Reactions between *trans*-Bis[1,2-bis(diethylphosphino)ethane]bis-(dinitrogen)molybdenum and Hydrogen Chloride in Tetrahydrofuran: A Mechanistic Study

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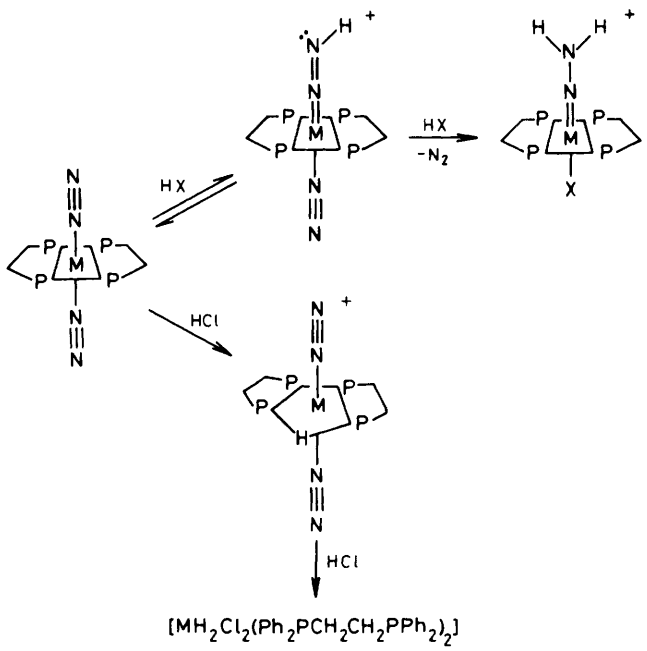
The reactions between *trans*-$[Mo(N_2)_2(depe)_2]$ [depe = 1,2-bis(diethylphosphino)ethane] and hydrogen chloride in tetrahydrofuran have been studied. The initial reaction involves rapid formation of the isolable $[MoH(N_2)_2(depe)_2]^+$ [k_1 = (2.7 ± 0.2) × 10^3 dm^3 mol^{-1} s^{-1}]. Subsequent rate-limiting dinitrogen loss [k_2 = (4.5 ± 0.4) × 10^{-4} s^{-1}] results, at low concentrations of acid ([HCl] < *ca.* 0.3 mol dm^{-3}), in the predominant formation of $[MoH_2Cl_2(depe)_2]$. At higher concentrations of acid the major product is *trans*-$[Mo(NNH_2)Cl(depe)_2]^+$. Discrimination between the two products occurs after the rate-limiting loss of dinitrogen. Detailed analysis shows that the two products are formed, at various concentrations of hydrogen chloride, according to the expression $[Mo(NNH_2)Cl(depe)_2^+]/[MoH_2Cl_2(depe)_2] = 8.0[HCl]^2$.

Studies on the reactions of the acids HX (X = Cl, Br, or HSO_4) with complexes of the type $[M(N_2)_2L_4]$ (M = Mo or W, L = monotertiary phosphine or L_2 = bidentate phosphine) give valuable information about the initial sites of protonation in the reduction of the dinitrogen ligand as far as the hydrazido(2−)-stage, $[M(NNH_2)X(L_4)]^+$ [equation (1)].[1,2]

trans-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ + 2HX ⟶
trans-$[M(NNH_2)X(Ph_2PCH_2CH_2PPh_2)_2]^+ + X^- + N_2$ (1)

Previous studies on the mechanism of reaction (1) in tetrahydrofuran (thf) showed the different consequences of initial protonation at the metal or the dinitrogen.[1,3] Protonation at dinitrogen is essential for the reaction to proceed through to the hydrazido(2−)-product, whereas protonation of the metal deactivates the dinitrogen ligands towards protic attack, resulting ultimately in the formation of $[MH_2Cl_2(Ph_2PCH_2CH_2PPh_2)_2]$ (Scheme 1). The work described herein on the reaction between *trans*-$[Mo(N_2)_2(depe)_2]$ [depe = 1,2-bis(diethylphosphino)ethane] and HCl complements this earlier study, and demonstrates that initial protonation at the metal can under certain conditions activate dinitrogen as far as the hydrazido(2−)-stage.



Scheme 1. $\overbrace{P\ \ P}$ = $Ph_2PCH_2CH_2PPh_2$

Results and Discussion

The reaction between *trans*-$[Mo(N_2)_2(depe)_2]$ (A) and HCl in thf occurs in two distinct steps: the initial rapid protonation of the metal gives $[MoH(N_2)_2(depe)_2]^+$ (B), and this is followed by its slow decomposition to yield *trans*-$[Mo(NNH_2)Cl(depe)_2]^+$ (G) or $[MoH_2Cl_2(depe)_2]$ (E). It is most convenient to discuss each of these stages separately. These reactions are summarised in Scheme 2; some species have been isolated and fully characterised as shown in Table 1.

The Formation of $[MoH(N_2)_2(depe)_2]^+$ (B).—The seven-co-ordinate hydrido-complex $[MoH(N_2)_2(depe)_2]^+$ (B) is the initial species formed in the reaction of *trans*-$[Mo(N_2)_2(depe)_2]$ (A) with HCl, under all conditions. The complex (B) is isolated as the HCl_2^- salt and its spectroscopic properties (Table 1) are very similar to those of the previously characterised analogue $[WH(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]HCl_2$ [3] {ν(N_2) 1 995 cm^{-1}. N.m.r.: ^1H, δ − 3.50 p.p.m. [t of t, $^2J(PWH)_A$ = 71.5, $^2J(PWH)_B$ = 10 Hz, W−H];[4] ^{31}P, δ −79.1 to −83.3 and −106.9 to −112.3 p.p.m., AA′XX′ system of PPh_2 mulitplets; ^{15}N,[5] δ −78.7 (N_α) and −52.7 (N_β) p.p.m., $^1J(^{15}N^{15}N)$ = 4 Hz}.[5] These properties are consistent with a pentagonal bipyramid structure with the hydrogen atom occupying an equatorial plane and with a face-capped octahedral configuration.

The complex (B) does not react with methyl iodide nor is it a sufficiently strong acid to be deprotonated by triethylamine in thf or methanol. However, its dinitrogen ligands can be replaced by carbon monoxide (but only in low yield) to give $[MoH(CO)_2(depe)_2]BPh_4$ (C). The spectroscopic properties of complex (C) (Table 1) indicate a structure analogous to that adopted by (B). It is isolated only in poor yield since the predominant pathway results in the formation of $[MoH_2Cl_2(depe)_2]$ (E) (see below), and successive fractional crystallisations are necessary to obtain pure samples of (C). Treatment of complex (B) with $LiBu^t$ in thf gives (A) in good yield (60% isolated).

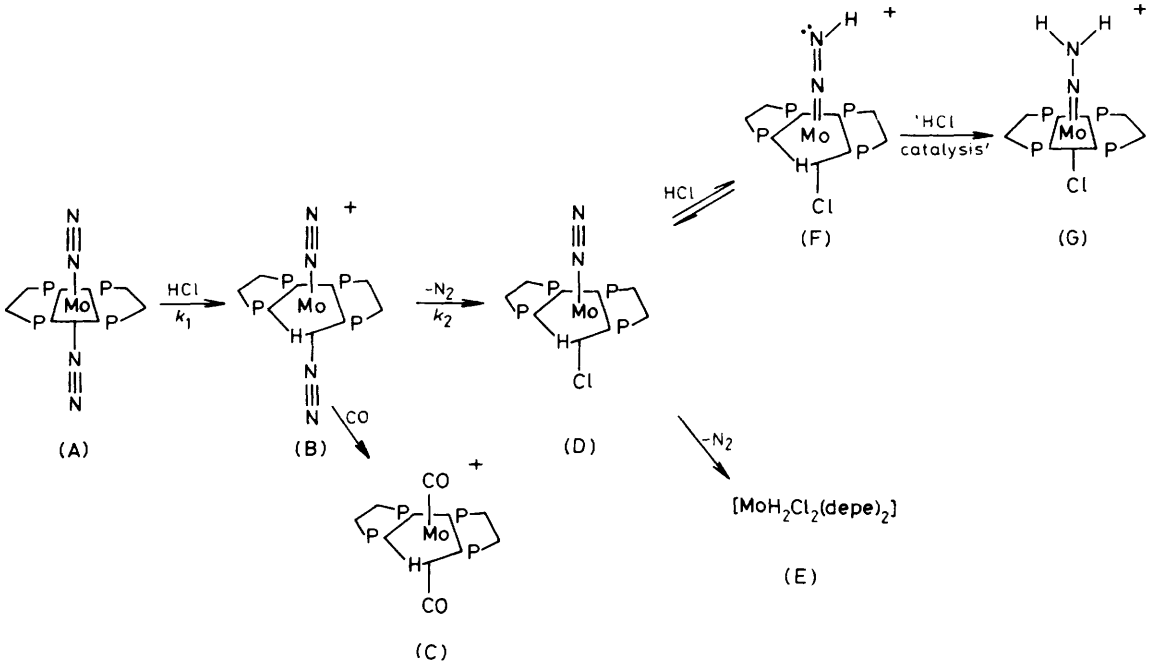
The kinetics for the formation of complex (B) exhibit a

Table 1. Analytical and spectroscopic characterisation of the complexes

Complex	Analysis [a] (%) C	H	N	I.r. spectrum, $\nu_{max.}$/cm^{-1}	N.m.r. spectra, δ/p.p.m. ^{31}P	^{1}H[b,c]	Other
(A) $[Mo(N_2)_2(depe)_2]$	42.6 (42.6)	8.8 (8.5)	9.7 (9.9)	ν(N_2) 1 925s	−84.4 (s)		
(B) $[MoH(N_2)_2(depe)_2]HCl_2$	37.5 (37.7)	7.5 (7.8)	8.8 (8.8)	ν(N_2) 1 980s ν(Mo–H) 1 800w	−63.1 to −66.8 (m), −94.4 to −97.9 (m) (PPh_2 multiplets of AA′XX′ pattern)	−5.15 (1) [d] [t of t, J(PMoH)$_A$ = 71.1, J(PMoH)$_B$ = 6.4 Hz, Mo–H]	^{15}N: −58.5 (s) (N_β), −42.8 (d) (N_α), J(^{15}N^{15}N) = 4.0 Hz
(C) $[MoH(CO)_2(depe)_2]BPh_4$	62.8 (62.4)	7.5 (7.8)	0.0 (0.0)	ν(CO) 1 840s	−63.1 to −66.9 (m), −89.7 to −93.4 (m) (PPh_2 multiplets of AA′XX′ pattern)	−6.99 (1) [e] [t of t, J(PMoH)$_A$ = 69.6, J(PMoH)$_B$ = 8.9 Hz, Mo–H]	
(E) $[MoH_2Cl_2(depe)_2]$	40.8 (41.0)	8.0 (8.5)	0.0 (0.0)	ν(Mo–H) 1 880, 1 840w	−66.8 (t), −98.3 (t), J(PMoP) = 35.0 Hz	−7.8 (1—2) (br, Mo–H), 1.10—1.50 (48) (depe)	
(G) $[Mo(NNH_2)Cl(depe)_2]HCl_2$	37.2 37.9 (37.2)	7.6 7.3 (7.7)	4.1 4.1 [f] (4.3)	ν(NH) 3 370, 3 110w (br)	−94.2 (s)	8.1 (2) [d,g] (NNH_2)	

* I.r.: s = strong, w = weak, br = broad. N.m.r.: s = singlet, d = doublet, t = triplet, and m = multiplet.

[a] Calculated values are given in parentheses. [b] Relative intensities are given in parentheses. [c] Poorly resolved signals attributable to depe ligand at 0.8—1.4 (24) (CH_3) and 1.6—2.3 (24) (CH_2) are present in all spectra except where noted. [d] Peak at 8.8—9.5 (br) attributable to HCl_2^-. [e] Signals at 7.0—7.4 (20) (m) attributable to $B(C_6H_5)_4$. [f] Product isolated from reaction in methanol. [g] Signal disappears on treatment with $C^2H_3O^2H$.



Scheme 2. $\overline{P\ \ P}$ = $Et_2PCH_2CH_2PEt_2$. Complexes (A)—(C), (E), and (G) have been isolated and characterised (Table 3). Cationic complexes are present as their HCl_2^- or BPh_4^- salts

first-order dependence on the concentrations of both (A) and HCl [equation (2)]. Despite this reaction being a relatively

$$k_{obs.} = (2.7 \pm 0.2) \times 10^3[HCl] \quad (2)$$

simple protonation, the second-order rate constant is significantly different from that of the diffusion-controlled processes associated with simple acid–base reactions.[6] This difference is a consequence of the diffuse electron density at the metal centre and the barrier to reorganisation of the co-ligands. The relatively slow protonation (and deprotonation) of metal centres has been observed before.[7,8] Indeed in the analogous reaction between *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ and HCl, where the encounter complex is preassembled, the proton transfer is still remarkably slow ($k_{obs.} = 2.7 \times 10^{-3}$ s^{-1}).[1]

The reaction between *trans*-$[Mo(N_2)_2(depe)_2]$ (A) and ^{2}HCl

Table 2. Kinetic data for the formation of $[MoH(N_2)_2(depe)_2]^+$ in tetrahydrofuran at 25 °C

$[Mo(N_2)_2(depe)_2]$/mmol dm^{-3}	$[^1HCl]$/mmol dm^{-3}	$k_{obs.}$/s^{-1}
0.25	2.5	7.0
	5.0	13.2
	10.0	28.1
	15.0	44.9
	20.0	55.4
	30.0	87.3
	40.0	115.1
0.50	5.0	12.1
	10.0	24.9
	20.0	56.3
	$[^2HCl]$/mmol dm^{-3}	
0.25	2.5	5.0
	5.0	11.1
	10.0	22.3
	15.0	33.0
	20.0	46.2
	30.0	66.1
	40.0	83.6

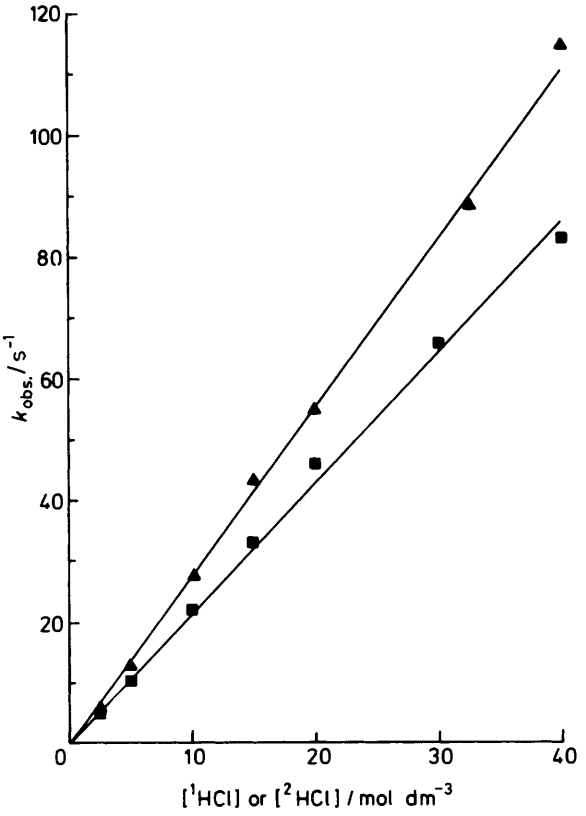


Figure 1. Kinetic plots for the formation of $[MoH(N_2)_2(depe)_2]^+$ (B) in the reaction between *trans*-$[Mo(N_2)_2(depe)_2]$ (A) and HCl in tetrahydrofuran: ▲ ^{1}HCl; ■ ^{2}HCl

exhibits a primary isotope effect, $k_H/k_D = 1.29$, consistent with rate-limiting protonation at the metal. The kinetic data are collected in Table 2, and illustrated in Figure 1.

A further feature of these data, when compared with those from the analogous studies with *trans*-$[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$,[1] is that although the latter exhibits an appreciable association constant with HCl ($K_{ass.} > 25$ dm^3 mol^{-1}), *trans*-$[Mo(N_2)_2(depe)_2]$ (A) does not: $K_{ass.} < 2.5$ dm^3 mol^{-1}. Although these data are too limited to make any generalisations, they may indicate that the association is primarily between the aromatic residues of the phosphine ligand and the protic end of the HX molecule.

Table 3. Kinetic data for the decomposition of $[MoH(N_2)_2(depe)_2]^+$ in methanol or tetrahydrofuran in the presence of HCl at 25 °C

$[MoH(N_2)_2(depe)_2^+]$	[HCl]		Isosbestic points,[a]
mmol dm^{-3}		$k_{obs.}$/s^{-1}	λ/nm
0.1	0.1	4.2	245, 342
		4.3 [b]	
		4.4 [c]	
0.05		4.1	
0.1	2.0	3.6	245, 342
	4.0	3.8	245, 344
	8.0	3.8	248, 344
		4.1 [b]	
	16.0	4.7	250, 344
	25.0	4.9	252, 344
	50.0	3.8	268, 344
		4.6 [c]	
0.05		4.2	
0.1	100.0	4.5	270, 344
	200.0	4.8	274, 344
	400.0	5.0	276, 344
		4.9 [b]	

[a] Measured in methanol. [b] Measurements made in tetrahydrofuran. [c] Studies using $[Mo^2H(N_2)_2(depe)_2]^+$.

Decomposition of $[MoH(N_2)_2(depe)_2]^+$ (B).—At low concentrations of acid ([HCl] < 0.4 mol dm^{-3}) in both methanol and thf the complex (B) reacts to yield predominantly $[MoH_2Cl_2(depe)_2]$ (E) with loss of dinitrogen as gas. The spectral characteristics of complex (E) (Table 1) are similar to those of $[MoH_2Cl_2(Ph_2PCH_2CH_2PPh_2)_2]$ {ν(Mo–H) 1 880 cm^{-1}. N.m.r.: ^{1}H, δ −4.55 p.p.m. [quintet ^2J(PMoH) = 48 Hz, Mo–H]; ^{31}P, δ −67.2(t) and −94.1 p.p.m.(t); J(PP) = 10.2 Hz}. However, the hydride resonance of (E) in the ^{1}H n.m.r. spectrum could not be resolved. The structure is probably similar to that adopted by $[WH_2Cl_2(PMe_2Ph)_4]$ [9] and $[TaH_2Cl_2(Me_2PCH_2CH_2PMe_2)_2]$.[10]

At high concentrations of acid ([HCl] > 0.4 mol dm^{-3}) in both methanol and thf the major product from the reaction between complex (B) and HCl is *trans*-$[Mo(NNH_2)Cl(depe)_2]$-HCl_2 (G). Although the analogous complex *trans*-$[Mo(NNH_2)Cl(Ph_2PCH_2CH_2PPh_2)_2]^+$ could not be prepared, owing to preferential formation of $[MoH_2Cl_2(Ph_2PCH_2CH_2PPh_2)_2]$,[1,3] the spectral characteristics of (G) are typical of hydrazido(2−)-complexes of this type.[3]

The kinetics for the formation of either complex (E) or (G) from (B), in both methanol and thf, are identical. The rate of formation of complex (E) or (G) is independent of the concentration of acid, and exhibits a first-order dependence on the concentration of (B) [$k_2 = (4.5 \pm 0.4) \times 10^{-4}$ (thf) and $(4.3 \pm 0.5) \times 10^{-4}$ s^{-1} (MeOH)]. The kinetic data for this reaction are in Table 3. The spectral changes during the course of this reaction in methanol exhibit well defined isosbestic points for at least three half-lives. The position of these isosbestic points depends upon the concentration of acid, consistent with the formation of complexes (E) and (G) in varying relative concentrations (Table 3). However, in thf the isosbestic points are maintained for only about one half-life. This may in part be attributable to the decomposition of thf by acid [reaction (3)].

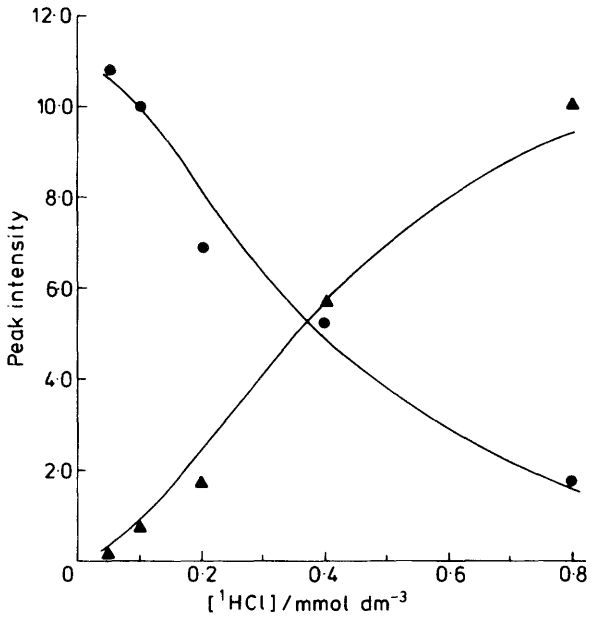


Figure 2. ^{31}P N.m.r. spectroscopic investigation of product variation with acid concentration: ●, $[MoH_2Cl_2(depe)_2]$; ▲, *trans*-$[Mo(NNH_2)Cl(depe)_2]^+$. Curves are those defined by equation (4). Total peak intensities are those measured on a 5 mmol dm^{-3} solution of complex (B) under the conditions described in the Experimental section

$$HCl + \overbrace{O(CH_2)_3CH_2} \longrightarrow HO(CH_2)_4Cl \xrightarrow{HCl} Cl(CH_2)_4Cl \quad (3)$$

The kinetics for the formation of complexes (E) or (G) are consistent with rate-limiting dinitrogen dissociation from $[MoH(N_2)_2(depe)_2]^+$ (B). This is further substantiated by studies on $[Mo^2H(N_2)_2(depe)_2]^+$ which reacts to yield complexes (E) and (G) at a rate identical to that of its protic analogue ($k_2 = 4.5 \times 10^{-4}\ s^{-1}$).

It is of interest to compare the dinitrogen dissociation rates from *trans*-$[Mo(N_2)_2(depe)_2]$ (A) and $[MoH(N_2)_2(depe)_2]^+$ (B). The dissociation rate for complex (A) ($k_{obs.} = 3.7 \times 10^{-6}\ s^{-1}$) is available from studies on the reaction between alkyl halides and this substrate.[11] Protonation at the metal therefore renders the dinitrogen ligand about a hundred times more labile.

Since the relative proportion of complexes (E) and (G) formed is a function of the acid concentration, which of these products is favoured must be decided by occurrences after the dinitrogen-dissociation step. By measuring the product distribution at various concentrations of HCl, the ratio of the rate laws for the formation of (E) and (G) was determined.[12] The absorption spectra of the products are not sufficiently diagnostic to be accurately resolved. However, ^{31}P n.m.r. spectroscopy allows a ready analysis of the product distribution. The peak heights attributable to the two products vary with the concentration of HCl as shown in Figure 2. With due regard to the problems associated with quantitative measurements in Fourier-transform spectroscopy,[13] the variation in peak intensity of a given product over a range of acid concentrations demonstrates that these data can be used at least semi-quantitatively.

The data shown in Figure 2 cannot be fitted to an expression exhibiting a first-order dependence on the concentration of HCl; in particular such an expression cannot simulate the rapid change in the product distribution over the relatively narrow range of acid concentration. The data can however be fitted to the expression shown in equation (4).

$$\frac{[Mo(NNH_2)Cl(depe)_2^+]}{[MoH_2Cl_2(depe)_2]} = 8.0[HCl]^2 \quad (4)$$

The Overall Mechanism.—We are now in a position to discuss the mechanism of the reactions between *trans*-$[Mo(N_2)_2(depe)_2]$ (A) and HCl. The initial site of protonation of (A) with HCl is the metal, to yield $[MoH(N_2)_2(depe)_2]^+$ (B) (Scheme 2). In general, protonation at the metal is deactivating since it withdraws electron density from the metal centre thus labilising the dinitrogen ligand and decreasing its basicity. Subsequent dinitrogen loss from (B), and attack of chloride ion at the vacated position, yields $[MoH(N_2)Cl(depe)_2]$ (D). At low concentrations of HCl, further dinitrogen loss results ultimately in the formation of $[MoH_2Cl_2(depe)_2]$ (E). However the dinitrogen ligand in (D) is sufficiently basic to be protonated at high concentrations of HCl to generate significant amounts of $[MoH(N_2H)Cl(depe)_2]^+$ (F). Then, as shown by the product analysis [equation (4)], complex (F) proceeds, *via* the acid-catalysed pathway, to yield *trans*-$[Mo(NNH_2)Cl(depe)_2]^+$ (G).

The origin of the second-order dependence on the concentration of HCl associated with the pathway from (D) to (G) is unclear. Either diprotonation of the dinitrogen ligand prior to metal–hydrogen cleavage, or the involvement of a molecule of HCl as a proton acceptor during metal–hydrogen cleavage of complex (F), is consistent with this rate law. Clearly this rate law does not support an intramolecular hydridic shift process. Attempts to determine the isotopic distribution of the products in the reaction between $[Mo^2H(N_2)_2(depe)_2]^+$ and ^1HCl, in particular to determine the fate of the metal–hydrogen group, were unsuccessful because of the extreme sensitivity of the ^1H resonance due to the hydrazido(2−)-ligand to trace moisture in the n.m.r. spectrum.

As outlined earlier, previous studies [1] on the reactions of *trans*-$[M(N_2)_2(R_2PCH_2CH_2PR_2)_2]$ (R = Et or Ph) with acid demonstrated that initial protonation at a dinitrogen ligand is an essential step for the formation of hydrazido(2−)-complexes (Scheme 1). Why then does the formation of *trans*-$[Mo(NNH_2)Cl(depe)_2]^+$ (G) adopt the pathway outlined in Scheme 2. The Two major reasons for this change in reactivity are (*i*) the weak acidity of HCl in thf and (*ii*) the strong electron-releasing capability of the depe ligand. The latter property renders the dinitrogen ligand poorly labile and thus the pathway (Scheme 1) involving initial protonation and rate-limiting loss of dinitrogen is relatively slow. This is compounded by the weak acidity of HCl in thf,[1] so that diprotonation prior to rate-limiting loss of dinitrogen does not make a significant contribution to the overall rate. Thus protonation at the metal is the fastest reaction, and the enforced pathway is that proceeding *via* $[MoH(N_2)_2(depe)_2]^+$ (B) (Scheme 2). However the same electron-releasing capability of the depe ligand renders the dinitrogen ligand in $[MoH(N_2)Cl(depe)_2]$ (D) sufficiently basic to be protonated, and the reaction proceeds *via* the acid-catalysed pathway through to *trans*-$[Mo(NNH_2)Cl(depe)_2]^+$ (G). In contrast $[MH(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]^+$ (M = Mo or W) is not activated towards protic attack at the dinitrogen ligands since the diphosphine is significantly less electron-releasing than depe.[1]

Experimental

All manipulations were performed under an atmosphere of dry dinitrogen using either standard Schlenk-tube and vacuum-

line or syringe techniques. Spectra were recorded on the following spectrometers: i.r., Pye-Unicam SP3-200 as KBr discs or Nujol mulls; ^{31}P and ^{1}H n.m.r., JEOL FX-90Q generally in thf or C^2HCl_3 respectively, using trimethyl phosphite (^{31}P) as external reference or tetramethylsilane (^{1}H) as internal reference.

Kinetic Measurements.—All kinetic measurements for the rapid reactions were made on an Aminco-Morrow stopped-flow spectrophotometer as described previously.[1] The stopped-flow traces were photographed and curve-fitted by the method of Thorneley.[14]

The slow reactions were monitored by measuring the absorption spectral changes in the range 230—450 nm on a Pye-Unicam SP1800 spectrophotometer. The rate constants were calculated from the normal semi-logarithmic plot.[15]

Materials.—All solvents were dried and freshly distilled immediately prior to use.

Stock solutions of anhydrous HCl were generated by mixing equimolar amounts of chlorotrimethylsilane and methanol in thf. All acid solutions were used within 1 h of their preparation. The stock solutions of HCl in thf were analysed by diluting an aliquot with water and then titrating against standard sodium hydroxide using phenolphthalein as indicator.

Preparations.—The ligand 1,2-bis(diethylphosphino)ethane (depe) was prepared by the method of Burt *et al.*,[16] and *trans*-$[Mo(N_2)_2(depe)_2]$ (A) by the literature method.[17]

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bis*(*dinitrogen*)*hydrido-molybdenum dichlorohydrogenate*(1−) (B). Compound (A) (0.50 g, 0.89 mmol) was suspended in thf (20 cm^3) and methanol (0.15 cm^3, 4.7 mmol) followed by chlorotrimethylsilane (0.52 cm^3, 4.7 mmol) was added. There was an immediate reaction and a bright yellow solid was deposited. The mixture was stirred at room temperature for 1 h and filtered; the solid obtained was washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo* (0.30 g, 53%). Recrystallisation from dichloromethane–diethyl ether afforded the compound (B) as a yellow microcrystalline solid.

The isotopically labelled complexes $[MoH(^{15}N_2)_2(depe)_2]HCl_2$ and $[Mo^2H(N_2)_2(depe)_2]HCl_2$ were prepared by an identical route. The former complex was prepared from isotopically enriched (50%) *trans*-$[Mo(^{15}N_2)_2(depe)_2]$. The latter complex was prepared using ^2HCl generated using equimolar amounts of MeO^2H and $SiMe_3Cl$ (Found: C, 37.9; H, 7.6; N, 8.7. Calc. for $C_{20}H_{48}{}^2H_2Cl_2MoN_4P_4$: C, 37.6; H, 7.8; N, 8.8%); ^2H n.m.r., δ −12.8 p.p.m. [t, $J(PMoH)_A = 10.9$ Hz], relative to C^2HCl_3.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*dicarbonyl*(*hydrido*)-*molybdenum tetraphenylborate* (C). Complex (B) (0.30 g, 0.47 mmol) and sodium tetraphenylborate (0.16 g, 0.47 mmol) were suspended in thf (15 cm^3) and carbon monoxide was bubbled through the solution for 4 h. The yellow-brown solution was evaporated to dryness *in vacuo*. Slow crystallisation of the solid from thf–diethyl ether gave complex (C) as a pale brown microcrystalline product (0.08 g, 19%).

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*dichlorodihydridomolybdenum* (E). A suspension of complex (B) (0.30 g, 0.47 mmol) in thf (15 cm^3) was stirred under dinitrogen for 4 h. The yellow solution was evaporated to dryness *in vacuo*. Careful crystallisation of the solid from thf–diethyl ether gave the product (E) as a yellow microcrystalline solid (0.20 g, 74%).

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*chloro*[*hydrazido*(2−)]-*molybdenum dichlorohydrogenate*(1−) (G). A suspension of complex (B) (0.30 g, 0.47 mmol) in thf or methanol (20 cm^3) was stirred vigorously while methanol (0.45 cm^3, 14.1 mmol) and chlorotrimethylsilane (1.54 cm^3, 14.1 mmol) were added. The solution was stirred for a further 4 h, and then the red solution evaporated to dryness *in vacuo*. Recrystallisation of the resulting solid from dichloromethane–diethyl ether yielded the product (G) as a red solid (0.19 g, 63%).

Product Analysis.—Solutions for the product analyses were prepared by adding a known weight of $[MoH(N_2)_2(depe)_2]HCl_2$ to the required standard solution of HCl in thf. The HCl was generated from the calculated volumes of methanol and chlorotrimethylsilane. The concentration of complex was 5 mmol dm^{-3}. The solution was stirred overnight after which the ^{31}P n.m.r. spectrum was recorded.

All spectra were proton-decoupled, recorded at 36.2 MHz, with a pulse width of 19 μs, and a pulse delay of 0.5 s over 4 219 scans. Corrections to the recorded intensity when comparing two spectra recorded at different Y gain (Y.G.) settings were made using equation (5), where b = measured

$$b' = b\left(\frac{\text{Y.G.}_A}{\text{Y.G.}_B}\right) \times 2^{(\text{N.G.B} - \text{N.G.A})} \qquad (5)$$

peak height in spectrum A, Y.G._A = Y gain setting in spectrum A, and N.G._A = normalized gain setting in spectrum A, *etc.*

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