Mechanistic Studies on Hydrazido(2−)-complexes. Cleavage of the Nitrogen–Nitrogen Bond in the Reaction of $[\mathrm{Mo\{N\overline{N(CH_2)_4C}H_2\}(Ph_2PCH_2CH_2PPh_2)_2}]$ with Acid

Richard A. Henderson,* G. Jeffery Leigh, and Christopher J. Pickett
AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ

The kinetics of the reaction between $[\mathrm{Mo\{N\overline{N(CH_2)_4C}H_2\}(dppe)_2}]$ (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) and $[\mathrm{NHEt_3}]\mathrm{BPh_4}$ to yield $\mathrm{\overline{NH(CH_2)_4C}H_2}$ and $[\mathrm{MoN(NCR)(dppe)_2}]\mathrm{BPh_4}$ (RCN is the solvent; R = Me, Et, or Ph) has been studied. In general the mechanism of the reactions involves two parallel pathways. Initial rapid protonation of the hydrazido(2−)-ligand and attack of a solvent molecule at the metal yields the spectrophotometrically detected hydrazidium species, *trans*-$[\mathrm{Mo\{N\overline{NH(CH_2)_4C}H_2\}(NCR)(dppe)_2}]^+$. This species can either undergo slow nitrogen–nitrogen cleavage or react *via* an acid-catalysed pathway involving *trans*-$[\mathrm{Mo\{NH\overline{NH(CH_2)_4C}H_2\}(NCR)(dppe)_2}]^{2+}$ to yield the products. The factors influencing whether protonation of hydrazido(2−)-ligands results in amine formation (N–N bond cleavage) or hydrazine formation (M–N bond cleavage) are discussed.

It has been known for some time that the protonation of dinitrogen complexes such as *cis*-$[\mathrm{M(N_2)_2(PMe_2Ph)_4}]$ (M = Mo or W) to yield both ammonia and hydrazine involves the common intermediacy of complexes containing the hydrazido-(2−)-ligand, such as $[\mathrm{M(NNH_2)X_2(PMe_2Ph)_3}]$ (X = halide).[1] Furthermore there is some evidence that the hydrazido(2−)-state can also be detected during turnover of the enzyme nitrogenase.[2] Despite this cardinal role for the hydrazido(2−)-residue in nitrogen fixation, no systematic mechanistic study on the factors influencing the rates of nitrogen–nitrogen cleavage has been reported. A major problem in studying the protonation reactions of hydrazido(2−)-complexes is that in general they are not analytically clean, often giving mixtures of ammonia and hydrazine,[3–5] or that the aprotic solvent is attacked by acid[6] over the protracted times necessary to complete the reaction. However, recently it has been shown that the reaction of an excess of acid with the alkylhydrazido(2−)-complex $[\mathrm{Mo\{N\overline{N(CH_2)_4C}H_2\}(dppe)_2}]$ (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) results in rapid cleavage of the nitrogen–nitrogen bond[7] [equation (1), thf = tetrahydrofuran]. This system forms the basis of the study described herein.

$$[\mathrm{Mo\{N\overline{N(CH_2)_4C}H_2\}(dppe)_2}] + 2\mathrm{HBr} \xrightarrow{\mathrm{thf}} \\ trans\text{-}[\mathrm{Mo(NH)Br(dppe)_2}]\mathrm{Br} + \mathrm{\overline{NH(CH_2)_4C}H_2} \quad (1)$$

Experimental

All manipulations in both the preparative and mechanistic aspects of this work were performed under an atmosphere of dinitrogen using standard Schlenk or syringe techniques as appropriate.

Kinetic Studies.—All kinetic studies were performed on an Aminco-Morrow stopped-flow apparatus modified for handling air-sensitive compounds.[8] The apparatus was interfaced to a B.B.C. microcomputer (Acorn Computers, Cambridge) *via* an analogue-to-digital converter operating at 3 kHz. Data were subsequently transferred to a PDP 1134A computer for analysis. The data were analysed by standard curve-fitting procedures. Analysis of the results was by the necessary straight line graphs, and errors on the slopes and intercepts of such graphs were established by a linear least-squares analysis.

For the kinetics experiments solutions of $[\mathrm{Mo\{N\overline{N(CH_2)_4C}H_2\}(dppe)_2}]$ were prepared in the required nitrile solvent containing 2% thf to solubilise the complex. In independent experiments the addition of greater amounts of thf, up to a maximum of 15%, had no effect on the rate constants.

Materials.—All solvents were distilled from the necessary drying agent immediately prior to all studies, in particular the nitrile solvents (MeCN, EtCN, and PhCN) were distilled from phosphorus pentoxide. The complex $[\mathrm{Mo\{N\overline{N(CH_2)_4C}H_2\}(dppe)_2}]$ was isolated as a black microcrystalline solid from the reaction of *trans*-$[\mathrm{Mo\{N\overline{N(CH_2)_4C}H_2\}Br(dppe)_2}]\mathrm{Br}$[9] with $\mathrm{LiBu^t}$ in hexane, and crystallised from a thf–hexane mixture. The salt $[\mathrm{NHEt_3}]\mathrm{BPh_4}$ was prepared as described earlier,[10] and $\mathrm{NEt_3}$ (B.D.H.) was used as supplied.

Product Analysis.—The metal-containing products from the reactions of $[\mathrm{Mo\{N\overline{N(CH_2)_4C}H_2\}(dppe)_2}]$ with $[\mathrm{NHEt_3}]\mathrm{BPh_4}$ were established both by isolation of the material from the reaction mixture and comparison of the *in situ* $^{31}\mathrm{P}$ n.m.r. spectrum of the reaction mixture with that of the same compound isolated by the alternative route (2).

$$trans\text{-}[\mathrm{Mo(NH)Cl(dppe)_2}]\mathrm{Cl} + 2\mathrm{NaBPh_4} + \mathrm{NEt_3} \xrightarrow{\mathrm{RCN}} \\ trans\text{-}[\mathrm{MoN(NCR)(dppe)_2}]\mathrm{BPh_4} + \\ 2\mathrm{NaCl} + [\mathrm{NHEt_3}]\mathrm{BPh_4} \quad (2)$$

trans-*Acetonitrilebis*[1,2-*bis*(*diphenylphosphino*)*ethane*]-*nitridomolybdenum*(IV) *Tetraphenylborate*, $[\mathrm{MoN(NCMe)(dppe)_2}]\mathrm{BPh_4}$.—To a vigorously stirred solution of *trans*-$[\mathrm{Mo(NH)Cl(dppe)_2}]\mathrm{Cl}$[11] (0.50 g, 0.51 mmol) in acetonitrile (*ca.* 20.0 cm^3) was added $\mathrm{NaBPh_4}$ (0.37 g, 1.1 mmol), followed by sufficient $\mathrm{NEt_3}$ to turn the solution yellow. After stirring the solution for a further 0.5 h at room temperature it was concentrated to about half the volume *in vacuo*. The precipitated NaCl was removed by filtration and then diethyl ether added until incipient crystallisation. The solution was set aside for

Table 1. Analytical and spectroscopic characterisation of complexes

Complex	Elemental analysis[a] (%) C	H	N	I.r.[b]/cm^{-1} ν(MoN)	ν(CN)	N.m.r. ^{1}H[c]	^{31}P[d]
$[\mathrm{Mo}\{\mathrm{N}\overline{\mathrm{N}(\mathrm{CH_2})_4\mathrm{C}}\mathrm{H_2}\}(\mathrm{dppe})_2]$	68.7 (69.1)	6.1 (5.9)	2.5 (2.8)			1.6, 0.8[e,f] [br, N(CH$_2$)$_4$CH$_2$]	−53.9 (s)[g,h] −54.4 (s)[i]
$[\mathrm{MoN(NCMe)(dppe)_2]BPh_4}$	73.8 (73.9)	6.2 (5.6)	2.2 (2.2)	998m	2 260w	1.24(3) (s, CH$_3$)	−80.2 (s)[i]
$[\mathrm{MoN(NCEt)(dppe)_2]BPh_4}$	73.5 (74.0)	5.7 (5.7)	1.9 (2.2)	998m	2 260w	0.68 (3) [t, CH$_3$, J(HH) = 7.2] 1.52 (2) [q, CH$_2$, J(HH) = 7.2]	−80.3 (s)[j]
$[\mathrm{MoN(NCPh)(dppe)_2]BPh_4}$	74.6 (75.0)	6.0 (5.5)	2.1 (2.1)	1 030m	2 235w[k]		−74.7 (s)[l]

[a] Calculated values in parentheses. [b] s = Strong, w = weak, and m = medium; recorded as Nujol mulls. [c] Chemical shifts relative to SiMe$_4$, J values in Hz; spectra recorded in CDCl$_3$. s = Singlet, t = triplet, q = quartet, and br = broad. All spectra show poorly resolved signals attributable to the dppe ligand at 1.6—2.3 (8) (CH$_2$) and 6.8—7.6 (20) (Ph), and nitrido-complexes also exhibit further complexities at 7.0—7.3 (m) attributable to BPh$_4$. [d] Chemical shifts relative to P(OMe)$_3$. [e] Solvent = [^{2}H$_8$]toluene. [f] Accurate integration in this spectrum is precluded because of signals due to the solvent. [g] Solvent = tetrahydrofuran. [h] Solvent = toluene. [i] Solvent = acetonitrile. [j] Solvent = propionitrile. [k] Signals attributable to co-ordinated PhCN indistinguishable from multiplets of other phenyl groups of dppe and BPh$_4$. [l] Solvent = benzonitrile.

several hours and then the needle crystals were removed by filtration, washed rapidly with two portions (5 cm^3) of ice-cold acetonitrile, followed by diethyl ether, and finally dried *in vacuo*.

The analogous EtCN and PhCN complexes were prepared in a similar fashion. The benzonitrile complex is thermally unstable over prolonged periods at room temperature and is thus best stored at −10.0 °C.

Analytical and spectroscopic characterisation of these complexes is shown in Table 1.

The presence of the amine was established (but not quantitatively estimated) by the reaction of $[\mathrm{Mo}\{\mathrm{N}\overline{\mathrm{N}(\mathrm{CH_2})_4\mathrm{C}}\mathrm{H_2}\}(\mathrm{dppe})_2]$ with 1 mol equivalent of [NHEt$_3$]Cl in MeCN. Subsequent addition of about 10 mol equivalents of anhydrous HCl (MeOH + SiMe$_3$Cl) resulted in the precipitation of $\overline{\mathrm{NH(CH_2)_4C}}\mathrm{H_2}\cdot\mathrm{HCl}$ whose authenticity was established by ^{1}H n.m.r. and i.r. spectroscopies.

Instrumentation.—Infrared and u.v.–visible spectra were recorded on a Perkin-Elmer 883 and a Philips Scientific SP1800 spectrophotometer respectively. All n.m.r. spectra were recorded on a JEOL FX90Q Fourier transform spectrometer.

Results

The System.—Attempts to study the kinetics of reaction (1) were unsuccessful because of its extreme rapidity: the reaction was complete within the dead-time of the stopped-flow apparatus (3.3 ms). However by using the much weaker acid [NHEt$_3$]BPh$_4$ in the basic solvent RCN (R = Me, Et, or Ph) the reaction becomes sufficiently slow to be monitored by the stopped-flow technique. The use of this acid has the further advantages that both the counter anion and the derived conjugate base are non-co-ordinating in this system. The stoicheiometry of the reaction studied is shown in equation (3).

$$[\mathrm{Mo}\{\mathrm{N}\overline{\mathrm{N}(\mathrm{CH_2})_4\mathrm{C}}\mathrm{H_2}\}(\mathrm{dppe})_2] + [\mathrm{NHEt_3}]\mathrm{BPh_4} \xrightarrow{\mathrm{RCN}} trans\text{-}[\mathrm{MoN(NCR)(dppe)_2}]\mathrm{BPh_4} + \overline{\mathrm{NH(CH_2)_4C}}\mathrm{H_2} + \mathrm{NEt_3} \quad (3)$$

The Kinetics.—The kinetics of reaction (3) were established by analogous studies for all three solvents, and so only the studies in acetonitrile will be described in detail. The observed rate constants in all three solvents are shown in Table 2, and the corresponding derived equilibria and elementary rate constants are summarised in Table 4.

Table 2. Kinetic data for the reaction between $[\mathrm{Mo}\{\mathrm{N}\overline{\mathrm{N}(\mathrm{CH_2})_4\mathrm{C}}\mathrm{H_2}\}(\mathrm{dppe})_2]$ and [NHEt$_3$]BPh$_4$ in RCN (R = Me, Et, or Ph) at 25.0 °C (λ = 400 nm, [Mo] = 0.25 mmol dm^{-3})

[NHEt$_3$$^+$] mmol dm^{-3}	[NEt$_3$] mmol dm^{-3}	$k_{\mathrm{obs.}}$/s^{-1} MeCN	EtCN	PhCN
0.5		10.8	1.2	0.32
1.0		15.2	1.4	0.35
2.0		24.4	1.7	0.33
4.0		35.6	2.0	
6.0		44.0	2.4	0.36
9.0		49.0	2.8	
12.0		52.0	3.2	0.36
15.0		52.3	3.3	
20.0		58.2	3.5	0.35
1.0	1.0	3.5		
	2.0	2.1		
	4.0	1.5		
	6.0	1.3		
	8.0	1.1		
	10.0	1.0		
2.0	1.0	7.5	1.1	0.35
	2.0	4.1	1.0	0.33
	4.0	2.5	1.0	0.35
	6.0	2.0	1.1	0.37
	8.0	1.8	1.1	0.37
	10.0	1.6	1.1	0.38
3.0	1.0	12.2		
	2.0	5.8		
	4.0	4.2		
	6.0	3.1		
	8.0	2.8		
	10.0	2.3		

The reaction between $[\mathrm{Mo}\{\mathrm{N}\overline{\mathrm{N}(\mathrm{CH_2})_4\mathrm{C}}\mathrm{H_2}\}(\mathrm{dppe})_2]$ (λ = 400 nm, ε = 7.0 × 10^3 dm^3 mol^{-1} cm^{-1}) and [NHEt$_3$]BPh$_4$ in acetonitrile occurs in two distinct phases: the initial rapid formation of a spectrophotometrically detected intermediate (λ = 400 nm, ε = 3.5 × 10^3 dm^3 mol^{-1} cm^{-1}), which is complete within the dead-time of the stopped-flow apparatus followed by the relatively slow conversion of the intermediate to

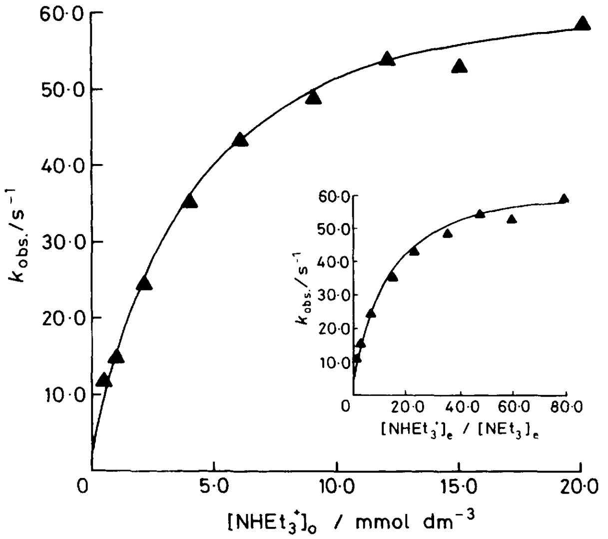


Figure 1. Dependence of $k_{obs.}$ on $[NHEt_3^+]_0$ for the reaction of $[Mo\{NN(CH_2)_4CH_2\}(dppe)_2]$ with $[NHEt_3]BPh_4$ in MeCN at 25.0 °C (λ = 400 nm, [Mo] = 0.25 mmol dm^{-3}); curve drawn is that defined by equation (4). Insert: derived dependence of $k_{obs.}$ on $[NHEt_3^+]_e/[NEt_3]_e$ as defined by equation (9); curve drawn is that defined by equation (7)

yield the products (λ = 400 nm, ε = 1.2 × 10^3 dm^3 mol^{-1} cm^{-1}). The decay of the intermediate occurs on the stopped-flow time-scale and the corresponding kinetics exhibits a first-order dependence on the concentration of the intermediate but a complicated dependence on the concentration of acid, as shown in Figure 1. Thus at low acid concentrations the reaction exhibits a first-order dependence of $[NHEt_3^+]_0$, whereas at high acid concentrations the reaction rate becomes independent of $[NHEt_3^+]_0$, as described by equation (4) (the '0' subscript denotes the added concentration). Here and throughout this paper $k_{obs.}$ is the observed pseudo-first-order rate constant.

$$k_{obs.} = 2.47 \times 10^4[NHEt_3^+]_0/(1 + 4.20 \times 10^2[NHEt_3^+]_0) \quad (4)$$

Before attempting to interpret equation (4) it is essential to appreciate the effect that the addition of NEt_3 has on the kinetics. In a series of experiments in which the concentrations of both the molybdenum complex and $[NHEt_3^+]_0$ were kept constant, but under conditions where the acid exhibited a first-order dependence on the rate of the reaction, the introduction of NEt_3 inhibits the reaction as shown in Figure 2 and described by equation (5).

$$k_{obs.} = 0.7 + 3.77[NHEt_3^+]_0/[NEt_3]_0 \quad (5)$$

There are three features of this reaction which are of prime importance in analysing the kinetic results. First, the kinetics being measured are those associated with the decomposition of a rapidly formed intermediate. Secondly, the non-zero intercept in Figure 2 demonstrates that the plot in Figure 1 also does not pass through the origin but has a small positive intercept, a feature which would have been missed if the studies with NEt_3 had not been performed. Finally, the form of equation (5) (exhibiting an inverse dependence on $[NEt_3]$) demonstrates that equation (4) should also be of this form. In respect of this last feature, using the value of $K_a = 3.47 \times 10^{-19}$ for the protolytic equilibrium shown in equation (6),[12] the equilibrium concentrations, $[NHEt_3^+]_e$ and $[NEt_3]_e$, were calculated for all the kinetic data, and the corrected data illustrated in the inserts of Figures 1 and 2.

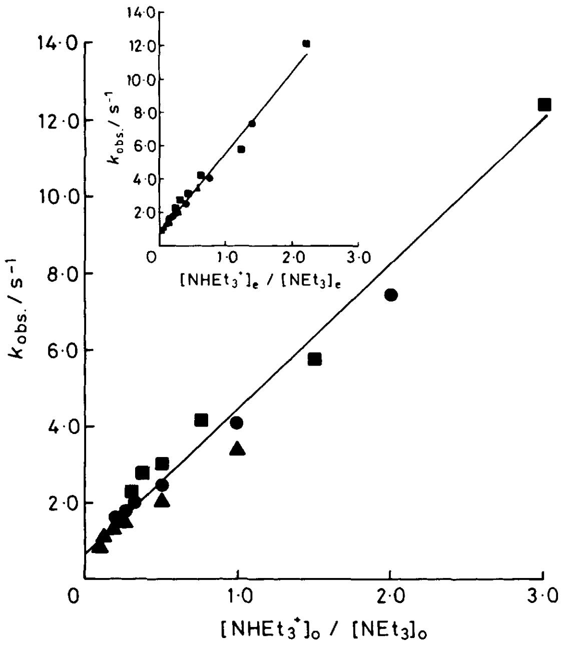


Figure 2. Dependence of $k_{obs.}$ on $[NHEt_3^+]_0/[NEt_3]_0$ for the reaction of $[Mo\{NN(CH_2)_4CH_2\}(dppe)_2]$ with $[NHEt_3]BPh_4$ in the presence of NEt_3 in MeCN at 25.0 °C (λ = 400 nm, [Mo] = 0.25 mmol dm^{-3}). Data points: $[NEt_3]_0$ = 1.0—10.0, $[NHEt_3^+]_0$ = 1.0 (▲), 2.0 (●), or 3.0 mmol dm^{-3} (■). The line drawn is that defined by equation (5). Insert: derived dependence of $k_{obs.}$ on $[NHEt_3^+]_e/[NEt_3]_e$ as defined by equation (9); line drawn is that defined by equation (8)

$$NHEt_3^+ + MeCN \overset{K_a}{\rightleftharpoons} NEt_3 + MeCNH^+ \quad (6)$$

In analysing the kinetic data we have further corrected the concentrations of $NHEt_3^+$ and NEt_3 by assuming that 1 mol equivalent of the acid is consumed (and hence 1 mol equivalent of NEt_3 is generated) as a consequence of the rapid conversion of $[Mo\{NN(CH_2)_4CH_2\}(dppe)_2]$ into the detected intermediate during the dead-time of the stopped-flow apparatus. This assumption is vindicated by the good agreement between the derived rate laws for the reaction under the two different conditions as shown in equations (7) and (8).

$$k_{obs.} = (0.7 \pm 0.05) + \frac{(6.9 \pm 0.8)[NHEt_3^+]_e/[NEt_3]_e}{1 + (0.12 \pm 0.01)[NHEt_3^+]_e/[NEt_3]_e} \quad (7)$$

$$k_{obs.} = (0.7 \pm 0.05) + (5.0 \pm 0.4)[NHEt_3^+]_e/[NEt_3]_e \quad (8)$$

The stoicheiometry of the reaction to generate the detected intermediate is open to further test. If the reaction between $[Mo\{NN(CH_2)_4CH_2\}(dppe)_2]$ and $NHEt_3^+$ is studied at a constant acid concentration but at variable complex concentrations, and the formation of the intermediate involves a single protonation step, the ratio $[NHEt_3^+]_e/[NEt_3]_e$ will be defined by the complex concentration as shown in equation (9).

$$[NHEt_3^+]_e/[NEt_3]_e = ([NHEt_3^+]_0 - [Mo])/([NEt_3]_0 + [Mo]) \quad (9)$$

Table 3. Kinetic data for the reaction between $[\mathrm{Mo}\{\mathrm{N\overline{N(CH_2)_4CH_2}}\}(\mathrm{dppe})_2]$ and $[\mathrm{NHEt_3}]\mathrm{BPh_4}$ in MeCN at 25.0 °C: dependence on the concentration of complex (λ = 400 or 580 nm)

$[\mathrm{NHEt_3}^+]$	[Mo]	
mmol dm^{-3}		$k_{\mathrm{obs.}}/\mathrm{s}^{-1}$
4.0	0.25	34.8
	0.50	27.2
	1.00	14.8
	2.00	7.6
1.5	0.125	29.0
	0.25	18.5
	0.50	14.5
	1.00	11.5

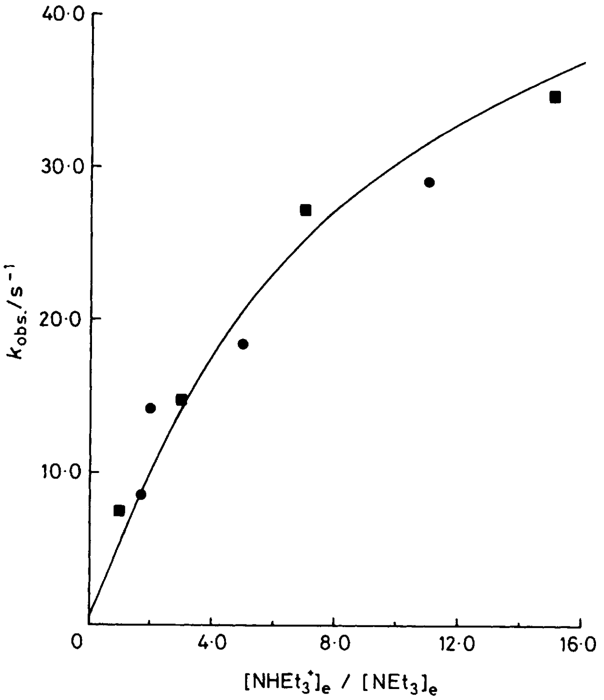
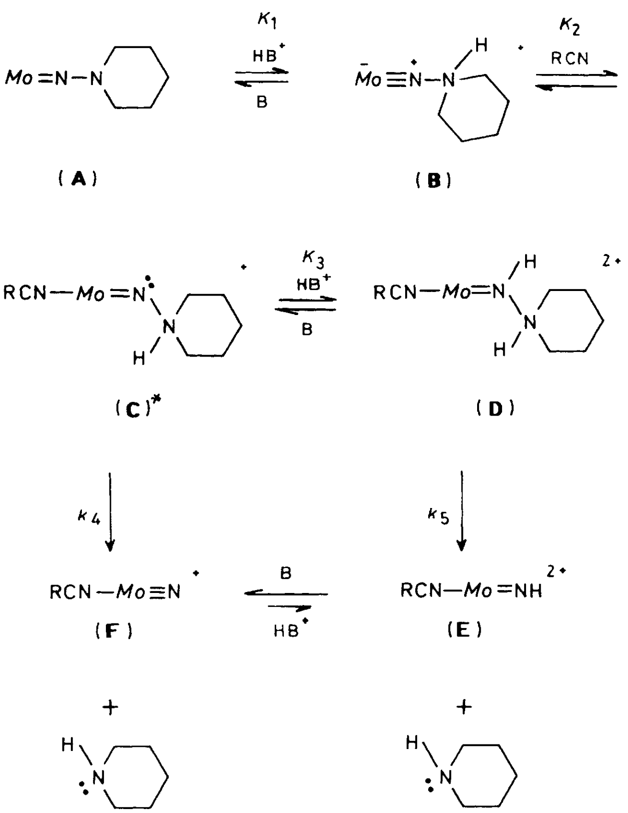


Figure 3. Dependence of $k_{\mathrm{obs.}}$ on $[\mathrm{NHEt_3}^+]_e/[\mathrm{NEt_3}]_e$ for the reaction of $[\mathrm{Mo}\{\mathrm{N\overline{N(CH_2)_4CH_2}}\}(\mathrm{dppe})_2]$ with $[\mathrm{NHEt_3}]\mathrm{BPh_4}$ in MeCN. Data points: $[\mathrm{NHEt_3}^+]_o$ = 4.0, [Mo] = 0.25—2.00 (■); $[\mathrm{NHEt_3}^+]_o$ = 1.5, [Mo] = 0.125—1.00 mmol dm^{-3} (●). The curve is that defined by equation (7)

As shown by the data in Table 3 and illustrated in Figure 3 the value of $k_{\mathrm{obs.}}$ varies with the complex concentration in a manner identical to that observed in the studies where the concentration of $[\mathrm{Mo}\{\mathrm{N\overline{N(CH_2)_4CH_2}}\}(\mathrm{dppe})_2]$ was kept low and constant.

One final feature of the kinetics of this system was revealed during the studies where the concentration of $[\mathrm{Mo}\{\mathrm{N\overline{N(CH_2)_4CH_2}}\}(\mathrm{dppe})_2]$ was varied. Even when the acid concentration was only slightly in excess of that of the complex ($[\mathrm{Mo}]/[\mathrm{NHEt_3}^+]$ = 0.67) the absorbance–time trace associated with the transformation of the intermediate to the products is exponential. Such an observation is implicit in the above analysis of the kinetics. After the initial rapid protonation of $[\mathrm{Mo}\{\mathrm{N\overline{N(CH_2)_4CH_2}}\}(\mathrm{dppe})_2]$ to generate the detected intermediate, the stoicheiometry of the reaction [equation (3)] dictates that the subsequent acid-dependent pathway must be catalytic in acid.



Scheme. The mechanism for the reaction of $[\mathrm{Mo}\{\mathrm{N\overline{N(CH_2)_4CH_2}}\}(\mathrm{dppe})_2]$ with $[\mathrm{NHEt_3}]\mathrm{BPh_4}$ in RCN (R = Me, Et, or Ph); *Mo* = Mo(dppe)$_2$. All species (**A**)—(**F**) have formally an eighteen-electron configuration. * Detected intermediate

Discussion

The Mechanism.—The mechanism of the reaction between $[\mathrm{Mo}\{\mathrm{N\overline{N(CH_2)_4CH_2}}\}(\mathrm{dppe})_2]$ and $\mathrm{NHEt_3}^+$ suggested by the kinetic analysis is shown in the Scheme.

Initial, rapid protonation of $[\mathrm{Mo}\{\mathrm{N\overline{N(CH_2)_4CH_2}}\}(\mathrm{dppe})_2]$ (**A**) at the nitrogen atom remote from the metal generates the hydrazidium species $[\mathrm{Mo}\{\mathrm{N\overline{NH(CH_2)_4CH_2}}\}(\mathrm{dppe})_2]^+$ (**B**). Protonation on the ligand will increase the positive charge on the metal and promote subsequent nucleophilic attack by a molecule of solvent at the five-co-ordinate metal centre and generate (**C**). However in order to maintain the formal eighteen-electron configuration around the molybdenum atom, upon attack of the nitrile ligand the nitrogenous residue has to adopt the bent configuration shown, in which the hydrazide ligand has changed from a formal four-electron donor to a formal two-electron donor. It is complex (**C**) which is the detected intermediate formed in the rapid phase of the reaction.

We cannot entirely discount the possibility that species (**C**) is formed by initial attack of solvent at the metal followed by protonation. The observation which favours the sequence shown in the Scheme is that the u.v.-visible absorption spectra and ^{31}P n.m.r. spectra of (**A**) are essentially the same in thf, MeCN, or toluene (Table 1), indicating little intimate interaction between the solvent and (**A**). Clearly though these techniques may not detect small concentrations of solvento-species. Irrespective of whether protonation precedes or follows binding of the solvent it is clear that (**C**) does contain a co-ordinated nitrile since both the rate of unimolecular decomposition (k_4) and basicity (K_3) of (**C**) depend on the

Table 4. Summary of the equilibrium and elementary rate constants for the reaction between $[\mathrm{Mo}\{\mathrm{N}\overline{\mathrm{N(CH_2)_4C}}\mathrm{H_2}\}(\mathrm{dppe})_2]$ with $[\mathrm{NHEt_3}]\mathrm{BPh_4}$ in RCN (R = Me, Et, or Ph) at 25.0 °C

RCN	k_4/s^{-1}	K_3	k_5/s^{-1}
MeCN	0.70 ± 0.05	0.12 ± 0.01	57.1 ± 1.5
EtCN	1.07 ± 0.02	0.045 ± 0.01	3.3 ± 0.2
PhCN	0.34 ± 0.02	*	

* In PhCN the acid-catalysed pathway is not detected because of the low basicity of species (**C**), R = Ph.

nature of the nitrile (Table 4). Thus when the electron-withdrawing benzonitrile ligand is present (**C**) is insufficiently basic to react *via* the acid-catalysed pathway.

Species (**C**) can either undergo nitrogen–nitrogen cleavage to yield $[\mathrm{MoN(NCR)(dppe)_2}]^+$ (**F**) and $\overline{\mathrm{NH(CH_2)_4C}}\mathrm{H_2}$ directly, or, if (**C**) is sufficiently basic (R = Me or Et), it is rapidly protonated to generate $[\mathrm{Mo}\{\mathrm{NH}\overline{\mathrm{NH(CH_2)_4C}}\mathrm{H_2}\}\text{-}(\mathrm{NCR})(\mathrm{dppe})_2]^{2+}$ (**D**) which subsequently undergoes nitrogen–nitrogen cleavage to generate $[\mathrm{Mo(NH)(NCR)(dppe)_2}]^{2+}$ (**E**) and the amine. In the nitrile solvent the imido-ligand in complex (**E**) is sufficiently acidic to release a proton and yield the product (**F**), thus completing the acid-catalysed nitrogen–nitrogen cleavage pathway by liberating the proton that was initially consumed in the protonation of (**C**).

It is important to re-emphasise at this point that the kinetics measured in this study is that associated with the conversion of the species (**C**) to yield the products $\overline{\mathrm{NH(CH_2)_4C}}\mathrm{H_2}$ and (**F**). If it is assumed that protonation of (**C**) by $\mathrm{NHEt_3}^+$ to generate (**D**) and $\mathrm{NEt_3}$ is a rapidly established equilibrium and that the nitrogen–nitrogen cleavage steps are rate-limiting, then the derived generalised rate law for the decomposition of the detected intermediate (**C**) is that shown in equation (10). This

$$-\mathrm{d}[(\mathrm{C})]/\mathrm{d}t = k_4 + \frac{(k_5K_3[\mathrm{NHEt_3}^+]_\mathrm{e}[(\mathrm{C})]/[\mathrm{NEt_3}]_\mathrm{e})}{1 + K_3[\mathrm{NHEt_3}^+]_\mathrm{e}/[\mathrm{NEt_3}]_\mathrm{e}} \qquad (10)$$

rate equation is identical in form to that observed experimentally for the studies in MeCN and EtCN herein and typified by equation (7) for the reactions in MeCN. However in PhCN the poor electron-releasing ability of this nitrile when a ligand results in only the k_4 pathway being observed. Comparison of the experimentally derived rate laws with equation (10) allows the determination of the values of the equilibrium constants and elementary rate constants observed in the three solvents as shown in Table 4.

The influence that the co-ordinated nitrile has on the basicity of the nitrogen atom adjacent to the metal was probed by spectrophotometrically determining the equilibrium constants for the protonation of $[\mathrm{MoN(NCR)(dppe)_2}]^+$ by acetic acid as defined by equation (11) (λ = 350 nm, [Mo] = 0.2 mmol

$$trans\text{-}[\mathrm{MoN(NCR)(dppe)_2}]^+ + \mathrm{MeCO_2H} \underset{K_4}{\overset{\mathrm{RCN}}{\rightleftharpoons}} trans\text{-}[\mathrm{Mo(NH)(NCR)(dppe)_2}]^{2+}\cdot\mathrm{MeCO_2}^- \qquad (11)$$

$\mathrm{dm^{-3}}$). When R = Me, $K_4 = (2.7 \pm 0.2) \times 10^2\ \mathrm{mol\ dm^{-3}}$; R = Et, $K_4 = (2.0 \pm 0.2) \times 10^2\ \mathrm{mol\ dm^{-3}}$; and R = Ph, $K_4 = (0.6 \pm 0.2) \times 10^2\ \mathrm{mol\ dm^{-3}}$. These equilibrium constants reflect the trend shown in the values of K_3. Thus the basicity of the nitrido-group decreases with *trans*-RCN along the series: R = Me > Et > Ph.

One dichotomy in the mechanism is the order in which the two nitrogen atoms become protonated. All the indications are that the first protonation occurs on the nitrogen atom remote from the metal, since the monoprotonated species (**C**) is capable of unimolecular cleavage to yield the products. Indeed for the benzonitrile system this is the exclusive pathway. It seems unlikely that protonation occurs initially at the nitrogen atom adjacent to the metal and then undergoes intramolecular rearrangement prior to the cleavage step. Furthermore it has recently been demonstrated that protonation of *trans*-$[\mathrm{W(N_2)_2(PMe_3)_4}]$ with HCl yields *trans*-$[\mathrm{W(NNH_3)Cl(PMe_3)_4}]^{2+}$, the hydrazidium residue having been established unambiguously in the solid state by *X*-ray crystallography.[13]

One feature of the collected rate and equilibrium constants shown in Table 4 which is not easy to rationalise concerns the relative rates of nitrogen–nitrogen cleavage of species (**D**). In particular the observation that in the EtCN system the cleavage step associated with the acid-catalysed pathway (k_5) is slower than the analogous step in the MeCN system is surprising since the corresponding rates for the decomposition of (**C**) by the uncatalysed route (k_4) are so similar for the two systems. It seems most likely that the origin of this effect resides both in the change of solvent from one study to the other, and in the steric effect imposed by the 'Mo(dppe)$_2$' core towards binding of the nitrile. The phenyl groups of the diphosphine ligand place constraints on the access of the metal towards nucleophiles. This steric effect must be particularly important when the nucleophile is not linear, as for EtCN, and the congestion is further compounded by the non-linear hydrazidium residue.

Finally, in mechanistic studies in aprotic solvents involving protonation reactions there is always the ambiguity concerning the nature of the 'active' form of the acid. The values of K_3 shown in Table 4 are defined with respect to the $\mathrm{NHEt_3}^+$–$\mathrm{NEt_3}$ pair. If, however, the 'active' acid–base pair were MeCNH^+–MeCN then the corresponding values of K_3 are given by the expression (12), where K_a is the protolytic equilibrium constant

$$K_3^{\mathrm{MeCN}} = K_3^{\mathrm{NEt_3}}/K_\mathrm{a} = 2.88 \times 10^{18}K_\mathrm{a} \qquad (12)$$

defined in equation (6). In the present study we are in a position to establish the 'active' form of the acid from analysis of the derived values of K_3. Since $K_3 = k_3/k_{-3}$, if k_{-3}^{MeCN} is diffusion-controlled then $k_3^{\mathrm{MeCN}} = 3.46 \times 10^{27}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, which is clearly impossible as it is faster than the diffusion-controlled limit.[14] On the other hand if the reaction is specifically catalysed by $\mathrm{NHEt_3}^+$ and $k_{-3}^{\mathrm{NEt_3}}$ is diffusion-controlled then the acceptable value $k_3^{\mathrm{NEt_3}} = 1.2 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ is derived.

The Formation of Ammonia versus *Hydrazine*.—Although ammonia is the exclusive nitrogenous product during the turnover of the enzyme nitrogenase, the stoicheiometric reactions of acid with simple transition-metal dinitrogen complexes can give either ammonia or hydrazine depending on the conditions.[1,3–5] Hydrazido(2−)-complexes have been detected as intermediates on both the hydrazine- and ammonia-forming pathways, but the factors which define whether metal–nitrogen cleavage (hydrazine formation) or nitrogen–nitrogen cleavage (ammonia formation) occurs have not been delineated, primarily because the systems are not analytically clean. For this reason we have preferred to look at the reactivity of alkyl- or aryl-substituted hydrazido(2−)-complexes.

Several studies[1,5,15,16] on complexes containing unsubstituted hydrazido(2−)-ligands have implicated a pathway for ammonia formation in which dinitrogen is also a product, as shown in a generalised form by equation (13). Labelling

$$2\mathrm{M}^{n+} + 2\mathrm{NNH_2}^{2-} + 2\mathrm{H}^+ \longrightarrow 2\mathrm{M}^{(n-1)+} + \mathrm{N_2} + 2\mathrm{NH_3} \qquad (13)$$

experiments have demonstrated that each hydrazido(2−)-species gives either dinitrogen or ammonia, and from a mechanistic point of view protons have clearly been transferred from one nitrogenous residue to another. Furthermore in a study particularly pertinent to the present work, the transfer of a proton from a sacrificial molecule of *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ to $[W(NNH_2)(dppe)_2]$ has been identified as a key step during the electrolysis of the former complex to give ammonia.[15] We must await further mechanistic studies on hydrazido(2 –)-complexes before the factors defining the transfer of protons to and from these species are fully understood, and bear in mind that such pathways are prohibited in the reactions of dialkylhydrazido(2 –)-complexes.

Of particular importance to the nitrogen fixation problem is understanding the factors which favour the cleavage of the nitrogen–nitrogen bond. Recent mechanistic studies[10] on reaction (14), R = Me or Ph, to yield the corresponding

$$[Mo(NNRPh)_2(S_2CNEt_2)_2] + 2HCl \xrightarrow{thf} [Mo(NNRPh)Cl_2(S_2CNEt_2)_2] + PhRNNH_2 \quad (14)$$

organohydrazine have demonstrated the intermediacy of $[Mo(NHNHRPh)(NNRPh)(S_2CNEt_2)_2]^{2+}$. In the present study we have demonstrated that an analogous species, $[Mo\{NH\overline{NH(CH_2)_4C}H_2\}(NCR)(dppe)_2]^{2+}$ (**D**), is also an intermediate but this time on a pathway that results in nitrogen–nitrogen cleavage. Although all the factors which discriminate between ammonia and hydrazine formation have yet to be defined it is clear that arguments based on the extent or position of protonation of the hydrazido(2 –)-residue are not sufficient. Rather it would seem that the ability of the metal to multiple bond to the nitrogenous residue plays a dominant role in defining the position of cleavage.

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References

1 R. A. Henderson, G. J. Leigh, and C. J. Pickett, *Adv. Inorg. Chem. Radiochem.*, 1983, **27**, 197 and refs. therein.
2 R. N. F. Thorneley, R. R. Eady, and D. J. Lowe, *Nature* (*London*), 1978, **272**, 557.
3 S. N. Anderson, M. E. Fakley, R. L. Richards, and J. Chatt, *J. Chem. Soc., Dalton Trans.*, 1981, 1973.
4 J. Chatt, A. J. Pearman, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1977, 1852.
5 J. A. Baumann, G. E. Bossard, T. A. George, D. B. Howell, L. M. Koczon, R. K. Lester, and C. M. Noddings, *Inorg. Chem.*, 1985, **24**, 3568.
6 G. E. Bossard, T. A. George, D. B. Howell, L. M. Koczon, and R. K. Lester, *Inorg. Chem.*, 1983, **22**, 1968.
7 W. Hussain, G. J. Leigh, and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 1982, 747.
8 R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1982, 917.
9 J. Chatt, W. Hussain, G. J. Leigh, and F. P. Terreros, *J. Chem. Soc., Dalton Trans.*, 1980, 1408.
10 J. R. Dilworth, R. A. Henderson, P. Dahlstrom, T. Nicholson, and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1987, 529.
11 J. Chatt and J. R. Dilworth, *J. Indian Chem. Soc.*, 1977, **54**, 13.
12 J. F. Coetzee, *Prog. Phys. Org. Chem.*, 1967, **4**, 45.
13 A. Galindo, A. Hills, D. L. Hughes, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1987, 1815.
14 R. P. Bell, 'The Proton in Chemistry,' 2nd edn., Chapman and Hall, London, 1973, ch. 7.
15 C. J. Pickett and J. Talarmin, *Nature* (*London*), 1985, **317**, 652.
16 I. A. Latham and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1986, 399.

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