Mechanisms of Reactions of Bases with *trans*-[Mo(NNH$_2$)X(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$ (X = F, Br, or *p*-MeC$_6$H$_4$SO$_3$)

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The mechanisms of the reactions between *trans*-[Mo(NNH$_2$)X(dppe)$_2$]$^+$ (X = F, Br, or *p*-MeC$_6$H$_4$SO$_3$; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) and the bases NEt$_3$ and MeO$^-$ under an atmosphere of dinitrogen, to give *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] have been investigated in both methanol and tetrahydrofuran. Initial deprotonation of the hydrazido(2−)-ligand generates *trans*-[Mo(NNH)X(dppe)$_2$] and the subsequent pathway adopted is determined by the relative labilities of X and the acid strength of the hydrazido(3−)-ligand. Rapid deprotonation of the hydrazido(3−)-complex (X = F or Br) yields *trans*-[Mo(N$_2$)X(dppe)$_2$]$^-$ which loses halide in the rate-limiting step to generate [Mo(N$_2$)(dppe)$_2$]. Subsequent attack by dinitrogen in solution yields the product. However, when X = *p*-MeC$_6$H$_4$SO$_3$, rapid loss of this ligand occurs from the hydrazido(3−)-complex, to generate, after attack by a molecule of solvent (S) the species *trans*-[Mo(NNH)S(dppe)$_2$]$^+$. Pathways leading to the product involving either rate-limiting deprotonation or exchange of the co-ordinated solvent for dinitrogen prior to deprotonation have been established, and the factors influencing the choice of pathway are discussed.

Previous studies on the mechanisms of formation of *trans*-[M(NNH$_2$)X(dppe)$_2$]$^+$ [M = Mo or W, X = Br or HSO$_4$, dppe = 1,2-bis(diphenylphosphino)ethane] from the reactions of HX with *trans*-[M(N$_2$)$_2$(dppe)$_2$] in tetrahydrofuran (thf) as shown in equation (1) have allowed only a qualitative determination of the base strengths of the dinitrogen ligand.

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] + 2\,HX \longrightarrow \textit{trans}\text{-}[M(NNH_2)X(dppe)_2]^+ + X^- + N_2 \quad (1)$$

Determination of the base strengths of the co-ordinated dinitrogen in these systems is precluded either by the lack of quantitative information on acid strengths in thf,[1,2] or (in the one study in methanol) the relative simplicity of the kinetics.[3]

Described herein are mechanistic studies on the reactions of *trans*-[Mo(NNH$_2$)X(dppe)$_2$]$^+$ with base (B) (X = F, B = MeO$^-$; X = Br or *p*-MeC$_6$H$_4$SO$_3$, B = NEt$_3$ or MeO$^-$) to give *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] as shown in equation (2). The absence of studies on the analogous chloro-complex is because the reaction of HCl with *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] yields [MoH$_2$Cl$_2$(dppe)$_2$] exclusively.[1,4]

$$\textit{trans}\text{-}[Mo(NNH_2)X(dppe)_2]^+ + 2\,B + N_2 \longrightarrow \textit{trans}\text{-}[Mo(N_2)_2(dppe)_2] + 2\,HB^+ + X^- \quad (2)$$

These studies demonstrate the several pathways by which the reaction shown in equation (2) is accomplished in both the protic solvent methanol and the aprotic solvent thf.

Results and Discussion

The complexes used in these studies, *trans*-[Mo(NNH$_2$)X(dppe)$_2$]$^+$ (X = F,[4] Br,[4] or *p*-MeC$_6$H$_4$SO$_3$[5]) and *trans*-[Mo(NNH$_2$)(Pr^{n}CN)(dppe)$_2$][HSO$_4$]$_2$,[6] were prepared by the methods described in the literature, and their analytical characterisation is shown in Table 1.

It is most convenient to discuss the various reactions and the corresponding mechanisms for each complex separately. At the end of the paper we will discuss the factors which influence the choice of pathway adopted.

Reactions of trans-[Mo(NNH$_2$)Br(dppe)$_2$]$^+$ (A; X = Br) *in Tetrahydrofuran.*—The reaction of (A; X = Br) with NEt$_3$ in thf occurs in two phases: an initial rapid absorbance jump [which is complete within the dead-time of the stopped-flow spectrophotometer (3.3 ms)], to generate an intermediate which reacts relatively slowly with base to yield the product, *trans*-[Mo(N$_2$)$_2$(dppe)$_2$]. This type of absorbance–time behaviour will recur in this paper and so it will be referred to as 'type 1 behaviour' for convenience.

Table 1. Analytical[a] characterisation of complexes

Compound	Analysis (%) C	H	N
trans-[Mo(NNH$_2$)Br(dppe)$_2$]Br·CH$_2$Cl$_2$	54.9 (54.4)	4.4 (4.4)	1.6 (2.3)
trans-[Mo(NNH$_2$)F(dppe)$_2$]BF$_4$	61.0 (60.7)	4.8 (4.9)	2.2 (2.7)
trans-[Mo(NNH$_2$)(*p*-MeC$_6$H$_4$SO$_3$)(dppe)$_2$][*p*-MeC$_6$H$_4$SO$_3$]	62.8 (62.7)	5.2 (5.1)	2.1 (2.2)
trans-[Mo(NNH$_2$)(Pr^{n}CN)(dppe)$_2$][HSO$_4$]$_2$	56.8 (56.8)	4.9 (5.0)	3.5 (3.6)
trans-[Mo(N$_2$)$_2$(dppe)$_2$][b]	65.7 (65.8)	5.1 (5.1)	5.9 (5.9)

[a] Calculated values in parentheses. [b] Isolated from the reaction of *trans*-[Mo(NNH$_2$)Br(dppe)$_2$]Br with NEt$_3$ in methanol.

Table 2. Kinetic data for the reactions of *trans*-[Mo(NNH$_2$)Br(dppe)$_2$]Br with base (NEt$_3$ or MeO$^-$) in thf or MeOH (T = 25 °C, λ = 370 nm, I = 0.1 mol dm^{-3} [NBu$_4$]BF$_4$)

Solvent	Base	[Base]/ mmol dm^{-3} [a]	[NEt$_3$H$^+$]/ mmol dm^{-3}	$k_{obs.}$/s^{-1}
thf	NEt$_3$	1.0		2.8
		2.0		5.8
		5.0		12.1
		10.0		17.3
		15.0		20.7
		20.0		25.1
		30.0		30.4
		10.0	0.50	4.3
			1.00	1.7
			2.50	0.8
			5.00	0.7
			7.00	0.4
			10.00	0.4
		20.0	0.25	14.6
			0.50	8.7
			1.00	5.7
			2.50	2.3
			5.00	1.3
			10.00	0.8
thf		40.0	0.25	25.2
			0.50	18.7
			1.00	12.3
			2.50	6.4
			5.00	3.1
			10.00	1.6
		40.0 [b]	10.00	1.5
		40.0 [c]	10.00	1.3
		10.0 [d]	1.00	1.8
		20.0	1.00	5.5
		40.0	1.00	12.1
		10.0 [e]		19.3
		10.0 [f]		20.2
		10.0 [g]		18.6
MeOH	MeO$^-$	0.25		19.1
		0.50		54.0
		1.00		121.4
		2.00		221.0
MeOH	NEt$_3$	0.40		9.8
		0.60		16.8
		1.00		20.0
		1.50		42.1
		2.00		58.9
		2.50		70.4
		3.00		91.1
		3.50		108.6
		4.00		116.3
		5.00		151.8
		0.50 [e]		14.8
		0.50 [f]		15.2
		0.50 [g]		14.5
		2.00	0.31	38.5
			0.63	31.1
			1.25	18.5
			2.50	10.9
			5.00	4.9
			10.00	2.0
		3.00	0.31	41.7
			0.63	32.7
			1.25	19.9
			2.50	13.1
			5.00	6.1
			10.00	2.8
MeOH	NEt$_3$	0.40	0.31	94.5
			0.63	75.1
			1.25	42.3
			2.50	25.5
			5.00	12.0
			10.00	5.8
		20.00	1.00	270.0
			2.00	157.6
			3.00	110.5
			4.00	80.5
			6.00	55.2
			8.00	39.5
			10.00	29.1
			12.00	25.2

[a] [Mo] = 1.0 × 10^{-4} mol dm^{-3}, unless otherwise stated. [b] [Mo] = 2.0 × 10^{-4} mol dm^{-3}. [c] [Mo] = 0.5 × 10^{-4} mol dm^{-3}. [d] Studies using *trans*-[Mo(NN^{2}H$_2$)Br(dppe)$_2$]$^+$ with NEt$_3$^{2}H$^+$. [e] [NBu$^n_4$Br] = 0.5 mmol dm^{-3}. [f] [NBu$^n_4$Br] = 2.0 mmol dm^{-3}. [g] [NBu$^n_4$Br] = 10.0 mmol dm^{-3}.

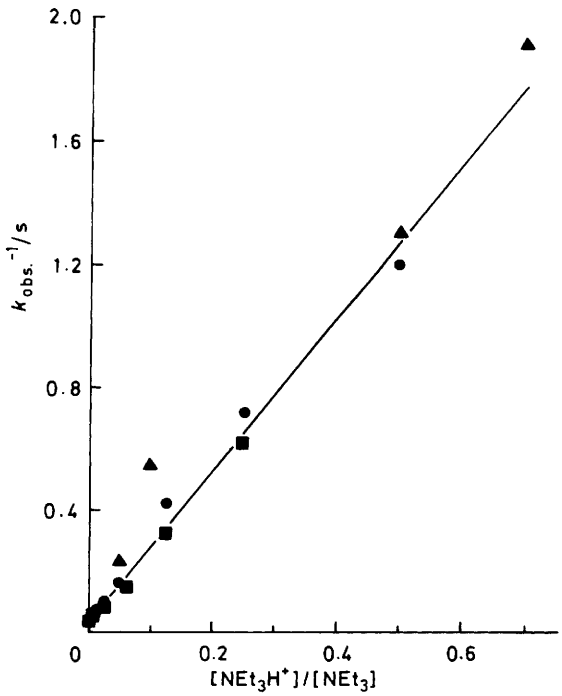


Figure 1. Graph of $k_{obs.}^{-1}$ against [NEt$_3$H$^+$]/[NEt$_3$] for the reaction of *trans*-[Mo(NNH$_2$)Br(dppe)$_2$]$^+$ in thf: [NEt$_3$] = 10.0 (▲), 20.0 (●), and 40.0 mmol dm^{-3} (■)

The kinetics of the slower phase exhibits a first-order dependence on the concentration of complex, and a complicated dependence on the concentration of NEt$_3$. At low concentrations of NEt$_3$ the reaction is first order in [NEt$_3$], but at high concentrations of NEt$_3$ the reaction is independent of the base as shown by the data in Table 2. It is important to stress at this point the necessity of strict anaerobic conditions for these studies. Oxygen damage to the complex in solution gives rise to anomalously fast reactions.

The reaction is inhibited by NEt$_3$H$^+$ in the manner described by the rate law shown in equation (3) and illustrated in Figure 1.

$$k_{obs.} = \frac{4.0(\pm 0.2) \times 10^{-1}([NEt_3]/[NEt_3H^+])}{1 + 8.1(\pm 0.5) \times 10^{-3}([NEt_3]/[NEt_3H^+])} \quad (3)$$

This rate law is applicable both to the studies using NEt_3 alone and the studies in the presence of an excess of $[NEt_3H]BPh_4$. This permits a determination of the stoicheiometry of the detected intermediate. In the studies with NEt_3 alone if it is assumed that the intermediate is *trans*-$[Mo(NNH)Br(dppe)_2]$ (**B**; X = Br), then $[NEt_3H^+] = [(A)]$ and $[NEt_3]_{free} = [NEt_3] - [(A)]$. The agreement of these data with those obtained in the presence of an excess of $[NEt_3H]BPh_4$ represents good evidence that the detected intermediate contains the hydrazido(3−)-residue. The visible absorption spectrum of (**B**; X = Br) is shown in Figure 2.

The rate of the reaction between (**A**; X = Br) and NEt_3 is unaffected by the presence of an excess of $[NBu_4]Br$, or by deuterium labelling in either (**A**) or $NEt_3{}^2H^+$. Therefore it is proposed that the mechanism of the reaction is as shown in Scheme 1 involving the initial rapid (and extensive) deprotonation of (**A**) to generate the spectrophotometrically detected hydrazido(3−)-complex (**B**). Subsequent rapid deprotonation of (**B**) by NEt_3 yields *trans*-$[Mo(N_2)Br(dppe)_2]^-$ (**C**; X = Br). Rate-limiting loss of bromide generates the five-co-ordinate, 16-electron species $[Mo(N_2)(dppe)_2]$ (**D**), which rapidly binds dinitrogen present in solution to yield the product, *trans*-$[Mo(N_2)_2(dppe)_2]$ (**E**). Assuming that the equilibrium between species (**B**) and (**C**) is established rapidly, relative to the rate of

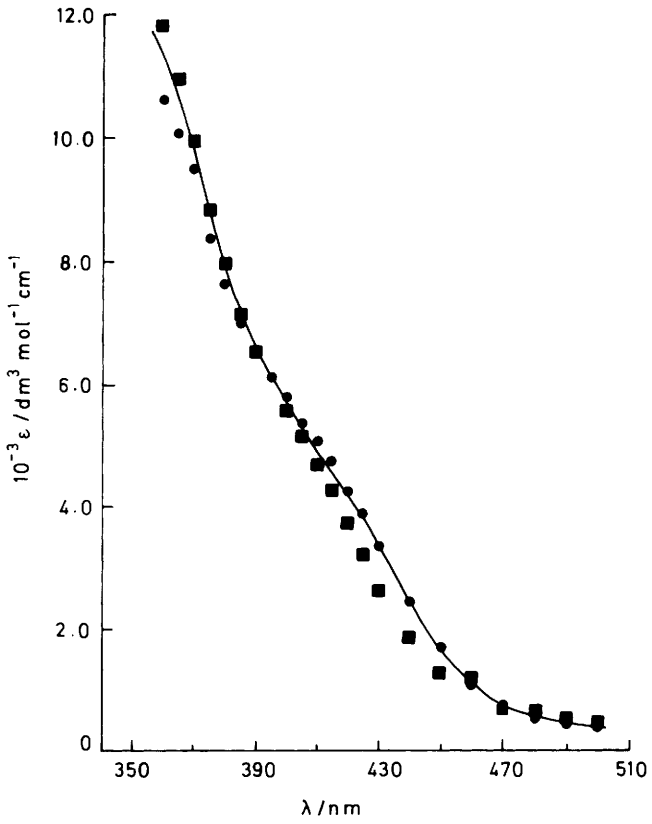


Figure 2. Visible absorption spectra of *trans*-$[Mo(NNH)Br(dppe)_2]$ detected in the reaction of *trans*-$[Mo(NNH_2)Br(dppe)_2]^+$ with NEt_3 in thf (■) and with NaOMe in MeOH (●)

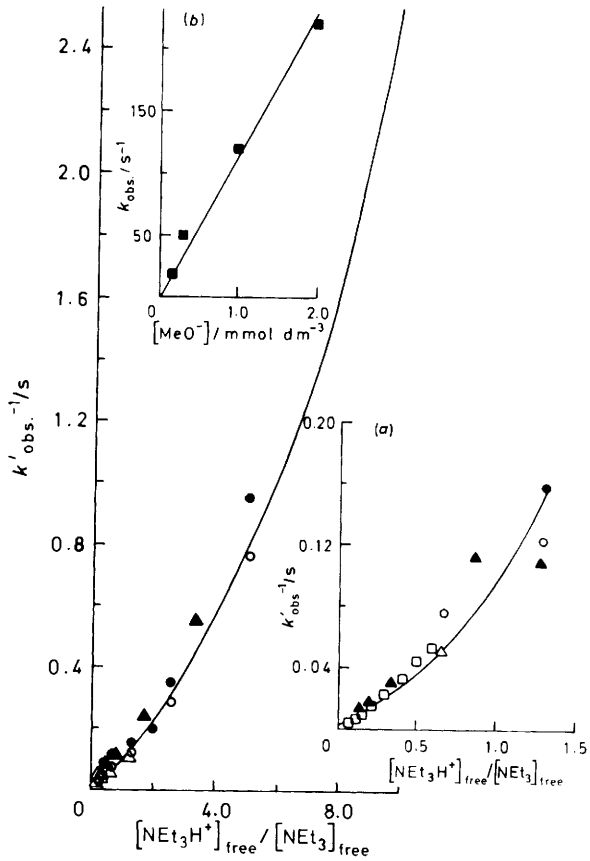
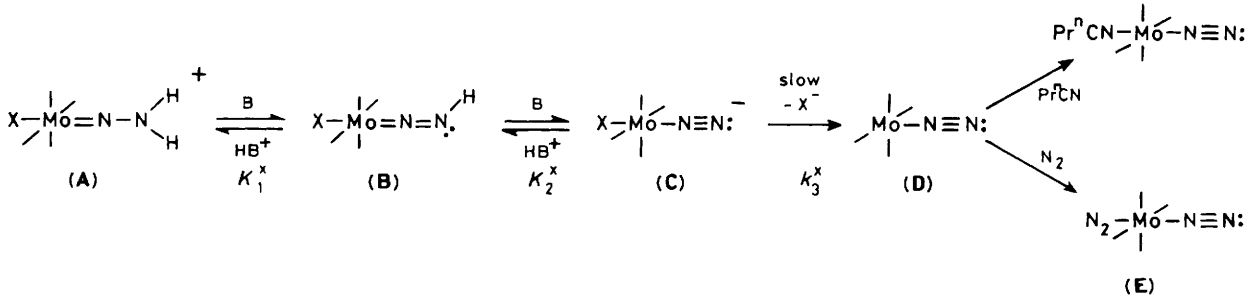


Figure 3. Graph of $k'^{-1}_{obs.}$ against $[NEt_3H^+]_{free}/[NEt_3]_{free}$ for the reaction of *trans*-$[Mo(NNH_2)Br(dppe)_2]^+$ in MeOH: $[NEt_3]$ = various with no added NEt_3H^+ (●), $[NEt_3]$ = 2.0 (▲), 3.0 (○), 4.0 (△), and 20.0 mmol dm^{-3} (□). Insert (*a*), expanded detail (near the origin) of the main graph. Insert (*b*), kinetic data for the reaction of *trans*-$[Mo(NNH_2)Br(dppe)_2]^+$ with MeO^- in MeOH



Scheme 1. Mechanism for the reactions of *trans*-$[Mo(NNH_2)X(dppe)_2]^+$ (X = F or Br) with base (B) in methanol or thf (phosphine ligands omitted)

loss of bromide, the derived rate law for the formation of (**E**) from (**B**) is as shown in equation (4).

$$k_{obs.} = \frac{k_3^{Br}K_2^{Br}([NEt_3]/[NEt_3H^+])}{1 + K_2^{Br}([NEt_3]/[NEt_3H^+])} \quad (4)$$

Comparison of equations (3) and (4) results in $k_3^{Br} = 50.0(\pm 0.2)\ s^{-1}$, and $K_2^{Br} = 8.1(\pm 0.5) \times 10^{-3}$.

Although this study does not allow a direct measurement of the rate of deprotonation of (**A**; X = Br) or the value of K_1^{Br}, limits of these values can be obtained giving $k_1^{Br} > 1 \times 10^6$ $dm^3\ mol^{-1}\ s^{-1}$, and $K_1^{Br} > 1.8 \times 10^2$. The value of k_1^{Br} probably represents a diffusion-controlled (or close to it) deprotonation. This is consistent with the studies on the deprotonation of *trans*-$[M(NNH_2)(Pr^nCN)(dppe)_2][HSO_4]_2$ (M = Mo or W) by NEt_3 in thf as shown in equation (5).

$$trans\text{-}[M(NNH_2)(Pr^nCN)(dppe)_2]^{2+} + 2\ NEt_3 \longrightarrow trans\text{-}[M(N_2)(Pr^nCN)(dppe)_2] + 2\ NEt_3H^+ \quad (5)$$

This simple deprotonation reaction is complete within the dead-time of the stopped-flow apparatus, $[NEt_3] = 0.5$ mmol dm^{-3}, demonstrating that both deprotonations of *trans*-$[M(NNH_2)(Pr^nCN)(dppe)_2]^{2+}$ occur at a rate in excess of $1 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$.

It has been possible to demonstrate that the reaction between (**A**; X = Br) and NEt_3 in thf proceeds *via* the 16-electron species (**D**). In the presence of a large excess of Pr^nCN, under either an atmosphere of dinitrogen or argon, *trans*-$[Mo(N_2)(Pr^nCN)(dppe)_2]$ is the exclusive product as detected by solution i.r. and ^{31}P n.m.r. spectroscopy. This product is formed within one minute of mixing (**A**; X = Br) and a mixture of NEt_3 and Pr^nCN, and thus is formed by 'trapping' the co-ordinatively unsaturated species (**D**) and not as a consequence of subsequent substitution of a rapidly formed *trans*-$[Mo(N_2)_2(dppe)_2]$. The latter pathway requires rate-limiting dinitrogen loss ($k = 2.8 \times 10^{-4}\ s^{-1}$, $T = 27\ °C$).[7]

Reactions of trans-$[Mo(NNH_2)Br(dppe)_2]^+$ (**A**; X = Br) *in Methanol*.—Despite the fact that *trans*-$[Mo(N_2)_2(dppe)_2]$ (**E**) is insoluble in methanol it has been possible to study the kinetics of reaction (2) in this solvent because the rate of this reaction is much faster than the rate of precipitation of (**E**).

The reaction of (**A**; X = Br) with NaOMe in methanol shows 'type 1 behaviour'. The visible absorption spectrum of the intermediate detected is essentially identical to that observed with NEt_3 in thf (Figure 2) strongly indicating that here too the intermediate is (**B**; X = Br). The kinetics of the subsequent decomposition of the intermediate to form (**E**) exhibit a first-order dependence on the concentrations of both (**B**; X = Br) and MeO^- as shown in Table 2 and Figure 3 [insert (*b*)]. The rate law is that defined by equation (6) where the concentration of MeO^- has been corrected for the initial rapid conversion of (**A**) to (**B**).

$$k_{obs.} = 1.2(\pm 0.1) \times 10^5[MeO^-]_{free} \quad (6)$$

This rate law is consistent with the mechanism shown in Scheme 1. Assuming that the equilibrium between (**B**) and (**C**) is established rapidly, relative to the slow bromide dissociation, then the rate law shown in equation (7) is derived.

$$k_{obs.} = \frac{k_3^{Br}K_2^{Br}([MeO^-]/[MeOH])}{1 + K_2^{Br}([MeO^-]/[MeOH])} \quad (7)$$

Under the conditions of the experiment $K_2^{Br}[MeO^-] > [MeOH]$, and using [MeOH] = 24.8 mol dm^{-3}, then $k_3^{Br}K_2^{Br} = 2.9(\pm 0.3) \times 10^6\ s^{-1}$.

With the studies of NEt_3 in methanol the behaviour is more complicated. Upon mixing the solutions of complex and NEt_3 there is a small absorbance jump, complete within the dead-time of the stopped-flow apparatus, followed by the relatively slow reaction to yield the product, *trans*-$[Mo(N_2)_2(dppe)_2]$ (**E**). The kinetics of this reaction exhibit a first-order dependence on the concentration of (**A**) but quantitative analysis of the data for the dependence on the concentration of base (Table 2) is complicated by the protolytic equilibrium shown in equation (8).

$$NEt_3 + MeOH \underset{}{\overset{K_B}{\rightleftharpoons}} NEt_3H^+ + MeO^- \quad (8)$$

Using the value of $K_B = 1.26 \times 10^{-6}$, calculated from the difference in $pK_a^{MeOH} = 16.6$[8] and $pK_a^{NEt_3H^+} = 10.7$,[9] to determine the equilibrium concentrations of methoxide by equation (9), it can be seen that the observed rate constants in the presence of NEt_3 are too large to be attributable entirely to the methoxide dependence described by equation (6), but rather that the reaction is subject to general base catalysis.

$$K_B = \frac{([NEt_3H^+] + [MeO^-]_{free})[MeO^-]_{free}}{([NEt_3] - [MeO^-]_{free})[MeOH]} \quad (9)$$

After correcting the observed rate constant for the methoxide-dependent pathway ($k'_{obs.}$) the data can be fitted, by an iterative method to equation (10), as shown in Figure 3 and insert (*a*).

$$k'_{obs.} = \frac{67.1(\pm 0.2)([NEt_3]_{free}/[NEt_3H^+]_{free})^2}{1 + 7.80(\pm 0.5)([NEt_3]_{free}/[NEt_3H^+]_{free}) + 0.34(\pm 0.04)([NEt_3]_{free}/[NEt_3H^+]_{free})^2} \quad (10)$$

This rate law is consistent with the mechanism shown in Scheme 1 but with the weaker base, NEt_3, deprotonation of both (**A**) and (**B**) is incomplete. The derived rate law under such conditions is shown in equation (11).

$$k'_{obs.} = \frac{k_3^{Br}K_1^{Br}K_2^{Br}([NEt_3]/[NEt_3H^+])^2}{1 + K_1^{Br}([NEt_3]/[NEt_3H^+]) + K_1^{Br}K_2^{Br}([NEt_3]/[NEt_3H^+])^2} \quad (11)$$

Comparison of equations (10) and (11) shows that $K_1^{Br} = 7.8(\pm 0.5)$, $K_2^{Br} = 4.3(\pm 0.5) \times 10^{-2}$, and $k_3^{Br} = 200(\pm 50)\ s^{-1}$.

The initial small absorbance jump observed in the reactions of (**A**; X = Br) with NEt_3 in methanol is attributable to the relatively low concentration of MeO^- present which rapidly deprotonates (**A**) to form (**B**). Since the reaction does not proceed exclusively *via* the methoxide-dependent route this indicates that the rate of perturbation of the equilibrium described by equation (8) is unable to keep up with the deprotonation rate of (**A**) by methoxide. This conclusion is consistent with the calculated rate of deprotonation of MeOH by NEt_3 (k_b). Since $K_B = 1.26 \times 10^{-6}$ and assuming diffusion-controlled deprotonation of NEt_3H^+ by MeO^- (k_{-b}), the value of $k_b = ca.\ 1 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$ can be calculated, which is at least a hundred times slower than the estimated rate of deprotonation of (**A**; X = Br) by MeO^-.

Reactions of trans-$[Mo(NNH_2)F(dppe)_2]^+$ (**A**; X = F) *in Methanol*.—It was not possible to study the reaction of (**A**; X = F) with NEt_3 in thf because of oxygen damage problems over the long times required to study the reaction. Furthermore in methanol with NEt_3, precipitation of the product, *trans*-$[Mo(N_2)_2(dppe)_2]$ (**E**), complicates the kinetics. However the

Table 3. Kinetic data for the reaction between *trans*-[Mo(NNH$_2$)F(dppe)$_2$]BF$_4$ and NaOMe in methanol (T = 25.0 °C, λ = 420 nm, I = 0.2 mol dm^{-3} [NBu$_4$]BF$_4$)

[Mo]/mmol dm^{-3}	[MeO$^-$]/mmol dm^{-3}	$k_{obs.}$/s^{-1}
0.05	5.0	0.27
	10.0	0.72
	20.0	0.88
	30.0	0.96
	40.0	1.70
	50.0	1.90
	80.0	2.60
	100.0	3.10
0.025	20.0	0.85
0.10	20.0	0.90

Table 4. Tabulation of pK_a values of nitrogenous residues on the 'Mo(dppe)$_2$' core

Residue	*trans* X	pK_a	Comments
=N–N$^{H}_{H}$	Br	9.8	
=N–N$^{H}_{H}$	F	≤11	Assuming >99% deprotonation by MeO$^-$ when [MeO$^-$] = 5 mmol dm^{-3}
=N=N^{H}	Br	12.1 (12.4)	Calculated from studies with NaOMe, using k_3^{Br} = 200 s^{-1}, measured with NEt$_3$
=N=N^{H}	F	14.2	
=NH	Cl, Br, or I	≤10	*
=NH	F	12.7	*

* R. A. Henderson, G. Davies, J. R. Dilworth, and R. N. F. Thorneley, *J. Chem. Soc., Dalton Trans.*, 1981, 40.

reaction between (**A**; X = F) and NaOMe in methanol was sufficiently rapid to be studied.

The reaction of (**A**; X = F) with NaOMe in methanol exhibits 'type 1 behaviour,' with the presumed intermediacy of *trans*-[Mo(NNH)F(dppe)$_2$] (**B**; X = F). The kinetics of the formation of (**E**) from the intermediate (**B**; X = F) exhibit a first-order dependence on the concentration of (**B**) and a complicated dependence on the concentration of MeO$^-$ (Table 3). At low concentrations of MeO$^-$ the reaction rate exhibits a first-order dependence on the concentration of MeO$^-$, but at higher concentrations the reaction rate is independent of the base concentration. The dependence of the reaction rate on the concentration of MeO$^-$ is described by equation (12), and illustrated in Figure 4.

$$k_{obs.} = \frac{66.1(\pm 0.4)[MeO^-]_{free}}{1 + 10.0(\pm 0.5)[MeO^-]_{free}} \quad (12)$$

Assuming that the pathway shown in Scheme 1 is adopted, the predicted rate law is as shown by equation (7). Comparison of equations (7) and (12) shows that k_3^F = 6.6(±0.4) s^{-1} and K_2^F = 248.0(±5.0).

The derived pK_a values of *trans*-[Mo(NNH$_2$)X(dppe)$_2$]$^+$ and *trans*-[Mo(NNH)X(dppe)$_2$] (X = F or Br) are summarised in Table 4.

Reactions of trans-[Mo(NNH$_2$)(*p*-MeC$_6$H$_4$SO$_3$)(dppe)$_2$]$^+$ (**A**; X = *p*-MeC$_6$H$_4$SO$_3$).—The formation of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (**E**) from the reaction of base with (**A**; X = *p*-MeC$_6$H$_4$SO$_3$) occurs by a different pathway to that already observed for (**A**; X = F or Br), and this is purely a consequence of the greater lability of the *p*-MeC$_6$H$_4$SO$_3^-$ group.

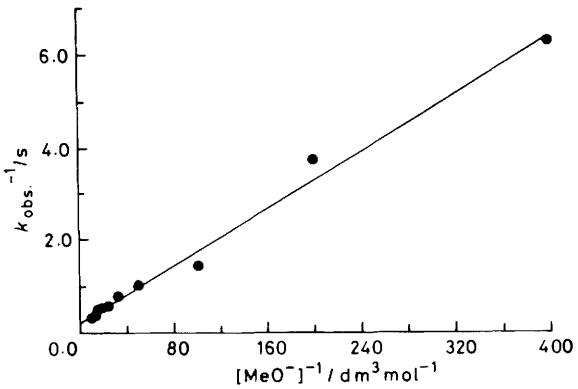


Figure 4. Graph of $k_{obs.}^{-1}$ against [MeO$^-$]$^{-1}$ for the reaction of *trans*-[Mo(NNH$_2$)F(dppe)$_2$]$^+$ with NaOMe in MeOH

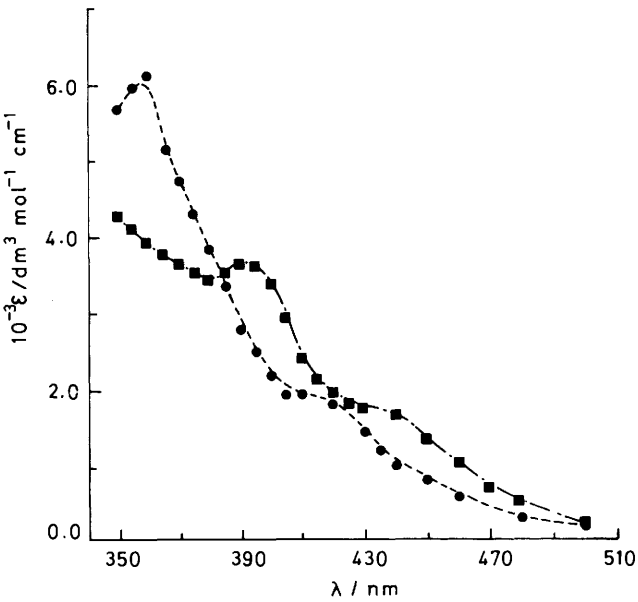


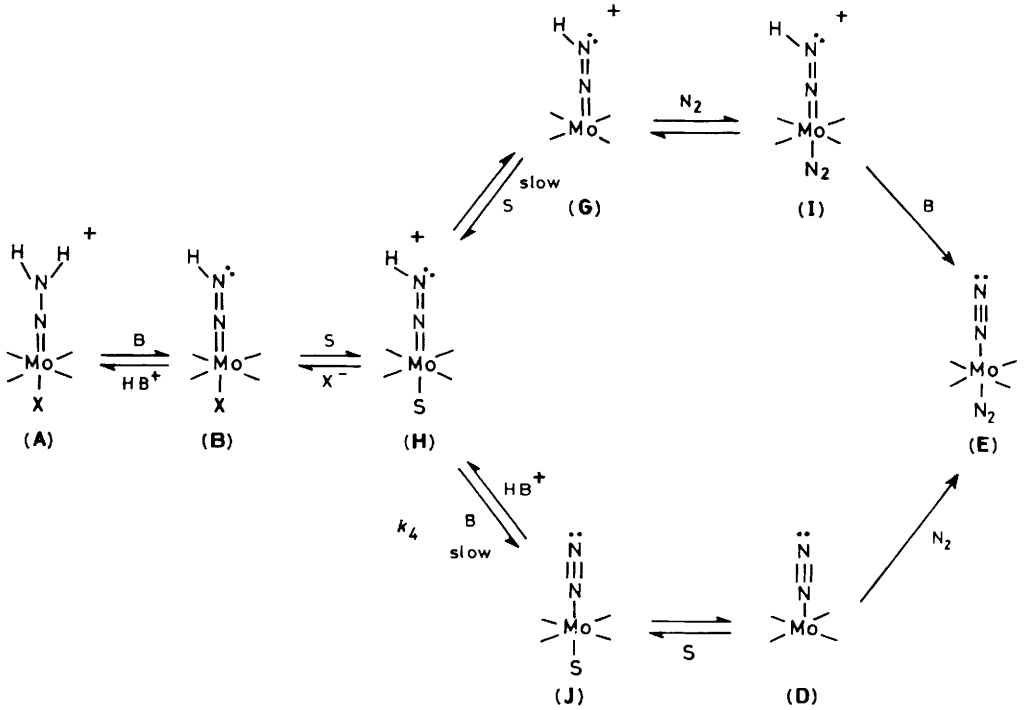
Figure 5. Visible absorption spectra of *trans*-[Mo(NNH)(thf)(dppe)$_2$]$^+$ (●) and *trans*-[Mo(NNH)(MeO)(dppe)$_2$] (■), generated in the reactions of *trans*-[Mo(NNH$_2$)(*p*-MeC$_6$H$_4$SO$_3$)(dppe)$_2$]$^+$ with base in the appropriate solvent

In both methanol and thf the reactions of base with (**A**; X = *p*-MeC$_6$H$_4$SO$_3$) exhibit 'type 1 behaviour'. However, in contrast to the studies with the bromo- and fluoro-complexes the spectra of the intermediates observed immediately upon mixing the two reagents (Figure 5) indicate that substitution of *p*-MeC$_6$H$_4$SO$_3$ for a molecule of solvent (S) has occurred, within the dead-time of the stopped-flow apparatus, thus the intermediate detected here is *trans*-[Mo(NNH)S(dppe)$_2$]$^+$ (**H**).†

In thf the kinetics for the formation of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (**E**) from (**H**) exhibit a first-order dependence on both the concentration of (**H**) and on the concentration of NEt$_3$ as described by equation (13), where a = 9.3(±0.2) × 10^4 dm^3 mol^{-1} s^{-1}.

$$k_{obs.} = a[NEt_3]_{free} \quad (13)$$

† In the species *trans*-[Mo(NNH)S(dppe)$_2$]$^+$ (**H**) and *trans*-[Mo(N$_2$)S(dppe)$_2$] (**J**) the charges given are for S = thf; those for S = MeO are one unit more negative.



Scheme 2. Mechanisms for the reactions of *trans*-$[Mo(NNH_2)(X)(dppe)_2]^+$ (X = *p*-$MeC_6H_4SO_3$) with base (B) in methanol or thf (phosphine ligands omitted)

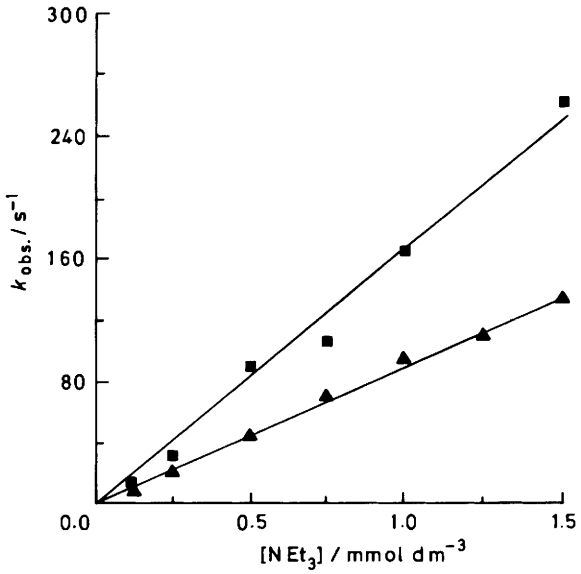


Figure 6. Dependence of the reaction rate on the concentration of NEt_3 for the reaction of *trans*-$[Mo(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ with NEt_3 in thf under an atmosphere (*ca.* 10^5N m^{-2}) of dinitrogen (▲) or carbon monoxide (■)

The kinetics of the reaction is unaffected by the presence of an excess of $[NEt_3H]BPh_4$, or deuterium labelling of the complex. These observations are consistent with the pathway shown in Scheme 2, in which the rapidly formed intermediate, *trans*-$[Mo(NNH)(thf)(dppe)_2]^+$ (**H**; S = thf) undergoes rate-limiting substitution of the co-ordinated solvent molecule by dinitrogen to yield *trans*-$[Mo(NNH)(N_2)(dppe)_2]^+$ (**I**). The strong electron-attracting capability of the dinitrogen ligand renders the hydrazido(3−)-residue sufficiently acidic that it is rapidly deprotonated by NEt_3 to yield the product, *trans*-$[Mo(N_2)_2(dppe)_2]$ (**E**). This mechanism is consistent with the observed sensitivity of the rate for this reaction to the presence of alternative substrates in the system. When the reaction between (**A**; X = *p*-$MeC_6H_4SO_3$) and NEt_3 is performed under carbon monoxide, the kinetics of the reaction shows a first-order dependence on both the concentrations of (**H**) and NEt_3 as described by equation (13), but at an enhanced rate with $a = 1.73(\pm0.3) \times 10^5$ dm^3 mol^{-1} s^{-1} as shown in Figure 6. This increased rate is due to the greater electron-attracting capability of CO over N_2 further increasing the acidity of the diazenido-ligand. A further consequence of this electronic effect of CO is that it renders the *trans*-dinitrogen ligand in the derived *trans*-$[Mo(CO)(N_2)(dppe)_2]$ sufficiently labile that rapid loss of dinitrogen and subsequent attack by CO yields *trans*-$[Mo(CO)_2(dppe)_2]$ (**F**).

In methanol the kinetics of the reaction between (**H**; S = MeO) and MeO^- exhibits a first-order dependence on the concentrations of both (**H**) and MeO^- as described by equation (14). It is proposed that the intermediate in this case is *trans*-$[Mo(NNH)(OMe)(dppe)_2]$ (**H**; S = MeO). The kinetic data are shown in Table 5.

$$k_{obs.} = 8.5(\pm0.3) \times 10^2[MeO^-]_{free} \qquad (14)$$

This reaction exhibits a primary isotope effect with $k_H/k_D = 1.11(\pm0.05)$ as shown in Figure 7 (insert), consistent with rate-limiting deprotonation of (**H**).

Quantitative analysis of the kinetic data for the reaction between (**H**; S = MeO) and NEt_3 is complicated by the protolytic equilibrium shown in equation (8). The concentration of MeO^- generated at each concentration of NEt_3 was calculated using equation (15). This equation is similar to equation (9) except that it makes allowance for the initial deprotonation of (**A**), and the (presumed) deprotonation of co-ordinated methanol necessary to generate the intermediate (**H**; S = MeO).

$$K_B = \frac{(2[(A)] + [NEt_3H^+] + [MeO^-]_{free})[MeO^-]_{free}}{([NEt_3] - 2[(A)] - [MeO^-]_{free})[MeOH]} \qquad (15)$$

Table 5. Kinetic data for the reaction between *trans*-[Mo(NNH$_2$)(*p*-MeC$_6$H$_4$SO$_3$)(dppe)$_2$][*p*-MeC$_6$H$_4$SO$_3$] and base (NEt$_3$ or MeO$^-$) in thf or MeOH (I = 25.0 °C, λ = 400 or 420 nm, I = 0.1 mol dm^{-3} [NBu$_4$]BF$_4$)

Solvent	[Mo] mmol dm^{-3}	Base	[Base] mmol dm^{-3}	[NEt$_3$H$^+$] mmol dm^{-3}	$k_{obs.}$ s^{-1}
thf	0.10	NEt$_3$	0.13[a]		10.4
			0.25		23.1
			0.50		47.0
			0.75		66.4
			1.00		91.2
			1.25		115.7
			1.50		139.6
	0.05		1.00		95.3
	0.20		1.00		90.8
	0.10	NEt$_3$	1.50	0.50	140.0
				1.00	130.3
				2.50	122.3
				5.00	131.0
				10.00	129.2
	0.10		0.13[b]		12.4
			0.25		20.6
			0.50		45.2
			0.75		66.4
			1.00		91.2
			1.25		114.7
			1.50		134.4
	0.10	NEt$_3$	0.13[c]		12.6
			0.25		28.0
			0.50		90.0
			0.75		104.7
			1.00		162.2
			1.50		270.0
MeOH	0.10	MeO$^-$	0.25[a]		0.08
			0.50		0.1
			1.00		0.5
			2.50		1.9
			5.00		4.2
			10.00		8.1
			15.00		14.1
			22.50		18.9
			30.00		25.4
			37.50		29.8
	0.10	MeO$^-$	1.00[b]		0.8
			2.00		1.5
			5.00		4.0
			10.00		8.1
			20.00		14.1
	0.05				14.3
	0.20				14.0
	0.10	MeO$^-$	1.00[c]		0.5
			2.00		2.0
			5.00		4.2
			10.00		8.3
			20.00		16.8
MeOH	0.10	NEt$_3$	5.00[a]		0.4
			10.00		0.8
			20.00		1.5
			30.00		2.3
			40.00		3.1
			50.00		3.5
			100.0		6.1
			25.0	1.25	1.4
				2.50	1.2
				5.00	0.9
				10.00	0.9
MeOH	0.10	NEt$_3$	5.00[b]		0.2
			10.00		0.7

Table 5 (*continued*)

Solvent	[Mo] mmol dm^{-3}	Base	[Base] mmol dm^{-3}	[NEt$_3$H$^+$] mmol dm^{-3}	$k_{obs.}$ s^{-1}
MeOH	0.10	NEt$_3$	20.00		0.8
			30.00		1.3
			50.00		2.4
			100.00		4.2
			5.00[b,c]		0.2
			10.00		0.7
			20.00		0.7
			50.00		2.6
			100.00		4.5

[a] Reactions studied under an atmosphere of dinitrogen. [b] Studies with *trans*-[Mo(NN^{2}H$_2$)(*p*-MeC$_6$H$_4$SO$_3$)(dppe)$_2$]$^+$. [c] Reactions studied under an atmosphere of carbon monoxide.

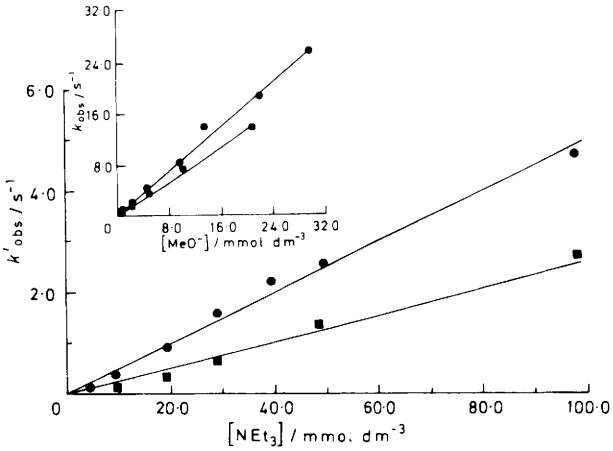


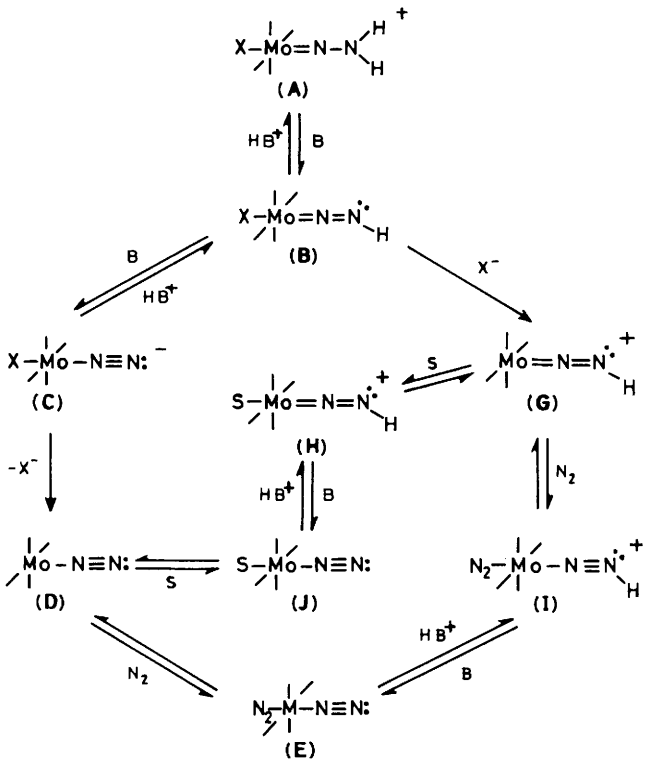
Figure 7. Dependence of the reaction rate on the concentration of MeO$^-$ (insert) and NEt$_3$, for the reactions of *trans*-[Mo(NNH$_2$)(*p*-MeC$_6$H$_4$SO$_3$)(dppe)$_2$]$^+$ (●) and *trans*-[Mo(NN^{2}H$_2$)(*p*-MeC$_6$H$_4$SO$_3$)(dppe)$_2$]$^+$ (■) in methanol

Analysis of the kinetic data shows that this reaction is subject to general base catalysis (Figure 7). By correcting the observed rate constants obtained in the studies with NEt$_3$, for the methoxide-dependent pathway using equation (14) the dependence of the reaction rate on the concentration of NEt$_3$ can be calculated. The only effect that [NEt$_3$H]Cl has on the kinetics in methanol is to perturb the concentration of MeO$^-$ according to equation (15). Thus the NEt$_3$-dependent formation of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] (**E**) from (**H**; S = MeO) is given by equation (16).

$$k'_{obs.} = 50.5(\pm 0.5)[NEt_3]_{free} \quad (16)$$

The NEt$_3$-dependent pathway also shows a primary isotope effect with k_H/k_D = 1.84(±0.12), Figure 7.

The primary isotope effects observed for the reactions of (**A**; X = *p*-MeC$_6$H$_4$SO$_3$) with both NEt$_3$ and MeO$^-$ are consistent with the pathway shown in Scheme 2, involving rate-limiting deprotonation of (**H**) by a base to generate *trans*-[Mo(N$_2$)(OMe)(dppe)$_2$]$^-$ (**J**; S = MeO) prior to the relative rapid loss of MeO$^-$ to form (**D**). Subsequent attack on (**D**) by dinitrogen yields the product (**E**). The second-order rate constants for the deprotonation of (**H**; S = MeO), k_4 = 50.5(±0.5) dm^3 mol^{-1} s^{-1}, base = NEt$_3$; k_4 = 8.5(±0.3) × 10^2 dm^3 mol^{-1} s^{-1}, base = MeO$^-$ are much slower than the diffusion-controlled limit observed in the reactions between conventional acids and



Scheme 3. Summary of the pathways for the reactions of *trans*-$[Mo(NNH_2)X(dppe)_2]^+$ (X = F, Br, or *p*-$MeC_6H_4SO_3$) with base (B) (phosphine ligands omitted)

bases and is probably due to a thermodynamically unfavourable deprotonation in the present reactions.

Conclusions

In conclusion the reaction described by equation (2) has been shown to proceed *via* three different pathways, which are summarised in Scheme 3. The common initial step for all the pathways is the deprotonation of the hydrazido(2−)-complex (**A**) to generate the hydrazido(3−)-species (**B**). The pathway adopted from this point is defined by the relative acidities of the hydrazido(3−)-ligand and the lability of the group X. When X = F or Br, relatively rapid deprotonation of (**B**) to generate the dinitrogen complex (**C**), followed by rate-limiting halide dissociation results in the formation of the product (**E**). Only when this pathway is followed, with rate-limiting dissociation of X, is it possible to determine the pK_a values of the hydrazido(2−)- and hydrazido(3−)-residues as shown in Table 4.

When X = *p*-$MeC_6H_4SO_3$ dissociation of this ligand from (**B**), and attack of solvent generates (**H**). Two further choices now result in the pathway to the product. Substitution of co-ordinated solvent (S = thf) for dinitrogen generates (**I**), this increases the acidity of the hydrazido(3−)-ligand, thus facilitating its subsequent deprotonation to yield the product (**E**). This pathway is characterised by a sensitivity of the reaction rate to the presence of other substrates (*e.g.* CO). Alternatively if dissociation of the solvent molecule is slow (S = MeO) rate-limiting deprotonation of (**H**) is enforced. This pathway is characterised by primary isotope effects, general base catalysis, and an insensitivity of the reaction rate to the presence of other substrates.

As shown in Table 4, despite the relatively limited amount of data, it can be seen that the acidity of the imido-ligand (NH) is more sensitive to perturbations of the 'Mo(dppe)$_2$' site than the hydrazido(2−)- (NNH_2) or hydrazido(3−)- (NNH) residues. Thus for a given change in the *trans* halide (*e.g.* Br to F), the pK_a values of the hydrazido(2−)- and hydrazido(3−)-ligands are affected by, at least, one unit less than the imido-ligand. This is almost certainly only a consequence of the closer proximity of the imido-ligand to the site.

The influence of the solvent (MeOH *versus* thf) on the pathway involving the intermediacy of species (**B**) and (**C**) is only relatively minor, affecting only the values of K_1^X, K_2^X, and k_3^X. However on the pathways involving species (**H**) the effect of the solvent is profound, since the rate of dissociation of a molecule of solvent from (**H**) defines the intimate mechanism of formation of *trans*-$[Mo(N_2)_2(dppe)_2]$.

Experimental

All manipulations in both the preparative and kinetic aspects of this work were routinely performed under an atmosphere of dinitrogen using Schlenk and syringe techniques as appropriate. All solvents were distilled from the appropriate drying agent immediately prior to use.

Kinetic Studies.—All kinetic studies were performed on an Aminco–Morrow stopped-flow spectrophotometer modified for the use of air-sensitive compounds as described earlier.[1] The spectrophotometer was interfaced to a B.B.C. microcomputer *via* an analogue to digital converter, operating at 3 kHz. Computer traces were analysed by standard curve fits to the exponential traces.[10]

For the studies under CO, the reacting solutions were saturated with CO, and the stopped-flow apparatus (*i.e.* behind the drive syringes and surrounding the mixing cell) was flushed with argon.

The kinetics was independent of the monitoring wavelength in the range λ = 350—500 nm for all reactions.

In all studies the ionic strength was maintained at 0.1 mol dm^{-3} with $[NBu^n_4]BF_4$, except in the studies with *trans*-$[Mo(NNH_2)F(dppe)_2]BF_4$ with NaOMe, where the ionic strength was 0.2 mol dm^{-3}.

Reagents.—Triethylamine (B.D.H.) was used as supplied. Sodium methoxide was prepared by the reactions of sodium with methanol, and standardised by titration against standard hydrochloric acid using phenolphthalein as indicator.

For solubility reasons $[NEt_3H]Cl$ was used in the studies in methanol and $[NEt_3H]BPh_4$ in the studies in thf. $[NEt_3H]Cl$ was prepared by the reaction of NEt_3 and anhydrous HCl in thf, and $[NEt_3H]BPh_4$ by the addition of $NaBPh_4$ to $[NEt_3H]Cl$ in methanol, and then removal of NaCl by washing with water. Both compounds were analytically pure.

Product Analyses.—The product of the reaction between *trans*-$[Mo(NNH_2)X(dppe)_2]^+$ (X = F, Br, or *p*-$MeC_6H_4SO_3$) and base under an atmosphere of dinitrogen is *trans*-$[Mo(N_2)_2(dppe)_2]$ as demonstrated by its isolation, followed by analytical (Table 1) and spectroscopic analysis [$\nu(N_2)$ at 1 970 cm^{-1}; ^{31}P n.m.r., δ −75.08 p.p.m. (*versus* trimethyl phosphate, tmp)] and *in situ* solution i.r. spectroscopy.

The product of the reaction between *trans*-$[Mo(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ and NEt_3 in thf under an atmosphere of carbon monoxide is *trans*-$[Mo(CO)_2(dppe)_2]$ as demonstrated by solution i.r. spectroscopy [ν(CO) at 1 825 cm^{-1}].

The product of the reaction between *trans*-$[Mo(NNH_2)Br(dppe)_2]^+$ and NEt_3 in thf, under an atmosphere of dinitrogen, but in the presence of an excess of Pr^nCN is *trans*-$[Mo(N_2)(Pr^nCN)(dppe)_2]$ as demonstrated by solution i.r. spectroscopy [$\nu(N_2)$ at 1 925 cm^{-1}] and ^{31}P n.m.r. spectroscopy (δ −72.42 p.p.m. *versus* tmp).

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References

1 R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1982, 917.
2 R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1984, 2259.
3 R. A. Henderson, *J. Organomet. Chem.*, 1981, **208**, C51.
4 J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 2074.
5 C. J. Pickett, personal communication.
6 J. Chatt, G. J. Leigh, H. Neukomm, C. J. Pickett, and D. R. Stanley, *J. Chem. Soc., Dalton Trans.*, 1980, 121.
7 W. Hussain, G. J. Leigh, H. Mohd-Ali, C. J. Pickett, and D. A. Rankin, *J. Chem. Soc., Dalton Trans.*, 1984, 1703.
8 R. Gut, *Helv. Chim. Acta*, 1964, **47**, 2262.
9 N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, 1932, **54**, 3469.
10 J. H. Espenson, 'Chemical Kinetics and Reaction Mechanisms,' McGraw-Hill, New York, 1979, ch. 2.

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