Mechanism of Ammonia Formation by Reaction of *trans*-[Mo(NH)X(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$ (X = F, Cl, Br, or I) with Base in Methanol

By **Richard A. Henderson, Geoffrey Davies, Jonathan R. Dilworth,** and **Roger N. F. Thorneley,*** A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ

At ambient temperatures in methanol the complexes *trans*-[Mo(NH)X(dppe)$_2$]$^+$ [where X = F, Cl, Br, or I and dppe = 1,2-bis(diphenylphosphino)ethane] are inert to acid, but give ammonia in high yield on treatment with methoxide. An initial rapid deprotonation of the substrate renders the *trans* halide labile and when X = Cl, Br, or I the halide is liberated rapidly ($k > 300$ s^{-1}) to yield a common species which on spectrophotometric evidence is an equilibrium mixture of the contact and solvent-separated ion pairs of [MoN(dppe)$_2$]$^+$ and X$^-$. This cation reacts with methoxide ion ($k = 1.7 \pm 0.4 \times 10^6$ dm^3 mol^{-1} s^{-1}), to yield [MoN(OCH$_3$)(dppe)$_2$] which rapidly abstracts a proton from solvent to give [Mo(NH)(OCH$_3$)(dppe)$_2$]$^+$. When X = F, the same sequence of reactions occurs but dissociation of fluoride from the intermediate [Mo(N)F(dppe)$_2$] is rate-limiting ($k = 1.78$ s^{-1}). The pK_a of *trans*-[Mo(NH)X(dppe)$_2$]$^+$ is very sensitive to the nature of the *trans* ligand and π-bonding influences dominate. [Mo(NH)(OCH$_3$)(dppe)$_2$]$^+$ reacts ($k = 1.57 \times 10^{-4}$ s^{-1} at 25 °C, $\Delta H^\ddagger = 50$ kJ mol^{-1}, $\Delta S^\ddagger = -143$ J K^{-1} mol^{-1}) in basic methanol with rate-limiting phosphine-chelate ring opening to give a product which gave a positive indophenol test for ammonia (70% yield). [Mo(NH)(OCH$_3$)(dppe)$_2$]$^+$ reacts with HX in methanol to form *trans*-[Mo(NH)X(dppe)$_2$]$^+$ with rate-limiting dissociation of methanol ($k_5 > 3.9 \times 10^2$ s^{-1}) formed by rapid protonation of the co-ordinated methoxy-group (pK_a < 1.8).

A SYSTEM which will produce catalytically high yields of ammonia from dinitrogen under ambient conditions has been sought for some time. Previous work [1] has shown that high yields of ammonia can be obtained from sulphuric acid treatment of a methanolic solution of [M(N$_2$)$_2$(PMe$_2$Ph)$_4$] (M = Mo or W). This system is very dependent upon the nature of the acid and phosphine ligands used. It has been suggested [2-4] that after the partial reduction of the dinitrogen molecule there is loss of phosphine followed by cleavage of the nitrogen–nitrogen bond to yield one molecule of ammonia and a nitrido-complex which yields a second molecule of ammonia on further protonation.

We now present a kinetic study of the reaction of methoxide ion with *trans*-[Mo(NH)X(dppe)$_2$]$^+$ [X = F, Cl, Br, or I and dppe = 1,2-bis(diphenylphosphino)ethane] which demonstrates the influence of π bonding involving *trans* ligands and co-ordinated phosphine on the basicity of nitrido- and imido-groups. The proposed mechanism explains why ammonia is surprisingly obtained under basic and not acidic conditions [5] from nitrido-complexes containing bidentate phosphine ligands.

EXPERIMENTAL

Materials.—Methanol used in the kinetic studies was freshly distilled under dinitrogen from magnesium methoxide in an all-glass still.

Lithium methoxide dimethanolate was obtained as a solid from the reaction of lithium metal with methanol, and standardised in methanol by titration with hydrochloric acid using phenolphthalein as indicator.

The complexes *trans*-[Mo(NH)X(dppe)$_2$]X (X = Cl or Br) and [Mo(NH)(OCH$_3$)(dppe)$_2$][BPh$_4$] were prepared by an analogous method to that of Chatt and Dilworth.[6]

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*imido*(*iodo*)-*molybdenum*(IV) *iodide*. Azidobis[1,2-bis(diphenylphosphino-ethane]nitridomolybdenum(IV) (0.5 g) was dissolved in a mixture of reagent grade methanol (10 cm^3) and dichloromethane (10 cm^3) and three drops of aqueous hydriodic acid were added. The solution immediately changed colour to mauve, and after allowing it to stand for 15 min the complex was precipitated by the addition of diethyl ether. This material was subsequently treated three times with hydriodic acid in methanol–dichloromethane to obtain a complex free of starting material. Recrystallisation from dichloromethane–diethyl ether yielded fine mauve needles.

trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*fluoro*(*imido*)-*molybdenum*(IV) *tetrafluoroborate*. Azidobis[1,2-bis(diphenylphosphino)ethane]nitridomolybdenum(IV) (0.5 g) was suspended in reagent grade methanol (20 cm^3) and three drops of aqueous hydrofluoric acid (40% B.D.H. Aristar) were added. There was an immediate reaction to yield an orange solution, to which, after 5 min, tetrafluoroboric acid (three drops) was added to precipitate the complex as an orange-yellow powder. Recrystallisation from dichloromethane–diethyl ether yielded orange needles

Analytical data for the complexes are shown in Table 1. Their conductivity (Λ = 112—120 ohm^{-1} mol^{-1}) establishes them as 1 : 1 electrolytes in methanol rather than seven-co-ordinate complexes.

Kinetic and Equilibrium Constants.—These were measured with either an Aminco–Morrow stopped-flow apparatus [7] or a Unicam SP1800 spectrophotometer.

Ammonia and Hydrazine Determinations.—Ammonia and hydrazine were determined by the standard reactions with indophenol [8] and *p*-dimethylaminobenzaldehyde,[9] respectively. A difference method was employed which involved the addition of known amounts of ammonia and hydrazine to duplicate samples.

Gravimetric Determination of Liberated Phosphine.—The compound *trans*-[Mo(NH)Br(dppe)$_2$]Br (0.092 mmol) was treated with triethylamine (3.84 mmol) in methanol (10 cm^3). The solution was heated to 35 °C and stirred at room temperature for 72 h. The white precipitate formed was removed by filtration, dried, and then weighed to give 1,2-bis(diphenylphosphino)ethane (0.12 mmol, 1.33 equivalents) (identified by a mixed melting point with an authentic sample).

Under the same conditions *trans*-[Mo(NH)Br(dppe)$_2$]Br (0.07 mmol) reacted with lithium methoxide (1.0 mmol) in methanol (10 cm^3) to give 1,2-bis(diphenylphosphino)ethane (0.11 mmol, 1.57 equivalents).

The yield of ammonia was identical (65 ± 1%) for both systems.

RESULTS AND DISCUSSION

The complexes containing the *trans*-bis[1,2-bis(diphenylphosphino)ethane]halido(imido)molybdenum(IV) cations {*trans*-$[Mo(NH)X(dppe)_2]^+$} (where X = F, Cl, Br, or I) are air-stable and dissolve as 1 : 1 electrolytes in anhydrous methanol. The cations exhibit spectral maxima at progressively longer wavelength with concomitant decreasing absorption coefficient, along the series from fluoro- to iodo-complex, as shown in Figure 1. These solutions are spectrally stable for *ca.* 45 min at room temperature in the presence of oxygen.

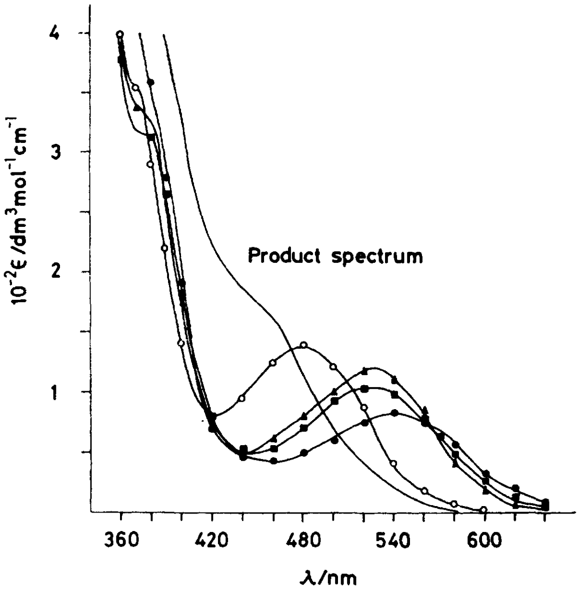


FIGURE 1 Spectra of *trans*-$[Mo(NH)X(dppe)_2]^+$ in methanol, where X = F (○), Cl (▲), Br (■), and I (●). The product spectrum is identical to that of $[Mo(NH)(OCH_3)(dppe)_2][BPh_4]$

TABLE 1

Analytical data of *trans*-$[Mo(NH)X(dppe)_2]^+$ salts

Formula	Analysis (%) [a] C	H	N	$\lambda_{max.}$/nm [b]	$\epsilon_{max.}/dm^3 mol^{-1} cm^{-1}$ [b]
$[Mo(NH)F(dppe)_2][BF_4]\cdot H_2O$	60.1	4.9	1.1	480	137
	(60.5)	(4.9)	(1.3)		
$[Mo(NH)Cl(dppe)_2]Cl\cdot H_2O$	63.1	5.2	1.3	525	120
	(62.7)	(5.1)	(1.4)		
$[Mo(NH)Br(dppe)_2]Br\cdot H_2O$	57.8	4.8	0.9	530	105
	(57.5)	(4.7)	(1.2)		
$[Mo(NH)I(dppe)_2]I\cdot H_2O$	52.8	4.5	1.6	540	83
	(52.9)	(4.3)	(1.2)		

[a] Calculated values are given in parentheses. [b] In methanol.

Stoicheiometry.—In methanol, *trans*-$[Mo(NH)X(dppe)_2]^+$ (X = F, Cl, Br, or I) reacts with one mole equivalent of triethylamine or lithium methoxide to give the common product $[Mo(NH)(OCH_3)(dppe)_2]^+$, Figures 1 and 2.

The complex *trans*-$[Mo(NH)X(dppe)_2]^+$ in dichloromethane exhibits an identical spectrum to that shown in methanol. However, in dichloromethane, addition of an excess of triethylamine resulted in the spectra shown in Figure 3, which are quite different from the spectrum of the product obtained with triethylamine in methanol. Addition of methanol (10% v/v) to the dichloromethane–triethylamine solutions of *trans*-$[Mo(NH)X(dppe)_2]^+$ yielded a single product whose spectrum was identical to that of the product formed in methanol.

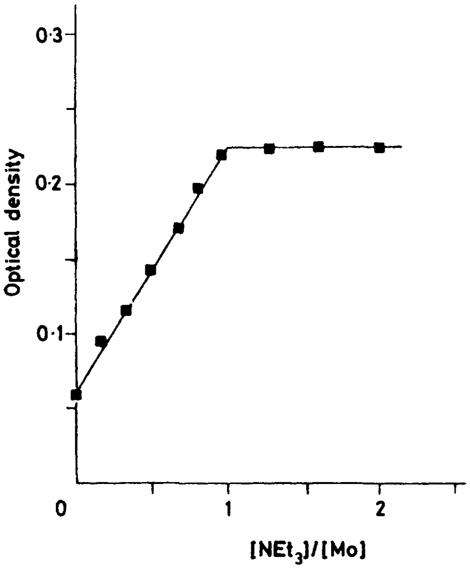


FIGURE 2 Typical spectrophotometric determination of the stoicheiometry of the reaction between triethylamine and $[Mo(NH)Br(dppe)_2]Br$ ([Mo] = 1.27 × 10^{-3} mol dm^{-3}, λ = 434 nm)

Kinetics.—The formation of ammonia from basic methanolic solutions of *trans*-$[Mo(NH)X(dppe)_2]^+$ occurs in two distinct stages. The rapid formation of $[Mo(NH)(OCH_3)(dppe)_2]^+$ which is complete within 1 s is followed by a slow reaction to yield ammonia ($t_{\frac{1}{2}} \sim 60$ min). The kinetics of both stages have been investigated.

The Formation of $[Mo(NH)(OCH_3)(dppe)_2]^+$.—The complex *trans*-$[Mo(NH)X(dppe)_2]^+$ (where X = Cl, Br, or I) (2.8 × 10^{-4} mol dm^{-3}) reacted in methanol with lithium methoxide (1 mmol dm^{-3}) to form $[Mo(NH)(OCH_3)(dppe)_2]^+$ within the time of mixing in the stopped-flow apparatus (3.3 ms). However when triethylamine (1—8 mmol dm^{-3}) was used, two distinct stages were observed, an initial rapid absorbance increase to yield an intermediate (formation complete within 3.3 ms) followed by a relatively low absorbance decrease ($t_{\frac{1}{2}}$ = 1—10 ms) to yield the spectrum of $[Mo(NH)(OCH_3)(dppe)_2]^+$.

TABLE 2

Influence of added halide ions on the spectrum of the five-co-ordinate intermediate [(C) and (D)] measured at λ = 380 nm, 25 °C in methanol

Complex	Concn. complex/ 10^{-4} mol dm^{-3}	Concn. triethylamine/ 10^{-3} mol dm^{-3}	Salt	Concn. salt/ 10^{-3} mol dm^{-3}	Absorbance
$[Mo(NH)I(dppe)_2]I$ *	5.7	1	$[NEt_4]I$	0	0.68
	5.7	1		5	0.90
	5.7	1		10	1.00
	5.7	1		15	1.07
	5.7	1		20	1.10
	5.7	1		30	1.10
	5.7	1		50	1.12
$[Mo(NH)Br(dppe)_2]Br$	5.6	1	$[NEt_4]Br$	0	0.89
	5.6	1		10	1.12
	5.6	1		20	1.15
$[Mo(NH)Cl(dppe)_2]Cl$	4.2	1	$[NMe_4]Cl$	0	0.67
	4.2	1		10	0.69
	4.2	1		20	0.70

* λ = 370 nm.

The spectrum of the intermediates derived from the chloro-, bromo-, and iodo-complexes was measured with [complex] = 1 × 10^{-3} mol dm^{-3} and $[NEt_3]$ = 2 × 10^{-3} mol dm^{-3} on the stopped-flow apparatus. Although the shapes of the spectra of all three intermediates were identical, the intensity of the spectrum derived from the iodo-complex was significantly lower than that of the other two, particularly at the shorter wavelengths. However, addition of tetraethylammonium iodide (5 × 10^{-3}—50 × 10^{-3} mol dm^{-3}) increased the absorbance of the intermediate but did not influence the spectrum of either starting material or product, Table 2 and Figure 4.

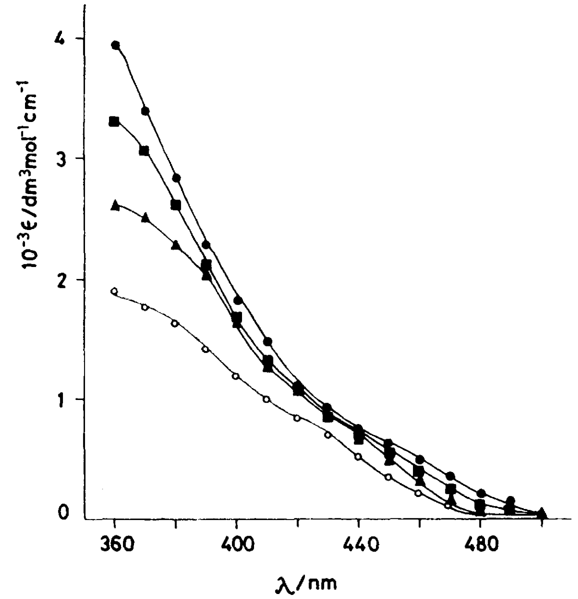


FIGURE 3 Spectra of *trans*-$[Mo(N)X(dppe)_2]$ generated from the reaction of triethylamine with *trans*-$[Mo(NH)X(dppe)_2]^+$ in chloromethane, where X = F (○), Cl (▲), Br (■), and I (●)

At low concentration of complex (<2.8 × 10^{-4} mol dm^{-3}) the common intermediate decayed with a rate constant which was first order in triethylamine concentration (k_{NEt_3} = 1.1 ± 0.2 × 10^5 dm^3 mol^{-1} s^{-1}) as shown in Table 3, Figure 5. The decay of this intermediate was exponential provided $[NEt_3]$ > [Mo], even when the concentration of triethylamine was much less than that required for pseudo-first-order conditions.

Variation of the concentration of the complex (2.8 × 10^{-4}—14 × 10^{-4} mol dm^{-3}) did not affect the first-order dependence of the rate of decay of the intermediate on the concentration of triethylamine. However, for the chloro- and bromo-complexes increasing the complex concentration resulted in a decreased rate constant

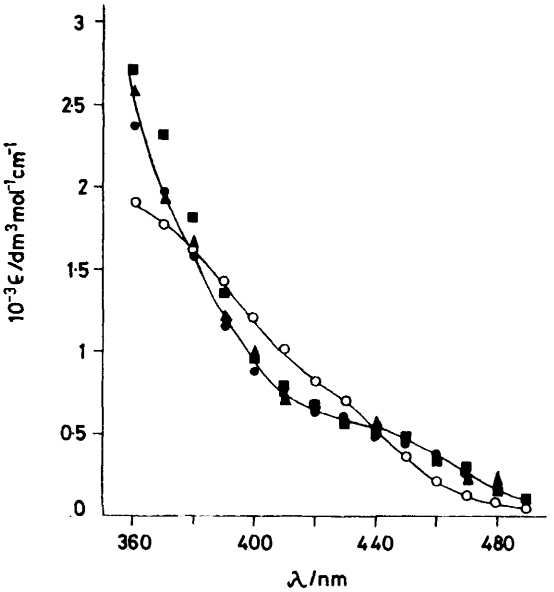


FIGURE 4 Spectra of the intermediates formed in the reaction between triethylamine and *trans*-$[Mo(NH)X(dppe)_2]^+$ where X = F (○), Cl (▲), Br (■), and I (●). For X = I, $[NEt_4I]$ = 0.05 mol dm^{-3} added to maximise intensity

(Table 3). This effect was most marked for the chloro-complex.

Addition of chloride or bromide ion (as tetra-alkylammonium salts) to solutions of the respective complexes also resulted in a decreased rate constant. This decrease was most marked for chloride ions and just discernable for iodide ion. A similar concentration of lithium perchlorate had little influence on the rate. These data are collected together in Table 4.

TABLE 3

Kinetic data for the reaction of triethylamine with *trans*-$[Mo(NH)X(dppe)_2]^+$ (where X = Cl, Br, or I) measured at λ = 440 nm and 25 °C in methanol

Complex	Concn. complex/ 10^{-4} mol dm^{-3}	Concn. triethylamine */ 10^{-3} mol dm^{-3}	$k_{obs.}$/ s^{-1}
$[Mo(NH)Cl(dppe)_2]Cl$	1.5	0.35	32
		0.85	106
		1.85	221
	2.8	1.0	104
		2.0	256
		3.0	405
		4.0	556
	7.0	0.3	14
		0.7	28
		1.8	60
		3.3	96
		9.3	276
	14.0	1.1	11
		4.6	44
		8.6	78
$[Mo(NH)Br(dppe)_2]Br$	1.5	0.35	37
		0.85	113
		1.85	211
	2.8	2.5	245
		5.0	518
		7.5	770
	7.0	0.3	18
		0.7	44
		1.8	117
		3.3	211
	14.0	1.1	56
		4.6	235
		8.6	438
$[Mo(NH)I(dppe)_2]I$	2.7	1.0	109
		2.0	147
		3.0	311
		4.0	460

* Concentration of triethylamine corrected to allow for initial deprotonation reaction, $[NEt_3]_{corr.} = [NEt_3] - [Mo]$.

The reaction of $[Mo(NH)X(dppe)_2]^+$ with triethylamine in dichloromethane was complete within 3 ms and gave a product whose spectrum was dependent on the nature of X, Figure 3.

The results are explained by the mechanism shown in Scheme 1. When *trans*-$[Mo(NH)X(dppe)_2]^+$ reacts with triethylamine in methanol an intermediate is rapidly formed ($k > 300$ s^{-1}). When X = Cl, Br, or I but not F, this intermediate is most likely $[Mo(N)(dppe)_2]^+$. Thus, *trans*-$[Mo(NH)X(dppe)_2]^+$ (A) is initially deprotonated by triethylamine to yield *trans*-$[Mo(N)X(dppe)_2]$ (B) which rapidly loses halide (X) to give the five-co-ordinate intermediates $[Mo(N)(dppe)_2]^+$ [(C) and (D)]. Species (C) is a contact ion pair of $[Mo(N)(dppe)_2]^+$ with X^-. Species (D) is either a solvent-separated ion pair or the free cation. A distinction between these descriptions of (D) is not relevant here. The presence of both (C and (D) is required by the dependence of the intensity, but not the shape of the intermediate's spectrum, on the concentration and nature of free halide ion (Table 2).

The ability of halide ion to increase the absorption of the intermediate at 380 nm is $I^- > Br^- > Cl^-$. This is consistent with the ion-pairing capabilities of these ions ($Cl^- > Br^- > I^-$) assuming that the contact ion pair formed by $[Mo(N)(dppe)_2]^+$ with X^- has a more intense spectrum than the corresponding solvent-separated ion pair or free cation. The spectrum of the contact ion pair (C) is independent of the nature of X since above 360 nm the charge-transfer spectrum is presumably dominated by transitions involving co-ordinated ligands.*

Evidence for the formation of the ion pairs between singly charged species in methanol has been obtained before. Pearson *et al.*[10] and Bosnich *et al.*[11] assigned a departure from first-order dependence for the reaction of *cis*-$[Co(en)_2Cl_2]^+$ (en = $H_2NCH_2CH_2NH_2$) with various anions to extensive ion-pair formation.

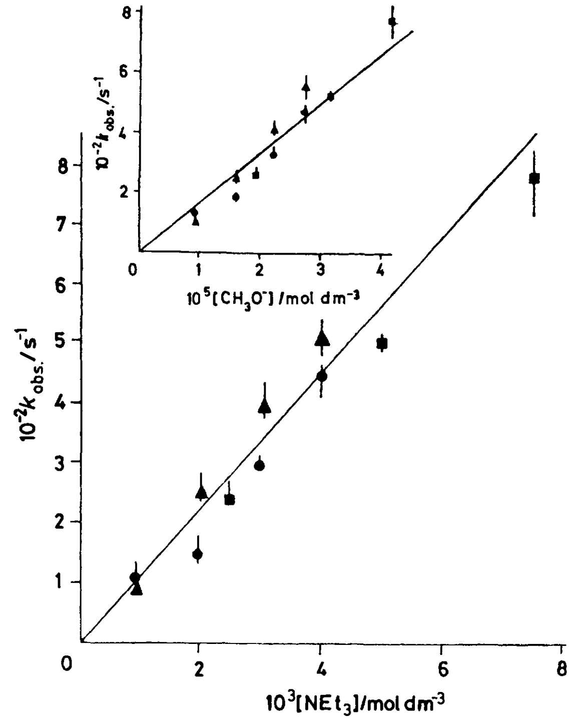


FIGURE 5 Plot of pseudo-first-order rate constants against the concentration of triethylamine for the reaction of triethylamine with $[Mo(NH)X(dppe)_2]^+$ where X = F (○), Cl (▲), Br (■), and I (●). The insert shows the dependence of $k_{obs.}$ on $[CH_3O]^-$. The concentration of CH_3O^- was calculated using equation (4) with $K_B = 1.26 \times 10^{-6}$. Data taken from Table 3. Data points with bars to cover the range of at least three experimental determinations

In the presence of an excess of triethylamine, the intermediates (C) and (D) react with methoxide ion (generated by the protolytic equilibrium between triethylamine and methanol) to give $[MoN(OCH_3)(dppe)_2]$

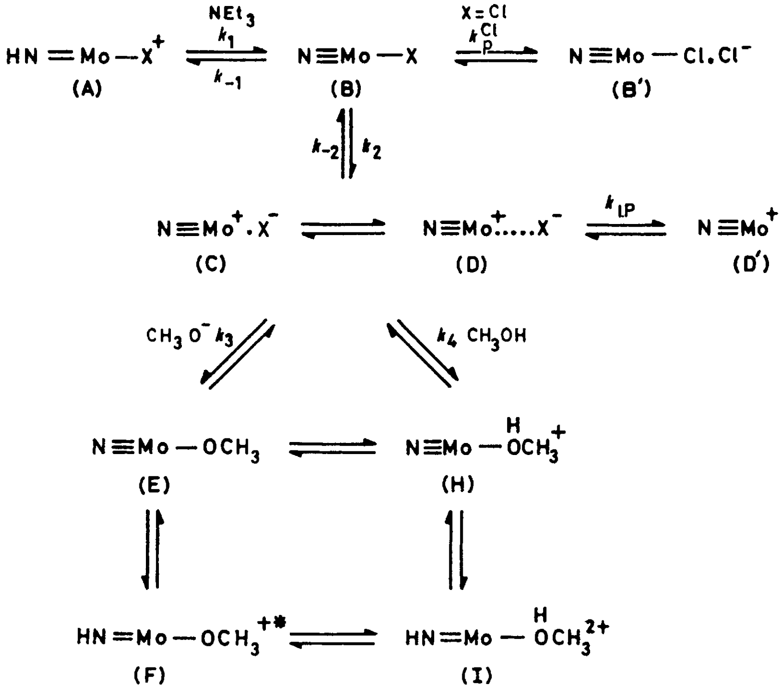
* See for example the spectra of $[Co(NH_3)_6]^{3+}\cdot X^-$ (X = Cl, Br, or I) (M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, 1953, **43**, 363).

TABLE 4

Influence of added halide ions on the reaction of *trans*-[Mo(NH)X(dppe)$_2$]$^+$ (X = Cl, Br, or I) with triethylamine measured at λ = 360 nm and 25 °C in methanol

Complex	Concn. complex/ 10^{-4} mol dm^{-3}	Salt	Concn. salt/ 10^{-3} mol dm^{-3}	Concn. triethylamine/ 10^{-3} mol dm^{-3}	Concn. triethyl-ammonium perchlorate/ 10^{-3} mol dm^{-3}	$k_{obs.}$/s^{-1}
[Mo(NH)Cl(dppe)$_2$]Cl	2.5	[NMe$_4$]Cl		1		105
	2.5		0.15	1		72
	2.5		0.50	1		52
	2.5		1.00	1		35
	2.5		2.50	1		18
	2.8		0.18	1		69
	2.8		0.18	1	0.35	38
	2.8		0.45	1		51
	2.8		0.45	1	0.70	30
	2.8		1.10	1		34
	2.8		1.10	1	1.40	15
	2.8		1.10	2	1.40	31
	2.5	Li[ClO$_4$]		1		110
	2.5		0.35	1		112
	2.5		0.70	1		103
	2.5		1.40	1		106
[Mo(NH)Br(dppe)$_2$]Br	2.5	[NEt$_4$]Br		1		114
	2.5		0.25	1		102
	2.5		0.50	1		86
	2.5		1.25	1		72
	2.5		2.50	1		60
[Mo(NH)I(dppe)$_2$]I	2.5	[NEt$_4$]I		1		107
	2.5		0.50	1		106
	2.5		2.50	1		100

(E). Since triethylamine is only a general base catalyst for this reaction, this explains why exponential traces were obtained even under non-pseudo-first-order conditions (Table 3). When [Mo(NH)X(dppe)$_2$]$^+$ (A) is in excess over triethylamine, the concentration of methoxide ion is so low that methanol competes effectively with methoxide for (C) and (D) to give [MoN(HOCH$_3$)(dppe)$_2$]$^+$ (H). Ion-pair formation does not affect the reactivity of [Mo(N)(dppe)$_2$]$^+$ with methoxide since when the concentration of (C) (X = I) was increased at the expense of (D) by the addition of iodide (shown by the increased absorbance at 370 nm, Table 2)



SCHEME 1 Mechanisms for the rapid reaction of triethylamine with [Mo(NH)X(dppe)$_2$]$^+$ (phosphine ligands omitted for clarity). *Alternative formulation: [MoN(HOCH$_3$)(dppe)$_2$]$^+$ (G)

no change in the rate of decay of (C) and (D) was observed (Table 4).

When (A) (1.5×10^{-4}—2.8×10^{-4} mol dm^{-3}) reacts in an excess of triethylamine, the rate constant for the decay of (C) and (D) is independent of the nature of X (Table 3, Figure 5). This supports the conclusion that (C) and (D) do not contain co-ordinated halide. Further evidence for the five-co-ordinate structure of (C) and (D) is the inhibition of the rate of formation of (D) observed when $[A] > 2.8 \times 10^{-4}$ mol dm^{-3} or when halide ion was added (Tables 3 and 4).

When X = Br (0.5—3.0 mmol dm^{-3}) the back reaction of (C) or (D) to give (B) becomes significant. It can be shown that equation (1) holds where $K_2^{Br} = k_{-2}/k_2 = 400$ dm^3 mol^{-1}, $k_3[CH_3O^-] = 120$ s^{-1}. Figure 6 curve Q

$$k_{obs.} = k_3[CH_3O^-]/(1 + K_2^{Br}[Br^-]_{free}) \qquad (1)$$

shows the dependence of $k_{obs.}$ on $[Br^-]_{free}$ (calculated for $k_{-2}/k_2 = 400$ dm^3 mol$^-$ and with $[Br^-]_{total} = 2[Mo] + [Br^-]_{added}$). When X = Cl, the data could not be fitted to the above rate expression. An additional equilibrium involving a second chloride ion is required, which results in equation (2) where $K_2^{Cl} = 625$ dm^3 mol^{-1}, $K_P^{Cl} = 555$ dm^3 mol^{-1}, $k_3[CH_3O^-] = 120$ s^{-1}. Figure 6 curve S shows the fit of the data points to this expression.

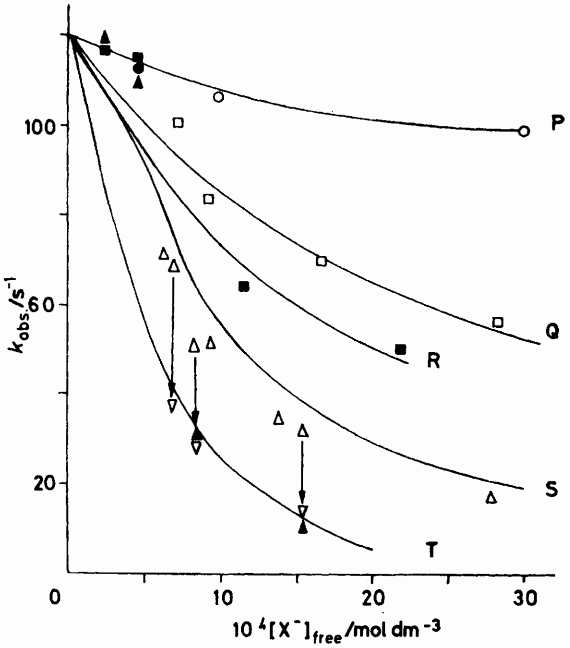


FIGURE 6 Dependence of $k_{obs.}$ on $[X^-]_{free}$ for the reaction of CH_3O^- with $[MoN(dppe)_2]^+$ generated from $[Mo(NH)X(dppe)_2]X$ by reaction with NEt_3 in methanol at 25 °C. Curves P, Q [equation (1)], and S [equation (2)] are for X = I (○), Br (□), and Cl (△), respectively with $[Mo] = 2.5 \times 10^{-4}$ mol dm^{-3} and when $[X^-]_{free}$ was varied by the addition of tetra-alkylammonium halides. Curves R and T, X = Br (■) and Cl (▲) respectively with $[X^-]_{free}$ varied by increasing [Mo] from 1.5×10^{-4} to 14×10^{-4} mol dm^{-3}, no tetra-alkylammonium halide added. For X = Cl, the points indicated by arrows move from curve S (△) to curve T (▽) on addition of $[NEt_3H][ClO_4]$ due to a decrease in $[CH_3O^-]$ according to equation (3). Data points taken from Tables 3 and 4

The dependence of $k_{obs.}$ on [A] (Table 3) is also explained by rate expressions (1) and (2), if an additional perturbation of the equilibrium between NEt_3 and CH_3OH is taken into account. Figure 6, curves R and T show the

$$k_{obs.} = \frac{k_3[CH_3O^-]}{1 + K_2^{Cl}[Cl^-]_{free} + K_2^{Cl}K_P^{Cl}[Cl^-]_{free}^2} \qquad (2)$$

dependence of $k_{obs.}$ on $[Cl^-]_{free}$ and $[Br^-]_{free}$ when (A) is increased from 2.8×10^{-4} to 14×10^{-4} mol dm^{-3} using the values of K_2^{Cl}, K_P^{Cl}, and K_2^{Br} calculated above. The data points on curves R and T lie significantly below the corresponding points obtained by adding tetra-alkylammonium halides with $[A] = 2.8 \times 10^{-4}$ mol dm^{-3} (curves Q and S). The lower values of $k_{obs.}$ obtained with high [A] for the same $[X^-]_{free}$ are due to the higher concentrations of NEt_3H^+ which result from the deprotonation of [A] by NEt_3. This causes the equilibrium in equation (3) to shift to the left with a consequent decrease in $[CH_3O^-]$. Since equations (1) and (2)

$$NEt_3 + CH_3OH \underset{}{\overset{K_B}{\rightleftharpoons}} \overset{+}{N}Et_3H + CH_3O^- \qquad (3)$$

contain the term $k_3[CH_3O^-]$, $k_{obs.}$ decreases as [A] increases. When $[NEt_3H][ClO_4]$ was added to solutions of [A] (2.8×10^{-4} mol dm^{-3}) at various $[Cl^-]_{free}$ the predicted decrease in $k_{obs.}$ was found (Table 4, and in Figure 6 the data points move from curve S to curve T).

The inhibition caused by the back reaction of (C) and (D) to give (B) is not reflected in changes in the amplitudes of the stopped-flow traces since the absorption coefficients at 360 nm for these species are very similar (Figures 3 and 4).

The negligible effect of added I$^-$ (Figure 6, curve P) and the first-order inhibition terms involving [Br$^-$] and [Cl$^-$] are easily rationalised by Scheme 1 with the affinities of $[Mo(N)(dppe)_2]^+$ for X$^-$ being $Cl^- > Br^- > I^-$. The equilibrium between (B) and Cl$^-$ to give (B′) gives rise to the $[Cl^-]_{free}^2$ term in equation (2). We feel a seven-co-ordinate structure, $[Mo(N)Cl_2(dppe)_2]^-$, for (B′) is unlikely for steric reasons and favour an interaction involving van der Waals forces. Pearson *et al.*[12] postulated a similar interaction, also in methanol, between the five-co-ordinate halidotris(*o*-diphenylarsinophenyl)arsineplatinum(1+) and thiourea and triphenylphosphine.

The rate constant (k_3) for the attack of methoxide ion on (C) and (D) was determined from the dependence of $k_{obs.}$ on $[CH_3O^-]$, Figure 5. The concentration of methoxide was calculated by solving equation (4) which is obtained from equation (3) together with an allowance for the NEt_3H^+ produced by the rapid initial deprotonation of (A). The insert to Figure 5 was drawn using

$$K_B = \frac{([Mo] + [CH_3O^-])[CH_3O^-]}{([NEt_3]_{total} - [CH_3O^-] - [Mo])[CH_3OH]} \qquad (4)$$

$K_B = 1.26 \times 10^{-6}$, calculated from the difference in $pK_a^{CH_3OH} = 16.6$[13] and $pK_a^{NEt_3H} = 10.7$.[14] The value of $k_3 = 1.7 \pm 0.4 \times 10^6$ dm^3 mol^{-1} s^{-1} is consistent with the rapid ($\tau < 1$ ms) reaction of (A) with methoxide ion (1 mmol) produced by dissolution of Li[OCH$_3$] in methanol. There is some uncertainty in k_3 since the value used for $pK_a^{NEt_3H}$ was determined in water and the $pK_a^{CH_3OH}$ is quoted for methanol as solvent at an ionic strength of 1 mol dm^{-3}. The absence of an intercept in Figure 5 indicates that methanol is a much poorer nucleophile for (C) and (D) than methoxide ion. However, spectrophotometric investigation of the reaction with triethylamine showed a good 1 : 1 stoicheiometry (Figure 2) clearly indicating that the product resulted from the nett addition of methanol and not methoxide to (C) and (D). Thus the attack of methoxide on (C) and (D) yields $[MoN(OCH_3)(dppe)_2]$ (E). The methoxy-group renders the *trans*-nitrido-group sufficiently basic that (E) rapidly abstracts a proton from the solvent to yield $[Mo(NH)(OCH_3)(dppe)_2]^+$, (F). This regenerates free methoxide ion and completes the base-catalysed reaction. An alternative formulation of the product would be as $[MoN(HOCH_3)(dppe)_2]^+$ (H), however we favour the imidomethoxy-designation for reasons discussed below.

TABLE 5

Reaction of *trans*-$[Mo(NH)X(dppe)_2]^+$ (X = Cl or Br) with sub-stoicheiometric concentrations of triethylamine measured at λ = 380 nm, 25 °C in methanol

Complex	Concn. complex/ 10^{-4} mol dm^{-3}	Concn. triethylamine/ 10^{-3} mol dm^{-3}	Concn. triethylammonium ion/ 10^{-3} mol dm^{-3}	Fast $k_{obs.}$/s^{-1}	Slow $k_{obs.}$/s^{-1}
$[Mo(NH)Cl(dppe)_2]Cl$	7	0.1		5.2	0.2
	7	0.2		5.1	0.25
	7	0.4		5.6	0.25
	7	0.6		6.0	0.32
	14	0.1		5.0	0.18
	14	0.6		6.2	0.42
	14	0.6	0	6.4	0.42
	14	0.6	0.3	6.0	0.35
	14	0.6	0.6	6.8	0.38
	14	0.6	0.9	6.4	0.40
$[Mo(NH)Br(dppe)_2]Br$	7	0.1		7.3	0.25
	7	0.2		6.5	0.32
	7	0.4		6.9	0.20

Sub-stoicheiometric Reaction.—When [A] > [NEt_3], (C) and (D) are rapidly formed (k > 300 s^{-1}) at a concentration equivalent to that of the NEt_3. (C) and (D) decay with a biphasic absorbance change to yield the corresponding concentrations of (F). The first-order rate constants for both absorbance changes are independent of the concentrations of triethylamine and complex (A). The addition of triethylammonium chloride also had no effect (Table 5). The first of the two consecutive reactions is most likely the attack of methanol on (C) and (D) [$k_4 = 5.9 \pm 0.8$ s^{-1} (X = Cl), 6.9 ± 0.4 (X = Br)] to yield $[MoN(HOCH_3)(dppe)_2]^+$ (H). The failure to observe a three-fold decrease in $k_{obs.}$ when $[X^-]_{free}$ increases from 8×10^{-4} to 20×10^{-4} is interesting since Scheme 1 and equations (1) and (2) predict this inhibition if methanol merely replaces methoxide as the attacking nucleophile on (C) and (D). Since there is a variation of *ca.* 30% in $k_{obs.}$ (Table 5) we can only conclude that a compensatory rate enhancement occurs as $[X^-]_{free}$ increases. Since methoxide reacts with (C) and (D) 10^6 times faster than methanol does, it is plausible that only a small perturbation of either the pK_a of methanol or the solvent structure compensates for the inhibition of halide.

It is proposed that the subsequent slower phase involves an isomerisation of (H) to (F) ($k_{obs.} = 0.3 \pm 0.1$ s^{-1}). Since the rate constant for this reaction is independent of the concentrations of complex (A) and NEt_3H^+, methanol-mediated prototropic shifts must dominate. Two mechanisms are shown in Scheme 1. One involves the initial rate-determining deprotonation of (H) by methanol to yield (E) which then rapidly abstracts a proton from solvent to give (F). The other involves an initial rate-determining protonation of the nitrido-group by methanol to give (I) followed by rapid deprotonation of the co-ordinated methanol to give (F). We are unable to distinguish between these two mechanisms but we note that the nitrido-group of (H) is likely to be significantly less basic than the nitrido-group in (E) and therefore proton addition to (H) may be less favourable.

The Fluoro-complex.—The complex *trans*-$[Mo(NH)F(dppe)_2]^+$ (A) exhibits an observable reaction with $Li[OCH_3]$ in methanol on the stopped-flow time scale. This reaction involves an initial rapid absorbance increase (k_1 > 300 s^{-1}) followed by a slow absorbance decrease at a rate ($k_2 = 2.0 \pm 0.1$ s^{-1}) independent of the concentration of methoxide ion ($[CH_3O^-] = 6.25 \times 10^{-3}$—$50.0 \times 10^{-3}$ mol dm^{-3}) to yield (F) (Table 6).

The reaction of (A) (X = F) with triethylamine in methanol resulted in similar absorbance changes except that the amplitude of the initial absorbance increase was dependent on [NEt_3] (Table 7). The subsequent decrease in absorbance occurred at a rate independent of the concentration of triethylamine ([NEt_3] = 1×10^{-3}—250×10^{-3} mol dm^{-3}) to again yield (F) ($k = 1.6 \pm 0.1$ s^{-1}) (Table 6).

When [NEt_3] > 0.125 mol dm^{-3} a ' saturated spectrum ' for the intermediate was obtained (Figure 4). This spectrum was identical to those obtained using either lithium methoxide in methanol or an excess of triethylamine in dichloromethane. This spectrum is different from that of (C) and (D) in that it is essentially featureless and does not contain the pronounced shoulder (λ = 440 nm, ε = 175 dm^3 mol^{-1} cm^{-1}).

TABLE 6

Kinetic data for the reaction of triethylamine with the *trans*-[Mo(NH)F(dppe)$_2$]$^+$ cation measured at λ = 400 nm, 25 °C in methanol

Concn. complex/ 10^{-4} mol dm^{-3}	Concn. base/ 10^{-3} mol dm^{-3}	$k_{\text{obs.}}$/s^{-1}
	[NEt$_3$]	
5	1.0	1.63
5	2.5	1.70
5	5.0	1.64
5	10.0	1.56
5	15.0	1.53
5	25.0	1.59
5	50.0	1.62
5	62.5	1.60
5	125.0	1.64
5	250.0	1.81
	[LiOCH$_3$]	
10	6.25	2.06
10	12.50	2.01
10	25.0	2.08
10	50.0	2.08
5	6.25	1.97
2.5	6.25	1.97

We conclude that the fluoride is retained in the inner co-ordination sphere after the initial rapid reaction and that the intermediate is (B) (X = F).

The imido-group of the fluoro-complex is significantly less acidic than when the other halogens are bound. Using the magnitude of the initial absorbance jump and the absorption coefficients of the intermediate (ε = 1 360 dm^3 mol^{-1} cm^{-1}) and the substrate (A) (ε = 173 dm^3 mol^{-1} cm^{-1}) at λ = 400 nm, the pK_a of (A) (X = F) was calculated to be 12.7 ($\pm$0.2) in methanol at 25 °C (Table 7). The independence of the amplitude of the initial rapid absorbance change on triethylamine concentration for (A) (X = Cl, Br, or I) shows that the pK_a's for these complexes are $<$10. The higher value for the pK_a of the fluoro-complex is unexpected when the stronger inductive influence of the fluorine atom relative to the other halogens is considered. An explanation would be that the fluoro-complex is the most acidic of the series but that with the other halogen complexes the acid–base equilibrium is coupled to the subsequent rapid dissociation of the halide ion. Although halide dissociation will undoubtedly affect the apparent pK_a of (A), this is not a dominant factor, since in dichloromethane (in which the halide is not liberated), only one equivalent of triethylamine is required to deprotonate completely (A) (X = Cl, Br, or I), but addition of one equivalent of triethylamine to the fluoro-complex yields an equilibrium mixture ($K_{\text{eq.}}$ = 3.4 × 10^{-3}, 'pK_a' = 13.2). The inability of fluoride to accept electron density in a π sense and its mesomeric electron-donating ability [15] accounts for the higher pK_a of (A) when X = F. The greater mesomeric electron-donating capability of methoxide [15] results in pK_a > 16 for [Mo(NH)(OCH$_3$)(dppe)$_2$]$^+$ (F) which is not deprotonated by excess of methoxide ion.

TABLE 7

Determination of pK_a of *trans*-[Mo(NH)F(dppe)$_2$]$^+$ in CH$_3$OH measured at λ = 400 nm, 25 °C in methanol, [Mo] = 5.5 × 10^{-4} mol dm^{-3}

Concn. triethylamine/ 10^{-3} mol dm^{-3}	Absorbance	$10^2K_{\text{eq.}}$	pK_a^{NH}
1	0.18	1.1	12.7
2.5	0.21	0.86	12.8
5.0	0.28	1.28	12.7
10.0	0.30	0.81	12.9
15.0	0.34	0.83	12.8
25.0	0.37	0.68	12.9
50.0	0.51	1.20	12.7
62.5	0.57	1.70	12.5
125.0	0.67	2.90	12.3
250.0	0.69	2.06	12.5

The subsequent exponential decay of *trans*-[Mo(N)F-(dppe)$_2$] (B) to yield (F) is essentially independent of the nature and concentration of base (k_2 = 1.8 $\pm$ 0.3 s^{-1}) (Table 6). This is consistent with the mechanism shown in Scheme 1 if the dissociation of fluoride from (B) is rate determining, followed by the rapid attack of methoxide on the five-co-ordinate intermediates (C) and (D).

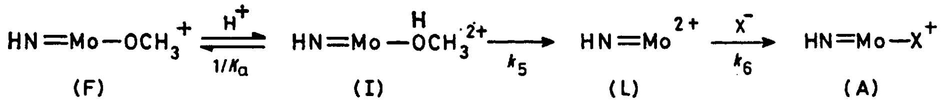
The Back Reaction.—The kinetics of the acid-catalysed anation of [Mo(NH)(OCH$_3$)(dppe)$_2$]$^+$ (F) have also been

TABLE 8

Kinetic data for the reaction of *trans*-[Mo(NH)(OCH$_3$)-(dppe)$_2$]$^+$ with acids, measured at λ = 440 nm, 25 °C in methanol

Concn. complex/ 10^{-4} mol dm^{-3}	Concn. acid [a]/ 10^{-3} mol dm^{-3}	$k_{\text{obs.}}$/s^{-1}
2.85 [b]	2	40.4
2.85	5	117
2.85	10	266
2.85	15	364
3.2 [c]	2	42.6
3.2	5	119
3.2	10	261
3.2	15	392
3.2 [d]	2	42.2
3.2	5	120
3.2	10	283
3.2	15	407
3.2 [e]	2	42.6
3.2	5	126
3.2	10	246
3.2	15	435
3.2 [f]	2	38.5
3.2	5	118
3.2	10	265
3.2	15	400
5.5 [c]	3.5 [g]	62.5
5.5	6.0 [g]	114
5.5	15 [g]	331
5.5	5 [h]	85
5.5	10 [h]	189
5.5	15 [h]	360

[a] Acid used was HBr unless otherwise stated. [b] Starting from [Mo(NH)(OCH$_3$)(dppe)$_2$][BPh$_4$]. [c] Generated in solution by reaction of triethylamine with [Mo(NH)Br(dppe)$_2$]Br. [d] Generated in solution by reaction of lithium methoxide with [Mo(NH)Br(dppe)$_2$]Br. [e] Generated in solution by reaction of triethylamine with [Mo(NH)Cl(dppe)$_2$]Cl. [f] Generated in solution by reaction of lithium methoxide with [Mo(NH)Cl-(dppe)$_2$]Cl. [g] Acid used was HCl. [h] Acid used was H$_2$SO$_4$.



SCHEME 2 Mechanism for the acid-catalysed anation of the $[Mo(NH)(OCH_3)(dppe)_2]^+$ cation (phosphine ligands omitted for clarity)

investigated (Scheme 2). The reaction of (F) with strong acids (HX) shows a single exponential decay whose initial absorbance at $\lambda = 440$ nm corresponds to that of (F) and whose final absorbance corresponds to that of (A).

The $[Mo(NH)(OCH_3)(dppe)_2]^+$ was prepared by three methods: isolation as the tetraphenylborate salt by the method of Chatt and Dilworth [6] and reaction of (A) with stoicheiometric amounts of either lithium methoxide or triethylamine in solution. The kinetics were independent of the method used to generate (F).

TABLE 9

Determination of the yields of ammonia from reaction of bases with *trans*-$[Mo(NH)X(dppe)_2]^+$ (X = Cl, Br, or CH_3O) in methanol

θ_c/°C	Complex	Concn. base/ 10^{-3} mol dm^{-3}	Base	Concn. complex/ 10^{-3} mol dm^{-3}	Concn. NH_3/ 10^{-3} mol dm^{-3}	Yield NH_3/ %	Yield N_2H_4/ %
25	$[Mo(NH)Cl(dppe)_2]Cl$	2.50	NEt_3	0.856	0.700 ($\pm$0.001)	82	0
25		5.00		1.150	0.710(14)	62	0.03
25		4.93	$Li[OCH_3]$	0.963	0.812(5)	84	0.029
25		9.96		0.786	0.622(9)	79	0
25		9.96		1.448	1.357(40)	94	0.02
35		10	NEt_3	1.70	0.889	52.4	
35		50		1.24	0.598	48.4	
35		8.1	$Li[OCH_3]$	1.38	0.807	58.5	
35		16.2		1.40	0.851	60.6	
47.5		10	NEt_3	1.38	0.624	45.2	
47.5		50		1.22	0.478	39.2	
25	$[Mo(NH)Br(dppe)_2]Br$	2.50	NEt_3	0.923	0.725(3)	79	0
25		2.50		1.168	0.932(10)	80	0.05
25		50		0.892	0.211	24	0.03
25		4.93	$Li[OCH_3]$	0.874	0.684(14)	78	0.02
25		4.98		0.812	0.788(4)	97	0.02
25		4.98		1.031	0.887(27)	86	0.03
35		25	NEt_3	0.636	0.317	47.8	
35		40.5	$Li[OCH_3]$	1.30	0.743	57.1	
45.5		4.1	$Li[OCH_3]$	0.918	0.505	55.0	
45.5		8.1		1.231	0.644	52.3	
45.5		16.2		1.655	0.763	46.1	
45.5		40.5		1.987	0.838	42.2	
47.5		5	NEt_3	1.69	0.642	38.0	
47.5		20		1.03	0.431	41.8	
25	$[Mo(NH)(OCH_3)(dppe)_2][PF_6]$	Excess	NEt_3	1.168	0.787(15)	68	0
		1.10	$Li[OCH_3]$	0.844	0.552(20)	65	0
25		2.20		0.533	0.437(12)	81	0

The reaction of (F) with an excess of acid proceeds at a rate dependent upon the concentration of hydrogen ion but independent of the anion (Table 8).

It is proposed that the mechanism is that shown in Scheme 2.

A protolytic pre-equilibrium between (F) and (I) is established within 3 ms followed by the rate-limiting dissociation of methanol from (I) ($k_5 > 3.9 \times 10^2$ s^{-1}) to give $[Mo(NH)(dppe)_2]^{2+}$ (L) which rapidly reacts with X^- ($k_6 > 1 \times 10^5$ dm^3 mol^{-1} s^{-1}) to yield (A).

The rate law derived from the mechanism proposed in Scheme 2 is given by equation (5) where, K_a is the acid dissociation constant of the co-ordinated methanol in (I). Since there was no observed departure from a first-order dependence of $k_{obs.}$ on $[H^+]$, $[H^+]/K_a < 1$, the pK_a of the co-ordinated methanol must be less than 1.8.

$$k_{obs.} = k_5(1/K_a)[H^+]/\{1 + (1/K_a)[H^+]\} \qquad (5)$$

The mechanism in Scheme 2 supports our previous conclusion that the product of the reaction of (A) with base is the methoxy-imido-complex (F) and not the nitrido-methanol complex (H). Clearly if the product were (H), protonation of a nitrido-group would have to labilise the co-ordinated methanol. This would be inconsistent with our conclusion that deprotonation of (A) strongly labilises the co-ordinated halide.

Ammonia Formation.—When (F) was left in basic solution, the yellow colour was slowly discharged and analysis of the resulting solution showed that ammonia had been produced in high yield (>70%).

To determine whether the ammonia was free or bound to molybdenum, the bleached solution obtained after kinetic runs was divided into two. The concentration of ammonia was determined directly on one aliquot. For the other aliquot, the solvent was removed *in vacuo* and the resulting residue redissolved in methanol, prior to an ammonia estimation. The two determinations were identical, strongly indicating that the ammonia was bound to the metal.

The data for ammonia yields (Table 9) allow two conclusions. (i) The yield of ammonia is independent of the concentration of base and nature of X in (A). (ii) The yield of ammonia decreases with increasing temperature. This latter observation is probably a consequence of solvolytic displacement of the co-ordinated ammonia with concomitant loss of the free ammonia from solution at the higher temperatures.

At higher concentrations of the complex, free phosphine was observed to precipitate from solution as the reaction proceeded. Between one and two equivalents of phosphine were liberated.

The kinetics of this reaction were investigated spectrophotometrically. The rate of bleaching was independent of the concentration of base ($k_7 = 1.57 \times 10^{-4}$ s^{-1} at 25 °C) and the temperature dependence of this reaction (Table 10) yielded activation parameters $\Delta H^\ddagger = 50$ kJ mol^{-1} and $\Delta S^\ddagger = -143$ J K^{-1} mol^{-1}.

TABLE 10

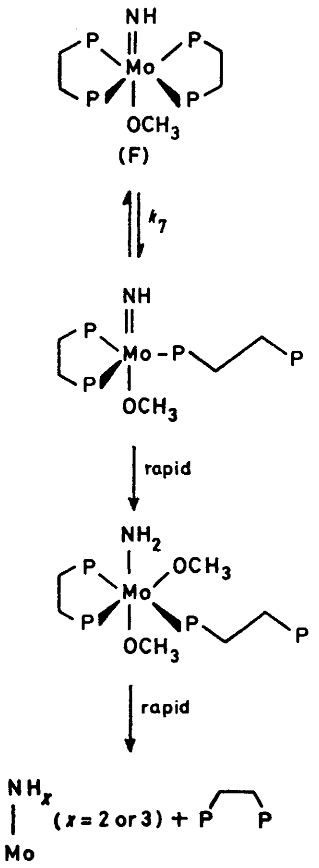
Kinetic data for the decomposition of *trans*-[Mo(NH)-(OCH_3)(dppe)$_2$]$^+$ in basic methanol, measured at $\lambda = 380$ nm

θ_c/°C	Concn. of complex [a]/ 10^{-4} mol dm^{-3}	Base	Concn. of base/ 10^{-4} mol dm^{-3}	$k_{obs.}$/ 10^{-4} s^{-1}
25	11.68	NEt_3	25.0	1.54
	2.59		25.7	1.57
	11.49		50.0	1.52
	5.82		57.6	1.33
	10.25		101.5	1.64
	7.92		150	1.25
	8.92		500	1.66
35	1.54		10	2.63
	1.70 [b]		10	2.74
	0.64		25	2.84
	1.24 [b]		50	3.42
47.5	1.69		10	7.18
	1.38 [b]		10	7.54
	1.03		25	7.46
	1.22		50	6.14
25	10.3	Li[OCH_3]	20	1.49
	8.12		20	1.91
	14.5 [b]		40	1.56
	7.86 [b]		40	1.98
	9.52 [b]		81.2	1.67
	7.88 [b]		81.2	1.60
36	13.9		20	3.21
	13.8 [b]		40	3.23
	14.1 [b]		80	3.55
47.5	19.9	Li[OCH_3]	20	7.15
	16.6 [b]		40	8.72
	12.3 [b]		80	7.18
	9.2		160	7.81

[a] [Mo(NH)(OCH_3)(dppe)$_2$]$^+$ generated from reaction of triethylamine with [Mo(NH)Br(dppe)$_2$]$^+$. [b] [Mo(NH)(OCH_3)-(dppe)$_2$]$^+$ generated from reaction of triethylamine with [Mo(NH)Cl(dppe)$_2$]$^+$.

The large negative entropy of activation and independence of the rate on the concentration of base is consistent with ring-opening of one of the phosphine chelate rings being the rate-determining step.

A mechanism for this reaction is shown in Scheme 3, where rate-limiting opening of a phosphine chelate ring is followed by the rapid attack of methoxide ion. The addition of this second methoxide group increases the basicity of the imido-group to such an extent that it abstracts a further one or two protons from the solvent. Whether the final product is an amido- or ammine complex of molybdenum is not clear since both types of complex would be expected to give ammonia under the aqueous alkaline conditions of the indophenol test for ammonia.



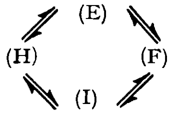
SCHEME 3 Mechanism for the formation of ammonia from the reaction of base with [Mo(NH)(OCH_3)(dppe)$_2$]$^+$

Conclusions.—It has been shown that *trans*-[Mo(NH)-X(dppe)$_2$]$^+$ reacts with base in methanol to give the five-co-ordinate intermediate [Mo(N)(dppe)$_2$]$^+$. The stability of this intermediate is not so surprising since similar 16-electron complexes [Mo(CO)(dppe)$_2$] [16] and [MoO($SCH_2CH_2PPh_2$)$_2$] [17] have been isolated. [Mo(N)(dppe)$_2$]$^+$ reacts rapidly with methoxide ion to yield [Mo(N)-(OCH_3)(dppe)$_2$]. This behaviour is again similar to that of [Mo(CO)(dppe)$_2$] which also adds two-electron donor ligands.[18] The complex [Mo(N)(OCH_3)(dppe)$_2$] abstracts a proton from methanol to yield [Mo(NH)(OCH_3)-(dppe)$_2$]$^+$. The basicity of the nitrido-group increases with the various *trans* ligands along the series $CH_3O^- > F^- > Cl^-$, Br^-, I^- because of π bonding between the *trans* ligand and molybdenum.

The strong *trans*-labilising effect of the nitrido-group,

TABLE 11

Summary of rate and equilibrium constants at 25 °C

Reaction	Rate or equilibrium constant	Comments
Scheme 1		
$NEt_3 + (A)^{a} \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} (B) + NEt_3H^{+\,b}$	$k_1 > 3 \times 10^5$ dm^3 mol^{-1} s^{-1}	X = F, Cl, Br, or I
	$k_{-1} > 30$ s^{-1}	X = F, Cl, Br, or I
$(B) \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} [(C) + (D)] \overset{K_{I.P.}{}^{c}}{\rightleftharpoons} (D) + X^-$	$k_2 > 300$ s^{-1}	X = Cl, Br, or I
	$K_{I.P.}{}^{Cl}\, k_{-2} > 2 \times 10^5$ dm^3 mol^{-1} s^{-1}	X = Cl
	$K_{I.P.}{}^{Br}\, k_{-2} > 1 \times 10^5$ dm^3 mol^{-1} s^{-1}	X = Br
	$K_{I.P.}{}^{I}\, k_{-2} > 2 \times 10^5$ dm^3 mol^{-1} s^{-1}	X = I
	$k_2 = 1.8 \pm 0.3$ s^{-1}	X = F
$Cl^- + (B) \overset{K_P{}^{Cl\,d}}{\rightleftharpoons} (B){\cdot}Cl^-$	$K_P{}^{Cl} = 5.5 \times 10^2$ dm^3 mol^{-1}	
$CH_3O^- + [(C) \rightleftharpoons (D)] \overset{k_3}{\rightleftharpoons} (E)$	$k_3 = 1.7 \pm 0.4 \times 10^6$ dm^3 mol^{-1} s^{-1}	Assuming p$K_a{}^{CH_3OH} = 16.6$, p$K_a{}^{NEt_3H+} = 10.7$
$CH_3OH + [(C) \rightleftharpoons (D)] \overset{k_4}{\rightleftharpoons} (H)$	$k_4 = 0.2 \pm 0.02$ dm^3 mol^{-1} s^{-1}	Average value for X = Cl and Br
	$k_{obs.} = 0.2 \pm 0.1$ s^{-1}	Prototropic isomerisation of (H) to (F) *via* (E) or (I), mechanism uncertain
Scheme 2		
$H^+ + (F) \overset{1/K_a}{\rightleftharpoons} (I)$	$K_a > 1.6 \times 10^{-2}$ mol dm^{-3}	
$(I) \overset{k_5}{\rightleftharpoons} (L) + CH_3OH$	$k_5 > 3.9 \times 10^2$ s^{-1}	
$X^- + (L) \overset{k_6}{\rightleftharpoons} (A)$	$k_6 > 1.0 \times 10^5$ dm^3 mol^{-1} s^{-1}	X = Cl or Br
Scheme 3		
$(F) \xrightarrow{k_7} MoNH_{x\,=\,2\text{ or }3} + dppe$	$k_7 = 1.6 \times 10^{-4}$ s^{-1}	$\Delta H^{\ddagger} = 50$ kJ mol^{-1}, $\Delta S^{\ddagger} = -143$ J K^{-1} mol^{-1}

[a] p$K_a{}^{A} < 10$ for X = Cl, Br, or I; p$K_a{}^{A} = 12.7$ for X = F. [b] p$K_a{}^{NEt_3H+} = 10.7$. [c] I.P. = Ion pair. [d] p = Pair.

which is formed by deprotonation of the imido-group, results in ready replacement of the *trans* halide by methoxide. It is this substitution which is the key step for labilisation of phosphine ligand, which leads to further substitutions by methoxide ion(s) and consequent increased basicity of the imido-group.

One of us (G. D.) is grateful to Northeastern University, Boston for sabbatical leave. We thank P. Maryan for technical assistance.

[0/732 *Received*, 16*th May*, 1980]

REFERENCES

[1] J. Chatt, A. J. Pearman, and R. L. Richards, *J.C.S. Dalton*, 1977, 1852.

[2] J. Chatt, A. J. Pearman, and R. L. Richards, *Nature*, 1976, **259**, 204.

[3] J. Chatt in 'Biological Aspects of Inorganic Chemistry,' eds. A. W. Addison, W. R. Cullen, D. Dolphin, and B. R. James, John Wiley and Sons, London, 1977, p. 229.

[4] J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589.

[5] J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1975, 983.

[6] J. Chatt and J. R. Dilworth, *J. Indian Chem. Soc.*, 1977, **54**, 13.

[7] R. N. F. Thorneley, *Biochem. J.*, 1975, **145**, 391.

[8] P. S. Maryan and W. T. Vorley, *Lab. Practice*, 1979, **28**, 251.

[9] G. W. Watt and J. D. Crisp, *Analyt. Chem.*, 1952, **24**, 2006.

[10] R. G. Pearson, P. M. Henry, and F. Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379, 5382.

[11] B. Bosnich, C. K. Ingold, and M. L. Tobe, *J. Chem. Soc.*, 1965, 4074.

[12] R. G. Pearson, M. M. Muir, and L. M. Venanzi, *J. Chem. Soc.*, 1965, 5521.

[13] R. Gut, *Helv. Chim. Acta*, 1964, **47**, 2262.

[14] N. F. Hall and M. R. Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

[15] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' G. Bell and Sons, London, 1969, p. 90.

[16] M. Sato, T. Tatsumi, T. Kodama, M. Hidai, T. Uchida, and Y. Uchida, *J. Amer. Chem. Soc.*, 1978, **100**, 4447.

[17] J. Chatt, J. R. Dilworth, J. A. Schmutz, and J. A. Zubieta, *J.C.S. Dalton*, 1979, 1595.

[18] J. Chatt, G. J. Leigh, H. Neukomm, C. J. Pickett, and D. R. Stanley, *J.C.S. Dalton*, 1980, 121.