Mechanism of the Base-catalysed Substitution of Halide for Methoxide in the Reactions of *trans*-$[W(NH)X(Ph_2PCH_2CH_2PPh_2)_2]^+$ (X = Cl, Br, or I)

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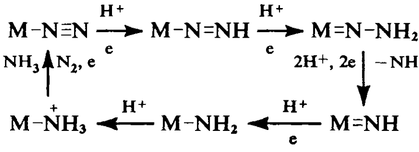
The kinetics of the reaction between *trans*-$[W(NH)X(dppe)_2]^+$ [X = Cl, Br, or I; dppe = 1,2-bis(diphenylphosphino)ethane] and triethylamine or lithium methoxide in methanol to yield the complex *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$ have been investigated. It is proposed that the reactions with both bases proceed *via* a common mechanism. This involves initial deprotonation of *trans*-$[W(NH)X(dppe)_2]^+$, to generate *trans*-$[W(N)X(dppe)_2]$. Rapid dissociation of the halide yields the relatively stable ion pair $[W(N)(dppe)_2]^+ \cdot X^-$. Subsequent rate-limiting attack of methoxide on the ion pair gives *trans*-$[W(N)(OCH_3)(dppe)_2]$ which rapidly abstracts a proton from a solvent molecule to yield the product *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$. The pK_a of *trans*-$[W(NH)X(dppe)_2]^+$ is sensitive to the nature of the *trans* ligand, and direct comparison of the pK_a for *trans*-$[M(NH)X(dppe)_2]^+$ (M = Mo or W, X = F or Cl) shows that the tungsten complexes are about a 1 000-fold less acidic than their molybdenum counterparts.

The reduction of dinitrogen to ammonia by both the enzyme nitrogenase and complexes of the type *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) has been proposed to occur *via* the pathway in Scheme 1.[1] The imido-ligand thus represents a possible intermediate in the fixation of dinitrogen, and clearly those factors which influence its reduction to ammonia are of significant interest.



Scheme 1

To date the only series of isolable, mononuclear complexes containing the imido-ligand are those of the general formula *trans*-$[M(NH)X(dppe)_2]^+$ [M = Mo or W; X = F, Cl, Br, or I; dppe = 1,2-bis(diphenylphosphino)ethane].[2,3] It was recently demonstrated that, under ambient conditions, *trans*-$[Mo(NH)X(dppe)_2]^+$ gives a high yield of ammonia (*ca.* 70%) in basic methanol, whereas in acidic media the starting material is recovered quantitatively, even in boiling methanol.[4] The crucial step in the reaction with base is the base-catalysed substitution of the *trans*-halide by methoxide to give *trans*-$[Mo(NH)(OCH_3)(dppe)_2]^+$. Subsequent replacement of the diphosphine chelate by the more electron-releasing methoxy-ligand permits the imido-ligand to protonate as far as the amido- or ammine stage. More recently the preparation of the tungsten analogues *trans*-$[W(NH)X(dppe)_2]^+$ has been reported,[3] and these have also been shown to yield ammonia (*ca.* 50%) in basic methanol *via* *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$. The mechanism of the base-catalysed formation of *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$ from the halido-substrates in methanol [equation (1)] is discussed herein.

$$trans\text{-}[W(NH)X(dppe)_2]^+ + CH_3O^- \xrightarrow[CH_3OH]{NEt_3} trans\text{-}[W(NH)(OCH_3)(dppe)_2]^+ + X^- \quad (1)$$

Results

The characterisation of the complexes *trans*-$[W(NH)X(dppe)_2]Y$ (X = F, Y = BF_4; X = Y = Cl, Br, or I; X = OCH_3, Y = I) has been described previously.[3] They dissolve in methanol as 1 : 1 electrolytes as evidenced by their molar conductivities (Λ = 103—120 Ω^{-1} cm^2 mol^{-1}).[5] The visible absorption spectra of these complexes (Figure 1 and Table 1) show similar characteristics to those of their molybdenum analogues.[4] Along the series F, Cl, Br, I the peak maxima progressively move to a higher wavelength with concomitant decrease in band intensity.

Stoicheiometry.—In methanol, treatment of *trans*-$[W(NH)X(dppe)_2]^+$ (X = Cl, Br, or I) with 1 mol equivalent of triethylamine or lithium methoxide yields *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$ [Figure 1 (insert)], as described in equation (1).

Kinetics of the Reactions with Triethylamine.—The reactions between the chloro-, bromo-, or iodo-substrates, *trans*-$[W(NH)X(dppe)_2]^+$, and triethylamine in methanol to yield *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$, equation (1), are characterised by a small increase in absorbance (λ = 370 nm), the initial and final absorbances being those of the substrate in question and *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$ respectively. The kinetics of the reactions with all substrates exhibit a first-order dependence upon the concentration of the complex, but the influence of triethylamine on the reaction with *trans*-$[W(NH)Cl(dppe)_2]^+$ differs from that on the bromo- or iodo-substrates. For this reason the results for the chloro-system (and their subsequent discussion) will be presented in a separate section.

(*a*) *trans*-$[W(NH)Cl(dppe)_2]^+$. The saturation kinetics observed in the reaction between the chloro-substrate and triethylamine (Figure 2) are consistent with either (*i*) a dependence upon the concentration of triethylamine as shown in equation (2), or (*ii*) a first-order dependence upon the concentration of methoxide (or the ratio $[NEt_3]_{free}/[NEt_3H^+]_{free}$), equation (3). The equivalence in equation (3) results from the

$$k_{obs.} = \frac{(68.1 \pm 1.1)[NEt_3]}{1 + (8.2 \pm 0.8)[NEt_3]} \quad (2)$$

$$\begin{aligned} k_{obs.} &= (1.9 \pm 0.3) \times 10^3[CH_3O^-] \\ &\equiv (5.9 \pm 0.9) \times 10^{-2}\,[NEt_3]_{free}/[NEt_3H^+]_{free} \quad (3) \end{aligned}$$

$$NEt_3 + CH_3OH \overset{K_B}{\rightleftharpoons} NEt_3H^+ + CH_3O^- \quad (4)$$

Table 1. Spectral and conductivity results for *trans*-$[W(NH)X(dppe)_2]^+$ (X = F, Cl, Br, or I)

Complex	Colour	Λ/ Ω^{-1} cm^2 mol^{-1} *	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/ dm^3 mol^{-1} cm^{-1}
trans-$[W(NH)F(dppe)_2]BF_4$	Yellow	116	446	244.7
trans-$[W(NH)Cl(dppe)_2]Cl$	Orange	108	488	137.3
trans-$[W(NH)Br(dppe)_2]Br$	Red	103	500	124.0
trans-$[W(NH)I(dppe)_2]I$	Mauve	120	502	122.5

* Concentration of complex = 0.5×10^{-3} mol dm^{-3}; cell constant = 1.35.

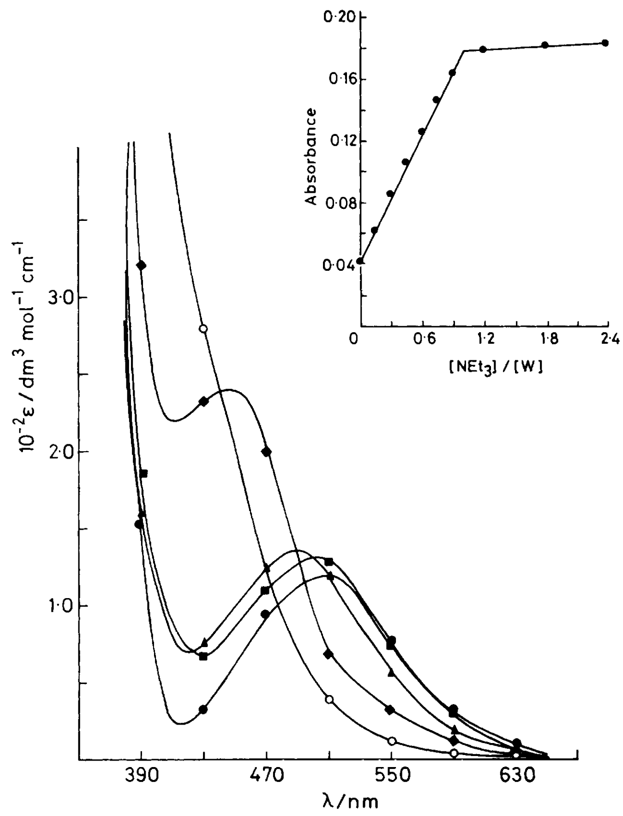


Figure 1. Spectra of *trans*-$[W(NH)X(dppe)_2]^+$ in methanol, where X = F (◆), Cl (▲), Br (■), I (●), and CH_3O (○). Insert: a typical spectrophotometric determination of the stoicheiometry of the reaction between triethylamine and *trans*-$[W(NH)Br(dppe)_2]Br$ ($[W] = 0.5 \times 10^{-3}$ mol dm^{-3}, λ = 410 nm)

protolytic equilibrium (4). The equilibrium constant $K_B = 1.26 \times 10^{-6}$ was calculated using the pK_a values for methanol (16.6)[6] and the triethylammonium ion (10.7).[7]

Consistent with the rate equation (2) rather than (3), the addition of triethylammonium perchlorate had little influence upon the rate of the reaction with triethylamine (see Table 2).

The reactions (both in the presence and absence of added triethylammonium perchlorate) are inhibited by the addition of tetra-alkylammonium chloride (Figure 3), as shown in

$$k_{obs.} = \frac{(68.1 \pm 1.1)\,[NEt_3]}{\{1 + (8.2 \pm 0.8)\,[NEt_3]\}(1 + K_{Cl}[Cl^-])} \qquad (5)$$

equation (5), where $K_{Cl} = 93.1 \pm 4.1$ dm^3 mol^{-1}. The kinetic data for the studies between *trans*-$[W(NH)Cl(dppe)_2]^+$ and triethylamine are collected in Table 2.

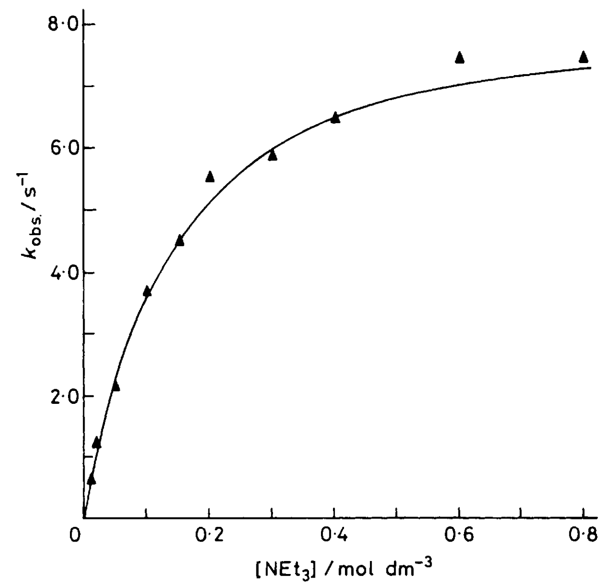


Figure 2. Graph of $k_{obs.}$ against the concentration of triethylamine, for the reaction between *trans*-$[W(NH)Cl(dppe)_2]Cl$ and triethylamine. The curve is that predicted by equation (2). The data are taken from Table 2

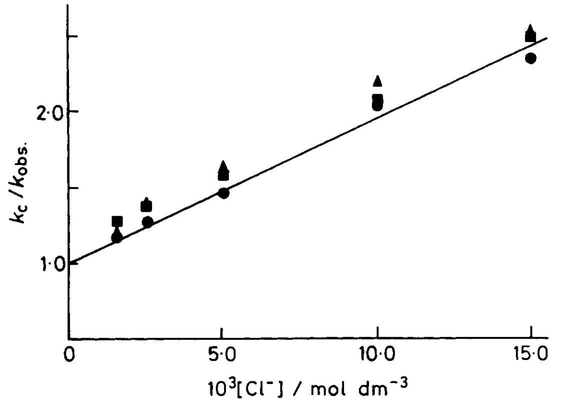


Figure 3. Graph showing the inhibition of the reaction between triethylamine and *trans*-$[W(NH)Cl(dppe)_2]Cl$ by chloride ions. Plot of $k_c/k_{obs.}$ {where $k_c = 68.1[NEt_3]/(1 + 8.2[NEt_3])$} against the concentration of chloride ions; $[NEt_3]$ = 0.1 (▲), 0.2 (■), and 0.4 mol dm^{-4} (●). The data are taken from Table 2

(b) *trans*-$[W(NH)Br(dppe)_2]^+$ and *trans*-$[W(NH)I(dppe)_2]^+$. The reaction of triethylamine with the bromo- or iodo-substrates exhibits an apparent first-order dependence on the

$$k_{obs.} = a[NEt_3] \qquad (6)$$

concentration of triethylamine, equation (6), over the concentration ranges amenable to study for each substrate (X = Br, $[NEt_3] \leqslant 50 \times 10^{-3}$ mol dm^{-3}; X = I, $[NEt_3] \leqslant 1.0 \times$

Table 2. Kinetic data for the reaction of triethylamine with *trans*-[W(NH)Cl(dppe)$_2$]$^+$ in methanol [a] measured at λ = 370 nm and 25 °C

[NEt$_3$]	[NEt$_3$HClO$_4$]	[Cl$^-$] [b]	$k_{obs.}$/s^{-1}
10^{-3} mol dm^{-3}			
5.0			0.45
10.0			0.63
20.0			1.18
40.0			2.00
50.0			2.31
100.0			3.65
150.0			4.44
200.0			5.56
300.0			5.91
400.0			6.25
600.0			7.40
800.0			7.69
100.0		1.25	2.82
		2.5	2.44
		5.0	2.13
		10.0	1.79
		15.0	1.46
200.0		1.25	4.00
		2.5	3.57
		5.0	3.28
		10.0	2.60
		15.0	2.30
400.0		1.25	5.46
		2.5	4.93
		5.0	4.08
		10.0	3.51
		15.0	3.26
100.0	2.5		3.8
	5.0		3.6
	10.0		3.6
	15.0		3.4
200.0	2.5		5.7
	5.0		5.9
	10.0		5.5
	15.0		5.1
400.0	2.5		6.2
	5.0		6.0
	10.0		5.7
	15.0		5.2
100.0	5.0	2.5 [c]	2.70
200.0	5.0	2.5	3.81
400.0	5.0	2.5	5.00
100.0	5.0	5.0	2.30
200.0	5.0	5.0	3.28
400.0	5.0	5.0	4.20
100.0	5.0	10.0	1.85
200.0	5.0	10.0	2.75
400.0	5.0	10.0	3.30
100.0	5.0	15.0	1.72
200.0	5.0	15.0	2.60
400.0	5.0	15.0	3.50

[a] Concentration of *trans*-[W(NH)Cl(dppe)$_2$]$^+$ = 0.25 × 10^{-3} mol dm^{-3}. [b] Chloride ion provided as the tetramethylammonium salt. [c] In studies with triethylammonium perchlorate, chloride ion provided as the tetrabutylammonium salt due to poor solubility of tetramethylammonium perchlorate.

10^{-3} mol dm^{-3}), where $a = (2.9 \pm 0.3) \times 10^3$ dm^3 mol^{-1} s^{-1} (X = Br) and $(1.6 \pm 0.2) \times 10^5$ dm^3 mol^{-1} s^{-1} (X = I).

The proposal that the dependence upon base is first order in triethylamine, and not first order in methoxide, concentration is well established over the large concentration range of triethylamine used in the study with the bromo-substrate (Figure 4). However, the very limited range of triethylamine amenable to study for the iodo-substrate does not define unambiguously the dependence upon the base. The dependence upon triethylamine is verified however upon analysis of the inhibition of these reactions by the respective tetrabutylammonium halide, and equation (6) shown to be the limiting form of a more complex rate expression. The inhibition of both systems is described by the general expression (7), and is illustrated for the bromo-system in Figure 4. When X = Br,

$$k_{obs.} = \frac{b[\mathrm{NEt_3}][\mathrm{CH_3O^-}]}{c[\mathrm{X^-}] + d[\mathrm{CH_3O^-}]} \qquad (7)$$

$b/c = (4.2 \pm 0.3) \times 10^3$ dm^3 mol^{-1} s^{-1} and $b/d = (2.9 \pm 0.3) \times 10^3$ dm^3 mol^{-1} s^{-1}, and when X = I, $b/c = (5.2 \pm 0.2) \times 10^5$ dm^3 mol^{-1} s^{-1} and $b/d = (1.0 \pm 0.3) \times 10^5$ dm^3 mol^{-1} s^{-1}.

Lithium perchlorate (in concentrations comparable to that of the halide salts) has little effect on the rate of the reaction of the bromo-substrate with triethylamine.

The reaction between triethylamine and *trans*-[W(NH)Br(dppe)$_2$]$^+$ is inhibited by the addition of triethylammonium perchlorate. The rate equation (7) is obeyed; the inhibition is the result of the perturbation afforded to equation (4), resulting in a decreased concentration of methoxide ion.

It was not possible to investigate the influence that triethylammonium perchlorate had upon the kinetics of the reaction between triethylamine and *trans*-[W(NH)I(dppe)$_2$]$^+$, because of the very low concentrations of triethylamine necessary to study this reaction, together with the problem of exact neutralisation in the preparation of triethylammonium perchlorate.

The kinetic data for the reactions between triethylamine and the bromo- and iodo-substrates are collected in Tables 3 and 4 respectively.

Influence of the Concentration of Complex upon the Rate of Reaction.—The chloro-, bromo-, and iodo-substrates react with triethylamine at a rate which exhibits a first-order dependence upon the concentration of substrate. However, increasing the concentration of substrate, at a constant concentration of triethylamine for the bromo- and iodo-complexes, results in a small (but discernible) decrease in the rate constant. The inhibition in both cases is merely a consequence of the increased halide-ion concentration, which is introduced as the counter ion to the substrate. The rate constants observed with various concentrations of substrate are well predicted by equation (7) for the bromo- and iodo-substrates, as shown in Table 5. This clearly indicates that the first-order dependence upon the concentration of triethylamine observed in the absence of tetra-alkylammonium halide for the bromo- and iodo-substrates [equation (6)] is misleading and that the more correct rate expression under these conditions is given by equation (7). The absence of a variation of the reaction rate with the concentration of the chloro-substrate is a consequence of the different rate equation, (2), for this complex.

Kinetics of the Reactions with Lithium Methoxide.—The reaction of *trans*-[W(NH)X(dppe)$_2$]$^+$ (X = Cl, Br, or I) with lithium methoxide occurs in essentially the same manner for

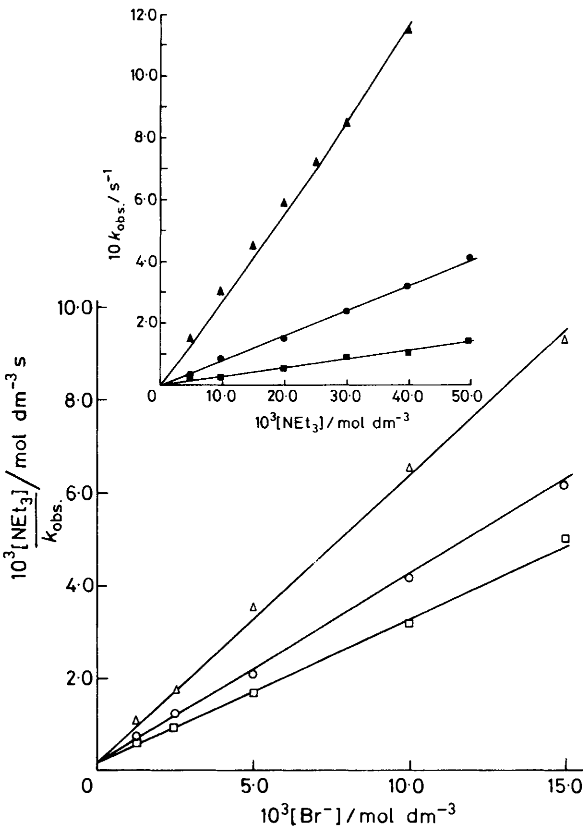


Figure 4. Graph of $[NEt_3]/k_{obs.}$ against the concentration of bromide ions for the reaction between *trans*-$[W(NH)Br(dppe)_2]Br$ and triethylamine, at a fixed concentration of triethylamine; $[NEt_3] = 5.0 \times 10^{-3}$ (△), 10.0×10^{-3} (○), and 20.0×10^{-3} mol dm^{-3} (□). Insert: graph of $k_{obs.}$ against the concentration of triethylamine, at a fixed concentration of tetrabutylammonium bromide; $[Br^-] = 0.25 \times 10^{-3}$ (*i.e.* complex only, note slight curvature of line) (▲), 5.0×10^{-3} (●), and 15.0×10^{-3} mol dm^{-3} (■). Lines drawn are those predicted by equation (7). The data are taken from Table 3

all substrates. There is an initial rapid increase in absorbance [complete within the dead-time of the stopped-flow apparatus (3.3 ms)], the extent of which (except for the chloro-substrate) is independent of the concentration of methoxide. This is followed by a relatively slow, methoxide-dependent, absorbance decrease to yield *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$. Both the spectra of the intermediates (Figure 5) and the rate of decay of these intermediates are dependent upon the nature of the substrate. In all cases the rate of decay of the intermediate exhibits saturation kinetics at high concentrations of methoxide (Figure 6). The decay of the intermediate is given by

$$k_{obs.} = h[CH_3O^-]/(1 + l[CH_3O^-]) \qquad (8)$$

the general expression (8). When X = Cl, $h = (1.4 \pm 0.2) \times 10^4$ dm^3 mol^{-1} s^{-1}, $l = 234.7 \pm 32.1$ dm^3 mol^{-1}; X = Br, $h = (5.4 \pm 0.3) \times 10^3$ dm^3 mol^{-1} s^{-1}, $l = 92.0 \pm 9.3$ dm^3 mol^{-1}; X = I, $h = (2.7 \pm 0.2) \times 10^3$ dm^3 mol^{-1} s^{-1}, $l = 46.6 \pm 6.4$ dm^3 mol^{-1}. The limiting rate constant for all three substrates is identical ($k_0 = 58.8 \pm 3.5$ s^{-1}).

Variation of the concentration of the substrate did not affect the rate of the reaction (Table 5) nor did the addition of tetrabutylammonium halide (or lithium perchlorate) affect the spectrum or kinetics of decay of the intermediate.

The kinetic data for the reactions of the three substrates with lithium methoxide are presented in Table 6.

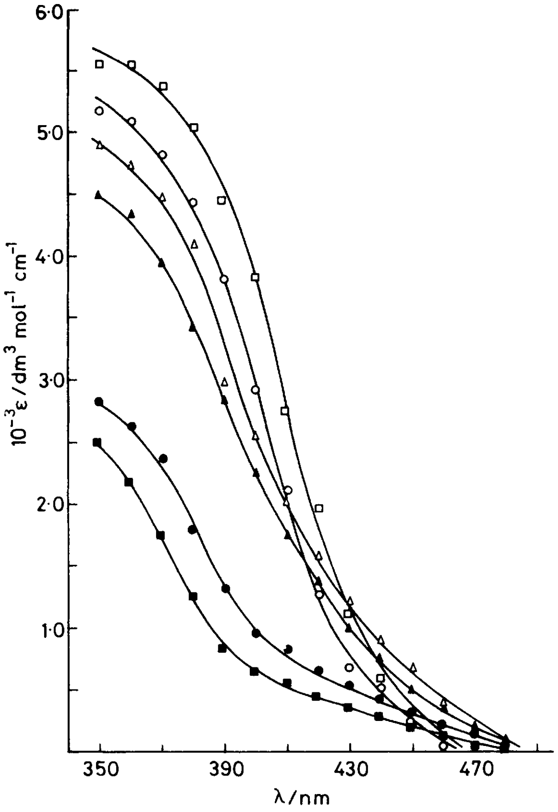


Figure 5. Spectra of the intermediates formed in the reactions between lithium methoxide ($[CH_3O^-] = 0.1$ mol dm^{-3}) and *trans*-$[W(NH)X(dppe)_2]^+$ [X = Cl (▲), Br (●), and I (■)] measured in methanol, and of *trans*-$[W(N)X(dppe)_2]$ [X = Cl (△), Br (○), and I (□)] measured in dichloromethane

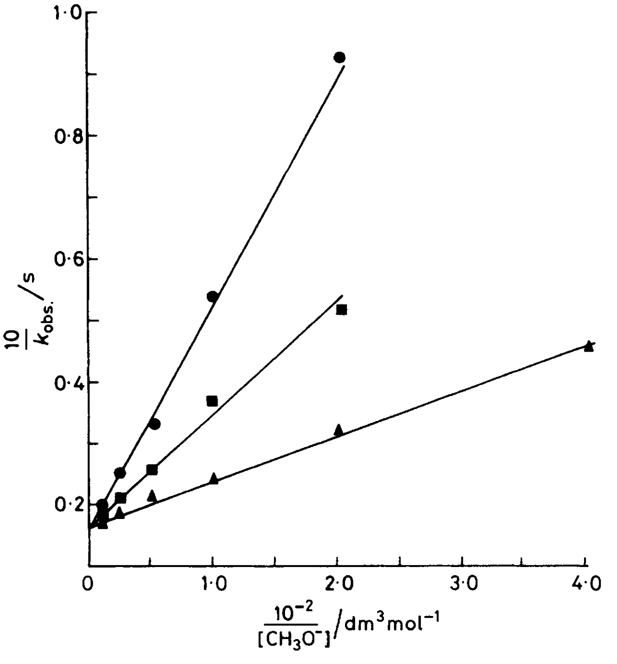


Figure 6. Graph of $1/k_{obs.}$ against $1/[CH_3O^-]$ for the reaction between lithium methoxide and *trans*-$[W(NH)X(dppe)_2]^+$ [X = Cl (▲), Br (■), and I (●)]. The data are taken from Table 6

Table 3. Kinetic data for the reaction of triethylamine with *trans*-$[W(NH)Br(dppe)_2]^+$ in methanol [a] measured at λ = 370 nm and 25 °C. Salt = NBu_4Br except where stated otherwise

$[NEt_3]$	$[NEt_3HClO_4]$	[Salt]	$k_{obs.}/s^{-1}$
	10^{-3} mol dm^{-3}		
2.5			6.60
5.0			15.60
10.0			30.30
15.0			48.81
20.0			58.14
25.0			75.76
30.0			90.90
40.0			113.6
50.0			128.2
10.0		1.25[b]	31.23
10.0		2.5[b]	30.61
10.0		5.0[b]	33.14
10.0		10.0[b]	33.52
10.0		15.0[b]	34.12
5.0		5.0	2.74
10.0		5.0	7.25
20.0		5.0	14.23
30.0		5.0	22.83
40.0		5.0	31.75
50.0		5.0	41.32
5.0		15.0	0.48
10.0		15.0	1.35
20.0		15.0	3.85
30.0		15.0	6.90
40.0		15.0	10.58
50.0		15.0	12.20
5.0		1.25	4.88
5.0		2.5	2.70
5.0		5.0	1.39
5.0		10.0	0.77
5.0		15.0	0.53
10.0		1.25	2.86
10.0		2.5	2.08
10.0		5.0	1.25
10.0		10.0	0.62
10.0		15.0	0.34
20.0		1.25	1.40
20.0		2.5	0.91
20.0		5.0	0.50
20.0		10.0	0.24
20.0		15.0	0.16
5.0	2.5		4.21
5.0	5.0		2.40
5.0	10.0		1.70
5.0	15.0		0.81
10.0	2.5		13.0
10.0	5.0		8.2
10.0	10.0		4.5
10.0	15.0		3.5
20.0	2.5		38.2
20.0	5.0		25.2
20.0	10.0		16.3
20.0	15.0		11.8

[a] Concentration of *trans*-$[W(NH)Br(dppe)_2]^+ = 0.25 \times 10^{-3}$ mol dm^{-3}. [b] Salt = $LiClO_4$.

Table 4. Kinetic data for the reaction of triethylamine with *trans*-$[W(NH)I(dppe)_2]^+$ in methanol [a] measured at λ = 370 nm and 25 °C

$[NEt_3]/10^{-3}$ mol dm^{-3}	$[I^-]$ [b]$/10^{-3}$ mol dm^{-3}	$k_{obs.}/s^{-1}$
0.30		38.5
0.35		41.7
0.40		52.6
0.45		62.5
0.50		80.0
0.75		133.3
1.00		170.2
0.50	1.25	19.6
0.50	2.5	11.4
0.50	5.0	6.3
0.50	10.0	4.4
0.50	15.0	2.9
1.00	1.25	58.8
1.00	2.5	35.7
1.00	5.0	20.8
1.00	10.0	15.6
1.00	15.0	9.9
2.00	1.25	138.9
2.00	2.5	96.2
2.00	5.0	51.2
2.00	10.0	43.5
2.00	15.0	35.7

[a] Concentration of *trans*-$[W(NH)I(dppe)_2]^+ = 0.25 \times 10^{-3}$ mol dm^{-3}. [b] Iodide ion supplied as the tetrabutylammonium salt.

Discussion

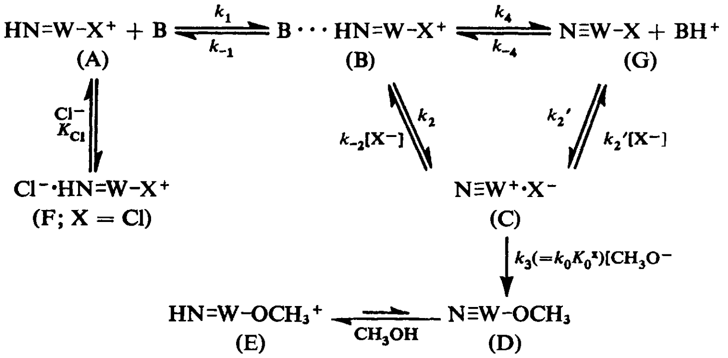
The present study of the base-catalysed formation of *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$ from *trans*-$[W(NH)X(dppe)_2]^+$ in methanol complements the earlier study on the reactions of *trans*-$[Mo(NH)X(dppe)_2]^+$ with triethylamine.[4] The mechanism of the reactions of the molybdenum complexes with triethylamine was shown to involve initial deprotonation and halide loss from the substrate. Subsequent rate-limiting attack of methoxide [$k = (1.7 \pm 0.4) \times 10^6$ dm^3 mol^{-1} s^{-1}] on the relatively stable $[Mo(N)(dppe)_2]^+$, followed by proton abstraction from the solvent, yields *trans*-$[Mo(NH)(OCH_3)(dppe)_2]^+$. However, in contrast to the molybdenum system where both the deprotonation and halide loss from the substrate are rapid ($k > 300$ s^{-1}) and complete within the dead-time of the stopped-flow apparatus, with the tungsten complexes the initial deprotonation is not extensive with triethylamine. This permits some important conclusions to be made about the deprotonation and halide-loss stages, and the influence that the metal has upon the basicity of the imido-ligands. All the discussion will centre around Scheme 2 and a summary of the derived rate and equilibrium constants is given in Table 9.

Reactions of trans-$[W(NH)X(dppe)_2]^+$ (X = Br *or* I).—The general rate expression for the reaction between the bromo- and iodo-substrates with triethylamine is described by equation (7), and is consistent with the mechanism shown in Scheme 2. Thus association of *trans*-$[W(NH)X(dppe)_2]^+$ (A) with triethylamine gives rise to the adduct (B). Deprotonation of the substrate generates the nitrido-group which is strongly *trans*-labilising and results in the rapid loss of the halide to yield the ion pair $[W(N)(dppe)_2]^+ \cdot X^-$ (C). Although, of course, the studies with triethylamine do not necessitate the ion pair, evidence for this species is obtained from the studies with lithium methoxide (see later). Subsequent attack of methoxide on (C) gives *trans*-$[W(N)(OCH_3)(dppe)_2]$ (D). The

Table 5. Kinetic data for the reactions of triethylamine or lithium methoxide with *trans*-$[W(NH)X(dppe)_2]^+$ (X = Cl, Br, or I) in methanol: influence of the variation of the concentration of complex. All data measured at λ = 370 nm at 25 °C

Complex	[Complex]/ 10^{-3} mol dm^{-3}	Base	[Base]/ 10^{-3} mol dm^{-3}	$k_{obs.}/s^{-1}$	$k_{calc.}/s^{-1}$
trans-$[W(NH)Cl(dppe)_2]Cl$	0.50	NEt_3	100.0	2.5	3.2 [a]
	0.25		100.0	3.0	3.2
	0.13		100.0	3.2	3.2
	0.50	$Li(OCH_3)$	10.0	41.9	
	0.25		10.0	42.0	
	0.13		10.0	41.7	
trans-$[W(NH)Br(dppe)_2]Br$	0.50	NEt_3	15.0	31.5	33.5 [b]
	0.40		15.0	36.2	36.0
	0.30		15.0	41.9	39.1
	0.20		15.0	45.0	42.0
	0.10		15.0	48.6	46.2
	0.50	$Li(OCH_3)$	10.0	38.5	
	0.40		10.0	40.8	
	0.30		10.0	40.0	
	0.20		10.0	38.5	
trans-$[W(NH)I(dppe)_2]I$	0.50	NEt_3	1.0	140	152 [c]
	0.40		1.0	153	160
	0.30		1.0	165	168
	0.20		1.0	169	173
	0.50	$Li(OCH_3)$	10.0	23.5	
	0.40		10.0	23.5	
	0.30		10.0	27.0	
	0.20		10.0	26.2	

[a] Based on equation (5). [b] Based on equation (7), using the parameters established for the bromo-system. [c] Based on equation (7), using the parameters established for the iodo-system.



Scheme 2. Mechanism for the reactions of base, B (triethylamine or lithium methoxide), with *trans*-$[W(NH)X(dppe)_2]^+$ (phosphine ligand omitted for clarity)

strongly electron-releasing methoxy-group renders the *trans*-nitrido-group sufficiently basic to abstract a proton from a molecule of solvent to yield the product *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$ (E) and 1 mol equivalent of methoxide. Thus, in this reaction, triethylamine has two roles: to deprotonate the substrate (A), and, as a general base catalyst, to generate methoxide [equation (4)]. The mol equivalent of methoxide which is consumed in the formation of (D) from (C) is subsequently regenerated in the formation of the product (E) from (D), giving rise to the observed stoicheiometry, $[W]/[NEt_3] = 1.0$.

The observed first-order dependence upon the concentration of triethylamine, and more specifically, the absence of an inverse dependence upon the concentration of triethylammonium ion, would be consistent with the halide-release step being catalysed by triethylammonium ion. This however seems unlikely and a more reasonable proposal is that the deprotonation and halide-loss steps are concerted. No doubt the strong *trans*-labilising influence of the nitrido-group and the coupling of the halide dissociation to the rapid deprotonation reaction results in the concerted process. A concerted deprotonation, halide-dissociation mechanism has previously been proposed[8] in the base hydrolysis of *cis*-$[CoX_2(L)]^+$ (X = Cl or Br, L = 1,4,7,10-tetra-azacyclododecane).

The principle of microscopic reversibility dictates that the reverse reaction (k_{-2}) also be concerted. The absence of a dependence upon the concentration of triethylammonium ion in the halide-dependent term of equation (7) is not inconsistent with this proposal. By far the most plentiful acid in the system is methanol, which would not be detected kinetically as it is the solvent.

For the mechanism shown in Scheme 2, application of the

Table 6. Kinetic data for the reaction of lithium methoxide with *trans*-$[W(NH)X(dppe)_2]^+$ (X = Cl, Br, or I) in methanol,[a] measured at λ = 370 nm and 25 °C

Complex	$[CH_3O^-]$/ 10^{-3} mol dm^{-3}	Salt	[Salt]/ 10^{-3} mol dm^{-3}	$k_{obs.}/s^{-1}$
$[W(NH)Cl(dppe)_2]^+$	2.5			21.74
	5.0			31.25
	10.0			41.67
	20.0			45.46
	40.0			52.63
	100.0			55.56
	20.0	NMe_4Cl	1.25 [b]	45.20
	20.0		2.5	44.62
	20.0		5.0	45.00
	20.0		10.0	43.12
	20.0		15.0	44.20
$[W(NH)Br(dppe)_2]^+$	5.0			19.23
	10.0			27.03
	20.0			38.76
	40.0			43.48
	50.0			47.62
	100.0			52.63
$[W(NH)I(dppe)_2]^+$	5.0			10.75
	10.0			18.76
	20.0			31.75
	40.0			39.22
	50.0			48.31
	100.0			50.00
	5.0	NBu_4I	5.0 [b]	10.10
	5.0		10.0	10.00
	5.0		20.0	8.33
	5.0		50.0	7.69
	5.0	$LiClO_4$	5.0	10.00
	5.0		10.0	10.10
	5.0		20.0	10.10
	5.0		30.0	9.21
	5.0		50.0	9.00

[a] Concentration of complex = 0.25 × 10^{-3} mol dm^{-3}. [b] Initial absorbance is identical to that in the absence of added tetra-alkylammonium halide salts, at all concentrations of salt.

steady-state approximation to species (C) gives equation (9),

$$k_{obs.} = \frac{K_1k_2k_3[NEt_3][CH_3O^-]}{k_{-2}[X^-] + k_3[CH_3O^-]} \qquad (9)$$

provided of course $K_1[NEt_3] < 1$. When X = Br, K_1k_2 = (2.9 ± 0.3) × 10^3 dm^3 mol^{-1} s^{-1}, k_{-2}/k_3 = 0.71 ± 0.11; when X = I, K_1k_2 = (1.6 ± 0.2) × 10^5 dm^3 mol^{-1} s^{-1}, k_{-2}/k_3 = 0.19 ± 0.05.

The ratio of the denominator terms, $k_{-2}[X^-]/k_3[CH_3O^-]$, represents the competition of halide and methoxide ion for $[W(N)(dppe)_2]^+\cdot X^-$ (C). However, direct comparison of the bromo- and iodo-values is not strictly meaningful because of the difference in the nature of (C).

The derivation of equation (9) does not uniquely define the rate-limiting step, the same equation being obtained whether loss of halide (k_2) or attack of methoxide on the five-co-ordinate intermediate (k_3) is rate-limiting. However, the studies with lithium methoxide and the bromo- or iodo-substrates resolves this ambiguity and further substantiates the mechanism shown in Scheme 2.

The reaction of the bromo- or iodo-substrates with lithium methoxide occurs with the rapid formation of an intermediate (k > 300 s^{-1}), which can be detected spectrophotometrically. The spectra of the intermediates (Figure 5) are clearly different, not only from one another, but also from those of *trans*-$[W(N)X(dppe)_2]$. It seems most likely that with the strong base, methoxide, the deprotonation of substrate (A) is total [(A) to (G), B = CH_3O^-] and that rapid loss of halide from (G) gives the ion pairs $[W(N)(dppe)_2]^+\cdot X^-$ (C), whose spectra are those measured. The proposed nature of the intermediate is consistent with the negligible influence that tetra-alkylammonium halides have on both the spectrum and the kinetics of the subsequent decay of the intermediate. Evidence for ion pairing between singly charged ions in methanol {including the species $[Mo(N)(dppe)_2]^+\cdot X^-$}[4] has been presented before.[9]

The decay of the intermediate to yield the product *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$ (E) occurs according to the rate equation (8), and is illustrated in Figure 6. Two mechanisms are consistent with this rate equation, and in particular the independence of the limiting rate constant (k_0 = 58.8 ± 3.5 s^{-1}) on the nature of the substrate, and the slight variation in the rate at low concentrations of methoxide ion: (1) formation of an ion-triplet precursor, prior to rate-limiting attack of methoxide, equation (10) for which the constants of equation

$$N{\equiv}W^+\cdot X^- + CH_3O^- \overset{K_0^x}{\rightleftharpoons} N{\equiv}W^+\cdot X^-\cdot CH_3O^- \xrightarrow[-X^-]{k_0}$$
$$N{\equiv}W{-}OCH_3 \overset{CH_3OH}{\rightleftharpoons} HN{=}W{-}OCH_3^+ \qquad (10)$$

(8) represent the values $h = K_0^xk_0$ and $l = k_0$, limiting constant = k_0; (2) formation of a steady-state ' activated ' complex, prior to rate-limiting attack of methoxide, equation (11)

$$N{\equiv}W^+\cdot X^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \{N{\equiv}W^+\cdot X^-\}^* \xrightarrow[-X^-]{k_b[CH_3O^-]}$$
$$N{\equiv}W{-}OCH_3 \overset{CH_3OH}{\rightleftharpoons} HN{=}W{-}OCH_3^+ \qquad (11)$$

for which the constants of equation (8) represent the values $h = k_ak_b/k_{-a}$ and $l = k_b/k_{-a}$, limiting constant = k_a.

It is impossible to distinguish between these two possibilities on the basis of the kinetic data. The ' activation ' process may be nothing more than the correct orientation of a molecule of solvent, ready for facile proton transfer after the attack of methoxide on the ion pair. Clearly, however, if the same intermediates are being generated with lithium methoxide (albeit in detectable concentrations) as with triethylamine, then the rate of decay of the intermediate must be inhibited by halide ions in the same manner as in the triethylamine reaction, equation (7). The extent of the inhibition by halide ion in the reactions with triethylamine is dependent upon the ratio $[X^-]/[CH_3O^-]$. Since the lowest concentration of lithium methoxide used (5 × 10^{-3} mol dm^{-3}) is greater than the highest concentration of methoxide generated in the reactions with triethylamine ($[NEt_3]$ = 40 × 10^{-3}, $[CH_3O^-]$ = 1.11 × 10^{-3} mol dm^{-3}) a correspondingly larger concentration of halide ion would be necessary to produce the same degree of inhibition.

Irrespective of the intimate details of the mechanism of attack of methoxide ion on the five co-ordinate intermediate (C), the fact that (for the bromo- and iodo-substrates) this step in the reactions with lithium methoxide is slower than halide loss dictates that, at the lower concentrations of methoxide ion generated in the triethylamine reaction, it too must be rate-limiting. This conclusion is numerically substantiated by comparison of the values for $K_1k_2[NEt_3]$ (rate of deprotonation and halide loss) and $K_0^xk_0[CH_3O^-]$\{= $k_3[CH_3O^-]$, rate of methoxide attack on (C)\}.

One further point of relevance to the reaction with tri-

Table 7. Determination of the equilibrium constant (K_T) for the process *trans*-$[W(NH)Cl(dppe)_2]^+ + CH_3O^- \rightleftharpoons [W(N)(dppe)_2]^+ \cdot Cl^- + CH_3OH$, in methanol,[a] measured at λ = 370 nm and 25 °C

$[CH_3O^-]$/ 10^{-3} mol dm^{-3}	Absorbance [b]	10^{-3} K_T
2.5	0.58	5.76
5.0	0.71	6.06
10.0	0.81	5.95
15.0	0.85	6.10
20.0	0.89	6.10
30.0	0.91	5.99
40.0	0.93	5.22
60.0	0.95	5.35
100.0	0.97	5.45

[a] Concentration of *trans*-$[W(NH)Cl(dppe)_2]^+$ = 0.25 × 10^{-3} mol dm^{-3}. [b] Values of K_T calculated using the absorption coefficients of *trans*-$[W(NH)Cl(dppe)_2]^+$ (ε = 1 448.3 dm^3 mol^{-1} cm^{-1}) and the intermediate (ε = 4 000.0 dm^3 mol^{-1} cm^{-1}) at λ = 370 nm.

ethylamine is that at high concentrations of triethylamine, where concentrations of methoxide are generated comparable to those used in the study with lithium methoxide ($[NEt_3]$ = 800 × 10^{-3}, $[CH_3O^-]$ = 5.0 × 10^{-3} mol cm^{-3}), the reaction with the iodo- or bromo-substrate is complete within the dead-time of the stopped-flow apparatus. This further substantiates the specific role of triethylamine as the base that deprotonates the substrate (A).

Reactions of trans-$[W(NH)Cl(dppe)_2]^+$.—Like the studies with the bromo- and iodo-substrates, the reaction between triethylamine and *trans*-$[W(NH)Cl(dppe)_2]^+$ exhibits a first-order dependence upon the concentration of triethylamine, at low concentrations of the base. However, at the much higher concentrations of triethylamine which can be employed with this substrate, limiting zero-order dependence upon triethylamine is observed. At all concentrations of triethylamine the initial absorbance is that corresponding to *trans*-$[W(NH)Cl(dppe)_2]^+$. This constrasts to the reaction with lithium methoxide ($[CH_3O^-]$ = 5.0 × 10^{-3} mol dm^{-3}, equivalent to $[NEt_3]$ = 800 × 10^{-3} mol dm^{-3}), which exhibits an initial increase in absorbance (k > 300 s^{-1}) followed by a decrease in absorbance to yield *trans*-$[W(NH)(OCH_3)(dppe)_2]^+$.

Indeed, *trans*-$[W(NH)Cl(dppe)_2]^+$ behaves in a very similar manner to the bromo- and iodo-substrates, in its reactions with lithium methoxide. The spectrum of the intermediate generated in the reaction between lithium methoxide and *trans*-$[W(NH)Cl(dppe)_2]^+$ (Figure 5) is very similar, but noticeably less intense than that of *trans*-$[W(N)Cl(dppe)_2]$. As noted earlier, it is proposed that this represents the ion pair $[W(N)(dppe)_2]^+ \cdot Cl^-$(C). The kinetics of decay of this intermediate are similar to those for the bromo- and iodo-substrates, obeying the rate equation (8) with the same limiting rate constant (k_0 = 58.8 ± 3.5 s^{-1}), consistent with the mechanism shown in equations (10) and (11).

Thus it is proposed that the mechanism of the reaction between triethylamine and *trans*-$[W(NH)Cl(dppe)_2]^+$ is identical to that already described for the bromo- and iodo-substrates (Scheme 2) involving initial rapid formation of the species (B). However, now the kinetic detection of an adduct between triethylamine and the chloro-complex (A) (K_1 = 8.2 ± 0.8 dm^3 mol^{-1}), which subsequently breaks down to yield the products (k_2 = 8.3 ± 0.6 s^{-1}), gives further credance to the proposed mechanism.

Table 8. Comparison of the pK_a for *trans*-$[M(NH)X(dppe)_2]^+$ (M = Mo or W, X = F or Cl) in methanol at 25 °C

Complex	pK_a	Ref.
trans-$[Mo(NH)F(dppe)_2]BF_4$	12.7 (13.2) *	4
trans-$[W(NH)F(dppe)_2]BF_4$	15.5	This work
trans-$[Mo(NH)Cl(dppe)_2]Cl$	<10	4
trans-$[W(NH)Cl(dppe)_2]Cl$	⩽12.8 (13.2) *	This work

* Determined in dichloromethane.

There is an important difference between the studies with the chloro-substrate and those of its bromo- and iodo-analogues. The reaction of all three complexes with lithium methoxide show similar behaviour, in which methoxide attack on the ion pair (C) is slower than the deprotonation, halide-loss steps. It is clear that, in the reactions of the bromo- and iodo-complexes with triethylamine, methoxide attack on (C) is also significantly slower (and hence rate-limiting) than the deprotonation, halide-loss step (Table 9). However, in the reaction of the chloro-substrate with triethylamine, the limiting rate constant (k_2 = 8.3 ± 0.6 s^{-1}) is less than that for methoxide attack upon (C), calculated using $k_3 = k_0K_0^{Cl}$, and the concentration of methoxide calculated using K_B = 1.26 × 10^{-6} for equation (4). This apparent anomaly between the studies of *trans*-$[W(NH)Cl(dppe)_2]^+$ with triethylamine and with lithium methoxide can be rationalised if the act of deprotonation within the adduct (B) is rate-limiting with triethylamine, but not with the stronger base methoxide. Certainly this postulate is consistent with the measured acidity of *trans*-$[W(NH)Cl(dppe)_2]^+$ (pK_a ⩽ 12.8, see later), rendering the deprotonation by triethylamine (but not by methoxide) thermodynamically unfavourable, and the different rate equation, (2), observed for the reaction between triethylamine and the chloro-substrate compared with that, (7), for the bromo- and iodo-substrates. From Scheme 2, if deprotonation within the adduct (B) is rate-limiting then equation (12) is obtained, in agreement with the observed form (2), where K_1 = 8.2 ± 0.8 dm^3 mol^{-1} and k_2 = 8.3 ± 0.6 s^{-1}.

$$k_{obs.} = \frac{K_1k_2[NEt_3]}{1 + K_1[NEt_3]} \qquad (12)$$

A significant difference between the reactions of the chloro-substrate and that of the iodo- or bromo-substrates resides in the influence of the respective tetra-alkylammonium halides upon the reactions with triethylamine. The inhibition of the reaction of *trans*-$[W(NH)Cl(dppe)_2]^+$ by tetra-alkylammonium chloride salts takes the form of equation (5), as illustrated in Figure 3. This is consistent with the formation of an ion pair (F) between the imido-proton of the substrate (A; X = Cl) and a chloride ion, K_{Cl} = 93.1 ± 4.1 dm^3 mol^{-1}, which hinders the deprotonation by triethylamine. The analogous reactions of the bromo- and iodo-substrates are inhibited by halide (over the same concentration range) because of the competitive attack by halide and methoxide ions on the ion pair (C). Clearly, for the chloro-substrate, when deprotonation is rate-limiting this type of inhibition is not observed. The bromo- and iodo-complexes show no detectable ion associations with their respective halide ions.

The Intimate Mechanism.—The factors which influence whether a particular complex chooses an interchange dissociative (I_d) or dissociative mechanism (D)[10] have been discussed before.[11] Certainly steric crowding of the intermediate, poorly nucleophilic solvents, strong labilising groups, and good

Table 9. Summary of rate and equilibrium constants at 25 °C

Reaction *	Rate or equilibrium constant	Comments
(*a*) Studies with triethylamine		
$NEt_3 + (A) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (B)$	$K_1{}^x = k_1/k_{-1}$	Outer-sphere association of NEt_3 with substrate
	$K_1{}^{Cl} = 8.2 \pm 0.8$ dm^3 mol^{-1}	X = Cl
	$K_1{}^{Br} < 4$ dm^3 mol^{-1}	X = Br
	$K_1{}^{I} < 200$ dm^3 mol^{-1}	X = I
$Cl^- + (A) \overset{K_{Cl}}{\rightleftharpoons} (F)$	$K_{Cl} = 93.1 \pm 4.1$ dm^3 mol^{-1}	Ion-pair association of Cl^- with the chloro-substrate
	K_{Br}, $K_I < 14$ dm^3 mol^{-1}	Ion-pair association of Br^- and I^- with the respective substrate
$(B) \underset{k_{-2}[X^-]}{\overset{k_2}{\rightleftharpoons}} (C) \xrightarrow{k_3[CH_3O^-]} (D)$	$k_2 = 8.3 \pm 0.6$ s^{-1}, X = Cl	Rate-limiting deprotonation of substrate by triethylamine
	$k_2 > 7.2 \times 10^2$ s^{-1}, X = Br $k_2 > 8.0 \times 10^2$ s^{-1}, X = I	Concerted, deprotonation and halide loss from (B)
	$k_{-2}/k_3 = 0.71 \pm 0.11$, X = Br	Nucleophilic competition ratio for halide and methoxide attack on the ion pair (C)
	$k_{-2}/k_3 = 0.19 \pm 0.05$, X = I	
	$k_{-2} = (3.8 \pm 0.7) \times 10^3$ dm^3 mol^{-1} s^{-1}, X = Br	Calculated using the nucleophilic competition ratio (k_{-2}/k_3), and the measured values of k_3 (= $k_0K_0{}^x$)
	$k_{-2} = (5.2 \pm 0.8) \times 10^2$ dm^3 mol^{-1} s^{-1}, X = I	
(*b*) Studies with lithium methoxide		
$CH_3O^- + (A) \overset{K_T}{\rightleftharpoons} (C) + CH_3OH$	$K_T = \frac{k_1}{k_{-1}} \cdot \frac{k_4}{k_{-4}} \cdot \frac{k_2'}{k_{-2}'}$ $K_T = (6.1 \pm 0.6) \times 10^3$, X = Cl $K_T > 4.5 \times 10^4$, X = Br or I	Equilibrium constant for the formation of the spectroscopically detected intermediate
$CH_3O^- + (C) \overset{K_0{}^x}{\rightleftharpoons} (C){\cdot}CH_3O^- \xrightarrow{k_0} (D)$	$K_0{}^{Cl} = 234.7 \pm 32.1$ dm^3 mol^{-1}, X = Cl	Attack of methoxide on (C). Alternative mechanism involving ' activated ' complex is discussed in the text
	$K_0{}^{Br} = 92.0 \pm 9.3$ dm^3 mol^{-1}, X = Br $K_0{}^{I} = 46.6 \pm 6.4$ dm^3 mol^{-1}, X = I	
	$k_0 = 58.8 \pm 3.5$ s^{-1}, X = Cl, Br, or I	

* See Scheme 2 for key.

leaving groups favour a dissociative mechanism. All these qualifications are met by the present system. The bulky nature of the phosphine ligand will tend to block the attack of nucleophiles at the five-co-ordinate intermediate as is evident in the crystal structure of the 16-electron species, [Mo(CO)(dppe)$_2$], in which the metal is 0.13 Å above the basal plane.[12] For reasons which are not entirely clear, methanol is a poor nucleophile for the five-co-ordinate intermediate (C), allowing the detection of the methoxide-dependent decay of this intermediate. The nitrido-group, which is generated by deprotonation of the imido-substrate, is certainly very strongly *trans*-labilising,[13] which operates not only on the halide leaving group, but also upon the attacking nucleophile. However, this nitrido-system can operate a unique ' switching ' process, in which the labilising force can be ' switched on ' or ' switched off ' by a simple proton-transfer step. As has been alluded to earlier, this may, in part, be responsible for the relatively slow formation of the product *trans*-[W(NH)(OCH$_3$)(dppe)$_2$]$^+$.

Influence of the trans *ligand and metal on the basicity of the nitrido-group.* In the reaction between *trans*-[W(NH)Cl(dppe)$_2$]$^+$ and lithium methoxide the magnitude of the initial absorbance jump is dependent upon the concentration of the base. Clearly, from the earlier discussion, the equilibrium constant calculated from this absorbance jump as shown in Table 7 [$K_T = (6.1 \pm 0.6) \times 10^3$] is the product of the equilibrium constant for deprotonation ($K_S = k_1k_4/k_{-1}k_{-4}$) with methoxide and the dissociation of chloride from (G) ($K_D = k_2'/k_{-2}'$). Thus using the literature value for the pK_a of methanol (16.6),[6] a limit for the pK_a of *trans*-[W(NH)Cl(dppe)$_2$]$^+$ in methanol can be calculated to be p$K_a \leqslant 12.8$. Deprotonation of the same substrate by triethylamine in the poorly ionising solvent dichloromethane gave a value of pK_a = 13.2.

There is no reaction between *trans*-[W(NH)F(dppe)$_2$]$^+$ and triethylamine in methanol, but with lithium methoxide absorbance changes corresponding to deprotonation of the substrate are observed, from which its pK_a was calculated to be 15.5.

The increased basicity of the nitrido-group (in the tungsten series) with the *trans* halide along the series F > Cl > Br, I is identical to that observed in the molybdenum analogues.[4] The order reflects the π-donating capabilities of the halide.[14]

It is now possible, by direct comparison with the previous study on the molybdenum complexes,[4] to assess, quantitatively the influence that the metal has upon the basicity of the nitrido-group. Direct comparison is possible only for the fluoro- and chloro-complexes, where it is seen that a tungsten complex is about a 1 000-fold more basic than its molybdenum counterpart (Table 8). The increased basicity of ligands when co-ordinated to the heavier elements of the transition-metal series (or increased basicity of the elements themselves) has been observed before.[15-17] This greater electron-releasing capability of the heavier elements manifests itself in other aspects of the chemistry associated with the ' site ' containing four phosphorus donor atoms co-ordinated to a metal atom. Thus the rate of formation of hydrazido(2−)-complexes from the reactions of acids with *trans*-[$M(N_2)_2(dppe)_2$] in tetrahydrofuran [18] and *cis*-[$M(N_2)_2(PMe_2Ph)_4$] in methanol [19] (M = Mo or W) is faster for the tungsten than molybdenum complexes. Related to this is the observation that *cis*-[$W(N_2)_2(PMe_2Ph)_4$] reacts in methanol alone to yield ammonia whereas the molybdenum counterpart requires the addition of acid.[20] Finally the relative rates of reaction of methyl iodide and *trans*-[$M(N_2CH_3)Br(dppe)_2$] ($k_W/k_{Mo} = 5.4$),[21] which occurs with S_N2 attack by the complex on the alkyl halide, also reflects the greater electron density on the alkyldiazenido-ligand when co-ordinated to tungsten.

Experimental

The tungsten complexes containing the cation *trans*-[$W(NH)X(dppe)_2$]$^+$ (X = F, Cl, Br, I, or CH_3O) were prepared by previously described methods.[3] Lithium methoxide was prepared and standardised with phenolphthalein as reported earlier.[4] Methanol was freshly distilled from magnesium methoxide in an all-glass still immediately prior to preparation of the solutions. Tetramethylammonium chloride (Aldrich), tetrabutylammonium chloride (Aldrich), tetrabutylammonium bromide (Lancaster Synthesis), and tetrabutylammonium iodide (B.D.H.) were used as received, as was lithium perchlorate (B.D.H.). Standard solutions of triethylammonium perchlorate were generated ' *in situ* ' by the addition of equimolar amounts of triethylamine (B.D.H.) and perchloric acid (B.D.H., Aristar).

All kinetic measurements were performed at 25 °C using an Aminco-Morrow stopped-flow spectrophotometer. The absorbance–time traces were curve-fitted by the method of Thorneley,[22] or by the normal semilogarithmic plot.[23]

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