Mechanism of the Reaction between *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(Ph_2PCH_2CH_2PPh_2)_2]^+$ and NEt_3: the Influence of the Metal on the Rates of Proton Transfer of Hydrazido(2−)-ligands

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The reaction between an excess of NEt_3 and *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane] in tetrahydrofuran, under an atmosphere of dinitrogen, ultimately to yield *trans*-$[W(N_2)_2(dppe)_2]$, has been studied. The mechanism of the reaction involves rate-limiting deprotonation of the hydrazido(2−)-residue to generate *trans*-$[W(NNH)(p\text{-}MeC_6H_4SO_3)(dppe)_2]$. The subsequent pathway involves the dissociation of $p\text{-}MeC_6H_4SO_3$ and deprotonation of the diazenido-residue to generate $[W(N_2)(dppe)_2]$. Rapid attack of dinitrogen, present in solution, yields the product. The influence of the metal (Mo or W) on the rates of proton transfer in this reaction is discussed.

The hydrazido(2−)-ligand (NNH_2^{2-}) probably represents the most important intermediate detected in the biological[1] and chemical[2] nitrogen fixation processes established so far. Currently there is much interest in the species *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane] which can be electrochemically reduced to yield ammonia.[3] Despite the fundamental importance of the role played by the hydrazido(2−)-species in the mechanisms of such reactions, relatively little is known about the protonation or deprotonation behaviour of simple transition-metal complexes containing this residue.

Previous studies[4] on the mechanism of the reactions of base with *trans*-$[Mo(NNH_2)X(dppe)_2]^+$ [X = F, Br, or $p\text{-}MeC_6H_4SO_3$] have shown that the reaction described by equation (1) can occur by a variety of pathways depending upon the nature of the *trans* substituent, the base (B), and the solvent.

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

In general the reactions of bases with the analogous tungsten complexes *trans*-$[W(NNH_2)X(dppe)_2]^+$ (X = F, Cl, or Br) do not proceed according to equation (1) but rather yield *trans*-$[W(N_2H)X(dppe)_2]$.[5] However, *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ does react with an excess of NEt_3 in tetrahydrofuran (thf) according to the stoicheiometry of equation (1). Described herein is a kinetic study of this last reaction which demonstrates that, in contrast to the behaviour of the molybdenum complexes,[4] deprotonation of the hydrazido(2−)-ligand is rate limiting. The influence of the metal on the rates of proton transfer in this reaction is discussed.

Results

The kinetics of the reaction between *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ and NEt_3 in thf were studied using an excess of NEt_3 ($[NEt_3]:[W] > 20:1$), and maintaining a constant ionic strength of 0.1 mol dm^{-3} using $[NBu^n_4]BF_4$, at 25.0 °C. At all wavelengths in the range 350—450 nm, the absorbance *versus* time traces were exponential with an initial absorbance corresponding to that of *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$, and a final absorbance corresponding to *trans*-$[W(N_2)_2(dppe)_2]$. The kinetic data are shown in the Table.

Table. Kinetic data for the reaction between *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ and NEt_3 in thf ($\theta_c = 25.0$ °C, $\lambda = 400$ nm, $I = 0.1$ mol dm^{-3} $[NBu^n_4]BF_4$)

$[NEt_3]^a$/ mmol dm^{-3}	$[NEt_3H^+]$/ mmol dm^{-3}	$k_{obs.}$/s^{-1}	$k'_{obs.}{}^b$/s^{-1}
2.0		0.05	
5.0		0.10	
5.0^c		0.10	
10.0		0.15	0.08
15.0		0.27	
25.0		0.40	0.25
25.0^c		0.38	
40.0		0.65	
50.0		0.80	0.54
75.0		1.12	0.89
100.0		1.50	1.15
100.0^c		1.52	
125.0		1.90	
150.0		2.25	1.62
150.0^c		2.40	
50.0	0.50	0.43	0.050
	1.00	0.28	0.030
	2.50	0.14	0.011
	5.00	0.08	0.005
	10.00	0.04	
100.0	0.50	1.05	0.18
	1.00	0.77	0.10
	2.50	0.42	0.040
	5.00	0.25	0.023
	10.00	0.14	0.010
150.0	0.50	2.69	0.40
	1.00	1.64	0.22
	2.50	0.98	0.10
	5.00	0.44	0.045
	10.00	0.30	0.028

[a] $[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2{}^+] = 5 \times 10^{-5}$ mol dm^{-3}, unless otherwise stated. [b] Studies using *trans*-$[W(NN^2H_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$. [c] $[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2{}^+] = 1 \times 10^{-4}$ mol dm^{-3}.

Under all the conditions described herein the kinetics of the reaction exhibit a first-order dependence on the concentration of complex, however the dependence on the concentration of NEt_3 is complicated. In the absence of $[NEt_3H]BPh_4$ the reaction exhibits a first-order dependence on the concentration of NEt_3 as described by equation (2), where $a = 14.3$ (± 0.2)

$$k_{obs.} = a[NEt_3] \quad (2)$$

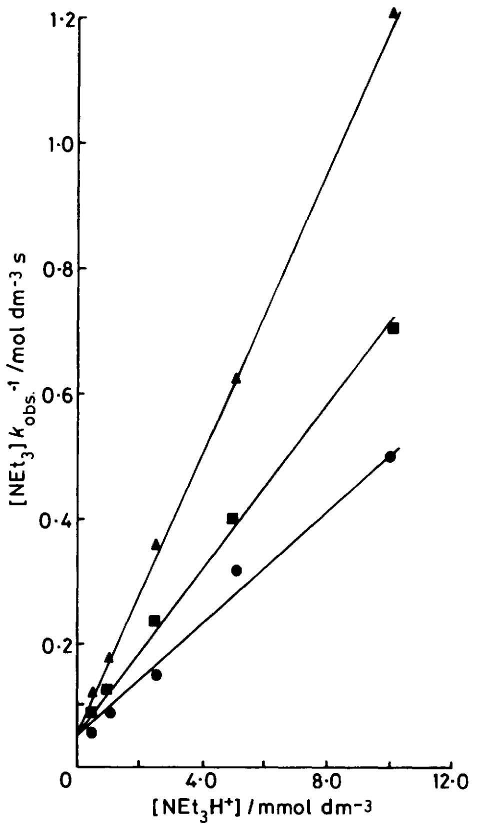


Figure. Plot of $[NEt_3]/k_{obs.}$ *versus* $[NEt_3H^+]$ for the reaction of *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ with NEt_3 in thf. $[NEt_3]$ = 50.0 (▲), 100.0 (■), or 150.0 mmol dm^{-3} (●)

dm^3 mol^{-1} s^{-1}. The addition of $[NEt_3H]BPh_4$ inhibits the reaction and, as shown by the Figure, the rate law under these conditions is that described by equation (3), in which $b = 1.49$ (± 0.1) $\times 10^{-1}$ dm^3 mol^{-1} s^{-1} and $c = 1.0(\pm 0.1) \times 10^{-2}$.

$$k_{obs.} = \frac{b[NEt_3]^2}{[NEt_3H^+] + c[NEt_3]} \qquad (3)$$

Study of the analogous reactions between NEt_3 and the isotopically substituted complex, *trans*-$[W(NN^2H_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ using $[NEt_3{}^2H]BPh_4$ as appropriate, gave kinetics of identical form to equations (2) and (3) but with the values: $a = 10.7$ (± 0.2) dm^3 mol^{-1} s^{-1}, $b = 1.10$ (± 0.1) $\times 10^{-1}$ dm^3 mol^{-1} s^{-1}, and $c = 1.0(\pm 0.1) \times 10^{-2}$.

Discussion

In the reaction of *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ with NEt_3 to produce *trans*-$[W(N_2)_2(dppe)_2]$ in thf, no intermediate is detected under the conditions described above. This, together with the rate laws under various conditions [equations (2) and (3)], is consistent with the mechanism shown in the Scheme.

Initial deprotonation of *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ by NEt_3 gives the diazenido-complex *trans*-$[W(NNH)(p\text{-}MeC_6H_4SO_3)(dppe)_2]$, a species previously detected during the electrolysis of the hydrazido(2−)-complex.[3] The subsequent fate of this intermediate depends upon whether its next encounter is with $[NEt_3H]^+$ or NEt_3. Reaction of the diazenido-complex with $[NEt_3H]^+$ regenerates the hydrazido(2−)-complex, whereas reaction with a further molecule of NEt_3 ultimately leads to *trans*-$[W(N_2)_2(dppe)_2]$. It is not possible to define unambiguously the intimate details of the latter pathway (see later) but the nett process involves the dissociation of $p\text{-}MeC_6H_4SO_3$ and deprotonation of the diazenido-residue to form the five-co-ordinate, 16-electron intermediate $[W(N_2)(dppe)_2]$. The subsequent pathway {possibly involving the solvento-species *trans*-$[W(N_2)(thf)(dppe)_2]$} in which dinitrogen, present in solution, binds to the tungsten atom, yields the product.

The derived rate law for this mechanism, as shown in equation (4), is obtained by treating *trans*-$[W(NNH)(p\text{-}MeC_6H_4SO_3)(dppe)_2]$ as a steady-state intermediate, and assuming that the deprotonation of this species is essentially irreversible.

$$k_{obs.} = \frac{k_1k_2[NEt_3]^2}{k_{-1}[NEt_3H^+] + k_2[NEt_3]} \qquad (4)$$

This equation is consistent with the experimentally determined rate law [equation (3)], and comparison of equations (3) and (4) gives $k_1 = 14.9$ (± 0.1) dm^3 mol^{-1} s^{-1} and $k_2/k_{-1} = 1.0$ (± 0.1) $\times 10^{-2}$. At low concentrations of $[NEt_3H]^+$, equation (4) reduces to $k_{obs.} = k_1[NEt_3]$ in excellent agreement with equation (2).

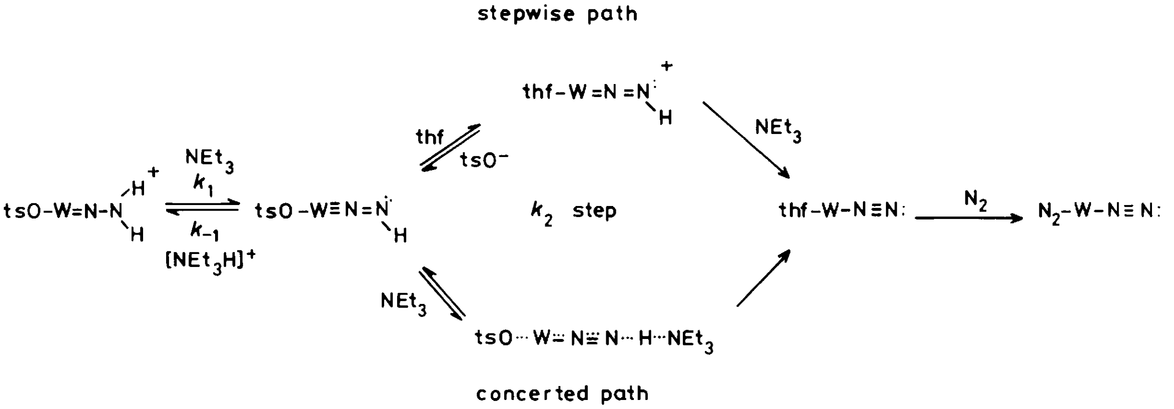
Investigation of the isotopically-substituted complex, *trans*-$[W(NN^2H_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ demonstrates that k_1 is associated with a primary isotope effect, $k_1^H/k_1^D = 1.37$ (± 0.10), confirming the interpretation that this rate constant corresponds to a proton-transfer reaction.

Although a primary isotope effect is to be expected for both k_{-1} and k_2 it is not possible to measure the effect on the individual rate constants. However there is no detectable isotope effect on the ratio k_2/k_{-1}; this is presumably a consequence of similar isotope effects associated with both processes.

The value of $k_1^H = 14.9$ (± 0.1) dm^3 mol^{-1} s^{-1} is *ca.* 10^9 times slower than the diffusion-controlled limit expected for thermodynamically favourable proton-transfer reactions.[6] This slow proton transfer is a consequence of the weak acidity of the hydrazido(2−)-ligand in thf rendering its deprotonation by NEt_3 thermodynamically unfavourable. An upper limit for the equilibrium constant associated with the deprotonation of *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ by NEt_3, $K_1^H = k_1^H/k_{-1}^H < 3.7 \times 10^{-6}$ can be calculated, since even at the highest concentration of base employed in this study no *trans*-$[W(NNH)(p\text{-}MeC_6H_4SO_3)(dppe)_2]$ can be detected. The limit for K_1^H is established assuming that less than 10% of the diazenido-intermediate is formed when $[NEt_3] = 150.0$ mmol dm^{-3}. Using the known value for k_1^H, the value of $k_{-1}^H > 4.0 \times 10^6$ dm^3 mol^{-1} s^{-1} can be calculated. This value probably represents the diffusion-controlled ($k_{-1}^H = 1 \times 10^{10}$ dm^3 mol^{-1} s^{-1})[7] protonation of the relatively basic diazenido-ligand by $[NEt_3H]^+$.

It is now possible to establish the limits for the value of k_2, *i.e.* $1 \times 10^7 > k_2 > 4 \times 10^4$ dm^3 mol^{-1} s^{-1}. In the light of the value of k_1^H, it is clear that k_2 cannot be associated with a simple deprotonation of *trans*-$[W(NNH)(p\text{-}MeC_6H_4SO_3)(dppe)_2]$. Certainly deprotonation of this species by NEt_3 would be thermodynamically less favourable than the deprotonation of the corresponding hydrazido(2−)-ligand, and would be correspondingly slower. Previous studies on *trans*-$[Mo(NNH_2)X(dppe)_2]^+$ (X = F or Br)[4] demonstrate that the two pK_a values in methanol of the dinitrogen residues differ by more than two units. In thf the corresponding equilibrium constants for NEt_3 with *trans*-$[Mo(NNH_2)Br(dppe)_2]^+$ differ by at least 10^5.

It is proposed that the anomalously high value for k_2 is a consequence, either, of the concerted deprotonation and dissociation of $p\text{-}MeC_6H_4SO_3$ from *trans*-$[W(NNH)(p\text{-}$



Scheme. Mechanism for the reaction of *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ with NEt_3 in thf (phosphine ligands omitted for clarity); tsO = $p\text{-}MeC_6H_4SO_3^-$

$MeC_6H_4SO_3)(dppe)_2]$, or the stepwise initial rapid dissociation of $p\text{-}MeC_6H_4SO_3$ followed by the deprotonation of the derived *trans*-$[W(NNH)(thf)(dppe)_2]^+$. It is not possible, from the kinetic studies, to distinguish between these two possibilities. It is the dissociation of $p\text{-}MeC_6H_4SO_3$ and subsequent binding of dinitrogen which allows the reaction to go to completion, despite the thermodynamically uphill proton-transfer reactions.

On the basis of equation (4) alone it is not possible to determine whether step k_1 or k_2 is rate limiting, however the observed value of $k_1^H = 14.9$ (± 0.1) dm^3 mol^{-1} s^{-1}, and the estimated value of $k_2 > 4 \times 10^4$ dm^3 mol^{-1} s^{-1}, demonstrate that under all conditions the initial deprotonation of *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ is the rate-limiting step.

The slow initial proton transfer between *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ and NEt_3 is a consequence of the weak acidity of the hydrazido(2−)-ligand. This contrasts with the analogous molybdenum system,[4] where the rate of deprotonation of the hydrazido(2−)-residue can be estimated as $k_1^H > 1 \times 10^6$ dm^3 mol^{-1} s^{-1}. This greater than 10^5 difference in the rates for analogous reactions of the two complexes is attributable to the greater electron-releasing capability of the heavier metal,[8] rendering the hydrazido(2−)-ligand correspondingly less acidic.

Previous studies have shown that the greater electron-releasing capability of the tungsten atom over that of molybdenum renders the imido-ligand in the complexes *trans*-$[M(NH)X(dppe)_2]^+$ (M = Mo or W, X = F or Cl) *ca.* 100 times less acidic when co-ordinated to tungsten.[9] The present study demonstrates how this electron-releasing effect of the metal can be manifest in the rates of proton-transfer reactions.

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. Tetrahydrofuran was distilled from sodium–benzophenone immediately prior to use.

Preparation of Complexes.—*trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2][p\text{-}MeC_6H_4SO_3]$ was prepared by the reaction of *trans*-$[W(N_2)_2(dppe)_2]$ with $p\text{-}MeC_6H_4SO_3H$ in thf, and recrystallised from MeOH–Et_2O by a method similar to that described for analogous complexes[10,11] (Found: C, 58.4; H, 5.0; N, 2.1. $C_{66}H_{64}N_2O_6P_4S_2W$ requires C, 58.6; H, 4.7; N, 2.1%).

The isotopically-substituted complex, *trans*-$[W(NN^2H_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2][p\text{-}MeC_6H_4SO_3]$ was prepared by the same method as described above but recrystallised from MeO^2H–Et_2O.

The product of the reaction between *trans*-$[W(NNH_2)(p\text{-}MeC_6H_4SO_3)(dppe)_2]^+$ and an excess of NEt_3 in tetrahydrofuran was identified as *trans*-$[W(N_2)_2(dppe)_2]$ by *in situ* solution i.r. spectroscopy [$\nu(N_2)$ at 1 955 cm^{-1}] and isolation of the product by the addition of methanol (Found: C, 60.0; H, 4.8; N, 5.4. $C_{52}H_{48}N_4P_4W$ requires C, 60.1; H, 4.6; N, 5.4%).

$[NEt_3{}^xH]BPh_4$ (x = 1 or 2) was prepared by the reaction of NEt_3 with anhydrous ^{x}HCl in thf, and then addition of the derived $[NEt_3{}^xH]Cl$ to $NaBPh_4$ in the corresponding MeO^{x}H. Sodium chloride formed as a by-product was removed by washing with water (Found: C, 85.9; H, 8.2; N, 3.1. $C_{30}H_{36}BN$ requires C, 85.5; H, 8.6; N, 3.3%); ν(N–^{1}H) at 3 140, ν(N–^{2}H) at 2 300 cm^{-1}.

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.[12] The spectrophotometer is 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.[13]

The ionic strength of the reaction solutions was maintained at 0.1 mol dm^{-3} with $[NBu^n{}_4]BF_4$. Triethylamine (B.D.H.) was used as supplied. All the kinetic studies were performed at 25.0 °C.

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References

1 R. N. F. Thorneley and D. J. Lowe, 'Molybdenum Enzymes,' ed. T. G. Spiro, John Wiley and Sons, New York, 1985, ch. 5, p. 221.
2 R. A. Henderson, G. J. Leigh, and C. J. Pickett, *Adv. Inorg. Radiochem.*, 1983, **27**, 197.
3 C. J. Pickett and J. Talarmin, *Nature (London)*, 1985, **317**, 652.
4 J. D. Lane and R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1986, 2155.
5 J. Chatt, A. J. Pearman, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1976, 1520.
6 M. Eigen, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 1.

7 R. P. Bell, 'The Proton in Chemistry,' Chapman and Hall, London, 1973, ch. 7, p. 111.

8 D. F. Shriver, *Acc. Chem. Res.*, 1970, **3**, 231.

9 R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1983, 51.

10 J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 2074.

11 C. J. Pickett, J. Talarmin, and K. Ryder, *J. Chem. Soc., Dalton Trans.*, 1986, 1453.

12 R. A. Henderson, *J. Chem. Soc., Dalton Trans.*, 1982, 917.

13 J. H. Espenson, 'Chemical Kinetics and Reaction Mechanisms,' McGraw-Hill, New York, 1979, ch. 2.

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