STUDIES OF THE KINETICS OF THE REACTIONS OF NITRILES WITH DINITROGEN COMPLEXES OF MOLYBDENUM(0) AND TUNGSTEN(0). FACTORS AFFECTING THE RATE OF DISSOCIATIVE LOSS OF DINITROGEN *

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Summary

The kinetics of the substitution of nitriles for dinitrogen in $trans$-$[M(N_2)_2(dppe)_2]$ (M = Mo, W; dppe = 1,2-bis(diphenylphosphino)ethane) and cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W) complexes have been studied in toluene solution at various temperatures. In the case of $trans$-$[Mo(N_2)_2(dppe)_2]$, one dinitrogen is replaced by a nitrile in toluene and the kinetic data support an $S_{N}1$ dissociative mechanism (k(PhCN) 3.6×10^{-4} s^{-1} at 303 K; E_a 28 kcal/mol; $\Delta H^{\ddagger}$ 27 kcal/mol; $\Delta S^{\ddagger}$ 15 cal/mol-deg). The analogous reaction with $trans$-$[W(N_2)_2(dppe)_2]$ was found to proceed only photochemically, with loss of one dinitrogen. The thermal activation energy for N_2 dissociation from $trans$-$[W(N_2)_2(dppe)_2]$ in toluene is estimated to be >38 kcal/mol. In the cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W) reactions in toluene, both dinitrogen ligands are replaced by nitriles in two consecutive dissociative steps (k(Mo)/k(W) $\approx 10^2$ for each step).

Introduction

Protonation of coordinated dinitrogen to yield hydrazine and/or ammonia has thus far been observed only for two classes of well characterized dinitrogen complexes, $\{(\eta^5\text{-}C_5Me_5)_2MN_2\}_2N_2$ (M = Ti, Zr) [1—3] and $[ML_4(N_2)_2]$ (M = Mo, W; L = PR$_3$) [4—10]. It is notable that for both classes there are two dinitrogen ligands per transition metal center. The vast majority of isolable (but inert) dinitrogen complexes contain only a single N$_2$ ligand in the first coordination

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* Dedicated to Joseph Chatt on the occasion of his 65th birthday.
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sphere of the metal. In light of this difference it has been suggested that in the former class $M-N_2$ dissociation may be a requirement for activation of the remaining dinitrogen ligand [11]. This suggestion would be in line with the observed stoichiometries wherein a maximum of one of the two molecules of N_2 per metal center is reduced, the other being evolved as free N_2. A comparison of the relative rates of N_2 protonation and reduction to that for N_2 dissociation would thus be revealing.

The rates of N_2 dissociation from $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ are such that they have been measured conveniently by ^1H and ^{15}N NMR spectrometry [3]. Terminal N_2 dissociation was found to proceed 10^2-10^3 times slower than the protonation/reduction sequence leading to hydrazine. For trans-$[W(N_2)_2(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane), a similar conclusion has been reached by Chatt, Leigh, and co-workers [12] concerning the relative rates of protonation of the ligated N_2 (~diffusion controlled) vs. the rate of N_2 dissociation ($k_1 < 10^{-7}$ s^{-1}). Thus the protonation of ligated N_2 for these two dinitrogen complexes proceeds readily without prior N_2 dissociation.

Alkylation of the coordinated dinitrogen of trans-$[M(N_2)_2(dppe)_2]$ (M = Mo, W) by alkyl bromides and iodides appears to proceed by a different mechanism, however [12—14]. The evidence suggests that the initial steps involve rate-determining dissociation of N_2 followed by halogen atom abstraction from RX by the five-coordinate species $[M(N_2)(dppe)_2]$ [12]. Furthermore, some differences in the protonation/reduction sequences have been noted for members of the series trans-$[Mo(N_2)_2(dppe)_2]$ (I), trans-$[W(N_2)_2(dppe)_2]$ (II), cis-$[Mo(N_2)_2(PMe_2Ph)_4]$ (III), and cis-$[W(N_2)_2(PMe_2Ph)_4]$ (IV).

It is apparent from the above discussion that a better understanding of the factors affecting the rate of loss of N_2 from metal—dinitrogen complexes is needed. Accordingly, we have performed an extensive kinetic study of the substitution of N_2 in complexes I—IV by nitriles. The results of this study and the conclusions we have drawn in regards to the reactivity of N_2 as a leaving group in molybdenum(0) and tungsten(0) complexes are reported herein.

Experimental

Materials and syntheses

All solvents used were reagent grade, obtained from MCB. All nitriles were freshly distilled from phosphorus(V) oxide, methanol was distilled from magnesium turnings, dichloromethane was distilled from Linde 4A molecular sieves, and THF was distilled from sodium/benzophenone. All other solvents were distilled from titanocene [15]. Molybdenum(V) chloride and tungsten(VI) chloride were obtained from ROC/RIC and purified by refluxing in CCl$_4$ under a nitrogen atmosphere for two days with visible irradiation [16,17]. 1,2-Bis(diphenylphosphino)ethane (dppe) and dimethylphenylphosphine were obtained from ROC/RIC, and triphenylphosphine was obtained from MCB. All were used without further purification.

All reactions were carried out under an inert atmosphere, using vacuum line and dry box handling techniques described earlier [3]. trans-$[M(N_2)_2(dppe)_2]$ and cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W) were prepared by published methods [8,18] with the following minor modifications: Magnesium amalgam was used

for all reductions, and 80% of the stoichiometric amount of phosphine was used in the synthesis of cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, W). The trans-$[Mo(N_2)$-(L)(dppe)$_2]$ (L = PhCN, p-TolCN, MeCN) complexes were prepared by published procedures [19].

cis-$[W(N_2)(PhCN)(PMe_2Ph)_4]$. 13.5 µl (0.13 mmol) of PhCN was added to 100 mg (0.13 mmol) of cis-$[W(N_2)_2(PMe_2Ph)_4]$ in 10 ml of toluene. After stirring for 3.5 h at room temperature, the solution was reduced to 2 ml of volume, and 1 ml of petroleum ether was added. This solution was stirred at −78°C for $\frac{1}{2}$ h and filtered cold. The green solid was washed twice with cold petroleum ether, and then quickly dried in vacuo. IR (cm^{-1}): 1995s, 1925s. ^{1}H NMR (benzene-d_6): P(CH$_3$)$_2$Ph, δ (ppm) 1.55 d ($J(^{31}$P—H) 5 Hz); δ 1.43 t ($J(^{31}$P—H) 3 Hz).

cis-$[W(PhCN)_2(PMe_2Ph)_4]$. 35 µl (0.34 mmol) of PhCN was added to 100 mg (0.13 mmol) of cis-$[W(N_2)_2(PMe_2Ph)_4]$ in 10 ml of toluene. After 10 h at 30°C, the solution was reduced in volume to 1 ml and 1 ml of petroleum ether was added. This solution was stirred at −78°C for $\frac{1}{2}$ h and filtered cold. The purple solid was washed twice with cold petroleum ether and quickly dried in vacuo. IR (cm^{-1}): 2030s, 1990s. ^{1}H NMR (benzene-d_6): P(CH$_3$)$_2$Ph; δ (ppm) 1.55 d ($J(^{31}$P—H) 5 Hz); δ 1.43 t ($J(^{31}$P—H) 3 Hz).

Analyses

Microanalyses were performed at Caltech. The results are presented in Table 1.

Reactions monitored by Toepler pump analyses

cis-$[W(N_2)(PhCN)(PMe_2Ph)_4]$: 200 µl (1.89 mmol) of PhCN was added to 75 mg (9.75 × 10^{-2} mmol) of cis-$[W(N_2)_2(PMe_2Ph)_4]$ in 200 ml of toluene. After stirring at 30°C for 1 h 40 min, the solution was cooled to −78°C. 8.1 × 10^{-2} mmol of N$_2$ was collected through a series of LN$_2$-cooled traps by Toepler pumping. The solution was then warmed to 30°C, and the reaction was allowed

TABLE 1

MICROANALYSES OF THE COMPOUNDS OBTAINED

Compound	Molecular formula	Analysis (Found (calcd.) (%))		
		C	H	N
trans-$[Mo(N_2)_2(dppe)_2]$	$C_{52}H_{48}MoN_4P_4$	65.31 (65.83)	5.15 (5.10)	5.93 (5.91)
trans-$[W(N_2)_2(dppe)_2]$	$C_{52}H_{48}N_4P_4W$	59.72 (60.24)	4.85 (4.67)	5.25 (5.40)
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	$C_{32}H_{44}MoN_4P_4$	54.37 (54.55)	6.25 (6.29)	7.97 (7.95)
cis-$[W(N_2)_2(PMe_2Ph)_4]$	$C_{32}H_{44}N_4P_4W$	49.14 (48.50)	5.64 (5.59)	6.85 (7.07)
trans-$[Mo(N_2)(PhCN)(dppe)_2]$	$C_{59}H_{53}MoN_3$	69.74 (69.21)	5.25 (5.22)	4.10 (4.11)
cis-$[W(N_2)(PhCN)(PMe_2Ph)_4]$	$C_{39}H_{49}N_3P_4W$	55.75 (53.99)	5.19 (5.69)	5.19 (4.84)
cis-$[W(PhCN)_2(PMe_2Ph)_4]$	$C_{46}H_{54}N_2P_4W$	59.93 (58.61)	5.96 (5.77)	3.23 (2.97)

to continue another 6.5 h. 1.04×10^{-1} mmol of N_2 was collected as before. In another experiment 15.5 μl (0.15 mmol) of PhCN was added to 120 mg (0.15 mmol) of cis-$[W(N_2)_2(PMe_2Ph)_4]$ in 10 ml of toluene. After 4 h at 30°C, 0.15 mmol of N_2 was collected as before. Similarly, 35 μl (0.34 mmol) of PhCN was added to 120 mg (0.15 mmol) of cis-$[W(N_2)_2(PMe_2Ph)_4]$ in 10 ml of toluene. After 8 h at 30°C, 0.29 mmol of N_2 was collected.

Spectroscopic measurements

All IR spectra used to identify the products were measured on a Perkin—Elmer 457 or Beckman IR 12 spectrophotometer using Nujol mulls. The proton NMR spectra of samples in C_6D_6 solutions were obtained on a Varian EM-390 spectrometer.

Kinetic measurements

The reactions of nitriles with trans-$[Mo(N_2)_2(dppe)_2]$ and cis-$[W(N_2)_2$-$(PMe_2Ph)_4]$ were monitored by following the change in the absorption spectrum (330—800 nm) of the solutions for two reaction half-lives, and in most cases for over three half-lives. The spectral measurements were performed on a Cary 15 spectrophotometer equipped with Cary 1116100 Program Times and Cary 115 Repetitive Scan accessories. The solutions were contained in anaerobic 1 mm Pyrex cells similar to those described by Shriver [20]. The cells were held in a thermostatable cell adapter, Cary 1444300, equipped with Pyrex windows. The volume was filled with distilled water to improve thermal contact between the cell and the cell adapter. A Masterline 2095 bath and circulator by Forma Scientific was used to maintain the desired temperatures.

The reactions were initiated by injection of the nitrile using a calibrated Hamilton gas tight syringe; the data collections were begun after allowing 5 min for temperature equilibration.

Reaction rates were determined under pseudo-first-order conditions. Plots of $-\ln(A_\infty - A)$ vs. time were linear over the reaction times monitored, and the observed rate constants were obtained from the slopes of the weighted least-squares fits to these lines [21,22]. The activation parameters were calculated using a simple least-squares program. In all cases, the calculated numbers are reported with their 95% confidence limits [21].

The reactions of nitriles with cis-$[W(N_2)_2(PMe_2Ph)_4]$ were monitored by following the change in the absorption spectrum of the solutions from 800 to 380 nm. Other experimental details were the same as before. For cis-$[W(N_2)_2$-$(PMe_2Ph)_4]$ the reaction was found to consist of two consecutive first-order steps [21]; the rate constants were obtained by a nonlinear least-squares fit [22] of the spectrum to an expression of the form [23]:

$$A(\text{obs}) = A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) + A_3$$

The activation parameters were calculated as before, and the calculated numbers are reported with their 95% confidence limits.

The slow reactions of nitriles with cis-$[Mo(N_2)_2(PMe_2Ph)_4]$ were monitored by following the change in the absorption spectrum of the solution at 600 nm for over two half-lives. The spectral measurements were made using a Cary 14 spectrophotometer equipped with the thermostatable cell adapter described
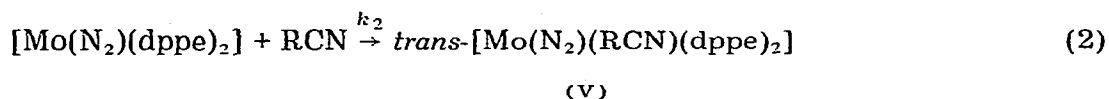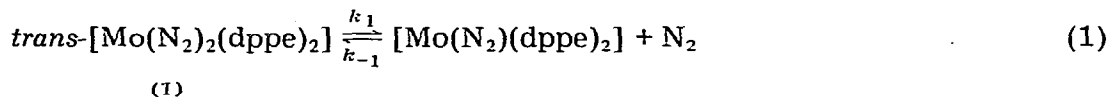
above. The solutions were contained in anaerobic 1 mm Pyrex cells similar to those described above, except that they were modified to accomodate two separate solutions that could be mixed quickly. To initiate the reaction, the cell assembly was removed from the constant temperature bath, tipped, and then shaken vigorously. The cell was placed in the thermostated cell adapter and data collections were started. This entire procedure took less than 20 s. All other experimental details and calculations were the same as for the reactions of cis-$[W(N_2)_2(PMe_2Ph)_4]$.

Results

The displacement of dinitrogen from complexes I—IV by nitriles was followed by the change in the absorption spectrum of each solution with time. Representative spectra for the reactions of I with benzonitrile and acetonitrile in toluene are shown in Figs. 1 and 2, respectively, and the plots of $-\ln(A_\infty^{600} - A^{600})$ vs. time and $-\ln(A_\infty^{450} - A^{450})$ vs. time are shown in Fig. 3 and 4, respectively. The kinetics of the reaction of I with PhCN in THF and toluene have also been studied by Chatt, Leigh, and coworkers [12]; where there is overlap our results are in good agreement with the earlier work.

The kinetic data we have obtained for the reactions of I with nitriles are given in Tables 2 and 3. These data are readily interpreted in terms of a dissociative (limiting S_N1) mechanism, as outlined in Scheme 1.

SCHEME 1

$$trans\text{-}[Mo(N_2)_2(dppe)_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Mo(N_2)(dppe)_2] + N_2 \tag{1}$$

(I)

$$[Mo(N_2)(dppe)_2] + RCN \overset{k_2}{\rightarrow} trans\text{-}[Mo(N_2)(RCN)(dppe)_2] \tag{2}$$

(V)

$$\text{rate} = \frac{d[V]}{dt} = k_{obs}[I], \quad k_{obs} = \frac{k_1 k_2 [RCN]}{k_{-1}[N_2] + k_2[RCN]}$$

The reactive, coordinatively unsaturated intermediate $[Mo(N_2)(dppe)_2]$ generated in the rate-determining step (k_1) is rapidly captured by N_2 (k_{-1}) or by nitrile (k_2). Thus, at low nitrile concentrations the rate increases with increasing $[RCN]$; it also increases when the reaction is carried out under Ar rather than 1 atm N_2. At sufficiently high concentrations of nitriles $([RCN]/[I] > 10)$, the rate is independent of the concentration and nature of the incoming group, as expected for a limiting dissociative process.

Compound II reacts with nitriles in toluene to yield the tungsten analog of V, but only in the presence of light. There was no detectable reaction of II with benzonitrile after 36 h at 70°C in the dark $(E_a > 38$ kcal/mol for W—N_2 dissociation); however, the reaction was found to proceed smoothly at 30°C upon irradiation in the spectrometer. Furthermore, the rate is slower if the reaction is constantly monitored at 605 nm rather than 380 nm.
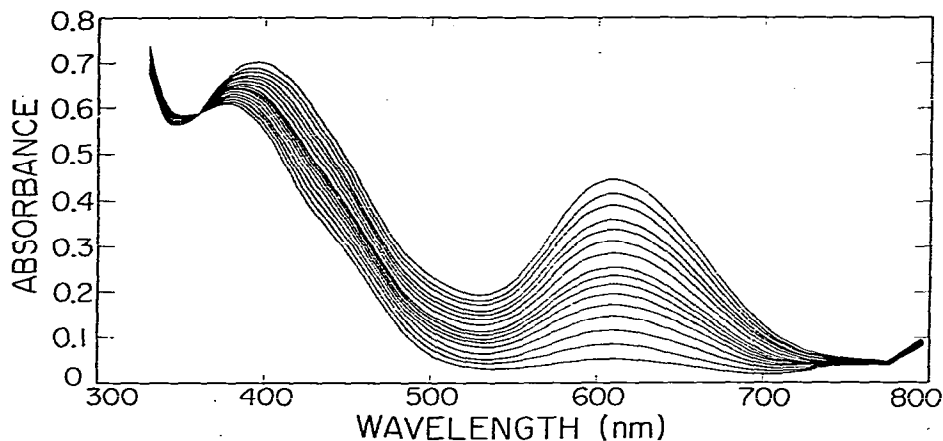
Fig. 1. Absorption spectral changes accompanying the reaction of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with benzonitrile in toluene at 303 K.

The reaction of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] with benzonitrile in toluene is somewhat more complex; a compound with λ_{max} 590 nm is formed initially, followed by a slower reaction to generate the final product with λ_{max} 540 nm (Fig. 5). On the basis of the following evidence, the reactions outlined in Scheme 2 are proposed: (i) Toepler pump analyses revealed that 0.85 equivalent of N$_2$ is evolved under conditions in which the maximum absorption at 590 nm is reached, and 1.95 equivalents N$_2$ correspond to the maximum absorption at 540 nm; (ii) analytical, IR, and ^{1}H NMR data for the isolated compounds established that *cis*-[W(N$_2$)(PhCN)(PMe$_2$Ph)$_4$] (VII) is the species

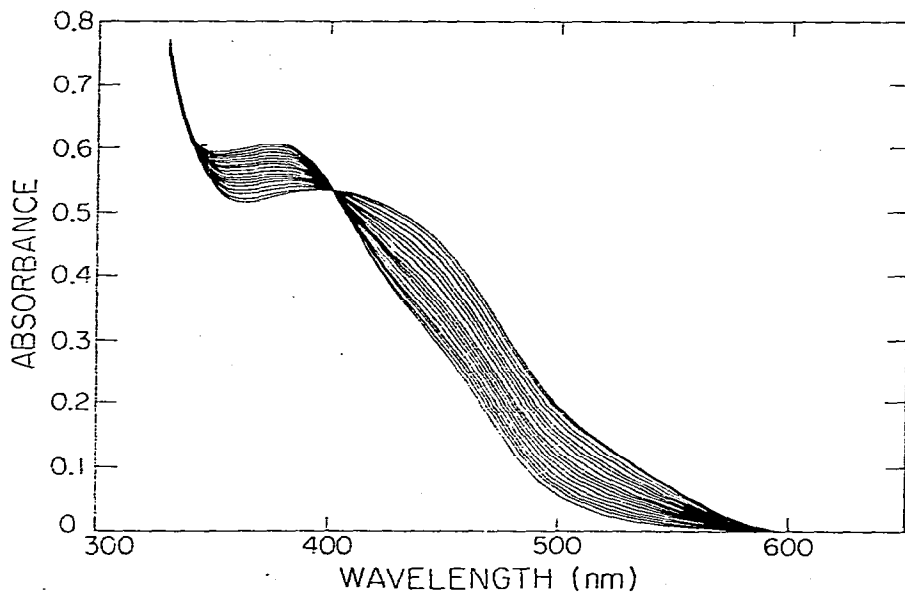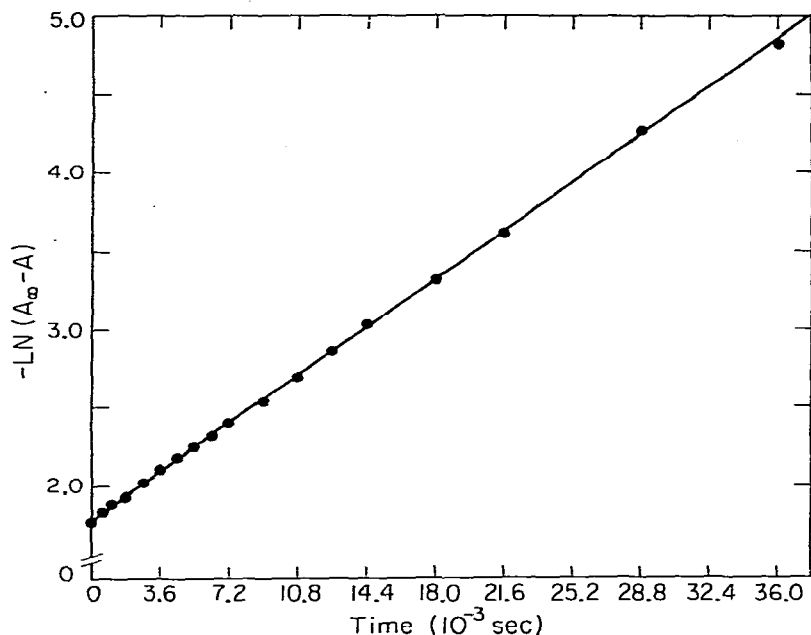Fig. 2. Absorption spectral changes accompanying the reaction of *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] with acetonitrile in toluene at 303 K.

Fig. 3. Plot of —ln(A∞ — A) vs. time for the reaction of benzonitrile with I (see Fig. 1).

with λ_{max} 590 nm and cis-[W(PhCN)$_2$(PMe$_2$Ph)$_4$] (VIII) is assigned λ_{max} 540 nm; (iii) computer fitting of the kinetic data (Table 4) indicated two consecutive first-order reactions (iv) neither rate was dependent on [PhCN] under pseudo-first order conditions; and (v) neither rate was affected by addition of substantial amounts of PMe$_2$Ph. The activation parameters obtained from rate data over the temperature range 294.5—314.1 K are E_a = 20.7 ± 0.8 kcal/mol,
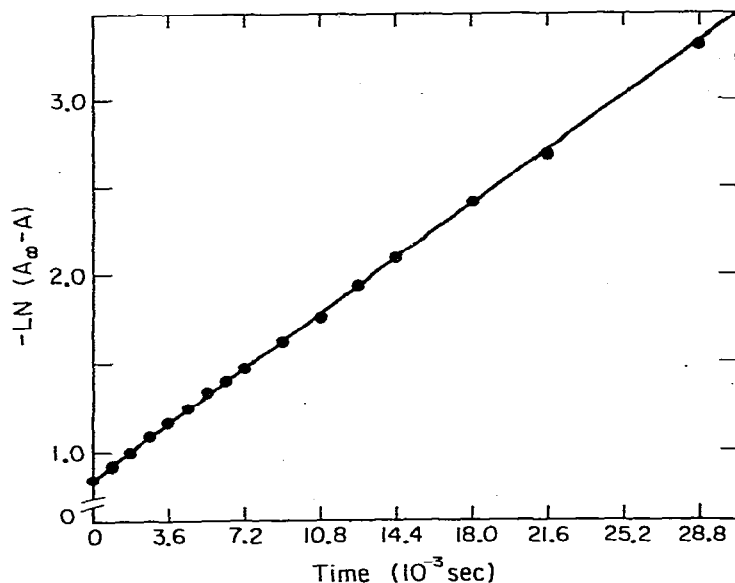

Fig. 4. Plot of —ln(A∞ — A) vs. time for the reaction of acetonitrile with I (see Fig. 2).

TABLE 2

OBSERVED RATE CONSTANTS FOR THE REACTIONS OF *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] WITH NITRILES IN TOLUENE

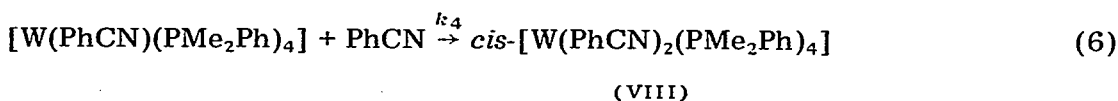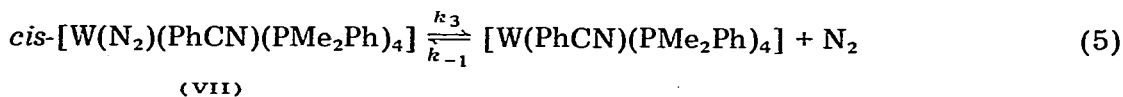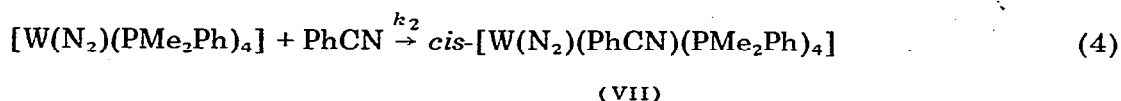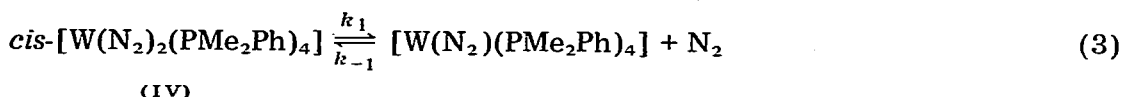| RCN	Temperature (K)	10^4 [Mo] (M)	10^3 [RCN] (M)	$10^4 k_{obs}$ (s^{-1})[a]
PhCN	293.90	5.02	49.8	8.81 ± 0.07
		4.94	48.7	8.66 ± 0.11
		4.99	50.4	8.92 ± 0.06
iPhCN	293.95	5.02	4.99	4.97 ± 0.05
	(under argon)	4.98	4.90	7.50 ± 0.06
PhCN	303.35	5.00	4.94	2.54 ± 0.06
		5.10	12.8	3.06 ± 0.10
		4.96	26.4	3.61 ± 0.04
		4.95	37.5	3.50 ± 0.30
		4.96	52.4	3.53 ± 0.04
p-TolCN	303.15	5.01	4.74	2.36 ± 0.04
		4.99	12.5	3.05 ± 0.02
		4.97	12.4	3.16 ± 0.29
		5.00	28.5	3.44 ± 0.05
		4.96	37.8	3.43 ± 0.04
		4.95	48.0	3.94 ± 0.03
MeCN	303.05	5.08	4.99	3.18 ± 0.25
		4.98	12.3	3.71 ± 0.17
		5.11	12.3	3.72 ± 0.07
		2.49	25.2	3.62 ± 0.23

[a] k_{obs} is given with 95% confidence limits.
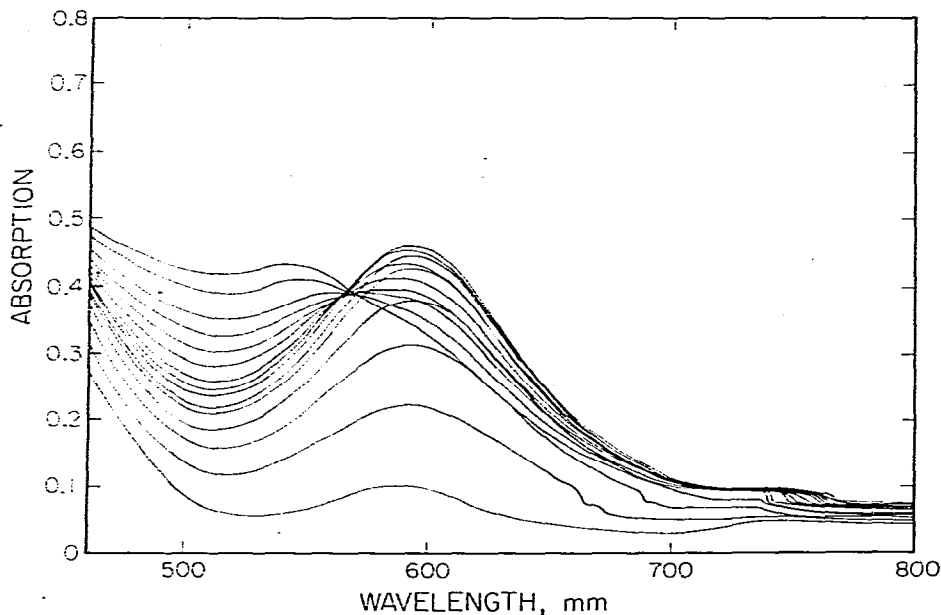
Fig. 5. Absorption spectral changes accompanying the reaction of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] with benzonitrile in toluene at 303 K.

$\Delta H^{\ddagger} = 20.1 \pm 0.8$ kcal/mol, and $\Delta S^{\ddagger} = -8.3 \pm 1.7$ cal/mol-deg for IV → VII and $E_a = 23.7 \pm 1.2$ kcal/mol, $\Delta H^{\ddagger} = 23.1 \pm 1.2$ kcal/mol, and $\Delta S^{\ddagger} = 1.1 \pm 2.7$ cal/mol-deg for VII → VIII.

The absorption spectral changes observed during the reactions of III with nitriles in toluene were similar to those for IV. Analysis of the amount of N_2 evolved indicated 0.91 equivalent at times corresponding to maximum absorbance at 600 nm and 1.95 equivalents at maximum absorbance of the final product at 545 nm. These nitrile complexes are even less stable than their tungsten analogues, and thus neither has been isolated in pure form. However, the results suggest that the mechanism by which III reacts with PhCN is entirely analogous to that presented for IV in Scheme 2. The kinetic data (Table 4) also indicate that two consecutive dissociative steps are involved.

SCHEME 2

$$cis\text{-}[W(N_2)_2(PMe_2Ph)_4] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [W(N_2)(PMe_2Ph)_4] + N_2 \qquad (3)$$
$$(IV)$$

$$[W(N_2)(PMe_2Ph)_4] + PhCN \overset{k_2}{\rightarrow} cis\text{-}[W(N_2)(PhCN)(PMe_2Ph)_4] \qquad (4)$$
$$(VII)$$

$$cis\text{-}[W(N_2)(PhCN)(PMe_2Ph)_4] \underset{k_{-1}}{\overset{k_3}{\rightleftharpoons}} [W(PhCN)(PMe_2Ph)_4] + N_2 \qquad (5)$$
$$(VII)$$

$$[W(PhCN)(PMe_2Ph)_4] + PhCN \overset{k_4}{\rightarrow} cis\text{-}[W(PhCN)_2(PMe_2Ph)_4] \qquad (6)$$
$$(VIII)$$

$$(\text{rate})_a = \frac{d[VII]}{dt} = k_a^{obs}[IV] \ , \ k_a^{obs} = \frac{k_1 k_2 [PhCN]}{k_{-1}[N_2] + k_2[PhCN]}$$

$$(\text{rate})_b = \frac{d[VIII]}{dt} = k_b^{obs}[VII]; \ k_b^{obs} = \frac{k_3 k_4 [PhCN]}{k_{-3}[N_2] + k_4[PhCN]}$$

Discussion

Our results and those of other workers [24—26] show conclusively that a principal pathway for the substitution of ligands for N_2 in six-coordinate metal complexes involves dissociative activation of M—N_2. The activation energy for Mo—N_2 dissociation from $[Mo(N_2)_2(dppe)_2]$ in toluene (28 kcal/mol) is marginally higher than that (24 kcal/mol) reported by Elson [26] in the case of the analogous molybdenum(I) derivative, $[Mo(N_2)_2(dppe)_2]^+$, in THF/MeOH solution. Activation enthalpies for M—N_2 dissociation also have been reported for several osmium(II) complexes (27—34 kcal/mol) [24] and for $[Ru(N_2)(NH_3)_5]^{2+}$ (28 kcal/mol) [25]. Comparisons of these $\Delta H^{\ddagger}$ values with those obtained for the molybdenum(0) and tungsten(0) complexes are not particularly meaningful, however, as multiple extrapolations (metal oxidation

TABLE 3

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REACTIONS OF *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] WITH NITRILES IN TOLUENE

RCN	Temperature (K)	k_1 (s^{-1}) [a]	E_a (kcal/mol) [b]	$\Delta H^{\neq}$ (kcal/mol) [b]	$\Delta S^{\neq}$ (cal/mol·deg) [b]
PhCN	293.90	8.80 ± 0.24 × 10^{-5}	27.7 ± 0.9	27.1 ± 0.9	15.1 ± 2.1
	303.35	3.55 ± 0.10 × 10^{-4}	27.7 ± 0.9	27.1 ± 0.9	14.9 ± 2.0
	312.35	1.471 ± 0.041 × 10^{-3}	27.7 ± 0.9	27.1 ± 0.9	15.0 ± 2.0
p-TolCN	292.5	7.17 ± 0.26 × 10^{-5}	27.8 ± 0.8	27.2 ± 0.8	15.6 ± 1.9
	303.15	3.60 ± 0.54 × 10^{-4}	27.8 ± 0.8	27.2 ± 0.8	15.5 ± 2.1
	313.75	1.704 ± 0.097 × 10^{-3}	27.8 ± 0.8	27.2 ± 0.8	16.4 ± 1.8
MeCN	293.35	9.34 ± 0.90 × 10^{-5}	26.8 ± 0.9	26.2 ± 0.9	12.4 ± 2.1
	303.05	3.68 ± 0.10 × 10^{-4}	26.8 ± 0.9	26.2 ± 0.9	12.1 ± 2.0
	313.40	1.675 ± 0.051 × 10^{-3}	26.8 ± 0.9	26.2 ± 0.9	12.2 ± 1.9

[a] The mean value of k_1 is given with 95% confidence limits. [b] All activation parameters are given with 95% confidence limits.

TABLE 4

OBSERVED RATE CONSTANTS FOR THE REACTION OF *cis*-[M(N$_2$)$_2$(PMe$_2$Ph)$_4$] WITH BENZONITRILE IN TOLUENE

M	Temperature (K)	10^4 [M] (M)	10^2 [RCN] (M)	10^2 [PMe$_2$Ph] (M)	k_a^{obs} (s^{-1}) [a]	k_b^{obs} (s^{-1}) [a]
W(IV)	303.3	9.87	6.60	7.72	(2.56 ± 0.16) × 10^{-4}	(4.77 ± 0.54) × 10^{-5}
		9.93	6.62	0.99	(2.93 ± 0.15) × 10^{-4}	(6.35 ± 0.64) × 10^{-5}
		9.93	7.37	0	(2.86 ± 0.60) × 10^{-4}	(4.44 ± 1.63) × 10^{-5}
		9.97	7.26	0	(2.89 ± 0.38) × 10^{-4}	(5.22 ± 1.03) × 10^{-5}
W(IV)	303.5	10.3	10.9	0	(3.24 ± 0.30) × 10^{-4}	(8.79 ± 0.70) × 10^{-5}
		9.87	9.51	0	(3.66 ± 0.47) × 10^{-4}	(7.8 ± 2.6) × 10^{-5}
		9.93	5.31	0	(3.56 ± 0.15) × 10^{-4}	(7.73 ± 0.72) × 10^{-5}
W(IV)	314.1	9.90	9.88	0	(11.36 ± 2.83) × 10^{-4}	(32.6 ± 11.8) × 10^{-5}
		9.90	9.60	0	(9.31 ± 1.53) × 10^{-4}	(31.9 ± 12.3) × 10^{-5}
		8.87	9.60	0	(11.21 ± 3.53) × 10^{-4}	(31.6 ± 18.7) × 10^{-5}
Mo(III)	292.6	9.90	10.16	0	(2.33 ± 0.30) × 10^{-2}	(7.5 ± 1.1) × 10^{-4}
Mo(III)	299.1	9.90	9.85	0	(3.49 ± 0.42) × 10^{-2}	(25.9 ± 7.2) × 10^{-4}
Mo(III)	304.6	9.88	7.05	0	(5.12 ± 0.28) × 10^{-2}	(46.7 ± 2.7) × 10^{-4}
Mo(III)	292.6	9.90	10.0	0.99	(2.49 ± 0.35) × 10^{-2}	(7.1 ± 1.1) × 10^{-4}
Mo(III)	292.6	9.9	10.0 [b]	0	(2.45 ± 0.35) × 10^{-2}	(7.8 ± 1.0) × 10^{-4}

[a] Observed rate constants are given with 95% confidence limits. [b] Reactant is acetonitrile.

state, nature of the nonlabile ligands, etc.) would be required.

If we restrict ourselves to the subset of dinitrogen-metal complexes examined in this work, we can make several observations about the factors that affect the rate of dissociative loss of N_2. Firstly, the nature of the central metal is very important, with $W-N_2$ dissociation being much slower than $Mo-N_2$. This result is consistent with a larger body of kinetic data on nd^6 low-spin-six-coordinate complexes; such data have establised that $5d$ complexes undergo dissociative ligand loss much slower than do analogous $4d$ complexes [27]. Secondly, the nonlabile ligand *trans* to the leaving N_2 appears to be influential, as judged by the apparent *trans*-effect order P-donor > N-donor in the complexes we have studied. It is logical to propose that a phosphorus donor atom competes effectively with N_2 for $d\pi$ electron density in the ground state of the *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ complexes, and that the transition state is stabilized by an increase in $d\pi \rightarrow P$ bonding interactions. Both effects operate to reduce the activation energies for $M-N_2$ dissociation in the *cis* complexes.

Finally, certain relatively thermally inert $M-N_2$ bonds may be labilized by irradiation into the electronic absorption bands of the complex in question. An outstanding example of $M-N_2$ photolabilization is provided by II. Elucidation of the nature of the photoactive states requires a knowledge of the relative energies and types of electronic transitions in such complexes; we are now preparing a sequel to this paper that will address these electronic spectroscopic matters directly.

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