

# Mechanism of the Decomposition Reaction of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] and of its Reaction with Pyridine

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The complex *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] **1** decomposes in benzene solution to give molybdenum, phosphine and dinitrogen. The kinetics of this process has been studied from absorbance vs. time curves which reveal two consecutive steps occurring at comparable rates. Relevant kinetic parameters for each step are  $k_1 = 0.52 \times 10^{-2} \text{ s}^{-1}$  at 10.0 °C,  $\Delta H_1^\ddagger = 75 \text{ kJ mol}^{-1}$ ,  $\Delta S_1^\ddagger = -29 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $k_2 = 2.13 \times 10^{-3} \text{ s}^{-1}$  at 10.0 °C,  $\Delta H_2^\ddagger = 38 \text{ kJ mol}^{-1}$ ,  $\Delta S_2^\ddagger = -163 \text{ J K}^{-1} \text{ mol}^{-1}$ . A mechanism is proposed in which there is an initial dissociation of PPh<sub>2</sub>Me to form a five-co-ordinate intermediate [Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>3</sub>] **2**. The presence of **2** in benzene solutions of **1** has been detected by <sup>1</sup>H NMR spectroscopy. In the next step associative attack on **2** occurs to form an unstable species **3** which probably contains co-ordinated solvent and decomposes rapidly. From kinetic data for solutions containing an excess of PPh<sub>2</sub>Me, the equilibrium constant for the phosphine dissociation step has been determined to be  $K_1 = 1.64 \times 10^{-3} \text{ mol dm}^{-3}$  at 10.0 °C. The formation of *trans*, *mer*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>3</sub>(py)] from **1** and pyridine (py) is kinetically controlled by phosphine dissociation.

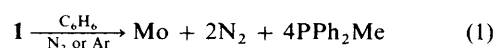
Although interest in the chemistry of vanadium and iron dinitrogen complexes has increased considerably in recent times<sup>1</sup> almost so as to obscure progress in other fields of nitrogen fixation, the possibilities of the analogous molybdenum complexes have not been fully exploited. Moreover, extensive work in the last two decades<sup>2</sup> has revealed many unresolved problems of relevance not only to nitrogen fixation but also to molybdenum chemistry itself. Of particular interest is the variety of derivatives obtained by substitution or reduction reactions, a field that has not been completely rationalised despite the progress in both synthetic and kinetic aspects of these reactions.<sup>2-4</sup>

The complex *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] **1** is a convenient material for the preparation of a series of related dinitrogen complexes because it allows replacement of one or more PPh<sub>2</sub>Me molecules by ligands such as phosphines,<sup>5,6</sup> CO,<sup>7</sup> pyridine and other N-donor molecules.<sup>8,9</sup> The synthesis of **1** has been reported by several groups<sup>6,10-12</sup> and the improved method of Morris and co-workers<sup>9</sup> is a facile route leading to pure samples in high yields. During the course of previous work<sup>13</sup> we observed that benzene solutions of **1** are not stable even for short periods and evidence was obtained that **1** decomposes with precipitation of molybdenum. This observation is apparently contradictory to the well established substitution behaviour of **1** and so we decided to investigate the nature and kinetics of the process.

## Results and Discussion

Benzene solutions of complex **1** at concentrations suitable for recording UV/VIS spectra ( $10^{-3}$ – $10^5 \text{ mol dm}^{-3}$ ) are unstable, as revealed by the changes observed in the spectra with time. There is an absorption band at 330 nm which disappears completely after 1–2 h, with formation of a small amount of precipitate. This solid is also obtained in experiments using  $10^{-2} \text{ mol dm}^{-3}$  solutions, and its infrared spectrum and elemental analysis suggest that it is mainly molybdenum contaminated by small amounts of PPh<sub>2</sub>Me.† These results are reproducible using an

atmosphere either of dinitrogen or of argon and complex concentrations up to  $10^{-2} \text{ mol dm}^{-3}$ , and they reveal complete decomposition of **1** according to reaction (1). There are previous



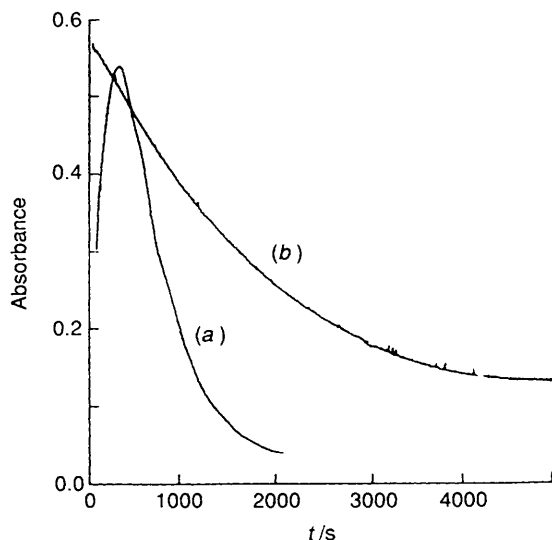
reports of reactions of **1** with arene solvents to give [Mo( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)(PPh<sub>2</sub>Me)<sub>3</sub>]<sup>12</sup> or [Mo( $\eta^6$ -PhPPhMe)(PPh<sub>2</sub>Me)<sub>3</sub>]<sup>8,14</sup> but under more drastic conditions than those used in our experiments, where no such compound was isolated or detected by NMR spectroscopy.

The observation of the decomposition process apparently contradicts literature data<sup>9</sup> that imply recrystallisation from benzene solutions is the best way to obtain pure complex **1**. In fact, although saturated solutions appear to be stable for several days, the same spectral changes are also observed upon dilution to concentrations suitable for recording electronic spectra.

Fig. 1(a) shows typical plots of the absorbance at 330 nm vs. time obtained in kinetic experiments. There is an initial increase in absorbance with a maximum after 80–500 s depending on the temperature, followed by a slower decrease. These biphasic curves suggest a mechanism involving two consecutive steps of comparable rates, and so they were analysed by non-linear least-squares procedures<sup>15</sup> as described in the Experimental section. The treatment leads to the rate constants in Table 1, where  $k_f^{\text{obs}}$  corresponds to the fast stage and  $k_s^{\text{obs}}$  to the slow, descending part of the curve. There are no significant differences in the  $k_f^{\text{obs}}$  and  $k_s^{\text{obs}}$  rate constants obtained under dinitrogen and argon, suggesting that N<sub>2</sub> is not released or attached in any of the kinetically observable stages of process (1). The rate of exchange of **1** with <sup>15</sup>N<sub>2</sub> has been reported<sup>9</sup> to be  $2 \times 10^{-4} \text{ s}^{-1}$  at 22.0 °C in thf (tetrahydrofuran), *i.e.* it is much slower than the reaction studied in this work. The passive role of N<sub>2</sub> in the early stages of the decomposition was confirmed by recording IR spectra of  $10^{-3}$ – $10^{-2} \text{ mol dm}^{-3}$  benzene solutions of **1**, which showed no significant changes in the position of the dinitrogen band at 1925 cm<sup>-1</sup> although its intensity decreases slowly.

For this type of biphasic process there are two mathematical solutions which differ mainly in the order of occurrence of the

† Elemental analysis: C, 24.20; H, 4.10; N, <0.3; P, 3.95%. This suggests a composition Mo·0.18PPh<sub>2</sub>Me (requires C, 24.35; H, 4.05; P, 3.95%).



**Fig. 1** Absorbance (330 nm) vs. time curves for the decomposition reaction of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] (benzene solvent, 10 °C, dinitrogen atmosphere). In (a) there is no added PPh<sub>2</sub>Me and in (b) there is an excess of phosphine, [PPh<sub>2</sub>Me] = 5.33 × 10<sup>-3</sup> mol dm<sup>-3</sup>

**Table 1** Observed rate constants for the decomposition of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] in benzene\*

T/°C	10 <sup>2</sup> k <sub>f</sub> <sup>obs</sup> /s <sup>-1</sup>		10 <sup>3</sup> k <sub>s</sub> <sup>obs</sup> /s <sup>-1</sup>	
	N <sub>2</sub>	Ar	N <sub>2</sub>	Ar
10.0	0.51(7)	0.49(4)	2.13(3)	2.02(2)
13.0	0.87(3)	0.81(8)	2.54(2)	2.55(1)
16.5	1.38(2)	1.40(2)	3.01(1)	3.04(2)
20.0	1.59(4)	1.73(7)	3.66(2)	3.97(6)
22.5	1.96(6)		4.54(2)	
25.0	2.69(4)		4.70(1)	

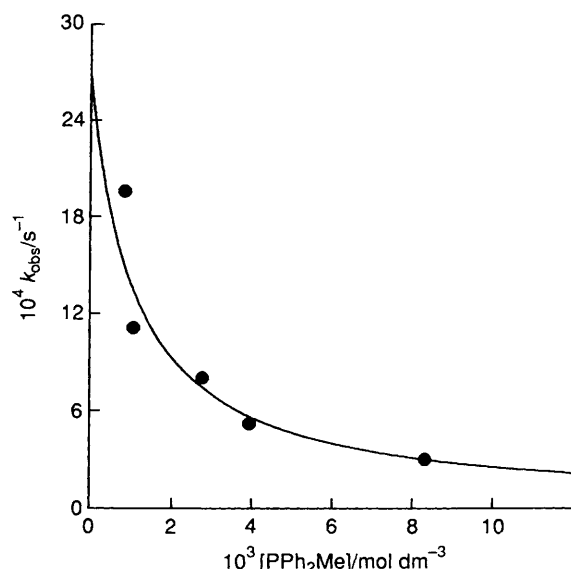
\* See text for the definition of k<sub>f</sub><sup>obs</sup> and k<sub>s</sub><sup>obs</sup>. Estimated standard deviations in the last significant digit are given in parentheses.

**Table 2** Observed rate constants for the decomposition of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] in the presence of an excess of PPh<sub>2</sub>Me<sup>a</sup>

10 <sup>3</sup> [PPh <sub>2</sub> Me]/ mol dm <sup>-3</sup>	10 <sup>4</sup> k <sub>obs</sub> /s <sup>-1</sup>	
	10 °C	15 °C
0.84		19.60(10)
1.06	12.00(10)	11.14(3)
2.17	8.64(1)	
2.75	6.46(5)	8.06(13)
3.95		5.25(3)
5.33	5.72(6)	
8.33	3.82(6)	3.06(3)
10.65	2.50(2)	
A <sup>b</sup> /s	486	371
B <sup>b</sup> /s dm <sup>3</sup> mol <sup>-1</sup>	2.97 × 10 <sup>5</sup>	3.52 × 10 <sup>5</sup>

<sup>a</sup> Benzene solvent and nitrogen atmosphere. Estimated standard deviations in the last significant digit are given in parentheses. <sup>b</sup> See text for the definition of A and B.

fast and slow steps.<sup>16a</sup> To solve this ambiguity, rate constants can be obtained in the presence of added PPh<sub>2</sub>Me and treated in a way similar to that used by Henderson *et al.*<sup>17</sup> for a similar problem. In the presence of an excess of PPh<sub>2</sub>Me the reaction (1) is inhibited and the initial increase in absorbance is not observed [Fig. 1(b)]. From such curves the values of k<sub>obs</sub> included in Table 2 were obtained by conventional linear treatment of ln(D<sub>t</sub> - D<sub>∞</sub>) vs. time data. Fig. 2 illustrates the changes of k<sub>obs</sub> with the concentration of PPh<sub>2</sub>Me and suggests

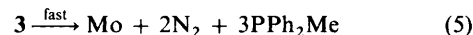
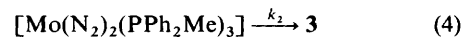
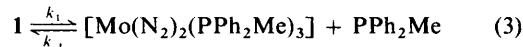


**Fig. 2** Dependence of k<sub>obs</sub> on [PPh<sub>2</sub>Me] for the decomposition reaction of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] (benzene solvent, 15 °C, dinitrogen atmosphere). The closed circles are the experimental results and the line was calculated from values of A and B as discussed in the text

an inverse linear dependence. The fit of these data by use of equation (2) gives values of A and B included in Table 2.

$$1/k_{\text{obs}} = A + B[\text{PPh}_2\text{Me}] \quad (2)$$

From the kinetic data and the well established substitution behaviour of complex 1 the mechanism in equations (3)–(5) is



proposed. Equation (3) represents the initial dissociation of one phosphine from 1 to give a five-co-ordinate intermediate [Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>3</sub>] 2 and the second step leads to the formation of an undetected and unstable species 3 which decomposes rapidly. If 2 is assumed to be formed under steady-state conditions, the rate equation would be (6) and comparison

$$k_{\text{obs}} = \frac{k_1 k_2}{k_2 + k_{-1}[\text{PPh}_2\text{Me}]} \quad (6)$$

with (2) leads to A = 1/k<sub>1</sub> and B = k<sub>-1</sub>/k<sub>1</sub>k<sub>2</sub> so that k<sub>1</sub> and k<sub>-1</sub>/k<sub>2</sub> can be obtained from the A and B values in Table 2.

These values obtained for k<sub>1</sub> (2.06 × 10<sup>-3</sup> s<sup>-1</sup> at 10.0 °C and 2.69 × 10<sup>-3</sup> s<sup>-1</sup> at 15.0 °C) correlate closely with the corresponding k<sub>s</sub><sup>obs</sup> of Table 1. On the other hand, k<sub>-1</sub>/k<sub>2</sub> is estimated to be 6.11 × 10<sup>2</sup> dm<sup>3</sup> mol<sup>-1</sup> at 10.0 °C and 9.49 × 10<sup>2</sup> dm<sup>3</sup> mol<sup>-1</sup> at 15.0 °C. So, k<sub>1</sub> = k<sub>s</sub><sup>obs</sup> and k<sub>2</sub> = k<sub>f</sub><sup>obs</sup>, *i.e.* the slow process occurs first. However, the activation parameters (ΔH<sub>f</sub><sup>‡</sup> = 75 ± 4 kJ mol<sup>-1</sup>, ΔS<sub>f</sub><sup>‡</sup> = -29 ± 3 J K<sup>-1</sup> mol<sup>-1</sup>; ΔH<sub>s</sub><sup>‡</sup> = 38 ± 7 kJ mol<sup>-1</sup>, ΔS<sub>s</sub><sup>‡</sup> = -163 ± 8 J K<sup>-1</sup> mol<sup>-1</sup>) suggest that the slow stage is associative, which makes doubtful the previous assignment of the slow and fast processes to k<sub>1</sub> and k<sub>2</sub>.

There is an alternative approximation which leads to a rate equation of the same mathematical form as that of (6) but different mechanistic meaning.<sup>16b</sup> If process (3) is considered to

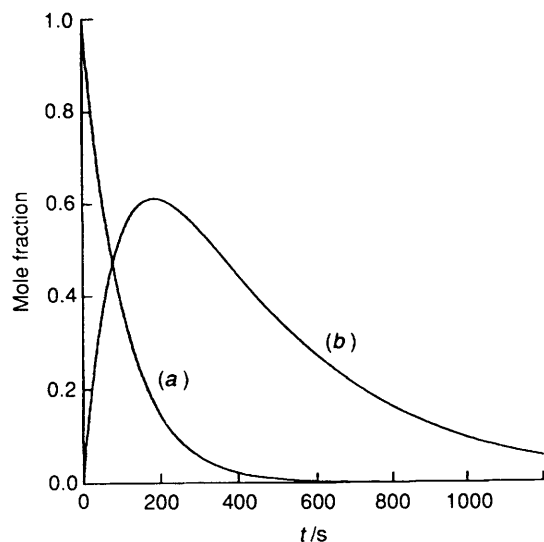


Fig. 3 Concentration vs. time profiles for *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] (a) and the proposed five-co-ordinate intermediate (b). The curves were calculated from kinetic data at 15 °C in benzene and a dinitrogen atmosphere in the absence of added PPh<sub>2</sub>Me

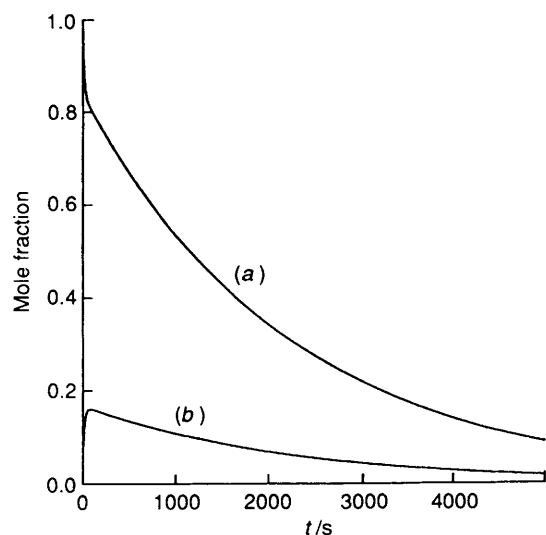


Fig. 4 Concentration vs. time profiles for *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] (a) and the proposed five-co-ordinate intermediate (b). The curves were calculated as in Fig. 3, except that [PPh<sub>2</sub>Me] was taken to be  $5 \times 10^{-3}$  mol dm<sup>-3</sup>

be a fast equilibrium with constant  $K_1$ , the rate expression would be (7) and comparison with (2) leads now to the

$$k_{\text{obs}} = \frac{k_2 K_1}{K_1 + [\text{PPh}_2\text{Me}]} \quad (7)$$

identification of  $k_2$  with the slow process. In this way, the equilibrium constant  $K_1$  can also be determined and, although accumulation of errors makes the values relatively unreliable,  $k_{-1}$  can be estimated from  $k_1$  and  $K_1$ . The resulting values at 10.0 °C are  $k_1 = 0.52 \times 10^{-2}$  s<sup>-1</sup>,  $k_{-1} = 3.05$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>,  $K_1 = 1.64 \times 10^{-3}$  mol dm<sup>-3</sup> and  $k_2 = 2.13 \times 10^{-3}$  s<sup>-1</sup>. This interpretation is in better agreement with the activation parameters, although the numerical values obtained for  $k_1$ ,  $k_{-1}$  and  $k_2$  indicate that the rate of approach to equilibrium (3) is only 4–25 times faster than  $k_2$ , depending on the actual excess of phosphine. Thus, the assumption that equilibrium (3) is much faster than process (4) is not very precise and the values obtained for  $K_1$  must be considered to be only approximate.

Although both mechanisms discussed above seem to be numerically reasonable, the main difference is the extent of

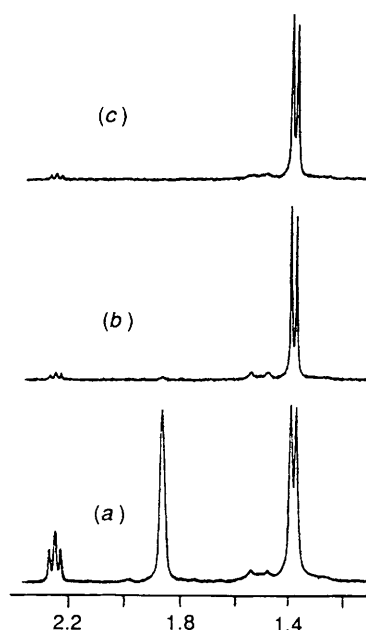


Fig. 5 Methyl region of <sup>1</sup>H NMR spectra taken during the decomposition of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] in the absence of added PPh<sub>2</sub>Me. Spectrum (a) was obtained after filtration of a saturated solution. Acquisition of spectrum (b) was started immediately after 1 : 10 dilution of the previous sample, and spectrum (c) was recorded 30 min later



Fig. 6 Methyl region of <sup>1</sup>H NMR spectra taken during the decomposition of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] in the presence of an excess of phosphine ([I] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> and [PPh<sub>2</sub>Me] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>). In spectrum (a) acquisition was started immediately after complex 1 was completely dissolved; (b) and (c) acquisition was started 30 and 60 min later, respectively

formation of the intermediate 2. If it is formed under steady-state conditions its concentration will be significantly smaller than that of 1 under all conditions we have studied. On the contrary, if it is in equilibrium with 1 very different concentration vs. time profiles will result depending on the concentration of added phosphine. Thus, Fig. 3 corresponds to an experiment in the absence of PPh<sub>2</sub>Me and shows that the concentration of complex 1 decreases very rapidly, and that intermediate 2 becomes the major species in solution, dis-

**Table 3** Kinetic data for the reaction of *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] with pyridine in benzene<sup>a</sup>

T/°C	Atmosphere	10 <sup>2</sup> [py]/mol dm <sup>-3</sup>	10 <sup>3</sup> k <sub>obs</sub> /s <sup>-1</sup>
10.0	N <sub>2</sub>	1.07	5.44 (0.2)
15.0	N <sub>2</sub>	0.20	8.6 (1.0)
	N <sub>2</sub>	0.57	10.8 (1.1)
	N <sub>2</sub>	1.07	10.3 (0.6)
	N <sub>2</sub>	1.67	8.5 (1.2)
	N <sub>2</sub>	2.30	9.9 (1.2)
	Ar	0.20	9.4 (0.6)
	Ar	2.30	9.6 (0.8)
	N <sub>2</sub>	1.67 <sup>b</sup>	9.1 (0.7)
	N <sub>2</sub>	1.67 <sup>c</sup>	9.4 (0.9)
	20.0	N <sub>2</sub>	1.07
25.0	N <sub>2</sub>	1.07	29.30 (1.5)

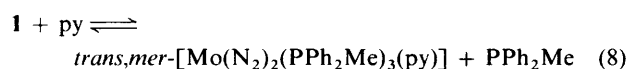
<sup>a</sup> Reported values correspond to the mean value of three measurements and estimated standard deviations are given in parentheses. <sup>b</sup> [PPh<sub>2</sub>Me] = 2.70 × 10<sup>-3</sup> mol dm<sup>-3</sup>. <sup>c</sup> [PPh<sub>2</sub>Me] = 6.70 × 10<sup>-3</sup> mol dm<sup>-3</sup>.

appearing more slowly in the last stage of the reaction. On the other hand, for experiments with an excess of PPh<sub>2</sub>Me (Fig. 4), the concentration of **1** is always higher than that of **2**, with both species disappearing at similar rates. Figs. 5 and 6 show the methyl region of the <sup>1</sup>H NMR spectra recorded under conditions resembling those for Figs. 3 and 4, although the initial concentration of **1** is high enough to obtain the spectra in a reasonable time (ca. 10 min). Fig. 5 shows that the signal at δ 1.87 previously assigned<sup>9</sup> to **1** is only the major signal in spectrum (a). In the same spectrum a doublet at δ 1.38 (*J* = 4.0 Hz) corresponding to free PPh<sub>2</sub>Me appears with an intensity showing that the reaction proceeds further than dissociation of only one PPh<sub>2</sub>Me from every molecule of the starting complex. The triplet at δ 2.25 (*J* = 4.1 Hz) can be tentatively assigned to the intermediate **2** because it remains upon dilution of the sample [spectrum (b)] and then its intensity decreases slowly [spectrum (c)]. In Fig. 6 the added phosphine causes the singlet assigned to **1** always to be more intense than the triplet of **2**, and they both disappear slowly, as expected from Fig. 4. Moreover, from the intensities of signals in the spectra of Fig. 6 and the initial concentrations of **1** and PPh<sub>2</sub>Me the value of *K*<sub>1</sub> is estimated to be 1.5 × 10<sup>-3</sup> mol dm<sup>-3</sup>, in excellent agreement with the values obtained from kinetic experiments. The doublet at δ 1.51 (*J* = 13.1 Hz) is more intense in the spectra of Fig. 6 and it may correspond to an unidentified intermediate product in process (5). The appearance of a triplet for the methyl protons of co-ordinated PPh<sub>2</sub>Me in intermediate **2** can be rationalised if coupling to the phosphorus in the same PPh<sub>2</sub>Me ligand is very small and then the triplet would be the result of coupling between methyl protons and two phosphorus atoms in adjacent phosphines. Another possibility is to consider the triplet as a consequence of virtual coupling of methyl protons with two *trans* phosphorus atoms, although in this case there should be a weak signal masked by other signals in the spectra.

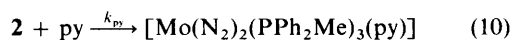
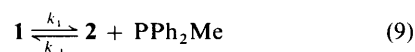
According to the previous discussion, both the NMR results and the activation parameters suggest that the second approximation is more adequate for the treatment of kinetic data. This indicates that the initial dissociation of PPh<sub>2</sub>Me from complex **1** is faster than process (4) and the value of Δ*H*<sup>‡</sup> for this process (75 kJ mol<sup>-1</sup>) is significantly smaller than the values usually observed for phosphine dissociation from other Group 6 compounds (105–125 kJ mol<sup>-1</sup>).<sup>14,18</sup> This low activation barrier is probably due to a weaker Mo–P bond resulting from steric interaction between four bulky phosphines in the equatorial plane of the complex molecule as revealed by X-ray crystal analyses.<sup>19</sup> Phosphine dissociation is slower in the case of the related complexes [Mo(η<sup>6</sup>-PhPPhMe)(PPh<sub>2</sub>Me)<sub>3</sub>]<sup>14</sup> and [Mo(η<sup>6</sup>-PhPPh<sub>2</sub>)(dppe)<sub>2</sub>(PPh<sub>3</sub>)] (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>-PPh<sub>2</sub>),<sup>20</sup> where steric interactions are not so important. No

information has been obtained on the nature of intermediate **3**, although dissociation of PPh<sub>2</sub>Me from **1** leads to a 16-electron species more suitable for an associative attack, and the activation parameters derived from the temperature dependence of *k*<sub>s</sub><sup>obs</sup> also suggest an associative mechanism for step (4). There is the possibility that this step involves the solvent, leading to the formation of an intermediate **3** such as [Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>-Me)<sub>3</sub>(solv)] or [Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>3</sub>]*nsolv*. However, no information has been obtained on the nature of the molybdenum–benzene interaction, although a strong bond with participation of the π electrons is not required because reaction (1) also occurs in solvents of different co-ordination ability (toluene, thf, cyclohexane), with the same kinetic behaviour and rate constants of the same order.

In order to test the mechanism proposed for the decomposition of complex **1** and its relevance to the kinetics of substitution reactions of this compound, reaction (8) was also



studied. The purple pyridine (py) complex shows an absorption maximum at 580 nm in benzene, close to the value of 555 nm reported for thf solutions.<sup>9</sup> Under pseudo-first-order conditions, the observed rate constant at 15.0 °C is not dependent on the concentration of pyridine, dinitrogen and PPh<sub>2</sub>Me (Table 3). Moreover the rate constants in Table 3 are essentially the same as the values of *k*<sub>f</sub><sup>obs</sup> included in Table 1, supporting the previous mechanistic interpretation of data for the decomposition reaction. The activation parameters derived from the pyridine reaction data, Δ*H*<sup>‡</sup> = 76 kJ mol<sup>-1</sup> and Δ*S*<sup>‡</sup> = -18.4 J K<sup>-1</sup> mol<sup>-1</sup>, also correlate well with those obtained for the first stage of the decomposition reaction. All this evidence suggests that the formation of the pyridine complex is kinetically controlled by phosphine dissociation in **1**, as proposed in (9) and (10), where **2** is now assumed to be formed under steady-



state conditions. The rate equation reduces to *k*<sub>obs</sub> = *k*<sub>1</sub> if *k*<sub>p</sub>[py] ≫ *k*<sub>-1</sub>[PPh<sub>2</sub>Me]. Thus, the behaviour of **1** towards substitution reactions seems to be similar to that of the closely related compound [Mo(η<sup>6</sup>-PhPPhMe)(PPh<sub>2</sub>Me)<sub>3</sub>],<sup>14</sup> although in that case dissociation of the labile PPh<sub>2</sub>Me is slower, probably because of weaker steric repulsion between co-ordinated phosphines.

## Experimental

The complex *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>] **1** was prepared by magnesium reduction of MoCl<sub>5</sub> in thf in the presence of PPh<sub>2</sub>Me.<sup>9</sup> A pure crystalline sample for kinetic runs was obtained by recrystallisation in benzene. Absorbance measurements were made with a Varian 2290 spectrophotometer interfaced to a Multitech P500 microcomputer. The temperature of the experiments was kept constant within 0.1 °C by thermostating the cell holder and the reaction vessel.

For the decomposition reaction of complex **1**, kinetic experiments were started by dissolving the required amount of **1** in previously thermostatted solvent (50 cm<sup>3</sup>) and then transferring the solution to the flow cell by using either a peristaltic pump or a Teflon tube. The time required to carry out these manipulations imposes an interval of 40–60 s in which data are lost. For experiments with excess of PPh<sub>2</sub>Me and with pyridine these reagents were added to the solvent before the addition of **1**. The concentration of **1** in the experiments was usually 5 × 10<sup>-5</sup> mol dm<sup>-3</sup>, although several runs were made in order to confirm the

independence of the observed rate constants of the concentration of **1** in the range  $(2.5\text{--}7.5) \times 10^{-5} \text{ mol dm}^{-3}$ . The kinetic results obtained in some experiments carried out in the dark were also similar to those of related experiments in the light. Absorbance readings were taken at 330 nm for all experiments except those involving pyridine, where data were recorded at 580 nm.

Data acquired as absorbance–time pairs were treated with different programs for linear and non-linear least-squares fit. For linear analysis,  $\ln(D_t - D_\infty)$  or  $\ln(D_\infty - D_t)$  data were fitted during two half-lives, with  $D_\infty$  readings taken after at least  $10t_{1/2}$ . An exception is the case of the pyridine reaction, where precipitation occurs after 4–5  $t_{1/2}$  and so more precise  $D_\infty$  values were determined by extrapolation. For biphasic absorbance *vs.* time curves data were fitted by equation (11)<sup>15</sup> using a non-

$$D = D_0 e^{-k_1 t} + \frac{\varepsilon_2 c_0 k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) + \frac{D_\infty}{k_2 - k_1} (k_1 e^{-k_2 t} - k_2 e^{-k_1 t}) + D_\infty \quad (11)$$

linear least-squares program adapted from program NL-REGR.<sup>21</sup> In these cases the initial concentration ( $c_0$ ) and the absorbance at equilibrium ( $D_\infty$ ) were kept constant and the rate constants ( $k_1, k_2$ ), the initial absorbance ( $D_0$ ) and the absorption coefficient of intermediate **2** ( $\varepsilon_2$ ) were refined until convergence was observed. Activation parameters were obtained from conventional Eyring plots of  $\ln(k/T)$  *vs.*  $1/T$ . In all cases the reported estimation of errors corresponds to the standard deviations of the fit, except for the case of the reaction of **1** with pyridine where it corresponds to the standard deviation of three independent measurements.

Elemental analyses were made by Butterworth Laboratories. Infrared spectra were obtained with a Philips Analytical SP3-300 spectrophotometer, NMR spectra at the probe temperature using either a Varian XL-200 or a Gemini 200 spectrometer. All manipulations were carried out under an atmosphere of dinitrogen or argon using standard Schlenk techniques. Solvents were dried by distillation from the appropriate drying agents and degassed immediately before use.

#### Acknowledgements

We thank Direccin General de Investigacion Cientifica y Tecnica for financial support (Grant PB88-0413) and also from the Junta de Andalucia. We also thank Professor G. J. Leigh who read the manuscript and made helpful comments.

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Received 4th November 1991; Paper 1/05595J