Kinetics of Substitution Reactions of *trans*-[Mo(N_2)$_2$(PPh$_2$Me)$_4$] with Tripodal Phosphines†

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The kinetics of substitution reactions of *trans*-[Mo(N_2)$_2$(PPh$_2$Me)$_4$] **1** with the tripodal ligands tris(2-diphenylphosphinoethyl)phosphine and tris(2-diphenylphosphinoethyl)amine has been studied in benzene solution at different temperatures. The absorbance *vs.* time profiles obtained at 25.0 °C are very complicated because of the existence of four consecutive steps. Although the curves can be fitted by consecutive exponentials, the values of the rate constants are very similar, which hinders a detailed interpretation of the data. The reactions have also been monitored by ^{31}P-{^{1}H} NMR spectroscopy to determine the order of occurrence of the different steps and to propose reasonable structures for the reaction intermediates. The proposed mechanism involves initial dissociation of PPh$_2$Me to form an intermediate which is also detected upon decomposition of **1**. This then reacts through two parallel pathways leading to complete decomposition of **1** and to the formation of reaction products with the tripodal phosphines. The second pathway goes through the formation of several intermediates containing one or two molecules of tripodal phosphine acting as mono-, bi-, tri- or tetra-dentate ligands.

Metal complexes of the tripodal compounds tris(2-diphenylphosphinoethyl)amine and tris(2-diphenylphosphinoethyl)phosphine have been prepared in recent years to study the co-ordination and activation of H_2, N_2, CO and small organic molecules.[1,2] Some of these complexes have been found to act as catalysts for the selective hydrogenation of organic substrates.[3] Both tripodal compounds have four donor atoms able to co-ordinate and in most complexes they act as tetradentate ligands, leaving one or two adjacent co-ordination sites which can be occupied by other ligands.[1,4] However, in some cases the bulky substituents in the terminal phosphine groups cause important steric interactions which result in tridentate co-ordination and a pendant PPh$_2$ group.[5,6] In the case of N(CH$_2$CH$_2$PPh$_2$)$_3$ there is also the possibility of tridentate co-ordination through the three P atoms, with the central nitrogen located far from the metal centre.[7] There are also some examples of polynuclear complexes with the tripod acting as a bridging ligand.[8]

An interesting complex is [Mo{P(CH$_2$CH$_2$PPh$_2$)$_3$}$_2$], which contains two tridentate ligands and was isolated unexpectedly from reaction mixtures of *trans*-[Mo(N_2)$_2$(PPh$_2$Me)$_4$] **1** and the tripod in 1 : 1 ratio.[6] Despite numerous attempts to prepare the analogous N(CH$_2$CH$_2$PPh$_2$)$_3$ complex, we have not yet been able to isolate it. The solids obtained under different reaction conditions usually give low analyses for C, H, N and P, which suggests that some decomposition is taking place with formation of molybdenum. In this context, we recently showed[9] that **1** decomposes in solution to give Mo, PPh$_2$Me and N_2. The kinetics of the process is biphasic with initial dissociation of PPh$_2$Me. Since there was the possibility that kinetic factors were responsible for the apparently different behaviours of both tripod compounds, we decided to carry out a kinetic study of the substitution reactions of *trans*-[Mo(N_2)$_2$(PPh$_2$Me)$_4$] with them.

Experimental

The complex *trans*-[Mo(N_2)$_2$(PPh$_2$Me)$_4$] and N(CH$_2$CH$_2$PPh$_2$)$_3$ were prepared according to literature procedures;[10,11] P(CH$_2$CH$_2$PPh$_2$)$_3$ was obtained from Aldrich. All the solvents used in the preparative and kinetic work were dried by refluxing them from appropriate drying agents and deoxygenated immediately before use.

The kinetic experiments were carried out by adding weighed amounts of solid **1** to previously thermostatted solutions of the tripodal compound. The resulting solutions, 5×10^{-5} mol dm^{-3} complex, were immediately transferred with a Teflon tube to a thermostatted flow cell. The time required to carry out these manipulations and starting-data acquisition was usually approximately 20 s. Absorbance *vs.* time data were recorded with a Varian 2290 or a Perkin-Elmer Lambda 3B spectrophotometer interfaced to PC-compatible computers. Finally, the data were transferred to an Acorn computer and analysed using the standard software of an Applied Photophysics stopped-flow instrument. Details of data analysis are given in the Results section.

Samples for NMR spectra were prepared inside a glove-box by placing weighed amounts of complex **1** and the tripodal compound in a tube fitted with a rubber septum. Immediately before recording the spectra, C_6D_6 was added with a Hamilton gas-tight syringe and the tube placed in the NMR spectrometer. The time required for this manipulation, locking and shimming was usually *ca.* 200 s. The ^{31}P-{^{1}H} NMR spectra were recorded at selected time intervals, using a Varian Unity 400 spectrometer, at the probe temperature (*ca.* 23 °C) to avoid a larger delay before starting acquisition. Infrared spectra at selected time intervals were recorded with a Mattson 5020 instrument using samples prepared in a way similar to those for kinetic determinations, except that the concentration of **1** was 5×10^{-3} mol dm^{-3}.

Results

Determination of Rate Constants.—The absorbance *vs.* time curves for solutions containing complex **1** and an excess of tripodal compound under pseudo-first-order conditions are very complicated and reveal the existence of several kinetically distinguishable steps. Thus, Fig. 1 corresponds to an experiment at 40.0 °C and shows a final slow decrease in absorbance preceded by poorly defined changes at short reaction times.

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† *Non-SI unit employed:* cal = 4.184 J.

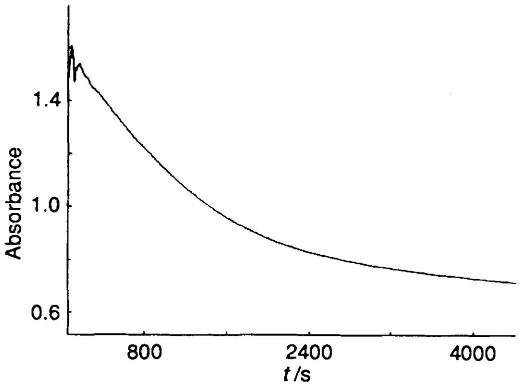


Fig. 1 Absorbance (330 nm) *vs.* time curve for the reaction of complex **1** with $N(CH_2CH_2PPh_2)_3$ (benzene solvent, 40.0 °C, argon atmosphere)

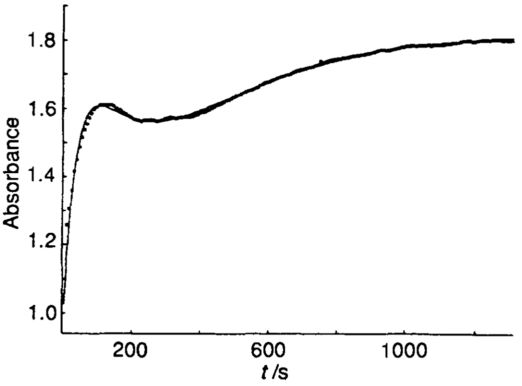


Fig. 2 Absorbance (330 nm) *vs.* time curve for the reaction of complex **1** with $N(CH_2CH_2PPh_2)_3$ (benzene solvent, 25.0 °C, argon atmosphere). The slow decrease in absorbance at longer reaction times is not shown

Table 1 Rate constants obtained from the slow decay of absorbance in the reaction of complex **1** with the tripodal phosphines[a]

		$10^4 k_s/s^{-1}$	
T/°C	Atmosphere	$P(CH_2CH_2PPh_2)_3$	$N(CH_2CH_2PPh_2)_3$
20.0	Ar	0.64 ± 0.01	
25.0	Ar	0.93 ± 0.02	0.39 ± 0.01
30.0	Ar	2.06 ± 0.05	0.72 ± 0.01
35.0	Ar	2.46 ± 0.15	1.45 ± 0.05
40.0	Ar	4.35 ± 0.25	2.50 ± 0.16
40.0	Ar[b]	4.43 ± 0.32	2.56 ± 0.19
40.0	N_2	4.30 ± 0.25	2.33 ± 0.22
45.0	Ar		4.74 ± 0.32

[a] Benzene solvent, λ = 330 nm. The values correspond to the mean and standard deviation from at least three measurements at different concentrations of phosphine ranging from 1.0×10^{-3} to 4.0×10^{-2} mol dm^{-3}. [b] In the presence of added PPh_2Me at concentrations ranging from 1.67×10^{-3} to 1.24×10^{-2} mol dm^{-3}.

These initial changes are better defined at lower temperatures, as shown in Fig. 2 which illustrates the changes in absorbance at 25.0 °C during the first 1200 s. The curve reveals the existence of three steps before the final slow decrease not shown. Similar curves were obtained when using different concentrations of tripodal compounds under an atmosphere of nitrogen or argon. The kinetic profile was not modified by the addition of PPh_2Me.

The slow descending part of the curves was analysed by conventional linear least-squares analysis to give the results in Table 1. This step is first order in the concentration of the starting complex and the rate constant is independent of the concentrations of the incoming tripodal compound, PPh_2Me and N_2. The activation parameters obtained from Eyring plots are $\Delta H^{\ddagger} = 17.0 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -20 \pm 3$ cal K^{-1} mol^{-1} for $P(CH_2CH_2PPh_2)_3$ and 22.6 ± 0.5 kcal mol^{-1} and -3 ± 2 cal K^{-1} mol^{-1} for $N(CH_2CH_2PPh_2)_3$.

Table 2 Rate constants obtained from the first part of the absorbance *vs.* time profile for the reactions of complex **1** with tripodal phosphines[a]

Phosphine	Atmosphere	$10^2k_a/s^{-1}$	$10^3k_b/s^{-1}$	$10^3k_c/s^{-1}$
$P(CH_2CH_2PPh_2)_3$	Ar	2.7 ± 0.4	5.2 ± 0.6	1.4 ± 0.7
	N_2	3.7 ± 1.3	18.1 ± 1.3	2.6 ± 0.5
	N_2[b]	3.5 ± 0.7	14.5 ± 0.9	2.6 ± 0.3
$N(CH_2CH_2PPh_2)_3$	Ar	2.2 ± 0.3	7.1 ± 0.6	3.4 ± 0.5
	N_2	1.9 ± 0.3	7.5 ± 0.7	1.5 ± 0.3
	N_2[b]	2.5 ± 0.7	3.1 ± 0.8	1.8 ± 0.2

[a] Benzene solvent, 25.0 °C, λ = 330 nm. The values correspond to the mean and standard deviation from at least four measurements at different concentrations of phosphine ranging from 1.0×10^{-3} to 4.0×10^{-2} mol dm^{-3}. [b] In the presence of added PPh_2Me at concentrations ranging from 1.67×10^{-3} to 1.24×10^{-2} mol dm^{-3}.

The kinetic analysis of the initial changes in absorbance is more complicated because of the existence of three steps with similar rate constants and it could be satisfactorily resolved only at 25.0 °C. Curves like that of Fig. 2 were fitted to three consecutive exponentials using equation (1), where D represents

$$D = Ae^{-k_at} + Be^{-k_bt} + Ce^{-k_ct} + E \qquad (1)$$

the absorbance at time t. All the seven unknown parameters (A–C, E, k_a, k_b, k_c) were refined to minimise the sum of squares of errors in the absorbance. Initial estimates for the parameters were obtained by non-linear single-exponential fits of the three parts of the curves. The results obtained under different conditions are shown in Table 2. As a consequence of the complicated analysis, the values obtained for the rate constants are affected by large errors which hinder the interpretation of the results.

An important observation is that the analysis described does not define the order of occurrence of the different kinetic steps. This is a general problem in the kinetics of consecutive reactions[12] and for this reason letters instead of numbers are used in Tables 1 and 2 as subindexes for the rate constants. In any case, these values suggest the existence of several reaction intermediates with lifetimes adequate for NMR observation. For this reason, NMR spectra of reaction mixtures were recorded at different time intervals in an attempt to check the quality of the fit of absorbance *vs.* time data. Moreover, these experiments also reveal the order of occurrence of the four steps, because in this case the observed changes in the signal intensities can be related to changes in the actual concentrations of reaction intermediates.

NMR Studies.—Although the complex *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ has often been used as a starting material for the synthesis of related dinitrogen complexes, there have been conflicting reports on its $^{31}P-\{^1H\}$ NMR spectrum.[10,13] In our experience only freshly prepared saturated solutions give spectra showing one singlet at δ 22.9. The spectra of more dilute solutions usually do not show this signal and a new singlet at δ 17.4 appears with an intensity which changes with time in a way similar to that expected for the intermediate previously proposed[9] in the decomposition of *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$. The phosphorus spectra of solutions containing the bis(dinitrogen) complex and $P(CH_2CH_2PPh_2)_3$ in 1:6 ratio are very complicated because of the presence of several species with different coupling patterns. The signal of the starting complex appears only in the first spectrum, and the intermediate with a signal at δ 17.4 appears in the spectra

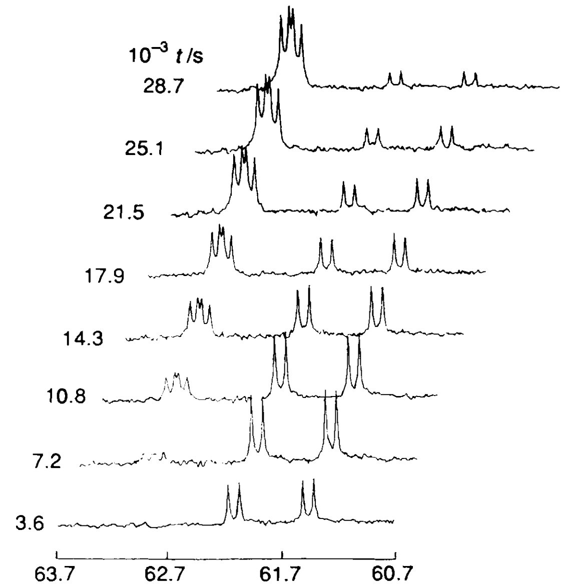


Fig. 3 The ^{31}P-{^1H} NMR spectra recorded during the reaction of complex **1** with $P(CH_2CH_2PPh_2)_3$ (C_6D_6 solvent, argon atmosphere) showing the different time dependences of two multiplets corresponding to different reaction intermediates

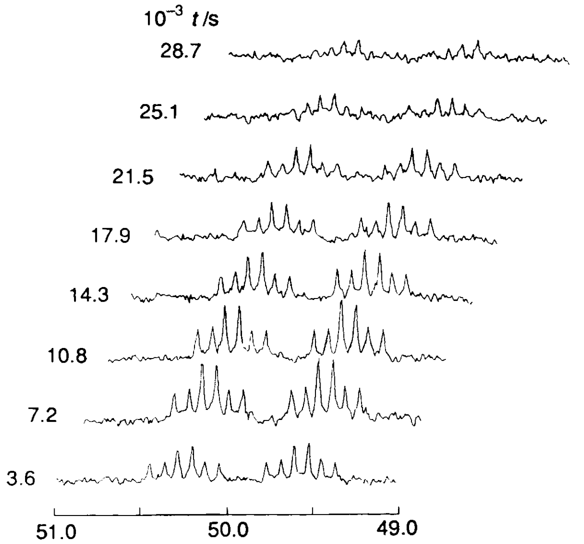
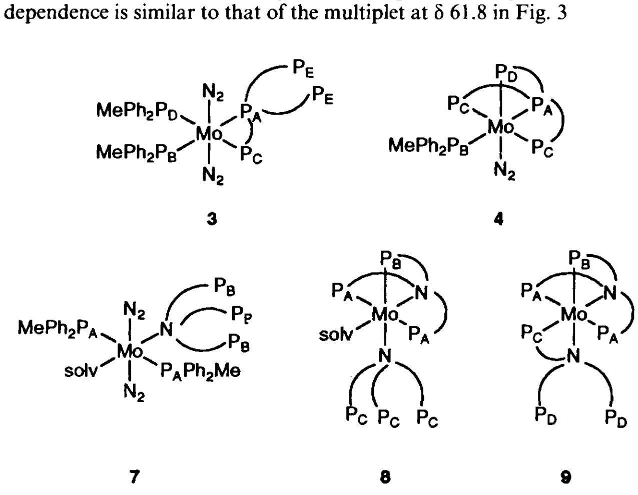


Fig. 4 Plot of a different region of the spectra in Fig. 3. The time dependence is similar to that of the multiplet at δ 61.8 in Fig. 3



Scheme 1 solv = Solvent

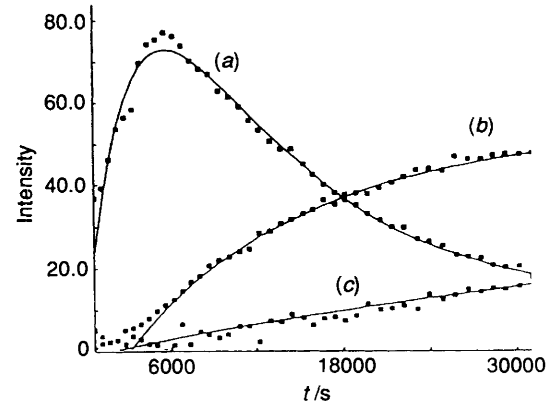


Fig. 5 Concentration *vs.* time profiles [(*a*) **3**, (*b*) **4** and (*c*) **5**] derived from NMR data for the proposed intermediates in the reaction of complex **1** with $P(CH_2CH_2PPh_2)_3$. The solid lines represent the best fits of experimental data (dots) to single- or double-exponential equations

recorded in the first 2000 s. The presence of signals corresponding to the excess of $P(CH_2CH_2PPh_2)_3$ and to free PPh_2Me also complicates the spectra. There are also signals corresponding to other reaction intermediates which can be assigned using the values of δ, *J* and the changes in intensity with time. Thus, Fig. 3 shows two multiplets at δ 61.8 and 63.1 which correspond to different reaction intermediates, as revealed by their different time evolutions. On the contrary, the intensity of the signal at δ 49.9 in Fig. 4 changes with time in the same way as that at δ 61.8, suggesting that they correspond to the same compound. For this compound there is also a doublet in a position typical of unco-ordinated PPh_2 groups of $P(CH_2CH_2PPh_2)_3$ (δ −13.5). This signal is coupled only with the one at δ 49.9, a reasonable position for the central P of a bidentate ligand. The signal at δ 61.8 is typical of co-ordinated PPh_2 groups of $P(CH_2CH_2PPh_2)_3$. The spectrum of this compound also shows two signals at δ 18.4 and 21.4 which can be assigned to two inequivalent PPh_2Me ligands because the signals are very similar to those of complexes **1** and $[Mo(N_2)(PPh_2Me)_2(solv)_2]$ **2**, which only contain PPh_2Me. In this way, the intermediates $[Mo(N_2)_2(PPh_2Me)_2\{P(CH_2CH_2PPh_2)_3\}]$ **3** and $[Mo(N_2)(PPh_2Me)\{P(CH_2CH_2PPh_2)_3\}]$ **4** have been identified. For **4** the NMR spectrum reveals the existence of tetradentate $P(CH_2CH_2PPh_2)_3$ and one co-ordinated PPh_2Me and so there is only one additional co-ordination site available for N_2. The structure proposed from these intermediates and the assignment of signals in their phosphorus spectra are included in Scheme 1 and Table 3. Since the structural assignments are based on ^{31}P NMR data, the arrangement of P atoms about molybdenum is well defined, although the same is not necessarily true for the other co-ordination sites, which can be vacant or occupied by N_2 or solvent. The signals of the previously reported[6] complex $[Mo\{P(CH_2CH_2PPh_2)_3\}_2]$ **5** appear only in the last spectra of the series. The spectra also contain other weak signals more difficult to analyse. However, a poorly defined multiplet at δ 43.5 and two doublets at δ 26.3 and −14.7 can be tentatively assigned to an intermediate **6** of composition $Mo(N_2)_2(PPh_2Me)_2\{P(CH_2CH_2PPh_2)_3\}$ in which the tripodal ligand would probably act in a monodentate manner through the central P, which is the more basic and less-hindered donor centre. Both PPh_2Me ligands would be mutually *trans* and the sixth co-ordination site could be vacant or occupied by N_2 or the solvent.

Fig. 5 shows the concentration *vs.* time profiles for the major species detected by ^{31}P NMR spectroscopy in reaction mixtures of **1** and $P(CH_2CH_2PPh_2)_3$. The vertical scale corresponds to the average intensity of all the signals observed for every compound. An absolute concentration scale cannot be defined because these intensities were obtained using vertical scale expansions in order to generate a good signal-to-noise ratio for

Table 3 ^{31}P-$\{^1H\}$ NMR spectral data for intermediates in the substitution of *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ by tropodal phosphines *

Compound	δ P_A	P_B	P_C	P_D	P_E	J/Hz
3	49.9	21.0	61.8	18.4	−13.5	$J(P_AP_B)$ = 107.7, $J(P_AP_D)$ = 13.4, $J(P_AP_E)$ = 25.3, $J(P_BP_C)$ = 16.0, $J(P_BP_D)$ = 14.0, $J(P_CP_D)$ = 105.8
4	144.9	22.4	63.1	66.3		$J(P_AP_B)$ = 107.4, $J(P_AP_C)$ = $J(P_AP_D)$ = 0, $J(P_BP_C)$ = 17.1, $J(P_BP_D)$ = 24.5, $J(P_CP_D)$ = 12.2
7	22.7	−22.3				
8	52.3	44.3	−21.2			$J(P_AP_B)$ = 7.1
9	51.0	46.6	47.8	−21.8		$J(P_AP_B)$ = 13.4, $J(P_AP_C)$ = 9.0, $J(P_BP_C)$ = 14.2

* See Scheme 1 for signal assignment. Solvent: C_6D_6. Reference: external 85% H_3PO_4.

each signal. However, the changes in concentration with time are well defined and provide useful kinetic information, especially when taken together with rate constants determined from spectrophotometric data. Since the time required to obtain a spectrum (*ca.* 500 s) is large compared to their half-lives, NMR data do not provide satisfactory results for compounds formed or consumed in the first stages of the substitution reaction. However, the curves obtained for compounds **3**–**5** can be analysed to give the fits shown in Fig. 5. Compound **3** is formed with a first-order rate constant of (0.86 ± 0.04) × 10^{-3} s^{-1} and disappears with a rate constant of (0.69 ± 0.02) × 10^{-4} s^{-1}. These results agree reasonably with the values of k_c and k_s, especially if the differences in temperature and experimental procedure are considered. The formation of **4** occurs after an induction period at the same time as **3** disappears, with a rate constant of (0.78 ± 0.03) × 10^{-4} s^{-1}, again similar to the value of k_s. Complex **5** is formed with a rate constant of (0.22 ± 0.02) × 10^{-4} s^{-1} which does not coincide with any of the spectrophotometrically determined values. Thus, it seems to be formed in a very slow step at the end of the reaction, probably with small changes in absorbance occurring during very large time intervals, thus this step can be neglected in the absorbance *vs.* time profiles.

The NMR study of the reaction between *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ and $N(CH_2CH_2PPh_2)_3$ also reveals the presence in solution of intermediate **2**, but there are also other signals which suggest the successive formation of complexes $[Mo(N_2)_2(PPh_2Me)_2\{N(CH_2CH_2PPh_2)_3\}(solv)]$ **8**, and $[Mo\{N(CH_2CH_2PPh_2)_3\}_2(solv)]$ **9**. The structures proposed for these compounds and the assignment of their phosphorus spectra are shown in Scheme 1 and Table 3. In this case, the existence of a central N instead of P simplifies the coupling patterns of the reaction intermediates and satisfactory spectra can be acquired in shorter times, resulting in a better definition of the processes occurring at the beginning of the reaction. Fig. 6 includes the concentration *vs.* time profiles derived from the NMR data for the different species during the first 2000 s. Although there are few experimental points, satisfactory fits can be obtained to give approximate values of the rate constants corresponding to the formation and disappearance of each species. Thus, intermediate **2** disappears with a rate constant of (4.5 ± 0.2) × 10^{-3} s^{-1}. The values obtained for the formation and decomposition of **7** are very similar, (1.8 ± 0.2) × 10^{-3} and (1.2 ± 0.1) × 10^{-3} s^{-1}. Intermediate **8** is formed with k = (2.4 ± 0.1) × 10^{-3} s^{-1} and disappears in a slower process not shown in Fig. 6, with k = (0.7 ± 0.2) × 10^{-4} s^{-1}. A similar value, (0.6 ± 0.1) × 10^{-4} s^{-1}, is obtained for the final formation of **9**. Fig. 6 also shows the formation of free PPh_2Me with a rate constant of (4.3 ± 0.2) × 10^{-3} s^{-1}.

Infrared Spectra.—The kinetic and NMR studies described above suggest the formation of new dinitrogen complexes in the early stages of the substitution reactions of *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ with the tripodal compounds. For this reason, infrared spectra of reaction mixtures under conditions similar to those of the kinetic studies were recorded at different times. Fig. 7 shows the changes observed in the case of $N(CH_2CH_2PPh_2)_3$ and reveals the rapid disappearance of the band at 1928 cm^{-1} and the formation of a new one at 1940 cm^{-1}. The time dependence of the intensity of these bands suggests that the first one corresponds to compound **2** and the second to **7**. In the reaction with $P(CH_2CH_2PPh_2)_3$ the band at 1928 cm^{-1} also disappears in the first 600 s, with parallel formation of a new one at 1945 cm^{-1} which can be assigned to intermediate **6** because its intensity increases with time to reach a maximum at *ca.* 900 s and then decreases slowly. A detailed kinetic study of the

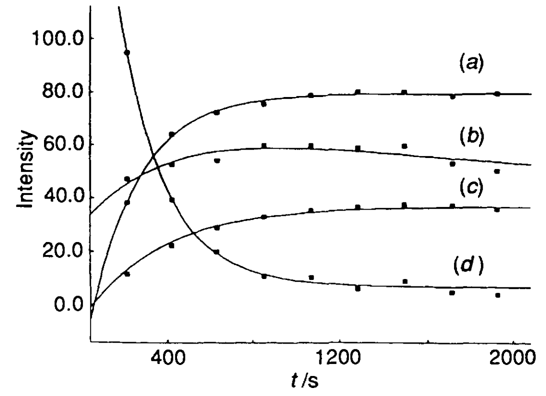


Fig. 6 Concentration *vs.* time profiles [(*a*) PPh_2Me, (*b*) **7**, (*c*) **8** and (*d*) **2**] derived from NMR data for the proposed intermediates in the reaction of complex **1** with $N(CH_2CH_2PPh_2)_3$ during the first 1200 s. The solid lines correspond to the fits discussed in the text

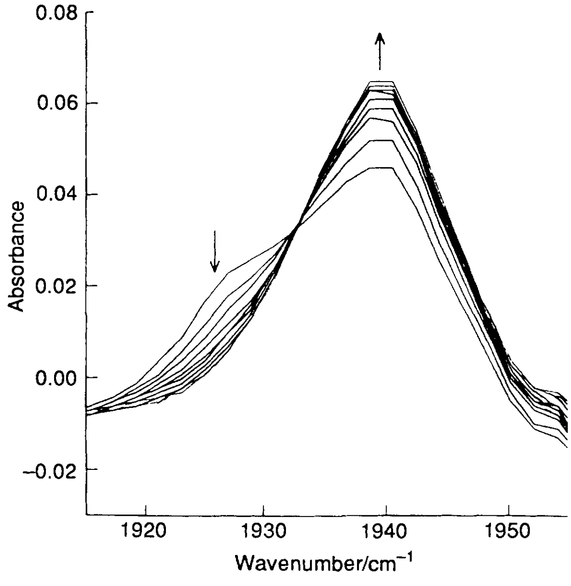


Fig. 7 Infrared spectra recorded at 64 s intervals during the reaction of complex **1** with $N(CH_2CH_2PPh_2)_3$

reactions has not been carried out because of the close proximity of the bands and the low resolution of the spectra. The available infrared data confirm the formation of new dinitrogen complexes during the course of both substitution reactions. Moreover, the appearance of just one ν(NN) band for intermediates **2**, **6** and **7** suggests that they are *trans*-bis(dinitrogen) or mono(dinitrogen) complexes. No evidence has been obtained for the formation of *cis* isomers.

Discussion

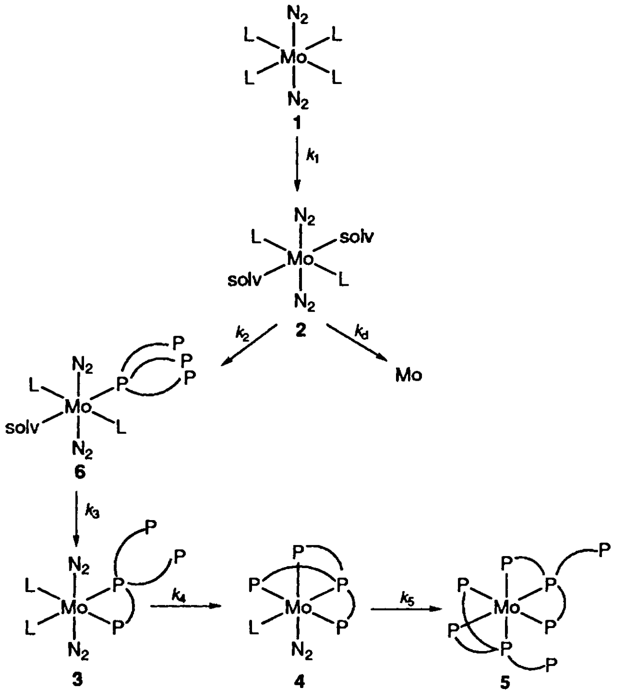
The complex *trans*-[Mo(N_2)$_2$(PPh_2Me)$_4$] has been often used to prepare other dinitrogen complexes because its substitution reactions occur with initial dissociation of PPh_2Me instead of the more common dissociation of N_2 found in most molybdenum dinitrogen complexes. In this way, complexes containing CO,[14] phosphines[15] and N-donor ligands[10,16] have been prepared. A kinetic study of the reaction with pyridine[9] shows that the substitution is controlled by phosphine dissociation, with a rate constant of 2.93×10^{-2} s^{-1} at 25.0 °C. In the same paper we showed that complex **1** decomposes in dilute solutions to give Mo, PPh_2Me and N_2. The kinetics of this process is biphasic, with initial dissociation of PPh_2Me followed by an associative step which probably corresponds to attack by the solvent. The observed rate constant for this second step is 4.70×10^{-3} s^{-1} at 25.0 °C which corresponds to a second-order rate constant of 4.18×10^{-4} dm^3 mol^{-1} s^{-1} for associative attack by the solvent. Complex **2**, characterized by a triplet in the methyl region of the proton NMR spectrum and a singlet at δ 17.4 ppm in the ^{31}P-{^{1}H} NMR spectrum, was detected as an intermediate in the decomposition process. Although a five-co-ordinate structure was previously[9] proposed for **2**, the NMR data are also consistent with octahedral co-ordination of two *trans* PPh_2Me, two N_2 and two solvent molecules. This structure is in better agreement with the results obtained in this work for the reactions with tripodal compounds.

The observation of intermediate **2** in the substitution reactions of complex **1** with the tripodal compounds is very helpful in understanding the complicated kinetics of these processes. Thus, according to previous work,[9] **2** must be formed with a rate constant of 2.93×10^{-2} s^{-1} (k_1), very similar to all the values of k_a in Table 2. Once complex **2** is formed, there is a pathway leading to complete decomposition with $k_d = 4.70 \times 10^{-3}$ s^{-1}. However, the formation of reaction products with the tripodal phosphines suggests a parallel pathway, k_2, such that **2** would disappear with a rate constant $k_d + k_2$. The only constant in Table 2 able to satisfy this condition is k_b. Moreover, previous work[9] showed that k_d decreases at 25 °C in the presence of added PPh_2Me according to equation (2) and

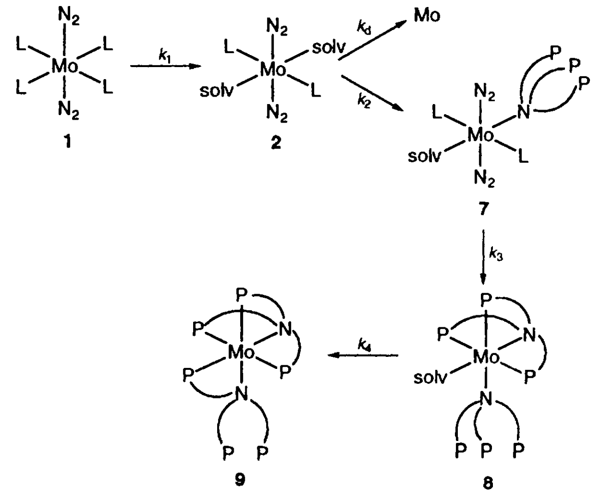
$$k_d = \frac{7.71 \times 10^{-6}}{1.64 \times 10^{-3} + [\mathrm{PPh_2Me}]} \qquad (2)$$

the same effect is observed in Table 2 for k_b, with both tripodal compounds. When the values obtained for the decomposition reaction are used to estimate the decrease in k_d at the concentrations used in the reactions with the tripodal compounds a decrease of (2.4–4.2) $\times 10^{-3}$ s^{-1} in k_b is expected if k_2 is not affected by the addition of phosphine. Despite the large standard deviations in Table 2, the decreases obtained for P($CH_2CH_2PPh_2$)$_3$ (3.6×10^{-3} s^{-1}) and N($CH_2CH_2PPh_2$)$_3$ (4.4×10^{-3} s^{-1}) agree satisfactorily with the previous estimation.

When all the available data are considered, the mechanisms shown in Schemes 2 and 3 can be proposed for the substitution reactions of complex **1** with the tripodal compounds. The correspondence of rate constants in the schemes with those of Tables 1 and 2 is $k_a = k_1$, $k_b = k_d + k_2$, $k_c = k_3$ and $k_s = k_4$. In the case of P($CH_2CH_2PPh_2$)$_3$ the NMR spectra reveal the existence of an additional step which leads to the formation of [Mo{P($CH_2CH_2PPh_2$)$_3$}$_2$]. The previous sequence implies the formation of metallic molybdenum in reaction mixtures of **1** with tripodal phosphines. Actually, the k_d pathway is more important than k_2 under some conditions, especially for N($CH_2CH_2PPh_2$)$_3$. Thus, Fig. 8 shows theoretical concentration *vs.* time profiles calculated using the kinetic results for N($CH_2CH_2PPh_2$)$_3$. For simplicity, the last step is ignored, but the figure shows clearly that the major product is Mo, although significant amounts of **7** and **8** are also formed. Difficulties in separating finely divided Mo could explain the low analyses for C, H, N and P found for solid samples isolated from the reaction mixtures of **1** and N($CH_2CH_2PPh_2$)$_3$. However, the same problem exists for P($CH_2CH_2PPh_2$)$_3$ and complex **5** could be isolated and its structure determined by X-ray diffraction.[6] Thus, the difficulties found in the former case seem to be related to the extreme instability of the compounds. The formation of crystalline solids was sometimes observed, but all attempts to isolate and characterize them were unsuccessful because decomposition occurs in a few minutes to give a mixture containing a white solid, probably free N(CH_2-CH_2PPh_2)$_3$.



Scheme 2 L = PPh_2Me, solv = solvent



Scheme 3

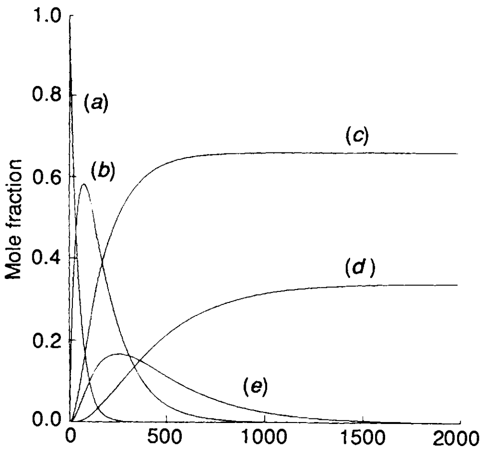


Fig. 8 Theoretical concentration *vs.* time profiles for intermediates [(*a*) **1**, (*b*) **2**, (*c*) Mo, (*d*) **8** and (*e*) **7**] in the reaction with $N(CH_2CH_2PPh_2)_3$. The curves were obtained using the rate constants and mechanism discussed in the text

Conclusion

Although the structures proposed for the intermediates cannot be considered definitive, the results from this work show that substitution reactions of complex **1** with tripodal phosphines occur through the formation of intermediates in which the ligands act in a mono-, bi-, tri- or tetra-dentate manner. In any case, the initial co-ordination to Mo seems to occur through the less sterically hindered central atom, N or P. Electronics effects and the smaller size of nitrogen facilitate co-ordination of the second $N(CH_2CH_2PPh_2)_3$ molecule. On the contrary the formation of $[Mo\{P(CH_2CH_2PPh_2)_3\}_2]$ is very slow, taking several days at room temperature.

An important conclusion of this work is that the reaction products with the tripodal phosphines are formed in competition with a parallel reaction leading to complete decomposition of the starting complex. The extent of decomposition depends on the relative rates of both pathways but, in any case, results in low yields of substitution products. If processes similar to the decomposition of **1** occur for other complexes they could be responsible for the low yields frequently obtained in reactions of molybdenum dinitrogen complexes.

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