

## Fe<sup>II</sup> COMPLEXES WITH TRIPOD PHOSPHINES, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> AND NEt<sub>3</sub>: STABILITY AND KINETICS OF FORMATION

M. ANGELES MÁÑEZ, M. JESUS FERNÁNDEZ-TRUJILLO and  
MANUEL G. BASALLOTE\*

Departamento de Ciencias de los Materiales, Ingeniería Megalúrgica y Química Inorgánica,  
Facultad de Ciencias, Universidad de Cádiz, Apartado 40, Puerto Real 11510, Cádiz, Spain

(Received 21 September 1994; accepted 27 October 1994)

**Abstract**—The formation constants of Fe<sup>II</sup> complexes with the tetradentate phosphines P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>, PP<sub>3</sub>, and N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>, NP<sub>3</sub>, have been determined spectrophotometrically in acetonitrile–toluene mixtures at 25.0°C and *I* = 0.05 mol dm<sup>-3</sup> Et<sub>4</sub>NBF<sub>4</sub>. The results for mixtures containing 60% v/v acetonitrile are log β<sub>11</sub> = 6.00 (PP<sub>3</sub>) and 5.37 (NP<sub>3</sub>). The bidentate phosphine Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, DPPE, and the monodentate amine NEt<sub>3</sub> have also been studied for comparative purposes. For the case of DPPE, the results are log β<sub>11</sub> = 4.07 and log β<sub>12</sub> = 7.10. The kinetics of formation of [FeL(CH<sub>3</sub>CN)<sub>x</sub>]<sup>2+</sup> complexes from [Fe(CH<sub>3</sub>CN)<sub>6</sub>]<sup>2+</sup> has been studied using the stopped-flow technique. The rate of complex formation is first order with respect to both Fe<sup>II</sup> and the incoming ligand. The second order rate constants in 60% v/v acetonitrile at 25.0°C and *I* = 0.05 mol dm<sup>-3</sup> are (in mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>): 10.1 10<sup>4</sup> (PP<sub>3</sub>), 8.6 10<sup>4</sup> (NP<sub>3</sub>), 0.6 10<sup>4</sup> (DPPE) and 5.4 10<sup>4</sup> (NEt<sub>3</sub>). These results can be rationalized with the classical Eigen–Wilkins mechanism assuming that the rate determining step is coordination of the central N or P of the tripod ligand. In all cases, the closure of chelate rings is rapid and the changes of log β and rate constants observed with different compositions of the solvent are small. The formation of *trans*-[Fe(DPPE)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>2+</sup> from [Fe(DPPE)(CH<sub>3</sub>CN)<sub>4</sub>]<sup>2+</sup> occurs slowly through a limiting dissociative mechanism.

Although polydentate phosphines are frequently used as coligands for the preparation of complexes able to activate H<sub>2</sub>, N<sub>2</sub> and other small molecules,<sup>1</sup> the knowledge of the solution behaviour of these species is still very limited. This is particularly true for the case of the tripod phosphines tris(2-diphenylphosphinoethyl)phosphine, PP<sub>3</sub>, and tris(2-diphenylphosphinoethyl)amine, NP<sub>3</sub>. These ligands form metal complexes that serve as catalysts for the hydrogenation of organic substrates.<sup>2</sup> Despite the great interest of these potential applications, little is known about the stability in solution and the kinetics of reaction of these complexes. For this reason, we decided to carry out a systematic study

devoted to determine the relative stabilities of NP<sub>3</sub> and PP<sub>3</sub> complexes compared with those of simpler phosphines and to detect possible differences in their kinetic behaviour. In a previous work,<sup>3</sup> we reported on the kinetics of reactions of these tripod phosphines with *trans*-[Mo(N<sub>2</sub>)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>4</sub>]. The results indicate that the process is very complicated, with several steps occurring at similar rates.

In this paper we report the stabilities and kinetics of formation of Fe<sup>II</sup> complexes with PP<sub>3</sub> and NP<sub>3</sub>. 1,2-Bis(diphenylphosphino)ethane (DPPE) and NEt<sub>3</sub> were also included in the study for comparative purposes. The starting material is the white compound Fe(an)<sub>6</sub><sup>2+</sup> (an = acetonitrile) that has been previously reported<sup>4</sup> to react with PP<sub>3</sub> and DPPE to give the coloured complexes *cis*-[Fe(PP<sub>3</sub>)(an)<sub>2</sub>]<sup>2+</sup> and *trans*-[Fe(DPPE)<sub>2</sub>(an)<sub>2</sub>]<sup>2+</sup>. Because of the low solubilities of the phosphines in

\* Author to whom correspondence should be addressed.

acetonitrile, mixtures containing a variable amount of toluene (tol) have been used as solvent. In any case, the results show a small effect of the composition of mixed solvent over the stability and the kinetics of complex formation.

## EXPERIMENTAL

Iron,  $\text{NOBF}_4$ ,  $\text{NEt}_3$ ,  $\text{PP}_3$  and  $\text{Me}_4\text{NBF}_4$  were obtained from Aldrich.  $\text{NP}_3$ ,  $[\text{Fe}(\text{an})_6](\text{BF}_4)_2$ ,  $[\text{Fe}(\text{PP}_3)(\text{an})_2](\text{BF}_4)_2$  and  $[\text{Fe}(\text{DPPE})_2(\text{an})_2](\text{BF}_4)_2$  were prepared by literature procedures.<sup>4-6</sup> All manipulations were carried out under  $\text{N}_2$  using the standard Schlenk techniques. Solvents were obtained from SDS and acetonitrile was dried by distillation from  $\text{P}_4\text{O}_{10}$ . The solvents were also deoxygenated by bubbling  $\text{N}_2$  immediately before use. NMR spectra were obtained with a Varian Unity 400 spectrometer and electronic spectra with a Perkin-Elmer Lambda 3B spectrophotometer.

For the determination of stability constants, a thermostated double walled Schlenk reactor was connected with Teflon tube to a flow cell placed in a thermostated cell-holder. The flow cell was also connected to a Hamilton gas-tight syringe. In this way, the sample can be transferred from the reactor to the cell and *vice versa* simply by operating the syringe. In a typical experiment,  $10.0 \text{ cm}^3$  of  $[\text{Fe}(\text{an})_6](\text{BF}_4)_2$   $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  in the appropriate solvent were placed in the reactor and titrated under  $\text{N}_2$  with a solution of the ligand. Spectra were recorded for solutions with  $c_L : c_M$  ratios from 0 to 2 and digitized at 5 nm intervals. At least eight spectra were used for every determination and the data were analysed with program SQUAD.<sup>7</sup> Results are reported as  $\log \beta_{mn} \pm \sigma$ , where  $\beta_{mn} = [\text{M}_m\text{L}_n]/[\text{M}]^m[\text{L}]^n$  and  $\sigma$  is the standard deviation of the fit. All the experiments were carried out at  $25.0^\circ\text{C}$  and  $I = 0.05 \text{ mol dm}^{-3} \text{ Me}_4\text{NBF}_4$ . Higher concentrations of electrolyte could not be used because of solubility problems in some of the mixtures. The stability of complexes with  $\text{NEt}_3$  could not be determined because a precipitate is formed during the titration.

The same conditions of temperature and ionic strength were used for the kinetic experiments carried out with an Applied-Photophysics DX17MV stopped-flow instrument. Stock solutions of  $[\text{Fe}(\text{an})_6](\text{BF}_4)_2$  and the ligands were prepared under  $\text{N}_2$  and transferred with Teflon tube to the syringes. The kinetics of reaction of  $[\text{Fe}(\text{an})_6](\text{BF}_4)_2$  with  $\text{PP}_3$  and DPPE were studied under pseudo first-order conditions using an excess of ligand. In these cases, rate constants were obtained by non-linear least-squares treatment of absorbance-time data. The wavelength was selected in preliminary

experiments using the kinetic spectral scanning facilities of the instrument. The reactions with  $\text{NP}_3$  and  $\text{NEt}_3$  could not be studied under pseudo first-order conditions because of solubility problems and/or small absorbance changes. For this reason, these reactions were studied using metal:ligand ratios close to 1 and the data were analysed using the method described by Roper and Elias in ref. 8. In these cases, the reported values of the observed second order rate constants,  $k_{2\text{obs}}$ , correspond to the mean of at least three experiments with different metal:ligand ratios.

The reaction of  $[\text{Fe}(\text{DPPE})(\text{an})_4]^{2+}$  with DPPE to form *trans*- $[\text{Fe}(\text{DPPE})_2(\text{an})_2]^{2+}$  is slow and experiments were started by adding solid  $[\text{Fe}(\text{DPPE})(\text{an})_4](\text{BF}_4)_2$  to thermostated solutions containing the ligand. The reaction was monitored with the Perkin-Elmer spectrophotometer and the analysis of the data carried out by conventional linear least-squares treatment of absorbance-time curves.

### Preparations

$[\text{Fe}(\text{NP}_3)(\text{an})_2](\text{BF}_4)_2$ . A solution of  $[\text{Fe}(\text{an})_6](\text{BF}_4)_2$  (0.47 g, 1 mmol) in acetonitrile ( $15 \text{ cm}^3$ ) was added to a solution of  $\text{NP}_3$  (0.65 g, 1 mmol) in dichloromethane ( $10 \text{ cm}^3$ ). The resulting red solution was stirred for 30 min and evaporated to dryness. Recrystallization from acetone (*ca*  $100 \text{ cm}^3$ ) led to the isolation of pure  $[\text{Fe}(\text{NP}_3)(\text{an})_2](\text{BF}_4)_2$  in yields close to 80% for different preparations (Found: C, 57.3; H, 5.2; N, 3.8.  $\text{C}_{46}\text{H}_{48}\text{N}_3\text{P}_3\text{FeB}_2\text{F}_8$  requires C, 57.2; H, 5.0; N, 4.3%).

$[\text{Fe}(\text{DPPE})(\text{an})_4](\text{BF}_4)_2$ . A solution of DPPE (0.40 g, 1 mmol) in toluene ( $10 \text{ cm}^3$ ) was added to a solution of  $[\text{Fe}(\text{an})_6](\text{BF}_4)_2$  (0.47 g, 1 mmol) in acetonitrile ( $10 \text{ cm}^3$ ),  $50 \text{ cm}^3$  more of toluene were added immediately upon mixing to precipitate a red solid that was washed several times with light petroleum. Satisfactory analysis could not be obtained because recrystallization from different solvents leads to a mixture of *trans*- $[\text{Fe}(\text{DPPE})_2(\text{an})_2]^{2+}$  and  $[\text{Fe}(\text{DPPE})(\text{an})_4](\text{BF}_4)_2$ .

However, NMR spectra show that solids prepared as described above do not contain *trans*- $[\text{Fe}(\text{DPPE})_2(\text{an})_2]^{2+}$  or free DPPE. So, the major impurity (*ca* 10%) is probably unreacted  $[\text{Fe}(\text{an})_6](\text{BF}_4)_2$ .

## RESULTS AND DISCUSSION

### Characterization and stability of complexes

It has been previously reported<sup>4</sup> that reaction of  $[\text{Fe}(\text{an})_6]^{2+}$  with  $\text{PP}_3$  in a mixture of acetonitrile

and CH<sub>2</sub>Cl<sub>2</sub> leads to the formation of *cis*-[Fe(PP<sub>3</sub>)(an)<sub>2</sub>]<sup>2+</sup>. In our case, this complex has been observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra of acetonitrile–toluene solutions containing [Fe(an)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> and PP<sub>3</sub> in different ratios ranging from 0.2:1 to 1:8. These spectra show the signals of *cis*-[Fe(PP<sub>3</sub>)(an)<sub>2</sub>]<sup>2+</sup> (AM<sub>2</sub>X system, δ<sub>A</sub> = 158.7 ppm, δ<sub>M</sub> = 54.0 ppm and δ<sub>X</sub> = 69.9 ppm, J<sub>AM</sub> = J<sub>AX</sub> = 26.7 Hz, J<sub>MX</sub> = 36.5 Hz) and, eventually, those of free PP<sub>3</sub>. The reaction of [Fe(an)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with the analogous ligand NP<sub>3</sub> leads to the formation of a closely related complex, *cis*-[Fe(NP<sub>3</sub>)(an)<sub>2</sub>]<sup>2+</sup> with signals at 38.5 ppm (d) and 42.7 ppm (t) (A<sub>2</sub>M system, J<sub>AM</sub> = 44.4 Hz). Thus, reaction of [Fe(an)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with both tripod phosphines leads to the formation of a single compound without evidence of formation of any additional species as [Fe(PP<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> or [Fe<sub>2</sub>(PP<sub>3</sub>)(an)<sub>4</sub>]<sup>4+</sup>. The spectrophotometric determination of the stability constants of the complexes leads to the results included in Table 1 and the inclusion of additional species does not lead to any significant improvement in the quality of the fit.

For the case of DPPE, the results are somewhat unexpected because the NMR spectra of reaction mixtures with different metal:ligand ratios do not show the signal at 49.92 ppm corresponding to the previously<sup>4</sup> reported complex *trans*-[Fe(DPPE)<sub>2</sub>(an)<sub>2</sub>]<sup>2+</sup>. In all the spectra there is a singlet at 78.31 ppm that had been<sup>4</sup> observed as a minor component in the crude reaction product. The stability calculations lead to the formulation of this complex as a 1:1 species, probably [Fe(DPPE)(an)<sub>4</sub>]<sup>2+</sup>. This species has been isolated as the BF<sub>4</sub><sup>-</sup> salt, although with impurities, as described in the Experimental. These results indicate that coordination of two phosphorus atoms seems to be enough to cause a spin change in Fe<sup>II</sup> yielding inert low spin *d*<sup>6</sup> species. Similar observations have been previously reported for the reaction of [Fe(an)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with monodentate phosphine ligands.<sup>9</sup>

The formation of *trans*-[Fe(DPPE)<sub>2</sub>(an)<sub>2</sub>]<sup>2+</sup> from [Fe(DPPE)(an)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> occurs very slowly, as will be shown below. For this reason, the concentration of *trans*-[Fe(DPPE)<sub>2</sub>(an)<sub>2</sub>]<sup>2+</sup> is too low to be detected during the time required to carry out the NMR and stability experiments. However, its formation constant can be determined using a batch titration procedure and allowing samples to reach equilibrium. The resulting value of log β<sub>12</sub> is also included in Table 1. The data in Table 1 indicate that the stability of the 1:1 complexes with the tripod phosphines is of the same order and higher than that of the 1:1 DPPE complex, as expected from coordination of four and two P atoms respectively. However, the stability of the *cis* complexes with PP<sub>3</sub> and NP<sub>3</sub> is lower than that of the *trans* complex *trans*-[Fe(DPPE)<sub>2</sub>(an)<sub>2</sub>]<sup>2+</sup> that also contains four coordinated phosphine groups in a less sterically demanding disposition. The data for both tripod phosphines indicate that the PP<sub>3</sub> complex is *ca* 4 times more stable than the NP<sub>3</sub> analogue despite the presumably higher basicity of the central N compared with the central P. However, phosphorus is capable of acting as a π-acceptor and it must be also considered that the log β<sub>11</sub> values also include contributions from the chelate ring closure processes that can not be separated from the stability resulting from initial monodentate coordination of the central atom. Thus, the higher stability of the PP<sub>3</sub> complex would reflect a lower strain of the chelate rings. Actually, it is well known that NP<sub>3</sub> frequently coordinates with elongation of the M—N bond<sup>10</sup> which must result in a lower stability of the chelate rings formed.

The changes observed in log β<sub>11</sub> for DPPE with the composition of the solvent are not very large and can be considered almost within the experimental error of the determination. Usually, tendencies in log β with solvent composition are correlated with the rates of formation and decomposition of the complexes.<sup>11</sup> In this sense, data in Table 1 show changes in the formation constants by a factor lower than three, what seems to indicate small changes in the rate constants or parallel compensating changes in the rates of formation and decomposition.

Unfortunately, there are few reports on the stability constants of polyphosphine–metal complexes<sup>12</sup> and our results are clearly different from those obtained by Tolazzi and coworkers<sup>12</sup> for Ag<sup>I</sup> complexes in DMSO. They found that significant amounts of Ag<sub>2</sub>L and AgL<sub>2</sub> complexes are formed when L = DPPE or PP<sub>3</sub>. However, a comparison between both series of data is not very appropriate because of the differences in the metal and the solvent. Moreover, as will be shown below, the

Table 1. Stability constants for the formation of Fe<sup>II</sup>–phosphine complexes in acetonitrile–toluene (60–40% v/v)

Ligand	Log β <sub>11</sub>	Log β <sub>12</sub>
DPPE	4.07 ± 0.03 <sup>a</sup>	7.10 ± 0.06
NP <sub>3</sub>	5.37 ± 0.05	
PP <sub>3</sub>	6.00 ± 0.08	

<sup>a</sup> Values for other solvent compositions are: 4.01 ± 0.02 (30% an); 4.08 ± 0.04 (40% an) and 4.25 ± 0.02 (50% an).

behaviour of Fe<sup>II</sup> can be well explained if it is considered that the closure of chelate rings is rapid and it avoids formation of Fe<sub>2</sub>L. On the other hand, the formation of low spin FeL complexes makes very slow the reaction with a second L to form FeL<sub>2</sub>. Consequently, these species are not observed in the stability studies unless special care is taken, as described above for the case of [Fe(DPPE)<sub>2</sub>(an)<sub>2</sub>]<sup>2+</sup>.

#### Kinetics of complex formation

The reaction of the white compound [Fe(an)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> with the different phosphines to give the low spin coloured 1:1 complexes occurs rapidly and the kinetics can be studied using the stopped-flow technique. Thus, the spectral changes observed during the formation of *cis*-[Fe(PP<sub>3</sub>)(an)<sub>2</sub>]<sup>2+</sup> under pseudo-first-order conditions show the appearance of a band at 475 nm. This band coincides with that observed for *cis*-[Fe(PP<sub>3</sub>)(an)<sub>2</sub>]<sup>2+</sup> in the stability experiments and there is no evidence for the accumulation of an intermediate

or any other reaction product containing more than one coordinated PP<sub>3</sub>. Absorbance–time curves can be fitted to a single exponential and the results for several concentrations of PP<sub>3</sub> are included in Table 2 and plotted in Fig. 1. Although the range of

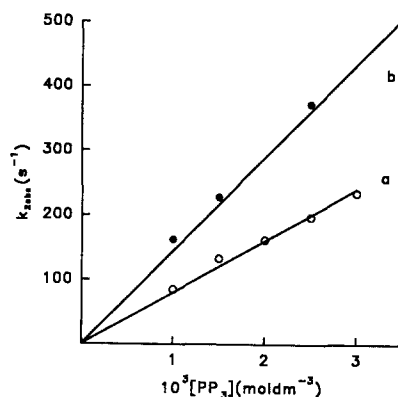


Fig. 1. Dependence of pseudo-first-order rate constant,  $k_{\text{obs}}$ , on the concentration of PP<sub>3</sub> for the reaction of [Fe(an)<sub>6</sub>]<sup>2+</sup> with PP<sub>3</sub>: (a) 30% v/v an; (b) 60% v/v an.

Table 2. Observed pseudo-first-order rate constants for the reaction of [Fe(an)<sub>6</sub>]<sup>2+</sup> with PP<sub>3</sub> and DPPE in acetonitrile–toluene mixtures<sup>a</sup>

(a) L = PP<sub>3</sub>

10 <sup>3</sup> [PP <sub>3</sub> ] (mol dm <sup>-3</sup> )	$k_{\text{obs}}$ (s <sup>-1</sup> )			
	30% an	40% an	50% an	60% an
0.5	—	69 ± 1	—	45 ± 1
1.0	85	112 ± 2	162 ± 8	—
1.2	—	—	—	99 ± 3
1.5	132	—	228 ± 8	154 ± 2
2.0	161	227 ± 12	—	217 ± 6
2.5	197	252 ± 17	372 ± 12	—
3.0	234	—	—	—
3.5	—	—	486 ± 8	—

(b) L = DPPE

10 <sup>3</sup> [DPPE] (mol dm <sup>-3</sup> )	$k_{\text{obs}}$ (s <sup>-1</sup> )			
	30% an	40% an	50% an	60% an
0.5	—	—	2.3 ± 0.1	3.0 ± 0.2
1.5	4.0 ± 0.2	5.9 ± 0.5	10.6 ± 0.2	10.0 ± 0.4
2.4	5.8 ± 0.3	9.0 ± 0.4	17.2 ± 0.3	16.2 ± 0.4
3.0	7.6 ± 0.2	11.8 ± 0.2	—	—
3.5	—	—	21.7 ± 0.5	22.2 ± 0.4
4.0	10.2 ± 0.2	14.2 ± 0.2	—	24.5 ± 0.5

<sup>a</sup>  $T = 25.0^\circ\text{C}$ ,  $I = 0.05 \text{ mol dm}^{-3}$  Et<sub>4</sub>NBF<sub>4</sub>, [Fe]<sub>0</sub> =  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ . The reported constants correspond to the mean value of at least three measurements.

concentration of PP<sub>3</sub> is small, the results indicate that the reaction is first order both in the iron complex and PP<sub>3</sub>, i.e. the rate law is eq. (1).

$$\frac{d[\text{cis-}[\text{Fe}(\text{PP}_3)_2(\text{an})_2]^{2+}]}{dt} = k_{2\text{obs}}[\text{Fe}(\text{an})_6]^{2+}[\text{PP}_3]. \quad (1)$$

A similar rate law is obtained when NP<sub>3</sub>, DPPE and NEt<sub>3</sub> are used instead of PP<sub>3</sub>. Because of solubility problems with the ligand or the reaction products, the kinetics of reactions with NP<sub>3</sub> and NEt<sub>3</sub> could not be studied under pseudo-first-order conditions and the analysis of the experimental curves was carried out as described in the Experimental. It is important to point out that no evidence of formation of 1:2 complexes was observed for any of the ligands in the first seconds following the mixture of reagents.

The values obtained for the second order rate constants ( $k_{2\text{obs}}$ ) for the different ligands and solvent compositions are included in Table 3 and illustrate several interesting aspects relevant to the kinetics of these reactions. Thus, for a given ligand there is a small change in the value of  $k_{2\text{obs}}$  with the changes in solvent compositions, in agreement with the results of stability determinations. Moreover, for the case of DPPE there is a good agreement between the tendencies of  $\log \beta_{11}$  and  $k_{2\text{obs}}$ , as shown in Fig. 2. Both the rate of complex formation and the stability constant reach a maximum at a composition of 50% acetonitrile. The observation of a maximum rate constant for an intermediate composition is general for the four ligands, as shown in Fig. 3. However, the composition corresponding to the maximum is different for every ligand, which seems to indicate that solvation effects in the initial and transition states are closely balanced and result in a lower activation barrier for intermediate compositions of the mixed solvent.

Comparison of Tables 1 and 3 also reveals a good correlation between the rate constants and the  $\log \beta_{11}$  values for the three phosphines, despite the

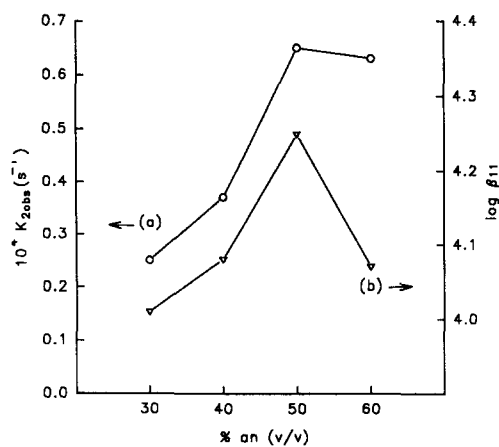


Fig. 2. Dependence of  $k_{2\text{obs}}$  (a) and  $\log \beta_{11}$  (b) on the composition of the solvent for the formation of  $\text{trans-}[\text{Fe}(\text{DPPE})_2(\text{an})_2]^{2+}$  from  $[\text{Fe}(\text{an})_6]^{2+}$  and DPPE.

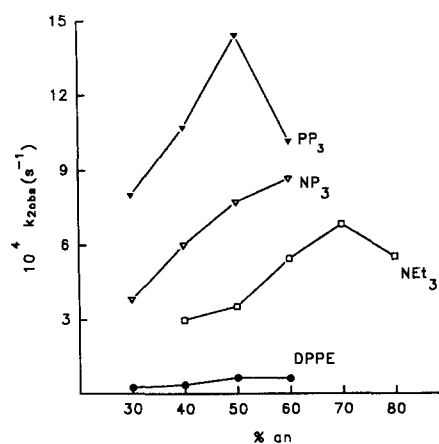


Fig. 3. Dependence of  $k_{2\text{obs}}$  on the composition of the solvent for the reaction of  $[\text{Fe}(\text{an})_6]^{2+}$  with the different ligands.

different number of P donors. The more stable complexes are formed faster and an acceptable linear free energy relationship (LFER) between  $\log k_{2\text{obs}}$  and  $\log \beta_{11}$  is observed for solutions containing

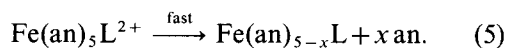
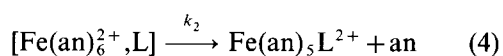
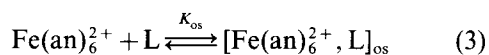
Table 3. Second order rate constants for the formation of Fe<sup>II</sup>-phosphine complexes in acetonitrile-toluene mixtures

Ligand	$10^{-4}k_{2\text{obs}}$ (mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> )					
	30% an	40% an	50% an	60% an	70% an	80% an
DPPE	0.25	0.37	0.65	0.63	—	—
NP <sub>3</sub>	3.82	5.99	7.72	8.65	—	—
PP <sub>3</sub>	8.00	10.70	14.41	10.15	—	—
NEt <sub>3</sub>	—	2.98	3.53	5.45	6.82	5.53

60% acetonitrile. The resulting equation for this LFER is eq. (2)

$$\log k_{2\text{obs}} = 1.16 + 0.66 \log \beta_{11} \quad (2)$$

and it suggests a common mechanism for all the reactions. As these reactions are complex formation processes from the solvated metal ion, it can be assumed that the classical Eigen–Wilkins<sup>8,13</sup> mechanism operates, with the process being kinetically controlled by the formation of the first metal–ligand bond.



Equation (3) represents outer-sphere complexation and eq. (4) corresponds to the rate limiting substitution of the first coordinated acetonitrile. Equation (5) indicates that all chelate rings are closed rapidly, as frequently found for complexation of polydentate ligands. Under the experimental conditions used in this work, the rate law reduces to eq. (6) that leads to  $k_{2\text{obs}} = k_2 K_{\text{os}}$ :

$$k_{2\text{obs}} = k_2 K_{\text{os}}[\text{L}]. \quad (6)$$

According to the proposed mechanism,  $k_2$  must be close to the rate of acetonitrile exchange,  $k_{\text{ex}}$ , in  $\text{Fe}(\text{an})_6^{2+}$ . The value of  $k_{\text{ex}}$  has been previously<sup>14</sup> determined in pure acetonitrile and if it is assumed that its change with solvent composition is small, then  $k_2$  can be considered to be *ca*  $6.6 \times 10^5 \text{ s}^{-1}$ . With this value and those in Table 3,  $K_{\text{os}}$  can be estimated for every ligand. The results are 0.12–0.22 for  $\text{PP}_3$ , 0.06–0.13 for  $\text{NP}_3$ , 0.004–0.010 for DPPE and 0.04–0.10 for  $\text{NEt}_3$ , where the couples of values result from the extreme values of  $k_{2\text{obs}}$  at different solvent compositions. In any case,  $K_{\text{os}}$  is always small, as expected for outer-sphere complexation between a divalent ion and a large neutral molecule.

One interesting observation from the data in Table 3 is that  $k_{2\text{obs}}$  for  $\text{NP}_3$  is close to the values for  $\text{NEt}_3$ , which suggests that  $\text{NP}_3$  coordinates initially through the more basic and less sterically demanding N atom. Coordination of this central atom serves as a bridgehead for subsequent rapid closure of the chelate rings. Initial coordination of  $\text{PP}_3$  would then occur through the central P atom and

the DPPE complex would be formed more slowly because of the larger cone angle of its phosphine groups. Thus, there seems to be a good correlation between the steric requirements of the donor centres and the rate of complex formation. For the case of donor atoms with bulky substituents, the metal–ligand distance in the outer-sphere complex must be large and this results in low values of  $K_{\text{os}}$  and  $k_{2\text{obs}}$ . In the presence of other donor atoms with smaller substituents, initial coordination will occur preferentially through these other centres.

The kinetic experiments described above show the fast formation of low-spin  $\text{Fe}^{\text{II}}$ –phosphine complexes with stoichiometry 1:1. However, the formation of complexes containing more than one coordinated polyphosphine is well illustrated for the case of DPPE and there are also precedents of formation of 1:2 complexes for molybdenum with  $\text{PP}_3$  and  $\text{NP}_3$ .<sup>3,15</sup> For this reason, the possible formation of 1:2 complexes was also examined both from the stability and the kinetic points of view. In the case of  $\text{PP}_3$  and  $\text{NP}_3$ , the spectral changes observed during very large periods of time are small and occur with rate constants in the order of  $10^{-5} \text{ s}^{-1}$ . However, the spectral changes are so small and occur over so large reaction times that a detailed analysis of the data is not possible. Thus, the formation in solution of species such as  $\text{Fe}(\text{PP}_3)_2^{2+}$  or  $\text{Fe}(\text{NP}_3)_2^{2+}$  cannot be ruled out, but if they exist their stability is very small relative to the corresponding 1:1 complexes and their formation is very slow. For the case of DPPE, the absorbance changes are larger and the rate constant corresponding to the formation of *trans*- $[\text{Fe}(\text{DPPE})_2(\text{an})_2]^{2+}$  from  $[\text{Fe}(\text{DPPE})(\text{an})_4](\text{BF}_4)_2$  was found to be independent of the concentration of DPPE. A value of  $k_{\text{obs}} = (1.8 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$  was determined at 25.0°C and 60% acetonitrile, using UV–vis and <sup>31</sup>P NMR spectroscopy. This result suggests that the substitution reactions of  $[\text{Fe}(\text{DPPE})(\text{an})_4](\text{BF}_4)_2$  occur by a limiting dissociative mechanism and are kinetically controlled by dissociation of acetonitrile. The closure of the chelate ring is also rapid in this case and no intermediate containing monodentate DPPE has been observed.

*Acknowledgements*—We thank Dirección General de Investigación Científica y Técnica (Grant PB91-0741) and Junta de Andalucía for financial support.

## REFERENCES

1. C. Bianchini, P. Innocenti, D. Masi, A. Meli and M. Sabat, *Organometallics* 1986, **5**, 72; C. Bianchini, C. Mealli, A. Meli, M. Peruzzini and F. Zanobini, *J.*

- Am. Chem. Soc.* 1987, **109**, 5548; C. Bianchini, M. Peruzzini and F. Zanobini, *J. Organomet. Chem.* 1987, **326**, C79; C. Bianchini, A. Meli, M. Peruzzini, P. Fedriani, C. Bohanna, M. A. Esteruelas and L. A. Oro, *Organometallics* 1992, **11**, 138; C. Bianchini, K. Linn, D. Masi, M. Peruzzini, A. Polo, A. Vacca and F. Zanobini, *Inorg. Chem.* 1993, **32**, 2366.
2. T. Suárez and B. J. Fontal, *J. Mol. Catal.* 1985, **32**, 191; C. Bianchini, A. Meli, M. Peruzzini, P. Fredriani, C. Bohanna, M. A. Esteruelas and L. A. Oro, *Organometallics* 1992, **11**, 138; C. Bianchini, C. Bohanna, M. A. Esteruelas, P. Fredriani, A. Meli, L. A. Oro and M. Peruzzini, *Organometallics* 1992, **11**, 3837.
  3. M. A. Máñez, M. J. Fernandez-Trujillo and M. G. Basallote, *J. Chem. Soc., Dalton Trans.* 1994, 1717.
  4. D. L. Du Bois and A. Miedaner, *Inorg. Chem.* 1986, **25**, 4642.
  5. B. J. Hathaway, D. G. Holah and A. E. Underhill, *J. Chem. Soc.* 1962, 2444.
  6. R. Morasi and L. Sacconi, *Inorg. Synth.* 1976, **16**, 174.
  7. D. J. Legget, in *Computational Methods for the Determination of Formation Constants* (Edited by D. J. Legget), Plenum Press, New York (1985).
  8. J. R. Roper and H. Elias, *Inorg. Chem.* 1992, **31**, 1202.
  9. C. J. Barbour, J. H. Cameron and J. M. Winfield, *J. Chem. Soc., Dalton Trans.* 1980, 2001; J. H. Cameron, A. G. Lappin, J. M. Winfield and A. McAuley, *J. Chem. Soc., Dalton Trans.* 1981, 2172; L. McGhee, R. M. Siddique and J. M. Winfield, *J. Chem. Soc., Dalton Trans.* 1988, 1309.
  10. L. Sacconi and M. Di Vaira, *Inorg. Chem.* 1978, **4**, 810.
  11. A. Y. Nazarenko, R. M. Izatt, J. M. Lamb, J. M. Desper, B. E. Matysik and S. H. Gellman, *Inorg. Chem.* 1992, **31**, 3990; R. Moreno-Esparza, M. López and K. H. Pannell, *J. Chem. Soc., Dalton Trans.* 1992, 1791.
  12. P. Di Bernardo, G. Dolcetti, R. Portanova, M. Tolazzi, G. Tmat and P. Zanonato, *Inorg. Chem.* 1990, **29**, 2859.
  13. R. Wilkins, *Acc. Chem. Res.* 1970, **3**, 408.
  14. M. J. Sisley, Y. Yano and T. W. Swaddle, *Inorg. Chem.* 1982, **21**, 1141.
  15. M. G. Basallote, P. Valerga, M. C. Puerta, A. Romero, A. Vegas and M. Martínez-Ripoll, *J. Organomet. Chem.* 1991, **420**, 371.