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KINETICS OF SUBSTITUTION REACTIONS OF Fe^{II}-PHOSPHINE COMPLEXES WITH Cl^-, Br^- AND SCN^- IN ACETONITRILE. A COMPARATIVE STUDY OF COMPLEXES CONTAINING BIDENTATE AND TRIPODAL PHOSPHINES

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

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

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Abstract—The kinetics of formation of $FeLX^+$ complexes from $FeLan_2^{2+}$ and X^- [$L = P(CH_2CH_2PPh_2)_3$, $N(CH_2CH_2PPh_2)_3$, $(Ph_2PCH_2CH_2PPh_2)_2$; X = Cl, Br, SCN; an = acetonitrile] has been studied in acetonitrile at 25.0°C and Et_4NBF_4 (0.05 mol dm^{-3}). All the reactions seem to go through initial substitution of one coordinated acetonitrile by X^- to form $FeLX^+$, although in some cases the reaction continues to the formation of $FeLX_2$. The values obtained for the rate constants corresponding to the first substitution process do not show large differences and indicate that the three $FeL(an)_2^{2+}$ complexes have a very similar behaviour, except that the $N(CH_2CH_2PPh_2)_3$ complex is intrinsically more labile towards substitution of coordinated acetonitrile. The stability quotients for the formation of $FeLX^+$ complexes have been also determined and they suggest some degree of steric selectivity in the reactions of $[Fe\{P(CH_2CH_2PPh_2)_3\}(an)_2]^{2+}$ with X^-. Copyright © 1996 Elsevier Science Ltd.

Most work dealing with iron complexes containing polydentate phosphines has concentrated on the synthesis, structure and reactivity of the complexes, especially from the point of view of the activation of small molecules[1] and their potential use as catalysts for hydrogenation processes.[2] Thus, metal complexes of the tripodal phosphine tris-(2-diphenylphosphinoethyl)phosphine, PP_3, are useful catalysts for the hydrogenation of organic substrates.[3] The proposed catalytic cycles include steps corresponding to substitution at coordination sites adjacent to the phosphine groups and also the opening of a chelate ring to create a vacant coordination site. The function of the catalyst can be conditioned in some cases by the relative rates of both processes. Thus, it is important to study the kinetic behaviour of metal complexes containing these phosphines and determine the effect of factors as the nature of metal ion, phosphine and incoming ligand.

As a first approximation to the problem, we decided to make a comparative study of the kinetics of substitution reactions of Fe^{II} complexes containing the bidentate phosphine 1,2-bis(diphenylphosphino)ethane, DPPE, and the tripodal ligands PP_3 and tris-(2-diphenylphosphinoethyl) amine, NP_3. The incoming ligands selected are Cl^-, Br^- and SCN^-, and the starting complexes are $Fe(PP_3)(an)_2^{2+}$ (**1**), $Fe(NP_3)(an)_2^{2+}$ (**2**) and *trans*-$[Fe(DPPE)_2(an)_2]^{2+}$ (**3**). All three complexes form readily and contain two acetonitrile ligands able to be substituted. The synthesis and characterization of these compounds has been previously reported.[4,5] Complexes **1** and **2** have a *cis* structure and differ only in the nature of the central atom of the tripod.[4,5] On the contrary, **3** is *trans* with four phosphine groups coordinated in a planar arrangement.[4]

In addition to the kinetic study, this work also

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* Author to whom correspondence should be addressed.

includes the determination of stability constants corresponding to the substitution reactions, in such a way that the effect of changing the nature of the phosphine and the incoming ligand can be analysed both from the thermodynamic and the kinetic points of view.

EXPERIMENTAL

All the preparative, stability and kinetic work was carried out under N_2 using Schlenk and syringe techniques. Acetonitrile was dried over P_4O_{10} and deoxygenated immediately before use.

Iron, $NOBF_4$, DPPE, PP_3, Et_4NBF_4, Me_4NCl, Me_4NBr- and Bu_4NSCN were obtained from Aldrich. The following compounds were prepared according to literature procedures: $[Fe(an)_6](BF_4)_2$,[6] $[Fe(PP_3)(an)_2](BF_4)_2$,[4] $[Fe(DPPE)_2(an)_2](BF_4)_2$,[4] NP_3[7] and $[Fe(NP_3)(an)_2](BF_4)_2$.[5] Samples of these compounds were available from previous work[5] and their purity had been checked by elemental analysis and NMR spectroscopy.

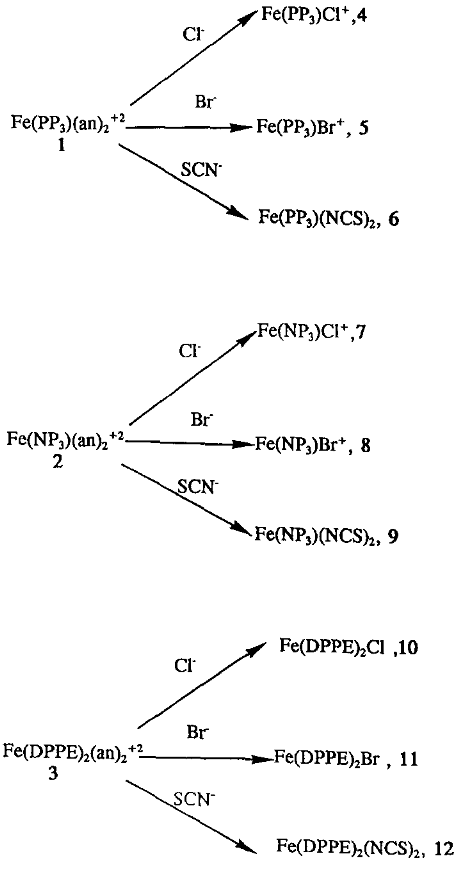
The stability constants were determined spectrophotometrically at 25.0°C and Et_4NBF_4 (0.05 mol dm^{-3}) using a Perkin–Elmer Lambda 3B instrument. Since the reactions studied are very slow, samples containing different concentrations of the starting iron complex and X^- were prepared under N_2 and allowed to reach equilibrium before recording the spectra. Typical ranges for the concentration of both reagents are $0.1–2.7 \times 10^{-3}$ mol dm^{-3} for the iron complexes and $0.1–1.0 \times 10^{-3}$ mol dm^{-3} for the X^- salt. The data were analysed with the program SQUAD,[8] which leads to the values of stability constants and the spectra of reaction products. These spectra are in good agreement with those previously published[9,10] for solid compounds isolated from analogous reaction mixtures.

Kinetic experiments were also carried out at 25.0°C and 0.05 mol dm^{-3} Et_4NBF_4 with the Perkin–Elmer instrument. The wavelength was selected for every reaction as that showing the maximum change of absorbance in preliminary spectral scanning experiments. These experiments were also used to check the independence of the observed rate constants on the concentration of the iron complex. Kinetic measurements were carried out under pseudo-first order conditions (X^- excess). The experiments were started by adding a weighed amount of solid complex to a previously thermostatted solution containing the desired concentration of X^- salt and the amount of Et_4NBF_4 required to adjust the ionic strength. The resulting solution, with a concentration of iron complex of 5×10^{-4} mol dm^{-3}, was transferred with a teflon tube to a thermostatted cell. The time required to carry out the transfer is not significant with respect to the reaction time. Rate constants were obtained by conventional least-squares analysis of absorbance versus time curves during two half-times.

RESULTS AND DISCUSSION

Stability of complexes

The analysis of equilibrium data corresponding to reactions of complexes **1** and **2** with X^- is satisfactorily carried out by considering the formation of the species shown in Scheme 1. The values derived for the formation constants are included in Table 1. When X^- is Cl^- or Br^- a single complex containing one coordinated X^- is formed and the inclusion of $FeLX_2$ species does not lead to any significant improvement in the quality of the fit. On the contrary, reactions with SCN^- lead to the formation of two species containing one or two coordinated SCN^-. These results agree well with literature reports[10] on the synthesis and characterization of complexes **4–9**. As revealed by X-ray structural determination,[9] the halocomplexes with PP_3 and NP_3 contain only one coordinated X^- and



Scheme 1.

Table 1. Stability quotients corresponding to the formation of Fe^{II}-phosphine-X complexes in acetonitrile at 25.0°C and $I = 0.05$ mol dm^{-3}[a]

Complex	L	X	log K_{11}	log K_{12}
1	PP_3	Cl	4.56 ± 0.18	—
		Br	2.22 ± 0.03	—
		SCN	4.50 ± 0.08	8.24 ± 0.14
2	NP_3	Cl	3.54 ± 0.05	—
		Br	3.99 ± 0.07	—
		SCN	4.02 ± 0.12	7.54 ± 0.24
3	DPPE	Cl	2.57 ± 0.06	—
		Br	2.66 ± 0.03	—

[a] The quotients are defined as $K_{11} = [FeLX]/([FeL][X])$ and $K_{12} = [FeLX_2]/([FeL][X]^2)$. The results are expressed as log $K \pm \sigma$, where σ represents the standard deviation of the fit.

are penta-coordinate because of the ability of the tripodal ligands to favour the formation of trigonal bipyramidal (tbp) complexes. Surprisingly, the equilibrium data for reactions of the DPPE complex are more difficult to analyse. The stability of the reaction products with SCN^- could not be determined because of precipitation in most reaction mixtures before reaching equilibrium. In addition, the results included in Scheme 1 and Table 1 for the reactions with Cl^- and Br^- can only be considered a partial description of the equilibrium system because they were derived from the analysis of spectra corresponding to samples with low X^- content. As the concentration of X^- increases, the differences between calculated and experimental spectra become more important, which suggests the formation of additional species. However, the inclusion of $Fe(DPPE)_2X_2$ does not represent any improvement of the equilibrium model and so its formation can be reasonably discarded. This result is in agreement with recent evidences in the sense that the compound $Fe(DPPE)_2Cl_2$ does not exist.[11] A white complex formulated as $Fe(DPPE)Cl_2$ has been isolated both from reaction of $FeCl_2$ with DPPE[11] and from protonation of $FeHCl(DPPE)_2$ with HCl excess.[12] As the reaction mixtures of complex **2** containing a large Cl^- excess become completely decolorized over several hours, it is reasonable to assume the formation of the tetrahedral dichloro complex, although the spectral changes observed in the equilibrium experiments suggest that the actual equilibrium model is more complicated.

The results included in Table 1 show that halo complexes of PP_3 and NP_3 are more stable than their analogues with DPPE, probably as a consequence of the ability of tripodal ligands to stabilize tbp complexes, what would result in reaction products with less strained chelate rings. This effect seems to be responsible for an increase of *ca* 2 log units in the stability quotients corresponding to the formation of the complexes. Another interesting observation is that the stability of $Fe(PP_3)Br^+$ is more than 2 log units lower than that of the Cl and SCN analogues. On the contrary, for the cases of NP_3 and DPPE the stability seems to be almost independent of the nature of X. This result suggests that **1** is more sterically selective than **2** and **3** and has more difficulty in accommodating the larger Br.

Kinetics of reaction

Compounds **1–3** are diamagnetic, octahedral low-spin d^6 complexes and their substitution reactions are sufficiently slow to be studied by conventional UV–vis spectroscopy. The kinetics of substitution reactions of complexes **1–3** with X^- has been studied under pseudo-first order conditions (X^- excess) and the values of the observed rate constants, k_{obs}, are included in Tables 2–4. Only one kinetic step is observed when X = Cl, Br, although reactions with SCN^- show a slower second step that was not studied in detail because the process was too slow, which made the determination of precise values of the rate constant difficult. However, it is important to point out that the spectra of intermediates formed in the first step are similar to those obtained for $LFe(NCS)^+$ complexes in the stability calculations. Thus, in all cases

Table 2. Observed rate constants for the substitution reactions of complexes **1–3** with Cl^- in acetonitrile at 25.0 C and $I = 0.05$ mol dm^{-3}

	$10^3 \times k_{obs}$ (s^{-1})		
$10^3 \times [Cl]$ (mol dm^{-3})	**1**	**2**	**3**
1.0	0.11	1.01	0.22
1.7	0.17		
2.0	0.18	1.26	0.30
3.0		1.96	0.46
3.6	0.28		
4.0		2.29	0.75
5.0	0.51	2.88	0.80
6.0	0.55	2.84	0.95
7.0	0.64	3.06	1.22
8.0	0.66	3.80	1.44
9.0	0.70	4.62	1.52
10.0	0.70	4.69	1.50

Table 3. Observed rate constants for the substitution reactions of complexes **1–3** with Br^- in acetonitrile at 25.0°C and $I = 0.05$ mol dm^{-3}

$10^3 \times [Br]$ (mol dm^{-3})	$10^3 \times k_{obs}$ (s^{-1}) **1**	**2**	**3**
0.7	0.062	—	—
1.0	0.066	0.57	0.29
1.2	—	0.65	—
1.7	0.072	—	—
2.0	—	1.13	0.58
3.0	0.096	1.44	—
4.0	0.110	1.67	0.95
5.0	0.117	1.73	1.13
5.5	—	2.29	—
6.0	0.127	2.39	1.20
7.0	0.138	2.77	1.55

Table 4. Observed rate constants for the substitution reactions of complexes **1–3** with SCN^- in acetonitrile at 25.0°C and $I = 0.05$ mol dm^{-3}

$10^3 \times [SCN]$ (mol dm^{-3})	$10^3 \times k_{obs}$ (s^{-1}) **1**	**2**	**3**
1.0	0.048	0.62	0.14
2.0	0.067	1.47	—
4.0	0.154	2.86	0.61
6.0	0.23	4.21	—
8.0	—	4.77	0.97
10.0	0.33	—	1.34
12.0	—	7.89	—
15.0	—	9.12	—
20.0	0.68	11.43	2.73
25.0	—	12.36	—
30.0	0.92	—	3.11
35.0	—	13.77	—
40.0	1.12	—	3.46
50.0	1.34	16.83	3.76

the values of k_{obs} correspond to the first substitution of coordinated acetonitrile by X^- and there is no evidence of kinetic effects caused by a rearrangement of coordinated NCS^-. In general, plots of k_{obs} versus [X] are linear for reactions with Cl^- and Br^-, but the data for SCN^- clearly indicate a tendency to saturation. Unfortunately, the lower solubility of the chloride and bromide salts hinders the observation of a similar effect for these ligands.

For all nine reactions studied, the experimental rate law is eq. (1) that reduces in some cases to eqs (2) or (3). The values of *a*, *b* and *c* are included in Table 5.

$$k_{obs} = a + \frac{b[X]}{1 + c[X]} \tag{1}$$

$$k_{obs} = a + b[X] \tag{2}$$

$$k_{obs} = b[X] \tag{3}$$

As the reactions are processes of complex formation, it can be reasonably assumed that substitution of coordinated solvent occurs through the Eigen–

Table 5. Rate constants corresponding to the formation of Fe^{II}-phosphine-X^- complexes[a]

Complex	L	X^-	a (s^{-1}) ($a = k_b$)	b (mol^{-1} dm^3 s^{-1}) ($b = k_2K_{os}$)	(b/c) (s^{-1}) ($b/c = k_2$)	c (mol^{-1} dm^3) ($c = K_{os}$)
1	PP_3	Cl^-	$(5 \pm 3) \times 10^{-5}$	0.076 ± 0.005	—	—
		Br^-	$(5.5 \pm 0.2) \times 10^{-5}$	0.012 ± 0.001	—	—
		SCN^-	—	0.038^b	$(4.2 \pm 0.3) \times 10^{-3}$	9 ± 1
2	NP_3	Cl^-	$(6 \pm 1) \times 10^{-4}$	0.41 ± 0.02	—	—
		Br^-	$(3 \pm 1) \times 10^{-4}$	0.35 ± 0.02	—	—
		SCN^-	—	0.86^b	$(2.7 \pm 0.2) \times 10^{-2}$	32 ± 3
3	DPPE	Cl^-	—	0.16 ± 0.01	—	—
		Br^-	$(1.4 \pm 0.6) \times 10^{-4}$	0.19 ± 0.01	—	—
		SCN^-	—	0.18^b	$(6.6 \pm 0.8) \times 10^{-3}$	28 ± 6

[a] See text for the definition of *a*, *b* and *c*. The table also shows the equivalences of a, b and c with rate constants in Scheme 2.

[b] Calculated from the values of *c* and *b*/*c*.

$$\mathrm{LFe(an)_2^{2+}} + \mathrm{X^-} \overset{K_{os}}{\rightleftharpoons} [\mathrm{LFe(an)_2^{2+}, X^-}]_{os}$$

$$[\mathrm{LFe(an)_2^{2+}, X^-}]_{os} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{LFe(an)X^+} + \mathrm{an}$$

$$\mathrm{LFe(an)X^+} \overset{K_3,\ \mathrm{fast}}{\rightleftharpoons} \mathrm{LFeX^+} + \mathrm{an}$$

Scheme 2.

Wilkins mechanism[13] (Scheme 2). In that case, the rate law would be eq. (4) with $k_b = (k_2[\mathrm{an}]^2)/(K_3+[\mathrm{an}])$. Identification of coefficients in eq. (4) with eqs (1)–(3) leads to the values of k_2, k_b and K_{os} included in Table 5. When $X^- = Cl^-$ or Br^-, the concentrations used are so low that $K_{os}[X]$ is always less than 1 and kinetic data only give the values of k_b and the product k_2K_{os}. On the contrary, separate values of k_2 and K_{os} can be obtained for the case of SCN^-. No attempts have been made to separate both constants in those cases without significant deviations from linearity in the k_{obs} versus [X] plots.

$$k_{obs} = k_b + \frac{k_2K_{os}[X]}{1+K_{os}[X]} \tag{4}$$

The rate constant for the reverse reaction, k_b, has been included in Table 5 only in those cases where the zero intercept is meaningful, although the errors associated with its determination are usually large and hinder a detailed analysis. In any case, the few data available seem to indicate that for a given complex k_b does not change very much with the nature of the incoming ligand and the lability of the reaction products decreases in the order $NP_3 >$ DPPE $> PP_3$. The rate constant for the direct reaction, measured as k_2K_{os}, also decreases in the order $NP_3 >$ DPPE $> PP_3$. However, although the rate of reaction of the DPPE complex is almost independent of the nature of X^-, the NP_3 complex and especially the PP_3 complex react at different rates with Cl^-, Br^- and SCN^-. The steric effect of the incoming ligand can be analysed more easily, making use of the quotient $(k_2K_{os})_{Cl}/(k_2K_{os})_{Br}$ that is close to 1 for the NP_3 and DPPE complexes and 6.3 for reactions of $Fe(PP_3)(an)_2^{2+}$. This result is in agreement with the stability constants in Table 1, which only show major changes for the case of the PP_3 complex. Thus, both the kinetic and the stability results suggest that $Fe(PP_3)(an)_2^{2+}$ is slightly more sensitive to the size of the incoming ligand.

Because the observed rate constants correspond to the product k_2K_{os}, the differences observed in the kinetic behaviour can be the result of changes in k_2, K_{os} or both. However, the values obtained for the reactions with SCN^- can be used to analyse separately the effect of both constants. For an interchange mechanism, the values of k_2 are expected to be close to k_{ex}, the rate constant for the exchange of coordinated acetonitrile with the solvent. The values of k_2 in Table 5 are very close for the PP_3 and DPPE complexes, but it is about six times higher for the NP_3, which means that coordinated acetonitrile is more labile in $Fe(NP_3)(an)_2^{2+}$. On the other hand, K_{os} corresponds to the equilibrium constant for the formation of an outersphere complex between a divalent cation and a monovalent anion in acetonitrile and values of the same order of magnitude have been reported for related systems.[14] The values of K_{os} for the reaction of complexes **2** and **3** are identical within the limits of error and about three times higher than the value for the analogous PP_3 complex, which can be interpreted as a consequence of a larger separation between both reagents in the outersphere complex.

If the DPPE complex is taken as a reference for establishing differences in the behaviour of compounds with both tripodal ligands, the conclusion is that all the three complexes show a very similar behaviour, except that $Fe(NP_3)(an)_2^{2+}$ is more labile towards substitution of coordinated acetonitrile and that $Fe(PP_3)(an)_2^{2+}$ is more selective to the size of the incoming ligand.

The DPPE complex is *trans* and allows the approximation of the incoming X^- in a direction perpendicular to the FeP_4 plane without important interactions between X^- and the phenyl substituents on the phosphine groups. For the case of the *cis* complexes of the tripodal ligands, the incoming ligand will approach the metal centre preferentially facing the edge defined by both coordinated acetonitriles, and steric interactions with the phenyls are expected to decrease the reaction rate. This effect is clearly seen in reactions of $Fe(PP_3)(an)_2^{2+}$, which reacts at rates that decrease with the size of the incoming X^-. However, $Fe(NP_3)(an)_2^{2+}$ behaves in a way more similar to the DPPE complex, probably as a consequence of the well known ability of NP_3 to form complexes with elongated M—N bonds.[15,16] Thus, the Fe—N distance in $Fe(NP_3)Br^+$ is 2.65 Å and the Fe—P_c distance in $Fe(PP_3)Br^+$ is 2.21 Å.[16] In the case of octahedral complexes, the distortion is usually not so pronounced, but theoretical calculations[17] indicate that the energy barrier for the displacement of N along the M—N direction to a non-bonding distance is very low for NP_3 (*ca* 8 kcal mol^{-1}) and considerably higher for the M—P_c bonds of PP_3 (*ca* 40 kcal mol^{-1}). Moreover, the conversion of tetradentate NP_3 in tridentate causes an important rearrangement of the frontier orbitals[15,17] and complexes with tridentate NP_3 can take up to three more ligands. Thus, for reactions of $Fe(NP_3)(an)_2^{2+}$ there is the possibility that the N separates from Fe^{II} as X^- approaches the metal centre, and this would result both in decreased steric interactions and in an acceleration of the substitution process because there would be a new orbital available to accept electron density from X^-. Once X^- is coordinated, theoretical calculations favour a tbp structure and dissociation of both acetonitriles would be fast. The acceleration observed for $Fe(NP_3)(an)_2^{2+}$ is not so large as to suppose a complete dissociation of the Fe—N bond, but a displacement of N in that direction would explain both the higher value of k_2 and the smaller steric interactions with X^-.

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