Reactions of Hexakis(acetonitrile)iron(II) Hexafluorophosphate in Acetonitrile. Ligation of Ammonia, Pyridine, and Trimethylamine to Iron(II) and the Behaviour of Trimethyl Phosphite and Trimethylphosphine towards Iron(II), Nitrogen Donor Ligand Complex Cations†

Laurence McGhee, Rana M. Siddique, and John M. Winfield *
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

Co-ordinated acetonitrile in the hexakis(acetonitrile)iron(II) cation is replaced readily by ammonia or pyridine (py) at room temperature to give $[FeL_6]^{2+}$, L = NH_3 or py. Only one trimethylamine ligand is co-ordinated to Fe^{II} under similar conditions. The cation $[Fe(NH_3)_6]^{2+}$ exists as a discrete entity in MeCN, whereas $[Fe(py)_6]^{2+}$ looses py to give $[Fe(py)_{6-x}(NCMe)_x]^{2+}$, x = 1 or 2. The cations react with trimethyl phosphite or trimethylphosphine in MeCN at room temperature to give low-spin Fe^{II} cations containing up to five ligated $P(OMe)_3$ or three ligated PMe_3 molecules. Both steric and electronic properties of the phosphorus ligands are important in determining the outcome of the reactions. The stereochemistry of the intermediate cations formed with $P(OMe)_3$ depends on the identity of the N-donor ligands present.

The hexakis(acetonitrile)iron(II) cation is a convenient starting point for the development of the non-aqueous co-ordination chemistry of iron(II) with simple ligands, and we have previously reported[1] its reaction with trimethyl phosphite to give low-spin $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$. Most of the intermediate steps in the reaction have been observed, and the kinetics of low-spin $[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$ formation are consistent with an interchange mechanism occurring *via* an outer-sphere complex.[2] We have extended this work to include reactions of high-spin Fe^{II} complexes having ligated ammonia, pyridine (py), or trimethylamine, with trimethyl phosphite and trimethylphosphine. The cations $[FeL_6]^{2+}$, L = NH_3 or py, are well known in the solid state,[3,4] but their chemistry in solution has been little studied. Iron(II) complexes with the ligand trimethylamine do not appear to have been reported previously.

Overall, the reactions of these high-spin Fe^{II} cations with phosphorus-donor ligands are very similar, however, three different types of behaviour can be distinguished. These may be rationalized in terms of the different steric properties of the N- and P-donor ligands involved.

Results and Discussion

Preparation and Characterization of Iron(II) *Cations with Nitrogen Donor Ligands.*—Co-ordinated acetonitrile in $[Fe(NCMe)_6]^{2+}$ is replaced readily by ammonia or pyridine (py) at room temperature. The off-white solids isolated from reactions of $[Fe(NCMe)_6][PF_6]_2$ with NH_3 in MeCN, or neat py, are identified on the basis of their analyses, electronic spectra (Table 1), and magnetic moments (5.7 ± 0.2 B.M. at 298 K), as high-spin $[FeL_6][PF_6]_2$, L = NH_3 or py. The $[Fe(NH_3)_6]^{2+}$ cation can be recovered unchanged after dissolution of $[Fe(NH_3)_6][PF_6]_2$ in MeCN; this is similar to the situation in liquid NH_3.[5]

The cation $[Fe(py)_6]^{2+}$ looses py in MeCN solution and the analysis of the colourless solid isolated from solution is consistent with it being $[Fe(py)_5(NCMe)][PF_6]_2$. However, it is likely that a mixture of cations $[Fe(py)_{6-x}(NCMe)_x]^{2+}$, x = 0 to at least 2, is present in solution. The product obtained from the reaction of $[Fe(NCMe)_6]^{2+}$ with py in MeCN is spectroscopically identical, Table 1. Solutions of these cations in MeCN are pale yellow at room temperature, but they become pink at 230 K, and red when frozen. The colour change is due to a red shift in the absorption edge of the charge-transfer band, from 390 at 273 to 404 nm at 233 K. A similar though less pronounced effect is observed for solid $[Fe(py)_{6-x}(NCMe)_x][PF_6]_2$. The origin of the reversible colour change is not clear but it is obviously associated with the presence of both ligated py and MeCN.

Table 1. Electronic spectra of high-spin iron(II) cations

	$\tilde{\nu}_{max.}/cm^{-1}$ ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) $^5T_{2g} \rightarrow {}^5E_g$
$[Fe(NCMe)_6]^{2+\,a}$	11 100 (10), 9 700 (sh)
$[Fe(NMe_3)(NCMe)_5]^{2+}$	11 200 (10), 10 000 (sh)
$[Fe(py)_{6-x}(NCMe)_x]^{2+\,b}$	12 000 (13), 10 500 (sh)
$[Fe(NH_3)_6]^{2+}$	12 400 (8), 9 000 (sh)

[a] Ref. 1. [b] $[Fe(py)_6]^{2+}$ dissolved in MeCN.

The reaction of trimethylamine with $[Fe(NCMe)_6]^{2+}$, in the presence or absence of MeCN, results in the ligation of only one NMe_3 molecule. The product isolated is colourless $[Fe(NMe_3)(NCMe)_4][PF_6]_2$, although its solution electronic spectrum, Table 1, is consistent with the presence of octahedral Fe^{II}, presumably $[Fe(NMe_3)(NCMe)_5]^{2+}$. Loss of one MeCN ligand during isolation of the solid is not surprising since MeCN is weakly bound to 3*d* divalent cations. Thermogravimetric analysis of $[Fe(NCMe)_6][PF_6]_2$ indicates that two MeCN ligands are lost at ⩽353 K. The ligand NMe_3 is inferior thermodynamically to mono- and di-methylamine with respect to complex formation towards copper(II) in methanol,[6] and the formation rate constants for the reactions of $[Ni(OH_2)_6]^{2+}$ with a series of amines decrease with increasing alkyl substitution.[7] The behaviour of $[Fe(NCMe)_6]^{2+}$ towards NH_3 and NMe_3 is consistent with these observations, and it emphasizes the importance of the steric properties of NMe_3 in determining the stoicheiometry of the complexes isolated.

The compounds described above are all moisture sensitive both in the solid state and in solution. In the absence of trace moisture there is no evidence, for example using cyclic voltammetry, for the reversible oxidation $Fe^{II} \rightleftharpoons Fe^{III}$, although hydrolysis does result in iron(III) formation.

Replacement of Nitrogen Donor Ligands at Iron(II) *by Trimethyl Phosphite.*—Trimethyl phosphite reacts with [Fe-

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† *Non-S.I. unit employed:* B.M. = 9.27×10^{-24} J T^{-1}.

Table 2. ^{31}P-$\{^1H\}$ N.m.r. data for iron(II)–trimethyl phosphite cations

	Spin system	Chemical shift *		Coupling constant
		δ_A/p.p.m.	δ_B/p.p.m.	$^2J_{AB}$/Hz
fac-$[Fe\{P(OMe)_3\}_3(py)_3]^{2+}$	A_3	155.6		
mer-$[Fe\{P(OMe)_3\}_3(py)_3]^{2+}$	AB_2	156.1	143.3	131
cis-$[Fe\{P(OMe)_3\}_4(py)_2]^{2+}$	A_2B_2	157.6	146.4	137
$[Fe\{P(OMe)_3\}_5(py)]^{2+}$	AB_4	156.0	148.4	131
trans-$[Fe\{P(OMe)_3\}_2(NMe_3)(NCMe)_3]^{2+}$	B_2		145.2	
cis-$[Fe\{P(OMe)_3\}_2(NMe_3)(NCMe)_3]^{2+}$	A_2	155.9		
fac-$[Fe\{P(OMe)_3\}_3(NMe_3)(NCMe)_2]^{2+}$	A_3	154.2		
mer-$[Fe\{P(OMe)_3\}_3(NMe_3)(NCMe)_2]^{2+}$	AB_2	157.5	147.1	130
cis-$[Fe\{P(OMe)_3\}_4(NMe_3)(NCMe)]^{2+}$	A_2B_2	157.6	146.6	137
trans-$[Fe\{P(OMe)_3\}_4(NMe_3)(NCMe)]^{2+}$	B_4		146.9	
$[Fe\{P(OMe)_3\}_5(NMe_3)]^{2+}$	AB_4	156.7	148.1	134
cis-$[Fe\{P(OMe)_3\}_4(NH_3)_2]^{2+}$	A_2B_2	165.4	149.8	130

* To low field of 85% H_3PO_4.

Table 3. Electronic spectra of $[Fe\{P(OMe)_3\}_5L]^{2+}$, L = py or NMe_3, cations

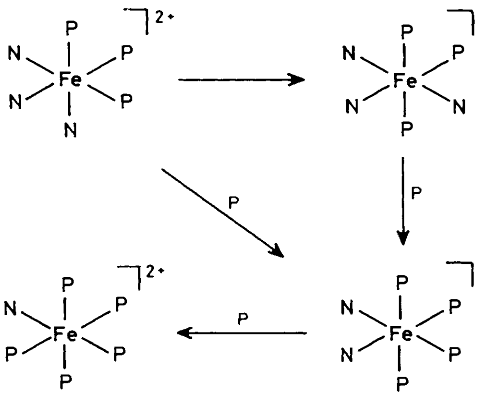
	$\tilde{\nu}_{max.}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) $^1A_1 \rightarrow {}^1E$	$\tilde{\nu}_{max.}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1}) $^1A_1 \rightarrow {}^1A_2$
$[Fe\{P(OMe)_3\}_5(py)]^{2+}$	26 700 (300)	32 600 (250)
$[Fe\{P(OMe)_3\}_5(NMe_3)]^{2+}$	27 900 (360)	32 600 (300)
$[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ [a]	26 700 (370)	32 700 (250)
$[Fe(CN)_5(OH_2)]^{3-}$ [b]	22 520 (444)	30 300 (100)

[a] Ref. 1. [b] Ref. 8.

$(py)_6][PF_6]_2$ or $[Fe(NMe_3)(NCMe)_4][PF_6]_2$ in MeCN at room temperature to give yellow, diamagnetic $[Fe\{P(OMe)_3\}_5L][PF_6]_2$, L = py or NMe_3. The solutions are red initially, rapidly become orange, and then pale yellow over a period of approximately 24 h. Approximately 7 d are required before substantial quantities of $[Fe\{P(OMe)_3\}_5L][PF_6]_2$ can be isolated. The ^{31}P-$\{^1H\}$ n.m.r. spectra of $[Fe\{P(OMe)_3\}_5L]^{2+}$ cations in MeCN are AB_4 spin systems (Table 2) and their electronic spectra, Table 3, consist of two bands assigned to $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E$ *d–d* transitions in C_{4v} symmetry by analogy with the spectrum of $[Fe(CN)_5(OH_2)]^{3-}$.[8]

Most of the intermediate cations in these reactions have been identified from ^{31}P-$\{^1H\}$ n.m.r. spectra of reaction mixtures, with electronic spectroscopy providing supporting evidence. N.m.r. assignments, Table 2, are made on the basis of the spin systems observed and, for species giving rise to singlets, their appearance/disappearance behaviour with time. Chemical shift assignments are internally consistent with the assumption that ^{31}P nuclei *trans* to nitrogen atoms are less shielded than those *trans* to phosphorus. The situation is identical to that found previously[1] in the reaction between $[Fe(NCMe)_6][PF_6]_2$ and $P(OMe)_3$.

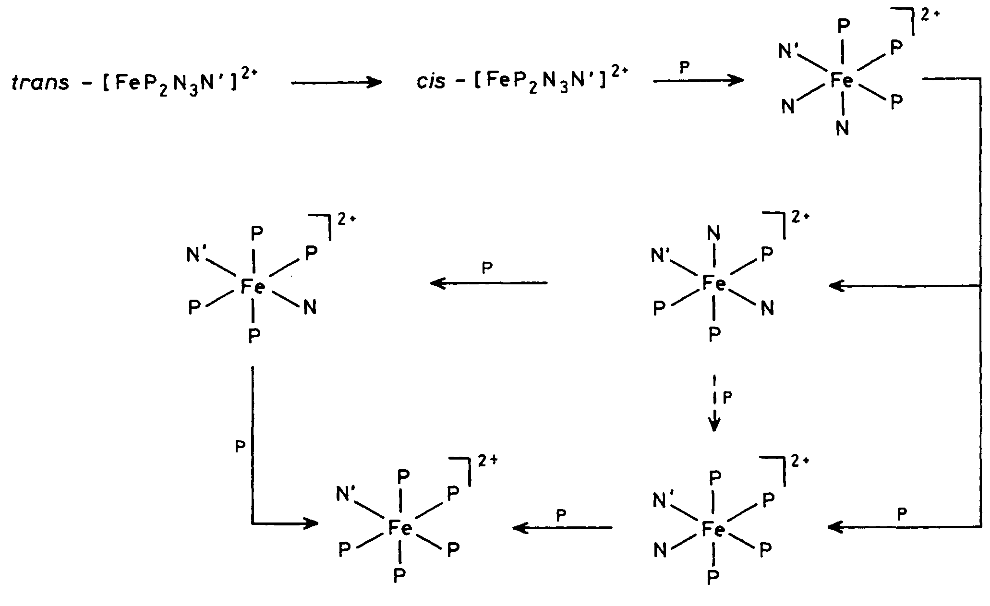
Replacement of acetonitrile, pyridine, or ammonia by trimethyl phosphite. The first low-spin cation to be formed in the reaction of $[Fe(NCMe)_6]^{2+}$ with $P(OMe)_3$ is *cis*-$[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$, identified by its ^{31}P n.m.r. and electronic spectra.[1,2] In the reaction between $[Fe(py)_6]^{2+}$ and $P(OMe)_3$ however no ^{31}P n.m.r. signals attributable to bis(trimethyl phosphite) cations are observed even when the reactants are mixed in an n.m.r. tube at 195 K, presumably due to rapid exchange involving cations such as $[Fe\{P(OMe)_3\}_2(py)_4]^{2+}$ and $[Fe\{P(OMe)_3\}_2(py)_3(NCMe)]^{2+}$. Formation of a low-spin species is observed by stopped-flow electronic spectroscopy, the visible spectrum, $\tilde{\nu}_{max.} = 22\,700$ cm^{-1}, $\varepsilon = 350$ dm^3 mol^{-1} cm^{-1}, being very similar to that observed for $[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$, $\tilde{\nu}_{max.} = 23\,000$ cm^{-1}, $\varepsilon = 320$ dm^3 mol^{-1} cm^{-1}, under identical conditions. The disappearance of this species, followed by electronic spectroscopy, is first order in trimethyl phosphite concentration. It results in the formation of *fac*-$[Fe\{P(OMe)_3\}_3(py)_3]^{2+}$ which itself undergoes further substitution.



Scheme 1. Proposed pathways for the latter stages of the reaction $[Fe(py)_6]^{2+}$ + $P(OMe)_3$; N = py or MeCN, P = $P(OMe)_3$

In its later stages the reaction between $[Fe(py)_6]^{2+}$ and $P(OMe)_3$ is essentially identical to that observed previously for $[Fe(NCMe)_6]^{2+}$ (ref. 1), and the pathways deduced are shown in Scheme 1. The rearrangement *fac* → *mer*-$[Fe\{P(OMe)_3\}_3(py)_3]^{2+}$ is observed, and there is a marked preference for *cis*-$[Fe\{P(OMe)_3\}_4(py)_2]^{2+}$ over the *trans* isomer. Approximately 20 h are required for *cis*-$[Fe\{P(OMe)_3\}_4(py)_2]^{2+}$ to become a major component of the reaction mixture and some of this species is still present after 7 d. These observations illustrate the sterically demanding nature of $P(OMe)_3$.

The reaction between $[Fe(NH_3)_6]^{2+}$ and $P(OMe)_3$ appears to be similar but little detailed information could be obtained. The only cation positively identified by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy is *cis*-$[Fe\{P(OMe)_3\}_4(NH_3)_2]^{2+}$, Table 2, but the



Scheme 2. Proposed pathways for the reaction $[Fe(NMe_3)(NCMe)_5]^{2+}$ + $P(OMe)_3$; N = MeCN, N′ = NMe_3, P = $P(OMe)_3$. The alternative structure for *mer*-$[Fe\{P(OMe)_3\}_3(NMe_3)(NCMe)_2]^{2+}$ cannot be excluded

salt could not be isolated free of bulk $P(OMe)_3$ suggesting the possibility of an outer-sphere interaction *via* N–H • • • O(Me) hydrogen bonding.

Replacement of acetonitrile in $[Fe(NMe_3)(NCMe)_5]^{2+}$ *by trimethyl phosphite.* The pathway deduced for this reaction is shown in Scheme 2. The stopped-flow visible electronic spectrum of a mixture of $[Fe(NMe_3)(NCMe)_5]^{2+}$ and $P(OMe)_3$, $\tilde{\nu}_{max.}$ = 22 700 cm^{-1}, ε = 340 dm^3 mol^{-1} cm^{-1}, is similar to those reported above but within the time of mixing the reagents to obtain a spectrum by conventional means the spectrum changes slightly, $\tilde{\nu}_{max.}$ = 23 500 cm^{-1}, ε = 400 dm^3 mol^{-1} cm^{-1}. Disappearance of the latter band is first order in $[P(OMe)_3]$. The $^{31}P-\{^1H\}$ n.m.r. spectrum, Table 2, obtained immediately after mixing the reactants at 243 K consists of two singlets at 145.2 and 155.9 p.p.m. assigned to *trans*- and *cis*-$[Fe\{P(OMe)_3\}_2(NMe_3)(NCMe)_3]^{2+}$ respectively. Over the first few minutes of reaction the intensity of the former singlet decreases, that assigned to the *cis* isomer remains approximately constant, and a new singlet tentatively assigned to *fac*-$[Fe\{P(OMe)_3\}_3(NMe_3)(NCMe)_2]^{2+}$ on the basis of its chemical shift, Table 2, is observed. It is necessary to assume that the three nitrogen ligands are equivalent on the n.m.r. timescale down to 243 K as a result of rapid exchange between NMe_3 and MeCN. The singlet assigned to *fac*-$[Fe\{P(OMe)_3\}_3(NMe_3)(NCMe)_2]^{2+}$ is replaced rapidly by AB_2 and A_2B_2 spectra assigned to *mer*-$[Fe\{P(OMe)_3\}_3(NMe_3)(NCMe)_2]^{2+}$ and *cis*-$[Fe\{P(OMe)_3\}_4(NMe_3)(NCMe)]^{2+}$ respectively, and a singlet assigned to *trans*-$[Fe\{P(OMe)_3\}_4(NMe_3)(NCMe)]^{2+}$, Table 2.

The final product $[Fe\{P(OMe)_3\}_5(NMe_3)]^{2+}$ can be formed from *fac*-$[Fe\{P(OMe)_3\}_3(NMe_3)(NCMe)_2]^{2+}$ *via* three possible routes, Scheme 2; of these, two are observed also for reactions involving $[FeL_6]^{2+}$, L = MeCN or py. In the latter stages of the reaction *trans*-$[Fe\{P(OMe)_3\}_4(NMe_3)(NCMe)]^{2+}$ is the dominant intermediate, only 4 h being necessary for this state to be achieved, and we suggest that the pathway involving this isomer is dominant in the reaction.

By analogy with the solvent exchange behaviour of 3*d* metal cations, $[M(solvent)_6]^{2+}$,[9] and the reactions of low-spin $[Fe(CN)_5(OH_2)]^{3-}$ with thiourea or N-substituted thioureas,[10] it is not unreasonable to assume that the reactions described here occur *via* dissociative interchange mechanisms in which the identity of the spectator ligands will be important. The effect of ligated NMe_3 on the observed reaction pathway is considered to be due to the fact that it is more sterically demanding than either py or MeCN. Replacement of an N–H by an N–Me substituent can have a pronounced effect on rates of substitution reactions, for example the enhanced rates of base hydrolysis observed for $[M(NH_2Me)_5(OSO_2CF_3)]^{2+}$, M = Co^{III}, Rh^{III}, or Cr^{III}, compared with their penta-ammine analogues,[11] and the greater lability of [M(*N*,*N*-dimethylacetamide)$_6$]$^{2+}$ cations towards solvent exchange compared with their *N*,*N*-dimethyl- and *N*,*N*-diethyl-formamide analogues.[9] Kinetic measurements have not been attempted in the present work because of the complex reaction behaviour but the different pathway observed starting from $[Fe(NMe_3)(NCMe)_5]^{2+}$, particularly the occurrence of *trans*-$[Fe\{P(OMe)_3\}_4(NMe_3)(NCMe)]^{2+}$, could be the result of the labilization of MeCN by NMe_3 in the *cis* position of *mer*-$[Fe\{P(OMe)_3\}_3(NMe_3)(NCMe)_2]^{2+}$.

Replacement of Nitrogen Donor Ligands at Iron(II) *by Trimethylphosphine.*—Trimethylphosphine reacts with $[FeL_6][PF_6]_2$, L = MeCN or py, or $[Fe(NMe_3)(NCMe)_4][PF_6]_2$ in MeCN at room temperature to form red solutions from which red, diamagnetic solids, predominantly $[Fe(PMe_3)_3L_3][PF_6]_2$ or $[Fe(PMe_3)_3(NMe_3)(NCMe)_2][PF_6]_2$ are isolated. Their $^{31}P-\{^1H\}$ (Table 4) and ^1H n.m.r. spectra indicate that cations in which the PMe_3 ligands have a *fac* configuration are the major species in each case. The electronic spectra of the products in MeCN, Table 5, consist of two bands assigned to $^1A_1 \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E$ transitions in C_{3v} symmetry by analogy with the spectrum of *fac*-$[Co(NH_3)_3(OH_2)_3]^{3+}$.[12]

The reaction between $[Fe(NH_3)_6]^{2+}$ and PMe_3 is similar to those described above but the $^{31}P-\{^1H\}$ n.m.r. spectrum of the product, Figure, shows that two major species are present. An A_3 spectrum is assigned to *fac*-$[Fe(PMe_3)_3(NH_3)_3]^{2+}$; the other species gives rise to an A_2B spectrum with a *fac* arrangement of PMe_3 indicated by the ^{31}P chemical shifts, Table 4. The electronic spectrum of the product is very similar to those obtained from the other reactions, Table 5, and its i.r. spectrum contains bands due to co-ordinated MeCN as well as

Table 4. $^{31}P-\{^1H\}$ N.m.r. data for iron(II)–trimethylphosphine cations

	Spin system	Chemical shift* δ_A/p.p.m.	Chemical shift* δ_B/p.p.m.	Coupling constant $^2J_{AB}$/Hz
fac-$[Fe(PMe_3)_3(NCMe)_3]^{2+}$	A_3	19.5		
mer-$[Fe(PMe_3)_3(NCMe)_3]^{2+}$	AB_2	20.1	10.4	56
cis-$[Fe(PMe_3)_4(NCMe)_2]^{2+}$	A_2B_2	13.3	2.7	51
fac-$[Fe(PMe_3)_3(py)_3]^{2+}$	A_3	19.5		
mer-$[Fe(PMe_3)_3(py)_3]^{2+}$	AB_2	20.1	10.4	56
cis-$[Fe(PMe_3)_4(py)_2]^{2+}$	A_2B_2	13.3	2.7	51
fac-$[Fe(PMe_3)_3(NMe_3)(NCMe)_2]^{2+}$	A_3	19.6		
mer-$[Fe(PMe_3)_3(NMe_3)(NCMe)_2]^{2+}$	AB_2	20.1	10.4	56
cis-$[Fe(PMe_3)_4(NMe_3)(NCMe)]^{2+}$	A_2B_2	13.3	2.7	51
fac-$[Fe(PMe_3)_3(NH_3)_3]^{2+}$	A_3	19.5		
fac-$[Fe(PMe_3)_3(NH_3)_2(NCMe)]^{2+}$	A_2B	18.9	21.9	80
mer-$[Fe(PMe_3)_3(NH_3)_3]^{2+}$	AB_2	20.1	10.4	55
cis-$[Fe(PMe_3)_4(NH_3)_2]^{2+}$	A_2B_2	13.3	2.7	51

* To low field of 85% H_3PO_4.

Table 5. Electronic spectra[a] of iron(II)–trimethylphosphine cations

	$\tilde{\nu}_{max.}/cm^{-1}$ ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) $^1A_1 \rightarrow E$	$\tilde{\nu}_{max.}/cm^{-1}$ ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) $^1A_1 \rightarrow {}^1A_2$
$[Fe(PMe_3)_3(NCMe)_3]^{2+}$	21 500 (250)	27 900 (300)
$[Fe(PMe_3)_3(py)_3]^{2+}$	21 600 (260)	28 400 (350)
$[Fe(PMe_3)_3(NH_3)_3]^{2+}$ + $[Fe(PMe_3)_3(NH_3)_2(NCMe)]^{2+}$	21 200 (300)	27 600 (310)
$[Fe(PMe_3)_3(NMe_3)(NCMe)_2]^{2+}$	21 500 (260)	27 900 (350)
$[Co(NH_3)_3(OH_2)_3]^{3+}$ [b]	18 950 (180)	27 500 (160)

[a] Assignments in C_{3v} symmetry. [b] Ref. 12.

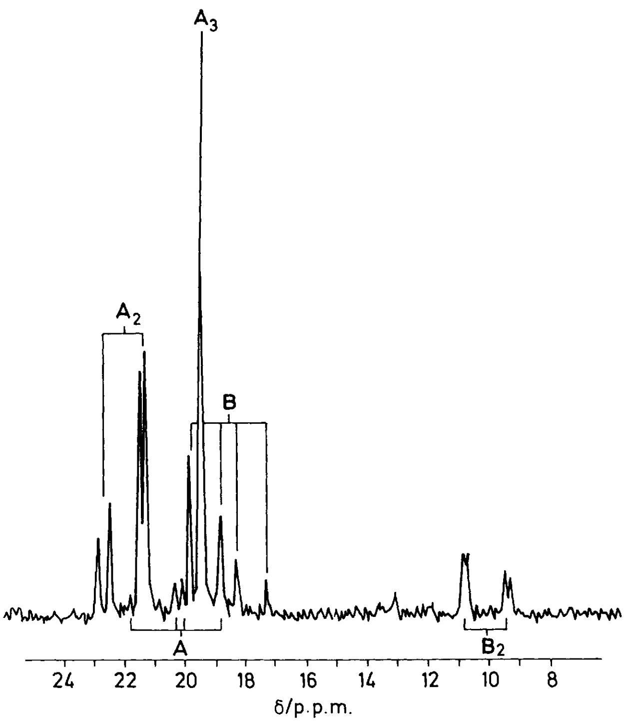


Figure. The $^{31}P-\{^1H\}$ n.m.r. spectrum of the product from the reaction $[Fe(NH_3)_6]^{2+}$ + PMe_3 in CD_3CN

to NH_3 and PMe_3. The signal assigned to MeCN in its ^1H n.m.r. spectrum is relatively broad. These observations are consistent with the presence of *fac*-$[Fe(PMe_3)_3(NH_3)_2(NCMe)]^{2+}$ and imply that exchange between NH_3 and MeCN is slow on the n.m.r. time-scale. In contrast the $^{31}P-\{^1H\}$ n.m.r. spectrum of *fac*-$[Fe(PMe_3)_3(NMe_3)(NCMe)_2]^{2+}$ is a singlet, Table 4, consistent with fast exchange between NMe_3 and MeCN.

The cations *mer*-$[Fe(PMe_3)_3L_3]^{2+}$, L = MeCN, py, or NH_3, or *mer*-$[Fe(PMe_3)_3(NMe_3)(NCMe)_2]^{2+}$ in which the relative positions of NMe_3 and MeCN are not determined, are minor products and *cis*-$[Fe(PMe_3)_4L_2]^{2+}$ or *cis*-$[Fe(PMe_3)_4(NMe_3)(NCMe)]^{2+}$ are formed in trace quantities. In contrast four MeCN ligands in $[Fe(NCMe)_6]^{2+}$ can be replaced readily using bidentate $Ph_2PCH_2CH_2PPh_2$ or tetradentate $P(CH_2CH_2PPh_2)_3$ ligands.[13]

Attempts to follow these reactions by low-temperature $^{31}P-\{^1H\}$ n.m.r. or electronic spectroscopy were unsuccessful since the reactions were complete within the time of mixing. Electronically, PMe_3 is expected to be a better σ donor to Fe^{II} than $P(OMe)_3$, but it has a larger steric requirement. For example, cone angles for the two ligands are 117 and 107° respectively.[14] Formation of less highly substituted products in the reactions with PMe_3 can be rationalized on this basis. Their outcome is determined solely by PMe_3. Only in reactions involving exchange between the N-donor ligand and solvent MeCN is the identity of the former important.

Experimental

All operations were carried out in a Pyrex vacuum line or an N_2-atmosphere glove box (Lintott, H_2O < 5 p.p.m.). Acetonitrile was purified.[15] Ammonia (BDH) was dried and purified by repeated low-temperature distillation over freshly cut sodium *in vacuo* and was stored over Na at 77 K. Trimethylamine (Matheson Inc.) was handled similarly replacing Na by P_2O_5. Pyridine (BDH AnalaR) was distilled from NaOH pellets and degassed over activated 4 Å molecular sieves. Trimethyl phosphite (BDH) was distilled, degassed, dried over

Table 6. Analytical data[a] for iron(II) complexes

Complex	Colour	Analysis (%) C	H	F	Fe	N	P
$[Fe(py)_6][PF_6]_2$	Off-white	42.4	3.6	28.1	6.8	10.0	7.8
		(42.9)	(3.6)	(27.8)	(6.8)	(10.2)	(7.6)
$[Fe(py)_5(NCMe)][PF_6]_2$[b]	Off-white				7.5	10.3	
					(7.2)	(10.7)	
$[Fe(NMe_3)(NCMe)_4][PF_6]_2$	Off-white	23.1	3.5	40.1	9.9	12.4	10.8
		(23.2)	(3.6)	(40.1)	(9.8)	(12.4)	(10.9)
$[Fe(NH_3)_6][PF_6]_2$	Off-white				12.3	18.6	
					(12.5)	(18.8)	
$[Fe\{P(OMe)_3\}_5(py)][PF_6]_2$[c]	Yellow	22.0	4.6	24.6	6.0	1.7	20.3
		(23.0)	(4.8)	(21.8)	(5.3)	(1.3)	(20.7)
$[Fe\{P(OMe)_3\}_5(NMe_3)][PF_6]_2$[d]	Yellow	20.5	5.0	23.0	5.7	2.0	22.4
		(21.0)	(5.2)	(22.3)	(5.5)	(1.4)	(21.2)
$[Fe(PMe_3)_3(NCMe)_3][PF_6]_2$	Red	26.0	5.0	32.5	8.2	6.2	22.0
		(25.8)	(5.1)	(32.7)	(8.0)	(6.0)	(22.2)
$[Fe(PMe_3)_3(NH_3)_2(NCMe)][PF_6]_2$ +	Red	20.0	5.6	35.9		6.6	24.5
		(20.4)	(5.5)	(35.0)		(6.4)	(23.8)
$[Fe(PMe_3)_3(NH_3)_3][PF_6]_2$		(17.3)	(5.7)	(36.4)		(6.7)	(24.8)

[a] Required values are given in parentheses. [b] The presence of $[Fe(py)_4(NCMe)_2][PF_6]_2$ which requires Fe, 7.5; N, 11.5% cannot be excluded. [c] *cis*-$[Fe\{P(OMe)_3\}_4(py)_2][PF_6]_2$ present as a minor product. [d] *trans*-$[Fe\{P(OMe)_3\}_4(NMe_3)(NCMe)][PF_6]_2$ present as a minor product.

Na, and stored over activated 4 Å sieves. Trimethylphosphine was obtained by thermal decomposition of its silver iodide complex (Aldrich) at <473 K *in vacuo*. $[Fe(NCMe)_6][PF_6]_2$ was prepared by the literature method.[1]

Reaction vessels fitted with poly(tetrafluoroethylene), Pyrex stop-cocks (J. Young or Rotaflo) had two limbs enabling solutions to be decanted under vacuum. Similar vessels with one limb replaced by an n.m.r. tube, Pyrex capillary, or 10-mm Spectrosil cell, were used to prepare solution samples for spectroscopic analysis. I.r. spectra of solids were obtained as Nujol or Fluorolube mulls between AgCl or Si plates. Solution i.r. spectra were obtained using disposable (Beckman) AgCl cells. Thermogravimetric analyses were carried out under Ar, samples in frangible ampoules being broken on to the balance pan which was quickly positioned within the oven to minimise hydrolysis. Heating rates were 5—20 °C min^{-1}.

Instrumentation was as follows: Raman, Spex Ramalog with 520.8 or 647.1 nm excitation; i.r., PE580 or PE983 with 3600 data station; electronic, Beckman 5270; stopped-flow, Hi-Tech SF-3L system with SFL-36 evacuable flow module and dry Ar line; n.m.r., Varian XL-100 at 40.5 MHz (^{31}P), Bruker WP200 (^{1}H); thermobalance, DuPont 951; atomic absorption, PE306. Microanalyses were by Malissa and Reuter, West Germany. Iron and nitrogen were determined also by atomic absorption and Kjeldahl methods respectively.

Reactions of Hexakis(acetonitrile)iron(II) *Hexafluorophosphate with Pyridine, Ammonia, or Trimethylamine*.—Mixtures of the compound $[Fe(NCMe)_6][PF_6]_2$ (0.42 mmol) with pyridine (5 cm^3) or NH_3 (2.9 mmol) in MeCN (5 cm^3), or NMe_3 (2.5 mmol) in MeCN (5 cm^3), were shaken for a few minutes at room temperature and in each case off-white solids were isolated after removal of volatile material. The products were identified by their analysis (Table 6) and spectra as hexakis(pyridine)iron(II) hexafluorophosphate, hexa-ammineiron(II) hexafluorophosphate, or tetrakis(acetonitrile)(trimethylamine)iron(II) hexafluorophosphate. Characteristic bands in their i.r. spectra were: $\tilde{\nu}_{max.}$ 1 603, 1 219, 1 160, and 1 010 cm^{-1} (co-ordinated py[16]); 2 315 and 2 280 cm^{-1} (co-ordinated MeCN[17]); 3 400, 1 220, and 630 cm^{-1} (co-ordinated NH_3[18]); 3 250, 1 478, and 1 048 cm^{-1} (co-ordinated NMe_3[19]); and 840 and 560 cm^{-1} (PF_6^- anion[20]).

Thermogravimetric analysis: $[Fe(py)_6][PF_6]_2$, loss of between two and three py at 338—413 K; $[Fe(NH_3)_6][PF_6]_2$, loss of six NH_3 at 368—438 K; $[Fe(NCMe)_6][PF_6]_2$, loss of two MeCN at 353 K.

Reactions between $[Fe(NCMe)_6][PF_6]_2$ and NMe_3, mole ratio 1:10 or 1:20, in the presence or absence of MeCN, gave off-white solids, spectroscopically and analytically identical to $[Fe(NMe_3)(NCMe)_4][PF_6]_2$ described above. Reactions above room temperature were not attempted due to the ready decomposition of $[Fe(NCMe)_6][PF_6]_2$.

The i.r. spectrum of $[Fe(py)_6][PF_6]_2$ in MeCN contained bands $\tilde{\nu}_{max.}$ 2 305, 2 280 (co-ordinated MeCN[17]); 1 600, 1 215, 1 155, 1 005 (co-ordinated py[16]); 1 578, 601, and 403 cm^{-1} (free py). The solid recovered from solution was spectroscopically identical to that obtained from $[Fe(NCMe)_6][PF_6]_2$ and py in the presence of MeCN. Its analysis (Table 6) corresponded to (acetonitrile)pentakis(pyridine)iron(II) hexafluorophosphate although the possibility of bis(acetonitrile)tetrakis(pyridine)-iron(II) hexafluorophosphate could not be excluded.

Reactions of Iron(II) *Cations with Trimethyl Phosphite*.—Mixtures of trimethyl phosphite (10.0 mmol), MeCN (5 cm^3), and $[Fe(py)_6][PF_6]_2$ or $[Fe(NMe_3)(NCMe)_4][PF_6]_2$ (0.3 mmol) were allowed to warm from 77 K to room temperature. The red solutions obtained became orange after 1 h and yellow after 24 h. Removal of volatile material after one week left yellow solids identified by their analysis (Table 6) as predominantly (pyridine)pentakis(trimethyl phosphite)iron(II) hexafluorophosphate or (trimethylamine)pentakis(trimethyl phosphite)iron(II) hexafluorophosphate. The major signals in their ^{31}P-$\{^{1}H\}$ n.m.r. spectra in CD_3CN were AB_4 multiplets (Table 2) but weak signals, A_2B_2 and a singlet respectively, were also present. Their i.r. spectra indicated that co-ordinated $P(OMe)_3$, $\tilde{\nu}_{max.}$ 793 and 719 cm^{-1},[21] and py or NMe_3 were present.

A mixture of $[Fe(NH_3)_6][PF_6]_2$ (0.3 mmol), $P(OMe)_3$ (10.0 mmol), and MeCN (5 cm^3) allowed to react for one week at room temperature gave an orange-yellow solid. Its ^{31}P-$\{^{1}H\}$ n.m.r. spectrum in CD_3CN consisted of an A_2B_2 multiplet and an intense singlet assigned to free $P(OMe)_3$. I.r.: $\tilde{\nu}_{max.}$ 3 400, 3 310, 1 620, 1 220 (co-ordinated NH_3[18]), 793 and 719 cm^{-1} [$P(OMe)_3$[21]].

Solution Studies.—Reactions between Fe^{II} cations and $P(OMe)_3$ in CD_3CN or $EtCN-CD_3CN$ were followed by $^{31}P-\{^1H\}$ n.m.r. spectroscopy with $[Fe^{II}] = 0.12$ mol dm^{-3} and $[Fe^{II}]:[P(OMe)_3]$ varied from 1:5 to 1:20. On occasion $P(OMe)_3$ was injected directly using a syringe and septum cap to an n.m.r. tube containing the Fe^{II} solution at 213 K. Visible spectra of transient intermediates were obtained from point-by-point (10-nm interval) determination of absorbance changes following stopped-flow mixing of MeCN solutions in which $[Fe^{II}] = 4 \times 10^{-3}$ mol dm^{-3} and $[P(OMe)_3] = 0.5$ mol dm^{-3}. Reactions were also followed by conventional electronic spectroscopy with $[Fe^{II}] = 4 \times 10^{-3}$ mol dm^{-3} and $[P(OMe)_3]$ in the range 0.1—0.8 mol dm^{-3}.

Reactions of Iron(II) *Cations with Trimethylphosphine.*—Mixtures of trimethylphosphine (2.0 mmol), MeCN (5 cm^3), and $[Fe(NCMe)_6][PF_6]_2$, $[Fe(NH_3)_6][PF_6]_2$, $[Fe(py)_6][PF_6]_2$, or $[Fe(NMe_3)(NCMe)_4][PF_6]_2$ (0.3 mmol in each case) were allowed to warm from 77 K to room temperature. Red solutions were obtained from which red solids were isolated after removal of volatile material. $^{31}P-\{^1H\}$ N.m.r. spectra of the solids in CD_3CN (Table 4) indicated that mixtures of cations were present, mainly tris(trimethylphosphine) species. Their ^1H n.m.r. spectra consisted of complex multiplets, δ_H = 1.53 and 1.35 p.p.m., assigned to PMe_3 protons *trans* to PMe_3 or to nitrogen-donor ligands respectively, and in some cases a singlet, δ_H = 1.96 p.p.m. assigned to protons from NMe_3 and MeCN. The analysis of the product from $[Fe(NCMe)_6][PF_6]_2$ was consistent with tris(acetonitrile)tris(trimethylphosphine)-iron(II) hexafluorophosphate, and that from $[Fe(NH_3)_6][PF_6]_2$ with a mixture of $[Fe(PMe_3)_3(NH_3)_2(NCMe)][PF_6]_2$ and $[Fe(PMe_3)_3(NH_3)_3][PF_6]_2$, Table 6. Their i.r. spectra indicated that co-ordinated PMe_3,[22] $\tilde{\nu}_{max.}$ 1 310, 1 295, 975, 950, 728, and 670 cm^{-1}, and MeCN, NH_3 and MeCN, py, or MeCN and NMe_3 were present.

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