Preparation of the Solvated Iron(II) Cation in Acetonitrile using High Oxidation-state Fluorides and its Reaction with Trimethyl Phosphite

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The cation $[Fe(NCMe)_6]^{2+}$ is formed from reactions in acetonitrile of iron metal with WF_6, MoF_6, PF_5, or the NO^+ cation and from the reaction of iron(II) fluoride with PF_5. Oxidation to Fe^{III} is not observed using binary fluorides or NO^+, but $[Fe(NCMe)_6]^{2+}$ is oxidised by chlorine in MeCN to give the tetrachloroferrate(III) anion. The MeCN co-ordinated to Fe^{II} is replaced by trimethyl phosphite giving $[Fe(NCMe)\{P(OMe)_3\}_5]^{2+}$ as the final product at room temperature. Some of the intermediate complexes in this reaction have been identified in solution by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy.

REACTIONS of the iron(II) cation in water are often complicated by oxidation to iron(III) and subsequent hydrolysis of the product. These problems may be circumvented by generating the cation under strictly anaerobic conditions using a dipolar aprotic solvent, for example sulphur dioxide [1] or acetonitrile.[2] In the latter solvent $[Fe(NCMe)_6]^{2+}$ has been prepared either by Lewis acid–base reactions between anhydrous iron(II) chloride and covalent chlorides,[2a] or by oxidation of iron metal with chlorine or bromine,[2b] however reactions of this cation have been little studied.

In this paper we report several reactions which produce the $[Fe(NCMe)_6]^{2+}$ cation and describe some of its reactions, notably with trimethyl phosphite. The preparative routes to the cation are similar to those described for other solvated metal cations,[3] and employ fluorides rather than chlorides. They have the advantage that the complex fluoro-counter-anions so formed are identified readily by spectroscopic methods, and have minimal co-ordinating tendencies. In addition, using a covalent fluoride ensures that rigidly anhydrous conditions are maintained.

RESULTS AND DISCUSSION

Preparation and Properties of Iron(II) *Salts.*—The $[Fe(NCMe)_6]^{2+}$ cation is formed in MeCN solution by the oxidation of iron metal with tungsten or molybdenum hexafluorides, or phosphorus pentafluoride, and by the reaction of PF_5 with anhydrous iron(II) fluoride. In each case the cation is identified by its electronic spectrum, consisting of a broad band, $\nu_{max.}$ 11 100 (ε *ca.* 10 dm^3 mol^{-1} cm^{-1}), 9 700 cm^{-1} (sh), which is assigned to the $^5E_g \leftarrow {}^5T_{2g}$ transition of an octahedral, high-spin d^6 system.[2] The magnetic moment of $[Fe(NCMe)_6]^{2+}$, determined by Evans' method [4] for the hexafluorophosphate salt in MeCN, is 5.4 ± 0.2 B.M.† at 293 K, within the range expected for octahedral, high-spin Fe^{II}.

The reaction between Fe^0 and PF_5 is very slow and that with MoF_6 is complicated by solvent attack. In all the other cases solid products were isolated and characterised as solvated iron(II) fluoro-anion salts.

The solid products isolated from the reaction of Fe^0 with WF_6 depend on the reaction conditions and the method of isolation. The Raman spectrum of the reaction mixture [Figure 1(*a*)] indicates that WF_6 and the anions, hexafluorotungstate(V) and heptafluorotungstate(VI), are present, and an additional band in the W–F stretching region is assigned to complexed tungsten pentafluoride. During the reaction a pale green solid precipitates from solution and an off-white solid is isolated from solution when volatile material is removed. The solids' Raman spectra show that both contain WF_6^- and WF_7^-, but proportionally more WF_6^- is found in the solid isolated from solution [Figure 1(*b*)]. The behaviour observed is accounted for by the solution equilibrium $WF_6 + WF_6^- \rightleftharpoons WF_5 + WF_7^-$, previously observed in the oxidation of other metals in MeCN by WF_6.[3a] If the concentration of WF_6 is limited, by allowing a mixture of WF_6 + MeCN vapour to react with Fe^0, the product is predominantly $[Fe(NCMe)_6][WF_6]_2$, and contained very little WF_7^- [Figure 1(*c*)].

The species Fe^0 and WF_6 do not react in nitromethane solution at room temperature, but reaction does occur when MeCN is added, sufficient to give a 1 : 6 Fe : MeCN mole ratio. The solid precipitated from solution contains $[Fe(NCMe)_6]^{2+}$ and WF_7^-. Evidently the relative insolubility of the WF_7^- salt displaces the equilibrium to the right-hand side. Although $MeNO_2$ is a poorer ligand than MeCN, a number of $[Fe(O_2NMe)_6]^{2+}$ salts are known.[2b,5] The lack of reaction in pure $MeNO_2$ is more likely to be of kinetic rather than thermodynamic origin, and we suggest that a weak $WF_6 \cdot NCMe$ complex is formed which is a better ligand to Fe^0 than is WF_6 alone.

The behaviour of high oxidation-state fluorides to Fe^0 may be compared with that of the nitrosonium cation.[6] The N–O stretching frequency of NO^+ in MeCN occurs at 1 865 cm^{-1} compared with 2 340 cm^{-1} in $[NO][PF_6]$, suggesting that NO^+ is highly solvated in MeCN solution. Notwithstanding, Fe^0 is oxidised by $[NO][BF_4]$ in MeCN to give the iron(II) salt,[6a] and we find that $[NO][PF_6]$ behaves similarly giving $[Fe(NCMe)_6][PF_6]_2$ as the major product. Oxidation also occurs in $MeNO_2$ solution; the product is presumed to be $[Fe(O_2NMe)_6][PF_6]_2$ although its characterisation was hampered by the exothermic reaction which produced purple, polymeric material even below room temperature. Rather different behaviour has been reported for the low-temperature reaction in

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† Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

$MeNO_2$ from which the product is a dark green solid, unstable above 253 K, and formulated as $[Fe_2(NO)_6][PF_6]_2$.[6b] At low temperature the reaction mixture in MeCN is dark green, and a small quantity of uncharacterised, dark brown solid is formed at room temperature in addition to the solvated iron(II) salt. Thus, although NO may be ligated at low temperature, there is no evidence for its being retained in the presence of the co-ordinating solvent MeCN.

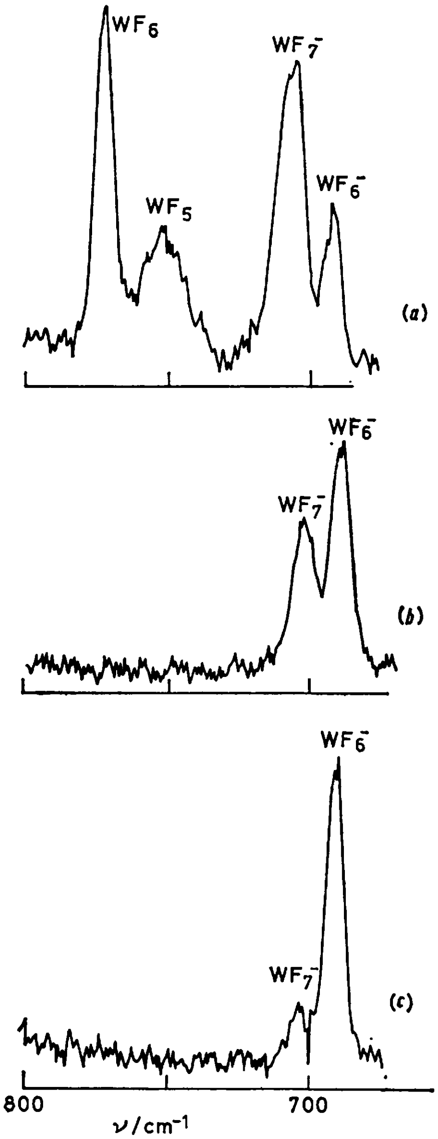

FIGURE 1 Raman spectra of the Fe, WF_6, MeCN system: (*a*) solution reaction mixture; (*b*) solid isolated by evaporation of the solution; (*c*) solid isolated from Fe(s) + WF_6(g) + MeCN(g)

The solvated Fe^{II} fluoro-anion salts do not decompose in the absence of moisture and oxygen, but decompose very slowly in MeCN solution over a period of several weeks. Fe^{II} is not oxidised by NO^+, PF_5, WF_6, or MoF_6 in MeCN but oxidation occurs rapidly in the presence of moist O_2 and slowly in the presence of Cl_2. In the latter case the sole iron-containing product is the tetrachloroferrate(III) anion; chlorination of MeCN also occurs.[7] The formal reduction potential of the Fe^{III}–Fe^{II} couple in MeCN has been estimated as 1.57 ± 0.05 V *versus* Ag–Ag^+,[8] and from cyclic voltammetry of $Ag[WF_6]$ and $Ag[MoF_6]$ in MeCN [9,*] it appears that MoF_6, but not WF_6, should be capable of oxidising $[Fe(NCMe)_6]^{2+}$ to $[Fe(NCMe)_6]^{3+}$. However, cyclic voltammetry of $[Fe(NCMe)_6][PF_6]_2$ in MeCN gave no indication of an oxidation wave, and we conclude that oxidation to Fe^{III} in MeCN is feasible only when other ligands are present.

In contrast to FeF_2, anhydrous iron(III) fluoride does not react with PF_5 or WF_6 in MeCN, a reflection of the greater lattice energy of FeF_3 compared with that of FeF_2, 5 870 *versus* 2 769 kJ mol^{-1}.[10]

Reaction of $[Fe(NCMe)_6]^{2+}$ *with Trimethyl Phosphite.*—Although a number of iron(II) phosphite complexes are known, for example [11] $Fe[P(OMe)_3]_3X_2$ (X = Cl, Br, or I) and $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$, direct replacement of co-ordinated MeCN in $[Fe(NCMe)_6]^{2+}$ by $P(OMe)_3$ has not been studied. The compound $[Fe(NCMe)_6][PF_6]_2$ reacts with an excess of $P(OMe)_3$ in MeCN at or below room temperature, to give a deep red solution whose colour changes to orange and finally yellow on standing. The time taken for the changes in colour depends on the Fe^{II} concentration and the mole ratio $Fe^{II} : P(OMe)_3$. The products isolated after several days are dimethyl methylphosphonate and a diamagnetic yellow solid identified as $[Fe(NCMe)\{P(OMe)_3\}_5][PF_6]_2$. The cation's ^{31}P-$\{^1H\}$ n.m.r. spectrum is identical to that of the analogous SbF_6^- salt, which was reported very recently as the product from the oxidation of $Fe[P(OMe)_3]_5$ by Ag^I or tropylium salts.[11b] In contrast $[Fe(NCMe)_6]^{2+}$ does not react with PF_3 or $P(OPh)_3$ under similar conditions, suggesting that the good σ-donor ability and small steric requirement of the $P(OMe)_3$ ligand are important.

TABLE 1

^{31}P-$\{^1H\}$ N.m.r. data for $[FeN_{6-n}P_n]^{2+}$ cations (n = 2—6) [N = MeCN, P = $P(OMe)_3$]

Cation	Spin system	Chemical shifts/p.p.m.		Coupling constant
		δ_A	δ_B	J_{AB}/Hz
$[FeN_4P_2]^{2+}$ [a]	A_2	155.4		
fac-$[FeN_3P_3]^{2+}$ [b]	A_3	157.7		
mer-$[FeN_3P_3]^{2+}$	AB_2	156.6	145.6	137.1
cis-$[FeN_2P_4]^{2+}$ [b]	A_2B_2	158.6	147.0	137.2
trans-$[FeN_2P_4]^{2+}$	B_4		148.7	
$[FeNP_5]^{2+}$	AB_4	157.7	150.1	129.2
$[FeP_6]^{2+}$	B_6		148.8	

[a] Tentative assignment, see text. [b] More abundant isomer.

The reaction between $[Fe(NCMe)_6]^{2+}$ and $P(OMe)_3$ in MeCN is a stepwise substitution process whose course can be followed by ^{31}P-$\{^1H\}$ n.m.r. spectroscopy. By examining ^{31}P-$\{^1H\}$ spectra of reaction mixtures at various times and over the temperature range 243—313 K most of the mixed-ligand cations can be observed and an internally consistent set of assignments (Table 1) is

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[*] The electrode potentials for WF_6^-–WF_6 and MoF_6^-–MoF_6 couples are 0.64 and 1.70 V respectively *versus* the cathodic peak potential for *in situ* Ag^+ reduction, D. W. A. Sharp, personal communication.

possible. The cations *mer*-$[FeN_3P_3]^{2+}$, *cis*-$[FeN_2P_4]^{2+}$, and $[FeNP_5]^{2+}$ [N = MeCN, P = $P(OMe)_3$] are unambiguously identified in solution by their second-order ^{31}P-$\{^1H\}$ multiplets, calculated spectra being in excellent agreement with those observed. Single peaks due to *fac*-$[FeN_3P_3]^{2+}$ and *trans*-$[FeN_2P_4]^{2+}$ are assigned from their chemical shifts, and by correlating their appearance (Table 2) with those of the *mer* and *cis* isomers.

TABLE 2

Cations $[FeN_{6-n}P_n]^{2+}$ [N = MeCN, P = $P(OMe)_3$] identified by ^{31}P-$\{^1H\}$ n.m.r. at various times in the reaction

Time after mixing/h	0.25	0.75	3	24	36
Solution colour	Red	Orange	Orange	Yellow	Yellow
Species identified [a]	$P(OMe)_3$	$P(OMe)_3$	$P(OMe)_3$		
	FeN_4P_2 [b]	FeN_4P_2 [b]			
	fac-FeN_3P_3	*fac*-FeN_3P_3	*fac*-FeN_3P_3	*fac*-FeN_3P_3 (minor)	*fac*-FeN_3P_3 (trace)
		mer-FeN_3P_3	*mer*-FeN_3P_3	*mer*-FeN_3P_3 (minor)	
		cis-FeN_2P_4 (trace)	*cis*-FeN_2P_4	*cis*-FeN_2P_4	*cis*-FeN_2P_4
				trans-FeN_2P_4	
				$FeNP_5$ (trace)	$FeNP_5$

[a] Cation charges not included. [b] Tentative assignment, see text.

Although the cation $[FeP_6]^{2+}$ has been reported,[11b,12] complete replacement of MeCN by $P(OMe)_3$ is not normally observed at room temperature even when the Fe^{II} : $P(OMe)_3$ mole ratio is 1 : 300. After several weeks however, the n.m.r. spectrum of the reaction mixture (Figure 2) contains a single peak assignable to the $[FeP_6]^{2+}$ cation in addition to the AB_4 and A_2B_2 multiplets.

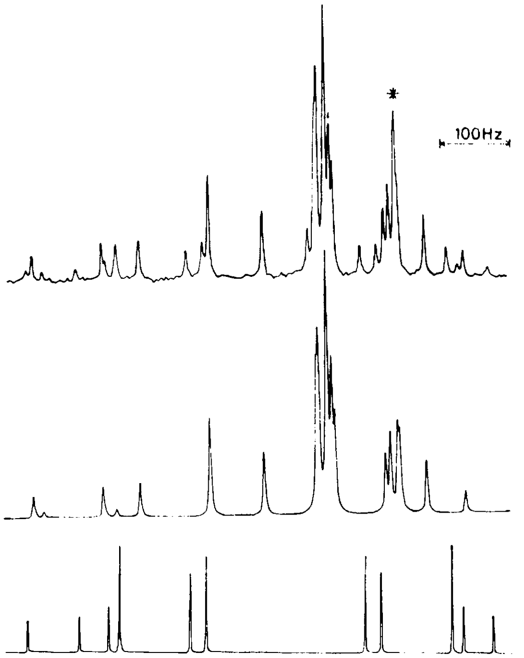

FIGURE 2 ^{31}P-$\{^1H\}$ n.m.r. spectrum of an $[Fe(NCMe)_6]^{2+}$ + $P(OMe)_3$ reaction mixture several weeks after mixing, and calculated AB_4 and A_2B_2 spectra. The peak assigned to $[Fe\{P(OMe)_3\}_6]^{2+}$ is marked with an asterisk

The information available from spectra recorded in the early stages of the reaction is limited, partly due to exchange between free and co-ordinated $P(OMe)_3$. For example the low-temperature spectrum recorded 15 min after mixing (Table 2) consists of a broad $P(OMe)_3$ signal and two relatively sharp singlets one of which is assigned to *fac*-$[FeN_3P_3]^{2+}$. Its intensity increases with time while that of the other decreases, and the second singlet is tentatively assigned to $[FeN_4P_2]^{2+}$. Its chemical shift implies a *cis* configuration, but equally it may be an exchange-averaged signal arising from *cis* and *trans* isomers. There is no direct evidence for $[FeN_5P]^{2+}$ in the spectra and we suggest that its formation and conversion to $[FeN_4P_2]^{2+}$ are complete within 15 min.

The electronic spectrum of $[Fe(NCMe)\{P(OMe)_3\}_5]^{2+}$ in MeCN consists of two bands at 26 700 (ε = 370) and 32 700 cm^{-1} (ε = 250 dm^3 mol^{-1} cm^{-1}) assigned to spin-allowed *d–d* transitions of the low-spin d^6 system. The spectrum of the isoelectronic $[Co\{P(OMe)_3\}_6]^{3+}$ cation contains bands at 29 350 ($^1T_{1g} \leftarrow {}^1A_{1g}$) and 32 650 cm^{-1} ($^1T_{2g} \leftarrow {}^1A_{1g}$),[13] and in the Fe^{II} cation there is no evidence of splitting due to the reduction in symmetry.

The electronic spectra of $[Fe(NCMe)_6]^{2+}$–$P(OMe)_3$ mixtures in MeCN are time and concentration dependent, and provide supporting evidence for the stepwise substitution reactions. Spectra of red solutions, recorded approximately 3 min after mixing, consist of two bands at 23 100 and 28 900 cm^{-1} (ε = 320 and 270 dm^3 mol^{-1} cm^{-1}) which over a period of several days change to give the spectrum of $[Fe(NCMe)\{P(OMe)_3\}_5]^{2+}$. The change is characterised by the successive appearance of at least two sets of isosbestic points and two other sets of peak maxima, but unambiguous assignment of the electronic spectra is not possible by comparison with the n.m.r. data alone, due to the large difference in solution concentration used in the two techniques.

In conclusion, this work has provided one of the few examples of a successive ligand-substitution process involving a first-row transition-metal cation in non-aqueous media. While the later steps in the reaction have been characterised, the point at which the high-spin–low-spin transition occurs is not yet clear.

EXPERIMENTAL

All operations were carried out in a Pyrex vacuum line or an Ar atmosphere glove box (Lintott Engineering Co., H_2O < 10 p.p.m.). Iron wire (Goodfellow Metals Ltd., 99.99%), anhydrous FeF_2 (Pierce and Warriner Ltd., 95%), anhydrous FeF_3 and $[NO][PF_6]$ (Fluorochem Ltd.) were used as received. The compounds WF_6, MoF_6, and PF_5 (Fluorochem Ltd. or Ozark Mahoning Inc.) were purified by low-temperature trap-to-trap distillation over NaF and were stored over NaF. The MeCN (Hopkin and Williams Ltd., reagent grade) was refluxed, twice over CaH_2 and twice over P_2O_5 for 8 h periods, degassed, and stored *in vacuo* over activated 4A sieves. The $MeNO_2$ (B.D.H. Ltd., reagent grade) was refluxed for 24 h over activated charcoal, filtered and distilled, passed through an alumina column, redistilled, degassed, and stored *in vacuo* over activated 4A sieves. The compound $P(OMe)_3$ (Hartman Organic Chemicals) was distilled, degassed, then dried over Na metal, and stored *in vacuo* over activated 4A sieves. Chlorine (B.D.H. Ltd., 99.9%) was dried over P_2O_5 *in vacuo*.

Reaction vessels, fitted with polytetrafluoroethylene stopcocks (Rotaflo) had two limbs to enable 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 examination. Infrared spectra of solids were obtained as Nujol mulls between AgCl windows, and those of solutions in sealed AgCl cells (Beckman RIIC Ltd.). Raman spectra of solids were obtained with samples contained in sealed Pyrex capillaries. Instrumentation was as follows: Raman, Spex Ramalog; i.r., PE 577; u.v.–visible, Beckman 5270; n.m.r., JEOL C60HL at 60 (^1H) or 56.4 MHz (^{19}F) and Varian XL-100 at 40.5 MHz (^{31}P). Chemical shifts were obtained with respect to external $SiMe_4$, CCl_3F, or H_3PO_4 and are reported as positive to low field. Microanalyses were by Malissa and Reuter F.R.G.

Reactions of Iron Metal with High Oxidation-state Fluorides.—(*a*) A mixture of Fe wire and WF_6 (mole ratio $WF_6 : Fe > 3 : 1$) in MeCN (5 cm^3), shaken for several days at room temperature, gave a pale green solid and a light brown solution. An off-white solid was isolated from the latter by decanting and removal of volatile material. Both solids contained bands in their Raman spectra assigned to co-ordinated MeCN, $\nu_{max.}$ 2 325, 2 295, and 940 cm^{-1},[14] and to the anions WF_7^- and WF_6^-, $\nu_{max.}$ 703 and 690 cm^{-1}.[3a] The $WF_7^- : WF_6^-$ peak height ratios were 2 : 1 (green solid) and 2 : 3 (off-white solid). The solution Raman spectrum of the reaction mixture contained bands at $\nu_{max.}$ 772 (WF_6), 706 (WF_7^-), 693 cm^{-1} (WF_6^-), and a band at 752 cm^{-1} assigned to WF_5. The solution's electronic spectrum showed that $[Fe(NCMe)_6]^{2+}$ was present.

(*b*) Iron wire (1.8 mmol) and a solution of WF_6 (3.5 mmol) in MeCN (5 cm^3), contained in two separate limbs of a reaction vessel, reacted over several days to give a fawn solid on the metal surface which could be dislodged with a magnet. The solid was identified from its spectra and analysis (Found: C, 15.6; H, 2.0; F, 25.3; Fe, 6.0; N, 10.5; W, 40.5. $C_{12}H_{18}F_{12}FeN_6W_2$ requires C, 16.0; H, 2.0; F, 25.4; Fe, 6.2; N, 9.4; W, 41.0%) as *hexakis(acetonitrile)iron*(II) *hexafluorotungstate*(V). Its Raman spectrum indicated that a very small quantity of WF_7^- was also present.

(*c*) A mixture of Fe, WF_6, and $MeNO_2$ did not react under conditions similar to (*a*) until sufficient MeCN was added to give a Fe : MeCN mole ratio of 1 : 6. A pale pink solid was precipitated from solution; its spectra indicated the presence of $[Fe(NCMe)_6]^{2+}$ and the sole band in the W–F stretching region of its Raman spectrum was at 706 cm^{-1}, assigned to WF_7^-.

(*d*) A mixture of Fe, PF_5, and MeCN reacted over several weeks to give a pale yellow solution from which a white solid was isolated. Its i.r. spectrum contained bands due to co-ordinated MeCN and bands at $\nu_{max.}$ 830 and 560 cm^{-1}, assigned to PF_6^-. The species Fe, MoF_6, and MeCN gave a solution whose electronic spectrum indicated $[Fe(NCMe)_6]^{2+}$, however a reaction between MoF_6 and MeCN prevented the solid product from being characterised.

Reaction of Iron Metal with Nitrosonium Hexafluorophosphate.—A mixture of Fe wire (0.9 mmol) and $[NO][PF_6]$ (1.7 mmol) in MeCN (5 cm^3) reacted at room temperature to give a non-condensible gas, a small quantity of brown insoluble solid, and a brown solution. A white solid was isolated from the latter and was identified by its spectra and analysis (Found: C, 25.6; H, 2.9; F, 38.0; Fe, 9.0; N, 14.0; P, 10.4. $C_{12}H_{18}F_{12}FeN_6P_2$ requires C, 24.3; H, 3.1; F, 38.5; Fe, 9.4; N, 14.2; P, 10.5%) as *hexakis(acetonitrile)iron*(II) *hexafluorophosphate*.

Reactions of Anhydrous Iron Fluorides with High Oxidation-state Fluorides.—A mixture of FeF_2 (1.3 mmol), PF_5 (2.5 mmol), and MeCN (5 cm^3), shaken for 2 days at room temperature, gave a pale yellow solution from which a white solid was isolated when volatile material was removed. The solid was identified by its spectra, solution magnetic susceptibility, and analysis (Found: C, 24.1; H, 3.1; F, 38.3; Fe, 9.6; N, 14.0; P, 10.6. $C_{12}H_{18}F_{12}FeN_6P_2$ requires C, 24.3; H, 3.1; F, 38.5; Fe, 9.4; N, 14.2; P, 10.5%) as *hexakis(acetonitrile)iron*(II) *hexafluorophosphate*. The compound's e.s.r. spectrum, recorded as a frozen MeCN solution, showed a characteristic Mn^{II} signal, suggesting that MnF_2 was a trace impurity in FeF_2 and had reacted with PF_5 in an analogous manner. This was confirmed in a separate reaction between MnF_2 and PF_5.

Anhydrous FeF_3, shaken with PF_5 or WF_6 in MeCN for several days, failed to yield any isolable products.

Reactions of Hexakis(acetonitrile)iron(II) *in Acetonitrile.*—(*a*) *With chlorine.* The compound $[Fe(NCMe)_6][PF_6]_2$ (0.2 mmol) reacted with Cl_2 (7.6 mmol) in MeCN (5 cm^3) to give a yellow solution. The reaction's progress was monitored over several days by electronic spectroscopy, and this revealed a decrease in the $[Fe(NCMe)_6]^{2+}$ band accompanied by the appearance and increase of bands at $\nu_{max.}$ 14 600, 16 150, 16 500, 18 900, 22 500, 27 800, 30 300, and 40 800 cm^{-1} assigned to $FeCl_4^-$.[2] No other iron-containing species were detected, and Cl_2 was not recovered from the reaction mixture. Gas chromatographic analysis of the solvent indicated that CH_2ClCN and CCl_3CN were present.[7]

(*b*) *With trimethyl phosphite.* A mixture of $[Fe(NCMe)_6][PF_6]_2$ (0.85 mmol), $P(OMe)_3$ (25.4 mmol), and MeCN (5 cm^3) allowed to warm from 77 K to room temperature became dark red as the mixture melted and gave a dark red solution at room temperature. The colour changed to orange after *ca.* 0.5 h and to yellow after a further 2 h. Removal of volatile material, a mixture of unchanged MeCN and a little dimethyl methylphosphonate, after 5 days left a yellow solid, identified as predominantly *acetonitrilepentakis(trimethyl phosphite)iron*(II) *hexafluorophosphate* (Found: C, 20.7; H, 4.7; F, 21.6; Fe, 5.2; P, 20.5. $C_{17}H_{48}F_{12}FeNO_{15}P_7$ requires C, 20.3; H, 4.8; F, 22.6; Fe, 5.5; P, 21.5%). Its i.r. spectrum indicated that co-ordinated MeCN, $\nu_{max.}$ 2 295 cm^{-1}, and $P(OMe)_3$, $\nu_{max.}$ 793 and 719 cm^{-1}, were present. The ^{31}P-{^1H} n.m.r. spectrum in CD_3CN consisted of an AB_4 multiplet identical to that reported previously,[11b] and a very weak A_2B_2 multiplet. Similar behaviour was observed when $[Fe(NCMe)_6][WF_6]_2$ reacted with $P(OMe)_3$ in MeCN.

Syntheses using shorter reaction times gave yellow or orange solids whose $^{31}P-\{^1H\}$ spectra were characteristic of $[Fe(NCMe)_{6-n}\{P(OMe)_3\}_n]^{2+}$ (n = 3 or 4) cations.

The reaction was followed by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. The results in Table 2 were obtained using a mixture in which $Fe^{II} : P(OMe)_3$ was 1 : 4.8 and Fe^{II} was 0.17 mol dm^{-3}, the reaction conditions being as follows: 2 h at 298 K, then 1 h at 313 K, then 21 h at 298 K, then 18 h at 323 K. Similar results were obtained when the mole ratio $Fe^{II} : P(OMe)_3$ was 1 : 15.

We thank Dr. D. S. Rycroft and Mr. A. Mackie for assistance in obtaining the $^{31}P-\{^1H\}$ n.m.r. and Raman spectra, Dr. A. McAuley (University of Victoria) for useful discussions, and the S.R.C., S.E.D., and N.A.T.O. for financial support.

[0/157 *Received, 28th January*, 1980]

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