Preparation, Redox and Substitution Reactions of Solvated Metal Ions in Non Aqueous Media.

by

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A thesis in fulfilment of the requirements of
the degree of Ph.D.

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October, 1980.

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Acknowledgements.

I would like to express my sincere thanks to my supervisor, Dr. J.M. Winfield, for all his help, advice and encouragement throughout the course of this work. I would also like to thank Dr. A.G. Lappin for his assistance and for some useful discussions, particularly with regard to the kinetic aspects.

Thanks are due to Drs. D.S. Rycroft, R. Keat and W. McFarlane for their aid in obtaining n.m.r. spectra on various occasions.

Finally, I thank my family and friends for their help, understanding and support over the last few years. Especial thanks to my mother and father for typing and checking, respectively, the bulk of this thesis.

I acknowledge financial support from the S.R.C. .

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Summary.

Solvated iron(II) , in MeCN solution, is prepared by oxidation of iron metal with WF_6 , $NOPF_6$ and PF_5 or by fluoride ion transfer from FeF_2 to PF_5 or AsF_5 . $Fe(NCMe)_6{}^{3+}$ is not produced from oxidation of iron metal, fluoride ion transfer from FeF_3 or oxidation of $Fe(NCMe)_6{}^{2+}$. $Fe(NCMe)_6{}^{2+}$ is oxidised, by Cl_2, producing $FeCl_4{}^-$. A ligand is necessary to stabilise Fe(III) in MeCN.

Vanadium metal is not oxidised by WF_6 , $NOPF_6$ or PF_5 , in MeCN solution. This is a result of kinetic control of the reaction. VO_2F undergoes fluoride ion transfer to PF_5 with subsequent reduction of $VO_2{}^+$, producing VO^{2+} .

Thallium(I) is formed, in MeCN solution, by reaction of TlF with PF_5 . The solid product has no coordinated acetonitrile. Tl(I) is oxidised, by $NOPF_6$ and PF_5 , to produce lemon coloured solids, containing mixtures of Tl(I) and Tl(III). TlF_3 reacts with PF_5 , in MeCN solution, but characterisation of the product is hindered by decomposition of the solvent, which produces dark red solutions.

$Fe(NCMe)_6{}^{2+}$ reacts with $P(OMe)_3$, in MeCN solution, to yield as the final product $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$. The reaction is a stepwise substitution of $P(OMe)_3$ for MeCN and the later stages are followed by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. Three species are identified unambiguously from their second order spectra.

The first step, formation of $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$, is followed by stopped-flow spectrophotometry. The rate of reaction is very slow, compared to solvent exchange at $Fe(NCMe)_6{}^{2+}$, and shows limiting behaviour which suggests that an Interchange mechanism is operating. The activation process may be I_a or I_d , the reaction

being sterically controlled by the bulky $P(OMe)_3$ group.

After substitution of one $P(OMe)_3$ for MeCN, the complex is low spin and the subsequent steps are extremely slow, in keeping with the 'substitution inert' behaviour of low spin, d^6 species. The later steps are followed by conventional spectrophotometry. Two distinct reactions are observed, formation of $[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$ which is first order in $P(OMe)_3$ and formation of $[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$, which is second order in $P(OMe)_3$. The results are obtained by computer modelling the reactions.

The final step, formation of $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$, is too slow to be followed conveniently.

$Fe(NCMe)_6^{2+}$ does not react with PF_3, $P(OPh)_3$, Et_2S and $^iPr_2S$ but reacts rapidly with 2,2'-bipyridyl, to form $Fe(bipy)_3^{2+}$.

Solvated Cu(I) and Cu(II) in MeCN solution, characterised in an earlier study,[11] react readily with $P(OMe)_3$. The product of the reaction of Cu(I) is $Cu\{P(OMe)_3\}_4^+$, which is characterised by n.m.r. spectroscopy. Cu(II) reacts via a purple transient intermediate to produce $Cu\{P(OMe)_3\}_4^+$, $MeP(O)(OMe)_2$ and $MeP(OMe)_3^+$. The decay of the intermediate, presumed to be a Cu(II) – $P(OMe)_3$ complex, is followed by stopped-flow spectrophotometry. The decay is second order in $P(OMe)_3$ and presumably involves formation of phosphorus radical species. The radical species must decompose with production of Me^+, which initiates the Arbusov rearrangement of $P(OMe)_3$. This accounts for formation of $MeP(O)(OMe)_2$ and $MeP(OMe)_3^+$ in the reaction.

$Cu(NCMe)_6^{2+}$ reacts readily with 2,2'-bipyridyl and 2,9-dimethyl-1,10-phenanthroline to produce $Cu(bipy)_3^{2+}$ and $[Cu(dmp)_2(NCMe)_2]^{2+}$.

The dmp complex oxidises Cu^o to produce $Cu(dmp)_2^+$.

Cu(I) in MeCN does not react with PF_3 but is oxidised by WF_6 . It is also oxidised by $[Ni(cyclam)(NO_3)_2]^+$ but not by $[Ni(cyclam)(NCMe)_2]^{3+}$.

The copper complexes, used in this work, are investigated by cyclic voltammetry. $Cu(NCMe)_6^{2+}$ is a relatively strong oxidising agent but it is stabilised by addition of the bidentate ligands, shown by the size of the respective $Cu^{2+}- Cu^+$ couples of the complexes. The large size of the $Cu^{2+}- Cu^+$ couple is attributed mainly to the stability of Cu^+ in MeCN.

$Cu\{P(OMe)_3\}_4^+$ reacts with PF_5 , via a P—P adduct, $F_5P-P(OMe)_3$, to produce $PF_2(OMe)$ and $PF(OMe)_2$ as major products. $PF(OMe)_2$ is capable of coordinating to Cu^+ to produce a labile complex. The other product of reaction is PF_4OMe which reacts with MeCN to yield POF_3 , F^- and $Me(MeCN)^+$. The solvent is attacked in the exothermic reaction, producing a yellow gel as the involatile product.

The reaction of $Cu\{P(OMe)_3\}_4^+$ with WF_6 is very violent and involves extensive decomposition of the solvent. The solvent polymerises, initiated by Me^+, to produce $Me(MeCN)_n^+$. These cations react to produce $Me(MeCN)_nPF_5^-$ species, which are characterised by their n.m.r. spectra. $PF(OMe)_2$, $PF_2(OMe)$ and PF_3 are also formed, the other product being WF_5OMe. WF_5OMe reacts with MeCN to produce WOF_4 , F^- and $Me(MeCN)^+$.

$[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ reacts only very slowly with PF_5 but with WF_6 it reacts , presumably via a W—P bonded adduct, to yield $MePF_4$. This is presumably formed by the same route as $Me(MeCN)_nPF_5^-$. In some cases the Arbusov product, $MePF(O)(OMe)$, is formed in the process, from reaction of Me^+ with $PF(OMe)_2$.

The small amount of Arbusov products formed in the above reactions is a function of the solvent, removing Me^+ from solution, and the metal ion, coordinating the phosphorus(III) species, preventing attack at the lone pair. The difference in behaviour of the two systems is due to the nature of the metal ions ; the labile Cu(I) and the 'substitution inert' Fe(II) .

Introduction.

The reaction of metal ions in solution has long been a subject of great interest. The vast majority of the work, quite naturally, has concerned aqueous systems and the behaviour of a large number of metal ions, in varying oxidation states, has been well characterised.

Unfortunately, a number of metal ions have oxidation states which are unstable with respect to redox or hydrolysis, in aqueous solution or cannot be prepared at all, without the use of stabilising ligands. For example, V(II) , although relatively well known in aqueous solution, is oxidised by water ; Fe(III) has a tendency to hydrolyse in aqueous solution and to obtain a solution containing mainly the pale purple $Fe(H_2O)_6^{3+}$ ion, the pH must be around zero ; Tl(III) in aqueous solution is subject to extensive hydrolysis but can be stabilised by addition of chloride ion, forming the very stable $TlCl_2^+$ (aq) species.[1]

To relieve these problems, workers have resorted to reactions which produce metal cations in non aqueous media, where rigorously anhydrous and anaerobic conditions can be maintained. This has involved the use of vacuum line and glove box techniques and has led to formation of solvated cations in 'unusual' oxidation states, for example Ag(II) and Tl(III) salts have been generated, in acetonitrile solution, by oxidation of the metals with molybdenum hexafluoride.[2] The salts are extremely moisture sensitive.

The behaviour of the metal ions in their 'common' oxidation states in the non aqueous media is also of great interest, as this allows direct comparison between the non aqueous solvent and water. This is potentially useful in producing ideas on the structuring of solvents, the effect that metal ions have upon the nature of the medium and the effect that the medium has upon the metal ion.

A wide variety of solvents are available, from dipolar hydrogen bonded solvents, such as methanol, which is very similar to water, through dipolar aprotic solvents, such as acetonitrile, to non polar solvents, such as benzene. The non polar solvents are of little use in these studies as they are poor solvating agents for metal ions. The other two categories, however, have received a great deal of attention.

Acetonitrile has proved particularly popular as a solvent for a number of reasons. It has a high dielectric constant for an organic liquid (37.5 at 293 K) and has good ability as a donor, through the lone pair of electrons on the nitrogen, which makes it a good solvent for metal ions. It is relatively simple to purify and its physical properties (m.pt. 228 K , b.pt. 354 K and high vapour pressure) give it a useful liquid range and allow it to be handled with ease in a vacuum system. A number of reports have appeared in the literature concerning the major impurities in reagent grade acetonitrile, along with methods for removing them. Purification can be done successfully on a laboratory scale.[3]

The role of acetonitrile as a donor solvent and the nature of the coordination to the metal centre has been fairly extensively reviewed.[4] By far the most common mode of coordination is via the nitrogen lone pair. This generally brings about an increase in the force constant of the $C\equiv N$ bond and hence an increase in the infra red stretching frequency of the bond, over that of the free solvent. This behaviour gives a useful spectroscopic method for determining if coordination of acetonitrile has been achieved.

A variety of methods has been used to produce solvated metal ions in acetonitrile. Many workers are content merely with dissolving the hexaquo ion directly in the solvent, generally as the perchlorate salt. This has the drawback that x moles of H_2O are introduced for every mole of metal ion (where x is the coordination number of the metal ion) . The effect that the presence of this amount of H_2O has upon the chemistry of the species is unknown. The situation is not merely one where a metal ion is dissolved in a solvent. A potential ligand exists in solution in significant amounts. As a trace amount of moisture may have a large effect, earlier work, which relies upon dissolution of the hydrated salt, will benefit from a re-examination under more careful conditions.

A number of first row transition metal cations have been generated, in MeCN solution, by oxidation of the pure metal. This has been done using $NOBF_4$ [5] or $NOClO_4$ [6] as oxidising agents, for example, with nickel metal,

$$\mathrm{Ni(s)} \quad + \quad 2\ \mathrm{NOBF_4(s)} \xrightarrow{\mathrm{MeCN}} \mathrm{Ni(BF_4)_2\ (solv.)} \quad + \quad 2\ \mathrm{NO}$$
$$\longrightarrow \mathrm{Ni(NCMe)_6(BF_4)_2\ (s)} \qquad (1)$$

This is a good preparative route to a number of metal ions but with copper a mixture of Cu(II) and Cu(I) species is produced.

Alternative syntheses have involved the use of Cl_2 , Br_2 and I_2 as oxidising agents.[7] A number of products of general formula $MX_2 \cdot 3MeCN$ have been produced. From their electronic reflectance spectrum, they are formulated as $M(NCMe)_6(MX_4)$ species. For example, the product of reaction of manganese metal with I_2 , in

MeCN solution, is formulated as $Mn(NCMe)_6(MnI_4)$. Although iron reacts with I_2 in an analogous fashion, to produce $Fe(NCMe)_6(FeI_4)$, the products of oxidation, using Cl_2 or Br_2 , are the interesting mixed oxidation state species $Fe(NCMe)_6(FeX_4)_2$. Two thirds of the iron exists as Fe(III) and one third as Fe(II) .

An extension of this approach has been the use of covalent high oxidation state fluorides as oxidising agents for the metals. This route is advantageous as the fluorides can be obtained rigorously anhydrous. The range of potential reagents for oxidation of metals is very large and the oxidation potential is variable. The relative oxidising potential of the second and third row transition metal fluorides has been discussed in a qualitative manner.[8] The electron affinity is found to increase with increasing atomic number and decreasing molecular volume. In fact PtF_6 has been found capable of oxidising the noble gas Xe , at room temperature.

The use of very strong oxidising agents in acetonitrile solution is not feasible as these reagents tend to interact with the solvent but the milder oxidising abilities of other metal hexafluorides have been used with great effect. For example, MoF_6 and WF_6 have been used to oxidise a number of metals, including Ag , Tl , Co , Ni and Cu .[2] The stronger oxidising ability of MoF_6 relative to WF_6 is demonstrated unambiguously, as MoF_6 oxidises Ag and Tl to Ag(II) and Tl(III) , while WF_6 oxidises these metals to Ag(I) and Tl(I) only. The products of reaction are isolated from solution as the hexafluorometallate(V) salts, for example $Tl(NCMe)_6(MoF_6)_3$. Subsequently UF_6 [9] and ReF_6 [10] have been used as oxidising agents.

UF_6 is found to be a strong agent, producing Tl(III) in reaction with Tl metal. ReF_6 , under the same conditions, is a weaker reagent, producing Tl(I) . Both UF_6 and ReF_6 react with acetonitrile, ReF_6 much more rapidly.

Of the group Va pentafluorides, PF_5 is found to slowly oxidise Cu metal to a Cu(I) salt, with the production of PF_3 ,[11]

$$2\ Cu(s) + 3\ PF_5(solv.) \xrightarrow{MeCN} 2\ CuPF_6(solv.) + PF_3(g) \qquad (2)$$

On the other hand AsF_5 , in MeCN solution, displays no oxidising ability toward Cu or Ag metals. This is ascribed to the formation of the adduct, $AsF_5.NCMe$ which is kinetically stable to reduction. AsF_5 has been used as an oxidising agent in SO_2 solution, to produce salts of the form, $Mn(AsF_6)_2$ or $Ni(AsF_6)_2.2SO_2$ [12].

The use of high oxidation state fluorides, as oxidising agents in acetonitrile solution, is a useful route to the solvated ion products. By using agents of differing oxidising power, the potential exists to generate different oxidation states of the same metal ion, cf. reactions of Tl with WF_6 and MoF_6 .

The final major route to solvated cations, in acetonitrile, is by Lewis acid - Lewis base reaction. A large number of such reactions has been done using chloride species as reagents. For example, solvated salts of Mn(II) , Fe(II) , Co(II) , Ni(II) and Cu(II) have been produced, with $FeCl_4^-$, $TlCl_4^-$, $SbCl_6^-$ or $SnCl_6^{2-}$ as the anion by reaction of MCl_2 with MCl_x ($x = 3,4$ or 5) , in the appropriate stoichiometry. [13]

More recently similar types of reaction have been done, using covalent high oxidation state fluorides as the Lewis acids and ionic fluorides as the Lewis bases. For example, WF_6 reacts with

CuF_2 , in MeCN solution to produce the blue solvated $Cu(WF_7)_2$ species, which is isolated from solution as $Cu(NCMe)_5(WF_7)_2$.[14] CuF_2 reacts in the same way with PF_5 , AsF_5 and TaF_5 , in MeCN, to produce the corresponding Cu(II) hexafluoroanion salts.[11]

Using binary fluoride compounds as starting materials has other benefits. As well as being able to obtain the reagents in an anhydrous condition, the formation of the complex fluoroanions, where the anion is diamagnetic, can be studied conveniently, by ^{19}F n.m.r. spectroscopy, and the behaviour of the anion in solution can be ascertained. Generally the complex fluoroanions show little or no tendency to coordinate to the metal ion, which is not true of the chloroanion species, formed in other reactions. This property of the fluoroanions is very important, as it means that the metal cation which is being studied, has only solvent in its primary coordination sphere. The chemistry of the metal ion is, to a great extent, free of the effect of the anion.

The aim of the work, described in this thesis, is the preparation of cations of a variety of metals, in different oxidation states. For the reasons described above, acetonitrile has been chosen as the solvent in the majority of the work. The most convenient preparative routes are oxidation of the metal by a covalent fluoride or by $NOPF_6$, and Lewis acid - Lewis base reactions between a covalent and an ionic binary fluoride. Where possible, the synthetic targets are PF_6^- salts, as this anion is very stable with respect to hydrolysis, in acetonitrile solution and the salts can be easily handled.

Once a number of salts of the different cations have been characterised, in MeCN solution, the aim was to investigate their behaviour in redox and substitution reactions. The electrochemistry of the species was investigated by cyclic voltammetry. The behaviour of Cu(II) and Cu(I) species, which have been characterised previously, was also studied.

Preliminary work has shown very interesting behaviour for Cu(II) , in MeCN, in reaction with $P(OMe)_3$ and with tetramethyl thiourea. The metal ion is reduced to Cu(I) with concomitant oxidation of the ligand.[15] This work was followed up and similar reactions attempted with other metal ions.

The present work has led to the formation of trimethyl phosphite complexes of Cu(I) and Fe(II) , which show very different kinetic behaviour ; Cu(I) is substitution labile and Fe(II) is substitution inert. These metal complexes were used to study the effect of the metal ion upon the fluorination reactions of the ligand, using WF_6 and PF_5 as the fluorinating reagent.

CHAPTER ONE

Preparation of Metal Cations in Acetonitrile Solution.

Introduction.

Previous work in this department has concerned the preparation of solvated ions of the transition elements, for example, Ni , Cu and Ag , and the post-transition elements, for example, Tl and Pb ,[2] in acetonitrile solution, by the methods previously described.

The present work is undertaken to extend the synthetic routes to other metal ions. The aim is to generate a particular metal in a particular oxidation state, examine the redox behaviour of the metal ions so produced, and measure, electrochemically, the potential between the various oxidation states of a metal, in acetonitrile solution. It is known that copper will exist, in MeCN, in both Cu(II) and Cu(I) states but that Cu(II) is a relatively powerful oxidant.[11] By examining other metal ions, in a similar way, it is expected that useful oxidising or reducing agents will be found for use in MeCN.

One metal of general interest is iron. The chemistry of iron ions and complexes is important from both an industrial and a biochemical point of view.[1] It is by far the most widespread and important transition metal with a functional role in living systems, for example in oxygen transport or electron transfer. In aqueous solution the Fe(II) and Fe(III) states are the most common.

In the absence of other complexing agents, aqueous solutions of iron(II) contain pale blue-green $[Fe(H_2O)_6]^{2+}$ and solutions of iron(III) contain pale purple $[Fe(H_2O)_6]^{3+}$. The potential of the Fe^{3+}- Fe^{2+} couple is 0.770 V , relative to the normal hydrogen electrode, and solutions of Fe(II) are oxidised to Fe(III) by molecular oxygen. On the other hand, solutions of $[Fe(H_2O)_6]^{3+}$ tend to hydrolyse, via a step equivalent to acid dissociation of the aquo ion, producing $[Fe(H_2O)_5(OH)]^{2+}$ and H^+ , unless the pH of the solution is around zero.

Fe(II) has been formed, in MeCN solution, as the $Fe(NCMe)_6{}^{2+}$ ion, as previously described (vide supra), by oxidation of iron metal or by reactions of $FeCl_2$ with a Lewis acid chloride. There is no evidence, in the literature, for formation of $Fe(NCMe)_6{}^{3+}$, but Fe(III) is known in complex ions, such as $FeCl_4{}^-$.

Both Fe(II) and Fe(III) form a wide variety of complexes, in aqueous solution, and these may be either high or low spin, depending upon the nature of the ligand. Some of the complexes exhibit 'spin crossover' behaviour, changing their spin state with temperature. For example, in the Fe(II) complex, $Fe(phen)_2(NCS)_2$, the magnetic moment varies from ca. 5.1 B.M. at 300 K to ca. 1.5 B.M. at $\leqslant 150$ K ,[16] and iron(III)-tris(dithiocarbamato) complexes have a magnetic moment which varies between ca. 2 B.M. at low temperatures and 5.9 B.M. at high temperature.[17]

Of the earlier first row transition metals, the aqueous solution chemistry of vanadium is very interesting. There are four well defined cationic species, $[V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $VO^{2+}(aq)$ and $VO_2{}^+(aq)$. $[V(H_2O)_6]^{2+}$ is violet in colour and is air sensitive. It is kinetically inert, due to the large crystal field stabilisation energy, of the d^3 configuration. Solutions of V(II) have been used in a number of reactions as a powerful reducing agent, for example in the reduction of the radical anions, $X_2{}^-$, in perchloric acid solution, to produce $V^{3+}(aq)$ and X^- (where X = Cl, Br, I) .[18]

$[V(H_2O)_6]^{3+}$ is blue in colour and its solutions are subject to aerial oxidation. The electronic spectrum of this ion has been extensively studied, as it is a good example of the octahedrally coordinated d^2 ion. The spectrum, which consists of three absorption bands, has been satisfactorily explained in terms of the ligand field model. V(III) forms six coordinate complexes, such as $[V(CN)_6]^{3-}$ and $[V(C_2O_4)_3]^{3-}$.

The oxovanadium(IV) ion, $[VO(H_2O)_5]^{2+}$, is blue and is formed by aerial oxidation of V^{3+}(aq) or by reduction of VO_2^+ . A large range of compounds with the V=O structural unit can be obtained from aqueous solutions of VO^{2+} . These can be cationic, neutral or anionic and five or six coordinate, depending upon the nature of the ligand, for example $[VO(bipy)_2Cl]^+$, $VO(acac)_2$ and $[VO(NCS)_4]^{2-}$.

VO_2^+ , in aqueous solution, is bent rather than linear, with its electronic spectrum being similar to octahedral complexes, such as <u>cis</u>-$[VO_2ox_2]^{3-}$ (ox = oxalate anion) .[19] The VO_2^+ ion has been used as an oxidising agent, for example, in the oxidation of thiourea in aqueous perchloric acid media, the final product being a VO^{2+} species.[20]

In MeCN solution, oxidation of V metal with Cl_2 , Br_2 or I_2 results in the formation of V(III) species, formulated as $[VCl_3(MeCN)_3]MeCN$, $[VBr_2(MeCN)_4]Br_3$ and $[V(MeCN)_6](I_3)_3$, each with six coordinate vanadium. The iodide complex is found to be unstable and quickly loses iodine.[21] $[V(MeCN)_6]^{3+}$ is also formed from the reaction of VCl_3 with $SbCl_5$ in MeCN solution, the product being formulated as $[V(MeCN)_6(SbCl_6)_3].3MeCN$.[22] Recently, electrochemical synthesis of V(II) halides, in MeCN, has been reported. The products precipitate from solution as $VCl_2.2MeCN$, $VBr_2.MeCN$ and VI_2 . [23]

The species $VO(MeCN)_5^{2+}$ has been identified by infra red spectroscopy, in an examination of the species formulated as $VO(MeCN)_6(SbCl_6)_2$. [24] VOF_3 is soluble in acetonitrile, giving a yellow solution but it is slowly reduced to produce a $V^{IV}O^{2+}$ species and HF. VOF_3 undergoes reaction with Me_3SiNEt_2 to yield species formulated as $VOF_{3-n}(NEt_2)_n$, as the major products. With $(Me_3Si)_2O$, VOF_3 reacts to produce VO_2F and Me_3SiF as the sole products. [25]

Of the post transition elements, thallium has received a great deal of attention. In aqueous solution, Tl(I) is distinctly more stable than Tl(III)(Tl^{3+}- Tl^{+} couple, E^{o} = 1.25 V relative to N.H.E.) . The chemistry of Tl(I) is very similar to the alkali or Ag(I) ions but gives rather few complexes. Solutions of Tl(I) salts are exceedingly toxic and trace amounts cause loss of hair.

Solutions of $[Tl(H_2O)_6]^{3+}$ are subject to extensive hydrolysis, forming $[Tl(H_2O)_5(OH)]^{2+}$ and H^+ . The Tl(III) state, however, is stabilised by complex formation and this is particularly noted with chloride ion, where, among other species, the very stable, linear $TlCl_2^+(aq)$ ion is formed. For this reason, much of the complex chemistry of Tl(III) has concerned the halide species, rather than $[Tl(H_2O)_6]^{3+}$. [26]

In the redox reactions of Tl(I) and Tl(III) , formation of a transient Tl(II) species has been proposed and it has been detected, by e.s.r. spectroscopy, as the product of γ-irradiation of solutions of Tl(III) . [27]

In MeCN solution, Tl(I) salts have been produced by Lewis acid - Lewis base reactions, for example, $Tl(NCMe)_2SbCl_6$ [28] or $TlAsF_6$,[11] or by oxidation of Tl metal with WF_6 .[2] Using a stronger oxidising agent, MoF_6 , the Tl(III) salt, $Tl(NCMe)_6(MoF_6)_3$ is produced.

The aim of the work described in this chapter is the preparation, in acetonitrile solution, of solvated cations of iron, as Fe(II) and Fe(III) , vanadium as V(II) , V(III) , VO(IV) and VO_2(V) and thallium, as Tl(I) and Tl(III) . The size of the redox potential of the various couples will be informative with regard to the role of the solvent in stabilising certain oxidation states. Some of these cationic species will have a use as mild oxidising or reducing agents, in MeCN solution. The Tl and V salts are particularly interesting as there is a potential to investigate the species by ^{205}Tl , ^{203}Tl or ^{51}V n.m.r. spectroscopy.

Results and Discussion.

Formation of Solvated Cations of Iron in MeCN Solution.

a) Iron(II).

Previous work has shown that iron metal is oxidised by WF_6, in MeCN solution, to produce solvated Fe(II) as the cationic product.[29] The anions are a mixture of WF_6^- and WF_7^-, the ratio being dependent upon the conditions of the reaction and the method by which the solid is isolated. The mixture arises due to operation of the equilibrium,

$$WF_6(\text{solv.}) + WF_6^-(\text{solv.}) \rightleftharpoons WF_7^-(\text{solv.}) + WF_5(\text{solv.}) \qquad (1)$$

This equilibrium has been observed in the reaction of WF_6 with other metals.[2] It is possible to force the equilibrium to either side, by altering the experimental conditions. For example, in $MeNO_2$ solution, Raman spectroscopy suggests that only the WF_7^- salt is formed, presumably due to the WF_7^- salt having a lower solubility in $MeNO_2$ than the WF_6^- salt. This results in the WF_7^- salt being precipitated from solution. By carrying out the reaction such that only WF_6 and MeCN vapour come into contact with the metal, the concentration of WF_6 at the surface of the metal is suppressed. The product which is formed is predominantly the WF_6^- salt, $Fe(NCMe)_6(WF_6)_2$. The 'vapour phase' reaction has been repeated in the course of the present work and the products are fully characterised, by spectroscopy and by microanalysis. The solid state vibrational spectra are listed in Table 1. The reaction of Fe with WF_6/MeCN vapour is fast, with reaction being complete within 24 hours, at room temperature.

Iron metal is also oxidised by PF_5, in acetonitrile, but only

Table 1.

Solid State Vibrational Spectra of $Fe(NCMe)_6(WF_6)_2$.

Infra-red (cm^{-1})	Raman (cm^{-1})	Assignment [2,28]
3260 w		comb. MeCN
3220 w		comb. MeCN
2320 s	2325 (15)	comb. MeCN
2295 s	2295 (90)	C≡N stretch
2240 w	2238 (90)	comb. MeCN
1040 m	1060 (25)	CH_3 rock
941 m	943 (35)	C—C stretch
790 w	782 (20)	overtone
	704 (20)	WF_7^-
	690 (100)	WF_6^-
595 vs		WF_6^-
	405 (60)	C-C≡N bend
230 m		Fe-N stretch

i.r. :- s, strong ; m, medium ; w, weak.

Raman :- scale 1-100

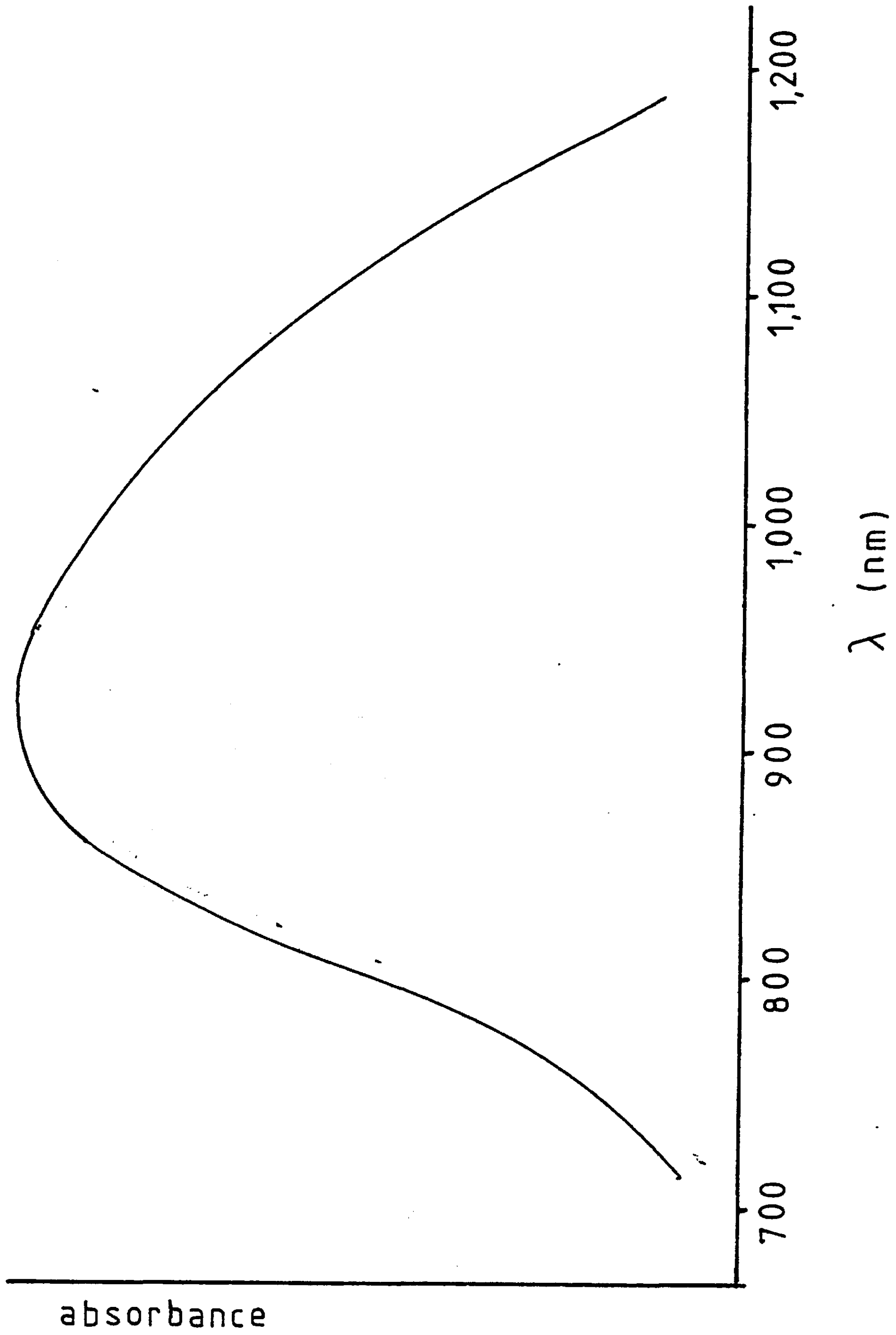
very slowly. The reaction takes several weeks to produce even a small amount of material. The product is characterised, by its electronic and infra red spectra, as $Fe(NCMe)_6(PF_6)_2$. The electronic spectrum of $Fe(NCMe)_6^{2+}$ in MeCN is shown in Figure 1. It consists of a broad band, $\bar{\nu}_{max}$ 11,100 cm^{-1} (ε ca. 10 dm^3mol^{-1} cm^{-1}) , 9,700 cm^{-1} (sh.) , assigned to the $^5E_g \leftarrow {}^5T_{2g}$ transition of an octahedral, high spin d^6 system. The band is broad due to a Jahn - Teller distortion in the excited state, deriving from a $t_{2g}^3\, e_g^3$ configuration. The slow rate of reaction of PF_5 with iron is in keeping with its reported behaviour in the oxidation of copper metal, in MeCN.[11]

In a preliminary experiment upon the nature of $NOPF_6$ in MeCN, it is found that $NOPF_6$ rapidly oxidises Ag metal. The white solid product is characterised by its spectra as a Ag(I) salt. A colourless gas is evolved as the other product, presumably NO. This is not coordinated to the metal at room temperature. On cooling to 77 K , however, a red colour develops which disappears on warming. This thermochromism is presumably due to coordination of NO to Ag(I) , at low temperatures. The colour results from a metal to ligand charge transfer interaction.

Earlier work on the reaction of metals in acetonitrile, found that iron metal is oxidised by $NOBF_4$, to give the Fe(II) salt.[5] In the present work, $NOPF_6$ is found to behave in a similar manner, to produce $Fe(NCMe)_6(PF_6)_2$. In the course of the reaction, the solution becomes dark brown and small amounts of an insoluble, dark brown solid are produced. Too little of this solid is formed to permit its identification but it is successfully removed from the

Figure 1.

Electronic Spectrum of $Fe(NCMe)_6^{2+}$.



major product by careful decanting. The solid product, isolated from solution, is off-white in colour.

In a separate experiment, concerning the nature of $NOPF_6$, in MeCN solution, the N—O stretching frequency is found to occur at 1865 cm^{-1}, compared with 2340 cm^{-1} in solid $NOPF_6$. This suggests that NO^+ is highly solvated in MeCN but this does not affect its usefulness as an oxidant. Iron metal is oxidised by $NOPF_6$ in $MeNO_2$ solution also, and the product is presumed to be $Fe(O_2NMe)_6(PF_6)_2$. Although $MeNO_2$ is a weaker ligand than MeCN, salts of this type are known.[7] Characterisation of this species is prevented due to formation of purple polymeric material, formed during the exothermic oxidation reaction. This behaviour differs from a recent report of the reaction of Fe with $NOPF_6$ in $MeNO_2$, at 253 K, where the product, a dark green solid, is formulated as $[Fe_2(NO)_6][PF_6]_2$.[30] This solid is unstable above 253 K. At low temperature, the Fe/$NOPF_6$/MeCN reaction mixture is dark green and though NO may be ligated, there is no evidence for it being retained at room temperature.

The reactions of PF_5 and AsF_5 with FeF_2, in MeCN, are facile and yield the $Fe(NCMe)_6^{2+}$ salts as the products. The magnetic moment of the PF_6^- salt, in MeCN solution, determined by Evans' method is 5.7 ± 0.4 B.M., within the range expected for a high spin d^6 species.[31]

An e.p.r. spectrum of $Fe(NCMe)_6(PF_6)_2$ in MeCN at 77 K shows a signal characteristic of Mn^{2+}.[15] The iron salt arises from reaction of FeF_2 with PF_5. The FeF_2 must contain some MnF_2 which reacts with PF_5 to produce $Mn(NCMe)_6(PF_6)_2$. The sensitivity of the e.p.r. experiment is such that even the very small amount of Mn^{2+} which is present is easily detected. A sample of MnF_2 itself, reacts with PF_5 to produce a salt whose spectra are in agreement with the above formulation. The rate of reaction is comparable to that of FeF_2, taking ca. 24 hours to produce a reasonable amount of product. The solvent, however, in the reaction of MnF_2, is subject to attack, giving rise to a brown colour in the reaction mixture and the infra red spectrum of the solid shows bands characteristic of N—H stretching.

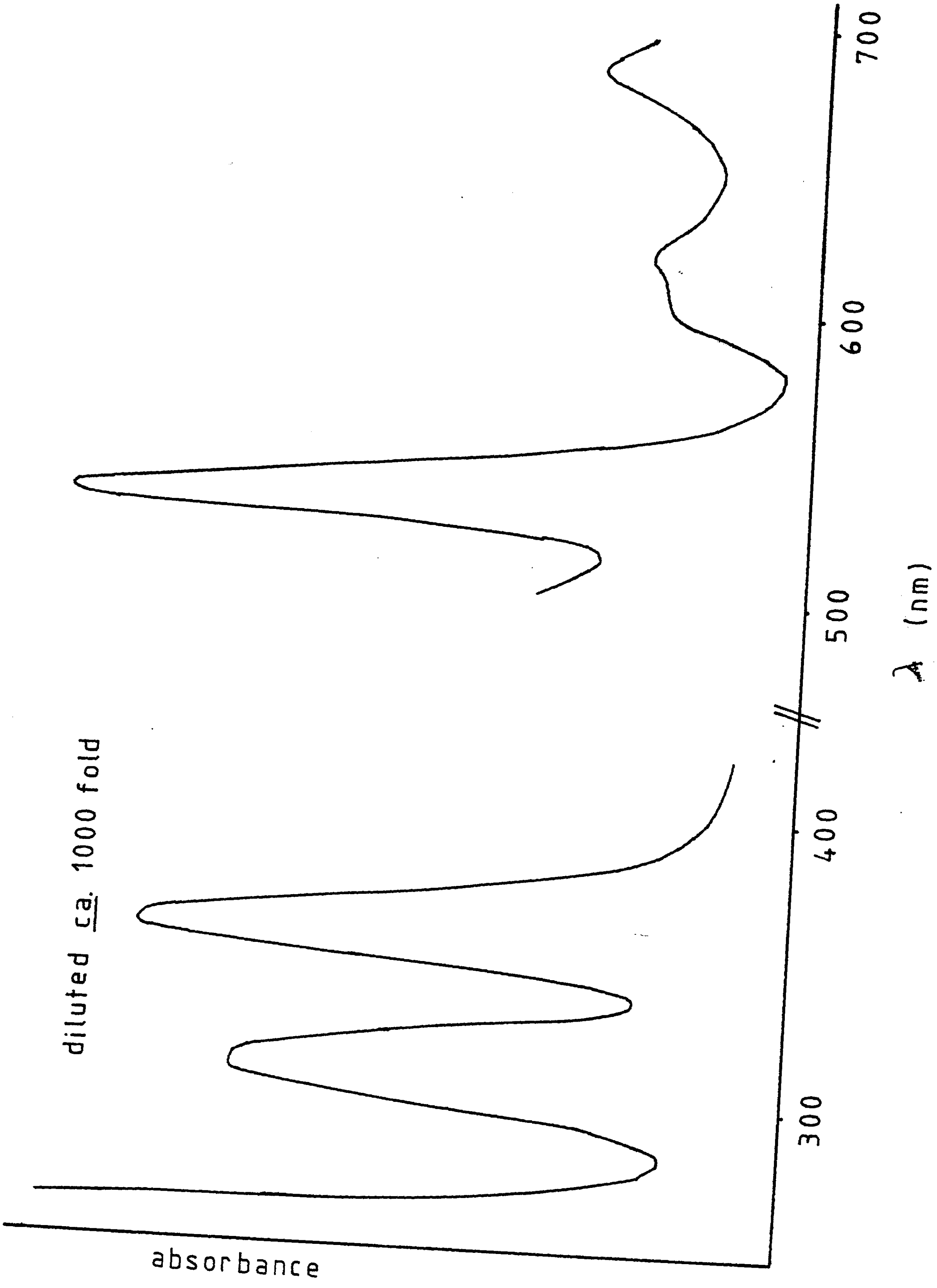
In the reaction of FeF_2 with IF_5 in MeCN, there is no evidence for formation of $Fe(NCMe)_6{}^{2+}$ in solution and no isolable products are formed. IF_5 is evidently too poor a fluoride ion acceptor to overcome the lattice energy of FeF_2 or, alternatively, the reaction may be very slow. In a similar reaction, involving CuF_2, the product is a molecular complex $CuF_2.4IF_5.4MeCN$ and not the $IF_6{}^-$ salt.[32]

b) Iron(III)

Iron metal is not oxidised to $Fe(NCMe)_6{}^{3+}$ by WF_6, PF_5 or NO^+, nor is $Fe(NCMe)_6{}^{2+}$. $Fe(NCMe)_6{}^{2+}$ is oxidised by Cl_2 in MeCN, but the product is $FeCl_4{}^-$, as shown by its electronic spectrum (Figure 2). In this reaction, all Fe(II) is converted to Fe(III) with solvated H^+ presumably acting as the cation. Examination of the solvent residues of the reaction by gas chromatography, reveals the presence of an appreciable quantity of CH_2ClCN and a little CCl_3CN.[33] In an earlier study of the oxidation of iron with chlorine, the product is $Fe(NCMe)_6(FeCl_4)_2$, with one third of the total iron concentration Fe(II) and two thirds Fe(III).[7] This

Figure 2.

Partial Electronic Spectrum of $FeCl_4^-$.



reaction is carried out by passing Cl_2 through the reaction mixture until a precipitate is obtained. The difference between the two systems is presumably a concentration effect, with the present study using a large excess of Cl_2 . In the earlier work, the solvent was not tested for chlorocarbon species.

Adding Cl_2 to MeCN results in a yellow solution. The colour arises from an intense band in the u.v. with a tail into the visible region. Over two days the solution becomes colourless but becomes yellow again, when more Cl_2 is added. Finally the solution becomes colourless once more. The colour is presumably due to solvated Cl_2 which reacts with MeCN, chlorinating the solvent. The chlorination process is probably photo-initiated though this was not investigated.

In the presence of moisture and O_2 , oxidation of Fe(II) to Fe(III) is very rapid and produces a dark brown solid, presumably an iron(III) oxide or hydroxide. This was found when air leaked into a reaction vessel containing $Fe(NCMe)_6^{2+}$ and NO^+ in MeCN .

Iron(III) fluoride does not behave as a fluoride ion donor toward PF_5 [29] or WF_6 in MeCN. A simple Born - Haber cycle for a fluoride transfer reaction is illustrated in the figure :- the reaction of MF with AF_5 is chosen for convenience.

$$\begin{tikzcd}
MF(s) \arrow[d, "U"'] & + & AF_5(solv.) \arrow[r] \arrow[d, "\Delta H_{solv.}"] & M^+(solv.) & + & AF_6^-(solv.) \\
M^+(g) \arrow[d] & + \; F^-(g) \; + & AF_5(g) \arrow[d, "\Delta H_{F^-}"] & & & \\
M^+(g) & + & AF_6^-(g) \arrow[uur, "\Delta H_{solv.}(M^+, AF_6^-)"'] & & &
\end{tikzcd}$$

where U is the lattice energy of MF , $\Delta H_{solv.}$ is the heat of solvation of the various species and ΔH_{F^-} is the fluoride ion affinity of $AF_5(g)$.

The major endothermic factor is the lattice energy of MF which, for the reaction to be feasible, must be balanced by the exothermic factors, most importantly $\Delta H_{solv.}(M^+)$ and ΔH_{F^-} .

In the reaction of FeF_3 the lattice energy is so large that it is not balanced by the solvation energy of Fe^{3+} and the fluoride ion affinity of PF_5 (calculated to be > 297 kJ mol^{-1}) .[34] The difference in behaviour between FeF_3 and FeF_2 is a reflection of the greater lattice energy of the trifluoride, 5870 <u>versus</u> 2769 kJ mol^{-1} .[35]

Reaction between FeF_3 and IF_5 yields a small amount of white solid as product but too little to be characterised. If this is a $FeF_3.xIF_5$ molecular complex, similar in form to the copper complex mentioned above, then the failure of FeF_2 to react with IF_5 must be interpreted as a kinetic effect rather than thermodynamic. The FeF_3 - IF_5 system requires further investigation, to characterise the product.

Discussion.

The solvated cation, $Fe(NCMe)_6^{2+}$, is readily prepared by a variety of synthetic routes while $Fe(NCMe)_6^{3+}$ is apparently not formed at all. This is in keeping with a study of the attempted oxidation of $Fe(NCMe)_6^{2+}$ with $Fe(phen)_3^{3+}$ which finds that the two species do not react.[36] The failure of the reaction is attributed to stabilisation of $Fe(NCMe)_6^{2+}$ by back donation from the metal to the ligand. In MeCN solution, $Fe(phen)_3^{3+}$ oxidises $Fe(TMP)_6^{2+}$, $Fe(DMF)_6^{2+}$ and $Fe(HMPA)_6^{2+}$ to the corresponding Fe^{3+} salt, (where

TMP is trimethyl phosphate, DMF, N,N'-dimethyl formamide and HMPA, hexamethylphosphoramide) .

The formal reduction potential of the Fe(III) - Fe(II) couple in acetonitrile has been measured, by coulometry, as 1.57 ± 0.05 V versus Ag/Ag^+ .[37] This is an increase of ca. 1.3 V over the potential in aqueous solution and shows that Fe(III) in MeCN is a very strong oxidising agent. This is attributed to an increase in stabilisation of Fe(II) and a decrease in stabilisation of Fe(III) ; the lower dielectric constant of MeCN, relative to H_2O , is not expected to stabilise species of high charge. The salt which was used in this study is hydrated $Fe(II)(ClO_4)_2$. Although this was treated with MeCN, to produce $Fe(ClO_4)_2.6MeCN$, there must be some doubt that all the H_2O was removed from the salt. In the electrochemical cell, upon oxidation, yellow colours were observed which are attributed to Fe(III)-hydroxy species. The presence of even trace amounts of moisture will have the effect of lowering the potential of the Fe(III) - Fe(II) couple and for this reason, the literature value may be lower than the true value. The effect of water on the system is illustrated, by using the hydrated salt in MeCN solution, without attempting to remove H_2O ; the potential of the couple is 1.1 V relative to Ag/Ag^+ .

In the course of the present work, a study of the Fe(III) - Fe(II) couple, by cyclic voltammetry, was attempted. Starting from $Fe(NCMe)_6(PF_6)_2$, no oxidation wave is observed, even when scanning to the solvent limit (ca. + 2.1 V versus Ag/Ag^+) , which suggests that the redox couple is larger than the literature value.

The conclusion drawn from this work is that a very strong oxidising agent is necessary to oxidise Fe(II) to Fe(III), in acetonitrile. $Fe(NCMe)_6^{3+}$, if it is formed, will be a very strong oxidising agent and will perhaps be capable of oxidising the solvent.

In the course of this work, the only Fe(III) species which are found are $FeCl_4^-$ and the brown Fe(III) species produced by oxidation of Fe(II) in the presence of moist air. The presence of Cl_2, H_2O or O_2 stabilises the Fe(III) state by their ability to act as ligands. This reduces the size of the redox couple and so oxidation is feasible, with the relatively mild agents which are used in this study. Acetonitrile is not a sufficiently good ligand to Fe(III) to stabilise this oxidation state. It is a general observation that Fe(III) has a low affinity for N donor ligands, except where strong-field ligands are involved, for example, simple ammine complexes do not exist in aqueous solution.[1]

Formation of Solvated Cations of Thallium in MeCN Solution.

a) Thallium(I).

Earlier work has shown that Tl(I) salts are produced successfully, in MeCN solution, by mild oxidation of Tl metal,[2] or by fluoride ion transfer from TlF.[11] In the present work, $TlPF_6$ is formed by reaction of PF_5 with TlF. This is a known compound and the crystal structure of a single crystal, formed by reaction of $TlClO_4$ with KPF_6 in MeOH, has been reported.[38] The structure is very similar to that of KPF_6. The solid salts of Tl(I) produced from MeCN solution are rather unusual, as they possess no coordinated MeCN.

b) Thallium(III).

The reaction of TlF_3 with PF_5 , in MeCN solution, is complicated by attack on the solvent. A preliminary study of the reaction suggested that the product, a brown solid, is best formulated as $TlF(PF_6)_2.3MeCN$, from its microanalysis,[39] although this was not confirmed, in the present study. The initial product of the reaction is a cream coloured solid whose infra red spectrum shows it to contain coordinated MeCN and PF_6^- . In the space of 24 hours, only a small amount is formed and the yield cannot be increased, as solvent attack follows rapidly. The infra red spectrum of the final brown solid contains strong bands due to N—H stretching and bending modes. Further investigation of this reaction is necessary to characterise the cream coloured solid.

TlF_3 reacts with IF_5 in acetonitrile, to produce a viscous, colourless liquid. This is ascribed as a molecular adduct between TlF_3 , IF_5 and MeCN.[40] In the present work this adduct has been prepared in situ and reacted with PF_5 . The reason for attempting this reaction is that fluoride ion transfer from TlF_3 is relatively slow and solvent attack is important in the later stages. By using the adduct, in which the fluoride ions of TlF_3 are already partially solvated, by IF_5 , the transfer reaction may be facile and proceed, without complication, to give the PF_6^- salt. The mixture of TlF_3 , PF_5 , IF_5 and MeCN is yellow, initially, but very rapidly darkens to a deep red colour, indicative of attack on the solvent. No solid products are isolated, merely a dark red viscous liquid. The reaction is presumably too exothermic, bringing about polymerisation of MeCN.

When TlF is reacted with an excess of PF_5 in MeCN, a golden yellow solution results, from which is isolated a lemon coloured solid. The infra red spectrum and microanalysis of the solid shows it contains coordinated acetonitrile. This suggests that the solid is a mixture of Tl(I) and Tl(III) salts, the excess PF_5 having behaved as an oxidising agent toward Tl(I) . Insufficient PF_5 was added to effect complete oxidation of Tl(I) .

The oxidation may occur via two pathways ; by two successive one electron oxidation steps from Tl(I) to Tl(III) as in (2),

$$\mathrm{Tl(I)} \quad + \quad 3\,\mathrm{PF_5} \longrightarrow \mathrm{Tl(III)} \; + \; 2\,\mathrm{PF_6^-} \; + \; \mathrm{PF_3} \qquad (2)$$

or by a single one electron oxidation followed by disproportionation, as in (3),

$$\begin{tikzcd} 2\,\mathrm{Tl(I)} + 3\,\mathrm{PF_5} \arrow[r] & 2\,\mathrm{Tl(II)} \arrow[d] + 2\,\mathrm{PF_6^-} + \mathrm{PF_3} \\ & \mathrm{Tl(I)} + \mathrm{Tl(III)} \qquad (3) \end{tikzcd}$$

A lemon solid, with similar properties is isolated from the reaction of $TlPF_6$ with $NOPF_6$ in MeCN . The infra red spectrum indicates that not all the $NOPF_6$ reacts, which suggests that, under the conditions of reaction, an equilibrium exists between Tl(I) and Tl(III) , in acetonitrile solution.

As stated above Tl(III) is formed by oxidation of Tl metal, using a large excess of MoF_6 . When the reaction is carried out using a mole ratio Tl : MoF_6 , ca. 1 : 2 , the product is a yellow solid, $Tl(I)Tl(III)[MoF_6]_4 \cdot 2MeCN$. The existence of mixed oxidation state salts is a consequence of the stability of the Tl(I) state and has been noted in other thallium salts, for example, '$TlBr_2$' which exists as $Tl(I)[Tl(III)Br_4]$.[41] '$TlBr_2$' is formed from $TlBr_3$ by loss of Br_2

and this occurs ca. room temperature. Further work is necessary to characterise the nature of the yellow solids.

Discussion.

Although formation of both Tl(I) and Tl(III) in acetonitrile is feasible, relatively strong oxidising agents are needed to reach the higher oxidation state in spite of the fact that Tl(III) is isoelectronic with Cu(I) , which is very stable in MeCN. This is probably a reflection of the stability of Tl(I) . Using milder oxidising agents, it is possible to produce a mixture of the two oxidation states. Whether this arises by two one electron oxidation steps or by one oxidation step followed by disproportionation is not clear from this work.

The participation of TlF_3 in fluoride ion transfer reactions is rather unusual, in view of the very large lattice energy, 5493 kJ mol^{-1} . This is only ca. 370 kJ mol^{-1} less than FeF_3 , which is known not to react. If the reactions are thermodynamically controlled, the deciding factor will be the relative enthalpy of solvation of the Tl(III) ion relative to Fe(III) in acetonitrile. If the $\Delta H_{solv.}$ for Tl(III) is much larger than for Fe(III) then this will offset the lattice energy contribution from TlF_3 and the reaction will be more feasible. An alternative explanation is that $\Delta H_{solv.}$ of Tl(III) is similar to that of Fe(III) and so both reactions are feasible, thermodynamically, but that the rate of the FeF_3 reaction is very slow. Thus the reactions are kinetically controlled.

The failure of some first row transition metal difluorides to react with PF_5 , in MeCN, for example, NiF_2, is interpreted in terms of kinetic control of the reaction. $Ni(NCMe)_6^{2+}$ is known in MeCN solution, and the lattice energy of NiF_2 is very similar to that of FeF_2 and CuF_2 , which both react readily with PF_5 .

An accurate determination of the thermodynamic parameters for the reactions is necessary, to decide between the alternatives.

<u>Formation of Solvated Cations of Vanadium in MeCN Solution</u>.

a) <u>Lower Oxidation States</u>.

Vanadium metal is not oxidised to V(II) or V(III) by PF_5 , WF_6 or $NOPF_6$, in MeCN, to any appreciable extent. This is unexpected, as there is no thermodynamic barrier to reaction. This is illustrated by comparing the behaviour of vanadium with that of iron, which reacts with all of these reagents. A simple Born - Haber cycle for formation of M^{2+} is illustrated in the figure, using WF_6 as the oxidising agent,

$$\begin{tikzcd}
M(s) \arrow[d, "\Delta H_{at}"'] & + & 2\,WF_6(\text{solv.}) \arrow[r] \arrow[d, "\Delta H_{solv}"'] & M^{2+}(\text{solv.}) + 2\,WF_6^-(\text{solv.}) \\
M(g) \arrow[d, "I_1+I_2"'] & + & 2\,WF_6(g) \arrow[d, "2\,E_a"'] & \\
M^{2+}(g) & + & 2\,WF_6^-(g) \arrow[uur, "\Delta H_{solv}(M^{2+},\ 2\,WF_6^-)"'] &
\end{tikzcd}$$

where $\Delta H_{at.}(M)$ is the heat of atomisation of the metal, I_1 and I_2 are the first and second ionisation energies of the metal, $E_a(WF_6)$ is the electron affinity of WF_6 and $\Delta H_{solv.}$ is the heat of solvation of the various species. The cycles for PF_5 and $NOPF_6$ are similar. Assuming that entropy contributions for Fe and V are similar, the reactions are discussed in terms of enthalpies alone.

The enthalpy of atomisation of vanadium is larger than that of iron, 514 <u>vs</u>. 415 kJ mol^{-1} , at 298 K but the first two ionisation energies of V are 650 and 1413 kJ mol^{-1} while those of Fe are 759 and 1560 kJ mol^{-1} . If the solvation energies of V^{2+} and Fe^{2+} , in MeCN, are similar then oxidation of V to V(II) is more favourable than the oxidation of Fe to Fe(II) . Unless there is an unusual thermodynamic contribution in MeCN solution, such as a greater enthalpy of solvation for Fe(II) relative to V(II) or an important entropy effect, the failure of vanadium to react is attributed to kinetic control of the reaction. The activation energy barrier for oxidation of vanadium is large and the rate of reaction is very slow.

In the presence of species which can act as ligands to the metal ion, for example Cl_2 , Br_2 , earlier work found that vanadium metal is oxidised to V(III) .[21] The products are isolated as $[VCl_3(MeCN)_3]$MeCN and $[VBr_2(MeCN)_4]Br_3$. In the presence of the coordinating halogen atom, the transition state is stabilised, lowering the activation energy for reaction and the oxidation occurs readily. The product from the reaction of V with I_2 is formulated as $[V(MeCN)_6(I_3)_3]$, although it is not well characterised. The solid is unstable, and loses I_2 rapidly.

In the present study, an attempt was made to generate I_2^+ <u>in situ</u> and use the cation as an oxidising agent for vanadium. I_2^+ is generated by reaction of I_2 with PF_5 in IF_5 solution, to produce a blue, paramagnetic solution.[42] In this work, no blue colour is observed and there is apparently no reaction with vanadium metal.

b) Higher Oxidation-states.

Preliminary studies have shown that VOF_3 reacts with $(Me_3Si)_2O$, in MeCN, to produce red VO_2F .[25] VO_2F reacts with fluoride ion acceptor fluorides, such as PF_5 and AsF_5 , <u>via</u> a yellow intermediate, to produce blue solutions, whose electronic spectra are characteristic of VO^{2+} .[43]

The reaction with PF_5 was repeated in the course of the present study and similar results were obtained. The infra red spectrum of the blue solid product of the reaction (Table 2) is consistent with the formulation, $[VO(NCMe)_5][PF_6]_2$. There are apparently two bands due to C—C stretching in coordinated MeCN, consistent with the presence of two binding sites to the metal, <u>trans</u> or <u>cis</u> to O . A band is observed due to the A_{1g} mode of PF_6^- . This mode is formally infra red inactive, as there is no net change in dipole moment during the totally symmetric stretch. This does not necessarily imply coordination of the anion to the metal, destroying the symmetry of PF_6^- but may be due to packing effects in the solid lattice.

The electronic spectrum of the species is shown in Figure 3 . The band has $\bar{\nu}_{max}$ 15,200 (sh.) , 15,750 and 16,400 (sh.) cm^{-1} . This is rather different from the bands reported in the literature for $VO(NCMe)_5^{2+}$, which are at $\bar{\nu}_{max}$ 12,750 and 14,800 cm^{-1} .[44]

The splitting of the energy levels in a compressed C_{4v} symmetry has been calculated. This is illustrated in Figure 4 and this diagram has been used to assign the electronic spectrum of $VO(H_2O)_5^{2+}$.[45] Three transitions are expected but the highest energy transition , $b_2 \rightarrow a_1$, is sometimes not observed, for VO^{2+} species, as it is obscured by charge transfer absorptions. For example, for $VO(H_2O)_5^{2+}$, only the $b_2 \rightarrow e$, at 13,100 cm^{-1} and $b_2 \rightarrow b_1$, at 16,000 cm^{-1} , are observed.

Table 2.

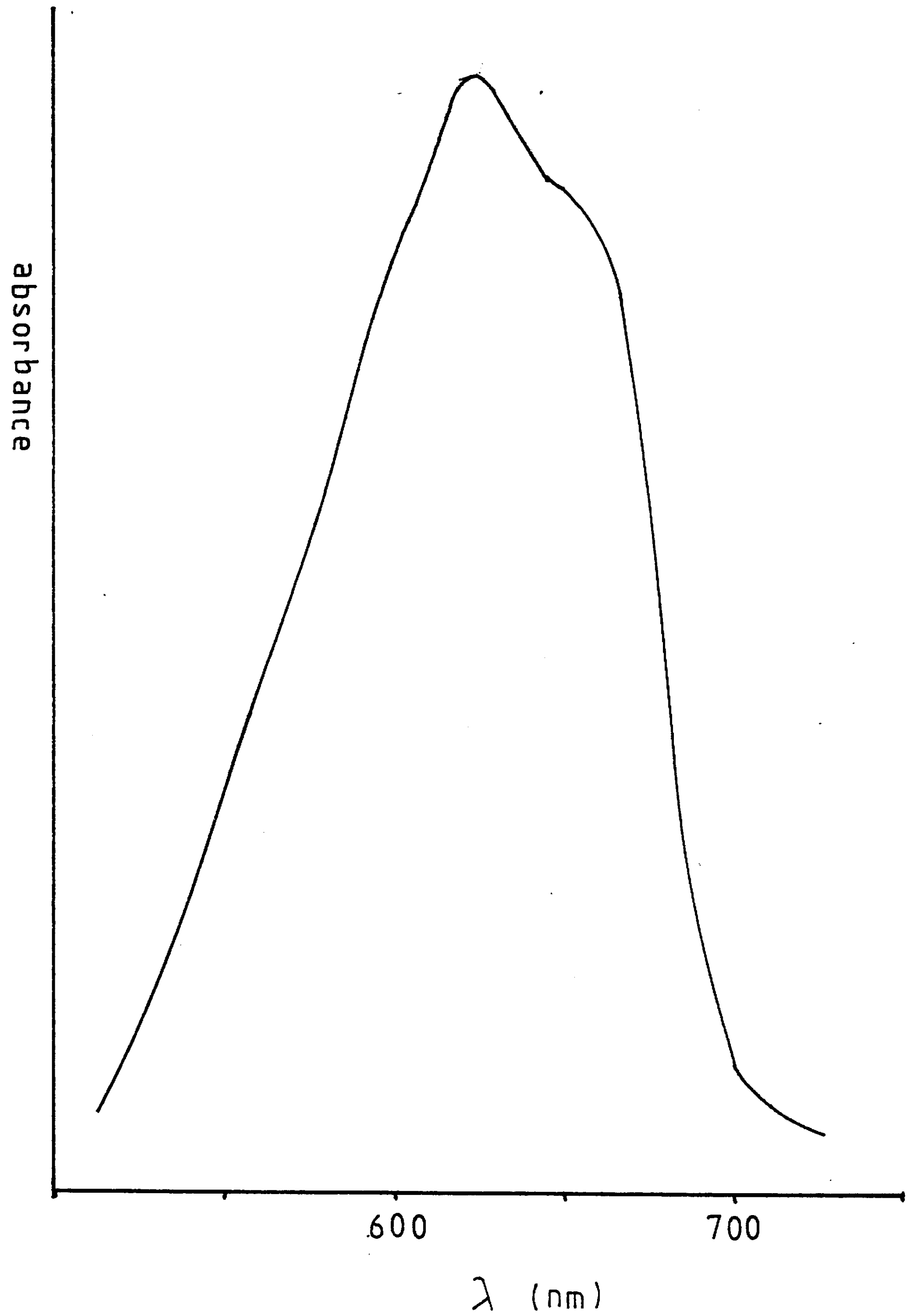
Solid State Infra-red Spectrum of $VO(NCMe)_5(PF_6)_2$.

wavenumber (cm^{-1})	assignment
2328 sh	comb. MeCN
2306 s	C≡N stretch
2260 w	comb. MeCN
1040 m	CH_3 rock
998 s	V=O stretch
954 m	C—C stretch
943 w	C—C stretch
835 vs	T_{1u} PF_6^-
740 w	A_{1g} PF_6^-
560 s	T_{1u} PF_6^-

sh, shoulder ; s, strong ; m, medium ; w, weak.

Figure 3.

Electronic Spectrum of VO^{2+} in MeCN.



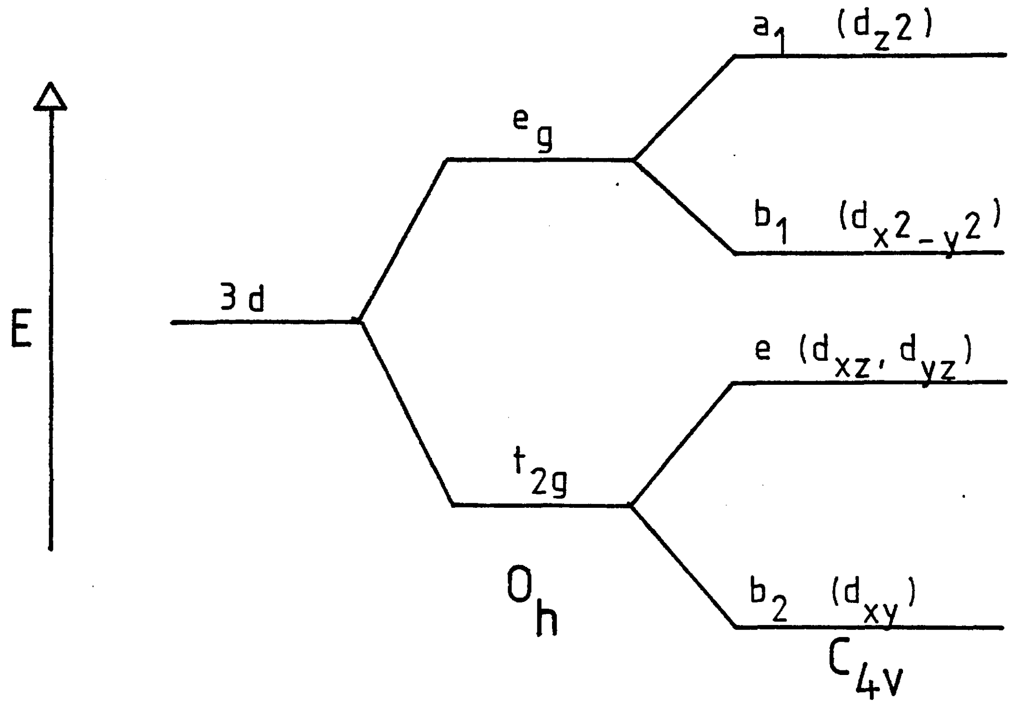


Figure 4. Energy levels in O_h and compressed C_{4v} symmetry.

The results of the present work, with a shift in position of the absorption bands and the evidence for an extra band, provided by a shoulder on the main peak, suggests that the VO^{2+} species does not possess a simple, compressed C_{4v} symmetry. This must be a result of coordination of an unknown species to the vanadyl ion, which alters the crystal field and the symmetry of the cation. The unknown species may arise from transfer of an oxygen from VO_2^+ to the solvent. It may be of the form $CH_3C(OH){=}NH$ rather than $CH_3CH{=}N{-}OH$, as there is no evidence from the infra red spectrum for a N—O stretch. The ^1H n.m.r. spectrum of the complex does not resolve this situation, due to the paramagnetic VO^{2+} which results in a very broad resonance.

The yellow intermediate formed in the initial stages of reaction is presumably solvated VO_2PF_6, the product of fluoride ion transfer from VO_2F to PF_5 . Solvated VO_2^+ is a relatively strong oxidising agent and presumably oxidises the solvent. In the reaction of $VO_2^+(aq)$ with thiourea, mentioned above, the final product of redox is $VO^{2+}(aq)$ which then complexes with excess ligand. [20] The oxygen is removed from the metal by protonation and loss as H_2O . This is not possible in the aprotic MeCN and the mechanism of oxygen abstraction is not clear.

The amount of PF_5 required for complete reaction is <u>ca</u>. 2.5 times the concentration of VO_2F . One equivalent is required to accept the fluoride ion of VO_2F and the other 1.5 equivalents reacts according to the equation

$$\tfrac{3}{2}\,PF_5(\text{solv.}) \longrightarrow PF_6^-(\text{solv.}) + \tfrac{1}{2}\,PF_3(g) \qquad (4)$$

The overall effect is to produce 2 equivalents of PF_6^- for every one of VO^{2+} and thereby balance the charge in the system. PF_3 is not detected as a product of the reaction but only a very small amount is formed and its presence is probably overlooked. It is not known which species is oxidised when PF_5 is reduced to PF_3 but a solvent associated species is the most likely candidate.

A great deal of work is necessary to fully characterise the products of the complex series of reactions of VO_2F with PF_5 . Until this is done it is impossible to provide a detailed mechanism for the formation of VO^{2+} .

Conclusions.

Solvated Fe(II) in acetonitrile is prepared by a variety of synthetic routes ; from oxidation of the metal or by transfer of fluoride ion from FeF_2 to an acceptor fluoride. The solvated salts, for example, $Fe(NCMe)_6(PF_6)_2$, are stable, in the absence of moisture and oxygen. The spectra of the salts are consistent with octahedrally coordinated Fe(II) and the magnetic moment shows the iron ion is high spin.

$Fe(NCMe)_6^{2+}$ cannot be oxidised to $Fe(NCMe)_6^{3+}$, in acetonitrile solution, either chemically or electrochemically. The oxidation potentials are such that MeCN will be oxidised before $Fe(NCMe)_6^{2+}$. The size of the Fe^{2+}– Fe^{3+} couple is a function of the stabilisation of Fe^{2+}, in MeCN solution, allied to a failure to stabilise Fe^{3+}, because of the high charge.

To effect oxidation of Fe(II) to Fe(III) it is necessary to introduce coordinating ligands to the system. Ligands, such as Cl^-, H_2O or O_2, coordinate to the metal and stabilise the Fe(III) state, thereby lowering the potential of the Fe^{2+}– Fe^{3+} couple.

The failure of MeCN to stabilise Fe^{3+} effectively results in a small enthalpy of solvation for this ion. The fluoride ion transfer reactions, from FeF_3 to PF_5 or WF_6, rely on a large $\Delta H_{solv.}$ to overcome the high lattice energy of FeF_3. As $\Delta H_{solv.}$ is small the transfer reaction may be thermodynamically forbidden.

Thallium(I) salts are prepared straightforwardly by fluoride ion transfer to acceptor fluorides. The Tl(I) salts are obtained from solution as solids, lacking coordinated MeCN, for example, $TlPF_6$.

$TlPF_6$ is partially oxidised by PF_5 or $NOPF_6$ to produce yellow species which contain coordinated MeCN and are presumably mixtures of Tl(I) and Tl(III) salts. It is not known if the Tl(I) : Tl(III) ratio is constant or if it is influenced by the reaction conditions.

Fluoride ion transfer from TlF_3 to PF_5 occurs, at least partially, but the characterisation of the products is prevented by decomposition of the solvent. In this case, $\Delta H_{solv.}$ of Tl^{3+} appears to be sufficiently large to aid in overcoming the high lattice energy of TlF_3 .

Vanadium metal is not oxidised, in MeCN, by PF_5 , WF_6 or $NOPF_6$. This is a result of kinetic control of the reaction. Comparison of the reactions of vanadium and iron shows that oxidation of V to V(II) is thermodynamically feasible, providing that there are no unusual solvation effects for V(II) in MeCN. To support the idea of very slow rates for oxidation of vanadium, small amounts of material can be isolated from reaction mixtures, using very long reaction times. Unfortunately, too little material is isolated to allow characterisation.

The reaction of VO_2F with PF_5 , in MeCN solution, is very complicated, involving formation of an intermediate presumed to be VO_2PF_6 (solvated). The final product is a blue VO^{2+} salt. The mechanism of this reaction is unknown and the system requires further study.

$NOPF_6$ is a useful oxidising agent, in MeCN solution. It is relatively powerful and the reduced product, NO gas, does not, under normal conditions, behave as a ligand and can be easily removed from the system.

Finally, preparation of solvated metal cations, in acetonitrile, is not always straightforward, with each system presenting its own problems. Some of the problems may be successfully circumvented, to allow formation of the desired cation and the chemistry of these species should prove very interesting.

Experimental.

All of the reactions, handling of reagents and products and the preparation of samples for spectroscopic analysis described throughout this work were carried out using a conventional high vacuum system (10^{-4} torr), an Ar or N_2 atmosphere glove box (Lintott Eng. Co. ; $H_2O < 10$ p.p.m.) or in apparatus modified for use with air and moisture sensitive materials. The vacuum system was constructed of Pyrex glass and the vacuum was provided by a rotary oil pump and mercury diffusion pump, working in series.

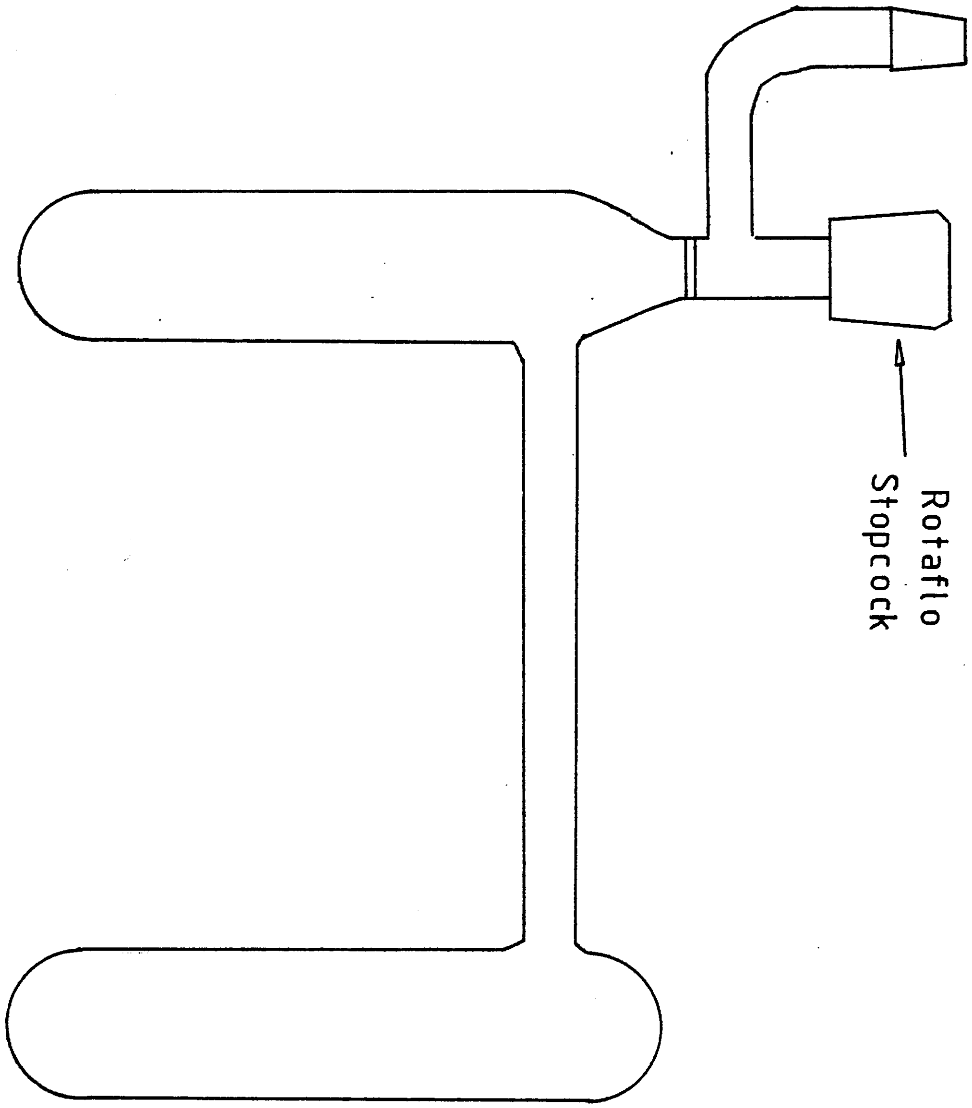
The reaction vessels were fitted with a P.T.F.E. stopcock (Rotaflo) and had two limbs, to allow solutions to be decanted under vacuum (Figure 5). Similar vessels, with one limb replaced by an n.m.r. tube, Pyrex capillary or 10 mm Spectrosil cell, were used to prepare solutions for spectroscopic examination. The flasks were evacuated and flamed out before use, to remove trace amounts of moisture.

Infra red spectra of solids were obtained, as Nujol or Fluorube mulls, between AgCl windows or, below 400 cm^{-1} , polythene windows. The i.r. spectra of solutions or liquids were obtained in throwaway AgCl cells (Beckman R.I.I.C. Ltd.) or from a film between AgCl windows. Raman spectra of solids and solutions were obtained from samples in sealed Pyrex capillaries.

The instruments used in measuring the spectra were as follows :- Raman, Spex Ramalog ; infra red, Perkin Elmer 577 ; electronic, Beckman 5270 ; n.m.r., J.E.O.L. C 60HL at 60 (^{1}H) or 56.4 MHz (^{19}F), Perkin Elmer R-32 at 90 MHz (^{1}H) , Varian XL-100 at 40.5 MHz (^{31}P) or 94.15 MHz (^{19}F) and a J.E.O.L. FX 90Q at 28.4 MHz (^{65}Cu) ,

Figure 5.

Typical Reaction Vessel.



26.5 MHz (^{63}Cu) and 40.5 MHz (^{31}P) . Chemical shifts were referenced externally, with respect to Me_4Si (^{1}H) , CCl_3F (^{19}F) and H_3PO_4 (^{31}P) and the results were reported as positive to low field. Microanalyses were by Malissa and Reuter, West Germany.

WF_6 , PF_5 , AsF_5 and IF_5 (Fluorochem Ltd. or Ozark Mahoning) were purified by low temperature trap-to-trap distillation over NaF and stored over NaF, at 77 K. IF_5 was additionally distilled over mercury metal and shaken for several hours, to remove I_2 . MeCN (Hopkin and Williams Ltd. ; reagent grade) was refluxed, twice over CaH_2 and twice over P_2O_5 , for eight hour periods, degassed and stored, in vacuo, over activated 4A molecular seives. MeCN, for use in electrochemical studies, was purified by a literature method involving successive refluxes over $AlCl_3$, $KMnO_4$, Li_2CO_3 , $K_2S_2O_7$ and CaH_2 .[3a] The purity was checked electrochemically. CD_3CN (C.E.A. Ltd. ; isotopic purity 99.6%) was degassed and stored, in vacuo, over activated 4A molecular seives. $MeNO_2$ (B.D.H. Ltd. ; reagent grade) was refluxed for 24 hours over activated charcoal, redistilled, degassed and stored, in vacuo, over 4A molecular seives. $P(OMe)_3$ (Hartman Organic Chemicals) was distilled, dried over sodium metal, degassed and stored, in vacuo, over 4A molecular seives.

Solid metal fluorides were used as received :- TlF (Ventron Alfa, 97%) ; TlF_3 (Cerac Inc., 99.9%) ; FeF_2 (Pierce and Warriner Ltd., 95%); FeF_3 , MnF_2 , VOF_3 (all Fluorochem Ltd.) and CuF_2 (Ozark Mahoning, 99.5%). $NOPF_6$ (Fluorochem Ltd.) ; vanadium (99.8%) and iron (99.99%) metal (both Goodfellow Metals Ltd.) were also used without further purification. Silver and copper metal, supplied as thin sheets, were treated with dilute HNO_3 , washed with water, dried, abraded and cut into small strips before use. Cl_2 (B.D.H. Ltd., 99.9%) was dried over P_2O_5 , *in vacuo*. 2,2'-bipyridyl and 2,9-dimethyl-1,10-phenanthroline (AnalaR [illegible]) were used as supplied. The solids were weighed in the glove box, using a Sartorius balance. The error in weighing was estimated to be ± 2 mg.

The experimental methods used, in the course of this work, are very similar throughout and are detailed only for the first reaction or where an unusual technique was used.

Preparation of Solvated Iron Cations in MeCN Solution.

1. Reactions of Iron Metal.

a) with tungsten hexafluoride.

Iron metal (0.08g ; 1.4 mmol) was added to one limb of a two limbed vessel, in the glove box. The vessel had been previously evacuated and flamed out on the vacuum line. The loaded vessel was attached to the vacuum line and re-evacuated. MeCN (4 ml) and WF_6 (0.31g ; 1.05 mmol) were distilled into the second limb of the flask, at 77 K and the system was allowed to warm to room temperature. After twenty minutes, the surface of the metal had a white coating. After 1.5 hours, the metal had a flaky, light brown solid deposit on its surface which was dislodged by disturbing the unreacted iron metal, using a magnet. After 24 hours, the reaction had gone to completion and the product was isolated, as a light brown solid, by cooling the limb containing the volatile material to 77 K and sealing the limb containing the solid. The solid was transferred to the glove box. A sample was characterised, by microanalysis, as *hexakis(acetonitrile) iron(II) hexafluorotungstate(V)* (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 %.)

A portion of the solid was added to a vessel with an n.m.r. tube as side arm. The flask was evacuated and MeCN (2 ml) added which produced a brown solution. The ^1H n.m.r. spectrum consisted of a broad solvent resonance, due to paramagnetic Fe(II) ; no signal was obtained on the ^{19}F n.m.r. spectrum. To obtain the solid state Raman spectrum, some of the solid was powdered and added to a Pyrex capillary, which was attached to a Rotaflo stopcock. The vessel was evacuated and the capillary sealed. The infra red spectrum was obtained as a Nujol mull. The results of the vibrational spectroscopic studies are listed in Table 1.

b) <u>with phosphorus pentafluoride</u>.

Iron wire (0.04g ; 0.72 mmol) was placed in a reaction vessel with a Spectrosil cell as side arm. MeCN (4 ml) and PF_5 (1.5 mmol) were distilled into the flask at 77 K . The quantity of PF_5 was measured by determining the pressure of a fixed volume of gas. The system was warmed to room temperature and was shaken for fourteen days. At the end of this period, the electronic spectrum consisted of a broad asymmetric band at $\bar{\nu}_{max}$ 11,050 cm^{-1} with a shoulder at 9,900 cm^{-1} , typical of $Fe(NCMe)_6^{2+}$ (Figure 1) .[7]

The reaction mixture was shaken for a further ten days and the concentration of product, monitored by observing the electronic spectrum, continued to increase. At the end of this time, the volatile material was removed by vacuum distillation, to leave a pale yellow solid as product. The infra red spectrum of the solid had bands due to coordinated solvent, appearing at the same position as those listed in Table 1, and there were bands due to PF_6^- , at $\bar{\nu}_{max}$ 835 cm^{-1} and 560 cm^{-1} .

c) with nitrosonium hexafluorophosphate.

Iron wire (0.1g ; 1.8 mmol) was placed in one limb of a two limbed reaction vessel, and $NOPF_6$ (0.45g ; 2.6 mmol) was added to the other. MeCN (4 ml) was distilled on to the $NOPF_6$ at 77 K and allowed to warm. The solid dissolved readily, to give a golden yellow solution. On tipping the solution on to the iron, a vigorous effervescence commenced from the metal surface, due to release of a non condensible gas, and the solution turned light brown in colour. Over a few hours, the solution became dark brown, most of the metal disappeared and a large amount of white solid was deposited from solution. The solution phase was decanted and the volatile material was back-distilled under vacuum, to leave an off-white solid as the product. The solid was characterised by infra red and electronic spectroscopy and by microanalysis as hexakis(acetonitrile) iron(II) hexafluorophosphate (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 %).

In the course of this reaction, a small amount of dark brown solid, insoluble in MeCN, was produced. This was present in too small an amount to be characterised, but was removed from the major product by careful decanting of the solution.

When this reaction was repeated in $MeNO_2$ solution, under the same conditions, rapid oxidation of iron occurred but the products were not characterised. This was due to the production of purple, polymeric material, formed during the exothermic reaction.

Polymerisation occurred even below room temperature. When the reaction mixture was cooled to 77 K , it became dark green.

2. Reactions of Iron(II) Fluoride.

a) with phosphorus pentafluoride.

In a typical reaction, FeF_2 (0.25g ; 2.8 mmol) was added to a two limbed flask, in the glove box and MeCN (5 ml) and PF_5 (5.0 mmol) were distilled in, at 77 K. The vessel was warmed and shaken for 24 hours at room temperature, at which time the solution was yellow. The solution was decanted from the solid residues and the volatile material was back-distilled to leave a white solid as the product. The solid was characterised, by infra red and electronic spectroscopy and by microanalysis, as hexakis(acetonitrile) iron(II) hexafluorophosphate, (Found, C, 24.1 ; H, 3.1 ; F, 38.3 ; Fe, 9.6 ; N, 14.0 ; P, 10.55 %. $C_{12}H_{18}F_{12}FeN_6P_2$ requires C, 24.3 ; H, 3.0 ; F, 38.5 ; Fe, 9.4 ; N, 14.2 ; P, 10.5 %).

The ^1H n.m.r. spectrum of the white solid, in MeCN solution consisted of a broadened solvent peak, shifted upfield from the normal resonance position. The ^{19}F n.m.r. spectrum had a 1:1 doublet, due to PF_6^- at -74 p.p.m., J_{P-F} 710 Hz. The magnetic moment of the salt was measured, in MeCN solution, using Evans' method. Me_4Si was used as the inert reference material (10% v./v. in MeCN) . The solutions of the Fe(II) salt were made up, in the glove box, by weighing the salt, dissolving and diluting to 5 ml. The concentrations of the solutions were 17 mmol dm^{-3} , 25 mmol dm^{-3} and 51 mmol dm^{-3} . A sealed capillary, containing the reference solution, was placed in an n.m.r. tube (5 mm o.d.) , a solution of the salt added and the tube sealed with a serum cap.

The ^1H n.m.r. spectrum was run and the frequency shift for Me_4Si was measured in Hz. The shifts caused by the iron(II) salt were 30 Hz, 48 Hz and 74 Hz respectively. The average magnetic moment was calculated to be 5.7 B.M. and the error in the result was estimated as ± 0.4 B.M.

b) with arsenic pentafluoride.

FeF_2 (0.2g ; 2.13 mmol) was placed in a reaction vessel and MeCN (5 ml) and AsF_5 (4 mmol) were distilled in at 77 K . The flask was warmed and shaken for 24 hours at room temperature. The solution, at this stage, was brown and a white solid and a small amount of brown solid had precipitated from solution. A portion of the solids was obtained by decanting and removing volatile material. The more soluble brown solid was removed from the mixture by adding MeCN and decanting the resulting brown solution. The infra red spectrum of the white solid, obtained by this method, was consistent with the formulation, $Fe(NCMe)_6(AsF_6)_2$. The peaks due to coordinated solvent were in the same position as those listed in Table 1 and the spectrum had peaks at $\bar{\nu}_{max}$ 700 cm^{-1} and 400 cm^{-1} , due to AsF_6^- . The AsF_6^- salt was less soluble than the corresponding PF_6^- salt.

c) with iodine pentafluoride.

FeF_2 (0.08g ; 0.85 mmol) was placed in a flask with a Spectrosil cell as side arm and IF_5 (0.95g ; 4.25 mmol) and MeCN (4 ml) were distilled in, at 77 K . The vessel was warmed to room temperature and shaken for several days. There was no evidence for formation of $Fe(NCMe)_6^{2+}$. When shaken for a further period of days, the solution slowly turned light brown in colour and had a peak in the electronic spectrum, at $\bar{\nu}_{max}$ 21,900 cm^{-1} . No products were isolated from solution.

3. Reactions of Iron(III) Fluoride.

a) with tungsten hexafluoride.

FeF_3 (0.12g ; 1.1 mmol) was added to a reaction vessel and WF_6 (0.32g ; 11 mmol) and MeCN (4 ml) were distilled in, at 77 K . After shaking for twenty days at room temperature, the solution had become golden yellow and a small amount of yellow-brown solid was obtained by decanting the solution and removing the volatile material. Insufficient material was produced to allow characterisation.

b) with iodine pentafluoride.

FeF_3 (0.23g ; 2.0 mmol) was placed in a reaction vessel and IF_5 (9.4g ; 42 mmol) and MeCN (5 ml) was distilled in, at 77 K . After shaking for twenty days at room temperature, the solution was colourless. Decanting the solution and removing the volatile material, left a small amount of viscous yellow oil. This was not characterised.

The reaction was repeated, in the absence of MeCN, using similar amounts of FeF_3 and IF_5 . After prolonged shaking, a small amount of white solid was produced from the solution by removing the volatile material. The solid was not characterised.

4. Oxidation of Solvated Iron(II) Salts.

a) with nitrosonium hexafluorophosphate.

$Fe(NCMe)_6(PF_6)_2$ (0.34g ; 0.57 mmol) was added to one limb of a two limbed flask and $NOPF_6$ (0.1g ; 0.56 mmol) was placed in the other limb. MeCN (4 ml) was distilled into the vessel and the two reagents dissolved. Adding the Fe(II) solution to the $NOPF_6$ solution produced no visible sign of reaction. Removing the volatile material left a white solid whose infra red spectrum showed it to be a mixture of the starting materials. A similar reaction , carried out in a vessel with a Spectrosil cell as side arm, became deep red in colour and the $Fe(NCMe)_6^{2+}$ peak disappeared from the electronic spectrum. A brown solid product was isolated, whose infra red spectrum had bands due to NO^+ , $\bar{\nu}_{max}$ 2,340 cm^{-1} , and OH , $\bar{\nu}_{max}$ 3,300 and 1,620 cm^{-1} . The flask was found, subsequently, to have a small hole in the glass. A further reaction was carried out in a similar vessel and no change in the concentration of $Fe(NCMe)_6^{2+}$ was observed.

b) with chlorine.

$Fe(NCMe)_6(PF_6)_2$ (0.1g ; 0.17 mmol) was added to a vessel with a Spectrosil cell as side arm and MeCN (4 ml) was distilled in, at 77 K , followed by Cl_2 (0.12g ; 3.3 mmol) . On warming to room temperature, the solution became yellow.

The electronic spectrum consisted of a band due to $Fe(NCMe)_6^{2+}$ and a tail into an intense band, the spectrum going off scale at 25,000 cm^{-1} . Over a period of twenty hours, the band due to $Fe(NCMe)_6^{2+}$ decreased in intensity as several other bands grew in, at $\bar{\nu}_{max}$ 14,600 ; 16,150 ; 16,500 ; 18,900 ; 22,500 ; 27,800 ; 30,300 and 40,800 cm^{-1} (Figure 2) . These bands were assigned to $FeCl_4^-$.[7] Over a further two days, the absorption due to $Fe(NCMe)_6^{2+}$ disappeared as the bands due to $FeCl_4^-$ continued to increase. No Cl_2 was recovered from the reaction mixture and g.l.c. analysis of the solvent indicated that CH_2ClCN and CCl_3CN

were present. [33]

c) by electrochemistry.

The electrochemical behaviour of $Fe(NCMe)_6(PF_6)_2$ was studied by cyclic voltammetry. The experimental method was that given in the appendix. No oxidation wave was identified, even upon scanning to the solvent limit.

Preparation of Solvated Thallium Cations in MeCN Solution.

1. Reaction of Thallium(I) Fluoride with PF_5.

a) TlF (1.04g ; 4.7 mmol) was placed in a reaction vessel and MeCN (5 ml) and PF_5 (4.4 ml) were distilled in, at 77 K . On warming to room temperature, the solution was pale yellow in colour and, on shaking for several hours, became colourless. The amount of solid had increased. The solution phase was decanted and the volatile material was removed, to leave a small amount of white solid as the product. This was characterised, by microanalysis, to be thallium(I) hexafluorophosphate, (Found, F, 32.2 ; P, 8.6 ; Tl, 58.4 %. F_6PTl requires F, 32.6 ; P, 8.6 ; Tl, 58.5 %) .

The infra red spectrum of the solid had bands at $\bar{\nu}_{max}$ 830 cm^{-1} and 560 cm^{-1} assigned to PF_6^- but no bands due to coordinated MeCN. The Raman spectrum had bands at $\bar{\nu}_{max}$ 742 cm^{-1} and 470 cm^{-1} due to PF_6^- . The ^1H n.m.r. spectrum of the reaction mixture had only a sharp peak due to the solvent and the ^{19}F n.m.r. spectrum consisted of a 1:1 doublet, at -73 p.p.m., J_{P-F} 707 Hz , due to PF_6^- .

b) TlF (0.66g ; 3 mmol), MeCN (5 ml) and PF_5 (6 mmol) were added together and the flask shaken for ten hours at room temperature. After this time, the solution was bright yellow and, by decanting and removing volatile material, a very soluble lemon solid was isolated. The infra red spectrum of the solid had bands due to PF_6^-, at $\bar{\nu}_{max}$ 830 cm^{-1} and 560 cm^{-1}, and coordinated MeCN, at $\bar{\nu}_{max}$ 2,300 cm^{-1}. Microanalysis of the solid showed the presence of small amounts of C, H and N (Found, C, 1.04 ; H, 0.16 ; F, 31.8 ; N, 0.6 ; P, 9.0 ; Tl, 57.0 % , Ratio F : P : Tl ; 6.0 : 1.05 : 1.0).

2. Reaction of Thallium(III) Fluoride.

a) with phosphorus pentafluoride.

TlF_3 (0.62g ; 2.4 mmol) was added to a reaction vessel and MeCN (5 ml) and PF_5 (7.2 mmol) were distilled in, at 77 K . The flask was shaken for two days at room temperature, after which time the solution was deep red-brown in colour. By decanting and removing the volatile material, the product was isolated as a dark brown solid.

The infra red spectrum of the solid had bands due to PF_6^-, at $\bar{\nu}_{max}$ 830, 740 and 560 cm^{-1}, and coordinated MeCN, at $\bar{\nu}_{max}$ 2,275, 2,305 cm^{-1}, as well as bands due to N—H groups, $\bar{\nu}_{max}$ 3,300 and 1,750 - 1,600 cm^{-1}. The ^{19}F n.m.r. spectrum consisted of a 1:1 doublet, at -73 p.p.m., J_{P-F} 710 Hz , due to PF_6^-.

By carrying out the reaction using a shorter time, the product was isolated as a cream coloured solid, but in very small yield. The infra red spectrum had bands due to PF_6^- and coordinated MeCN, $\bar{\nu}_{max}$ 2,290 cm^{-1} and 2,320 cm^{-1}.

b) with iodine pentafluoride.

TlF_3 (0.22g ; 0.85 mmol) was placed in a reaction vessel and IF_5 (3g ; 14 mmol) was distilled in, at 77 K . On warming to room temperature, the liquid phase was an olive green suspension. MeCN (3 ml) was added but the suspension remained. The flask was shaken for three days and the product obtained, by decanting and removing volatile material, was a small amount of a non volatile liquid. MeCN and PF_5 were added to the liquid and a yellow solution was formed. On shaking the mixture for one minute, a deep red colour formed and the involatile product was a dark red viscous liquid. This was not investigated further.

3. Oxidation of $TlPF_6$ in MeCN Solution. by Nitrosonium Hexafluorophosphate.

$TlPF_6$ (0.25g ; 0.73 mmol) was added to one limb of a two limbed vessel and $NOPF_6$ (0.53g ; 3.0 mmol) was placed in the other limb. MeCN (4 ml) was distilled on to the $NOPF_6$ which resulted in formation of a yellow solution. Upon tipping the solution on to $TlPF_6$, a gas was evolved and a golden yellow solution was formed. A lemon coloured solid was isolated from the solution.

The infra red spectrum of the solid had bands due to PF_6^- and NO^+ , $\bar{\nu}_{max}$ 2,335 cm^{-1} and the solution infra red spectrum had a band, at $\bar{\nu}_{max}$ 1,860 cm^{-1} , assigned to solvated NO^+ . The ^{19}F n.m.r. spectrum consisted of a 1:1 doublet, -70 p.p.m., J_{P-F} 710 Hz , due to PF_6^- .

Preparation of Solvated Vanadium Cations in MeCN Solution.

1. Reactions of Vanadium Metal.

a) with phosphorus pentafluoride.

V metal (1.0g ; 19 mmol) was placed in a reaction vessel and MeCN (5 ml) and PF_5 (7 mmol) were added. On shaking the flask, at room temperature, for several days, there was no visible sign of reaction and no product was isolated from the reaction mixture.

b) with tungsten hexafluoride.

V metal (0.38g ; 7.5 mmol) was placed in a reaction vessel and MeCN (5 ml) and WF_6 (0.76g ; 2.6 mmol) were added. The flask was shaken for several days at room temperature and the solution became faint brown in colour. Removing volatile material from the solution phase left a small amount of green-brown solid. A further portion of WF_6 (1.35g ; 4.6 mmol) was added and the flask shaken for several more days but too little solid was obtained to allow identification.

c) with nitrosonium hexafluorophosphate.

V metal (0.51g ; 10 mmol) and $NOPF_6$ (0.55g ; 3.1 mmol) were placed in a reaction vessel and MeCN (5 ml) was added. On warming, slight effervescence was observed. The flask was shaken for ten hours and a blue solution was found. Removing the volatile material left an inhomogeneous blue solid. The infra red spectrum of the blue solid had peaks due to NO^+ , PF_6^- and coordinated MeCN. The Raman spectrum had bands due to NO^+ and PF_6^- . The ^1H n.m.r. spectrum of the blue solid consisted of a broadened solvent resonance and the ^{19}F n.m.r. spectrum was a 1:1 doublet, due to PF_6^- .

d) with iodine in iodine pentafluoride.

Iodine (0.49g ; 1.93 mmol) was distilled into a reaction vessel and IF_5 (30g ; 0.14 mol) was added. A deep red solution resulted. PF_5 (3 mmol) was added, to bring about formation of I_2^+ but no colour change was observed. Upon adding the mixture of I_2 / IF_5 / PF_5 to V (0.1g ; 1.9 mmol), there was no visible sign of a reaction. After shaking for ten days, the volatile material was distilled off, leaving unreacted V metal as the product.

2. Reaction of VO_2F with PF_5.

VO_2F (0.05g ; 0.5 mmol), prepared by reaction of VOF_3 with $(Me_3Si)_2O$,[25] was placed in a reaction vessel and MeCN (5 ml) and PF_5 (0.25 mmol) were added. On warming to room temperature, a yellow solution was formed, containing a great deal of suspended solid. As this gradually cleared from solution, the colour changed to blue. The electronic spectrum of the solution had peaks at $\tilde{\nu}_{max}$ 15,200 (sh), 15,750 and 16,400 (sh) cm^{-1} . Adding successive aliquots of PF_5 (0.25 mmol) resulted in a decrease in the amount of solid and an increase in intensity of the absorptions until a total of 1.25 mmol PF_5 had been added. At this stage, all the solid had disappeared. When the volatile material was removed, the product was isolated as a dark blue solid. The infra red spectrum of the blue solid had bands assigned to PF_6^- , coordinated MeCN and V=O (Table 2).

Other Reactions.

1. Reaction of Manganese(II) Fluoride with PF_5 in MeCN Solution.

MnF_2 (0.25g ; 2.7 mmol), MeCN (5 ml) and PF_5 (5 mmol) were added together in a reaction vessel. The flask was shaken for 24 hours, after which the solution was yellow. The shaking was continued for a further 24 hours and the solution became light brown. An off white solid was obtained by removing the volatile material. The infra red spectrum of the solid showed the presence of PF_6^- and coordinated MeCN, $\tilde{\nu}_{max}$ 2,320 , 2,295 , 1,045 , 943 cm^{-1} . There were also bands, at $\tilde{\nu}_{max}$ 3,250 and 1,750 - 1,600 cm^{-1} , due to N—H groups. On the basis of the spectra, the product was formulated as $Mn(NCMe)_6(PF_6)_2$.

2. Reaction of Silver Metal with $NOPF_6$ in MeCN Solution.

Ag (0.25g ; 2.3 mmol) and $NOPF_6$ (0.46g ; 2.63 mmol) were added together in a reaction vessel and MeCN (5 ml) was distilled in. On warming to room temperature, vigorous bubbling commenced, the metal was consumed and the solution became yellow. Freezing the solution to 77 K resulted in formation of a deep red colour and this colour change was reversible.

A white solid was obtained by removing the volatile material. The infra red spectrum of the solid had bands due to PF_6^- , coordinated MeCN, at $\bar{\nu}_{max}$ 2,318 and 2,290 cm^{-1} , and NO^+ , at $\bar{\nu}_{max}$ 2,338 cm^{-1} . The Raman spectrum had bands, at $\bar{\nu}_{max}$ 742, 568 and 470 cm^{-1} , assigned to PF_6^- , at $\bar{\nu}_{max}$ 2,321 , 2,293 , 2,237 , 941 and 392 cm^{-1} , due to coordinated MeCN, and at $\bar{\nu}_{max}$ 2,346 cm^{-1} , due to NO^+ . The ^1H n.m.r. spectrum, in MeCN solution, consisted of a sharp singlet, due to the solvent resonance and the ^{19}F n.m.r. spectrum was a 1:1 doublet, at −75 p.p.m., J_{P-F} 720 Hz , assigned to PF_6^- . On the basis of the spectra, by comparison with other silver salts, the product was formulated as $Ag(NCMe)_2PF_6$.[11]

3. $NOPF_6$ in MeCN Solution.

$NOPF_6$ (0.5g ; 2.9 mmol) was placed in a flask and MeCN (5 ml) was added, producing a golden yellow solution. The solution infra red spectrum had bands due to PF_6^- , MeCN and a band, at $\bar{\nu}_{max}$ 1,860 cm^{-1}, assigned to NO^+(solvated). Removing the volatile material left a white solid, whose infra red spectrum was identical to that of $NOPF_6$, $\bar{\nu}_{max}$ (NO^+) 2,338 cm^{-1} .

4. Chlorine in MeCN Solution.

Chlorine (0.077g ; 1.1 mmol) was added to MeCN (4 ml) in a vessel fitted with a Spectrosil cell as side arm. On warming the solution became yellow. The electronic spectrum consisted of a tail into an intense band, going off scale at 27,000 cm^{-1} . After four days at room temperature, the solution had gone colourless. The electronic spectrum had shoulders, at $\bar{\nu}_{max}$ 28,500 and 33,000 cm^{-1} , and went off scale, at $\bar{\nu}_{max}$ 36,400 cm^{-1} . Upon adding a further portion of Cl_2 , the solution became yellow but again became colourless, on standing for 12 hours.

CHAPTER TWO

Substitution Reactions of Solvated Iron(II) Cation in Acetonitrile Solution.

Introduction.

The most useful method of determining the mechanism of a reaction is the study of kinetics. While an experimental rate law may not always provide an unambiguous answer as to the mechanism which operates, it is a very important step on the way to understanding the nature of the reaction.

The simplest reaction which can be envisaged for a metal cation in solution, is the substitution of a neutral, monodentate ligand for a coordinated solvent molecule in the primary coordination sphere of the metal ion. The common situation of a hexasolvated cation is illustrated;

$$MS_6^{n+} + L \longrightarrow MS_5L^{n+} + S \qquad (1)$$

where S represents solvent, M, the cation and L, the incoming ligand. If L and S are the same species, then equation 1 describes solvent exchange at the cation.

As this is the simplest situation a great deal of effort has been expended upon investigation of reactions of this type. The majority of these studies have concerned, naturally, the most common solvent, water and a great deal is now known about the behaviour of a wide variety of cations of varying charge and size in aqueous solution.[46]

These reactions fall into two main classes, dissociative and associative, and each of these can be further subdivided to give the following four mechanisms for ligand substitution.

Dissociative (D) Mechanism.

This is also termed the S_N1(lim.) mechanism. In this mechanism a five coordinate transient intermediate is formed which is sufficiently long lived to discriminate between potential nucleophiles. This nucleophile may be an incoming ligand or a solvent molecule.

$$MS_6^{n+} \underset{+S}{\overset{-S}{\rightleftharpoons}} MS_5^{n+} \xrightarrow{L} MS_5L^{n+} \tag{2}$$

The rate determining step is the breaking of the M—S bond to generate the five coordinate intermediate.

<u>Dissociative Interchange (I_d) Mechanism</u>.

This mechanism involves formation of a transition state which has considerable extension of a M—S bond; the incoming ligand has little effect. The mechanism does, however, involve an association of the solvated metal ion and ligand, prior to substitution, forming an outer sphere complex. The incoming ligand is thus suitably placed to enter the inner coordination sphere of the metal ion, once bond breaking to the solvent has been achieved; this is the interchange step.

$$\begin{tikzcd} MS_6^{n+} \arrow[r, shift left, "+L"] & MS_6,L^{n+} \arrow[l, shift left, "-L"] \arrow[r] & {[MS_5—S,L]^{n+\ddagger}} \arrow[dl] \\ & MS_5L^{n+} + S & \end{tikzcd} \tag{3}$$

The breaking of an M—S bond is still rate determining.

<u>Associative Interchange (I_a) Mechanism</u>.

This is very similar to the I_d mechanism, the difference being that the association of the reacting species assumes a greater importance in determining the rate of the reaction. The incoming ligand is weakly bound to the metal in the transition state and has a greater influence on the M—S bond breaking step.

$$\begin{tikzcd} MS_6^{n+} \arrow[r, shift left, "+L"] & MS_6,L^{n+} \arrow[l, shift left, "-L"] \arrow[r] & {[MS_6—L]^{n+\ddagger}} \arrow[dl] \\ & MS_5L^{n+} + S & \end{tikzcd} \tag{4}$$

Associative (A) Mechanism.

This is also termed the S_N2(lim.) mechanism. In this mechanism a seven coordinate transient intermediate is formed which then reacts to form the products.

$$MS_6^{n+} \underset{-L}{\overset{+L}{\rightleftharpoons}} MS_6L^{n+} \longrightarrow MS_5L^{n+} + S \qquad (5)$$

The rate determining step of this mechanism is formation of the M—L bond and is thus dependent upon the nature of L.

There are no clear cut boundaries between these four mechanisms. A continuous gradation exists, extending from one limiting extreme to another and encompassing a large number of reactions. The assignment of a particular mechanism to a reaction reflects the extent of interaction of the incoming ligand with the solvated metal ion in the transition state; from no interaction in the D mechanism to complete interaction in the A mechanism.

The correlation of a reaction with a particular mechanism may be achieved by a number of means. These include, determination of the rate law of the reaction, comparing the rate of a reaction of a metal ion with different ligands, especially in solvent exchange, and evaluating the activation parameters of the reaction, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$.

Some time ago, it was recognised by Eigen, Wilkins and co-workers that the rates of reaction and the activation parameters for complex formation are generally similar for a given metal ion in aqueous solution.[47] This is particularly true for divalent metal ions reacting with neutral, unidentate ligands. The rates and activation parameters are also very similar to those determined for solvent exchange at that metal ion. This suggests that a rate determining dissociative step is involved. The rates, however, are dependent to some extent upon the nature and concentration of the incoming ligand and so the mechanism cannot be purely dissociative. This led to the proposal that there is a rapid equilibrium of reactants prior to substitution to produce an outer sphere complex. This, then is the I_d mechanism, and is sometimes termed the Eigen - Wilkins mechanism. A large body of evidence now exists for the operation of this mechanism in aqueous solution, particularly from investigation of reactions of nickel(II) and it seems to apply to virtually all first row M(II) cations. Ni(II) is particularly favoured as the rates of reaction of this ion are in a range that can be monitored conveniently.

Recently studies of complex formation in non aqueous media have been carried out and there is evidence that Ni(II) reactions in a number of solvents follow the Eigen - Wilkins mechanism.[48] A paucity of data exists for reactions of other M(II) cation in non aqueous media which prevents generalisation of the Eigen - Wilkins mechanism to the reactions of these ions in the non aqueous solvents.

The aim of this study is to investigate the substitution behaviour of $Fe(NCMe)_6^{2+}$ in MeCN with a number of potential ligands. Although the solvated cation has been known for some time, with a variety of counter ions, the substitution behaviour has not been investigated previously.

The ligands chosen for the investigation were the monodentate phosphorus donor, $P(OMe)_3$, and the bidentate nitrogen donor, 2,2'-bipyridyl.

Iron-trimethyl phosphite species have received a great deal of attention in recent years, principally due to the interesting steric and electronic properties of the ligand. The alkyl phosphites are less sterically demanding than the corresponding alkyl phosphines and, due to the more electronegative substituents on the phosphorous, have greater ability as π- acceptors.[49]

A great deal of work stems from the preparation of $Fe\{P(OMe)_3\}_5$ by sodium amalgam reduction of $Fe[P(OMe)_3]_3Cl_2$ in the presence of excess $P(OMe)_3$.[50] This species is very interesting both physically and chemically. It is fluxional in solution but at 168 K exhibits an A_2B_3 second order spectrum on the ^{31}P n.m.r., indicative of a trigonal bipyramidal geometry.[51] There is no fast exchange between $Fe[P(OMe)_3]_5$ and free $P(OMe)_3$. The chemistry of the species is dominated by the high electron density on the iron atom. The relatively basic iron atom can be protonated or alkylated to produce six coordinate species.

$$Fe[P(OMe)_3]_5 \quad + \quad MeI \longrightarrow [Fe\{P(OMe)_3\}_5Me]^+ + I^- \qquad (6)$$

$Fe[P(OMe)_3]_5$ may also be oxidised by Ag(I) or tropylium salts in MeCN. The product of two consecutive one electron transfers is $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$.[52] $Fe[P(OMe)_3]_6{}^{2+}$ was prepared from $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ and $P(OMe)_3$ by precipitation from solution by addition of a similarly sized anion. Recently a number of species corresponding to the general formula $[Fe\{P(OMe)_3\}_5X][Y]$ have been prepared, either by oxidation of $Fe[P(OMe)_3]_5$ (for $X=H,Me,CF_3$) or by addition of $P(OMe)_3$ to $Fe(THF)_2X_2$ (for $X=Cl,Br,I$). A $^{31}P-\{^1H\}$ n.m.r. study of these six coordinate iron species finds the spectra to be complex second order,

AB_4 patterns.

$Fe[P(OMe)_3]_6^{2+}$ was also prepared as the BPh_4^- salt, by refluxing anhydrous $FeCl_2$ and $NaBPh_4$ in the presence of excess $P(OMe)_3$ for four hours in MeOH solution.[53] The product is a white precipitate which has low solubility in all common solvents. Very recently reports of zero valent, five coordinate $Fe\{P(OMe)_3\}_3$(diene) species have appeared in the literature (e.g. $Fe\{P(OMe)_3\}_3$(butadiene)) which have been prepared by metal atom evaporation techniques.[54] These species are fluxional and have been used to examine the mechanisms for exchange in five coordinate species.

While the present work was in progress, the synthesis of iron (II) phosphite complexes by reaction of $FeCl_2.2H_2O$, $NaBH_3CN$ and excess $P(OMe)_3$ in acetonitrile solution was reported.[55] The product was $Fe\{P(OMe)_3\}_4(BH_3CN)_2$ in both cis and trans isomers. An interesting result of this study is that metathesis yields a cis : trans ratio of 30 : 70 while electrochemical synthesis produces a cis : trans ratio of 65 : 35.

The products of the reaction of $P(OMe)_3$ and $Fe(NCMe)_6^{2+}$ in MeCN were thus of great interest.

Reactions of metal ions with multidentate ligands have long proved a fruitful area for study. Kinetics of formation reactions of metal ions with di-imine ligands, such as 2,2'-bipyridyl (bipy), and 1,10-phenanthroline (phen), have been studied in aqueous, non aqueous and mixed aqueous solvents. In water the formation reactions conform to the Eigen - Wilkins mechanism with rate determining interchange, followed by rapid ring closure to give the chelate product.[56]

$$MS_6{}^{2+} + L\text{-}L \rightleftharpoons [MS_6{}^{2+},L\text{-}L] \xrightarrow{r.d.s.} MS_5L\text{-}L^{2+} + S \qquad (7)$$

$$MS_5L\text{-}L^{2+} \xrightarrow{fast} MS_4L_2{}^{2+} + S \qquad (8)$$

(r.d.s. is the rate determining step)

In non aqueous media the situation is less clear. While the Eigen - Wilkins mechanism operates for the reaction of Ni^{2+} with bipy in EtOH, in DMSO the r.d.s. shifts to being the ring closing step and the solvent competes successfully with the non ligated N for Ni^{2+} in the intermediate, $MS_5L\text{-}L^{2+}$.[57]

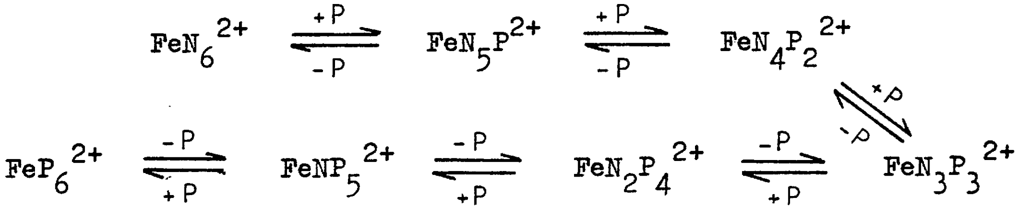
Complexes of the iron(II) ion with di-imine ligands have been well characterised in both aqueous and non aqueous solvents. Indeed the distinctive electronic spectrum of $Fe(bipy)_3{}^{2+}$ forms the basis for an analytical determination of the concentration of iron(II). The slow hydrolysis of $Fe(phen)_3{}^{2+}$ derivatives has been studied in both aqueous[58] and mixed aqueous[59] media, and a mechanism involving an association step has been postulated to account for the observed results. The formation reactions of iron - bipyridyl and iron - phenanthroline complexes have also been studied in aqueous solution. The formation in aqueous solution of both $FeL_3{}^{2+}$ [60] and, more recently, FeL^{2+} [61] has been observed and the kinetic results rationalised. Direct comparison of results in other solvents may thus be made. A study of the reaction of $Fe(NCMe)_6{}^{2+}$ with 2,2'-bipyridyl in MeCN should be informative in that results may yield information, not only on the mechanism of substitution at $Fe(NCMe)_6{}^{2+}$, but also on the mechanism of reaction of metal ions with bidentate ligands in MeCN.

Results and Discussion.

Reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$ in MeCN.

The reaction of $P(OMe)_3$ with $Fe(NCMe)_6^{2+}$ proceeds via a stepwise substitution of $P(OMe)_3$ for coordinated MeCN, as shown in scheme 1.

Scheme 1.



where N represents NCMe and P represents $P(OMe)_3$.

$^{31}P-\{^1H\}$ n.m.r. study.

The stepwise nature of the substitution reaction is clearly shown by the $^{31}P-\{^1H\}$ n.m.r. study. A number of species which give rise to only a single peak on the $^{31}P-\{^1H\}$ n.m.r. spectrum are involved, which could lead to ambiguity in assignment of a single peak to a specific isomer. This problem is solved by correlating the appearance of the singlets with the appearance of the second order multiplet spectra which are also involved, and which can be assigned unambiguously to a specific isomer. For example, in the early stages of the reaction a singlet is observed which is increasing in intensity. Allied to this is the appearance of an AB_2 multiplet due to the meridional isomer of $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$. Thus the singlet can be assigned with confidence to the facial isomer of the same complex ion. By extending this approach it is possible to identify the seven species listed in Table 1.

Table 1.

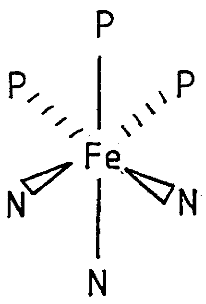
$^{31}P-\{^{1}H\}$ N.M.R. Data for $[FeN_{6-n}P_n]^{2+}$ Cations (n = 2-6).

(N= NCMe , P= $P(OMe)_3$)

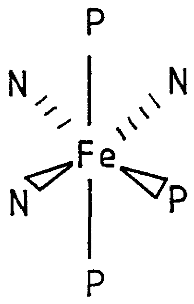
Cation	Spin System	Chemical Shifts (p.p.m.)		Coupling Const. (Hz)
		δA	δB	J_{A-B}
$FeN_4P_2^{2+}$	A_2	155.4		
fac-$FeN_3P_3^{2+}$ [a]	A_3	157.7		
mer-$FeN_3P_3^{2+}$	AB_2	156.6	145.6	137.1
cis-$FeN_2P_4^{2+}$ [a]	A_2B_2	158.6	147.0	137.2
trans-$FeN_2P_4^{2+}$	B_4		148.7	
$FeNP_5^{2+}$	AB_4	157.7	150.1	129.2
FeP_6^{2+}	B_6		148.8	

[a] more abundant isomer

The structure of the isomers are :-

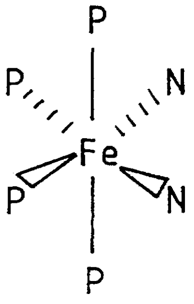


fac

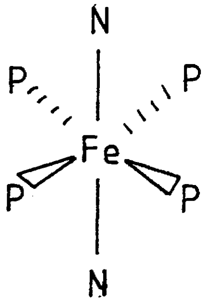


mer

$[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$



cis

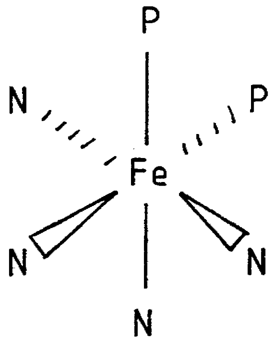


trans

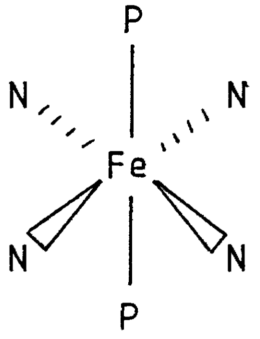
$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$

In addition to the signals due to the species listed in Table 1, a broad singlet is observed due to the exchange of free $P(OMe)_3$ with $P(OMe)_3$ associated with the metal ion. The exchange can be slowed by reducing the temperature of the solution.

Under the conditions of the experiment, the first two steps of scheme 1 are too fast to be observed but the subsequent steps can be followed conveniently. The chemical shift of the singlet, by comparison with spectra of the later species, suggests that the complex exists as the <u>cis</u> isomer rather than the <u>trans</u>.



cis



trans

$[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$

The decay of this species to produce $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ is fast, being complete in about 20 minutes at room temperature. The remaining steps are slow, production of $[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$ requiring several hours at room temperature. Formation of $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ requires two days at room temperature but can be accelerated by heating the sample at 335 K for several hours. This is effectively the final product of the substitution reaction. Although there is evidence for $Fe\{P(OMe)_3\}_6^{2+}$ after several weeks of reaction, the amount is so small and the rate of reaction so very slow that the reaction can be considered complete at the five substituted stage.

As the theory behind second order spectra is well established,[62] it is possible to calculate spectra for particular values of chemical shift and coupling constant. Figure 2 shows calculated A_2B_2 and AB_4 spectra along with the spectrum of the reaction mixture at a late stage of the reaction. A comparison of calculated frequencies of transition with experimentally observed results is listed in Table 2 for AB_2 , A_2B_2 and AB_4 spectra. Representative spectra at different reaction times are illustrated in Figure 1.

The very slow rate of substitution at the sixth coordination position is presumably a function of the bulk of the $P(OMe)_3$ ligand, relative to the 'rod like' NCMe . The large $P(OMe)_3$ ligand finds it sterically very difficult to enter the primary coordination sphere of the metal ion, at the expense of a solvent molecule, under the mild conditions used in these reactions. The relative rates of these steps may be appreciably varied by altering the conditions of temperature and concentration. No attempt was made to extract

Figure 1.

Representative ^{31}P N.M.R. Spectra for the Reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$

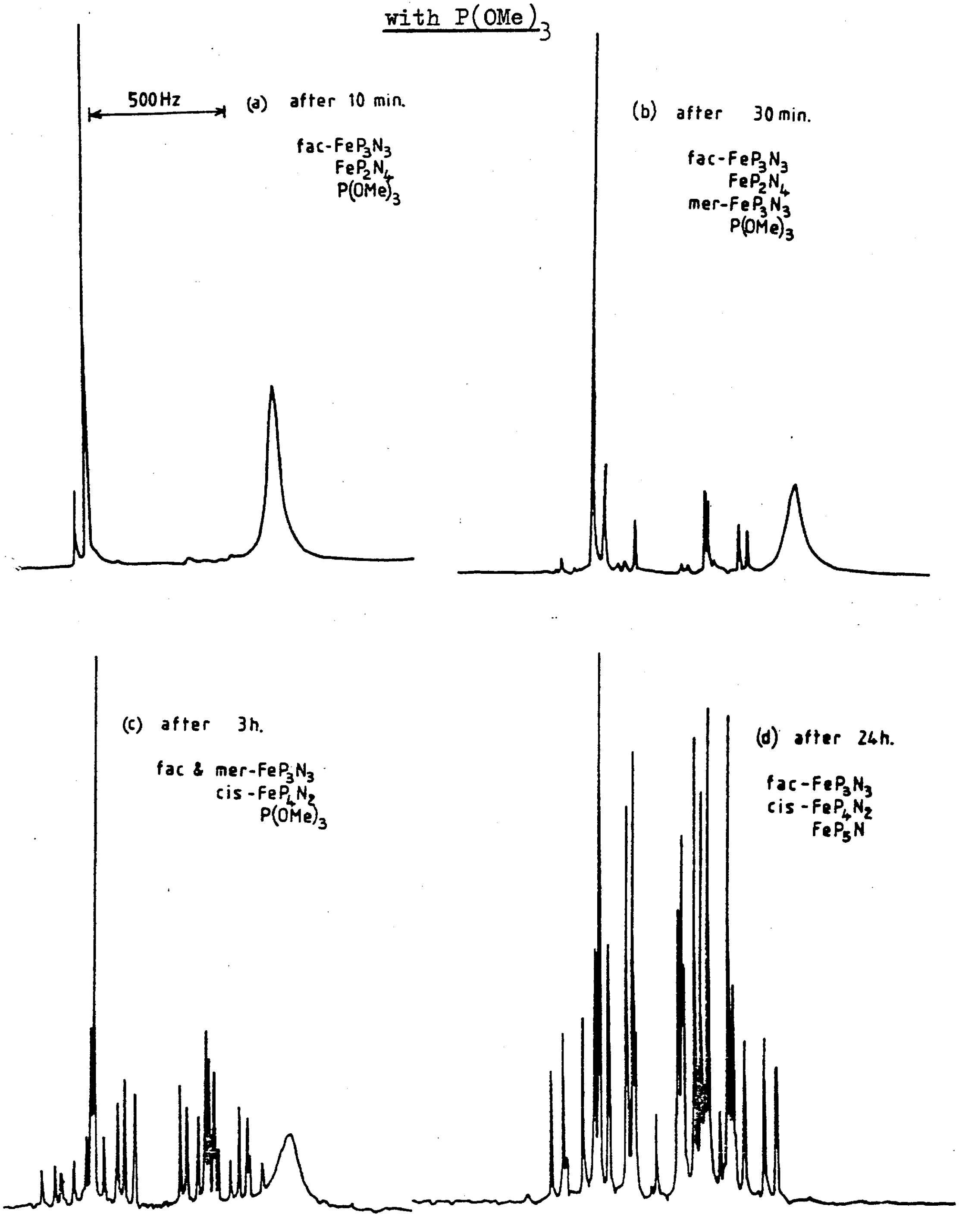


Figure 2.

Observed and Calculated ^{31}P N.M.R. Spectra for the Reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$.

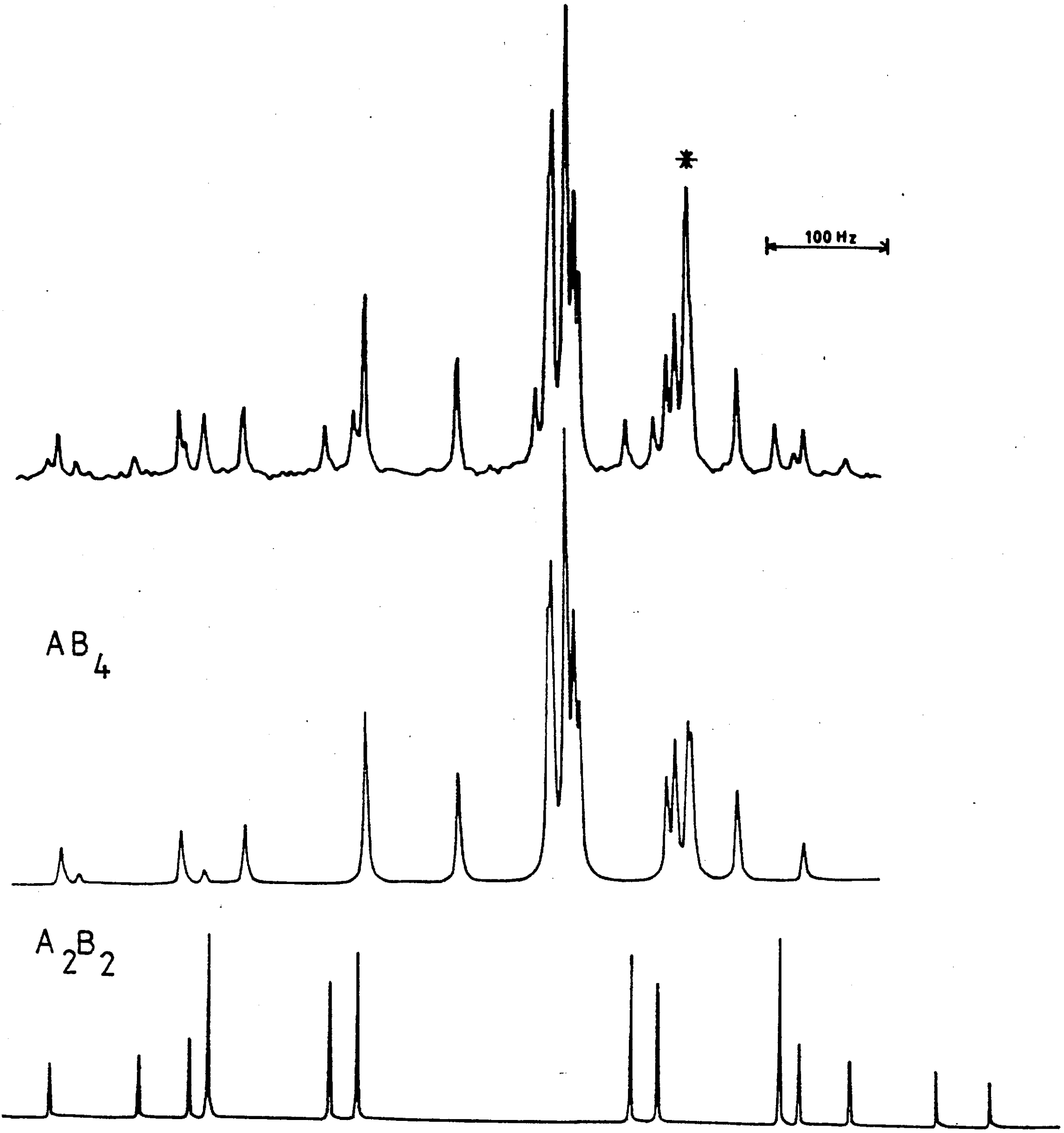


Table 2.

Observed and Calculated Frequencies of Second Order Spectra for AB_2, A_2B_2 and AB_4 Systems.

(AB_2 data from mer-$[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$, A_2B_2 from cis-$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$ and AB_4 from $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$).

AB_2 obs.	AB_2 calc.
6498.5	6498.0
b	6384.4
6343.2	6343.6
6229.7	6229.9
5961.9	5962.0
5949.9	5950.6
5836.8	5836.9
5807.3	5807.5
a	5414.5

A_2B_2 obs.	A_2B_2 calc.
6587.1	6587.3
6543.8	6543.7
6471.0	6471.0
6429.1	6429.2
6413.1	6413.1
6312.8	6312.9
6290.0	6290.2
6063.8	6063.9
6041.1	6041.2
5941.0	5941.0
5924.7	5924.9
5882.7	5883.1
5810.2	5810.4
5766.5	5766.8

AB_4 obs.	AB_4 calc.
a	6686.7
a	6614.8
6545.5	6545.3
a	6531.3
6445.3	6445.3
a	6427.0
6392.7	6392.6
6392.5	6292.6
6216.0	6216.4
6140.0	6141.2
6137.0	6131.2
6126.0	6127.5
6125.0	6126.1
6119.1	6120.3
6114.5	6115.9
6042.5	6044.0
6035.2	6036.9
6024.6	6026.2
6021.7	6023.2
5984.0	5985.5
5929.2	5930.6

[a] too weak to be observed

[b] hidden by more intense peak

quantitative rate data from the n.m.r. experiments.

Experimentally, under normal conditions, it is found that, kinetically, $P(OMe)_3$ will substitute in a position trans to NCMe rather than trans to $P(OMe)_3$. In the formation of $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$, the fac isomer is formed first. As the reaction proceeds the mer isomer becomes more important, presumably as a result of rearrangement of the fac isomer. The mer isomer is stereochemically less hindered than the fac.

$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$ exists mainly as the cis isomer, very little trans being formed in spite of the fact that the cis form is sterically more hindered. When the volatile material is removed from a reaction mixture in which the $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ species is dominant, the major product is trans-$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$. The product is being precipitated from a very concentrated solution of $P(OMe)_3$ and this alters the kinetics of the reaction. The preferred isomer is now the trans which, once precipitated, cannot isomerise.

The ^{31}P chemical shift of the $P(OMe)_3$ complexes exhibit a shift to lower field with respect to free $P(OMe)_3$. The range of shifts fall into two distinct groups :- complexes which have $P(OMe)_3$ trans to NCMe, have ^{31}P chemical shifts in the range +15 - +19 p.p.m. from free $P(OMe)_3$ and complexes which have $P(OMe)_3$ trans to $P(OMe)_3$ have ^{31}P chemical shifts in the range +5 - +10 p.p.m.. There is apparently no single explanation to account for the isomer ratios and the chemical shift data.

Electronic Spectroscopic Study.

The complexes $[Fe\{P(OMe)_3\}_n(NCMe)_{6-n}]^{2+}$ (n = 2-6) are low spin.

This is shown by a combination of the n.m.r. spectra, which indicate that all the observed species are diamagnetic, and the electronic spectra of the species.

The electronic spectra of $[Fe\{P(OMe)_3\}_{6-n}(NCMe)_n]^{2+}$, (n = 1-5) are given in Table 3. The two bands which are observed for each of these species are assigned, by analogy with the isoelectronic $Co\{P(OMe)_3\}_6^{3+}$, as the two spin-allowed transitions of a low spin, d^6 species ; $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$.[63]

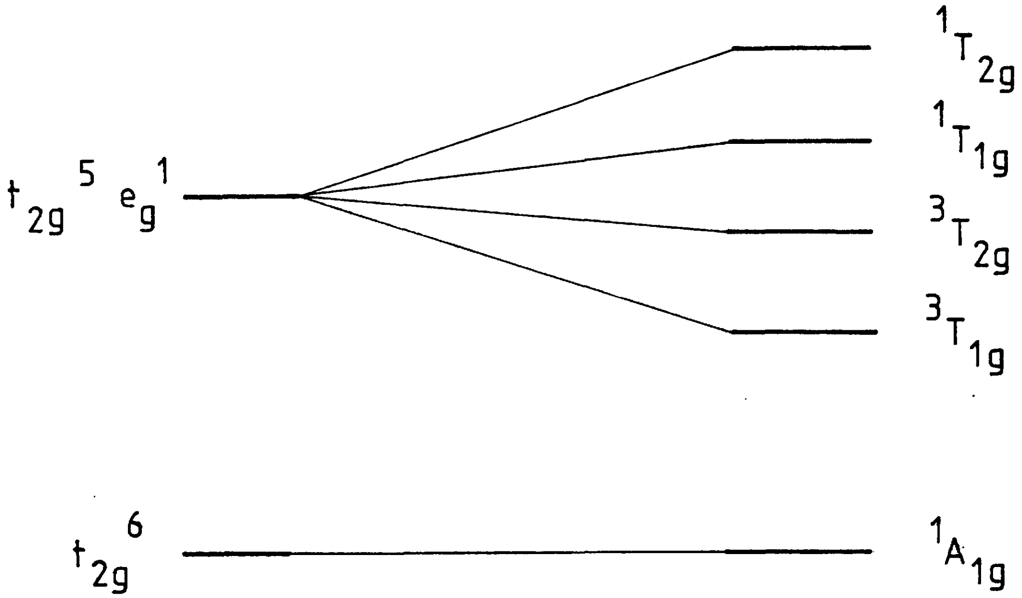


Figure 3. Energy levels for d^6 species in a strong O_h ligand field.

The predicted splitting of these bands as the symmetry is lowered from O_h is not observed for $[Fe\{P(OMe)_3\}_{6-n}(NCMe)_n]^{2+}$ although the bands are not Gaussian, which suggests that the splitting is present but not resolved. The high ligand field splitting caused by alkyl phosphites is not explicable in terms of σ-donor character alone. It is attractive to propose that extra stability of the $^1A_{1g}$ level takes place via a metal - phosphorus π-bonding interaction.

The extinction coefficients of the two bands of

Table 3.

Electronic Spectra of $FeP_nN_{6-n}^{2+}$ (n = 1-5).

(N = NCMe , P = $P(OMe)_3$)

Cation	Assignment [a] (cm^{-1})	
	$^1T_{1g} \leftarrow {}^1A_{1g}$	$^1T_{2g} \leftarrow {}^1A_{1g}$
$FePN_5^{2+}$	23,300 (320)	29,000 (270)
$FeP_2N_4^{2+}$	24,100 (290) [b]	29,400 (250) [b]
$FeP_3N_3^{2+}$	24,900 (300) [b]	30,000 (250) [b]
$FeP_4N_2^{2+}$	25,650 (350)	30,700 (240)
FeP_5N^{2+}	26,700 (370)	32,700 (250)

extinction coefficients ($dm^3\ mol^{-1}\ cm^{-1}$) are given in brackets

[a] see text

[b] estimated

$[Fe\{P(OMe)_3\}_{6-n}(NCMe)_n]^{2+}$ (ε ca. 300 $dm^3\ mol^{-1}\ l^{-1}$) are rather large for d-d transitions but are in keeping with values for $Co\{P(OR)_3\}_6^{3+}$ (ε ca. 10^2- 10^3 $dm^3\ mol^{-1}\ l^{-1}$). The bands may be borrow$\{P(OR)_3\}_6^{3+}$ intensity from the charge transfer bands which are visible at higher energy ($>$ 37,000 cm^{-1}). In the $[Fe\{P(OMe)_3\}_{6-n}(NCMe)_n]^{2+}$ complexes, the reduction in symmetry from O_h may also play a part, by relaxing the selection rules and allowing the 'mixing-in' of orbitals of different quantum number.

Kinetic Studies of the Substitution Reactions.

a) Stopped-flow Spectrophotometry.

The principles of the stopped-flow method are given in the appendix. The traces from the reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$ in the region 17,000 to 33,000 cm^{-1}, show the formation of a single species. This is assumed to be $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$, the product of the first step of scheme 1. The alternative explanation is that the species is a complex of higher substitution, for example $[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$, and the earlier complex is not observed.

Formation of an unobservable intermediate complex does not seem reasonable and the species is assigned as $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$. The electronic spectrum of the species (Table 3), is consistent with a low spin complex and so the high spin - low spin transition occurs upon substitution of one $P(OMe)_3$ ligand for NCMe.

The reaction was studied under pseudo first order conditions, $[P(OMe)_3]$ was in, at least, a fifty fold excess over $[Fe(NCMe)_6^{2+}]$. The rate of formation of $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ is,

$$\text{Rate} = \frac{d[FeN_5P^{2+}]}{dt} = k_{obs}[FeN_6^{2+}] \qquad (9)$$

where P = $P(OMe)_3$ and N = NCMe .

$$[\mathrm{Fe}^{\mathrm{II}}]_{\mathrm{total}} = [\mathrm{FeN}_6{}^{2+}] + [\mathrm{FeN}_5\mathrm{P}^{2+}]$$

thus,

$$\frac{d[\mathrm{FeN}_5\mathrm{P}^{2+}]}{dt} = -\frac{d[\mathrm{FeN}_6{}^{2+}]}{dt} = k_{\mathrm{obs}}[\mathrm{Fe}^{\mathrm{II}}]_{\mathrm{total}} - k_{\mathrm{obs}}[\mathrm{FeN}_6{}^{2+}] \qquad (10)$$

k_{obs} is determined from a plot of $-\log(\mathrm{O.D.}_{\infty} - \mathrm{O.D.}_t)$ <u>vs</u>. t, using data obtained by monitoring the reaction at 23,300 and 29,000 cm^{-1}, the absorption maxima of $[\mathrm{Fe}\{\mathrm{P(OMe)}_3\}(\mathrm{NCMe})_5]^{2+}$.

The electronic spectrum of $[\mathrm{Fe}\{\mathrm{P(OMe)}_3\}(\mathrm{NCMe})_5]^{2+}$ is obtained from the point by point spectrum of the absorbance change, at 10 nm intervals, determined using the stopped-flow technique. The spectrum is found to be in good agreement with the spectrum of the first species observed in the conventional spectrophotometric study.

The values of k_{obs} for the formation of the complex, at 23,300 and 29,000 cm^{-1}, are listed in Table 4, as a function of $[\mathrm{P(OMe)}_3]$. The quoted errors are those evaluated from a least squares determination of the data. In general there is good agreement between the values from the two wavelengths. The plot of k_{obs} (averaged for the two wavelengths) against $[\mathrm{P(OMe)}_3]$ is given in Figure 4. This shows that the reaction has a complex rate dependence upon the concentration of $\mathrm{P(OMe)}_3$, k_{obs} tending to a limiting value at high $[\mathrm{P(OMe)}_3]$.

Behaviour of this type can be accounted for by a rate expression of the form ,

$$\mathrm{Rate} = k_{\mathrm{obs}}[\mathrm{FeN}_6{}^{2+}] = \frac{a[\mathrm{FeN}_6{}^{2+}][\mathrm{P}]}{1 + b[\mathrm{P}]} \qquad (11)$$

for some constants, a and b .

When $b[\mathrm{P}] < 1$, the expression becomes ,

$$\mathrm{Rate} = k_{\mathrm{obs}}[\mathrm{FeN}_6{}^{2+}] = a[\mathrm{FeN}_6{}^{2+}][\mathrm{P}] \qquad (12)$$

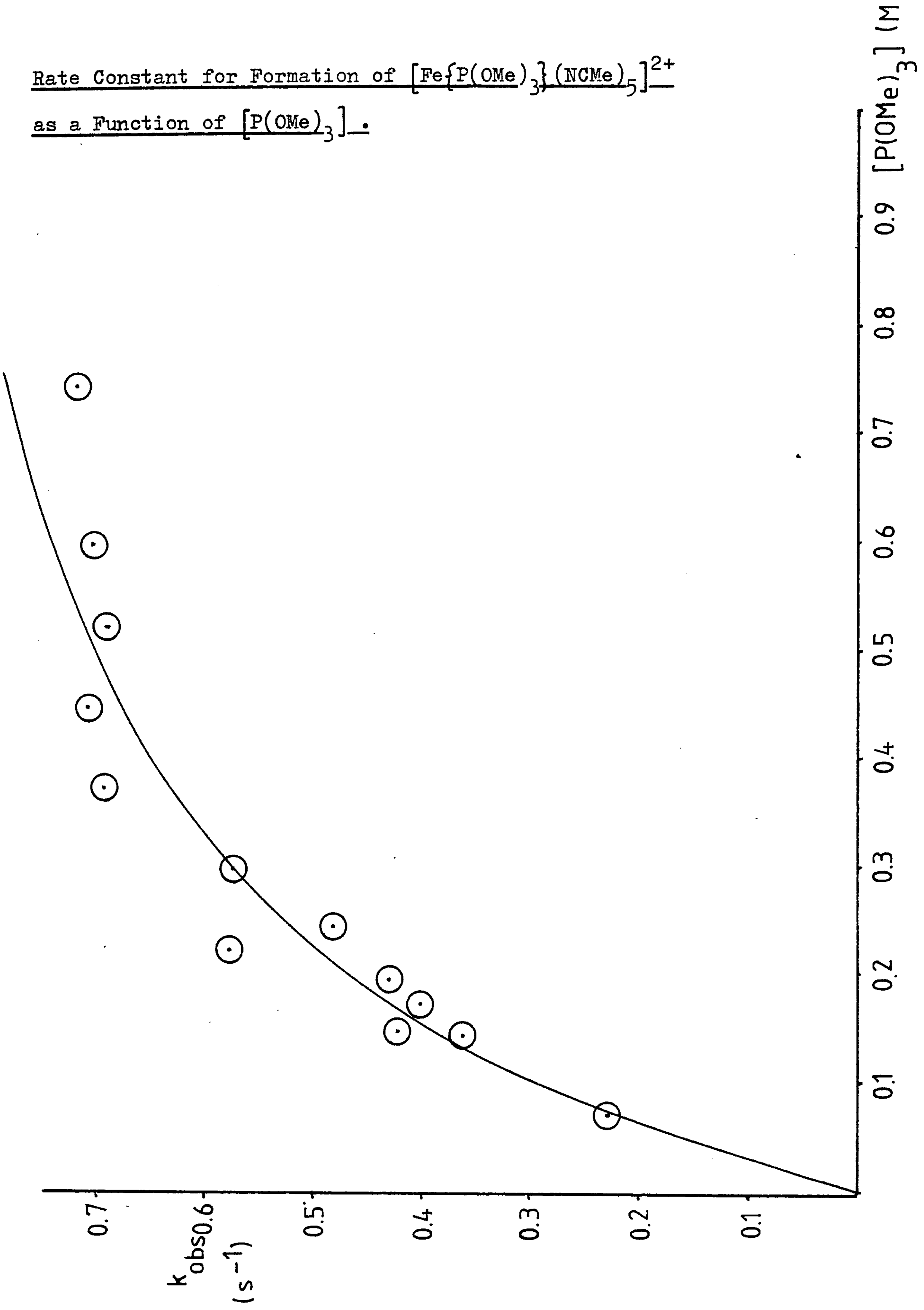
Table 4.

Observed Rate Constants for Formation of $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$.

$[P(OMe)_3]$ (mol l^{-1})	k_{obs} (s^{-1})	
	at 23,300 cm^{-1}	at 29,000 cm^{-1}
0.075	0.226 ± 0.007	0.233 ± 0.004
0.150	0.398 ± 0.007	0.460 ± 0.009
0.150	0.350 ± 0.005	0.372 ± 0.008
0.175	0.396 ± 0.003	0.399 ± 0.003
0.200	0.443 ± 0.004	0.413 ± 0.004
0.225	0.582 ± 0.005	0.588 ± 0.008
0.250	0.492 ± 0.003	0.500 ± 0.005
0.300	0.573 ± 0.005	0.598 ± 0.007
0.375	0.674 ± 0.007	0.680 ± 0.006
0.450	0.690 ± 0.009	0.758 ± 0.012
0.525	0.671 ± 0.009	0.753 ± 0.011
0.600	0.633 ± 0.008	0.753 ± 0.010
0.750	0.734 ± 0.007	0.733 ± 0.014

Figure 4.

Rate Constant for Formation of $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ as a Function of $[P(OMe)_3]$.



At low $[P(OMe)_3]$, the reaction is thus first order in $P(OMe)_3$ and second order overall. As $[P(OMe)_3]$ increases and $b[P]$ becomes greater than 1 , expression (11) becomes ,

$$\text{Rate} \quad = \quad k_{obs}[FeN_6{}^{2+}] \quad = \quad \frac{a}{b}[Fe^{2+}] \qquad (13)$$

The rate is now independent of $[P(OMe)_3]$ and is first order overall. Values for a and b may be determined by using a reciprocal plot , $\frac{1}{k_{obs}}$ versus $\frac{1}{[P]}$. From (11) ,

$$k_{obs} \quad = \quad \frac{a[P]}{1 + b[P]} \qquad (14)$$

$$\frac{1}{k_{obs}} \quad = \quad \frac{1}{a[P]} + \frac{b}{a} \qquad (15)$$

A reciprocal plot has gradient $\frac{1}{a}$ and intercept b/a. The reciprocal plot of the data in Table 4 is shown in Figure 5. $\frac{1}{a}$ is found to be 0.240 and b/a 0.97 . These data come from a least squares fit of the straight line which has a correlation coefficient of 0.973 .

The observed rate law, expression (11), can be explained by a number of the mechanisms for substitution which were outlined above. The D , I_d and I_a mechanisms can all give rise to this type of rate law. The rate law is thus of little help in assigning a mechanism. This situation can be resolved by comparing the rate of this substitution reaction with the rate of solvent exchange at $Fe(NCMe)_6{}^{2+}$, which has been determined by ^{14}N n.m.r. studies.[64] The rate constants for this exchange, and for exchange of solvent at Fe^{2+} , in other media are given in Table 5 . These rates of exchange are all very fast and the rate of exchange of MeCN is <u>ca</u>. 10^6 times faster than the rate of substitution of $P(OMe)_3$ on $Fe(NCMe)_6{}^{2+}$ (k_{obs} of the order of 1 s^{-1} at the upper limit) .

Figure 5.

Reciprocal Plot of Observed Rate Constant vs. $[P(OMe)_3]$.

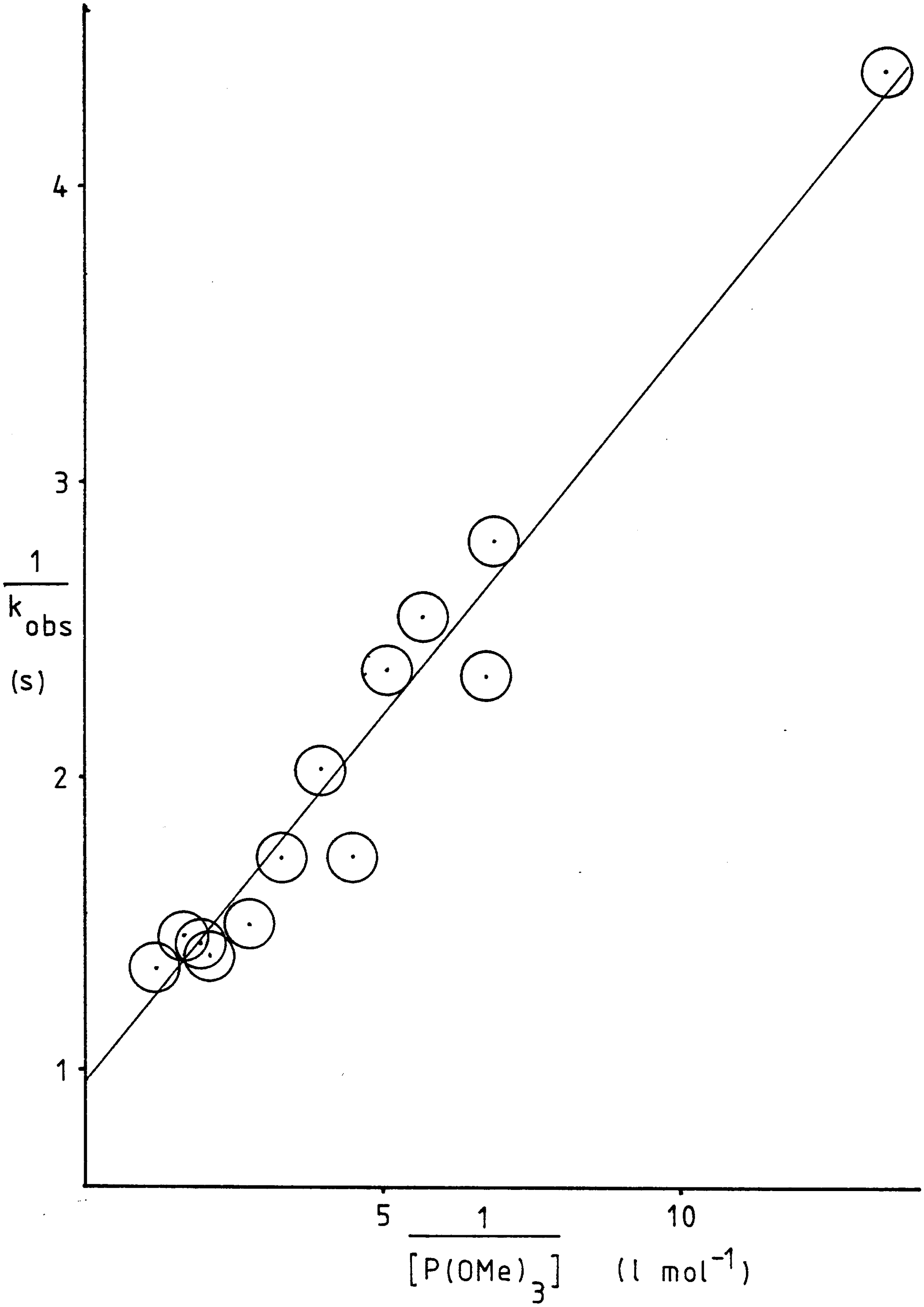


Table 5.

Rate Constants for Solvent Exchange at Fe(II).

Solvent	k_{ex} (s^{-1})
H_2O [b]	3.2×10^6
MeOH [b]	5.0×10^4
MeCN [a]	5.5×10^5
DMSO [b]	1.0×10^6
DMF [b]	1.7×10^6

[a] ref. 64

[b] ref. 65

This would seem to preclude involvement of a mechanism which has a dissociation process as the rate determining step. The ligand obviously has a great effect in determining the rate. The likely mechanism is thus associative interchange, I_a .

$$FeN_6^{2+} \quad + \quad P \quad \underset{}{\overset{K_{o.s.}}{\rightleftharpoons}} FeN_6^{2+},P \xrightarrow{k} FeN_5P^{2+} \quad + \quad N \qquad (16)$$

The outer-sphere complex stability constant is ,

$$K_{o.s.} = \frac{[FeN_6^{2+}, P]}{[FeN_6^{2+}][P]} \qquad (17)$$

The rate law is now ,

$$Rate = \frac{kK_{o.s.}[FeN_6^{2+}][P]}{1 + K_{o.s.}[P]} \qquad (18)$$

and a and b correspond to $kK_{o.s.}$ and $K_{o.s.}$ respectively. Thus $k = 1.03\ s^{-1}$ and $K_{o.s.} = 4.03\ M^{-1}$.

The small value of k for the reaction is presumably a function of the steric requirement of $P(OMe)_3$ in forming the transition state. The approach of $P(OMe)_3$ to the metal ion is hindered and the rate of reaction is slowed.

This value for $K_{o.s.}$ is somewhat larger than that found for outer sphere complexation of metal(II) ions with neutral ligands in aqueous solution ; for example, in the reaction of Ni(II) (aq) with ammonia, $K_{o.s.}$ is 0.15 M^{-1} , at 298 K .[66] An increase in $K_{o.s.}$ is expected from consideration of the relative size of the dielectric constant of water and acetonitrile ; 78 for H_2O and 37 for MeCN , at 293 K . The much lower dielectric constant of acetonitrile will favour a greater degree of association between the cation and the ligand .

The assignment of an I_a mechanism to this reaction is unusual , the majority of studies having been interpreted, as discussed above, in terms of the Eigen - Wilkins, I_d , mechanism. While the Eigen - Wilkins mechanism operates for M(II) in aqueous solution, in other media the mechanisms are often substantially different.

Recently evidence has been presented for a changeover in the mechanism for solvent exchange, from associative to dissociative, in the divalent cations of the first row transition elements in methanol solution.[67] This evidence is derived from measurement of volumes of activation for solvent exchange at Mn(II) , Fe(II) , Co(II) and Ni(II) . The ratio of the volume of activation to the solvent partial molar volume, $\Delta V^{\ddagger}/V^{\circ}$, was found to be negative for Mn(II) , <u>ca</u>. 0 for Fe(II) and positive for Co(II) and Ni(II) . For a Dissociative process, this ratio should be +1 and for an Associative process, it should tend to -1 . Interchange processes should have values which fall between these limits. On the basis of the results for solvent exchange at the M(II) ions, it was predicted that in substitution reactions, in methanol solution, Mn(II) would react via an I_a mechanism, Co(II) and Ni(II) would react via an I_d mechanism and Fe(II) , which is on the borderline, may react via I_a or I_d , depending upon the nature of the ligand which is involved in the reaction. Similar studies have been carried out for Co(II) and Ni(II) in MeCN and in N,N-dimethyl formamide (DMF) and in these solvents the results suggest that an I_d mechanism operates for both metal ions, although Co(II) is apparently less dissociative in nature than Ni(II) .[68] The results of these studies are given in Table 6.

This trend of behaviour across the transition series, for solvent

Table 6.

Activation Volumes for Solvent Exchange at M(II) Cations.

	MeOH		MeCN		DMF	
	$\Delta V^{\ddagger}$ $cm^3 mol^{-1}$	$\Delta V^{\ddagger}/V^{\circ}$	$\Delta V^{\ddagger}$ $cm^3 mol^{-1}$	$\Delta V^{\ddagger}/V^{\circ}$	$\Delta V^{\ddagger}$ $cm^3 mol^{-1}$	$\Delta V^{\ddagger}/V^{\circ}$
Ni(II)	+11.4 (307 K)	+0.28	+9.6 (294 K)	+0.18	+9.1 (297 K)	+0.12
Co(II)	+8.9 (279 K)	+0.22	+9.9 (260 K)	+0.20	+6.7 (296 K) +9.2 (253 K)	+0.09 +0.12
Fe(II)	+0.4 (255 K)	+0.01				
Mn(II)	-5.0 (279 K)	-0.12				

exchange was rationalised by noting that, in the absence of π-bonding, the t_{2g} orbitals are essentially non-bonding whereas the e_g orbitals are anti-bonding. There is no change in occupancy of the e_g orbitals in going from Mn(II) to Ni(II) and the trend toward less associative behaviour would seem to depend upon the occupancy of the t_{2g} orbitals. Increased occupancy of these orbitals makes approach of a seventh ligand less and less favourable.

Behaviour of this type is observed in the reactions of Cr(III) , t_{2g}^3 , which is known to react via an I_a mechanism, whereas low spin Co(III) , t_{2g}^6 , reacts via an I_d mechanism.[69] Similarly reactions of low spin Fe(II) , t_{2g}^6 , are known to proceed via a D mechanism.[70] The contraction in size of the ions in going from Mn(II) to Ni(II) will also tend to make association less favourable on steric grounds.

If these results for MeOH solution can be extrapolated to MeCN, then the results of the reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$ may be rationalised. If, in MeCN, the Fe(II) ion is near the mechanism crossover point, as it is in MeOH, then the mechanism which operates will be sensitive to the nature of the ligand and the substitution reaction of $P(OMe)_3$ on $Fe(NCMe)_6^{2+}$ may well occur via an I_a mechanism.

A very recent report of solvent exchange in MeCN for the five coordinate complexes $[CoL(NCMe)]^{2+}$ and $[NiL(NCMe)]^{2+}$ (where L = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) suggests that an I_a mechanism operates.[71] This is based upon large negative $\Delta S^{\ddagger}$ values and low values of $\Delta H^{\ddagger}$ for the reactions. The corresponding six coordinate species $[ML(NCMe)_2]^{2+}$ undergo solvent exchange via the I_d mechanism ; $\Delta S^{\ddagger}$ is large and positive for these reactions. This is an elegant illustration of the intuitive prediction that the geometry of the complex will have an influence on the mechanism of reaction.

Although the I_a mechanism is the most attractive candidate to account for the observed kinetics, the results are not completely unambiguous. It is not possible to identify the activation process at the metal centre (I_a or I_d) if the relatively slow rate of formation, as shown by the small value of k, is ascribed to steric control.

In recent years it has become accepted that in the chemistry of phosphorus ligands, steric effects are at least as important as electronic effects, and in some cases may dominate.[72] Reactions of phosphorus ligands with Ni^o could not be rationalised in terms of an electronic effect alone which led to the introduction of the parameter, ligand cone angle, θ .[73] This was based upon the observation that the order of decreasing binding of phosphorus ligands was reflected by the increasing steric crowding around the bonding face of the phosphorus, as revealed by molecular models. Cone angles are measured from space filling molecular models assuming a M—P bond length of 2.28 Å and that the substituents on the phosphorus are in a strain free conformation. The measurement of such angles for ligands of fixed geometry can be made relatively easily and confidently but more complex ligands can cause problems due to their greater flexibility and thus greater inaccuracies exist. The cone angle has, however, proved a useful aid in explaining some experimentally observed phenomena. Cone angles for a representative group of phosphorus ligands are given in Table 7.

Table 7.

Cone Angles for Selected PR_3 Ligands.

ligand	minimum cone angle (degrees)
PF_3	104 ± 2
$P(OMe)_3$	107 ± 2
PMe_3	118 ± 4
$P(OPh)_3$	121 ± 10
PPh_3	145 ± 2

The mechanism for substitution may be I_d with a sterically controlled interchange step. This ambiguity can be resolved only by studying the reactions of $Fe(NCMe)_6^{2+}$ with other potential ligands.

PF_3 , $P(OPh)_3$, Et_2S and $^iPr_2S$ were all tried as ligands but all fail to react with $Fe(NCMe)_6^{2+}$ under the conditions used in these experiments. PF_3 has a smaller steric requirement than $P(OMe)_3$ and is an excellent π-acceptor ligand [74] and its failure to react is interpreted in terms of its poor ability as a σ-donor. On the other hand, the ability of $P(OPh)_3$ as a σ-donor would be expected to be of the same order as that of $P(OMe)_3$ and $P(OPh)_3$ has been shown to have ability as a π-acceptor [75] and so its failure to react is interpreted in terms of its larger steric requirement. The cone angle of $P(OPh)_3$ is subject to a large error due to the flexibility of the substituents, but it is larger than $P(OMe)_3$; 121° versus 107° .

The failure of the sulphide species to react with $Fe(NCMe)_6^{2+}$ may also be a steric effect, despite having only two substituent groups on the donor atom. The alkyl phosphines are more bulky than the alkyl phosphites and it may be that the alkyl sulphides are sufficiently bulky to prevent reaction.

In considering substitution reactions in solution, the steric requirement of the ligand must be taken into account, as well as the electronic properties. In some cases the bulk of the ligand dominates the course of the reaction.

b) Conventional Spectrophotometric Study.

The first species observed in a conventional study is spectroscopically identical to the species assigned as $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ in the stopped-flow study. The subsequent reaction of this species with $P(OMe)_3$ can be followed by conventional electronic spectroscopy. In fact two steps are observed, each characterised by a set of three isosbestic points. A representative trace is shown in Figure 6. The isosbestic points appear at :- step 2 , 24,750 , 27,800 and 29,850 cm^{-1} and step 3 , 24,200 , 28,100 and 29,850 cm^{-1} . An isosbestic point is found at a wavelength where the absorbance of the solution does not change during the course of the reaction.[76] The occurrence of such points strongly suggests that the original reactant is being replaced by one product. The absence of appreciable amounts of reaction intermediates can thus be implied. The criteria for the appearance of such points have been discussed.[77] The case for a reaction $A \rightarrow B$ is illustrated below.

$$O.D._0 = \varepsilon_A[A]_0 \quad \text{and} \quad O.D._\infty = \varepsilon_B[B]_\infty$$

at an isosbestic point , $O.D._0 = O.D._\infty \therefore \varepsilon_A[A]_0 = \varepsilon_B[B]_\infty$

Further , $[A]_0 = [B]_\infty \therefore \varepsilon_A = \varepsilon_B$ at the isosbestic point.

Thus , at time t , where $[A]_t = [A_0 - x]$ and $[B] = [x]$

$$O.D._t = \varepsilon_A[A_0 - x] + \varepsilon_B[x]$$
$$= \varepsilon_A[A_0] - \varepsilon_A[x] + \varepsilon_B[x]$$

but $\varepsilon_A = \varepsilon_B$

$$\therefore O.D._t = \varepsilon_A[A_0] \quad \text{for any time t .}$$

For a reaction ,

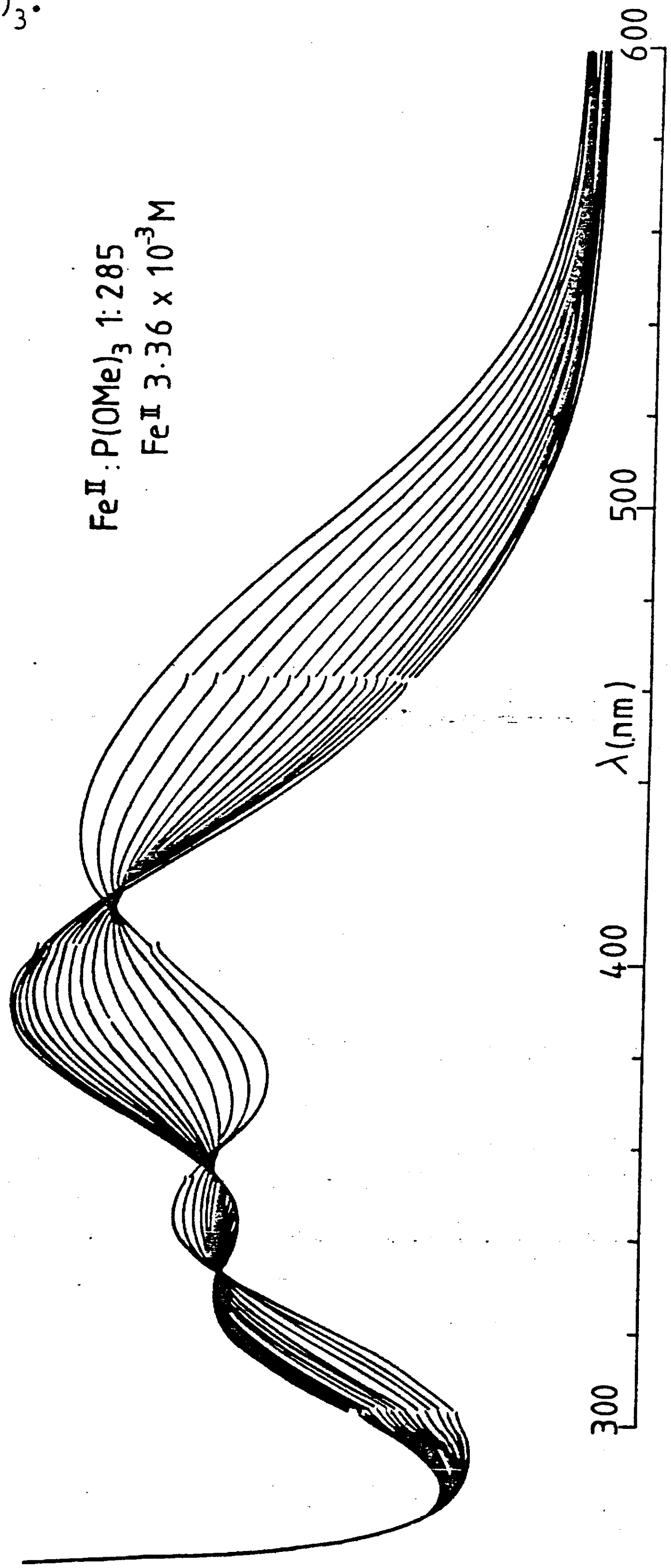
$$A \longrightarrow B + C$$

the criterion for appearance of an isosbestic point is

$\varepsilon_A = \varepsilon_B + \varepsilon_C$ at a particular point, which is far less likely

Figure 6.

Consecutive Electronic Spectra for the Reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$.



to occur.

The kinetics of the reactions are studied under pseudo first order conditions, the concentration of $P(OMe)_3$ held in great excess over that of $Fe(NCMe)_6^{2+}$.

The reactions are followed at 470 nm . The system can be considered to be two consecutive pseudo first order reactions, of the type ,

$$A \xrightarrow{k_{1\ obs}} B \xrightarrow{k_{2\ obs}} C$$

It is possible to computer model reactions of this type, knowing the initial concentration of A , the extinction coefficients of A , B and C , and the values of $k_{1\ obs}$ and $k_{2\ obs}$, the pseudo first order rate constants. The program for this calculation is listed in Table 8 .[78] The output of the calculation is the total O.D. of the solution and the individual concentrations of A , B and C as a function of t , at a particular wavelength. The input parameters are varied until the calculated O.D. agrees with the experimentally observed O.D. .

The first step in the reaction , $A \rightarrow B$, was treated by the initial rate method. The results are listed in Table 9 and plotted as a function of $[P(OMe)_3]$, in Figure 7 . This shows the reaction to be first order in $P(OMe)_3$. Two straight lines are found in Figure 7 , arising from the use of two stock solutions of $Fe(NCMe)_6^{2+}$. These were nominally the same concentration but the results suggest a difference of ca. 5 % between the two solutions. The rate constants for the initial rate treatment are in units of absorbance min^{-1} .

In order to use the computer modelling treatment and the initial

Table 8.

Program for Modelling Reaction A→B→C .

```
0010  PRINT "EXTINCTION COEFFICIENTS A, B, C."
0020  INPUT A;
0025  PRINT ,;
0030  INPUT B;
0035  PRINT ,;
0040  INPUT C
0045  PRINT "RATE (FIRST ORDER) K1, K2"
0050  INPUT K1;
0055  PRINT ,;
0060  INPUT K2
0062  PRINT "INIT. TIME AND STEP"
0063  INPUT T;
0064  PRINT ,;
0065  INPUT S
0070  PRINT "INIT. CONC. A AND STOP"
0075  INPUT D;
0076  PRINT ,;
0077  INPUT R
0080  LET E=D*EXP(-K1*T)
0090  LET F=D*K1*(EXP(-K1*T)-EXP(-K2*T))/(K2-K1)
0100  LET G=D-(E+F)
0110  LET H=E*A+F*B+G*C
0120  PRINT T, E, F, G, H
0130  LET T=T+S
0140  IF T=R THEN GO TO 0160
0150  GO TO 0080                      0160  END
```

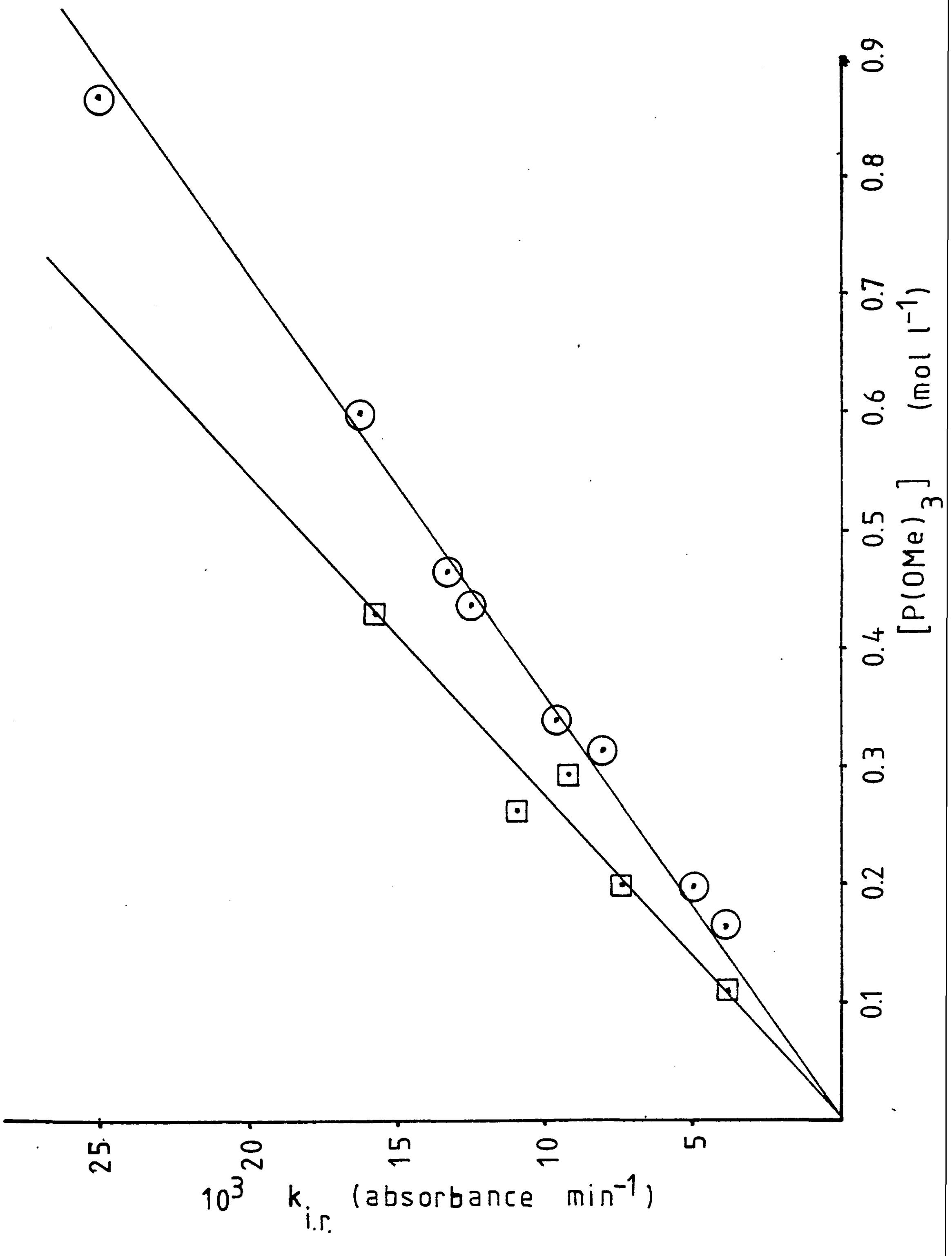
Table 9.

Initial Rate Data for the Reaction of $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ with $P(OMe)_3$.

$[P(OMe)_3]$ (mol l^{-1})	k_{obs} x 10^3 (absorbance min^{-1})
0.108	3.9
0.163	3.9
0.192	7.6
0.193	4.9
0.260	10.9
0.289	9.3
0.307	8.0
0.334	9.6
0.364	7.8
0.423	15.8
0.434	12.5
0.457	13.2
0.591	16.2
0.862	24.9

Figure 7.

Plot of Initial Rate Constant vs. $[P(OMe)_3]$ for the Reaction of $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ with $P(OMe)_3$.



rate data, it is necessary to know the extinction coefficients of A , B and C at 470 nm . The extinction coefficients of A and C are obtained from O.D.$_0$ and O.D.$_\infty$ respectively but the extinction coefficient of B is more difficult to calculate.

It is possible to obtain a value for ε_B by noting that, at high concentrations of $P(OMe)_3$, the process A ⟶ B is rate determining, with B ⟶ C being very rapid. The total reaction, A ⟶ C is treated as being first order and a plot of $-\log(A - A_\infty)$ vs. t for this process is linear for ca. 80 % of reaction. The rate constant obtained from this treatment is the rate constant for A ⟶ B , in min^{-1}.

This value is related to the initial rate value by the equation ,

$$k_{1\ obs}\ (\text{min}^{-1}) \quad = \quad \frac{k_{i.r.}}{\Delta\varepsilon_{A\rightarrow B}[FeP]} \qquad (19)$$

where $k_{i.r.}$ is the initial rate value , $\Delta\varepsilon_{A\rightarrow B}$ is the change in extinction coefficient from A ⟶ B and $[FeP]$ is the total concentration of iron (= $[Fe(II)]_{total}$) .

Knowing $\Delta\varepsilon_{A\rightarrow B}$, ε_B is calculated. It is thus possible to use the computer modelling program. Initial estimates for $k_{1\ obs}$ are obtained from the initial rate data. Some typical results of modelling the reaction are shown in Figure 8. The pseudo first order rate constants, $k_{1\ obs}$ and $k_{2\ obs}$ calculated by this method are listed in Table 10. The plot of $k_{1\ obs}$ vs. $[P(OMe)_3]$ is shown in Figure 9. This clearly shows that A ⟶ B has a first order dependence upon $P(OMe)_3$.

As the concentration of $P(OMe)_3$ increases the rate of B ⟶ C increases very rapidly and at high concentrations of $P(OMe)_3$, this step is not observed. A plot of the values of $\frac{k_{2\ obs}}{[P(OMe)_3]}$ vs. $[P(OMe)_3]$

Figure 8.

Observed and Calculated Optical Density vs. Time for the Reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$.

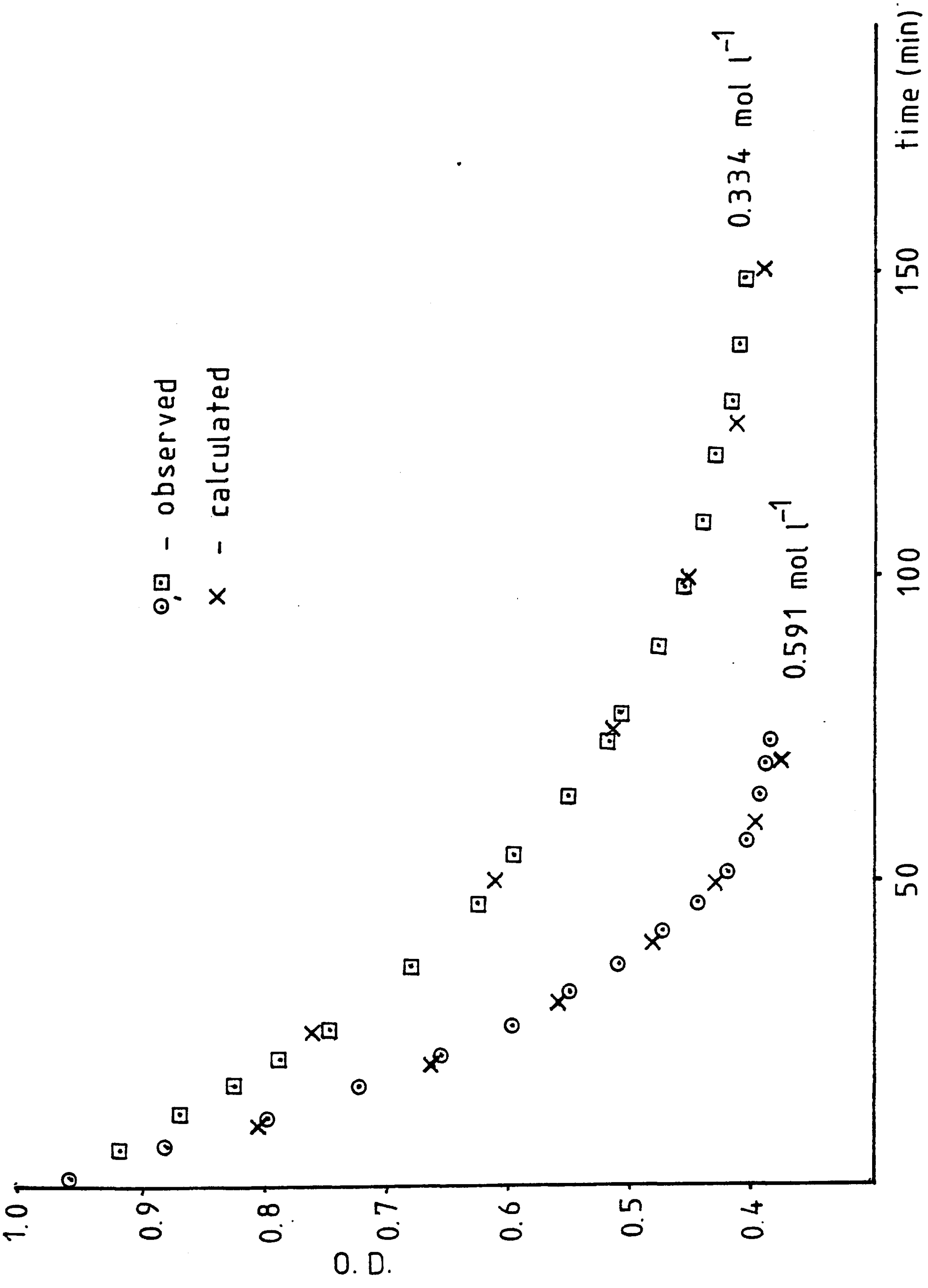


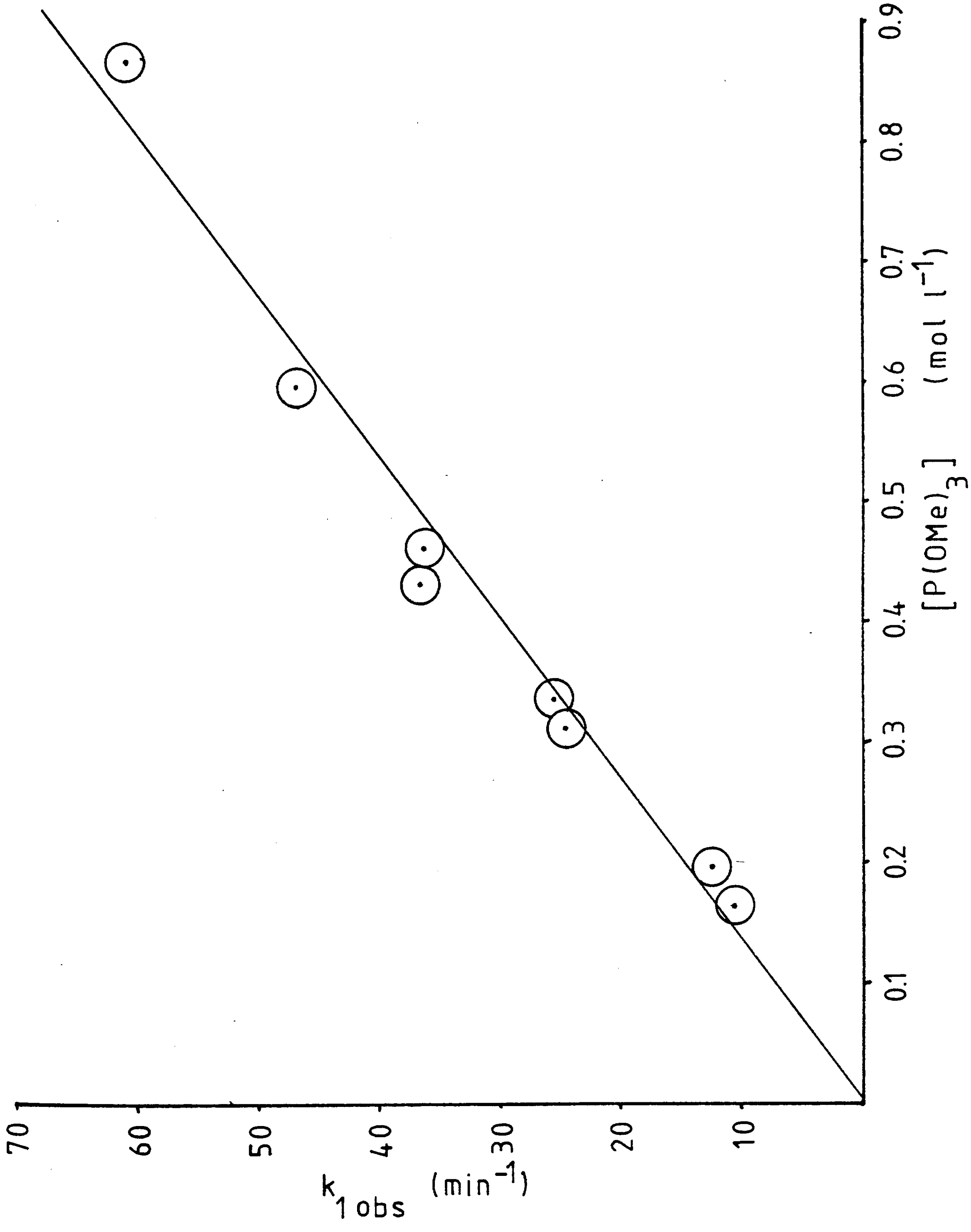
Table 10.

Observed Rate Constants for the Reaction $A \rightarrow B \rightarrow C$.

$[P(OMe)_3]$ (mol l^{-1})	$k_{1\,obs} \times 10^3$ (min^{-1})	$k_{2\,obs} \times 10^3$ (min^{-1})
0.163	11.0	3.7
0.193	13.0	6.5
0.307	25.0	22.0
0.334	26.0	18.0
0.434	37.0	23.0
0.457	37.0	29.0
0.591	47.0	65.0
0.862	61.0	-

Figure 9.

Plot of Observed Rate Constant vs. $[P(OMe)_3]$ for the Reaction of $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ with $P(OMe)_3$.



for low concentrations of $P(OMe)_3$ shows that $B \rightarrow C$ has a greater than first order dependence upon $P(OMe)_3$, probably second order. This plot is shown in Figure 10.

The observed kinetics can be explained in the following way. The rate law for $A \rightarrow B$ is ,

$$\text{Rate} = -\frac{d[FeN_5P^{2+}]}{dt} = k_1[FeN_5P^{2+}][P] \qquad (20)$$

where the total iron concentration exists as $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$.

Substitution reactions of low spin iron(II) complexes are generally very slow and these complexes have consequently been termed 'substitution inert' . This is clearly shown in the present work with the rate constant being very small. The dramatic lowering of the rate of reaction, relative to high spin Fe(II) has been rationalised in terms of a large increase in the net crystal field activation energy (CFAE) in going from high spin d^6 , $t_{2g}^4 e_g^2$ to low spin d^6 , $t_{2g}^6 e_g^0$. The CFAE is defined as the loss of stabilisation in going from the normal geometry of the reactant complex to the geometry of the activated complex. In a series of reactions where other contributions to the overall activation energy are constant then the higher the value of CFAE the more likely a reaction is to be slower.

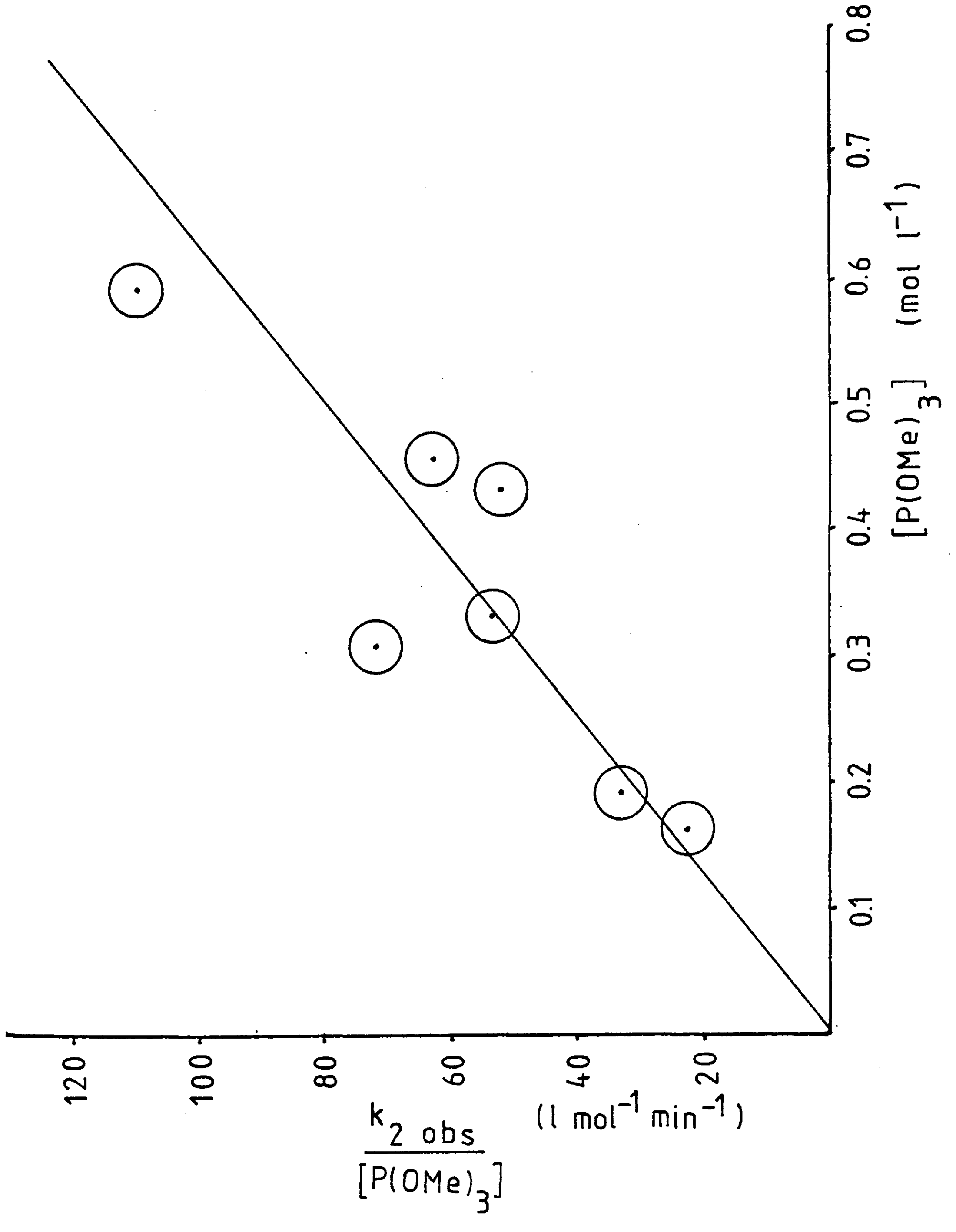
The observed rate law may be explained in one of two ways. Firstly the overall second order nature is that expected for an associative mechanism with a simple bimolecular reaction between the complex ion and ligand. Secondly the mechanism may be dissociative,

$$FePN_5^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FePN_4^{2+} + N \qquad (21)$$

$$FePN_4^{2+} + P \xrightarrow{k_2} FeP_2N_4^{2+} \qquad (22)$$

Figure 10.

Plot of Observed Rate Constant Over $P(OMe)_3$ vs. $[P(OMe)_3]$ for the Reaction of $[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$ with $P(OMe)_3$.



The rate law for this reaction is ,

$$\text{Rate} = \frac{k_1 k_2[\mathrm{FeN_5P}^{2+}][\mathrm{P}]}{k_{-1} + k_2[\mathrm{P}]} \qquad (23)$$

if k_2 is small and $k_{-1} \gg k_2[\mathrm{P}]$ and so this reduces to ,

$$\text{Rate} = k_{obs}[\mathrm{FeN_5P}^{2+}][\mathrm{P}] \qquad (24)$$

and the kinetics are overall second order.

Both associative and dissociative mechanisms have been postulated for reactions of low spin Fe(II) . The reaction between $\mathrm{Fe(bipy)_3}^{2+}$ and $\mathrm{CN^-}$ in aqueous solution follows the rate law ,[79]

$$-\frac{d[\mathrm{Fe(bipy)_3}^{2+}]}{dt} = \left\{k_1 + k_2[\mathrm{CN^-}]\right\}[\mathrm{Fe(bipy)_3}^{2+}] \qquad (25)$$

The bimolecular part of the rate law was ascribed to an association of the nucleophile and the complex ion on the basis of several pieces of evidence, including comparison of the activation parameters of the reaction with the analogous reaction of $\mathrm{Fe(phen)_3}^{2+}$. Later, determination of the volume of activation for reactions of both $\mathrm{Fe(bipy)_3}^{2+}$ and $\mathrm{Fe(phen)_3}^{2+}$, found to be of the order of $+20\ \mathrm{cm^3\ mol^{-1}}$ for both complexes , led to a proposal that the reactions proceeded by a dissociative interchange mechanism.[80] Very recently a report appeared which indicated that desolvation of the nucleophile is an important factor in determining volumes of activation, and that associative reactions may still have positive $\Delta V^{\ddagger}$.[81]

The rate of reaction of $[\mathrm{Fe(CN)_5H_2O}]^{3-}$ with a number of aromatic nitrogen heterocycles was found to be relatively independent of the nature of the incoming ligand,[82] which suggests that a dissociative mechanism is operative. Similarly, as stated above,[70] substitution at $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ with a variety of charged and uncharged ligands are known to occur via a D mechanism.

To discriminate between the two possibilities, further reactions of low spin iron(II) in MeCN must be investigated. If the rates of other reactions are similar to those of substitution at $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ then this would be good evidence for a common dissociative mechanism. In the absence of such data, however, it seems reasonable to propose that the reaction occurs via a dissociative mechanism.

The rate law for the succeeding step is ,

$$\text{Rate} = -\frac{d[FeP_2N_4^{2+}]}{dt} = k_2'[FeP_2N_4^{2+}][P]^2 \qquad (26)$$

The mechanism of this reaction is rather less certain. The second order nature can be accounted for by assuming that a relatively fast equilibrium exists, involving $[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$, followed by a slow substitution step ,

$$FeP_2N_4^{2+} + P \underset{}{\overset{K}{\rightleftharpoons}} FeP_3N_3^{2+} + P \xrightarrow{k_2} FeP_4N_2^{2+} \qquad (27)$$

The fact that isosbestic points are observed for this reaction indicates that, either very little $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ is present in solution, or the extinction coefficients of $[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$ and $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ are very similar, at 470 nm .

The rate law for this process is ,

$$\text{Rate} = \frac{k_2K[FeP_2N_4^{2+}][P]^2}{1 + K[P]} \qquad (28)$$

If K is small, the rate law simplifies to ,

$$\text{Rate} \quad = \quad k_2K[FeP_2N_4{}^{2+}][P]^2 \qquad (29)$$

The product of the second step may be $[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$. The mechanism of the substitution steps is unknown but may be dissociative, by analogy with the step,

$$[Fe\{P(OMe)_3\}(NCMe)_5]^{2+} \longrightarrow [Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$$

The data for the later stages of reaction are open to different interpretation but this explanation seems reasonable. The apparent differences in behaviour between the kinetic and n.m.r. studies are the result of the large concentration differences between the two techniques. This is particularly important in influencing the equilibrium ,

$$FeP_2N_4{}^{2+} \quad + \quad P \quad \overset{K}{\rightleftharpoons} \quad FeP_3N_3{}^{2+} \qquad (30)$$

While only a small amount of $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ may exist in the kinetic studies, large amounts exist in the n.m.r. studies.

Estimation of Errors in the Kinetic Studies.

All of the kinetic results for the $Fe(NCMe)_6{}^{2+}$: $P(OMe)_3$ system are subject to appreciable error, both in the calculation and , more importantly, from the nature of the experiments. The major source of this error arises in determining the concentration of the solution of $P(OMe)_3$.

With the stopped-flow experiments the solutions were made up in a glove box by weighing the appropriate amount of reagent, to ± 2 mg, and diluting to a standard volume with MeCN. The problem arises with the volatility of the $P(OMe)_3$, which is particularly important at low concentrations. The transfer of solutions was done as quickly as possible to minimise this loss. The error in calculation, using a least squares fit of the data, is small, but due to the probable error in $[P(OMe)_3]$, the rate constant is subject to an estimated error of ± 10 % .

For the conventional spectrophotometric studies, the solutions were made by distilling the appropriate weight of $P(OMe)_3$, to ± 0.2 mg , into a flask with a Spectrosil cell attachment which had been charged with a solution of the metal complex. Allowance was made for the volume of $P(OMe)_3$ which was added but the volume of mixing of the two solutions was assumed to be negligible. The error in the values of the rate constants for these reactions is estimated to be ± 10 % .

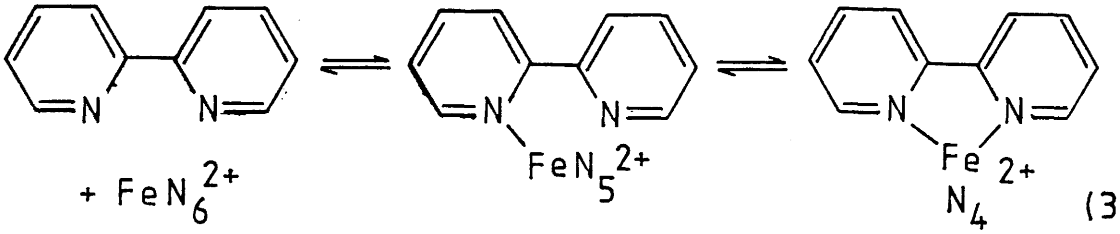
Formation of $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$.

The last stage of the substitution reaction of $P(OMe)_3$ with $Fe(NCMe)_6^{2+}$ is too slow to be followed conveniently under the conditions used in these experiments. The large deceleration in the rate of reaction in going from $[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$ to $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ is a result of the large steric effect of $P(OMe)_3$. This also accounts for the extremely slow formation of $Fe\{P(OMe)_3\}_6^{2+}$.

Reaction of $Fe(NCMe)_6^{2+}$ with 2,2'-bipyridyl in MeCN.

The solvated iron(II) ion reacts with three equivalents of bipyridyl to produce $Fe(bipy)_3(PF_6)_2$ and this was characterised spectroscopically. An attempt to investigate the kinetics of this substitution reaction failed as the rate is so fast that the reaction is complete within the dead time of the stopped-flow instrument. The dead-time was estimated to be 0.05 s and this sets a lower limit for the pseudo first order rate constant of ca. 80 s^{-1} .

The first step in the reaction of $Fe(NCMe)_6^{2+}$ with bipy is illustrated here ,

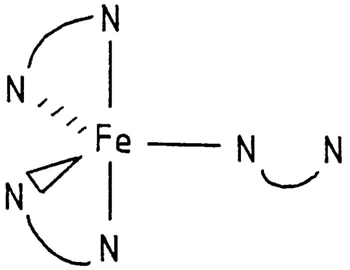


(31)

If the fast rate of formation of the iron(II) - bipyridyl complex is compatible with the rate of solvent exchange at $Fe(NCMe)_6^{2+}$, then this would suggest that the reaction occurs via an Eigen - Wilkins , I_d , mechanism. The rate determining step would be solvent loss, with complex formation and ring closure both being fast. This is the situation found in aqueous solution.[56]

In DMSO [57], an alternative mechanism has been proposed where ring closure becomes the rate determining step and this may apply to other non aqueous solvents. Accurate evaluation of the kinetics is necessary to aid in deciding between these two possible mechanisms.

The results from reactions between $Fe(bipy)_3^{2+}$ and $P(OMe)_3$, and $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ and bipyridyl are very interesting. The failure of $P(OMe)_3$ to react with $Fe(bipy)_3^{2+}$ may be a reflection of poor ligand ability of $P(OMe)_3$ relative to bipy. On the other hand, and more likely in the light of the above discussion, $P(OMe)_3$ may be too bulky to approach the metal ion and enter the inner coordination sphere, even assuming that such a reaction goes via a dissociative mechanism with generation of the five coordinate intermediate (I) . It has been proposed that hydrolysis of

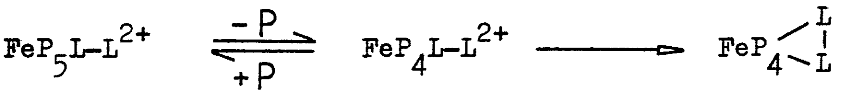


I

$Fe(phen)_3^{2+}$ occurs via an associative mechanism and, if this is true, it makes attack by $P(OMe)_3$ even less likely.

Bipyridyl does react with $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ to yield as a product a red solid which contains no coordinated MeCN but, apparently, has both $P(OMe)_3$ and bipy coordinated to the metal. The complex ion may be of the form $[Fe\{P(OMe)_3\}_4bipy]^{2+}$ which may arise from attack of bipyridyl on $Fe\{P(OMe)_3\}_5^{2+}$, the intermediate generated by loss of MeCN from $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$.

$$FeP_5N^{2+} \underset{+N}{\overset{-N}{\rightleftharpoons}} FeP_5^{\,2+} \xrightarrow{L-L} FeP_5L\text{–}L^{2+} \qquad (32)$$



$$FeP_5L\text{–}L^{2+} \underset{+P}{\overset{-P}{\rightleftharpoons}} FeP_4L\text{–}L^{2+} \longrightarrow FeP_4\begin{smallmatrix}\diagup L\\ \mid\\ \diagdown L\end{smallmatrix} \qquad (33)$$

L–L represents bipy .

The red solid, assumed to be $[Fe\{P(OMe)_3\}_4bipy][PF_6]_2$, is unstable in solution and decomposes fairly rapidly. Further investigation of this system is necessary to clarify the situation.

Conclusions.

Substitution of $P(OMe)_3$ for MeCN on $Fe(NCMe)_6^{2+}$ in acetonitrile solution proceeds via a stepwise ligand substitution process. This is clearly shown from $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ onwards, by n.m.r. spectroscopic studies. The kinetics of three of the five substitution steps were followed by electronic spectroscopy. The first step, substitution on high spin $Fe(NCMe)_6^{2+}$, is relatively fast and appears to proceed via an associative interchange, I_a, mechanism.

In aqueous solution, substitution reactions of M(II) generally proceed via an Eigen - Wilkins, I_d, mechanism. The result of this study suggests that, while the Eigen - Wilkins mechanism is, obviously, still very important, it is perhaps not so widespread in its application as originally believed ; the nature of the solvent has a great influence in determining mechanism. Although based on only one example, this conclusion agrees with previous work in non aqueous media with Ni(II) where it was concluded that "rate constants and activation parameters for ligand substitution strongly depend upon the nature of the solvent, and in DMSO and MeCN, on the ligand as well".[83] These workers also concluded that the ligand dependence of substitution in MeCN could be rationalised in terms of steric effects and that further work with unidentate ligands of varying steric requirement would be necessary to determine what constituted "normal" substitution in acetonitrile solution. This echoed earlier work which found that different types of ligand were affected in quite different ways by the structural features of a particular solvent.[84] Thus, until the solvent structures of non aqueous media are better understood, it is not valid to relate the mechanism of a reaction in one solvent to that in another.

Once substitution of one $P(OMe)_3$ has been achieved, the complex $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ is low spin and the rate of subsequent substitution is very slow, in keeping with the increased Crystal Field Activation Energy.

The kinetics of the reactions of $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ and

$[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$ with $P(OMe)_3$ do not point to a particular mechanism, but the reactions are presumed to proceed via the dissociative , D , mechanism , in common with other reactions of low spin complexes of iron(II) .

The slow rate of the reactions is also a function of the steric requirement of $P(OMe)_3$. The failure to produce significant amounts of $Fe\{P(OMe)_3\}_6^{2+}$ in this work and the fact that $Fe(NCMe)_6^{2+}$ does not react with $P(OPh)_3$ is further evidence for the idea that steric considerations can dominate in the reaction of phosphorus ligands.

On the other hand, the failure of $Fe(NCMe)_6^{2+}$ to react with PF_3 must be an electronic effect. Both concepts must be invoked in any study of phosphorus ligands.

$Fe(NCMe)_6^{2+}$ reacts readily and very rapidly in MeCN to produce $Fe(bipy)_3^{2+}$. The mechanism could not be assigned but further study of the kinetics of the reaction may make this possible.

The study of ligand substitution at $Fe(NCMe)_6^{2+}$ in MeCN is feasible and by using different types of ligand with different electronic and steric properties, it should be possible to produce a greater understanding of the role of the solvent in the substitution reactions of solvated metal ions.

Experimental.

1. Reaction of $Fe(NCMe)_6(PF_6)_2$ with $P(OMe)_3$ in MeCN

In a typical reaction, $P(OMe)_3$(1.5 ml ; 12.7 mmol) was added to $Fe(NCMe)_6(PF_6)_2$ (0.25g ; 0.42 mmol) in MeCN (3 ml) at 77 K. As the temperature was raised, the $P(OMe)_3$ melted and flowed down on to the frozen MeCN solution; a peach colour formed which darkened to a deep red as the temperature continued to rise. When all the MeCN had melted, the solution had a deep red colour. Over a period of twenty minutes to an hour, the colour changed through brownish red to orange. Finally over a period of hours the solution became yellow. The rate of the reaction, as marked by the colour changes, was very dependent upon the concentration of $P(OMe)_3$. A yellow solid was isolated from the final yellow solution by removing volatile material; the volatile material was found, by ^1H n.m.r. spectroscopy, to be a mixture of MeCN, unreacted $P(OMe)_3$ and some $MeP(O)(OMe)_2$. The solid was characterised as predominantly acetonitrile pentakis(trimethyl phosphite)iron(II) hexafluorophosphate. The result of three analyses, together with the required result, are listed in Table 11. The results of the analyses were in poor agreement with the required result due to the presence of complexes of a lower degree of substitution, as shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. The major signal was the expected AB_4 pattern of $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ but there were also minor signals due to cis-$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$ and fac-$[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$. The electronic spectrum in MeCN solution consisted of two bands, at 26,700 cm^{-1} (ε 370 $dm^3mol^{-1}cm^{-1}$) and 32,700 cm^{-1} (ε 250 $dm^3mol^{-1}cm^{-1}$). The infra-red spectrum gave

Table 11.

Analyses of $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$.

Element	Sample (%)			Required (%)
	I	II	III	
C	21.7	20.7	20.8	20.3
H	5.0	4.7	4.6	4.8
F	21.5	21.6	22.1	22.6
Fe	5.4	5.2	5.3	5.5
N			1.5	1.4
(O) [a]			(24.5)	23.9
P	20.8	20.5	21.1	21.5

[a] not analysed; value calculated by difference

evidence for coordinated MeCN, $\bar{\nu}_{max}$ 2,295 cm^{-1} , and $P(OMe)_3$, $\bar{\nu}_{max}$ 793 and 719 cm^{-1} .

N.m.r. Studies.

The reaction was followed by $^{31}P-\{^1H\}$ n.m.r. , typically using $Fe(NCMe)_6(PF_6)_2$ (0.2g ; 0.34 mmol) and $P(OMe)_3$ (0.21g ; 1.67 mmol) in CD_3CN (2 ml) (mole ratio Fe(II) : $P(OMe)_3$, 1 : 4.9). The $P(OMe)_3$ was distilled on to the solid in MeCN at 77 K in a vessel fitted with an n.m.r. tube. The mixture was warmed until liquid, shaken and a portion decanted into the n.m.r. tube and sealed off.

On warming from 77 K to 243 K, a red solution was obtained and the $^{31}P-\{^1H\}$ n.m.r. spectrum at this temperature showed three singlets, one, due to $P(OMe)_3$, broadened by exchange. As the temperature was allowed to rise, one of the singlets increased in intensity as the other decreased. Accompanying this increase in intensity of the singlet was the appearance of a second order, AB_2 multiplet. The singlet and multiplet were assigned to the fac and mer isomers of $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ respectively. The relative amount of free $P(OMe)_3$ had reduced during this time. The singlet which decreased in intensity was assigned to $[Fe\{P(OMe)_3\}_2(NCMe)_4]^{2+}$. After fifteen minutes at room temperature, $[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ was virtually the only iron containing species in solution. After a further forty five minutes at room temperature, small peaks had become visible, due to the A_2B_2 multiplet of cis-$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$. After heating for five hours at 330 K, the major signal was that of cis-$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$ and a significant amount of $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ was now present, as shown by its AB_4

spectrum. A singlet assigned to trans-$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$ was also visible and the singlet of fac-$[Fe\{P(OMe)_3\}_3(NCMe)_3]^{2+}$ was still discernible though very much reduced in intensity. There was now no evidence for free $P(OMe)_3$. When a reaction mixture was left for several weeks at room temperature, a small singlet assigned to $Fe[P(OMe)_3]_6^{2+}$ was obtained, along with the dominant AB_4 multiplet.

The reaction was also followed by ^1H n.m.r. spectroscopy but the results were very difficult to interpret due to the smaller range of chemical shifts being studied. Separate signals were identified for both free and bound $P(OMe)_3$. The free $P(OMe)_3$ was found to be undergoing rapid exchange in the early stages of the reaction.

Spectrophotometric Studies.

a) Stopped Flow.

The reaction was also followed by electronic spectroscopy. The first step, formation of the red species, $[Fe\{P(OMe)_3\}(NCMe)_5]^{2+}$ was followed by stopped flow spectrophotometry. This involved 3×10^{-3} mol l^{-1} solutions of $Fe(NCMe)_6^{2+}$ in MeCN, mixed with solutions of $P(OMe)_3$ in MeCN varying in concentration from 0.15 mol l^{-1} to 1.5 mol l^{-1}, ensuring that pseudo first order conditions were maintained. The solutions were made up in the glove box by diluting the appropriate weight of $P(OMe)_3$ to the desired volume, generally 25 ml. The $P(OMe)_3$ was weighed to ± 2 mg in each case and the solution was made up quickly to minimise loss of $P(OMe)_3$ by evaporation. The error in concentration of the $P(OMe)_3$ solutions was the major source of error in the system.

The stopped flow apparatus was thermostatted to 24.0 ± 0.1 °C . The experimental method was that described in the appendix.

b) Conventional Spectrophotometric Studies.

The later stages of the reaction were followed by conventional electronic spectroscopy. This involved, typically, 3.4×10^{-3} mol l^{-1} solutions of $Fe(NCMe)_6^{2+}$ in MeCN and solutions of $P(OMe)_3$, in MeCN, varying from 0.11 mol l^{-1} to 0.86 mol l^{-1} . The reaction mixtures were made by distilling a weighed amount of $P(OMe)_3$ into flasks with a Spectrosil cell side arm. These flasks had been loaded with the solution of $Fe(NCMe)_6^{2+}$ in the glove box. MeCN was also added to bring the total solution volume to 5 ml. Allowance was made for the volume of $P(OMe)_3$ to be added but the volume of mixing was assumed to be negligible, within the limits of the experiment.

The reaction mixtures were held at 77 K until they were required and then rapidly warmed before being placed in a thermostatted cell holder. The temperature was controlled to 24.0 ± 0.1 °C . An estimated five minutes elapsed before temperature equilibration of the solution was achieved. The spectra were run initially at 2.5 minute intervals ; the time interval was enlarged as the changes in the spectrum grew less. The rate of the reaction was found to be very dependent upon the concentration of $P(OMe)_3$. The first spectrum consisted of two bands, at 23,300 cm^{-1} (ε 320 $dm^3mol^{-1}cm^{-1}$) and 29,000 cm^{-1} (ε 270 $dm^3mol^{-1}cm^{-1}$) which decayed, via a series of three isosbestic points at 24,750 cm^{-1} , 27,800 cm^{-1} and 29,850 cm^{-1}, to produce a second species. This species also had two bands at 24,100 cm^{-1} (ε 290 $dm^3mol^{-1}cm^{-1}$) and 29,400 cm^{-1} (ε 250 $dm^3mol^{-1}cm^{-1}$)

and it, in turn, decayed via a second series of three isosbestic points, at 24,200 cm^{-1} , 28,100 cm^{-1} , 29,850 cm^{-1} to produce a third species. This species had two bands, at 25,650 cm^{-1} (ε 350 $dm^3mol^{-1}cm^{-1}$) and 30,700 cm^{-1} (ε 240 $dm^3mol^{-1}cm^{-1}$). The decay of this species to produce the final product was so slow that it could not be followed under these conditions.

2. Reaction of $Fe(NCMe)_6(WF_6)_2$ with $P(OMe)_3$ in MeCN.

$Fe(NCMe)_6(WF_6)_2$ reacted with $P(OMe)_3$ in MeCN in an identical manner to the PF_6^- salt, under the same conditions. The cationic products were trimethyl phosphite complexes of the same type as in the above reactions.

3. Reaction of $Fe(NCMe)_6(PF_6)_2$ with $P(OPh)_3$ in MeCN.

$Fe(NCMe)_6(PF_6)_2$ (0.05g ; 0.084 mmol) was dissolved in MeCN (5 ml) in a flask fitted with a Spectrosil cell side arm. $P(OPh)_3$ (ca.1g ; 3.2 mmol) was added to the flask by pasteur pipette in the glove box (mole ratio Fe(II) : $P(OPh)_3$, 1 : 38). Continuous monitoring of the electronic spectrum revealed no change, even after the reaction mixture had been shaken for several days.

4. Reaction of $Fe(NCMe)_6(PF_6)_2$ with PF_3 in MeCN.

$Fe(NCMe)_6(PF_6)_2$ (0.07g ; 0.12 mmol) was dissolved in MeCN (5 ml) in a flask fitted with a Spectrosil cell side arm. The flask was attached to a vacuum line and PF_3 gas was released into the line to a pressure of 6 cm. The PF_3 was allowed to stand over the solution of $Fe(NCMe)_6^{2+}$ for several hours. There was no observable change during this time. The flask was resealed and the excess PF_3 pumped away. The electronic spectrum of the solution showed no change over the course of the reaction. The mixture was allowed to stand for several weeks at room temperature with no change evident.

5. Reaction of $Fe(NCMe)_6(PF_6)_2$ with $^iPr_2S$ in MeCN.

$^iPr_2S$ (0.4g ; 3.4 mmol) was added to $Fe(NCMe)_6(PF_6)_2$ (0.2g ; 0.34 mmol) (mole ratio Fe(II) : $^iPr_2S$, 1 : 10) in MeCN (4 ml). There was no visible evidence for reaction. After shaking for several hours, the volatile material was removed leaving a white solid. The infra red spectrum of this solid was identical with that of $Fe(NCMe)_6(PF_6)_2$.

6. Reaction of $Fe(NCMe)_6(PF_6)_2$ with Et_2S in MeCN.

Et_2S (0.43g ; 4.78 mmol) was added to $Fe(NCMe)_6(PF_6)_2$ (0.25g ; 0.42 mmol) (mole ratio Fe(II) : Et_2S , 1 : 11.5) in MeCN (4 ml). There was no visible evidence for reaction. After shaking for several hours, the volatile material was removed, leaving a white solid. The electronic and infra red spectra of the solid were identical to those of $Fe(NCMe)_6(PF_6)_2$. The ^1H n.m.r. spectrum of the volatile material showed it to consist of unreacted Et_2S and MeCN.

7. Reaction of $Fe(NCMe)_6(PF_6)_2$ with 2,2'-bipyridyl in MeCN.

$Fe(NCMe)_6(PF_6)_2$ (0.2g ; 0.34 mmol) and 2,2'-bipyridyl (0.16g ; 1.02 mmol) (mole ratio Fe(II) : bipy, 1 : 3) were loaded into separate limbs of a two limbed flask in the glove box. Where small amounts of solid bipy came into contact with the solid $Fe(NCMe)_6(PF_6)_2$, a pronounced pink colour developed. The flask was evacuated and MeCN (2 ml) was distilled into each limb. On warming from 77 K both solids dissolved. The solution of the iron salt was pink due to the small amount of bipy which had mixed in with the iron salt during transfer to the vessel. When the two solutions were added together, an intense red colour formed within the time of mixing. Removing the volatile material from the reaction mixture left a dark red solid. The electronic, infrared, and ^{1}H n.m.r. spectra of the solid were in good agreement with published data for the $Fe(bipy)_3^{2+}$ cation. The spectroscopic results are listed in Table 12. Bands on the infra red spectrum, at $\bar{\nu}_{max}$ 840 cm^{-1} and 560 cm^{-1}, confirmed the presence of PF_6^-.

A study of the reaction by stopped flow spectrophotometry was attempted. The solutions used were 3×10^{-3} mol l^{-1} in $Fe(NCMe)_6^{2+}$ and ca.10^{-4}mol l^{-1} in bipy (mole ratio Fe(II) : bipy, ca.15 : 1). The rate of the reaction was found to be too fast to be followed under these conditions, reaction being complete within the dead-time of the instrument.

8. Reaction of $Fe(bipy)_3(PF_6)_2$ with $P(OMe)_3$ in MeCN.

Excess $P(OMe)_3$ was distilled into a flask with a Spectrosil cell side arm, which had been charged previously with a solution of $Fe(bipy)_3(PF_6)_2$ (5×10^{-5}mol l^{-1}). The electronic spectrum did not change from the spectrum of the initial solution, even after shaking for several days at room temperature.

9. Reaction of $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ with 2,2'-bipyridyl in MeCN.

2,2'-bipyridyl (0.046g ; 3×10^{-4}moles) was added to $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ (0.1g ; 10^{-4}moles) in MeCN and immediately a red colour developed indicative of formation of an iron - bipyridyl species. The infra red spectrum of the red solid product which was isolated from the reaction mixture, revealed the presence of both $P(OMe)_3$, $\bar{\nu}_{max}$ 1,040 cm^{-1}, 1,180 cm^{-1} and bipy, $\bar{\nu}_{max}$ 765 cm^{-1}

Table 12.

Observed Spectroscopic Parameters of $Fe(bipy)_3(PF_6)_2$.

1. Electronic Spectrum in MeCN Solution.

$\bar{\nu}$ (cm^{-1})	ε (dm^3 mol^{-1} cm^{-1}) [a]
19,300	8,600
20,200 sh	(7,700)
24,200 sh	(2,400)
25,800 sh	(3,500)
28,750	6,400
33,900 sh	(55,000)
34,700	64,000
38,200 sh	(18,000)
41,000	27,500
42,000	24,000

2. ^1H N.M.R. Spectrum in MeCN Solution.

δ (p.p.m.)	assignment [b]
7.40	6
7.48	5
8.15	4
8.57	3

Key

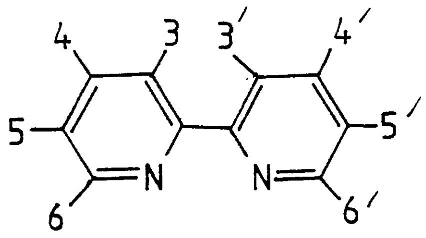


Table 12 (continued).

3. Infra-red Spectrum, Nujol and Fluorube Mulls.

$\bar{\nu}$ (cm^{-1})	Corresponding Band of Free Ligand (cm^{-1}) [c]
1606 s	1582 s
1465 s	1460 s
1444 s	1422 s
1318 m	
1243 m	1254 s
1163 s	1140 s
1128 m	
1073 m	1091 s
1050 m	1040 s
962 m	976 m
840 vs [d]	
765 s	759 vs
734 m	741
560 s [d]	

[a] ref. 85

[b] ref. 86

[c] ref. 87

[d] PF_6^- bands

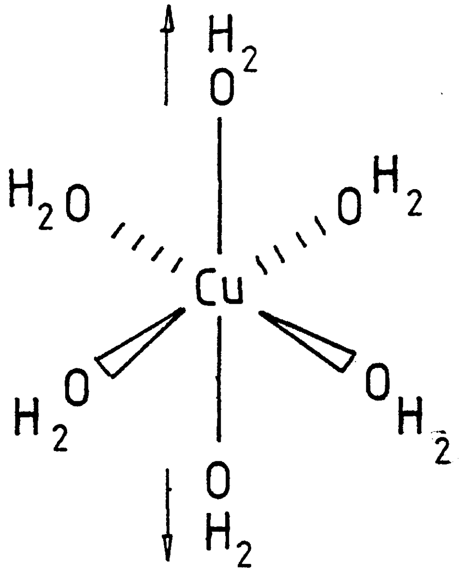
and 1,585 cm^{-1} . There was no evidence for coordinated MeCN. On standing for a day at room temperature, the red solution went colourless and the electronic spectrum showed only one peak, at 27,550 cm^{-1} , which was not assigned.

CHAPTER THREE

Redox and Substitution Reactions of Copper(II) and Copper(I) Cations in Acetonitrile Solution.

Introduction.

The chemistry of copper complexes has been widely studied in both aqueous and non aqueous media. The Cu(II) state has been studied to the greatest extent as it is the most common oxidation state in aqueous solution and the d^9 configuration makes the electronic spectra of such species very interesting.[88] To a first approximation Cu(II) species, in an octahedral environment, should exhibit a simple one band spectrum, corresponding to promotion of one electron from the t_{2g} to the e_g set of orbitals. The d^9 configuration, however, has a degenerate ground state and is thus subject to Jahn - Teller distortion.[1] The observed spectra may thus have an asymmetric band or indeed may even be split resolvably. This is exemplified by the electronic spectrum of $[Cu(H_2O)_6]^{2+}$ which exhibits a band with a broad shoulder on the low energy side. This results from a tetragonal distortion of the cation in solution, with two of the H_2O ligands being further from the metal than the other four.[1]



Cu(II) species exhibit great versatility in their stereochemistry and adopt a geometry ranging from a distorted octahedron, as in $[Cu(H_2O)_6]^{2+}$, through trigonal bipyramidal, in $[Cu(bipy)_2I]^+$,[89] to a flattened tetrahedral structure in Cs_2CuCl_4 . This potential for variable geometry gives Cu(II) salts some very interesting properties and makes them worthy of study.

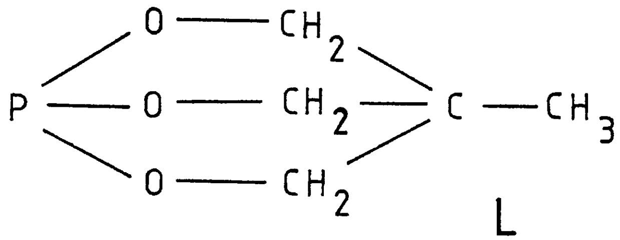
Recently, great interest has been aroused by the discovery of distorted tetrahedral binding sites for copper ions in a number of proteins, including the low molecular weight species, plastocyanin and azurin. Because of the intense colour of these species, they are termed 'copper - blue' proteins. The electronic spectra of the copper(II) ions have very large extinction coefficients, 1,000 to 5,000 $dm^3 mol^{-1} cm^{-1}$, and the ions have high reduction potentials. In the proteins, the copper ion is coordinated via two imine nitrogens from histidine residues and two sulphurs, from a methionine and a cysteine residue.[90] In both azurin and plastocyanin, the copper utilises the oxidation states II and I and the protein is involved in electron transport ; in plastocyanin, from photosystem II to photosystem I, and azurin, between cytochrome C_{551} and cytochrome oxidase.

The mechanism of electron transfer in these species is of great interest. A number of studies have been carried out to investigate oxidation of the reduced form of the protein, with inorganic complexes as the redox partners, for example Co(III) with various substituted 1,10-phenanthroline ligands.[91] The kinetics of the oxidation reaction are consistent with an association of the protein and the inorganic complex prior to electron transfer. Studies with different complexes, of varying steric requirement, led to the proposal that more than one binding site exists on the protein and thus different pathways for electron transfer exist within the protein, specific for certain reagents.[92] Much interesting chemistry remains to be done on such systems.

There has been a great deal of effort expended in the production of compounds to act as models for the biological systems. These compounds possess the same set of four donor atoms and have a similar geometry to the copper ions in the proteins.[93]

In acetonitrile solution, Cu(I) is the favoured state due to the very effective solvation of the cation and, in fact, Cu(II) is a relatively powerful oxidising agent.[1] For this reason the redox and substitution reactions of Cu(II) and Cu(I) in acetonitrile solution are worthy of study. Both species have been well characterised in MeCN and have been prepared by a variety of synthetic routes.[5,11] In some cases the Cu(II) salt is isolated from solution as the salt $Cu(NCMe)_5(PF_6)_2$ but the electronic spectrum, in MeCN solution, suggests that it exists as the tetragonally distorted $Cu(NCMe)_6^{2+}$ ion.[11] Both the Cu(II) and Cu(I) salts are stable in the absence of moisture and oxygen. Preliminary work has shown that Cu(II) , in acetonitrile, reacts with an excess of $P(OMe)_3$ to produce $Cu\{P(OMe)_3\}_4^+$ and dimethyl methyl phosphonate.[15] The reaction involves the rapid formation and subsequent decay of a purple intermediate. It is possible to study the decay of the intermediate by stopped-flow spectrophotometry.

This work stemmed from earlier work on reactions of Cu(II) with alkyl phosphites ; some years ago it was discovered that $[Cu(H_2O)_6]X_2$ ($X{=}ClO_4,NO_3$) reacted with 4-methyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane (L) in ethanol solution to produce the CuL_4^+ salt as product.[94] A later study by the same group



L

showed that the Cu(II) salts also reacted with $P(OMe)_3$ to produce $Cu\{P(OMe)_3\}_4^+$ salts.[95]

Complexes of Cu(II) and Cu(I) with bipy, phen and substituted derivatives have received a great deal of attention in recent years, due in part to controversy over the stereochemistry of some of these species. The complex $[Cu(bipy)_2(H_2O)_2]^{2+}$ is thought to exist in a cis octahedral stereochemistry ; the two bipyridyl ligands are unable to assume a square coplanar conformation about the copper(II), due to steric interactions between hydrogen atoms.[96] As stated above, a number of complexes of the form $Cu(bipy)_2X_2$ have a pseudo trigonal bipyramidal structure around the metal, for example when X=I and the crystal structure of this complex is known.[97] The crystal structure of $Cu(bipy)_3^{2+}$ shows it to be a distorted octahedron, in agreement with the prediction of the Jahn - Teller theorem. The complex has four 'short' Cu-N bonds in a plane, mean distance 2.031 Å and two 'long' bonds, 2.450 Å and 2.226 Å . The inequality of length in the 'long' bonds is unusual and there is no apparent reason why it should occur, although crystal packing effects are the most likely cause.[98]

The complex of Cu(II) with 2,9,-dimethyl-1,10-phenanthroline (dmp) , $Cu(dmp)_2(ClO_4)_2$, is thought to have a distorted tetrahedral environment around the Cu(II) but it is reported to be hygroscopic, absorbing H_2O to form a five or six coordinate species.[99] This Cu(II) species is easily reduced to the corresponding Cu(I) complex, which is assumed to have a pseudo tetrahedral geometry around the metal. During the course of the present work, the crystal structure of the 6,6'-dimethyl-2,2'-bipyridine (dmbp) complex of Cu(I) , $Cu(dmbp)_2BF_4$ was reported.[100] The complex has a distorted tetrahedral environment around Cu(I) and the BF_4^- anion remains uncoordinated.

The potential of the $Cu^{2+}- Cu^+$ couple has been measured in aqueous solution and is 0.158 V relative to the normal hydrogen electrode (N.H.E.) .[1] The potential of the couple in MeCN solution was measured, a number of years ago, to be 1.24 V relative to N.H.E., using voltammetry at a rotating Pt electrode and using $Cu(H_2O)_6(ClO_4)_2$ as the starting material.[101] The large increase in potential of the redox couple was attributed to the extra stability of the Cu(I) solvate, allied to the low solvation energy of Cu(II) and high solvation energy of Cu(I) in MeCN. Addition of four per cent water to the MeCN solution alters the reduction potential to 1.04 V and 68% water to 0.64 V . This change in potential reflects the increase of solvation energy of the Cu(II) ion. This result emphasises the effect water may have in metal ion systems and highlights also the interesting results which can be found in rigorously anhydrous conditions. Due to the low freezing point of

MeCN solutions and the large potential of the Cu^{2+}– Cu^{+} couple, this system has been suggested for use in a battery for working at low temperatures.[102]

The aim of the present work is the examination of the redox and substitution behaviour of solvated Cu(II) and Cu(I), in acetonitrile solution, in the absence of moisture. The major study involves the reaction of Cu(II) with $P(OMe)_3$, mentioned above, where the aim is to characterise the nature of both the intermediate and the products. The kinetics of the decay of the intermediate are evaluated, in an attempt to produce a mechanism for the reaction.

To provide a comparison with the behaviour of Cu(II) with $P(OMe)_3$, the reactions of Cu(II) with bipy and 2,9-dimethyl-1,10-phenanthroline (dmp) , in acetonitrile, are studied. The nature, in MeCN solution, of the complexes produced from these reactions is studied by spectroscopic techniques.

The final part of the work concerns evaluation of the redox potentials of the solvated Cu(II) and Cu(I) salts and the various copper complexes, in MeCN. This is done using the technique of cyclic voltammetry, which has become widely used in measuring redox potentials in inorganic systems.[103] It is interesting to compare the aqueous with the rigorously non aqueous system and also to determine the effect that different ligands have upon the potential of the Cu^{2+}– Cu^{+} couple in MeCN.

Results and Discussion.

Reaction of $Cu(NCMe)_6^{2+}$ with H_2O in solution.

The behaviour of the solvated Cu(II) species with H_2O is of interest, as it is possible that the presence of trace amounts of water has a great influence upon the course of the reactions. Adding water to MeCN and $MeNO_2$ solutions of $Cu(NCMe)_5(PF_6)_2$ merely shifts the position of the absorption band of the electronic spectrum to lower energy. This is the expected result for H_2O substituting for MeCN at the metal centre, the band moving from 13,500 cm^{-1} for $Cu(NCMe)_6^{2+}$ towards 12,500 cm^{-1} for $Cu(H_2O)_6^{2+}$.[1] There is no evidence for hydrolysis of coordinated MeCN.

Reaction of $Cu(NCMe)_4^+$ with $P(OMe)_3$ in MeCN solution.

As a Cu(I) -phosphite complex is found as a product, in the preliminary study of the Cu(II) -phosphite reaction, in MeCN, it is important to characterise the product of the reaction of $Cu(NCMe)_4^+$ with $P(OMe)_3$. The $Cu(NCMe)_4^+$ ion reacts very readily and smoothly with $P(OMe)_3$, with or without the presence of MeCN, to produce $Cu\{P(OMe)_3\}_4PF_6$. This species is characterised by spectroscopy and by microanalysis. The infra-red and Raman data are listed in Table 1. The n.m.r. data for a variety of nuclei (^{63}Cu, ^{65}Cu, ^{31}P, ^{19}F and ^{1}H) are listed in Table 2 and illustrated in Figure 1 and are in good agreement with results of other workers. ^{63}Cu and ^{65}Cu both have spin I = $^3/2$ and thus have an associated electric quadrupole moment, which leads to rapid relaxation of the nuclear spin. For this reason coupling to these nuclei is not normally observed unless the quadrupolar nucleus has a high degree of symmetry. The regular tetrahedral geometry around the copper

Table 1.

Infra-red and Raman Bands of $Cu\{P(OMe)_3\}_4^+$.

Infra-red (cm^{-1}) (solid state)	Raman (cm^{-1}) (MeCN solution)	Assignment[126]
3020 w	3018 (10)	ν_{asym} CH_3
2965 m		ν_{sym} CH_3
2856 m	2855 (14)	$2\,\delta$ CH_3
	1470 (8)	δ_{asym} CH_3
1180 s		γ CH_3
	1060 (10)	ν_{sym} $P(OC)_3$
1030 vs	1020 (10)	ν_{asym} $P(OC)_3$
840 s		T_{1u} PF_6^-
784 s	775 (20)	ν_{sym} $P(O)_3$
	750 (26)	ν_{asym} $P(O)_3$
735 s		ν_{asym} $P(O)_3$
	715 (16)	comb.
560 m		T_{1u} PF_6^-
523 m	515 (8)	asym $P(OC)_3$ bend

i.r. intensities :- w, weak ; m, medium ; s, strong.

Raman intensities :- scale 1-25

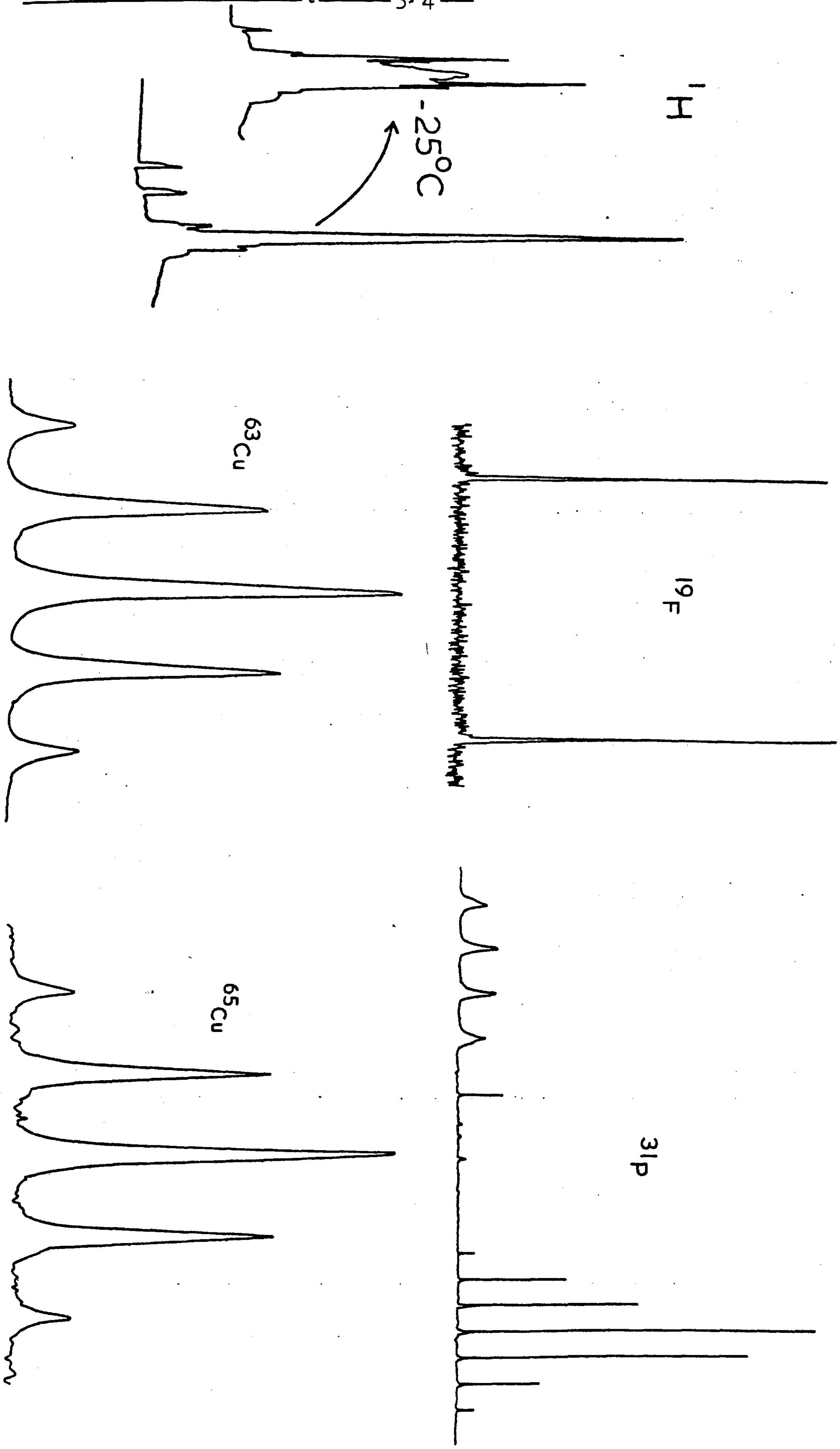
Table 2.

N.M.R. Spectra of $Cu\{P(OMe)_3\}_4PF_6$ in CD_3CN Solution.

Nucleus	Chem. Shift δ (p.p.m.)	Coupling Const. (Hz)	Type of Signal
^{31}P	125.6 -144.6	J_{Cu-P} 1231 J_{P-F} 706	1:1:1:1 quartet 1:6:15:20:15:6:1 septet
^{19}F	-71.5	J_{P-F} 707	1:1 doublet
^{63}Cu		J_{Cu-P} 1221	1:4:6:4:1 quintet
^{65}Cu		J_{Cu-P} 1311	1:4:6:4:1 quintet
^{1}H	3.72		290 K broad singlet 248 K $[A_9X]_4$ multiplet

Figure 1.

N.M.R. Spectra of $Cu\{P(OMe)_3\}_4^+$.



is confirmed by measurement of the ^{31}P n.m.r. spectrum of $Cu\{P(OMe)_3\}_4ClO_4$.[104] The $^{31}P-\{^1H\}$ spectrum, measured in this work, shows two sets of overlapping 1:1:1:1 quartets due to coupling of the ^{31}P with a ^{63}Cu or a ^{65}Cu nucleus. The outer peaks are smaller and have a pronounced shoulder because the coupling constants, $J_{^{63}Cu-P}$ and $J_{^{65}Cu-P}$ are significantly different and so the quartets do not exactly overlap. Both ^{63}Cu and ^{65}Cu n.m.r. spectra consist of 1:4:6:4:1 quintets due to coupling with four equivalent phosphorus nuclei. The copper spectra have previously been obtained by indirect means.[105] The spectra of ^{63}Cu, ^{65}Cu and ^{31}P are broadened due to some residual quadrupolar relaxation, caused by a lowering of the symmetry. This results from asymmetric vibration of the Cu-P bonds and from ligand exchange reactions. Reducing the temperature of the solution causes these bands to sharpen as vibration diminishes. The lowering of temperature also reduces the rate of exchange of the trimethyl phosphite ligands. At 248 K, exchange is sufficiently slow that the ^1H n.m.r. spectrum appears as the band characteristic of an $[A_9X_4]_4$ spin system (where $A={}^1H$ and $X={}^{31}P$), with a broad central band, flanked by two sharp outer lines.[105]

Reaction of $Cu(NCMe)_4^+$ with PF_3 in MeCN solution.

To test the ability of $Cu(NCMe)_4^+$ to partake in other substitution reactions, with tervalent phosphorus species, in acetonitrile solution, a reaction with PF_3 was attempted but met with no success. This is presumably due to the high stability of the solvated cation. For an incoming ligand to react, it must have potential to produce a more stable cation. The potential to stabilise the cation must be a function of the relative σ-donor :

π-acceptor ability of the ligand. PF_3, though an excellent π-acceptor, is too poor a σ-donor to react. In liquid SO_2, a much poorer solvent for Cu^+, PF_3 does react with Cu^+ to produce the 1:1 adduct $[CuPF_3]^+$, which can be isolated as the AsF_6^- salt.[106] This salt is stable for several weeks at room temperature, if it is stored in a sealed vessel. In SO_2 solution, the cation does not possess the same inherent stability as in MeCN solution. The activation energy barrier for the reaction is smaller and so the reaction of Cu^+ with PF_3 is feasible.

Reactions of $Cu(NCMe)_6^{2+}$ with $P(OMe)_3$ in MeCN solution.

The species $Cu(NCMe)_6^{2+}$, in MeCN solution, reacts with $P(OMe)_3$ to produce, initially, a purple intermediate which decays rapidly. The final products of the reaction are $Cu\{P(OMe)_3\}_4PF_6$, dimethyl methyl phosphonate and the trimethoxymethyl phosphonium cation, $[MeP(OMe)_3^+]$. The metal salt is identified using a combination of n.m.r. spectroscopy and infra-red spectroscopy and comparing the spectra with data obtained from a sample of $Cu\{P(OMe)_3\}_4PF_6$, prepared and characterised by the reaction of $Cu(NCMe)_4^+$ with $P(OMe)_3$ (vide supra). $MeP(O)(OMe)_2$ is identified by its infra spectrum and by ^1H n.m.r. spectroscopy. $MeP(OMe)_3^+$ is identified by ^1H n.m.r. spectroscopy. The ^{31}P chemical shifts of the two organophosphorus species are obtained by heteronuclear decoupling of the ^1H spectrum and are in good agreement with published data ; 32.8 p.p.m. for $MeP(O)(OMe)_2$ (literature,[107] 32.0 p.p.m.) , 53.5 p.p.m. for $MeP(OMe)_3^+$ (literature,[108] 53.9 p.p.m.) .

The formation of the intermediate is extremely rapid but the decay is followed by stopped flow spectrophotometry. The spectrum of the purple species is obtained by plotting the change in optical density, determined from stopped flow spectrophotometry, as a function of wavelength. The results of an experiment, using solutions 5×10^{-4} mol l^{-1} in Cu(II) and 5×10^{-2} mol l^{-1} in $P(OMe)_3$, are given in Table 3 and are shown plotted in Figure 2. The absorption maximum occurs at 29,000 cm^{-1} and has an extinction coefficient of ca. 3×10^3 dm^3 mol^{-1} cm^{-1} . The spectrum does not change upon reducing the concentration of the $P(OMe)_3$ solution to 5×10^{-3} mol l^{-1} , which is the lowest concentration for which reproducible data are obtained.

The band is assigned as the d-d band of the $[Cu\{P(OMe)_3\}_x(NCMe)_{6-x}]^{2+}$ cation, where x is unknown. For $Cu(NCMe)_6^{2+}$, the d-d band occurs at 13,500 cm^{-1} and thus considerable strengthening of the crystal field has occured upon substitution of $P(OMe)_3$ for NCMe . There are no data in the literature concerning the electronic spectra of comparable species. The large size of the extinction coefficient probably arises from a combination of two factors :- i) a lowering of the symmetry of the cation, which allows the mixing-in of orbitals of other symmetry into the electronic wave function, which relaxes the selection rule, and ii) intensity stealing, from the very intense charge transfer bands which occur at higher energy ($>$40,000 cm^{-1}).

The rate of ligand substitution at Cu(II) in solution is known to be extremely fast. This effect is due to the Jahn - Teller distortion, which results in two solvent molecules being further from the metal centre than the other four, and thus more readily lost in a reaction. The lower limit for solvent exchange at $Cu(NCMe)_6^{2+}$, as determined by ^{14}N n.m.r. studies, is 1.6×10^7 s^{-1}

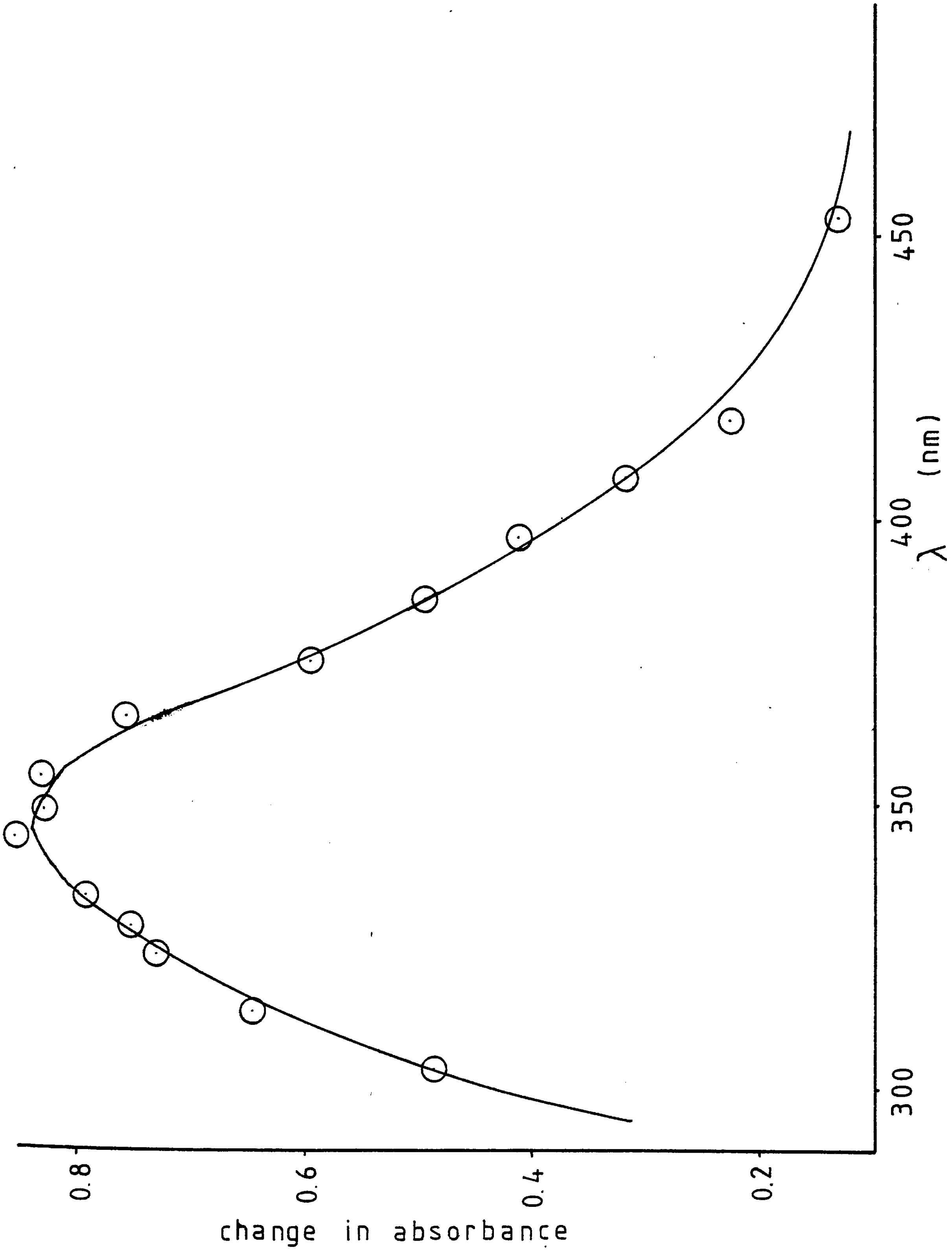
Table 3.

Total Change in Optical Density for the Reaction of $Cu(NCMe)_6^{2+}$ with $P(OMe)_3$ as a Function of Wavelength.

λ (nm)	Δ O.D.
450	0.128
415	0.222
405	0.310
395	0.403
385	0.480
375	0.579
375	0.580
365	0.736
355	0.807
350	0.810
345	0.830
340	0.774
340	0.836
335	0.771
330	0.735
325	0.715
315	0.632
305	0.477

Figure 2.

Electronic Spectrum of the Intermediate Complex Formed in the Reaction of $Cu(NCMe)_6^{2+}$ with $P(OMe)_3$.



at 228 K.[109] Assuming that the stability constants for complex formation between Cu(II) and $P(OMe)_3$ are large, at least for the early stages of substitution, then it seems likely that substitution of $P(OMe)_3$ for NCMe at the copper centre will proceed to a fairly high degree within the observation time, under the experimental conditions. A consequence of this is that the observed spectrum of the intermediate (Figure 2) arises from a mixture of cations of general formula $[Cu\{P(OMe)_3\}_x(NCMe)_{6-x}]^{2+}$, although one species may predominate.

One way to resolve this problem of which species contribute to the purple colour, is to investigate the reaction by e.s.r. spectroscopy. Cu(II) species with different numbers of $P(OMe)_3$ ligands will show separate resonances due to hyperfine coupling of the unpaired electron with different numbers of phosphorus nuclei.

The rate of decay of the purple intermediate is measured, by stopped flow spectrophotometry, as a function of the concentration of $P(OMe)_3$. The results are listed in Table 4. The reaction is carried out under pseudo first order conditions, with $P(OMe)_3$ being in large excess ; at least 15 fold over the concentration of Cu(II). When $P(OMe)_3$ solutions with smaller ratios of $P(OMe)_3$: Cu(II) are used, the results show deviations from first order behaviour. The largest concentration of $P(OMe)_3$ which is used is 7.5×10^{-2} mol l^{-1} ; at higher concentrations, the decay is too fast to be followed, the reaction being complete within the dead time of the instrument. The decay has a second order dependence upon the concentration of $P(OMe)_3$, shown by the plot of k_{obs}, the pseudo first order rate constant, against the square of the concentration of $P(OMe)_3$

Table 4.

k_{obs} for the Reaction of $Cu(NCMe)_6^{2+}$ with $P(OMe)_3$ as a Function of $[P(OMe)_3]$ and $[P(OMe)_3]^2$.

a) λ = 345 nm

$[P(OMe)_3]$ (10^2 mol l^{-1})	$[P(OMe)_3]^2$ (10^4 mol^2 l^{-2})	k_{obs} (s^{-1})	k_{obs} average (s^{-1})
0.75	0.56	0.32	0.32
1.50	2.25	0.59	0.595
		0.60	
2.50	6.25	1.94	1.75
		1.89	
		1.41	
3.75	14.06	3.78	4.23
		4.67	
5.00	25.00	5.11	6.24
		5.18	
		8.00	
		6.67	
5.50	30.3	15.00	15.00
6.50	42.3	15.70	15.70
7.50	56.3	18.75	18.75

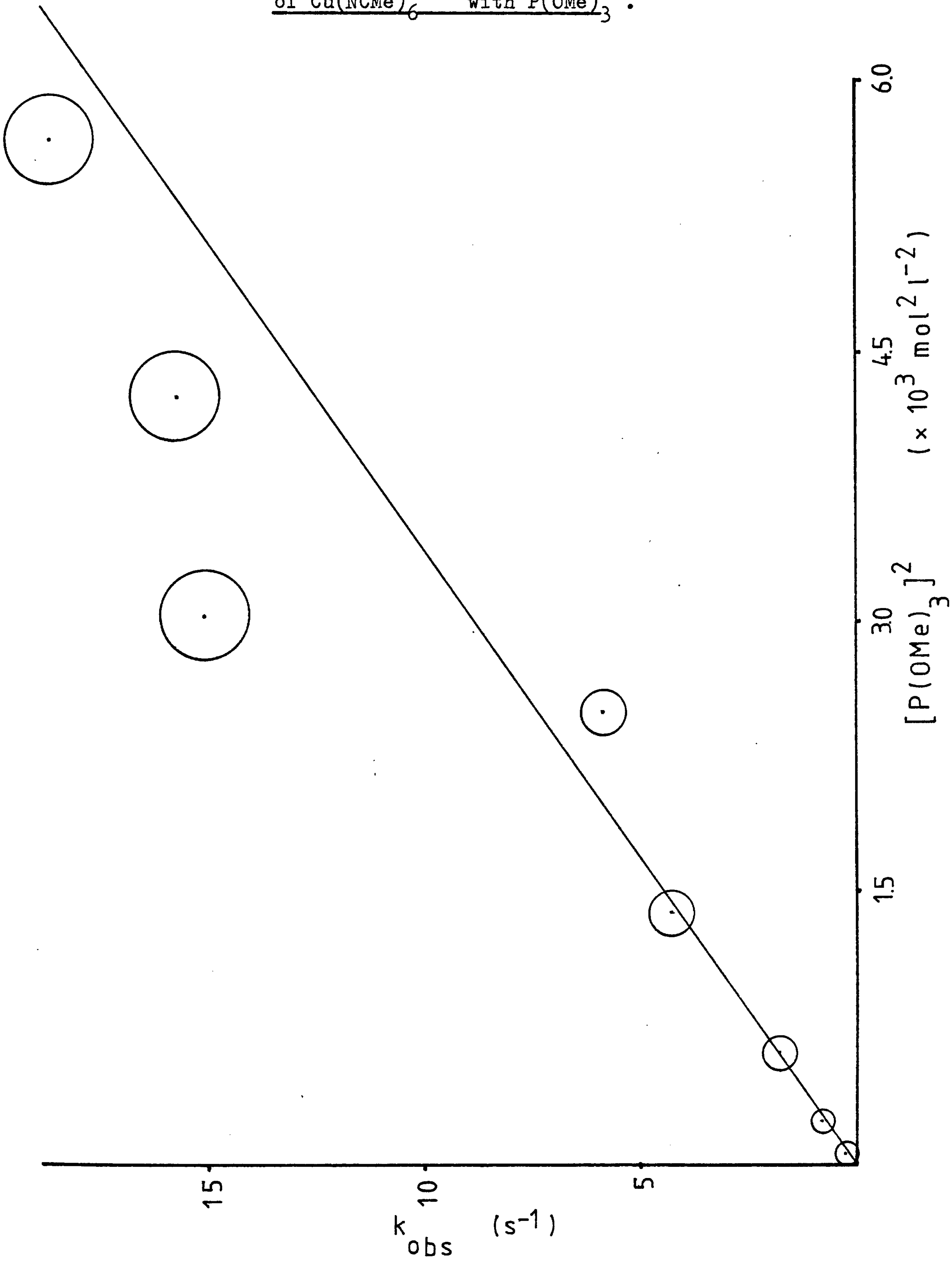
Table 4(continued).

b) λ = 405 nm

$[P(OMe)_3]$ (10^2 mol l^{-1})	$[P(OMe)_3]^2$ (10^4 mol^2 l^{-2})	k_{obs} (s^{-1})	k_{obs} average (s^{-1})
2.5	6.25	4.88	
		2.00	2.62
		0.98	
5.0	25.00	10.22	
		10.00	9.77
		9.00	

Figure 3.

Plot of Observed Rate Constant vs. $[P(OMe)_3]^2$ for the Reaction of $Cu(NCMe)_6^{2+}$ with $P(OMe)_3$.



(Figure 3) . The gradient of the line is the overall third order rate constant for the reaction and is found to be $2.8 \times 10^{3}\ l^{2}\ mol^{-2}\ s^{-1}$.

The results are calculated as detailed in the appendix on stopped flow spectrophotometry. The straight line of Figure 2 is biased toward the points obtained at low concentration of $P(OMe)_3$ for two reasons ; i) the points in most cases are an average of at least two separate determinations, with different Cu(II) solutions and, ii) the traces are less subject to error from random interference, as the time scale which is used is much longer. The major experimental error arises from the making up of the $P(OMe)_3$ solutions. These are made up in the glove box by weighing the appropriate amount of $P(OMe)_3$ and diluting to a standard volume. This is done as rapidly as possible to avoid loss by evaporation of the volatile $P(OMe)_3$. The error in concentration is assumed to be of the order of ± 10% .

Assuming that $[Cu^{II}] = [Cu^{II}P_x]$, that is $K_1, K_2, \ldots K_x$ are large, the observed rate law for the reaction is

$$\text{Rate} = -\frac{d[Cu^{II}P_X]}{dt} = k[Cu^{II}P_X][P]^2 \qquad (1)$$

where $Cu^{II}P_x$ is the purple species and P is $P(OMe)_3$. The second order dependence of $P(OMe)_3$ is, at first sight, difficult to rationalise. It may be accounted for by considering the following mechanism :- if there is an equilibrium step between the redox active $Cu^{II}P_x$ species and a species of lower substitution, $Cu^{II}P_{x-1}$, of the form,

$$Cu^{II}P_{X-1} + P \xrightleftharpoons{K} Cu^{II}P_X \qquad (2)$$

then the rate of decay has dependence upon one mole of $P(OMe)_3$. If a further mole of $P(OMe)_3$ is necessary in the actual decay step, in order to allow formation of a dimeric radical cation,

$$Cu^{II}P_x \quad + \quad P \quad \xrightarrow{k'} \quad Cu^{I}P_{x-1} \quad + \quad P_2^{+\cdot} \qquad (3)$$

then the decay is dependent upon two moles of $P(OMe)_3$ and the full rate expression is :-

$$\text{Rate} = -\frac{d[Cu^{II}P_x]}{dt} = \frac{k'K[Cu^{II}P_{x-1}][P]^2}{1 + K[P]} \qquad (4)$$

If the value of K is small and $[P]$ does not become large, then $K[P] \ll 1$ and (4) reduces to,

$$\text{Rate} = -\frac{d[Cu^{II}P_x]}{dt} = k'K[Cu^{II}P_{x-1}][P]^2 \qquad (5)$$

which is of the same form as (1) .

The proposition that a second mole of $P(OMe)_3$ is involved in the decay, necessary for formation of the dimeric radical cation, is not unreasonable. Dimeric radical cations of tervalent phosphorus have been known for some time and have been characterised by e.s.r. spectroscopy, for example $(Et_3P)_2^{+\cdot}$ and $(Bu_3P)_2^{+\cdot}$, obtained by γ-irradiation, at 77 K .[110] Dimer phosphine radicals of the form $[X_3P{-}{-}PX_3]^{+\cdot}$ have been prepared by electrochemical oxidation. It was proposed that the unpaired electron exists in a σ^* molecular orbital formed from 3s and 3p atomic orbitals on phosphorus. The two phosphorus atoms of the dimer are equivalent and have a pseudo tetrahedral geometry.[111] The dimeric radical cation of $P(OMe)_3$, $[(MeO)_3P{-}{-}P(OMe)_3]^{+\cdot}$, has been prepared by γ-irradiation of a single crystal at 77 K .[112] The only other product observed from this experiment was the monomeric radical anion, $P(OMe)_3^{-\cdot}$. There was no evidence for the monomeric radical cation, $P(OMe)_3^{+\bullet}$ and it seems that the dimeric species is preferred over the monomeric.

The mode of breakdown of the dimer is speculative but may be of the form,

$$(MeO)_3P—P(OMe)_3^{+\bullet} \longrightarrow (MeO)_3P + {}^\bullet P(O)(OMe)_2 + Me^+ \qquad (6)$$

The Me^+ cation will react with $P(OMe)_3$ to generate the trimethoxy methyl phosphonium cation.

$$Me^+ + P(OMe)_3 \longrightarrow MeP(OMe)_3^+ \qquad (7)$$

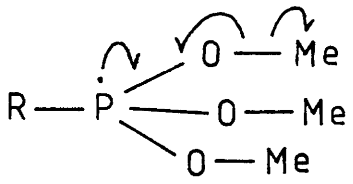
This cation is the ionic intermediate which is expected for an Arbusov rearrangement of the tervalent phosphorus and it has been shown to decompose to $MeP(O)(OMe)_2$ and Me^+ .[113] The Me^+ which is generated may then react with a further molecule of $P(OMe)_3$, and the process continues until all the excess $P(OMe)_3$ has been used up. This accounts for the formation of the major phosphorus containing products observed in the reaction. The fate of $\dot{P}(O)(OMe)_2$, if it is formed, is unknown but it may react or decompose to give a variety of phosphorus compounds and the ^1H n.m.r. spectrum of the reaction mixture does yield evidence for the existence of small amounts of unidentified species which have $^{31}P — ^1H$ coupling.

This pathway for the breakdown of the dimer is preferred over another which produces a $Me^\bullet$ radical, rather than Me^+ cation. The $Me^\bullet$ radical will not bring about the free radical Arbusov reaction, which must be postulated to account for $MeP(O)(OMe)_2$ in the products.

$$R^\bullet + (MeO)_3P \longrightarrow RP(O)(OMe)_2 + Me^\bullet \qquad (8)$$

For such a reaction to occur, the alkyl radical must be reasonably reactive, or else the β-scission step to produce the products must be rapid.[114] The reaction occurs when $R^\bullet = Ph^\bullet$ but not when

$R^{\bullet} = Me^{\bullet}$. An e.s.r. study of the reaction will characterise the



β - scission step

radical species which are involved.

The value of x in the Cu(II) species is open to debate. As substitution reactions of copper(II) are normally very fast, the important factor will be the magnitude of the stability constants, K_n , for the successive substitution steps. If these are large for the early steps, then the purple species will be a fairly highly substituted complex. The stability constants for complex formation between $Cu(H_2O)_6{}^{2+}$ and NH_3 have been determined as $K_1 = 12{,}000$; $K_2 = 3{,}000$; $K_3 = 800$; $K_4 = 120$; $K_5 = 0.3$; $K_6 = 0$.[115]

An attractive proposition is that substitution occurs, rapidly and easily, until virtually all the Cu(II) is present as $[Cu\{P(OMe)_3\}_4(NCMe)_2]^{2+}$. The value of K for the next substitution is small, by analogy with the Cu(II)-NH_3 system. When a further molecule of $P(OMe)_3$ manages to substitute at the copper centre, to form $[Cu\{P(OMe)_3\}_5NCMe]^{2+}$, the Cu(II) ion, which is a very strong oxidising agent, rapidly oxidises one of the coordinated $P(OMe)_3$ groups. This produces $Cu\{P(OMe)_3\}_4{}^{+}$ directly and the oxidised ligand dimerises with a molecule of free $P(OMe)_3$. Thus, in the above reaction scheme, $x = 5$. Complexes with $x < 5$ are also strong oxidising agents. This is shown by the reaction of $Cu(NCMe)_6{}^{2+}$ with $P(OMe)_3$ in a mole ratio of greater than 1:1 . The reaction proceeds, with formation of an intermediate, which decays, but much more slowly than when $P(OMe)_3$ is in excess. This suggests that, thermodynamically, the lower complexes are strong oxidising agents, but, kinetically, the redox step is slow. In the absence of excess $P(OMe)_3$ in solution, the subsequent reaction follows a different pathway. Any Me^+ cation, generated under these conditions, presumably attacks the solvent which very rapidly decomposes to produce a dark brown, sticky material.

The ability of Cu(II) species to act as oxidising agents to coordinated ligands has been noted in other systems. As stated above, reactions of hydrated copper(II) salts with trialkyl phosphites, in ethanol solution, produced CuL_4^+ species, but no colour changes, comparable to the system in MeCN, were observed. The intense purple coloured intermediate, observed in this work, is a function of the absence of O_2 and H_2O in the system. When O_2 and H_2O are present, the reaction presumably occurs so quickly that no intermediate is detected. Thus it appears that $Cu\{P(OR_3)\}_x^{2+}$ species in general, are very strong oxidising agents. In some cases, they are so strong that they oxidise a ligand molecule to produce a Cu(I) complex. This oxidising ability of the Cu(II) species arises from two sources. Firstly, increasing steric effects, upon substitution of the bulky $P(OR)_3$ group for NCMe at the Cu(II) centre, will tend to destabilise the pseudo octahedral Cu(II) species and favour formation of the less sterically demanding tetrahedral Cu(I) species. Secondly, the presence of extensive metal to ligand π-bonding in the copper complexes will reduce the effective electron density at the metal centre. This will make the Cu(II) more willing to accept an electron in a redox reaction, as the electron density which is gained will be partially delocalised over the π-bonding system. Both of these effects will increase the oxidation potential of the Cu(II) species. In keeping with the existence of π-bonding in copper-$P(OR)_3$ complexes is the ^{31}P chemical shift of the coordinated $P(OMe)_3$ in $Cu\{P(OMe)_3\}_4^+$. The resonance of the ^{31}P nucleus of $P(OMe)_3$, coordinated to Cu^+, is shifted to a higher field than free $P(OMe)_3$. This increased shielding of the phosphorus can be ascribed to substantial π-donation from the metal to the ligand.

Cu(II) species, in reaction with thiourea and substituted thioureas, also undergo reduction to yield the Cu(I) complexes as products, along with the oxidised ligand. In these reactions rose to purple coloured intermediates were observed, in both aqueous and non aqueous solvents. In MeCN solution, in the reaction of Cu(II) with tetramethyl thiourea, (tmtu), workers characterised the red intermediate as a Cu^{II}— S bonded species by e.s.r. spectroscopy.[116] The final products were $Cu(tmtu)_4^+$ and $[(Me_2N)_2C\text{-}S\text{-}S\text{-}C(NMe_2)_2]^{2+}$. Recently this was confirmed by the crystal structure of [Cu(t[Cu(tmtu)], obtained as the major product of reaction of tmtu with $CuCl_2 \cdot 2H_2O$ in aqueous solution, which clearly shows the coordination of the sulphur to the metal.[117]

In the reaction of Cu(II) with $P(OMe)_3$ in MeCN solution, when the kinetics of decay are measured at 24,700 cm^{-1} rather than 29,100 cm^{-1}, the rate of decay is found to be significantly faster. This is due to the presence of small amounts of the complexes of lower substitution. These react via complexation, or redox to give other products, which absorb at different wavelengths. Allied to the small absorbance of the major species at this wavelength, the presence of these lower species makes the rate of reaction appear to be much more rapid. Some of the results for decay at 24,700 cm^{-1} are listed in Table 4.

Reaction of $Cu(NCMe)_6^{2+}$ with bidentate nitrogen donor ligands in MeCN solution.

Further substitution reactions of Cu(II) were investigated using the bidentate nitrogen donor ligands, 2,2'-bipyridyl and 2,9-dimethyl-1,10-phenanthroline.

The $Cu(NCMe)_6^{2+}$ cation reacts readily with an excess of bipy to produce the dark blue $Cu(bipy)_3^{2+}$ species, isolated as the PF_6^- salt. This is clearly shown by electronic spectroscopy. In one reaction an olive green colour was formed but this changed, over a few days to give the dark blue colour of $Cu(bipy)_3^{2+}$. The electronic spectra showed the decay of an absorption, probably due to a copper-bipyridyl species of unusual coordination. This species reacts slowly to produce the normal trisubstituted cation.

The cation, $Cu(bipy)_3^{2+}$, is well known [88] and, as stated in the introduction, the crystal structure has been reported.[98]

In one instance a royal blue solution resulted from the reaction of Cu(II) with bipyridyl. The electronic spectrum of this species, by analogy with $[Cu(bipy)_2(H_2O)_2]^{2+}$, is consistent with the formulation $[Cu(bipy)_2(NCMe)_2]^{2+}$. The aquated cation has a cis pseudo octahedral stereochemistry, as discussed above and, from the similarity of the electronic spectra (Table 5), it is likely that the acetonitrile solvated ion adopts the same geometry.

The Cu(II) ion also reacts rapidly with 2,9-dimethyl-1,10-phenanthroline (dmp), in MeCN solution, to produce the solvated,

Table 5.

Electronic Spectra of Some Copper(II) Complexes.

Complex	$\bar{\nu}_{max}$ (cm^{-1})	Ref.
$Cu(H_2O)_6^{2+}$	12,500	88
$Cu(NCMe)_6^{2+}$	13,500	this work
$Cu(bipy)_3^{2+}$	14,700	88
	(14,800)	this work
$Cu(bipy)_2I^{+}$	12,500	125
$Cu(bipy)_2(H_2O)_2^{2+}$	10,500 ; 13,900	88
$Cu(bipy)_2(NCMe)_2^{2+}$	10,900 ; 13,700	this work
$Cu(dmp)_2(NCMe)_2^{2+}$	9,900 ; 13,800	this work
$Cu\{P(OMe)_3\}_x(NCMe)_{6-x}^{2+}$ (x= 5?)	29,000	this work

green species, $Cu(dmp)_2^{2+}$. Some controversy existed over the nature of this species in solution, concerning the presence or absence of solvent molecules in the inner coordination sphere of the metal. The purple anhydrous species $Cu(dmp)_2(ClO_4)_2$ was reported to react rapidly with moisture, to form a green species with five or six coordination of the copper.[99] In this work, the infra red spectrum of the green solid, isolated from acetonitrile solution, confirms the presence of coordinated acetonitrile. Moreover the electronic spectrum of the green species, in acetonitrile solution, consists of two bands, at 9,900 cm^{-1} and 13,800 cm^{-1}, of similar intensity. Spectra of this type have been observed for species which have a cis octahedral geometry about the metal,[97] as discussed above for $[Cu(bipy)_2(H_2O)_2]^{2+}$,[88] and so the green species, in MeCN solution, is assigned as cis-$[Cu(dmp)_2(NCMe)_2]^{2+}$. Whether both MeCN molecules or only one remain coordinated in the solid state remains to be determined.

A number of reports comment upon the ease of reduction of the Cu^{II}-dmp species. Indeed solvated $Cu(dmp)_2^{2+}$ is a relatively powerful oxidising agent and has been used in the study of the oxidation of SCN^- and thiourea, in aqueous solution and in MeOH.[118] The reduced product of these reactions is $Cu(dmp)_2^{+}$. This ion is well characterised and formation of this brightly coloured species is the basis of an analytical determination of copper. In these studies, $[Cu(dmp)_2(NCMe)_2]^{2+}$ and $[Cu(bipy)_2(NCMe)_2]^{2+}$ rapidly oxidised copper metal, in MeCN solution, to produce a bright red and dark red solution, respectively. This is due to formation of $Cu(dmp)_2^{+}$ and $Cu(bipy)_2^{+}$. These cations have a distorted tetrahedral structure about the metal, confirmed by the crystal structure of $Cu(dmp)_2NO_3$ [119] and the related $Cu(dmbp)_2BF_4$, [100] mentioned previously. They are extremely stable, thermodynamically, and for this reason the corresponding Cu(II) complexes are relatively powerful oxidising agents and will oxidise copper metal to Cu(I) in MeCN. The electronic spectra of a number of Cu(II) complexes, pertinent to this work, are listed in Table 5.

Oxidation of $Cu(NCMe)_4^+$ in MeCN solution.

The high stability of the solvated Cu(I) ion in MeCN solution leads to a large oxidation potential for this ion. Thus relatively strong oxidising agents are necessary to produce solvated Cu(II) in MeCN. Copper metal is oxidised by tungsten hexafluoride, in MeCN, to the Cu(II) solvate and so WF_6 is a strong enough oxidising agent to oxidise Cu(I).[2] Earlier work upon the reaction of $CuWF_6$ with WF_6 in MeCN had found the redox step to be temperature dependent. As the temperature was reduced from 295 K to 255 K, the amount of Cu(II) in solution increased.[120] This was shown by a number of spectroscopic techniques and by the observation of a colour change from yellow to blue. The reaction was thought to involve the equilibria

$$Cu^{+}(solv.) \rightleftharpoons Cu^{2+}(solv.) + e^{-} \qquad (9)$$

$$WF_6(solv.) + e^{-} \rightleftharpoons WF_6^{-}(solv.) \qquad (10)$$

$$WF_6^{-}(solv.) + WF_6(solv.) \rightleftharpoons WF_5(solv.) + WF_7^{-}(solv.) \qquad (11)$$

Addition of WF_6 to a solution of $CuPF_6$ in MeCN, gives rise to a blue colour, well below room temperature, corresponding to formation of $Cu(NCMe)_6^{2+}$. This colour persists at room temperature and the electronic spectrum is consistent with formation of the Cu(II) species. Removal of the volatile material generates an off white solid, presumably a mixture of Cu(II) and Cu(I) solvated salts.

The potential of the couple $WF_6 - WF_6^-$ in MeCN solution has recently been measured, using cyclic voltammetry, to be 0.82 V relative to the saturated Calomel Electrode (S.C.E.) .[121] This is somewhat less than the 1.0 V measured for the $Cu^{2+} - Cu^+$ couple, in MeCN,[101] which had a little H_2O also present but the relative values are subject to considerable error. This arises from different measurement techniques and, more importantly, the different methods of referencing, $Cu^{2+} - Cu^+$ directly against S.C.E. and $WF_6 - WF_6^-$, by measuring the potential relative to an internal $Cp_2Fe - Cp_2Fe^+$ couple and adjusting the value to S.C.E. .

Oxidation of $Cu(NCMe)_4^+$ in MeCN was also attempted using Ni(III) salts :- $[Ni(cyclam)(NCMe)_2][ClO_4]_3$ and $[Ni(cyclam)(NO_3)_2][NO_3]$, where cyclam is the tetradentate macrocycle, 1,4,8,11-tetraazacyclotetradecane. $[Ni(cyclam)(NCMe)_2]^{3+}$ does not oxidise Cu(I) but instead decomposes photochemically in solution. This was shown conclusively by following the decay of the strong absorption band on the electronic spectrum of the Ni(III) salt, in the light and in the dark, with or without added Cu(I) salt. On the other hand, $[Ni(cyclam)(NO_3)_2]^+$ very rapidly oxidises Cu(I) to the Cu(II) solvate. This suggests that the size of the $Ni^{3+} - Ni^{2+}$ couple for these two species depends markedly upon the nature of the axially coordinated ligands and that, in terms of oxidation potential,

$$[Ni(cyclam)(NCMe)_2]^{3+} < \underline{ca.}\ 1.0 \text{ to } 1.2\ V \text{ (relative to N.H.E.)} < [Ni(cyclam)(NO_3)_2]^+$$

Alternatively, the size of the redox potential may not be the controlling factor but it may depend upon the mechanistic pathway of the reaction. For example, NO_3 has potential to act as a bridging ligand in electron transfer, whereas MeCN cannot, and this may account for the observed results. The redox potential of the $Ni^{3+}-Ni^{2+}$ couple has been measured in MeCN, by cyclic voltammetry, as + 1.47 V relative to N.H.E. .[122] Thus the MeCN complex should be a strong enough oxidising agent for $Cu(NCMe)_4^+$ and the failure to observe a reaction suggests that the mechanistic criterion is the controlling factor. Accurate evaluation of the redox potential of the couples for various Ni^{III} salts in MeCN solution will help to resolve this situation.

Cyclic Voltammetry of Some Copper Complexes in MeCN Solution.

The results of cyclic voltammetry studies are listed in Table 6. The results are all internally referenced with respect to added ferrocene, as discussed in the appendix. The results quoted in this section, except where noted will be with respect to the $Cp_2Fe-Cp_2Fe^+$ couple in MeCN. All the couples are pseudo-reversible with the exception of $Cu\{P(OMe)_3\}_4^+$ where only the oxidation wave is observed. This appears at *ca.* + 1.8 V , which shows the $Cu^{II}\{P(OMe)_3\}_4$ species to be a very strong oxidising agent, as is expected from the kinetic studies. The Cu(II) centre oxidises a coordinated $P(OMe)_3$, chemically removing the Cu(II) species, hence no reduction wave is observed.

The results for the $Cu^{2+}-Cu^+$ couple in MeCN, in the absence of added ligand, are very complicated, starting either from the Cu(II) or the Cu(I) salt. The couple is very far from being reversible, the average peak to peak distance being *ca.* 500 mV. There is an

Table 6.

Results of Cyclic Voltammetry Studies of Some Copper Complexes in MeCN Solution.

Complex	$E_{\frac{1}{2}}$ (V) [a]	Peak to Peak(V)
$Cu(NCMe)_5(PF_6)_2$	+0.510	0.420
$Cu(NCMe)_4PF_6$	+0.840	0.570
$Cu(dmp)_2(NCMe)_x(PF_6)_2$	+0.250	0.105
$Cu(bipy)_3(PF_6)_2$	-0.320	0.140
$Cu\{P(OMe)_3\}_4PF_6$ [b]	+1.800	-

[a] relative to $Cp_2Fe - Cp_2Fe^+$

[b] oxidation wave only is observed

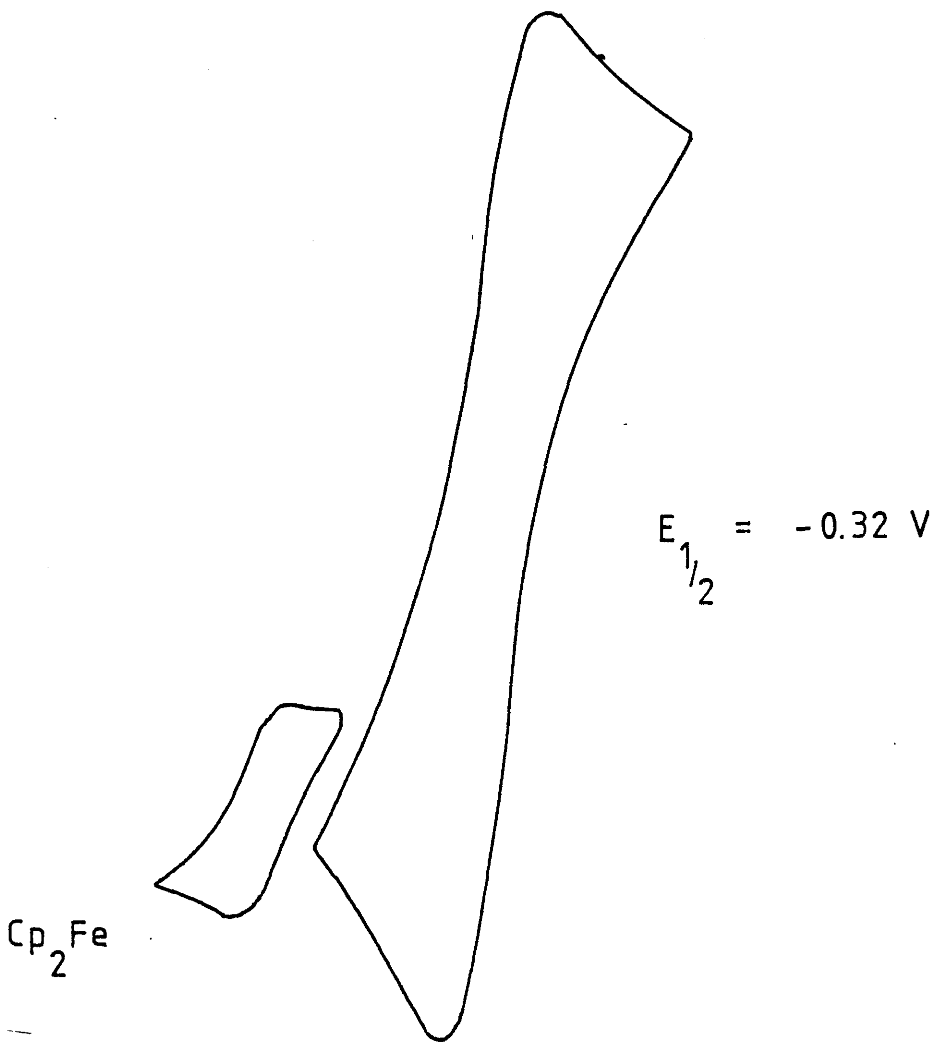
added complication in that the metal solvates react in some way when ferrocene is added to the solution. The oxidation and reduction waves broaden and undergo a shift which is apparently not reproducible from experiment to experiment. The nature of the reaction was not explored but it may be some outer sphere association of the copper ions with ferrocene, which slightly alters the potential of the redox couple. The oxidation peak of the couple, using both Cu(II) and Cu(I) salts as starting materials, is relatively well defined, while the reduction peak is very broad and suggests that more than one species is being reduced. There is a large peak due to the major reducing species but also a smaller 'hump' at a potential much closer to the oxidation peak and thus more nearly reversible. These two reducing species are presumably due to Cu(II) solvated species of differing coordination number. Accepting that, in MeCN solution, the six coordinate Cu(II) solvate undergoes a tetragonal distortion to obey the Jahn - Teller theorem, then loss of one MeCN ligand from an axial position is relatively easy ; this is the reason proposed for the extremely fast rate of ligand substitution at Cu(II) solvated species. The mechanism of substitution at Cu(II) in MeCN has not been determined, but extrapolating the results of Merbach and co-workers, for the earlier first row divalent cations, it seems reasonable to propose an I_d mechanism for substitution. In solution, at any one instant of time, a proportion of the Cu(II) species will exist as the transition state of the I_d mechanism, with one coordinated solvent molecule very close to complete dissociation. The reduction potential of this species will be different from that of the six coordinate tetragonally distorted species which is the 'normal' species found in solution. As the potential across the solution is varied, species of differing geometry will be reduced at differing potentials and a broadened wave will be obtained. This is not unlike exchange averaging effects in n.m.r. spectrometry. This effect accounts for the very broad peak observed for the reduction of solvated Cu(II) in MeCN. The presence of such a broad peak makes determination of the half wave potential very difficult and hence results are subject to a large error. The redox couple for $Cu^{2+} \rightharpoonup Cu^{+}$ in MeCN is + 0.675 ± 0.15 V, from an average of the studies using Cu(II) and Cu(I) as starting materials.

As discussed above, the high stability of $Cu(dmp)_2^{+}$ makes $[Cu(dmp)_2(NCMe)_2]^{2+}$ a relatively strong oxidising agent and it is capable of oxidising copper metal in acetonitrile. The half wave potential occurs at + 0.25 V. This is ca. 0.4 V less oxidising than $Cu(NCMe)_6^{2+}$ and this drop in potential is a reflection of the stabilisation of the Cu(II) state by the bidentate ligand.

This stabilisation effect is apparent to a greater extent for $Cu(bipy)_3^{2+}$. The half wave potential occurs at − 0.32 V, nearly 1 V less oxidising than $Cu(NCMe)_6^{2+}$. The tris chelation imparts a high stability to the complex. The couples of the complexes with dmp and bipy are much closer to complete reversibility than that of the solvated ion, peak to peak distances being 105 mV and 140 mV respectively. That they are only pseudo reversible is due to the geometry changes which accompany the electron transfer. An example of a cyclic voltammogram obtained in this study is given in Figure 4.

Figure 4.

Cyclic Voltammogram of $Cu(bipy)_3(PF_6)_2$ in MeCN Solution.



scan rate 20 mVs^{-1}
x,y scale 100 $mVcm^{-1}$
amplification 20 μAV^{-1}

An early determination of the redox potential of $Cu(dmp)_2SO_4.5H_2$ in aqueous solution gave a value of + 0.624 V relative to N.H.E. .[12] A later study of the salts $Cu(dmp)_2X_2$ ($X=NO_3$,Cl,Br) by voltammetry at a rotating Pt electrode in MeCN solution, found that the potential varied with the anion ; + 0.637 V for NO_3 and + 0.615 V for Br and Cl relative to S.C.E. .[124] This was attributed to a differential solvation effect for the salts. These results are very close to the value found for $Cu(dmp)_2(NCMe)_2^{2+}$, in this work. The potential in aqueous solution is approximately 0.2 V less oxidising than the salts in MeCN, again illustrating the changes brought about by excluding moisture from a system. In aqueous solution, the Cu(II) species is stabilised and consequently the potential of the couple is lowered.

Conclusions.

Addition of H_2O to solutions of Cu(II) in MeCN does not result in hydrolysis of coordinated MeCN but, instead, substitution occurs to produce mixed ligand complexes.

Ligand substitution of $P(OMe)_3$ for NCMe at $Cu(NCMe)_4^+$ is very rapid and facile, to produce $Cu\{P(OMe)_3\}_4^+$ which is fully characterised by n.m.r. spectroscopy. PF_3 will not react with $Cu(NCMe)_4^+$. This is a function of the weaker donor ability of PF_3 relative to $P(OMe)_3$.

The reaction of $Cu(NCMe)_6^{2+}$ with $P(OMe)_3$ in MeCN occurs via a purple intermediate to produce $Cu\{P(OMe)_3\}_4^+$, $MeP(O)(OMe)_2$ and $MeP(OMe)_3^+$ as the major products. The intermediate is a $Cu\{P(OMe)_3\}_x^{2+}$ species which is a very strong oxidising agent, and it oxidises a coordinated $P(OMe)_3$ ligand. The value of x is uncertain but it may be 5.

The kinetics of the decay give a rate law with a second order dependence upon $P(OMe)_3$. This can be accounted for by a mechanism which has a complex formation step prior to redox and also a reaction to produce a dimer radical cation, after redox has occurred.

$Cu(NCMe)_6^{2+}$ reacts rapidly in MeCN with dmp or bipy, in mole ratio 1:2, to produce brightly coloured species whose electronic spectra suggest that they are the cis pseudo octahedral cations, $[Cu(LL')_2(NCMe)_2]^{2+}$ (LL' = dmp or bipy). Using excess bipy, $Cu(bipy)_3^{2+}$ is produced.

The majority of these Cu(II) complexes are strongly oxidising in MeCN. This is due to the high stability of the corresponding tetrahedral Cu(I) species. For $Cu\{P(OMe)_3\}_x^+$ the presence of strong metal ligand π-bonding also stabilises Cu(I) relative to Cu(II) and accounts for the very large oxidation potential of the $Cu\{P(OMe)_3\}_x^{2+}$ species. The presence of bidentate nitrogen donors has a stabilising effect on the Cu(II) state which results in a marked lowering of the oxidation potential of the complexes. This is clearly shown by the relative potentials of $Cu(dmp)(NCMe)_2^{2+}$ and $Cu(bipy)_3^{2+}$, as determined by cyclic voltammetry.

The high stability of Cu(I) species in MeCN necessitates the use of very strong oxidising agents to produce the Cu(II) species.

Experimental.

Reactions of Solvated Cu(II) in MeCN Solution.

a) with trimethyl phosphite.

The nature of the reaction was very dependent upon the conditions which were used. i) $P(OMe)_3$ in greater than ten fold excess $P(OMe)_3$ (0.44g ; 3.6 mmol) was added to $Cu(NCMe)_5(PF_6)$ prepared as in the literature[11] (0.2g ; 0.36 mmol) in MeCN (4 ml) at 77 K. On warming, a deep purple colour developed as the $P(OMe)_3$ melted and flowed on to the frozen MeCN. The colour decayed rapidly, even at temperatures below 230 K. The final solution was straw yellow in colour. The volatile products consisted of two fractions ; a very volatile fraction, containing unchanged MeCN, and a sparingly volatile fraction, containing dimethyl methyl phosphonate, $MeP(O)(OMe)_2$, identified by ^1H n.m.r. spectroscopy. The latter assignment was confirmed by ^{31}P decoupling experiments, which gave a ^{31}P chemical shift of + 32.8 p.p.m. .

Removing the volatile material from the reaction mixture isolated a white solid. This was shown to be $Cu\{P(OMe)_3\}_4PF_6$, by comparison of the vibrational and n.m.r. spectra of the solid with those of a sample of the salt, characterised from the reaction of $Cu(NCMe)_4^+$ with $P(OMe)_3$. ^1H n.m.r. spectroscopy also identified $MeP(OMe)_3^+$, the trimethoxy methyl phosphonium cation, among the solid products, presumably as the PF_6^- salt. This was confirmed by ^{31}P decoupling experiments which gave a ^{31}P chemical shift of 53.5 p.p.m. .

ii) $P(OMe)_3$ in slight excess.

$Cu(NCMe)_5(PF_6)_2$ (0.14g ; 0.24 mmol) was added to a cell, with a

Spectrosil cell as side arm, in the glove box. MeCN (4 ml) was distilled into the flask and the electronic spectrum was run. $P(OMe)_3$ (0.037g ; 0.297 mmol) was then distilled in. On warming from 77 K, the purple colour developed and decayed, as witnessed in the above reaction. When the flask reached room temperature, the solution was blue, but the electronic spectrum revealed a drop in the absorbance at the maximum of the Cu(II) band, from 1.55 to 1.40 absorbance units. After standing at room temperature for two days, the solution was colourless and the electronic spectrum revealed the absence of the band due to $Cu(NCMe)_6^{2+}$.

iii) Cu(II) in excess.

$Cu(NCMe)_5(PF_6)_2$ (0.3g ; 0.53 mmol) was dissolved in MeCN (4 ml) and $P(OMe)_3$ (0.05g ; 0.40 mmol) was distilled into the flask at 77 K. On warming, the deep purple colour developed and decayed, more slowly than in previous reactions. At room temperature, the solution was blue and the electronic spectrum showed the band due to $Cu(NCMe)_6^{2+}$. Overnight the solution became very dark brown in colour, indicative of solvent attack. The reaction was followed by ^1H n.m.r. spectroscopy, under these conditions. The broadened solvent peak gradually shifted downfield and sharpened a little, over a period of twenty minutes. Over a few days the solution turned dark brown.

iv) Kinetic studies.

The reaction was studied by stopped flow spectrophotometry. The experimental method is detailed in the Appendix. The concentration of $Cu(NCMe)_5(PF_6)_2$ was maintained at 5×10^{-4} mol l^{-1} and the concentration of the solutions of $P(OMe)_3$ was varied between

7.5×10^{-3} mol l^{-1} and 7.5×10^{-2} mol l^{-1} , maintaining pseudo first order conditions. The system was thermostatted to 24.0 ± 0.1°C . Attempts to study the reaction at higher concentrations of $P(OMe)_3$ were unsuccessful, as the rate was too fast to be followed ; reaction was complete within the dead time of the instrument (0.05 s) . Similarly attempts to study the reaction at very low concentrations, ($< 5 \times 10^{-4}$ mol l^{-1}) , met with failure ; the traces which were obtained proved irreproducible and thus did not yield trustworthy results. The spectrum of the deep purple intermediate was determined by measurement of the total change in optical density at points over a wide range of wavelengths. Results calculated for a ten-fold and a hundred-fold excess of $P(OMe)_3$ were identical ; the maximum was at 29,000 cm^{-1} (ε ca. 3×10^3 dm^3 mol^{-1} cm^{-1}) . The decay of the intermediate was first order in total copper(II) and second order in $P(OMe)_3$. The overall third order rate constant was 2.8×10^3 l^2 mol^{-2} s^{-1} .

b) with water.

$Cu(NCMe)_5(PF_6)_2$ (0.15g ; 0.26 mmol) was dissolved in MeCN (4 ml) and some H_2O was distilled into the solution at 77 K . On warming to room temperature there was no visible change in the solution but the maximum in the electronic spectrum had shifted from 13,500 cm^{-1} to 12,850 cm^{-1} . An infra red spectrum of the solution showed new bands, at 3,500 cm^{-1} and 1,630 cm^{-1} , due to H_2O .

In a similar study, $Cu(NCMe)_5(PF_6)_2$ (0.15g ; 0.26 mmol) was dissolved in $MeNO_2$ (4 ml) and some H_2O was distilled into the solution at 77 K . On warming to room temperature, a cloudy suspension was observed which gradually settled out to leave a light blue solution with a small amount of turquoise solid at the bottom of the vessel. The electronic spectrum of the solution had a maximum at 12,500 cm^{-1} . The spectrum of $Cu(NCMe)_5(O_2NMe)^{2+}$ in $MeNO_2$ solution, is identical to that of $Cu(NCMe)_6^{2+}$ in MeCN solution, with a maximum at 13,500 cm^{-1} . In a separate test, water and $MeNO_2$ were found to be immiscible, forming two layers, the aqueous layer on top.

c) <u>with 2,2'-bipyridyl</u>.

i) $Cu(NCMe)_5(PF_6)_2$ (0.07g ; 0.125 mmol) and bipy (0.06g ; 0.385 mmol) were added together in a flask and MeCN (1.5 ml) was distilled in at 77 K (mole ratio Cu(II) : bipy, 1:3) . On warming to room temperature, a turquoise solid was formed which was rather insoluble in the small volume of MeCN. On standing, the solution became royal blue. A further portion of MeCN (4 ml) was added and a dark blue solution was found, standing above a white solid. A sample of the blue solution was taken and the electronic spectrum suggested that the major species was $[Cu(bipy)_2(NCMe)_2]^{2+}$, $\tilde{\nu}_{max}$ 10,900 cm^{-1} , 13,700 cm^{-1} . A strip of copper metal was added to the blue solution and a reaction occurred, over the space of twenty minutes, to produce a red coloured solution, presumed to contain $Cu(bipy)_2^+$.

ii) The reaction was repeated, with $Cu(NCMe)_5(PF_6)_2$ (0.1g ; 0.18 mmol) and bipy (0.11g ; 0.72 mmol) (mole ratio Cu(II) : bipy, 1:4) . The solids were loaded into separate limbs of a two limbed flask and MeCN (2 ml) was distilled over each solid. The resulting blue solution of Cu(II) was added to the colourless solution of bipy and immediately a deep olive green colour formed. The volatile material was removed by distillation to leave a deep olive coloured solid. The ^{1}H n.m.r. spectrum of the solid, in MeCN, consisted solely of a broadened solvent peak ; there were no resonances due to bipyridyl. The infra red spectrum (Table 7) was consistent with a mixture of free bipyridyl and $Cu(bipy)_3^{2+}$. The electronic spectrum had a band at 14,900 cm^{-1} , consistent with $Cu(bipy)_3^{2+}$, and, unassigned, stronger bands at 19,300 cm^{-1} (sh) and 22,700 cm^{-1}. After three days at room temperature, the solution turned from olive green to blue and this was reflected by a change in the electronic spectrum of the solution. The maximum was now at 14,800 cm^{-1} , with weaker bands at 19,200 cm^{-1} and 20,400 cm^{-1} (sh) .

iii) The reaction was repeated using $Cu(NCMe)_5(PF_6)_2$ (0.2g ; 0.36 mmol) and bipy (0.17g ; 1.08 mmol) in MeCN (5 ml) (mole ratio Cu(II) : bipy, 1:3) . The solution was initially turquoise but turned deep blue and a dark blue solid was isolated by removing the volatile material. This dark blue solid had an electronic spectrum identical to that of the final blue solution, in (ii) (<u>vide supra</u>) , assigned to $Cu(bipy)_3^{2+}$.

d) <u>with 2,9-dimethyl-1,10-phenanthroline (dmp)</u> .

$Cu(NCMe)_5(PF_6)_2$ (0.2g ; 0.36 mmol) and dmp (0.15g ; 0.72 mmol) (mole ratio Cu(II) : dmp, 1:2) were loaded in separate limbs of a two limbed flask and MeCN (2 ml) was distilled over each solid. When the blue solution of Cu(II) was added to the yellow solution of dmp, there was immediate formation of an intense emerald green colour. Removing the volatile material by vacuum distillation, left a dark green solid. The electronic spectrum of the solid consisted of two bands, $\bar{\nu}_{max}$ 9,900 cm^{-1} and, slightly less intense, 13,800 cm^{-1} . The infra red spectrum of the solid (Table 8) showed bands due to

Table 7.

Infra-red Spectrum of $Cu(bipy)_3(PF_6)_2$ in the Solid State.

$\bar{\nu}_{max.}$ (cm^{-1})	Assignment [87]
1600 s	coord. lig.
1580 m	free lig.
1568 m	free lig.
1492 m	coord. lig.
1440 s	coord. lig.
1316 s	coord. lig.
1247 m	coord. and free lig.
1175 m	coord. lig.
1163 s	coord. lig.
1138 w	free lig.
1106 w	coord. lig.
1090 w	free lig.
1063 m	coord. and free lig.
1040 w	free lig.
1022 m	coord. lig.
905 m	coord. lig.
840 vs	T_{1u} PF_6^-
758 s	coord. lig.
736 s	coord. lig.
652 m	coord. lig.
560 s	T_{1u} PF_6^-

coordinated MeCN and coordinated ligand. When a strip of copper metal was added to a green solution of Cu(II) and dmp, a rapid reaction took place, with attack on the metal, to form a deep red coloured solution. This solution contained the species $Cu(dmp)_2^+$.

Reactions of Solvated Copper(I) in MeCN Solution.

a) with trimethyl phosphite.

$Cu(NCMe)_4PF_6$ made by a literature method [11] (0.13g ; 0.35 mmol) was loaded in a vessel and $P(OMe)_3$ (2 ml, ca. 17 mmol) was distilled in at 77 K . On warming to room temperature, a yellow solution formed, standing over a white solid. The volatile material, identified by ^1H n.m.r. spectroscopy as mainly $P(OMe)_3$ with, traces of $MeP(O)(OMe)_2$ and MeCN, was removed, under static vacuum, to isolate a white solid as the product. This solid was identified by spectroscopy and microanalysis as tetrakis (trimethyl phosphite) copper(I) hexafluorophosphate. (Found, C, 21.6 ; H, 5.0 ; Cu, 8.8 ; F, 15.9 ; P, 21.6 %. $C_{12}H_{36}CuF_6O_{12}P_5$ requires C, 20.5 ; H, 5.2 ; Cu, 9.0 ; F, 16.2 ; P, 22.0 %.) The ^{31}P, ^{19}F, ^{63}Cu, ^{65}Cu and ^1H n.m.r. spectra of the salt, in CD_3CN solution, are listed in Table 2 and illustrated in Figure 1. The solid state vibrational spectra are listed in Table 1. The spectroscopic studies were in good agreement with earlier work.

When the reaction was repeated, using similar quantities of reagents, but using MeCN (3 ml) as a solvent, the course of the reaction was similar, but all the solid dissolved. The products of the reaction were identical to the reaction in neat $P(OMe)_3$. $Cu(NCMe)_4AsF_6$ behaved in an identical manner to the PF_6^- salt.

Table 8.

Infra-red Spectrum of $Cu(dmp)_2(NCMe)_x(PF_6)_2$ in the Solid State.

(x = 1 or 2)

$\bar{\nu}_{max}$ (cm^{-1})	Assignment [87]
2315 m	comb. band, coord. MeCN
2295 m	C≡N stretch, coord MeCN
1620 m	coord. lig.
1597 s	coord. lig.
1569 m	coord. lig.
1520 sh	coord. lig.
1500 s	coord. lig.
1300 m	coord. lig.
1224 m	coord. lig.
1207 w	coord. lig.
1161 m	coord. lig.
1110 w	coord. lig.
1063 m	coord. lig.
991 w	
840 vs	T_{1u} PF_6^-
729 m	coord. lig.
682 w	
661 w	
560 s	T_{1u} PF_6^-

b) with phosphorus trifluoride.

$Cu(NCMe)_4PF_6$ (0.2g ; 0.54 mmol) was dissolved in CD_3CN (2 ml) in a flask with an n.m.r. tube as a side arm. A pressure of 70 torr of PF_3 was introduced into the flask and the system allowed to stand for several hours. There was no visible evidence for a reaction. Some of the PF_3 was distilled into the flask at 77 K and the remainder was pumped away. After shaking the flask for several days at room temperature, the infra red spectrum of the vapour phase revealed the presence of only CD_3CN and PF_3 . The ^{19}F n.m.r. spectrum showed only a doublet, due to PF_6^- . The solid state infra red spectrum of the white solid product, isolated by distilling off the volatile fraction, suggested that the product was $Cu(NCCD_3)_4PF_6$, with bands at $\bar{\nu}_{max}$ (CN) 2286 cm^{-1} , $\bar{\nu}$(CD) 2118 cm^{-1} $\delta(CD_3)$ 1033 cm^{-1} , $\nu(PF_6^-)$ 840 cm^{-1} and 560 cm^{-1} .

c) with tungsten hexafluoride.

$Cu(NCMe)_4PF_6$ (0.16g ; 0.43 mmol) was dissolved in MeCN (5 ml) in a flask, with a Spectrosil cell as side arm, to give a colourless solution. WF_6 (0.37g ; 1.24 mmol) was distilled in at 77 K and the flask allowed to warm. At ca. 240 K, a blue colour was observed in the solution, which persisted up to room temperature. The electronic spectrum of the solution exhibited a band at 13,500 cm^{-1} , consistent with formation of $Cu(NCMe)_6^{2+}$. Removal of the volatile material produced an off-white solid, presumably a mixture of Cu(II) and Cu(I) solvates.

d) with nickel(III) salts.

i) Some solid $[Ni(cyclam)(NCMe)_2](ClO_4)_3$ was added to an acetonitrile solution, $10^{-2}M$ in $Cu(NCMe)_4PF_6$, at room temperature.

There was immediate formation of a green colour and the electronic spectrum was identical to that of the Ni(III) salt alone. Over a period of days, the concentration of Ni(III) fell to zero. In a separate experiment $Ni(cyclam)(NCMe)_2(ClO_4)_3$ was found to undergo photochemical decomposition in MeCN solution at the same rate as when Cu(I) is present. A solution of Cu(I) and Ni(III) in MeCN (in a Cu(I) : Ni(III) ratio <u>ca</u>. 100:1) , showed no decomposition even after several weeks, when stored in the dark. When the solution was eventually subjected to the light, the Ni(III) salt decomposed.

ii) $Cu(NCMe)_4PF_6$ (0.075g ; 0.20 mmol) and $[Ni(cyclam)(NO_3)_2]NO_3$ (0.05g ; 0.10 mmol) were added together in a flask with a Spectrosil cell as side arm and MeCN (4 ml) was distilled in at 77 K. Immediately upon warming above the melting point of the solution, it became green and a green insoluble solid was also present. The spectrum gave evidence for Cu(II) in solution with a band at $\bar{\nu}_{max}$ 13,800 cm^{-1} , which shifted slightly to 13,600 cm^{-1} over a period of an hour. On standing overnight, the solution darkened to a deep brown colour and there were no distinct peaks visible on the electronic spectrum, merely a tail in the visible region from intense bands, at higher energy.

The reaction was repeated in $MeNO_2$ solution, using $Cu(NCMe)_4PF_6$ (0.07g ; 0.18 mmol) and $[Ni(cyclam)(NO_3)_2][NO_3]$ (0.05g ; 0.1 mmol) . The result was similar, with rapid formation of a Cu(II) species, which had a maximum at 12,900 cm^{-1} . The mixture decomposed on standing overnight, producing an olive coloured solution and a green solid, but this was not investigated further.

Cyclic Voltammetry of Copper Complexes in MeCN Solution.

Cyclic voltammetry studies were carried out using the experimental procedure described in the Appendix. The complexes which were studied were $Cu(NCMe)_5(PF_6)_2$, $Cu(NCMe)_4PF_6$, $Cu\{P(OMe)_3\}_4PF_6$, $Cu(bipy)_3(PF_6)_2$ and $Cu(dmp)_2(NCMe)_2(PF_6)_2$. All of the species showed pseudo reversible redox couples, with the exception of $Cu\{P(OMe)_3\}_4PF_6$ which was completely irreversible. The results are listed in Table 5.

CHAPTER FOUR

Reactions of Coordinated Trimethyl Phosphite with Covalent High Oxidation-state Fluorides.

Introduction.

The chemistry of species containing phosphorus – fluorine bonds has received a great deal of attention over the years. This is due both to the interesting chemical behaviour of such species and to the extreme toxicological action of some of the compounds with the P—F functional group. A major factor in increasing their popularity as a field of study is that they are amenable to study by ^{31}P and ^{19}F n.m.r. spectroscopy.

The range of compounds with P—F bonds is vast and the variation in physical and chemical properties has been extensively reviewed.[127] Further reviews have appeared on the chemistry of fluorophosphoranes,[128] R_nPF_{5-n} and fluorophosphines,[129] R_nPF_{3-n} . A number of synthetic routes to P—F bonded species are known but the most general route, to both fluorophosphoranes and fluorophosphines, involves halogen exchange between a fluorinating agent and the corresponding chloro compound, for example,[130]

$$3\ RPCl_2 \quad + \quad 2\ SbF_3 \xrightarrow{\text{pyridine}} 3\ RPF_2 \quad + \quad 2\ SbCl_3 \qquad (1)$$

The yield of P(III) compounds is variable, but can be up to 85% . A number of fluorinating agents have proved successful in such reactions, for example HF, AsF_3, SbF_3 and KF .[128] The fluorophosphoranes have also been synthesised by oxidative fluorination of the chlorophosphine compound, for example,[131]

$$3\ MePCl_2 + 4\ AsF_3 \longrightarrow 3\ MePF_4 + 2\ As + 2\ AsCl_3 \qquad (2)$$

Another interesting synthetic route to alkyl tetrafluorophosphoranes involves fluorination of a phosphoryl bond using SF_4 , for example,[132]

$$PhP(O)F_2 \quad + \quad SF_4 \longrightarrow PhPF_4 \quad + \quad SOF_2 \qquad (3)$$

The scope of this type of reaction is very wide and it has been used to produce a large number of P—F species. Compounds of general formula RPF_4 have long been of interest as they are stereochemically non rigid. They have been used to study the nature of the fluorine exchange reaction, and the energy barrier to exchange, for five coordinate complexes. They are particularly useful in such studies as they can be examined by both ^{31}P and ^{19}F n.m.r. spectroscopy, and a number of variable temperature studies have been carried out.[133]

An interesting reaction of RPF_4 species is their ability to add fluoride ion, to form organopentafluorophosphates. These species have six coordinate phosphorus in a pseudo octahedral stereochemistry and, at the time of their discovery, were among the few known groups with this coordination about phosphorus. Subsequent work resulted in the formation of similar species, such as $[CF_3PF_5]^-$, $[(CF_3)_2PF_4]^-$ and $[(CF_3)_3PF_3]^-$ [134] and also $[HPF_5]^-$.[135] The RPF_5^- species were originally formed from rearrangement reactions of $RPF_3NR'_2$ to give, as products, $RPF(NR'_2)_2^+$ and RPF_5^- .[136] When R=Ph, the ^{19}F n.m.r. spectrum is second order, but for R=Me, a first order spectrum is found, with a doublet of doublets for the resonance of the equatorial fluorines and a doublet of quintets for that of the axial fluorine.[137] The ^{31}P n.m.r. spectra of both species consist of a doublet of quintets, from coupling with the two types of fluorine. The ^{31}P chemical shift is very close to that of PF_6^- which confirms the six coordinate structure about the phosphorus.

Fluorophosphines containing P—N bonds are obtained by reactions involving exchange of NMe_2 groups on phosphorus with F from the fluorinating agent, for example,[138]

$$P(NMe_2)_3 \quad + \quad BF_3 \longrightarrow Me_2NPF_2 \quad + \quad (Me_2N)_2BF \qquad (4)$$

Similar reactions involving PF_5 lead to isolation of a series of solid adducts containing P—P bonds.[139] When heated the P—P

$$P(NMe_2)_3 \quad + \quad PF_5 \longrightarrow PF_5-P(NMe_2)_3 \qquad (5)$$

adducts decompose to yield a variety of P—F species,

$$PF_5-P(NMe_2)_3 \longrightarrow PF_4NMe_2 \quad + \quad PF_3(NMe_2)_2 \text{ (trace)}$$
$$+ \quad PF_2(NMe_2)_3 \text{ (trace)} \quad + \quad PF(NMe_2)_4 \qquad (6)$$

Fluorine containing compounds with P—O bonds, the fluorophosphites, are generally formed from the corresponding chlorophosphite and these reactions are invariably strongly exothermic.[140] Alternatively they may be formed by exchange of F for OR in pet. ether as solvent. BF_3 is found to react vigorously with $P(OMe)_3$ at 273 K to produce a mixture of $PF(OMe)_2$ and $PF_2(OMe)$, as the phosphorus containing products.[141] This result disagrees with a similar study which finds that fluorination does not occur but that BF_3 merely catalyses the Arbusov reaction of $P(OMe)_3$, producing $MeP(O)(OMe)_2$ as the product.[142] This second study, however, uses only a small amount of BF_3, which is recovered as BF_2OMe. This implies that BF_3 does fluorinate $P(OMe)_3$ by exchange of F for OMe, and, at some stage in the reaction, presumably Me^+ is generated, which is the catalyst for the Arbusov reaction.

In the reaction of PF_5 with $P(OMe)_3$, in diethyl ether or pentane solution, it is not possible to isolate a P—P bonded adduct.[113] The first products which are identified are PF_4OMe and $PF(OMe)_2$. These undergo further reaction, via a complex reaction scheme, to produce a variety of products, including $[(MeO)_3PMe]PF_6$ and

$PF_2(O)(OMe)$ as the major species, along with small amounts of $PF_2(O)Me$ and $PF_2(OMe)$.

In an investigation of the properties of WF_6 , it is found that reactions between WF_6 and $P(OMe)_3$, in the absence of solvent, result in violent explosions, unless the conditions are carefully controlled.[143] Using an excess of $P(OMe)_3$, the initial products are $PF(OMe)_2$ and, presumably, WF_5OMe. The WF_5OMe is not observed, due to further reaction with $P(OMe)_3$ and the final products are $[MeP(OMe)_3][WOF_5]$, $MeP(O)F(OMe)$ and $MeP(O)(OMe)_2$. In some cases $MeP(O)F_2$ is also formed.

The reaction of BF_3 with zero valent metal complexes having $P(OMe)_3$ ligands has been studied.[142] These are complexes of the form $Fe(CO)_{5-x}\{P(OMe)_3\}_x$ (x=1,2) and $Ni(CO)_{4-x}\{P(OMe)_3\}_x$ (x=1-4) . The products of reaction are coordinated $PF(OMe)_2$ or $PF_2(OMe)$, depending upon the stoichiometry, and BF_2OMe.

Interest in the coordinating ability of fluorophosphines stems from early studies on Pt(II)—PF_3 complexes which suggested that PF_3 had similar ligand properties to CO .[144] The bonding in PF_3 complexes has been discussed in terms of σ-donation from phosphorus to the metal and π-back donation from metal to phosphorus, the process operating synergically. Replacing one or more of the fluorines of PF_3 with other groups has the effect of altering the ligand properties, for example Me_2NPF_2 is a much better donor ligand than PF_3 .

Large numbers of complexes with various fluorophosphine ligands are known, with the metal generally in a zero valent or low oxidation state.[129] It has been noticed that fluorophosphines mainly stabilise the metal in an electron configuration which maximises the number of d electrons, that is where the metal is in a low, zero or formally negative oxidation state. In fact some metal salts have been reduced directly from a high to a zero valent state by the coordinating ligand, for example,[145]

$$PtCl_4 + 6\ PF_3 \longrightarrow Pt(PF_3)_4 + 2\ PF_3Cl_2 \qquad (7)$$

The aim of the work described in this chapter is the in situ fluorination of $P(OMe)_3$ coordinated to Fe(II) and Cu(I), using WF_6 and PF_5 as reagents. The purpose of this is three fold. Firstly, to investigate the role that the metal ion plays in determining the course of the reaction. This may be in moderating or even changing the course of the reaction, as compared with the reaction of free $P(OMe)_3$. Using complexes of metal ions which are so different in electronic structure adds to the scope of these experiments, that is, using Fe(II), $t_{2g}^{6}\ e_{g}^{0}$ and Cu(I), $t_{2g}^{6}\ e_{g}^{4}$. Secondly, a study of the ability of fluorophosphites to coordinate to metal cations of different charge and electronic structure may lead to some useful information about bonding in fluorophosphite complexes. Finally, any specificity in the reactions could lead to new synthetic routes to some P—F bonded species.

Earlier work on coordination of fluorophosphites in iron complexes has been concerned with mainly zero valent iron, in complexes of the type $Fe(CO)_4[PF(OMe)_2]$.[146] Recently the complex $[Fe^{II}Cl(PhPF_2)_5][Fe^{III}Cl_4]$ has been reported, from the reaction of $FeCl_3$ with $PhPF_2$ in Et_2O and the crystal structure has been determined.[147] Little information exists concerning fluorophosphine complexes of Cu(I) but CuCl will form complexes with

Me_2NPF_2 .[148] These are of the form $CuCl(Me_2NPF_2)_x$ (x = 1 or 2) . Interestingly, in similar reactions with $CuCl_2$, Cu(II) complexes are not isolated but oxidation of the ligand occurs, with concomitant reduction of the metal, to produce $[CuCl(Me_2NPF_2)]_4$ and $Me_2NPF_2Cl_2$. This is a general observation for reaction of Cu(II) - halides with phosphines.[149] In the course of the present work, a $Cu—PF_3^+$ complex was reported. This is formed by reaction of $CuAsF_6$ with PF_3 in SO_2 solution and is isolated as a white solid.[106]

Caution must be observed at all times in dealing with P—F bonded species, as compounds with this functional group have been found to be extremely toxic. This is true for PF_3 which has been shown to bind to haemoglobin in much the same way as CO. Compounds of general formula $PF(O)R_2$ are particularly toxic. Members of this group include the nerve gases, Sarin, $MePF(O)(O^iPr)$, DFP , $PF(O)(O^iPr)_2$ and Soman, pinacolyl - P(O)FMe.

The biological effects of fluorophosphates was first noted in 1932 [150] and this behaviour was exploited during World War Two in the search for new chemical warfare agents. These species deactivate cholinesterase. When a nerve impulse passes down nerve fibres to the terminus, acetylcholine is released to trigger the required response, for example, muscle contraction. In the presence of acetylcholine, the response will continue to operate and some mechanism is required to remove acetylcholine from the system. This is the function of cholinesterase.

In the presence of a nerve gas, there is a build up of acetylcholine in the nervous system. The effects are similar to those of the powerful nerve poisons, nicotine and muscarine and, in the most severe cases, curare. Symptoms progress from nausea and abdominal cramps to the full effects of overwhelming stimulation of the parasympathetic nervous system, for example, difficulty in breathing, mental confusion and death, primarily from respiratory failure.[151]

In the course of the reaction of PF_5 with $(EtO)_3P$,[113] the investigators noticed the toxic behaviour of the products, causing constriction of the pupils and difficulty in breathing, even in very low concentrations. This is presumably due to $PF(O)(OEt)_2$, the homologue of DFP . Methyl esters such as MePF(O)(OMe) , a Sarin homologue, hydrolyse much more quickly than Sarin, in moist air, but must still be treated with extreme care.

Results and Discussion.

Fluorination of $P(OMe)_3$ coordinated to Fe(II) or Cu(I) is not a straightforward process but involves a series of reactions. The products obtained from complexes of the two cations are different, showing that the metal has a great influence upon the course of the reaction.

The reactions of $Cu\{P(OMe)_3\}_4^+$ with WF_6 and PF_5, in MeCN, are very exothermic and strict control of the temperature is advised, particular when using large concentrations of WF_6. The PF_5 reaction is less violent than that of WF_6, where the solvent invariably turns deep red due to the solvent being attacked. No explosions were encountered in the course of this work but it must be remembered that the reactions are very violent and that, in the PF_5 reaction, large volumes of gas are evolved as products. These facts and the potential toxicity of the products make the systems dangerous to the unwary and great caution is counselled in dealing with these, and similar reactions. The major source of the heat energy, and the driving force for the reaction, is the high energy of formation of W=O or P=O bonds formed in the processes.

1. Reaction of $Cu\{P(OMe)_3\}_4^+$ with WF_6 in CD_3CN.

Although there is no variation in the nature of the major products of the reaction, the relative amounts, and the appearance of some minor products, depend to a large extent upon the conditions of temperature and the mole ratio of WF_6 to $P(OMe)_3$. In all of the reactions the ^{19}F n.m.r. signal ascribed to WF_6 is broadened and shifted upfield due to a rapid exchange reaction between WF_6 and WF_7^-. This exchange reaction has been observed in the addition of

WF_6 to $TlWF_7$ in MeCN .[14] ^{19}F and ^{31}P n.m.r. spectroscopic data for the products are presented in Table 1. Corresponding data from the literature are listed in Tables 3 and 4.

a) mole ratio WF_6 : $P(OMe)_3$, ca. 2:1 ; reaction moderated by cooling .

The final major products of fluorination of $P(OMe)_3$ are MePF(O)(OMe) , two species of the form RPF_5^- (in the ratio ca. 3:1) and a trace of $PF_2(OMe)$. The species are assigned as RPF_5^- from the similarity of their n.m.r. spectra to those of $MePF_5^-$. The ^{31}P n.m.r. spectra of some RPF_5^- species are shown in Figure 1. The R groups arise from polymerisation of the solvent, initiated by Me^+ , which is formed in the reaction. The ^1H n.m.r. spectra are very complicated and cannot be assigned. The different degrees of polymerisation give rise to R groups which are spectroscopically non equivalent. The ^{31}P and ^{19}F n.m.r. spectra of the various RPF_5^- groups are therefore slightly different.

The degree of polymerisation depends upon the conditions of the reaction and so altering the conditions yields different ratios of the RPF_5^- species. Temperature is particularly important in this respect. When the reaction is moderated, the amount of RPF_5^- species is apparently less and, in one case, $MePF_4$ is observed as a product.

$Me-C{\equiv}N-Me^+$ is known, being formed by reaction of MeCN with methyl 2,4,6-trinitrobenzenesulphonate.[152] This species can react with more MeCN to form $[MeC(NCMe)NMe]^+$, which will continue to add successive molecules of MeCN, until the positive charge is trapped by reaction or the cation becomes sufficiently stable that reaction ceases.

Table 1.

^{19}F and ^{31}P N.M.R. Data on the Products of Reactions Between $Cu\{P(OMe)_3\}_4^+$ and WF_6 in CD_3CN.

Species	δ ^{31}P (p.p.m.)	δ ^{19}F (p.p.m.)	Coupling Constants (Hz)		
			$^1J_{P-F}$	$^2J_{F-F}$	$^1J_{W-F}$
1 a) $PF_2(OMe)$		-51.0	1300		
$MePF(O)(OMe)$	39.2	-66.9	1064		
RPF_5^-	-149.8	-61.2 eq	803 eq	47.5	
			747 ax		
$R'PF_5^-$	-150.7	-66.9 eq	799 eq	47.0	
$WOF_4.NCCD_3$		67.0			
$W_2O_2F_9^-$		62.0 eq		57.0	
		-145.0 br			
1 b) $PF(OMe)_2$		-59.3	1208		
$MePF(O)(OMe)$	38.8		1058		
RPF_5^-	-148.8	-61.3 eq	812 eq	47.5	
			740 ax		
$R'PF_5^-$	-150.8	-62.0 eq	797 eq	48.0	
		-73.0 ax	746 ax		
WOF_5^-		50.1 eq		46.0	
$W_2O_2F_9^-$		62.5 eq		58.4	
		-144.0 br			
$(W_2O_2F_9^-)'$		61.3 eq		56.5	
		-144.4 br			

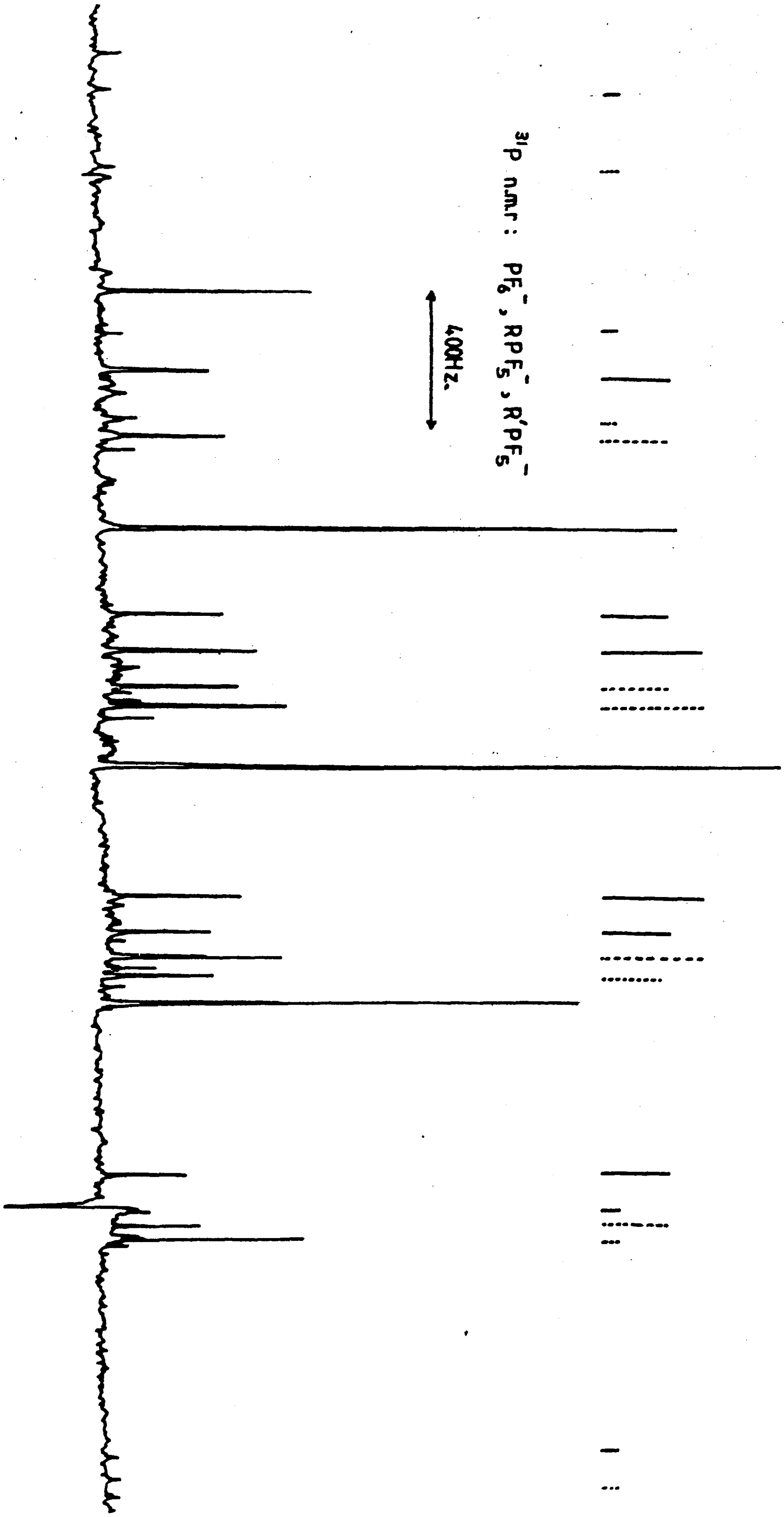
Table 1 (continued).

Species	δ ^{31}P (p.p.m.)	δ ^{19}F (p.p.m.)	Coupling Constants (Hz)		
			$^{1}J_{P-F}$	$^{2}J_{F-F}$	$^{1}J_{W-F}$
1 c) $MePF(O)(OMe)$	39.0	-67.1	1075		
$MePF_4$	-28.2	-44.6	975		
PF_3 (trace)	101.0		1403		
RPF_5^-	-149.7	-61.3 eq	804 eq		
			744 ax		
$R'PF_5^-$ (trace)		-67.0 eq			
$WOF_4.NCCD_3$		67.6			
$W_2O_2F_9^-$		62.1 eq		59.0	72.0
		-145.4 br			
1 d) $PF(OMe)_2$		-59.1	1216		
$PF_2(OMe)$		-51.0	1310		
$MePF(O)(OMe)$		-67.0	1065		
WF_5OMe		113.6 eq		66.0	42.0
		69.3 ax			
$WOF_4.NCCD_3$		67.1			70.0
$W_2O_2F_9^-$		62.3 eq		58.3	

nature of R, R' :- see p 183

Figure 1.

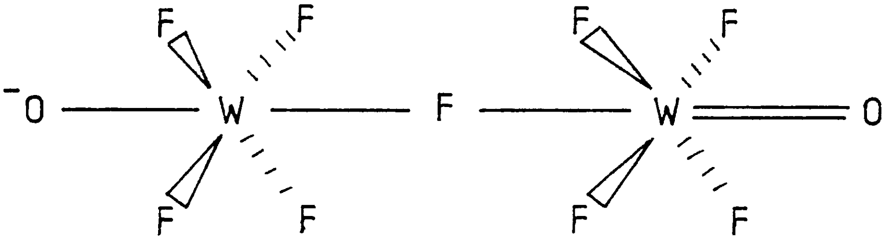
^{31}P N.M.R. Spectrum of RPF_5^- Species.



R_3C^+ , formed in the reaction of R_3CX with NO_2BF_4 , has been found to add to MeCN , forming $[R_3CNCMe]^+$.[153] This is hydrolysed to the corresponding acetamide , $R_3CN(H)C(O)Me$.

At its simplest, therefore, R in RPF_5^- is $MeC{=}N{-}Me^+$, and RPF_5^- is $MeC({=}NMe)PF_5^-$. The charge is balanced by the presence in solution of a $Me(MeCN)_n^+$ cation. The RPF_5^- species are perhaps better termed as $Me(MeCN)_nPF_5^-$.

The tungsten containing product of reaction is $W_2O_2F_9^-$ (I) , previously noted as the product of reaction of WOF_4 and WOF_5^- in



I

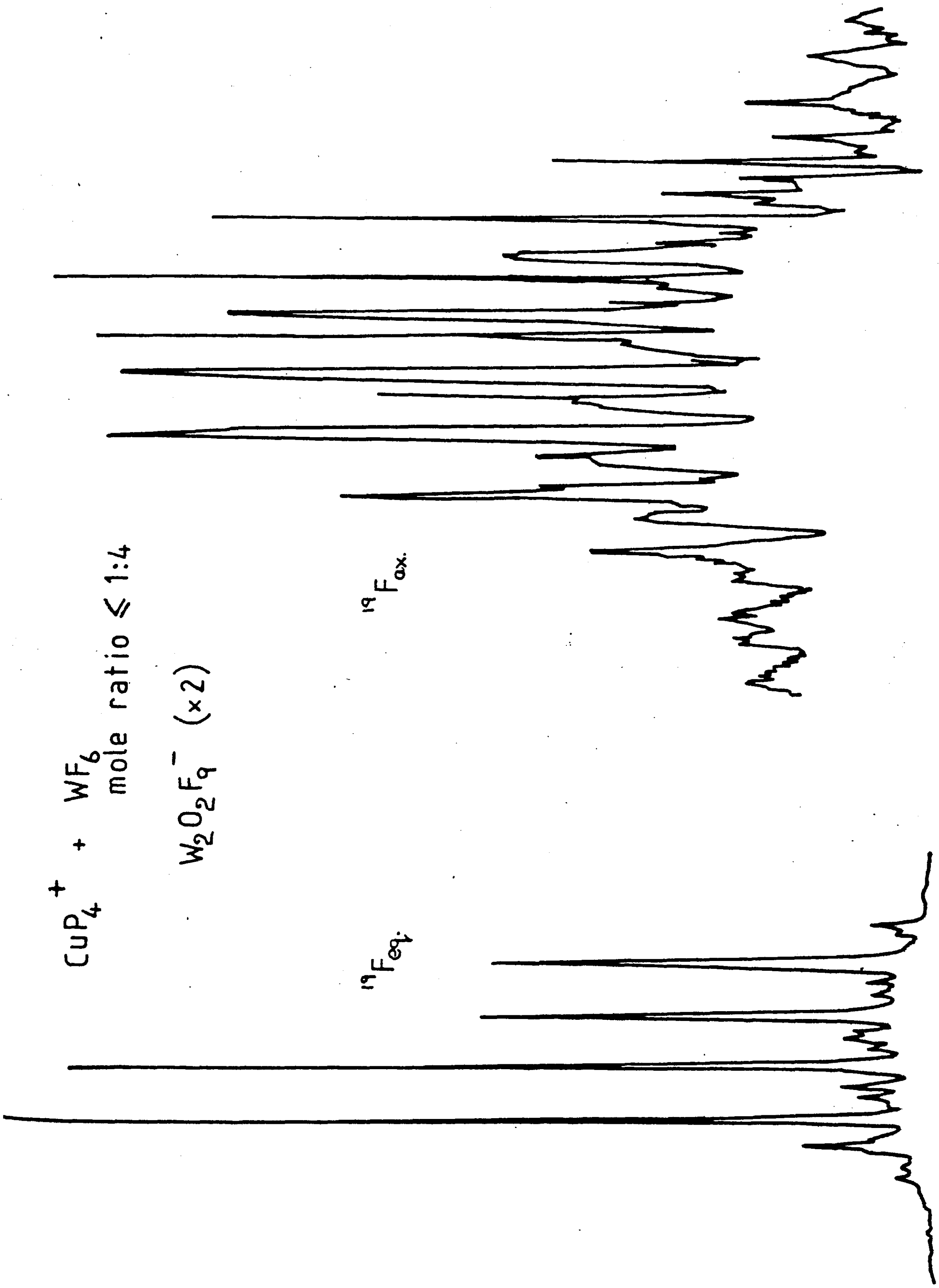
MeCN.[107] WOF_4 is observed as an intermediate in the present work. Attack on the solvent is rapid, the solution becomes dark red in a few hours. Over a period of a few days, the solution becomes very viscous, which causes the n.m.r. spectra to be broadened and poorly resolved.

b) <u>mole ratio WF_6 : $P(OMe)_3$; ca. 1:1 ; no temperature control</u>.

The major fluorinated products are MePF(O)(OMe) , $PF(OMe)_2$ and the same two RPF_5^- species observed in a) (in the ratio <u>ca</u>. 1:3) . The tungsten containing products are $W_2O_2F_9^-$, WOF_5^- and a species formulated as $(W_2O_2F_9^-)'$. This species has ^{19}F n.m.r. parameters very similar to $W_2O_2F_9^-$ but slightly shifted (Figure 2) . This suggests that the terminal oxygens in $W_2O_2F_9^-$ are further coordinated perhaps to the polymeric cationic species, $Me(MeCN)_n^+$,

Figure 2.

^{19}F N.M.R. Spectrum of $W_2O_2F_9^-$ and $(W_2O_2F_9)^{-\prime}$.



present in solution. Any coordination involves both O atoms and must be to very similar species. This is shown by the ^{19}F n.m.r. spectrum of $(W_2O_2F_9^-)'$ which suggests that the symmetry of the anion is preserved, and both tungsten atoms are in an identical chemical environment. Solvent attack is much slower in this case, taking two days to reach the dark red stage.

c) mole ratio $WF_6 : P(OMe)_3$ ca. 4:1 ; temperature held at 273 K.

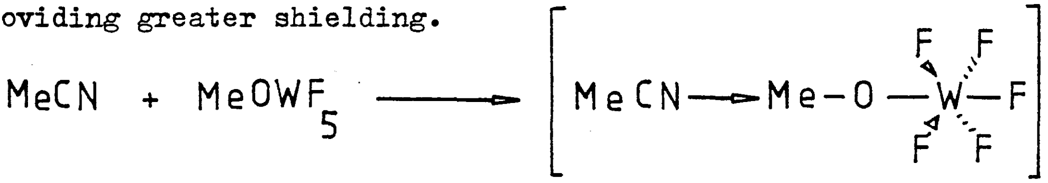
The major products of fluorination are MePF(O)(OMe) , $MePF_4$ and one species, RPF_5^- . There are also trace amounts of PF_3 and another RPF_5^- species. The tungsten containing products are WOF_4 and $W_2O_2F_9^-$. In this case the solution turns deep red within two hours at 273 K.

d) mole ratio $WF_6 : P(OMe)_3$ ca. 3:1 ; temperature strictly controlled .

The temperature of the solution was strictly controlled by use of cold baths and the various stages of the reaction are followed. At 253 K , $PF(OMe)_2$ is present and undergoing rapid exchange, presumably with $PF(OMe)_2$ coordinated to the metal ion, shown by broadening of the ^{19}F n.m.r. spectrum.

The ^{63}Cu and ^{65}Cu n.m.r. spectra of the reaction mixture, at low temperature, show no evidence for coordination of P—F species and only a very broad signal is found. The symmetry about the copper ion is no longer tetrahedral, due to the presence of the fluorophosphite ligand, and the electric field gradient at the nucleus is not zero. The nuclear quadrupole is active and brings about rapid relaxation of the spin system. There is no fine structure evident on the spectra.

The tungsten containing products are WF_5OMe and some $WOF_4.NCCD_3$. The ^{19}F n.m.r. spectrum of WF_5OMe is rather different from that reported in the literature.[143] The signal due to the equatorial fluorine atom, a 1:1 doublet, is shifted to slightly higher field but the change is not large considering the temperature and solvent difference. The signal due to the axial fluorine atom, however, a 1 : 4 : 6 : 4 : 1 quintet, is shifted upfield by 20 p.p.m. . This increase in electron density on the axial fluorine atom can be explained in terms of the interaction of WF_5OMe with the solvent. It is known that WF_5OMe reacts very rapidly with MeCN.[154] If the first step of the decomposition involves donation from a solvent lone pair to the Me group, this will have the effect of pushing electron density through the system, on to the fluorine atoms, providing greater shielding.



(8)

WF_5OMe exists, in MeCN, as the solvated form and this accounts for the observed shift in the ^{19}F n.m.r. spectrum. A similar effect is observed in <u>cis</u>-$WF_4(OMe)_2$ where the fluorine atoms <u>trans</u> to OMe are shifted to higher field relative to a fluorine atom in the same environment in WF_5OMe. This arises from replacement of one fluorine by a less electronegative OMe group.[107] The remaining fluorine atoms receive a greater share of the electron density and so are more shielded.

As the temperature of the reaction mixture is raised, $PF_2(OMe)$, MePF(O)(OMe) and one RPF_5^- species appear. The concentration of WF_5OMe decreases rapidly and those of WOF_4 and $W_2O_2F_9^-$ increase.

At 263 K the signals due to $PF(OMe)_2$ are relatively sharp, which suggests that coordination of $PF(OMe)_2$ to the metal ion, at this temperature , is either involved in a fast exchange process between free and bound $PF(OMe)_2$, or else does not occur, coordination only being possible at lower temperature.

An attempt was made to carry out the reaction in the absence of CD_3CN , to eliminate solvent interaction. This involved use of $CFCl_3$ as a heat transfer medium. The reaction failed, presumably because solvation of the reactants is necessary, prior to reaction.

2. Reaction of $Cu\{P(OMe)_3\}_4^+$ with PF_5 in CD_3CN .

a) mole ratio PF_5 : $P(OMe)_3$, ca. 2.5 : 1 ; no temperature control.

The volatile products of the reaction are POF_3 and $PF_2(OMe)$ with trace amounts of PF_3 and $PF_2(O)(OMe)$ also present (Tables 2 and 3 , experimental and literature n.m.r. parameters) . The involatile material, a yellow gel, soluble in CD_3CN contains POF_3 and $PF_2(O)(OMe)$, as well as species of the form RPF_5^- but the spectra are not well resolved and are difficult to assign.

b) mole ratio PF_5 : $P(OMe)_3$, 1:1 ; temperature strictly controlled.

At 243 K , the ^{31}P and ^{19}F n.m.r. spectra show signals due to $F_5P—P(OMe)_3$, PF_4OMe and $PF_5.NCMe$, as the major species. The spectra are shown in Figures 3 and 4. The P—P bonded adduct is characterised by its ^{19}F and ^{31}P n.m.r. parameters (Table 3) . Corresponding literature data are listed in Table 3. The n.m.r. spectra show signs of second order effects, particularly the ^{19}F spectrum, but are assigned on the basis of a first order approximation and are consistent with the adduct having the structure (II) .

Table 2.

^{19}F and ^{31}P N.M.R. Data on the Products of Reaction Between $Cu\{P(OMe)_3\}_4^+$ and PF_5 in CD_3CN.

Species	δ ^{31}P (p.p.m.)	δ ^{19}F (p.p.m.)	Coupling Constants (Hz)			
			$^1J_{P-F}$	$^1J_{P-P}$	$^2J_{P-F}$	$^2J_{F-F}$
2 a) POF_3	-35.3		1065			
$PF_2(OMe)$	113.5		1289			
PF_3 (trace)	103.0		1400			
$PF_2(O)(OMe)$ (trace)	-19.7		1025			
2 b) $F_5P—P(OMe)_3$	49.6 (P^{III})	-48.1 eq	875 eq	1205	285 eq	57
	-145.6 (P^V)	-79.9 ax	787 ax		0 ax	
PF_4OMe	-76.7	-66.9	872			
POF_3	-35.5	-87.9	1064			
$F_5P.NCCD_3$	-144.8		770			
$MePF(O)(OMe)$		-84.1	1000			
$MeP(OMe)_3^+$ [a]	54.0					
PF_6^- [a]	-145.2	-71.6	707			

[a] observed in reactions of AsF_6^- salt

Table 3.

^{19}F and ^{31}P N.M.R. Data on Selected Compounds, from the Literature.

Species	δ ^{31}P (p.p.m.)	δ ^{19}F (p.p.m.)	Coupling Constants (Hz)		Ref.
			$^{1}J_{P-F}$		
PF_3	97.0	-34.0	1410		163
$PF_2(OMe)$	111.0	-53.0	1275		163
$PF(OMe)_2$	131.6	-63.4	1210		164
PF_5	-80.3	-71.5	930		164
PF_4Me	-29.7	-45.4	966		165
PF_4OMe	-79.0	-68.0	870		113
$PF_5.NCMe$	-146.0		770		166
POF_3	-35.5	-93.3	1055		164
$PF_2(O)(OMe)$	-19.6	-87.5	1088		164
$MePF(O)(OMe)$	31.7	-62.0	1039		164
PF_6^-	-145.0	-71.7	710		163
PF_5H^-		-56.4 eq	817 eq	$^{2}J_{F-F}$= 41	135
		-66.2 ax	729 ax		
PF_5Me^-	-126.0	-45.0 eq	830 eq	$^{2}J_{F-F}$= 39	167
		-57.0 ax	691 ax		
$F_5P—PMe_3$	24.0(P^{III})	-51.3 eq	890 eq	$^{1}J_{P-P}$=720	155
	-120.0(P^{V})	-77.3 ax	780 ax	$^{2}J_{F-F}$= 52	
				$^{2}J_{P-F}$= 175 eq 0 ax	
$MeP(OMe)_3^+$	54.0				108

Table 4.

^{19}F N.M.R. Data on W—F Species, Taken from the Literature.

Species	$\delta\ ^{19}F$ (p.p.m.)	Coupling Constants (Hz)		Reference
		$^1J_{W-F}$	$^2J_{F-F}$	
WOF_4	73.9	64		158
WOF_5^-	49.4 eq	70	53	158
	-82.8 ax	58		
$W_2O_2F_9^-$	63.0 eq	70	58	107
	-142.0 br	49		
WF_6	162.0	44		107
WF_7^-	143.0			14
WF_5OMe	118.5 eq	43	66	107
	89.5 ax	33		

Figure 3. ^{31}P N.M.R. Spectrum of the Cu$\{P(OMe)_3\}_4^+$ – PF_5 Reaction Mixture.

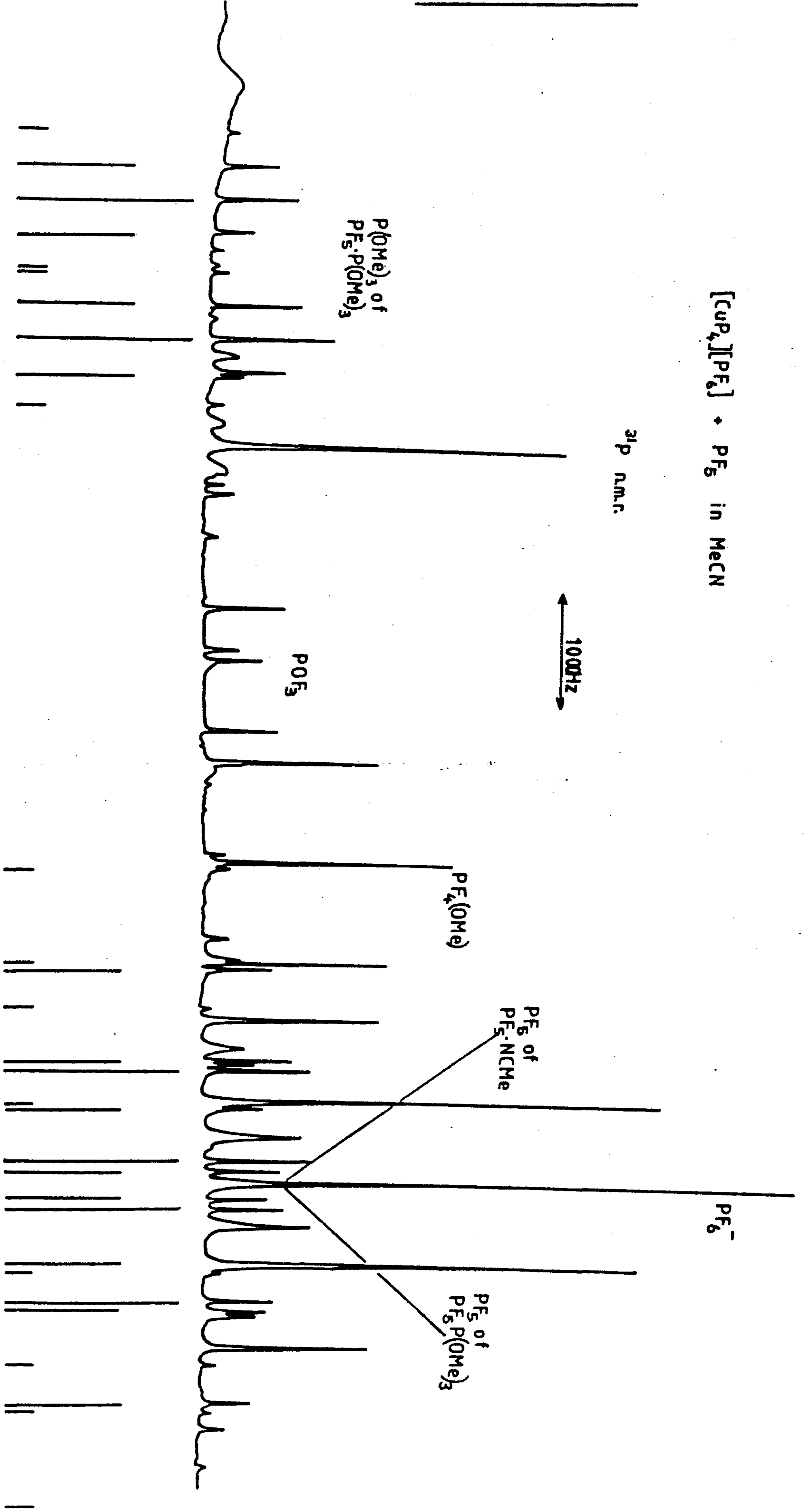
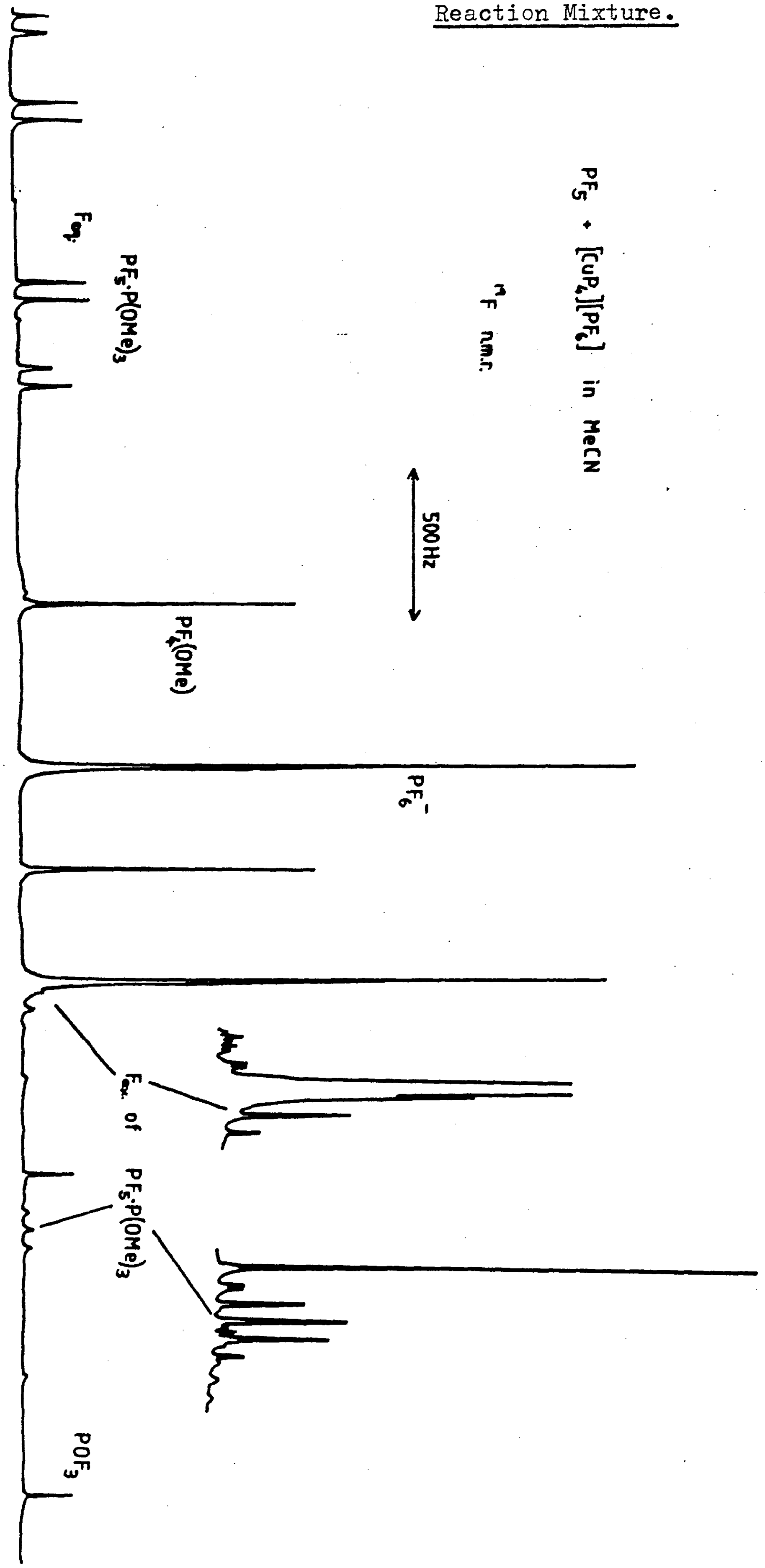
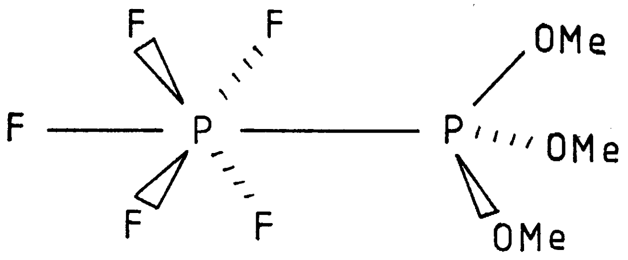


Figure 4. ^{19}F N.M.R. Spectrum of the $Cu\{P(OMe)_3\}_4^+ - PF_5$ Reaction Mixture.





II

The ^{31}P n.m.r. spectrum consists of two resonances. The signal due to P(III) is a doublet of quintets, from coupling with the directly bonded phosphorus atom, P(V) , followed by coupling with the four equivalent fluorine atoms of P(V). Coupling of the axial fluorine on P(V) to P(III) is not observed. The signal of the P(V) nucleus is a doublet of doublet of quintets, from coupling with the directly bonded phosphorus atom, followed by coupling with the axial fluorine, followed by coupling with the four equivalent equatorial fluorines.

The ^{19}F n.m.r. spectrum also consists of two resonances. The first resonance, that of the equatorial fluorines, is a doublet of doublet of doublets, from coupling with the directly bonded phosphorus atom (P(V)) , followed by coupling with the P(III) atom, followed by coupling with the axial fluorine. The resonance of the axial fluorine is a doublet of quintets, from coupling with the directly bonded P(V) , followed by coupling with the four equivalent fluorines. Coupling with the P(III) atom is not observed.

A similar P(V) - P(III) bonded species, $F_5P—PMe_3$, has been reported as the product of the reaction of PF_5 with PMe_3 .[155] This is prepared by direct addition of PF_5 to PMe_3 to yield the product as a white crystalline solid, which is stable at room temperature, *in vacuo* . The n.m.r. parameters of the adduct are included in Table 3 and the spectra are very similar to those of $F_5P—P(OMe)_3$. The major difference is the large increase in the size of the coupling constants, between the two phosphorus atoms (720 to 1205 Hz) and between P(III) and the equatorial fluorine atoms of P(V) (175 to 285 Hz) . At 1205 Hz , $F_5P—P(OMe)_3$ has the largest known value for ${}^1J_{P-P}$. Spin - spin coupling constants between directly bound phosphorus atoms have an extremely large range and can be of either sign. Decoupling experiments show the sign of ${}^1J_{P-P}$ to be positive for $F_5P—PMe_3$ but a similar experiment was not attempted in the present studies.

It has been shown that the major contribution to the magnitude of a spin - spin coupling constant comes from the Fermi contact interaction between nuclear moments and electron spins in s orbitals, which leads to electron spin polarisation.[156] This means that non vanishing magnetic fields exist which act on other nuclei. The increase in size of ${}^1J_{P-P}$ and ${}^2J_{P-F}$ of $F_5P—P(OMe)_3$ relative to $F_5P—PMe_3$ is ascribed to a large increase in the Fermi contact contribution.

The observation that ${}^2J_{P-F}$ is zero in both PF_5 adducts follows a general trend that the magnitude of $\underline{P}—P—\underline{F}$ coupling depends upon the P—P—F angle. For an angle of 90° , ${}^2J_{P-F}$ is 285 Hz (in $F_5P—P(OMe)_3$) or 175 Hz (in $F_5P—PMe_3$) . In compounds such as $F_2P—PF_2$, where the P—P—F angle is intermediate between 90° and 180° , the values of J reduce to around 65 - 80 Hz .[157] This phenomenon of decreasing size of coupling constant with increasing angle is also observed for ${}^2J_{H-F}$ in $H—P^V—F$ species.[135] When the $H—P^V—F$ angle is 90° , for example in $[HPF_5]^-$ and $[CF_3PF_4H]^-$, the coupling constant ${}^2J_{H-F}$ is <u>ca</u>. 120 Hz . Increasing the angle to ca. 120° , in RPF_3H species causes $^2J_{H-F}$ to fall to ca. 30 Hz . Finally, when the angle is 180° , in $[HPF_5]^-$, $^2J_{H-F}$ falls to zero. The increase in angle of the X—P—F group causes a decrease in the Fermi contact interaction of the X and F nuclei, which manifests itself in a reduction in the size of $^2J_{X-F}$.

The signal due to $PF_5.NCMe$ on the $^{31}P-\{^1H\}$ n.m.r. spectrum is a 1:5:10:10:5:1 sextet. PF_4OMe gives a quintet on the $^{31}P-\{^1H\}$ n.m.r. spectrum and a doublet on the $^{19}F-\{^1H\}$ n.m.r. spectrum, showing the four fluorines to be equivalent. There is a possibility that solvent will coordinate to the phosphorus to give a six coordinate species but the ^{31}P chemical shift (-76.7 p.p.m.) is indicative of a five coordinate rather than a six coordinate species (cf. $PF_5.NCMe$, $\delta_{^{31}P}$ = -144.8 p.p.m.) . The fluorines are equivalent due to a rapid fluorine exchange process.

Signals due to POF_3 are also apparent and, when the reaction is carried out, under the same conditions, using the AsF_6^- salt as starting material, PF_6^- is found as a product. There is also evidence, in the reaction of the AsF_6^- salt, for formation of a small amount of $MeP(OMe)_3^+$. A gaseous infra red spectrum of the volatile material shows some SiF_4 is among the products.

When the reaction mixture containing the AsF_6^- salt is allowed to warm above room temperature, a dark brown solid is precipitated from solution. This material is presumably the AsF_6^- salts of the polymeric cations derived from the solvent but this was not investigated. The AsF_6^- salts of the cations are obviously less soluble in CD_3CN than are the PF_6^- salts.

Discussion of the Reactions.

From these observations of the products of reaction, and particularly from the reactions where the temperature is strictly controlled, it is possible to produce mechanisms for the reactions of $Cu\{P(OMe)_3\}_4{}^+$ with PF_5 and WF_6 . The PF_5 reaction is presented first, as better evidence exists for this system due, in part, to its lower reactivity and because the phosphorus of PF_5 gives a more direct n.m.r. handle on the reaction, than does the tungsten of WF_6 .

Reaction of $Cu\{P(OMe)_3\}_4{}^+$ with PF_5 .

The first step in the reaction of $PF_5.NCMe$ with $Cu\{P(OMe)_3\}_4{}^+$ is the formation of a phosphorus – phosphorus bonded adduct, $F_5P—P(OMe)_3$. This adduct is postulated to be the intermediate in the reaction of PF_5 with $P(OMe)_3$, in Et_2O or pentane , but it proved too unstable to be identified.[113] The first species which are identified from this reaction are the products of breakdown of the adduct, PF_4OMe and $PF(OMe)_2$, formed by F / OMe transfer between phosphorus atoms.

In the present work the reaction mixture, at low temperature, contains PF_4OMe but apparently no $PF(OMe)_2$ (Figure 3 , Table 2) . The $PF(OMe)_2$ is presumably coordinated to the metal ion and the signal is to broad to be observed. Broadening of the signals is enhanced by a rapid exchange reaction between free and bound $PF(OMe)_2$.

PF_4OMe is unstable and breaks down presumably by reaction with MeCN , eliminating the components of MeF , to produce POF_3 . No MeF is observed in these reactions, so loss of Me^+ and F^- is not concerted. The F^- which is produced adds to PF_5 to yield $PF_6{}^-$.

The Me^+ presumably adds to the solvent to form a cation, $(MeCN)Me^+$ which initiates solvent polymerisation. The production of involatile gels from the reaction shows that the solvent is attacked.

In Et_2O or pentane, PF_4OMe is proposed to decompose via the reaction,[113]

$$2\ PF_4OMe \longrightarrow PF_2(O)(OMe) + MePF_6 \qquad (7)$$

but there is evidence in the present work for only a trace of this phosphoryl species. Formation of $PF_2(O)(OMe)$, however, will also arise from reaction of $P(OMe)_3$ with POF_3 by F /OMe transfer, the other product being $PF(OMe)_2$. The mechanism of decomposition of PF_4OMe is obviously solvent dependent and this accounts for the difference in products between this study and the earlier reactions.

$PF(OMe)_2$ undergoes further reaction with PF_5, presumably via formation of a P—P bonded adduct, although such a species is not observed. The products are $PF_2(OMe)$ and PF_4OMe. The phosphorane breaks down as before, to POF_3, Me^+ and F^-.

The volatile products of reaction of $Cu\{P(OMe)_3\}_4^+$ with PF_5 in CD_3CN (mole ratio $P(OMe)_3 : PF_5$, 1:2.5), where no temperature control is applied are POF_3, $PF_2(OMe)$ and traces of PF_3 and $PF_2(O)(OMe)$. The PF_3 must come from further reaction of PF_5 with $PF_2(OMe)$. The involatile products of the reaction contain some six coordinate phosphorus - fluorine species of unknown formula ; the n.m.r. spectra are broad and indistinct but the species are probably similar to the RPF_5^- species, observed in the reaction of WF_6 with $Cu\{P(OMe)_3\}_4^+$.

The proposed pathway for the reaction of PF_5 with $Cu\{P(OMe)_3\}_4^+$

in MeCN is shown in Scheme 1.

Reaction of $Cu\{P(OMe)_3\}_4^+$ with WF_6 in CD_3CN Solution.

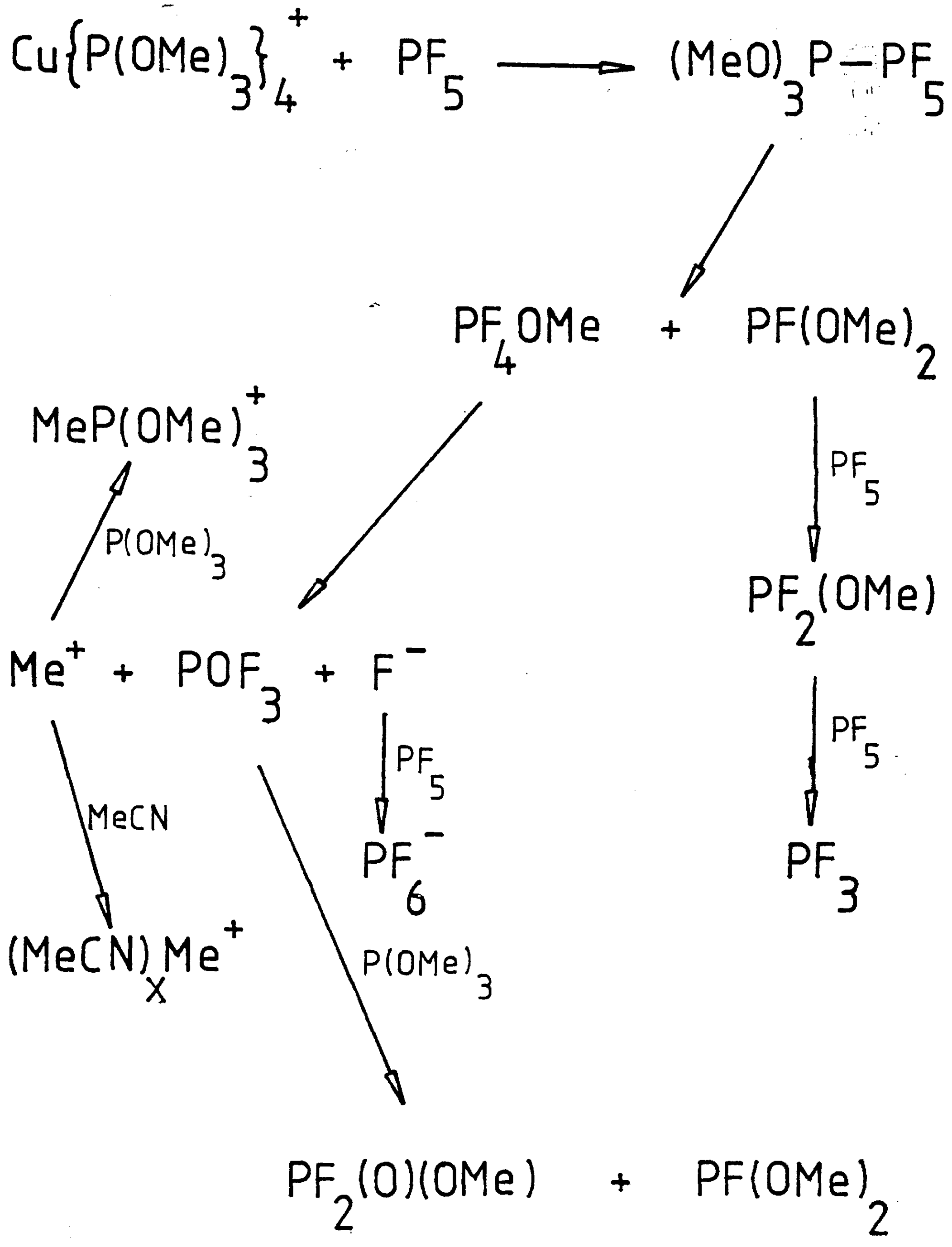
The reaction was carried out under controlled conditions, in an attempt to gain evidence for a W—P bonded adduct, analogous to the P—P bonded species. Unfortunately there are no signals, on either the ^{31}P or ^{19}F n.m.r. spectra, which can be assigned to such a species. An ambiguity exists, as $P(OMe)_3$ can donate to WF_6 from the lone pairs on either P or O , depending upon the relative affinity that WF_6 has for these two donor atoms. Identification of the P—P bonded adduct, in the PF_5 reaction, removes the ambiguity in that case. A W^{VI}—P^{III} bonded species is known. The seven coordinate tungsten species $F_6W.PMe_3$ has been prepared and characterised by analysis. The ^{19}F n.m.r. spectrum is a doublet, due to P—F coupling ($^2J_{P-F}$ = 73 Hz) , with associated ^{183}W satellites.[158] All six fluorines are equivalent due to a rapid exchange process. The adduct, an orange solid, is relatively stable, decomposing in vacuum at 353 K but, in solution, it decomposes quite rapidly ; in MeCN, at 298 K , the half life is ca. one day.

In the absence of conflicting data, therefore, it seems reasonable to propose that WF_6 reacts with $P(OMe)_3$ via a W—P bonded intermediate.

The first products which are identified in these studies are WF_5OMe and $PF(OMe)_2$, the products of an F /OMe transfer reaction between WF_6 and $P(OMe)_3$. The decomposition of WF_5OMe in MeCN is rapid, even at 263 K . The products are a solvento cation , $[MeCN-Me]^+$, WOF_4 and F^- . The ^{19}F n.m.r. spectrum has a signal

Scheme 1.

Reaction of $Cu\{P(OMe)_3\}_4^+$ with PF_5 in MeCN Solution.



due to $WOF_4.NCCD_3$ and an exchange broadened signal due to WF_6 / WF_7^-, showing that F^- has been produced, as well as the signals due to WF_5OMe . At a later stage in the reaction, there is evidence for formation of $PF_2(OMe)$, MePF(O)(OMe) and trace amounts of PF_3 .

The evidence suggests that the reaction is following a very similar pathway to the reaction of PF_5 , and involves fluorination by F /OMe transfer reactions in W—P bonded adducts. The proposed reaction pathway is shown in Scheme 2 .

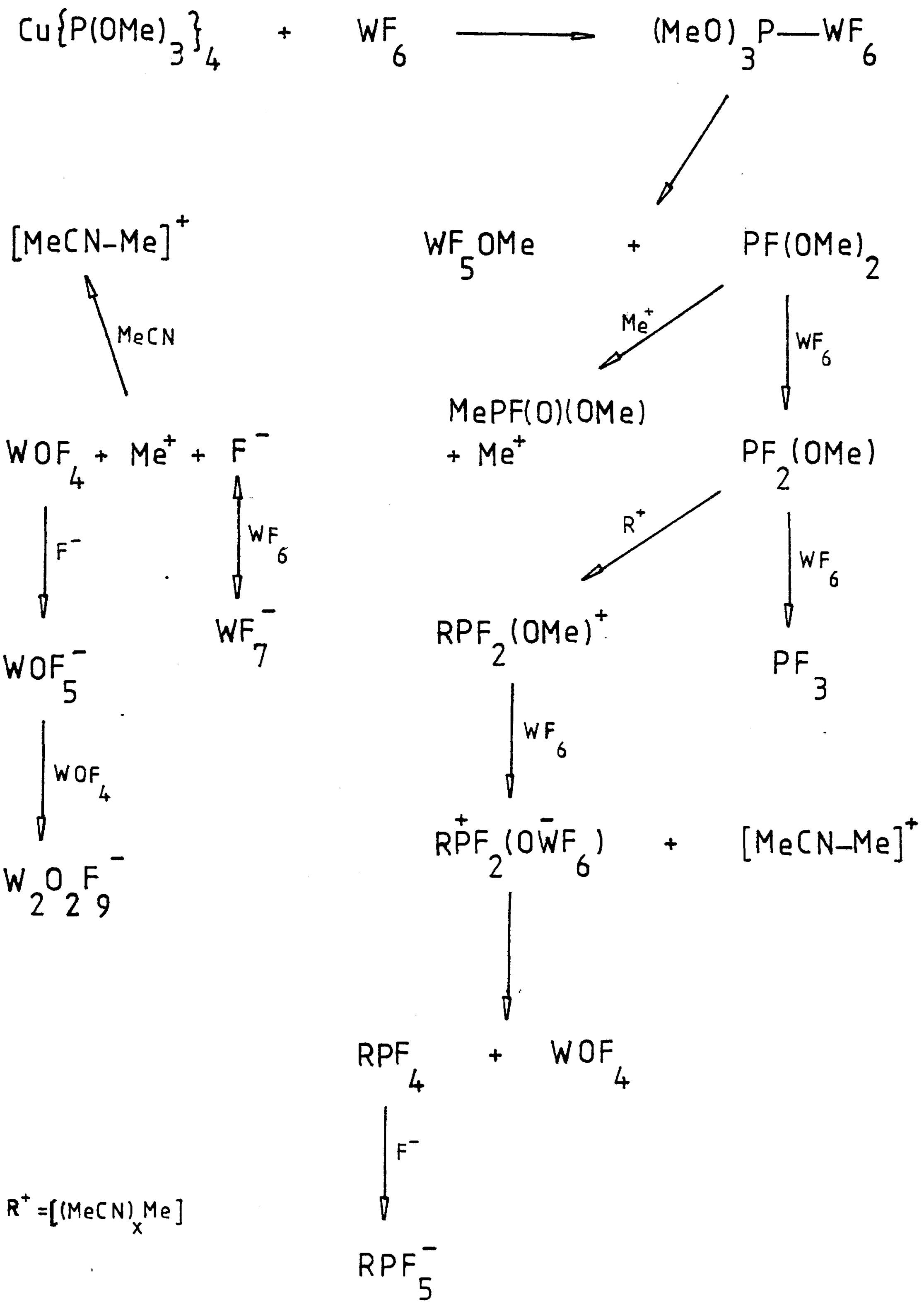
The major difference between the reactions of WF_6 and PF_5 with the copper salt is that, with WF_6 , there is considerable formation of MePF(O)(OMe) and species of the form RPF_5^- . MePF(O)(OMe) is the product of an Arbusov reaction of $PF(OMe)_2$ and formation of this phosphoryl species suggests that Me^+ is present in the reaction mixture. This reacts with $PF(OMe)_2$ to initiate the valency expansion reaction. Once formed, MePF(O)(OMe) plays no further part in the reaction.

The formation of the RPF_5^- species occurs by another mechanism and the nature of this is speculative.

It does not seem reasonable to propose that PF_3 is involved in the reaction, reacting with R^+ and F^- from solution, to form, initially, RPF_4 which then adds another fluoride ion to produce RPF_5^- . The reactions of PF_3 contain no analogies and it is too poor a base to react with R^+. Another potential source of RPF_4 is by fluorination of $RP(O)F_2$ by WF_6. There is evidence in the literature for WF_6 fluorinating $(MeO)_3P=O$ to produce, as one of the products, PF_6^- , so evidently fluorination of a P=O bond is possible.[159] In the reaction of WF_6 with $P(OMe)_3$, however , $MeP(O)F_2$

Scheme 2.

Reaction of Cu{P(OMe)$_3$}$_4^+$ with WF$_6$ in MeCN Solution.



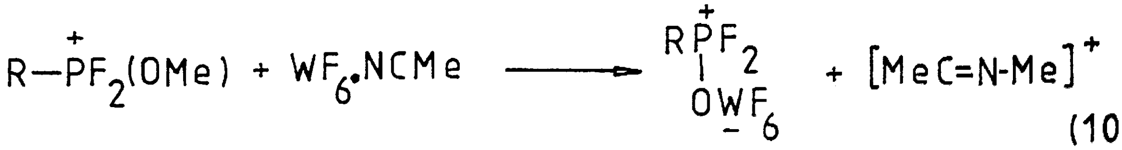
R$^+$ = [(MeCN)$_x$Me]

is one of the products and there is no evidence for $MePF_4$ being formed. The formation of RPF_5^- as a result of fluorination of a P=O bond seems unlikely in the present work.

One possible route to RPF_5^- species is that they arise from attack of R^+ upon $PF_2(OMe)$ to form an intermediate, analogous to that formed in an Arbusov reaction.

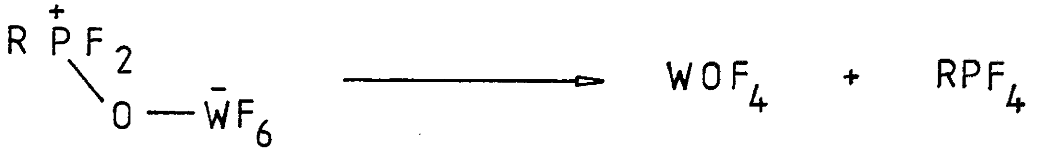
$$R^+ \quad + \quad PF_2(OMe) \longrightarrow [R{-}PF_2(OMe)]^+ \qquad (9)$$

Rather than eliminate Me^+ to form a phosphoryl species, this intermediate may then form an adduct with solvated WF_6, via a lone pair on the oxygen atom, eliminating $[MeC{=}N{-}Me]^+$.



$$R{-}\overset{+}{P}F_2(OMe) + WF_6.NCMe \longrightarrow \underset{\underset{O\underset{-}{W}F_6}{|}}{R\overset{+}{P}F_2} + [MeC{=}N{-}Me]^+ \qquad (10)$$

This adduct can then rearrange to produce two neutral species, by transfer of fluorine atoms to the phosphorus.



(11)

RPF_4 is capable of acting as a Lewis acid to fluoride ion and forms the observed, RPF_5^-.

The Role of the Solvent and the Copper Ion in the Reactions of PF_5 and WF_6.

The presence of the solvent is very important in determining the course of the reactions. In the absence of acetonitrile, there is, of course, no mechanism to produce the solvento cations. Also, without solvation of WF_6, the reaction of the cationic intermediate, $[RPF_2(OMe)]^+$, does not proceed. In the absence of MeCN, the corresponding intermediate is $[MePF_2(OMe)]^+$ which does not add WF_6, but eliminates Me^+ to form $MeP(O)F_2$.[143] In MeCN solution, the positive charge is stabilised by the large R group and elimination of Me^+ is not favoured.

Under the milder conditions of the PF_5 reaction, little or no attack of $Me(MeCN)_n^+$ on the fluorophosphite species occurs. No Arbusov products are detected and little or no RPF_5^- species are formed.

To test the belief that the solvent plays a major role in dictating the course of the reaction, WF_6 was reacted with $P(OMe)_3$, (mole ratio WF_6 : $P(OMe)_3$, 2:1) , with MeCN added as a solvent. In the absence of a solvent, this reaction is very violent, even explosive and great care must be taken in controlling the conditions.[143] The products of the reaction, without solvent, are MePF(O)(OMe) and $MeP(O)F_2$.

In MeCN solution, when the solution is warmed slowly to room temperature, the products are MePF(O)(OMe) , PF_6^- , and $Me(MeCN)_nPF_5^-$ (with four different values of n) . The n.m.r. data are listed in Table 5. The tungsten containing products are WOF_4 , WF_7^- and $W_2O_2F_9^-$ and a small amount of a 'WOF' species, which remains unidentified.

The formation of PF_6^- arises, presumably, by the same mechanism as the $Me(MeCN)_nPF_5^-$ species, but with PF_5 dissociating at some point, releasing $Me(MeCN)_n^-$. The PF_5 then reacts with F^- from solution. Alternatively, as HF is known to exist in the reaction mixture, shown by the formation of SiF_4 , then this could react with RPF_4 to produce RH and PF_5 . The HF is produced due to the intense heat generated in the reaction. PF_6^- has also been observed as a product from the reaction of $Cu\{P(OMe)_3\}_4AsF_6$ with WF_6 .[160] MePF(O)(OMe) once formed,

Table 5.

^{19}F and ^{31}P N.M.R. Data on the Products of Reaction of $P(OMe)_3$ with WF_6 in CD_3CN Solution.

Species	$\delta\ ^{31}P$ (p.p.m.)	$\delta\ ^{19}F$ (p.p.m.)	Coupling Constants (Hz)		
			$^1J_{P-F}$	$^1J_{W-F}$	$^2J_{F-F}$
MePF(O)(OMe)	41.7	-66.8	1064		
PF_6^-	-142.6	-72.8	707		
RPF_5^-	-147.3	-61.4 eq	803 eq		48.5
			748 ax		
$R'PF_5^-$	-142.9	-57.4 eq	836 eq		45.0
			726 ax		
$R''PF_5^-$	-148.2	-67.2 eq	798 eq		48.0
			745 ax		
$R'''PF_5^-$	-146.0		815 eq		
			742 ax		
$WOF_4 \cdot NCMe$		67.3		69	
$W_2O_2F_9^-$		62.1 eq		71	
		-145.2 br			
WF_7^-		143.8			
'WOF' (?)		62.5			

takes no part in the reaction, as is found in the reaction of the copper salt with WF_6 .

As a further test, WF_6 was added to $Cu\{P(OMe)_3\}_4^+$ in $CFCl_3$ but no reaction occurs until a little MeCN is added to the mixture. While $CFCl_3$ will act as a heat transfer reagent, it cannot solvate the reagents, preventing any reaction.

The role of the copper ion in the reactions of PF_5 and WF_6 is to limit the concentration of free $P(OMe)_3$ in solution and hence the amount available for fluorination. This leads to moderation of the reaction and different conditions from the free $P(OMe)_3$ reactions. There is little evidence, in the present work, for the formation of Arbusov rearrangement products of $PF(OMe)_2$ and $PF_2(OMe)$. Such species are formed in the reactions of free $P(OMe)_3$ and their absence can be ascribed to both the action of the solvent and the metal ion.

The solvent reacts with Me^+ , removing it from solution. In the absence of Me^+ the fluorophosphites have no trigger to undergo the Arbusov reaction. The cation may play a part by coordinating the fluorophosphite. The phosphorus lone pair is then not available to react with Me^+ . Cu^+ is known to coordinate PF_3 in SO_2 solution, but not in MeCN.[106] The better donor ability of $PF(OMe)_2$ and $PF_2(OMe)$ relative to PF_3 makes them better potential ligands.

In the reaction of WF_6 , some Arbusov product, $MePF(O)(OMe)$, is formed and its formation is ascribed to the higher temperature conditions in the reaction.

The variation in the extent of fluorination with the amount of PF_5 has not been investigated but fluorination obviously proceeds to the second step very readily. Presumably, by adjusting the conditions,

$PF(OMe)_2$ will be obtained as a major product. The limiting factor in the production of PF_3 will be the ability of $PF_2(OMe)$ to form an adduct with PF_5 . $PF_2(OMe)$ may not be a sufficiently good σ-donor to form the adduct with PF_5 .

The generality of the reaction, with respect to the nature of $P(OR)_3$, has not been examined. It is possible to produce $Cu\{P(OR)_3\}_4{}^+$ species, using a number of different alkyl phosphites and it will be interesting to investigate the reaction of these ions with PF_5 . It may be possible to produce simple routes to $PF_2(OR)$ and $PF(OR)_2$ involving no Arbusov rearrangements reactions and very mild reaction conditions.

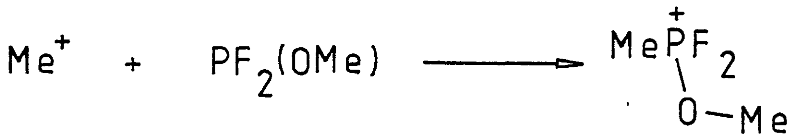
The reaction of $Cu\{P(OMe)_3\}_4{}^+$ with WF_6 is much more difficult to control as it is very exothermic. Further attempts to moderate the reaction may prove fruitful, for example by increasing the volume of solvent. It will also be interesting to vary the solvent, perhaps to use propionitrile or higher nitriles, to investigate the effect of the R group upon formation of $Me(RCN)_n{}^+$ species. The larger R group of the solvent will stabilise the carbonium ion, by greater inductive donation of electron density. This may make the carbonium ion less reactive to further attack by the solvent. The overall effect will be to limit the number of different solvent cations, $Me(RCN)_n{}^+$, perhaps to one , $Me(RCN)^+$. Hence only $Me(RCN)PF_5{}^-$ will be formed.

Reaction of $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ with WF_6 in MeCN Solution.

In contrast to $Cu\{P(OMe)_3\}_4{}^+$, the reaction of $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ with WF_6 is very mild and takes several weeks to reach completion, even when large amounts of WF_6 are used. The colour of the solution changes very slowly from light to dark yellow, indicating that attack on the solvent is very slow. This is in keeping with the lower temperature under which the reaction is carried out. The ^{31}P and ^{19}F n.m.r. spectra are shown in Figure 5 and 6 and listed in Table 6.

The major product of fluorination is $MePF_4$. This is formed, presumably, by a route similar to that presented for formation of RPF_5^-, except that Me^+ rather than R^+ is involved. The mechanism of the first two steps, reaction of $P(OMe)_3$ with WF_6 to produce $PF_2(OMe)$ is the same as for the Cu^+ salt.

$PF_2(OMe)$ reacts with Me^+ to produce an Arbusov type intermediate,



$$Me^+ + PF_2(OMe) \longrightarrow Me\overset{+}{P}F_2(OMe) \tag{12}$$

This then reacts with $WF_6.NCMe$ with elimination of $[MeCN\text{-}Me]^+$,

$$[MePF_2(OMe)]^+ + WF_6.NCMe \longrightarrow Me\overset{+}{P}F_2(O\overset{-}{W}F_6) + [MeCN\text{-}Me]^+ \tag{13}$$

The adduct breaks down with transfer of fluorine atoms to produce two neutral species.

$$Me\overset{+}{P}F_2(O\overset{-}{W}F_6) \longrightarrow MePF_4 + WOF_4 \tag{14}$$

Under these conditions, $MePF_4$ is too poor an acceptor to compete with WF_6 for fluoride ion and so does not react further to produce $MePF_5^-$.

It is possible that $MePF_4$ will act as a Lewis acid to MeCN and exist as a six coordinate species in solution, $MePF_4(NCMe)$. Earlier work finds that there is no significant amount of complex formation of RPF_4 with MeCN (where R = Me, Et, Ph).[137] This is confirmed in the present work, where the ^{31}P chemical shift and the P—F coupling constant of $MePF_4$ are in keeping with five rather than

Table 6.

^{19}F and ^{31}P N.M.R. Data on the Products of Reaction of $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ with WF_6 in CD_3CN.

Species	$\delta\ ^{31}P$ (p.p.m.)	$\delta\ ^{19}F$ (p.p.m.)	Coupling Constants (Hz)				
			$^{1}J_{P-F}$	$^{1}J_{W-F}$	$^{2}J_{F-F}$	$^{2}J_{P-H}$	$^{3}J_{F-H}$
$MePF_4$	-26.6	-44.8	968			20	ca.5
MePF(O)(OMe)	38.9	-67.0	1063				
RPF_5^-		-61.8 eq	802 eq		48		
$R'PF_5^-$		-67.5 eq	797 eq		47		
$WOF_4.NCCD_3$		66.8		69			
$W_2O_2F_9^-$		61.7 eq -145.6 br		70.5	58		

Figure 5. ^{31}P N.M.R. Spectrum of the $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ – WF_6 Reaction Mixture.

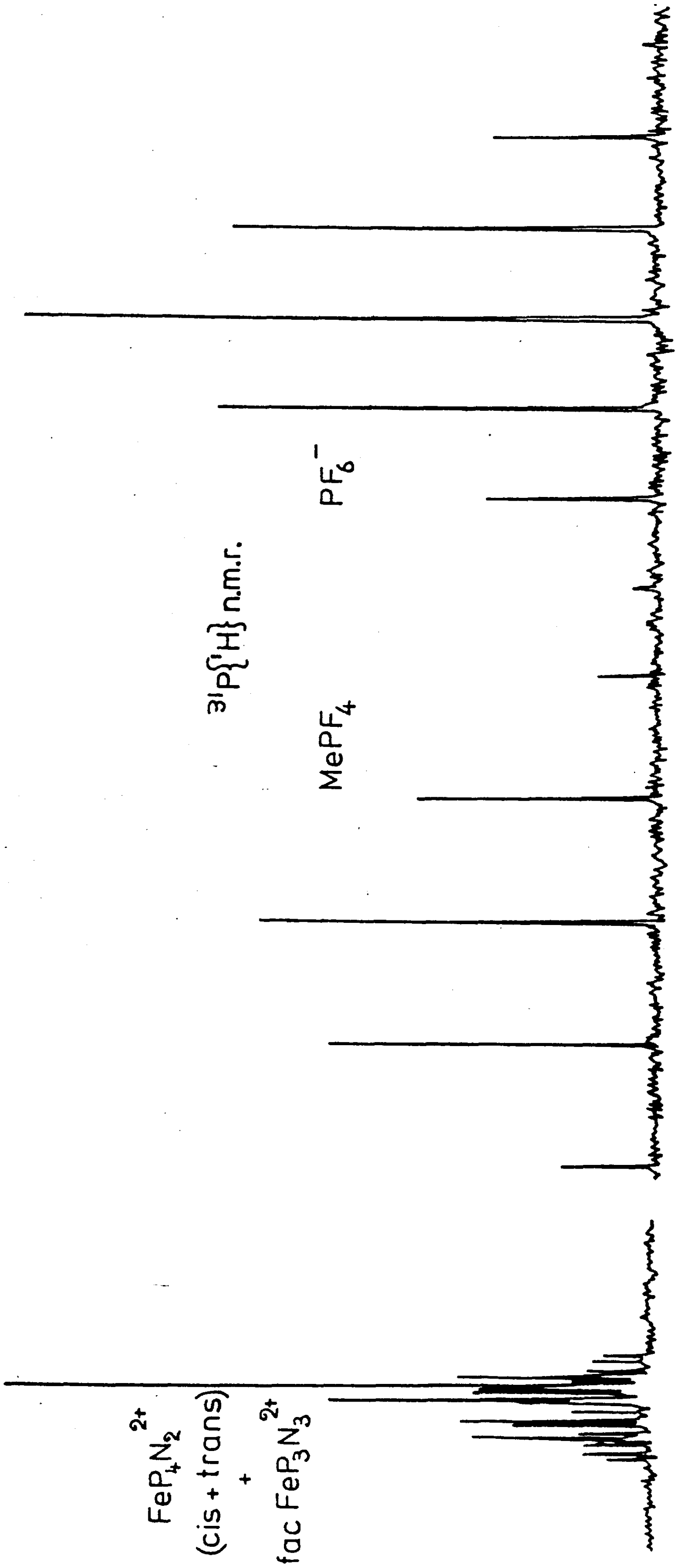
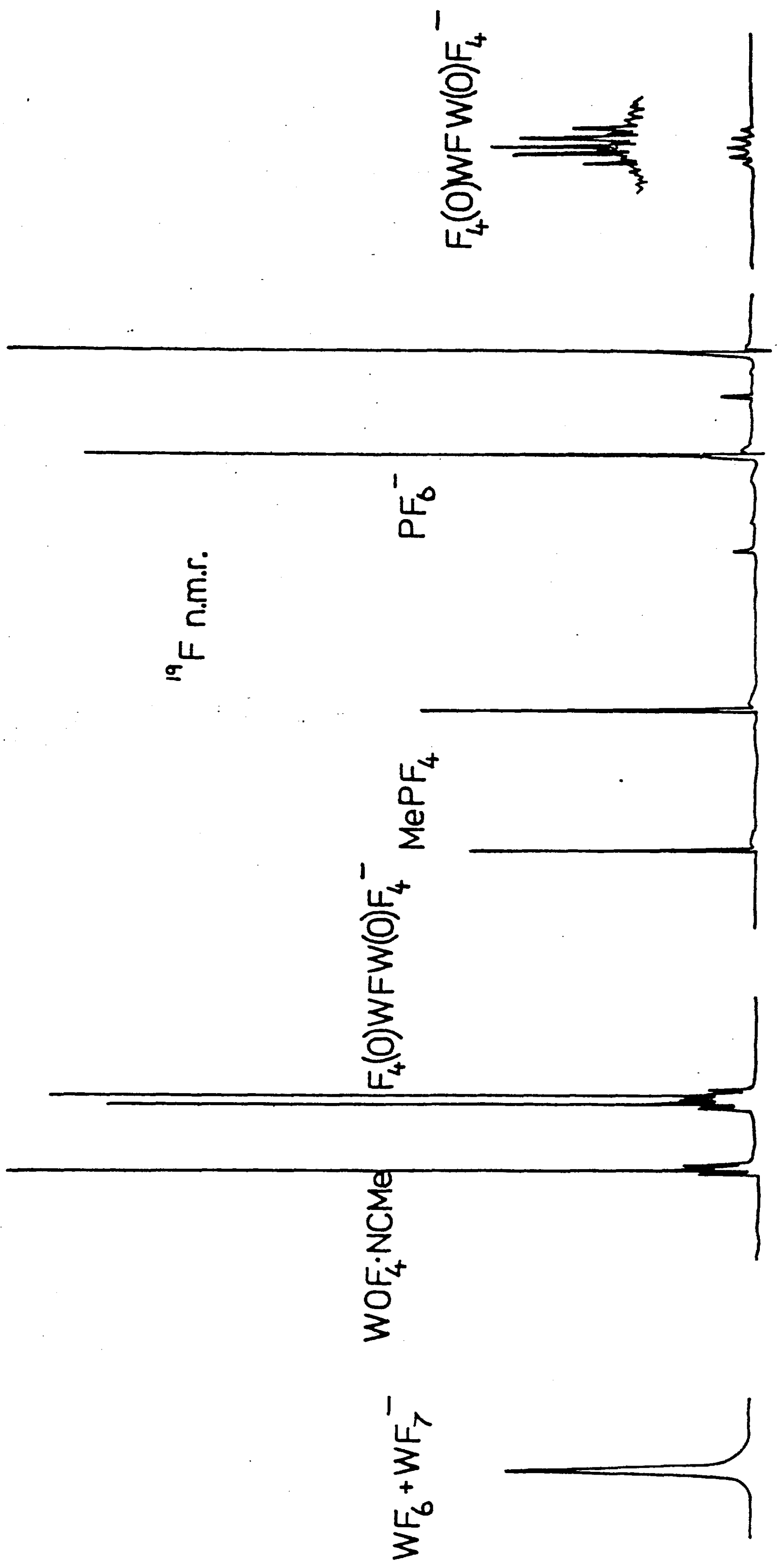


Figure 6. ^{19}F N.M.R. Spectrum of the $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ - WF_6 Reaction Mixture.



six coordinate phosphorus (Tables 3 and 6) .

In one reaction of WF_6 with $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$, significant amounts of $MePF(O)(OMe)$ and $W_2O_2F_9^-$ are formed, as well as $MePF_4$ and WOF_4 . This reaction mixture contained 50 % less WF_6 , relative to the reactions where only $MePF_4$ and WOF_4 are formed. This is rationalised as follows. In the initial fluorination step, the reaction proceeds via formation of a W—P bonded species, as discussed above. This breaks down to produce WF_5OMe and $PF(OMe)_2$. In the presence of a large excess of WF_6 , $PF(OMe)_2$ reacts rapidly to form another W—P bonded species and hence $PF_2(OMe)$. When less WF_6 is available, solvated Me^+ competes successfully with WF_6 for $PF(OMe)_2$, to form $MePF(OMe)_2^+$. This species, instead of being fluorinated, loses Me^+ to the solvent to form the Arbusov product, $MePF(O)(OMe)$.

This difference in behaviour of the two intermediates , $MePF(OMe)_2^+$ and $MePF_2(OMe)^+$ is probably a reflection of the relative kinetic stability of the two species, in MeCN solution. If $MePF(OMe)_2^+$ is very short lived, it will rapidly lose Me^+ to give the Arbusov product. If $MePF_2(OMe)^+$ is longer lived, it will be able to form an adduct with WF_6 , and hence produce $MePF_4$.

The formation of $W_2O_2F_9^-$ is also accounted for by an argument based upon the smaller concentration of WF_6 . WF_5OMe breaks down rapidly, in MeCN solution, releasing F^- to the solution. In the presence of a large excess of WF_6 , all the fluoride ion is used in forming WF_7^- . There is a rapid exchange process between WF_6 and WF_7^- . When less WF_6 is present, WOF_4 competes more successfully with WF_6 for the fluoride ion and some WOF_5^- is formed. The WOF_5^-

adds another WOF_4 group to form the fluorine bridged anion, $W_2O_2F_9^-$.

The proposed reaction pathway is outlined in Scheme 3. The metal ion plays a very important role in dictating the products. Low spin iron(II) is 'substitution inert' and dissociation of $P(OMe)_3$ from $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ is very slow. Thus, at any instant in time, the amount of free $P(OMe)_3$ in solution is very small. There is a very large excess of WF_6 in solution and reaction to produce $MePF_4$, or MePF(O)(OMe) , occurs very rapidly. As very little fluorination occurs at any particular time, the heat energy produced is readily dissipated and there is no noticeable rise in temperature. The reaction conditions are much milder, particularly for polymerisation of the solvent.

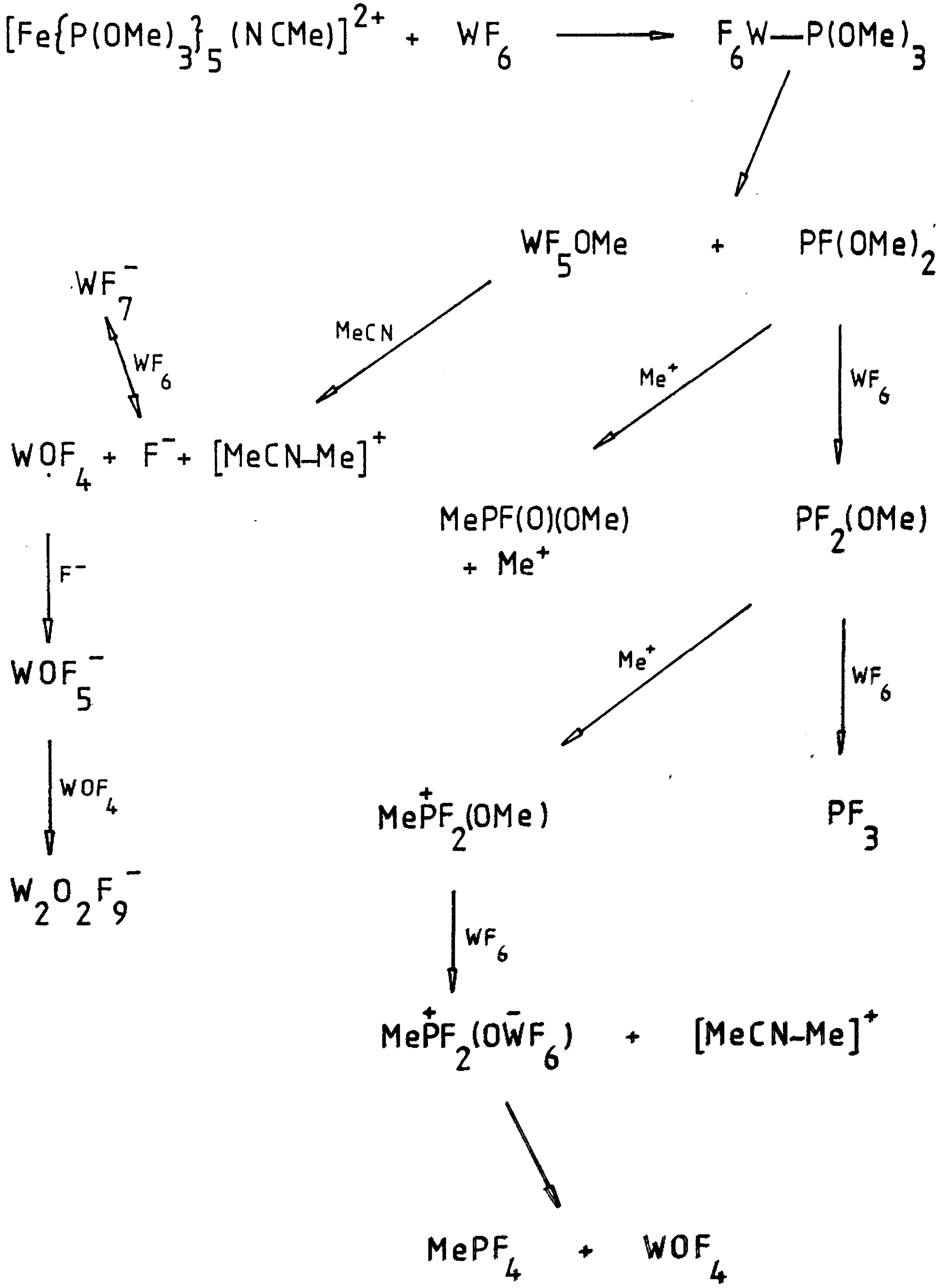
The solvent is also crucial in dictating the course of the reaction by acting as a solvating agent for the two reagents, by dissipating the heat energy produced in the reaction and by acting as a source of Me^+ and $Me(MeCN)_n^+$. The role of the solvent in the reaction is illustrated by using $CFCl_3$ as the liquid phase. $CFCl_3$ cannot solvate the reagents and no reaction occurs.

The reaction of $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ with PF_5 in MeCN , is very slow indeed. Following the reaction by ^{31}P n.m.r. , over a period of weeks, a slow change in the spectrum is observed, corresponding to the appearance of Fe(II) - $P(OMe)_3$ complexes with lower numbers of $P(OMe)_3$ groups, for example <u>cis</u>-$[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$. No products of fluorination are observed, but they are presumably present. The reaction is less suitable for study compared with the WF_6 system, due to the very slow rate.

The formation of $MePF_4$ as the product of fluorination of $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ with WF_6 is quite striking. That, in the

Scheme 3.

Reaction of $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$ with WF_6 in MeCN Solution.



presence of a large excess of WF_6 , it is the sole phosphorus containing product is even more intriguing, for this makes the method a potentially useful synthetic route to $MePF_4$. Many routes to $MePF_4$ are known, as described in the introduction. This route, however, is one of the very few where the methyl group is not attached to the phosphorus, prior to the fluorination reaction. Another example of a reaction where an alkyl group is transferred to phosphorus, is the reaction between PF_5 and R_4Sn (R = Me, Et, vinyl and ^{n}Pr)[161] and (R = Ph)[162]. The products are RPF_4 and R_3SnF.

The use of the reaction of $[Fe\{P(OR)_3\}_5NCMe]^{2+}$ with WF_6 is limited. This is a function, not of the fluorination reaction, but of the availability of the starting material, $[Fe\{P(OR)_3\}_5NCMe]^{2+}$. The formation of these complexes is very dependent upon the steric and electronic properties of the $P(OR)_3$ moiety , as discussed in an earlier chapter. It should be possible, however, to produce $[Fe\{P(OEt)_3\}_5NCMe]^{2+}$ and the reaction between this complex and WF_6, in MeCN solution, will be illuminating.

Conclusions.

The reactions of coordinated $P(OMe)_3$ with WF_6 and PF_5 are very dependent upon the conditions of the reaction. The conditions of importance are, the nature of the metal ion to which $P(OMe)_3$ is coordinated, the nature of the solvent used as the reaction medium and the temperature at which the reaction is carried out. The major exothermic contribution to the reaction is formation of the strong W=O or P=O bonds.

When MeCN is used as the solvent for the fluorination reactions, it becomes involved by reacting with Me^+ . This limits the availability of Me^+ which is important in preventing formation of Arbusov products. The phosphoryl compounds, produced in the Arbusov reaction, are major products of the reaction of WF_6 and PF_5 with free $P(OMe)_3$ but little or none of these species are observed in the reactions in MeCN solution. The exception is formation of some MePF(O)(OMe) , the Arbusov product of $PF(OMe)_2$, in some of the reactions of WF_6 .

The species, PF_4OMe and WF_5OMe , are very unstable in MeCN solution and break down to form POF_3 and WOF_4 respectively. Me^+ is transferred to the solvent and F^- to PF_5 or WF_6 . There is no MeF produced in either reaction.

The reaction of WF_6 with $[Fe\{P(OMe)_3\}_5NCMe]^{2+}$ is slow but proceeds , under mild conditions, to produce $MePF_4$ as the fluorinated product. This reaction has potential as a synthetic route to $MePF_4$.

The reaction of WF_6 with $Cu\{P(OMe)_3\}_4{}^+$ is very fast and is violently exothermic. The products of reaction are a number of $Me(MeCN)_nPF_5{}^-$ species , where n is variable , and MePF(O)(OMe) . The value of n is dependent upon the temperature of the solution during the course of the reaction.

The products of both reactions arise by effectively the same mechanism. The difference between the two is a function of the temperature of the reaction medium , which in turn depends upon the nature of the metal ion.

The Fe(II) complex is low spin, d^6 , and is substitution inert. Loss of $P(OMe)_3$ from this complex is very slow. The heat produced in the fluorination step is rapidly dispersed and hence the internal temperature of the solution does not rise dramatically.

The Cu(I) complex is labile, as is shown by its ^{1}H n.m.r. spectrum. A higher concentration of free $P(OMe)_3$ is present in solution at any instant in time and so reaction proceeds more rapidly. The heat produced is not easily dissipated and the temperature of the solution rises rapidly.

The initial steps in the fluorination of $P(OMe)_3$ by WF_6 , to produce $PF(OMe)_2$ and $PF_2(OMe)$, proceed via W—P bonded adducts. This is based upon evidence from the reaction of $Cu\{P(OMe)_3\}_4^+$ with PF_5 which proceeds via a P—P bonded intermediate , $F_5P-P(OMe)_3$. This adduct is characterised by ^{19}F and ^{31}P n.m.r. spectroscopy.

Under the milder conditions of the PF_5 reaction , less attack on the solvent occurs and the products of fluorination reactions are the fluorophosphite species , particularly $PF_2(OMe)$.

$PF(OMe)_2$ is capable of coordinating to Cu(I) in MeCN but the complex is labile and undergoes a rapid exchange reaction. The exchange reaction is slowed by reducing the temperature of the solution.

The reaction of free $P(OMe)_3$ with WF_6 , in MeCN solution , is very different from when no solvent is used. This is a result of the moderating effect of the solvent on the temperature , as well as the participation of MeCN in the reaction. The solvent polymerises, initiated by Me^+ , forming $Me(MeCN)_n^+$ cations.

Experimental.

1. Reaction of $Cu\{P(OMe)_3\}_4 PF_6$ with WF_6 in CD_3CN Solution.

a) WF_6 (1.2g ; 4 mmol) was added to $Cu\{P(OMe)_3\}_4PF_6$ (0.38g ; 0.54 mmol) in CD_3CN (2 ml) at 77 K in a flask with an n.m.r. tube as side arm (mole ratio, WF_6 : $P(OMe)_3$, 1.88 : 1) . At ca. 233 K, as solid WF_6 dissolved, the liquid phase was bright yellow. As the flask continued to warm, violent bubbling began from the undissolved solid in the bottom of the flask and the solution darkened in colour. The bubbling ceased when all the solid had dissolved and the solution was dark brown. When the flask reached ca. 278 K, the solution was straw yellow in colour and the flask became very hot. This was accompanied by a vigorous reflux of the solution up the side of the vessel. The reaction was moderated by cooling and reflux ceased. The solution, now amber, was decanted and sealed in the n.m.r. tube. The following species were identified by ^{19}F n.m.r. spectroscopy (Tables 1, 3 and 4) ; WF_6 (broadened and shifted to higher field from literature value) , WOF_4 , $W_2O_2F_9^-$ and PF_6^- . Over a period of hours, the signal due to WOF_4 decreased, effectively to zero, that due to $W_2O_2F_9^-$ increased and the solution became dark red. After 24 hours, the solution was opaque and the following species were identified by ^{19}F n.m.r. spectroscopy ; WOF_4 (trace) $W_2O_2F_9^-$, PF_6^- , RPF_5^- . No further changes were observed over a period of days. The ^{19}F n.m.r. spectrum of the involatile residues was identical to that of the reaction mixture. After twenty days at room temperature, the n.m.r. spectra were broad, due to the high viscosity of the solution. The following species were identified from the ^{19}F and

^{31}P F.T. n.m.r. spectra ; $W_2O_2F_9^-$, PF_6^- , RPF_5^- , $R'PF_5^-$, MePF(O)(OMe) , PF_2(OMe) (trace) , and small amounts of other F or P containing species were also present which were not identified. The ratio of RPF_5 : $R'PF_5$ was ca. 3 : 1 .

b) Reaction a) was repeated using WF_6 (0.55g ; 1.84 mmol) with $Cu\{P(OMe)_3\}_4PF_6$ (0.38g ; 0.54 mmol) in CD_3CN (2 ml) (mole ratio WF_6 : $P(OMe)_3$, 0.86 : 1) . No attempt was made to moderate the reaction by cooling. The reaction showed the same behaviour as witnessed in a) . After 30 minutes reaction, the following species were identified by ^{19}F n.m.r. spectroscopy ; WF_7^- , $W_2O_2F_9^-$, PF_6^- , $PF(OMe)_2$, WOF_5^- (trace) . After two days, the solution had become deep red. The ^{19}F n.m.r. spectrum revealed the presence of $W_2O_2F_9^-$, $(W_2O_2F_9^-)'$, WOF_5^- , PF_6^- , RPF_5^- , $R'PF_5^-$ and $PF(OMe)_2$. After ten days at room temperature, the only change was an additional resonance due to MePF(O)(OMe) with a concomitant decrease in the signal due to $PF(OMe)_2$. The ratio RPF_5^- : $R'PF_5^-$ was ca. 1 : 3 . A number of other small resonances due to P or F containing species remained unassigned. The gas infra red spectrum of the volatile residues showed bands characteristic of SiF_4 .

c) Reaction a) was repeated using WF_6 (2.4g ; 8 mmol) with $Cu\{P(OMe)_3\}_4PF_6$ (0.38g ; 0.54 mmol) in CD_3CN (2 ml) (mole ratio WF_6 : $P(OMe)_3$, 3.7 : 1) . The reaction mixture was held at 273 K for two hours to moderate the reaction. After this time the solution was deep red. The ^{19}F n.m.r. spectrum of the mixture indicated the presence of the following species ; WOF_4 , $W_2O_2F_9^-$ (trace) , PF_6^- . There was also an extremely broad signal at ca. 150 p.p.m. assigned to WF_6 , undergoing rapid exchange.

After 48 hours the spectrum indicated a large increase in the amount of $W_2O_2F_9^-$, relative to WOF_4 , and also the presence of RPF_5^- . After a further period of several days, the only change was in the ratio WOF_4 : $W_2O_2F_9^-$ which had decreased still further. As well as the major signals the ^{31}P and ^{19}F F.T. n.m.r. spectra showed signals due to small amounts of the following species, MePF(O)(OMe) , $MePF_4$ and trace amounts of PF_3 and $R'PF_5^-$. The ^{19}F n.m.r. spectra of the volatile residues showed signals due to PF_3 , $MePF_4$ and WF_6 . The gaseous infra red spectrum of the volatile residues at 195 K indicated that SiF_4 , PF_3 and WF_6 were present.

d) $Cu\{P(OMe)_3\}_4PF_6$ (0.54 mmol) was generated in situ from $Cu(NCMe)_4PF_6$ (0.2g ; 0.54 mmol) and $P(OMe)_3$ (1.05g ; 8.4 mmol) in MeCN (3 ml) . The volatile material was removed by vacuum distillation to leave the product as a cream coloured solid. CD_3CN (1.5 ml) was distilled into the flask, followed by WF_6 (1.82g ; 6.11 mmol) , (mole ratio WF_6 : $P(OMe)_3$; 2.84 : 1) . The flask was warmed from 77 K to 253 K at which stage the solution was light brown in colour. A portion was decanted and sealed in an n.m.r. tube, without being warmed above 253 K. The ^{19}F and ^{31}P n.m.r. spectra were run at this temperature and gave evidence for the presence of PF_6^- , WOF_4 , WF_5OMe and $PF(OMe)_2$. The $PF(OMe)_2$ signal was broadened by fluorine exchange. Other small signals were not assigned. There were very broad signals, on the ^{19}F n.m.r. spectrum above 100 p.p.m., due to WF_6 exchanging with WF_7^- . The n.m.r. tube was allowed to warm to 273 K and the mixture turned bright yellow. The ^{19}F n.m.r. spectrum of the sample, at 243 K, showed the presence of WF_7^- and PF_6^- as major species, WF_5OMe , WOF_4

and $W_2O_2F_9^-$, $PF(OMe)_2$ (broadened doublet) . There were also a number of small peaks which were not assigned. The mixture was warmed again, to above 273 K and the tube became hot. The high field ^{19}F n.m.r. spectrum was measured, at 263 K and showed the presence of PF_6^- (major species) , $PF(OMe)_2$, MePF(O)(OMe) (small amount) and $PF_2(OMe)$ (trace amount) .

e) Reaction a) was repeated using WF_6 (2.0g ; 6.7 mmol) with $Cu\{P(OMe)_3\}_4PF_6$ (0.38g ; 0.54 mmol) in $CFCl_3$ (5 ml) (mole ratio WF_6 : $P(OMe)_3$; 3.1 : 1) . On warming from 77 K, the solid floated on top of the $CFCl_3$ and no reaction was observed, even after shaking for several days. CD_3CN (0.045g) was distilled into the flask and, on warming, a yellow colour developed. After twelve hours, the white solid had been deposited as an involatile, viscous, yellow oil. The ^{19}F n.m.r. spectrum of the oil showed PF_6^- and $W_2O_2F_9^-$ as the only identifiable fluorine containing species.

2. Reaction of $Cu\{P(OMe)_3\}_4AsF_6$ with WF_6 in CD_3CN Solution.

WF_6 (0.44g ; 1.46 mmol) was added to $Cu\{P(OMe)_3\}_4AsF_6$ (0.36g ; 0.48 mmol) in CD_3CN (2 ml) at 77 K, in a flask with an n.m.r. tube side arm (mole ratio WF_6 : $P(OMe)_3$; 0.76 : 1) . The solution was warmed slowly and follows a similar reaction pathway to 1 b) (*vide supra*) . The ^{19}F n.m.r. spectrum of the reaction mixture indicated the presence of $W_2O_2F_9^-$, WOF_5^- and $PF(OMe)_2$. After four days, at room temperature, the solution was very dark red in colour and the ^{19}F n.m.r. spectrum showed the appearance of $(W_2O_2F_9^-)'$ as the only change.

3. Reaction of $Cu\{P(OMe)_3\}_4$ PF_6 with PF_5 in CD_3CN Solution.

a) $Cu\{P(OMe)_3\}_4PF_6$ (0.38g ; 0.54 mmol) was reacted with PF_5

(5.1 mmol) in CD_3CN (2 ml) in a flask with an n.m.r. tube side arm (mole ratio PF_5 : $P(OMe)_3$; 2.4 : 1) . As the flask warmed from 77 K, the adduct, $PF_5.NCCD_3$, was deposited on the walls of the vessel and this dissolved, as the temperature continued to rise, to give a yellow-green solution. After the flask had warmed to ca. 278 K, the solution commenced to bubble vigorously, grew very hot and turned bright yellow in colour. As the system cooled down, the liquid phase became very viscous. The volatile material was removed by vacuum distillation to leave a yellow gel which was soluble in CD_3CN. The ^{19}F n.m.r. spectrum showed a broadened doublet, due to PF_6^- , as the only major signal. The ^{19}F n.m.r. spectrum of the volatile products of reaction indicated that POF_3 and $PF_2(OMe)$ were present. The gas phase infra red spectrum of the volatile products confirmed the n.m.r. results. The gaseous infra red spectrum of the vapour phase, above the yellow gel, showed bands due to POF_3 and $PF_2(OMe)$. The ^{31}P F.T. n.m.r. spectrum confirmed the above results and gave evidence for trace amounts of PF_3 and $PF_2(O)(OMe)$ in both the volatile products and in the gel. The gel contained species of the form RPF_5^- , as well as trace amounts of a number of other phosphorus containing products which were not identified.

b) Reaction a) was repeated using PF_5 (1.92 mmol) with $Cu\{P(OMe)_3\}_4PF_6$ (0.38g ; 0.54 mmol) in CD_3CN (2 ml) , under controlled conditions of temperature (mole ratio PF_5 : $P(OMe)_3$; 0.89 : 1) . The flask was allowed to warm over a period of three hours to ca. 268 K, at which time an infra red spectrum, of the gaseous phase, indicated the presence of POF_3 , SiF_4 and PF_5 . The material which was volatile at 195 K was pumped away and a portion of the reaction mixture was isolated in an n.m.r. tube. The ^{19}F and ^{31}P F.T. n.m.r. spectra were determined at 243 K. The spectra showed the presence of $F_5P{-}P(OMe)_3$, PF_4OMe , POF_3 , PF_6^- and $PF_5.NCMe$. There was also a very broad, (ca. 1,400 Hz) , asymmetric peak around 125 p.p.m., on the ^{31}P spectrum, with no fine structure. There was also a strong singlet at 12 p.p.m., which was not assigned.

4. Reaction of $Cu\{P(OMe)_3\}_4$ AsF_6 with PF_5 in CD_3CN Solution.

a) PF_5 (1.92 mmol) was reacted with $Cu\{P(OMe)_3\}_4AsF_6$ (0.36g ; 0.48 mmol) in CD_3CN (2 ml) (mole ratio PF_5 : $P(OMe)_3$, 1 : 1) . The solution was allowed to warm slowly from 243 K. At ca. 273 K the solution was yellow but began to darken, through orange to red and a dark brown solid precipitated from solution, as the mixture continued to warm. The ^{19}F n.m.r. spectrum of the reaction mixture, at this stage showed a broadened doublet, due to PF_6^- as the only major fluorine containing species. The ^{19}F n.m.r. spectrum, and gas phase infra red spectrum, of the volatile products, indicated the presence of POF_3 and $PF_2(OMe)$.

b) PF_5 (1.62 mmol) was reacted with $Cu\{P(OMe)_3\}_4AsF_6$ (0.36g ; 0.48 mmol) in CD_3CN (2 ml) (mole ratio PF_5 : $P(OMe)_3$; 0.84 : 1) under controlled temperature conditions. The mixture was warmed slowly to 268 K and the gas phase infra red spectrum was measured at this temperature. This showed the presence of POF_3 and PF_5 . The ^{31}P and ^{19}F F.T. n.m.r. spectra of the reaction mixture were run at 243 K and these spectra indicated the presence of PF_4OMe , PF_6^- and a trace of $PF_5.NCCD_3$. There was also a very broad signal on the

^{31}P spectrum at around 125 p.p.m.. There was a further singlet at 53.9 p.p.m. due to $MeP(OMe)_3^+$ and also some other singlets which were not assigned.

5. Reaction of $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ with WF_6 in CD_3CN Solution.

a) WF_6 (0.9g ; 3 mmol) was added to $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ (0.2g ; 0.2 mmol) in CD_3CN (2 ml) at 77 K, in a vessel fitted with an n.m.r. tube side arm (mole ratio WF_6 : $P(OMe)_3$; 3 : 1) . As the flask warmed to room temperature, the WF_6 dissolved and the solution bubbled vigorously, to produce a yellow solution, deeper in colour than that of the trimethyl phosphite complex alone. The ^{19}F n.m.r. spectrum of the reaction mixture, after one hour, revealed the presence of WF_6 (undergoing exchange) , WOF_4 and PF_6^- . After six days at room temperature, the ^{31}P n.m.r. spectrum indicated there was no change from the starting material. After a further fourteen days, the ^{19}F n.m.r. spectrum showed that WF_6 (broadened) , WOF_4 , PF_6^- and $MePF_4$ were present. This was confirmed by the ^{31}P n.m.r. spectrum which also showed that the relative quantities of the complexes, of general formula $[Fe\{P(OMe)_3\}_n(NCMe)_{6-n}]^{2+}$, had altered from that of the starting material. There was now proportionally more $[Fe\{P(OMe)_3\}_4(NCMe)_2]^{2+}$. Over a period of two months, the ratio of the complexes continued to change, accompanied by a strengthening of the signals due to $MePF_4$. The presence of a trace amount of RPF_5^- was also evident. A ^{19}F n.m.r. spectrum of the volatile residues indicated that WF_6 and $MePF_4$ were present, and $MePF_4$ was further identified by ^1H n.m.r. spectroscopy. The infra red spectrum of the solid residues gave evidence for $[Fe\{P(OMe)_3\}_n(NCMe)_{6-n}][PF_6]_2$ and $WOF_4.NCCD_3$.

b) WF_6 (0.38g ; 1.2 mmol) was added to $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ (0.15g ; 0.15 mmol) in CD_3CN (2 ml) at 77 K (mole ratio WF_6 : $P(OMe)_3$; 1.6 : 1) . The reaction proceeded in a similar manner to 5 a) , above. After 24 hours the ^{19}F n.m.r. spectrum showed that the following species were present ; PF_6^- , WOF_4 , $W_2O_2F_9^-$ and WF_6 (broadened and shifted upfield). After five days, proportionally more $W_2O_2F_9^-$ was present, relative to WOF_4 , and there was now evidence for $MePF_4$. The ^{31}P n.m.r. spectrum confirmed this and indicated that MePF(O)(OMe) had also been produced. Over several weeks, $W_2O_2F_9^-$ became the major W—F species, the relative amount of $MePF_4$ increased and a minute trace of $R'PF_5^-$ appeared on the ^{19}F n.m.r. spectrum.

c) WF_6 (0.72g ; 2.4 mmol) was added to $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ (0.2g ; 0.2 mmol) in $CFCl_3$ (3 ml) at 77 K (mole ratio WF_6 : $P(OMe)_3$; 2.4 : 1) . The solid was insoluble in $CFCl_3$ and remained on the surface of the solution. There was no evidence for reaction, even after shaking the mixture for several days.

6. Reaction of $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ with PF_5 in CD_3CN Solution.

PF_5 (0.25 mmol) was added to $[Fe\{P(OMe)_3\}_5(NCMe)][PF_6]_2$ (0.05g ; 0.05 mmol) in CD_3CN (2 ml) at 77 K . On warming to room temperature, there was no immediate evidence for a reaction. The sole change, after four weeks at room temperature, was a change in the relative distribution of $[Fe\{P(OMe)_3\}_n(NCMe)_{6-n}]^{2+}$ species. $[Fe\{P(OMe)_3\}_4(NCMe)]^{2+}$ became much more favoured with respect to $[Fe\{P(OMe)_3\}_5(NCMe)]^{2+}$.

7. Reaction of $P(OMe)_3$ with WF_6 in MeCN Solution.

$P(OMe)_3$ (0.33g ; 2.63 mmol) and WF_6 (1.6g ; 5.41 mmol) (mole ratio WF_6 : $P(OMe)_3$; 2.1 : 1) , together with MeCN (5 ml) were added to a flask at 77 K . The mixture was allowed to warm very slowly to room temperature, in a fume cupboard, by enclosing the vessel in a large dewar flask, which had been previously cooled to 77 K . After several hours, with the mixture still frozen, a golden yellow colour had developed. Over a period of twelve hours the flask warmed to ca. 273 K , and the solution was brown-red in colour. Removing the volatile fraction, by vacuum distillation, left a dark red, viscous liquid. A portion of the liquid was transferred, to a vessel with an n.m.r. tube as side arm, in the glove box. The flask was evacuated and a small volume of CD_3CN was distilled in. A portion of the mixture was decanted and sealed in the n.m.r. tube. The ^{31}P n.m.r. spectrum showed the presence of PF_6^- , MePF(O)(OMe) and four species of the form RPF_5^- , of varying intensity. This was confirmed by the ^{19}F n.m.r. spectrum which also showed the presence of WF_7^- (trace) , WOF_4 (small amount) , $W_2O_2F_9^-$ (large amount) and a 'WOF' species of undetermined nature. There was also a large singlet, at -66 p.p.m. which was not assigned. The ^{19}F n.m.r. spectrum of the unknown 'WOF' species was a doublet of doublets and had ^{183}W satellites, J_{W-F} ca. 70 Hz . The coupling constant of the doublets were very small, 1.3 Hz and 2.2 Hz . The ^{1}H n.m.r. spectrum of the red solution showed two 1:3:3:1 quartets, at 2.6 p.p.m. and 3.6 p.p.m. which were not related by a coupling constant. The coupling constant in the 1:3:3:1 quartets was ca. 2 Hz . The spectra were not assigned.

Appendix I.

Cyclic Voltammetry.

Introduction.

The theory and techniques of voltammetry have been extensively discussed,[168] and only a very brief outline is given here.

The basic apparatus consists of two electrodes, a working and a reference, immersed in a solution of the species being studied. The potential of the working electrode is varied and the current is measured. A typical voltammogram is shown in Figure 1.

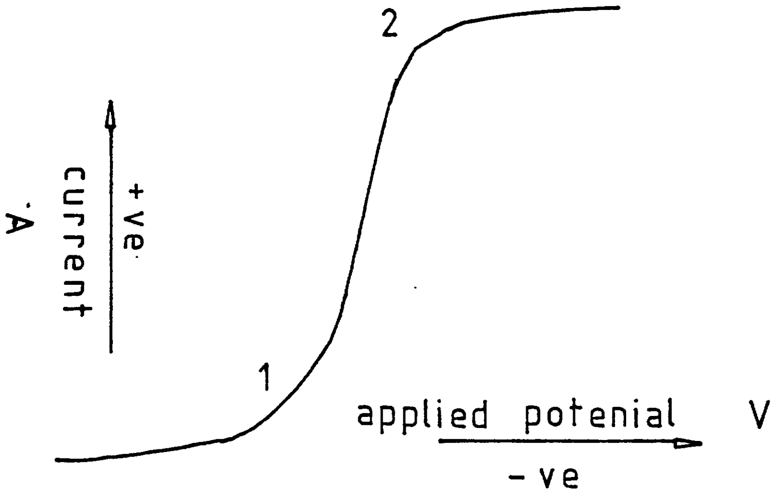


Figure 1. Current vs. Applied Potential.

The situation discussed is for a one electron reduction but the same arguments apply for an oxidation step.

As the applied potential becomes increasingly negative, the current rises slowly. This residual current is due to a condenser current, a consequence of charging of a double layer at the electrode surface, and a diffusion current, due to traces of oxidisible or reducible material in the solution. At point 1, near the formal electrode potential of the redox active species, the current rises sharply as reduction of the species begins. The current rises sharply to 2, at which point the approach of the species to the electrode, and the subsequent reduction, are at a maximum, determined by diffusion. At higher negative potentials, the current rises slowly due to residual current. This behaviour gives rise to the wave form on the current vs. voltage plots.

For a reversible wave, $E_{\frac{1}{2}} \approx E^{o}$, where $E_{\frac{1}{2}}$ is the half wave potential (the potential corresponding to a position halfway up the curve) and E^{o} is the formal electrode potential. For a non-reversible wave, $E_{\frac{1}{2}}$ is not equal to E^{o} and so systems must be tested for reversibility before equating $E_{\frac{1}{2}}$ with E^{o} .

Some waves are not reversible because one of the species in the couple is involved in a chemical reaction. Consider,

$$A \longrightarrow B^{+} \longrightarrow C^{+}$$

A is oxidised electrochemically to produce B^{+} , but this species is chemically reactive, forming C^{+} . The potential for reduction of C^{+} will be different from B^{+} and so the wave is not reversible. It is important to test reversibility in a system and a simple method of doing so, is to use cyclic voltammetry.

In cyclic voltammetry, the potential of the working electrode is changed, at a constant rate, backwards and forwards between two limits. These limits are adjusted to lie within the voltammetric range of the solution. A typical cyclic voltammogram for a reversible one electron step is shown in Figure 2, for the Cp_2Fe / Cp_2Fe^{+} couple in MeCN.

For a reversible system it has been shown that

$$E_{red} = E_{1/2} - \frac{0.0285}{n} \quad V \qquad (1)$$

where E_{red} is the potential of the reduction peak, $E_{\frac{1}{2}}$ is the half wave potential and n is the number of electrons transferred. Similarly,

$$E_{ox} = E_{1/2} + \frac{0.0285}{n} \quad V \qquad (2)$$

where E_{ox} is the potential of the oxidation peak.

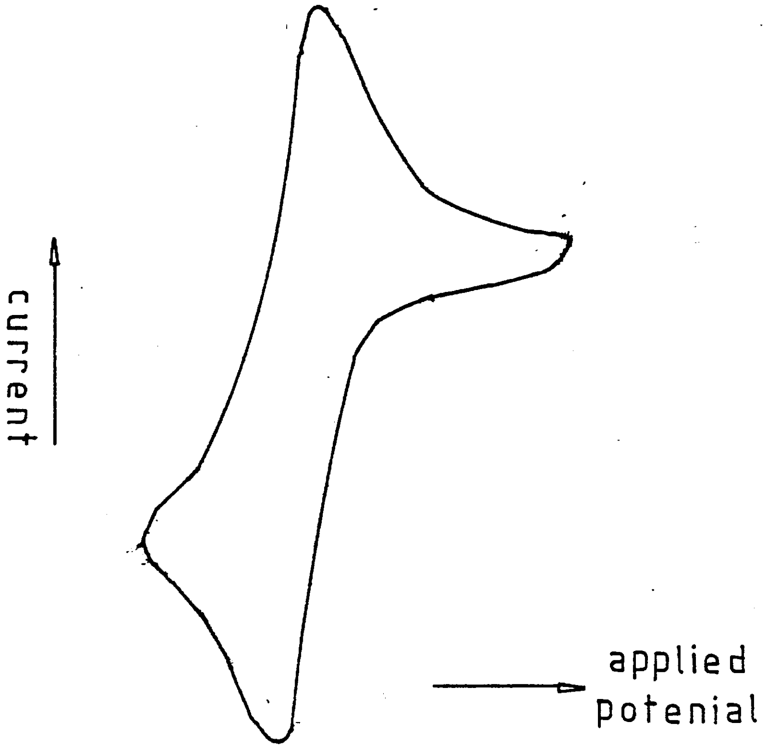


Figure 2. Cyclic Voltammogram of Cp_2Fe .

The separation of the peak potentials for a reversible, one electron transfer is thus, $E_{ox} - E_{red} = 57$ mV . If the redox step is irreversible then the peak-to-peak distance is increased.

If one half of a redox couple is involved in a chemical reaction, for example, the oxidised form, then the size of the reduction peak will be much smaller than that of the oxidation peak, or may be absent altogether. This arises because some (or all) of the oxidised form is used up in the reaction and is not reduced on the return sweep. This situation is exemplified by the behaviour of $Cu\{P(OMe)_3\}_4^+$ in MeCN solution, described in chapter 3.

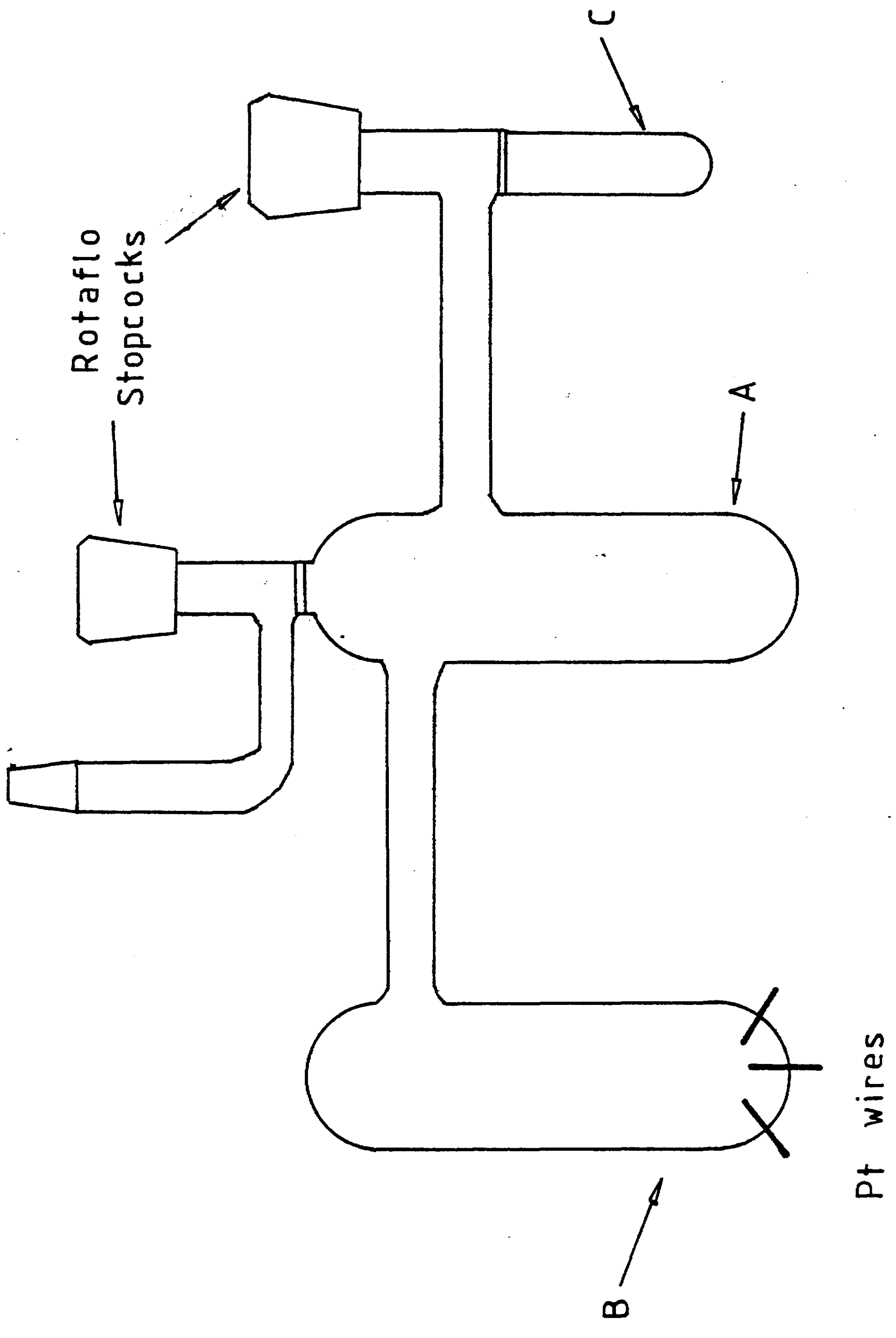
Cyclic voltammetry has become a widely used technique in inorganic chemistry, in recent years, and many workers now use it as an analytical tool in the characterisation of their complexes. The common usage is illustrated by several examples from the very recent literature :- a) concerning the influence of substituted pyridines on the redox reactions of iron porphyrin complexes[169] b) complexes of Ru(II) and Ru(III) with cyclam[170] and c) novel dithiocarbamato complexes of Os(IV) .[171] The ease and rapidity with which measurement of half wave potentials can be made by cyclic voltammetry ensures that the technique will remain popular.

Experimental Method.

The cell which was used in this work is illustrated in Figure 3. It consisted of three compartments. A was used to make up the MeCN solution of the backing electrolyte and the species under investigation. B was the working part of the cell, with three Pt wires fused into the glass, to function as electrodes ; one as a working electrode, one as a reference and the third as an auxiliary electrode. The function of the auxiliary electrode is to remove the need to pass current through the reference electrode. If current does pass through the reference electrode, polarisation occurs and the potential is no longer stationary. This potential drift must be avoided, if the reference is to function reliably. Compartment C was used to store a little of the internal reference material, ferrocene. C remained sealed until the ferrocene was

Figure 3.

Vessel for Cyclic Voltammetry Experiment.



required.

Ferrocene was chosen as the internal reference material because the one electron oxidation to ferricinium ion is well defined and reversible. This is illustrated in Figure 2. A backing electrolyte is required in solution for two reasons. Without it, an electrical migration current (e.m.c.) exists, in addition to the diffusion current. The e.m.c. is suppressed by added electrolyte. The electrolyte serves to keep the resistance of the solution low by acting as a current carrier. In this work, Et_4NBF_4 was used as the backing electrolyte.

The solvent for electrochemical work must be freed of all oxidisible and reducible impurities. Acetonitrile is useful as it can be fairly easily purified by a series of refluxes. The treatment of the MeCN, used in this work, followed a literature method of purification with additional refluxes over CaH_2 and P_2O_5 , to remove moisture from the solution as thoroughly as possible.[3a)] The limiting potentials of acetonitrile for oxidation and reduction are + 2.4 and - 2.7 V respectively vs. Ag / AgCl[121] which, allied to its ability as a solvent, makes it a very good medium for electrochemical work. Each batch of solvent was tested for impurities, prior to experiment, by checking the limiting potentials.

The typical experimental technique was as follows. The flask was evacuated for several hours and then transferred to the glove box. Et_4NBF_4 (0.1g ; 0.46 mmol) was added to limb A, followed by the salt being examined (ca. 3 mg) . Cp_2Fe (ca. 2 mg) was added to compartment C and the stopcock closed. MeCN (5 ml) was then added to limb A and the flask sealed. The solid material was dissolved and the solution tipped into limb B, covering the electrodes. The flask was removed from the glove box, linked to the C.V. instrumentation and the voltammogram recorded. The scan rate, current amplification factor and the voltage scale factor were varied depending upon the species which was being investigated. For example $Cu(bipy)_3(PF_6)_2$ was studied using a scan rate of 20 mV s^{-1} , a current amplification factor of 20 μA V^{-1} and a voltage scale factor of 100 mV cm^{-1} . Once the cyclic voltammogram had been recorded, the ferrocene was added to the solution. The voltammogram was re-recorded to indicate the position of the redox couple with respect to the Cp_2Fe - Cp_2Fe^+ couple. By using only a tiny amount of Cp_2Fe , the effect on the system should be minimal. Thus the redox couples obtained for different complexes, in MeCN solution, vs. the Cp_2Fe - Cp_2Fe^+ couple, may be directly compared.

The apparatus used to obtain the cyclic voltammograms was a model CV-1A (Bioanalytical Systems Inc.), linked to a JJ 'XY' plotter, type PL51.

In the present work, where only relative values of the redox potentials of the various species are required, it is valid to use Cp_2Fe as a reference. For more accurate work, it is necessary to use a standard electrode whose potential is invariant. A Ag - AgCl electrode has been used in MeCN solution and is commercially available. Using such an electrode it will be possible to produce a scale of redox potentials with respect to the reference. It is not valid, however, to relate such a scale to the scale of standard electrode potentials in aqueous solution. It is difficult, then, to obtain a quantitative list of the relative oxidising or reducing properties of a particular ion in a range of solvents.

Earlier work, in MeCN solution, has involved referencing to the aqueous saturated Calomel electrode or a Ag - Ag^+ standard. The Cp_2Fe - Cp_2Fe^+ couple has been measured, with respect to aq. S.C.E., in MeCN solution, as + 0.35 V [172] or + 0.31 V.[173] The moisture content of the reagents used in the early work may have been significant and, as the potential is known to be very sensitive to moisture, the early results will benefit from examination under more stringent conditions.

Appendix II.

Stopped-flow Spectrophotometry.

Introduction.

The study of the kinetics of a reaction has long been a topic of interest, especially as an aid to providing a mechanism for a reaction. The classical method of investigating the rate of a reaction involves the use of so called "static techniques". With "static techniques" the reactants are mixed and the course of the reaction is followed by monitoring the variation in one of the physical properties of the reaction mixture, for example the absorption of visible radiation, using conventional techniques.

Many chemical reactions, however, occur at rates so fast or involve the formation of intermediates which have such a transitory existence, that they cannot be observed by use of conventional instrumentation, and recourse to other techniques is necessary. The most often used methods are those involving 'flow' or 'rapid mixing' where the time taken to mix the reactants is greatly reduced. The reaction is then followed by recording the change in a physical property of the mixture, with time. These techniques are useful for reactions with half lives in the range
$1 \text{ min} \geqslant t_{\frac{1}{2}} \geqslant 10^{-3} \text{ s}$.

To investigate even faster reactions the use of relaxation methods has become popular. These fall into two categories :
a) a system at equilibrium is very rapidly disturbed by a single stimulus, generally by a pressure or a temperature jump, and the rate of re-attainment of equilibrium is measured, and b) the system is continuously disturbed, for example by the application of

ultrasonic waves or by radio frequency signals, as in the n.m.r. experiment. Relaxation techniques can be used to study very fast reactions, $t_{\frac{1}{2}} \leqslant 0.1$ s, and have even been used to investigate reactions at rates up to the diffusion controlled limit of ca. 10^{10} s^{-1} .

In the course of the present work, relatively fast reactions were encountered which were studied using the stopped-flow technique.

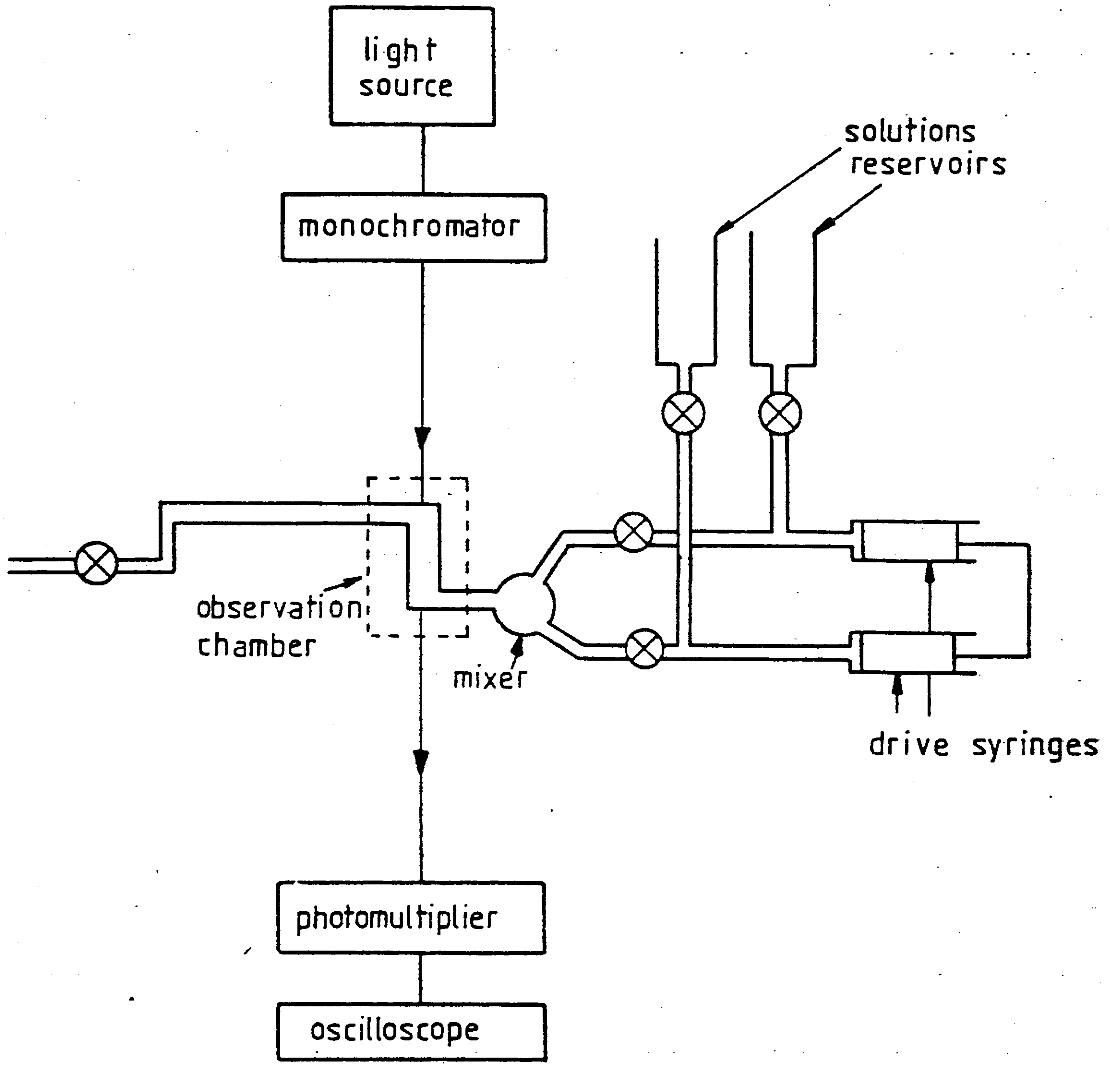
Stopped-flow Apparatus.

A diagrammatic representation of a stopped-flow system is depicted in Figure 1. Stock solutions of the reagents are stored in the reservoir syringes from where they are fed into the drive syringes. The drive syringes are driven, with constant pressure, provided by a cylinder of nitrogen, forcing the solutions to rapidly mix, in the mixing chamber. The resulting solution is then forced into the observation chamber. This consists of a quartz cell through which light from a monochromator is passed. The transmitted light is detected by a photomultiplier which is connected to an oscilloscope. The oscilloscope is triggered when the syringes are fully depressed, that is when flow is stopped, and a trace of the reaction is obtained on the oscilloscope screen. This trace is a direct measurement of the changes in light intensity, due to the absorbance changes occurring in the reaction. The trace is photographed and retained for future measurement.

By carrying out the experiment, point by point, over a range of wavelengths, throughout the region of interest at, for example 10 nm intervals, it is possible to build up a spectrum of the species under investigation. This is accomplished by plotting the

Figure 1.

Schematic Diagram of Stopped-flow Instrument.

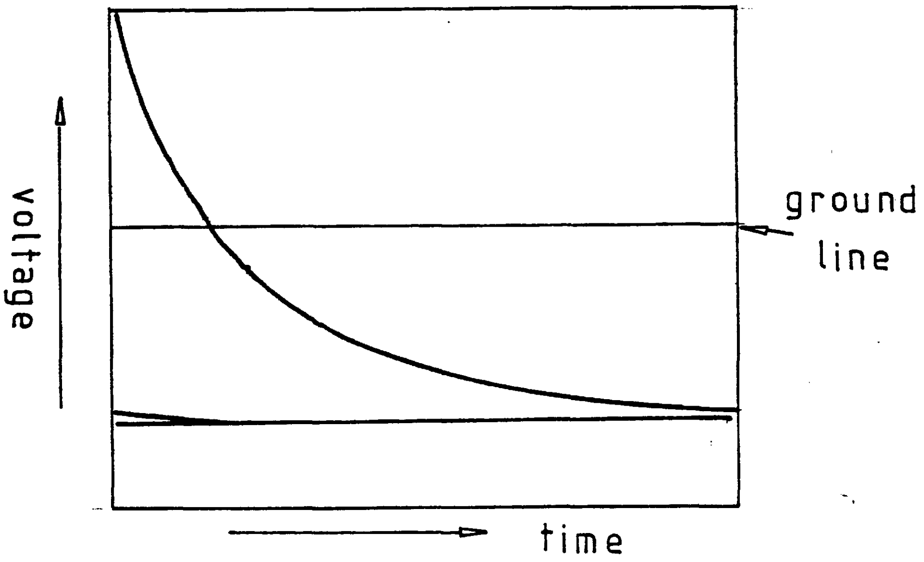


total change in absorbance during the reaction as a function of wavelength. An example of this is shown in Figure 1 of Chapter 3 for the reaction of Cu(II) with $P(OMe)_3$, in MeCN solution. Plotting the spectrum is particularly important in this case as a transient intermediate is involved whose spectrum cannot be obtained in any other way.

The stopped-flow instrument used in this work was adapted to allow it to be flushed with nitrogen gas for several hours prior to a run and the system was additionally well flushed with anhydrous acetonitrile to ensure that conditions are as moisture free as possible.

Calculation of Results.

A typical trace is illustrated in Figure 2.



The trace measures volts of transmitted light, thus a decrease on the trace indicates an increase in absorption of the solution, and vice versa. Figure 2, therefore, shows the formation of a species.

The transmitted light is converted to a voltage which is 'backed-off' , with the aid of a helipot , to yield the ground line. From the value of the 'back-off' and a calibration factor for the instrument , in this case 0.005535 , the absolute voltage of the ground line can be determined. Knowing the gain of the oscilloscope , it is straightforward to correlate any point on the trace with a voltage.

The optical density of a solution is related to the intensity of transmitted light by ,

$$\text{O.D.} \quad = \quad \log \frac{I_0}{I_t} \qquad (1)$$

where I_o is the intensity of light initially and I_t is the intensity of the transmitted light. Since the measured voltages are directly proportional to the intensities of the light , this becomes ,

$$\text{O.D.} \quad = \quad \log \frac{V_0}{V_t} \qquad (2)$$

where V_o is the voltage initially and V_t is the voltage of light transmitted.

Equation 2 can be used to calculate the change in O.D. as a function of time. When V_o is the voltage at time 0 and V_t is the voltage at time t then expression 2 calculates the change in optical density from time 0 to time t . The total optical density of the solution includes any residual absorption from the solvent or any species not taking part in the reaction. It is thus important to obtain the absorption spectra of the reactants in the region to be studied , prior to an experiment , and , especially in the case of a decay , the spectrum of the final products. This allows calculation of the total optical density of the solution.

Using expression 2 it is possible to measure the change in O.D. at intervals from t_o to t_∞ .

The kinetics are followed under pseudo first order conditions, that is where the concentration of the ligand is held in very large excess over the concentration of the metal ion (generally greater than ten fold) . For a first order reaction, $A \xrightarrow{k} B$, the rate expression is given by ,

$$\text{Rate} = -\frac{d[A]}{dt} = k[A] \qquad (3)$$

which, on integration, becomes ,

$$\ln[A]_o - \ln[A]_t = kt \qquad (4)$$

Now, let $[A]_t = [A_o - x]$ where $[x] = [B]$

then (4) becomes ,

$$\ln[A]_o - \ln[A_o - x] = kt \qquad (5)$$

and $[A] = \frac{O.D._A}{\varepsilon_A l}$, so expression (5) becomes ,

$$\ln\left(\frac{O.D._{A_o}}{\varepsilon_A l}\right) - \ln\left(\frac{O.D._{A_o}}{\varepsilon_A l} - \frac{O.D._{B_t}}{\varepsilon_B l}\right) = kt \qquad (6)$$

but $[A]_o = [B]_\infty$ and so $\left(\frac{O.D._{A_o}}{\varepsilon_A l}\right) = \left(\frac{O.D._{B_\infty}}{\varepsilon_B l}\right)$

and expression 6 becomes ,

$$\ln\left(\frac{O.D._{B_\infty}}{\varepsilon_B l}\right) - \ln\left(\frac{O.D._{B_\infty}}{\varepsilon_B l} - \frac{O.D._{B_t}}{\varepsilon_B l}\right) = kt \qquad (7)$$

A plot of $-\ln(O.D._{B_\infty} - O.D._{B_t})$ *vs.* t is linear with a gradient of k .

For the data from the oscilloscope trace, a plot of $-\log(O.D._\infty - O.D._t)$ *vs.* t will be linear with slope $k/2.303$

A representative set of data for the reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$ is given in Table 1 and the plot is illustrated in Figure 3.

Table 1.

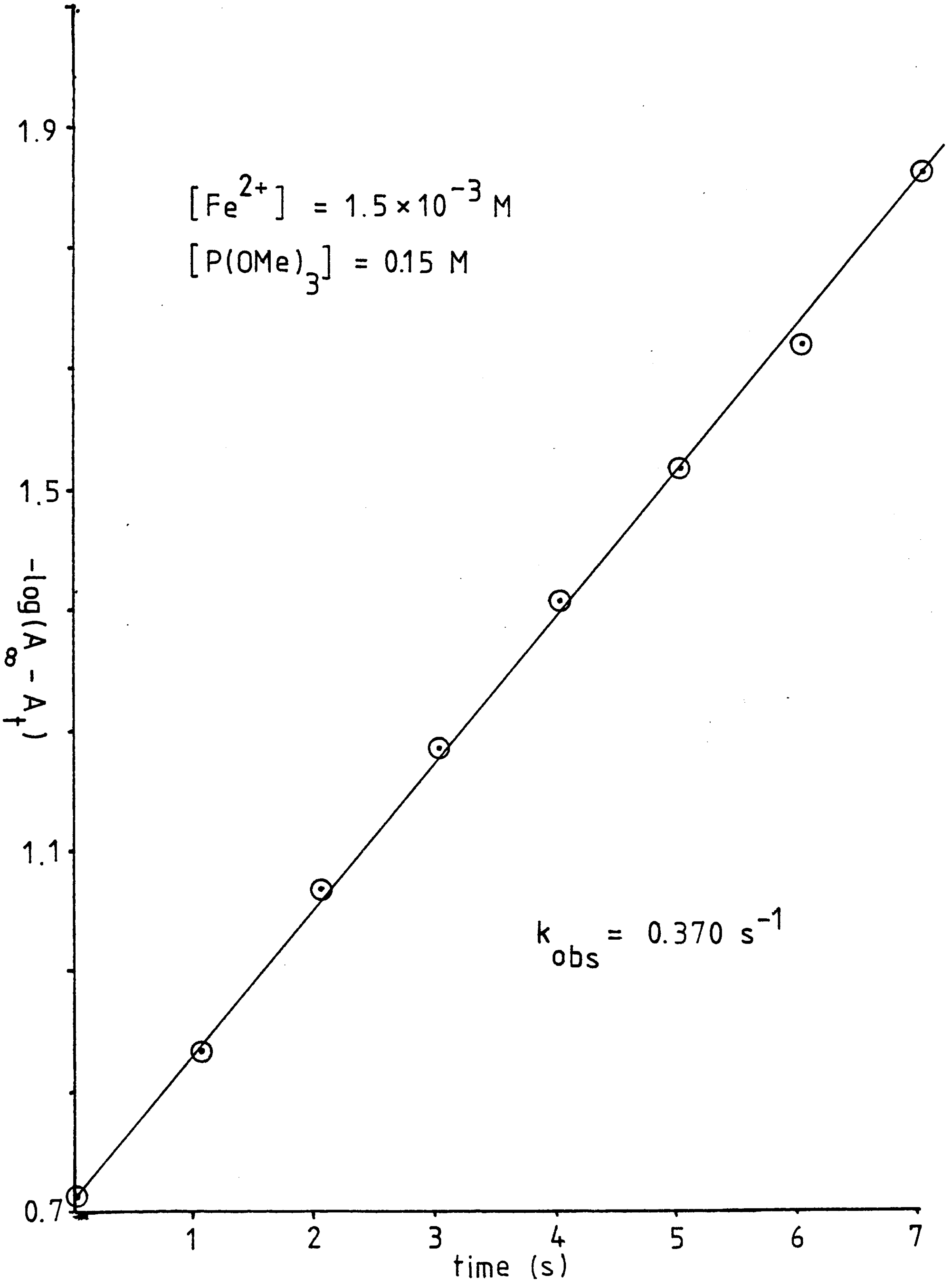
$-\log(O.D._{\infty} - O.D._{t})$ Versus Time for the Reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$ in MeCN.

$[Fe(NCMe)_6^{2+}] = 1.5 \times 10^{-3}$ mol l^{-1}, $[P(OMe)_3] = 0.15$ mol l^{-1}
T = 24.0 ± 0.1 °C.

time (s)	$O.D._t$ (= $\log \frac{V_o}{V_t}$)	$-\log(O.D._{\infty} - O.D._t)$
0	0	0.719
1	0.060	0.883
2	0.104	1.060
3	0.130	1.215
4	0.149	1.377
5	0.161	1.523
6	0.169	1.658
7	0.177	1.854
∞	0.191	—

Figure 3.

Plot of $-\log(A_\infty - A_t)$ vs. Time for the Reaction of $Fe(NCMe)_6^{2+}$ with $P(OMe)_3$.



To reduce the work involved in calculating the results, the various computational stages are included in a simple computer program. The program includes a least squares determination for fitting the straight line.[174]

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