

CATIONIC ARYLAZO COMPLEXES OF IRON

by

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ABSTRACT

A series of p-substituted diazonium salts have been reacted with tricarbonyl bis (triphenylphosphine) iron (0). The salts so obtained have been characterised by various spectroscopic and physical means. Most techniques indicate the salts to contain a five-coordinate cation of general formula $[(PPh_3)_2(CO)_2FeNNAr]^+$, although the formulation does not at present appear to be consistent with the observed Mössbauer and magnetic data. Possible reasons for these discrepancies, and the merits of alternative formulations are discussed. The infrared spectra of these salts show an unusually intense absorption band $\nu(N=N)$ at a frequency (1710 cm^{-1}) which is high by comparison with other arylazo compounds but similar to that observed for some complexes containing a terminal dinitrogen ligand.

Concurrently, it was found that p- $Et_2NC_6H_4N_2^+BF_4^-$ reacted differently from the other diazonium salts to give a product containing no iron, that has been shown to be $[Et_2NC_6H_4-N=N-PPh_3]^+BF_4^-$, a salt containing the new phosphodiazonium ion. Subsequent research has shown that the compound is formed by the reaction of p- $Et_2NC_6H_4N_2^+BF_4^-$ with triphenylphosphine and that other Lewis bases, eg., SPh_2 may react similarly.

To Nuala

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CHAPTER 1
INTRODUCTION

This thesis describes work in the field of investigation of the interaction of aryldiazonium ions with transition metal complexes. The research was attempted for two main reasons. Firstly, the known examples of stable cationic species which co-ordinate to transition metals are relatively few. One example is the nitrosonium cation, with which some nitrosyl complexes have been synthesised¹⁻³, although the majority of nitrosyl complexes have been synthesised by other techniques. The electronic structure of the nitrosonium cation is obviously very similar to the diazo part of the diazonium cation, and hence it seemed feasible that the latter might also be capable of co-ordination, in a fashion similar to that of NO^+ . Indeed, a limited number of examples were already known at the start of this work⁴⁻⁹.

Secondly, at present much interest is being shown in the biological system nitrogen reductase. This enzyme reduces dinitrogen to ammonia, and the transition metals iron and molybdenum are crucial in the fixing and reducing of dinitrogen by, as yet, an unresolved mechanism. Naturally there is much current activity in biochemical circles to determine how these metals are implicated in the mechanism. At the same time, inorganic chemists have been synthesising a wide variety of metal-dinitrogen complexes, in which N_2 co-ordinates either terminally or as a bridge structure (Figs. 1-I and 1-II respectively), and investigating the ease with which these may

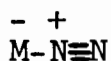


Fig. 1-I

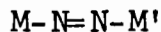


Fig. 1-II

be protonated or reduced to ammonia or intermediates. Until recently little success was accomplished in this area due to the complete inertness of these dinitrogen complexes towards mild reducing agents. Therefore, as an alternative model system it seemed to be worthwhile to attempt to synthesise and examine a series of iron complexes in which co-ordinated N_2 is replaced by co-ordinated diazonium ion (Fig. 1-III). Formally this can be

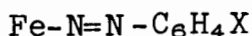


Fig. 1-III

viewed as the replacement of M' in Fig. 1-II with a substituted aryl ring. If X is varied in Fig. 1-III it is possible to vary the electronic structure within the diazo group and at the iron atom, which is impossible in the terminal dinitrogen complexes and less easy in the bridging complexes. Consequently it might be possible to produce, by obtaining the correct electronic circumstances, a system which facilitated reduction of the $\text{N}=\text{N}$ bond.

This thesis describes the successful synthesis and characterisation of such a series of arylazo complexes with the general formula $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2\text{NNC}_6\text{H}_4\text{X}]^+ \text{Y}^-$. Since Johnson¹⁰ had already reported the analogous nitrosyl complex $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2\text{NO}]^+ \text{Y}^-$, the feasibility of preparing the series appeared high. Indeed

the synthesis went according to plan, except in one case ($X = p\text{-NEt}_2$), where an entirely different compound was synthesised. However, none of the complexes in the series could be mildly reduced and hence the aim of the study was not completely achieved. Nevertheless, the results obtained are of interest and tentative conclusions are drawn with reference to other related complexes.

As the work described in this thesis bears indirectly on the question concerning the role of iron in biological nitrogen fixation, a brief review of the biological system and of some of the models which other workers have utilised to attempt to simulate the natural case, follows.

The Problem of Nitrogen Fixation

Nitrogenase (hereafter abbreviated as N_2 ase) is an enzyme system found in certain bacteria, some of which are free living and others symbiotic. Although the latter are biologically the more important it is the former that have been studied in more detail since they can be extracted in a pure form far more easily. The role of N_2 ase in nature is to catalyse the reduction of di-nitrogen to ammonia, although, unlike most enzymes, it is not specific to this substrate. For instance, all of the following are also reduced: - organic nitriles and isonitriles, the cyanide ion, nitrous oxide, acetylene and the azide ion. The ability of this enzyme to reduce unsaturated sites appears to be as follows: -

1. It can reduce $N=N$, $N=C$ or terminal $C\equiv CH$. It will not, however, reduce $C\equiv O$.

2. It will cleave $N\equiv N$, $N\equiv C$ or $N=O$ (in N_2O), but not $C\equiv C$ bonds.
3. $C=C$ is reduced only if conjugated with CN or an allylic system.
4. Rates are affected markedly by steric considerations, and hence short, linear, unbranched molecules are reduced far more quickly than their larger or branched counterparts.

Since the natural product of this type of enzyme is ammonia, there are possibilities of utilising this natural system in two ways: chemically and biologically. If one could, for example, by mutation, impart nitrogen fixing ability to common soil bacteria (e.g. E. coli) then the widespread application of synthetic nitrogenous fertilisers would not be as necessary, if necessary at all: this is the biological approach. The chemical approach would be to use the enzyme, or, more likely, a model thereof, as a catalyst in a new process to replace the Haber process. The Haber process requires, for the optimum yield-rate ratio, a temperature of $450^\circ C$ and a pressure of 100 atmospheres. With these conditions one pass of the starting gases (H_2 and N_2) gives a 7% yield. (The remaining gases are of course recycled.) Consequently if a process is devised using a catalyst comparable to the enzyme both the temperature and the pressure requirements would be reduced decisively, if not completely, down to ambient conditions. The yield-rate ratio would almost certainly increase at the same time. The cost saving would, needless to say, be immense. Therefore, if the mechanism and structure of N_2ase can

be determined the use of such knowledge could be considerable.

Structure of Nitrogenase

Unfortunately, as yet, the exact structure of any of these enzymes is not known. However, N₂ases from Azotobacter vinelandii have been crystallised in what appears to be high purity, and can be separated into two fractions. The one with the larger molecular weight, which is called by a variety of names including azofermo, has a molecular weight of between 2 and 3×10^5 . It has one, or less probably two, atoms of molybdenum and about 15 atoms of iron per atom of molybdenum. H₂S is liberated on the addition of acid in the ratio 1 mole per iron atom. The smaller fraction, called azofer, has a molecular weight of ca 7×10^4 and contains two atoms of iron and two ions of "labile sulphide". This, in conjunction with a high sulphur content, has resulted in the suggestion that the metals are in a "sulphur environment".

Neither the azofermo nor the azofer show nitrogenase action on their own, but a mixture is immediately active, even if the two fractions come from different types of bacteria, providing they are sufficiently closely related. If the bacteria chosen for the two fractions become too unrelated to each other then the activity of the enzyme drops off markedly.

As yet the environment of the metals has not been unambiguously assigned, so one can only speculate with reference to other iron-sulphur proteins. The rubredoxin from Clostridium pasteurianum has been subjected to X-ray diffraction by Jensen et al.¹¹ This showed that the iron atom is tetrahedrally sur-

rounded by four sulphur atoms, which are part of cysteine residues. Other rubredoxins have had their amino acid sequences determined¹²⁻¹⁴ and this shows that the four cysteines are found in two pairs, each pair having two other amino acid residues in between the two cysteine residues, i.e. cys-X-Y-cys. With ferredoxins, however, only two of the five cysteines are in such a pair. This pair is probably bonded to the iron atom. The other three cysteine residues are randomly situated along the protein chain, of which some or all may be bonded to the iron atom. It should be remembered that Jensen¹⁵ has shown that ferredoxins in nature have more than one iron atom, indeed they have clusters of four iron atoms which share alternate corners of a cube with four sulphur atoms. The azofer has been shown to have similar properties to other iron-sulphur proteins and its two iron atoms have been found not to be equivalent; there is no e.p.r. signal unless the protein is either oxidised or reduced. This would suggest that the iron atoms are in an even oxidation state, either low-spin Fe^{II} or Fe^{O} depending on the co-ordination of the iron. Although as yet the structure of a N_2 ase is uncertain, within a few years this will undoubtedly be elucidated.

Postulated Mechanisms and Roles of Fe and Mo

Three metals are essential for bacterial nitrogen-fixing activity, namely, iron, molybdenum and magnesium. However it has been found that vanadium can be substituted for molybdenum, though accompanied by a decrease in efficiency¹³. The amount of molybdenum needed for the enzyme to function is minute

(ca 0.004 ppm). Iron is also needed only in a trace amount. N_2 ase is, however, compared with other enzymes, quite inefficient in terms of energy, more carbohydrate being required than might be expected. For instance, the most efficient of the laboratory systems fixes only about 15 mg of nitrogen for every gram of glucose consumed. In natural conditions N_2 ases may be up to three times as efficient, but nonetheless by this criterion they are somewhat inefficient. Also, N_2 ase requires considerable amounts of adenosine triphosphate (ATP) to function. Approximately 15 moles of ATP are hydrolysed in reducing 1 mole of dinitrogen to 2 moles of ammonia. This is equal to about 105 kcal/mole N_2 . If dinitrogen and dihydrogen were to react to equilibrium at atmospheric pressure and room temperature the reaction would be exothermic with close to 100% yield of ammonia: therefore, the high energy requirement is puzzling.

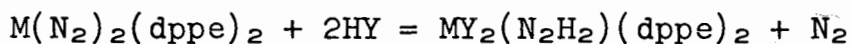
In the natural system there is no evidence for the intermediates hydroxylamine, hyponitrous acid, di-imine, hydrazine or any other thermodynamically possible intermediate. So it appears that the dinitrogen is held by the enzyme throughout the reduction process until ammonia is liberated. This is supported by the fact that the enzyme is poisoned by hydrazine, which it fails to reduce.

When N_2 ase is treated with $Na_2S_2O_4$, dihydrogen gas is evolved as long as there is ATP available. Although H_2 is itself an inhibitor of N_2 fixation, it can act as an electron donor to ferredoxin, which in turn can function as an electron donor in

support of N_2 fixation by anaerobic organisms. Hydrogenase, which in certain bacteria is found in conjunction with nitrogenase, contains molybdenum. Hence it has been suggested that an iron atom provides the binding site and the molybdenum atom the reducing site, with an electron-transfer chain through more iron atoms.

Whether the dinitrogen is reduced via nitride, terminal dinitrogen or bridging dinitrogen coordination during the reaction is not yet known. All three types of complex are known in transition metal chemistry. N_2 is bound terminally to Fe^{II} in the complexes $FeH_2(N_2)(PPh_2Et)_3$ and $[FeH(N_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$. Terminal dinitrogen complexes of molybdenum also exist, eg., $Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2$

Chatt¹⁶ has put forward two schemes for the reduction mechanism, one via a nitride (see Fig. 1-IV) and one via di-imine and hydrazine formation from a terminal dinitrogen complex (Fig. 1-V). Chatt has gained evidence for the mechanism shown in Fig. 1-IV from the observation that certain tungsten and molybdenum dinitrogen complexes can be reduced by adding a hydrogen halide¹⁷, viz: -



Here dppe is an abbreviation for $Ph_2PCH_2CH_2PPh_2$.

This reaction occurs at $0^\circ C$ in tetrahydrofuran. The complexes are reduced no further, however, under these conditions.

Hardy¹⁸, meanwhile, has suggested a mechanism involving a bridge intermediate (Fig. 1-VI) which assumes that the two metals are linked by a sulphur bridge.

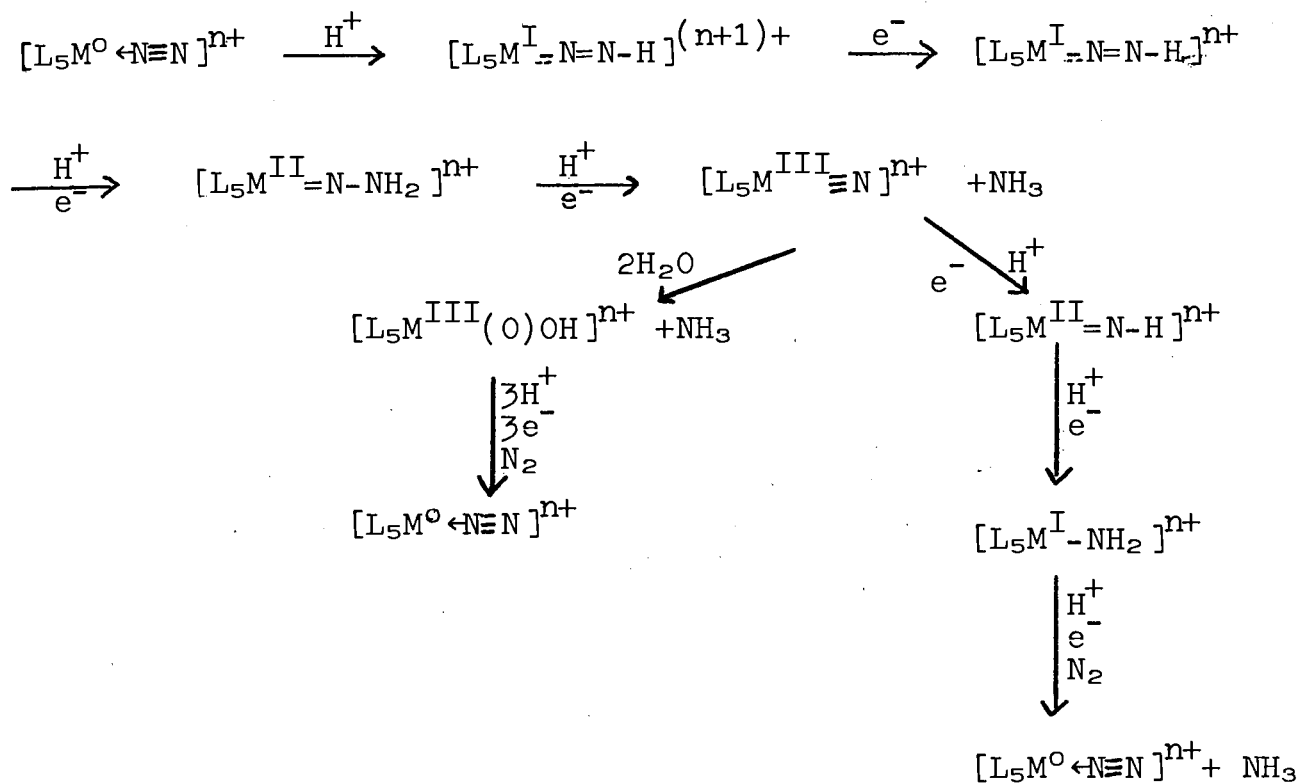


Fig. 1-IV

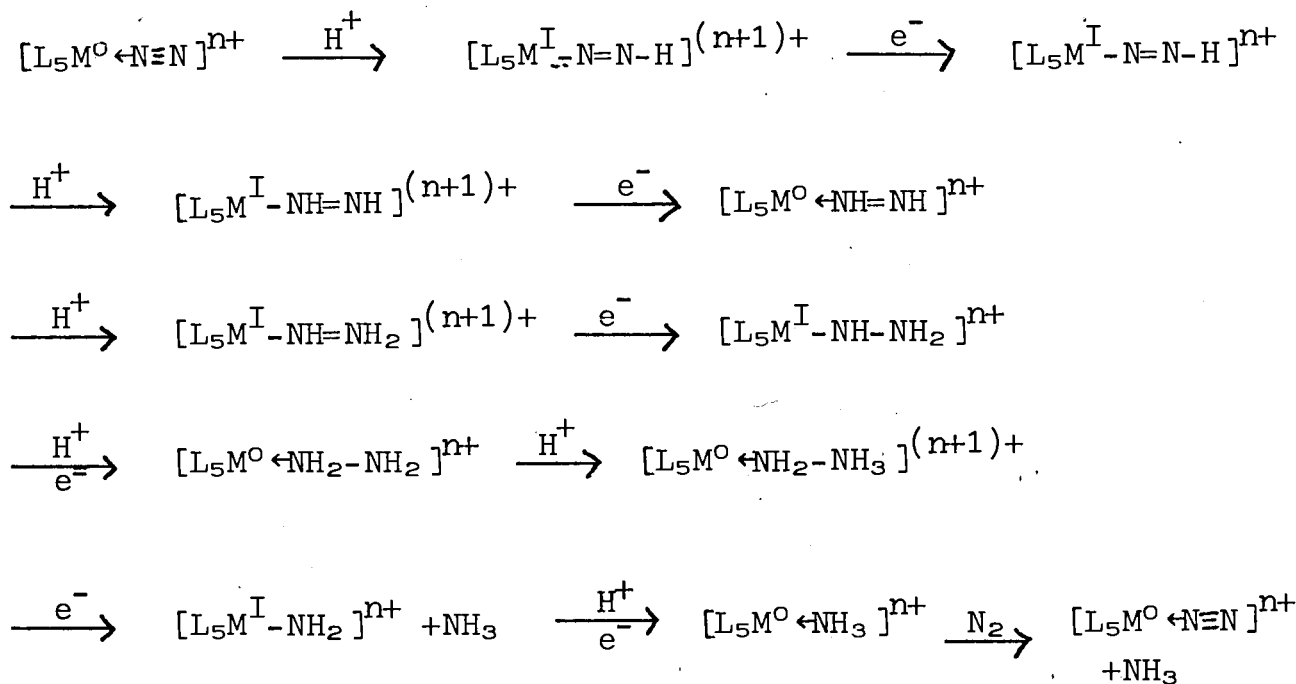


Fig 1-V

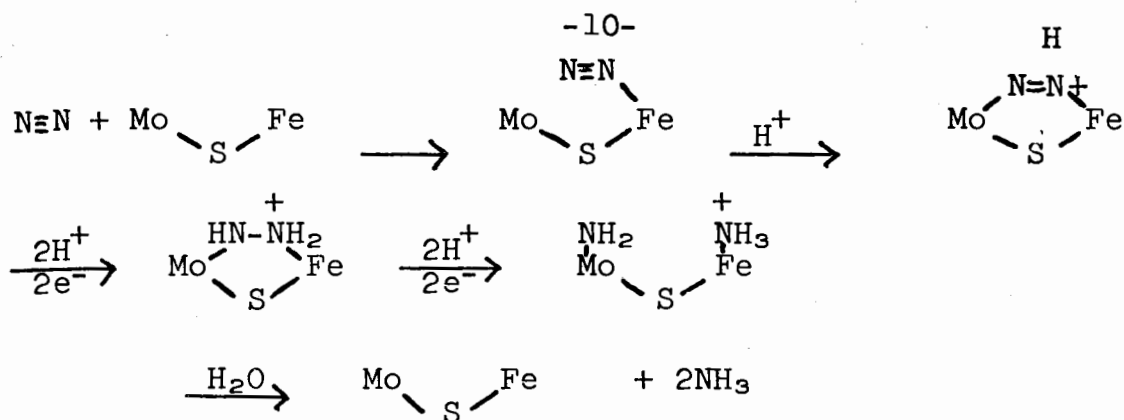


Fig. 1-VI

A bridging dinitrogen type of mechanism has also been considered by Chatt¹⁸; this will be dealt with later in connection with model systems.

This has been a necessarily brief outline, and more details of the chemical and biological aspects of nitrogen fixation are to be found in several recent reviews^{16, 18-22}.

Model Systems

Chemical models for biological reduction of dinitrogen range from some which are quite similar to the natural system to those which seem to bear little similarity. For instance Schrauzer et al.²³ have reported that a mixture of organic thiols, sodium molybdate and ferrous sulphate in the presence of a reducing agent, e.g. Na₂S₂O₄ or NaBH₄ gives substantial reduction of those dinitrogen analogues which are reduced by the natural system. Thus acetylene is reduced this way, but dinitrogen is only reduced in trace amounts at 2000 p.s.i. pressure. Many observed conditions were similar at those of the natural system: without molybdenum no ammonia was produced; other transition

metals such as Cu, Ni or Pd would not substitute for Fe. However, on the other side it was found that carbon monoxide did not act as an inhibitor. Using the same method, but with cysteine as the reducing agent, Hill and Richards²⁴ managed to reduce dinitrogen, at one atmosphere pressure, in trace amounts to ammonia.

Another model with close analogies to the natural system is that discovered by Shilov²⁵, in which dinitrogen is reduced to hydrazine. Here, the essential catalyst to produce hydrazine is a reduced molybdenum or vanadium salt in the presence of a substantial proportion of magnesium ions. This method produces hydrazine, but no NH₃, at ambient conditions. The yield per molybdenum atom is, however, increased a hundred fold if the temperature is elevated to between 50 and 100° C together with a pressure of 50 to 150 atmospheres. The reductant used is Ti^{III}, although V^{II} or Cr^{II} can also be utilised. This system is poisoned by carbon monoxide; also, as in the natural case, Mg is needed, possibly to keep the Ti^{III} ions apart as in the mechanism postulated by Shilov (Fig. 1-VII).

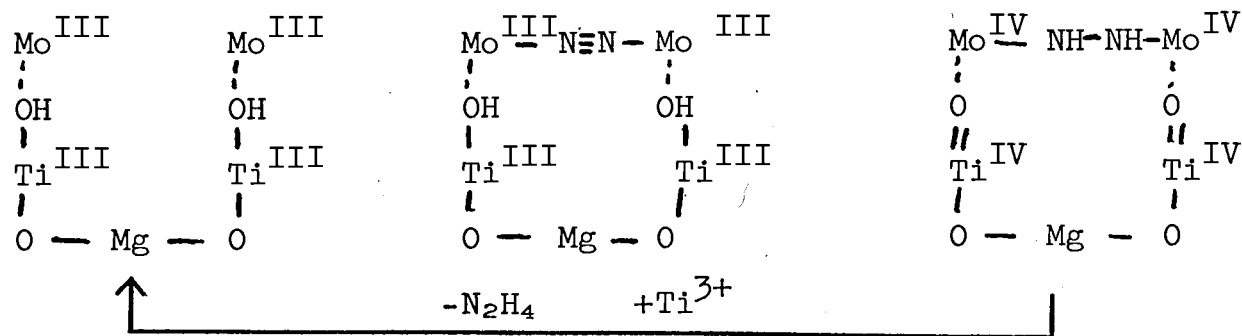
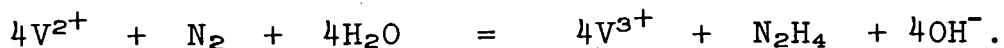


Fig. 1-VII

Although this parallels the natural system in some respects its capacity is at best 1% of that found in nature. If vanadium (II) is substituted for both the molybdenum and titanium then at high pH's rapid reduction occurs according to the equation: -



This is, of course, getting further away from the natural system. Van Tamelen²⁶⁻²⁸ has also produced some model systems which depend on titanium as a catalyst.

Chatt and co-workers have prepared a number of complexes in which dinitrogen bridges between rhenium and a second metal or non-metal, and have deduced a possible nitrogen fixation mechanism from their results. When such a bridge is formed the $N \equiv N$ bond can be weakened to greater or smaller amounts depending on the electron structures of the two metals, in accordance with an electron "push-pull" mechanism. Table 1-I shows the ν_{N_2} observed when $trans-[ReCl(N_2)(PMe_2Ph)_4]$ is reacted with various Lewis acids to produce the bridged complexes. From Table 1-I it should be noted that the Lewis acids which have empty d-orbitals weaken the N-N bond more than those with partially filled (i.e. d^3 or greater) or no available d-orbitals: this can be attributed to the population of the π -molecular orbitals shown in Fig. 1-VIII. Here, the $1e$ level is filled by four π -electrons from the N_2 molecule and the $2e$ and $1b_2$ levels by six 5d-electrons from the rhenium (I) atom. Thus any d electrons possessed by the second metal will start filling the $2b_2$ and $3e$ levels, which are seen to be bonding in the N-N region. This

TABLE 1-I

ADDUCTS OF VARIOUS LEWIS ACIDS WITH TRANS-[ReCl(N₂)(PMe₂Ph)₄]

Lewis Acid	ν_{N_2} cm ⁻¹
None	1925
AlMe ₃	1894
Pt ₂ Cl ₄ (PEt ₃) ₂	1890
CoCl ₂ (THF) _{1.5}	1855
TiCl ₃ (THF) ₃	1805
MoCl ₄ (Et ₂ O) ₂	1795 or 1680
PF ₅	1640

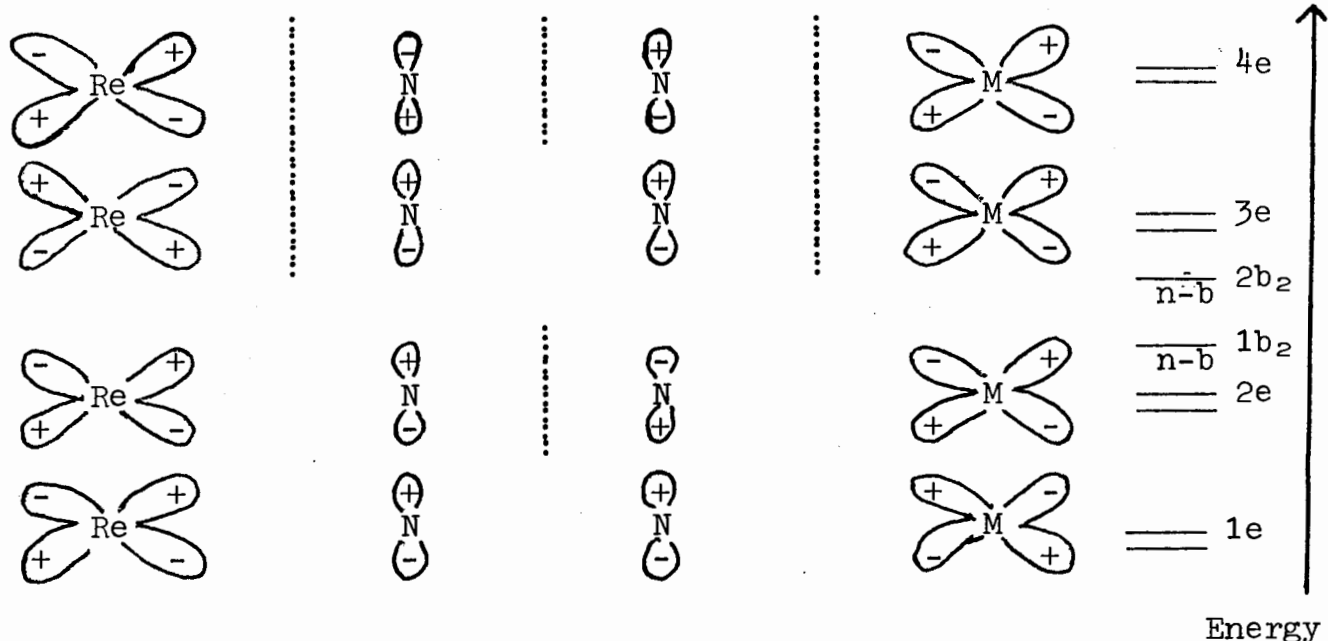
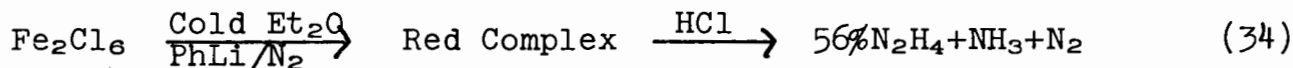
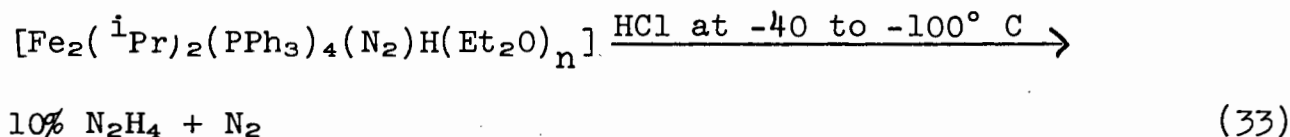
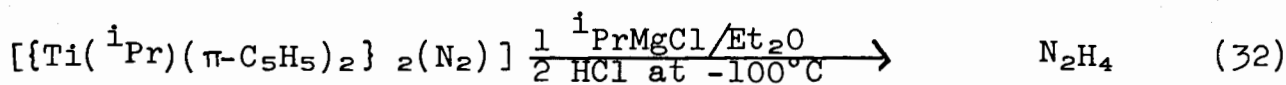


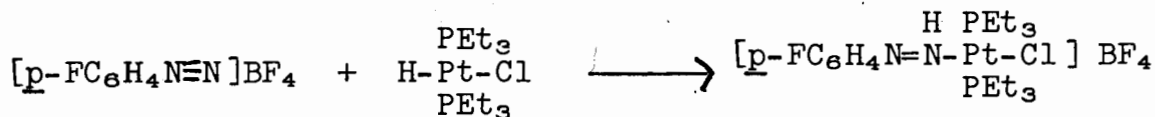
Fig. 1-VIII

also compensates for any electron withdrawal from the N-N σ -system or the $1e$ π -system, which of course is the main factor in the d^0 and d^2 cases. Thus, a decrease in N-N bond order is anticipated in coordination to a d^0 - d^2 element, but a successive re-strengthening of N-N is expected as the number of d electrons of the Lewis acid is increased further up to d^6 . Further information on dinitrogen complexes can be read in many good reviews 18,19,29-31.

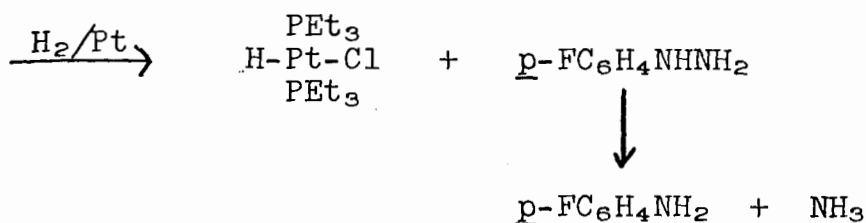
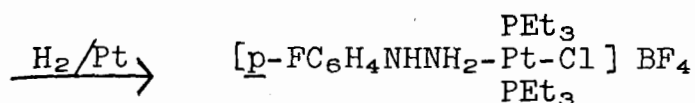
It has now been shown that some stable dinitrogen complexes can be reduced ³²⁻³⁴, as in the following schemes: -



The final model system to be discussed is that reported by Parshall^{35,36}. This investigation showed that it was possible to reduce diazonium salts with a platinum complex as a catalyst. The reaction scheme is as follows: -



(I)



This reaction occurs at 1 atm. pressure and 25° C. It was suggested by Parshall that perhaps N₂ase had a similar mechanism where some form of activated dinitrogen molecule inserted into either an iron-hydride or a molybdenum-hydride bond. Indeed he finds quite a number of similarities between his model system and the natural enzyme. Despite the fact that quite a vigorous catalyst is used in this scheme, it does suggest that further study of arylazo complexes might be one way of obtaining further insight into the factors influencing the question of nitrogen fixation.

Further Arylazo Complexes

Further study of arylazo-transition metal complexes of iridium³⁷ and rhodium^{38,39} has been carried out by D. Sutton's group. An extension of this study to arylazo complexes of iron seemed worthwhile for the following reasons: -

1) Several arylazo complexes have been prepared with relative ease.

2) Parshall had shown that, without undue difficulty, such complexes might be reduced with aid of a catalyst.

3) Despite the obvious chemical difference between dinitrogen and a diazonium salt, any arylazo complex that might be formed would have analogies with the "compounds" suggested by Hardy and Chatt in their postulated bridging mechanisms (Figs. 1-VI and I-VII), the main difference being that the second metal is now replaced by an aryl ring.

4) By varying the substituents on the aryl ring of the original diazonium salt the electronic environment of the metal could be changed. This would then throw light on the "push-pull" model.

5) Since the natural system incorporates iron, an iron complex should be studied.

6) Since Sacco and Rossi⁴⁰ had found similarities between N_2ase and $CoH(N_2)(PPh_3)_3$, it appeared that the presence of PPh_3 ligands need not be detrimental to the model.

7) Although the enzyme is able to reduce dinitrogen, it can also reduce many analogous compounds; therefore the use of diazonium salts is not totally irrelevant to the enzyme mechanism.

The complexes prepared and investigated in this work are described in the following chapters.

CHAPTER 2

ARYLAZO CATIONS OF IRON

Introduction

Since Johnson had prepared and investigated the analogous series of complexes $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2\text{NO}]^+ \text{Y}^-$, the synthesis of $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2\text{NNC}_6\text{H}_4\text{X}]^+ \text{Y}^-$ (I) seemed a viable possibility. Johnson had prepared certain of his nitrosyl complexes by reacting $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$ with the nitrosonium salt. Therefore, by replacing the nitrosonium salt by diazonium salt it was hoped that a similar reaction would occur, and indeed, the observed reaction appeared similar. Furthermore, the analysis of the products for $\text{X} = \text{H}, \text{NO}_2, \text{F}, \text{Cl}, \text{Br}, \text{OCH}_3,$ and OH , together with their properties were found to be consistent with the expected product (I), as detailed below. Other possible formulations are also discussed. In this chapter the following features of the compounds, which were investigated, are discussed: -

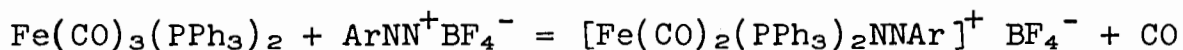
- (1) The stereochemistry and co-ordination of the cation.
- (2) The various components of the complexes, especially the N-N entity, which were characterised by using several physical methods.
- (3) The observed trends in the properties of the complexes formed by varying the substituents on the aryl ring of the original diazonium salt.
- (4) The chemical properties and reactions of the complexes, particularly with reference to reduction.

In all, seven arylazo iron cations of type (I) were prepared and fully investigated. These seven all had Y^- as BF_4^- and

X = p-NO₂, -H, -F, -Cl, -Br, -OCH₃, -OH. The only substituent which did not yield compounds of type (I) was p-NEt₂. A completely different reaction was found to occur, giving a product containing no iron. This is discussed in Chapter 3.

Preparation

An acetone solution of the diazonium salt was added dropwise to a benzene solution of tricarbonylbis(triphenylphosphine)-iron(0), in an inert, N₂, atmosphere. Gas evolution was observed and at the same time the colour changed from yellow to orange. Further investigation, using a quantitative volumetric gas analysis system similar to a Toëpler pump, showed that one mole of CO was evolved per mole of Fe(CO)₃(PPh₃)₂ consumed. The CO was analysed by high resolution mass spectroscopy. This evidence supports a reaction similar to that found by Johnson using the nitrosyl salts, i.e.: -



The compounds are orange-brown in colour, stable in air, and soluble in polar organic solvents such as alcohols, ketones, acetonitrile, nitromethane, dichloromethane and chloroform. They are, however, insoluble in water and common non-polar solvents such as benzene, ether and toluene.

Stereochemistry and Co-ordination

Empirical formulae were established by elemental analysis (see Table 2-I). I.r. spectra included the bands characteristic of BF₄⁻. The results of molecular weight, electrical

TABLE 2-I

ANALYTICAL DATA FOR COMPLEXES (I)

p-substituent	Colour	%age Found				%age Calculated				Yield				
		C	H	N	O	Br	Fe*	C	H		N	O	Br	Fe
H	Brown	56.08	4.00	2.87				63.6	4.23	3.38			6.78	30%
NO ₂	Orange	60.27	3.86	4.84			6.23	60.4	3.89	4.82			6.39	45%
	-brown													
OCH ₃	Brown	62.78	4.20	3.22			5.94	62.9	4.31	3.26			6.52	35%
F	Orange	62.38	4.15	3.50			6.84	62.3	4.02	3.31			6.60	50%
	-brown													
Cl	Orange	61.04	4.09	3.08			6.60	61.2	3.94	3.25			6.47	60%
	-brown													
Br	Orange	58.28	3.89	3.11		8.58	6.54	58.3	3.75	3.08		8.82	6.16	70%
	-brown													
OH	Yellow	62.34	4.31	3.19			6.40	62.5	4.15	3.32			6.62	35%
	-brown													
Br I ⁻ †	Orange					3.61						3.39		

* From Atomic Absorption measurements.

† Obtained from the tetrafluoroborate salt + NaI.

conductivity and further spectroscopic studies described below identified the molecular formulae as (I).

Although it was considered likely that the products were salts containing the pentaco-ordinate complex cation shown in Fig. 2-I (where simple replacement of an equatorial carbonyl group by ArNN^+ has occurred), other pentaco-ordinate isomers involving both trigonal bipyramidal (2-II to 2-V) and square based pyramidal (2-VI to 2-XI) geometry warranted consideration. Furthermore, more complex structures such as those involving o-metallation of the arylazo (2-XII) or triphenylphosphine (2-XIII) ligands, or polynuclear arrangements such as (2-XIV) or (2-XV) could not be ignored at this stage. Considerable physical data were therefore accumulated in order to establish the correct molecular formula and stereochemistry.

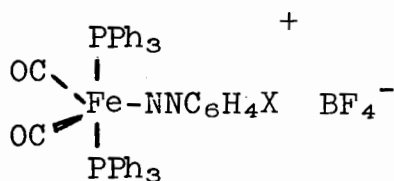


Fig 2-I

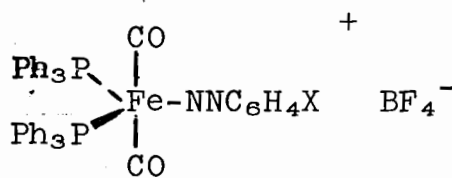


Fig 2-II

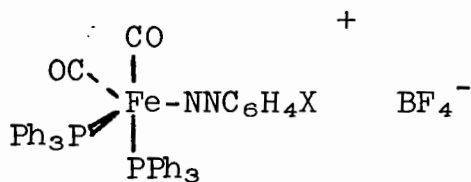


Fig 2-III

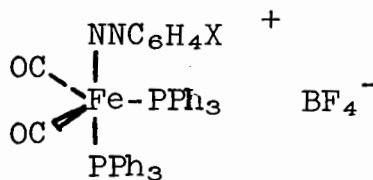


Fig 2-IV

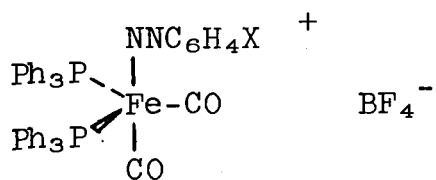


Fig 2-V

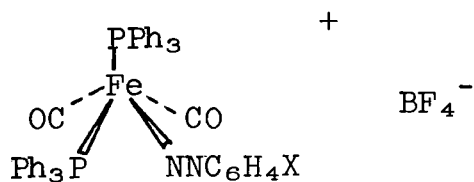


Fig 2-VI

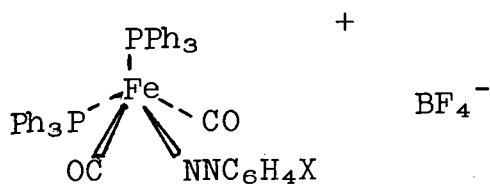


Fig 2-VII

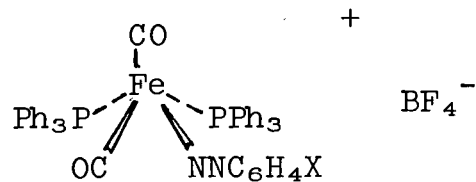


Fig 2-VIII

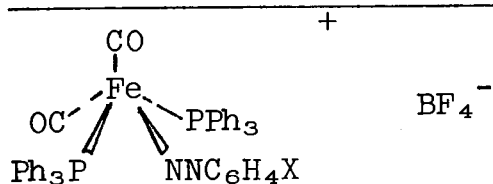


Fig 2-IX

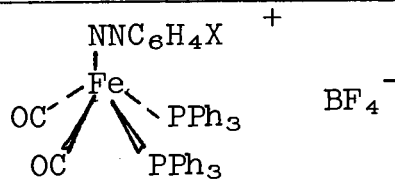


Fig 2-X

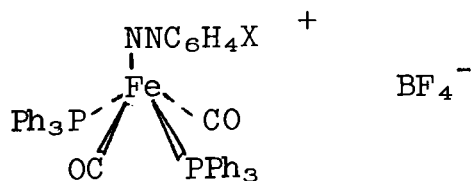


Fig 2-XI

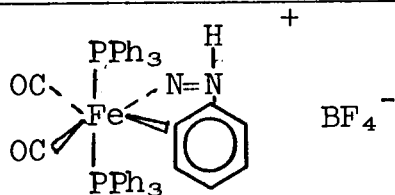


Fig 2-XII

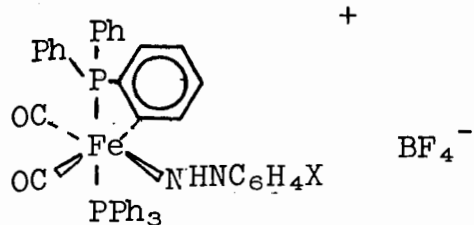


Fig 2-XIII

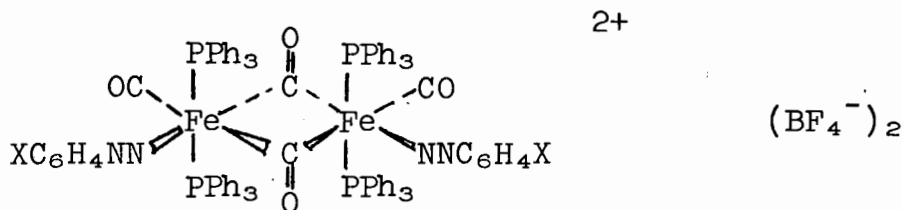


Fig 2-XIV

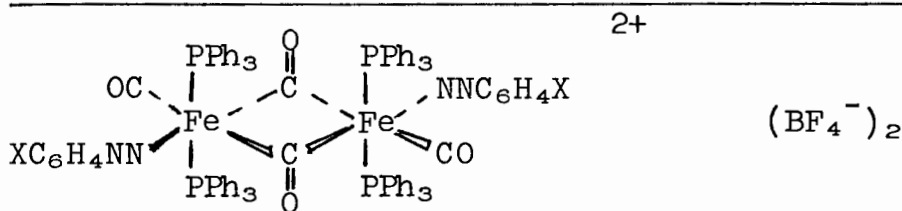


Fig 2-XV

An absorption band of some intensity at ca 1720 cm^{-1} suggested that a bridging carbonyl system might indeed be present. However, this band was found to be shifted when the complex was prepared using the ^{15}N isotope, and hence was assigned to the N=N stretch, as is discussed in more detail below. Further evidence for the lack of bridging carbonyls was furnished by the fact that pyridine did not cleave the molecule. Consequently, this extra fact and the lack of a band corresponding to a bridging carbonyl stretch ruled out the type of structure represented in Figs 2-XIV and

2-XV. Indeed, this conclusion was further supported by electroconductivity measurements and a molecular weight determination, which is also discussed more fully below.

N.m.r. spectroscopy was utilised to help resolve which of the remaining possibilities was in fact the correct structure. It was hoped that information would arise from the spectra obtainable both from the ^1H nuclei present and the ^{31}P nuclei. Although the complexes were investigated in d_6 -acetone and d_1 -chloroform, neither solvent system was concentrated enough to give rise to a discernable ^{31}P n.m.r. spectrum. Fortunately, due to their greater susceptibility, the ^1H nuclei produced spectra. The spectra obtained from a selection of the compounds were virtually identical; the best resolved being the p-Br derivative (Diag. 2-I), which showed two principal absorptions due to aryl protons. One was an apparent triple peak centred at τ 2.38 and the other an apparent singlet at τ 2.62. The latter peak had small shoulders, which would suggest the possibility of an overlapping of peaks. The integration of the two peaks was ca 64:27, which for 34 protons corresponds with a ratio of 24:10. Interpretation of these results is, at best, speculative and no evidence on stereochemistry is revealed.

The analogue $[\text{Fe}(\text{CO})_2(\text{PPh}_2\text{Me})_2\text{NNC}_6\text{H}_4\text{Cl}]^+ \text{BF}_4^-$ was prepared and the ^1H n.m.r. investigated in d_6 -acetone in order to utilise the expected virtual coupling between the P-atoms and the CH_3 resonances to gain stereochemical information. The spectrum of the methyl protons (Diag. 2-II) appears as a 1:1 doublet of

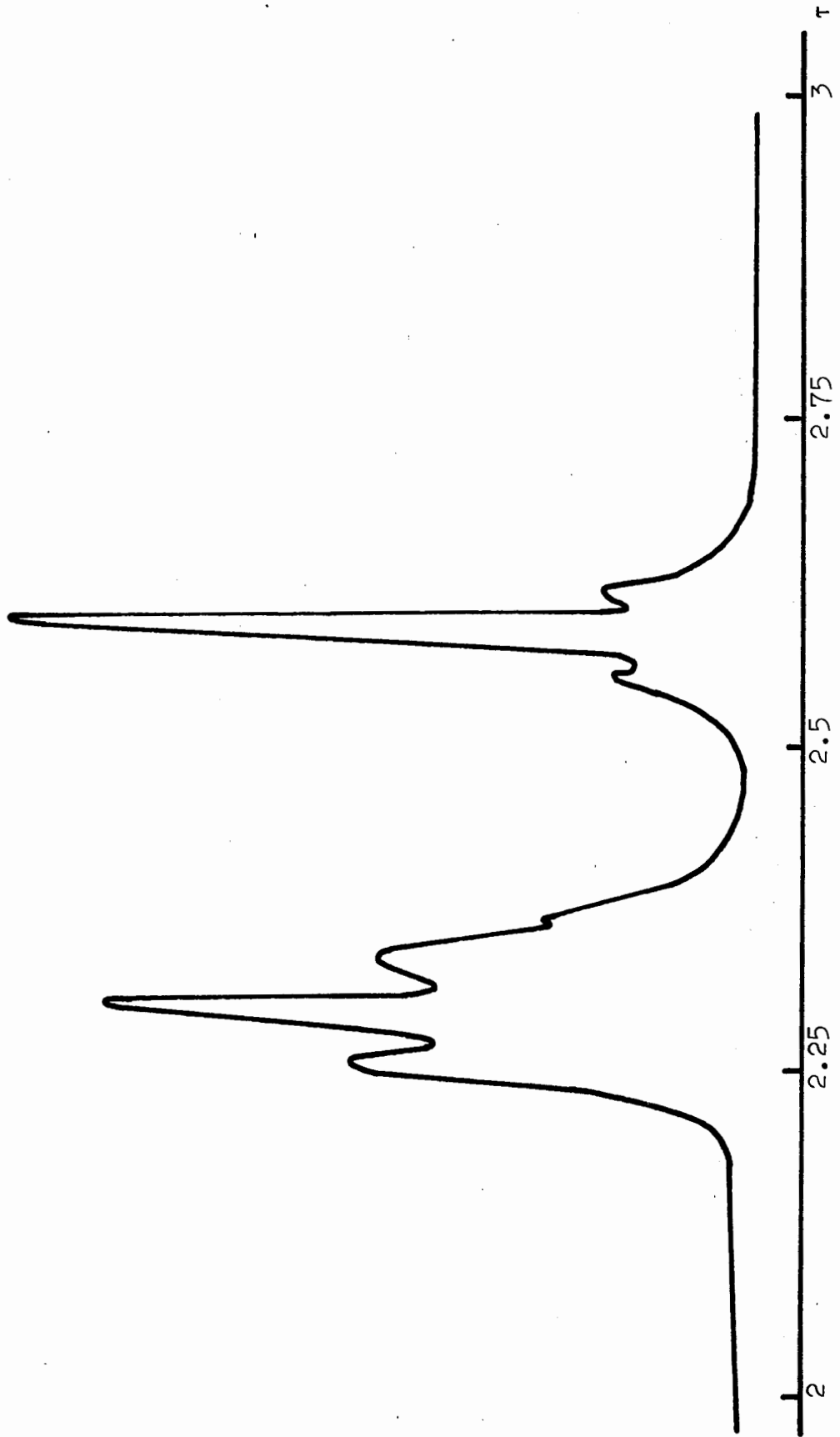


DIAGRAM 2-I. N.M.R. SPECTRUM OF $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NnC}_6\text{H}_4\text{Br}]^+ \text{BF}_4^-$.

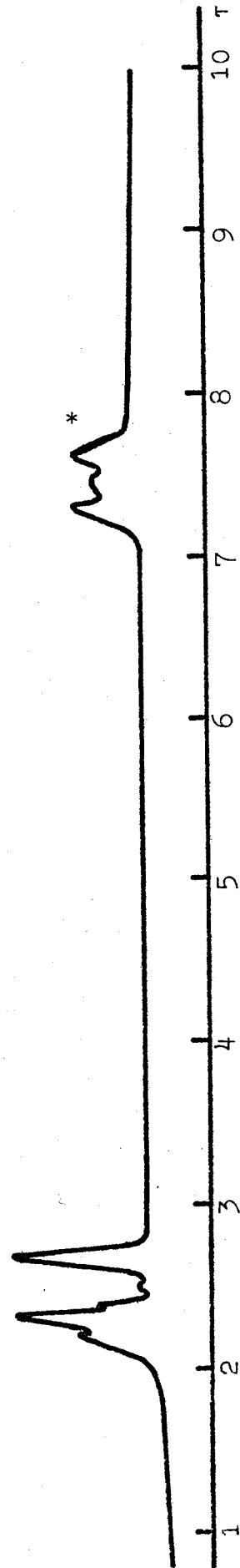
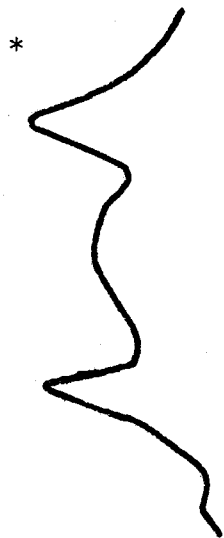


DIAGRAM 2-II. N.M.R. SPECTRUM OF $[\text{Fe}(\text{CO})_2(\text{PPh}_2\text{Me})_2\text{NNC}_6\text{H}_4\text{Br}]^+ \text{BF}_4^-$.

separation 8.9 Hz centred at τ 7.42 separated by a broad unresolved resonance having approximately the same integrated intensity as the outer doublet. Thus, the spectrum is typical of intermediate phosphorus-phosphorus virtual coupling^{41,42} and $|J_{P-H} + J'_{P'-H}| = 8.9$ Hz. Although no definite stereochemical information may be drawn from this result alone it should be noted that $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{Me})_2$ gives a similar spectrum as does the analogous nitrosyl complex², consistent with a similar trans-arrangement of phosphines in all three cases.

The i.r. spectra of all complexes show two peaks attributable to terminal carbonyl stretches (at ca 1980 and 2030 cm^{-1}) and one due to a N=N stretch (see Table 2-II), which was mentioned above. A compound of C_{2v} symmetry would be expected to give the observed spectra for the carbonyl stretches. Also in Table 2-II the corresponding bands for the starting material, $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, and for the analogous nitrosyl complex are shown. It can be seen that ν_{CO} values for the nitrosyl complex are almost identical with those for the electron withdrawing arylazo complexes. The trigonal bipyramidal $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ gives the expected single carbonyl peak at a much lower wavenumber. Raman spectroscopy showed little, since the C=O stretches are only weakly active in the Raman. As with the n.m.r., striking similarities between the arylazo series and the nitrosyl analogue are again apparent.

The electroconductivities of this series were investigated and a molecular weight determination achieved. The former are to be found in Table 2-III: the concentrations were calculated

TABLE 2-II
 INFRARED AND RAMAN DATA OF COMPLEXES (I)

p-substituent	Infrared		Raman	ν/ν_0 [†]
	ν_{CO} cm ⁻¹	ν_{N_2} cm ⁻¹		
-NO ₂	2040s	1715vs	-	0.743
-F	2035s	1718vs	1714w	0.747
-Cl	2022s	1715vs	1715w	0.749
H	2038s	1724vs	-	0.750
-Br	2029s	1721vs	1714w	0.752
-Br ¹⁵ N complex	-	1691vs	1690w	-
-OCH ₃	2020s	1722vs	1724w	0.763
-OH	2022s	1725vs	1719w	0.767
NO analogue	2040s	$\nu_{NO} = 1775vs$	-	0.785*
Fe(CO) ₃ (PPh ₃) ₂	1887s	-	-	-

† $\nu = \nu_{N_2}$ complex $\nu_0 = \nu_{N_2}$ diazonium salt. ν_{N_2} diazonium salts obtained from refs. 39 and 43.

* Values obtained from ref. 2.

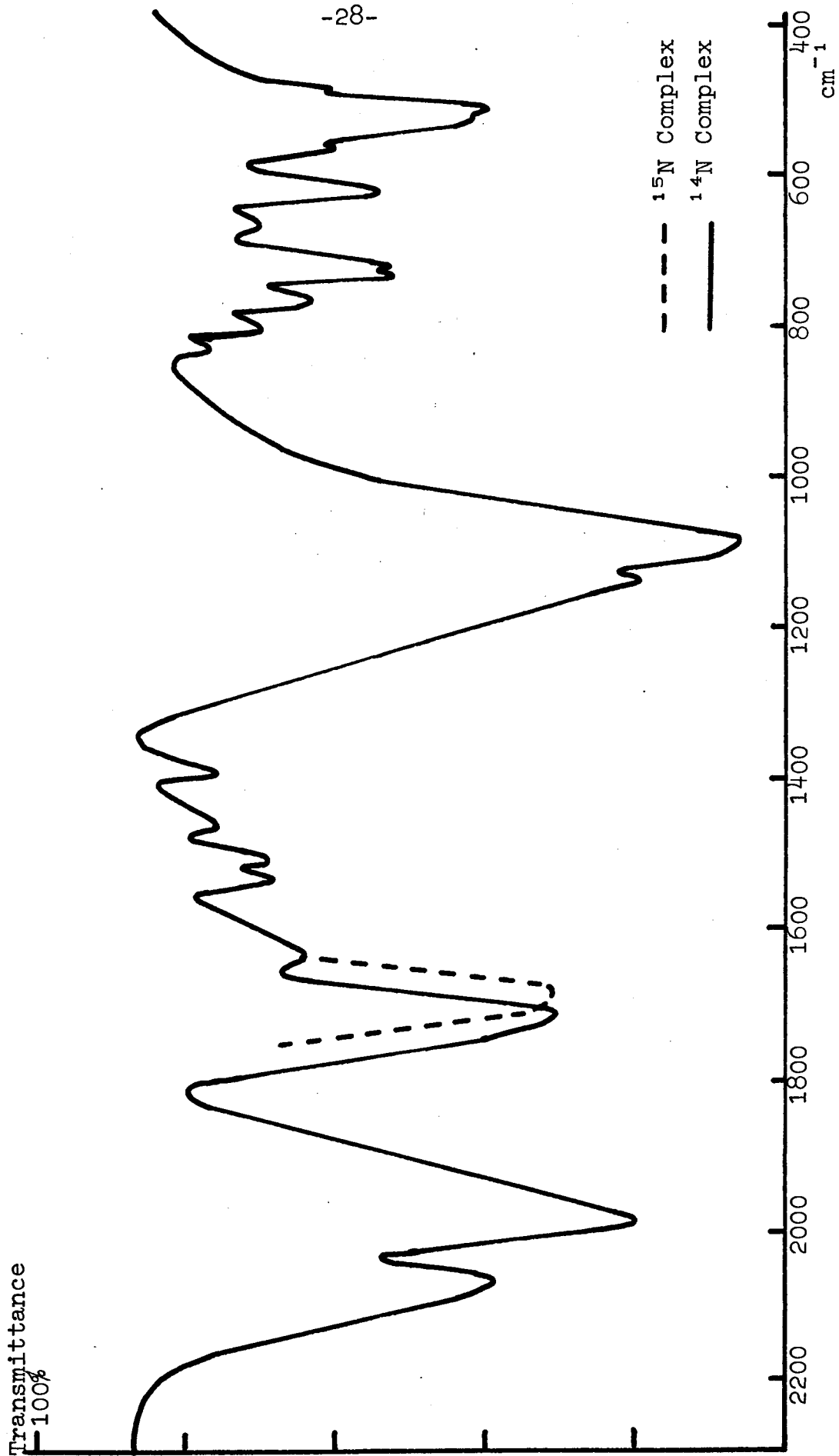


DIAGRAM 2-III. INFRARED SPECTRA OF $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNCeH}_4\text{Br}]^+\text{BF}_4^-$.

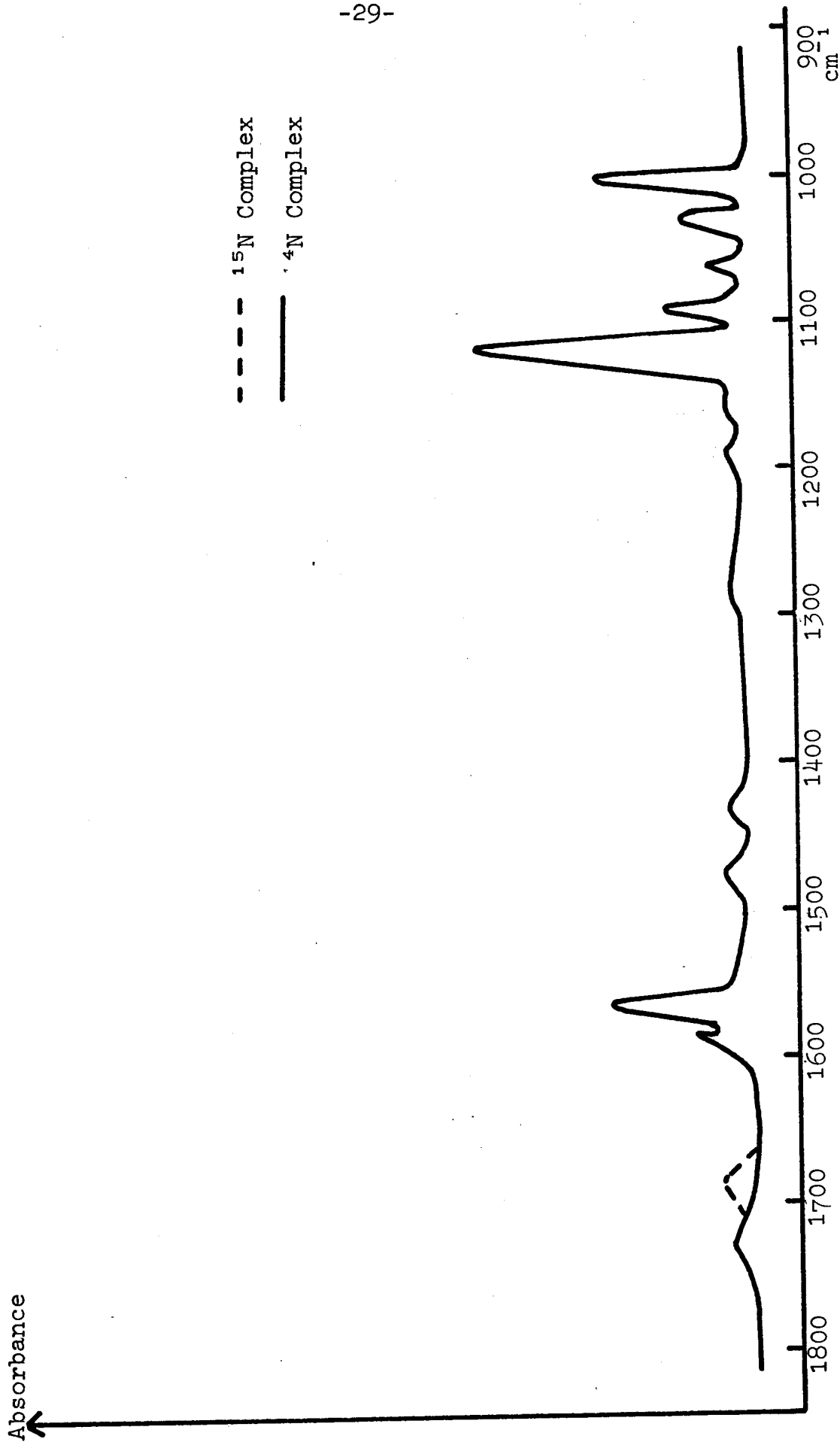


DIAGRAM 2-IV. RAMAN SPECTRA OF $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{Br}]^+\text{BF}_4^-$.

using the monomer's molecular weight. When the molecular weight of the dimer was used instead, the results obtained gave rise to discrepancies, especially when the result of the molecular weight experiment was considered also. The molecular weight determination of the p-Br complex gave a molecular weight of 498 ± 3 , which

TABLE 2-III

ELECTROCONDUCTIVITIES (IN ACETONE SOLUTION) OF COMPLEXES (I)

<u>p</u> -substituent	Λ_e (mho $\text{cm}^2 \text{mole}^{-1}$)	Concentration
-NO ₂	103.0 (75.7*)	$9.22 \times 10^{-5} \text{M}$ ($9.17 \times 10^{-4} \text{M}^*$)
-OCH ₃	117.3	$5.63 \times 10^{-5} \text{M}$
-F	129.1	$1.13 \times 10^{-4} \text{M}$
-Cl	126.6	$1.09 \times 10^{-4} \text{M}$
-Br	128.7	$1.03 \times 10^{-4} \text{M}$
-OH	144.2	$9.98 \times 10^{-5} \text{M}$

* For solution in nitromethane.

is consistent with a 1:1 electrolyte of molecular weight 907 that is 82% dissociated. The electroconductivities also are within the limits expected for 1:1 electrolytes⁴⁴ both in acetone and nitromethane (i.e. $\Lambda_e = \text{ca } 100\text{-}160 \text{ mho cm}^2 \text{mole}^{-1}$ for acetone and $\text{ca } 65\text{-}100 \text{ mho cm}^2 \text{mole}^{-1}$ for nitromethane).

Another useful aid in determining the stereochemistry of iron is Mössbauer spectroscopy, so the ⁵⁷Fe Mössbauer spectra of these compounds were compared with the spectra from $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NO}]^+\text{BF}_4^-$ and $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$. The measurements were kindly made by Prof. C. H. W. Jones of this Department.

The parameters quoted in Table 2-IV are with respect to sodium

TABLE 2-IV
MOSSBAUER SPECTRAL DATA

Compound	Chemical Shift δ mm sec ⁻¹	Quadrupole Splitting Δ mm sec ⁻¹
Fe(CO) ₃ (PPh ₃) ₂	+0.15 ± 0.01	2.75 ± 0.01
[Fe(CO) ₂ (PPh ₃) ₂ NO] ⁺ BF ₄ ⁻	+0.17 ± 0.01	1.85 ± 0.01
[Fe(CO) ₂ (PPh ₃) ₂ NNC ₆ H ₄ Br] ⁺ BF ₄ ⁻	+0.18 ± 0.01	0.94 ± 0.01
[Fe(CO) ₂ (PPh ₃) ₂ NNC ₆ H ₄ Cl] ⁺ BF ₄ ⁻	+0.16 ± 0.01	0.90 ± 0.02

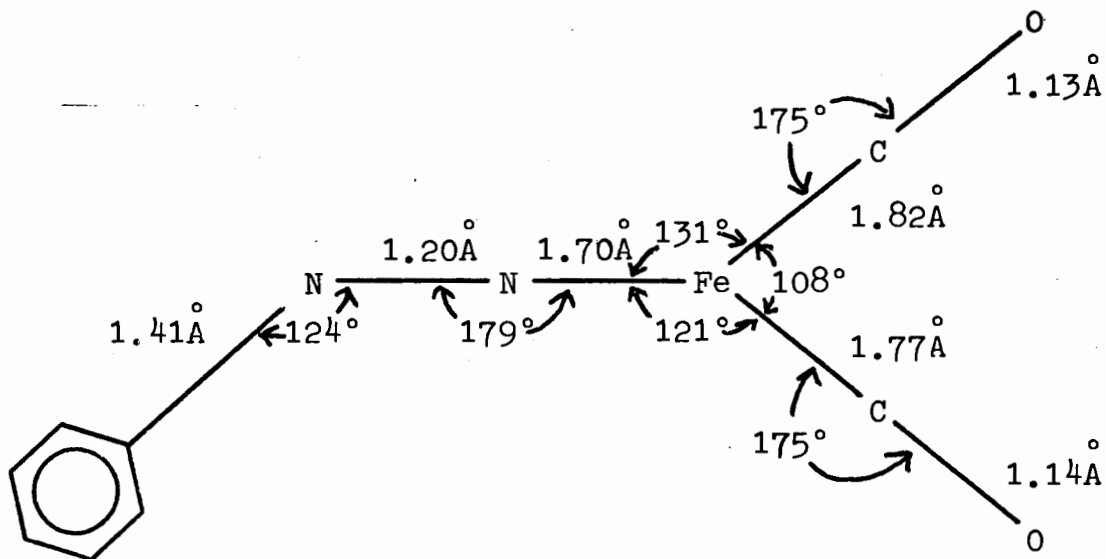
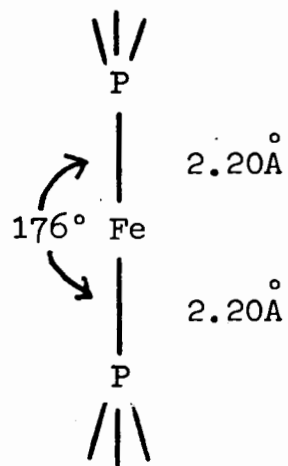
nitroprusside. The results for Fe(CO)₃(PPh₃)₂ agree well with reported values⁴⁵ and are typical of a trigonal bipyramidal Fe⁰ stereochemistry. The results for the other compounds are somewhat different in their quadrupole splittings, and at first sight it would suggest a different stereochemistry. The possible reasons for these results, being consistent with a trigonal bipyramidal stereochemistry, are discussed below.

The overall inference drawn from the accumulated data was that the complex appeared to be a 1:1 ionic species with the stereochemistry portrayed in Fig. 2-I. This structure has recently been independently confirmed by X-ray crystallographic techniques by Haymore and Ibers⁴⁶, see Fig. 2-XVI.

Features of the Azo Group

As mentioned briefly above, all of these complexes have an extremely intense band in the i.r. at ca 1720 cm⁻¹. This

View along equatorial plane, ignoring ligands in that plane.



View along z-axis, ignoring ligands in that direction.

Fig. 2-XVI. STRUCTURE OF $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NnC}_6\text{H}_5]^+$, FOLLOWING X-RAY CRYSTALLOGRAPHIC STRUCTURE OF HAYMORE AND IBERS.

band is also present in the Raman spectra, but is much weaker. By using the p-Br diazonium salt $\text{BrC}_6\text{H}_4^{14}\text{N}=\text{}^{15}\text{N}^+ \text{BF}_4^-$, which was prepared by using $\text{Na}^{15}\text{NO}_2$, the corresponding isotopically substituted arylazo complex was synthesised and investigated by i.r. and Raman spectroscopy. The only band which shifted was that at 1721 cm^{-1} in the i.r., which shifted to 1691 cm^{-1} , and its counterpart in the Raman, which shifted from 1714 to 1690 cm^{-1} . Hence it was possible to assign this absorption to the N=N stretch.

This band is at a reasonably high wavenumber for this type of bond, the majority falling into the range $1440\text{-}1620 \text{ cm}^{-1}$; ^{5,7-9,47} however, both Robinson⁴⁸ and Ibers⁴⁹ have found values in excess of this, the latter finding a value of 1868 cm^{-1} for $[\text{IrCl}(\text{NNC}_6\text{H}_5)(\text{PPh}_3)_2]^+$, and the former the even higher value of 1882 cm^{-1} for $\text{RuCl}_3(\text{NNC}_6\text{H}_5)(\text{PPh}_3)_2$. The other, perhaps more striking thing about this peak is its unusually high intensity in the i.r., and its weakness in the Raman, cf. $\text{Rh}(\text{NNAr})\text{Cl}_2\text{-(PPh}_3)_2$ ³⁹. The high frequency absorbed indicates a strong N=N bond. A strong N=N bond in bridging dinitrogen complexes would be due to a partially filled d-shell on the Lewis acid, as was discussed in Chapter 1. Here the d-shell has been replaced by the π -cloud of the aromatic ring. If it is fair to consider the aryl ring as the Lewis acid in a dinitrogen bridging complex, then the substituents on the ring should reduce the ν_{N_2} if they are electron withdrawing and increase it if they are electron donating. Indeed, if the ν_{N_2} of the complex is compared with the

ν_{N_2} of the free diazonium salt (see Table 2-II) then the fraction is $p\text{-OH} > p\text{-OCH}_3 > p\text{-Br} > H > p\text{-Cl} > p\text{-F} > p\text{-NO}_2$, which is in good agreement with the hypothesis.

The intensity in the i.r. spectra shows that there is a considerable dipole moment change associated with the ν_{N_2} . From work by Ibers⁵⁰ on nitrosyl complexes it appears that two extreme types of co-ordination in these complexes exist as yet. The two types are shown in Figs. 2-XVII and 2-XVIII; in Fig. 2-XVII the nitrosyl ligand is considered formally as NO^+ and in 2-XVIII as NO^- . There is no known example of the intermediate neutral species. Extending these structures to the analogous co-ordinated arylazo complexes the three possible structures shown in Figs. 2-XIX, 2-XX and 2-XXI arise. Here, Fig. 2-XIX is

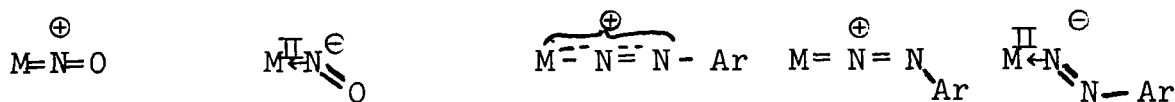


Fig. 2-XVII Fig. 2-XVIII Fig. 2-XIX Fig. 2-XX Fig. 2-XXI

analogous to Fig. 2-XVII, 2-XXI to 2-XVIII and 2-XX lying in between 2-XVII and 2-XVIII, perhaps analogous to the neutral possibility mentioned above. Fig. 2-XIX involves a formal $ArNN^+$ ligand behaving as a σ -donor, π -acceptor to the iron atom. Fig. 2-XXI is related to 2-XIX by a formal transfer of two electrons from metal to ligand so that the ligand now behaves as $ArNN^-$. In Fig. 2-XX the Fe to ligand electron transfer may be considered to have taken place to such an extent as to involve a full $M=L$ double bond but falling short of the complete transfer

envisaged in Fig. 2-XXI. Both Figs. 2-XX and 2-XXI indicate the existence of a dipole across the N=N group of a fair magnitude. In Fig. 2-XIX the dipole would be expected to be smaller due to the less discrete charge difference between the two nitrogen atoms. From the dimensions shown in Fig. 2-XVI it can be seen that the actual structure approximates most closely to Fig. 2-XX, with the nitrogen atom nearest the iron sp hybridised and the other nitrogen atom sp² hybridised. This structure has an associated dipole, which is the case, also, if it tends to incorporate a little of the structure portrayed by Fig. 2-XIX; an above average N=N bond strength would arise, since the bond order would be increased.

Comparisons with the Nitrosyl Analogue

It has been shown that stereochemically the two cations $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NO}]^+$ and $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{X}]^+$ are similar. Nevertheless, within the cation itself there are some differences accountable by the change in ligand, and the consequent change in the electronic environment of the iron. From Table 2-II it is clear that whereas $\nu/\nu_0(\text{N}_2)$ is in the order $\underline{p}\text{-OH} \gg \underline{p}\text{-NO}_2$ the $\nu(\text{CO})$'s are in the reverse order. This suggests that the diazonium groups compete effectively with the CO ligands for the d-electrons. In the case of $\underline{p}\text{-NO}_2$ and $\underline{p}\text{-F}$, where the $\nu(\text{CO})$'s are similar to those of the nitrosyl complex, it would seem that these two diazonium groups and the nitrosyl group have similar π -acceptor properties. With the less electron-withdrawing groups the $\nu(\text{CO})$'s decrease suggesting a poorer π -acceptor, which is

hardly surprising since there is no longer as great a drain for the electrons accepted. However if the values of ν/ν_0 are considered, then that for the NO group is far greater than any of the diazonium groups. Hence, the evidence is conflicting. However, it has also been found that, whereas NO^+ will replace the p-Br diazonium group in the cation, p- $\text{BrC}_6\text{H}_4\text{NN}^+$ will not replace the nitrosyl group, even in aqueous media. This other piece of evidence suggests that the Fe-N bond is stronger in the nitrosyl complex; i.e. that the nitrosyl ligand is indeed the better π -acceptor of the two.

The other obvious method of investigating electronic effects is with electronic spectroscopy. Solutions in ethanol were used in preference to solutions in acetone due to interference from the carbonyl $\pi^* \leftarrow \pi$ transition of the latter at ca 275 nm. Table 2-V shows the results obtained from the series, the nitrosyl analogue and $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$. The results of Gray et al.⁵¹ for $\text{Fe}(\text{CO})_5$ are also included. The extinction coefficients are very high and the higher energy absorptions are almost certainly due to charge-transfer. The lower energy band at ca 300 nm could be a $\pi^* \leftarrow \pi$ transition in accord with its lower extinction coefficient. In Gray's analysis of $\text{Fe}(\text{CO})_5$ the bands at 200 nm and 240 nm were assigned to M \rightarrow L charge-transfer. It is, therefore, probable that the absorptions at 204 - 211 nm observed in the arylazo complexes and other carbonyl compounds in Table 2-V correspond to the former and that those between 226 and 251 nm to the latter. The band observed at 282 nm in $\text{Fe}(\text{CO})_5$

TABLE 2-V
ELECTRONIC SPECTRAL DATA

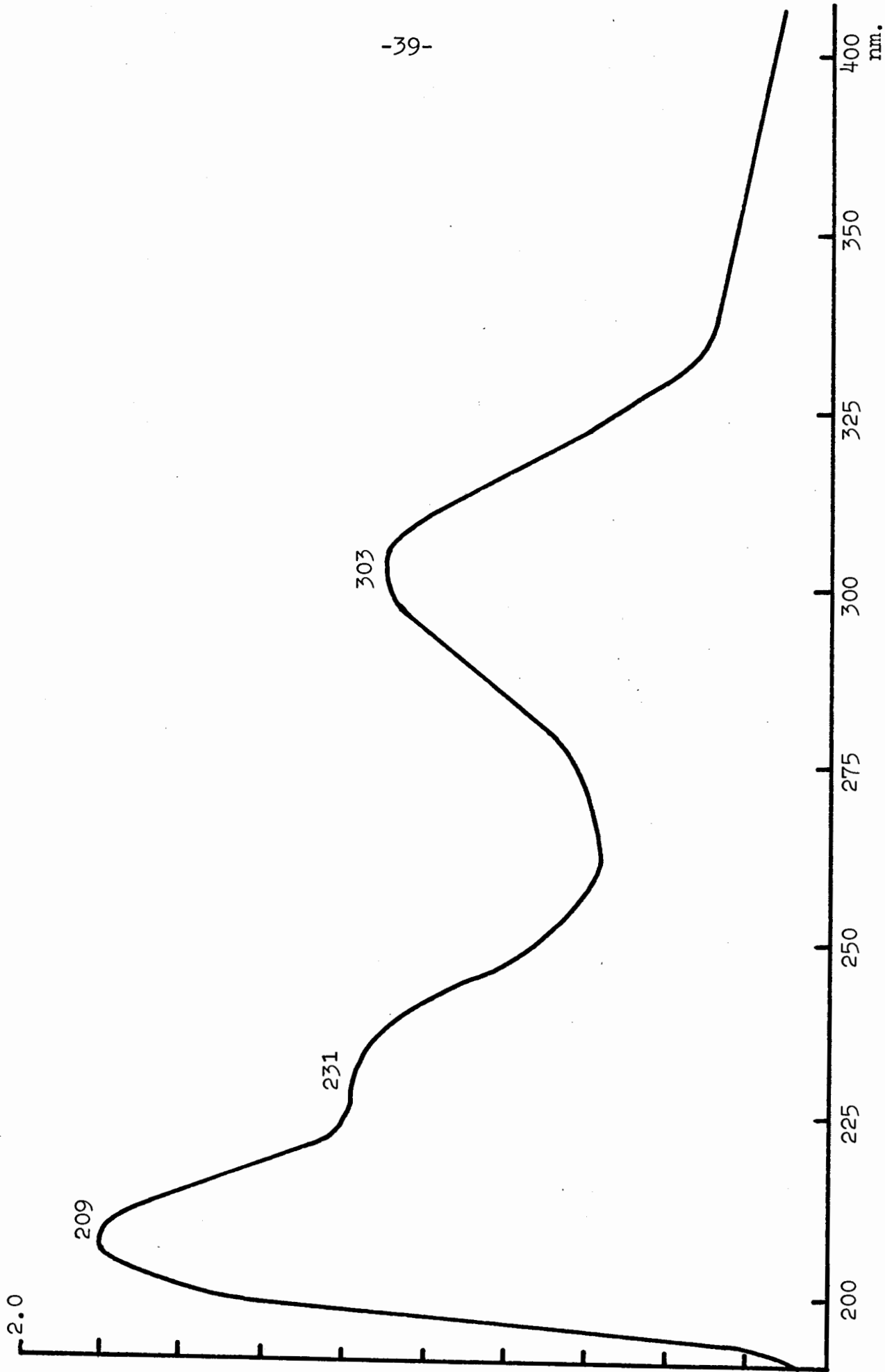
Compound	λ_{max} (nm.)		$(\epsilon_{\text{max}} \times 10^{-3} \text{ in parenthesis.})$	
Fe(CO) ₅	200 (37)	240 (10.2)	282 (3.8)	
Fe(CO) ₃ (PPh ₃) ₂	204 (12.5)	225sh (4.9)	251 (3.9)	
<u>p</u> -NO ₂ complex	211 (20.9)	242 (15.4)		305 (9.7)
<u>p</u> -F complex	206 (14.0)	230sh (7.9)		298 (7.1)
<u>p</u> -Cl complex	210 (16.9)	230 (11.1)		301 (10.2)
<u>p</u> -Br complex	209 (17.7)	231 (11.7)		303 (10.8)
<u>p</u> -OCH ₃ complex	209 (32.3)	226sh (23.8)		295sh 317 (11.3)
<u>p</u> -OH complex	210 (20.2)	227sh (15.8)		293sh 322 (11.6)
NO analogue	210 (74)	230sh (48)		302 (17.6)

does not seem to be present in the other complexes. Hence the band at about 300 nm would appear to be peculiar to the new ligand. (It is also absent in $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$.) Consequently a $\pi^* \leftarrow \pi$ transition of the azo (or nitrosyl) chromophore is tentatively assigned to it. The interesting fact is that in the electronic spectra the nitrosyl complex has practically the same λ_{max} as the p-Cl arylazo complex. Their extinction coefficients are, however, different, the former being far the larger of the two. Thus, if the $\pi^* \leftarrow \pi$ transition is that of the Fe-N π -system then the π -acceptor qualities of the two analogous ligands are similar. If, however, the π -system in question is that of the N-N (or N-O) then the evidence is coincidental, since the energy gaps in the orbital schemes of these two complexes are not expected to be of identical magnitude.

Miscellaneous Measurements

With one possible exception, all of the results described so far are explicable in terms of the trigonal bipyramidal structure suggested. This exception was the Mössbauer spectroscopic study, the results of which are outlined in Table 2-IV. The results obtained for $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ are typically consistent with its known trigonal bipyramidal Fe^0 structure. By comparison, quadrupole splitting in $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NO}]^+ \text{BF}_4^-$ is substantially

Absorbance



-39-

DIAGRAM 2-V. ELECTRONIC SPECTRUM OF $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{Br}]^+\text{BF}_4^-$.

decreased and that in $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNAr}]^+ \text{BF}_4^-$ decreased still further. Such quadrupole splittings are highly atypical of most trigonal Fe^0 complexes. The large Δ -values these normally display are due to a considerable electric field gradient which results from the asymmetric (i.e. non-cubic) environment in these complexes. The replacement of CO by NO^+ and NNAr^+ therefore appears to reduce the electric field gradient despite the fact that the ligand environment of the iron atom is rendered more asymmetric by the removal of the trigonal symmetry of the equatorial plane. From the various other techniques used there was no evidence to support the other possibilities of BF_4^- co-ordination, o-metallation of an aromatic ring, or close contact of an o-hydrogen atom with the metal, all of which would result in a pseudo-octahedral complex. It seems therefore that the explanation for this effect must lie in the electronic properties of the co-ordinated nitrosyl and arylazo ligands, and may arise from the increased π -acceptor character of these ligands in comparison with that of the carbonyl group as evidenced in the i.r. data already discussed.

The magnetic data obtained for these complexes are extremely difficult to explain. All the arylazo complexes were found to be paramagnetic, as was also the nitrosyl analogue. $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, however, was diamagnetic as expected. The results are tabulated in Table 2-VI. Taken at their face value they fall into two distinct groups, firstly those with p-substituents which have μ_M effects, and secondly those with

TABLE 2-VI
MAGNETIC DATA OF COMPLEXES (I)

Complex	μ_{eff} at R. T. (B. M.)		
<u>p</u> -NO ₂	2.26*	2.09**	2.04***
<u>p</u> -OCH ₃	2.26*		
<u>p</u> -OH	1.92*		
<u>p</u> -Cl	1.24*	1.39**	
<u>p</u> -Br	0.88*		
<u>p</u> -F	0.64*		
NO analogue	0.84*		

* Using Faraday Magnetic Balance

** Using Proton Resonance Shift method⁵²

*** μ_{eff} at 85° K.

only ± 1 effects. The former (p-NO₂, p-OCH₃, p-OH) give a μ_{eff} corresponding to about one unpaired electron, whereas the latter (p-F, p-Cl, p-Br) give a smaller μ_{eff} corresponding somewhere between the values expected for zero and one unpaired electrons. This paramagnetism can be explained by one of three causes: firstly, that they possess inherent first-order paramagnetism; secondly, that there is a trace of impurity present; thirdly, that the complexes exhibit temperature independent (or second-order) paramagnetism. As mentioned above formal oxidation states in the complexes can be considered as Fe⁰-L⁺, Fe^I-L, or Fe^{II}-L⁻ (L = NNC₆H₄X). The Fe^I system would indeed be paramagnetic having two unpaired electrons, one on the iron and one on the ligand.

However, both the Fe^0 and the Fe^{II} systems would be diamagnetic due to the ligand field splitting obtained in a trigonal bipyramidal field for a low-spin d^8 or d^6 shell. Since all the results fall into the range between zero and two unpaired electrons' μ_{eff} 's the first possibility cannot be ruled out, despite the fact that none of the results correspond exactly to the spin-only expectation for an integral number of unpaired electrons.

It is difficult to believe that the values obtained are due to impurities, as these values are remarkably consistent. Different batches of the same complex give the same μ_{eff} , as did crystals obtained by different crystallisation techniques. If these paramagnetic susceptibilities were due to impurities, it would be unlikely that the impurity would always be present in the same amount. Furthermore, the analyses suggest that if an impurity is present in any amount, then the impurity must have a strong analytical resemblance to the pure complexes. What is more no spectral impurities were detected in any of the spectra investigated.

This paramagnetism was also examined in solution by Evan's proton resonance shift method⁵², using tert.-butanol as the internal reference in chloroform solution, with results in general agreement with solid state values. However, no line broadening was observed in any of the ^1H n.m.r. spectra, nor did the complexes exhibit e.p.r. spectra, both of which are in agreement with the absence of first-order paramagnetism.

Therefore, the observed paramagnetism is tentatively attributed to second-order Zeeman effects (temperature independent paramagnetism) despite the rather high values of μ_{eff} observed.

Chemical Reactions

These orange compounds are quite air-stable at room temperature, unlike the nitrosyl, which decomposes very slowly. They do, however, decompose on melting -- the melting points are listed in Table 2-VII. As mentioned above they are soluble

TABLE 2-VII
MELTING POINTS

Complex	M. Pt.
<u>p</u> -NO ₂	184° C
<u>p</u> -OCH ₃	128° C
<u>p</u> -F	204° C
<u>p</u> -Cl	132° C
<u>p</u> -Br	160° C
<u>p</u> -OH	203° C

in polar solvents, with the notable exception of water, but not in non-polar solvents.

Reactions with NO⁺

When NO⁺BF₄⁻ was added to an acetone solution of the p-Br arylazo complex and stirred under N₂ at room temperature for three hours, approximately 50% was found to have been converted

to the nitrosyl complex. However, addition of p-Br diazonium salts to the nitrosyl complex under similar conditions gave no evidence of formation of the arylazo complex, even after 48 hours. Even the addition of a small quantity (10%) of water to the solvent had no noticeable effect.

Reduction of the N=N Group

The strength of the N=N bond already apparent from the high wave number of its band in the i.r. was further emphasized in its resistance to reduction. There was no evidence of reduction of the complexes with dihydrogen gas alone when stirred at room temperature in acetone for 24 hours, or even in the presence of a palladium catalyst (Pd/BaCO₃) under similar conditions. The p-Br complex was, however, reduced by NaBH₄ in ethanol solution and the resulting products were investigated. These products appear to be numerous and it is difficult to characterise them all. Nevertheless, from the mass spectrum there are two peaks of equal intensity at m/e = 200 and 202 with corresponding fragmentation patterns. These two peaks are characteristic of ions differing by the two common bromine isotopes. The m/e values and the fragmentation pattern determine these peaks to be due to the ion [p-BrC₆H₄NHNH₂-BH₃]⁺ as shown in Table 2-VIII. There was no concrete evidence of further reduction, although the possibility cannot be ruled out entirely since all the products were not identified.

The apparent difficulty with which these complexes are reduced is therefore as expected. Parshall's work showed that

TABLE 2-VIII

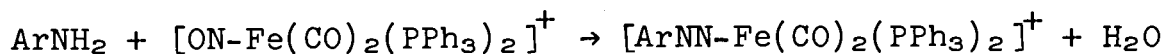
FRAGMENTATION PEAKS OF p-BrC₆H₄NHNH₂-BH₃⁺

m/e	Abundance	Assignment
200,202	15	p-BrC ₆ H ₄ NHNH ₂ -BH ₃ ⁺
183,185	15	p-BrC ₆ H ₄ NN ⁺
172,174	5	p-BrC ₆ H ₄ NH ₃ ⁺
155,157	5	p-BrC ₆ H ₄ ⁺
79,81	20	Br ⁺
77	100	C ₆ H ₅ ⁺
76	25	C ₆ H ₄ . ⁺
17	includes OH ⁺ from C ₂ H ₅ OH	NH ₃ ⁺
16	90	NH ₂ ⁺
15	100	NH ⁺
14	90	N ⁺ , BH ₃ ⁺
13	25	BH ₂ ⁺

with a N=N stretching frequency of 1463 cm⁻¹, the p-F arylazo complex of platinum could be reduced by dihydrogen gas in the presence of a Pt catalyst³⁶. However when the $\nu_{N=N}$ value is increased in arylazo complexes then more powerful reducing agents are required, as is described in papers by van Tamelen^{26-28, 53}, where he resorts to sodiumnaphthalide as the reducing agent for dinitrogen complexes. Consequently, these results are in keeping with other published results.

Miscellaneous Syntheses

It was hoped that investigation of another possible synthetic route to arylazo complexes would prove successful. The reaction tried was a parallel to the Mills reaction of organic nitroso-compounds, namely: -



Unfortunately, no reaction was observed under the conditions tried. Even using the dehydrating solvent $\text{CH}_3\text{C}(\text{OCH}_3)_2\text{CH}_3$ there was no evidence, from i.r. spectra, of the arylazo complex being formed. Apparently there must be sufficient difference in the chemical nature of the NO group between an inorganic nitrosyl complex and an organic nitroso complex to prevent the analogous reaction from occurring.

To try and obtain further understanding of this system, it was decided to investigate the isoelectronic aryl nitriles and isonitriles. It is known that N_2 ase is able to reduce nitriles and isonitriles and consequently it was hoped that the starting material for the arylazo complexes would also react with either benzonitrile or phenylisonitrile, i.e. to form $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2 \text{NCPH}$ and $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2 \text{CNPh}$ respectively. However, in neither case was evidence of success shown, even when a less polar solvent (benzene) was used.

Conclusions

It has been shown that arylazo complexes of iron can be synthesized with relative ease quite successfully. These complexes are stereochemically analogous to the corresponding

nitrosyl complex. They are, however, more air-stable than the nitrosyl complex even though the latter is the more thermodynamically stable. There is no evidence of a disubstituted arylazo complex although the possibilities were not fully investigated. The N=N bond is reasonably strong but, as with bridging dinitrogen complexes, this strength is decreased by electron withdrawing groups substituted on the aromatic ring. Furthermore, this bond requires quite strong reducing agents for reduction to occur. However, if the ring is heavily substituted with electron withdrawing groups, it is possible that reduction might be facilitated. The reduction of this bond was as difficult as expected from its $\nu_{N=N}$ value. Although the various techniques used have slightly conflicting interpretations, it can be said that the arylazo ligand appears to be quite a good π -acceptor of approximately equal strength to the nitrosyl ligand.

Unfortunately, due to the relative difficulty with which these complexes reduce, this series of complexes has little in common with nitrogen reductase and, as such, has little apparent use as a model. Nevertheless the results obtained are all explicable by factors brought out by some of the other models of the enzyme, and hence with different ligands perhaps the model might have been more successful.

CHAPTER 3

PHOSPHODIAZONIUM SALTS

Introduction

As mentioned previously, one diazonium salt, the p- $\text{NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$, reacted very differently from the others with $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$. This chapter describes the properties of the compound thus formed and the analogues also prepared.

With the above mentioned reaction, an intense orange-red colouration was immediately observed with no gas evolution. Furthermore, it was found that when the reactants were added in equimolar amounts, only half the iron complex was utilized whereas all the diazonium salt was expended. Atomic absorption measurements showed, however, that only trace amounts of iron were present in the product, as impurity. This was further supported by Mössbauer spectra of the product.

After some investigation it was found that this compound could also be prepared by adding the p- NEt_2 diazonium salt directly to triphenylphosphine, forming a 1:1 adduct. Furthermore, it was found that all diazonium salts appear to react with PPh_3 in this fashion. However, the products from all except p- OCH_3 and p- NEt_2 decomposed in solution. Those with -M substituents were transient species under these conditions, decomposing totally within seconds: those with only inductive substituents or m-substituted mesomeric substituents decomposed a little more slowly, lasting in solution about a minute. The two mentioned with +M substituents were fortunately isolable in

the solid state. Nevertheless the p-OCH₃ derivative is only stable as a solid at 0° C, but the greater electron-donating diethylamino group seems to be sufficient to allow the complex to be quite stable at room temperature. Analytical data on the decomposed adducts showed the reaction to yield the phosphonium salt PPh₃Ar⁺BF₄⁻ with evolution of N₂ (e.g. for Ar = m-MeO C₆H₄, analysis was: found C 66.84, H 4.98, N 0.0%; required C 64.6, H 4.72%). The analysis of the p-NEt₂ derivative was found to fit that for the 1:1 adduct p-NEt₂C₆H₄NNPPh₃⁺ BF₄⁻ very well. The results shown in Table 3-I are those obtained for the complex

TABLE 3-I
ANALYTICAL DATA FOR PHOSPHODIAZONIUM SALTS

For <u>p</u> -NEt ₂ C ₆ H ₄ NNPPh ₃ BF ₄				For <u>p</u> -MeOC ₆ H ₄ NNPPh ₃ BF ₄		
	From Fe(CO) ₃ (PPh ₃) ₂		From PPh ₃			
	Observed	Calculated	Observed	Calculated	Observed	Calculated
C	64.27%	64.01%	63.97%	64.01%	62.31%	62.03%
H	5.52%	5.56%	5.56%	5.56%	4.83%	4.54%
N	9.18%	8.00%	7.98%	8.00%	5.25%	5.79%
P	4.36%	5.90%	5.94%	5.90%		
F	13.55%	14.50%		14.50%		

formed by the two different methods. From Table 3-I it can be seen that the complex was of greater purity when prepared from PPh₃.

\underline{p} - $\text{NEt}_2\text{C}_6\text{H}_4\text{NN}^+\text{BF}_4^-$ was found to react similarly with PPh_2Me , but in this case an unstable compound was formed, decomposing slowly at room temperature, even when in an inert (N_2) atmosphere. Although an i.r. spectrum was obtained, due to the instability of the complex this spectrum was of a poor quality. The results from this spectrum are discussed below. The complex was too unstable to allow a Raman spectrum or an electronic spectrum to be obtained.

Similar reactions were tried with SPh_2 , AsPh_3 and SbPh_3 . With SPh_2 and AsPh_3 oils were obtained after 2 or 3 days, but there was no apparent reaction with SbPh_3 . The diazonium salt was also mixed with triethyl and triphenyl phosphites and triphenyl phosphine oxide: however, in all these attempts no reaction occurred. Consequently, it appears that the only stable and preparable compound of the series $\text{ArNNMR}_3^+\text{BF}_4^-$ is with $\text{M}=\text{P}$, $\text{Ar}=\underline{p}\text{-NEt}_2\text{C}_6\text{H}_4$, and $\text{R}=\text{Ph}$. Thus, most of the other evidence described is necessarily that obtained for this one compound, with inferences from the others. The physical properties measured for this compound were i.r. spectra, Raman spectra, electronic spectra, n.m.r. spectra, molecular weight determinations and electroconductivity measurements. I.r. and Raman spectra were also obtained for the ^{15}N substituted compound $\underline{p}\text{-NEt}_2\text{C}_6\text{H}_4\text{}^{14}\text{N}^{15}\text{NPPh}_3^+\text{BF}_4^-$.

Physical Properties

Since the salt obtained by adding the $\underline{p}\text{NEt}_2$ diazonium salt straight to PPh_3 was purer, this was the salt studied.

This compound is a stable red needle crystalline solid which is soluble in polar organic solvents such as acetone, ethanol, chloroform, and nitromethane. It is, however, unstable in solution, especially in chloroform where it decomposes with loss of N_2 to a brown oil in a day or so. It is insoluble in water and non-polar organic solvents such as benzene, toluene, carbon tetrachloride, and ether. Melting points were taken both for the p- NEt_2 and p- OCH_3 derivative, giving $164^\circ C$ and $92^\circ C$ respectively. Both, however, decomposed completely on melting and the latter started to decompose well prior to this value (ca $40^\circ C$).

An electroconductivity experiment on an acetone solution of $1.37 \times 10^{-4} M$ (assuming a molecular weight of 525) gave a result of $184 \text{ mho cm}^2 \text{ mole}^{-1}$. This value is relatively high for a 1:1 electrolyte⁴⁴ which normally exhibits values in the range 120 to $175 \text{ mho cm}^2 \text{ mole}^{-1}$ for this concentration; however, the expected values for a 2:1 electrolyte are far higher, in the range 230 to $290 \text{ mho cm}^2 \text{ mole}^{-1}$. A molecular weight determination on an acetone solution of $4.25 \times 10^{-3} M$ indicated a molecular weight of 320. This result corresponds to a 67% dissociation of a 1:1 electrolyte of molecular weight 525. Consequently, it appears that the compound is a direct adduct of the p- NEt_2 diazonium salt and PPh_3 in a 1:1 ratio.

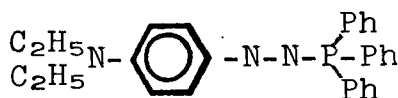
Vibrational Spectra

Particularly important bands in the infrared spectra obtained for three compounds are listed in Table 3-II as are the Raman

TABLE 3-II
INFRARED AND RAMAN SPECTRA

Compound	$\nu_{P-N} \text{ cm}^{-1}$		$\nu_{N-N} \text{ cm}^{-1}$	
	I.r.	Raman	I.r.	Raman
<u>p</u> -NEt ₂ C ₆ H ₄ NNPPh ₃ BF ₄	1222	1212	888	883
<u>p</u> -NEt ₂ C ₆ H ₄ NNPPh ₂ MeBF ₄	1265?	--	873?	--
<u>p</u> -OCH ₃ C ₆ H ₄ NNPPh ₃ BF ₄	1249?	--	878?	--
<u>p</u> -NEt ₂ C ₆ H ₄ ¹⁴ N ¹⁵ NPPPh ₃ BF ₄	1210	1200	878	877

results for p-NEt₂C₆H₄NNPPh₃⁺BF₄⁻ and the ¹⁵N results mentioned above. Spectra are illustrated in Diag. 3-I and 3-II. The results shown for p-NEt₂C₆H₄NNPPh₃BF₄ are unambiguous; those for the other two compounds are only tentatively assigned by comparison. All the other bands in the spectra could be accredited to either the PPh₃ or the aryl diazonium moieties or BF₄⁻, as they were also found in the spectra of the starting materials. From the evidence thus achieved it seems most probable that the complex is formed in the following configuration: -



The bond orders have been deliberately omitted from this figure.

Fig. 3-I

The assignment of the vibrational bands is in reasonable agreement with the results found by Bock, Schnoller and Diek⁵⁴; these results and other results⁵⁵ for P-N and N-N bonds are tabulated in Table 3-III.

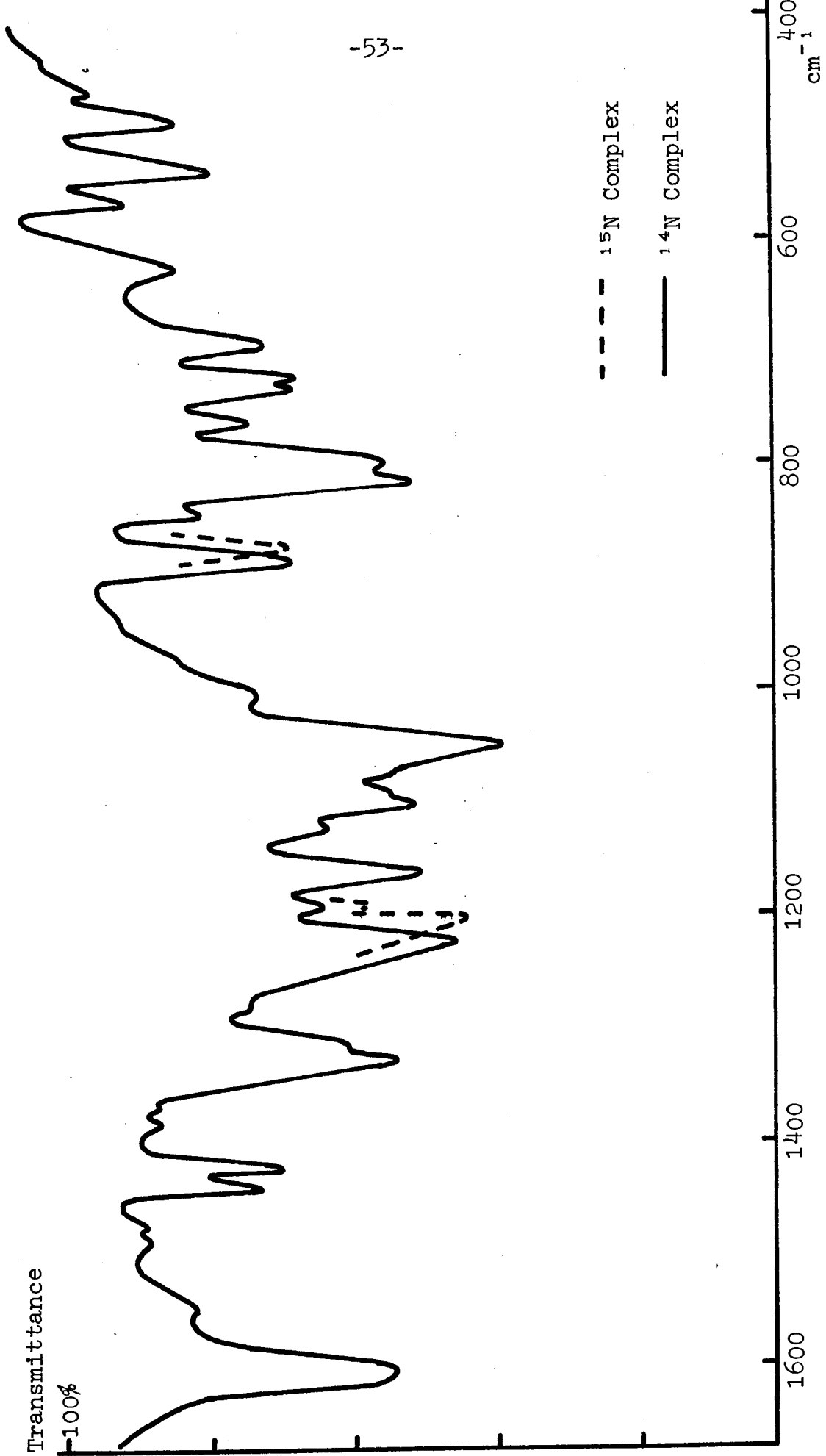


DIAGRAM 3-I. INFRARED SPECTRA OF [p-NEt₂C₆H₄NNPPh₃]⁺BF₄⁻.

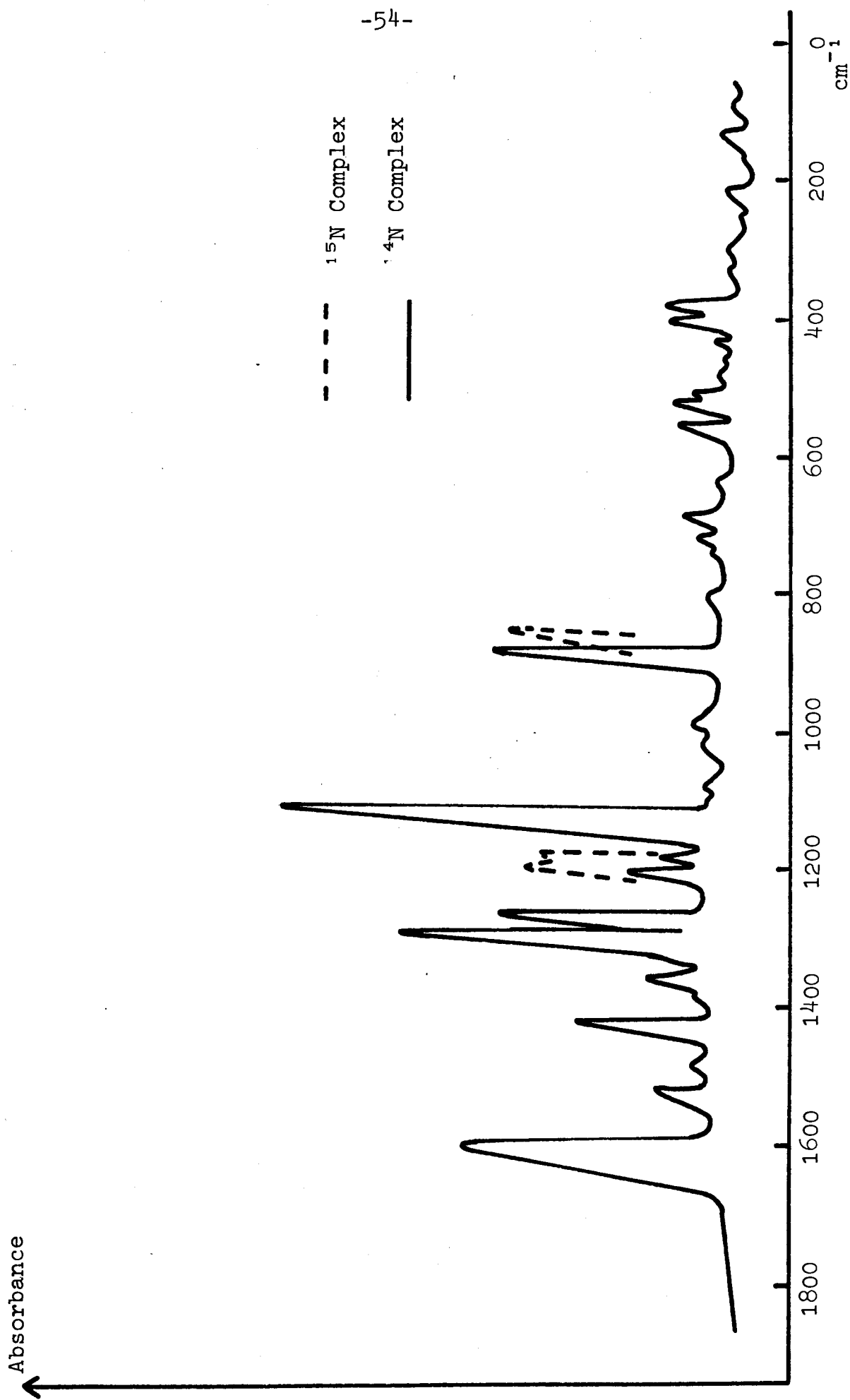


DIAGRAM 3-II. RAMAN SPECTRA OF [p-NEt₂C₆H₄NNPPh₃]⁺BF₄⁻.

TABLE 3-III
SPECTRAL DATA OF SIMILAR COMPOUNDS

Compound	$\nu_{\text{P=N}} \text{ cm}^{-1}$	$\nu_{\text{N-N}} \text{ cm}^{-1}$
$\text{Ph}_3\text{P=N-N=CH}_2$	1053	847
$\text{Ph}_3\text{P=N-N=CD}_2$	1012	799
$\text{Ph}_3\text{P=NPh}$	1344	--
$\text{Ph}_2\text{EtP=NPh}$	1330	--
$\text{Ph}_3\text{P=NCH}_3$	1230	--
$\text{Ph}_3\text{P=NSO}_2\text{CH}_3$	1152	--

From Table 3-III it can be seen that $\nu_{\text{P=N}}$ lies between 1000 and 1350 cm^{-1} , whereas $\nu_{\text{N-N}}$ is far lower in the order of 800 cm^{-1} . $\nu_{\text{P-N}}$ has been shown to be in the range of 860 to 910 cm^{-1} ^{5e}, and in hydrazines and azo complexes $\nu_{\text{N-N}}$ and $\nu_{\text{N=N}}$ are found to be between 850 and 1050 cm^{-1} and 1550 and 1650 cm^{-1} respectively. Since it would seem correct to assume that either P-N or N-N tends to a single bond order, whilst the other tends to a double bond order, the assignment adopted seems the most reasonable choice by comparison. Neither the infrared nor Raman spectra show any sign of bands attributable to N-H or P-H, indicating these to be absent.

From the evidence so far three possible basic structures can be formulated. The first (Fig. 3-II) is shown in two limiting resonance structures and the other two (Figs. 3-III to 3-VII) can have protons in the various positions shown.

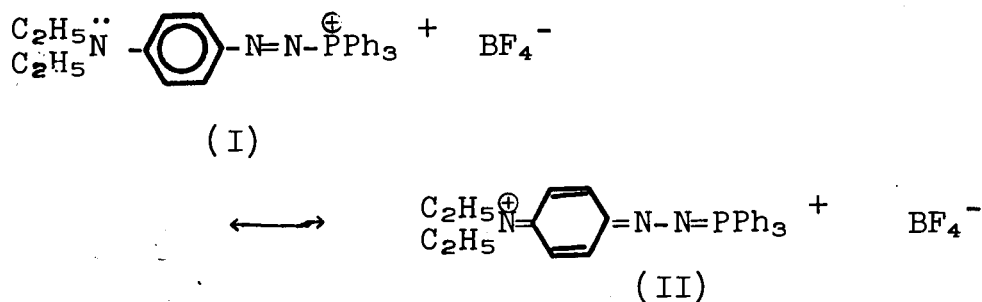


Fig 3-II

The i.r. and Raman evidence suggests that the compound has the structure corresponding to Fig. 3-II and that resonance structure (II) is the predominant one. Likewise, the strong colouration of the complex is suggestive of the larger chromophore that arises from resonance structure (II).

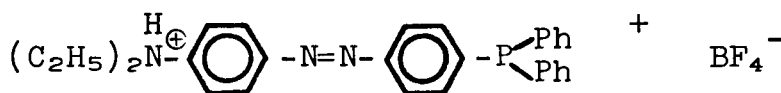


Fig 3-III

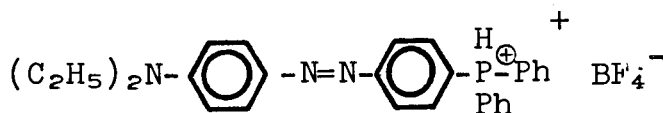
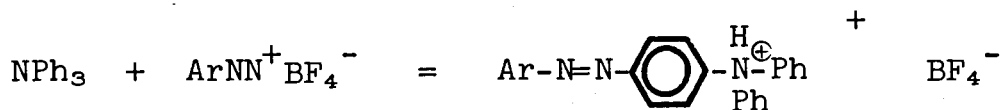


Fig 3-IV

Figs. 3-III and 3-IV are derived by analogy with the structure obtained from the reaction between diazonium salts and tertiary aromatic amines i.e.: -



These structures, however, have two important discrepancies: firstly, the absence of $\nu_{\text{P-H}}$ and $\nu_{\text{N-H}}$ in the spectra and

secondly, there is no longer any P-N bond, and hence the new i.r. assignments would be $\nu_{\text{N=N}}$ at 1222 cm^{-1} and $\nu_{\text{C-N}}$ at 888 cm^{-1} , both of which are in poor agreement with published results for these stretching frequencies.

Structures shown in Figs. 3-V to 3-VII again lack evidence for N-H bonds and in these structures the P-N bond has to be of single bond order, which would mean the assignments made for $\nu_{\text{P=N}}$ and $\nu_{\text{N-N}}$ would no longer be valid. The assignments now would be $\nu_{\text{N=N}}$ at 1222 cm^{-1} and $\nu_{\text{P-N}}$ at 888 cm^{-1} . However this value for $\nu_{\text{N=N}}$ is far lower than that normally found for formal N=N double bonds.

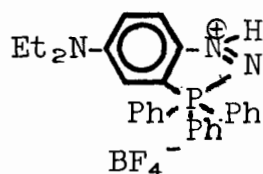


Fig 3-V

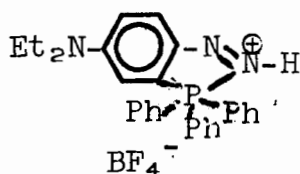


Fig 3-VI

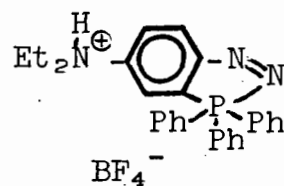


Fig 3-VII

Electronic Spectra

As already mentioned, these compounds are an intense orange-red in colour. However, due to instabilities in solution only the one complex was investigated by electronic spectroscopy. The results obtained are tabulated in Table 3-IV, together with results for PPh_3 and $\text{p-NEt}_2\text{C}_6\text{H}_4\text{NN}^+\text{BF}_4^-$. The very intense band at 506 nm can be seen to be due to some totally new chromophore in the compound, and is of course the absorbance that gives rise to the visible colouration. This colour would suggest a large

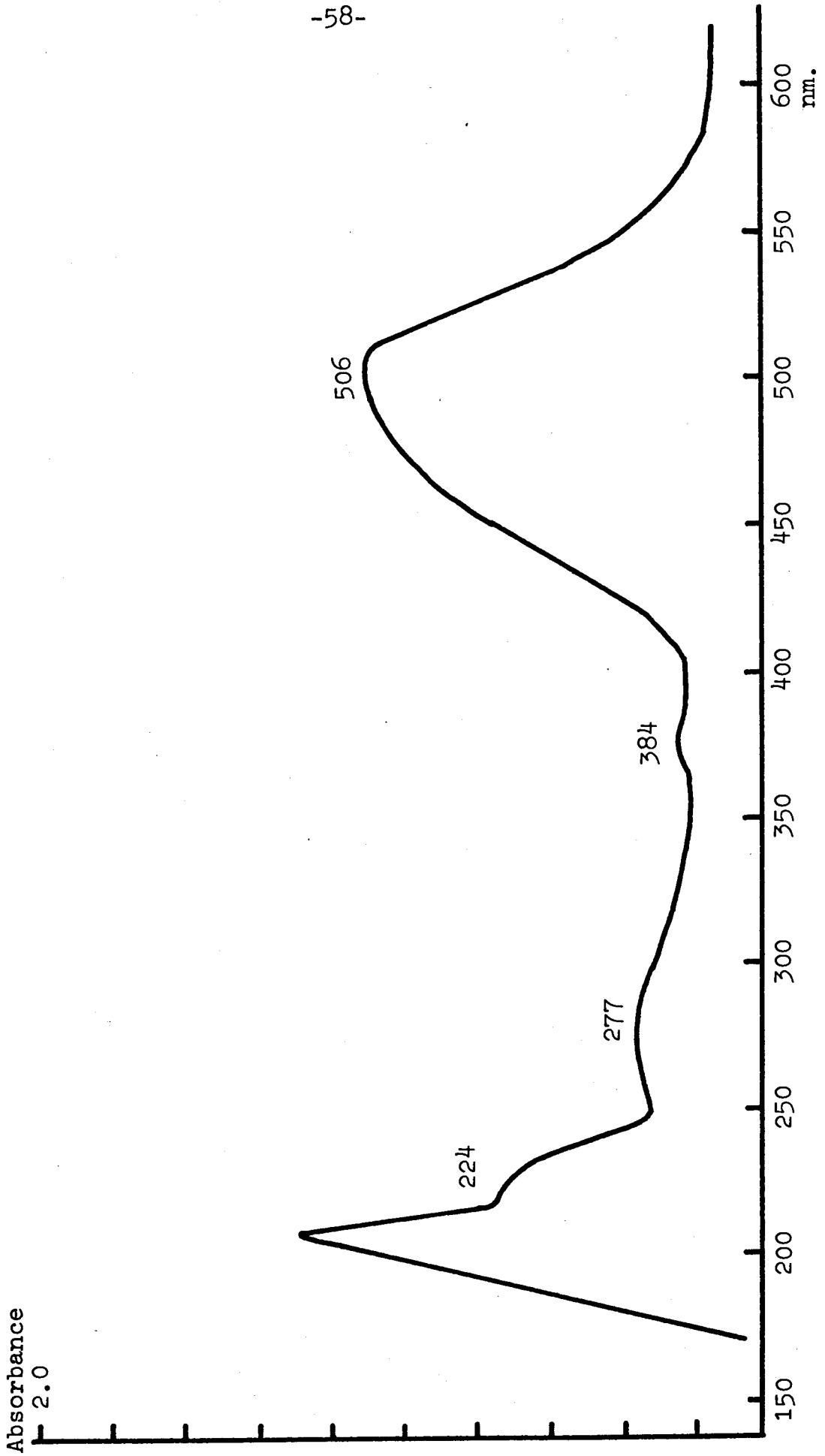


DIAGRAM 3-III. ELECTRONIC SPECTRUM OF $[p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNPPh}_3]^+ \text{BF}_4^-$.

TABLE 3-IV
ELECTRONIC SPECTRAL DATA IN ETHANOL SOLUTION

$p\text{-NEt}_2\text{C}_6\text{H}_4\text{NN}^+\text{BF}_4^-$	λ_{max} (nm)		$\epsilon \times 10^{-3}$
	PPh_3	$p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNPPh}_3^+\text{BF}_4^-$	
	cut off at <u>ca</u> 200 nm		
--	214 vs	224 sh	14
255 w br	265 s	277	6.3
381 vs	--	384	4.1
--	--	506	23

conjugated system as is evident from Fig. 3-II. The extinction coefficient for this absorption band is indicative of a $\pi^* \leftarrow \pi$ transition.

Nuclear Magnetic Resonance Measurements

The ^1H n.m.r. spectrum of this compound showed three main peaks centred at τ 8.76, 6.39 and 2.37 (Diag. 3-IV). The peak at τ 8.76 is due to a CH_3 group being split by CH_2 , and that at τ 6.39 to a CH_2 group being split by CH_3 . That at τ 2.37 is a multiplet due to aromatics. The peaks integrate in the ratio 20:14:56. The ratio should be 6:4:19, which is in reasonable agreement.

There is one further peak in the spectrum, occurring at τ 3.10 and integrating for one proton per six protons in CH_3 groups. This is a doublet of splitting 9 Hz. In the spectrum

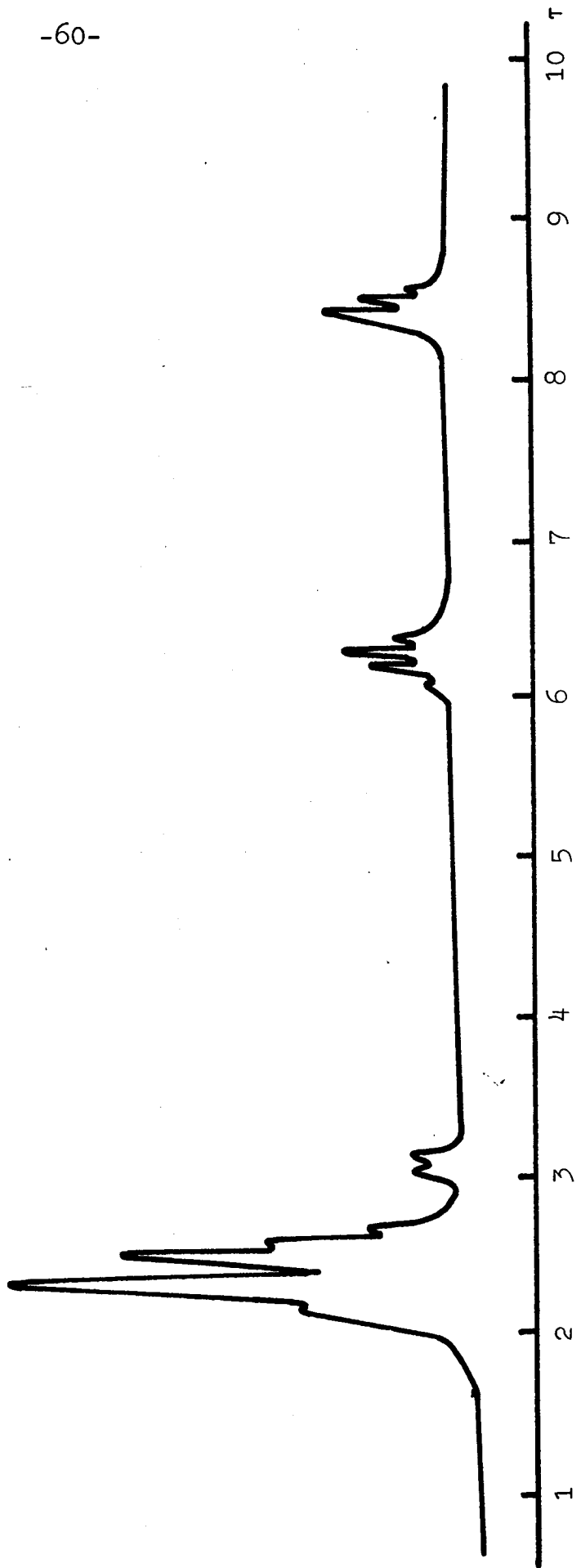


DIAGRAM 3-IV. N.M.R. SPECTRUM OF [p-NEt₂C₆H₄NNPPh₃]⁺BF₄⁻.

for the ^{15}N substituted compound, the peak becomes a triplet with the same splitting. The very small splitting rules out both N-H and P-H for this peak, since both normally have a splitting of a far greater magnitude. Why, however, this peak is a doublet with ^{14}N , and its associated quadrupole, and a triplet with ^{15}N , which has only a spin of $\frac{1}{2}$, remains a mystery. Consequently assignment of this non-equivalent proton cannot be made with any satisfaction.

Further Structural Evidence

In order to totally eliminate the possibility of the structures shown in Figs. 3-III and 3-IV the complex was prepared between \underline{p} - $\text{NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$ and tri(para-methoxy-phenyl) phosphine. This was chosen for two reasons: firstly, if the complex formed with triphenyl phosphine was bonded through the para position on one of the phenyl rings this would now be impossible without the loss of a methoxy group, and secondly, if it bonded through the ortho position instead, then the methyl protons of the methoxy groups would be chemically inequivalent and would show as such in the ^1H n.m.r.

On adding the two reactants together the familiar red colouration formed immediately. When the product was isolated and investigated by i.r. spectroscopy it was found to be identical to the triphenyl phosphine adduct, with the exception of peaks attributable to the para substituent. The analytical data was as follows: C 60.6%, calc. 60.6%; H 5.74 %, calc. 5.69%; N 6.95%, calc. 6.84%.

The n.m.r. obtained from this complex proved conclusively that the system was N-P bonded since, as can be seen from Diag. 3-V, the methyl protons of the methoxy groups are all equivalent and integrate for nine protons per molecule. Integration of the spectrum gives the ratio 64:32:16:24 for aromatics: methoxy protons: methylene protons: methyl protons. The ratio should be 64:36:16:24, and, consequently, little doubt is left about the structure of the complex. The aromatic region itself appears to be in four distinct absorptions integrating in the ratio 8:24:24:8, however, although this could be interpreted favourably for the structure, due to second order effects and the complexity normally observed for a AA'BB'X type spectrum the shape and integration observed seem quite coincidental.

Further experimental investigations showed that the adducts obtained with other diazonium salts with (p-CH₃OC₆H₄)₃P were decidedly more stable than those obtained with PPh₃. However a full investigation of all the salts has not been attempted.

Other Experiments

Since Wilkinson's catalyst (RhCl(PPh₃)₃) possibly dissociates to give free, or at least loosely bound, PPh₃ in its mechanistic route, it seemed a viable proposition to add p-NEt₂C₆H₄NNBF₄ to this compound. The two reactants were stirred in degassed benzene/acetone in an inert (N₂) atmosphere. However no immediate red colouration occurred as with Fe(CO)₃(PPh₃)₂, and only after 24 hours was there any sign of a red colouration. After 48 hours the solvent was stripped off and the resulting residue shown to

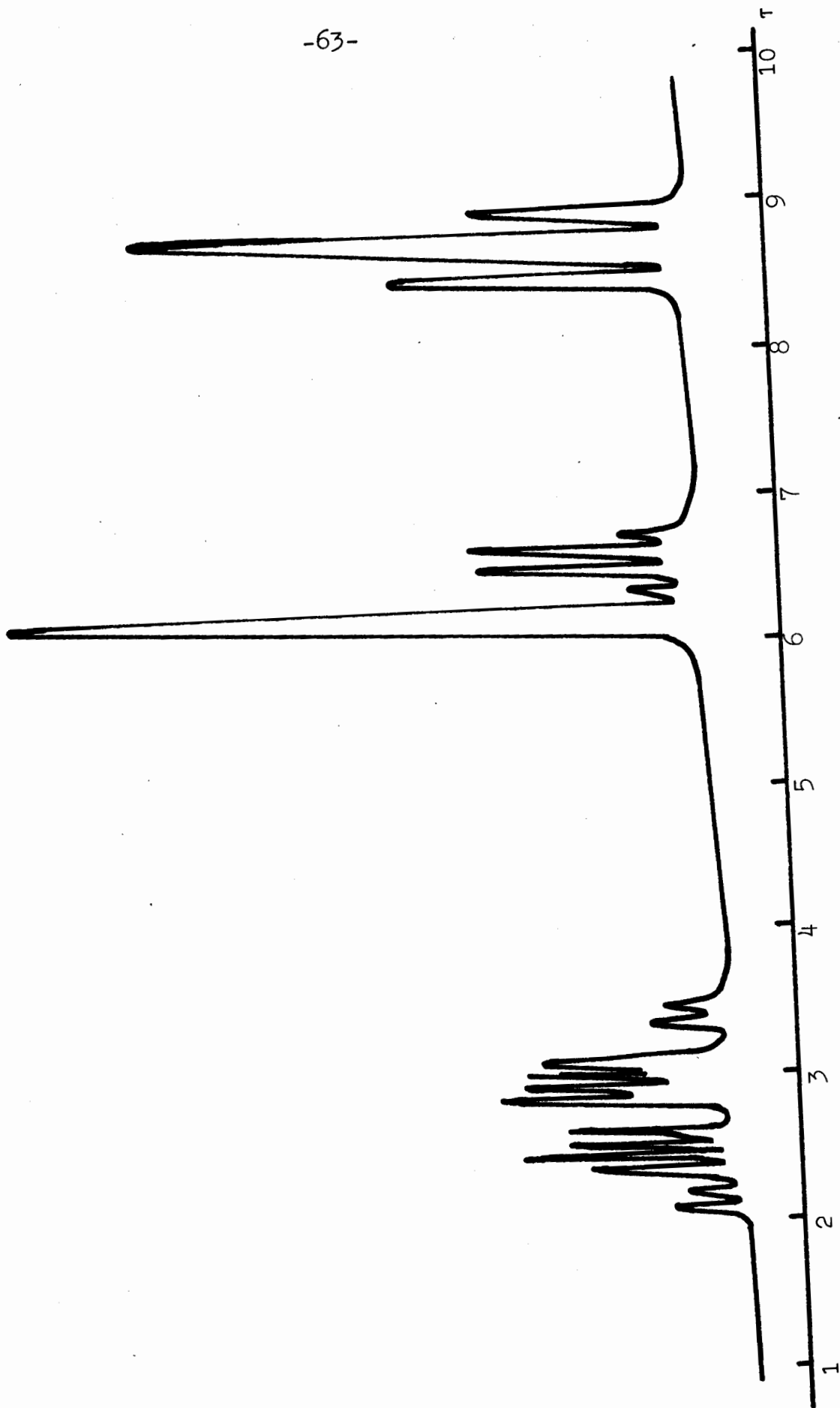


DIAGRAM 3-V. N.M.R. SPECTRUM OF $[(p-CH_3CC_6H_4)_3PNNC_6H_4NEt_2]^+ BF_4^-$.

contain an amount of $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNPPh}_3\text{BF}_4$. I.r. spectroscopy was utilised to show this.

From this evidence it appears that the suggested equation: -



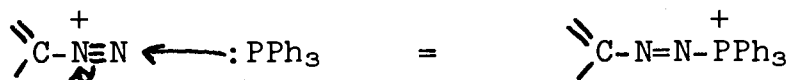
is either incorrect or else the equilibrium lies very far to the left. Whichever alternative is right it would appear that the suggested mechanistic route is in fact incorrect.

$p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$ was also added to $\text{PtCl}_2(\text{PPh}_3)_2$ and to $\text{PdCl}_2(\text{PPh}_3)_2$ using ethanol as the solvent in both cases. In neither case was there any sign of the phosphodiazonium salt produced.

Conclusion

It can be seen that the compound formed, initially by the reaction of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ with $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$, is a 1:1 adduct of PPh_3 with the diazonium salt. The salt resulting appears to be the only salt in the series that is stable at room temperature, and indeed one of the few isolable ones.

A proposed mechanism for the reaction involves σ -donation by the lone pair on phosphorus i.e.: -



However, it seems that for the complex to be stable, delocalisation of charge is essential: hence a +M substituent on the original diazonium salt is required. Equally, it would appear that a \underline{o} - or \underline{p} - +M or a \underline{o} - +I substituent on the phenyl rings of the PPh_3 would have a similar effect. This is supported by

the greater instability found when one of the phenyl groups of the phosphine is replaced by a methyl group, and the increased stabilities with (*p*-CH₃OC₆H₄)₃P.

Since the delocalisation can only be successful by the possible formation of a N=P bond requiring low lying vacant orbitals on the P atom (in this case 3d) this explains why NPh₃ reacts differently. Also, the vacant 4d and 5d orbitals of As and Sb respectively will form a far smaller overlap with the 2p orbital of the N in the order 2p-3d > 2p-4d > 2p-5d - hence the apparent fall off of reaction down the series. PPh₃ is of course a far better base than SPh₂, which might explain why SPh₂ is reluctant to react in the same way.

This series of compounds seems to fall into an unmapped area of a well studied field. Many similar compounds have been described in the literature. One of the pioneers of this study was H. Staudinger who published several papers⁵⁷⁻⁵⁹ on the series with general formula RR'R''P=N-N=CX₂: here X and R, R', R'' are aliphatic and aromatic groups, which may, or may not be identical.

More recently similar complexes have been made between C₅H₄N₂ and PPh₃⁶⁰ and between PPh₃ and the diazonium salt shown in Fig. 3-VIII⁶¹. However, it should be noted that in all these

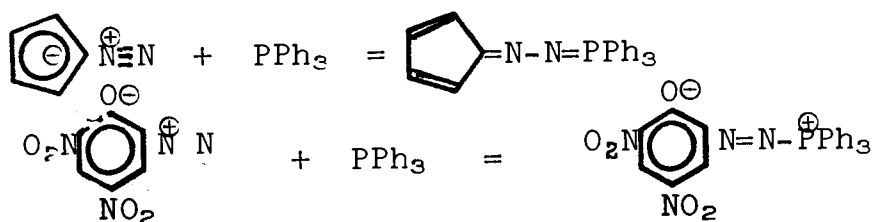


Fig 3-VIII

cases the final products have overall neutrality, even, though, as in the illustrated case, they are invariably zwitter-ions.

CHAPTER 4

EXPERIMENTAL PROCEDURES

Preparation of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$; Reaction of $\text{Fe}_3(\text{CO})_{12}$ with PPh_3 .

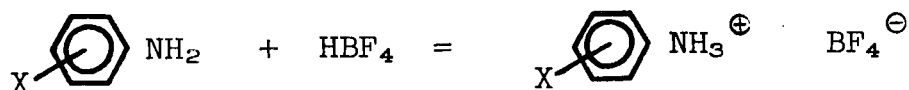
The procedure was that used by Clifford and Mukherjee⁶². An excess of PPh_3 (ca 10 g) was dissolved in 200 ml of tetrahydrofuran. To this 2.5 g $\text{Fe}_3(\text{CO})_{12}$ was added. This mixture was then refluxed in an inert atmosphere (N_2) until the green colour disappeared. On cooling, the solution was filtered and the filtrate reduced in volume to ca 20 ml in vacuo. 50 ml of ethanol was then added and the yellow crystals that resulted were filtered and washed with petroleum-ether. The solid was crystallised from benzene-ethanol, and shown to be $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ by analysis and i.r. spectroscopy.

Preparation of $\text{Fe}(\text{CO})_3(\text{PPh}_2\text{Me})_2$; Reaction of $\text{Fe}_3(\text{CO})_{12}$ with PPh_2Me .

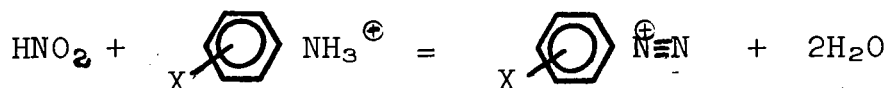
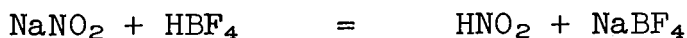
This reaction was performed as above, using PPh_2Me in lieu of PPh_3 and using a tenth scale of the quantities described above.

Preparation of Diazonium Salts

The reaction used was that described by A. Roe⁶³ viz. the tetrafluoroborate salt of the corresponding aniline was made in water by the addition of excess HBF_4 (aq.):



This aqueous solution was cooled to 0°C and then a similarly cooled solution of NaNO_2 was added dropwise, with stirring: -



The diazonium salt produced has comparatively low solubility at 0° C and was filtered off. The resulting crude product was then recrystallised from acetone-ether.

Reaction of p-BrC₆H₄NNBF₄ with Fe(CO)₃(PPh₃)₂

Fe(CO)₃(PPh₃)₂ (0.5 mM, 332 mg) was dissolved in 30 ml of deoxygenated benzene. This solution was stirred at room temperature under N₂ in a round bottom flask with a reflux condenser. p-BrC₆H₄NNBF₄ (0.5 mM, 136 mg) in 15 ml deoxygenated acetone was added dropwise and the resulting mixture was stirred for 2 hours. The solvent was then stripped off in vacuo leaving an orange residue. This residue was recrystallised from acetone-ether and shown to be [Fe(CO)₂(PPh₃)₂NNC₆H₄Br]⁺ BF₄⁻.

Reaction of XC₆H₄NNBF₄ With Fe(CO)₃(PPh₃)₂, (X = p-NO₂, p-F, p-Cl, p-OCH₃, p-OH and p-H)

These reactions were identical to the preparation of [Fe(CO)₂(PPh₃)₂NNC₆H₄Br]⁺ BF₄⁻ substituting p-BrC₆H₄NNBF₄ with the appropriate diazonium salt. In the case of the p-NO₂ salt 25 ml of acetone were required to obtain a solution.

Reaction of [Fe(CO)₂(PPh₃)₂NNC₆H₄Br]⁺ BF₄⁻ With NaI.

An excess of a saturated acetone solution of NaI was added to 0.5 mM of [Fe(CO)₂(PPh₃)₂NNC₆H₄Br]⁺ BF₄⁻ in 20 ml acetone

at room temperature. The mixture was stirred for 10 minutes. 200 ml water were then added and an orange precipitate of $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{Br}]^+ \text{I}^-$ was filtered off and washed with water.

Reaction of $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{Br}]^+ \text{BF}_4^-$ with H_2

1 mM of $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{Br}]^+ \text{BF}_4^-$ was dissolved in CHCl_3 (25 ml) and stirred at room temperature. Through the solution dihydrogen gas was bubbled at a rate of ca 5 ml min^{-1} for 24 hours. After this time the solvent was stripped off on the vacuum line and the resulting solid investigated by i.r. spectroscopy. Results showed that the solid was in fact the starting material. The reaction was repeated exactly with the addition of 0.02 g Pd/BaCO_3 to the reaction mixture. Again after 24 hours there was no evidence of the complex having been reduced.

Reaction of $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{Br}]^+ \text{BF}_4^-$ With NaBH_4 .

1 mM $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{Br}]^+ \text{BF}_4^-$ was dissolved in 25 ml $\text{C}_2\text{H}_5\text{OH}$ and to this solution was added 1.5 g NaBH_4 . The resulting mixture was stirred in an inert (N_2) atmosphere at room temperature for 24 hours. After this time the mixture was frozen with liquid nitrogen and transferred to the vacuum line. Here the products were distilled, and fractions collected in cold traps at -196° , -33° and -16°C . These fractions were then investigated by i.r. spectroscopy and mass spectroscopy. These results showed that reduction had occurred in this case;

the N=N bond was shown to have been hydrogenated to give p-BrC₆H₄NHNH₂ as the BH₃ adduct (trapped at -16° C) as well as many other unidentified products.

Reaction of p-Cl and p-BrC₆H₄NNBF₄ with Fe(CO)₃(PPh₂Me)₂

The procedure was similar to the reaction with Fe(CO)₃(PPh₃)₂, except that half scale quantities were used. However, due to the instability of the products, once the orange colouration appeared the whole solution was frozen with liquid nitrogen and freeze-dried on the vacuum line. (If the extraction was attempted at room temperature a brown solid was initially obtained: when subjected to attempted recrystallisation from acetone-ether, the solution became green within 5 minutes to yield a green solid.) Consequently the solid obtained from the freeze-drying could not be purified by recrystallisation, and was therefore washed with benzene and water and dried.

Reaction of [Fe(CO)₂(PPh₃)₂NNC₆H₄Br]⁺ BF₄⁻ with NO⁺BF₄⁻

1 mM of each of the two reactants were stirred together in 50 ml of acetone under an inert (N₂) atmosphere. 5 ml aliquots were withdrawn at 15 min intervals and the solvent stripped off in vacuo. The resultant residue was then washed with water, dried and investigated by i.r. spectroscopy.

Reaction of [Fe(CO)₂(PPh₃)₂NO]⁺ BF₄⁻ with p-BrC₆H₄NNBF₄

This reaction was performed twice. The first time the conditions were identical with the previous experiment described. The second case differed by the addition of 5 ml water to the


solution at the start of the experiment.


Reaction of $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{Br}]^+ \text{BF}_4^-$ with $\text{C}_5\text{H}_5\text{N}$

$[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{Br}]^+ \text{BF}_4^-$ (1 mM) was dissolved in 50 ml acetone to which 1 ml of pyridine was added. The mixture was stirred at 48° C in an inert (N_2) atmosphere. 1 ml aliquots were removed at specific times. These aliquots were dried in vacuo and investigated by i.r. spectroscopy.

Reaction of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ with $p\text{-BrC}_6\text{H}_4\text{NNBF}_4$ to Give Quantitative CO Measurements

A mixture of 40 ml of benzene and 10 ml acetone was totally degassed on the vacuum line. This mixture was then distilled in vacuo into the reaction vessel containing 1 mM $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ and 1 mM $p\text{-BrC}_6\text{H}_4\text{NNBF}_4$. The reaction vessel was then sealed and allowed to react with stirring for 24 hours. After this time the vessel was returned to the vacuum line, the seal broken and the volume of gas in the flask measured using a system similar to a Töepler pump. A sample of this gas was collected in a capillary tube and submitted to high resolution mass spectroscopy. The volume corresponded to 1.07 mM CO.

Reaction of $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NO}]^+ \text{BF}_4^-$ with X--NH₂

$[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NO}]^+ \text{BF}_4^-$ (0.5 mM) was added to 2 mM of X--NH₂, where X = NO₂, OCH₃, F, using 2,2-dimethoxypropane as the solvent. The mixture was stirred at room temperature for 24 hours, but no reaction was observed; the mixture was then refluxed for 24 hours, again with no sign of reaction, as shown by i.r. spectroscopy.

Reaction of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ with $\text{C}_6\text{H}_5\text{CN}$

$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ (0.5 mM) was dissolved in CHCl_3 (20 ml) and stirred at room temperature with 1 ml $\text{C}_6\text{H}_5\text{CN}$ in an inert (N_2) atmosphere for 48 hours. The solvent was stripped off in vacuo. The starting materials were recovered. The reaction was also tried in benzene (25 ml) under the same conditions with the same results.

Reaction of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ with $\text{C}_6\text{H}_5\text{NC}$

$\text{C}_6\text{H}_5\text{NC}$ was made in situ by the carbylamine reaction, i.e. KOH (100 mg) was dissolved in a minimum of ethanol and added dropwise to 25 ml CHCl_3 , in which 0.5 mM $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ and 1 ml $\text{C}_6\text{H}_5\text{NH}_2$ were dissolved. The resulting reaction mixture was stirred for 72 hours under an inert (N_2) atmosphere at room temperature. The solvent was then stripped off in vacuo and the starting material $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ recovered alone with $\text{C}_6\text{H}_5\text{NC}$.

Reaction of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ with $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$

$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ (0.9750 g) was dissolved in 30 ml benzene. To this solution $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$ (0.3750 g) dissolved in 10 ml acetone was added dropwise. The solution turned red immediately and later red crystals formed at the bottom of the reaction flask. After 2 hours of stirring at room temperature under an inert (N_2) atmosphere the solution was filtered. The filtrate was stripped of solvent in vacuo and the solid thus obtained was found to weigh 0.4747 g. From i.r. spectroscopy this solid was identified as $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$. From the weights recorded it was

calculated that for every mole of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ that reacts, 2.11 moles of $\text{p-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$ are needed, which within experimental errors is a 1:2 ratio.

Reaction of Diazonium Salts with PPh_3

PPh_3 (1 mM) was dissolved in 10 ml of acetone. To this, 1 mM of a concentrated acetone solution of the required diazonium salt was added, with stirring, at 0°C . In all cases the combined solutions immediately turned a deep red. However, in all cases, except p-OCH_3 and p-NEt_2 , gas evolution began at once in conjunction with a loss of colour. In each case a solid was obtained by recrystallisation by adding ether to the solution. Only the p-OCH_3 and p-NEt_2 analysed correctly as the diazo phosphonium moiety, the remainder analysing as the quaternary phosphonium salt of general formula $\text{Ph}_3\text{PAr}^+ \text{BF}_4^-$. The p-OCH_3 complex is only stable as a solid at 0°C and hence has to be kept in the refrigerator. The p-NEt_2 derivative is quite stable at room temperature as a solid.

Reaction of PPh_2Me with $\text{p-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$

PPh_2Me (1 ml) was mixed with an acetone solution of 0.3 mM $\text{p-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$ and stirred in an inert (N_2) atmosphere. A red colouration occurred immediately. After stirring for 1 hour the solvent was stripped off in vacuo. A red residue formed, but started to decompose slowly, both in vacuo and under 1 atm. pressure of N_2 . It did, however, last sufficient time for an i.r. spectrum to be obtained, although the spectrum was not well

defined.

Reaction of $(p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}$ with $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$

$(p\text{-CH}_3\text{OC}_6\text{H}_4)_3\text{P}$ ($\frac{1}{2}$ mM) was dissolved in 5 ml of acetone. To this $\frac{1}{2}$ mM of a concentrated acetone solution of $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$ was added with stirring. The red colouration occurred immediately. The solution was reduced in volume in vacuo and the resulting residue recrystallised from acetone-ether. The i.r. and n.m.r. spectra, together with analytical data showed that the complex was the 1:1 adduct.

Reaction of $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$ with $\text{PtCl}_2(\text{PPh}_3)_2$ and $\text{PdCl}_2(\text{PPh}_3)_2$

In both cases $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$ (1/10 mM) was added to the metal complex (1/10 mM) in 10 ml ethanol. The resulting solutions were stirred for 48 hours at which time there was no spectroscopic evidence of the phosphodiazonium salt having been synthesised.

Reaction of $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$ with $\text{Rh}(\text{PPh}_3)_3\text{Cl}$

30 ml benzene and 5 ml acetone were fully degassed in vacuo, and then distilled on the vacuum line into a reaction vessel containing 0.0925 g $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and 0.0263 g $p\text{-NEt}_2\text{C}_6\text{H}_4\text{NNBF}_4$. The reaction vessel was then sealed with a stir-bar inside and the mixture was stirred for 48 hours. After 18 hours a red colouration was observed, which gradually deepened. After 48 hours the vessel was returned to the vacuum line and the solvent removed. A red crystalline solid was obtained from recrystallisation with acetone-ether, and shown to be

[p-NEt₂C₆H₄NNPPh₃]⁺ BF₄⁻ by i.r. spectroscopy.

Reaction of p-NEt₂C₆H₄NNBF₄ with SPh₂, AsPh₃, SbPh₃, P(OCH₃)₃, P(OPh₃)₃ and OPPh₃

In all these cases ca 0.25 mM p-NEt₂C₆H₄NNBF₄ was added to an equimolar amount of the other reactant in 15 ml of acetone. The mixtures were then allowed to stir for 24 hours under a N₂ atmosphere. After this time only the solutions with SPh₂ and AsPh₃ showed any signs of reaction, having turned green and greenish-brown respectively. The solvent was stripped off on the vacuum line leaving an oil in both cases, neither of which gave a discernable i.r. spectrum. In all the other cases where there was no sign of reaction after 24 hours, the reaction mixture was allowed to stir from between another 72 hours and 2 weeks. In no case was there any evidence for a reaction having occurred (other than a small amount of the diazonium salt having decomposed), i.r. spectroscopy showing a retrieval of the starting materials.

Instrumentation Utilised

Infrared spectroscopy was investigated on the following instruments: - Perkin Elmer 457 for routine spectra, Beckman IR 12 for accurate wavenumber calibrations ($\pm 1 \text{ cm}^{-1}$). In both cases the samples were pressed in KBr.

Raman spectra ($\pm 1 \text{ cm}^{-1}$) on solid samples at room temperature were recorded using a Cary 81 spectrometer with unfocussed He-Ne laser excitation from a Spectra-Physics Model 125 laser producing 70 mW at source.

Proton n.m.r. spectra were recorded at 60 MHz and 100 MHz using Varian A-60 and HA-100 spectrometers: τ values are relative to $(\text{CH}_3)_4\text{Si}$ ($\tau = 10.0$) as internal standard. ^{31}P n.m.r. spectra were obtained at 40.5 MHz using the Varian HA-100.

Mössbauer spectra were recorded (by Dr. C. H. W. Jones of the Simon Fraser University Chemistry Department) with the absorbers at $80 \pm 1^\circ \text{K}$ and a $^{57}\text{Co}/\text{Pd}$ source (New England Nuclear, 10 mCi) at room temperature. A Technical Measurement Corporation constant acceleration spectrometer was used, providing 2 x 200 channel spectra. The spectrometer was calibrated using a N.B.S. Standard absorber: $\text{Na}_2 \text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ ($\Delta = 1.172 \text{ mm. sec}^{-1}$, $\delta (^{57}\text{Co}/\text{Pd}) = -0.442 \text{ mm. sec}^{-1}$)

Magnetic susceptibility measurements were made at room temperature on a Faraday apparatus calibrated against $\text{HgCo}(\text{NCS})_4$. The value obtained for the p- NO_2 iron complex at 85°K was kindly measured by Dr. G. W. Rayner Canham using the automatic variable temperature Faraday balance at York University, Ontario. The results obtained over the temperature range $85 - 280^\circ \text{K}$ are plotted in Diagram 4-I. The magnetic susceptibilities obtained by Evans¹⁴⁹ method were determined from the n.m.r. downfield contact shift of the methyl resonance of added t-butanol using the Varian A-60 and HA-100 spectrometers.

Molecular weights were determined from osmometric measurements on acetone solutions using a Perkin-Elmer Hitachi Model 115 calibrated with benzil. Electrical conductances were determined at room temperature using a standard conductivity meter. The cell constant was determined as 0.0095. Elemental analyses

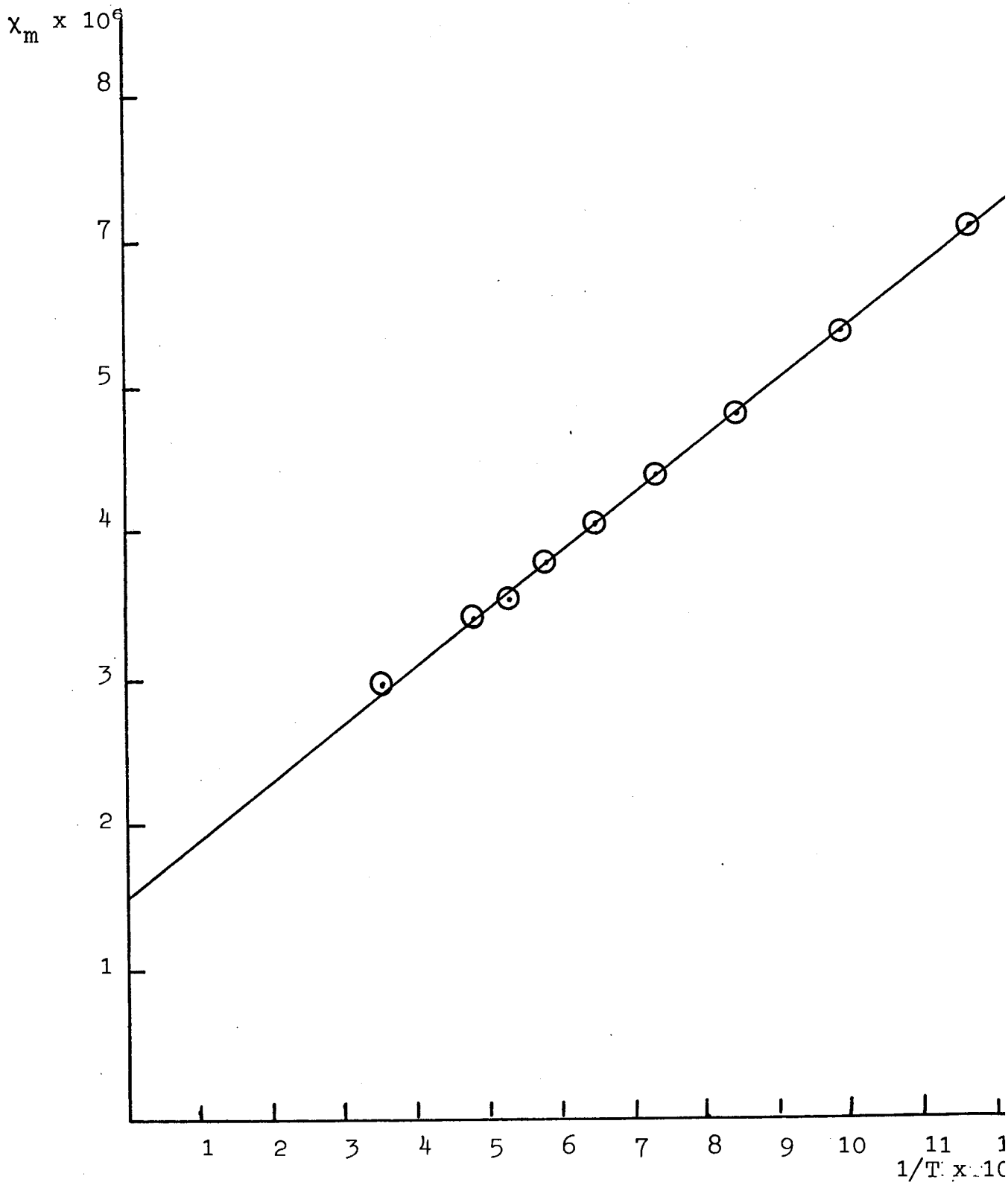


DIAGRAM 4-I. GRAPH OF MAGNETIC DATA FOR $[\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\text{NNC}_6\text{H}_4\text{NO}_2]^+$
 BF_4^- .

for non-metal content were determined by the S. F. U. Micro-analytical Laboratory, by A. Bernhard, Germany and Chemanalytics, Tempe, Arizona. Iron was determined by atomic absorption spectroscopy using a Perkin-Elmer Model 305.

Electronic spectra were performed on a Unicam SP800 spectrometer using ethanol solutions in quartz cells.

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