A STUDY OF THE SYNTHESIS, STRUCTURE AND POTENTIAL USES OF SOME COMPLEXES OF RHODIUM

by

IBRAHIM ISMAIL BHAYAT

A Thesis presented for the degree of
Doctor of Philosophy
in the
University of Aston in Birmingham

SEPTEMBER 1972

TO

PAKEEZAH

SUMMARY

The complexes of rhodium(III) halides with uni-, bi- and terdentate N-heterocyclic ligands such as 4-phenyl pyridine, 4-methyl pyridine, 2.2'-bipyridyl, 4.4'-diphenyl 2.2'-bipyridyl, 4.4'-dimethyl 2.2'-bipyridyl, 1-10-phenanthroline and 2.2'.2"-terpyridyl are synthesized and characterized by various physical techniques.

The rhodium(III) complexes with uni- and terdentate ligands are non-ionic while the complexes of bidentate ligands are ionic. The far infra-red spectra of these complexes are surveyed. It is concluded from the far infra-red study that when the ligand is of considerable molecular complexity e.g. terpyridyl, the assignments of V(RhX) (x = Cl, Br, I) are difficult. Also when the ligand is unidentate such as 4-methyl pyridine and 4-phenyl pyridine, differentiation of cis and trans isomers, using infra-red data alone is virtually impossible. However, far infra-red spectroscopy is more informative in the case of charged complexes. Thus cationic complexes e.g. $[Rh(chelate)X_2]^+$ are readily differentiated from the anionic $[Rh(chelate)X_4]$ (chelate = 2.2'-bipyridyl, 4.4'-diphenyl 2.2'-bipyridyl, 4.4'-dimethyl 2.2'-bipyridyl and 1-10-phenanthroline). It is also noted that the range of frequencies for V(RhBr) is considerable and that the useful relationship V(RhBr) = V(RhCl) x 0.78 does not hold because of the coupling of V(RhBr) and V(RhN) which are expected in the same spectral region for complexes of pyridine derivatives. The polymorphus of $[Rh(phen)_2.Cl_2].Cl$. α and ε are synthesized and it is found that the spectra did not appear to be sensitive to polymorphism.

The reduction of rhodium(III)-2.2'-bipyridyl (1:2) with sodium borohydride in methanolic medium under an atmosphere of nitrogen is studied and it is considered that the reduction proceeds via labile hydride intermediate species which can be trapped by addition of triphenyl phosphine   Addition of organic halides to this medium affords new complexes of the type $[Rh(bipy)_2.RX](ClO_4)$. When sodium borohydride is replaced by sodium amalgum the same compounds are formed. These complexes are considered to arise from the oxidative-addition of RX to a mono 2.2'-bipyridyl rhodium(III) species.

The reaction of $[Rh(chelate)_2\ X_2]\ x$ (chelate = 2.2'-bipyridyl, di-2-pyridyl amine and X = Cl, Br) in alkaline ethanol and in the presence of excess triphenyl phosphine is studied. The known compound $HRh(PPh_3)_4$ is isolated from this reaction. The reactions of $HRh(PPh_3)_4$ with dilute mineral acids are studied.

The reduction of nitrobenzene and nitrosobenzene by sodium borohydride in the presence of $Co(bipy)_3{}^{2+}$ is studied. The reaction products aniline and azobenzene are isolated and characterized. Evidence is considered to favour a hydride transfer mechanism for the reduction rather than the electron transfer process originally proposed by Vlček.

This work was carried out between
1968 and 1972 at The University of
Aston in Birmingham. It has been
done independently and has not
been submitted for any other degree.

I. I. BHAYAT.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to Dr. W. R. McWhinnie for his supervision and encouragement during the course of this study.

I should like to thank Dr. G. C. Kulasingam and Dr. J. D. Miller for many helpful suggestions and discussions.

My thanks go also to Mr. W. E. Sabin for making glassware, to Mr. M. C. Perry, for recording I.R.Spectra, to Mr. E. J. Hartland for the preparation of N.M.R. Spectra, to Mr. M. J. Houghton for recording mass spectra, to Mrs. B. Taylor for performing the elemental analysis, and to Dr. A. McCarthy and Mrs. M. M. Thorn for the X-ray powder photography.

I am most greatful to Mr. H. Khalfey, Mrs. Amina Khalfey and their children for creating a homely atmosphere during the course of this study.

Finally, I am indebted to the British Council for an Overseas Student's Fee Award.

CONTENTS

CHAPTER ONE

INTRODUCTION

The chemistry of coordination compounds has become a highly specialized branch of science in recent years. When two or more species associate together they form a compound known as a complex. If one of them is a metal ion then the product obtained is known as a metal complex. It is also known that the metal atom occupies the central position and in a complex it may be considered to form covalent bonds to its immediate neighbours accepting electron pairs from each ligand atom.

The ligand is thus the molecule which donates electron pairs in order to form complexes (Lewis base). There are some ligands which attach to the metal atom by more than one donor atom in such a way as to form a Heterocyclic ring.

An example of this ring is the one formed by glycinate ion [1].

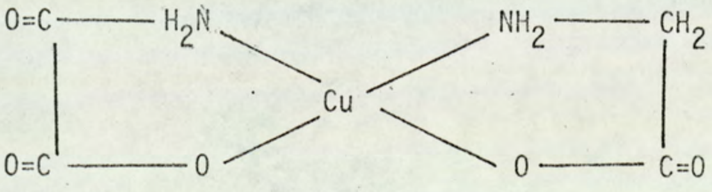
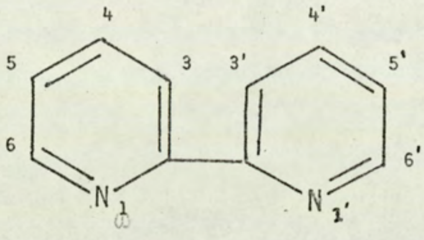


Fig.1

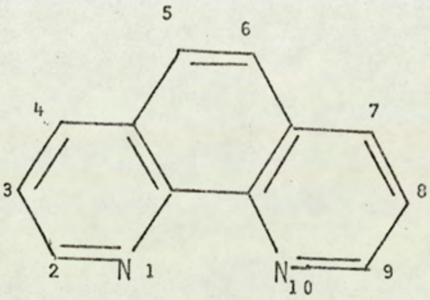
The ring is known as chelate ring and the molecule or ion which forms such a type of chelate ring is known as the chelating agent. There are so many ligands which form such chelate rings e.g. γ-hydroxy quinoline, ethylene diamine, acetyl acetonate, dimethyl glyoxime. Also organic heterocyclic molecules containing the -N=C-C=N- group such as

2-2'-bipyridyl 1-10-phenanthroline and also 2-2'-2"-terpyridyl have been known as chelating agents for many years.

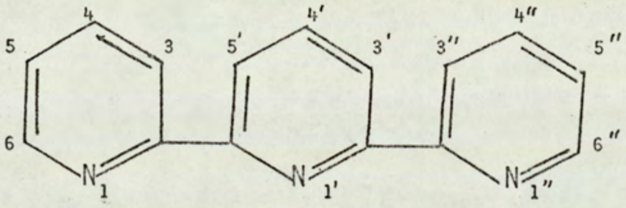
The term 2-2'-bipyridyl(1), 1-10-phenanthroline(2) and 2-2'-2"-terpyridyl(3) are the nomenclature and the abbreviation used are bipy, phen and terpy.



(1)



(2)



(3)

Fig.2.

These ligands are heterocyclic diamines (bipy and phen) and triamine (terpy) and have been studied and are used in making co-ordination compounds with many metals and are also used in analysis.

The ligands 2-2'-bipyridyl and 1-10-phenanthroline were first used as coordinating agents by Blau in 1888-1889. He first observed the reaction of 2-2'-bipyridyl and iron(II) salts with the formation of an intense red substance who then isolated in a salt as $Fe(bipy)_3^{2+}$. The molecule known as 1-10 diazaphenanthrene was prepared by Gerdeisson[2] and Blau[3] synthesized it and gave the name α-phenanthroline to compare its behaviour in the formation of metal complexes with 2-2'-bipyridyl. After 30 years Walden et al[4] made use of this coordination phenomenon in analytical chemistry. While the triamine-terpyridyl was first obtained as a by-product in the dehydrogenation of pyridine with ferric chloride[5]. It forms remarkable coordination compounds and Morgan and Burstall[6] prepared compounds of this ligand with many metal ions. It is now known that bipyridyl type chelate molecules are amongst the most versatile of coordinating agents in terms of the number and variety of their complexes.

2-2'-bipyridyl as a free ligand exists in a trans-planar configuration. The crystal structure[7] and dipolemoment study suggests that the rings in 2-2'-bipyridyl are co-planar but in the transposition. But in metal complexes the rings are in the cis-position.

1-10-phenanthroline has a cis structure and coordination occurs in such a way that the chelate ring containing the metal atom is coplanar with the rest of the molecule. N.M.R. studies for the bipyridyl and phenanthroline have been carried out in various solvents [10-20]. According to Castellano et al[10] bipyridyl shows different configurations in an inert and proton donor solvent. In an inert solvent the molecule is trans planar while in proton donor solvents mono and diprotonated species exist in transoid skew confirmations. While Spotswood and Tanzer[14] suggest no change from trans confirmation with solvent. While 1-10-phenanthroline is a rigid molecule. These ligands when coordinated to metal ions show small changes in the proton n.m.r. chemical shifts [10, 18-20].

2-2'-2" terpyridyl which is symmetrically planar can coordinate to a metal atom in an octahedral fashion surrounding it occupying 6-coordination positions as under:

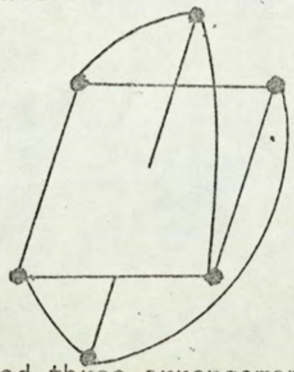


Fig. 3.

Morgan and Burstall suggested three arrangements of the two chelate molecule only one satisfies the coplanarity of the pyridine rings. According to Corbridge and Cox[21] the terpyridine molecule has been shown to remain flat when coordinated to zinc(II) ion. Thus dichloro terpyridine zinc(II) has a distorted trigonal bipyridyl structure, the chlorine atoms and central pyridine nitrogen atom occupying the equatorial plane.

2-2'-bipyridyl, 1-10-phenanthroline and terpyridyl are very weak bases and form monoprotonated species. Charlton[22] found typical values for the first stability constant (pka). The pka values at 25^{o}C for bipyridyl and phenanthroline are 4.5 and 4.8 respectively. 2-2'-bipyridyl forms high spin complexes with V(II), Mn(II), Co(II) but forms low spin complexes with Cr(II) and Fe(II)[23,24]. The corresponding phenanthroline has similar properties to their bipyridyl analogous. The <u>tris</u>-bipyridyl or phenanthroline Fe(II) complexes are anomalously high in the stability sequence. The step-wise formation constants for bipyridyl and phenanthroline complexes with divalent metal ions were obtained by Irving and Mellor[25]. They found that for Fe(II), the trend is $K_1 > K_2 < K_3$ and thus Fe(II) <u>tris</u> bipyridyl and phenanthroline complexes do not follow the usual Irving-Williams order of stabilities.

Jørgenson[26] obtained Δ values (ligand-field splitting parameter) for complexes with ethylenediamine, bipyridyl and phenanthroline and suggested that the spectro chemical position of 2-2'-bipyridyl and 1-10-phenanthroline is higher than ethylene-diamine. The Δ values for tris-complexes of ethylenediamine, bipyridyl and phenanthroline are $[Ni(en)_3]^{2+}$ = 11200 cm^{-1}; $[Ni(bipy)_3]^{2+}$ = 12650 cm^{-1} and $[Ni(phen)_3]^{2+}$ = 12700 cm^{-1}. 2-2'-2"-terpyridyl is believed to be a more highly conjugated amine than 2-2'-bipyridyl[27] and it behaves as a weak base. Mono and bis complexes of terpyridine with various metal ions have been studied by Hogg and Wilkins[28].

These ligands form complexes with many metal ions in their normal oxidation states (+2, +3 are normal oxidation states). However, both 2-2'-bipyridyl and 1-10-phenanthroline complexes, generally $[ML_2]^{n+}$ or $[ML_3]^{n+}$ (where L = 2-2'-bipyridyl or 1-10-phenanthroline)can be reduced giving stable species with the same formula but with charges of +1, 0 or -1. It is thus generally accepted that molecules such as 2-2'-bipyridyl or phenanthroline stabilize low oxidation states by functioning as electron donors as well as electron acceptors due to the presence of delocalized Π-orbitals associated with their aromatic ring systems. Herzog and his co-workers [29] have prepared many bipyridyl complexes with metal ions in their low oxidation states and classified bipyridyl or phenanthroline as a Π-acid type ligands. It is also known that terpyridyl gives similar complexes.

Bipyridyl and phenanthroline also stabilize high oxidation states which can be explained by their ability to denote electrons and by chelate effect rather than the ability to accept electrons from metal ions. Complexes of many metal ions in their high oxidation states such as Vanadium, Manganese, Tungsten, Silver[30-36] have been reported in recent years.

The substitution of other groups for hydrogen in 2,2'-bipyridyl and 1-10-phenanthroline may lead to increased stability of the metal complexes due to increased basic strength or Π-acceptor properties of the ligand. While on the other hand stabilities of metal complexes can be lowered because of the lower basic strength of ligands or by virtue of steric hinderance caused by substituent groups[37,38,39]. The substitution of the electrophilic bromo or nitro group in the 4-4' position of 2,2'-bipyridyl or 4-7 position in phenanthroline lowers the basic strength and hence reduces the stabilities of metal complexes. However, methyl substituents in these positions should increase the stabilities.

Qualitative investigations have been carried out for the effect of substitution of methyl groups in the phenanthroline ring upon the stabilities of Fe(II) and Cu(II) complexes [40,41] and it has been found that the order of stabilities is as under:

4-7 position > 5-6 position > 3-8 position

while in the case of 2,2'-bipyridyl, substituents in 3-3'-position make such a change in chelating ability that either no complex is formed or the complex of low stability.

The element Rhodium is the member of Group-VIII - transition elements and is in the second row of the transition series. It belongs to the Platinum group metals which are Ruthenium, Osmium, Rhodium, Iridium, Platinum and Paladium. Its electronic configuration is 2, 8, 18 | 2, 6, 8 | 1 and is considered as a d block element. Rhodium chemistry centres mainly around the valence states one and three. Oxidation state one in square planar complexes of rhodium is important and complexes in oxidation state one are obtained with Π-acid ligands such as carbon monoxide, tertiary phosphines, tertiary arsines, stabines, and alkenes. These complexes are coordinatively unsaturated and have been found effective catalysts for the homogeneous hydrogenation of alkenes and alkynes [42].

Oxidation state three is more common and more extensively studied in the field of rhodium chemistry. A large number of octahedral complexes: cationic, neutral and anionic are known for this metal with all types of ligands. Rhodium forms stable ionic and neutral complexes with pyridine, 2-2'-bipyridine, 1-10-phenanthroline and their substituted derivatives.

It is now known that the rhodium(III) ion can coordinate one, two or three molecules of 2-2'-bipyridyl. Jaeger and Van Dijk[43] first described rhodium(III) compounds with 2-2'-bipyridyl. They reported different compounds, their preparations and isolations. According to them a yellow compound with the formula $[Rh(bipy)_2.Cl_2].Cl$, an impure (now it is recognised as such) <u>tris</u> chelated brown compound with the formula $[Rh(bipy)_3.Cl_3]$ and a number of less characterized mono chelated compounds with varying amounts of ionizable chlorine were obtained by the reaction of rhodium(III) chloride and 2-2'-bipyridyl. In many experiments a sparingly soluble pink compound $Rh_2bipy_3Cl_6$

was obtained in which rhodium is in both cation and anion and can be formulated as $[Rh(bipy)_2.Cl_2][Rh(bipy)Cl_4]$. While Martin and Waind[44] used different procedures for the preparation of rhodium(III) complexes with bipyridyl. They isolated both bis and tris complexes by a simple fusion of rhodium(III) chloride and 2-2'-bipyridyl. Harris and McKenzie[45] also described varieties of coloured chelated salts.

Rhodium(III) complexes of 1-10-phenanthroline are known and were obtained as bis-chelated compounds with formulations such as $[Rh(phen)_2.\ X_2]\ X\ nH_2O$ and as mono chelates $[Phen\ H]\ [Rh\ phen\ X_4]$ where X = Cl, Br, I[46,47]. Bis-terpyridyl complexes of rhodium(III) have been synthesized [45] to interpret colours of these compounds in terms of charge transfer from the anions to the colourless cations. No other information was available with regard to rhodium(III) terpyridyl complexes.

More recent studies on rhodium(III) complexes with these chelate forming ligands such as 2-2'-bipyridyl and 1-10-phenanthroline mainly centre around their more convenient preparative methods and stereochemistry of these complexes [46,48,49,50]. Attempts have been made to prepare pure compounds containing the $[Rh(bipy)_2.Cl_2]^+$ cation[43] but the products described in the above preparation are difficult to separate from other reaction products. Also tris-bipyridyl rhodium(III) trichloride obtained by Martin and Waind[44] was an impure product. In these preparations when alcohol was used as a solvent to dissolve 2-2'-bipyridyl, the formation of little amount of $[Rh(bipy)_2.Cl_2]^+$ cation is mainly due to the catalytic effect of alcohol. It has also been found that when acetone is used to dissolve the ligand, $[Rh(bipy)_2.Cl_2]^+$ cation is formed very slowly and in lower yield. The addition of a little alcohol catalyses the reaction and formation of the carbon takes place rapidly.

Delepine[51] has showed that ethanol and other alcohols catalyse the formation of trans-dichloro tetrapyridine rhodium(III) cation, thus rapid preparations of rhodium(III) species can be carried out by using alcohol as a solvent. Gillard and Wilkinson[52] have found that in the absence of alcohol only trichloro tripyridine rhodium(III) can be obtained by the reaction of rhodium tricloride and pyridine in water. This can be easily converted catalytically to tetrapyridine salt by using hypophosphorous acid, sodium hypophosphite or hydrazinium chloride in a hot solution. Thus ethanol and other reducing agents are widely used in the preparation of rhodium(III) complexes.

Also hydrochloric acid may be used to synthesize mono chelated compounds such as $[bipyH][Rh\ bipy\ Cl_4]$ and $[phen\ H][Rh\ phen\ Cl_4]$. [50,53]. The use of acid conditions manitains a low concentration of 2-2'-bipyridyl or 1-10-phenanthroline and at the same time a high concentration of bipyridilium or phenanthrolium ion. This favours the synthesis of mono complexes. These complexes can readily be converted to bis-chelated complexes in ethylene glycol[53].

Formerly the cation $[Rh(phen)_2.Cl_2]^+$ together with the analogous bipyridyl compound and also their bromo-analogues have been assigned a trans-octahedral geometry on the basis of their ability to form an adduct with hydrochloric acid [47,48]. Also on the basis of catalytic formation of these cations in the presence of ethanol, trans-stereochemistry has been suggested[54]. It is well established that trans complexes afford adducts with acids more rapidly than the cis-complexes. This is not reliable evidence to suggest trans-stereochemistry for these complexes.

On steric grounds these compounds with the formula $[M(chelate)_2 X_2] X$ (where chelate = 2.2'-bipyridyl or 1-10-phenanthroline and X = Cl, Br or I) can be regarded as having the cis-configuration. McKenzie[55] suggested that for the phenanthroline or bipyridyl molecules in planar coordination there is considerable steric interaction between the hydrogen atoms of opposite ligands. Thus in an octahedrally coordinated metal complex this steric hindrance would lead to increased stability of the cis over the trans isomer of a complex $[M(chelate)_2 X_2]^{n+}$.

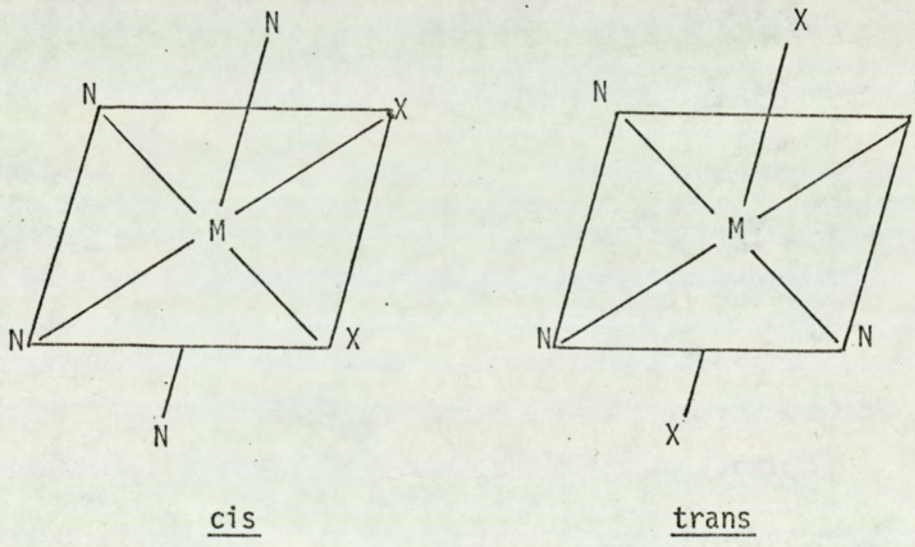


Fig. 4.

Palade[56] also carried out geometric analysis of the complex trans $[Co(phen)_2.Cl_2]^+$ and suggested that the repulsion of ortho hydrogen atoms of the phenanthroline molecules makes its existence impossible.

Using the x-ray powder technique the cations: $[Rh(chelate)_2\,X_2]^{2+}$ have been shown to be cis [48,50]. The compounds $[Co(phen)_2.Cl_2].Cl$ and $[Cr(phen)_2.Cl_2].Cl$ and analogous bipyridyl compounds have been known from their x-ray structural analysis and solid state spectra to be cis[57]. Rhodium forms analogous compounds with different crystallisation forms, α, β and ε. According to McKenzie et al[50] the preparative methods for $[Rh(phen)_2.Cl_2]Cl$ gave one or the other of crystalline forms of cis isomer. No other isomerism probably trans occurs. Far infrared and Raman investigations have been carried out to distinguish cis and trans configurations.[48,49]. On the basis of rhodium-halogen frequencies in these complexes: $[Rh(bipy)_2\,X_2]\,X$ $[Rh(phen)_2.X_2]\,X$ (where X = Cl or Br), the cis-stereochemistry has been assigned. Also cis-configuration is suggested for $[Rh(phen)_2.Cl_2]^{2+}$ cation from its 'H n.m.r. studies[49] which gives similar spectrum to that of $[Co(phen)_2.Cl_2].Cl$. Thus after a number of earlier assignments of configuration without having any concrete evidence it is now generally accepted from the above techniques and other studies that the cations $[Rh(phen)_2\,X_2]^{2+}$ and $[Rh(bipy)_2\,X_2]^{2+}$ where X = Cl. Br or I) have the cis-configuration.

Reaction of transition metal complexes, especially those of rhodium [58-61] and Iridium [59,62,63,64] with reducing agents has lately been of interest and extensively investigated. Reducing agents used are sodium borohydride, sodium amalgum, hypophosphorous acid, alcohol, alcoholic potassium hydroxide and molecular hydrogen. The action of these reducing agents on rhodium(III) systems can be classified into three categories:

(i) The catalysis of the formation of rhodium(III) complexes.

(2) The formation of hydrido rhodium(III) complexes by the formation of hydride H^- ion.

(3) The reduction of tervalent oxidation state of rhodium(III) complexes to lower valence state.

The first type of behaviour can be found in the synthesis of rhodium(III) complexes by catalytic action of alcohols. The preparation of dichloro tetrapyridine(III) complex in the presence of alcohol is known to be a catalytic reaction [51]. Rund has suggested a mechanism for the formation of this salt by the catalytic effect of a reducing agent[65]. According to him the reducing agent was thought to produce rhodium(I) which being labile rapidly underwent substitution by pyridine ligands. This being a planar rhodium(I) complex, it then formed a bridged imtermediate with an inert rhodium(III) ion.

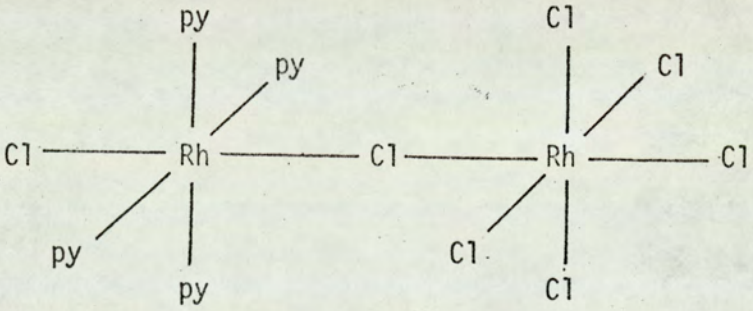


Fig. 5.

Finally, the two rhodium atoms exchanged oxidation states giving the product and a new molecule of rhodium(I) catalyst. Dwyer[37] observed intensely coloured violet solutions by treating mixtures of rhodium trichloride and 2-2'-bipyridyl in methanol with zinc amalgum. This was found to turn rapidly yellow in air. Martin et al[58] reported that the reduction of rhodium(III) bipyridyl complexes with sodium amalgum or with alkaline sodium borohydride in an inert atmosphere gives low valent complexes. The complexes are:

(1) $[Rh(I)(bipy)_2(ClO_4).3H_2O]$

(2) $[Rh(I)(bipy)_2(NO_3).\ 3H_2O]$

(3) $[Rh(II)(bipy)_2.Cl.NO_3.2H_2O]_n$

(4) $[Rh(II)(bipy)_2.Cl.CLO_4.2H_2O]_n$

known. It has been found that complexes (1), (3) and (4) are diamagnetic and complex (2) is paramagnetic. All these complexes form the same species, probably $[Rh(bipy)_2(H_2O)_2^+]$ in dilute ethenolic solution.

The kinetics of the reduction of $[Rh^{III}L_2Cl_2]^+$ cations (where L is bipyridyl, phenanthroline or their substituted derivatives) in alkaline ethenolic solution at 60° under a hydrogen atmosphere were investigated by following the rate of $[Rh^{I}(L)_2]^+$ production spectrometrically. An autocatalytic mechanism with hydrogen gas as the reducing agent is suggested [66].

The behaviour of rhodium(III) systems containing other nitrogen ligands with sodium borohydride in aqueous solutions contrast sharply with the reactions of rhodium(III) bipyridyl systems.[60]. Aqueous solutions of dichloro<u>bis</u>ethylene diamine rhodium(III), dichlorotriethylenetetreamine rhodium(III), dihelogenotetrapyridine rhodium(III) and chloropentaamine rhodium(III) complexes react with sodium borohydride to give hydrido complexes. In all these cases nucleophilic displacement of the halogen ion by hydride ion takes place[60,61]. Evidence for hydride species is obtained both by infra red and proton magnetic resonance spectroscopy. The following table shows some hydride complexes of rhodium(III) with Nitrogen ligands.

Hydridoamine complexes of Rhodium(III)[60]

Compound	$V(M\text{-}H).cm^{-1}$	$\tau(M\text{-}H)$
cis-$[Rh\ HCl\ trien]^+$	2081	28.5, doublet, J_{Rh-H} = 27c/s
cis-$[Rh\ H_2.\ trien]^+$	-	27.1, doublet, J_{Rh-H} = 30c/s
trans-$[Rh\ HCl\ en_2]^+$	2093-2100	31, doublet, J_{Rh-H} = 31c/s
$[Rh\ H(NH_3)_5\ ]^{2+}$	2079	Solution was too dilute
trans-$[Rh\ Cl_2(DMG)_2]^- + BH_4$	-	26.4
trans-$[Rh\ Cl_2py_4]^+ + BH_4$	-	28.6

Both cis-and trans-$[Rh\ Cl_2\ en_2]^+$ yield the same hydride species on treatment with borohydride. The tetraphenylborate precipitate is chloride free. These facts suggest the following displacement reactions:

$$\begin{tikzcd}
\text{cis-or trans-}[Rh\ Cl_2\ en_2]^+ \arrow[r, "B\bar{H}_4"] & \text{trans-}[Rh\ HCl\ en_2]^+ \arrow[d, "B\bar{H}_4"] \\
 & \text{cis-}[Rh\ H_2\ en_2]^+
\end{tikzcd}$$

Trans-stereochemistry has been assigned to the monohydride cation because of the ready replacement of the second chloride. Cis stereochemistry is indicated for the dihydride by the τ value of its high field line, which is considerably greater than would be expected for a trans-dihydride.

The products obtained from the reaction of bis-bipyridyl rhodium(III) complexes correctly formulated as rhodium(III) complexes rather than hydrides[58,60]. Tris bipyridyl cobalt(II) ion as well as rhodium(III) amine complexes which form hydrides, catalyze the reduction of aromatic nitro compounds by borohydride [67,68]. This reduction may take place by hydride transfer via the catalyst is suggested by the fact that quinone is reduced to hydroquinone on shaking it with an aqueous methanotic suspension of [Rh HCl trien][BPh_4]. The presence of Co-H bonds can be suggested by rapid isomerization of trans-[Co Cl_2 en_2]Cl to cis-[Co Cl_2 en_2].Cl by sodium borohydride via intermediate hydrido species.

CHAPTER TWO

EXPERIMENTAL

(A) CHEMICALS

Rhodium trichloride trihydrate was obtained from Johnson Matthey and Co. 4-phenyl pyridine was purchased from 'The Koch-Light Laboratories Ltd.'England and was used without further purification. 4-methyl pyridine was obtained from B.D.H. and purified by drying over sodium hydroxide pellets and redistilled before use. 2.2'-bipyridyl, 4.4'-dimethyl 2.2'-bipyridyl and 2,2':6',2"-terpyridyl were obtained from I.C.I. (Dyestuffs) as a gift. 2.2'-bipyridyl was purified by steam distillation and recrystallised from water-ethanol. 4.4'-dimethyl 2.2'-bipyridyl was recrystallised from water-ethanol mixture before use. 2.2':6' 2"-terpyridyl was used with no further purification. 4.4'-diphenyl 2.2'-bipyridyl was synthesized by the procedure of Sasse and Carrey[69]. 1-10-phenanthroline monohydrate was purchased from B.D.H. and was used with no further purification. The triphenyl phosphine was obtained from Albright and Wilson Limited and was recrystallised from benzene-ethanol before use. (The triphenyl phosphine used after purification showed no mass spectroscopic evidence of contamination with triphenyl phosphine oxide) The triphenyl phosphine oxide was purchased from Phase separations Ltd. Sodium borohydride was obtained from B.D.H.Chemicals Ltd. and was kept in the sealed bottle. The other chemicals used were all A.R. grade.

(B) SOLVENTS

All the solvents used were reagent grade and were purified by the literatur methods.

The procedure adopted for the purification and drying of each solvent was as under:

(1) Ethyl Alcohol

Ethyl alcohol (ethanol) used was obtained as commercially available 'absolute alcohol' and was used without further purification.

(2) Methyl Alcohol

Anhydrous calcium sulphate was added to the methyl alcohol (methanol) and also kept for a few days. The methanol was then decanted and filtered to get a clean solvent. The methanol was then distilled under reduced pressure. The pure methanol obtained was kept over molecular sieves (type 3A) as a drying agent.

(3) Nitrobenzene

The nitrobenzene was treated with sulphuric acid to remove the impurities and was then separated and distilled. It was then dried with calcium chloride and redistilled under reduced pressure.

(4) Nitromethane

Phosphorous pentoxide was added to the nitromethane and then it was kept for a few days. The nitromethane was then decanted from the phosphorous pentoxide and centrifuged to remove any trace of phosphorous pentoxide. Finally the nitromethane was distilled under reduced pressure with great care. Pure nitromethane has a boiling point of 101^o - 102^oC. (760 mm Hg).

(5) Dimethyl Sulphoxide

Dimethyl sulphoxide was refluxed for several hours in contact with calcium oxide. It was then distilled through a fractionating column under reduced pressure.

(6) Chloroform

The chloroform was shaken five to six times with a small volume of concentrated sulphuric acid. It was then thoroughly washed with water, dried over anhydrous calcium chloride. Finally the chloroform was distilled and pure chloroform which has a boiling point of 61^oC at 760 mm was kept in the dark to avoid photochemical formation of phosgene.

(7) Carbon tetrachloride

The carbon tetrachloride was treated with potassium hydroxide dissolved in an equal weight of water and rectified spirit (100 ml). The mixture was vigorously shaken for 30 minutes at 50^o-60^oC. After washing with water, the process was repeated with half the quantity of potassium hydroxide. The alcohol was then removed by shaking several times with water (500 ml), followed by shaking with small portions of concentrated sulphuric acid until there was no colouration. The carbon tetrachloride was then washed with water, dried over anhydrous calcium chloride and distilled.

(C) INSTRUMENTAL TECHNIQUES

(a) SPECTRA

(1) Diffuse Reflectance spectra

Diffuse reflectance spectra (50250-11050 cm^{-1}) were recorded for finely powdered specimens using a Unicam SP 800 spectrophotometer.

(2) 'H nuclear magnetic resonance spectra

'H nuclear magnetic resonance spectra at 100 MH_z were recorded for nitromethane or chloroform solutions of complexes using TMS as an internal reference, with a Perkin Elmer R.14 instrument.

(3) Mass spectra

Mass spectra were recorded at 70 ev with an AEI MS9 mass spectrometer.

(4) Infra-red spectra

Infra-red spectra were recorded for nujol mulls in caesium iodide supports between 4000 cm^{-1} and 250 cm^{-1} with a Perkin Elmer 457 instrument.

(5) Far infra-red spectra

(i) Far infra-red spectra were recorded for nujol mulls in caesium supports in the region of 400 cm^{-1} and 200 cm^{-1} with a Perkin Elmer 225 spectrometer.

(ii) Far infra-red spectra in the region of 400-60 cm^{-1} were recorded for nujol mulls in polythene plates with RIIC Fourier spectrophotometer (RIIC FS 720). The entire optical system is enclosed and evacuated to a pressure of less than 0.1 in order to prevent atmospheric water vapour absorption. The output from the interferometer was computed using the University ICL 1600 computer.

(b) X-RAY POWDER PHOTOGRAPHS

X-ray powder photographs were taken with Cu(K)α radiation. The "Solus-Schall" London generator and "Phillips" camera were used.

(c) CONDUCTIVITY

Molar conductivities of freshly prepared solutions were determined with a Mullard conductivity bridge, using standard conductivity cell type E 7591/B and cell constant 1.36. 10^{-3} molar solutions were prepared in purified nitromethane and in some cases, in dimethyl sulphoxide for the measurement of conductivity.

(d) ANALYSIS

Microanalysis for carbon, hydrogen and nitrogen were carried out by Mrs. Taylor, Microanalytical Laboratory, Chemistry Department, Aston University; Dr.F.Strauss, Microanalytical Laboratory, 10 Carlton Road, Oxford; and also by A.Bernhardt, 5251 Elbach Uber Engelskirchen, West Germany. The analyses which were done within this department were carried out on F and M Scientific Instrument, Model "185", C.H.N. auto-analyser. The carbon, hydrogen and nitrogen were analysed on F and M instrument by the combustion of sample on a combustion bar (with flux at the end) and the gas produced, followed by gas-liquid chromatographic analysis.

CHAPTER THREE

PREPARATIONS AND SPECTROSCOPIC STUDIES OF RHODIUM(III) HALIDE COMPLEXES WITH NITROGEN HETEROCYCLIC LIGANDS

(A) INTRODUCTION

Infrared spectroscopy has become increasingly important as a technique for studying metal-ligand bonding in Inorganic and Co-ordination compounds. Commercially available far-infrared spectrometers operating in the region of 400-20 cm^{-1} provide a valuable tool for the examination of many different types of systems including the study of weak interactions and the vibrational spectra of heavier mass systems. Metal-ligand vibrations can be included in the latter category. Direct examination of ligand-metal and metal-halogen vibrations is a more satisfactory way of determining the structure of complexes of transition metal ions of the first row. When the metallic element is heavier it is often difficult to elucidate the structure on the basis of infrared due to the reduced coupling of vibrations.

For the chemistry of rhodium(III) complexes there is little positive information available for the assignments of rhodium-bromine and rhodium-iodine vibrations when the ligands attached to the rhodium(III) halide are complex derivatives of pyridine. Even for the rhodium-chlorine frequencies in the complexes of bis-chelated rhodium(III) (where chelate = 2.2' bipyridyl and 1-10-phenanthroline), there is a controversy about the precise location of rhodium-chlorine bands[47,48].

It has been found that the study of the co-ordination chemistry of rhodium has been hampered by the slow and often inconvenient preparative methods required, and by the inert nature of the complexes formed. In this section synthesis of rhodium(III) complexes which are convenient and quickly performed are presented. This section deals with the preparations and characterisation and spectroscopic studies of rhodium(III) complexes with 4-phenyl pyridine, 4-methyl pyridine, 2.2'-bipyridyl, 4.4'-diphenyl, 2.2'-bipyridyl, 4.4'-dimethyl, 2.2'-bipyridyl, 1.10-phenanthroline and 2.2'.2"-terpyridine. The complexes of rhodium(III) with 2.2'-bipyridyl and 1.10-phenanthroline which have been known previously [44-50] are also prepared for the assignment of rhodium-chlorine vibrations more positively. The structure of these complexes and cis-trans isomerism can also be established with the use of V(RhX) assignments (where X = Cl,Br,I).

(B) PREPARATION OF COMPLEXES

(a) Rhodium(III) halide complexes with 4-phenyl pyridine

(1) Trichloro Tris (4-phenyl pyridine) rhodium(III)

Rhodium trichloride trihydrate (0.26 gm 1 m mole) was dissolved in water (5 ml) and to this a solution of 4-phenyl pyridine (.62 gm 4m mole) in ethanol (20 ml) was added. The fawn (pinkish) product was heated under reflux. The product redissolved on refluxing and the colour of the solution changed from brownish-yellow through red-brown to orange yellow. On further refluxing orange crystals deposited. After about 90 minutes of refluxing the orange product was filtered through a sintered glass crucible (porasity -4) while the solution was still hot. The orange crystals were washed with hot ethanol several times. It was then dried over P_4O_{10} under vacuum.

Found: C,58.3%; H,4.0%; N,6.3%

$C_{33}H_{27}Cl_3RhN_3$

Requires:C,58.8%; H,4.0%; N,6.2%

(2) Tribromo Tris (4-phenyl pyridine) rhodium(III)

Rhodium trichloride trihydrate (0.26 gm 1m mole) was dissolved together with a tenfold excess of potassium bromide in water (10 ml) and to this a solution of 4-phenyl pyridine (0.62 gm 4m mole) in ethanol (20 ml) was added. The intense dark brown product obtained was heated under reflux for 90 minutes. The brown crystals obtained as a final product were filtered through a sintered glass crucible (porasity -4) while the solution was hot, washed with hot ethanol several times and dried over P_4O_{10} under vacuum.

Found: C,52.6%; H,3.3%; N,5.8%

$C_{33}H_{27}Br_3RhN_3$

Requires: C,49.0%; H,3.3%; N,5.2%.

(3) <u>Triiodo *Tris* (4-phenyl pyridine) rhodium(III)</u>

Rhodium trichloride trihydrate (0.26 gm 1m mole) was dissolved together with a tenfold excess of sodium iodide in water (10 ml) and to this a solution of 4-phenyl pyridine (.62 gm 4m mole) in ethanol (20 ml) was added. The dark brown product was then heated under reflux for 90 minutes. A brown compound was filtered as a final product while the solution was hot, washed with hot ethanol and then dried over P_4O_{10} under vacuum.

Found: C,41.2%; H,2.7%; N,4.5%.

$C_{33}H_{27}I_3RhN_3$

Requires: C,41.7%; H,2.8%; N,4.4%

(b) <u>Rhodium(III) complexes with 4-methylpyridine</u>

(4) <u>Trichloro *Tris* (4-methyl pyridine) rhodium(III)</u>

Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved in water (5 ml) and to this a solution of 4-methyl pyridine (3.5 ml 4m mole) in ethanol (20 ml) was added. The fawn product was redissolved on heating under reflux. The colour of the clear solution was changed from brown to orange yellow. The solution was refluxed for nearly one hour. It was then concentrated and cooled on ice. Orange yellow crystals were deposited on cooling and filtered through a sintered glass crucible, washed with ice cold ethanol and dried over P_4O_{10} under vacuum.

Found: C,44.4%; H,4.7%; N,8.6%.
$C_{18}H_{21}Cl_3RhN_3$
Requires: C,44.3%; H,4.3%; N,8.6%.

(5) Tribromo tris (4-methyl pyridine) rhodium(III)

Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved together with a ten fold excess of potassium bromide in water (10 ml) and to this a solution of 4-methyl pyridine (3.5 ml 4m mole) in ethanol (20 ml) was added. The brown product thus obtained was then heated under reflux for 90 minutes. The product redissolved giving a clear orange brown solution. It was concentrated and on cooling on ice, orange brown crystals were deposited. It was then filtered, washed with ice cold ethanol and dried over P_4O_{10} under vacuum.

Found: C,36.5%; H,3.4%; N,7.0%.
$C_{18}H_{21}Br_3RhN_3$
Requires: C,34.7%; H,3.4%; N,6.8%.

(6) Triiodo Tris (4-methyl pyridine) rhodium(III)

Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved in water (10 ml) together with a tenfold excess of sodium iodide and to this a solution of 4-methyl pyridine (3.5 ml 4m mole) in ethanol was added and the resulting dark brown product was heated under reflux for 90 minutes. The final product which was reddish brown was filtered while the solution was hot, washed with hot ethanol and dried over P_4O_{10} under vacuum.

Found: C,30.1%; H,2.8%; N,5.8%.

$C_{18}H_{21}I_3RhN_3$

Requires: C,28.3%; H,2.8%; N,5.5%.

(C) Rhodium(III) complexes with 2.2'-2"-Terpyridyl

(7) Trichloro (terpyridyl) rhodium(III)

Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved in water (5 ml) and to this a solution of 2.2'-2"-terpyridyl (.233 gm 1m mole) in ethanol (20 ml) was added. A brown product was heated under reflux for 90 minutes. The colour changed from brown through reddish-brown to orange. Finally the orange product was filtered while the solution was hot. It was washed with hot ethanol and dried over P_4O_{10} under vacuum.

Found: C,41.1%; H,2.4%; N,10.0%.

$C_{15}H_{11}Cl_3RhN_3$

Requires: C,40.7%; H,2.5%; N,9.5%.

(8) Tribromo (terpyridyl) rhodium(III)

Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved in water (10 ml) together with a tenfold excess of potassium bromide, and to this a solution of terpyridyl (.233 gm 1m mole) in ethanol (20 ml) was added. A pink-brown product was then heated under reflux for 90 minutes. The colour changed from pinkish-brown to orange brown. This final product was filtered through a sintered glass crucible while the solution was hot. It was washed with hot ethanol and dried over P_4O_{10} under vacuum.

Found: C,31.6%; H,2.1%; N,7.2%.
$C_{15}H_{11}Br_3RhN_3$
Requires: C,30.9%; H,1.9%; N,7.2%.

(9) Triiodo (terpyridyl) rhodium(III)

Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved in water (10 ml) together with a tenfold excess of sodium iodide and to this a solution of terpyridyl (0.233 gm 1m mole) in ethanol (20ml) was added. The dark brown product was heated under reflux for 90 minutes. The final product, which was intense dark, was filtered while the solution was hot. It was washed with hot ethanol and dried over P_4O_{10} under vacuum.

Found: C,25.1%; H,2.8%; N,5.8%.
$C_{15}H_{11}I_3RhN_3$
Requires: C,24.9%; H,2.8%; N,5.5%.

(d) Complexes of 4.4'-dimethyl 2.2'-bipyridyl with Rhodium(III)halides

(10) Dichloro *bis*(4.4'-dimethyl 2-2'-bipyridyl) rhodium(III) chloride

Rhodium tricloride trihydrate (.26 gm 1m mole) was dissolved in water (5 ml) and to this a solution of 4.4'-dimethyl-2.2'-bipyridyl (0.368 gm 2m mole) in ethanol (20 c.c.) was added. The pinkish-brown product was heated under reflux for one hour. The product redissolved giving an orange yellow solution. The bulk of this solution was reduced to nearly 10 ml. On setting aside overnight in a cool place a yellow crystalline product was deposited. The crystals were filtered through a sintered glass crucible (porasity-4), washed with ice-cold ethanol and dried over P_4O_{10} under vacuum.

Found: C, 47.5 %; H, 4.7 %; N, 9.1 %.

$C_{24}H_{24}Cl_3RhN_4$

Requires: C, 47.7%; H, 4.5 % N, 9.3 %;

(11) 4.4'-dimethyl-2.2'-bipyridylium tetra bromo-4.4'-dimethyl-2.2'-bipyridyl rhodate(III)

Rhodium tricloride trihydrate (.26 gm 1m mole) was dissolved in water (10 c.c.) together with a tenfold excess of potassium bromide and to this a solution of 4.4'-dimethyl 2.2'-bipyridyl (.368 gm 2m mole) in ethanol (20 ml) was added and the resulting brown product was heated under reflux for 90 minutes. The product redissolved giving an orange yellow solution. It was then concentrated to 10 ml and it was set aside overnight in a cool place. Orange yellow crystals were deposited, filtered and washed with ice-cold ethanol.

The crystals were dried over P_4O_{10} under vacuum

Found: C,36.4%; H,3.2%; N,7.2%.

$C_{24}H_{25}Br_4RhN_4$

Requires: C,36.4%; H,3.2%; N,7.0%

(e) Complexes of 4-4'-diphenyl-2.2'-bipyridyl with Rhodium(III)halides

Ligand 4.4'-diphenyl-2.2'-bipyridyl was prepared as under by dehydrodimerisation of 4-phenylpyridine over rhodium on charcoal[69].

Degassing of Catalyst

The catalyst used was rhodium on charcoal.

The catalyst (1 gm) was heated in a round bottom flask at 160-180° for 2 hours at less than 0.1 mm pressure. After being cooled to room temperature under vacuum it was used for the following reaction.

Preparation of 4.4'-diphenyl-2.2'-bipyridyl

Molten 4-phenylpyridine (12 gms) was added under vacuum to the catalyst (1 gm) and heated under reflux for 100 hours in an atmosphere of dry oxygen free nitrogen. The reaction mixture was treated with chloroform and filtered. The chloroform was removed and the residue crystallized from hot petrolium ether (fraction 60/80) to give 4.4'-diphenyl 2.2'-bipyridyl. Mother liquors on fractional crystallization gave more 4.4'-diphenyl-2.2'-bipyridyl. The total yield was about 4 gm. m.p. 188°C.

(12) Dichloro *bis*(4.4'-diphenyl-2.2'-bipyridyl) rhodium(III) chloride

Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved in water (5 ml) and to this a hot solution of 4.4'-diphenyl-2.2'-bipyridyl (0.616 gm 2m mole) in ethanol (20 ml) was added. The pinkish-brown precipitate obtained was redissolved on heating under reflux to afford an orange-yellow solution. After one hour the solution was concentrated to 10 ml and on cooling, yellow crystals were deposited. The product was filtered and washed with ice-cold ethanol. Finally it was dried over P_4O_{10} under vacuum.

Found: C,61.3%; H,4.2%; N,6.5%.
$C_{44}H_{32}Cl_3RhN_4$
Requires: C,63.9%; H,3.9%; N,6.7%

(13) Dibromo *bis* (4.4'-diphenyl-2.2'-bipyridyl) rhodium(III)bromide

Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved in water (10 ml) together with a tenfold excess of potassium bromide and to this a hot solution of 4.4'-diphenyl-2.2'-bipyridyl (.616 gm 2m mole) in ethanol (20 ml) was added. A dark brown precipitate was then heated under reflux for 90 minutes. The final product which was orange yellow was filtered while the solution was hot and washed several times with hot ethanol and finally dried over P_4O_{10} under vacuum.

Found: C,55.2%; H,3.4%; N,5.9%.
$C_{44}H_{32}Br_3RhN_4$
Requires: C,55.1%; H,3.4%; N,5.8%.

(14) Diiodo bis-(4.4'-diphenyl-2.2'-bipyridyl) rhodium(III) iodide

Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved in water (10 ml) together with tenfold excess of sodium iodide and to this a hot solution of 4.4'-diphenyl-2.2'-bipyridyl (.616 gm 2m mole) in ethanol (20 ml) was added. A reddish dark product was heated under reflux for 90 minutes to afford an orange brown compound. This was filtered while the solution was hot, washed several times with hot ethanol and dried over P_4O_{10} under vacuum.

Found: C,46.2%; H,3.0%; N,4.8%.
$C_{44}H_{32}I_3RhN_4$
Requires: C,48.0%; H,3.0%; N,5.1%.

Complexes of 2.2'-bipyridyl and 1-10-phenanthroline are known and have been reported several times together with their preparative methods [46,48,49,50]. However, different preparative routes may afford different combinations of products, hence it is necessary to describe in detail the methods of synthesis used in this work.

(f) Complexes of 2.2'-bipyridyl with Rhodium(III) halides

(15) Dichloro bis (2.2'-bipyridyl) rhodium(III) tetrachloro (2.2'-bipyridyl) rhodate(III) di hydrate

(16) Dichloro bis (2.2'-bipyridyl) rhodium(III) chloride di hydrate

(15) To the cold solution of rhodium trichloride trihydrate (.26gm 1m

mole) in water (5 ml) was added a hot solution of 2.2'-bipyridyl (.312 gm 2m mole) in ethanol (20 ml). A fawn precipitate obtained at once was heated under reflux for 90 minutes. The colour of the product changed from pink-brown to orange. During this period orange crystals were obtained as a final product. The crystals were filtered through a sintered glass crucible, washed with hot ethanol and finally dried over P_4O_{10} under vacuum.

The orange crystals had properties consistent with the formulation:

$[Rh(bipy)_2.Cl_2][Rh(bipy)\ Cl_4].2H_2O$

Found: C,38.5%; H,2.9%; N,9.1%.

$C_{30}H_{28}Cl_6Rh_2N_6O_2$

Requires: C,39.0%; H,3.0%; N,9.1%.

(16) The yellow filtrate from the above preparation was concentrated to reduce its volume to 5 ml. On cooling yellow crystals were deposited. These crystals were washed with ice-cold ethanol and then dried over P_4O_{10} under vacuum.

The yellow crystals were formulated as:

$[Rh(bipy)_2.Cl_2.].Cl.\ 2H_2O.$

Found: C,43.0%; H,3.7%; N,10.1%.

$C_{20}H_{20}Cl_3RhN_4O_2$

Requires: C,43.1%; H,3.6%; N,10.0%.

(17) Dibromo bis(2.2'-bipyridyl) rhodium(III) tetra bromo (2.2'-bipyridyl) rhodate

(18) Dibromo bis(2.2'-bipyridyl) rhodium(III) bromide dihydrate

(17) A cold solution of rhodium trichloride trihydrate (.26 gm 1m mole) in water (10 ml) together with a tenfold excess of potassium bromide was treated with a hot solution of 2.2'-bipyridyl (.312 gm 2m mole) in ethanol (20 ml). The brown-fawn precipitate was then heated under reflux for 90 minutes. The final product, obtained as orange-brown crystals, was filtered while the solution was hot and washed several times with hot ethanol and dried over P_4O_{10} under vacuum.

This was formulated as:

$$[Rh(bipy)_2Br_2][Rh(bipy)\ Br_4]$$

Found: C,31.5%; H,2.1%; N,7.2%.

$C_{30}H_{24}Br_6Rh_2N_6$

Requires: C,31.2%; H,2.1%; N,7.3%.

(18) The orange filtrate obtained from the above preparation was concentrated and on cooling it afforded orange yellow crystals. It was washed with ice-cold ethanol and dired over P_4O_{10}under vacuum.

Analysis shows this to be:

$$[Rh(bipy)_2.Br_2].Br.2H_2O$$

Found: C,35.03%; H,3.12%; N,8.08%.

$C_{20}H_{20}Br_3RhN_6O_2$

Requires: C,34.81%; H,2.92%; N,8.104%.

It was observed that when excess of ethanol was used in this preparation only one compound [Rh(bipy)$_2$.Br$_2$][Rh(bipy) Br$_4$] was isolated. No other product, namely, [Rh(bipy)$_2$Br$_2$].Br; 2H$_2$O was isolated from the filtrate.

(19) Diiodo bis (2.2'-bipyridyl) rhodium(III) tetra iodo (2.2'-bipyridyl) rhodate(III)

and

(20) Diiodo bis (2.2'-bipyridyl) rhodium(III) iodide

(19) Rhodium trichloride trihydrate (.26 gm 1m mole) in water together with tenfold excess of sodium iodide was treated with a hot solution of 2.2'-bipyridyl (.312 gm 2m mole) in ethanol (20 ml) and the resulting dark brown precipitate was heated under reflux for nearly 2 hours. During this period a dark reddish-brown solid was obtained in the solution. It was filtered while the solution was hot. Washed with hot ethanol and dried over P_4O_{10} under vacuum.

The analysis showed that the product was

[Rh(bipy)$_2$.I$_2$][Rh(bipy)I$_4$]

Found: C,24.8%; H,1.75%; N,6.07%.

$C_{30}H_{24}Br_6Rh_2N_6$

Requires: C,25.07%; H,1.67%; N,5.85%.

(20) A reddish-brown filtrate from the above preparation afforded brick-red crystals after reducing its volume and on cooling. The crystals were filtered, washed with ice-cold ethanol and dried over P_4O_{10} under vacuum.

Found: C,30.36%; H,2.13%; N,7.07%.

$C_{20}H_{16}I_3RhN_4$

Requires: C,30.02%; H,2.03%; N,7.04%.

(21) 2.2'-Bipyridylium-tetrachloro-(2.2'-bipyridyl) rhodate(III)

2.2'-bipyridyl (.312 gm 2m mole) was added to the hot solution of rhodium trichloride trihydrate (.26 gm 1m mole) in hydrochloric acid (30 ml 2M) and the solution was heated on a water bath for 10 minutes. Orange-yellow crystals were separated. These were filtered off, washed with hydrochloric acid (2 M) and water and dried over P_4O_{10} under vacuum.

Found: C,42.7%; H,31.1%; N,9.9%.

$C_{20}H_{17}RhN_4Cl_4$

Requires: C,43.0%; H,3.0%; N,10.1%.

(g) Complexes of 1-10-phenanthroline with Rhodium(III) halides

(22) Dichloro *bis* (1.10-phenanthroline) rhodium(III) tetra chloro (1.10-phenanthroline) rhodate(III)

(23) Dichloro *bis* (1.10-phenanthroline) rhodium(III) chloride

(22) Rhodium trichloride trihydrate (.26 gm 1m mole) was dissolved in water (5 ml) and to this a hot solution of 1.10-phenanthroline monohydrate (0.4 gm 2m mole) in ethanol (20 ml) was added and the brown precipitate obtained was then heated for one hour under reflux. The colour of the product changed and an orange crystalline product formed. This was then filtered while the solution was hot. It was then washed with hot ethanol and dried over P_4O_{10} under vacuum.

This was formulated as:

$[Rh(phen)_2.Cl_2][Rh(phen)\ Cl_4]$

Found: C,44.50%; H,2.68%; N,8.75%.

$C_{36}H_{24}Cl_6Rh_2N_6$

Requires: C,45.05%; H,2.50%; N,8.76%.

(23) The orange-yellow filtrate from the above preparation afforded yellow crystals after concentration and cooling. These were washed with ice-cold ethanol and dried over P_4O_{10} under vacuum.

The analysis suggested formula was:

$[Rh(phen)_2.Cl_2].Cl.2H_2O$

Found: C,48.0%; H,3.2%; N,9.5%.

$C_{24}H_{20}Cl_3N_4RhO_2$

Requires: C,47.5%; H,3.4%; N,9.6%.

Recrystallization of $[Rh(phen)_2.Cl_2].Cl.nH_2O$ was carried out in order to get α and ε forms.

(1) The α-form of $[Rh(phen)_2.Cl_2].Cl.nH_2O$ was obtained by recrystallization of this salt from methanol.

(2) The ε form of $[Rh(phen)_2.Cl_2].Cl.nH_2O$ was obtained by recrystallization from water or hydrochloric acid.

They were identified by their characteristic x-ray powder photographs [50].

(24) Dibromo *bis*(1.10-phenanthroline) rhodium(III) *tetra* bromo (1.10-phenanthroline) rhodate(III)

and

(25) Dibromo *bis* (1.10-phenanthroline) rhodium(III) bromide trihydrate

(24) A cold solution of rhodium trichloride trihydrate (.26 gm 1m mole) in water (5 ml) together with a tenfold excess of potassium bromide was treated with a hot solution of 1.10-phenanthroline monohydrate (.4 gm 2m mole) in ethanol (20 ml) and the brown precipitate was heated under reflux for 2 hours. The orange-brown crystalline product obtained was filtered off while the solution was hot. It was washed with hot water and then with hot ethanol and finally dried over P_4O_{10} under vacuum.

This product was formulated as:

$$[Rh(phen)_2Br_2][Rh(phen)\ Br_4]$$

Found: C,36.0%; H,1.8%; N,7.02%.

$C_{36}H_{24}Br_6Rh_2N_6$

Requires: C,35.25%; H,1.95%; N,6.85%.

(25) The orange-brown filtrate from the above preparation afforded orange-yellow crystals on concentration and cooling. It was washed with ice-cold ethanol and then dried over P_4O_{10} under vacuum.

The analysis suggested it was:

$[Rh(phen)_2.Br_2].Br.\ 3H_2O$

Found: C,37.62%; H,2.63%; N,7.40%.

$C_{24}H_{22}Br_3RhO_3N_4$

Requires: C,38.05%; H,2.89%; N,7.4%.

(26) Diiodo bis(1.10-phenanthroline) rhodium(III) tetra iodo (1.10-phenanthroline) rhodate(III)

Rhodium trichloride trihydrate (.26 gm 1m mole) in water (5 ml) together with a tenfold excess of sodium iodide was treated with a hot solution of 1.10-phenanthroline monohydrate (.4 gm 2m mole) in ethanol (20 ml) and the deep brown precipitate was heated under reflux for 2 hours. The final product obtained was chocolate-brown in colour. This was then filtered off, washed with hot water and hot ethanol. Finally it was dried over P_4O_{10} under vacuum.

The product was formulated as:

$[Rh(phen)_2.I_2][Rh(phen)\ I_4]$

Found: C,29.03%; H,1.60%; H,5.48%.

$C_{36}H_{24}I_4Rh_2N_6$

Requires: C,28.72%; H,1.60%; N,5.58%.

(27) Phenanthrolinium Tetrachloro (1.10-phenanthroline)rhodium(III)

1.10-phenanthroline monohydrate (.4 gm 2 m mole) was added to the hot solution of rhodium trichloride trihydrate (.26 gm 1m mole) in hydrochloric acid (15 ml, 2M) and the solution was heated on a water bath for 10 minutes. The orange crystals separated. These were filtered off, washed with hydrochloric acid (2 M) then with water and dried over P_4O_{10} under vacuum.

The compound was identified by x-ray powdered photograph [50]

as $[\ phen\ H]\ [Rh(phen).Cl_4]$

Found: C,48.26%; H,3.02%; N,9.30%.

$C_{24}H_{17}Cl_4RhN_4$

Requires: C,47.55%; H,2.83%; N,9.2%.

[C] RESULTS

Solid state data and molar conductivity for the complexes of rhodium(III) halides with 4-phenyl pyridine, 4-methyl pyridine, 2.2'.2"-terpyridyl, 4.4'-dimethyl 2.2'-bipyridyl, 4.4'-diphenyl 2.2'-bipyridyl, 2.2'-bipyridyl and 1-10-phenanthroline are gathered in Table 1. These complexes are sufficiently soluble either in nitromethane or dimethyl sulphoxide. The solvolysis of some bromo- and iodo- complex of 4-phenyl pyridine, 4-methyl pyridine and 2.2'.2"-terpyridyl are examined and conductivity as a function of concentration is given in figure 6, 7 and 8.

The infra-red spectra in the region of 4000-400cm^{-1} shows similar absorption patterns and therefore are not tabulated. The far infra-red spectra in the region of 400-40 cm^{-1} of all these complexes together with some known complexes of rhodium(III) halides with 1.10-phenanthroline and 2-benzoyl pyridine are given in Table 2. Some typical spectra in this region are shown in figures 10, 12 & 12a.

The 'd' spacings of some new complexes from their X-ray powder photographs are given in Table 3.

TABLE: 1 SOLID STATE DATA AND MOLAR CONDUCTIVITIES OF RHODIUM(III) HALIDE COMPLEXES WITH N-HETROCYCLIC LIGANDS

Compound	Molar Conductivities (10^{-3}M)	Reflectance minima(kK)
(a) Complexes with 4-phenyl pyridine		
1. $[Rh(4Phpy)_3.Cl_3]$	10*	27.0, 23.0
2. $[Rh(4Phpy)_3.Br_3]$	24*	27.0, 22.5
3. $[Rh(4Phpy)_3.I_3]$	28*	25.5(b), 19.7, 17.2(sh)
(b) Complexes with 4-methyl pyridine		
4. $[Rh(4Mepy)_3.Cl_3]$	13*	22.5
5. $[Rh(4Mepy)_3.Br_3]$	8*	26.2, 22.0
6. $[Rh(4Mepy)_3.I_3]$	31*	24.5, 19.0, 15.0(sh)
(c) Complexes with 2.2'.2"-Terpyridyl		
7. $[Rh(terpy)Cl_3]$	8†	23.5, 19.5(sh)
8. $[Rh(terpy)Br_3]$	11†	22.0
9. $[Rh(terpy).I_3]$	21†	20.0(b)
(d) Complexes with 4.4'-dimethyl 2.2'-bipyridyl		
10. $[Rh(4.4'diMe.2.2'\text{-}bipy)_2.Cl_2].Cl$ 1.5 H_2O	66*	25.0
11. $[4.4'.diMe.2.2'\text{-}bipy\ H][Rh(4.4'diMe\text{-}2.2'\text{-}bipy)Br_4]$	79*	24.5
(e) Complexes with 4.4'-diphenyl 2.2'-bipyridyl		
12. $[Rh(4.4'\text{-}diPh\ 2.2'\text{-}bipyl)_2.Cl_2].Cl$	69*	

continued

TABLE: 1 continued..

Compound	Molar Conductivities (10^{-3}M)	Reflectance Minima(k^K)
13. $[Rh(4.4' \text{ diph } 2.2'\text{-bipy})_2.Br_2]$ Br	68*	21.5(sh)
14. $[Rh(4.4' \text{ diph.} 2.2'\text{-bipy})_2.I_2]I$	79*	
(f) <u>Complexes with 2.2'-bipyridyl</u>		
15. $[Rh(bipy)_2.Cl_2][Rh(bipy)Cl_4].2H_2O$	20†	27.0,22.0, 17.5(sh)
16. $[Rh(bipy)_2.Cl_2]\ Cl.2H_2O$	83*	26.0
17. $[Rh(bipy)_2.Br_2][Rh(bipy)Br_4]$	45†	26.9,21.0
18. $[Rh(bipy)_2.Br_2].Br.$	74*	
19. $[Rh(bipy)_2.I_2][Rh(bipy)I_4]$	22.27	
20. $[Rh(bipy)_2.I_2].I$	95.63*	
21. $[bipy\ H][Rh\ bipy\ Cl_4]$	43†	26.5,22.0
(g) <u>Complexes with 1.10-phenanthroline</u>		
22. $[Rh(phen)_2.Cl_2][Rh(phen)Cl_4]$	20.4†	
23. $[Rh(phen)_2.Cl_2].Cl$	79*	
24. $[Rh(phen)_2.Br_2][Rh(phen)Br_4]$	20.6†	
25. $[Rh(phen)_2.Br_2].Br$	87.8*	
26. $[Rh(phen)_2.I_2][Rh(phen)I_4]$	20†	
27. $[phen\ H][Rh\ phen\ Cl_4]$	21†	

* Measured in nitromethane.

† Measured in Dimethyl sulphide (10^{-3} tetra-n-methyl ammonium iodide gives $\lambda M = 55$ in DMSO)

TABLE: 2 FAR INFRA-RED SPECTRA OF SOME RHODIUM(III) HALIDE COMPLEXES*

Complex	I.r. absorption maximum (400 - 60 cm^{-1})
(a) 4-phenyl pyridine	389w, 378w, 350m, 327m, 245s, 94w
$[Rh(4Phpy)_3.Cl_3]$	395w, 389sh, 365m-s, 331s, 307s, 297w-m, 257m-s, 253m, 231m-s, 225sh, 209m, 197m, 182m, 170m, 146m, 137sh, 116w, 95w.
$[Rh(4Phpy)_3.Br_3]$	392m, 388sh, 364w, 352sh, 328m, 300sh, 295s, 278w, 255m, 245sh, 228sh, 216m, 205m, 188v.br,s ($\Gamma 1/2 = 34\ cm^{-1}$) 161sh, 142w, 87v.w, 59v.w.
$[Rh(4Phpy)_3.I_3]$	397sh, 358m, 339m-w, 297sh, 280w-m, 250sh, 245m, 210w, 206w, 182br,m. 166s, 155sh,m, 115m.
(b) 4-methyl pyridine	
$[Rh(4Mepy)_3.Cl_3]$	382m, 376sh, 364v.w., 344v.s., 334v.s., 303sh, 290v.s., 266s, 237w.m. 209s.
$[Rh(4Mepy)_3.Br_3]$	376m-w, 335s, 307v.w, 287s, 266sh, 260s, 246s, 207sh.
$[Rh(4Mepy)_3.I_3]$	392m-w, 379v.w, 371v.w, 345m, 337m, 322w, 297w, 275s, 260m, 240w, 205s.

continued...

TABLE: 2 continued

Complex	I.r absorption maximum (400 - 60 cm^{-1})
(c) 2.2'.2"-terpyridyl	352s, 344s, 328sh, 279w, 244w, 194sh, 189s, 116sh, 111s.
[Rh(terpy).Cl$_3$]	379s, 352w, 340s, 330m, 322sh, 306m, 278s, 274sh, 258w, 241m-s, 233m, 155m, 145m, 137m, 129m, 118sh, 96m, 78w,sh,59w, 51w.
[Rh(terpy).Br$_3$]	376w, 370w, 338w, 326sh, 320m, 300sh, 293s, 274m, 253sh, 250, 209v.s, 205v.s, 184w, 156sh, 150s, 144sh, 138m, 129m,111w, 107w, 95m-s, 44m-s,
[Rh(terpy).I$_3$]	374w, 364w, 336m, 324w, 311sh, 303w-m, 295w-m, 270s, 178s, 156w, 136m-s, 132sh, 126sh, 116w, 99w-m, 79sh, 87w-m, 63sh, 52w.
(d) 4.4'-dimethyl 2.2'-bipyridyl	368m, 352m, 344sh, 220m-w, 137m, 90m-w, 86m-w.
[Rh(4.4'-diMe 2.2'-bipy)$_2$.Cl$_2$] 1.5 H$_2$O	395w, 365m, 349s, 341s, 311w, 300m, 288s, 240m, 141w.
[4.4' diMe 2.2 bipy H] [Rh(4.4'-diMe 2.2 bipy).Br$_4$]	391w, 379w, 366w, 349w, 338w, 308m, 298m, 264s, 258s, 240w, 192m,br.

continued.

TABLE: 2 continued

Complex	I.r.absorption maximum (400 - 60 cm^{-1})
(e) 4.4' diphenyl 2.2' bipyridyl	388w-m, 355m,br, 328w-m, 247m-w,br.
$[Rh(4.4'diPh\ 2.2'bipy)_2.Cl_2]Cl.$	367m, 358s, 348sh, 313m, 300m, 291m, 220m, 188m, 138m, 109m.
$[Rh(4.4'diPh\ 2.2'bipy)_2.Br_2]Br.$	303m,br, 288m, 283sh, 245s, 234s, 189sh, 183s, 138w-m, (poor spectrum)
$[Rh(4.4'diPh\ 2.2'bipy)_2.I_2].I.$	398m, 352w, 344sh, 306w, 292w, 254w, 231m-s, 172m-s, 137w.
(f) 2.2'-bipyridyl	
$[Rh(bipy)_2.Cl_2].Cl.2H_2O$	376sh, 371w, 357s, 350.5s, (For a thick mull: 354v.s, 349v.s) 333w, 289sh, 283m, 268m, 248m-w, 223m, 170m, 161m, 154m, 144m.
$[Rh(bipy)_2.Br_2].Br.$	375sh, 371m, 352.7m, 342s, 317s, 273w, 248.5m, 216s, 205s.
$[Rh(bipy)_2.I_2].I$	374s, 367.5s, 368s, 360sh, 326s, 312-308s, 305sh, 270m, 256sh, 240s, 213m, 184s, 178sh, 159-156s, 142sh, 118sh, 117sh, 108s, 85s, 78s.
$[bipyH^+][Rh(bipy).Cl_4]$	395w, 338s, 333s, 327s, 316sh, 294w, 270m, 253m-w, 241w, 226m, 216w, 172s, 168s, 161sh, 153w, 116m-w.
$[Rh(bipy)_2Cl_2][Rh(bipy).Cl_4]$	373w, 357s, 350s, 336s, 328s, 321sh, 316sh, 279w, 268w, 253m, 224m, 208m, 199m, 151br, 114w-m, 95w-m.

continued

TABLE: 2 continued

Complex	I.r absorption maximum (400 - 60 cm^{-1}
(f) continued	
$[Rh(bipy)_2.Br_2][Rh(bipy).Br_4]$	372w-m, 353w-m, 340w, 320m, 312m, 303m-w, 287sh, 275sh, 271m, 257m-w, 249sh, 215s, 206s, 195s, 188s, 183s, 141w.
$[Rh(bipy)_2.I_2][Rh(bipy). I_4]$	373.5-369s, 345w, 322.5s, 312.5m, 296.5m, 282.5-279.5m, 270m, 258sh, 254sh, 244s, 299sh, 223sh, 215sh, 209m, 203.5w.
(g) 1-10-phenanthroline	
$[Rh(phen)_2.Cl_2].Cl.2H_2O$ (as freshly prepared)	355sh, 347s, 324m, 311m, 290m, 280m-ws, 261m, 256m, 239m-w, 223w, 172m-s, 147m, 115m-w.
$[Rh(phen)_2.Cl_2].Cl.nH_2O$ recrystallised from (a) H_2O	
[ε-form]	354sh, 347s, 324m, 311m, 290m, 280m-w, 261m, 256m, 239m-w, 228w.
(b) Methanol	
[α-form]	353sh, 345.5s, 328m, 312m, 292m, 282m-w, 263sh, 256m, 241m, 228sh.
(c) HCl	
[ε-form]	354sh, 349s, 328m, 313m, 293m, 283m-w, 264m, 256m, 237m, 228w.

continued

TABLE: 2 continued

Complex	I.r. absorption maximum (400 - 60 cm^{-1})
(g) continued	
[Rh(phen)$_2$.Br$_2$].Br	380w, 348w, 335w, 330w, 313w-m, 304v-w, 297m-s, 275m-s, 259m-s, 244m-s, 241m-s, 204s, 190v-s, 176m, 122v.br, (Composite), 96w, 90w.
[phenH][Rh(phen).Cl$_4$]	383w, 350m, 344m, 329sh, 324m-s, 318sh, 297m, 287w, 266w, 250m, 238m, 225m, 197w, 178m, 171m, 156m, 136m, 115m-w, 89m, 84m.
[phenH][Rh(phen).Br$_4$]	350m-w, 333m-w, 324sh, 310m-w, 306sh, 297w, 281sh, 276m, 261w, 253sh, 239m, 205s, 192v-s, 182sh, 170sh, 117w, 99w.
[phenH][Rh(phen).I$_4$]	328w, 318w, 284w, 270w, 252m, 242m, 237m, 177m-s, 162w, 150s, 108br.
[Rh(phen)$_2$.Cl$_2$][Rh(phen).Cl$_4$]	355.5sh, 346s, 325s, 311sh, 299s, 283m, 267sh, 258s, 242m, 237w, 224m.
[Rh(phen)$_2$.Br$_2$][Rh(phen).Br$_4$]	334s, 325m, 312s, 294sh, 279s, 260s, 252w, 240s.
[Rh(phen)$_2$.I$_2$][Rh(phen).I$_4$]	283s, 279sh, 267.5s, 249sh, 242s.

continued

TABLE: 2 continued

Complex	I.r. absorption maximum (400 - 60 cm^{-1})
(h) 2-benzoylpyridine	
$[Rh(PhCOpy)_2.Cl_2].ClO_4$ (orange)	384w, 374s, 340m, 310w, 294m, 282w, 270m, 254m, 195w, 180w, 151sh, 140s, 131sh, 117m, 107m, 90w, 76sh.
$[Rh(PhCOpy)_2.Br_2].ClO_4$	393w, 380w, 365m, 350m, 338sh, 333m, 295m, 276m, 261m, 234s, 184m, 100m, 94m.
$[Rh(PhCOpy)_2.Cl_2][Rh(PhCOpy).Cl_4]$	382w, 368s, 343s, 335s, 313m, 302w, 284m, 275w, 253m, 225w, 215m, 195m, 179m, 161sh, 154s,br, 116w, 88m.
$[Rh(PhCOpy)_2.Br_2][Rh(PhCOpy).Br_4]$	383w, 366w, 350w, 335w, 312w, 297m, 288w, 276m, 259m, 240s, 201sh, 193s, 183sh, 176m, 155w, 137w, 131w.

* Bands assignable as rhodium halogen stretching frequencies are underlined.

s-strong, m-medium, w-weak, vw-very weak, sh-shoulder, br-broad

TABLE: 3 'd' SPACINGS FOR SOME RHODIUM(III) HALIDE COMPLEXES

Complex	d spacings
(a) <u>4-phenyl pyridine</u>	
$[Rh(4\text{-}phpy)_3.Cl_3]$	12.5s, 7.5w, 6.4s, 5.6m, 4.8m, 4.5m, 4.2m, 3.6w, 3.45w, 3.25vw,3.13w, 2.9w. 2.75w, 2.6w, 2.46m, 2.35m, 2.18v.w, 2.04w, 1.91v.w, 1.85v.w, 1.75v.w,1.72v.w,
$[Rh(4\text{-}phpy)_3.Br_3]$	12.5s, 9.5s, 8.2m, 7.5w, 6.5s, 6.1w, 5.6m, 4.8w, 4.25w, 3.6s, 3.45v.w, 3.35w, 3.15m, 2.95w, 2.85m, 2.75w, 2.64w, 2.5m, 2.35v.w, 2.23v.w, 2.07m, 1.95v.w, 1.85w, 1.8m, 1.75v.w.
$[Rh(4\text{-}phpy)_3.I_3]$	12.45s, 11.0s, 9.3s, 7.6w, 6.4s, 5.88w, 5.5w, 5.2w, 4.4v.w, 4.2s, 3.7m, 3.5m, 3.3w, 3.2m, 2.6v.w.
(b) <u>4-methyl pyridine</u>	
$[Rh(4Mepy)_3.Cl_3]$	7.7s, 7.0w, 6.35m, 5.25w, 4.75s, 4.25m, 3.9v.w, 3.63w, 3.5m, 2.95v.w, 2.65v.w, 2.45v.w, 2.16v.w, 1.85m, 1.8m.
$[Rh(4Mepy)_3.Br_3]$	8.0s, 7.25m, 6.5s, 5.3w, 4.75m, 4.3m, 3.9v.w, 3.7v.w, 3.55s, 3.3w, 3.15w, 2.95w, 2.85v.w, 2.65m, 2.22v.w, 1.82v.w.
$[Rh(4Mepy)_3.I_3]$	8.0s, 7.25s, 6.2w, 4.75m, 4.2v.w, 3.65m, 3.5w, 3.25w, 3.05m, 2.9w, 2.83m, 2.45v.w, 2.25v.w, 2.05m, 1.85w.

TABLE: 3 continued

Complex	d spacings
(c) <u>2.2'.2"-terpyridyl</u>	
[Rh(Terpy).Cl_3]	7.5s, 6.57s, 6.2s, 5.75w, 4.75m, 3.8s, 3.65s, 3.25w, 2.83s, 2.65v.w, 2.55v.w, 2.35w, 2.2v.w, 2.1m, 1.97v.w, 1.95s, 1.93w, 1.88m, 1.78w, 1.75w, 1.7w, 1.67w, 1.6w.
[Rh(Terpy).Br_3]	7.7s, 6.7s, 5.9m, 4.7m, 3.88m, 3.7m, 3.35s, 3.2w, 3.1s, 2.85w, 2.75v.w,2.68w, 2.55w, 2.47w, 2.38s, 2.33m, 2.25w, 2.15s, 2.05m, 2.03m, 1.95m, 1.92m, 1.8v.w 1.7w. 1.68m, 1.65m.
[Rh(Terpy).I_3]	8.0v.w, 7.0m, 6.2s, 4.8w, 4.4w, 3.98s, 3.8s, 3.05m, 2.83s, 2.58v-m, 2.46w, 2.36m, 2.28m, 2.22v-w, 2.05v-w, 1.85w.
(d) <u>4.4'-diMethyl 2.2'-bipyridyl</u>	16.5s, 12.5m, 10.5s, 8.0s, 6·8s, 6.3w, 5.8w, 5.3w, 4.7s,
[Rh(4.4'-diMebipy)$_2$.Cl_2].Cl.	4.25w, 3.8m, 3 65v.w, 3.5m, 3.3w, 3.08m, 2.9w, 2.8w, 2.6m, 2.45w, 2.33v.w, 2.15v.w, 2.05v.w, 1.925v.w, 1.875v.w, 1.8v.w, 1.725v.w.
[4.4'-diMebipy H][Rh(4.4'-diMebipy).Br_4]	17.0s, 13.0w, 11.0s, 8.0s, 6.8w, 6.0s, 5.25s, 4.85w, 4.45m, 4.15s, 3.8m, 3.5m, 3.2w, 3.05m, 2.85w, 2.7w, 2.4m, 2.135w, 2.035w, 1.925w, 1.825w, 1.75v.w,

continued..

TABLE: 3 continued

Complex	d spacings
(e) 4.4'-diphenyl 2.2'-bipyridyl	
[Rh(4.4'-diPhbipy)$_2$.Br$_2$].Br	15.0s, 13.0s, 11.0s, 8.75v.w, 7.5s, 6.15s, 5.5s, 5.15m, 4.75s, 4.5w, 4.25m, 4.15s, 3.85m, 3.6v.w, 3.3w, 3.07s, 2.85m, 2.7s, 2.6v.w, 2.45v.w, 2.33w,2.25v.w,
[Rh(4.4'-diPhbipy)$_2$.I$_2$]I	14.0s, 11.5m, 9.0v.w, 8.0s, 6.25s, 5.5m, 4.85v.w, 4.5v.w, 4.25s, 3.9w, 3.7w, 3.3m, 3.1v.w, 3.0v.w, 2.9w, 2.76v.w, 2.55v.w, 2.4v.w, 2.3v.w, 2.2v.w.

s-strong, m-medium, w-weak, vw-very weak.

[D] CHARACTERIZATION OF NEW COMPLEXES

All the new complexes prepared for the present work are well characterized and their molecular formulae are established by the combination of their elemental analysis and molar conductivities. The presence of water in some complexes is supported by its characteristic absorptions in the infra-red spectra.

These complexes are distinguished into two classes according to their behaviour in solution: (1) Ionic complexes and
(2) Non-ionic complexes.
Ionic complexes are those of 4.4'-diphenyl 2.2'-bipyridyl, 4.4'-dimethyl 2.2'-bipyridyl, 2.2'-bipyridyl and 1-10-phenanthroline. While the complexes of monodentate ligands such as 4-phenyl pyridine, 4-methyl pyridine and terdentate ligand 2.2'.2"-terpyridyl are non-ionic.

The complexes of rhodium(III) halides with 4.4'-diphenyl 2.2'-bipyridyl and 4.4'-dimethyl 2.2'-bipyridyl are easily prepared and the synthesis of these complexes afforded only one product in each case. These complexes are soluble in nitromethane and give conductivities which are characteristic of uni-univalent electrolytes. The bromo-complex of rhodium(III) with 4.4'-dimethyl 2.2'-bipyridyl is characterized as $[4.4'\text{-diMe } 2.2'\text{-bipyH}][Rh(4.4'\text{-diMe } 2.2'\text{-bipy})Br_4]$ by elemental analysis, molar conductivity and far infra-red spectroscopy. The other complexes with these ligands tabulated in Table 1 are <u>bis</u> complexes.

Reaction between rhodium(III) chloride and 2.2'-bipyridyl in aqueous ethanol gives two different compounds. The one which is known as dichloro <u>bis</u> (2.2'-bipyridyl) rhodium(III) chloride is isolated from the filtrate after the separation of the orange compound obtained during the reaction. This orange complex has the stoichiometry, $[Rh(bipy)_{1.5}Cl_3]$. The molar conductivity of this complex by assuming it as $Rh_2bipy_3Cl_6$ in dimethyl sulphoxide is low when compared with the known compound $[bipyH][Rh\ bipy\ Cl_4]$, prepared from the reaction of rhodium trichloride and 2.2'-bipyridyl in hydrochloric acid and characterized by X-ray powder data[50]. The far infra-red spectrum of this orange compound suggests that this compound $(Rh\ bipy_{1.5}Cl_3)$ should be formulated as $[Rh(bipy)_2.Cl_2][Rh(bipy).Cl_4]$. The orange-brown compound separated during the synthesis of dibromo <u>bis</u> (2.2'-bipyridyl) rhodium(III) bromide from the reaction of rhodium trichloride and 2.2'-bipyridyl in aqueous ethanol in the presence of excess of potassium bromide is formulated as $[Rh(bipy)_2.Br_2][RhbipyBr_4]$ using similar arguments. Similar reaction has been observed during the reaction of rhodium trichloride and 2.2'-bipyridyl in aqueous ethanol in the presence of excess sodium iodide. The dark reddish-brown compound which is separated first is formulated as $[Rh(bipy)_2.I_2][Rh\ bipy\ I_4]$. The filtrate from the above reaction gives crystals of a brick-red compound which is characterized as $[Rh(bipy)_2.I_2].I$ by elemental analysis and molar conductivity. All these complexes:

$[Rh(bipy)_2.Br_2][Rh(bipy)Br_4]$ and $[Rh(bipy)_2.I_2][Rh(bipy)I_4]$ in dimethyl sulphoxide and

$[Rh(bipy)_2.Br_2].Br.2H_2O$ and $[Rh(bipy)_2.I_2]I$ in nitromethane show molar conductivities expected for a uni-univalent electrolytes.

1.10-phenanthroline gives similar types of complexes and they are all characterized well by their elemental analysis, molar conductivities and far infra-red spectroscopy.

The complexes of rhodium(III) chloride with 4-phenyl pyridine, 4-methyl pyridine and 2.2'.2"-terpyridine are prepared by the direct reaction of rhodium trichloride and appropriate ligands in aqueous ethanol. The bromo and iodo complexes of these ligands are synthesized in the presence of excess of potassium bromide or sodium iodide. 4-phenyl pyridine and 4-methyl pyridine give tris complexes while 2.2'.2"-terpyridyl affords mono complexes. All the complexes of rhodium(III) with these ligands are reasonably expected to be non-electrolytes, particularly chlorides. But the bromides and more particularly the iodides show far from negligible degrees of dissociation in nitromethane and dimethyl sulphoxide. This can be explained by the fact that these two solvents are potentially co-ordinating solvents and show solvolysis reaction as under:

$$RhL_3X_3 + S \rightleftarrows RhL_3X_2S + X^-$$

(where L = 4-phenyl pyridine and 4-methyl pyridine and
X = Br^- or I^-)

Thus when conductivity is examined as a function of concentration; for the bromo and iodo complexes of 4-phenyl pyridine, 4-methyl pyridine and 2.2'.2"-terpyridyl, the characteristic behaviour of weak electrolyte is observed (See figure 6, 7 and 8). This supports the above solvolysis reaction and thus the ionic formulation for the above complexes is not considered in view of the solvolysis of these complexes in the solution.

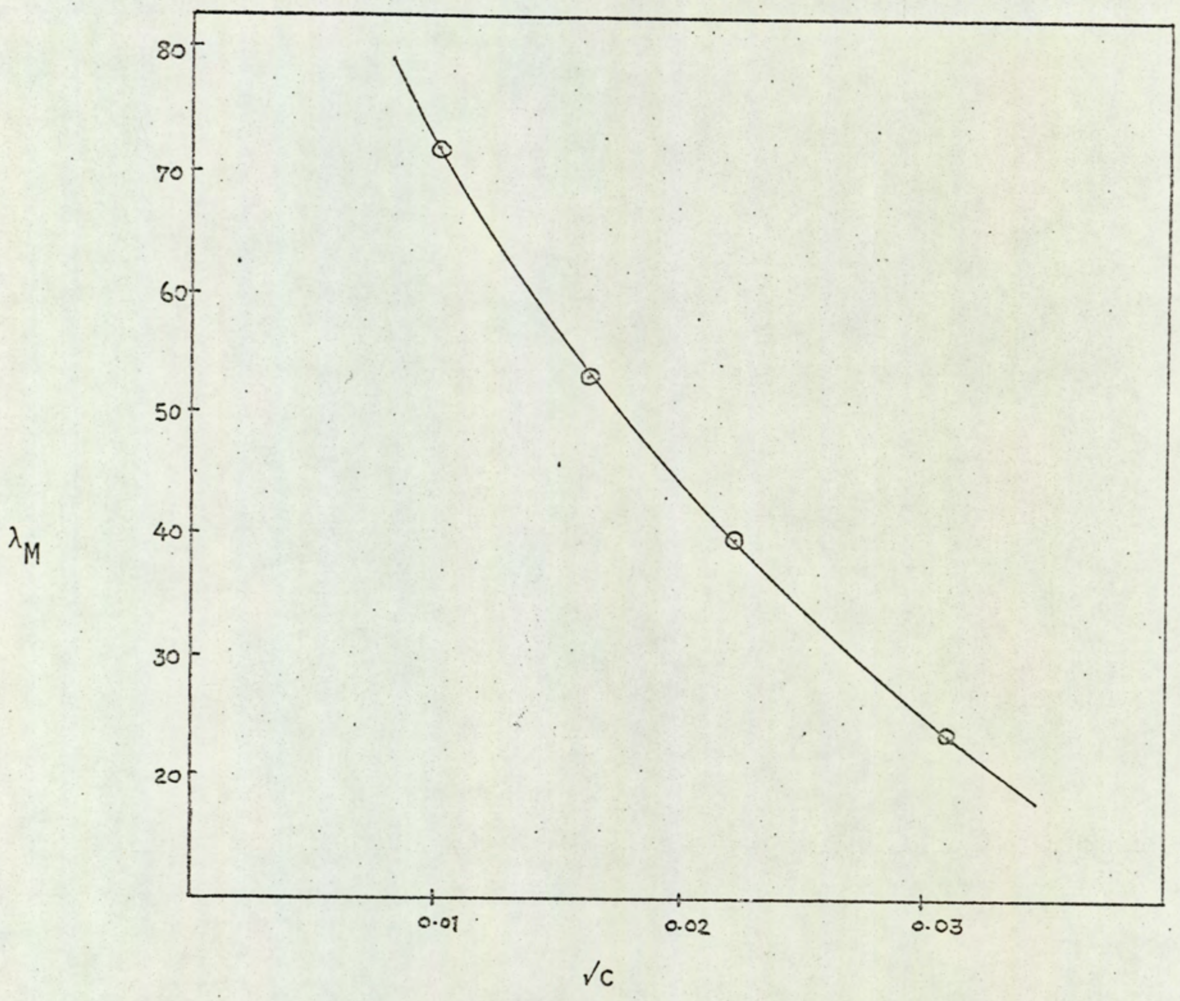


Fig: 6 Graph of square root of concentration against molar conductivity for $Rh(4.Phpy)_3.I_3$

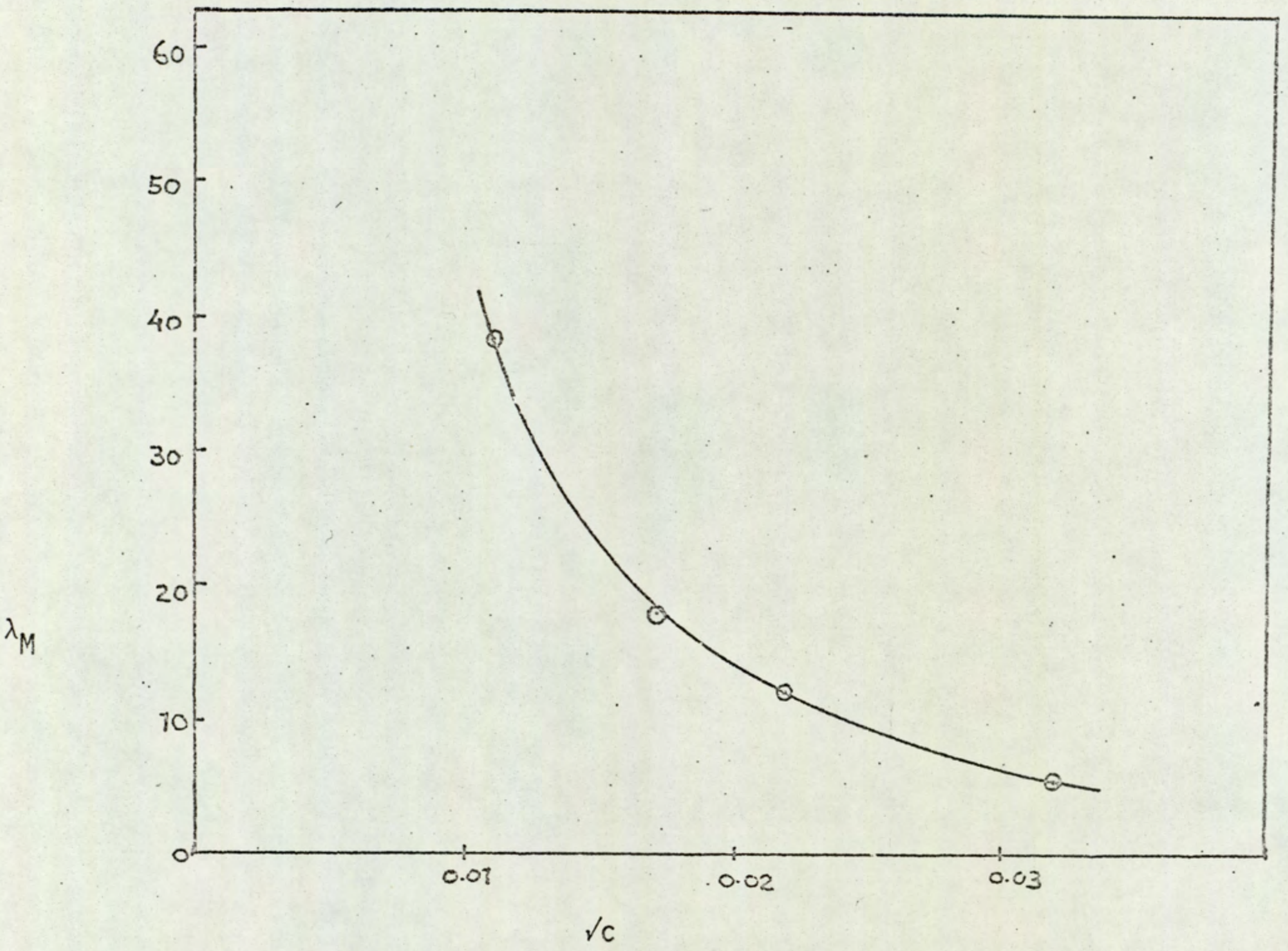


Fig: 7 Graph of square root concentration against molar conductivity for Rh(Terpy)I_3

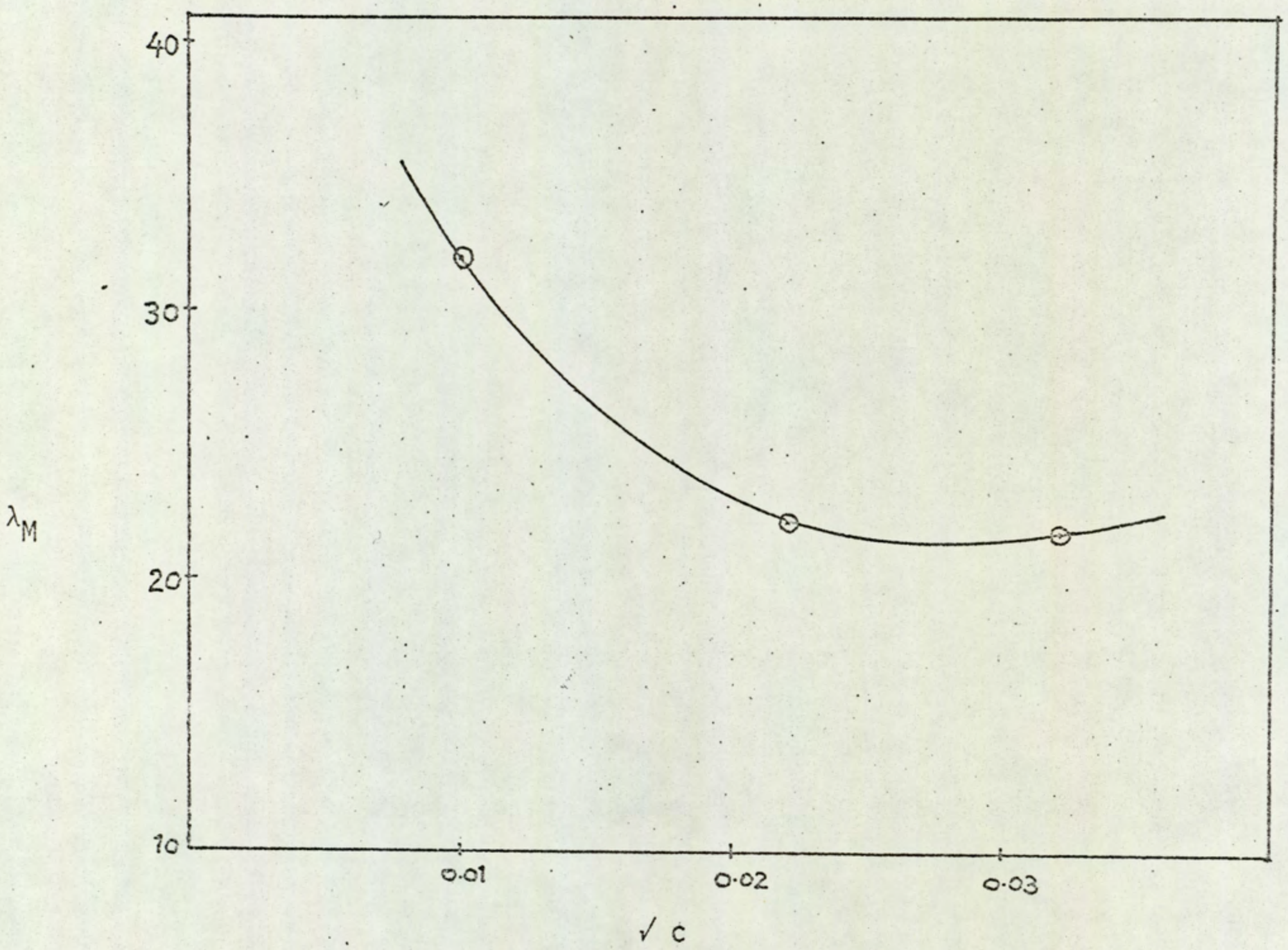


Fig: 8 Graph of square root of concentration against molar conductivity for $Rh(4\text{-}Phpy)_3.Br_3$.

[E] DISCUSSION

The steriochemistry of the rhodium(III) halide complexes with N-heterocyclic ligands such as pyridine and its substituted derivatives is derived from their far infra-red study. The spectra of these complexes in the region of below 400 cm^{-1} is more complicated than would be anticipated (see Table 2). When these ligands co-ordinate to the metal ions new bands are observed which are not present in the free ligands. Nakamoto and his co-workers recently proved for 2.2'-bipyridyl and 1.10-phenanthroline complexes that on co-ordination new ligand modes are activated[70]. They have studied the metal-isotopic effect on the metal-ligand vibrations in the tris-chelate complexes of the type $[M(bipy)_3]^{2+}$ and $[M(phen)_3]^{2+}$ (where M = Fe, Ni, and Zn). They have found that these complexes belong to D_3 symmetry. Thus M-N stretching modes (A_2 and 2E) are expected to be infra-red active. The M-N stretching frequencies in these complexes are established as 380-360 cm^{-1} for Fe(II), 300-240 cm^{-1} for Ni(II) and 240-175 cm^{-1} for Zn(II). Hence the order of M-N frequencies was established as Fe(II) $\gg$ Ni(II) $>$ Zn(II). In the study of rhodium(III) complexes this fact is considered and it is assumed that the greater mass of rhodium would lower the frequencies. Also the increased charge on Rh^{3+} can compensate this and the Rh-N frequencies for these heterocyclic ligands are expected to occur in the region of 300-200cm^{-1}. The far infra-red study of cis- and trans- $[Rh(pyridine)_3Cl_3]$ complexes were carried out by Clark and Williams[71] and they have assigned V(RhN) stretching frequencies: 266,245 cm^{-1} for cis - $[Rh(py)_3Cl_3]$ and 265,245, 230 cm^{-1} for trans-$[Rh(py)_3Cl_3]$

Also rhodium-bromine frequencies can be expected in this region where Rh-N frequencies are expected and the two types of metal-ligand vibration may couple. Thus it is improbable that the simple relationship $V(RhBr) \simeq 0.76 \times V(RhCl)$ will hold.

Since the present work suggests two different classes of complexes they are discussed separately.

(1) Non-ionic Tri-halogeno- complexes

The complexes of 4-phenyl pyridine, 4-methyl pyridine and 2.2'-2"-terpyridyl are considered as non-ionic.

Complexes of 2.2'-2"-terpyridyl

The solid state diffuse reflectance (see Table 1) of the three halogeno (chloride, bromide and iodide) complexes are similar showing shifts of the broad charge transfer absorption band to high wavelength in the order Cl < Br < I (see figure 9). This suggests that the rhodium ions in the three complexes are in similar environments. This can also be proved by the X-ray powder photographs. This is necessary for the valid assignment of spectra by comparison of chloro-, bromo- and iodo complexes. The spectra are recorded for polycrystalline materials, this may only be valid if they all crystallize with the same space group. X-ray powder data show, on calculation of 'd' values (see Table 3) that the three compounds are isomorphous. However, the assignments are not easy to make. These complexes are of unambiguous stereochemistry. Three rhodium halogen stretching frequencies are observed for $Rh(terpy)X_3$ where X = Cl,Br,I.

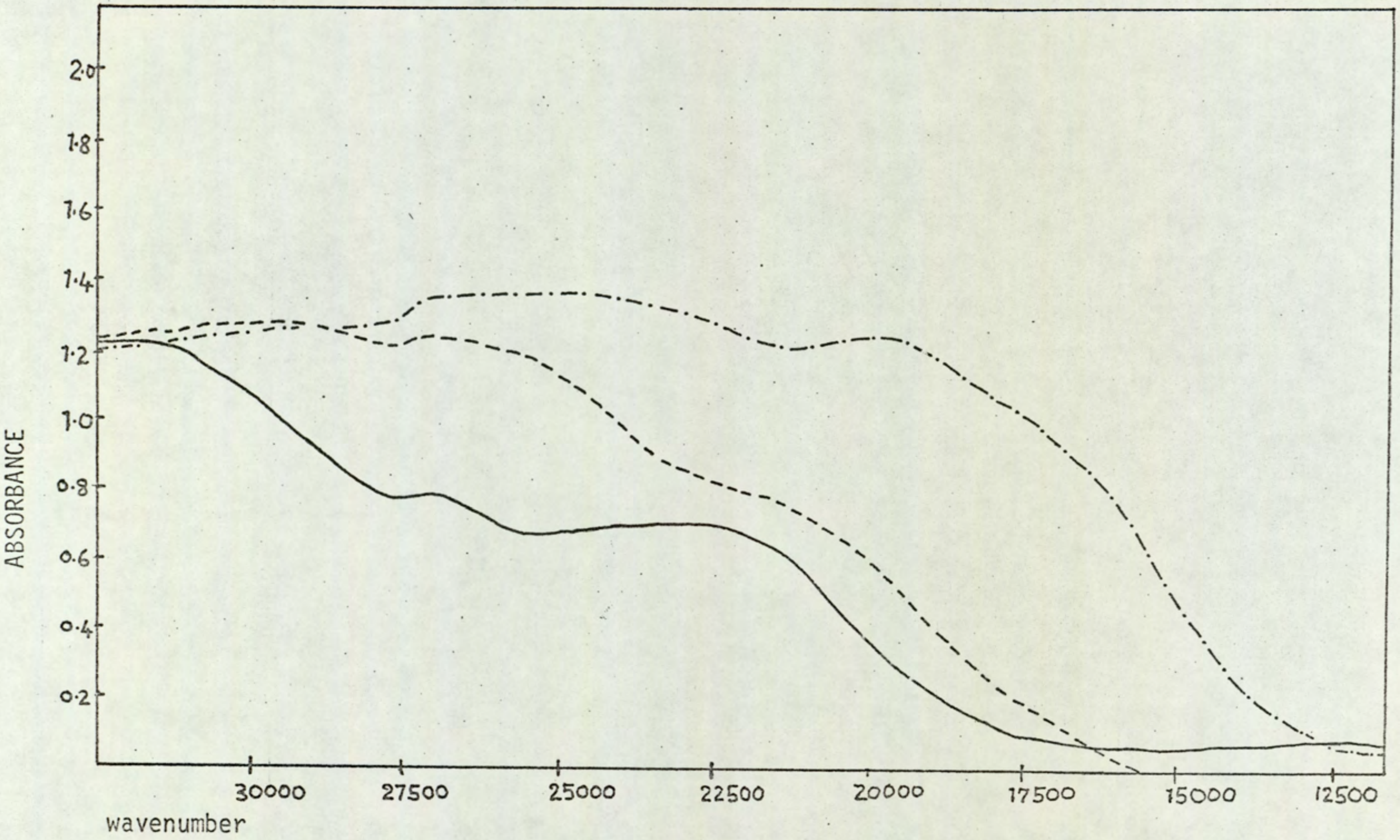


Fig: 9 The Diffuse Reflectance spectra of [Rh(Terpy)X_3] where X = Cl(———); Br(-----) and I(—·—·—).

Clark and Williams[71] observed three rhodium-chlorine stretching frequencies: 355 cm^{-1}, 332 cm^{-1}, and 295 cm^{-1} in the trans-$[Rh(py)_3Cl_3]$. The lowest frequency V(Rh-Cl) is weaker than the other two. Hence they suggested that this may be the symmetric (a_1) vibration of the Cl - Rh - Cl group. The strong to medium intensity bands at 379 cm^{-1}, 340 cm^{-1} and 330 cm^{-1} in $Rh(terpy)Cl_3$ are possibly due to the three Rh-Cl vibrations. The higher values for V(RhCl) in $Rh(terpy)Cl_3$ than in trans - $[Rh(py)_3.Cl_3]$ are due to the lower basic strength of 2.2'.2"-terpyridyl than pyridine. The bands at 209 cm^{-1} and 205 cm^{-1} which are more intense in $Rh(terpy)Br_3$ are likely to be V(RhBr). While the mode at 150 cm^{-1} can be considered as the third Rh-Br frequency. When the spectra of $Rh(terpy)Cl_3$ and $Rh(terpy)Br_3$ are compared, the assignments of Rh-Cl and Rh-Br frequencies do not show the usual relationship of $V(RhBr) \simeq 0.76(RhCl)$. In the complex $Rh(terpy)I_3$ the assignment of Rh-I is more complicated but the band at 178 cm^{-1} is assigned as one of the three expected rhodium-iodine frequencies. The comparison of the spectra of $Rh(terpy)X_3$ (where X = Cl,Br,I) is shown in the figure: 10.

Complexes of 4-methyl pyridine and 4-phenyl pyridine:

Complexes of rhodium(III) with pyridine have been well studied[46]. Rhodium forms both ionic and non-ionic complexes with pyridine as a ligand. The substitution of the other groups for hydrogen on the pyridine ring could produce some differences in the co-ordination ability of pyridine and properties of metal complexes. The position of the substitution in the pyridine ring also decides the stereochemistry of the complexes. More stable complexes can be obtained with 4- substituents for mono substituted pyridines. The

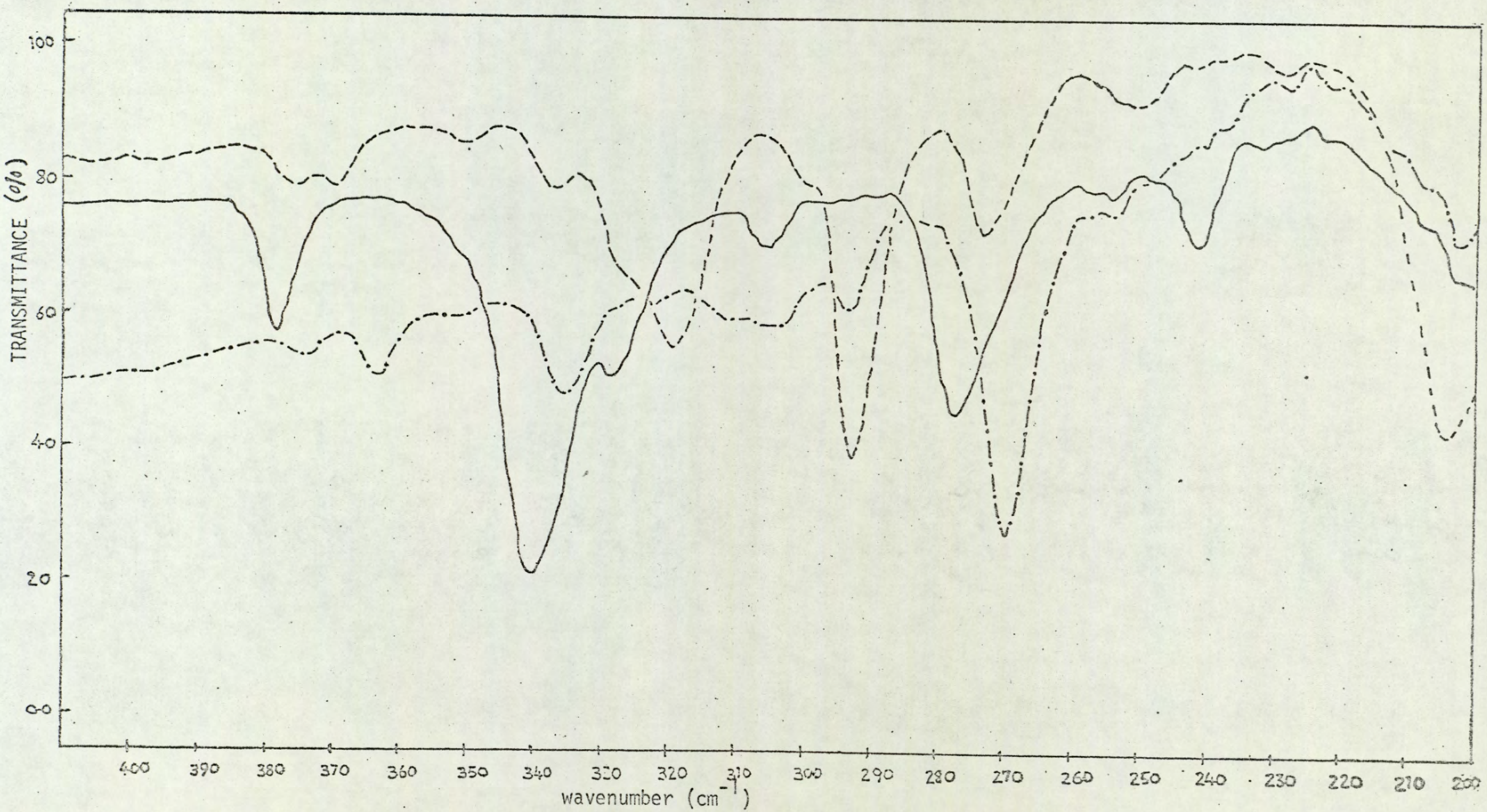


Fig: 10 Far infra-red spectra of [Rh(terpy)X$_3$] where X = Cl(———); Br(-----) and I(—·—·—).

substitution of electron attracting groups lowers the electron density on pyridine ring and decreases the bascity of the ligand. On the other hand substitution of electron releasing groups increases the electron density on the pyridine ring and strengthen the σ-bonding property of the ligand. It has been found that the infra-red frequencies of the complexes with electron attracting substituents are higher than, and those with electron-releasing substituents are a little lower than, that of the pyridine complexes. The study of the substituent effects upon the metal-nitrogen (ligand) and metal-chlorine stretching frequencies in the far infra-red region of a series of Cu(II) complexes with 4- substituted pyridine was carried out by Wong and his co-workers[72]. According to them the electron-releasing and electron-attracting groups appear to increase the chlorine-copper stretching frequencies. Also the metal-nitrogen stretching frequencies are appreciably changed by the effect of different substituents in the 4-position of the pyridine ring.

Rhodium forms monomeric, non-ionic complexes with 4-methyl pyridine and 4-phenyl pyridine. The complexes of the type RhL_3X_3 (where L = 4-Phpy and 4-Mepy and X = Cl,Br,I) give similar X-ray powder photographs and isomorphism is observed within the series of chloro-, bromo- and iodo- complexes on the basis of calculation of d values (see Table 3). The solid state diffuse reflectance spectra of these complexes are also similar showing shifts of the charge transfer band to high wavelength in the order Cl < Br < I (see figure 11). The possibility of cis- trans isomerism is considered but the differentiation by far infra-red spectroscopy is not a simple matter in practice. The assignment of RhCl

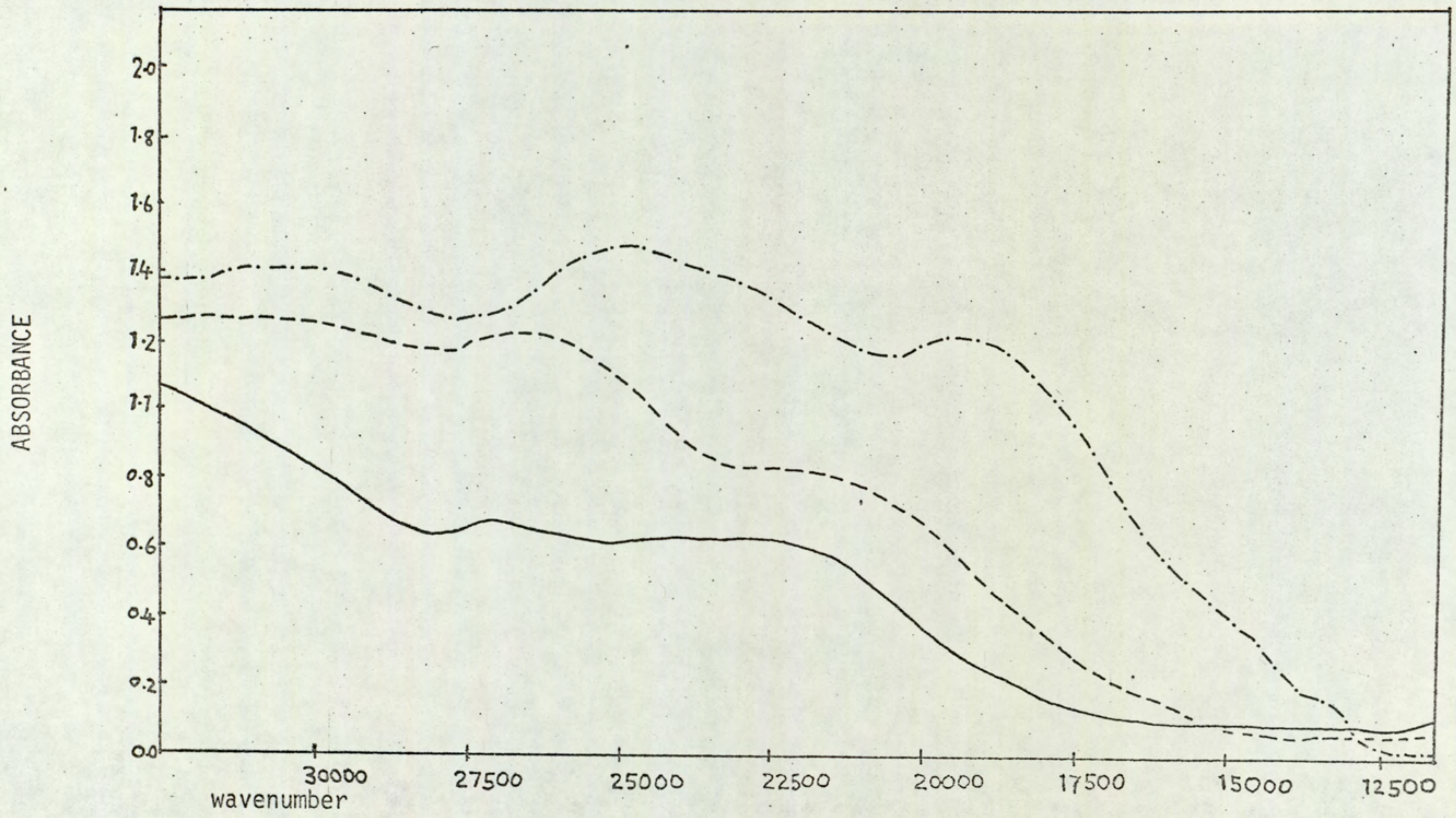


Fig: 11 The Diffuse Reflectance spectra of $[Rh(4\text{-}Phpy)_3X_3]$ where X = Cl(———); Br(- - - - -) and I(—·—·—).

stretching frequencies is not so easy since the complexes are of complex derivatives of N-heterocyclic ligands. The complex $Rh(4\text{-}Phpy)_3.Cl_3$ gives three Rh-Cl frequencies at 365 cm^{-1}, 331 cm^{-1} and 307 cm^{-1} on careful consideration of the spectra. This indicates the trans stereochemistry for the complex. The assignment of Rh-Br frequencies is very difficult since it gives a very complicated spectrum below 200 cm^{-1}. Bands at 205 cm^{-1} and 188 cm^{-1} may be considered as having some V(RhBr) character, but positive assignment is very difficult. While in the $Rh(4\text{-}Phpy)_3.I_3$ complex the band at 166 cm^{-1} is considered as V(RhI). Figure: 12 shows the more complicated spectrum for $Rh(4\text{-}Phpy)_3.X_3$ (where X = Cl,Br,I) in the region of 400-200 cm^{-1}. In the case of the complex $Rh(4\text{-}Mepy)_3.Cl_3$ the band at 344 cm^{-1} may be assigned as V(RhCl). The ligand 4-methyl pyridine is more basic than pyridine, thus the assignment of second rhodium chlorine frequency at 382 is not compelling. The band at 246 cm^{-1} is considered as due to the V(RhBr) for the complex $Rh(4\text{-}Mepy)_3Br_3$. The complexes of the type RhL_3X_3 are typical and far infra-red spectroscopy does not provide useful information for the structural investigations since assignments of metal ligand vibrations cannot be made with sufficient confidence for the normal symmetry arguments to be applied.

(2) Ionic complexes

Complexes of 2.2'-bipyridyl and 1-10-phenanthroline

The various compounds derived from the reaction of rhodium trichloride with 2.2'-bipyridyl and 1.10-phenanthroline in aqueous ethanol and in the presence of an excess of potassium bromide or

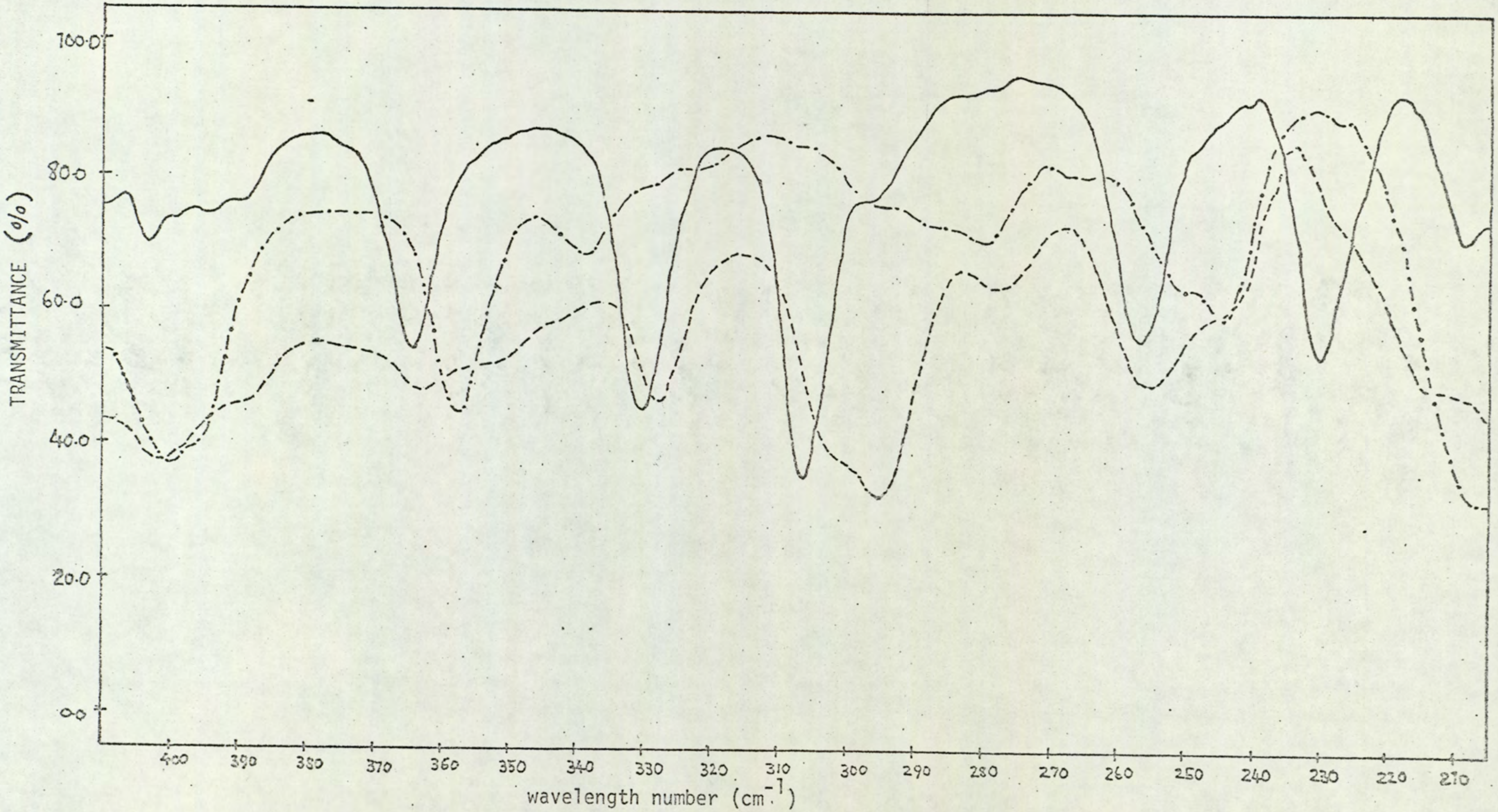


Fig: 12 Far infra-red spectra of $[Rh(4Phpy)_3X_3]$ where X=Cl(———); Br(-----) and I(–·–·–)

sodium iodide (in case of bromo- and iodo- complexes) are given in Table 1. These complexes have been prepared by different workers [48,49,50]. Salts of the cations $[Rh^{III}(chelate)_2.X_2]^+$ theoretically can exist in two geometrical isomers. However, only one such isomers has been obtained in all cases and assigned as having cis- octahedral geometry. The assignment of the geometrical isomerism from the electronic absorption spectra is not possible, since in these compounds the d-d band positions are obscured by other more intense absorptions of the complexes. The assignment of the cis configuration is based on a detailed study of the X-ray powder patterns of the solid salts of these cations and also from far infra-red and 'H.n.m.r. studies. Since the complexes $[Rh(bipy)_2.Cl_2].Cl$ and $[Rh(phen)_2.Cl_2]Cl$ are considered as having cis- stereochemistry (C_2 symmetry) they would have two coincident metal-chlorine bands in both the infra-red and Raman (A+B) spectra.

The present study of far infra-red spectroscopy for the known complexes such as $[Rh(bipy)_2.Cl].Cl$ and $[Rh(phen)_2Cl_2].Cl$ is considered mainly due to the current confusion about the precise location of rhodium-chlorine frequencies in the literature. Gillard and Heaton have observed two metal-chlorine frequencies for the complex $[Rh(bipy)_2.Cl_2].Cl$. Thus the bands at 356 cm^{-1} and 349 cm^{-1} are considered due to the V(RhCl)[48]. On the other hand Kulasingam et al[49] have reported the bands at 352 cm^{-1} and 348 cm^{-1} for V(RhCl). To overcome this confusion more convenient preparative methods are performed to synthesize these complexes and on careful observations of the far infra-red spectra it is found that the above results are reproduceable particularly for $[Rh(bipy)_2.Cl_2].Cl$. When different sampling techniques are applied the results observed are different. Using thin nujol mull the results are reproduced which have been reported by Gillard and Heaton. While thick nujol mull gives good agreement with that reported by Kulasingam and his co-workers (see Table 2). Similarly for the complex $[Rh(phen)_2.Cl_2].Cl$ assignment for the V(RhCl) is satisfactory when compared with that reported by Gillard and Heaton[48]. Thus in the case of $[Rh(phen)_2.Cl_2].Cl$ the bands at 354 cm^{-1} and 347 cm^{-1} are due to the V(RhCl). The band at 324 cm^{-1} is now considered as ligand vibration.

For the bromo complexes of rhodium(III) with 1.10-phenanthroline two different compounds are previously reported and they are characterized as mono and bis complexes such as $[phenH][Rh(phen)Br_4]$ and $[Rh(phen)_2.Br_2].Br$ by their elemental analysis, conductivity and 'H.n.m.r. spectroscopy. These compounds do not give spectra similar to that reported as $[Rh(phen)_2.Br_2].Br.2H_2O$ by Gillard et al[48]. In table 2 the assignments for the V(RhBr) are given and it is observed that the simple relationship for V(RhBr) $\simeq$ 0.76(RhCl) does not hold.

The synthesis of rhodium(III) complexes with bidentate ligands such as 2.2'-bipyridyl and 1.10-phenanthroline gives a variety of complexes. In the series of halogeno complexes of rhodium(III) with these ligands at least two complexes are isolated (but not in the case of iodide complex with 1.10-phenanthroline). This can be explained by the fact that various combinations of LH^+, $RhL_2X_2{}^+$,

X^- and $RhLX_4^-$ may afford a variety of products. The products which are prepared are a function of solvent composition and temperature. When more alcohol is used the major product obtained is $[RhL_2X_2][RhLX_4]$. While more water favours the formation of $RhL_2X_2^+$. Thus a variety of complexes are synthesized and identified. Since the carbon, hydrogen figures change with the addition of water molecules, elemental analysis does not unambiguously identify those complexes. Thus far infra-red is a more useful technique for the identification of these complexes. In the case of cationic complexes, rhodium-halogen frequencies occur at higher wavenumber than in the anionic complexes. Thus the compound $Rh_2.bipy_3.Cl_6$ is formulated as $[Rh(bipy)_2.Cl_2]$ $[Rh(bipy)Cl_4]$ despite its low conductivity value. Similarly $[Rh(bipy)_2.Br_2][Rh(bipy)Br_4]$ is identified which gives reasonable conductivity for uni-univalent electrolyte, although there is some evidence for overlap between the regions for V(RhBr) (cationic) and V(RhBr) anionic.

Mono complexes of the formula $[phenH][RhphenX_4]$ (where X = Cl,Br,I) have been reported previously[49]. Also the complex $[bipyH][RhbipyCl_4]$ is prepared from the reaction of rhodium trichloride and 2.2'-bipyridyl in hydrochloric acid. These complexes belong to the C_{2v} point group and should therefore have four infra-red active metal-halogen stretching frequencies. For $[bipyH][RhbipyCl_4]$ bands at 338, 333, 327 and 316 cm^{-1} are assigned to rhodium-chlorine stretching. (Fig.12a).

$[Rh(phen)_2.Cl_2].Cl.nH_2O$ crystallizes into two different polymorphic forms. They are α and ε. The α form is obtained when

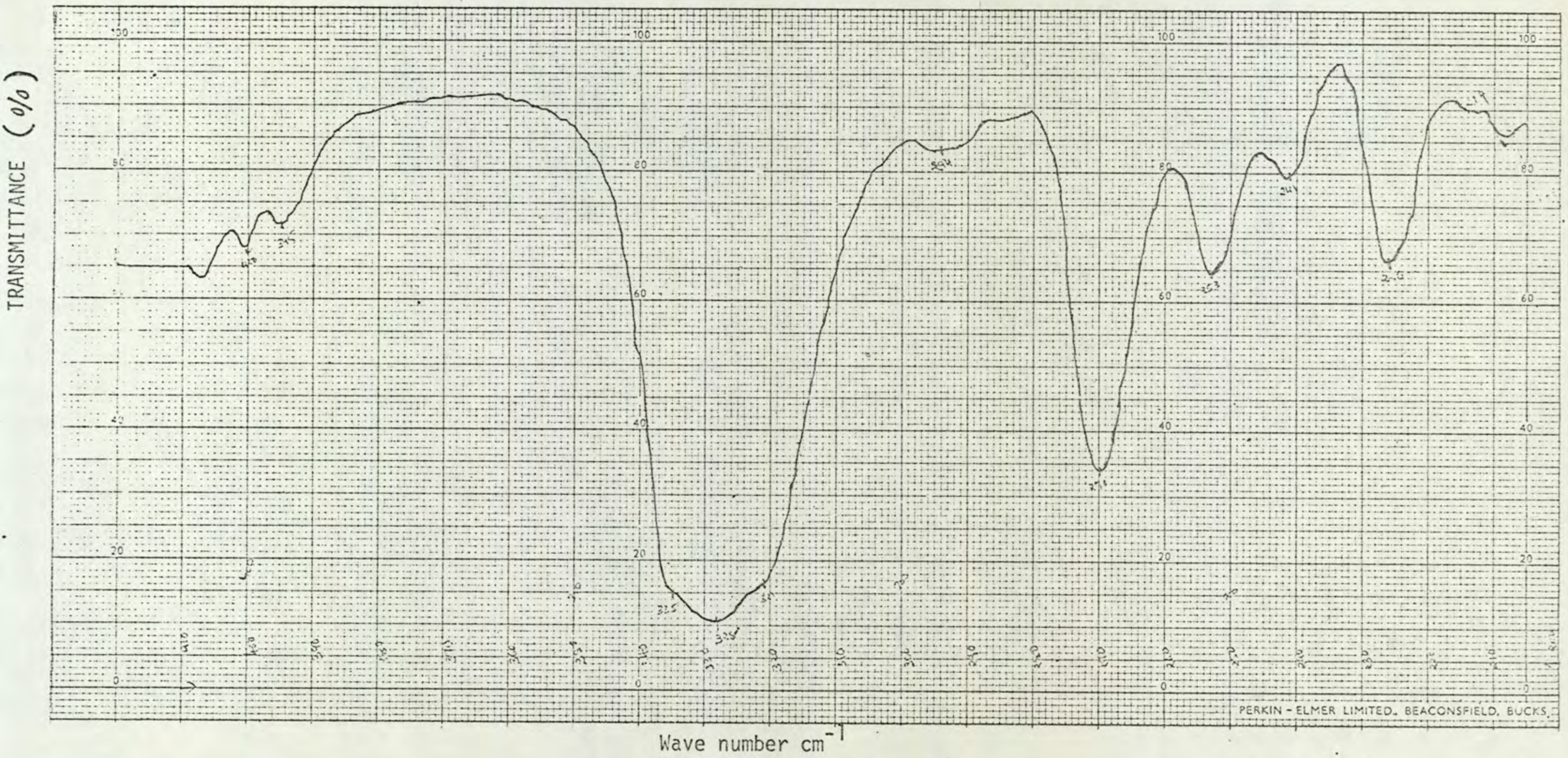


Fig:12a Far-infrared spectra of [bipyH$^+$][Rh(bipy).Cl$_4$] in the region of 400 - 200 cm^{-1}.

the complex is recrystallized from methanol and the ε form is obtained by recrystallisation from water or dilute hydrochloric acid. The spectra of these α and ε forms are relatively insentitive to charge of polymorph.

Complexes of 2-benzoyl pyridine

The complexes of rhodium(III) with 2-benzoyl pyridine (PhCOpy) are known[73]. Rhodium trichloride and 2-benzoyl pyridine in ethanol affords the complex of the formula $[Rh(PhCOpy)_2.Cl_2][Rh(PhCOpy)Cl_4]$. The cation can be obtained as perchlorate in two different isomeric forms e.g. orange and yellow and both have trans chloride ligands. Also the complexes of the type $[Rh(PhCOpy)_2.Cl_3]$,$[Rh(PhCOpy)Cl_3]$ and $[Rh(PhCOpy)_2.Br_3]$,$[Rh(PhCOpy)Br_3]$ have also been reported. These complexes were not synthesized as they were obtained directly from the previous worker[72] and were used without further purification for their detail far infra-red study. The assignment of V(RhCl) for the complexes of $[Rh(PhCOpy)_2.Cl_2].ClO_4$ - (1) and $[Rh(PhCOpy)_2.Cl_2][Rh(PhCOpy)Cl_4]$ - (2) is in good agreement with that reported previously[72]. Thus the bands at 374 cm^{-1} in - (1) and at 343-335 cm^{-1} in - (2) are due to the V(RhCl). The assignment of V(RhBr) in the complex $[Rh(PhCOpy)_2.Br_2].ClO_4$ is now necessary and the band at 234 cm^{-1} is now considered as V(RhBr). The complexes $[Rh(PhCOpy)_2.Cl_2].ClO_4$ and $[Rh(PhCOpy)_2.Br_2].ClO_4$ now appear to be trans complexes on the basis of their metal-halogen frequencies.

Complexes of substituted Bipyridyl

Substitution in 2.2'-bipyridyl may increase or lower the stabilities of metal complexes due to the increased or decreased basic strength of ligand. The substitution of 4.4'-position at bipyridyl may favour the stability of complexes depending upon the substitution groups. Both 4.4'-diphenyl 2.2'-bipyridyl and 4.4'-dimethyl 2,2'-bipyridyl give stable ionic complexes with rhodium(III) halides. The cations $[Rh(4.4'\text{-diMe } 2.2'\text{-bipy})_2.Cl_2]^+$ and $[Rh(4.4'\text{-diPh } 2.2'\text{-bipy})_2.Cl_2]^+$ are shown to be the cis-isomers as anticipated by their far infra-red data (see Table 2). Since the effects of both the electron-releasing and electron-attracting groups (as substituents for the hydrogen at the 4.4'-position in 2.2'-bipyridyl) appear to increase the metal-halogen stretching frequencies and the strengthening of metal-halogen bonds. The substitution gives a stronger metal-nitrogen bond; thus a higher electron density on the metal atom results (in the case of electron releasing groups) which enhances the drift of electron density from metal to halogen and strengthens the $d\pi$-$d\pi$ metal to chlorine bonding. Thus a rough correlation can be noted between V(RhCl) for the cationic complex $[RhL_2.Cl_2]^+$ and the anticipated σ donon power. The ease of σ bonding increases as:

2-benzoyl pyridine < 4.4'-diphenyl 2.2'-bipyridyl < 4.4'-dimethyl 2.2'-bipyridyl ~ 2.2'-bipyridyl.

The bromo complexes with these substituted bipyridyls illustrate some difficulty. Similar preparative methods gave $[Rh(4.4'\text{-diPh } 2.2'\text{-bipy})_2.Br_2]Br$ with 4.4'-diphenyl 2.2'-bipyridyl and

[4.4'-diMe 2.2'-bipyH][Rh(4.4'-diMe 2.2'bipy)Br_4] with 4.4'-dimethyl 2.2'-bipyridyl. The latter compound can easily be identified by its far infra-red spectrum. The band at 192 cm^{-1} in the <u>mono</u> complex can be assigned to V(RhBr). Whereas bands at 245 cm^{-1} and 234 cm^{-1} are assigned due to the V(RhBr) in [Rh(4.4'-diPh 2.2'-bipy)$_2$ Br_2].Br.

[F] CONCLUSION

Far infra-red spectroscopy is a rapidly expanding technique which is even now providing results of use to the inorganic and co-ordination chemist. Thus the technique is likely to be used increasingly in inorganic chemistry to assist in stereochemical assignments of new complexes containing metal-halogen bonds. However, the investigation suggests considerable limitations of far infra-red spectroscopy as a structure tool for the study of a complex molecule. The study of complexes of N-heterocyclic pyridine derivatives have shown that a variety of vibrational modes may occur in the same spectral region which make it more difficult to eliminate ligand vibrations confidently.

In the case of neutral complexes of rhodium(III) halides the assignment of the V(RhX) (where X = Cl, Br, I) is not easy. This virtually makes stereochemical assignment impossible on the infra-red data alone. On the other hand charged complexes give more promising results since cationic and anionic complexes may be differentiated more readily. The reaction of rhodium(III) halides with 2.2'-bipyridyl and 1.10-phenanthroline may afford a variety of products, routine scans of far infra-red spectra will serve as a useful tool to identification of these complexes. Also the confusion about the precise location for the rhodium-chlorine frequencies in the literature in the <u>bis</u>-chelated complexes is now removed. Since Nakamoto and his co-workers[70] have proved that metal-nitrogen modes occur in the same region, the isotopic substitution experiments with the combination of infra-red and Raman studies are necessary to achieve detailed assignments for these compounds which are considered for the present study.

CHAPTER FOUR

ASPECTS OF THE CHEMISTRY OF RHODIUM(III) COMPLEXES WITH 2.2'-BIPYRIDYL UNDER REDUCING CONDITIONS

[A] INTRODUCTION

Transition metal complexes of d^8 and d^{10} electronic configuration having particularly "soft ligands" have been found to co-ordinate and activate small molecules, e.g. CO, NO etc. These complexes are co-ordinatively unsaturated and undergo oxidative-addition and insertion reactions into the metal-carbon or metal-hydrogen bonds. The cobalt(I) ion, which is stabilized by tetradentate, conjugate chelating systems having nitrogen and oxygen as donor atoms, behaves as a powerful nucleophilic species and undergo oxidative-addition reactions[74]. Complexes with a stable Co^{111}-C σ bond can be obtained from these reactions. Recently Mestroni et al[75] have reported a new series of stable σ and π-allylic cobalt dimetallo - organic complexes with 2.2'-bipyridine and 1.10-phenanthroline as ligands. These cobalt(III) complexes containing cobalt to carbon σ- bonds have prompted us to synthesise similar types of complexes with rhodium.

It has been known for some years that intensely coloured solutions are obtained when rhodium(III) complexes of 2.2'-bipyridyl are treated with reducing agents such as sodium borohydride or sodium amalgum. This was thought to be a rhodium(I) species[58].

The major species present in the solution was believed to be bis-(2.2'-bipyridyl) rhodium(I) cation. At that time this cation was considered as having trans- stereochemistry[58]. During the recent years numerous papers have been published and the impossibility of this stereochemistry for bis-(2.2'-bipyridyl)complex has been established[76]. However, the recent crystal structure determination of the nitrate monohydrate of the isoelectronic $[Pd(bipy)_2]^{2+}$ ion establishes the description "distorted planar" to be preferable to "tetrahedral" [76a,77]. The compound bis-(1.10-phenanthroline) palladium(II) ion is known to be labile[78] and in this property might reasonably parallel by the rhodium(I) 2.2'-bipyridyl analogue.

In this section the possibility of an oxidative addition reactions to some co-ordinatively unsaturated rhodium(I)-2.2'-bipyridyl complexes are demonstrated. Reacrions of dichloro bis-(2.2'-bipyridyl) rhodium(III) chloride-dihydrate with reducing agents such as sodium borohydride and sodium amalgum in the presence of organic halides and triphenyl phosphine are discussed. The use of alkaline ethanol as a reducing agent is known and the reaction of rhodium(III) complexes of 2.2'-bipyridyl and di-2-pyridyl amine in alkaline ethanol in the presence of a tenfold molar excess of triphenyl phosphine is carried out. The recent synthesis of the known compound hydrido tetrakis-(triphenyl phosphine) rhodium(I) [79, 80] is performed to compare the products obtained from the above reactions.

[B] PREPARATIONS OF SOME NEW COMPLEXES OF RHODIUM(III) WITH 2.2'-BIPYRIDYL AND ORGANIC HALIDES OR TRIPHENYL PHOSPHINE AS LIGANDS

General observations

The apparatus was designed in order to perform reactions under an inert atmosphere. The reactions are conveniently performed in a three neck 250 ml round bottomed flask fitted with a condenser and a nitrogen inlet. The reaction solutions are stirred magnetically.

(1) Iodo phenyl *bis* (2.2'-bipyridyl) rhodium(III) perchlorate

Rhodium trichloride trihydrate (0.26 gm 1 m mole) was dissolved in nitrogen saturated methanol (100 ml). An excess of iodo benzene was added to the solution. This was then followed by the addition of the solution of 2.2'-bipyridyl (0.312 gm 2 m mole) in nitrogen saturated methanol (20 ml). Sodium borohydride was slowly added to the solution which was maintained under an atmosphere of nitrogen. The colour of the solution was changed from a pink-brown through red-violet to brown. The addition of borohydride is complete at this stage. The resulting solution was then refluxed for two hours under the atmosphere of nitrogen. The solution was then cooled and filtered to remove insoluble material. An excess of sodium perchlorate was added to the clear brown solution. The solution was kept aside for a few minutes. The excess solvent was then removed on a rotatory evaporator. The remaining solid residue was washed well with water to remove the soluble components. Then it was thoroughly washed with ether to remove iodobenzene. The resulting brownish-yellow solid was then dried over P_4O_{10} under vacuum. On recrystallization from a water-methanol mixture a yellow crystalline product was obtained.

Found: C,42.3%; H,3.2%; N,7.8%.
$C_{26}H_{21}IN_4$.Rh ClO_4
Requires: C,43.4%; H,2.9%; N,7.6%

(2) Chloro benzyl bis (2.2'-bipyridyl) rhodium(III) perchlorate

Rhodium trichloride trihydrate (0.26 gm 1m mole) was dissolved in nitrogen saturated methanol (100 ml). To this a solution of 2.2'-bipyridyl (0.312 gm 2m mole) in nitrogen saturated methanol (20 ml) was added followed by benzyl chloride. Sodium borohydride was gradually added to the reaction mixture which was kept under the nitrogen atmosphere. A change in the colour of the solution was observed from pink through reddish-violet to dark brown. At this stage the addition of sodium borohydride is completed. The resulting solution was then refluxed for 2 hours under an atmosphere of nitrogen. The solution was cooled and it was then filtered to remove insoluble material. To the dark-brown solution an excess of sodium perchlorate was added. The excess of solvent was removed on a rotatory evaporator. The brown residue obtained was treated with water to remove soluble components. Water was removed by filtration and the remaining solid residue was again washed with water and then with ether to remove excess benzyl chloride. The product was dried over P_4O_{10} under vacuum.

The crude product was recrystallized from acetone water mixture to give brown-yellow crystals.

Found: C,50.6%; H,3.7%; N,8.8%.
$C_{26}H_{23}.Cl\ N_4Rh\ ClO_4$
Requires: C,50.5%; H,3.6%; N,8.7%.

(3) Bromo benzyl *bis* (2.2'-bipyridyl) rhodium(III) perchlorate

(a) To the solution of rhodium trichloride trihydrate (0.26 gm 1m mole) in nitrogen saturated methanol (100 ml) was added the solution of 2.2'-bipyridyl (0.312 gm 2m mole) in methanol (20 ml) saturated with nitrogen together with an excess of benzyl bromide. Sodium borohydride was slowly added to the reaction mixture which was maintained under the atmosphere of nitrogen until the colour changed through red violet to dark brown. The resulting solution was then refluxed for 2 hours under nitrogen atmosphere. It was then cooled and filtered. To the dark brown solution an excess of sodium perchlorate was added. The excess solvent was removed on a rotatory evaporator. The solid residue was treated with water in order to dissolve soluble components. The remaining solid residue was then filtered and washed thoroughly with water and then several times with ether to remove the excess of benzyl bromide. The final product was recrystallized from methanol-water mixture to afford brownish-yellow crystals of the pure complex. The crystals were dried over P_4O_{10} under vacuum.

Found: C,48.2%; H,3.8%; N,8.0%.

$C_{26}H_{23}$ BrN_4Rh ClO_4

Requires: C,47.3%; H,3.4%; N,8.3%.

(b) A separate experiment was carried out for the synthesis of Bromo benzyl bis (2.2'-bipyridyl) rhodium(III) perchlorate by using sodium mercury as a reducing agent.

To the solution of $[Rh(bipy)_2.Cl_2].Cl.2H_2O$ (prepared and characterized as described in the Chapter 3) (0.24 gm) in nitrogen saturated methanol (100 ml) freshly prepared sodium amalgum was added under the atmosphere of nitrogen. A reduction was continued until the solution assumed a reddish-purple colour. When the reduction was complete the amalgum was removed from the reaction medium. To the remaining solution an excess of benzyl bromide was added under nitrogen atmosphere. The colour of the solution was immediately changed to an orange-yellowish-brown. The solution was filtered and the excess of sodium perchlorate was added. The excess solvent was then removed on a rotatory evaporator. The remaining solid residue was treated with water to dissolve soluble components. It was then filtered again, washed with water and finally with ether to remove the excess of benzyl bromide. The final product was recrystallized from methanol-water mixture to afford orange-brown crystals of the complex. The complex prepared is identical to that prepared by the borohydride reduction.

(4) Iodo methyl bis (2.2'-bipyridyl) rhodium(III) perchlorate

Rhodium trichloride trihydrate (0.26 gm 1m mole) was dissolved in nitrogen saturated methanol (100 ml). An excess of methyl iodide was added to the solution together with the solution of 2.2'-bipyridyl (0.312 gm 2m mole) in methanol (20 ml) saturated with nitrogen. The reaction mixture was then reduced by sodium borohydride under nitrogen atmosphere. Sodium borohydride was added until the colour of the solution changed through red-violet to brownish-yellow. The resulting solution was then refluxed for nearly two hours under the atmosphere of nitrogen. The solution was then cooled and filtered to remove solid insoluble material. The dark brown filtrate was cooled and the excess of sodium perchlorate was then added. The excess solvent was then removed on a rotatory evaporator. The remaining solid residue was treated with water to dissolve soluble components. Finally the product was washed with water and then with ether. On recrystallization of the crude product from methanol-water mixture, orange-yellow crystals of the complex were obtained. The crystals were filtered, washed with ice-cold water and dried over P_4O_{10} under vacuum.

This preparation was repeated in which methyl iodide was added after the reduction of the reaction mixture containing rhodium trichloride and 2.2'-bipyridyl by borohydride. The product obtained was identical.

Found: C,37.8%; H,2.9%; N,8.0%.

$C_{21}H_{19}I.N_4Rh\ ClO_4$

Requires: C,38.4%; H,3.0%; N,8.5%.

(5) Iodo ethyl-*bis* (2.2'-bipyridyl) rhodium(III) perchlorate

To the solution of rhodium trichloride trihydrate (0.26 gm 1m mole) in nitrogen saturated methanol (100 ml) was added the solution of 2.2'-bipyridyl (0.312 gm 2m mole) in nitrogen saturated methanol (20 ml) followed by an excess of ethyl iodide. Sodium borohydride was slowly added to the solution which was maintained under an atmosphere of nitrogen until the colour of the solution was changed through reddish-violet to dark brown. The resulting mixture was then refluxed for 2 hours under the atmosphere of nitrogen. The solution was then cooled. The solid material remaining after the reflux period was removed by filtration. An excess of sodium perchlorate was added to the dark brown filtrate. The solvent was then removed on a rotatory evaporator. The remaining solid residue was treated with water to dissolve soluble components. The solid was then filtered, washed with water and then with ether to remove the excess ethyl iodide. The crude product was recrystallized from methanol-water mixture to afford orange brown crystals of the complex. The crystals were filtered and dried over P_4O_{10} under vacuum.

Found: C,37.8%; H,3.0%; N,8.0%;

$C_{22}H_{21}I\ N_4Rh\ ClO_4$

Requires: C,39.3%; H,3.1%; N,8.3%.

(6) Dihydrido bis (triphenyl phosphine) mono (2.2'-bipyridyl) rhodium(III) perchlorate

Pure $[Rh(bipy)_2.Cl_2].Cl.2H_2O$ (0.24 gm) was dissolved in nitrogen saturated methanol (50 ml) under an atmosphere of nitrogen. To this solution an excess of sodium borohydride was added. When the colour of solution was changed to a reddish-violet a tenfold molar excess of triphenyl phosphine was rapidly introduced. The solution was vigorously stirred and the colour of the solution changed to pink-brown. At this stage the reaction was complete and the reaction solution was kept aside for one hour. The solution was then filtered and to the clean solution an excess sodium perchlorate was added. A white crystalline product was obtained. The crystals were filtered, washed with water then with ice-cold methanol and finally with ether and dried over P_4O_{10} under vacuum.

A similar experiment was carried out which was identical except for the replacement of sodium borohydride by sodium amalgum. No hydrido complex was obtained.

Found: C,62.4%; H,3.4%; N,4.5%.

$C_{46}H_{40}N_2P_2Rh\ ClO_4$

Requires: C,62.4%; H,3.1%; N,4.6%.

[C] The reaction of rhodium(III) compounds with triphenylphosphine in alkaline ethanol

The reduction of $Rh(bipy)_2.Cl_2.Cl.2H_2O$ complex with sodium borohydride and sodium amalgum in the presence of a tenfold molar excess of triphenyl phosphine has lead for the further investigation of the reduction of rhodium(III) compounds in alkaline ethanol.

The following experiments were performed.

(1). Pure $[Rh(bipy)_2.Cl_2].Cl.2H_2O$ (0.24 gm) was suspended in ethanol (50 ml). To this potassium hydroxide (0.5 gm approximately) was added followed by a tenfold molar excess of triphenylphosphine. The reaction mixture was then heated under reflux for 2 hours. The pale yellow colour of the solution disappeared with the formation of an orange-yellow microcrystalline product. These crystals were filtered when the solution was hot through a sintered glass crucible. The product was then washed several times with hot ethanol and finally with water. The crystals were dried over P_4O_{10} under vacuum.

(2) A similar experiment was carried out except for the replacement of $[Rh(bipy)_2.Cl_2].Cl.2H_2O$ by $[Rh(bipy)_2.Br_2].Br$. The orange-yellow product obtained was identical to that obtained in the above preparation.

(3) Dichloro bis (di-2-pyridylamine) rhodium(III) chloride was used in a separate experiment. A reduction of this complex was carried out in alkaline ethanol with triphenylphosphine in excess. The orange-

yellow microcrystalline product was obtained when the solution was heated under reflux for 2 hours.

The conditions employed here are essentially those reported recently by Robinson and his co-workers [79]. It is thus observed that rhodium may be introduced as the trichloride, as $[Rh(bipy)_2X_2.X]$ (where X = Cl, Br) or as dichloro bis (di-2-pyridylamine) rhodium(III) chloride and the product obtained in each case was "$HRh(PPh_3)_4$". Thus the orange-yellow peoducts obtained under air (V(RhH)= 2140 cm^{-1}) correspond in description to specimens of $HRh(PPh_3)_4$ given by Robinson's earlier method using borohydride as the reducing agent[80].

The orange-yellow crystalline product was identified as $HRh(PPh_3)_4$ by elemental analysis, infrared and 'H n.m.r. data.

The above experiments were performed under an atmosphere of nitrogen and argon separately. In both cases yellow products were obtained in good yield (V(RhH) = 2140 cm^{-1}). These also corresponded to products obtained more recently by Robinson[77].

Found: C,74.7%; H,5.4% - (a)
C,72.9%; H,5.2% - (b)

$C_{72}H_{61}P_4Rh$

Requires: C,74.9%; H,5.3%

[(a) $HRh(PPh_3)_4$ - synthesised from $Rh(bipy)_2.Cl_2.Cl.\ 2H_2O$ under argon.

(b) Synthesis of $HRh(PPh_3)_4$ from $Rh(bipy)_2.Cl_2.Cl.\ 2H_2O$ under air.]

Synthesis of $HRh(PPh_3)_4$

The compound $HRh(PPh_3)_4$ is known and the methods of preparation are described in the literature [79,80]. For the comparison of its infrared spectra and mass spectra with those obtained by the reaction of rhodium(III) compounds in alkaline ethanol, the synthesis of $HRh(PPh_3)_4$ is carried out by the methods known in the literature. The preparative methods are described briefly.

(i) Using Sodium borohydride as a reducing agent

Rhodium trichloride trihydrate (0.13 gm,0.5m mole) in nitrogen saturated warm ethanol (10 ml) and sodium borohydride (0.10 gm 2.5m mole) in nitrogen saturated warm ethanol (10 ml) were added rapidly and successively to a vigorously stirred solution of triphenylphosphine (1.31 gm, 5.0 m mole) in boiling nitrogen saturated ethanol (40 ml) which was maintained under an atmosphere of nitrogen. The reaction mixture was heated under reflux for about 5 minutes under the atmosphere of nitrogen. Then it was cooled to 30^oC, filtered and the precipitate washed with water, ethanol, and n-hexane to give the product as orange-yellow microcrystals.

$$[V(RhH) = 2140\ cm^{-1}]$$

Found: C,76.49%; H,5.6%.

$C_{72}H_{61}P_4Rh$

Requires: C,75.0%: H,5.35%.

(ii) Using alkaline ethanol as a reducing agent

Solutions of rhodium trichloride trihydrate (0.26 gm 1m mole) in nitrogen saturated warm ethanol (20 ml) and potassium hydroxide (0.4 gm) in nitrogen saturated warm ethanol (20 ml) were added in rapid succession to a vigorously stirred solution of triphenyl phosphine (2.62 gm 10 m mole) in boiling nitrogen saturated ethanol (80 ml) which was also kept under an atmosphere of nitrogen. The reaction mixture was then heated under a nitrogen atmosphere for 10 minutes. It was then cooled to 30^o, filtered, and the precipitate washed with ethanol, water, ethanol and finally n-hexane. It was then dried over P_4O_{10} under vacuum to give the required product as yellow microcrystals.

m.p. 145 - 147^o

Found: C,75.9%; H,5.9%.

$C_{72}H_{61}P_4Rh$

Requires: C,75.0%; H,5.35%.

[D] Reaction of Hydrido tetrakis (triphenyl phosphine) rhodium(I) with 2.2'-bipyridyl

Pure $HRh(PPh_3)_4$ (0.115 gm 1m mole) was dissolved in ethanol (50 ml). An excess of 2.2'-bipyridyl together with an excess of sodium perchlorate was added and the solution was heated under reflux for 2 hours. The colour of the solution was changed from an orange-yellow through reddish-brown to pinkish-brown. The solution was cooled and the excess solvent was removed on a rotatory evaporator. The solid residue was then treatedwith water to dissolve soluble components. The remaining solid was filtered, washed several times with water, then with ether. Finally it was washed with benzene and dried over P_4O_{10} under vacuum. The product was extracted with boiling petrolium ether (80/100 fraction) to remove excess bipyridyl. The product obtained was a pinkish-white in colour, identical to that prepared by the reaction of $[Rh(bipy)_2.Cl_2]Cl.2H_2O$ with sodium borohydride in the presence of a tenfold molar excess of triphenylphosphine which was characterized as $[Rh(bipy)(PPh_3)_2H_2]ClO_4$.

Found: C,62.1%; H,3.5%; N,4.3%.

$C_{46}H_{40}N_2P_2Rh\ ClO_4$

Requires: C,62.4%; H,3.1%; N,4.6%.

[E] Reactions of $HRh(PPh_3)_4$ with dilute mineral acids

(i) Reaction with dilute Nitric acid:

Pure $HRh(PPh_3)_4$ (0.1 gm) was suspended in dilute nitric acid (4M, 50 ml) and refluxed for 2 hours. The colour of the compound changed from an orange-yellow through brown to green. The resulting green product was filtered while the solution was hot, washed several times with water and dried over P_4O_{10} under vacuum.

The green compound is formulated from its infra-red spectrum, conductivity and elemental analysis and mass spectrum as

$$Rh(Ph_3PO)_2(NO_2)(NO_3)$$

Found: C,55.1%; H,3.9%; N,5.4%.
$C_{36}H_{30}N_3P_2RhO_7$
Requires: C,55.3%; H,3.8%; N,5.4%.

(ii) Reaction with dilute Hydrochloric acid:

Pure hydrido <u>tetrakis</u> (triphenyl phosphine) rhodium(I) (0.1 gm) was suspended in dilute hydrochloric acid (4M 50 ml) and refluxed for 2 hours. The colour was changed from an orange-yellow through orange brown to red. The final red product was filtered while the solution was hot, washed several times with water and finally dried over P_4O_{10} under vacuum.

The red product is formulated as pure [Rh$(PPh_3)_3$.Cl] which is known [42] from infra-red and elemental analysis.

Found: C,70.38%; H,5.11%;

$C_{54}H_{45}ClRhP_3$

Requires: C,70.1%; H,5.0%.

(iii) Reaction with dilute perchloric acid:

Pure HRh$(PPh_3)_4$ (0.1 gm) was suspended in dilute perchloric acid (4M, 50 ml) and refluxed for 2 hours. The colour of the compound was changed from an orange-yellow to red. The final red product was filtered while the solution was hot, washed several times with water and dried over P_4O_{10} under vacuum.

Immediate infra-red spectrum was obtained which showed that the perchlorate was ionic. The red compound gradually changed its colour and after keeping for a few days a brown coloured compound was obtained. This brown compound showed co-ordinated perchlorate in the infra-red region.

The product obtained by the reaction of HRh$(PPh_3)_4$ with dilute perchloric acid is not characterized.

[F] RESULTS

In Table 4 molar conductivities in pure nitromethane for some new compounds of rhodium(III) are given. These complexes are of the type $[Rh(bipy)_2RX](ClO_4)$ where RX is an organic halide. Also data for the new complex $[Rh(bipy)(PPh_3)_2H_2].ClO_4$ are given. The products obtained from the reaction of rhodium(III) compounds in alkaline ethanol in the presence of a tenfold molar excess of triphenyl phosphine are given. The reaction products from the reaction of $HRh(PPh_3)_4$ with mineral acids are given with their conductivity data.

TABLE:4 MOLAR CONDUCTIVITIES OF SOME NEW RHODIUM COMPLEXES

Complex	Molar Conductivities λM (10^{-3} Molar Solution) in Nitromethane.
1. $[Rh(bipy)_2(Ph)I].ClO_4$	84
2. $[Rh(bipy)_2(PhCH_2)Cl].ClO_4$	59
3. $[Rh(bipy)_2(CH_3)I].ClO_4$	123
4. $[Rh(bipy)_2(C_2H_5)I].ClO_4$	105
5. $[Rh(bipy)_2(PhCH_2)Br].ClO_4$	69
6. $[Rh(bipy)(PPh_3)_2(H_2)].ClO_4$	78
7. $[H(PPh_3)_4Rh]$	~ 0 *
8. $[Rh(PhPO)_2(NO)_2(NO_3)]$ †	~ 0
9. $[Rh(PPh_3)_3.Cl]$	~ 0

* decomposed

† green product from the reaction of $HRh(PPh_3)_4$ with dilute HNO_3

[G] DISCUSSION

The use of a methanolic solution of sodium borohydride suggests the most convenient synthetic route for the synthesis of new rhodium(III) complexes. These complexes are believed to be obtained by oxidative-addition reactions to some co-ordinatively unsaturated rhodium(I) complexes of 2.2'-bipyridyl. Under an atmosphere of nitrogen bis-(2.2'-bipyridyl) rhodium(III) complexes can be reduced by sodium borohydride. Thus, when bis-(2.2'-bipyridyl)rhodium(III) compounds are reduced by methanolic solution of sodium borohydride an intense reddish-violet colour is obtained. On addition of a tenfold molar excess of triphenyl phosphine, the reddish-violet colour disappeared. Addition of an excess of sodium perchlorate to this solution afforded a white crystalline material. Infra-red, ^{1}H.n.m.r. elemental analysis and conductivity data suggest the possible formulation of this white material as $[Rh(bipy)(PPh_3)_2.H_2].ClO_4$.

The high field ^{1}H.n.m.r. spectrum (see figure 13) showed a quartet centred on $\tau = 25.7$ (1:3:3:1). This possibly arises from a pair of overlapping triplets (1:2:1) and implies that $J_{Rh-H} \simeq J_{PH} \simeq$ 15 Hz. Spin-spin coupling of the M-hydrogens with other nuclei in the complex, in particular with the central metals is observable with the Rh^{103}, Pt^{195} and W^{183} nuclei, provides strong evidence for direct M-H bonds. Coupling with other ligands attached to the central metal atom can also be observed. For example in the phosphine hydrides the P^{31} nucleus will couple with the hydrogen. It has been found that the phosphorous-hydrogen coupling constants (J_{PH}) can provide evidence for the configuration of various

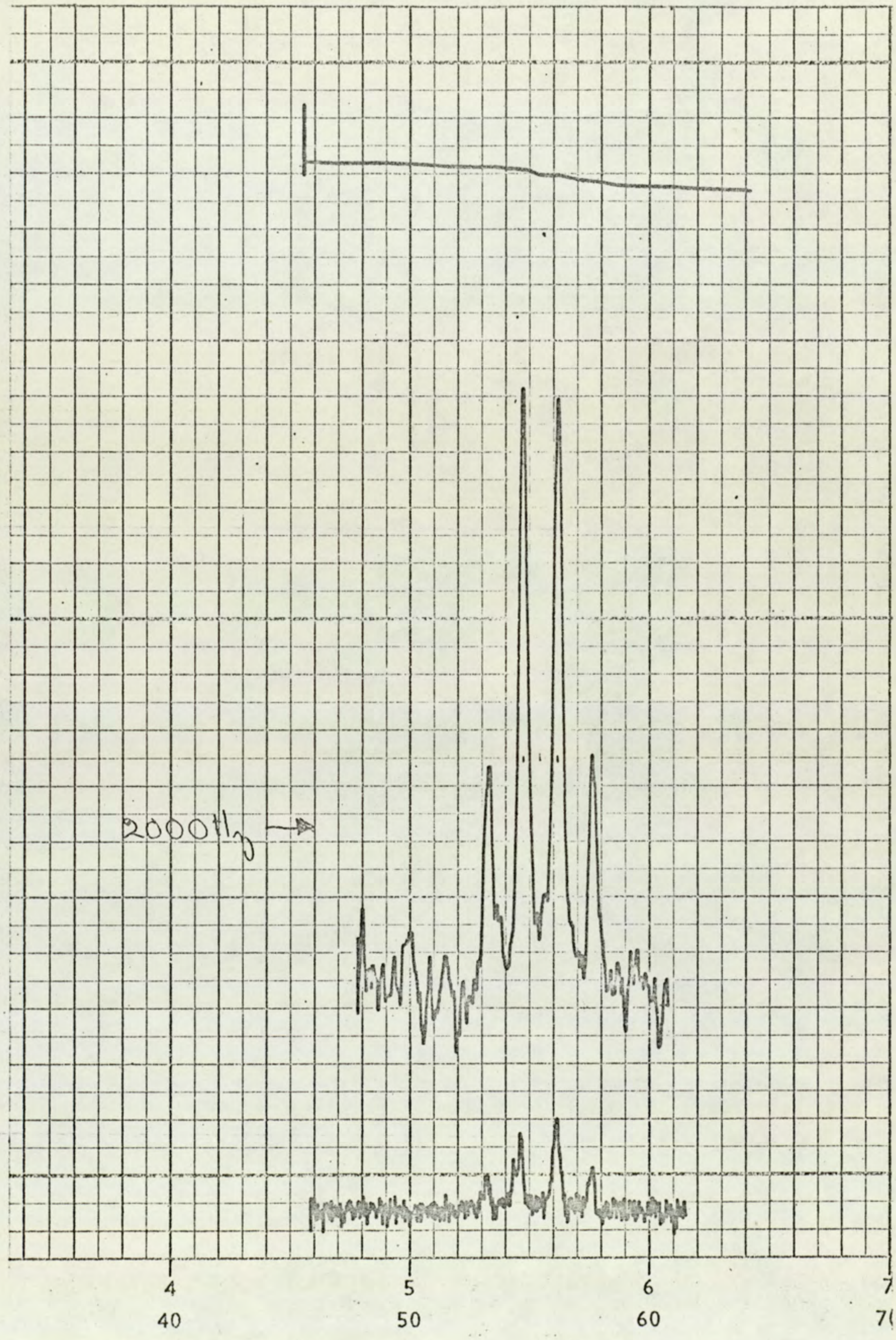


Fig:13 'H.n.m.r. spectrum of $[Rh(bipy)(PPh_3)_2.H_2].ClO_4$ in nitromethane.

geometrical isomers e.g. cis and trans. For the number of octahedral hydride-phosphine complexes it has been found that H-^{31}P coupling constants are greater (J = 80-150 cps) for hydrogen occupying a position trans to a phosphorous atom than for hydrogen cis to phosphorous (coupling constants 15 cps).[81]. The spectrum and the value of J_{PH} suggest that phosphine ligands are located cis to equivalent hydrogen atom [82]. Also the τ values for hydrogen trans to phosphorous are generally lower than those when hydrogen is trans to a halide or a similar ligand[83]. The high hydride shifts which can be explained by assuming that a nitrogen atom is trans to hydrogen. Chatt and his co-workers[84] have suggested that in octahedral transition metal complexes a hydride ligand in a trans position to tertiary phosphine or carbon monoxide ligands has chemical shifts within the range τ 18-22, while larger shifts are shown when the hydrid is trans to a chloride ligand. The effect of 2.2'-bipyridyl must not be very different from that of chloride ligand.

The infra-red spectrum (see figure 14) shows a split band (2120, 2050 cm^{-1}) for Rh-H stretching frequencies (ca. 2000 cm^{-1} for transition-metal and hydrogen bonds). This is to be expected for cis-dihydrido groups and it suggests the cation to be cis-dihydrido trans-(triphenyl phosphine) mono (2.2'-bipyridyl) rhodium(III).

Thus on the basis of infra-red and ^{1}H.n.m.r. studies the possible structure for the cation $[Rh(bipy)(PPh_3)_2H_2]^+$ is given

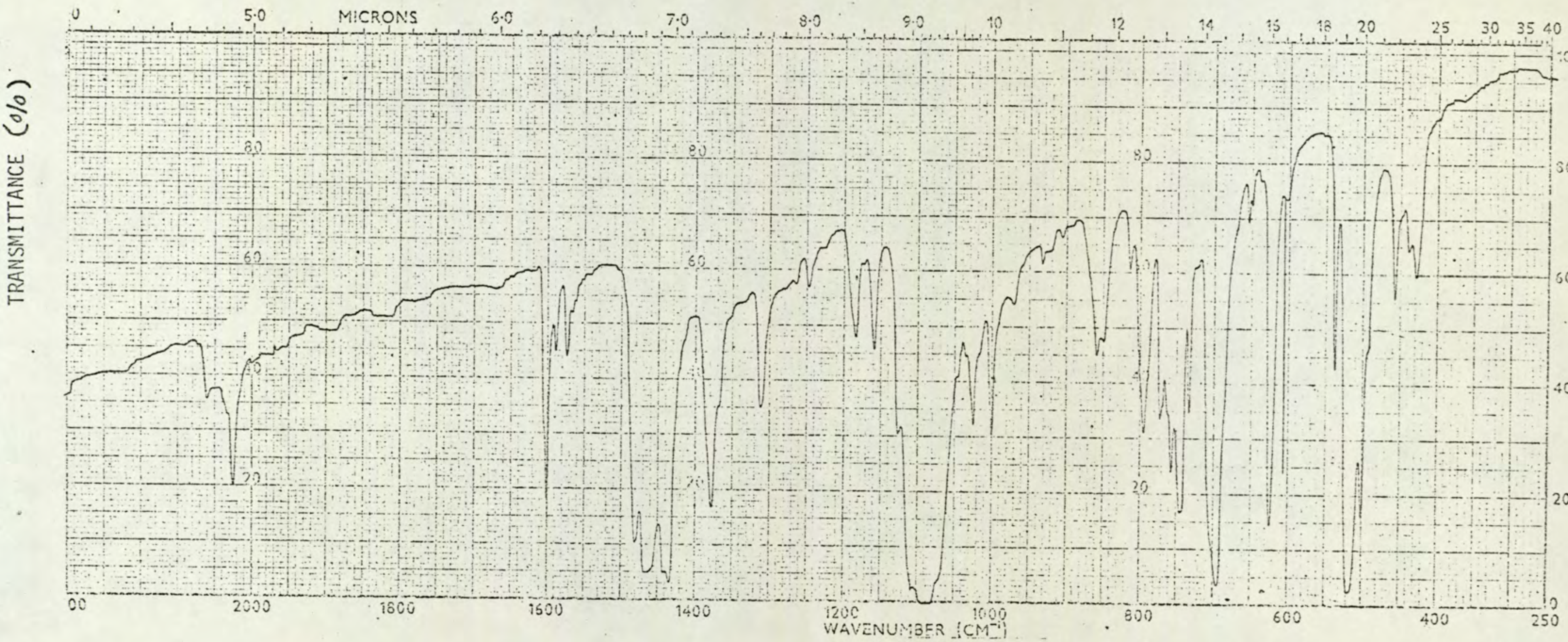


Fig: 14 Infrared spectra of $[Rh(bipy)(PPh_3)_2H_2].ClO_4$

as under:

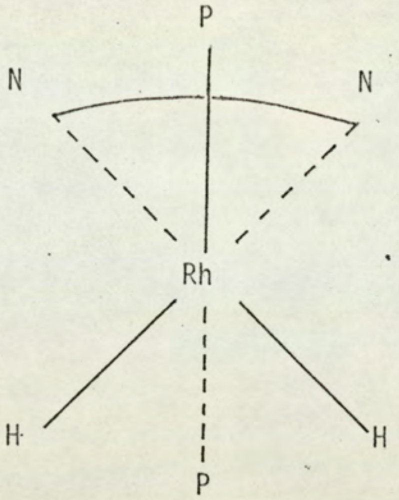


Fig. 15

The above structure is supported by the most recent dihydride cobalt complexes of bipyridyl and phosphine as ligands reported by Mestroni and his co-workers[85]. On the basis of PMR spectra of the complexes of the type $[Co(bipy)(PR_3)_2H_2]$. ClO_4 (where PR_3=PEt_3, PPr_3, PB_{43}, PEt_2Ph) they suggested above structure.

Recently Mestroni et al[86] have synthesised the same compound $[Rh(bipy)(PPh_3)_2H_2].ClO_4$ by completely different methods and also this compound is less well characterized. The isolation of this complex is a significant in this context for two reasons:

(1) It establishes the existence of <u>mono</u>-2.2'-bipyridyl rhodium species under the experimental conditions which are performed for the reduction of rhodium(III) complexes with 2.2'-bipyridyl.

(2) It also indicates the possible involvement of hydrido species under the same experimental conditions.

So far there is only one indication in the literature about the possible formulation of <u>mono</u> 2.2'-bipyridyl species. This was suggested by the kinetic study of the reduction of rhodium(III) complexes of 2.2'-bipyridyl with sodium borohydride[58]. Also the recent kinetic study of the reduction of rhodium(III) complexes of the absorption of gases by transition metal complexes has been carried out within this department and it was suggested that mono-species may be involved during the reduction of rhodium(III) 2.2'-bipyridyl complexes.[66].

That borohydride ions may function as a source of hydride ion has been suggested by Gillard and Wilkinson[60]. Several chloro complexes of rhodium(III) with amines as ligands on treatment with sodium borohydride in aqueous solution undergo a notable change in colour from yellow to pale brown. On examination of these solutions in the n.m.r. spectrum show the presence of the characteristic high field proton resonance line associated with a metal-hydrogen bond. In certain cases hydrido-complexes could be isolated as their insoluble tetraphenyl borates whose infra-red spectra contain a band which can be assigned as V(Rh-H). This suggests that in the reactions of borohydride ions with amino complexes of rhodium(III) substitution reactions may occur to afford mono- or di - hydrido complexes. The products obtained from the reduction of 2.2'-bipyridyl complexes of cobalt(II) and rhodium(III) were postulated as the complexes of univalent metals. No high-field line in the n.m.r. spectra of these complexes have been found[44,58,60]. However, it has been observed that reduction of the yellow dichloro <u>bis</u>-(2.2'-bipyridyl) rhodium(III) cation gives first a brown solution which was found as diamagnetic[60]. The solid obtained by the precipitation with tetraphenylborate from the above intermediate brown solution (obtained by the reduction of dichloro <u>bis</u>-2.2'-bipyridyl rhodium(III)) showed a weak peak at 2016 cm^{-1} in the infra-red region[60]. This absorption may be due to the Rh-H stretching frequency. Since the analogous dichloro *tetrakis*(Pyridine) rhodium(III) cation gives a hydride ion on treatment with borohydride, a common first stage may occur, of the type

$$\begin{tikzcd}
{[Rh^{III}B_4Cl_2]^+} \arrow[r, "H^-"] & {[Rh\ B_4ClH]^+ \ (1)} \arrow[r] \arrow[d, "H^-"] & {[Rh^{I}B_4]^+ + HCl \ (2)} \\
 & {[Rh^{III}B_4H_2]^+} \arrow[r, "-H_2"] & {[Rh^{I}B_4]^+}
\end{tikzcd}$$

The second stage then appears to occur only with the complex containing bipyridyl; this is presumably due to the greater π-bonding capacity of bipyridyl and its well known ability to stabilise lower oxidation states.

Similarly Kulasingam has been able to synthesise a hydrido-species by the reaction of dichloro *bis*-(di 2-pyridyl amine) rhodium(III) salts [87]. This hydrido complex is not well characterized and is probably polymeric. The stoicheiometry establishes that one molecule of bidentate base is lost. This observation is reproduced but the isolation of $[Rh(dipyam)(PPh_3)_2H_2].ClO_4$ failed due to the insolubility of Kulasingan's compound $[Rh(dipyam)H_2.ClO_4]$.

Thus the following reaction sequence may occur

$$\begin{tikzcd}
{[Rh(bipy)_2Cl_2]^+} \arrow[r, "\overline{BH}_4"] & {[Rh(bipy)_2H_2]^+ \ (A)} \arrow[d, "-bipy"] & \\
{[Rh(bipy)(PPh_3)_2H_2]^+} & {[Rh(bipy)H_2]^+ \ (B)} \arrow[l, "PPh_3"'] \arrow[r, "-H_2"] & {[Rh(bipy)]^+ \ (C)}
\end{tikzcd} \quad (1)$$

Since the reaction (1) occurs via different stages such as (A),(B) and (C), the completion of the reaction(1) depends upon the ligand selected. Thus ethylene-diamine completes the reaction at stage (A); di-2-pyridyl amine ends the reaction at stage (B) while the reaction stops at stage (C) when 2.2'-bipyridyl is selected. Triphenyl phosphine stabilises hydrido species, it is used to stabilise labile intermediate (B) and the formation of $[Rh(bipy)(PPh_3)_2H_2]^+$ cation favours the above mechanism. The organic halides may react with (B) or (C). Gillard and Wilkinson[60] have showed that the hydrido-species could not be obtained when sodium amalgum is used as a reducing agent. Similar experiments are carried out using sodium amalgum as a reducing agent. It was not possible to form $[Rh(bipy)(PPh_3)_2H_2]ClO_4$ under these conditions by addition of triphenyl phosphine to the reaction of dichloro bis-(2.2'-bipyridyl) rhodium(III) salts with sodium amalgum. But oxidative-addition of organic halide is observed with the formation of $[Rh(bipy)_2(C_6H_5.CH_2)Br]ClO_4$ when benzyl bromide was added to the same reaction with sodium amalgum.

Thus, the following mechanism is suggested for the reaction of organic halides with borohydride as a reducing agent for rhodium:

$$\begin{tikzcd}
{[Rh^{III}(bipy)H_2]^+} \arrow[r, shift left] & {[Rh^{I}(bipy)]^+ + H_2} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "RX"] & {[Rh^{III}(bipy)H_2]^+} \arrow[l, shift left] \\
 & {[Rh^{III}(bipy)RX]^+} \arrow[r, "bipy"] & {[Rh^{III}(bipy)_2RX]^+}
\end{tikzcd}$$

(2)

Hence the compounds represented in the Table 4 having rhodium to carbon σ-bonds are believed to be obtained by the oxidative-addition of organic halides to the co-ordinatively unsaturated rhodium(I) complex, this in our view providing further strong evidence for the real existence of rhodium(I) under these experimental conditions.

The efficiency of base alcohol reducing systems involving sodium carbonate, sodium formate, triethylamine, potassium hydroxide has been known for some years. Potassium hydroxide-alcohol was found to be a particularly effective reducing system and it is known that alkaline ethanol may reduce rhodium(III) in the presence of 2.2'-bipyridyl[49]. Also it has been found that the rate equation for the reduction of the same system with molecular hydrogen contains a hydroxide dependent term[66]. Hydroxide ion could act as the reducing agent by the reaction:

$$O\bar{H} \longrightarrow O\dot{H} + \bar{e}$$

$$2O\dot{H} \longrightarrow H_2O_2$$

provided that only traces of hydrogen peroxide are produced.

Recently a number of rhodium and iridium phosphine complexes have been synthesised by the use of the potassium hydroxide-ethanol system[79]. And it has been found that clean and rapid synthesis can be carried out by the use of alkaline-ethanol. The reaction of dichloro <u>bis</u> (2.2'-bipyridyl rhodium(III) salts in ethanolic solution of potassium-hydroxide has been studied kinetically[66] in the presence of molecular hydrogen and it has been found that rhodium(I) species are formed. According to the mechanism -(1) the intermediate hydride species can be stabilized by triphenyl phosphine when the reduction of rhodium(III) compounds of 2.2'-bipyridyl carried out with sodium borohydride as the reducing agent. This leads to the new reaction of $[Rh(bipy)_2.Cl_2]^+$ in potassium-hydroxide-ethanol solution in the presence of excess of triphenyl phosphine.

The reaction of $[Rh(bipy)_2.Cl_2].Cl\ 2H_2O$ in potassium hydroxide-ethanol in the presence of a tenfold excess of triphenyl phosphine in air affords an orange yellow compound. The same reaction when carried out in an atmosphere of nitrogen or argon affords a nice yellow product in good yield. Also the compounds $[Rh(bipy)_2.Br_2].Br$ or $[Rh(dipyam)_2.Cl_2].Cl$ under these conditions affords identical orange-yellow or yellow compounds depending upon the atmospheric conditions.

These reactions are represented as under:

$$[Rh(chelate)_2X_2]X + PPh_3(\text{in excess}) \xrightarrow[\text{KOH/ethanol}]{\text{in air}}$$

$$\longrightarrow \text{Orange-yellow product} \qquad (1)$$

$$[Rh(chelate)_2X_2]X + PPh_3(\text{in excess}) \xrightarrow[\text{KOH/ethanol}]{\text{in Argon or } N_2}$$

$$\longrightarrow \text{yellow product} \qquad (2)$$

[chelate = 2.2'-bipyridyl or di-2-pyridyl amine and X = Cl or Br]

The infra-red spectra for both these orange-yellow and yellow compounds are identical (see figure16,17) and they are identified as hydrides. The band at 2140 cm^{-1} is considered as Rh-H stretching frequency. The analytical figures for carbon fluctuated over several per cent being higher for the products from the experiments performed under an atmosphere of argon. The orange-yellow compound obtained in air resembled in characteristic a specimen of the known compound hydrido <u>tetrakis</u>-(triphenyl phosphine) rhodium(I) prepared by Robinson and his co-workers from the reaction of rhodium trichloride and triphenyl phosphine in tenfold molar excess using sodium borohydride as the reducing agent[80]. It is found that the orange compound obtained from the above reaction -(1) is more stable than the compound prepared by Robinson's method using sodium borohydride as the reducing agent even under the atmosphere of nitrogen. The compound $HRh(PPh_3)_4$ decomposes with time and gives a product which has no rhodium-hydrogen stretching frequency in the infra-red. The yellow compounds obtained from the reaction -(2) under the atmosphere of nitrogen or argon resembled the specimen $HRh(PPh_3)_4$ prepared by Robinson's more recent method[79] using ethanolic potassium hydroxide as the reducing agent.

The reactions performed by Robinson and his co-workers are represented as under:

$$RhCl_3 + PPh_3 \text{ (in excess) } \xrightarrow[\substack{\text{in ethanol} \\ \text{under } N_2 \\ \text{(ref.80)}}]{BH_4} HRh(PPh_3)_4 \tag{3}$$

$$RhCl_3 + PPh_3 \text{ (in excess) } \xrightarrow[\substack{\text{under } N_2 \\ \text{(ref.79)}}]{KOH/EtOH} HRh(PPh_3)_4 \tag{4}$$

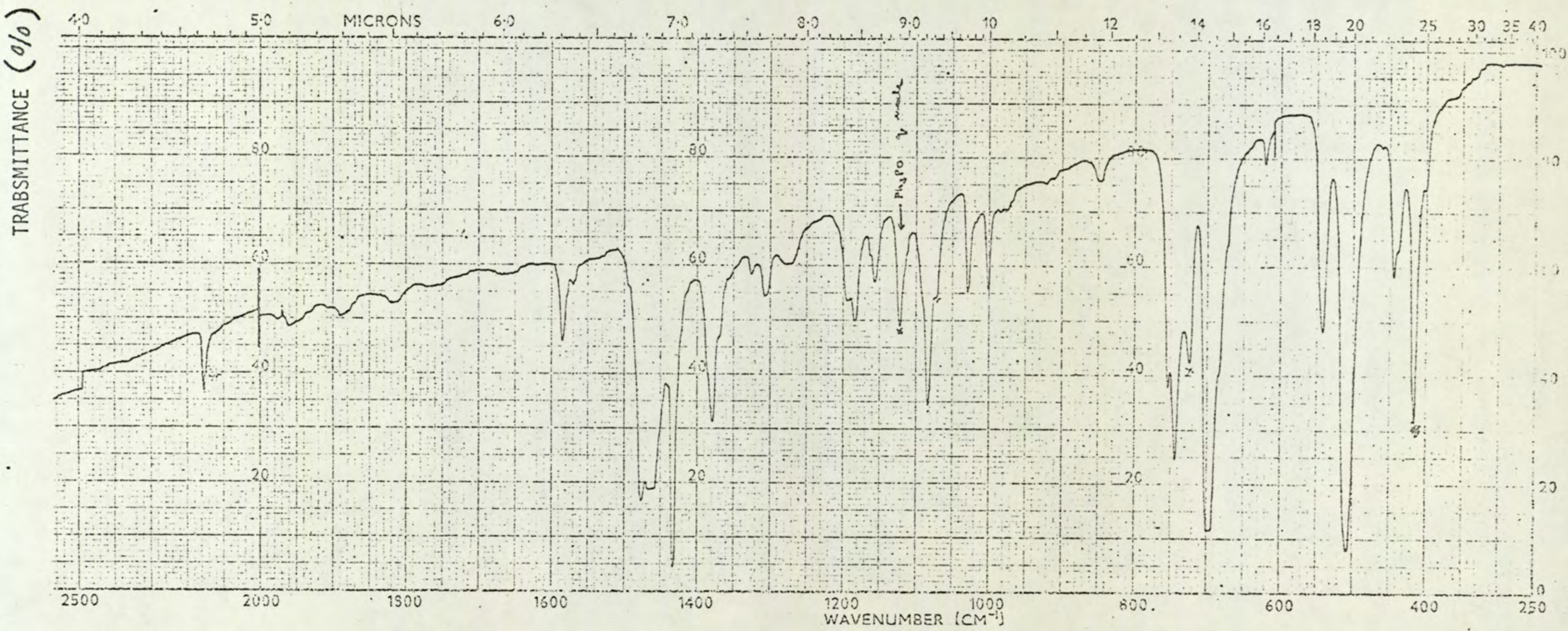


Fig: 16 Infra-red spectra of [$HRh(PPh_3)_4$] obtained by the reaction of [$Rh(bipy)_2.Cl_2.2H_2O$ and PPh_3(in excess) in alkaline ethanol in air. (orange-yellow)

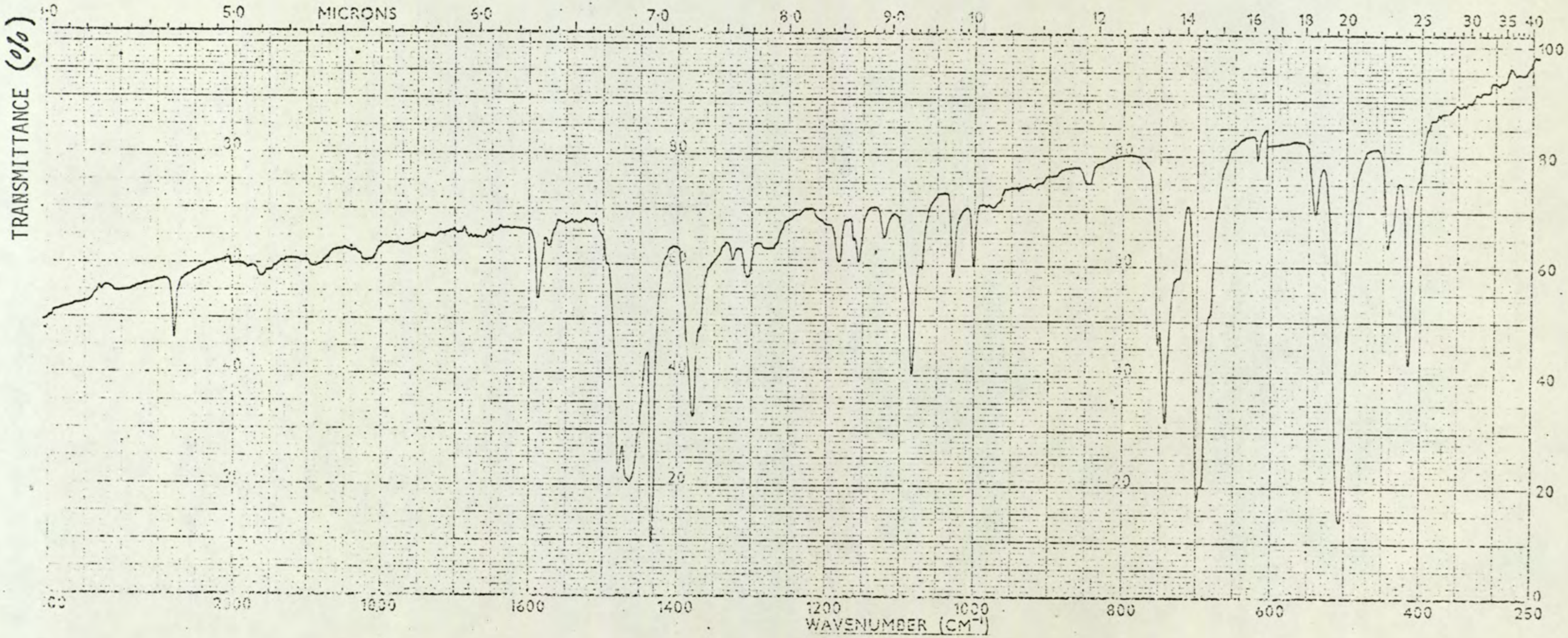


Fig: 17 Infra-red spectra of $[HRh(PPh_3)_4]$ obtained by the reaction of $[Rh(bipy)_2.Cl_2].Cl.2H_2O$ and excess PPh_3 in alkaline ethanol under the atmosphere of Argon.- (yellow)

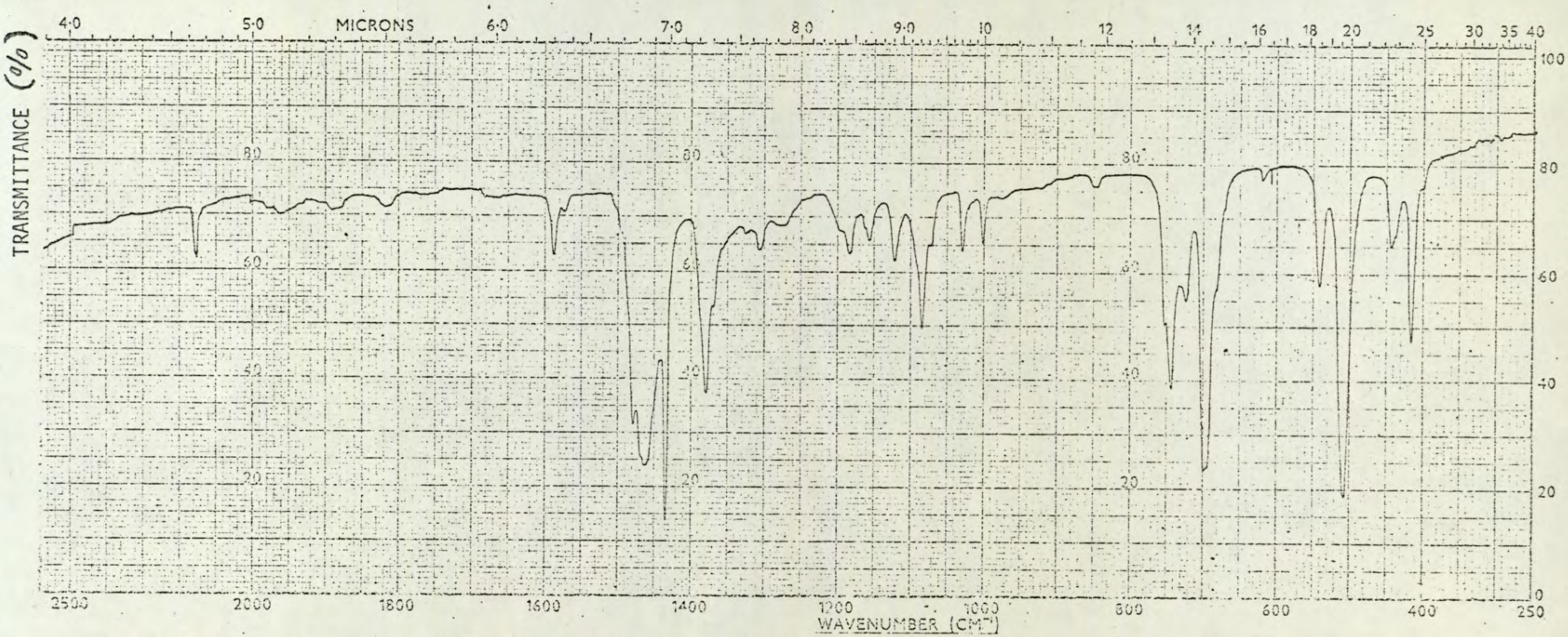


Fig: 18 Infra-red spectra of [HRh(PPh$_3$)$_4$] prepared by the Robinson method in alkaline ethanol under notrogen atmosphere.

The identification of the orange-yellow and yellow compounds obtained from reactions -(1) and (2) are carried out by comparison with Robinson's specimens and also by infra-red spectra (see figure 18) and elemental analysis. These compounds are also characterized as HRh(PPh$_3$)$_4$. The close study of mass spectra of these compounds prepared under various conditions are carried out. Only the fragmentation patterns of the phosphine ligands are observed and no parent ion peak was observed in either case. In addition to the expected fragmentation pattern of triphenyl phosphine[88] peaks at m/e] 278 and 277 are also observed (see figure 19a,b). On accurate mass determination this proved to be the P$^+$ and (P-1)$^+$ ions of triphenyl phosphine oxide. Also the expected fragmentation pattern of oxide was observed[88]. The presence of 277$^+$ for triphenyl phosphine oxide was not surprising in those specimens where the reactions were carried out in air. But the presence of 277$^+$ was seen in <u>all</u> the mass spectra of <u>all</u> the specimens even when extreme care was taken to exclude air during the preparation. Triphenyl phosphine used in all the reactions was purified and no evidence of 277$^+$ peak was found in the mass spectrum. We also found evidence for the presence of traces of triphenyl phosphine oxide in the known compounds such as [Rh(PPh$_3$)$_3$.Cl] and [HRh(PPh$_3$)$_4$] which are prepared by literature methods [42, 79, 80] with great care. The comparisons of 277$^+$ and 262$^+$ peaks in the mass spectra of <u>all</u> the complexes prepared under different conditions are given in figure 19ab together with those prepared by known methods.

The infra-red spectra of all these complexes on closer examination also revealed the presence of triphenyl phosphine oxide.

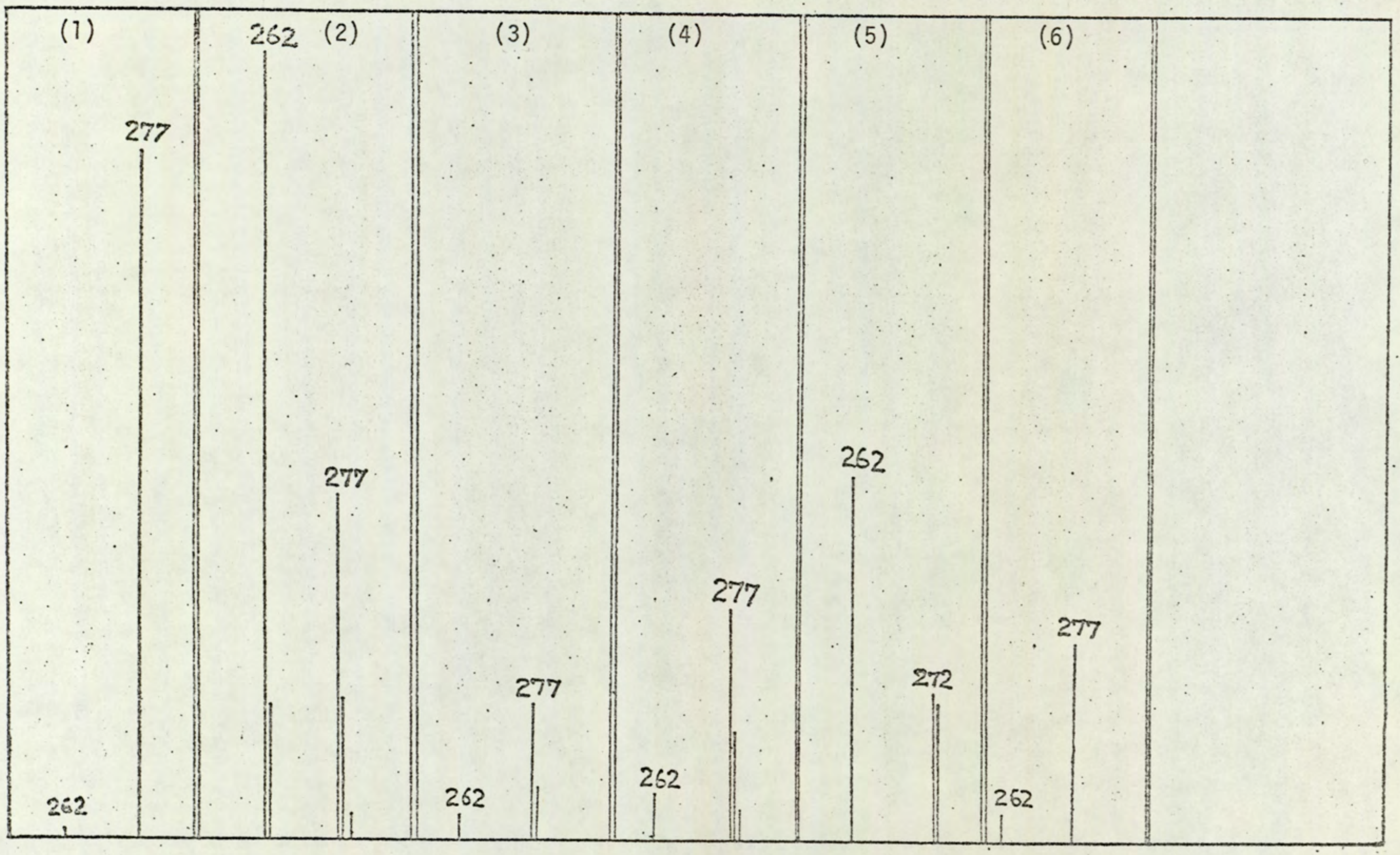


Fig:19a.The comparisons of 277^+ and 262^+ peaks in the mass spectra of the compounds prepared under different conditions by the reaction of $[Rh(bipy)_2.Cl_2]Cl$. with triphenyl phosphine in alkaline ethanol.*

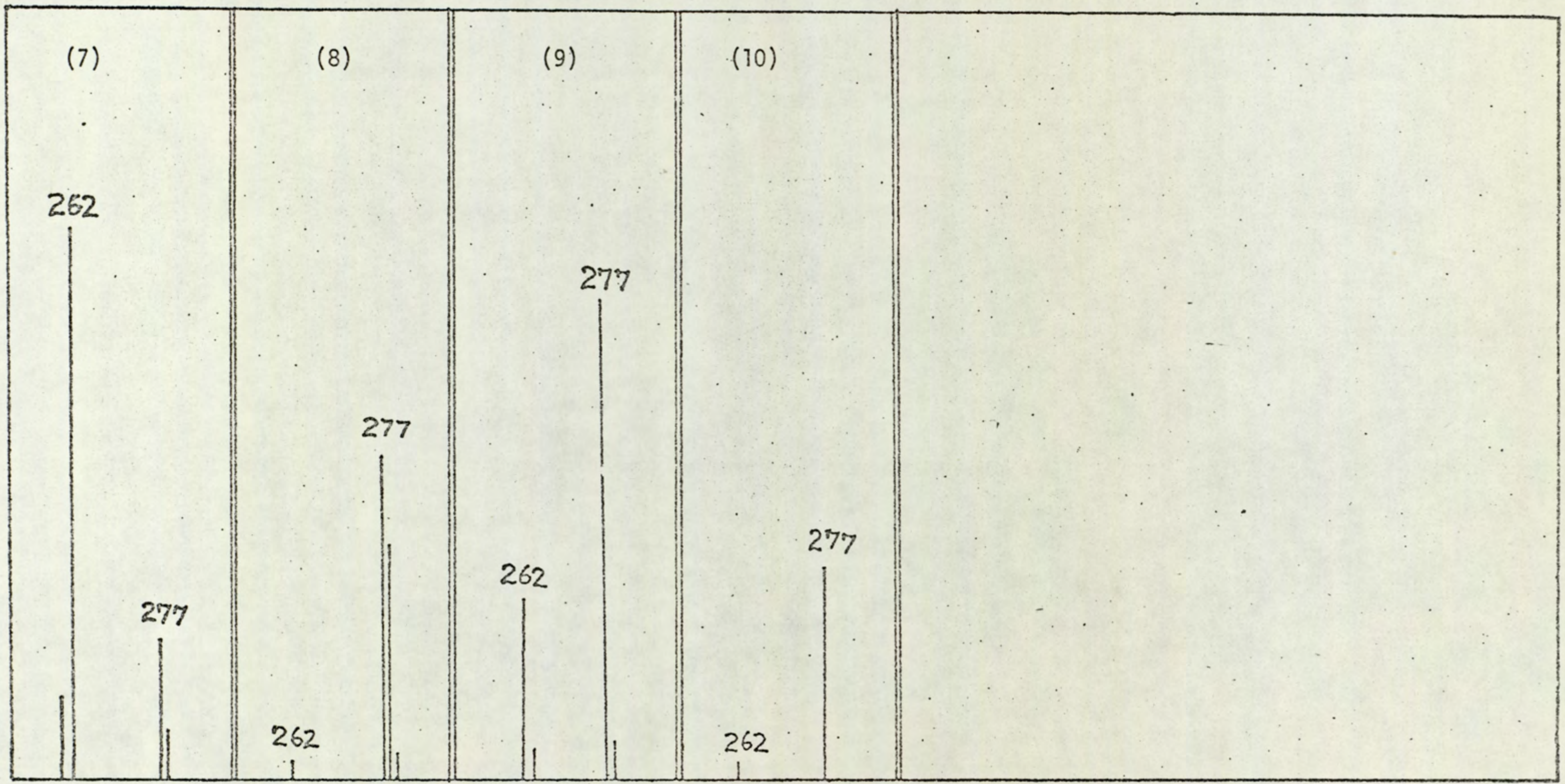


Fig: 19b. The comparisons of 277^+ and 262^+ peaks in the mass spectra of the compound $HRh(PPh_3)_4$ prepared by Robinson's method[79,80].*

* $HRh(PPh_3)_4$ obtained from the reaction of $RhCl_3.3H_2O$ or $Rh(bipy)_2.Cl_2.Cl.2H_2O$ with triphenyl phosphine in alkaline ethanol.

1. $[Rh(bipy)_2.Cl_2]Cl + PPh_3 \xrightarrow{\text{in air}}$ orange yellow

2. $RhCl_3 + PPh_3 \xrightarrow{\text{under Ar}}$ yellow.

3. $[Rh(bipy)_2.Cl_2].Cl] + PPh_3 \xrightarrow{\text{under } N_2}$ orange yellow.

4. $[Rh(bipy)_2.Cl_2].Cl + PPh_3 \xrightarrow{\text{under Ar}}$ orange yellow

5. $[Rh(bipy)_2.Cl_2].Cl + PPh_3 \xrightarrow{\text{under } N_2}$ yellow

6. $[Rh(bipy)_2.Cl_2].Cl + PPh_3 \xrightarrow{\text{under Ar}}$ orange yellow

$HRh(PPh_3)_4$ prepared by Robinson's method [79,80].

7. $RhCl_3 + PPh_3 \xrightarrow[\text{under } N_2]{KOH/EtOH}$ yellow

8. $RhCl_3 + PPh_3 \xrightarrow[\text{in air}]{BH_4^-/EtOH}$ pink (unstable)

9. $RhCl_3 + PPh_3 \xrightarrow[\text{under } N_2]{BH_4^-/EtOH}$ orange yellow

10. $RhCl_3 + PPh_3 \xrightarrow[\text{under } N_2]{KOH/EtOH}$ yellow

It is observed that in those cases where mass spectra showed the largest 277^+ peaks the intensity for the band at 1122 cm^{-1} is greater. This band at 1122 cm^{-1} is not reported for the free triphenyl phosphine ligand but corresponds to the q-mode of the phenyl ring for the oxide[89]. Cotton et al have found that on co-ordination the P=O stretching frequency which occurs at 1193 cm^{-1} in free triphenyl phosphine oxide, shifts to lower values even as far as the q-mode[89]. Thus the band at 1122 cm^{-1} may be due to the triphenyl phosphine oxide (see figure 16).

The reaction of triphenylphosphine oxide instead of triphenylphosphine with $[Rh(bipy)_2.Cl_2].Cl$ in ethanolic-potassium hydroxide was carried out under an atmosphere of nitrogen. The intense reddish-violet coloured solution obtained which is identical to that reported for "$Rh(bipy)_2{}^+$" (λ_m = 557 nm). However, the stability to air oxidation seems to be superior in the presence of triphenyl phosphine oxide[58].

Reactions of $HRh(PPh_3)_4$ with dilute mineral acids

When the yellow hydrido tetrakis (triphenyl phosphine) rhodium(I) was heated with mineral acids under reflux, different compounds are obtained.

With dilute hydrochloric acid after two hour reflux a red product was obtained. This red compound was characterized as pure chloro tris-(triphenyl phosphine) rhodium(I) reported by Wilkinson and his co-workers by direct reaction of rhodium trichloride and excess of triphenyl phosphine in ethanol[42]. The analysis and infra-red are in good agreement. There is no evidence for triphenyl phosphine oxide in the mass spectrum.

The reaction of $HRh(PPh_3)_4$ with dilute nitric acid afforded reproducibly a green complex. The infra-red is more complex. The spectrum is consistent with the presence of nitrosyl groups [$V(NO) = 1646, 1635$, Sh, and 1539 (?) cm^{-1}] and nitrato groups [1539(?), 1271, 985, 829, 790 cm^{-1}]. Elemental analysis suggests the empirical formula $C_{36}H_{30}N_3P_2RhO_7$. Thus on the basis of infra-red the complex appears to be the nitrate analogue of $RhCl_2(NO)(PPh_3)_2$ for which the NO stretching frequency = 1630 cm^{-1}[90]. The examination of mass spectrum shows the fragmentation pattern for triphenyl phosphine oxide <u>only</u> and there is no evidence for P^+ peak (m/e = 262) for triphenyl phosphine. Thus on the present evidence the alternative formulation of $[Rh(Ph_3PO)_2(NO)_2(NO_3)]$ is preferred. The strong band at 1098 cm^{-1} may be considered as $V(P{=}O)$, while the band at 1539 cm^{-1} in infra-red maybe $V(NO)$ rather than a nitrate mode (see figure 20).

The reaction of $HRh(PPh_3)_4$ with dilute perchloric acid gives more confused results. The product obtained after the reflux period was red in colour and shows a broad perchlorate band centred on 1100 cm^{-1} indicating perchlorate is ionic (see figure 21). After two-three days the red compound changed its colour and gave a grey-brown coloured compound. The infra-red spectrum of this compound shows the bands at 1150 - 1120 - 1090 - 1040 - 1000 cm^{-1}

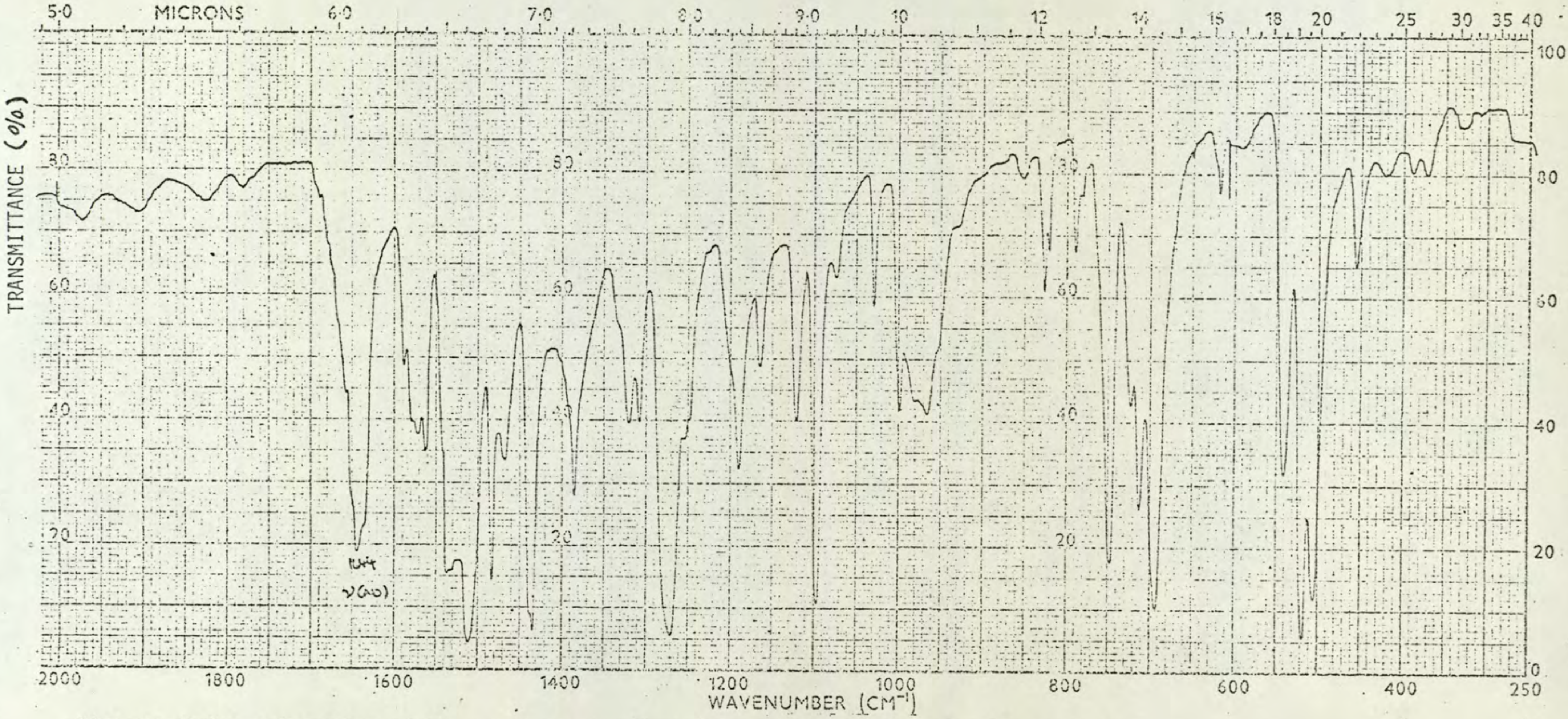


Fig: 20 Infra-red spectra of the green compound[possibly $Rh(Ph_3PO)_2(NO)_2(NO_3)$] obtained by the reaction of tetrakis (triphenyl phosphine) rhodium(I) with dilute nitric acid.

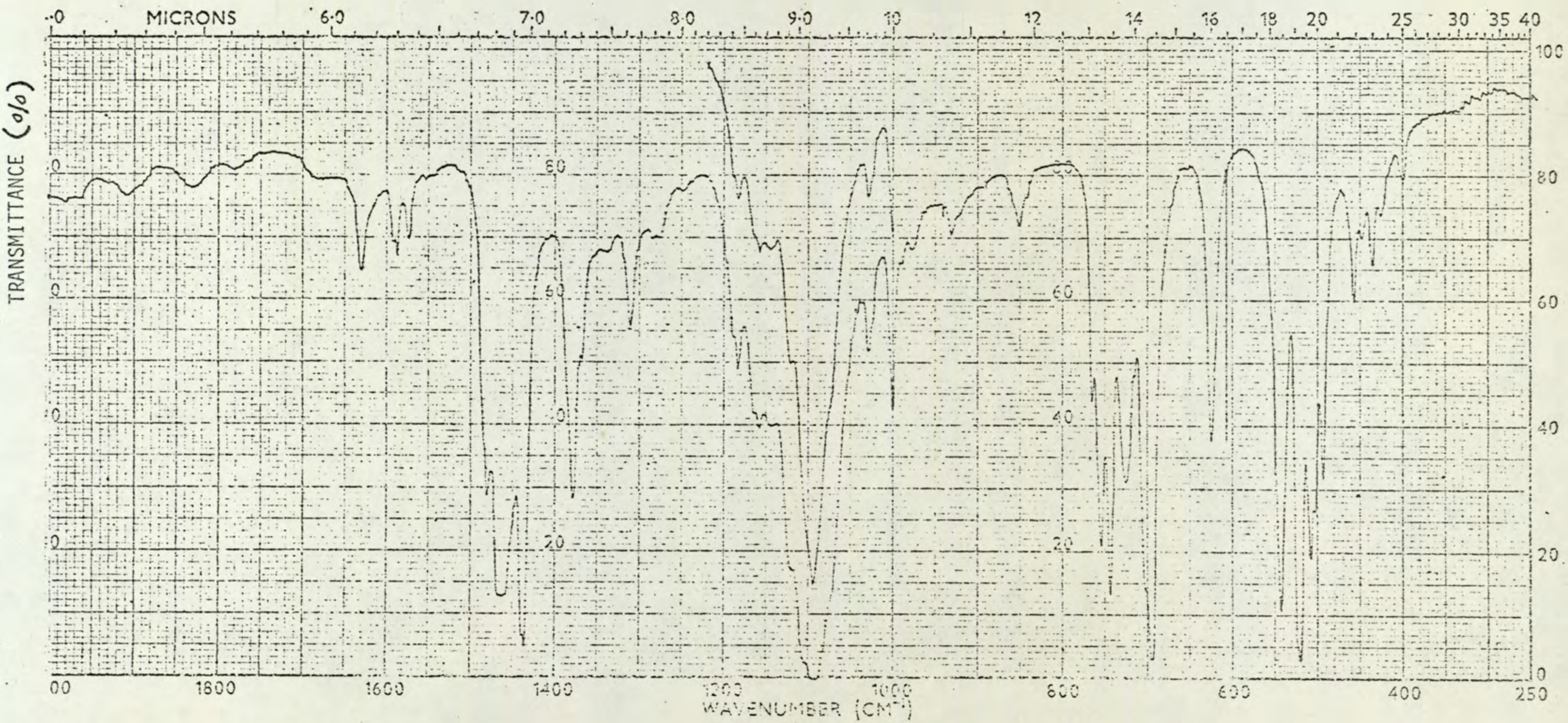


Fig: 21. Infra-red spectra of the red-brown product obtained by the reaction of tetrakis (triphenyl phosphine) rhodium(I) with dilute perchloric acid.

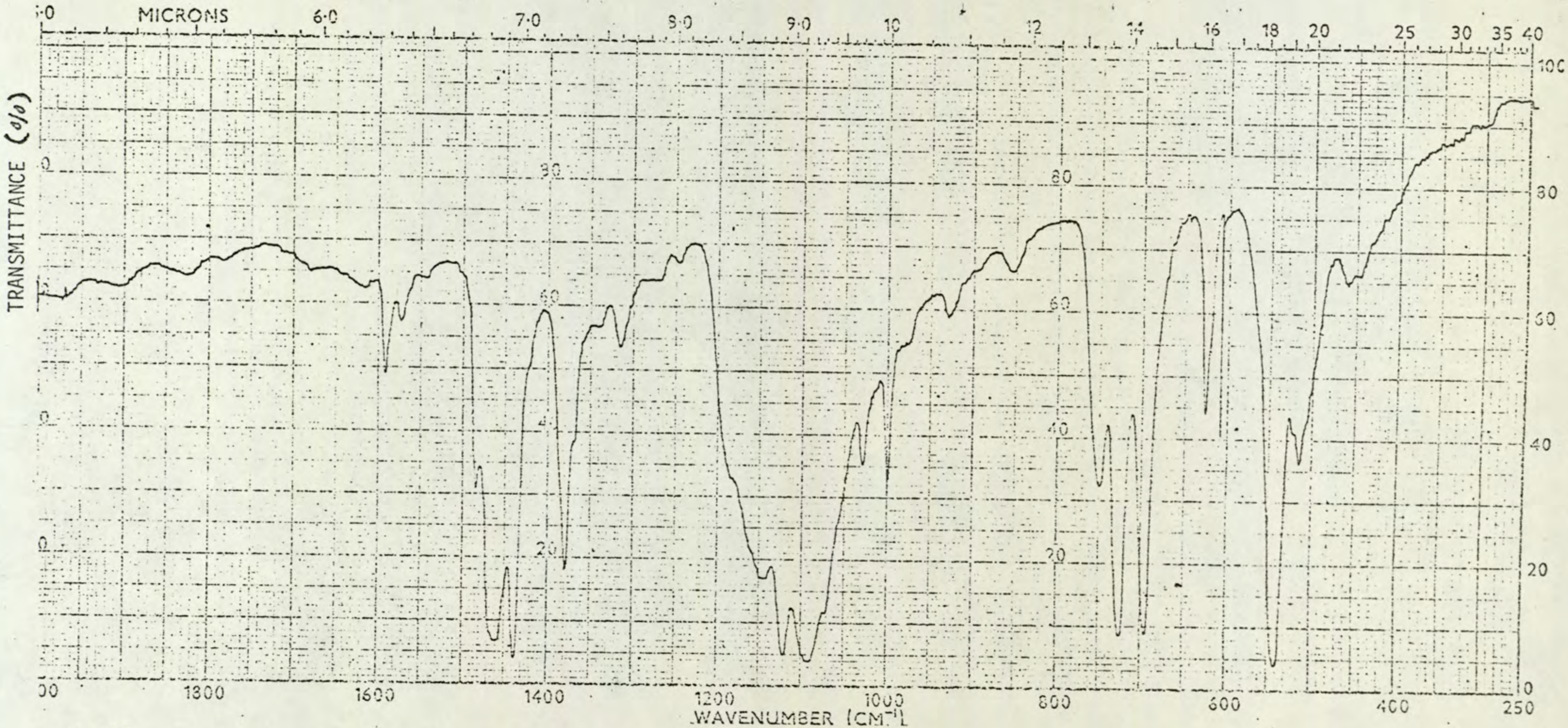


Fig:22. Infra-red spectra of the decomposed product of the compound obtained by the reaction of tetrakis (triphenyl phosphine) rhodium(I) with dilute perchloric acid.

indicating the presence of perchlorate group as weakly co-ordinated (see figure 22). Thus the following mechanism may be suggested

$$HRh(PPh_3)_4 + HClO_4 \longrightarrow H_2 + Rh(PPh_3)_4^+ ClO_4$$

$$Rh(PPh_3)_4 ClO_4 \xrightarrow{O_2} \text{oxidised product containing } Ph_3PO.$$

<u>Reaction of HRh(PPh$_3$)$_4$ with 2.2'-bipyridyl in ethanol</u>

When the compound $HRh(PPh_3)_4$ was reacted with 2.2'-bipyridyl in hot ethanol the colour of the compound changed and a dark reddish-brown coloured solution was obtained. The product isolated from this reaction as a perchlorate was identical to that $[Rh(bipy)(PPh_3)_2H_2].ClO_4$ obtained by the reaction of $[Rh(bipy)_2.Cl_2]Cl$ with sodium borohydride in the presence of an excess of triphenyl phosphine. The presence of hydride group is established by infra-red (see figure 23) and ^1H.n.m.r. spectroscopy. The elemental analysis also supports that the compound obtained from the above reaction is $[Rh(bipy)(PPh_3)_2H_2].ClO_4$. Thus, the following reaction sequence may occur:

$$\begin{tikzcd}
Rh(bipy)_2.Cl_2^+ \arrow[rr, "KOH/EtOH", "PPh_3"'] \arrow[dr, "BH_4^-", "PPh_3"'] & & HRh(PPh_3)_4 \arrow[dl, "bipy"] \\
& {[Rh(PPh_3)_2(bipy)H_2]^+} &
\end{tikzcd}$$

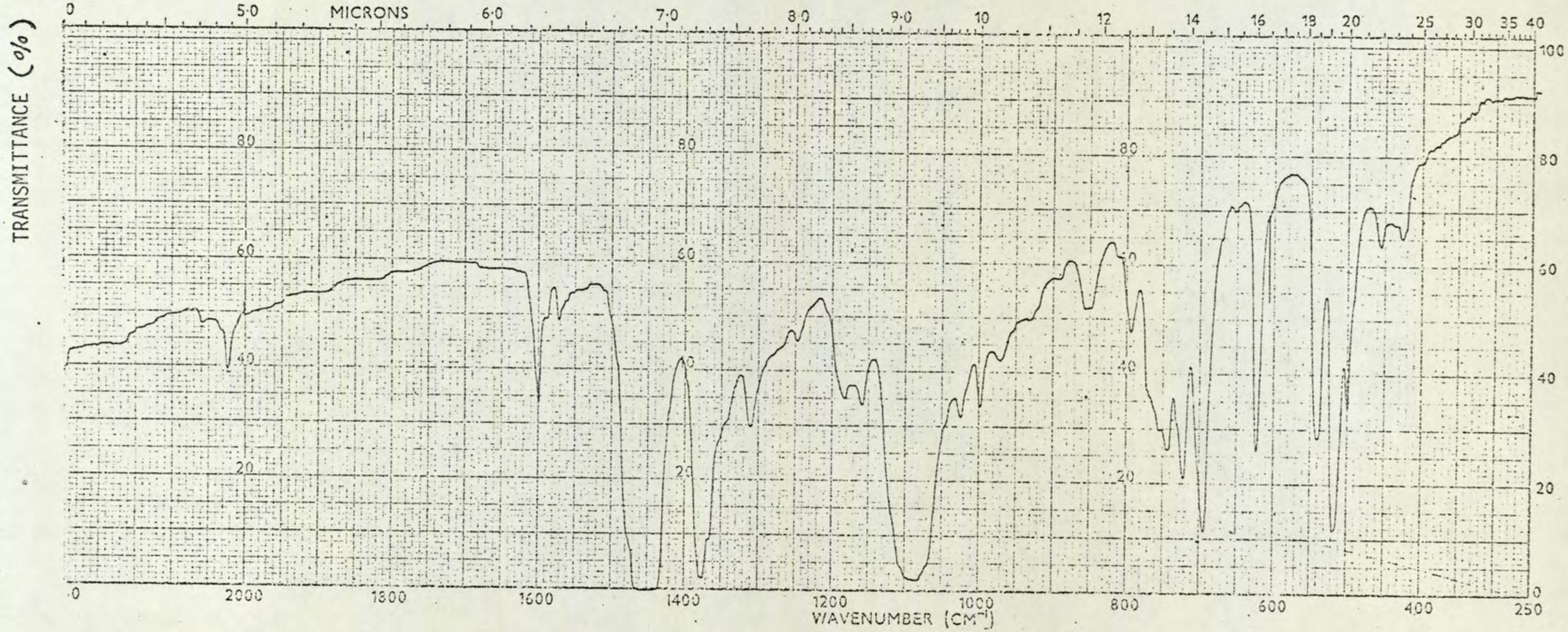


Fig:23 Infra-red spectra of $[Rh(bipy)(PPh_3)_2H_2].ClO_4$

CHAPTER FIVE

SOME INVESTIGATIONS WITH LOW-VALENT COBALT-2.2'-BIPYRIDYL COMPOUNDS AS CATALYSTS IN THE REDUCTION OF ORGANIC NITRO-COMPOUNDS

[A] INTRODUCTION

The use of various metal hydrides as selective reducing agents has attracted a considerable amount of interest in recent years. Sodium borchydride which is an effective reducing agent has been known as a mild reducing agent. Contrary to the general belief that sodium borohydride is not a particularly powerful reducing agent and will not reduce, for example, aromatic nitro or azoxy group readily, it has been found that aromatic nitro compounds are reduced to some extent by sodium borohydride in aqueous or aqueous-alcoholic alkali ar room temperature[91]. The overall reduction of nitrobenzene occurs in three sequential steps:

$$\begin{tikzcd}
\text{Nitrobenzene} \arrow[r] & \text{azoxybenzene} \arrow[r] \arrow[dr] & \text{azobenzene} \arrow[d] \\
 & & \text{aniline}
\end{tikzcd}$$

Also the reduction of organic nitro compounds by sodium borohydride in polar solvent such as dimethylsulphoxide or sulfone has been known to be very slow at mild temperatures. However, at higher temperatures ready reduction of organic nitro compounds in dimethylsulphoxide or sulfone by sodium borohydride has been observed to initially afford azoxy compounds which may be further reduced to mixtures of corresponding azo derivatives or amines[92].

Transition metal ions or their complexes have been known to be effective catalysts for many organic synthesis. It has been found that in the presence of some cobalt complexes, the reduction of organic nitro or nitroso compounds by sodium borohydride can be achieved easily. Thus the catalysis by cobalt complexes of the sodium borohydride reduction of organic nitro or nitroso- arenes has been of great interest in recent years. These cobalt complexes include tris- (2.2'-bipyridyl) cobalt (I); bis-(dimethyl glyoximate) cobalt(I); cobalt bromide and trans - [aquobromo - bis (dimethyl glyoximate) cobalt(III)] and also vitamin B_{12} complex of cobalt. The reduction of aromatic nitro compounds by sodium borohydride in the presence of cobalt complexes is known to be rapid and more effective than in the absence of the catalyst.

Nitrobenzene and various derivatives are readily reduced in the presence of cobalt ion and 2.2'-bipyridyl. The active species, being tris-(2.2'-bipyridyl)cobalt(I)[67]. Sal'nikova and Khidekel have been observed that nitrobenzene is reduced by sodium borohydride in the presence of platinum and bis-(dimethyl glyoximate)cobalt(I)[93]. The conversion of 4-nitroso-N.N'-dimethyl aniline to azoxybenzene and azobenzene can readily be carried out by sodium borohydride in the presence of cobalt bromide or trans-[aquobromo bis-(dimethyl glyoximate)cobalt(III)][94]. Hill and Williams et al have found that the reduction of nitrobenzene, nitrosobenzene and azoxybenzene by potassium borohydride is catalysed by hydroxo-cobalamine and the products obtained from the reduction with nitrobenzene include aniline and azobenzene[95].

The mechanism of the catalysis by cobalt complexes by sodium borohydride reduction has been of major interest and different mechanisms have been suggested. They are:

(1) electron transfer

(2) nitrene intermediate

(3) Hydride transfer

The electrochemical reduction of nitrobenzene is known to proceed via the intermediates, nitrosobenzene, phenylhydroxylamine, azoxybenzene, azobenzene, and hydroazobenzene[96]. Thus the organic nitro- and nitroso- compounds are very easily reduced at a mercury electrode by an electron transfer mechanism[97]. According to Vlček and Rusina[67] cobalt-bipyridyl complexes can be used as the catalytic system. They found that sodium borohydride does not react in solution (aqueous-ethanol) with nitrobenzene and other organic-nitro-compounds at all readily. An addition of a small amount of $Co(bipy)_3(ClO_4)_3$ to this solution causes reduction of nitro-compounds at a rate dependent on the amount of cobalt complex added. The complexes $Co(bipy)_3^{3+}$ and $Co(bipy)_3^{2+}$ react readily with sodium borohydride with the formation of univalent cobalt $Co(bipy)^+_3$. The redox potential of the system $Co(bipy)_3^{2+} \longrightarrow Co(bipy)_3^{+}$ is -0.91v

with respect to the saturated calomal electrode in 50% ethanolic solution. The reduction of nitrobenzene occurs by one electron redox process

$$Co^{I} \longrightarrow Co^{II}$$

Also a two electron transfer, $Co^{I} \longrightarrow Co^{(III)}$ looks convenient for processes such as

$$PhN{:}N(O)Ph \longrightarrow PhN{:}N(O^{2-})Ph \xrightarrow[OH^{-}]{H^{+}} PhN{:}NPh.$$

However, cobalt(III) is very strongly oxidising in the bromide systems, while for the oxime case half wave data point to a potential of about -0.55 for $Co^{(III)} \longrightarrow Co^{I}$. Thus thermodynamically the one electron path is preferable to the two in these systems[98].

Gillard and Wilkinson[57] have suggested a possible alternative to the electron-transfer mechanism for the catalysis is a hydride transfer. They have found that the reduction of aromatic-nitro compounds by borohydride can be carried out in the presence of complexes of rhodium(III) which form hydrides and in each case, nitrobenzene was reduced to aniline, when an aqueous-methanolic solution of the complex of rhodium was used. When an aqueous-methanolic solution of the tetraphenyl borate salt of hydrido chloro triethylene tetramine rhodium(III) was shaken with aqueous solution of quinone, quinol could be extracted from the mixture. This indicates that the cation-hydrido chloro triethylene tetraamine rhodium(III) acts as a hydride transfer reagent.

Reduction of azoxybenzene to azobenzene is also a hydride transfer. The complex bis-(dimethyl glyoximato) cobalt(I) forms a hydride[99,100] and involvement of a hydride would provide a convenient pathway for hydrogen transfer in the reduction of azoxybenzene[98].

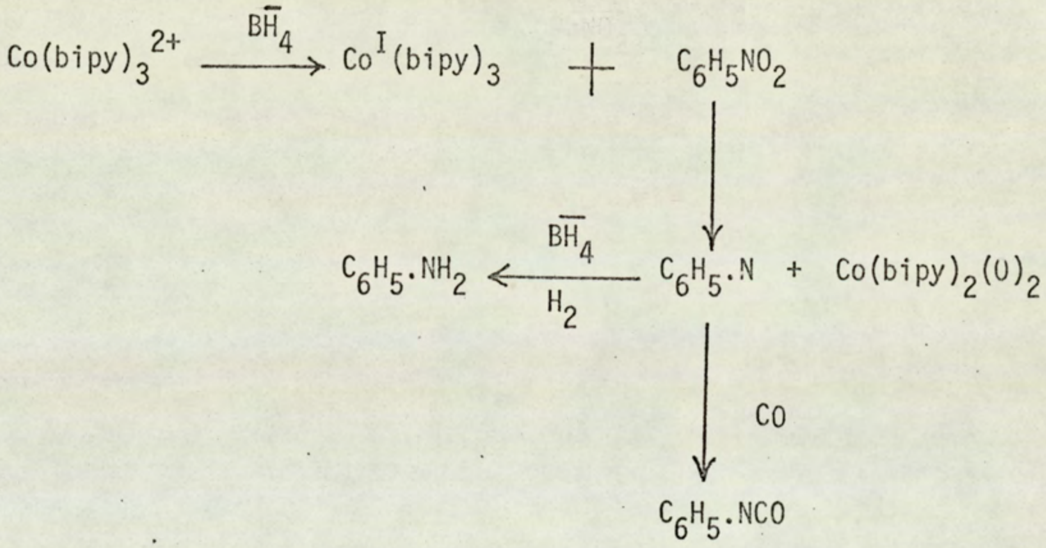
$$\mathrm{PhN{:}N(O)Ph + CoH \longrightarrow PhN{:}NPh + O\bar{H} + Co^{(III)}}$$

The most recent work on this system[95] presented mechanism for the reduction of organo-nitro compounds. Thus in the presence of a cobalt complex, nitrobenzene is reduced to nitrosobenzene, this then forms hydroxylamine. The final product would be aniline depending on the amount of borohydride used. The following mechanism has been suggested for the reduction of nitrobenzene of cobalt complex

$$\begin{tikzcd}
 & \mathrm{PhNO_2} \arrow[rr, "B_{12s}\mathrm{(fast)}", "\mathrm{KBH_4(v.slow)}"'] & & \mathrm{PhNO} \arrow[d, "\mathrm{KBH_4(slow)}", "\begin{matrix}B_{12s}\\ \mathrm{fast}\end{matrix}"'] & \\
\mathrm{PhN(O){:}NPh} \arrow[d, "\begin{matrix}\mathrm{KBH_4}\\ \mathrm{(v.slow)}\end{matrix}", "\begin{matrix}B_{12s}\\ \mathrm{(fast)}\end{matrix}"'] & & & \mathrm{PhNHOH} \arrow[lll, "\mathrm{+PhNO}"', "\mathrm{(v.fast)}"] \arrow[r, "\mathrm{KBH_4}", "\mathrm{(slow)}"'] & \mathrm{ANILINE} \\
\mathrm{PhN{:}NPh} \arrow[rrr, "?\ \mathrm{KBH_4}", "B_{12s}"'] & & & \mathrm{PhNH\text{-}NHPh} \arrow[r] & \mathrm{PhNH_2}
\end{tikzcd}$$

In order to understand the mechanism for the reduction of aromatic-nitro compounds, various intermediate products such as, nitrosobenzene, azoxybenzene, azobenzene, hydroxylamine have also been used for the reduction[95,98]. The final product aniline or azobenzene in these reactions suggested the path of the reaction.

It has also been known that phenyl isocyanate can be prepared by the direct reaction of organo-nitro compounds and carbon monoxide in the presence of a metal catalyst (particularly transition metal ion) under increased pressure. In the reduction of nitrobenzene by borohydride and in the presence of $Co(bipy)_3^{2+}$ as a catalyst if it is a nitrene intermediate can we trape it with carbon monoxide and get a new and cheap route to phenylisocyanate by the following mechanism.



In this section reduction of nitrobenzene and nitrosobenzene by sodium borohydride in the presence of $Co(bipy)_3^{2+}$ complex is described. The reduction of nitrobenzene in the absence of borohydride but in the presence of univalent cobalt is given. Reduction of nitrobenzene by sodium borohydride with carbon monoxide in the presence of cobalt-bipyridyl is carried out. Products obtained are separated and characterized. The possible mechanism is discussed.

[B] EXPERIMENTAL

(1) Preparation of tris-(2.2'-bipyridyl)cobalt(II) perchlorate

Tris-(2.2'-bipyridyl) cobalt(II) perchlorate was used as the catalyst and was prepared as under.

Hydrated cobalt(II) perchlorate (3.67 gm. 10m mole) was dissolved in ethanol (50 ml). To this a solution of 2.2'-bipyridyl (4.68 gm. 30 m mole) in ethanol (20 ml) was added. The dark brown crystals obtained were filtered and washed with ice-cold ethanol and dried over P_4C_{10} under vacuum.

Found: C,49.0%; H,3.34%; N,11.45%.

$C_{30}H_{24}N_6CoCl_2O_8$ requires

C,49.3%; H,3.30%; N,11.55%.

(2) General Procedure

The reduction of nitrobenzene and nitrosobenzene was carried out by sodium borohydride in the presence of tris-(2.2'-bipyridyl) cobalt(II) perchlorate in different solvents. The solvents used are aqueous-ethanol and methanol. All the solvents and nitrobenzene were saturated with nitrogen to remove any dissolved oxygen.

The solution of tris-(2.2'-bipyridyl)cobalt(II) perchlorate was prepared as under which was then used in the reduction of nitrobenzene and nitrosobenzene.

Tris-(2.2'-bipyridyl) cobalt(II) perchlorate (1 gm) was dissolved in water-ethanol mixture (10%, 200 ml) or in methanol (about 200 ml, when reduction was carried out in methanol) and it was then frozen with liquid nitrogen. The space above the frozen solid was evacuated. After the stop cock was shut, the frozen solid was melted with an electric hair drier. The air which was dissolved in the solution bubbled vigorously. The solution was again frozen and the space above the solid was avacuated. This procedure was repeated three times. Under these conditions all oxygen was removed from the reaction mixture.

Similarly the aqueous solution of sodium borohydride and the washed solution containing no dissolved oxygen were prepared.

(3) Reduction of Nitrobenzene by sodium borohydride in the presence of *tris* -(2.2'-bipyridyl) cobalt(II) perchlorate and carbon monoxide

Reaction was carried out in an oxygen free nitrogen atmosphere. A three-necked round-bottomed flask (250 ml) was used for the reaction. The flask was fitted with a condenser and a nitrogen and carbon monoxide inlet.

Tris-(2.2'-bipyridyl) cobalt(II) perchlorate (prepared by the method described on page 126) was dissolved in a water-ethanol mixture (150 ml). The clear brownish-yellow solution was then deaerated by the frozen method (described on page 126). The process was repeated three to four times in order to remove dissolved oxygen. Pure nitrobenzene (5 ml) was introduced to this solution and it was then saturated with nitrogen. Carbon monoxide was bubbled at the same time for one hour. Freshly prepared nitrogen saturated solution of sodium borohydride in water was added to the reaction mixture under the atmosphere of nitrogen and in the presence of carbon monoxide. The solution was stirred vigorously with an electro-magnetic stirrer. The colour of the solution was changed to a reddish-brown and an oily layer was separated during this reaction. When the colour changed to blue the reaction was ceased.

The top oily layer was then extracted with ether. The ether extract was collected and aqueous layer was kept for further investigation.

Investigation of reaction product from ether extract

Ether was removed under vacuum and the green liquid was obtained, which was then used for the further investigation.

Fractional distillation was carried out for the green liquid and different fractions were obtained at different temperatures.

During the distillation the temperature was raised gradually and as the temperature reached 180°C, a colourless liquid was distilled out, which on exposure to air turned to deep brown in colour. The temperature gradually increased up to 184° at which colourless liquid distilled out more readily and this temperature remained constant while all colourless liquid was distilled. It was collected for identification. As the colourless liquid ceased to distil out, the temperature was again raised and at temperature 208° to 212°C a few drops of yellow liquid were distilled out which was also collected for identification. The remaining part was then heated and as the temperature reached 220°C a reddish-brown liquid distilled out with the temperature gradually increasing. The reddish-brown liquid was immediately solidified giving a reddish-crystalline semi-solid product. This reddish-brown liquid was obtained as the temperature reached 250°C. No other product was obtained from the greenish liquid beyond 250°C.

The fractions obtained are as under:

(a)	fraction (i)	colourless liquid which turned to deep-brown at 184°C.
(b)	fraction (ii).	yellow-liquid (few drops only) at 208-210°C

(c) fraction (iii) reddish-brown liquid which changed to a semi-solid at temperature 208-210^{o}C.

Identification of the products obtained by fractional distillation of green liquid

fraction (i) Product obtained from fraction (i) is identified as "ANILINE" from its infra-red, n.m.r. and B.P.

fraction (ii) The yellow liquid from fraction (ii) is characterized as "NITROBENZENE" (this was unreacted during the reaction) by its B.P., infra-red and n.m.r.

fraction(iii) The reddish-brown semi-solid isolated from fraction(iii) was difficult to identify due to its complicated infra-red spectrum and also its uncertain m.p.

By assuming that the fraction (iii) may contain more than one component, qualitative analysis was carried out on reddish-brown crystalline semi-solid product. A thin layer chromatograph technique was applied for the qualitative test. The technique which was applied is described in brief.

Silica jel was suspended in methanol to get slurry and transparent glass plates were dipped in and dried in the oven. The dry plates were preserved in the desiccator before use.

Fraction (iii) which was a reddish-brown crystalline semi-solid was dissolved in carbon tetrachloride and concentrated solution was obtained. Tow or three tiny drops were put on the thin film made on the glass plate. Different solvents were used to separate the components.

The following figures show how different components were separated by using different solvents

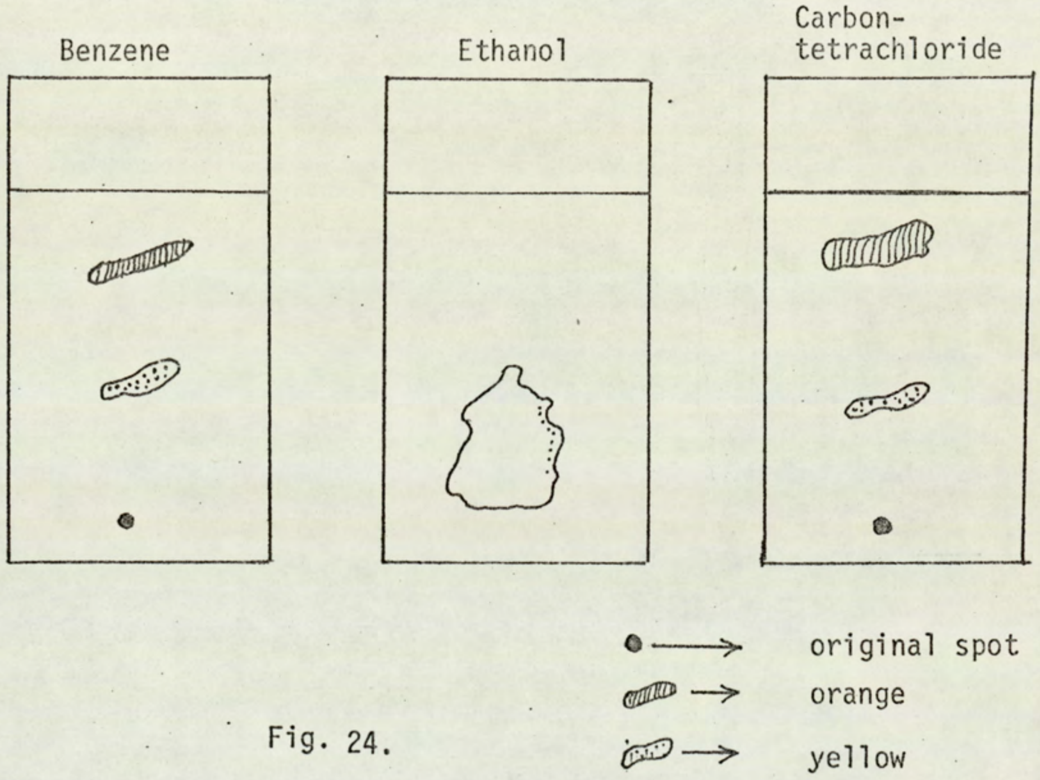


Fig. 24.

It was observed from the thin layer spot chromatography that the reddish-brown semi-solid (fraction iii) contains at least three components. The purification of fraction (iii) is thus essential for the identification of the products.

Purification of fraction (iii)

The reddish-brown semi-solid was dissolved in carbontetrachloride and insoluble material was removed by filtration. The clear solution was shaken with an aqueous solution of ferrous sulphate. The deep red colour formed in the aqueous layer. Two layers were then separated by using a separating funnel. Carbontetrachloride layer was repeatedly shaken with ferrous sulphate solution in water until the red colour in the aqueous layer was not observed. The formation of red colour in the aqueous layer was due to the reaction of free 2.2'-bipyridyl and ferrous ion.

Carbon tetrachloride layer was finally separated and collected. On evaporation of carbontetrachloride, the dark red product was obtained, this was then recrystallized from petroleum ether (60/80-fraction). The orange-red crystallized product was deposited on cooling the solution.

The orange-red product was identified as "AZOBENZENE" by its infra-red, n.m.r., mass spectrum and m.p.

Thus, the products isolated from the green liquid are as under.

(1) Aniline - fraction (i).
(2) Nitrobenzene - (unreacted) - fraction (ii).
(3) Azobenzene - fraction (iii).

Attempts were made to isolate a cobalt complex from the aqueous layer but the solid obtained was a mixture of components which were difficult to separate.

(4) Preparation of Nitrosobenzene

Pure nitrosobenzene was prepared by the known method[101].

In a 2-litre bolt-head round-bottomed flask, equipped with an efficient mechanical stirrer, pure nitrobenzene (30 gm. 25 ml) was placed together with a solution of ammonium chloride (15 gm) in water (500 ml). The solution was stirred vigorously and to this a good quality of zinc powder (about 90 per cent purity - 38 gm) was added in small portions over a period of 5 minutes. The main reaction occurred about 5 minutes after the addition with the rising in temperature. When the temperature reached about 65°C, enough ice was added to the well stirred mixture to reduce the temperature to 50 - 55°C. The solution was filtered through a Buchner funnel twenty minutes after the first portion of zinc-powder was introduced. The zinc oxide residue was washed with boiling water (500-600 ml). The filtrate and washings were transferred to a 3 litre beaker and it was cooled immediately to 0 to -1° by the addition of sufficient crushed ice and at least 250 gm was left unmelted. Without delay, a cold solution of concentrated sulphuric acid (75 ml of the concentrated sulphuric acid to which sufficient ice has been added to reduce the temperature to 15°) was added with stirring. Then an ice-cold solution of crystallized sodium dichromate (17 gm) in water (65 ml) was added as rapidly as possible to the stirred solution. After 2-3 minutes, the straw-coloured precipitate of nitrosobenzene was filtered on a Buchner funnel and washed it with water. The nitrosobenzene was steam distilled from an all-glass apparatus (since cork and rubber are readily attacked) as rapidly as possible. The receiver was cooled in ice because the compound has a high vapour pressure at room temperature. The nitrosobenzene condensed to a green liquid, which solidified to a white solid. Care was taken that the solid did not clog the condenser by turning off the water supply from time to time. The distillation was stopped when the yellow oily material appeared in the condenser. It was filtered and the nitrosobenzene was ground in a glass mortar with a little water. Then it was filtered at the pump, washed it with water until the washings were no longer brown. It was dried between layers of filter paper.

The nitrosobenzene was recrystallized from a small volume of alcohol with good cooling. The compound was kept for longer periods at 0^oC.

(5) Reduction of Nitrosobenzene by sodium borohydride in the presence of *tris*-(2.2'-bipyridyl)cobalt(II) perchlorate

The apparatus used in this reaction was the same described in experiment 3. Reaction was carried out in an atmosphere of nitrogen.

Tris-(2.2'-bipyridyl) cobalt(II) perchlorate was dissolved in water-ethanol mixture (150 ml). The solution was then de-aerated by the freezing method described on page 126 . This process was repeated three to four times to remove dissolved oxygen. Finally the solution was saturated with nitrogen. An excess of sodium borohydride was added to this solution under the nitrogen atmosphere. The colour of the solution was changed from brownish-yellow through green to blue. Freshly prepared nitrosobenzene was introduced to this reduced system and the reaction mixture was stirred vigorously under the atmosphere of nitrogen. After an hour the reaction was stopped and the solution was filtered. The organic material was then extracted with chloroform. The chloroform layer was separated. The extraction was repeated two-three times. All the chloroform extract was collected and chloroform was then removed under vacuum. The residue which was reddish-yellow was then dissolved in carbontetrachloride and the clear solution was shaken several times with an aqueous solution of ferrous sulphate. The red colour in the aqueous layer showed the presence of free 2.2'-bipyridyl. Carbontetrachloride layer was separated and the solvent was removed under vacuum. The reddish-orange product obtained was recrystallized from petrolium ether (60/80 fraction) which finally gave a nice orange-red crystalline product.

The compound was identified by n.m.r., infra-red, mass spectrum and m.p. as "AZOBENZENE".

m.p.: 67^{o}C. (lit. 66-68^{o}C)

(6) Reduction of Nitrobenzene by sodium borohydride in the presence of tris-(2.2'-bipyridyl) cobalt(II) perchlorate

Tris-(2.2'-bipyridyl) cobalt(II) perchlorate was dissolved in methanol (100 ml) and the solution was de-aerated by the frozen method described on page 126. The process was repeated two or three times to remove dissolved oxygen and then the solution was saturated with nitrogen. Pure nitrobenzene (5 ml) was introduced under the atmosphere of nitrogen. An excess of sodium borohydride was added to the reaction mixture. The colour immediately changed to a dark brown.

When the reaction was complete after an hour time the solution was filtered and the excess methanol was removed on a rotatory evaporator The residue was then treated with water to dissolve soluble component. An oily layer separated on the top of the aqueous layer which was extracted with chloroform and the chloroform extract was collected. The chloroform was removed under vacuum and the residue, a brown liquid was then dissolved in carbontetrachloride. It was shaken with ferrous sulphate solution to remove free bipy present. The red colour in the aqueous layer immediately obtained indicates the presence of bipyridyl in the system. Carbontetrachloride layer was separated and the solvent was removed under vacuum. The residue, a brown liquid was collected and identified by its B.P., infra-red and n.m.r. as "ANILINE". No other product was obtained in the reduction of nitrobenzene.

(7) Reaction of Nitrobenzene in the presence of $Co^{I}(bipy)_3(ClO_4)$

Reaction was carried out in an oxygen free nitrogen atmosphere. A three necked round-bottomed flask (250 ml) was used for the reaction. The flask was fitted with a condenser and a nitrogen inlet.

Preparation of univalent cobalt complex.

Tris-(2.2'-bipyridyl) cobalt(II) perchlorate was dissolved in a water-ethanol mixture (150 ml). The clear brownish-yellow solution was de-aerated by the frozen method (described on page 126). The process was repeated two to three times in order to remove dissolved oxygen. An excess of sodium botohydride was added to the clear solution under the atmosphere of nitrogen. The colour of the solution changed from brownish-yellow through green to blue and precipitates of the same colour was obtained. At this stage the reduction of cobalt complex was complete and sodium borohydride addition was also complete. The blue coloured complex of the univalent cobalt was filtered through a sintered glass crucible under the atmosphere of nitrogen. The complex was washed several times with water and ethanol saturated with nitrogen and dried under nitrogen. This univalent cobalt-bipyridyl complex was then used for further reaction with nitrobenzene.

Reaction of nitrobenzene with $Co^{I}(bipy)_3(ClO_4)$

Univalent cobalt-bipyridyl complex (prepared by the above method) was added to nitrobenzene (5 ml) (saturated with nitrogen) under the atmosphere of nitrogen. The reaction mixture was shaken vigorously by the use of electro-magnetic stirrer, for nearly two hours. The colour of the solution changed to brownish-red. It was then filtered and the clean solution was tested for identification. The infra-red spectrum showed no characteristic absorption bands due to aniline or azobenzene. It showed the bands due to nitrobenzene and cobalt complex (dissolved in nitrobenzene).

The above experiment suggests that no reaction was obtained between nitrobenzene and univalent cobalt complex under these conditions.

(8) Preparation of Dihydrido bis-(triphenyl phosphine) mono (2.2'-bipyridyl) cobalt(II) perchlorate

(1) Tris-(2.2'-bipyridyl) cobalt(II) perchlorate (.726 gm) was dissolved in methanol (100 ml) saturated with nitrogen. A tenfold molar excess of triphenyl phosphine was added and the solution was stirred vigorously. An excess of sodium borohydride was added to the reaction mixture under the atmosphere of nitrogen. The solution was stirred continuously. The colour of the solution changed from brownish-yellow through blue to dark brown. At this stage the reaction was complete. The solution was then filtered and to the clear dark brown solution an excess of sodium perchlorate was added. No desired product, $[Co(bipy)(PPh_3)_2H_2]^+(ClO_4)$, was isolated from the solution.

(2) To the solution of tris-(2.2'-bipyridyl) cobalt(II) perchlorate (.726gm in methanol) (100 ml - saturated with nitrogen) an excess of sodium borohydride was added under an atmosphere of nitrogen. The colour of the solution changed from brownish-yellow through green to blue. A tenfold molar excess of triphenyl phosphine was added to the reduced system and the reaction mixture was vigorously stirred for nearly two hours. The colour of the solution changed from blue to yellow. The solution was then filtered and an excess of sodium perchlorate was added to the clean solution. No $[Co(bipy)(PPh_3)_2H_2]$ ClO_4 was isolated.

Recently complexes of the type $[Co(bipy)(PR_3)_2H_2].ClO_4$ (where PR_3 = PEt_3, PPr_3, PBu_3, PEt_2Ph) have been synthesized[85] but the complex with triphenyl phosphine is <u>not</u> reported, and our failure to isolate the complex of the type $[Co(bipy)(PPh_3)_2H_2].ClO_4$ is less surprising. Presumably the complex with PPh_3 is too soluble in the reaction medium even as perchlorate.

[C] RESULTS AND DISCUSSION

The reactions of aromatic nitro- and nitroso compounds with borohydride in the presence of $Co(bipy)_3^{2+}$ were carried out in different solvents such as water-ethanol, and methanol and it was found that the reactions studied were exothermic. Since the reactions of organo nitro- and nitroso- compounds with sodium borohydride in the presence of various cobalt complexes as catalysts afford different products, it is necessary to understand the role of both borohydride and the catalyst. The products obtained during the reduction of nitrobenzene and nitrosobenzene by sodium borohydride in the presence of $Co(bipy)_3^{2+}$ as a catalyst are listed in Table 5.

All the products obtained were characterized by their boiling points, infra-red characteristic bands, n.m.r. peaks and mass spectral evidence. Azobenzene which was the major product in two cases, the reduction of nitrobenzene in the presence of carbon monoxide and also in the reduction of nitrosobenzene, was identified by its melting point and mass spectrum. The expected fragmentation pattern of azobenzene was observed and the peak at $m/e = 182$ proved to be of azobenzene. Aniline which was the major product in the reaction of nitrobenzene with sodium borohydride in the presence of $Co(bipy)_3^{2+}$ was identified by its boiling point and characteristic absorption in the infra-red region. (see figure 25,26). However, when the same experiment was performed in the presence of carbon monoxide, aniline and azobenzene were the major products.

TABLE: 5 PRODUCTS OF REDUCTION OF AROMATIC NITROGEN COMPOUNDS USING SODIUM BOROHYDRIDE AND A COBALT COMPLEX AS CATALYST

Starting Material	Catalyst	Solvent	Reducing Agent	Products
Nitrobenzene	$Co(bipy)_3^{2+}$	Methanol	$NaBH_4$	ANILINE
Nitrobenzene*	$Co(bipy)_3^{2+}$	Water/ethanol	$NaBH_4$	ANILINE AZOBENZENE
Nitrosobenzene	$Co(bipy)_3^{2+}$	Water/ethanol	$NaBH_4$	AZOBENZENE

* Reaction was carried out in the presence of carbon monoxide.

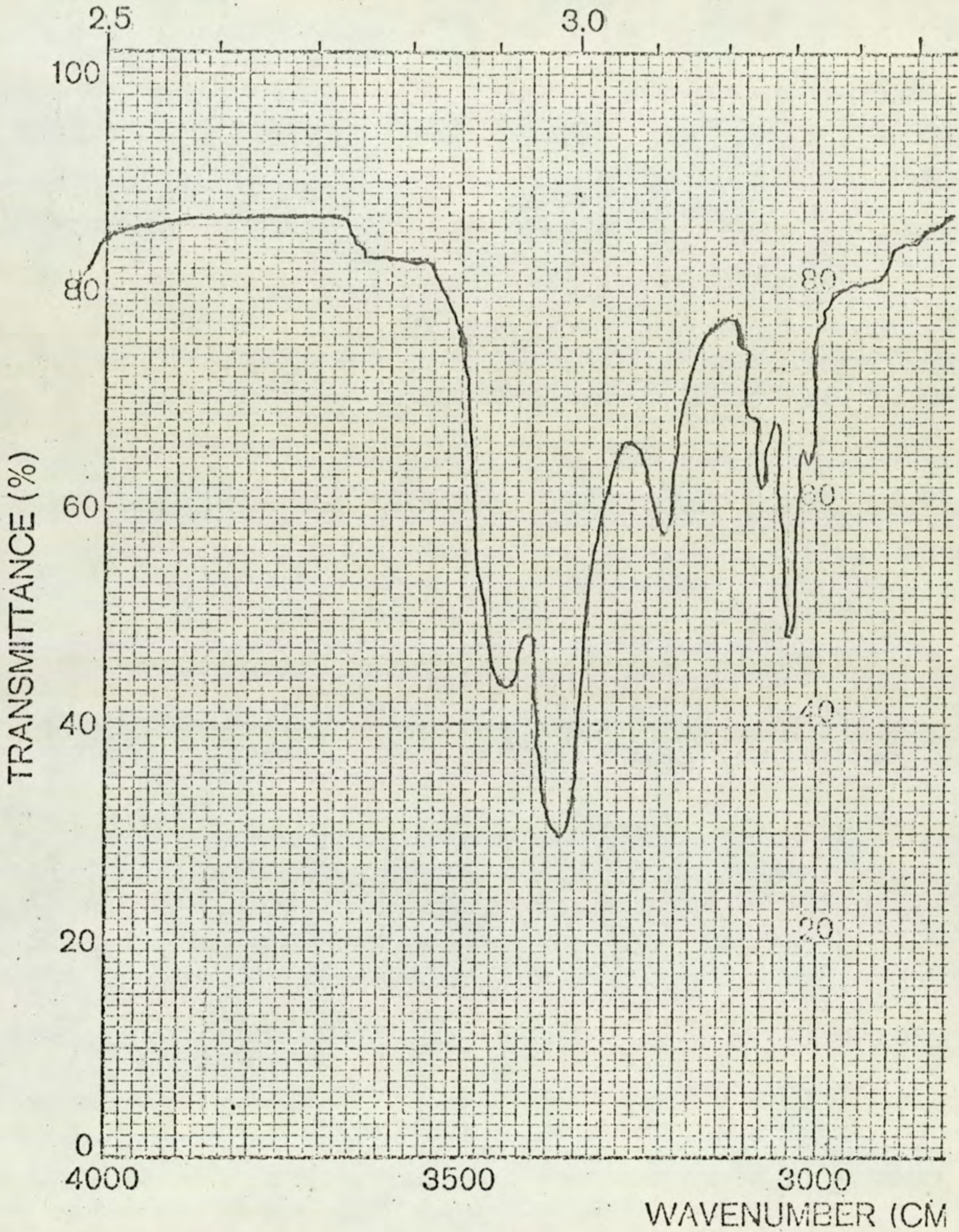


Fig: 25 Reduction of Nitrobenzene by sodium borohydride in the presence of $Co(bipy)_3^{2+}$ and carbon monoxide.

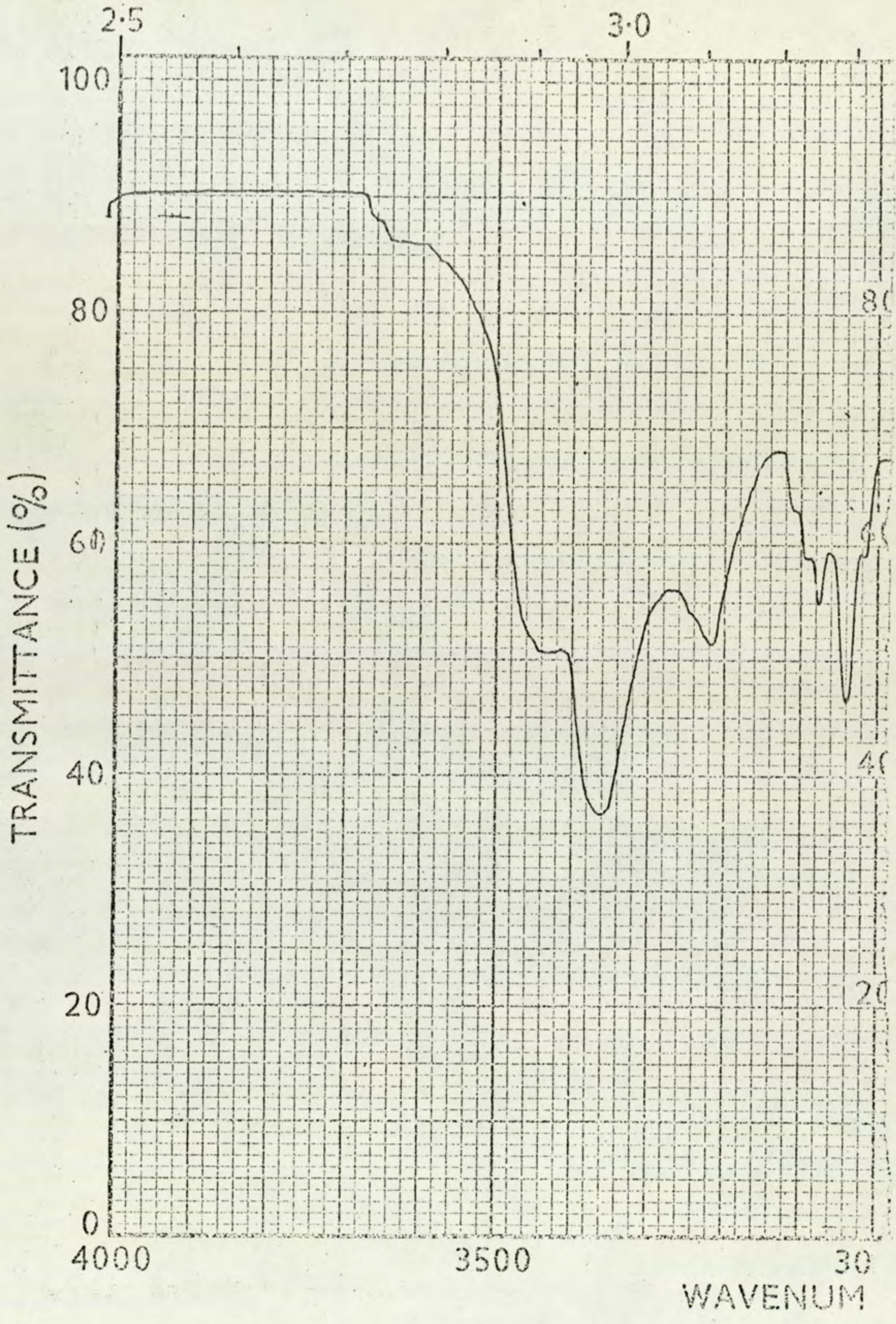
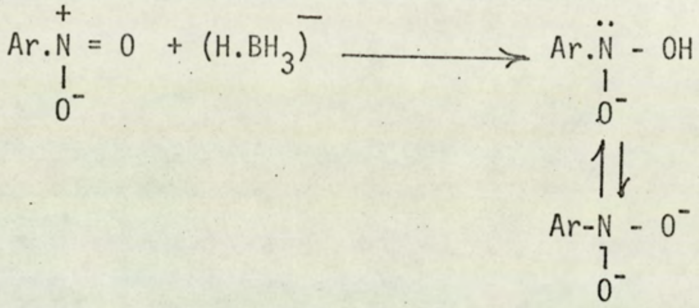
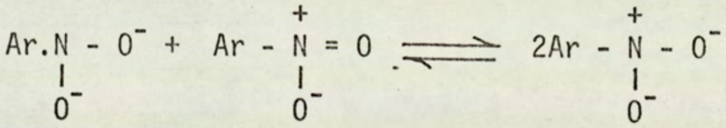


Fig: 26. Reduction of Nitrobenzene by sodium borohydride in the presence of $Co(bipy)_3^{2+}$ in methanol.

It is now known that the reaction of nitrobenzene with borohydride gives a radical anion. Since borohydride does not act other than by hydrogen transfer[91], the radical anion formation takes place as under



$$\begin{array}{ccc} Ar.\underset{\underset{O^-}{|}}{\overset{+}{N}} = O + \overline{(H.BH_3)} & \longrightarrow & Ar.\underset{\underset{O^-}{|}}{\ddot{N}} - OH \\ & & \upharpoonleft\downharpoonright \\ & & Ar\text{-}\underset{\underset{O^-}{|}}{N} - O^- \end{array}$$



$$Ar.\underset{\underset{O^-}{|}}{N} - O^- + Ar - \underset{\underset{O^-}{|}}{\overset{+}{N}} = O \rightleftharpoons 2Ar - \underset{\underset{O^-}{|}}{\overset{+}{N}} - O^-$$

When the reduction of nitrobenzene by sodium borohydride is carried out in the absence of catalyst, the products obtained are azoxybenzene with small amounts of azobenzene; but no aniline is formed. However, the same reaction when catalysed, gives as the major products aniline, azobenzene and azoxybenzene[95].

The role of catalysts in these systems can be explained in different ways. According to Vlček and Rusina[67] nitrobenzene and other organo-nitro compounds are readily reduced in the presence of cobalt ion and bipyridyl and the active species being tris-(2.2'-bipyridyl) cobalt(I) and the electron transfer mechanism has been postulated. But in our view this is not the case since no reduction products were isolated when the reaction of nitrobenzene is carried out with uni-valent cobalt-bipyridyl complex. Thus electron-transfer mechanism is not involved during the reduction of nitrobenzene by $Co^{I}(bipy)_3(ClO_4)$ as a catalyst.

The reduction of nitrobenzene to aniline via a nitrene intermediate has also been suggested and it has been found that dodecacarbonyl tri ruthenium may promote the reduction of nitrobenzene to aniline by carbon monoxide and hydrogen[102] and carbon dioxide was detected spectroscopically in the final reaction mixtures. This makes one believe that stoicheometry of the reaction would be

$$PhNO_2 + 2CO \longrightarrow PhN + 2CO_2$$

$$\begin{tikzcd}
H_2NPh \arrow[dr] & PhN^{\cdot} \arrow[l, "+H_2"'] \arrow[r, "+CO"] & PhNCO \arrow[dl] \\
& PhNHCONHPh &
\end{tikzcd}$$

The nitrene intermediate in this reaction is not believed to be present as such in a solution even for short periods of time. However, this species can be stabilized by complex formation.

The ruthenium-catalysed reduction of nitrobenzene to aniline as occurring through the formation of an

$$C_6H_5NO_2 + 2CO + H_2 \longrightarrow C_6H_5.NH_2 + 2CO_2$$

intermediate complex formation is thus regarded as the attractive feature of the reaction.

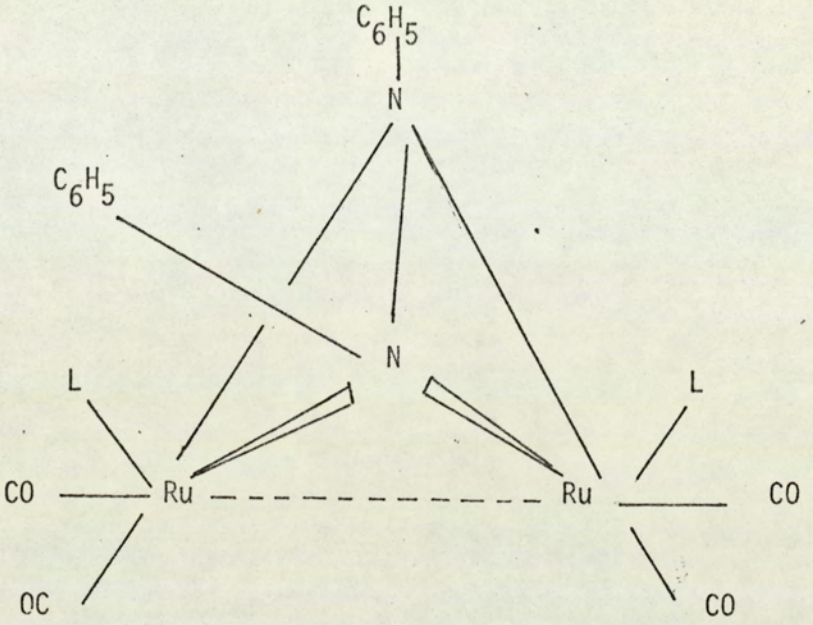


Fig. 27

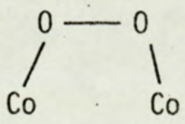
The ligands L on the ruthenium atoms may be either carbon monoxide groups or hydrido ligands. Ruthenium complex (figure 27) can then undergo hydrogenation to aniline.

The reduction of nitrosobenzene to azoxybenzene by tervalent phosphorous reagents **via** an intermediate nitrene has been known for many years[103]. The first record of this type of reaction was the reaction of substituted nitrosobenzene but <u>not nitrosobenzene itself</u>, with triphenyl phosphine to give the corresponding azoxybenzene[104].

$$ArNO + Ph_3P \longrightarrow ArN + Ph_3PO$$

$$ArN: + ArNO \longrightarrow ArN = N(O)Ar$$

Green and Swindon[98] have ruled out the possible involvement of a nitrene intermediate in the reduction of nitrosobenzene to azoxybenzene (and hence azobenzene) on the basis of an NN bond formation which might occur either through the nitrosobenzene dimer or condensation after initial reduction of the monomer. Further support for the impossibility of nitrene intermediate involvement is obtained by our own work. When nitrobenzene is reduced by sodium borohydride in the presence of tris-(2.2'-bipyridyl) cobalt(II) perchlorate as a catalyst and carbon monoxide, aniline and azobenzene were obtained as the final product. Failure to synthesize phenylisocyante from this reaction suggests that there is no evidence for the nitrene intermediate which can be readily traped by carbon monoxide. Also the possibility of nitrene intermediate can be ruled out on the basis of the above reaction. An attempt was made to isolate any peroxy complex of the cobalt with bridging oxygen, such as



No evidence in the infra-red is obtained when cobalt complex was recovered from the reaction mixture after the reduction of nitrobenzene was complete. Thus, the possible mechanism of the nitrene intermediate in this reaction is not considered.

The reduction of nitrobenzene by sodium borohydride in the presence of $Co(bipy)_3^{2+}$ and carbon monoxide and also the reduction of nitrosobenzene by sodium borohydride in the presence of $Co(bipy)_3^{2+}$ to azobenzene can easily be explained in terms of hydride transfer.

Thus the reduction of azoxybenzene to azobenzene would provide sufficient proof for the formation of azobenzene.

$$\mathrm{Ph{:}N(O)Ph} + \mathrm{CoH} \longrightarrow \mathrm{PhN{:}NPh} + \mathrm{OH^-} + \mathrm{Co^{III}}$$

It is now well established in the case of both cobalt and rhodium that hydride species are formed when the reduction of bipyridyl-complex of cobalt and rhodium is carried out by sodium borohydride. Our own work which is presented in Chapter Four suggests the hydride intermediate in the reduction of dichloro <u>bis</u>-(2.2'-bipyridyl) rhodium(III) chloride complex which is trapped by the addition of triphenyl phosphine. Also the formation of hydrido- cobalt-bipyridyl complexes in the presence of phosphine ligands[85] suggests the involvement of hydride intermediate in the reduction of cobalt-bipyridyl complex. The following mechanism is thus suggested for the formation of cobalt species during the reduction by sodium borohydride.

$$\begin{tikzcd}
\mathrm{Co(bipy)_3}^{2+} \arrow[r, "2H^-"] & \mathrm{Co(bipy)_2H_2}^{+} \arrow[r, shift left, ""] & \mathrm{Co(bipy)H_2}^{+} + \mathrm{L} \arrow[l, shift left] \arrow[d, shift left, "-H_2"] \\
\mathrm{Co(bipy)_3}^{2+} \arrow[r, shift left, "-L"] & \mathrm{Co(bipy)_2}^{2+} \arrow[l, shift left, "+L"] \arrow[r, shift right, "+L"'] & \mathrm{Co(bipy)}^{+} \arrow[u, shift left, "+H_2"] \arrow[l, shift right, "-L"'] \arrow[d, shift left, "+L"] \\
 & & \mathrm{Co(bipy)_2}^{+} \arrow[u, shift left, "-L"] \arrow[d, shift left, "+L"] \\
 & & \mathrm{Co(bipy)_3}^{+} \arrow[u, shift left, "-L"]
\end{tikzcd}$$

Thus, on the basis of experimental results and our own rhodium work and the recent work on cobalt[85] we believe that the reduction of organo nitro- and nitroso compounds by borohydride in the presence of $Co(bipy)_3^{2+}$ proceeds via a hydride transfer mechanism.

REFERENCES

1. Dwyer, F.P. and Mellor, D.P. Chelating agents and metal chelates. Academic Press, New York and London - 1964, p2.
2. Gerdeisson. Ber 22. 244 (1889).
3. Blau Montash 19 666 (1898).
4. Walden, G.H., Hemmet, L.P., and Chapman R.P., J.Am.Chem.Soc. 53 3908 (1931).
5. Burstall, F.H. J.Chem.Soc. 1662 (1938)
6. Morgan, T.G. and Burstall, F.H. J.Chem.Soc. 1498 (1934)
7. Cogle, F.W. Acta Cryst. 1 658 (1948).
8. Fielding, P.E. and Le Fèvre, R.J.W. J.Chem.Soc. 1811 (1951)
9. Goethals, C.H. Rec.trev.Chim. 54, 299. (1935)
10. Castellano, S., Günther, H. and Ebersole, S.J. J.Phys. Chem. 69, 4166 (1965).
11. Gil, V.M.S. Mol.Phys. 9 97 (1965).
12. Kramer, F.A., and West, R. J.Phys.Chem. 69, 673 (1965).
13. Murell, J.N., Gil, V.M.S., and Duijneweldt, F.B. Rec. Trav. Chim. 84 1399 (1965).
14. Spotswood, T.M., and Tanzer, C.I. Australian J.Chem.20, 1227 (1967).
15. Blears, D.J., and Danyluk, S.S. Tetrahedron 23, 297 (1967).
16. Carman, R.M., and Hall, J.R. Australian J.Chem. 17, 1354 (1964).
17. Donckt, E. Wander, Martin, R.H.. and Geerts-Everard, F. Tetrahedron 20 1495 (1964).
18. Miller, J.D., and Prince, R.H. J.Chem.Soc. 3185 (1965).
19. Miller, J.D., and Prince, R.H. J.Chem.Soc. 4706 (1965).
20. Rosenberger, H., and Pettig, M. Z.Chem.6, 30 (1966).
21. Corbridge, D.E.C., and Cox, E.G. J.Chem.Soc. 594 (1956).

22. Charlton, M., J.Org.Chem. 31 3739 (1966).

23. Burstall, F.H., and Nyholm, R.S. J.Chem.Soc. 3570 (1952)

24. Hein, F., and Herzog, S., Z.Anarg. .Allgem Chem. 267 337 (1952).

25. Irving, H., and Mellor, D.H. J.Chem.Soc. 5222 (1962).

26. Jørgenson, C.K. Acta.Chem.Scand. 9, 1362 (1955).

27. James, B.R., and Williams, R.J.P. J.Chem.Soc. 2007 (1961).

28. Hogg, R., and Wilkins, R.G. J.Chem.Soc. 341 (1962).

29. Herzog, S., and Taube, R. Z.Chem. 2, 225 (1962).

30. Funk, H., Weiss, W., and Zeising, M.
Z.Ancrg. Allgem Chem. 296, 36 (1958).

31. Nyholm, R.S., and Turco, A., Chem. and Ind.(London) 74 (1960).

32. Carmichael, W.M., Edwards, D.A. and Watton, R.A.
J.Chem.Soc. A 97 (1966).

33. Brown, I.M., and McCarley, R. U.S.At.Energy Comm. 15-741 (1964).

34. Barbieri, G.A., and Malaguti, A. Chem.Abstr. 45 55e (1951).

35. Morgan, G.T., and Burstall, F.H. J.Chem.Soc. 1649 (1937).

36. Selbin, J., and Shamburger, B. J.Inorg. and Nucl.Chem. 24.1153
(1962).

37. Brandt, W.W., Dwyer, F.P., and Gyarfas, E.C.
Chem. Rev. 54 959 (1954).

38. James, B.R., and Williams, R.S.P. , Parris, M.
J.Chem.Soc. 4630 (1961)

39. Irving, H. and Mellor, D.H. J.Chem.Soc. 5237 (1962)

40. Brandt, W.W., and Smith, G.F. Anal.Chem. 21 1313 (1949).

41. McCurdy, W.H., and Smith, G.F. Analyst 77, 846 (1952).

42. Osborn, J.A., Jardine, F.H., Young, J.F. and Wilkinson, G.
J.Chem.Soc. A. 1711 (1966).

43. Jaeger, F.M., and Van Dijk, J.A.

(a) Proc.Acd.Sci. Amsterdam 37, 284 (1934)

(b) Chem.Abst. 29, 1733 (1935).

44. Martin, B., and Waind, G.M. J.Chem.Soc. 428 (1958).

45. Harris, C.M., and McKenzie, E.D.

J.Inorg. and Nucl. Chem. 25, 171 (1963).

46. Gillard, R.D., Osborn, J.A. and Wilkinson, G.

J.Chem.Soc. 1951 (1965).

47. Kulasingam, G.C., and McWhinnie, W.R.,

J.Chem.Soc. 7145 (1965).

48. Gillard, R.D. and Heaton, B.T., J.Chem.Soc. A 451 (1969).

49. Kulasingam, G.C., McWhinnie, W.R. and Miller, J.D.

J.Chem.Soc. A,521 (1969)

50. McKenzie, E.D., and Plowman, R.A.,

J.Inorg.and Nucl. Chem. 32, 199 (1970).

51. Delepine, M., Bull.Soc.Chim.France 45, 235 (1929)

also Compt. rend., 236, 559 (1953).

52. Gillard, R.D., and Wilkinson, G. J.Chem.Soc. 1640 (1964).

53. Broomhead, J.A., and Grumely, William.

Inorg. Chem. 10, 2002 (1971).

54. Rund, J.V., Basolo, F., and Pearson, R.G.

Inorg. Chem. 3, 658 (1964).

55. McKenzie, E.D., Ph.D.Thesis, University of New South Wales, 1962.

56. Palade, D.M. Russ.J.Inorg.Chem. 14(3), 359 (1969).

57. Gibbson, J.G., and McKenzie,E.D. J.Chem.Soc.A,2637 (1969).

58. Martin, B., McWhinnie, W.R., and Waind, J.M.

J.Inorg.and Nucl.Chem. 23, 207 (1961).

59. Lewis, J., Nyholm, R.S., and Reddy, G.K.N. Chem. and Indust. 1389 (1960).

60. Gillard, R.D., and Wilkinson, G. J.Chem.Soc. 3594 (1963).

61. Figgis, B.N., Gillard, R.D., Nyholm, R.S. and Wilkinson, G. J.Chem.Soc. 5189 (1964).

62. Vaska, L., and DiInzio, J.W., J.Am.Chem.Soc.84, 4989 (1962).

63. Chatt, J., Coffey, R.S. and Show, B.L. J.Chem.Soc. 7391 (1965).

64. Areno, A. Gazzetta 95, 1431 (1965).

65. Rund, J.V. Inorg.Chem.7, 24 (1968).

66. Oliver, F.D., Ph.D.Thesis, University of Aston in Birmingham 1971.

67. Vlček, A.A., and Rusina, A. Proc. Chem. Soc. 161 (1961).

68. Bath, S.S., and Vaska, L. J.Am.Chem.Soc. 85, 3500 (1963).

69. Carey, J.C., and Sasse, W.H.F. Australian J.Chem. 21,207 (1968).

70. Hutchinson, B., Takemoto, J., and Nakamoto, K. J.Am.Chem.Soc. 92 3335 (1970).

71. Clark, R.J.H., and Williams, C.S. Inorg.Chem. 4, 350 (1965).

72. Wong, Patric T.T., and Brewer, D.G. Canad.J.Chem.46,131 (1968).

73. Osborn, R.R., and McWhinnie, W.R., J.Chem.Soc.(A),2153 (1968).

74. Carra, S., and Ugo, R. Inorganica Chim.Acta Rev. 1,49 (1967).

75. Mestroni, G., Camus, A., and Mestroni, E. J.Organomet, Chem.24, 775 (1970).

76. McKenzie, E.D., Co-ord Chem.review 6.187 (1971).

76a. Carty, A.J., and Chieh, P.C. J.C.S.Chem.Comm. 158 (1972).

77. Hinamoto, M., Ooi, S., and Kuroya, H. J.C.S.Chem.Soc. 356 (1972).

78. Livingstone, S.E., and Wheelahan, B. Aust.J.Chem.17, 219(1964).

79. Ahmad, N., Robinson, S.D., and Uttley, M.F. J.Chem.Soc. Dalton 843 (1972).

80. Levison, J.J., and Robinson, S.D., J.Chem.Soc.A 2947 (1970).

81. Malatesta, L., Angoletta, M., Araneo, A., and Caziani, F.
Angew.Chem. 73 273 (1961).

82. Dewhurst, K.C., Kein, W., and Reilly, C.A.
Inorg. Chem. 7 546 (1968).

83. Powell, J., and Shaw, B.L. J.Chem. Soc. (A), 3879 (1965).

84. Chatt, J., Coffey, R.S., and Shaw, B.L.,
J.Chem.Soc.(A) 7391 (1965).

85. Camus, A., Cocevar, C., and Mestroni, G.
J.Organomet.Chem. 40, 355 (1972).

86. Cocevar, C., Mestroni, G., and Camus, A.
J.Organometal.Chem. 35, 389 (1972).

87. Kulasingam, G.C., Ph.D.Thesis, London University, 1967, also
McWhinnie, W.R., Coord.Chem.Review. 5, 293 (1970).

88. Williams, D.H., Ward, R.S., and Cooks, R.G.
J.Am. Chem. Soc. 90, 960 (1968).

89. Deacon, G.R., and Green, J.H.S. Spectrochimica Acta 24A 845
(1968).

90. Cotton, F.A., Barnes, R.D., and Bannister, E.
J.Chem.Soc. 2199 (1960)

91. Swanwick, M.G., and Waters, W.A. Chem.Comm. 63 (1970).

92. Milewski, C., and Maryanoff, Bruce.
J.Organ.Chemistry, 36, 803 (1971).

93. Sal'nikova, E.N., and Khidekel, M.L. Izvest.Akad.Nank.S.S.S.R.
Ser. Khim., 223 (1967).

94. Green, M., Mawby, R.J., and Swinden, G.,
Inorganic. Nucl. Chem. Letters 5, 73 (1968).

95. Brealy, A.E., Gott, H., Hill, H.A.O., O'Roirdan, M. Pratt, J.M., Williams, R.J.P. J.Chem.Soc.(A), 612 (1971).

96. Zuman, P., and Perrin, C.L. 'Organic Polarography', Interscience, New York 1969.

97. Bastiansen and Hassel. Acta.Chem.Scand. 1, 489 (1971).

98. Green, M., and Swinden, G. Inorganica Chemica Acta 5,49 (1971).

99. Schrauzer, G.N., and Khohnle, J. Chem.Ber. 97, 3056 (1964).

100. Schrauzer, G.N., and Windgassen, R.J., J.Am.Chem.Soc. 89, 1999 (1967).

101. Vogel, A.I., A Text book of practical organic chenistry, Longmans and Green and Co. p.630.

102. L'eplattenier, F., Matthys, P., and Calderazzo, F. Inorg.Chem. 9, 342 (1970).

103. Cadogan, J.I.G., Quarterly Reviews - Chem.Soc.22 ,222 (1968).

104. Hoffmann, H., and Horner, L. Angew.Chem.68, 743 (1956).

105. Boyer, J.H. and Ellzey, S.E., J.Am.Chem.Soc. 82, 2525 (1960).