A STUDY OF THE REACTIVITY OF IMINOPYRIDINIUM COMPOUNDS WITH METAL IONS

by

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SUMMARY

Several known resonance-stabilized carbonyl ylides of general formula $\overset{+}{A} - \overset{-}{B}COAr$ (where $A = C_5H_5N$, $(CH_3)_3N$, or $(C_6H_5)_3P$; $B = N$ or CH; and $Ar = C_6H_5$ or *m* or *p* $C_6H_4\text{-}CH_3$) and their salts (some of them previously unknown) have been prepared and fully characterized. Reported literature methods were used for their synthesis but in some cases modifications were incorporated. Detailed spectroscopic data for these ylides are presented and are discussed.

All the available literature on the reactions of these ylides with metal salts are described and a comprehensive literature survey on the well-known *ortho*-metallation reaction is presented and the available data are critically reviewed.

N-aminopyridinium perchlorate, like the corresponding chloride, bromide and iodide in solution behaves as a 1:1 electrolyte and shows no sign of any association. However, in the solid form, under the influence of high pressure, the anion and cation of N-aminopyridinium perchlorate interact *via* hydrogen bonding possibly to give chain polymers or cyclic oligomers. Ample spectroscopic evidence is presented to support this interaction.

Attempts to use N-iminopyridinium imine as a donor molecule towards some transition metal salts have failed and resulted in the protonation of the free ylide. This behaviour of the N-iminopyridinium imine is in direct contrast to that of isoelectronic pyridine-N-oxide

and a possible explanation for its greater tendency for protonation rather than co-ordination is the very much higher basicity as reflected by its pK_a value (=13.4).

The reaction of the carbonyl ylides mentioned above, with halide salts of palladium (II), platinum (II), rhodium (III) and iridium (III) affords products containing metallated betaines. Spectroscopic data (*i.r.* 'H and ^{13}C.*n.m.r*) show unambiguously that the aryl group (Ar) has become metallated in a position *ortho* to the carbonyl group and also that the ylide is bidentate *via* the group B (N or CH). There is good evidence to indicate that the mechanism of the reaction involves preliminary co-ordination of the ylide followed by intramolecular electrophilic attack by the metal.

Palladium tends to give di-μ-halogeno-complexes; $[Pd(L\text{-}H)Hal]_2$, whereas in the case of platinum it is possible to prepare $[Pt(L\text{-}H)_2]$ which has *cis* Pt-C bonds. Reaction with rhodium (III) affords ionic compounds *cis* $[Rh(L\text{-}H)_2(H_2O)_2]^+\bar{X}$ (where X = Cl, Br, I, BPh_4)which with 2,2'-bipyridyl give $[Rh(L\text{-}H)_2(bipy)]^+\bar{Cl}$. Iridium gives a non-ionic derivative $[Ir(L\text{-}H)_2(H_2O)Cl]3H_2O$. Reactions of the complexes with Ph_3P or Bu^n_3P give new compounds containing phosphine oxide such as $[Pd(L\text{-}H)(Ph_3PO)Cl]$, $[Pt(L\text{-}H)(Ph_3PO)Cl]$, $[Rh(L\text{-}H)_2(Bu^n_3PO)Cl]$ and $[Ir(L\text{-}H)_2(Ph_3PO)Cl]$. The Pd-Cl and Pt-Cl bonds are *trans* to nitrogen when L = $C_5H_5\overset{+}{N}\text{-}\bar{N}COPh$ with which most of the metallation reactions have been done.

Carbon monoxide reacts reversibly with palladium and iridium complexes of $C_5H_5\overset{+}{N}\text{-}\bar{N}COPh$, under ambient conditions, to give $[Pd(L\text{-}H)(CO)Cl]$

and $[Ir(L-H)_2(CO)_2]Cl$. Infra-red evidence suggests the carbon monoxide to be *cis* to the Pd-C bond in the palladium complex and other observations suggest that the mode of formation is not simple.

The generality of the *ortho*-metallation reaction was tested on two other related ylides namely N-phenacylidene pyridinium betaine and N-(*p*-toluenesulphonyl)iminopyridinium betaine and no metallated products were isolated in either case. In these cases, a competing reaction exists between the reduction of the metal and the reaction of metal with the ylide.

The donor ability of N-benzoyliminopyridinium betaine as a ligand towards some first row transition metals such as Cu^{II}, Co^{II}, Fe^{II} and Ni^{II}, and coinage metals Ag^{I} and Hg^{II} was investigated. With these metals, no *ortho* metallation was observed, and the reactions resulted in the formation of several stable co-ordination compounds in which the betaine is O-co-ordinated to the metal except with Cu^{II} and Hg^{II} where N-co-ordination is indicated. Reaction with anhydrous copper chloride results in the cleavage of the N-N bond in the betaine well below its m.p. and evidence is presented for the copper-catalized formation of phenyl isocyanate. All the co-ordination compounds prepared, have been characterized by a combination of physical methods such as *i.r.*, *n.m.r.*, and electronic spectroscopy, conductivity and magnetic measurements.

This work was carried out between 1971 and 1974 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

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Finally, I am indebted to the University of Sri Lanka (Vidyalankara Campus) for granting me study leave to carry out this work.

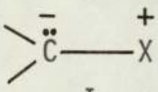
CONTENTS

CHAPTER ONE

INTRODUCTION

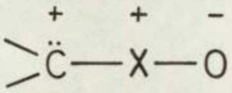
There has been a growing interest in new methods of synthesis of organic compounds and in particular, in the understanding of mechanisms of already known syntheses. Consequently, a special class of dipolar molecules, commonly known as ylides, has attracted the attention of many workers all over the world, not only because of the variety of different types of reaction they can undergo in view of the dipolar nature, but also, perhaps mainly, because some of them are believed to be the intermediates in some well-known rearrangements and reactions.

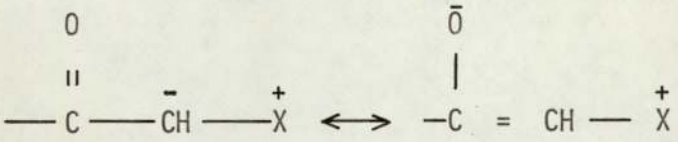
The term ylide appears to have been used very loosely in the chemical literature. Originally it was defined by Johnson(1) as a substance in which a carbanion is attached directly to a heteroatom carrying a high degree of positive charge - represented by the general formula I.



I

(where X = P, N, As, Sb, S, Se)

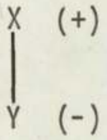
including those molecular systems whose heteroatoms carry less than a formal full positive charge such as structure II  and resonance hybrid molecule III in which there is an important contributing structure which meets the original definition.



$$-\overset{\overset{O}{\|}}{C}-\overset{-}{CH}-\overset{+}{X} \longleftrightarrow -\overset{\overset{\bar{O}}{|}}{C}=CH-\overset{+}{X}$$

III

The important criterion, he has stressed is the presence of the formal charges on adjacent atoms. This definition has now been extended to include those substances that resemble ylides in their chemical and physical properties and/or by virtue of their molecular structure. All the known substances that have been referred to as ylides can be represented by the general formula IV



$$\begin{array}{l} X\ (+) \\ | \\ Y\ (-) \end{array}$$

where X = NR_3, SR_2, PR_3, AsR_3, SbR_3, SeR_2.

Y = CR_2 or NR.

IV

The anion portion of an ylide can be stabilized by delocalization of the unshared pair of electrons on the "Y atom" and this delocalization can occur in two different ways. First of all, the adjacent "onium" atom may withdraw electrons into a vacant orbital, forming a *pi*-bond. Secondly, the carbanion or imino anion may contain electron withdrawing groups, such as carbonylor phenyl groups, which stabilize the anion. These factors could, thus, account for many ylides being isolable as stable crystalline substances. In the literature, the term, "stabilized ylide" is taken to imply an ylide that can be isolated, purified, usually stored in the atmosphere and used in a subsequent experiment.

It will be noted that each of the six heteroatoms mentioned above has vacant low energy d-orbitals with the exception of nitrogen. The stabilization of the ylide has been partly attributed to the overlap of the filled carbanionic or imino anionic 2*p*-orbital with an empty d-orbital of the "onium atom". Thus one would expect the ammonium group to be less effective for anion stabilization than the "onium" group of the other heteroatoms. Indeed, this expectation has been borne out experimentally. For instance $R_3\overset{+}{P}-\bar{N}H$ are surprisingly stable in marked contrast to the corresponding amine imines $R_3N^+ - \bar{N}H$ which are nonexistent in the absence of complexing agents(2). Further, the nitrogen ylides are, in general, more difficult to prepare and less stable than other ylides.

The vast majority of ylides prepared thus far are phosphorus ylides. A large number of nitrogen ylides has also been prepared. Sulphur(3), antimony, arsenic, selenium(6), and tellurium(7) ylides, however, have been studied only in recent years and mainly as an extrapolation of phosphorus chemistry.

The reactivity of these compounds depends both on the properties of the carbanion or imino anion and on the possible involvement of the heteroatom. The most important reaction due to the latter was discovered by Wittig(8) in 1953, and this stimulated an extensive investigation of the properties and reactions of phosphorus ylides and of organophosphorus chemistry in general. Several reviews on ylide chemistry have appeared(9) in recent years, including a comprehensive book(1).

Because of the dipolar nature, the ylides have mainly been studied as reactive intermediates in organic synthesis.

The various classes of ylides have characteristic reactions and since the work to be discussed subsequently in this thesis is mainly on nitrogen ylides, our concern will mostly centre around such ylides and in particular on pyridinium ylides.

On the basis of the deuteroxide-catalyzed exchange of deuterium in tetramethylammonium and tetramethylphosphonium salts(11), and greater basicity of nitrogen ylides as against the corresponding sulphur, phosphorus, or arsenic ylides(12) and many other observations of a similar nature, it has been assumed generally that an ammonium group is capable of stabilizing an adjacent carbanion or imino anion only by an electrostatic interaction between the opposite charges, since they can derive no stabilization by d-orbital carbanion delocalization. It must, however, be pointed out that the absence of other than electrostatic stabilization by positively charged nitrogen has not been rigorously proven.

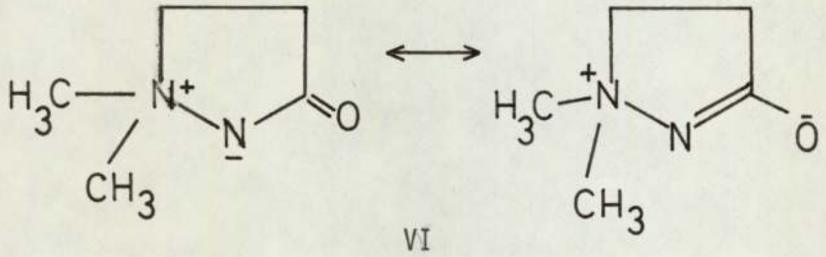
Although nitrogen ylides are relatively less stable, a large variety of such ylides are isolable when suitable substituents are present to stabilize the charges.

The nomenclature of N-N ylides is varied; the majority of investigators use the aminimide nomenclature because they are isoelectronic with amine oxides. Thus V is named trimethylamine-benzimide.

$$(CH_3)_3\overset{+}{N} - \overset{-}{N}COC_6H_5$$

V

Other investigators have used the names ammonium ylides, imines amido ammonium compounds or even nitrogen betaines. Chemical Abstracts in the Seventh Collective Index names this class as hydrazenium hydroxide inner salts. e.g. compound V is indexed as hydrazenium, 2-benzoyl-1,1,1-trimethylhydroxide, inner salt. Further, it has been pointed out(13) that even the IUPAC Nomenclature of Organic Chemistry fails for cyclic aminimides such as VI.



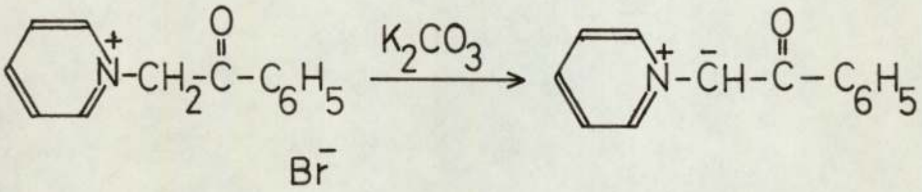
VI

Although Kronhnke(14) in 1935 reported the first nitrogen ylide to be prepared, the evolution of the chemistry of nitrogen ylides really began with the early attempts to demonstrate the existence of pentavalent nitrogen by workers such as Schlenk and Holtz(15), and Hager and Marvel(16).

In the recent years, several workers have reviewed (13,17,18,19,20) the interesting and varied chemistry of this synthetically useful and mechanistically important class of compounds.

Nitrogen ylides like other ylides undergo two basic types of reaction: those in which only the imino anion or carbanion is involved mechanistically and those in which both the anion and the heteroatom portion are involved. The former group consists basically of those reactions which any carbanion or imino anion, regardless of structure, would undergo, e.g. Alkylation etc. The presence of the heteroatom portion of the ylide usually is reflected only in its effect on the nucleophilicity exhibted by the carbanion. The most interesting reactions of ylides are the second group which involves both the anion and the heteroatom portion. The well known Wittig reaction falls into this category and the discovery of this and related reactions has aroused a tremendous activity in the field of ylide chemistry during the last decade(21).

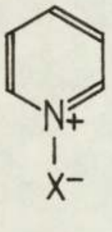
Kronhke(14), by treatment of N-phenacyl pyridinium bromide with potassium carbonate isolated the crystalline ylide VII of m.p. 74°C.



VII

Subsequently analogous ylides also were prepared using the corresponding quinolinium and isoquinolinium salts.

These were but the first of a series of ylides of general structure VIII



VIII

where $X = CR_1 R_2$

$= NR$

In order for the ylide to be capable of isolation at least one of the groups R, R_1 or R_2 must be capable of stabilizing the carbanion by resonance.

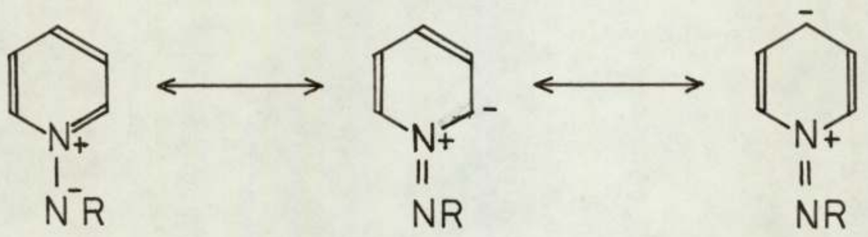
e.g. R = CH_3CO, C_6H_5CO, CO_2Et .

The importance of resonance stabilization of these ylides is shown by the low carbonyl stretching frequencies in their infrared spectra. For example, all the amine acylimides show strong absorptions in the region 1545 - 1590 cm^{-1}, thus supporting the resonance structures as shown below.

$$\mathrm{R-\underset{\underset{O}{\|}}{C}-\overset{-}{N}-\overset{+}{N}R_3 \longleftrightarrow R\,\underset{\underset{O^-}{|}}{C}=N-\overset{+}{N}\,R_3}$$

When X = NR, the compounds are known as pyridinium imines. Pyridinium ylides appear to be much more stable than ammonium ylides, probably due to stabilization of the anion by resonance with the pyridinium ring.

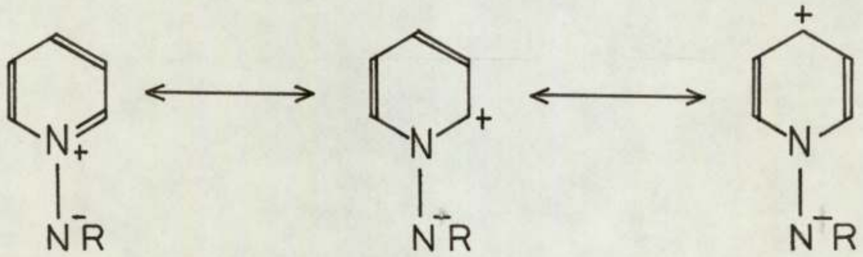
e.g.



etc.

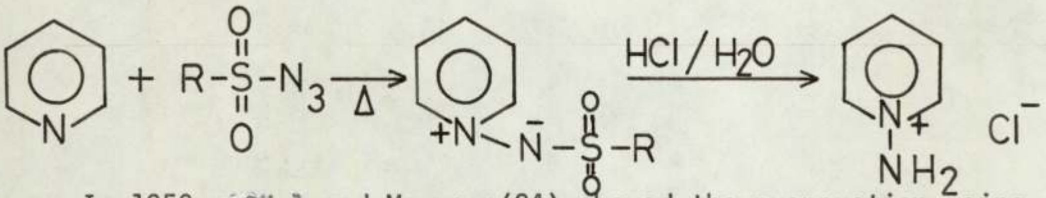
The positive charge also can be delocalized over the ring carbon atoms.

viz:

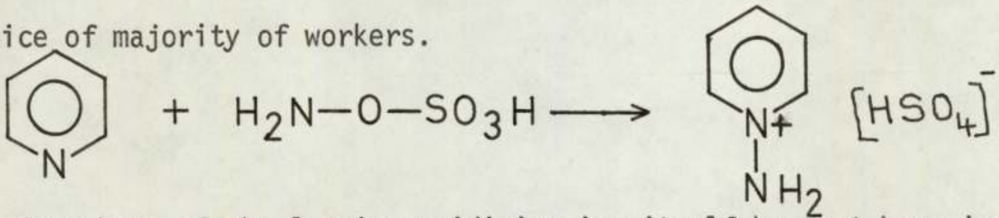


etc.

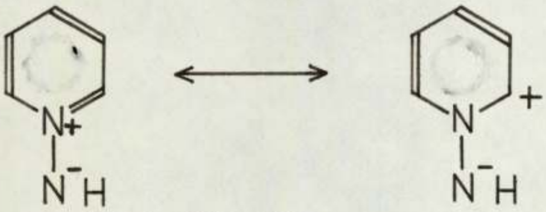
Ashley, Buchanan and Easson(22) were the first to prepare the 1-aminopyridinium ion (R = H_2) in a re-investigation of earlier work of Curtius(23).



In 1959, Gösl and Meuwson(24) showed the preparation using hydroxylamine-O-sulphonic acid and to date this method has been the choice of majority of workers.



The free base of the 1-aminopyridinium ion itself has not been isolated, although its transient existence as the 1,3-dipolar azomethine imine



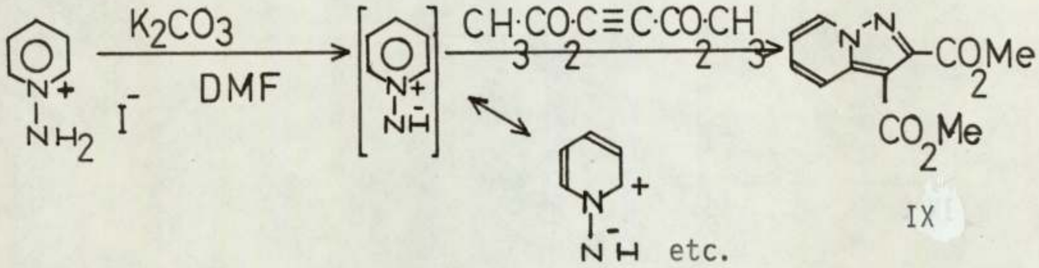
has been well established(25,26).

A large number of investigations has been carried out into the organic chemistry of pyridinium imines. Various nucleophilic and electrophilic substitution reactions and reactions involving nitrogen-nitrogen bond cleavage have been studied.

The majority of the published work has been carried out by the Japanese School of Okamoto and his co-workers as described in a series of recent papers(27,28,29,30).

Reactions of these compounds previously investigated include (a) 1,3-dipolar cycloadditions(25,26,31,32,33) with a variety of dipolarophiles.

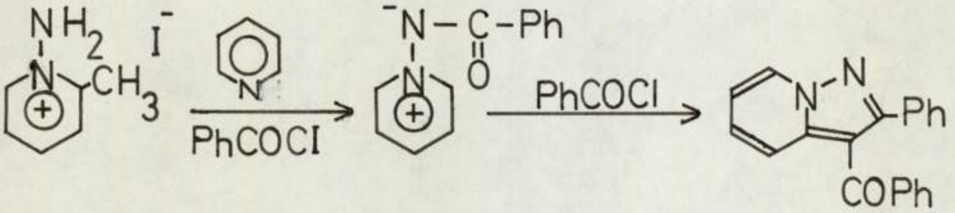
For example, Huisgen *et al*(25,26) showed that treatment of 1-aminopyridinium ion with potassium carbonate in N.N. dimethyl formamide, followed by reaction with dimethyl acetylene dicarboxylate gave methyl pyrazolo [1,5-a] pyridine -2,3 dicarboxylate IX.



IX

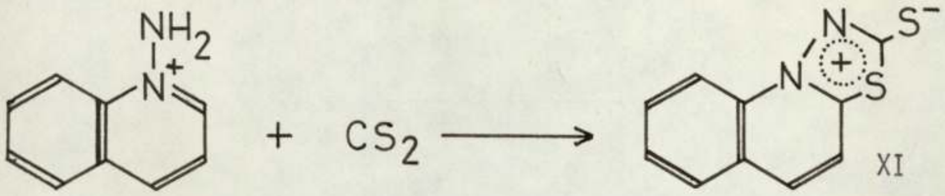
Okamoto *et al*(29,34) showed that 1-aminopyridinium salts react with HCN to give S-triazolo [1,5-a] pyridine - a reaction analogous to the acetylenic 1,3 dipolar cycloaddition reactions.

Potts, Singh and Bhattacharrya(35) have demonstrated that treatment of 1-amino -2-methyl pyridinium iodide in pyridine with benzoyl chloride yielded 3-benzoyl-2-phenyl pyrazolo [1,5-a] pyridine X.



X

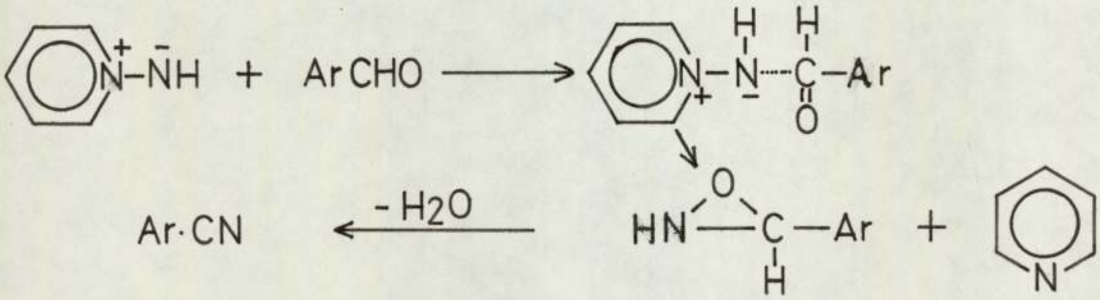
Huisgen *et al*(25) have also demonstrated a similar ring expansion reaction of 1-aminoquinolinium ion with carbon disulphide to give the ring-fused mesoionic 1,3,4-thiodiazole system XI.



XI

The chemistry of mesoionic compounds has attracted considerable attention in recent years(36). Thus, 1,3-dipolar nature of the free base offers an attractive starting point for the synthesis of novel ring-fused mesoionic systems.

(b) Reactions with carbonyl compounds(37) and heterocumulenes(38)

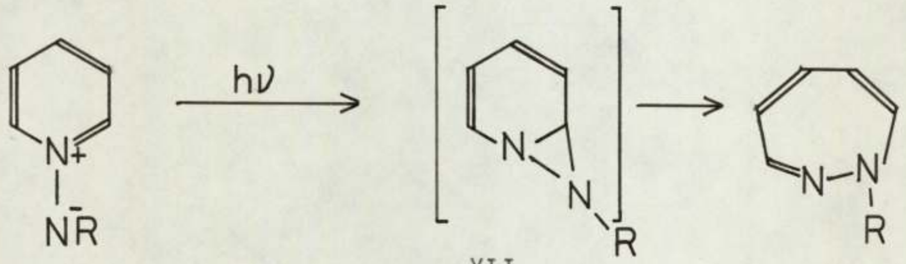


Dugas(38) has studied the reactions of 1-aminopyridinium ion with β-diketones and heterocumulenes such as isocyanates and isothiocyanates and with the latter reactions, 1-ureido (or thioureido) pyridinium hydroxide inner salts have been isolated. For example, 1-amino-4-methyl pyridinium iodide and phenyl isocyanate had yielded 1-(3-phenylureido)-4-picolinium hydroxide inner salt.

A general study of the physical and chemical properties of heteroaromatic-N-imides, particularly designed to test their susceptibility to electrophilic and nucleophilic substitution has been carried out and the initial results have been reported by Katritzky and co-workers(39,40). They have demonstrated that N-aminopyridinium cations and their acylated and sulphonylated derivatives readily undergo deuterium exchange at the 2- and 6-positions on base catalysis but are not susceptible to acid catalysed deuteriation.

(c) Photoisomerization to 1(1H), 2-Diazepines

On irradiation, N-iminopyridinium ylides have been found to undergo ring expansion to afford seven membered 1(1H),2-Diazepines XIII(41 - 47) in good yields.



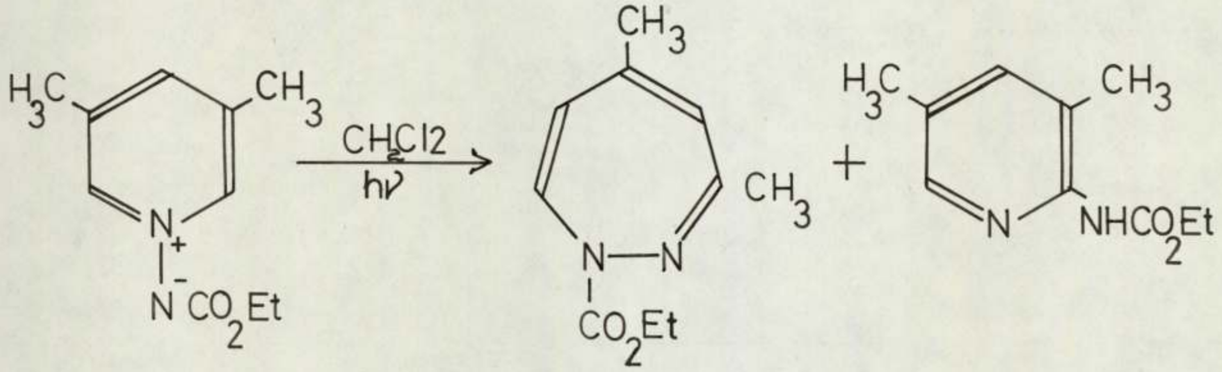
XII

XIII

It is believed that the reaction goes through the hypothetical diaziridine intermediate XII which then undergoes valence isomerization to the diazepine. The isolation of a 2-substituted pyridine derivative besides the normal product, in some cases, has been taken to indicate the possible participation of this diaziridine intermediate. For instance, Snieckus *et al*(47) on irradiation of 3,5-dimethyl-1-carbethoxyiminopyridinium ylide XIVa obtained 2-carbethoxyamino-3,5-dimethyl pyridine XIVb besides the expected diazepine XIVc.

41%

31%



XIVa

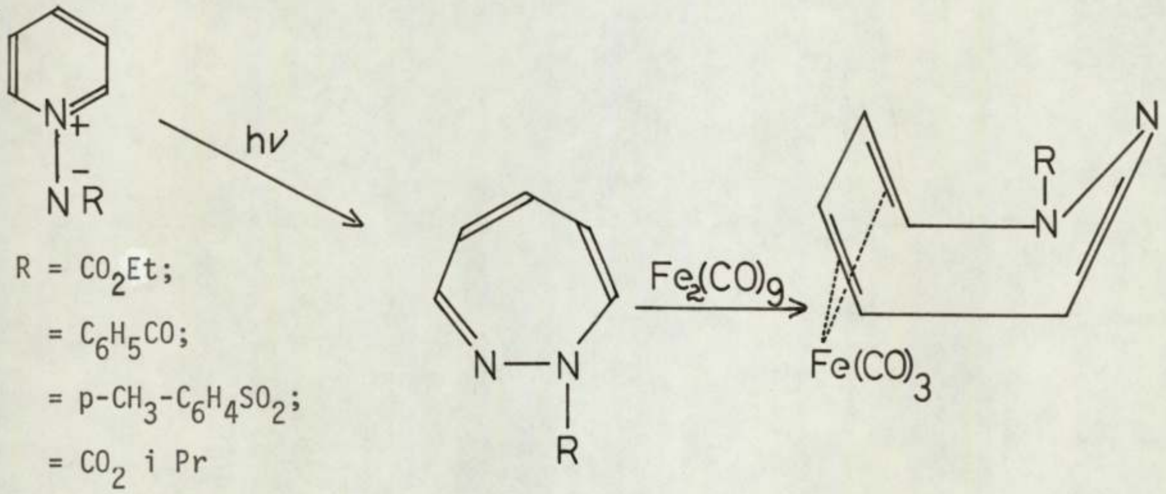
XIVc

XIVb

Of the various physical methods namely *ir, uv, and n.m.r.* used to characterize these compounds, *n.m.r.* spectra have been extremely useful due to the dramatic change in the absorption pattern in going from the ylide to the diazepine.

The photoisomerization products of many N-aminopyridinium ylides have been isolated in the form of metal carbonyl adducts(48 - 50).

E.g.



R = CO_2Et;
= C_6H_5CO;
= $p\text{-}CH_3\text{-}C_6H_4SO_2$;
= CO_2 i Pr

Allman(50) by X'ray studies, and Snieckus and co-workers(51) by *i.r.* mass spectra, *Mössbauer and n.m.r.* studies have shown that the seven membered heterocycles are co-ordinated to the metal atom *via* two olefinic double bonds in typical diene fashion.

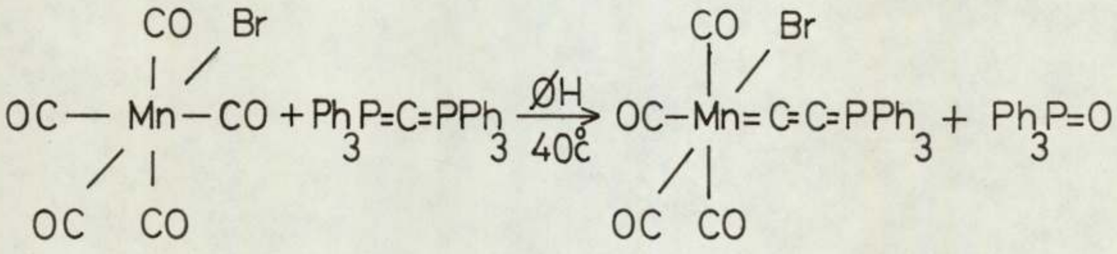
These are, perhaps, the only instances where these nitrogen ylides have ever been treated with metal compounds.

Ylides, thus exhibit a broad spectrum of chemical reactivity with a variety of organic compounds and yet their potential chemistry as co-ordinated ligands to transition metal complexes has been scantily explored.

In view of the tremendous interest in the Wittig reaction, it is not surprising to find that phosphorus ylides have been the subjects of the majority of such investigations.

Several successful attempts(52 - 56) have been made in the past to apply the Wittig reaction to transition metal carbonyls, using phosphorous ylides.

Thus, Mitchell, Korte and Kaska(52) reported the formation of bromotetracarbonylphoranylideneketenmanganese [1] as an organometallic ylide by reacting Hexaphenylcarbodiphosphorane with bromopentacarbonylmanganese.

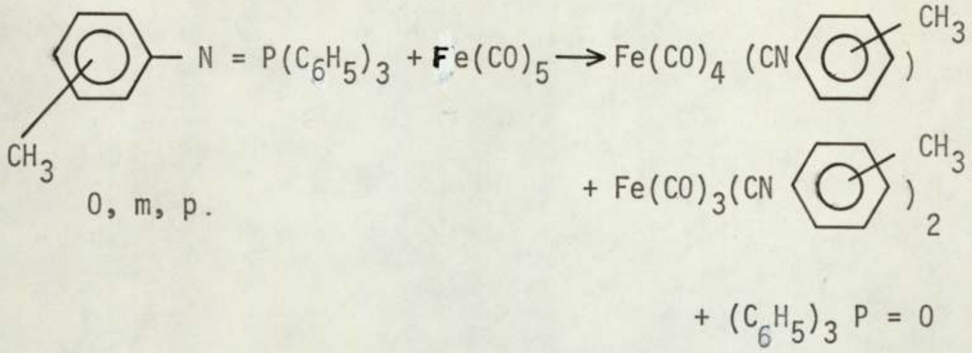


$$OC-\underset{OC\ \ CO}{\overset{CO\ \ Br}{Mn}}-CO + Ph_3P{=}C{=}PPh_3 \xrightarrow[40^{\circ}C]{\emptyset H} OC-\underset{OC\ \ CO}{\overset{CO\ \ Br}{Mn}}{=}C{=}C{=}PPh_3 + Ph_3P{=}O$$

(A *bis* ylide)

The ylide structure $Ph_3\overset{+}{P} - C \equiv \overset{-}{C}$ of the above complex has been confirmed by X'ray studies(53).

A Wittig-like reaction with N-tolyltriphenyl phosphine imines and iron pentacarbonyl has been reported by Alper and Partis(54), where deoxygenation of a carbonyl group of iron pentacarbonyl occurs without cleavage of M-C bond.



Others have observed only substitution of carbon monoxide by the ylide carbon atom on reacting with transition metal complexes (57 - 63) For example,

$$Ph_3P = CHR + M(CO)_6 \longrightarrow M(CO)_5(PH_3P = CHR) + CO$$

where M = Cr; Mo; W.

R = Ph; $CH = CH_2$; $CH = CHCH_3$; CH = CHPh

and

$$Ph_3P = NH + M(CO)_6 \longrightarrow [M(CO)_4(PH_3P = NH)_2] \text{ where } M = Mo, W.$$

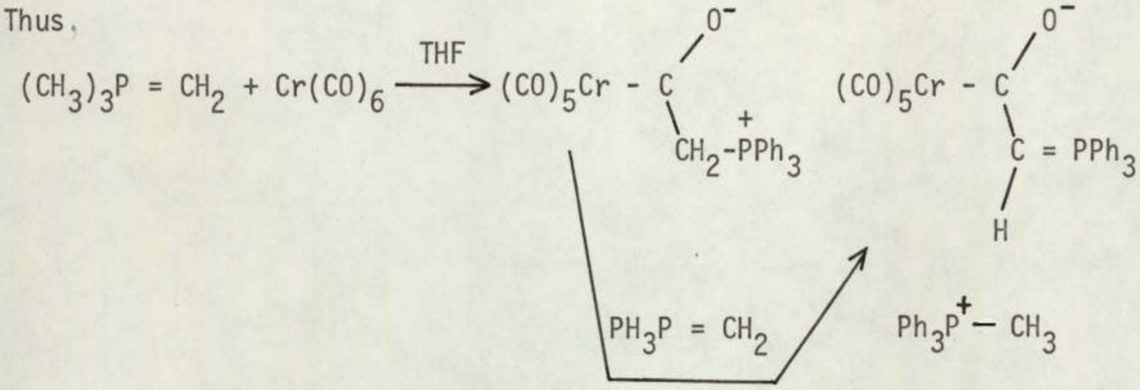
Refluxing the reagents at higher temperatures in petroleum ether or benzene, sometimes had resulted in the formation of *bis*-ylide metal tetracarbonyls,

$$2Ph_3P = CHPh + M(CO)_6 \longrightarrow M(CO)_4(Ph_3P = CHPh)_2 + 2CO$$

The failure of Wittig-like reactions in these cases has been attributed to the reduced basicity of the resonance-stabilized ylide.

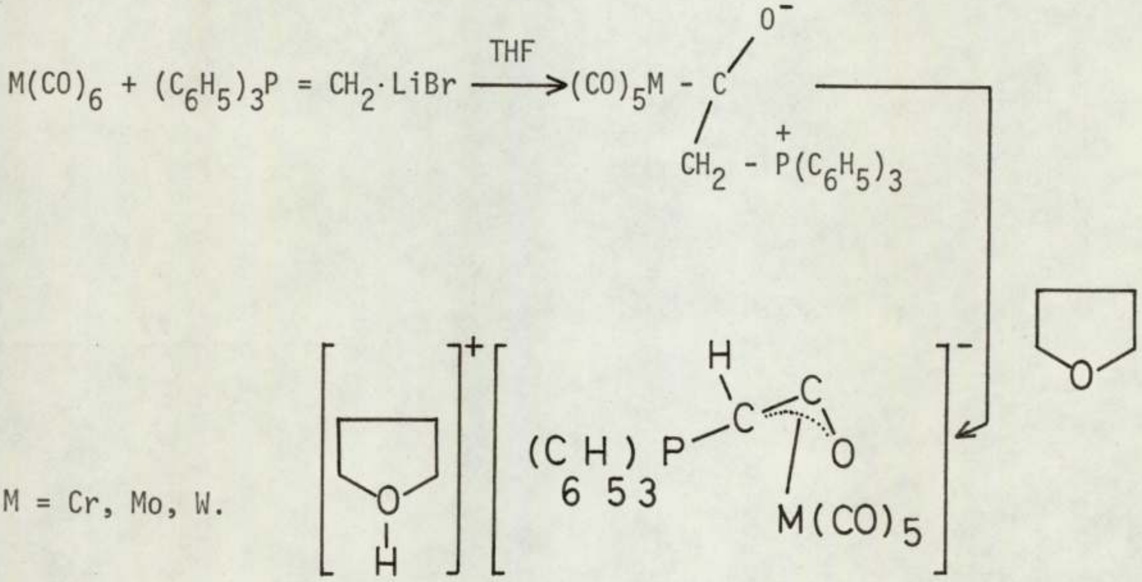
As against the above reports which emphasize only substitution of CO by the ylide, a facile addition to the metal co-ordinated carbon monoxide has been observed by Mitchell and Kaska(64), to yield ylide-carbene complexes.

Thus,



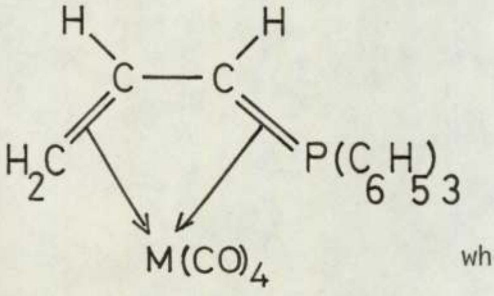
They also have prepared the analogous tungsten complex.

Greco(65), using triphenylmethylene phosphorane generated *'in situ'*, has prepared a series of 1:1 adducts and has postulated a π-allylic structure with a THF oxonium cation.



M = Cr, Mo, W.

Allylidenetriphenyl phosphorane is also reported by the same authors to form π-complexes and preliminary X'ray analysis of the Mo complex has revealed the presence of a non-classical allylic system on the metal.



where M = Mo or W.

Kreisse and co-workers(66) have quite recently reported that secondary and tertiary alkyl phosphines react with alkoxycarbene or (alkylthiocarbene) pentacarbonyl complexes of Cr(0) and W(0) at low temperatures to give the corresponding ylidepentacarbonyl metal complexes under addition of the phosphines to the carbene carbon atom, without cleavage of either methanol or a ligand.

$$PX_3 + (CO)_5M[C(OCH_3)Z] \longrightarrow (CO)_5M[C(PX_3)(YCH_3)Z]$$

OR $(CO)_5W[C(SCH_3)CH_3]$

when $M = Cr, \; Z = C_6H_5$

where $M = W, \; Z = CH_3$

$X_3 = (CH_3)_3$ $\qquad$ $M = Cr, W$

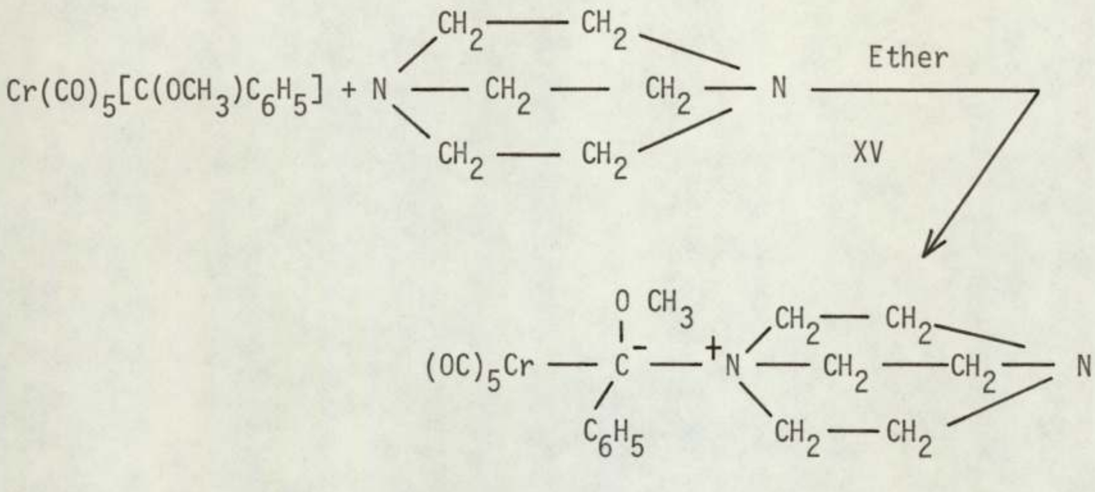
$= (C_2H_5)_3$ $\qquad$ $Y = O, S$

$= (n\text{-}C_4H_9)_3$ $\qquad$ OR $\qquad$ $Z = CH_3, C_6H_5$

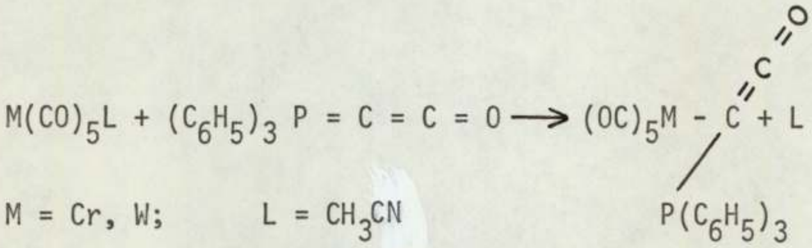
$= (CH_3)_2H$

The above behaviour is in contrast with the reaction of ammonia, primary and secondary amines and with thiols or selenols, which results in the cleavage of alcohol to give the corresponding amino(67), thio(68), and seleno(69) carbene complexes. In the case of aminolysis involved in these reactions, a nitrogen ylide complex has been assumed as an intermediate(70).

The above observation had prompted the same workers to extend these reactions to tertiary amines and, indeed, they have isolated a novel nitrogen ylide-transition metal complex(71) by reacting 1,4-diazabicyclo [2,2,2] octane XV with phenylmethoxy carbene pentacarbonyl chromium [0]



Berke and Lindner(72) have prepared a series of phorphorus ylide complexes of group VI metal carbonyls with carbonylmethylene triphenyl phosphorane.



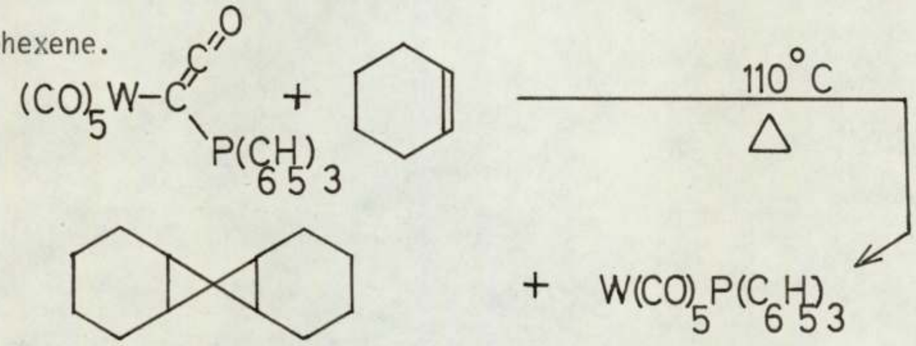
$$M(CO)_5L + (C_6H_5)_3P=C=C=O \longrightarrow (OC)_5M-C(=C=O)P(C_6H_5)_3 + L$$

M = Cr, W; L = CH_3CN

M = Mo, L = CO.

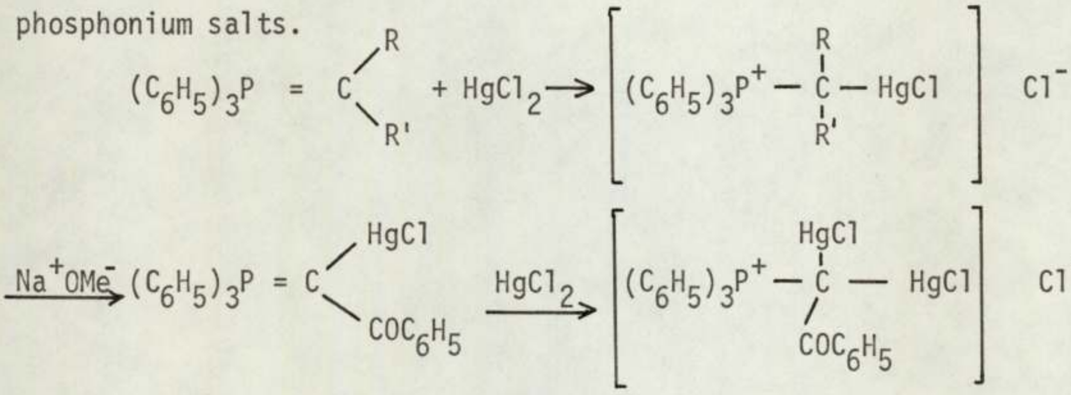
The mass spectra of the resultant complexes have been found to be characterized by thermolysis reactions involving rearrangements; $M(CO)_5P(C_6H_5)_3$ and C_2O occur as products of thermolysis and a carbene; intermediate is believed to be involved and, indeed, has been trapped with cyclohexene.

E.g.



This behaviour has been taken by them to indicate the potential of the phosphorus ylide complexes of group VI as sources of carbonyl methylene.

Besides, metal carbonyls, metal halides also have been reacted with trialkylphosphine methylene and their derivatives. Nesmeyanov, Novikov and Reutov(73) have reacted a series of resonance-stabilized triphenyl phosphine methylene ylides with mercuric chloride and have observed ready addition of mercuric chloride to form mercurated phosphonium salts.



$$(C_6H_5)_3P = C\begin{matrix}R\\R'\end{matrix} + HgCl_2 \rightarrow \left[(C_6H_5)_3P^+ - \overset{R}{\underset{R'}{C}} - HgCl\right] Cl^-$$

$$\xrightarrow{Na^+OMe^-} (C_6H_5)_3P = C\begin{matrix}HgCl\\COC_6H_5\end{matrix} \xrightarrow{HgCl_2} \left[(C_6H_5)_3P^+ - \overset{HgCl}{\underset{COC_6H_5}{C}} - HgCl\right] Cl^-$$

A doubly mercurated phosphonium salt.

Where $R = H$ or C_6H_5

$R' = CO_2CH_3$

$= COCH_3$

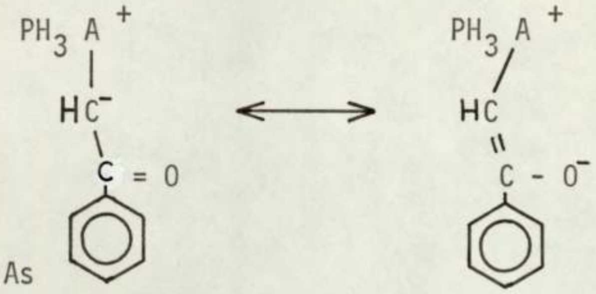
$= COC_6H_5$

$= COC_6H_4C_6H_5$.

They have also used arsenic ylides in these reactions and obtained analogous products. The infrared carbonyl stretching frequency has been used as a criterion to distinguish O-versus C-modes of attachment of stabilized phosphorus ylides in mercuric halide complexes and have concluded that in all cases the ylide is C-co-ordinated.

The position of the carbonyl stretching frequency in the complexes as compared with that in the free ylides has also been used by Buckle and Harrison(74) to establish the site of co-ordination in the series of tin and lead complexes they prepared with triphenyl arsine and triphenyl phosphine phenacyclides.

L =



where A = P or As

With triorgano tin and lead halides, irrespective of the metal, ligand ratio or nature of the ligand, always 1:1 adducts were formed.

$$\begin{array}{l} R_3PbX \\ \\ R_3SnX \end{array} + L \longrightarrow R_3MX(L)$$

The phosphorus ylide was found to be O-co-ordinated whilst the arsenic ylide was C-co-ordinated. With diorganotin dichlorides, the nature of adduct formed depended on the nature of the ylide and the groups attached to tin. For example, with dimethyltin dichloride, triphenyl phosphine C-acetyl methylene and triphenyl phosphine C-carbomethoxy methylene give adducts of the stoichiometry $3R_2SnCl_2.4(ylide)$; whilst triphenylphosphine C-benzoyl methylene and triphenyl arsine -C-benzoyl methylene yield products of $5R_2SnCl_2.4(ylide)$. These stoichiometries, they suggest, are best rationalized on the basis of ionic formulation.

E.g. $[R_2Sn(ylide)_4]^{2+}$ $2[R_2SnCl_3]^-$

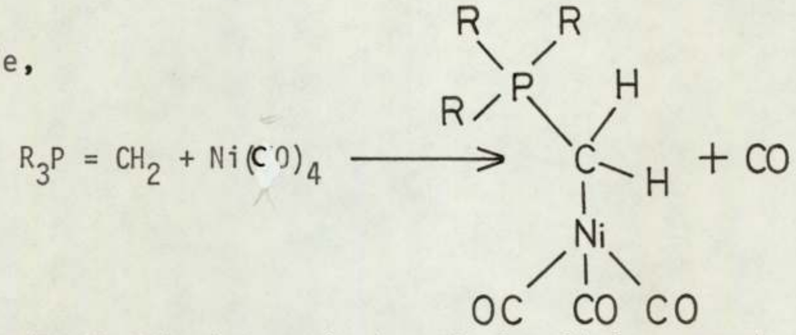
$[R_2Sn(ylide)_2]_2^{2+}$ $2(R_2SnCl_3)^-(R_2SnCl_4)^{2-}$

The predicted O-co-ordination on the basis of infrared carbonyl stretching frequency of the trimethyl tin - triphenylphosphine acetyl methylene complex was confirmed by crystal and molecular structure determinations(75).

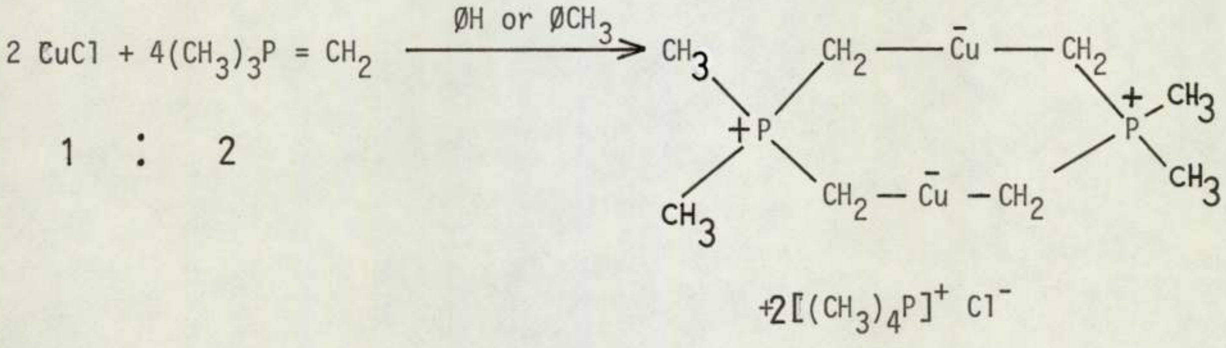
Triphenyl phosphine methylene also gives analogous C-stannylated salts with organotin halides(76).

Heydenreich and co-workers(77) by means of *i.r, n.m.r.,* and X'ray structural determinations have confirmed that in the case of trialkyl phosphine methylene complexes, the ylide is bonded to the metal through the C-atom with resulting hybridization from sp^2 towards sp^3.

For example,

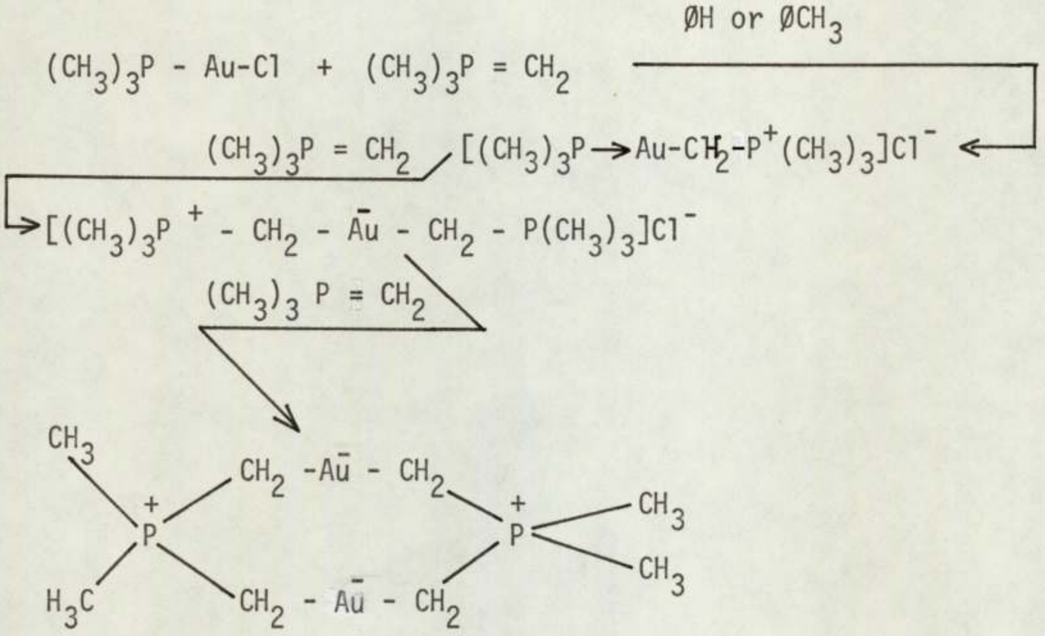


It is known(78,79,80) that replacing simple alkyl groups by trimethyl silylmethyl group, often, effects considerable stabilization of organometallic compounds. Schmidbaur and co-workers(81,82) have found that this effect of the $(CH_3)_3Si\text{-}CH_2$ group is greatly exceeded by that of the isoelectronic phosphonium group $(CH_3)_3P^+ - CH_2^-$, and that Cu-C and Ag-C units become capable of existence under normal conditions when this ligand is used.



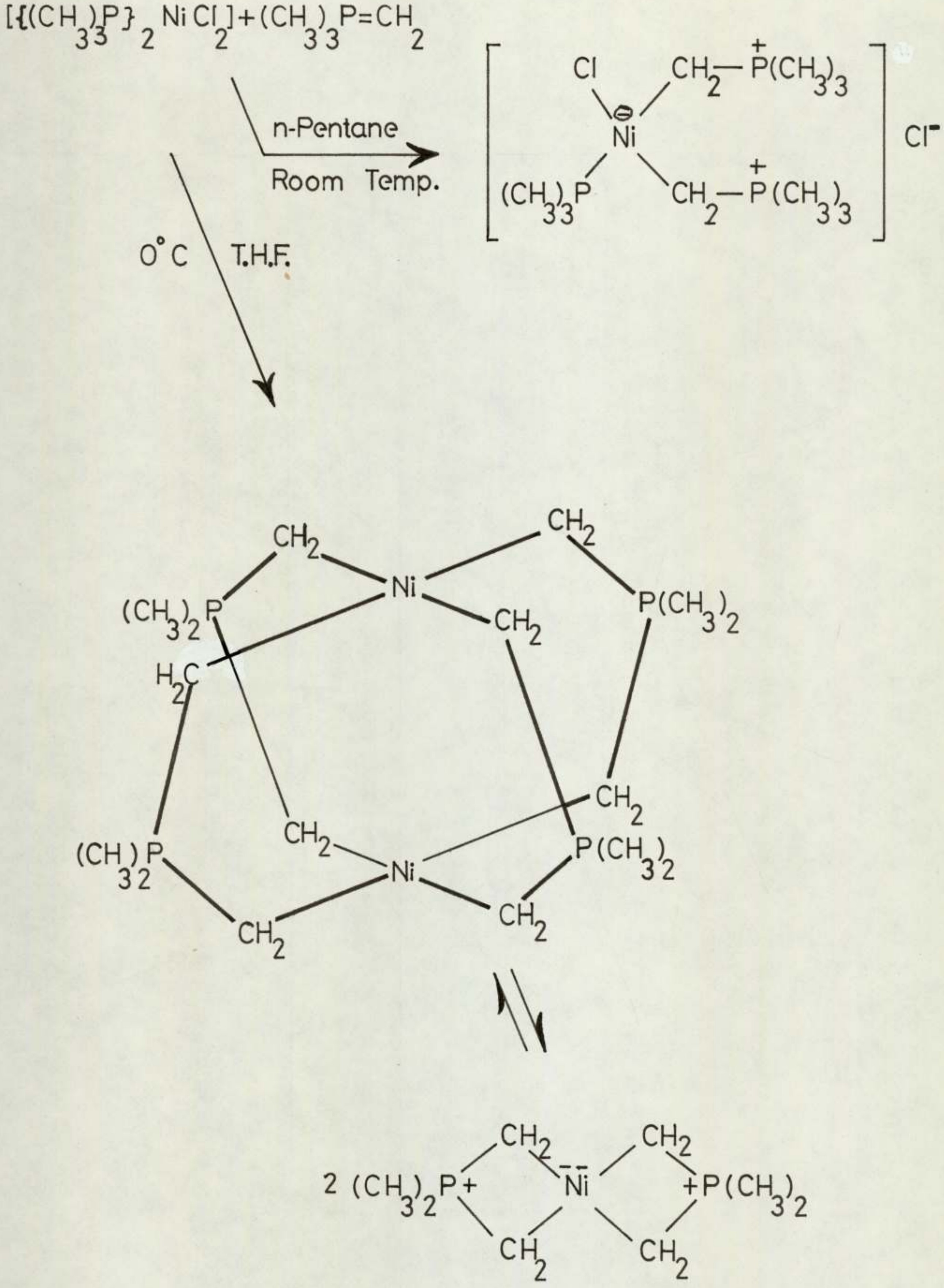
The analogous silver complex is better prepared from the tetrameric (trimethyl phosphine) silver chloride.

In the case of the gold complex, they have shown that not only the first, but also a second Au-C σ-bond is stabilized to an unexpectedly great extent by a neighbouring onium centre.

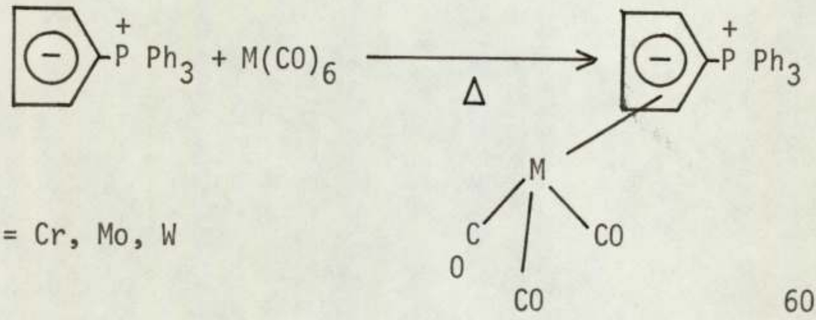


The effect of introducing an onium centre on otherwise unstable M-C structural units is exemplified by the unusual properties of these compounds.

Schmidbaur and Karsch(83) have synthesized a similar nickel complex which has a binuclear structure with no less than four Ni-C σ-bonds attached to each of the two $\underline{d}^8$-nickel atoms.


[{(CH3)3P}2NiCl2]+(CH3)3P=CH2
n-Pentane
Room Temp.
Cl⁻
0°C
T.H.F.
2

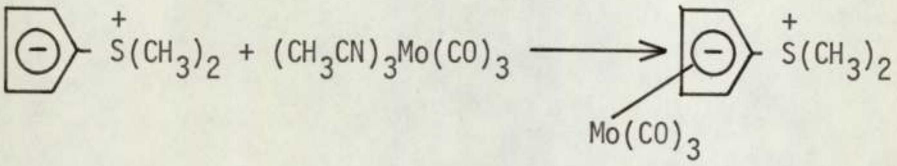
Another stable triphenyl phosphine ylide that has been reacted with metal compounds is the triphenyl phosphonium cyclopentadienide which has been found to form several stable complexes with group VI metal carbonyls(84 - 86)



M = Cr, Mo, W

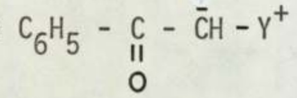
60% yield

Quite recently Zdanovitch and co-workers(87) reported the synthesis and characterization of a similar complex of molybdenum with the analogous sulphur ylide.



The ylide, thus, behaving as a formal six-electron donor ligand in complexing with transition metals. However, in the case of 1:2 complexes prepared by Barney(88) with the above sulphur ylide and tetramethylene sulphonium cyclopentadienylide, co-ordination of the ylides through sulphur rather than the cyclopentadienide ring, has been strongly suggested on the basis of infrared, and *n.m.r.* data. Further, on comparing the stretching frequency of the sulphur - "anionic carbon atom" bond in the free ylide with that of complexes, he suggests position one of the ring in these sulphur ylides as the site of co-ordination in the 1:1 complexes with Hg I_2. Cd I_2 $ZnCl_2$ and $AgNO_3$.

Alper and Partis(89) have treated a series of phosphorus ylides of general structure p-$XC_6H_4CH = P(C_6H_5)_3$ (where X = H, CH_3, or OCH_3) with iron carbonyls and obtained low - reasonable yields of the corresponding stilbenes, in addition to some unstable, and unidentified purple-red organometallic complexes. Also, using ylides of type $RCH = P(C_6H_5)_3$, when R is alkyl, the corresponding substituted ethylenes have been isolated. Further, 1,4-diphenylbutane -1,4 dione in various *cis/trans* ratios has been obtained using the carbonyl stabilized ylides of general structure



$$C_6H_5 - \underset{\underset{O}{\|}}{C} - \bar{C}H - Y^+$$

Where $Y = P^+(C_6H_5)_3$;

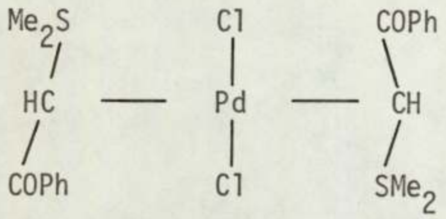
$= P^+(p\text{-}F\ C_6H_4)_3$;

$= \overset{+}{N}C_5H_5$

$= \overset{+}{S}(CH_3)_2$

on reaction with iron pentacarbonyl. The mechanism for the formation of alkenes or 1,4 diketones in these reactions is unknown, although the formation of 1,2,3-tribenzoyl cyclopropane as the major product from the sulphur ylide has been explained as being due to its thermal decomposition in refluxing tetrahydrofuran.

Recently a preliminary report by Bravo and co-workers(90) on the donor properties of several carbonyl stabilized sulphonium ylides of general structure p-X $C_6H_4CO\bar{C}H\text{-}\overset{+}{S}Me_2$(where X = H, Me, OMe) towards palladium dichloride has appeared and in general the ylide displaces the two styrene or benzonitrile ligands in the starting palladium complex to yield *bis*-ylide palladium dichloride complexes. X'ray analysis of a single crystal of the phenacyclidene dimethyl sulphonium ylide - complex has shown that it exists in the solid state in a *d,l-trans* square planar structure with the two ylidic ligands bound to palladium through the anionic carbon atoms which now appear tetrahedral in a perfectly equivalent spatial arrangement as shown below.



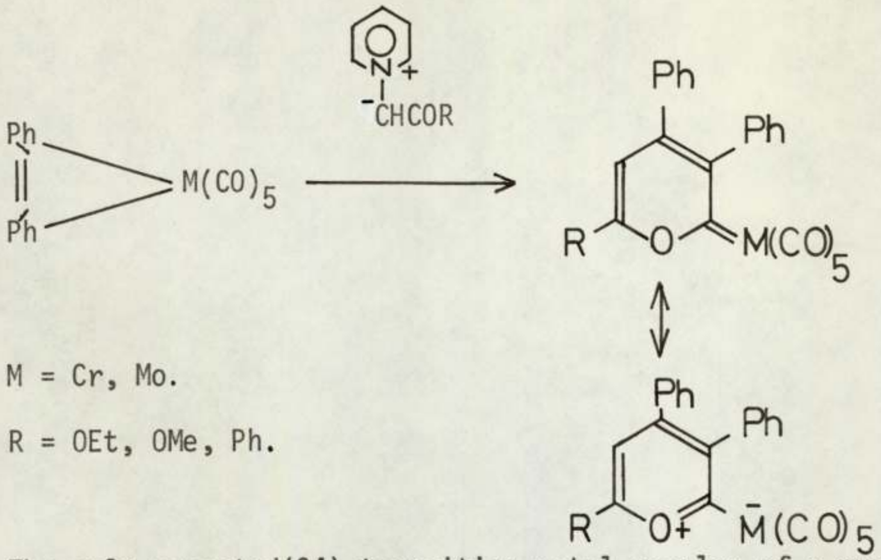
These workers also have used the *i.r.* absorption of the carbonyl group as a criterion to establish the C-co-ordination of the ylides.

However, the above ylide is reported(91) to have undergone protonation when reacted with copper halides in methanol.

$$(CH_3)_3\ S^+\bar{C}HCOPh + CuCl_2 \xrightarrow[\text{Room temp.}]{\text{MeOH}} [(Me_2S^+\text{-}CH_2COPh)\bar{Cl}]_2 \cdot CuCl_2$$

Bis ylide - complexes of phenacylidene triphenyl phosphorane, Ph_3P^+-$\bar{C}$ HCOPh with palladium and platinum dichloride have been reported (92) and again, the infrared carbonyl absorption criterion is relied upon to establish the C-co-ordination for the ylide. However, the conditions used for the preparation of these complexes have not been reported.

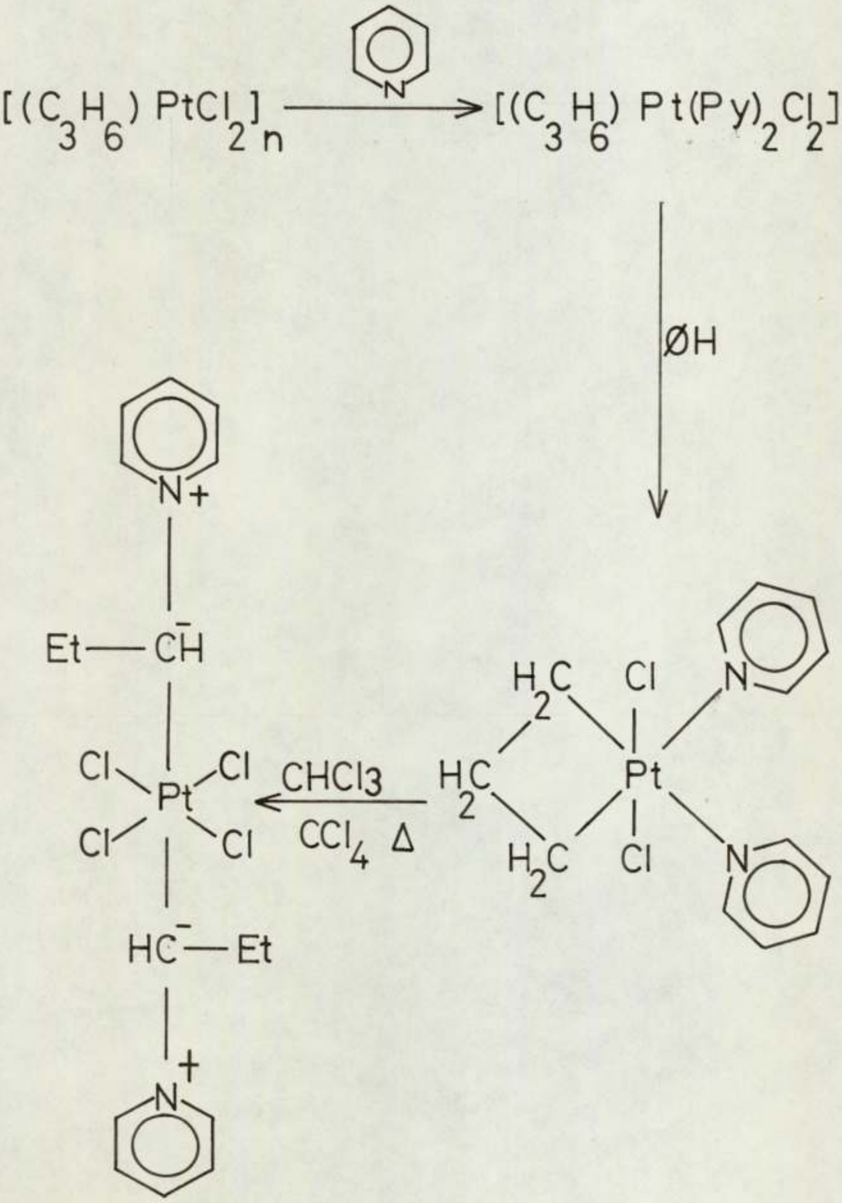
An interesting conversion of a metal complex of one class of carbene (the 2πcyclopropenylidenes) into another class (the 6π - pyranylidene) of carbene complex has been achieved(93) by reacting stable pyran-2-ylidene complexes of chromium and molybdenum carbonyls with some pyridinium ylides.



When M = Cr, Mo.

R = OEt, OMe, Ph.

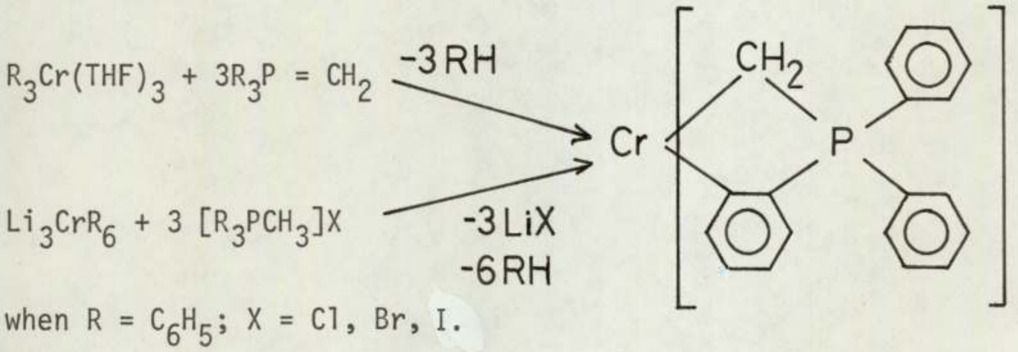
The only reported(94) transition metal complex of a pyridinium ylide had resulted unexpectedly from the reaction of polymeric cyclopropane platinum chloride with pyridine.



X-ray studies had indicated that the σ-bonded carbon atom (bonded to Pt) is not trigonal planar and therefore the complex is considered not to be a carbene by them.

A unique instance where a substitution of a hydrogen attached to a ylide by a metal atom has recently been reported by Kurras, Rosenthal, Mennenga and Oehme(95).

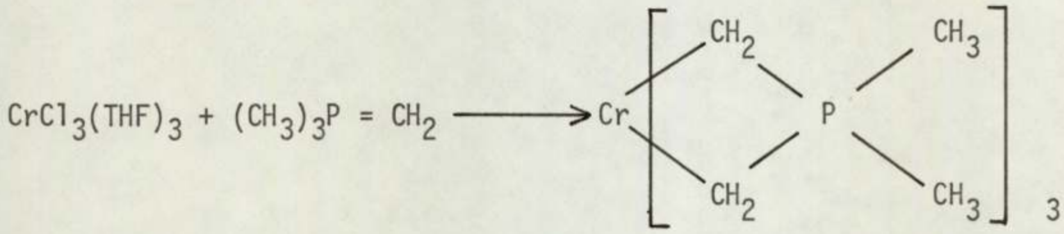
They have found that reaction of methylene triphenylphosphorane with triphenyl *tris*(tetrahydrofuran) chromium(iii) or of a methyl triphenyl phosphonium halide with lithium hexaphenyl) chromate (III) leads to the chelate complex XVI where the *ortho* hydrogen of a phenyl group attached to the phosphorus has been replaced by the metal.



XVI

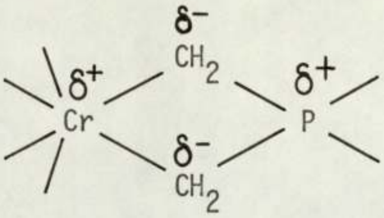
when R = C_6H_5; X = Cl, Br, I.

An analogous complex with $(CH_3)_3P = CH_2$ ylide has also been obtained.



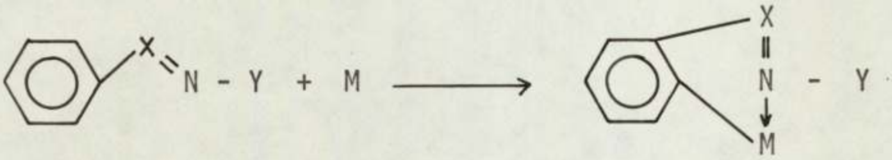
tris(dimethylphosphorium *bis*methylide)
chromium(iii)

These compounds give typical reactions of organometallic compounds and a charge distribution shown schematically below, is believed to stabilize the polar Cr-C σ bond.



These are but first reported examples of ylides undergoing a well documented reaction referred to as *ortho*-metallation reaction which has received widespread attention in recent years (96 - 100).

In this reaction, an aryl or alkyl C-H bond in a donor ligand of a transition metal complex reacts with the central metal atom to form a metal - carbon σ-bond as part of the resultant metalocycle. Metallation on a phenyl group most commonly occurs at the *ortho* position of the phenyl group and hence the term *ortho-metallation*.



$M = PdCl/_2$
$= Mn(CO)_4$
$= Re(CO)_4$ etc.

where X = RC, N
Y = alkyl, aryl, OH etc.

These metallation reactions are generally intramolecular, leading to the formation of, usually, five membered metalocycles and hence are to be distinguished from the direct metallation of organic compounds by organometallic reagents such as organolithium reagents(101) and organo mercury reagents(102).

$$RLi + R'H \longrightarrow RH + R'Li$$

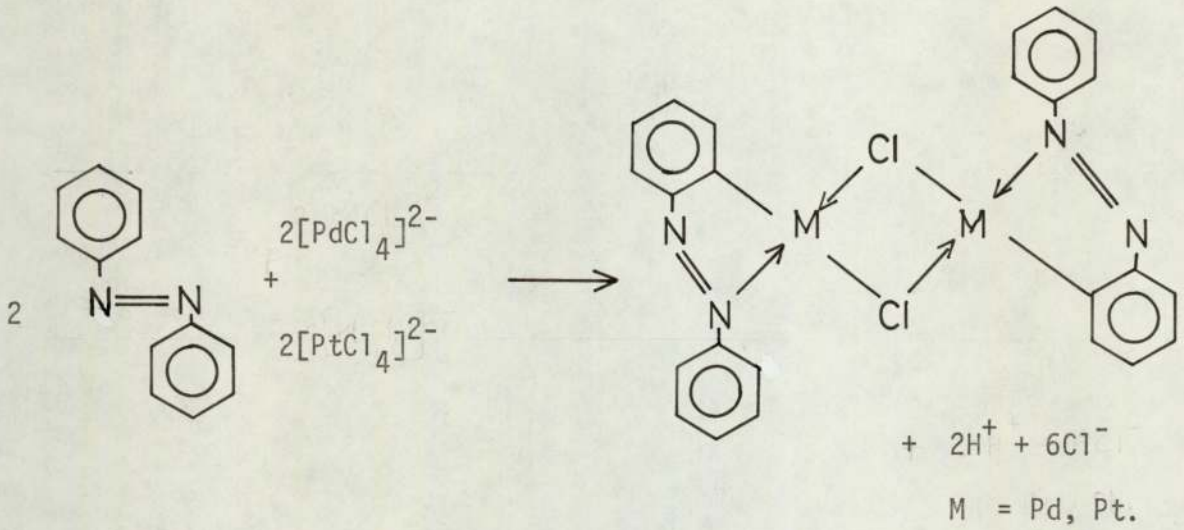
$$PhHgCl + PdCl_2 \longrightarrow PhPdCl + HgCl_2$$

A variety of metals (Fe, Co, Ni, Mn, Ru, Rh, Ir, Pd, Pt etc.) and ligands including amines(103,104),Schiff bases(105 - 109) azo compounds (110 - 123), phosphites(124 - 129), phosphines(98, 130 - 136), oximes(137), and ketones(138) are known to undergo this internal metallation. Recently Alper and Chan(97) reported the first examples of sulphur donor ligand *ortho*-metallated complexes by reaction of various thiobenzophenones with diiron enneacarbonyl in benzene at room temperature. The same workers have subsequently reported the preparation of several more sulphur donor ligand *ortho*-metallated complexes(139 - 141).

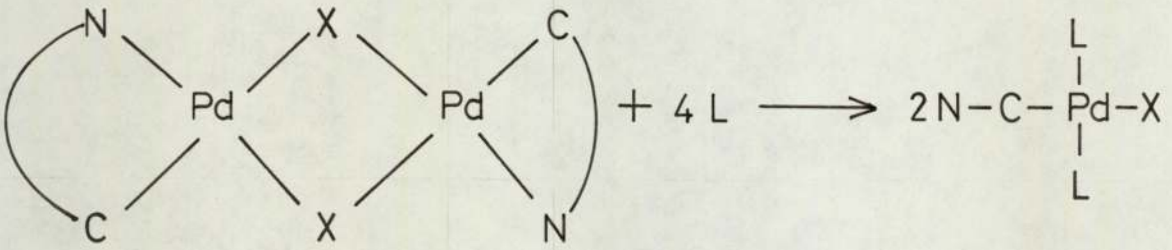
Recent reviewers(142 - 144) of transition metal-carbon compounds have suggested, mainly from spectroscopic and bond-length data, that the long-held view of inherently weak bonding is unfounded, and further, in view of the large number and wide variety of organic compounds undergoing facile *ortho*-metallation of appropriately substituted benzenes, it seems possible that this type of reaction occurs even more commonly than is recognised. Such reactions are likely to be involved in many transition metal catalyzed syntheses(96, 112, 115)

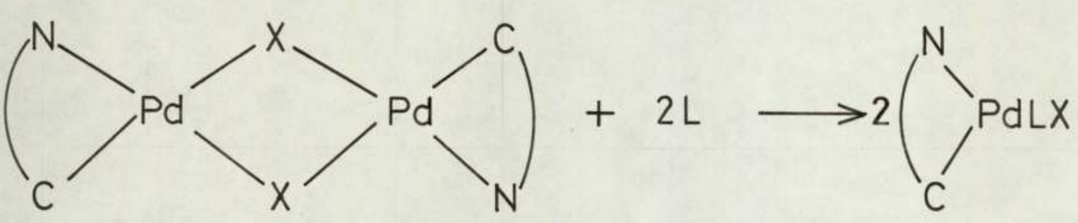
The substitution of an aryl group which is part of an N-donor ligand molecule has been studied most extensively with palladium. With platinum such reactions are, in general, slower. The ligand in these complexes is bonded to the metal *via* a nitrogen lone-pair and a carbon metal σ-bond. Azobenzenes and other similar N.donor ligands with Pd(II) and Pt(ii) usually form dimeric products with halogen bridges.

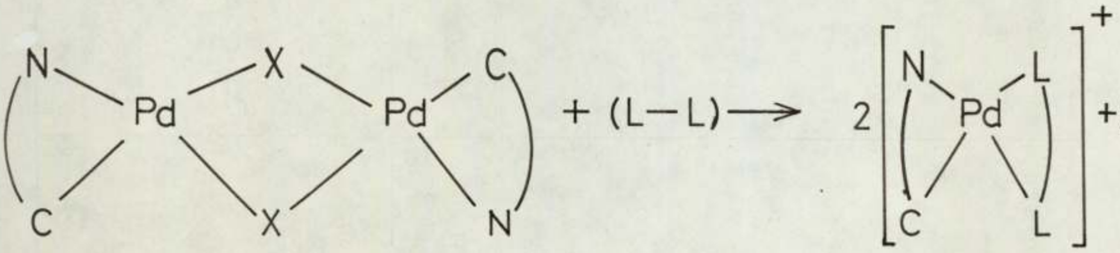
Thus:



These bridged complexes undergo various bridge-aplitting reactions with amines and phosphines to give monomeric products(118,145).

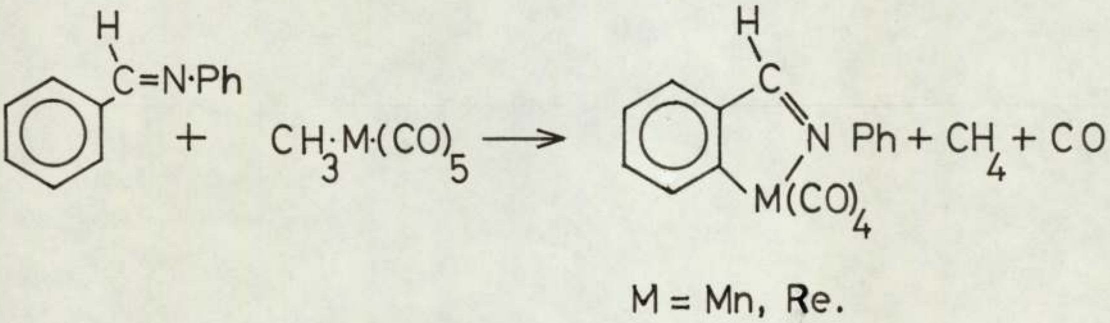




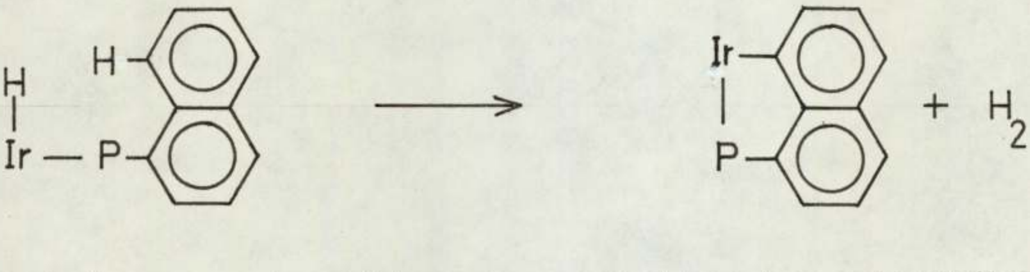


The *ortho*-substitution reaction involves proton elimination and thus it is promoted by proton acceptors such as tributylamine, acetate anion or excess of the ligand itself(98,118,132,137). However, it is suggested(96) that the effect is probably kinetic rather than thermodynamic because several compounds are known(132) to undergo metallation even in dilute acids.

There are several fates available for the displaced hydrogen:
(a) It can be expelled as an alkane from alkyl metal complexes(98,108, 136,148). Thus, with benzylidene aniline(108), methyl manganese and rhenium pentacarbonyls reacted to give the metallated complexes as shown below:

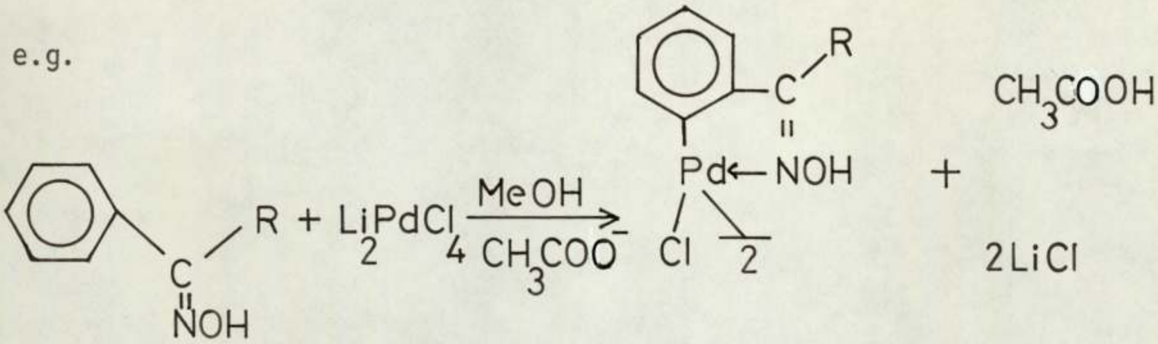


(b) It can be expelled as H_2 from metal hydride complexes(132).

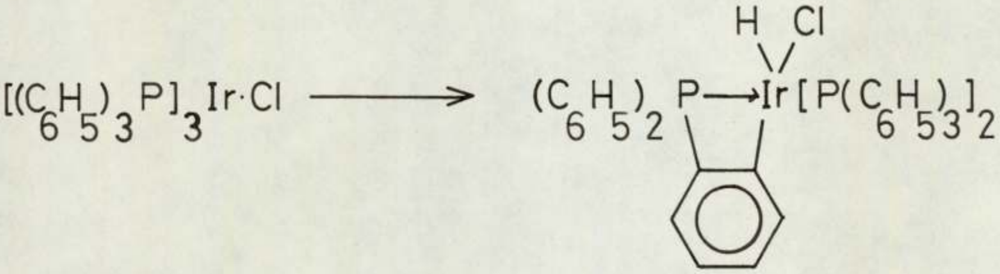


or simply as a proton which may be accepted by a base molecule(137) - usually another molecule of the ligand undergoing internal metallation or a solvent molecule.

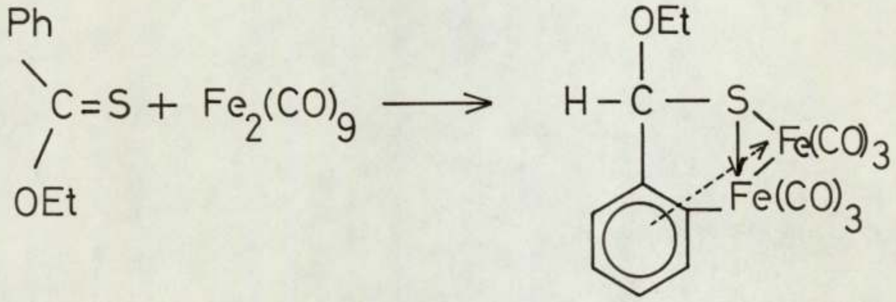
e.g.



In cases where the displaced hydrogen is retained in the complex it may add to the metal oxidatively(146).



or transferred to another atom of the ligand(121, 135,139).



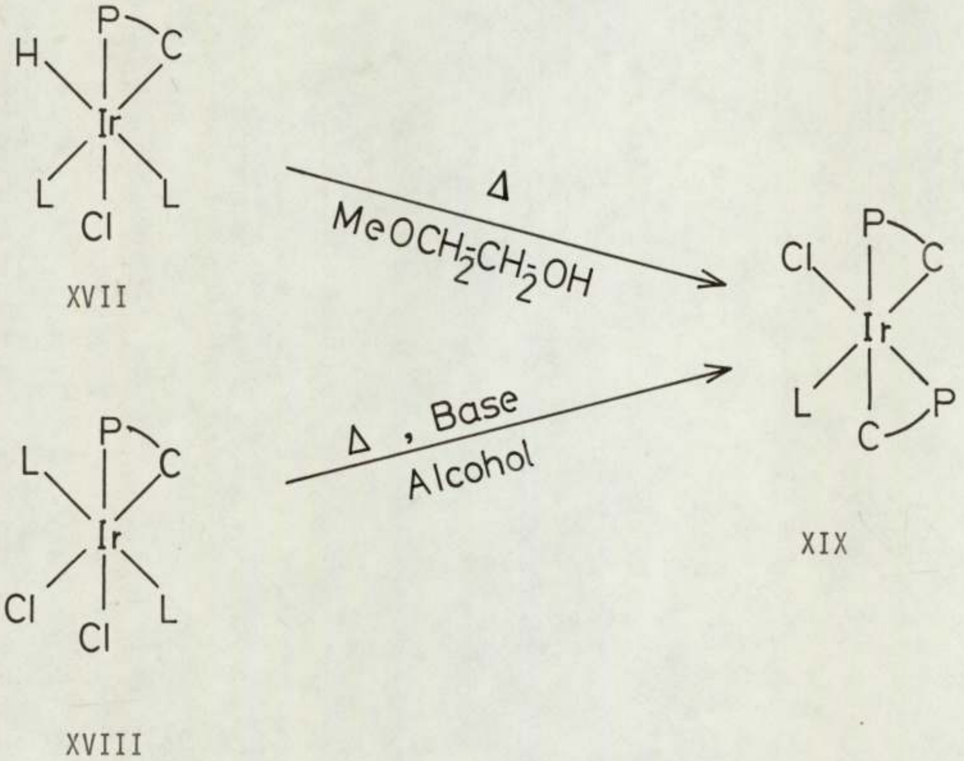
Several factors are known to influence these internal metallation reactions but their precise role has not been fully understood. In general, the electron donating substituents on the phenyl ring favours the internal metallation reaction (96,112,146).

Alper and Chan(139) studying the susceptibility for *ortho*-metallation of O-ethyl thiobenzoate and NN-dimethylthiobenzamide by enneacarbonyl diiron pointed out the influence of the hetero atom on the *ortho*-metallation reactions.- Nitrogen being a better donor than oxygen completely inhibits *ortho*-metallation whilst oxygen is a more effective donor than a benzene ring and consequently donor ligand complexation predominates over *ortho*-metallation.

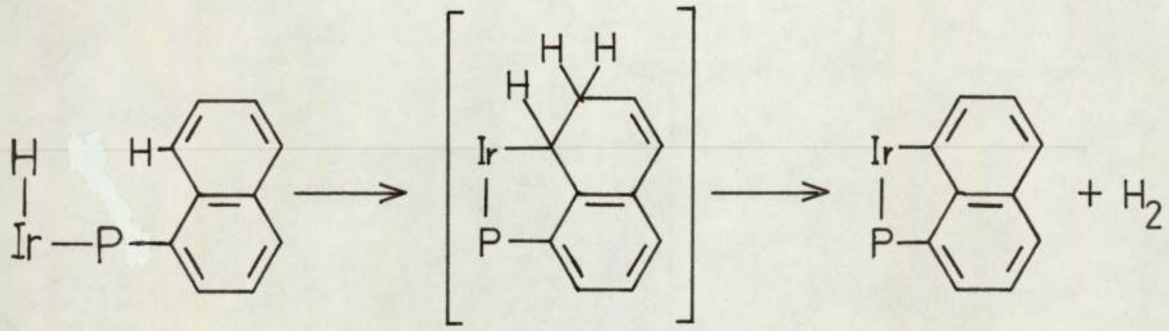
Bulky substituents have been shown(132, 147 - 149) to promote internal metallation of tertiary phosphines by platinum(ii) or palladium(ii). Steric effects are known(150) to increase the size of the ring from the normal five-membered to six-membered. Many instances are known where the nature of the anion (leaving group) on the metal influenced the Metal-Carbon bond formation(98,109,148).

The mechanism of *ortho*-metallation reactions seems to be dependent on the nature of the ligand and the oxidation state of the metal. Thus palladation of azobenzenes and related ligands appears to involve an electrophilic attack by the metal(96,103,111,120). However, this mechanism seems very unlikely for reactions involving low-valent electron rich metal complexes, e.g. $MeMn(CO)_5$ etc. for which a nucleophilic mechanism has been suggested(115). Recently, Bruce, Goodall and Stone (100) claim to have confirmed the above two mechanisms in the *ortho*-metallation of *m*-substituted azobenzenes. In the case of phosphorus ligands the results available to date indicate that different mechanisms may be involved, i.e. sometimes the metal appears to be acting as a nucleophile and sometimes as an electrophile(96,124,131).

Duff and Shaw(132) in their studies on the internal metallation of dimethyl (1-naphthyl) and methylphenyl (1-naphthyl) phosphine by iridium(iii) and rhodium(iii) found that some of the internal metallation reactions required the presence of a base and also they could be reversed by hydrochloric acid; whilst others, e.g. the conversion of *mer*-$[IrCl_3L_3]$ to $[IrCl_2(P\text{-}C)L_2]$ where L = dimethyl(1-naphthyl) phosphine and P-C = peri (or eight) metallated dimethyl (1-naphthyl) phosphine, occur even in acid solution. Further they found a hydride XVII prepared by a different method underwent conversion into the doubly metallated complex XIX much more readily than the singly metallated complex XVIII.



On the basis of these observations they suggest that the function of the base is to promote hydride formation, with the alcohol solvent as the source of hydrogen and tentatively a hydride addition-elimination mechanism shown below has been postulated.

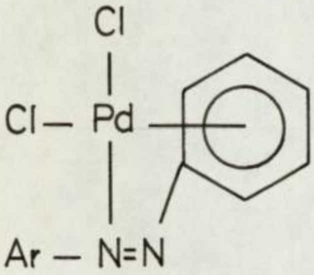


Since oxidative additions during the internal metallation reaction of phosphorus donor ligands are sometimes involved, the effect of various substituents on phosphorus donor ligands is less clear. Thus, although Bennett and Milner(146) have shown that electron-donating substituents on the aromatic ring promote *ortho*-substitution and that the rates decrease in the series $CH_3 > OCH_3 > H \gg F$, the effect of the substituents could be due to either or both of two effects: (1) an enhancement of the electron density in the ring, thus promoting electrophilic substitution or (2) enhanced electron density on the metal atom, thus promoting 'oxidative addition' to the metal. Even the more common reactions where the initial and final oxidation states of the metal are the same may involve(96) oxidative addition when the metal is co-ordinatively unsaturated, followed by a 'reductive-elimination'.

Whatever the detailed mechanism involved may be, there seems to be wide-spread agreement, especially in view of direct conversions of fully unmetallated complexes to partially or fully metallated complexes(98,132). that initial co-ordination *via* the donor atom precedes chelation.

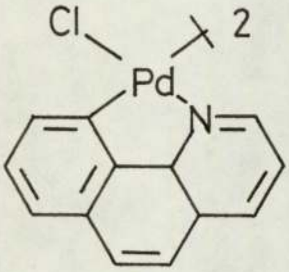
Parshall(96) in his review suggested the formation of a π-arene complex:

e.g.



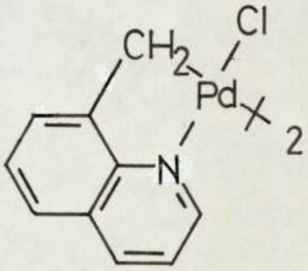
as the first significant interaction between the metal atom and the aromatic ring. However, the preparation of Pd(ii) and Pt(ii) complexes from planar quinoline ligands(151).

e.g.



Benzo(h) quinoline

&



8-methyl quinoline

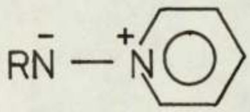
excludes a π-arene complex as a necessary intermediate in the metallation reaction.

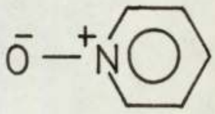
Many of these *ortho*-metallated complexes undergo typical reactions of M-C bonds including insertion of carbon monoxide(112) etc., and hence are very useful synthetic intermediates.

Due to the low volatility and poor solubility in common organic solvents, many of these *ortho*-metallated complexes are difficult to characterize(96,99). 'H *n.m.r. and i.r.* spectroscopy have proved to be invaluable in characterizing these compounds. Although ^{13}C *n.m.r.* spectroscopy could, in principle, be extremely useful in elucidating the structure, specially the location of the metal-carbon σ-bond of these complexes, to the best of our knowledge, there is but one reported instance(153) where this powerful tool has been made use of.

Cope *et al*(111) who were among the first to recognise and report these *ortho*-metallation reactions, found that these reactions are, however, not general, and outlined three requirements that must be fulfilled by the ligand before it could undergo this reaction: (i) the nitrogen must be tertiary, (ii) it must be possible to form a planar five membered ring containing the metal, (iii) the metal must displace a hydrogen ion from an aromatic carbon atom that is not highly deactivated towards electrophilic attack. The majority of ligands employed up to date have conformed to these Cope's requirements.

The pyridinium imines of general structure are



isoelectronic with pyridinium N-oxides; 

which type ligands are quite versatile, in that metal complexes with several stoichiometries have been obtained depending on the anions, the reaction conditions and the type of metal ion(154).

In spite of nitrogen being a better donor than oxygen, and the isoelectronic nature of the two systems, it is unfortunate that pyridinium imines have been totally neglected in the past, as potential donor ligands towards transition metal salts.

Further, when R = COAr etc., the pyridinium imines, indeed, conform to Cope's requirements for *ortho*-metallation.

Also, due to the presence of an unusual N-N bond in the molecule, they may be expected to undergo interesting reactions and re-arrangements in the presence of transition metal salts.

CHAPTER TWO

EXPERIMENTAL

(A) CHEMICALS

All the precious metal salts (Rh^{III}, Pd^{II}, Pt^{II}, Ir^{III} and Ir^{IV}) were purchased from Johnson Matthey Chemicals Limited, and were used as obtained. Other chemicals were obtained from other commercial sources and "Analar R" grades were used wherever possible. Hydroxylamine-O-sulphonic acid obtained from commercial sources was found to be less than 85% pure (iodometric titration) and hence it was prepared by a literature method(155) and purified by adding seven volumes of acetic acid to an aqueous solution. The final product had a purity of 98 to 99%, as judged by its oxidation of iodide ion.

(B) SOLVENTS

All solvents were obtained from commercial sources and were purified where necessary by literature methods; e.g. nitromethane(158), acetonitrile(156), and NN-dimethylformamide(157). In general, all solvents were distilled prior to use and kept over molecular sieves (Linde 3A). Pyridine was dried and distilled from barium oxide.

(C) INSTRUMENTAL TECHNIQUES

(a) SPECTRA

(1) Infrared Spectra

The infrared spectra between 4000 cm^{-1} and 250 cm^{-1} were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer for nujol and fluorochemical mulls supported between caesium iodide plates unless otherwise indicated. KBr discs were used for all solid samples. The spectra were calibrated against polystyrene film.

Far infra-red spectra were recorded for nujol mulls in caesium iodide or polythene plate supports in the region of 400 cm^{-1} to 200 cm^{-1} with a Perkin Elmer 225 Spectrometer. Far infra-red spectra in the region of 400 - 40 cm^{-1} were recorded for nujol mulls in polythene plates with a Fourier Spectrometer (R.I.I.C.FS720 - FS200). The output from the interferometer was computed using the University ICL 1605 computer.

(2) Electronic Spectra

Electronic absorption spectra in the ultra violet and visible region were obtained on Unicam SP700 and SP800 instruments using matched silica cells.

Diffuse reflectance spectra for finely powdered specimens, were obtained on the Unicam SP700 equipped with SP735 diffuse reflectance attachment. Magnesium oxide was used as the reference and also as a diluent wherever necessary.

(3) Nuclear Magnetic Resonance Spectra

'H nuclear magnetic resonance spectra, at 100 MHz were measured with Varian HA100D or Perkin Elmer R.14 Spectrometers. Proton decoupled natural abundance ^{13}C *n.m.r.* spectra were obtained on a Varian XL100FT spectrometer at 25.2 MHz. Spectra run in either deuteriochloroform or carbon tetrachloride were referenced to the internal standard - tetramethylsilane, whilst those run in dimethylsulphoxide were referenced to the dimethylsulphoxide signal positioned at $\tau = 7.36$. ^{13}C *n.m.r.* spectra were obtained in dimethylsulphoxide (d_6) and the values given are relative to the ^{13}C *n.m.r.* signal of trimethylsilane used as an external standard.

(4) Mass Spectra

The mass spectra were recorded on an AEI MS9 mass spectrometer at an ionizing voltage of 70 eV unless otherwise stated. Source temperature was 250^{o}C and the probe temperature was just below the m.p. of the sample. Accurate mass determinations were performed using heptacosafluorotri-N-butylamine as the standard.

(b) X-Ray Powder Photographs

X-ray powder photographs were taken with Cu(K)α radiation using a "Solus-Schall" London generator and "Philips" camera. An exposure time of 2-3 hours was generally used.

(c) Thermal Analysis

Thermogravimetric curves were recorded on a Du Pont 950 thermogravimetric analyzer, using ca. 2mg samples and a heating rate of 5^{o}C/minute.

(d) Magnetic Susceptibility Measurements

Paramagnetic susceptibilities were measured by the Gouy method at room temperature. A semi-micro balance (Stanton Instruments Ltd.) was used in conjunction with an electromagnet. For all measurements a current of 10 amps was used unless otherwise indicated. The tube constants α and β were determined using $Hg\ Co(CNS)_4$ as calibrant and taking its specific susceptibility $\chi_g = 16.44 \times 10^{-6}$ c.g.s. units at 20^{o}C.

Magnetic susceptibilities were calculated using the standard equation

$$10^6\chi = \frac{\alpha + \beta f'}{w}$$

with α = 0.016 mg; β = 0.209;

f' = effective force on the sample in mg.

w = weight of the sample in g.

Diamagnetic corrections were made from Pascals Constants as listed in Figgis and Lewis(159).

The diamagnetic susceptibility of N-benzoylimino pyridinium betaine, was, however, experimentally determined and had a value of 94.16 x 10^{-6} c.g.s. units.

Effective magnetic moments (μ_{eff}) were calculated using the following formula

$$\mu_{eff} = 2.83\ (X'_{M}T)^{\frac{1}{2}}$$

where X'_{M} is the molar susceptibility corrected for diamagnetism and T is the absolute temperature.

(e) Conductivity

Molar conductivities of freshly prepared solutions were determined with Henelec or Mullard conductivity bridges, using a standard conductivity cell of the type E7591/B and cell constant 1.33. Measurements were made for 10^{-3}M solutions.

(f) Analysis

Microanalysis for carbon, hydrogen, nitrogen, halogen and phosphorus were carried out by: Dr. F. Strauss, Microanalytical Laboratory, 10 Carlton Road, Oxford and Mrs.B.Taylor, Microanalytical Laboratory, Chemistry Department, Aston University. Precious metal, phosphorus, halogen and in some cases oxygen analysis were provided by A.Bernhardt, Fritz-Pregl-Strasse, Elbach-über, Engelskirchen, West Germany.

First row transition metal analysis was carried out by several different methods which include atomic absorption spectroscopy, gravimetric methods and complexometric titrations.

(1) Miscellaneous (General Information)

Melting points were determined on a Gallenkamp capillary melting point apparatus and are uncorrected. For column chromatography, neutral aluminium oxide "Camag" M.F.C. (100-250 mesh), MN-Kieselgel Silica Gel G/UV$_{254}$ or Florisil (Hopkin and Williams) initially packed in light petroleum (b.p. 40 - 60^{0}) were used. Thin layer chromatography was performed, for convenience, on various precoated sheets from Camlab, Cambridge.

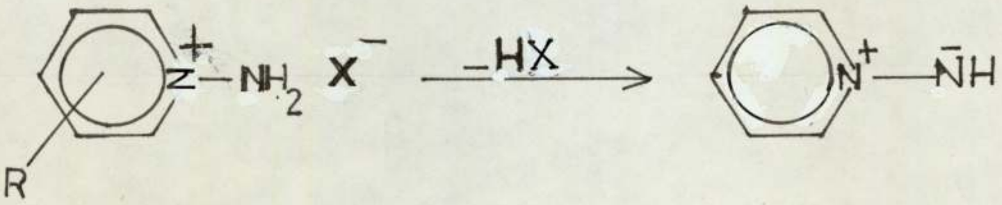
A standard eluotropic series of solvents was used. Chromatograms were developed with iodine or a dilute solution of dichlorofluorescein in ethanol.

CHAPTER THREE

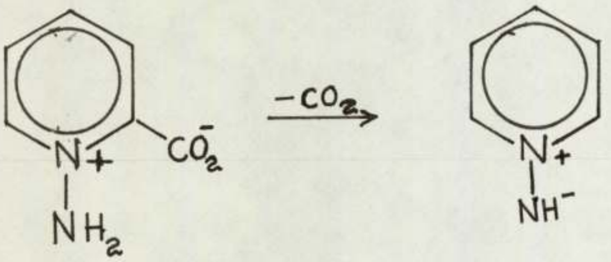
(A) INTRODUCTION

The bulk of the published work on ylides has been concerned with their syntheses. There are a number of related methods of general applicability which may be used for the preparation of nitrogen imines. These methods include reaction of the parent amine with acid azides (34, 43, 47, 160 - 167) such as arenesulphonyl azides and acyl azides, chloramine(168), hydroxylamine-O-sulphonic acid (24, 34, 169 - 174) rearrangement (175 - 177) and reaction of pyrylium salts (1,165, 178 - 182) and pyrans (183) with hydrazines. Aminimides involving, usually, tertiary aliphatic amines have been prepared by the alkylation of various sulphonyl (184 - 187) and acyl (188 - 198) hydrazides or their hydrazinium salts (199 - 201). Recently a new method involving ring opening of N-(2,4-dinitrophenyl) pyridinium chlorides with hydrazine followed by recyclization has been described (202) for the preparation of N-amino pyridine derivatives. Of all these methods, the one using hydroxylamine-O-sulphonic acid, due to its convenience, has been the choice of many workers, and it has recently been improved (203) by the case of O-mesitylene sulphonyl hydroxylamine for the N-amination of tertiary amines. N-amino pyridinium and other quaternary ammonium halides prepared by the above methods can be converted into ylide-type imino compounds by dehydrohalogenation.

$$R_3\overset{+}{N} - NH_2\ X^- \xrightarrow{-HX} R_3\overset{+}{N} - \overset{-}{N}H$$



The preparation of ylides *via* abstraction of a proton from an onium salt has been employed almost to the exclusion of other routes An attractive alternative which has received little attention in the literature involves the decarboxylation of an appropriate betaine (204). Eg.

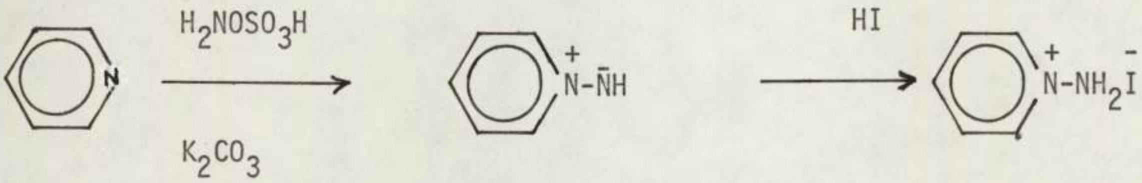


The need for efficient and economic methods of synthesis of these aminimides continuesto be justified in view of the increasing number of applications the aminimides are finding in industry (13), for example, as adhesives, antistatic agents in polymers, photographic materials, detergents, shrink-proofing agents in textiles, surface coating agents, elastomers and pharmaceuticals.

(B) SYNTHESIS OF YLIDES

(a) N-aminopyridinium salts

N-aminopyridinium salts were most conveniently prepared by the method of Gösl (172) using hydroxylamine-O-sulphonic acid.



N-aminopyridinium iodide, thus prepared (yield 70%) after recrystallization from absolute ethanol/animal charcoal has m.p. 160-161^{o}C {lit(172), 160-162^{o}C}. The chloride m.p. 157-158^{o}C {lit(34), 160^{o}C} and the bromide m.p. 159-160°C were prepared in a similar way, except that the methanolic solution was treated with concentrated HCl and concentrated HBr respectively, evaporated and the residue crystallized from methanol/ether and then ethanol. The corresponding perchlorate, m.p.203°C {lit (39), 203-204°C} was prepared in almost quantitative yield from the iodide by anion exchange with sodium perchlorate (39).

The analytical, conductivity and electronic data are given in Table 1.

TABLE I

N-aminopyridinium salt	Elemental Analyses, Theoretically calculated value is within brackets. %age.				Conductivity CH_3NO_2 in $ohm^{-1} cm^2 m^{-1}$ λ_M	H_2O λ_{Max} -nm
Iodide	C	H	N	X		
$C_5H_5N^+-NH_2\bar{I}$	27.16 (27.05)	3.31 (3.18)	12.79 (12.62)	57.06 (57.16)	98	203(Strong) 230(V.strong) 260(W.shoulder)
Bromide						
$C_5H_5N^+-NH_2\bar{Br}$	35.21 (34.30)	4.68 (4.00)	16.91 (16.01)	46.21 (45.69)	99	
Chloride						
$C_5H_5N^+-NH_2\bar{Cl}$	46.21 (45.99)	5.87 (5.37)	21.38 (21.46)	27.35 (27.18)	99	
Perchlorate						
$C_5H_5N^+-NH_2\ \bar{ClO_4}$	30.82 (30.85)	3.65 (3.68)	14.31 (14.42)	- -	105	202(strong) 250(strong & broad)

(b) N-Substituted pyridinium imines and their salts

(i) 1-(N-benzamino)pyridinium iodide or 1-(N-benzoyl)aminopyridinium iodide $C_5H_5\overset{+}{N}\text{-}NHCOPh\overset{-}{I}$

N-iminopyridinium ylide prepared by Gösl method(172) was extracted with acetone (about 100 ml) and then water (200 ml) was added. The resultant orange solution was then treated with solid K_2CO_3 (11.2g 0.08M), followed by benzoyl chloride (10.4g 0.08M) in acetone (80 ml). The benzoyl chloride solution was added dropwise over 1.5 hours. The mixture was stirred for 2 hours and then concentrated HI was added to pH2. Recrystallization of the precipitated iodide from absolute ethanol/animal charcoal gave pale yellow needles, m.p. 229°C {lit(39) 228-230°C} in 61.3% yield.

Found: C,44.46%; H,3.98%; N,8.43%; I,40.00%.

$C_{12}H_{11}IN_2O$

Requires: C,44.24%; H,3.43%; N,8.61%; I,39.71%.

Conductivity. $\lambda_M^{CH_3NO_2} = 63\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

(ii) 1-(N-benzoyl)iminopyridinium ylide. $C_5H_5\overset{+}{N}\text{-}\overset{-}{N}COPh$

This was prepared by treatment of 1-(N-benzamido)pyridinium iodide with a sodium hydroxide solution as described by Katritzky(39). The product obtained in 90.7% yield, was twice recrystallized from benzene/animal charcoal to yield snow-white feathers, m.p. 178-179°C {lit.(39), 179-180°C}

Found: C,72.48%; H,5.13%; N,14.06%.

$C_{12}H_{10}N_2O$

Requires: C,72.73%; H,5.05%; N,14.14%.

λ_{max}^{EtOH} = 230 nm; 312 nm.

ε = 13250; 4500

lit(34) λ^{EtOH}_{max} = 230 nm; and 313 nm.
(13200) (4430)

Mass spectrum: $M^{+\cdot}$ m/e = 198

(iii) 1-(N-benzoyl)aminopyridinium perchlorate $C_5H_5N^+$-NHCOPhClO$_4^-$

This was prepared simply by adding a dilute solution of perchloric acid (20 ml.) to a solution of N-benzoyliminopyridinium ylide (~1g) in distilled water (10 ml.). The perchlorate salt precipitated out immediately, in almost quantitative yield (98%). The isolated product was recrystallized from 1:1 mixture (v/v) of ethanol and methanol using animal charcoal to obtain colourless plates, m.p. 231-232^{o}C.

Found: C,47.96%; H,3.87%; N,9.19%; Cl,12.02%.

$C_{12}H_{11}ClN_2O_5$

Requires: C,48.26%; H,3.71%; N,9.38%; Cl,11.87%.

Conductivity (λ_M CH_3NO_2) = 88 ohm^{-1} cm^2 mol^{-1}.

(iv) 1-(N-benzoyl)aminopyridinium tetraphenylborate $C_5H_5N^+$-NHCOPhBPh$_4^-$

1-(N-benzoyl)iminopyridinium ylide (~1g) was dissolved in distilled water (10-15 ml.) and concentrated HCl (3 ml.) were added. No precipitate of the chloride was obtained, probably due to its greater solubility. However, when an aqueous solution of NaBPh$_4$ was added to the above solution, immediately a white precipitate separated out, which was recrystallized from a 1:2 mixture (v/v) of ethanol and ether to obtain 1-(N-benzoyl)amino pyridinium tetraphenylborate in quantitative yield, m.p. 128-130^{o}C.

Found: C,82.62%; H,6.36%; N,5.63%;

$C_{36}H_{31}BN_2O$

Requires: C,83.43%; H,5.99%; N,5.41%.

(v) 1-(N-benzoyl)aminopyridinium bromide $C_5H_5N^+$-NHCOPhBr^-

This was prepared by a method similar to the one used for the preparation of the analogous perchlorate, except that the solution after addition of the HBr was concentrated to half its volume and left in the refrigerator when a pale yellow precipitate was deposited. The isolated product was recrystallized from ethanol/animal charcoal. m.p. 222-224^{o}C(d).

Found:	C,52.21%;	H,4.51%;	N,10.34%;	Br,29.31%.
$C_{12}H_{11}BrN_2O$				
Requires:	C,51.63%;	H,3.94%;	N,10.04%;	Br,28.65%.

Conductivity λ_M CH_3NO_2 = 72 ohm^{-1} cm^2 mol^{-1}.

(vi) 1-(N-*m and p*-toluoyl)iminopyridinium ylides $C_5H_5N^+$-$\bar{N}COC_6H_4$-CH_3

They were prepared by a method similar to the one reported for the syntheses of 1-(N-benzoyl)iminopyridinium ylide by Snieckus *et al* (47). viz:

N-aminipyridinium iodide (8.88g = 0.04M) was dissolved in a mixture of ethanol (100 ml.) and methanol (100 ml.). To this solution, potassium hydroxide (4.5g = 0.08M) in methanol (100 ml.) and *m*-methylbenzoyl chloride (12g = 0.08M) in methanol (20 ml.) were added concurrently and dropwise with constant stirring. The rate of addition of potassium hydroxide solution was regulated to maintain a blue violet colouration of the solution during the addition of *m*-methylbenzoyl chloride solution. The resultant solution was stirred for a further 2 hours; and concentrated to dryness in a rotatory film evaporator between 40-50^{o}C to obtain a yellow residue which was dissolved in 10% aqueous potassium carbonate solution and extracted with methylene chloride. The methylene chloride extract was dried with anhydrous sodium sulphate and concentration followed by addition of ether produced a white precipitate which was recrystallized from benzene/animal charcoal. yield: 70.7%, m.p.96-97°C {lit:(205) 87-88°C}.

Found: C,73.46%; H,5.90%; N,13.46%.

$C_{13}H_{12}N_2O$

Requires: C,73.55%; H,5.70%; N,13.20%.

Mass spectrum: M^{+}; m/e = 212.

1-(N-*p*-toluoyl)iminopyridinium ylide was prepared by a strictly analogous method. yield = 75% m.p.166-167°C {lit:(205) 164-166°C}

Found: C,73.52%; H,5.85%; N,13.31%.

$C_{13}H_{12}N_2O$

Requires: C,73.55%; H,5.70%; N,13.20%.

Mass spectrum: M^{+}; m/e = 212.

(vii) 1-(N-toluenesulphonyl)iminopyridinium ylide

$C_5H_5N^+\text{-}\bar{N}SO_2\text{-}C_6H_4\text{-}pCH_3$

This was prepared by the method of Snieckus *et al* (47). yield = 55%. m.p. 215-216°C {lit (47), 215-217°C}

λ_{max}^{MeOH} = 242 nm; 316 nm:

ε = (14,000); (2175).

lit (47) λ_{max}^{MeOH}, 240 nm; 317 nm.

ε (14,000); (2180)

Mass spectrum: M^{+}; m/e = 248.

(c) N-phenacylpyridinium salts

(i) N-phenacylpyridinium iodide $C_5H_5N^+\text{-}CH_2COPh\bar{I}$

This was prepared by the method of King (206). The crude product was recrystallized from water/animal charcoal. yield = 85%.

m.p. 218-219°C {lit:(206) 215-219°C}

Found: C,48.38%; H,4.02%; N,4.52%.

$C_{13}H_{12}INO$

Requires: C,48.01%; H,3.69%; N,4.31%.

(ii) N-phenacylpyridinium perchlorate $C_5H_5N^+\text{-}CH_2COPhClO_4^-$

This too was prepared by the method of King (206). Recrystallization of the crude product from aqueous methanol/animal charcoal afforded colourless plates. yield 90%

m.p. 188-189°C(d). {lit(206), 189-190°C}

Found: C,53.02%; H,5.10%; N,4.82%.

$C_{13}H_{12}ClNO_5$

Requires: C,52.45%; H,4.03%; N,4.71%.

(d) 1-benzoyl-2,2,2-trimethyl hydrazinium iodide and its ylide

(i) 1-benzoyl-2,2,2-trimethyl hydrazinium iodide $(CH_3)_3N^+\text{-}NHCOPh\bar{I}$

It was prepared by a literature method (188). yield = 50%.

m.p. 175-176°C lit:(188) 194-196°C
lit:(209) 174-176°C

Found: C,39.23%; H,5.13%; N,9.05%.

$C_{10}H_{15}IN_2O$

Requires: C,39.21%; H,4.90%; N,9.01%.

$\lambda_M^{CH_3NO_2} = 117\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

(ii) Trimethylamine-benzimide. $(CH_3)_3N^+-\bar{N}COPh$

This too was prepared by the same literature method (188) referred to above. yield = 98%.

m.p. 168-169°C {lit:(188); 168-169°C}

Found: C,67.23%; H,7.75%;- N,15.62%.

$C_{10}H_{14}N_2O$

Requires: C,67.42%; H,7.86%; N,15.72%.

mass spectrum: M^+; m/e = 178.

(e) Phenacyltriphenylphosphonium bromide and its ylide

(i) Phenacyltriphenylphosphonium bromide. $PH_3P^+-CH_2COPhB\bar{r}$

This was prepared by a literature method (208). yield = 62.6%.

After recrystallization from water/animal charcoal it had a m.p.271-272°C {lit:(208) 271-272°C}

Found: C,67.85%; H,4.95%; Br,17.98%;

$C_{26}H_{22}BrOP$

Requires: C,67.70%; H,4.77%; Br,17.34%.

(ii) Triphenylphosphinebenzoyl methylene. $Ph_3P^+-\bar{C}HCCPh$

This too was prepared by the same literature method (208).

yield = 80%.

After recrystallization from benzene/animal charcoal, it had a m.p. 178-180°C {lit:(208) 178-180°C}

Found: C,82.32%; H.5.81%.

$C_{26}H_{21}OP$

Requires: C,82.11%; H,5.53%.

mass spectrum: M^+; m/e = 380.

(C) A FEW COMMENTS ON SYNTHESIS OF THE YLIDES

Of the ylides and their salts mentioned above, the preparation of 1-(N-benzoyl) aminopyridinium perchlorate and tetraphenylborate salts are new. Attempts to isolate the free ylide, N-phenacycledenepyridinium ($C_5H_5N^+-\bar{C}HCOC_6H_5$) by treating either the perchlorate or the iodide salt with a 10% aqueous solution of sodium carbonate failed. Although the free ylide seems to be liberated on basification, it decomposes to a tarry or gummy material during the work-up procedure. The relative instability of this ylide is also reflected in its reported (207), comparatively low m.p. 93-96°C. Further, in the preparation of N-benzoyl substituted derivatives of N-iminopyridinium ylide, the general procedure of benzoylating the present iodide in the presence of a base was found to be unnecessary since direct benzoylation of the N-iminopyridinium ylide freshly prepared by reaction of hydroxylamine-O-sulphonic acid and pyridine could be achieved as effectively. This possibility has been mentioned by Katritzky *et al* (39); but, however, details or even a mention of this could not be traced in the reference (4) given by them. Finally, the use of animal charcoal as a decolourizing agent during recrystallization was extremely rewarding, especially in the case of iodide salts, and always helped to obtain clean and analytically-pure samples.

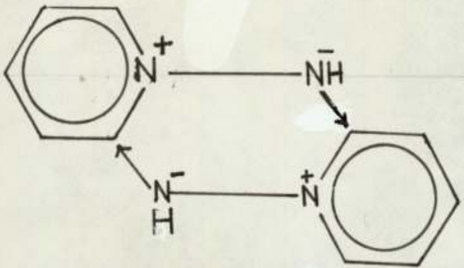
N-aminopyridinium salts prepared, are stable in the solid form showing no sign of decomposition against air or light. A similar stability was found in solution under neutral or acidic conditions. The salts under neutral conditions showed a *u.v.* absorption maximum at about 250 nm in water, which was replaced by a very intense band at 325 nm on basification with sodium hydroxide solution. Acidification regenerates the spectrum of the starting salt.

Treatment of N-aminopyridinium salts with bases such as NaOH, KOH, Na_2CO_3. K_2CO_3,$(C_2H_5)_3N$, NH_3, liberates a compound which imparts a red-purple colouration to the organic solvents. Extraction of this species with organic solvents such as chloroform gave only reddish tarry material. A band at *ca* 540 nm in the visible region seems to be associated with this deep-red purple colour. The absorption maximum of this long wavelength band was found to be solvent dependent as shown under.

Solvent	λ_{max} (nm)
Ethanol(95%)	562
dimethylsulphoxide	551
acetonitrile	550
N.N.dimethylformamide	543
methylene dichloride	542
chloroform	541
acetone	450

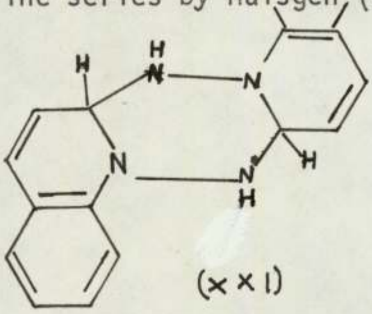
Variation in the wavelength is in keeping with the variation of the polarity of the solvents except for acetone where the observed low wavelength suggests the existence of probably a different species.

What exactly is responsible for this red-purple colour is unknown. Huisgen (25,217) believed that the purple colouration observed was probably not due to the N-imine and Lunt (40) suggested that the purple absorption may in fact be due to a charge-transfer band and this charge-transfer complex in its simplest form could involve a dimerization of the N- iminopyridinium itself as in XX



(XX)

The possibility of additional association to trimeric and higher states is considered by Lunt to explain the minor wavelength changes observed on standing and on evaporation to the solid state. The formation of a definite chemical dimer XXI presumably *via* an associated species similar to XX has indeed been observed in the corresponding quinoline series by Huisgen (217) and Okamoto (170).



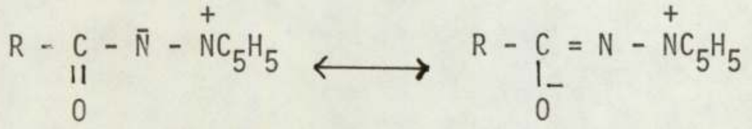
(XXI)

Whereas the origin of the purple band is far from clear, the existence of the free N-iminopyridinium ylide as the predominant species in solution containing the N-aminopyridinium cation and base has been very well demonstrated by them (40, 25, 217). All attempts to isolate the free N-iminopyridinium ylide in the solid form, e.g. by evaporation of solutions with organic solvents, in vacuo, etc., were unsuccessful.

(D) SPECTRAL CHARACTERISTICS OF THE YLIDES AND THEIR SALTS PREPARED

The *i.r. and n.m.r.* data of all the ylides and some of their salts are gathered in Tables 2, 3, 4, 5 and 6. The electronic data were only obtained for compounds for which such data are reported in the literature and hence only served for further characterization of these compounds. The origin of these bands are uncertain although a relatively strong band near 200 nm in the case of carbonyl ylides is probably a transition of the C = 0 double bond in conjunction with the non-bonded electrons on the adjacent nitrogen (13).

The infra-red spectra of acylaminimides show a very strong absorption in the 1543-1600 cm^{-1} region which is assigned to the stretching frequency of the $\bar{O}C = N$ bond (13) in the resonance form B.



$$R - \underset{\underset{O}{\|}}{C} - \bar{N} - \overset{+}{N}C_5H_5 \longleftrightarrow R - \underset{\underset{O}{|_{-}}}{C} = N - \overset{+}{N}C_5H_5$$

A. B.

This form seems to make a major contribution to the actual structure in the free ylide, since the carbonyl frequency in the N-protonated form of the ylide at about 1700 cm^{-1} is completely suppressed. The phenacyclide of pyridine and triphenylphosphine also show the expected lowering of the carbonyl stretching frequency at about 1520 cm^{-1} which moves to the typical value around 1700 cm^{-1} in the protonated salts. A similar delocalization of the negative charge on the imino nitrogen would certainly account for the lowering of the $-SO_2-$ stretching frequencies down to 1270 cm^{-1} and 1130 cm^{-1} in the corresponding sulphonyl ylide (13).

Another very strong absorption observed in the N-N ylides is the one associated with N-----N bond stretching occurring between 1280 cm^{-1} and 1335 cm^{-1} in the ylides prepared in this study. This assignment is in reasonable agreement with the values reported by Russian workers (182), at 1341 cm^{-1} for 2,4,6-trimethyl-1(-N-benzoyl)iminopyridinium betaine. This assignment seems to be justified by the observed downward shift of this bond to 1270 cm^{-1} in the N-protonated forms.

Another region of interest in the infra-red spectra of these compounds is the region between 670 cm^{-1} and 855 cm^{-1} where the out-of-plane deformation modes of aromatic C-H bonds occur. In the case of pyridinium ylides, by comparison, it is possible to associate a band at ~790 cm^{-1} and a very strong and sharp band at ~ 770cm^{-1} with the pyridine ring having five adjacent hydrogens while the strong bands at ~ 715 cm^{-1} and ~ 680 cm^{-1} with the phenyl ring having five adjacent hydrogens. These bands are little affected due to protonation and further in the case of phenyl ring-substituted ylides the bands assigned to γ(CH) phenyl (with 5 adjacent hydrogens) do, indeed, shift according to the position of substitution, to positions characteristic of the 3-disubstituted or 4-disubstituted rings (211) as the case may be. These features, as discussed in subsequent chapters, have been diagnostically useful in the characterization of the metal compounds prepared. The far infra-red region (400 - 200 cm^{-1}) of these ylides are unfortunately not free of absorptions and hence presented difficulties in the characterization of the metal compounds.

The most interesting feature in the *n.m.r.* spectra of these compounds is the occurrence of α proton resonance of the pyridine as a doublet (J = 6-7 Hz) in the low field distinctly separated from the other resonances of the ylides; thus enabling the spectrum to be unequivocally integrated to obtain the total number of protons in the system. In addition usually the γ and β proton resonances of the pyridine ring also appear as well separated triplets in the low field and hence may be used to confirm the integration of the spectrum. The protons of the unsubstituted phenyl group of the ylides usually occur as two multiplets in the ratio of 2:3.

The α-protons of the pyridine ring absorb at lower field than those in the corresponding free ylide and this shift is to be expected because of the overall increase in electron density in the free ylide.

TABLE 2

I.R. DATA (KBr discs)

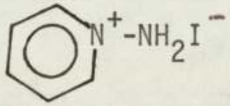
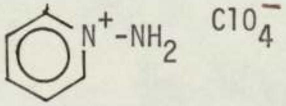
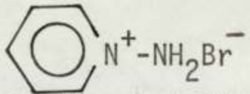
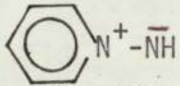
	3180 m,br; 3062 m,br; 1625 W,br; 1585 W,Sh; 1505 S,Sh; 1480 S,Sh; 1372 W,Sh; 1200 W; 1145 W,Sh; 1058 W; 978 W; 908 m,br; 785 m-s; 761 S,Sh; 670 S,Sh; 480 m,Sh; 411,w; 360 w-m,br.
	3350 W; 3180 m-s; 3110 S; 3050 S; 1622 w-m; 1595 m,Sh; 1515 V.S.Sh; 1480 V.S.Sh; 1385 m,Sh; 1150 S; 1110 S; 1090 S; 935 m,br; 790 S; 765 S; 670 S.Sh; 637 S; 626 S; 542 W; 485 m-s; 458 m; 390 W.
Nujol mull CsI	3342 m; 3200 m; 3080 m; 1640 m,br; 1505 S; 1482 S; 1378 m; 1320 W; 1240 W; 1085 S,br; 910 W,br; 770 S; 670 S; 622 S; 480 m; 340 W.br.
 Hexachlorobutadiene mull	3170 m,br; 3060 m,br; 1610 W; 1585 W; 1560 S; 1505 S,Sh; 1478 S; 1070 m,br; 1145 W,Sh; 980 S; 942 m-s; 795 S; 765 m,Sh; 672 m; 658 S,Sh.
 in EtOH	3150 S,br; ν(N-H); 1065 S,br; 885 m.

TABLE 3 (KBr disc cm^{-1})

$C_5H_5N^+$-NHCOPhI^-	C_5H_5 N^+-NHCOPhBr^-	C_5H_5 N^+-NHCOPhClO_4^-	C_5H_5 N^+-NHCOPhBPh_4^-	C_5H_5 N^+-$\bar{N}$COPh	Assignments
2930 W,br 2890 W,br	2780 m,br	3240 m,br	3260 m,Sh	-	ν(N-H)
3120 V.W. 3040 m,br	3100 W. 3040 m,br	3125 m. 3070 W	3118 W.Sh. 3075 m,Sh 3055 m,Sh 3018 W,Sh 3000 W,Sh 2995 W,Sh	3100 W.Sh. 3070 m	ν(C-H)
1698 V.S.	1690 V.S.	1700 V.S.	1708 V.S.Sh.	1550 V.S.	ν(>C=O)
1516 m	1515 m	1530 m	not seen	-	N-H bend
1625 S,Sh 1600 W,Sh 1580 W-m 1495 W 1480 S 1450 S	1621 S,Sh 1598 W,Sh 1578 W,Sh 1478 S,Sh 1460 S 1445 W	1628 S,Sh 1600 m,Sh 1585 m,Sh 1482 S 1462 S	1626 S,Sh 1600 W 1570 W-m 1500 W 1480 S 1460 m 1445 W 1429 m	1650 W 1620 W-m 1595 S,Sh 1485 m,Sh 1470 S 1449 W	C = C and C = N Str.

continued

TABLE 3 continued

$C_5H_5N^+$-NHCOPhI^-	$C_5H_5N^+$-NHCOPh$\bar{Br}$	$C_5H_5N^+$-NHCOPhClO_4^-	$C_5H_5N^+$-NHCOPhBPh_4^-	$C_5H_5N^+$-$\bar{N}$COPh	Assignments
1285 V.S.	1283 V.S.	1285 V.S.	1270 V.S.	1335 V.S.	ν(N------N)
1250 m	1252 m	1252 m	1238 W.		
1200 W	1235 W	1240 W	1180 W		
1150 W	1195 W	1205 m.Sh	1150 W,br		C - H in plane
1090 m	1178 V.W.				and
1070 W	1140 W				
1055 W	1088 m		1085 W	1299 m	
1030 W	1068 W			1255 W	C - C Str.
970 V.W.	1055 W		1068 W-m	1200 W	in-plane bend
942 W	1029 W		1035 W	1182 m	β(=CH)
915 W	970 W	950 W,br	1025 W,Sh	1160 W	
850 V.W.	912 m	920 W,br		1100 W	
	850 V.W.	850 V.W.	955 W	1068 m	
			850 W,br	1050 W	
				1030 m	
				980 W	
				952 W	
				930 W	
				908 m,Shn	
				870 W	
-	-	1110 V.S.br	-	-	ν_3,F_2 in Td(ClO_4^-)
		620 S,Sh			ν_4,F_2 in Td(ClO_4^-)
795 W-m	792 W,Sh	792 W,Sh	788 V.W.	805 W	
772 V.S.Sh	772 V.S.Sh	770 V.S.Sh	769 S.Sh	765 V.S.Sh	γ(C-H)Pyridine

continued

TABLE 3 continued

$C_5H_5N^+\text{-NHCOPh}\bar{I}$	$C_5H_5N^+\text{N- HCOPh}\bar{Br}$	$C_5H_5N^+\text{NHCOPhClO}_4^-$	$C_5H_5N^+\text{-NHCOPhBPh}_4^-$	$C_5H_5N^+\text{-}\bar{N}\text{COPh}$	Assignments
716 V.S.Sh	715 V.S.Sh	715 V.S.Sh	740 S	715 V.S.Sh	γ(C - H)Phenyl
			710 V.S.Sh		
688 S.Sh	685 S.Sh	684 S.Sh	685 m.Sh	690 S,Sh	with 5 adjacent protons
665 S.Sh	662 S.Sh	665 S.Sh	665 m,Sh	668 S.Sh	
645 W.Sh	640 W.Sh		640 W	640 W.Sh	C - C bond
			625 W		
580 W	572 W	578 W	600 m-S	570 W	
535 W,br	471 W,sh.	520 V.W.br	575 W	510 W,Sh	
472 W,Sh	435 W	471 W,Sh	478 W	470 S	
		421 W			C - C bond
432 W		400 W	460 W	400 W-m	
398 W	395 W,Sh		420 V.W.		and
			380 V.W.	318 m	
305 W	305 W Sh.	305 m,Sh	305 V.W.		ring torsion

TABLE 4

$C_5H_5N^+-\bar{N}COC_6H_4{}^{m}CH_3$	$C_5H_5N^+-\bar{N}COC_6H_{4p}CH_3$	$C_5H_5N^+-\bar{N}SO_2C_6H_{4p}CH_3$	$(CH_3)_3N^+-NHCOPh\bar{I}$	$(CH_3)_3N^+-\bar{N}COPh$	Assignments
			3450 m,br		
-	-	-	3100 m,br	-	ν(N-H)
3100 W,Sh 3065 m.br	3100 W,Sh 3050 m.br	3130 V.W.Sh 3120 W.Sh 3060 V.W.br	3060,V.W. 3015 W,Sh	3100 V.W. 3055 W. 3038 W.	ν(C-H) Aromatic
2920 V.W.	2920 V.W.	2940 W.br	2930 m,br	2960 W.br	ν(C-H) methyl gr.
1545 V.S.	1543 V.S.	-	1698 V.S.	1600 V.S.	ν(>C=O)
-	-	-	1530 S	-	N-H bend
1620 W 1605 V.W. 1592 W. 1468 W. 1460 m	1615 W 1585 S 1505 V.W. 1485 V.W. 1460 S 1400 W.	1612 m 1598 W. 1490 W 1400 W.	1605 W,Sh 1585 W 1488 m,Sh. 1450 S,br 1430 W,Sh 1415 W.	1485 m,Sh 1450 W. 1430 W. 1400 W.	C = C and C = N Str. and $C-H(-CH_3)$deformation
1335 V.S.	1330 V.S.	1465 V.S.	1280 V.S.	1335 V.S.	ν(N-----N)
-	-	1270 V.S.	-	-	$\nu_{as}(>SO_2)$
		1130 V.S.			$\nu_{sym}(>SO_2-N)$
1280 W. 1250 W	1295 m, 1250 W	-	1245 m	1300,W	
					continued

TABLE 4 continued

$C_5H_5N^+\text{-}\bar{N}COC_6H_{4m}CH_3$	$C_5H_5N^+\text{-}\bar{N}COC_6H_{4p}CH_3$	$C_5H_5N^+\bar{N}SO_2C_6H_{4p}CH_3$	$(CH_3)_3N^+\text{-}NHCOPhI$	$(CH_3)_3N^+\text{-}\bar{N}COPh$	Assignments
1218 m	1205 W.		1185 W.	1265 W	C - H
1190 W.		1162 W.	1160 W.	1238 W.	in
1150 W.	1180 S.		1100 W.	1175 W.	plane
1085 W.	1100 W.	1095 m.	1122 m.	1170 W.	and
1045 W.	1050 W.	1045 W.		1120 W	
978 W.	1020 W.	1030 W.	1075 W.		
960 W.	978 W.	1015 W.	1028 W.	1070 m	C - C - Str.
920 W.	950 W.	940m	1000 W.	1030 W-m	
		920 S.	980 W	1000 W.	
			940 m	965 W.	
			880 m	945 W.	
			800 W.	890 m	
				860 W.	
				810 W.	
792 W.	788 W.	798 W.	-	-	γ(C - H)
765 V.S.Sh.	760 V.S.Sh.	778 V.S.	-	-	Pyridine
855 m.	-	-	-	-	γ(C-h) of 1,3 di-
740 V.S.Sh	-	-	-	-	substituted
					Phenyl group
	832 m,Sh.	812 m	-	-	γ(C-H)of 1,4 disub-
	745V.S.Sh	760 s			stituted phenyl group
-	-	-	718 V.S.Sh.	728 V.S.	γ(C-H)phenyl group
-	-	-	690 M,Sh.	690 m.	with 5 adjacent
					protons
685 S.	690 W.	655 S.	670 W.	670 W-m	
670 m.	670 S.	640 W.			
640 W.Sh.	635 W.Sh.	622 m,Sh.			C - C bend

TABLE 4 continued

$C_5H_5N^+-\bar{N}COC_6H_4\,mCH_3$	$C_5H_5N^+-\bar{N}COC_6H_4\,pCH_3$	$C_5H_5N^+-\bar{N}SO_2C_6H_4\,pCH_3$	$(CH_3)_3N^+-NHCOPhI$	$(CH_3)_3N^+-\bar{N}COPh$	Assignments
520 W.	560 W.	560 S.Sh.	528 W.br	525 V.W.	
490 W.	508 W.	540 S.Sh		500 W.	
470 W-m	480 W.	495 m.Sh.	460 W.	468 W.	C - C bond
440 V.W.	460 S.Sh.	430 m.	435 W.	440 V.W.	
410 V.W.	420 m.				
400 W.			395 W.	412 W.	
400 W.		360 W.	352 W.	390 W.	C - C bond ring torsion
355 W.	350 W.			360 m,br	
308 W.	308 m.	325 W.			

TABLE 5

$C_5H_5N^+$-CH_2COPhI^-	$C_5H_5N^+$ $CH_2COPhClO_4^-$	Ph_3P^+-CH_2COPh Br^-	Ph_3P^+-$\bar{C}HCOPh$	Assignment
3130 W.	3140 m,Sh.	3060 W.	3050 W.br.	ν(C - H)
3050 W.	3080 m,br	3040 W.		Aromatic
2920 W.	3010 W,Sh.	2990 V.W.	-	ν(C - H)
2870 W.	2960 m,Sh.	2950 W.		CH_2 group
2820 W.br				
1695 V.S.	1705 V.S.	1660 V.S.	1520 V.S.br.	ν(>C = 0)
1630 m.S.	1640 S.Sh.	1595 W.	1588 m,S.Sh	
1590 W.	1600 m.	1580 W.		
1580 W.	1585 m.			
1500 W.	1508 W.	1488 W,Sh.	1482 W.	
1485 S.	1493 S.Sh			
1445 m.	1450 m,Sh.	1450 W.Sh.	1435 S.	
	1438 V.W.	1435 m,Sh.		
			1385 V.S.br	ν(P--C--0)
1365 V.W.	1358 M.	1380 W.Sh.		$\nu(\overline{C{=}C})$
1350 S.	1305 W-m.	1325 W.	1300 W.	
1300 W.				
1230 W.	1238 W.	1300 W.		
1210 m.	1218 m.	1208 W.		
1150 W.		1185 W.	1195 W-m	
		1160 V.W.	1182 W-m	
		1110 m.	1100 s	
	1090 V.S.br			$\nu_3(ClO_4^-)$
1070 V.W.		1028 V.W.	1062 V.W.	
1055 W.			1050 W.	
1025 W.			1025 W.	
995 S.	990 W.	990 m.	1000 W.	
938 W.	950 W.		970 V.W.	
845 W.	850 W.Sh.	860 W.	920 V.W.	

TABLE 5 continued

$C_5H_5N^+-CH_2COPhI^-$	$C_5H_5N^+-CH_2COPhClO_4^-$	$Ph_3P^+-CH_2COPh\ Br^-$	$Ph_3P^+\bar{C}HCOPh$	Assignment
		820 W. 790 W	890 S 870 S 840 W 800 W,Sh.	$\nu(Ph_3P=C)$
750 V.S.br 670 V.S.br	755 V.S.br 678 V.S.br			γ(C-H) Pyridine and Phenyl rings
-	620 S.	-	-	$\nu_4(ClO_4^-)$
		745 V.S. 715 S.Sh. 685 V.S.	745 V.S. 710 V.S. 688 V.S.	γ(C-H)Phenyl with 5 adjacent hydrogens.
560 S. 449 W-m 399 V.W. 370 V.W. 295 W.	568 S. 452 W-m. 400 W. 372 W. 300 W.	512 S.Sh 500 m. 492 S.Sh. 460 W. 428 W. 400 W. 312 W.	560 W. 550 m. 510 V.S.br 460 W. 430 W. 395 V.W. 285 W-m.	

TABLE 6 100 MH_z 'H n.m.r. data (DMSO Solution)

Compound	Pyridine ring protons			Benzene ring protons			Others
	2,6	3,5	4	2,6	3,5	4	
$C_5H_5N^+$-NH_2 I^-	1.15 d J=7Hz (2H)	1.90 t J=7Hz (2H)	1.75 t J=7Hz (1H)	-	-	-	-
$C_5H_5N^+$-$NHCOC_6H_5$ I^-	0.60 d J=6Hz (2H)	1.54 t J=6Hz (2H)	1.10 t J=7Hz (1H)		1.72-2.00m (2H)	2.06-2.44 m (3H)	-
$C_5H_5N^+$-$NHCOC_6H_5$ ClO_4^-	0.64 d J=7Hz (2H)	1.56 t J=5Hz (2H)	1.12 t, J=8Hz (1H)		1.75-2.00 m (2H)	2.04-2.40 m (3H)	-
$C_5H_5N^+$-$NHCOC_6H_5$ $B(C_6H_5)_4^-$	0.66 d J=6Hz (2H)	1.64 t J=6Hz (2H)	1.23 t J=7Hz (1H)		1.74-1.94 m (2H) + 2.40-2.74 m (8H)	2.00-2.37 m (3H) + 2.76-3.18 m (12H)	
$C_5H_5N^+$-$\bar{N}COC_6H_5$	1.10 d J=7Hz (2H)	2.05 t J=2Hz (2H)	1.65-1.93, m, (3H)	(3H)		2.40-2.60, m (3H)	

continued

TABLE 6 continued 100MHz 'H n.m.r. data (DMSO Solution)

Compound	Pyridine ring protons			Benzene ring protons			Others
	2.6	3,5	4	2,6	3,5	4	
$C_5H_5N^+$-$\bar{N}COC_6H_4$-*m*CH_3 (in $CDCl_3$)	1.25 d J=7Hz (2H)		1.92-2.10 m (1H)	2.14-2.77 m (6H) H_3 and H_5P_y+ H_2,H_4,$H_5$and H_6 Ph			7.63 S (3H) CH_3
$C_5H_5N^+$-$\bar{N}COC_6H_4$-*p*CH_3	1.20, d, J=6Hz (2H)	2.40, t, J=7Hz (2H)	2.15 t J=7Hz (1H)	1.90, d, J=8Hz (2H)	2.77 d J=8Hz (2H)		7.62 S (3H) CH_3
$C_5H_5N^+$-$\bar{N}COC_6H_4$-*p*CH_3 (in DMSO-d_6)	1.18 d J=6Hz (2H)	1.80-2.38 m (5H)			2.72-2.93, m, (2H)		7.65 S (3H) CH_3
$C_5H_5N^+$-$\bar{N}SO_2C_6H_4$-*p*CH_3 (in $CDCl_3$)	1.41, d J=7Hz (2H)	1.92-2.45, m (3H)		2.73 d J=8Hz (2H)	2.63, d, J=8Hz (2H)		7.57 S (3H) CH_3
$C_5H_5N^+$-$CH_2COC_6H_5$ I^-	0.80 d J=6Hz (2H)	1.60 t J=6Hz (2H)	1.14, t, J=7Hz (1H)	1.71-1.90, m (2H)	2.00-2.37, m (3H)		3.27 S (2H) -CH_2-
$C_5H_5N^+$-$CH_2COC_6H_5$ ClO_4	0.91, d J=6Hz (2H)	1.66 t J=7Hz (2H)	1.20, t J=7Hz (1H)	1.77-1.94, m, (2H)	2.00-2.34, m, (3H)		3.43 S (2H) -CH_2-

TABLE 6 continued 100MHz 'H n.m.r. data (DMSO Solution)

Compound	Pyridine ring protons			Benzene ring protons			Others
	2,6	3,5	4	2,6	3,5	4	
$(CH_3)_3N^+-\bar{N}COC_6H_5$ (in $CDCl_3$)	-	-	-	2.23-2.48, m (2H)	2.86-3.14, m (3H)		6.90, S (9H) $(CH_3)_3$
$(C_6H_5)_3P^+-CH_2COC_6H_5\ \bar{Br}$	-	- -	-	1.70-2.50 m (20H)			3.55 d J_{P-H}=14Hz (2H) CH_2
$(C_6H_5)_3P^+-\bar{C}HCOC_6H_5$	-	-	-	1.90-2.40 m (15H) $(C_6H_5)_3P^+$ + 2.45-2.60 m (5H) (C_6H_5-CO-)			5.43 d J_{P-H}=24Hz (1H) - CH -

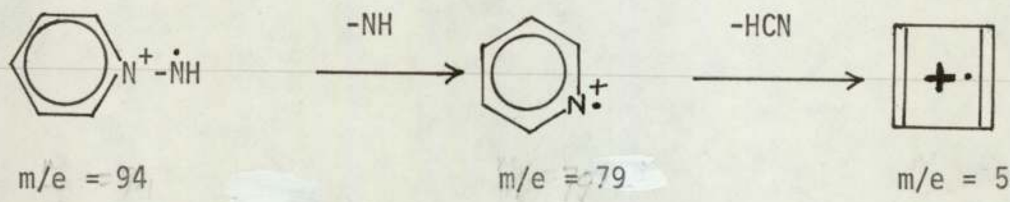
Tabulation follows the order chemical shift (τ value), multiplicity (S=singlet,d=doublet,t=triplet, m=multiplet), coupling constant and the number of protons responsible for the signal.

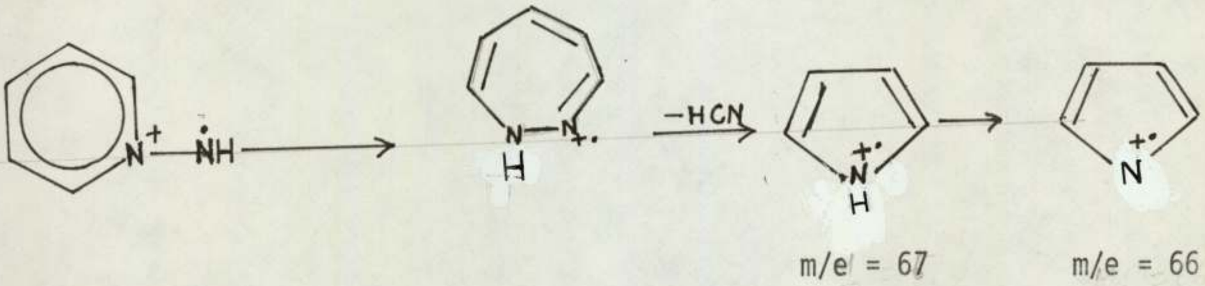
The mass spectra of all the N-aminopyridinium salts showed peaks due to the N-aminopyridinium cation ($C_5H_5\overset{+}{N}\text{-}NH_2$ at m/e = 95; to the N-iminopyridinium ylide at m/e = 94 and an intense peak at m/e = 79 corresponding to the pyridine redical ion.

E.g. Some of the selected peaks from the spectrum of N-aminopyridinium iodide salt are given below together with their relative abundance.

m/e = 127 (87.4%) = I^+
m/e = 95 (4%) = $[C_5H_5\text{-}NH_2]^+$
m/e = 94 (30%) = $[C_5H_5N\text{-}NH]^+$
m/e = 79 (100%) = $[C_5H_5N]^+$
m/e = 67 (7%) = $[C_4H_4NH]^+$
m/e = 66 (4%) = $[C_4H_4N]^+$
m/e = 52 (63%) = $[C_4H_4]^+$
m/e = 51 (98%) = $[C_4H_3]^+$

The observed mass spectra were in agreement with those reported by Ikeda and co-workers(210), who have rationalized the breakdown pattern as follows



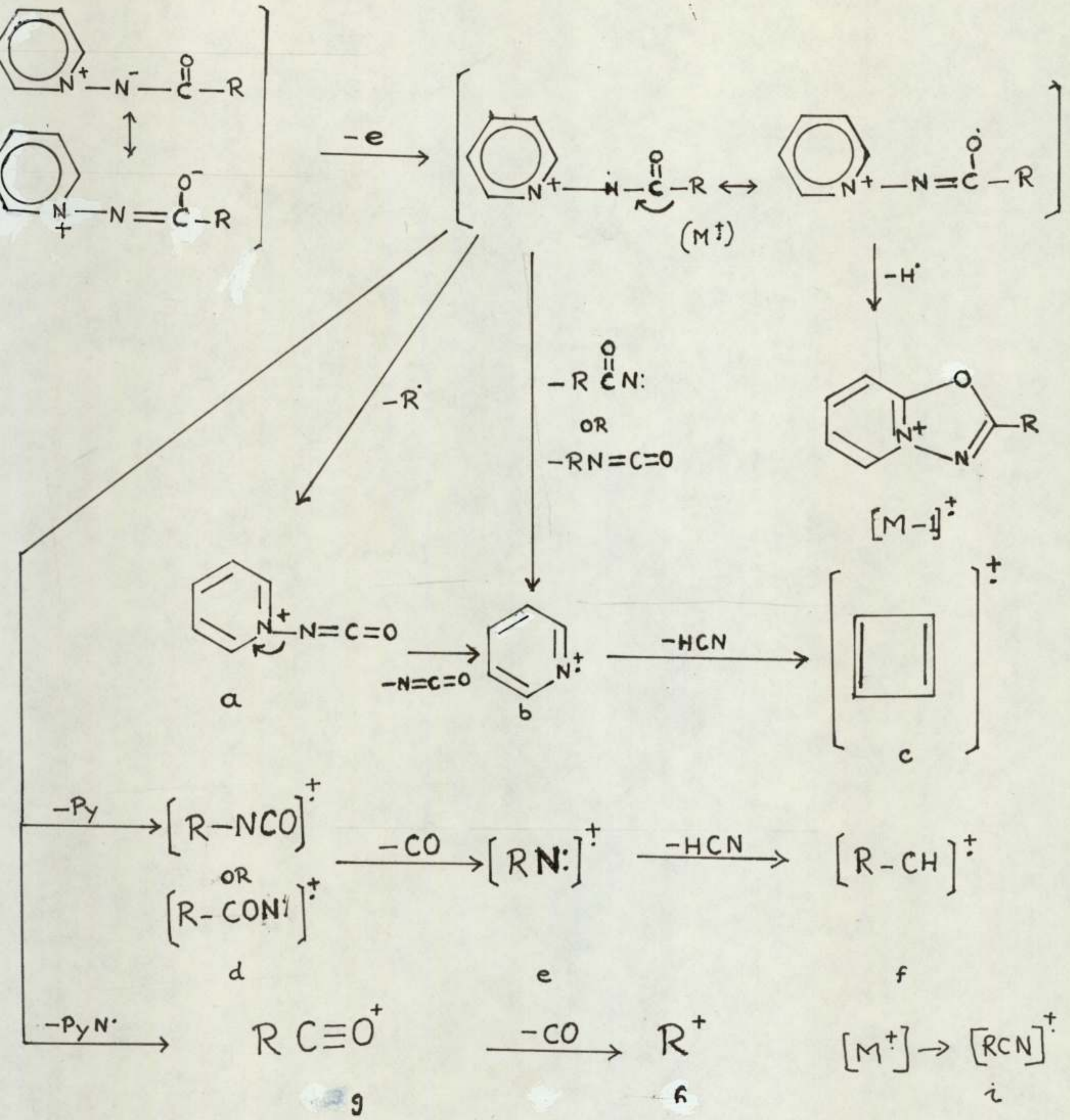


The mass spectra of all the ylides prepared showed a peak due to the parent ion and the salts of the ylides showed similar spectra except for the additional peak due to the protonated cation. The fragments arising due to the cleavage of the ylidic bonds viz. $\overset{+}{N}\text{-}\overset{-}{N}$, $\overset{+}{N}\text{-}\overset{-}{C}$, $\overset{+}{P}\text{-}\overset{-}{C}$ were clearly observed

e.g. $(CH_3)_3N^+\text{-}\overset{-}{N}COPh$ showed the following major fragments.

M^+ at m/e = 178 (100%)
$[M\text{-}CH_3]^+$ " " = 163 (73%)
$[M\text{-}(CH_3)_3N]^+$ " " = 119 (74%)
$[C_6H_5CO]^+$ " " = 103 (99%)
$[M\text{-}C_6H_5]^+$ " " = 101 (84%)
$[C_6H_5]^+$ " " = 77 (91%)
$[(CH_3)_3N]^+$ " " = 59 (99%)

It is surprising that the above ylide $(CH_3)_3N^+\text{-}\overset{-}{N}COPh)$ is reported (13) not to have given a parent peak. The mass spectral fragmentation behaviour of benzoylated N-iminopyridinium derivatives are interesting in that it is the $[M\text{-}1]^+$ ion and not $[M]^+$ that is most abundant, thus implying a ready loss of a hydrogen from the molecular ion. This process is accompanied by a large metastable peak in all the spectra which exhibit the $[M\text{-}1]^+$ ions. This and the origin of other fragments have been studied in detail by Ikeda *et al* (212) and the following fragmentation pattern has been well established.



The mass spectrum of 1-(N-benzoyl)iminopyridinium observed was identical with what is reported by Ikeda *et al* (212) except for some differences in the relative abundances of the peaks. By comparison with the above scheme, the peaks of the previously unreported mass spectrum of 1-(N-*p*-toluoyl and *m*-toluoyl)iminopyridinium betaines were assigned and are gathered in Table 7.

TABLE 7 Principal Mass spectral peaks in the spectra (70eV) of N-benzoyliminopyridinium betaines (% Relative Intensity)

Compound	$[M]^+$	$[M-1]^+$	(a)	(d)	(g)	(i)	(e)	(b)	(h)	(f)	(c)
$C_5H_5N^+\text{-}\bar{N}COC_6H_5$	198	197	121	119	105	103	91	79	77	64	52
	(46)	(88)	(100)	(14)	(18)	(13)	(16)	(88)	(45)	(12)	(90)
$C_5H_5N^+\text{-}\bar{N}COC_6H_4\text{-}m\text{CH}_3$	212	211	121	133	119	117	105	79	91	78	52
	(71)	(100)	(87)	(21)	(17)	(7)	(6)	(76)	(41)	(25)	(39)
$C_5H_5N^+\text{-}\bar{N}COC_6H_4\text{-}p\text{CH}_3$	212	211	121	133	119	117	105	79	91	78	52
	(57)	(100)	(73)	(15)	(31)	(22)	(7)	(70)	(46)	(32)	(40)

None of these ylides, nor their salts, showed a peak corresponding to $[M-2]^+$ radical ion, whereas, as indicated in Chapter IV many precious metal derivates of these ylides do show such an ion in their mass spectra.

(E) SOME CHARACTERISTICS OF N-AMINOPYRIDINIUM PERCHLORATE SALT.

$C_5H_5N^+$-NH_2 ClO_4^-

Reference to Table 1 would show that N-aminopyridinium perchlorate, like the chloride, bromide and iodide, in solution has a conductivity (105 ohm^{-1} cm^2 $mole^{-1}$) acceptable for a 1:1 electrolyte, thus showing little evidence of any association between the anion and cation. This conclusion is further supported by the infra-red spectrum of the perchlorate, taken as a nujol mull, in which the typical broad band of the ionic perchlorate group centered at 1085 cm^{-1} (ν_3, F_2 in Td) together with a sharper band at 622 cm^{-1} (ν_4, F_2 in Td) can be seen (Figure 1). However, when pressed into a KBr disc the ν_3 and ν_4 bands split (Table 8 and Figure 2) and a new band of medium intensity appears at 458 cm^{-1}.

Figure 1. Infra-red spectrum of $C_5H_5\overset{+}{N}-NH_2\overset{-}{(ClO_4)}$(Nujol mull/CsI)

Figure 1.cont. Infra-red Spectrum of $C_5H_5N\text{-}\overset{+}{N}H_2(ClO_4^-)$ (Nujol mull/CsI)

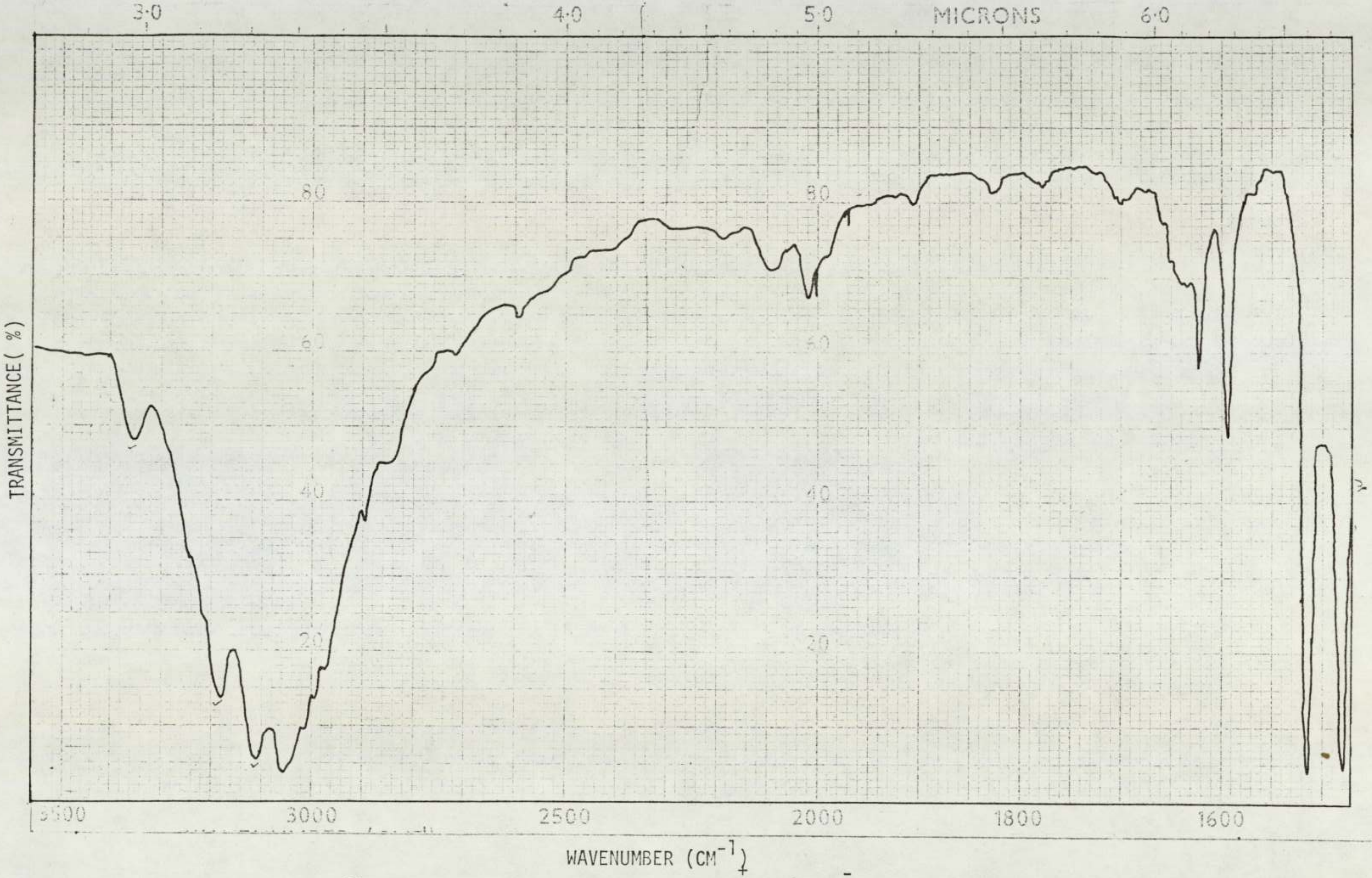


Figure 2. Infra-red Spectrum of $C_5H_5\overset{+}{N}-NH_2(Cl\overset{-}{O_4})$(KBr disc)

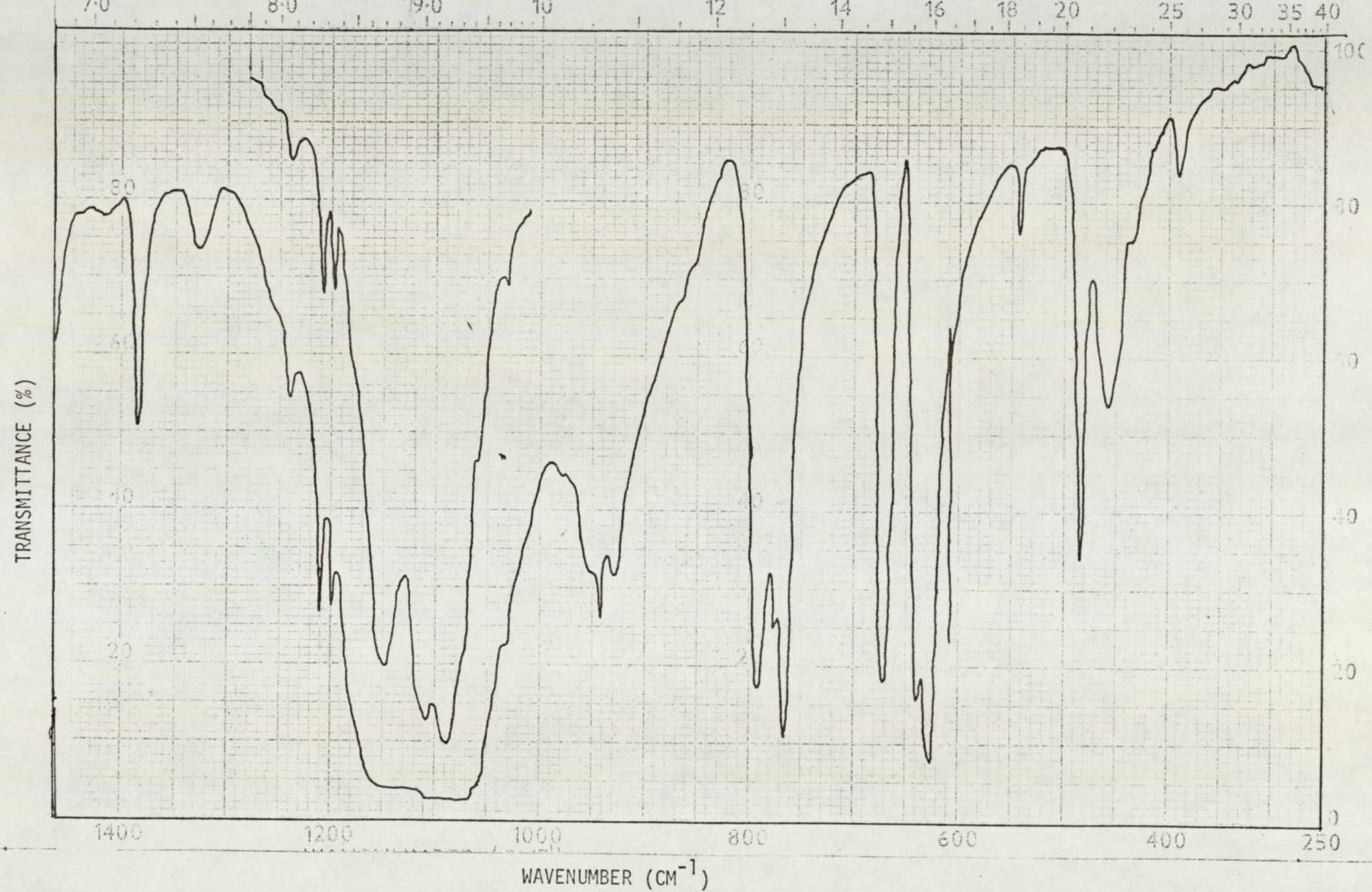


Figure 2. contd Infrared Spectrum of $C_5H_5\overset{+}{N}-NH_2Cl\bar{O}_4$ (KBr disc)

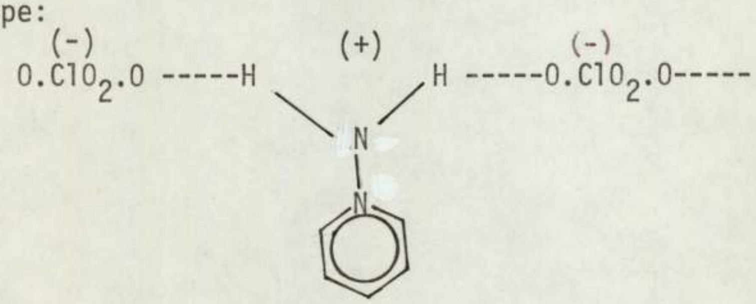
TABLE 8 Some features of the *i.r.* spectrum of 1-aminopyridinium perchlorate (cm^{-1})

Nujol mull/C_sI plates	KBr disc (15-18 tons/ sq.in. pressure)	Assignment
3342 m	3350 W	ν(N-H)
3200 m	3180 m,br	
3080 Sh	3010 S	
2440 m-W	2440 W	ν(N-D)
2300 m	2290 W,Sh	
2282 m-W	2280 m	
	1150 S	B_2(as. Str)
	1110 S	B_1(as.Str)
1085 S		ν_3 (Td)
	1090 S	A_1 (S.Str)
	637 S	A_1(S.bend)
622 S		ν_4(Td)
	626 S	B_1 (rock)
	458 m	A_1(S.bond)

The splitting is well resolved (Figure 2) and this dramatic change is difficult to attribute to a low site symmetry for the perchlorate group in a new polymorphic form of the crystal. The spectrum suggests that the perturbation has reduced the effective symmetry of the perchlorate group to C_{2v}(213). The A_1 mode for $C_{2\nu}$ perchlorate anticipated at 930 cm^{-1} is obscured by vibrations of the 1-aminopyridinium group.

The spectrum of the 1-aminopyridinium cation also undergoes change when examined as a disc rather than as a mull. In particular intensity ratios change in the region above $3000cm^{-1}$ and bands attributable to ν(NH) undergo small shifts to low frequency and become broader. The assignments of the stretching vibrations of the $-NH_2$ group have been aided by a study of the partially deuteriated compound prepared by refluxing a specimen with D_2O and crystallizing. The ν(ND) bands undergo the changes noted above for the ν(NH) vibration on change from mull to disc.

A reasonable explanation of the above observations is that the anions and cations interact, *via* hydrogen bonding, in the high pressure modification of the material to give chain polymers or cyclic oligomers of the type:



Such change of crystalline phase when materials are subjected to pressures of the order of those used to prepare potassium bromide discs is known(214). but almost certainly reports describing similar behaviour for perchlorate groups in an organic compound are, however, unknown, although in co-ordination and organometallic chemistry there are several precedents (215). Possibly the most closely analogous observation is that of Chow and McAulffe (216) who reported that pressing the complex

$$[Cu(ArgH)_2(H_2O)][ClO_4]_2$$

where ArgH $= H_2N^+ = C(NH_2).(CH_2)_3.CH(NH_2).CO\bar{O}$

into a KBr disc resulted in the appearance of the spectrum of

$$[Cu(ArgH)_2(ClO_4)_2] \text{ (plus water)}$$

with bidentate ($C_{2\nu}$) perchlorate groups. The splittings of the perchlorate vibrations (ν_3 and ν_4) observed by them are very similar indeed to those observed by us, implying, simplistically, equally strong (or weak) interaction of the perchlorate group with its environment in the two cases.

(F) ATTEMPTS TO USE N-IMINOPYRIDINIUM YLIDE AS A DONOR LIGAND

In view of the isoelectronic nature of the N-iminopyridinium ylide with pyridine N-oxide which is known to form numerous complexes with transition metal salt, generally bringing out their highest co-ordination number, it was thought - that transition metal salts might be able to stabilize the imine and that some interesting co-ordination or organometallic compounds might result.

Various complexation reactions of N-iminopyridinium ylide were attempted by two different methods. Firstly, the salts of the ylide (perchlorate, iodide etc.) were treated with transition metal salts in aqueous or alcoholic media, in the presence of calculated amounts of weakly co-ordinating bases such as triethylamine, n-butylamine etc., thus liberating the imine in *situ*. Secondly, the free ylide was liberated by addition of base (e.g. NaOH, K_2CO_3 etc.) to aqueous solutions of the N-aminopyridinium salts, the free ylide was extended into organic solvents such as methylenedichloride and treated with transition metal salt in an organic solvent - usually methanol or ethanol. The reaction carried out with cupric chloride dihydrate typifies the general procedure adopted.

N-aminopyridinium perchlorate (9.7 g = 0.05M) was dissolved in distilled water (40 ml) and treated with solid potassium carbonate (3.5 g = 0.025M). The liberated ylide was extended with methylene dichloride (100-150 ml) and to this solution cupric chloride dihydrate (2.13 g = 0.0125M) dissolved in absolute ethanol (75 ml) was added with stirring. Almost immediately after the addition, a greenish yellow product separated out which was filtered, washed with ethanol and then dried under vacuo over silica gel.

The metal salts treated in this way, include halide and perchlorate salts of Cu^{II}, Ni^{II}, Co^{II}, Fc^{III}, Fe^{II}, Cr^{III} and potassium tetrachloroplatinite (K_2PtCl_4). In all cases the product obtained contained the protonated imine as shown by the *i.r.* and mass spectra (m/e 95 very intense). The transition metal precipitates as the basic hydroxide with N-aminopyridinium as the cation. Analytically it was found that these compounds were ill-defined and showed no sign of N-iminopyridinium being present as a neutral ligand. In all cases the addition of sodium hydroxide and an organic solvent (e.g. $CHCl_3$) to an aqueous solution of the metal complex resulted in the generation of the free imine as indicated by a purple colouration in the organic phase.

The products obtained from cupric halides and platinum salt seemed to be well defined compounds with transition metal halide anion and

N-aminopyridinium cation. Three of the well defined complexes are given below

(a) $C_5H_5N^+\text{-}NH_2\ CuCl_3$ (green-yellow)

Found: C,22.18%; H,2.84%; N,10.44%; Cl,39.62%; Cu,23.41%.

$C_5H_7Cl_3CuN_2$

Requires: C,22.63%; H,2.67%; N,10.56%; Cl,40.13%; Cu,23.96%.

μ_{eff} = 1.98 B.M.

$\lambda_M^{CH_3NO_2}$ = 76 ohm^{-1} cm^2 mole^{-1}

i.r. (KBr disc) 3260W; 3210W, 3125m, ν(N-H)
cm^{-1} 318 V.S., 285 V.S., ν(Cu-Cl)

Mass spectrum m/e = 95 N-aminopyridinium cation.

(b) $C_5H_5N^+\text{-}NH_2\ CuBr_3^-$ (yellow)

Found: C,15.03%; H,1.63%; N,6.73%; Br,59.63%; Cu,15.82%.

$C_5H_7Br_3CuN_2$

Requires: C,15.07%; H,1.78%; N,7.03%; Br,60.19%; Cu,15.95%.

$\lambda_M^{CH_3NO_2}$ = 75 okm^{-1} cm^2 mole^{-1}

i.r. (KBr disc) 3265w-m, 3190W, 3125W, ν(N-H)
cm^{-1}

Mass spectrum: m/e=95 N-aminopyridinium cation.

(c) $[C_5H_5N^+\text{-}NH_2]_n$ $[PtCl_3^-]_n$ (yellow-orange)

Found: C,15.04%; H,1.63%; N,7.41%; Cl,25.82%;

$C_5H_7Cl_3N_2Pt$

Requires: C,15.16%; H,1.78%; N,7.08%; Cl,26.90%.

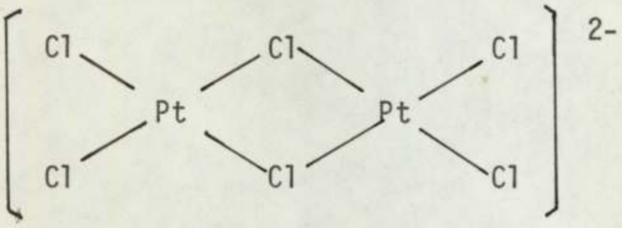
$\lambda_M^{CH_3NO_2} = 87$ ohm^{-1} cm^2 $mole^{-1}$ assuming n = 1

i.r. (KBr disc) 3250m,br, 3128m,br, ν(NH) cm^{-1}

(Nujol mull/CsI cm^{-1}) 310 s.br, 235 w. ν(Pt-Cl)

Mass spectrum: m/e = 95 N-aminopyridinium cation.

Most probably the anion involved in this salt is dimeric with platinum-chlorine bridges as follows:



and on this dimeric formulation the conductivity would be 87 x 2 = 174 ohm^{-1} cm^2 $mole^{-1}$ - a value acceptable for a 2:1 electrolyte with bulky ions. Further, the far infra-red spectrum reveals two absorptions of which the one at 310 cm^{-1} could be assigned to "terminal" platinum-chlorine stretching frequency and the one at 235 cm^{-1} is possibly the "bridging" platinum-chlorine stretching frequency.

Since the *i.r.* spectra indicated beyond doubt, the presence of the protonated ylide, these compounds were not investigated any further.

Thus, it appears that the tendency of the imine is to undergo protonation rather than co-ordination and is thus remarkably different from the behaviour of analogous pyridine N-oxide. This is not too surprising in view of the very much greater basicity of the imine with a pKa of 13.4 (40) as compared with that of pyridine N-oxide with a pKa of 0.67 (218) .

CHAPTER FOUR

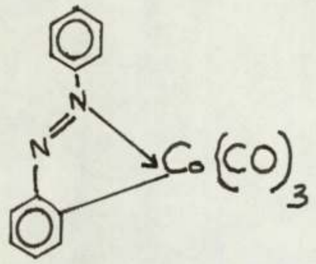
ORTHO-METALLATION REACTIONS WITH N-BENZOYLIMINO-PYRIDINIUM BETAINE AND RELATED COMPOUNDS

(A) INTRODUCTION

Of the chemical reactivities of ylides, the donor properties are of special interest. From the dipolar formula they might be expected to be very powerful donor molecules and hence form numerous complexes with various kinds of Lewis acid.

Transition metal aromatic ring σ-bonded complexes are important for studying the mechanism of aromatic substitution reactions and the study of the properties of these complexes will help to find out new synthetic methods. For a long time it has been known that various olefinic complexes of palladium chloride and other metal salts react with carbon monoxide to form carbonyl compounds and they are useful intermediates in organic syntheses. Furthermore, the carbonylation of amines can be carried out in the presence of palladium chloride to give isocyanates substituted ureas oxamides and formamides(112). In these carbonylation reactions, it is assumed that a σ-bond between palladium and carbon or nitrogen atom should be formed as a prerequisite of the carbonylation. Takahashi and Tsuji(112) found that palladium σ-bonds with carbon atom are very reactive towards carbon monoxide and undergo carbon monoxide insertion. They have succeeded in effecting carbonylation of several symmetrically and asymmetrically substituted azobenzene complexes of palladium under mild conditions (~100^{o}C and 100 atmosphere) in protic solvents to give 2-aryl-3-imazolinones.

Heck(219) prepared the *ortho*-metallated azobenzene complex of cobalt carbonyl



and considered it to be the reaction intermediate of the carbonylation of azobenzene catalysed by dicobalt octacarbonyl.

Further, the intermediacy of nitrenes has been frequently predicted in reactions of organo-nitrogen compounds in the presence of transition metals(220). For example, nitrenes have been postulated (221-223) as key intermediates in the reactions of RN_3, RNCO and RNO_2 with iron carbonyls and in the copper-catalysed decomposition of benzene sulphonyl azide (224). In fact, recent studies(223,225) indicate that nitrenes may be "trapped" as ligands in metal carbonyl complexes.

Nitrogen-nitrogen ylides are potential nitrene producing compounds. Further, the resonance-stabilized carbonyl derivatives of these ylides are thermally stable but decomposing at or above their melting points. The influence of metal ions on the thermal stability of the N-N bond in these compounds would be interesting and might result in the formation of metallated nitrenes. In addition, the geometry of resonance stabilized N-benzoyliminopyridinium betaine suggested that in some instances the *ortho*-metallation reaction should be observed. *Ortho*-metallation should be possible on either phenyl ring or pyridine ring. In the former case, co-ordination of either exocyclic nitrogen or oxygen would result in a five membered metalocycle whereas in the latter possibility, only co-ordination of oxygen can result in a five membered ring.

In this chapter, the reactions of this betaine and of related compounds with rhodium(III), iridium(III), palladium(II) and platinum(II) are described.

(B) PREPARATION OF COMPLEXES

(a) Palladium(II) halide complexes

(1) Chloro(2-carbonyliminopyridinium)phenylpalladium(II)

Palladium dichloride (1.0g, 5.6m Mol) was dissolved in hot water (200 ml) and filtered. N-benzoyliminopyridinium betaine (2.0g, 10m Mol) was added to the warm solution which was then refluxed for 2 hours with vigorous stirring. The yellowish green *product* was recrystallized from water and then dried over P_4O_{10} under vacuum. Addition of sodium perchlorate to the filtrate from the reaction mixture afforded crystals of the perchlorate salt of the protonated betaine - $[C_5H_5\overset{+}{N}\text{-NHCOPh}][ClO_4^-]$. The product could also be recrystallized from ethanol, Chloroform and dichloromethane. Products obtained from dichloromethane contained variable amounts of solvent (analysis, *i.r.*, *'H n.m.r.*) and were yellow in contrast to the yellowish-green products obtained from water or ethanol. The product from chloroform was also yellow. No differences in *i.r.*, *'H n.m.r.* or mass spectra were observed between the green and yellow forms.

Yield = 1.85g (97%)

m.p. of the yellowish-green form = 266 - 267°c(d).

m.p. of the yellow product (from $CHCl_3$)= 240 - 245°C(d)

Found: C,42.68%; H,2.75%; N,8.25%; Cl,10.34%; Pd,31.10%.

$C_{12}H_9ClN_2OPd$

Requires: C,42.47%; H,2.94%; N,8.26%; Cl,10.43%; Pd,31.31%.

$\lambda_M{}^{CH_3NO_2}$ = 5 ohm^{-1} cm^2 mol^{-1}.

(2) Bromo(2-carbonyliminopyridinium)phenylpalladium(II)

This was prepared by refluxing a suspension of the above product (either form, 0.6g) in water (75 ml) containing an excess of lithium bromide (~3g). The dark green product was washed with cold water, and recrystallized from dibromomethane. There was no apparent change in the colour during recrystallization. The isolated product was washed with ether and dried under vacuuo over P_4O_{10}.

Yield = 0.68g (98%).

m.p. = 245°C(d).

Found: C,37.42%; H,3.34%; N,6.70%; Br,19.69%; Pd,27.90%.

$C_{12}H_9BrN_2OPd$

Requires: C,37.56%; H,2.35%; N,7.30%; Br,20.84%; Pd,27.75%.

$\lambda_M{}^{CH_3NO_2}$ = 4 ohm^{-1} cm^2 mol^{-1}

(3) Dichlorobis(N-benzoyliminopyridinium betaine)palladium(II)

Potassium tetrachloropalladate(II) (0.98g, 3m mol) and sodium acetate (0.49g, 6m mol) were dissolved in water (75 ml). N-benzoylimino-pyridinium betaine (1.2g, 6m mol) was added and the reaction mixture was stirred at room temperature for 2 hours and set aside overnight. The amber coloured *product* was washed with water, methanol and ether and dried *in vacuo*.

Yield = 1.5g. (87%).
m.p. = 195 - 196^{o}c(d).

Found: C,49.06%; H,3.70%; N,9.40%; Cl,11.92%.
$C_{24}H_{10}Cl_2N_4O_2Pd$
Requires: C,50.22%; H,3.49%; N,9.76%; Cl,12.36%.

$\lambda_M^{DMF} = 2\ ohm^{-1}\ cm^2\ mol^{-1}$

The product could be converted to chloro(2-carbonyliminopyridinium) phenylpalladium by refluxing in ether toluene or benzene for 3-4 hours.

(4) Chloro(N-benzoyliminopyridinium betaine)(2-carbonylimino pyridinium)-phenylpalladium(II)dihydrate

The above procedure was followed with the exception that the solution was stirred for 2 hours under reflux. The amber material changed to a greenish yellow *product* which was filtered, washed with water, methanol and ether and dried *in vacuo*.

Yield = 1.6g (98%)
m.p. = 165 - 166^{o}C(d)

Found: C,51.10%; H,3.50%; N,9.87%; Cl,6.50%.
$C_{24}H_{23}ClN_4O_4Pd$
Requires: C,51.89%; H,3.78%; N,10.09%; Cl,6.39%.

$\lambda_M^{CH_3NO_2} = 5\ ohm^{-1}\ cm^2\ mol^{-1}$

This product too could be converted to chloro(2-carbonyliminopyridinium) phenylpalladium(II) by refluxing the compound in benzene for 3-4 hours.

(5) *Chloro(2-carbonylimino-4 methyl)phenylpalladium(II)*

Palladium dichloride (0.35g, 2m Mol) was dissolved in hot water (50 ml) and filtered. N-*m*-toluoyliminopyridinium betaine (0.5g;2.4 m mol) was added to the warm solution and then refluxed for 2 hours, with vigorous stirring. Within about 5 minutes a bright yellow *product* separated and was recrystallized from a 1:1 (v/v) mixture of chloroform and methanol. After washing with ether, the product was dried *in vacuo*.

Yield = 0.71g (99%)
m.p. 229 - 230^oC(d)

Found: C,43.56%; H,3.30%; N,7.60%; Cl,9.62%.

$C_{13}H_{11}ClN_2OPd$

Requires: C,44.18%; H,3.12%; N,7.93%; Cl,10.04%.

$\lambda_M^{CH_3NO_2} = 3\ ohm^{-1}\ cm^2\ mol^{-1}$

(6) *Chloro(2-carbonyliminopyridinium-5 methyl)phenylpalladium(II)*

This was prepared by following the procedure given above except that N-*p*-toluoyliminopyridinium betaine was used as the ligand. The greenish yellow *product* was recrystallized from acetone and dried *in vacuo*.

Yield = 0.68g (96%)
m.p. = 255 - 257^oc(d)

Found: C,44.30%; H,3.46%; N,7.63%; Cl,9.67%

$C_{13}H_{11}ClN_2OPd$

Requires: C,44.18%; H,3.12%; N,7.93%; Cl,10.04%.

$\lambda_M{}^{CH_3NO_2} = 4\ ohm^{-1}\ cm^2\ mol^{-1}$

It was noted that the reaction with the *m*-toluoyl betaine was complete in a very short time. If fact, when the reaction of the benzoyl, *m*-toluoyl and *p*-toluoyl betaines were compared under the same conditions, it was observed that the reaction rates were, qualitatively

m-toluoyl $\gg$ benzoyl $>$ *p*-toluoyl

(7) *Chloro(2-carbonyliminotrimethylammonium)phenylpalladium(II)*

Palladium dichloride (1.8g, 10m mol) and lithium chloride (0.85g, 20 m ml) were dissolved in methanol (40 m) giving a homogeneous solution to which were added N-benzoyliminotrimethylammonium betaine (1.8g, 10m mol) in methanol (10 ml) and sodium acetate (0.82g, 10m mol). The mixture was heated under reflux for 2 hours, when a dirty green residue separated out. This material was filtered and recrystallization from acetone afforded a green crystalline *product* which was dried *in vacuo*.

Yield = 2.8g (88%)

m.p. 220°C(d)

Found: C,38.04%; H,4.04%; N,8.86%; Cl,10.50%; Pd,31.75%.

$C_{10}H_{13}ClN_2OPd$

Requires: C,37.51%; H,4.34%; N,8.79%; Cl,10.49%; Pd,31.49%.

$\lambda_M{}^{CH_3NO_2} = 3\ ohm^{-1}\ cm^2\ mol^{-1}$.

(8) *Chloro(2-carbonylmethylenetriphenylphosphonium)phenylpalladium(II)*

Triphenylphosphinebenzoylmethylene (1.9g, 5m mol) was dissolved in anhydrous methanol (50 ml) containing sodium acetate (0.41g, 5m mol). To this solution was added, with stirring, palladium dichloride (0.89g, 5m mol) and the resulting mixture was then heated under reflux for 2 hours. A greenish product contaminated with a black material separated out. This material was treated with dichloromethane and filtered to remove the black contaminant and the filtrate, on concentration in a rotatory film evaporator gave a green *product*. The product was washed several times with dry ether and dried *in vacuo*.

Yield = 1.95g (75%)

m.p. 250 - 255^{o}C(d)

Found: C,58.82%; H,3.58%; P,5.73%; Cl,7.02%

$C_{26}H_{20}ClOPPd$

Requires: C,59.79%; H,4.02%; P,5.94%; Cl,6.79%

$\lambda_M^{CH_3NO_2}$ = 3 ohm^{-1} cm^{2} mol^{-1}.

(9) *Dichlorobis(triphenylphosphinebenzoylmethylene betaine)palladium(II)*

Palladium dichloride (1.0g, 5.6m mol) was dissolved in hot water (200 ml) and filtered. Triphenylphosphinebenzoylmethylene betaine (3.8g, 10m mol) in ethanol (20 ml) was added to the warm solution and it was then heated under reflux for 2 hours when a greenish product with a little black residue separated out. The black contaminant was separated by dissolving the crude product in chloroform and filtering. The filtrate which was greenish-yellow on concentration and addition of ether afforded a yellowish *product*. The product after washing thoroughly with ether was dried *in vacuo*.

Yield = 4.46g(85%)

m.p. = 228 - 231^{o}C(d) lit:(92)m.p. 225 - 230^{o}C(d)

Found: C,66.21%; H,4.71%; P,6.56%; Cl,8.29%.

$C_{52}H_{42}Cl_2O_2P_2Pd$

Requires: C,66.58%; H,4.48%; P,6.61%; Cl,7.57%.

λ_M^{DMF} = 2 ohm^{-1} cm^2 mol^{-1}

(b) Platinum(II) chloride complexes

(1) Chloro(N-benzoyliminopyridinium betaine)(2-carbonyliminopyridinium)phenylplatinum(II)dihydrate

Potassium tetrachloroplatinate(II) (1.0g, 2.4m Mol) in water (75 ml) was treated with N-benzoyliminopyridinium betaine (1.2g, 6m Mol) and the mixture was heated under reflux for 2 hours. After about 30 minutes of heating, the original reddish brown, clear solution turned yellowish and a yellowish *product* separated out. The yellowish product was recrystallized from ethanol. Addition of a hot aqueous solution of sodium tetraphenylborate to the filtrate from the reaction afforded the tetraphenylborate salt of the protonated betaine.

Yield = 0.95g (60%)

m.p. = 218 - 219^{o}C(d)

Found: C,45.34%; H,3.78%; N,8.60%; Cl,5.41%; Pt,30.23%.

$C_{24}H_{23}ClN_4O_4Pt$

Requires: C,43.52%; H,3.48%; N,8.46%; Cl,5.36%; Pt,29.48%.

$\lambda_M^{CH_3NO_2}$ = 6 ohm^{-1} cm^2 mol^{-1}.

(2) Bis{(2-carbonyliminopyridinium)phenyl}platinum(II)

A mixture of potassium tetrachloroplatinate(II) (1.6g, 4m Mol) sodium acetate (0.66g, 8m Mol) and N-benzoyliminopyridinium betaine (1.6g, 8m Mol) in water (75 ml) was heated under reflux for 4 hours. The greenish-yellow solid which separated was found to be a mixture by *t.l.c.* Extraction of 2.2g material with dry benzene (150 ml) in a sohxlet apparatus gave the compound (1.1g) described above leaving a yellowish-orange residue. Dichloromethane extraction afforded an amber material (0.4g) (not yet characterized) and the greenish-yellow residue was shown to be pure by *t.l.c.* and characterized as the *bis*-metallated compound.

Yield = 0.7g (30%)

m.p. = 280 - 282^{o}C(d)

Found: C,48.21%; H,3.25%; N,9.24%; Pt,33.40%.

$C_{24}H_{18}N_4O_4Pt$

Requires: C,48.88%; H,3.05%; N,9.50%; Pt,33.11%

$$\lambda_M^{CH_3NO_2} = 5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}.$$

(c) Rhodium(III) halide complexes

(1) Diaquobis{(2-carbonyliminopyridinium)phenyl}rhodium(III)chloride

Rhodium trichloride hydrate (0.5g) and N-benzoyliminopyridinium betaine (2.0g, 10m Mol) were dissolved in water (75 ml) containing ethanol (10 ml) and the resultant clear reddish-brown solution was refluxed for 2 hours. The greenish-yellow *product* separated during the reaction and was recrystallized from ethanol/benzene. Addition of an aqueous solution of sodium perchlorate to the filtrate after isolation of the product afforded the perchlorate salt of the protonated betaine. Further, the repetition of the reaction in the presence of sodium acetate gave the same product in slightly shorter time.

Yield = 0.83g (77%)
m.p. = 273 - 275^{o}C(d)

Found: C,50.79%; H,3.89%; N,9.74%; Cl,6.26%; Rh,18.86%.
$C_{24}H_{22}ClN_4O_6Rh$
Requires: C,50.66%; H,3.87%; N,9.85%; Cl,6.24%; Rh,18.10%.

$\lambda_M^{H_2O}$ = 91 ohm^{-1} cm^{2} mol^{-1}

λ_M^{DMF} = 12 ohm^{-1} cm^{2} mol^{-1}

$\lambda_M^{CH_3NO_2}$ = 10 ohm^{-1} cm^{2} mol^{-1}

(2) *Diaquobis{(2-carbonyliminopyridinium)phenyl}rhodium(III)bromide*

This was prepared by refluxing an aqueous suspension of the above chloride (0.5g, 0.9 m Mol) in water, (50 ml) in the presence of excess of sodium bromide (~3g) for half-an-hour. The greenish-yellow *product* was recrystallized from ethanol/benzene.

Yield = 0.49g(88%).
m.p. > 300^{o}C

Found: C,47.48%; H,3.59%; N,9.74%; Br,13.52%; Rh,17.38%.
$C_{24}H_{22}BrN_4O_6Rh$
Requires: C,46.99%; H,3.59%; N,9.14%; Br,13.03%; Rh,17.06%.

$\lambda_M^{H_2O} = 106 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

$\lambda_M^{CH_3NO_2} = 21 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

(3) *Diaquobis{(2-carbonyliminopyridinium)phenyl}rhodium(III)iodide*

This was prepared by the method described above for the preparation of the bromide except that excess of sodium iodide (~4g) was used instead of sodium bromide. The yellow *product* was recrystallized from ethanol/benzene.

Yield = 0.53g(90%).

m.p. > 300

Found: C,42.34%; H,3.27%; N,7.79%; I,18.83%.

$C_{24}H_{22}IN_4O_6Rh$

Requires: C,43.64%; H,3.33%; N,8.49%; I,19.23%.

$\lambda_M^{DMF} = 99 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

(4) *Diaquobis{(2-carbonyliminopyridinium)phenyl}rhodium(III) tetraphenylborate*

The rhodium(III)chloride complex {(C)(i)}, (0.2g, 0.4m Mol) was dissolved in boiling water (100 ml) to obtain a clear solution and to the hot solution was added sodium *tetra*phenylborate (4g) in water. A yellow *product* separated out immediately on mixing the two solutions. The product was filtered, washed with water and dried *in vacuo*.

Yield = 0.32g (95%)

m.p. > 300°C.

Found: C,68.00%; H,5.22%; N,6.82%.

$C_{48}H_{42}BN_4O_6Rh$

Requires: C,67.61%; H,4.93%; N,6.57%.

$\lambda_M^{DMF} = 60\ ohm^{-1}\ cm^2\ mol^{-1}$

The same product was obtained with the analogous rhodium(III) bromide {(C)2} and rhodium(III) iodide {(C)3} complexes.

(5) *Diaquobis{(2-carbonyliminopyridinium-5-methyl)phenyl} rhodium(III)chloride*

Rhodium trichloride hydrate (0.3g,~ 1m Mol) was dissolved in water (30 ml) containing ethanol (10 ml) and N-*p*-toluoyliminopyridinium betaine (0.64g, 3m mol) was then added to reddish-brown solution. The resultant solution was refluxed for 2 hours when a greenish *product* separated out. The product was washed with ethanol and dried *in vacuo*.

Yield = 0.57g (83%)

m.p. $>$ 300°C

Found: C,50.87%; H,4.17%; N,9.15%; Cl,5.96%.

$C_{26}H_{26}ClN_4O_4Rh$

Requires: C,52.30%; H,4.36%; N,9.39%; Cl,5.94%.

$\lambda_M^{H_2O} = 108\ ohm^{-1}\ cm^2\ mol^{-1}$

$\lambda_M^{CH_3NO_2} = 5\ ohm^{-1}\ cm^2\ mol^{-1}$

(d) Iridium(III)chloride complexes

(1)*Chloroaquobis{(2-carbonyliminopyridinium)phenyl}iridium(III) trihydrate*

An exactly similar preparative procedure to that for the rhodium(III) chloride complex {(C)1} was followed, replacing rhodium(III)chloride hydrate by sodium (or ammonium)*hexa*chloroiridate(IV) (0.5g). The reddish-orange *product* was washed with water, ethanol and dried *in vacuo*. The same product could be obtained even with sodium *hexa*chloroiridite(III) but however, it was about a week after eight hours of refluxing before the product separated out. The product was recrystallized from benzene/chloroform.

Yield = 0.36g (47%) (with sodium *hexa*chloroiridate(IV)

m.p. > 300°C

Found: C,41.67%; H,3.57%; N,7.96%; Cl,4.74%; Ir,27.57%

$C_{24}H_{26}ClIrN_4O_6$

Requires: C,41.51%; H,3.75%; N,8.07%; Cl,5.11%; Ir,27.70%

$\lambda_M^{DMF} = 7\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

(2)*Chloroaquobis{(2-carbonyliminopyridinium-5-methyl)phenyl} iridium(III) trihydrate*

N-*p*-toluoyliminopyridinium betaine (0.6g, 3m mol) was added to ammonium-*hexa*chloroiridate(IV) (0.4g, 0.9m mol) in water (75 ml) and the resultant solution was refluxed for 2 hours. A reddish-brown precipitate separated out, which dissolved in ethanol to give a reddish solution. Addition of ether to the ethanolic solution reprecipitated the *product*.

Yield = 0.15g (23%)

m.p. 210 - 220°C(d)

Found: C,40.18%; H,3.69%; N,7.29%; Cl,4.76%

$C_{26}H_{30}ClIrN_4O_6$

Requires: C,43.22%; H,4.16%; N,7.76%; Cl,4.91%;

$$\lambda_M^{CH_3NO_2} = 4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

(e) Reactions with tertiary phosphines and other Lewis bases

(1) Reaction of chloro(2-carbonyliminopyridinium)phenyl palladium(II) with triphenylphosphine

The palladium complex (0.5g, 1.5m Mol) was dissolved in hot 1:4 dioxane(25ml)and of excess triphenylphosphine (~2g) was added to the clear hot solution. The reaction mixture was then heated under reflux for 30 - 40 minutes. The reaction was conducted in an atmosphere of dinitrogen. The reaction mixture was allowed to cool to room temperature and *n*-hexane was added to precipitate the *product* which was recrystallized from chloroform/carbontetrachloride to afford the pale-yellow crystalline product.

Yield = 0.74g (80%)

m.p. 170 - 180°C(d)

The analysis showed that the product was

$[Pd(L-H)(Ph_3PO)Cl]$ where L = N-benzoyliminopyridinium betaine

Found: C,58.28%; H,4.18%; N,4.22%; Cl,6.25%; P,5.06%.

$C_{30}H_{24}ClN_2O_2PPd$

Requires: C,58.34%; H,4.05%; N,4.54%; Cl,5.75%; P,5.02%.

$$\lambda_M^{CH_3NO_2} = 3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

i.r.(KBr.disc): 1095 (S), ν(→ PO)

Mass Spectrum = m/e = 278 (Ph_3PO); m/e = 262 (PH_3P)

(2) *Reaction of chloro(N-benzoyliminopyridinium betaine)(2-carbonyliminopyridinium)phenylpalladium dihydrate with triphenylphosphine*

The palladium complex (0.21g, 0.4m Mol) was covered with benzene (75 ml) (de-aerated by passing N_2) and triphenyl phosphine (0.53g, 1.6m Mol) was then added maintaining the dinitrogen atmosphere. The resultant mixture was then refluxed for 30 minutes, when a pale green clear solution was obtained. On cooling to room temperature a white *product* was obtained. The product was dried *in vacuo*.

Yield = 0.20g (70%)

m.p. 180 - 187^{o}C(d)

The analysis showed that the product was

$[Pd(L\text{-}H)(Ph_3PO)Cl]C_6H_6$. where L = N-benzoyliminopyridinium betaine.

Found: C,61.41%; H,5.29%; N,4.07%; Cl,5.23%; P,4.51%.

$C_{36}H_{30}ClN_2O_2PPd$

Requires: C,62.17%; H,4.32%; N,4.03%; Cl,5.10%; P,4.46%.

$\lambda_M^{CH_3NO_2} = 5\ ohm^{-1}\ cm^2\ mol^{-1}$.

i.r.(KBr.disc): 1098 cm^{-1}(S), ν(→P-O)

Mass Spectrum: m/e = 278 (Ph_3PO); m/e = 262 (Ph_3P).

(3) *Reaction of Chloro(2-carbonyliminotrimethylammonium)phenylpalladium(II) with triphenylphosphine*

The palladium complex (0.21g, 0.6m Mol) and triphenylphosphine (0.64g, 2.4m Mol) were covered with benzene (75 ml) (de-aerated by passing N_2) and refluxed under dinitrogen for 30 minutes. Concentration of the reaction mixture in a rotatory film evaporator afforded a pale green crystalline *product* which was recrystallized from chloroform.

Yield = 0.35g (98%)
m.p. 195 - 200^{o}C(d)

The pale green crystals were formulated as

$[Pd(L\text{-}H)(Ph_3PO)Cl]$ where L=N-benzoyliminotrimethylammonium betaine.

Found: C,57.17%; H,5.19%; N,4.70%; Cl,5.68%; P,5.06%.

$C_{28}H_{28}ClN_2O_2PPd$

Requires: C,56.30%; H,4.69%; N,4.69%; Cl,5.94%; P,5.19%.

$$\lambda_M^{CH_3NO_2} = 6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\lambda_M^{DMF} = 7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

i.r.(KBr disc): 1095 cm^{-1}(S), ν(P-O)

Mass spectrum: m/e = 278 (Ph_3PO); m/e = 262 (Ph_3P).

(4) *Reaction of chloro(N-benzoyliminopyridinium betaine)(2-carbonyliminopyridinium)phenylplatinum(II)dihydrate with triphenylphosphine*

The platinum complex (0.32g, 0.5m Mol) and triphenylphosphine (0.5g, 1.9m Mol) were covered with de-aerated benzene (50 ml) and refluxed for 30 minutes under dinitrogen. On cooling a cream coloured *product* separated out, which was washed with ether and dried *in vacuo*.

Yield = 0.24g, (60%)

m.p. 183 - 185^{o}C(d)

The analysis showed that the product was

$[Pt(L-H)Ph_3POCl]C_6H_6$

Found: C,54.77%; H,4.56%; N,3.43%; Cl,4.34%; P,3.63%.

$C_{36}H_{30}ClN_2O_2PPt$

Requires: C,55.13%; H,3.83%; N,3.57%; Cl,4.52%; P,3.95%.

$\lambda_M^{CH_3NO_2} = 6$ ohm^{-1} cm^2 mol^{-1}

i.r. (KBr.disc): 1098 cm^{-1}(S) ν(P -O)

Mass spectrum: m/e = 278 (PH_3PO); m/e = 262 (Ph_3P).

(5) Reaction of Diaquobis{2-carbonyliminopyridinium)phenyl} rhodium(III)chloride with tri-n-butylphosphine

The rhodium complex (1.14g, 2m Mol) and tri-*n*-butyl phosphine (1.63g, 8m Mol) were covered with de-aerated benzene (75 ml) and refluxed under dinitrogen for 30 minutes. The greenish-yellow product was filtered and washed with dry benzene, ether and dried *in vacuo*.

Yield = 1.23g, (82%).
m.p. 205^{o}C(d)

The analysis showed that the product was

$[Rh(L-H)_2(Bu^n_3PO)Cl]$ where L = N-benzoyliminopyridinium betaine.
and Bu^n_3PO = tri-*n*-butylphosphine oxide

Found: C,57.55%; H,6.08%; N,7.58%; Cl,5.42%

$C_{36}H_{45}ClN_4O_3PRh$

Requires: C,57.56%; H,6.00%; N,7.46%; Cl,4.72%;

$\lambda_M^{CH_3NO_2} = 20\ ohm^{-1}\ cm^2\ mol^{-1}$

i.r. (KBr.disc): 2955 cm^{-1}(m), 2930 cm^{-1}(m), 2870 cm^{-1}(W-m)- ν(CH)butyl group.. 1092 cm^{-1}(S) ν(P-O).

Mass spectrum: m/e = 218 {$(nC_4H_9)_3PO$}; m/e = 202 {$(nC_4H_9)_3P$}

(6) *Reaction of diaquobis{(2-carbonyliminopyridinium)phenyl} rhodium(III)chloride with 2,2'-bipyridyl*

The rhodium complex (0.57g, 1m Mol) dissolved in hot dichloromethane (100 ml) was treated with 2,2'-bipyridyl (0.94g, 6m Mol) and heated under reflux for 1.5 hours. After concentration and addition of *n*-hexane a yellow *product* was obtained which was recrystallized from dichloromethane/*n*-heptane (1:2 v/v) and dried *in vacuo*.

Yield = 0.55g (80%)
m.p. 270 - 290°C

The analysis suggested the formulation of this compound as

$[Rh(L-H)_2(bipy)]^+Cl^-$ where L = N benzoyliminopyridinium betaine.

Found: C,59.56%; H,3.92%; N,12.30%; Cl,5.65%.

$C_{34}H_{26}ClN_6O_2Rh$

Requires: C,59.26%; H,3.78%; N,12.20%; Cl,5.15%.

$$\lambda_M^{CH_3NO_2} = 82 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

(7) *Reaction of chloroaquobis{(2-carbonyliminopyridinium)phenyl} iridium(III)trihydrate with triphenylphosphine*

The iridium complex (0.35g, 0.5m Mol) and *tri*-phenylphosphine (0.66g, 2.5m Mol) were covered with de-aerated benzene (75 ml) and refluxed under dinitrogen for 35 minutes. On cooling to room temperature a yellow *product* separated out and was washed with benzene, ether and dried *in vacuo*.

Yield = 0.45g (99%).
m.p. 230 - 233^{o}C(d)

This was formulated as

$[Ir(L-H)_2(Ph_3PO)Cl]$ where L = N-benzoyliminopyridinium betaine.

Found: C,56.31%; H,4.08%; N,5.79%; Cl,3.73%.

$C_{42}H_{33}ClIrN_4O_3P$

Requires: C,56.01%; H,3.67%; N,6.22%; Cl,3.94%.

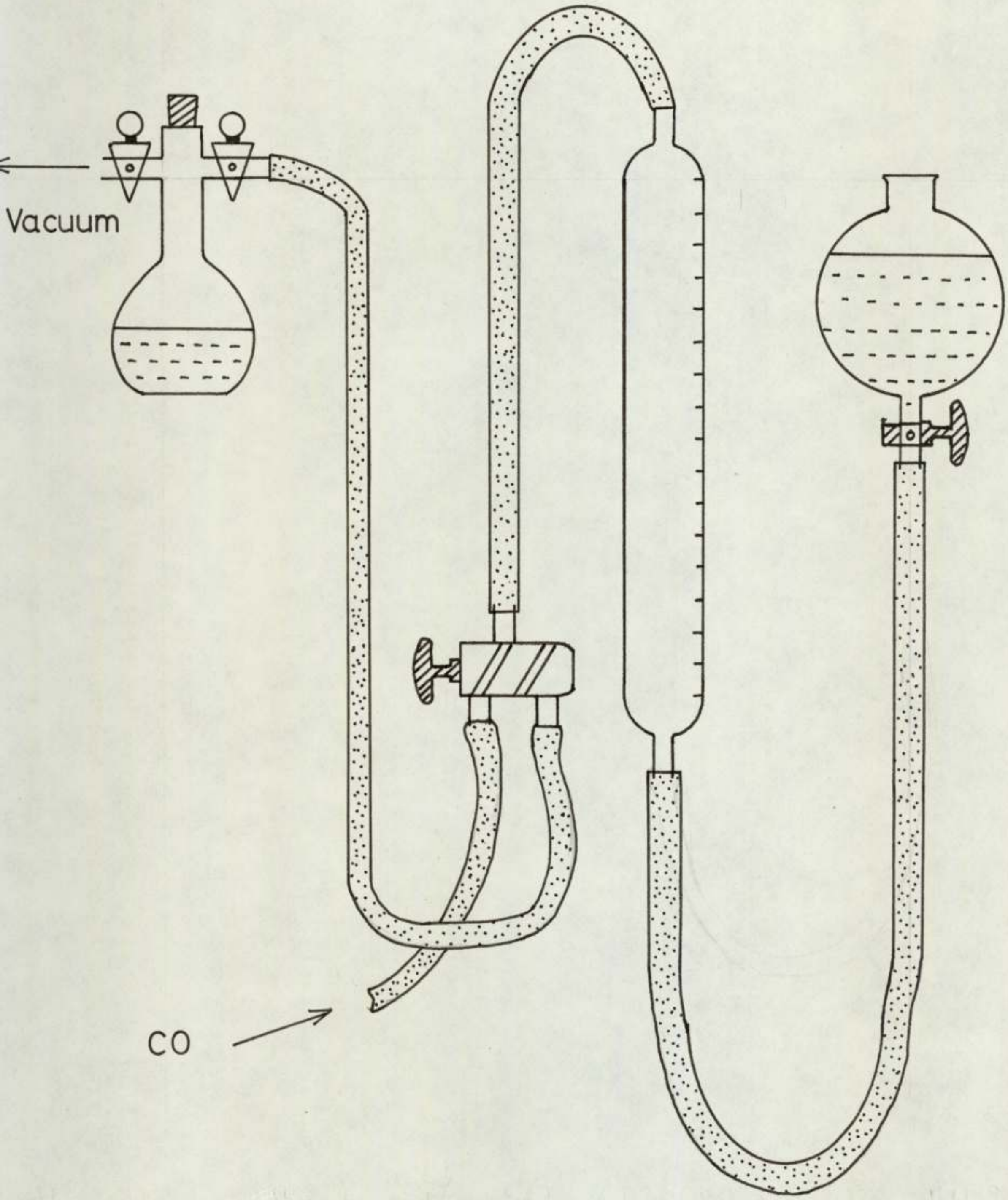
$$\lambda_M^{DMF} = 7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

i.r. (KBr.disc): 1088 cm^{-1}(S) $\nu(\rightarrow P\text{-}O)$

Mass spectrum: m/e = 278 (Ph_3PO); m/e = 262 (Ph_3P).

(f) Reactions with carbon monoxide

The preparations were carried out in a Schlenk flask at room temperature and atmospheric pressure and the gas uptake was monitored by means of a gas burette.



THE APPARATUS USED FOR CO ABSORPTION STUDIES

(1) Palladium complexes

(i) Reaction of chloro(2-carbonyliminopyridinium)phenyl palladium(II) with carbon monoxide

The palladium complex (1.0g, 3m Mol) in suspension in dry benzene (75 ml) saturated with carbon monoxide, was treated with carbon monoxide over 4 hours, after which time gas uptake was complete. During the gas uptake the original greenish-yellow colour of the solution gradually disappeared and a colourless product was formed together with some palladium metal. When the carbon monoxide atmosphere was removed and the reaction flask gently warmed to about 35°C, the original greenish-yellow product was formed; thus indicating that the reaction is reversible. The colourless product decomposed when isolation was attempted. The colourless filtrate on concentration afforded a pale green precipitate which was washed with ether.

Yield = 0.39g (35%).
m.p. 265°C(d)

The analysis shows this compound to be

[Pd(L-H)COCl] where L = N-benzoyliminopyridinium betaine

Found: C,43.21%; H,3.43%; N,7.79%.

$C_{13}H_9ClN_2O_2Pd$

Requires: C,42.51%; H,2.45%; N,7.63%.

$$\lambda_M^{CH_3NO_2} = 4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

The same product could be obtained when carbon monoxide was allowed to interact with the complex in ethanol, methanol or acetone. In the case of acetone, the reaction was not reproducible in that sometimes the product isolated by concentration of the acetone solution did not contain any co-ordinated carbon monoxide (*i.r.*) but its place had been taken by co-ordinated acetone (*i.r.*). Exactly the same behaviour was observed when the products obtained in benzene, ethanol or methanol were recrystallized from acetone in the absence of carbon monoxide. Further when the complexes were heated to about 60°C, the co-ordinated carbon monoxide was readily lost (*i.r.*)

(ii) Reaction of bromo(2-carbonyliminopyridinium(phenyl palladium(II) with carbon monoxide

The same conditions as mentioned above were used and similar behaviour was observed. The isolated *product* was pale yellow in colour.

Yield = 0.99g(80%).

m.p. 232 - 235°C(d)

The pale yellow product was formulated as

[Pd(L-H)COBr] where L = N-benzoyliminopyridinium betaine

Found: C,36.86%; H,2.58%; N,6.31%; Br,18.50%.

$C_{13}H_9BrN_2O_2Pd$

Requires: C,37.92%; H,2.20%; N,6.80%; Br,19.41%.

$$\lambda_M^{CH_3NO_2} = 5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

The *dichlorobis(N-benzoyliminopyridinium betaine)palladium(II)* complex did not react with carbon monoxide under the above mentioned conditions. Even on prolonged (12 hours) treatment with carbon monoxide there was no sign of any reaction and the starting material could be isolated unchanged.

(2) Platinum complex

Chloro(N-benzoyliminopyridinium betaine)(2-carbonyliminopyridinium) phenylplatinum(II)dihydrate (∼0.2g) was treated with carbon monoxide using the same conditions as for palladium complexes. The reaction was very slow and the gas uptake was complete after about 14 hours at which stage the presence of the unchanged yellow starting material together with a grey material could be seen. The impure product showed an absorption at 2080 cm^{-1} along with the characteristic absorptions of the ligand in its *i.r.* spectrum indicating the presence of terminal carbon monoxide group. All attempts to isolate pure compounds were unsuccessful. Hence this compound was not investigated any further.

(3) Iridium complex

The rhodium complexes were totally unreactive to carbon monoxide under the above conditions, yet, by contrast, the iridium complex, *chloroaquobis{(2-carbonyliminopyridinium)phenyl}iridium(III)trihydrate* undergoes a rapid and clean reaction to afford an amber coloured precipitate as the final *product*. The initial product was green but subsequently changed to amber and this was washed with ether and dried *in vacuo*.

The amber coloured *product* was formulated as

$Ir(L-H)_2(CO)_2Cl$

Yield = 0.197g (98%)

m.p. > 300°C

Found: C,46.00%; H,3.21%; N,7.46%; Cl,5.80%.

$C_{26}H_{18}ClIrN_4O_4$

Requires: C,46.03%; H,2.66%; N,8.26%; Cl,5.23%.

$$\lambda_M^{CH_3NO_2} = 3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Refluxing the dicarbonyl complex in water regenerates the starting iridium complex. Further, experiments involving a gas burette confirmed the uptake of 2 moles of carbon monoxide but suggested that at first 4 moles of carbon monoxide are consumed with the subsequent release of 2 moles to give the observed final *product*. The results of this experiment are given below.

Weight of the iridium complex (starting material) = 0.2056g (0.296 m Mol)

Time	Volume of gas absorbed
0	0.0 ml
10 mts.	26.0 ml corresponds to 3.918 moles of CO per 1 mole of complex.
30 mts.	19.0 ml corresponds to 2.865 moles of CO per 1 mole of complex
50 mts.	14.0 ml corresponds to 2.11 mole of CO per 1 mole of complex
70 mts.	14.0 ml
90 mts.	14.0 ml

(g) Attempted *ortho*-metallation reactions

(1) Ligand = Phenyl 2-pyridyl Ketoxime. (prepared by a literature method (226))

(i) Rhodium trichloride hydrate (0.5g,~ 1m Mol) and *syn-& anti.* phenyl-2-pyridyl ketoxime (1.98g, 10m mol) were dissolved in 10% aqueous ethanol (80 ml) and the resultant solution was heated under reflux for 2 hours. A yellow *product* separated out which was recrystallized from chloroform/carbon tetrachloride and dried *in vacuo*.

Yield = 1.1g (65%)

m.p. $>$ 300°C

Use of *syn* or *anti* phenyl 2-pyridyl ketoxime instead of the mixture resulted in the same *product* as above. Addition of sodium chloride or sodium acetate did not alter the nature of the final *product*.

Analysis suggested the formulation of this compound as

$[Rh_2(L\text{-}H)_3Cl_3]$ where L = phenyl-2-pyridyl ketoxime

Found: C,49.22%; H,3.24%; N,9.34%; Cl,11.08%; O,5.50%.

$C_{36}H_{27}Cl_3N_6O_3Rh_2$

Requires: C,47.82%; H,2.99%; N,9.30%; Cl,11.78%; O,5.31%.

$\lambda_M^{CH_3NO_2} = 5\ \mathrm{ohm}^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$

(ii) The above rhodium complex (~0.5g) was refluxed in 10% aqueous ethanol (70 ml) containing a large excess of potassium iodide (~5g) for 2 hours. The reddish *product* was washed with water, ethanol and dried *in vacuo*.

m.p. $>$ 300°C

Analysis showed this compound to be

$[Rh_2(L\text{-}H)_3I_3]$

Found: C,37.52%; H,2.61%; N,7.39%; I,32.73%.

$C_{36}H_{27}I_3N_6O_3Rh_2$

Requires: C,36.68%; H,2.29%; N,7.13%; I,32.32%.

$\lambda_M^{DMF} = 8\ \mathrm{ohm}^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$

(iii) The rhodium chloride complex $[Rh_2(L-H)_3Cl_3]$ (where L = phenyl-2-pyridyl ketoxime) (~0.5g) was heated under reflux in 10% aqueous ethanol (50 ml) containing an excess of lithium bromide (~3g) for 2 hours. An orange precipitate appeared, which was washed with ethanol, ether and dried *in vacuo*.

m.p. 300^oC

The analytical data are consistent with the formulation of it as

$[Rh_2(L-H)_2LBr_4]$

Found: C,38.47%; H,3.03%; N,7.06%; Br,28.52%.

$C_{36}H_{28}Br_4N_6O_3Rh_2$

Requires: C,38.66%; H,2.51%; N,7.52%; Br,28.60.

$\lambda_M^{DMF} = 8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

(2) Ligand=N-(*p*-toluenesulphonyl)iminopyridinium betaine

(i) Potassium tetrachloropalladate(II) (1.96g, 6m Mol) and N-(*p*-toluenesulphonyl)iminopyridinium betaine (1.49g, 6m Mol) were dissolved in 50% aqueous methanol and heated under reflux for 2.5 hours. A tan coloured product separated out which was washed with ether and dried *in vacuo*.

Yield = 2.5g

The *i.r.* spectrum of this compound revealed strong absorptions at 1320 cm^{-1} $\nu_{asym.}(>SO_2)$; 1145 cm^{-1}, $\nu_{sym}(>SO_2)$; 330 cm^{-1}, ν(Pd-Cl). Except for these three absorptions, the *i.r.* spectrum is identical with that of the free ligand and in view of the lack of change in the 850 cm^{-1} to 500 cm^{-1}, it was concluded that no metallation of the phenyl or pyridyl ring has taken place. This compound was hence not further dealt with.

When the above procedure was repeated in the presence of triethylamine (3 ml), immediately the tan coloured product changed to dark grey and later palladium metal was deposited.

(ii) Rhodium trichloride trihydrate (0.3g, 1.22 m Mol) was dissolved in 5% aqueous ethanol (60 ml) and N-(*p*-toluenesulphonyl)iminopyridinium betaine (0.5g, ~ 2m Mol) was added to the clear reddish-brown solution when immediately a black residue (probably rhodium metal) was deposited. Even in the presence of sodium acetate, reduction of the rhodium salt took place and hence this reaction was not investigated any further.

(3) Ligand = N-phenacylpyridinium betaine

(i) N-phenacylpyridinium perchlorate (3g, 10 m Mol) was added to 20% sodium hydroxide solution (100 ml) and extracted with chloroform (40 ml). The chloroform extract was then added to a solution of rhodium trichloride hydrate (0.6g, 2m Mol) in ethanol (75 ml) and refluxed for 10 minutes. Then, *tri-n*-butylamine (2.2g 12m Mol) was added to the reaction mixture and the solution was again heated under reflux. On heating, a brown tarry mass was deposited and it did not crystallize out on standing. Concentration of the filtrate afforded rhodium trichloride hydrate co-precipitated with the protonated betaine.

(ii) N-phenacylpyridinium perchlorate (3g,~10 m Mol) and potassium carbonate (0.8g,~5 m Mol) were dissolved in water (100 ml) and to this solution, palladium dichloride (1.0g,~6 m Mol) was added with stirring. On heating the solution a grey residue of palladium metal was deposited.

(C) RESULTS

The infra-red spectra in the region of 4000 - 250 cm^{-1} show similar absorption patterns in the complexes of each ligand and therefore are not tabulated.

The infra-red spectra of metallated (Figure 3) and unmetallated (Figure 4) palladium complexes of N-benzoyliminopyridinium betaine are presented and they may be considered as typical spectra of the complexes of this betaine. Infra-red spectroscopic data relevant to the discussion which follows are gathered in Tables 9 and 10. Attempts were made to obtain 'H *n.m.r.* data for each complex prepared but due to poor solubility properties they were not successful in many cases. 'H *n.m.r.* data are presented in Table 11 and the spectra of the rhodium chloride complex $[Rh(L-H)_2(H_2O)_2]^+Cl^-$, as a representative type, together with the spectra of the free ylide and of the protonated salt for comparison, are given in Figures, 5, 6 and 7. ^{13}C *n.m.r.* data for two betaines and their rhodium chloride complexes are given in Table 12, and the actual spectra observed are reproduced in Figures 8 to 11. In general, the mass spectra of all the complexes of each ligand were similar showing the characteristic fragmentation pattern of the ligand but none of them revealed a peak corresponding to the molecular ion of the complex. Further, attempts to obtain molecular weight data using a Mechrolab Vapour Phase Osmometer failed due to the limited solubility of the compounds at 37°C. All the metal complexes prepared with the betaines were found to be diamagnetic. X-ray powder data established isomorphism for the series $[Rh(L-H)_2(H_2O)_2]^+ \bar{X}$ where X = Cl,Br,I; L = $C_5H_5\overset{+}{N}\text{-}\bar{N}COC_6H_4$-*ortho*. While they indicated that $[Rh(L-H)_2(H_2O)_2]^+Cl^-$ and $[Ir(L-H)_2(H_2O)Cl]3\ H_2O$ are <u>not</u> isomorphous.

TABLE 9 - Infra-red data for metal derivatives of resonance stabilized ylides (cm^{-1}) (KBr disc)

Compound	ν(OH)	ν(>C=O)	νN-----N	γ(CH)-phenyl	γ(CH)-pyridyl	*C ν(M-X)
(a)(1)$[Pd(L\text{-}H)Cl]_n$	-	1645(v.s.)	1315(s)	738(s.sh.)	675(s.sh) 772(s.sh.)	344; 292.
(2)$[Pd(L\text{-}H)Br]_n$	-	1640(v.s.)	1312(s)	735(s.sh)	670(s.sh) 770(s.sh)	-
(3) $[PdL_2Cl_2]$	-	1620(v.s.)	1338(v.s.)	695(v.s.sh.) 722(v.s.sh)	670(s.sh) 770(v.s.sh)	338
(4) $[Pd(L\text{-}H)LCl]2H_2O$	3420(m.br)	1610(v.s.) 1630(v.s.)	1322(v.s.)	695(m.sh) 718(s.sh) 735(s.sh)	670(s.) 778(s.sh)	346
(5) $[Pd(L^{III}\text{-}H)Cl]_n$	-	1630(v.s.sh) 1608(s.)	1302(s)	850(m) 760(s.sh)	675(m.sh) 768(s.sh)	344, 289
(6) $[Pd(L^{IV}\text{-}H)Cl]_n$	-	1640(v.s.)	1308(s)	835(m)	670(s) 768(s)	325, 375
(7) $[Pd(L^{I}\text{-}H)Cl]_n$	-	1640(v.s.)	1290(s)	740(v.s.sh)	-	360, 321
(8) $[Pd(L^{II}\text{-}H)Cl]_n$	-	1630(v.s.)	-	682(s);715(v.s.) 745(s);770(s.sh)	-	328, 295
(9) $[Pd(L^{II}{}_2Cl_2]$	-	1635(v.s.)	-	682(v.s.);710(s) 745(s)	-	330, 294

TABLE 9 - Infra-red data for metal derivatives of resonance stabilized ylides (cm^{-1}) (KBr disc)
continued

Compound	ν(OH)	ν(>C=O)	νN-----N	γ(CH)-phenyl	γ(CH)-pyridyl	*C ν(M-X)
(b)(1)$[Pt(L-H)LCl]2H_2O$	3450(s)	1620(s.br) 1650(v.s.sh)	1320(v.s.)	690(s.sh) 719(m.sh) 748(s.sh)	668(s.sh) 770(s.sh)	333
(2) $[Pt(L-H)_2]$	-	1630(v.s.)	1285(s)	730(s.sh)	672(s.sh) 765(m.sh)	-
(c)(1)$[Rh(L-H)_2(H_2O)_2]^{+}Cl$	3400-3140 (s.br)	1609(v.s.)	1332(v.s.)	755(s.sh)	675(m.sh) 768(s.sh)	-
(2) $[Rh(L-H)_2(H_2O)_2]^{+-}Br$	3600-3140 (s.br)	1600(v.s.br)	1330(v.s.)	750(s.sh)	670(m) 768(s.sh)	-
(3) $[Rh(L-H)_2(H_2O)_2]^{+-}I$	3620-3200 (s.br)	1600(v.s.br)	1325(s)	738(s)	668(s) 765(m)	-
(4)$[Rh(L-H)_2(H_2O)_2]^{+}$ $[Ph_4B]^{-}$	3570(m) 3500(m.sh)	1628(v.s.) 1652(s)	1330(s)	755(s.br) 708(s.sh)	768(s) 670(s)	-
(5)$[Rh(L^{IV}-H)_2(H_2O)_2]^{+-}Cl$	3400-3120 (v.s.br)	1585(v.s.)	1320(v.s.)	835(m)	678(s) 765(s.sh)	-
(d)(1)$[Ir(L-H)_2(H_2O)Cl]$ $3H_2O$	3660-3100 (v.s.br)	1590(v.s.br)	1325(v.s.)	740(m.sh) 758(s.sh)	675(s) 770(m)	341
(2)$[Ir(L^{IV}-H)_2(H_2O)Cl]$ $3H_2O$	3600-3200 (v.s.br)	1585(v.s.)	1315(s)	830(m)	675(s) 765(s)	375

TABLE 9 - Infra-red data for metal derivatives of resonance stabilized ylides (cm^{-1}) (KBr disc)
continued

Compound	ν(OH)	ν(>C=O)	νN-----N	γ(CH)-phenyl	γ(CH)-pyridyl	*C ν(M-X)
(e)(1)[Pd(L-H)(Ph$_3$PO)Cl]	-	1638(v.s.)	1315(s)	738(s)	670(m.sh)	320
(2)[Pd(L-H)(Ph$_3$PO)Cl]C$_6$H$_6$	-	1638(v.s.)	1315(v.s.)	738(s.sh)	678(s) 760(s.sh)	318
(3)[Pd(L^I-H)(Ph$_3$PO)Cl]	-	1628(v.s.)	1300(m)	740(v.s.)	-	285
(4)[Pt(L-H)(Ph$_3$PO)Cl]C$_6$H$_6$	-	1645(v.s.)	1310(s)	740(s.sh)	678(s) 768(m.sh)	290
(5)[Rh(L-H)$_2$(Bu$^n_3$PO)Cl]	-	1615(v.s.)	1308(v.s.)	738(v.s.sh)	675(s) 770(s)	353
(6)[Rh(L-H)$_2$(bipy)]$^+$Cl$^-$	-	1610(v.s.sh)	1320(v.s.)	745(v.s.)	678(m) 695(w) 775(s)	-
(7)[Ir(L-H)$_2$(Ph$_3$PO)Cl]	-	1620(v.s.)	1300(s)	740(s) 755(m.sh)	675(s) 772(w)	351
(f)(1)(i) [Pd(L-H)COCl]	-	1650(v.s.) 2110(v.s.) ν(C≡O)	1318(v.s.sh)	740(s.sh)	675(s.sh) 775(s.sh)	273
(ii)[Pd(L-H)COBr]	-	1645(v.s.) 2108(v.s.) ν(C≡O)	1315(v.s.)	738(v.s.sh)	670(s.sh) 770(s.sh)	233

TABLE 9 - Infra-red data for metal derivatives of resonance stabilized ylides (cm^{-1}) (KBr disc)
continued

Compound	ν(OH)	ν(>C=0)	νN-----N	γ(CH)-phenyl	γ(CH)-pyridyl	^{*C} ν(M-X)
(2)[Pt(L-H)COCl]	-	1620(v.s.br) 2080(s) ν)C≡0)	1310(s.br)	740(s)	670(s.sh) 768(s,sh)	260
(3)$[\mathrm{Ir(L{-}H)}_2(\mathrm{CO})_2\overset{+-}{]}\mathrm{Cl}$	-	1632(v.s.) 1985(s.sh) ν(C≡0) 2000(v.s.sh) ν(C≡0)	1300(v.s.)	750(v.s.)	670(s) 770(m.sh)	-

Notes: (a) Numbers of compounds are as given in the text under Preparation of Complexes.

(b) (L-H) = Ligand, less one *ortho*-proton (c) Nujol mull/Polythene plates

v = very; s = strong; sh = sharp; br = broad; m = medium

TABLE 10 - Infra-red spectral data of phenyl-2-pyridyl ketoxime and its rhodium(III)complexes (KBr disc)

Compound	Infra-red absorptions (4000-250cm^{-1})
Syn & Anti phenyl-2 pyridyl ketoxime(L^V)	3480-2800(v.s.br), ν(OH) + ν(C-H); 1618(w); ν(C=N); 1587(s), 1560(m), 1490(m); 1470(s) 1430(s), ν(C-C); 1325(s), 1282(m), 1240(m), 1180(s.sh), 1155(s.sh),1100(w),1060(w),1050(m) 1032(m), 992(v.s.), ν(N-O); 945(s); 910(m); 780(s.br); 740(s.br); 690(s.br). γ(C-H); 565(w); 490(m), 468(w), 455(m), 400(m.sh); 335(w), 250(w).
(g)(1)(i) $[Rh_2(L^V-H)_3Cl_3]$	3075(w), 3040(v.w.), ν(C-H); 1600(w-m), 1575(w); 1532(m), 1488(m), 1470(s), 1442(m), ν(C-C); 1380(v.w), 1300(m.br), 1215(m), 1185(w), 1160(w), 1130(s), 1115(w), 1070(w), 1030(m), 1000(w), 980(w), 820(m.br), 775(s), 755(m), 745)m.sh), 705(m), γ(C-H).615(w) 518(v.w), 491(m), 440(m), 378(w), 350(s), and 300(m-s), ν(Rh-Cl)
(ii)$[Rh_2(L^V-H)_3I_3]$	3082(v.w), 3070(w), ν(C-H); 1600(m), 1580(w), 1572(w), 1530(s), 1490(m), 1470(s), 1445(s,sh) ν(C-C); 1300(m.br), 1220(m,br); 1182(w), 1162(w-m), 1130(s), 1120(v.w), 1070(w), 1030(m), 1000(w), 978(m); 880(w), 815(m,br), 775(s.sh), 759(s.sh), 745(s.sh), 705(s), γ(C-H); 658(w), 615(m), 515(w), 488(w), 440(w), 400(v.w), 380(w); 345(v.w), 300(w), 268(w).
(iii)$[Rh_2(L^V-H)_2L^VBr_4]$	3640-3100(s.br), ν(O-H); 3065(w), 3025(w), ν(CH); 1630(w,br), 1600(m), 1580(w), 1525(m-s) 1488(m), 1470(s), 1445(s), ν(C-C); 1300(w-m,br), 1220(w), 1185(v.w), 1160(w), 1135(m), 1115(w), 1070(w), 1030(s.sh), 1005(v.w), 978(m), 885(v.w), 820(w.br), 778(s.sh), 762(m-s.sh), 745(s.sh), 705(s), γ(C-H); 660(w), 600(w,br), 515(w), 486(w), 440(w), 400(v.w), 380(v.w), 300(w), 270(v.w). *230(s) ν(Rh-I)

Note: (L^V-H) = ligand less the hydroxyl hydrogen. * From the *i.r.* spectrum from 400-200 cm (Nujol mull/Caesium iodide plates)
Other abbreviations have the usual meaning.

TABLE 11

Compound*	'H *n.m.r.* data[(a)]. (τ values) (DMSO Solutions)
(a)(1) $[Pd(L\text{-}H)Cl]_n$	1.03(d,2H,H_2+H_6Py); 1.43(t,1H,H_4Py); 1.73-2.03(m,3H,H_3,H_5Py+H_2Ph); 2.43-2.60(m,1H,H_5Ph); 2.70-2.90(m,2H,H_3+H_4Ph).
(2) $[Pd(L\text{-}H)Br]_n$	1.02(d,2H,H_2+H_6Py); 1.46(t,1H,H_4Py); 1.71-2.02(m,3H,H_3H_5Py+H_2Ph); 2.36-2.60(m,1H,H_5Ph); 2.63-2.86(m,2H,H_3+H_4Ph).
(3) $[PdL_2Cl_2]$	1.00(m,2H,H_2+H_6Py); 1.30-1.70(m,1H,H_4Py); 1.73-2.10(m,4H,H_3H_5Py+H_2H_6Ph). 2.24-2.59(m,2H,,Ph); 2.60-2.90(m,1H,Ph)
(4) $[Pd(L\text{-}H)LCl]2H_2O$	1.06(d,2H,H_2+H_6Py); 1.29-2.24(m,6H,Py+Ph); 2.30-3.06(m,4H,aromatic)
(5) $[Pd(L^{III}\text{-}H)Cl]_n$	1.01(d,2H,H_2+H_6Py); 1.44(t,1H,H_4Py); 1.86(t,2H,H_3+H_5Py); 2.66(s,1H,H_2Ph);, 2.81-2.96(m,2H,H_4+H_5Ph). methyl resonance masked by solvent.
(6) $[Pd(L^{IV}\text{-}H)Cl]_n$	0.83(d,2H,H_2+H_6Py); 1.00-1.33(m,1H,H_4Py); 1.50-1.90(m,3H,H_3+H_5Py+Ph);

TABLE 11
continued '

Compound	'H *n.m.r.* data (τ values) (DMSO Solutions)
(7) $[Pd(L^{I}-H)Cl]_n$	1.80-2.15(m,1H,Ph); 2.25-2.75(m,3H,Ph) methyl resonance masked by solvent.
(8) $[Pd(L^{II}-H)Cl]_n$	1.60-2.03(m, aromatic protons). methine proton not detected due to dilute solution.
(b)(2) $[Pt(L-H)_2]$	1.15(d,2H,H_2+H_6Py); 1.54-3.00(m,7H,H_3,H_4,H_5Py+H_2,H_3,H_4,H_5Ph).
(c)(1)$[Rh(L-H)_2(H_2O)_2]^+Cl^-$	0.66(d,2H,H_2+H_6Py); 1.53(t,1H,H_4Py); 1.93(t,2H,H_3+H_5Py); 2.36-2.74(m,2H,H_2+H_5Ph); 2.79-3.17(m,2H,H_3+H_4Ph).
(2) $[Rh(L-H)_2(H_2O)_2]^+Br^-$	0.66(d,2H,H_2[H_6Py); 1.50(t,1H,H_4Py); 1.91(t,2H,H_3+H_5Py); 2.30-2.71(m,2H,H_2+H_5Ph) 2.72-3.10(m,2H,H_3+H_4Ph).
(3) $[Rh(L-H)_2(H_2O)_2]^+I^-$	0.68(d,2H,H_2+H_6Py); 1.51(t,1H,H_4Py); 1.94(t,2H,H_3+H_5Py); 2.40-2.78(m,2H,H_2+H_5Ph); 2.80÷3.20(m,2H,H_3+H_4Ph).
(5($[Rh(L^{IV}-H)_2(H_2O)_2]^+Cl^-$	0.75(d,2H,H_2+H_6Py); 1.61(t,1H,H_4Py); 2.01(t,2H,H_3+H_5Py); 2.70(d,1H,H_5Ph); 2.90-2.98(m,1H,H_2Ph); 3.20-3.33(m,1H,H_3Ph); 7.81(s.3H,CH_3).
(d)(1) $[Ir(L-H)_2(H_2O)Cl]3H_2O$	0.57-0.90(m,2H,aromatic); 1.24-1.60(m,2H,aromatic); 1.65-2.15(m,4H,aromatic); 2.25-2.69(m,3H,aromatic); 2.70-3.13(m,4H,aromatic);
(e)(1) $[Pd(L-H)Ph_3POCl]$	0.99(d,2H,H_2+H_6Py); 1.49(t,1H,H_4Py); 1.89(t,2H,H_3+H_5Py); 2.00-2.59(m,16H,aromatic); 2.85-3.05(m,1H,aromatic); 3.20-3.60(m,2H,aromatic).

* Numbers and symbols as in Table 10.

Notes (a) Tabulation of data follows the order: tau value, multiplicity (d=doublet, s=singlet,m=Multiplet,t=triplet) number of protons responsible for the signal; and the likely assignment of the signal.

(b) Solvent used was DMSO(d_6).

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
L	168.4	143.1	129.4	137.8	137.5	126.3	127.2	127.4			
$[Rh(L-H)_2(H_2O)_2]^+Cl^-$	174.9 2,J=5 Hz	146.3	137.5	141.9	126.6	129.2	121.5	133.0	126.0	159.0 d,J=32.5 Hz	
L^{IV}	168.6	143.6	138.2	139.4	135.3	128.5	128.0	126.8			22.8
$[Rh(L^{IV}-H)_2(H_2O)_2]^+Cl^-$	177.6	148.3	140.5	143.8	136.9	128.5	127.9	124.6	135.6	160.5 d,J=33.0 Hz	23.4

Note: Numbering of the carbon atoms is as given in Figures 8, 9, 10 and 11.

TABLE 12: ^{13}C.*n.m.r.* data, 25.2 Hz Spectra in DMSO (d_6) with 'H nucleus spin decoupler chemical shifts (ppm) relative to TMS^{13}C as external reference.

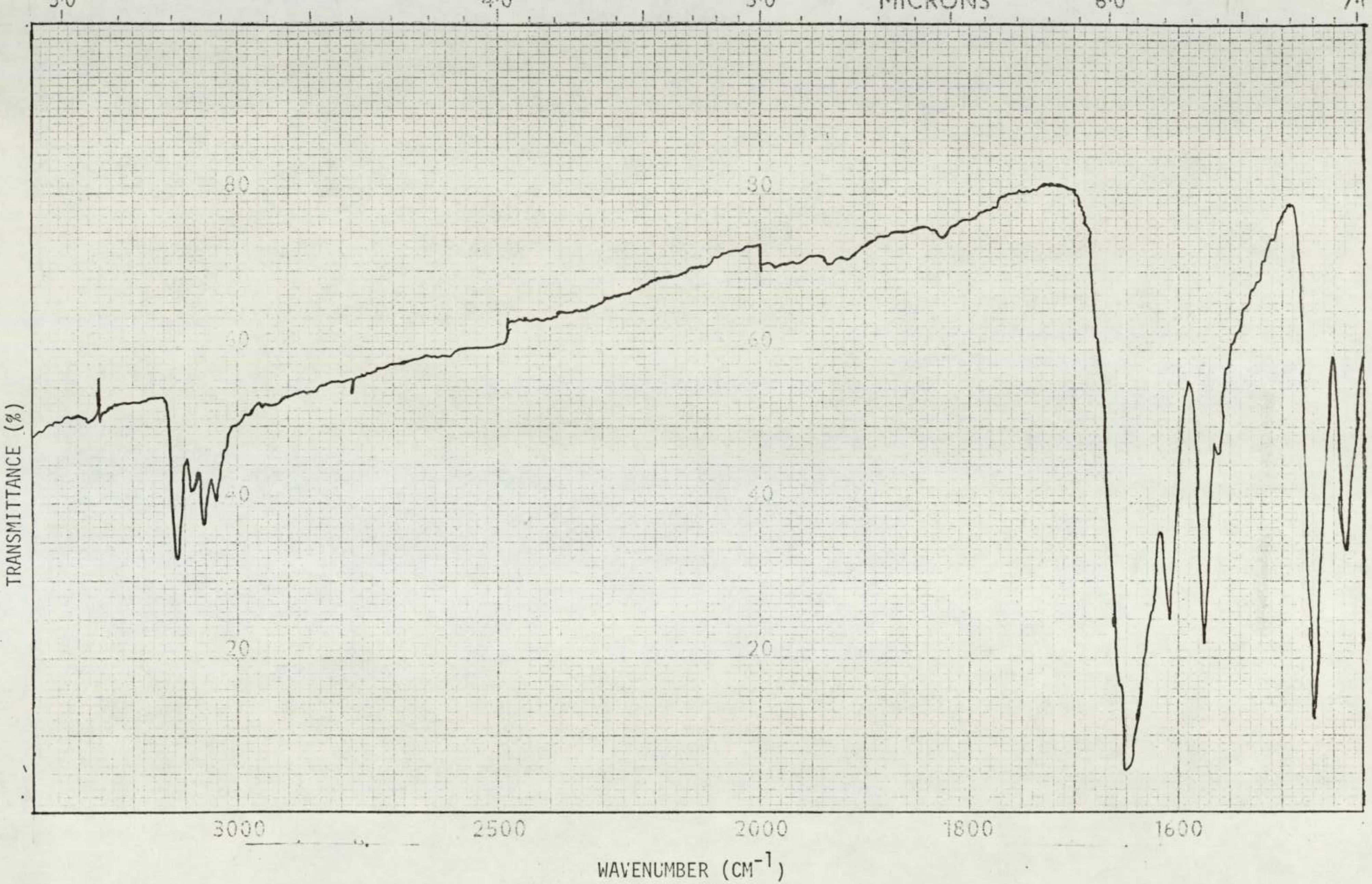


Figure 3. Infra-red Spectrum of $[Pd(L-H)Cl]_n$ (KBr disc)

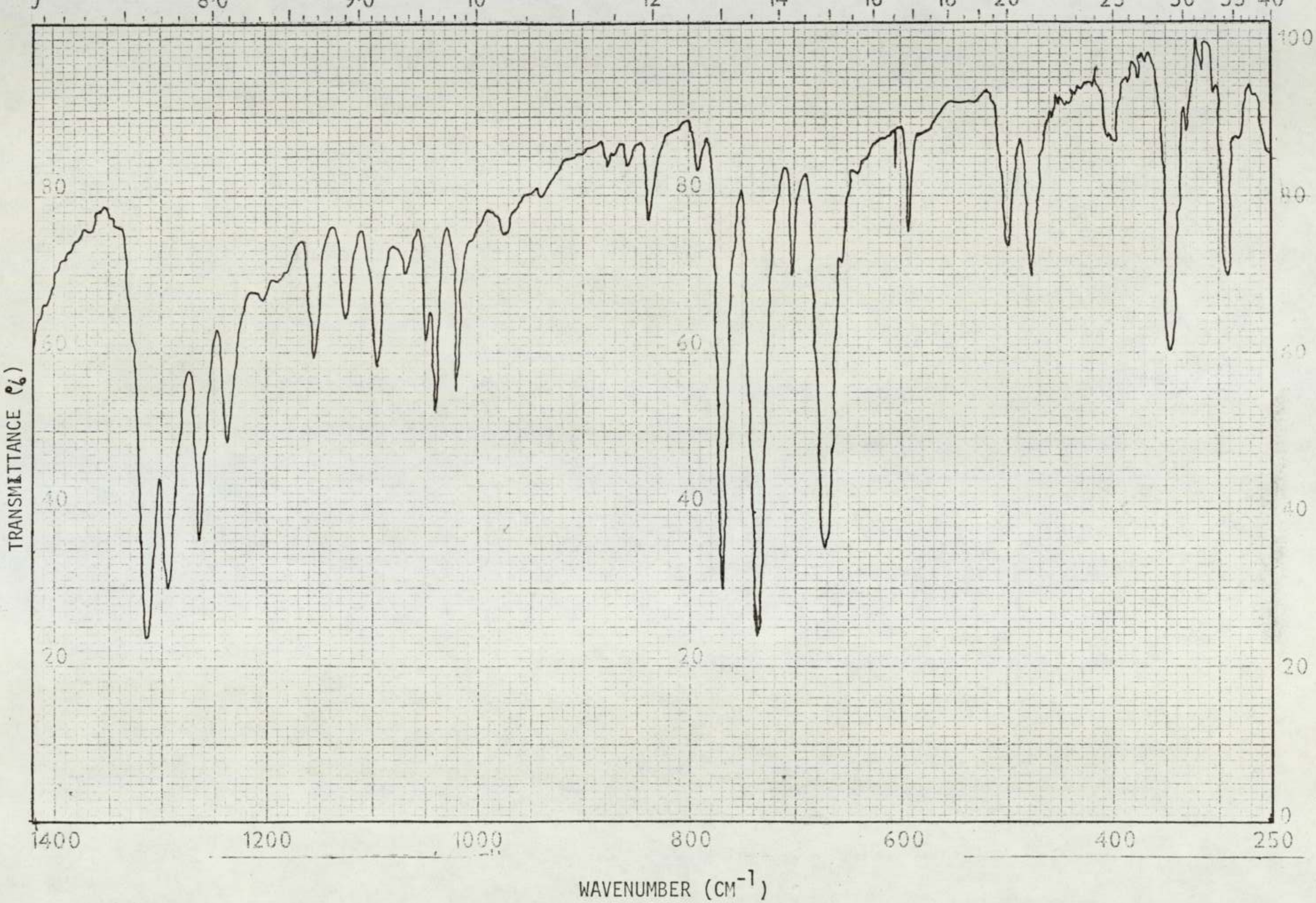


Figure 3. contd. Infra-red Spectrum of $[Pd(L-H)Cl]_n$ (KBr disc)

Figure 4. Infra-red Spectrum of [PdL_2Cl_2] (KBr disc)

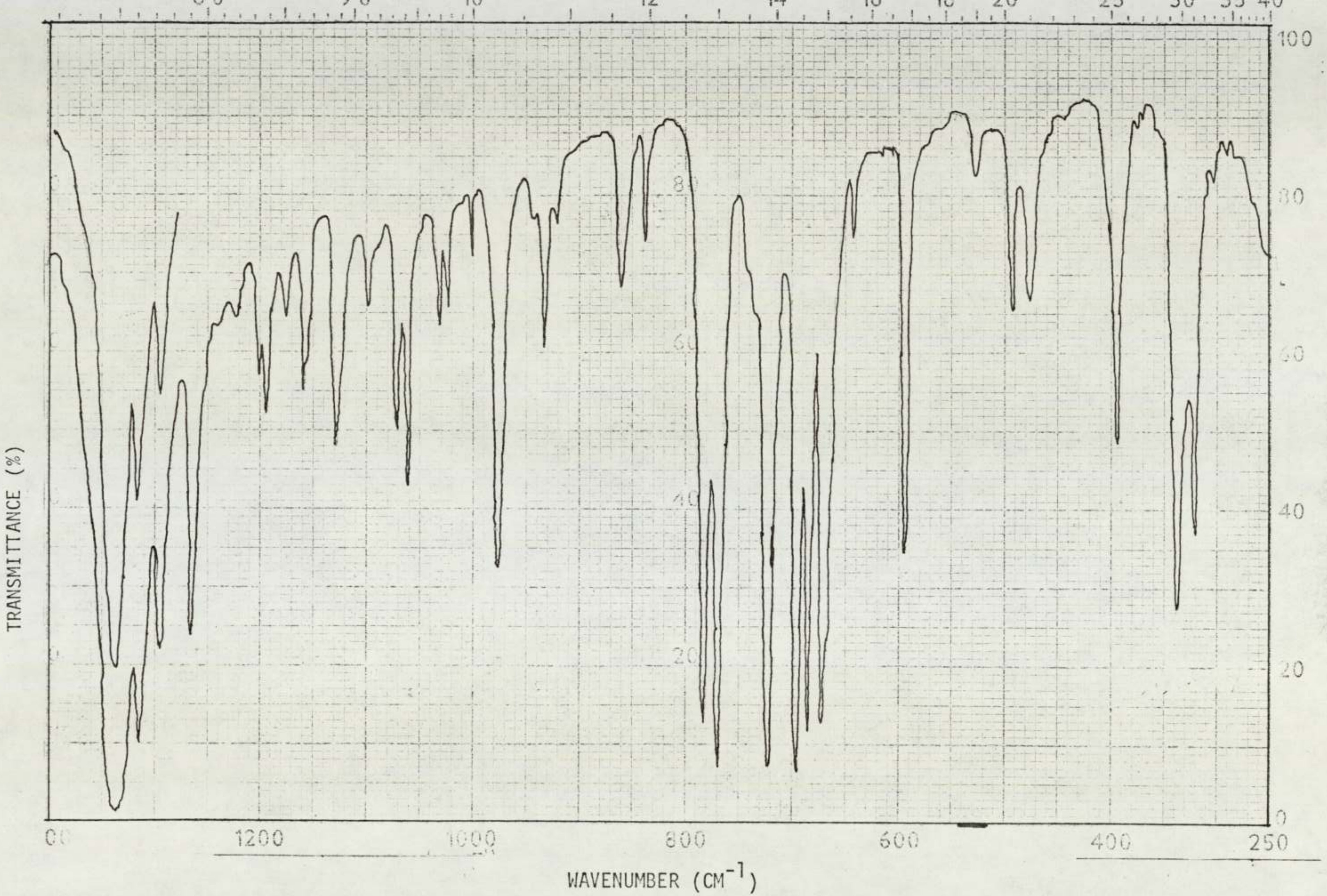


Figure 4. contd. Infra-red Spectrum of [PdL_2Cl_2] (KBr disc)

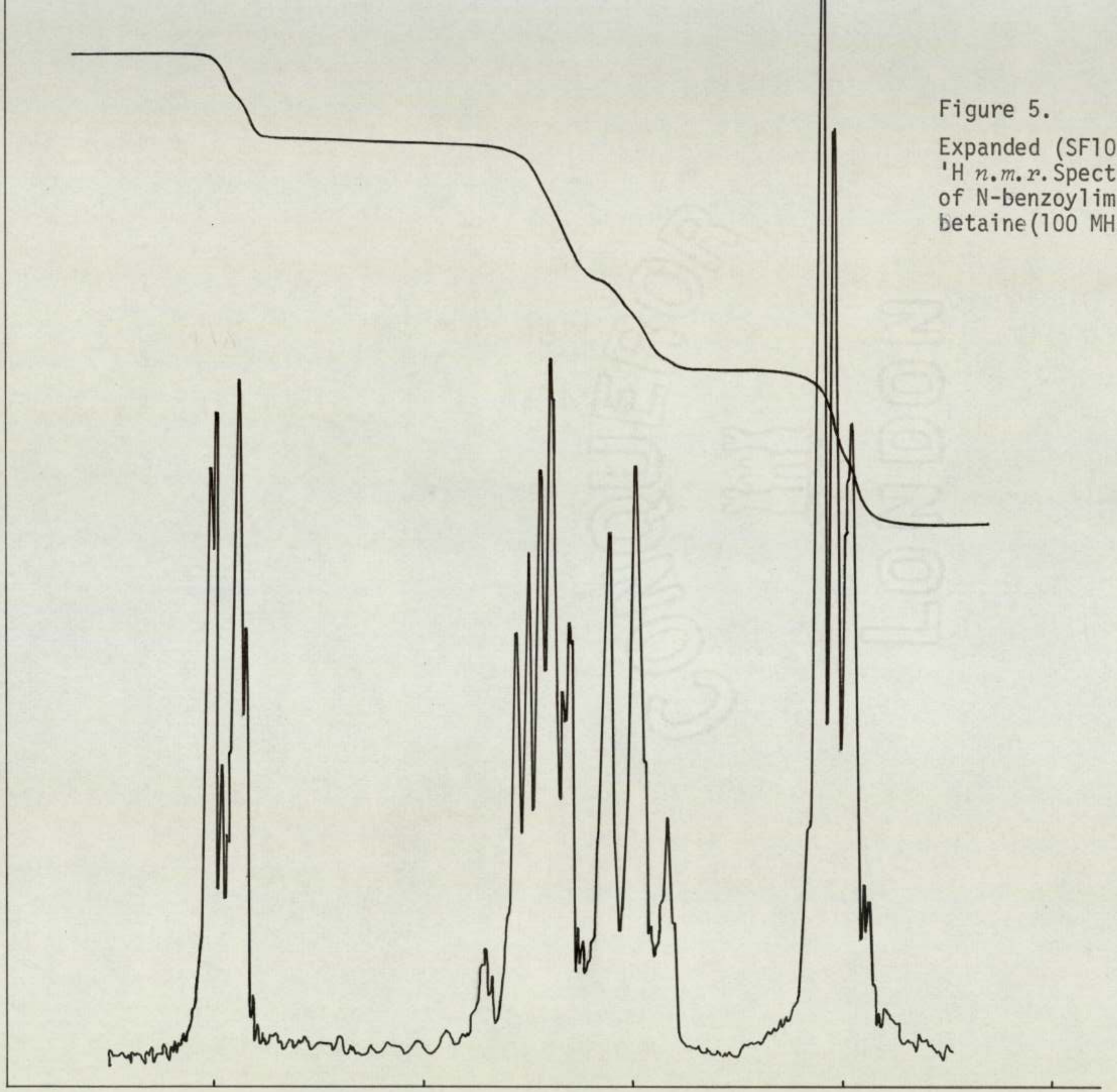


Figure 5.

Expanded (SF10)
'H *n.m.r.* Spectrum
of N-benzoyliminopyridinium
betaine(100 MHz)in DMSO.

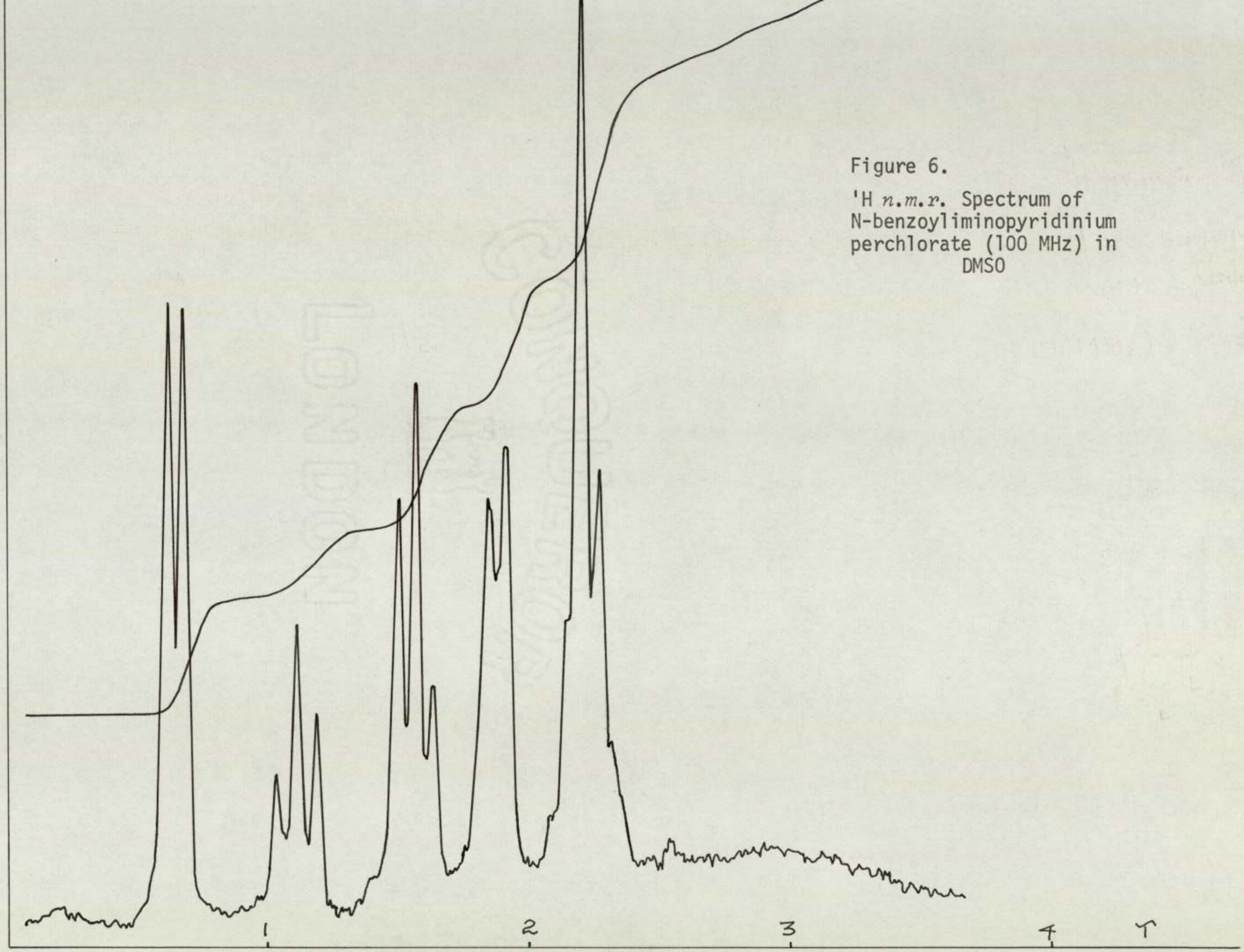


Figure 6.

'H *n.m.r.* Spectrum of N-benzoyliminopyridinium perchlorate (100 MHz) in DMSO

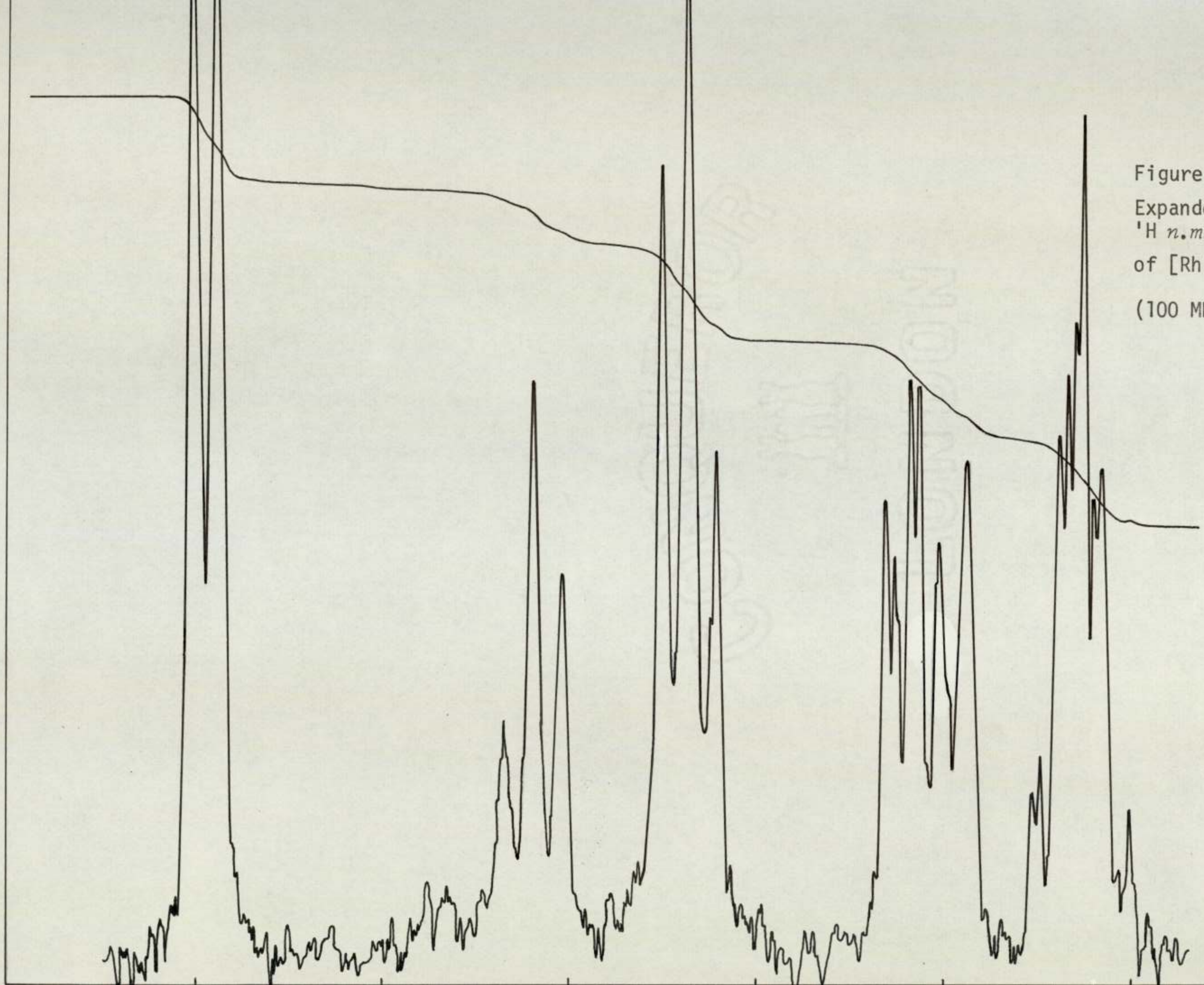


Figure 7.
Expanded (SF10)
'H *n.m.r.* Spectrum
of $[Rh(L-H)_2(H_2O)_2]^+Cl^-$
(100 MHz) in DMSO

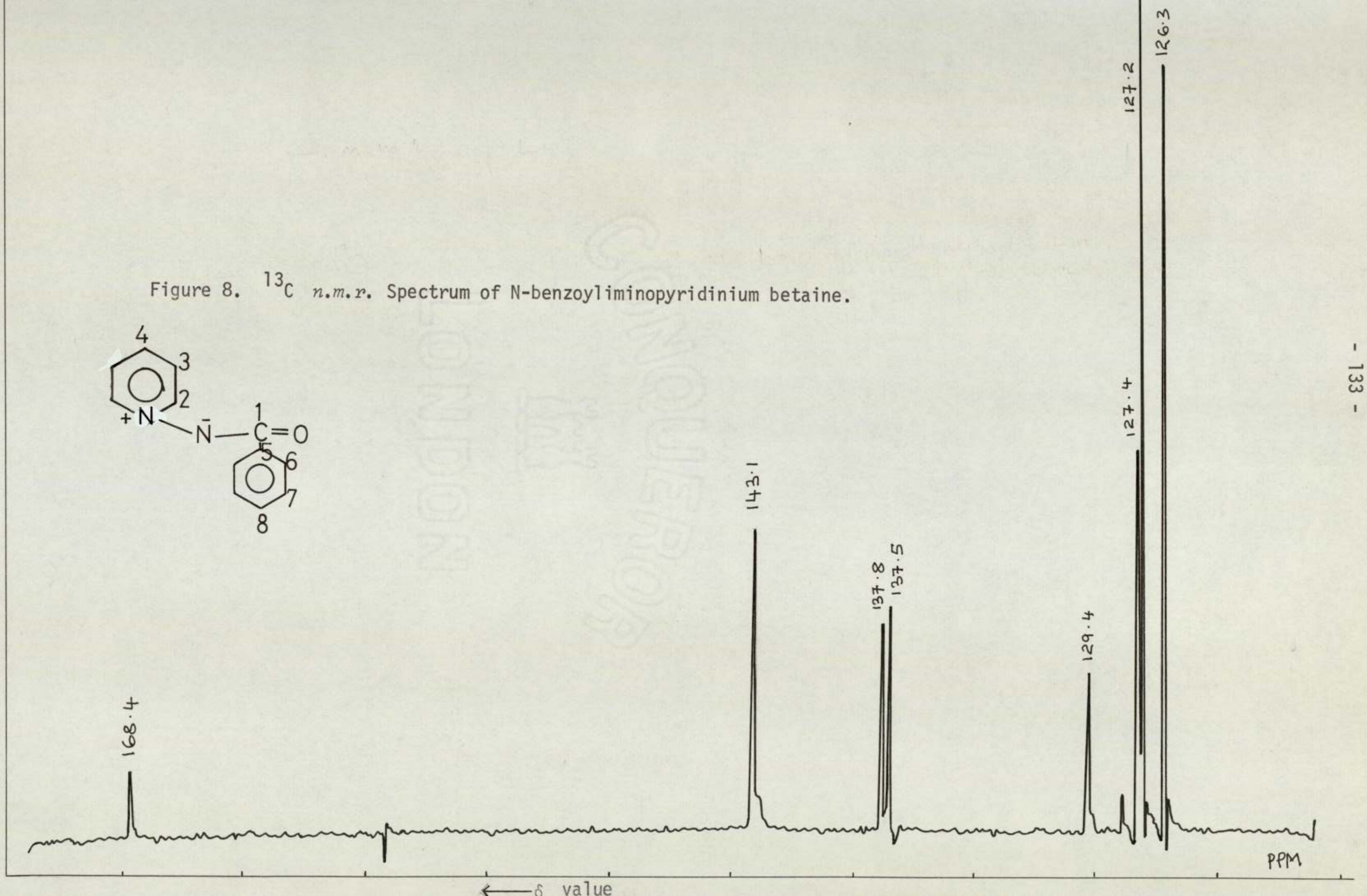


Figure 8. ^{13}C *n.m.r.* Spectrum of N-benzoyliminopyridinium betaine.

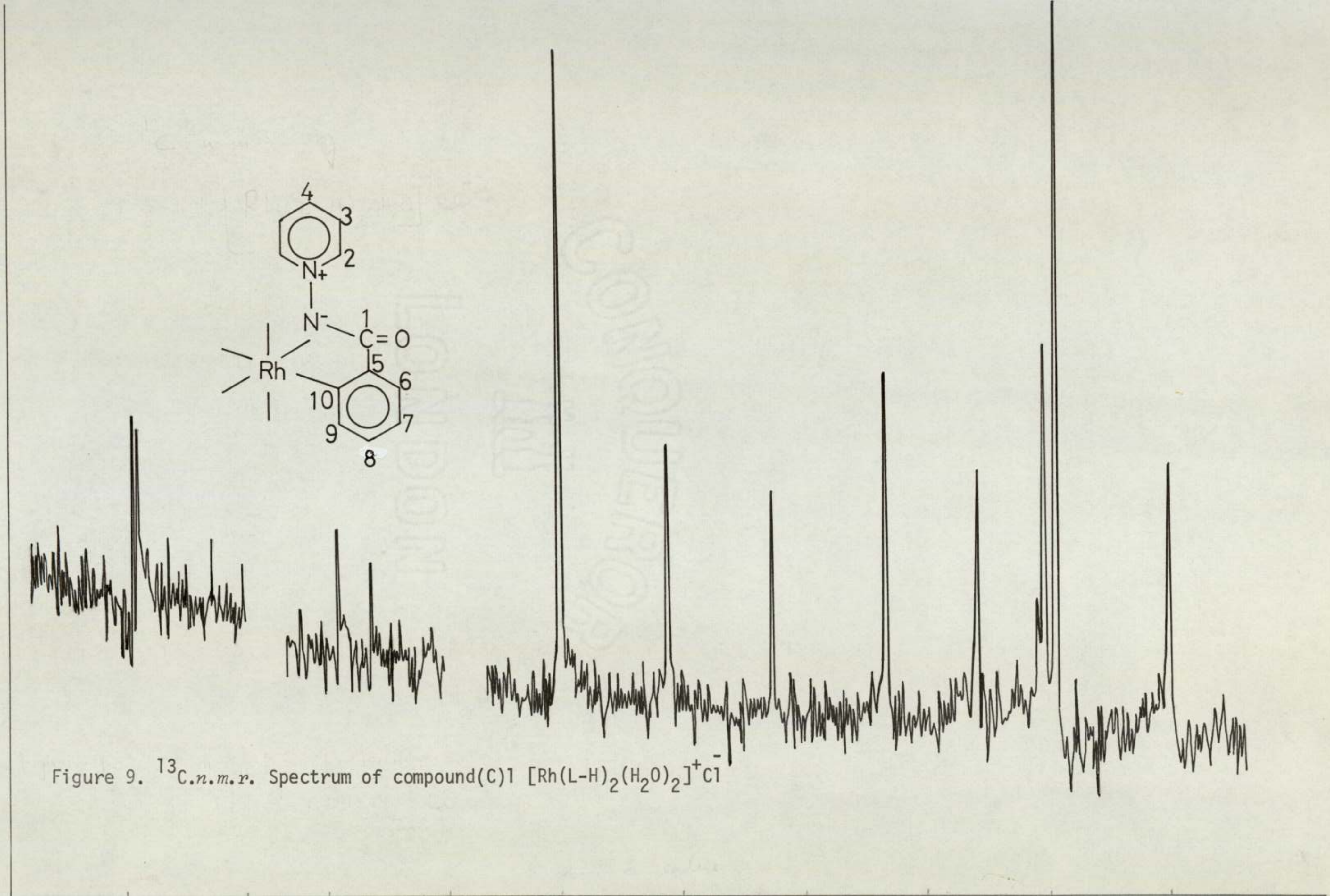


Figure 9. ^{13}C.*n.m.r.* Spectrum of compound(C)1 $[Rh(L-H)_2(H_2O)_2]^+Cl^-$

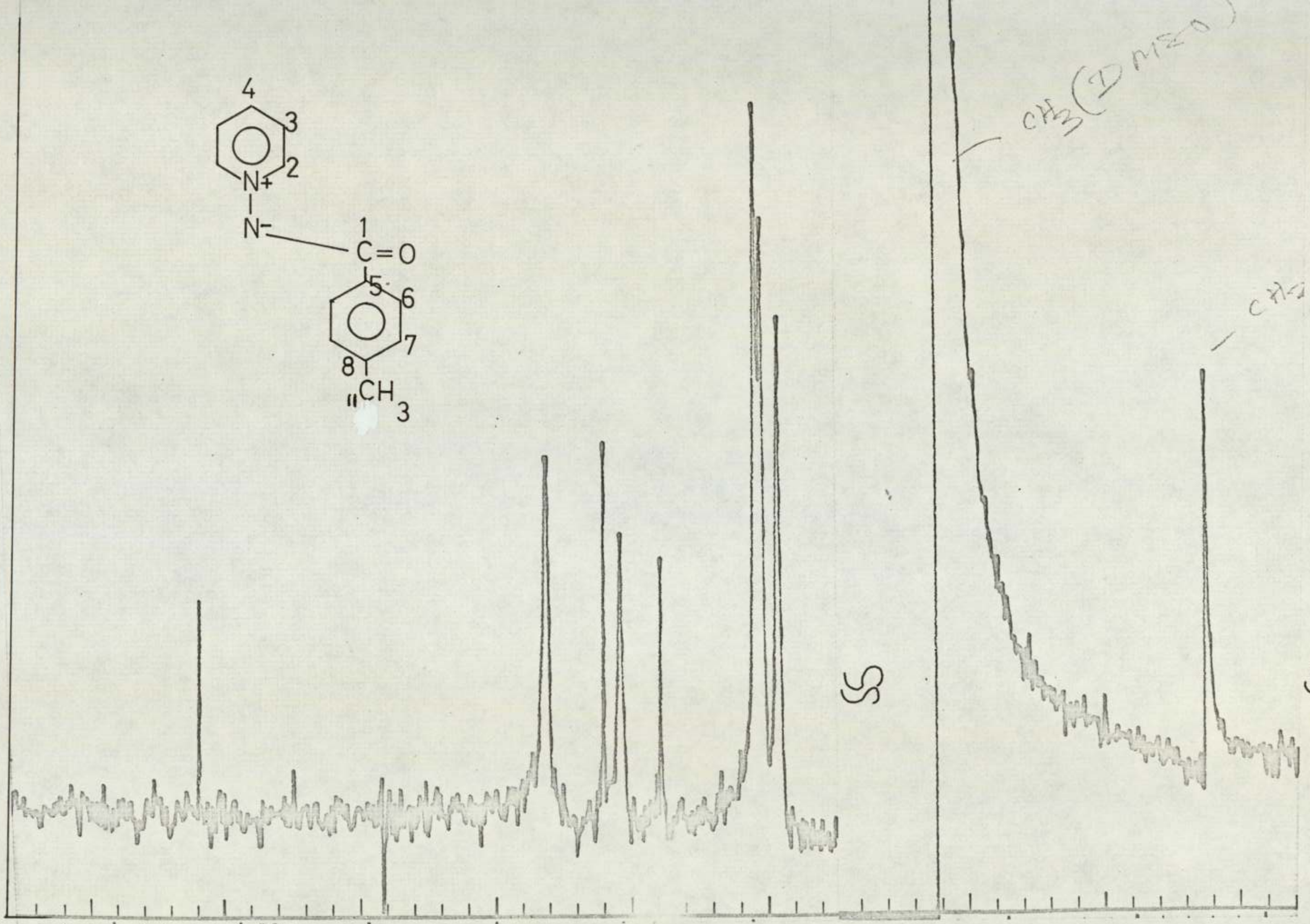


FIGURE 10. ^{13}C *n.m.r.* Spectrum of N-(*p*-toluoylimino)pyridinium betaine.

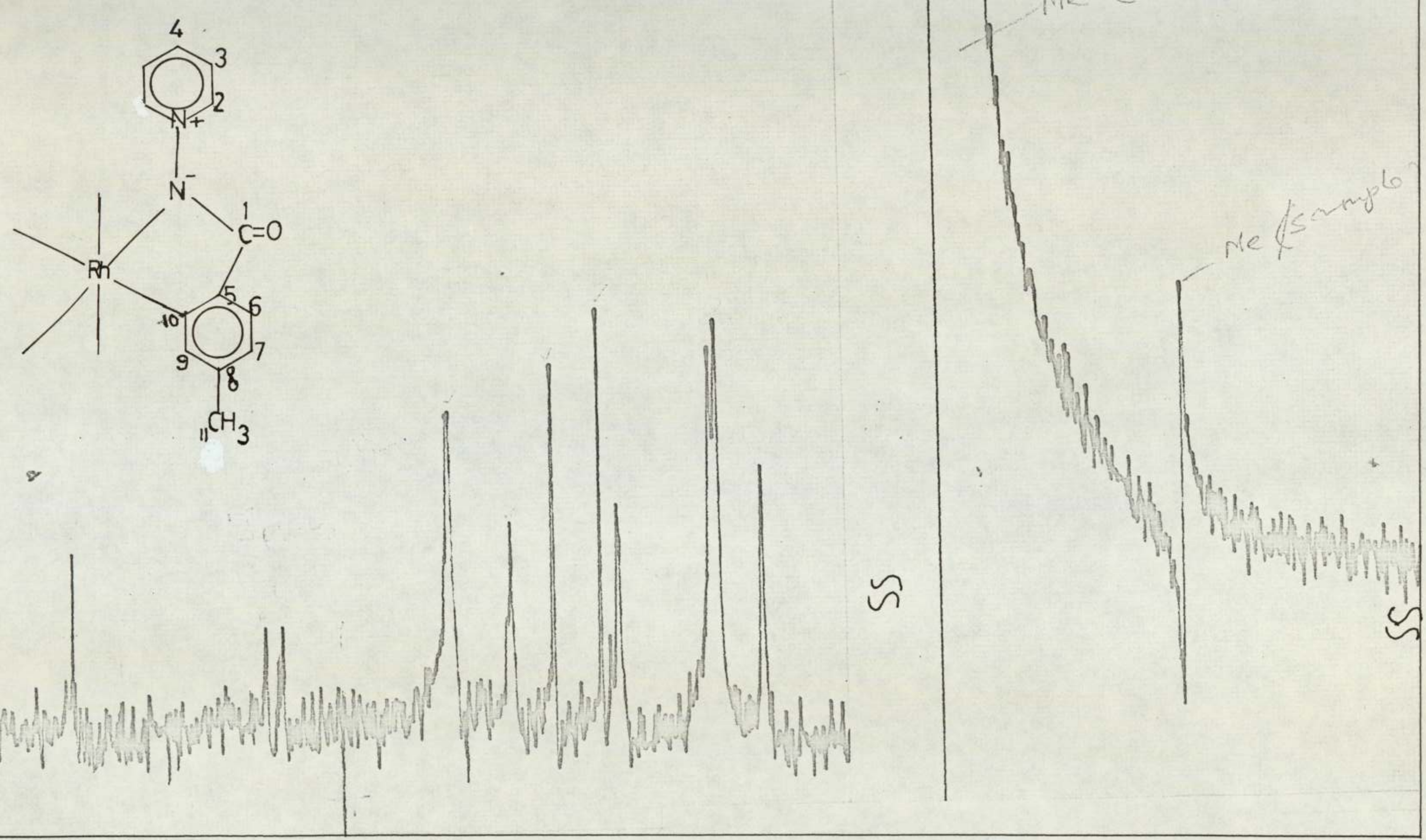


FIGURE 11. ^{13}C *n.m.r.* Spectrum of compound (C)5 $[Rh(L^{IV}-H)_2(H_2O)_2]^+Cl^-$

(D) DISCUSSION

All the complexes prepared were characterized by the combination of their elemental analyses, molar conductivities and spectroscopic data. The presence of water and trialkyl or aryl phosphine oxide in some complexes is supported by their characteristic absorptions in the infrared spectra.

(a) *Ortho*-metallation

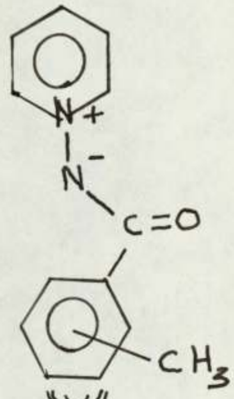
The analytical data for compounds derived from the reaction of palladium, platinum, rhodium and iridium salts with various resonance stabilized ylides suggested that, in some cases, the organic subtrate has lost one proton and a detailed investigation of the spectroscopic data of these complexes confirmed this loss and further indicates that it is an *ortho* hydrogen of the phenyl group that has been replaced by the metal. The spectroscopic evidence which argues rather convincingly for the presence of a sigma bond between the metal and a carbon atom on the phenyl ring of the resonance-stabilized ylides in these compounds thus providing further examples of the *ortho*-metallation reaction is presented below.

(i) Infrared Spectroscopic evidence

It is well known that mono- and 1,2-disubstituted benzenes have characteristic spectra in the γ(CH) region of the *i.r.* spectrum(211,227). *Ortho*-metallation of N-benzoyliminopyridinium betaine in the phenyl ring will generate a 1,2-disubstituted benzene and should lead to characteristic changes in the 680 - 800 cm^{-1} region; this criterion has also been used by others (105, 109, 111, 228), to confirm *ortho*-metallation of the phenyl group. It was observed that whenever the phenyl ring of the betaine is unaffacted during reactions such as N-protonation to form salts (Table 3) and donor ligand co-ordination through N or O (Chapter V) the two strong absorptions at 690 cm^{-1} and 715 cm^{-1} in the *i.r.* spectrum of the free ylide are hardly affected. Comparison of the *i.r.* spectra in this region with various other ylides and their salts suggests that these two strong absorptions are probably out of plane carbon-hydrogen bending modes and are associated with the presence of an unsubstituted phenyl ring in the compounds. Table 9 shows that in all cases where the analytical data suggest loss of a ligand proton, changes characteristic of the metallation reaction are noted in the infra-red spectrum; in particular two bands at ~ 690 and 715 cm^{-1} are replaced by one band at 740 cm^{-1}. Moreover when both metallated and unmetallated ligand molecules are present as in compounds (a) 4 and (b) 1, this fact is clearly evident from the *i.r.* spectrum. In the case of N-(*m*-toluoyl)iminopyridinium betaine L^{III}, the *i.r.* spectrum (Table 4) reveals strong absorptions at 855 cm^{-1} γ(=CH) 1 free hydrogen and at 740 cm^{-1}, γ(=CH) 3 free hydrogens, characteristic of a 1,3-disubstituted phenyl ring, whilst in its palladium complex (a) 5, these absorptions occur at 850 cm^{-1} γ(=CH) 1 free hydrogen, and at 760 cm^{-1} γ(=CH) 2 free hydrogens (Table 9), thus indicating the presence of a 1,2-4trisubstituted benzene. Similarly, in the case of compounds (a) 6, (c) 5, and (d) 2, the changes in *i.r.* spectra observed are consistent with the change from a 1,4-*di* L^{IV} to a 1,2-5-trisubstituted benzene.

Perhaps, less important, are the changes observed in the ν(CH) region of the *i.r.* spectra of these metallated complexes. The absorptions between 3100 cm^{-1} and 3000 cm^{-1} also undergo changes in its pattern (as compared with the free ligand and its salts) on metallation but it is less clear if these changes can directly be related to substitution of the phenyl ring.

The *ortho*-metallation reaction is generally accompanied by the formation of a chelate ring, and preferably a five membered planar ring. Inspection of structure "y" indicates that planar five membered chelate rings could be formed by co-ordination through the imino-nitrogen atom or *via* the carbonyl oxygen atom.



"Y"

It is observed that protonation on the imino nitrogen atom results in a considerable shift to higher energy of $\nu(CO)$(13) (see Table 3 and 4) and this is to be expected since protonation prevents the delocalization of the negative charge on to oxygen. On the otherhand, co-ordination of, say, cobalt(II) (Chapter V) *via* the carbonyl oxygen atom causes a lowering of $\nu(CO)$ compared to the free base. Since $\nu(CO)$ undergoes a shift to higher frequency in the compounds considered here, co-ordination *via* nitrogen is indicated. Further, the observed lowering of ν(N-----N) in the complexes as in the N-protonated ligands (Table 3 and 4), is consistent with co-ordination through nitrogen and also implies a weakening of the NN bond in the complexes.

The phosphorus ylide L^{II} also shows an increase in $\nu(CO)$ on complex formation in compounds (a) 8 and 9 thus implying co-ordination *via* the anionic carbon atom. Arnup and Baird(92) reported no example of *ortho*-metallation reactions with this ylide. Possibly the experimental conditions used here were more forcing.

Finally, none of the complexes showed any absorptions attributable to ν(M-H) in their *i.r.* spectra.

(ii) Nuclear Magnetic Resonance Spectroscopic evidence

As discussed in Chapter III, one of the most interesting features of the *n.m.r.* spectra of the pyridinium betaines is the occurrence of the resonance of the α-protons of the pyridine ring well separated downfield from other resonances in the aromatic region, a fact which enables us to perform meaningful integrations of the spectra. The *n.m.r.* spectra of the metal derivatives also revealed this feature and further, their spectra were similar to those of the protonated ylides. Thus the ratio of the low field doublet (J ≃ 7Hz) to the other aromatic resonances is 2:8 for the free ylide (N-benzoylimino pyridinium betaine) but in complexes (a) 1,2, (b) 2 and (c) 1 - 3 the ratio is 2:7. Further, the characteristic pattern of the pyridine resonances is unaltered thus indicating the loss of proton from the phenyl ring. In compound (a) 3, however, the ratio, 2:8 is seen which is consistent with the view that this is a simple co-ordination compound. In the cases where two ylide molecules are present, the results indicate that these molecules are magnetically equivalent. However, in the case of the iridium(III) complex (d) 1, it was not possible to carry out a meaningful integration of the spectrum based on the α-doublet, a result which supports the non-equivalence of the ligands implied by its formula.- The α-doublet of the pyridine ring undergoes a shift to low field on protonation (Table 6) of the imino-nitrogen atom of the ylide indicating that the α-protons become more deshielded. The same resonance undergoes a very slight downfield shift in the Pd(II) and Pt(II) complexes, but in complexes of the tripositive ions Rh(III) and Ir(III) the degree of deshielding produced is comparable to that produced by a proton. These observations confirm the *i.r.* indication that the imino-nitrogen atom is the point of attachment of the ligand to the metal ion and also that the ylide has undergone no major rearrangement on co-ordination and metallation. The 'H *n.m.r.* data also provided adequate proof of the metallation reactions with ligands L^{I}, L^{III} and L^{IV} (Table 11). It should be added that none of these complexes showed a signal due to a metal-bonded hydrogen below τ40.

In view of the excellent 'H *n.m.r.* spectra (Figure 7) given by the rhodium complexes and of the 100% abundance of $^{103}Rh(I = \frac{1}{2})$ the rhodium complexes of $C_5H_5\overset{+}{N}\text{-}\overset{-}{N}COR$(R = Ph, or $p$$CH_3\text{-}C_6H_4$) were selected for ^{13}C *n.m.r.* investigations which should provide unambiguous proof of the metallation reaction. Details are given in Table 12 and the spectra are illustrated in Figures 8,9,10 & 11.The proton decoupled spectra show a single sharp band for each magnetically distinct carbon atom, thus $C_5H_5\overset{+}{N}\text{-}\overset{-}{N}COPh$ shows eight resonances. The metallated complex has ten magnetically inequivalent carbon atoms and, indeed, the spectrum of complex (c) 1 (Figure 9) shows ten distinct resonances one of which has undergone a large downfield shift and is split into a doublet (J_{RhC} = 32.5 Hz). The deshielding clearly indicates that this is the resonance due to C_{10} (Table 12) and the splitting is of the order expected for J_{RhC}(153).

The data for L^{IV} and complex (c) 5 are very similar and it is noted that the resonance of the methyl carbon is a sharp singlet thus confirming that the two ligand molecules are magnetically equivalent.. However, a small splitting ($5H_2$) of the carbonyl resonance for compound (c) 1 is observed and in view of other evidence which suggests that the two ligand molecules are equivalent, the possibility of long distance coupling with ^{103}Rh seems to be a likely explanation. In the case of compound (c) 5, this splitting of the carbonyl carbon resonance is absent (Figure 11) and it may be due to an electronic effect of the methyl group.

Although experiments to assign all the peaks of the spectra were not quite successful, the assignments of C_1, C_5, C_{10} and C_{11} are most definite (Table 12). The assignment of C_1 and C_5 was established with accuracy by rapid pulsing which attenuates all signals relaxing slowly - mostly those arising from carbon atoms without any protons attached. The ^{13}C *n.m.r.* data of metal complexes available in the literature are very limited and further the variation of chemical shifts of carbons attached to metals is so wide. In view of these difficulties the assignments of resonances due to other carbons in the complex are only tentative but the appearance of a well separated low field doublet in the complexes but not in the free ylides most certainly indicates the presence of direct Rh-C σ-bond.

(iii) Mass Spectra

The mass spectra of the complexes show the characteristic fragmentation pattern of the parent ylides (Chapter III), thus confirming the presence of the unaltered ligand skeleton. Even more interesting is the fact that in complexes containing the metallated ligand the molecular ion peak of the ligand is extremely weak or even absent, and unlike in the free ylide, peaks at [M-2] and [M-3] can be seen in low abundance (15 - 25%). Further, a new peak at m/e 104 in the metallated complexes of N-benzoyliminopyridinium betaine is seen and is attributable to $[C_6H_4CO]^+$ the benzoyl fragment less a proton. The palladium complex (a) 1 shows peaks at m/e 223 and 225 and they could be due to the $[C_6H_4CONPd]^+$ fragment ion formed by loss of pyridine. However, the presence of ions corresponding for loss of a hydrogen from the phenyl group is not diagnostic of the presence of *ortho*-metallated ligands(108). These observations are thus in keeping with other indications that a phenyl proton has been lost.

(b) The Formation and Structures of the Complexes

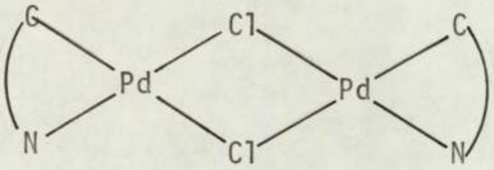
The metallation reactions described above occur smoothly in aqueous media and, in the case of the palladium complexes, it is possible by slight variation of the experimental conditions to isolate compounds (a) 3 and 4 which may be regarded as intermediates in the path to the final product {compound(a) 1} since it is possible to convert both to compound (a) 1.

$$PdCl_2 \ + \ 2L \longrightarrow PdL_2Cl_2 \longrightarrow [Pd(L\text{-}H)LCl] \longrightarrow [Pd(L\text{-}H)Cl]$$

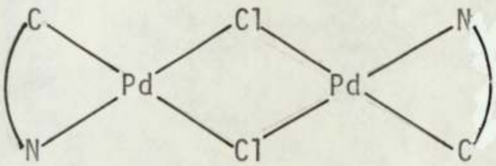
Therefore it appears that the first step is the formation of a simple co-ordination compound, the ligand then undergoes internal metallation. The imino nitrogen directs, by co-ordination, the palladium into the *ortho* position of the benzene ring. This is in direct analogy with the proposed mechanism for *ortho*-palladation(96) and *ortho*-mercuration (229) of azobenzene. As recently pointed out(100), if substituents in the phenyl ring are to be used to aid mechanistic studies the results will be more readily interpreted if an electron releasing substituent is *meta*-(i.e. *ortho or para*- to the position attacked by the metal). Although no rigorous mechanistic studies were carried out in this study, comparison of the rates of formation of complexes (a) 1, 5 and 6 showed the relative rates to be (a)5 >> (a)1 > (a)6. Thus the *meta*-methyl substituent gives the greater rate suggesting strongly that the metallation involves electrophilic attack by the palladium on the N-co-ordinated ligand.

The *ortho* hydrogen seems to be expelled in the form of a proton as is evident from the isolation of the protonated ligand from the reaction mixture and also from the fact that proton acceptors such as acetate ion etc. facilitate the reaction.

Compound (a) 1 is obtainable in greenish-yellow or bright yellow modifications (see experimental section) and the elemental analyses of both forms gave the molecular formula $C_{12}H_9N_2OPd$. Hence, the possibility of a *cis* - *trans* isomerism, as shown under, was considered,



cis

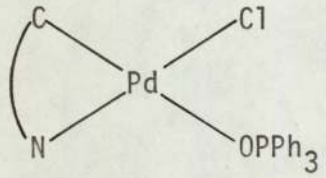


trans

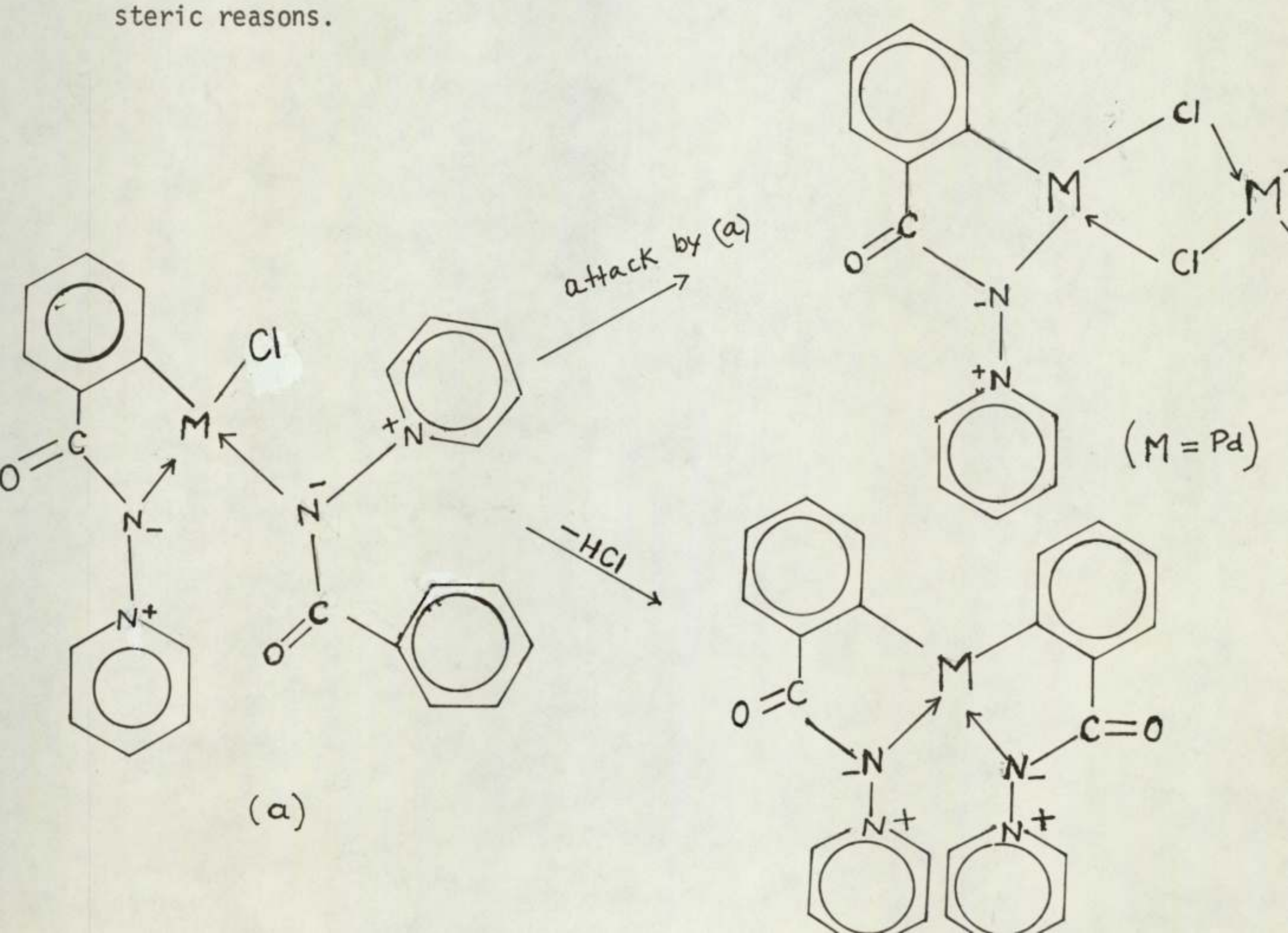
Infra-red and 'H *n.m.r.* spectra for these two forms would be expected to be different, yet the observed spectral differences between the forms were marginal. Further, the modification obtained is a function of crystallization solvent and the yellow form can trap solvent molecules such as $CHCl_3$, CH_2Cl_2 etc, (therefore more open structure?). In view of these observations it appears that they are better treated as dimorphic forms rather than isomers or differing oligomeric forms. The X-ray powder photographs of the two forms are different, but this would be expected whatever the difference between the material. Far infra-red spectra (400 - 200 cm^{-1}) of these two forms are also identical and show ν(PdCl) at 344 and 292 cm^{-1} and these values compare well with data for corresponding dimeric azobenzene derivatives(145) thus indicating that the complex (a) 1 is also a chlorobridged complex. That compound (a)2 shows no ν(PdBr) above 200 cm^{-1} is consistent with *di*-μ-bromo structure. The evidence for the presence of chloride bridges in analogous complexes is also good. The reaction of the chlorobridged complexes afford compounds {(e)1 and 3} which probably arise from a bridge-splitting reaction. The presence of triphenyl phosphine oxide in these complexes and others {(e)2, 4 and 7} is supported by their *i.r.* and mass spectra (230). In addition to the expected fragmentation pattern of triphenyl phosphine(230), peaks at m/e = 278 and 277 are also observed in their mass spectra. On accurate mass determination this proved to be the P^+ and $(P-1)^+$ ions of triphenyl phosphine oxide. Also, the expected peak at m/e = 218, corresponding to tri-*n*-butylphosphine oxide was observed in the mass spectrum of (e)5. However the mass spectra of neither triphenyl phosphine nor tri-*n*-butylphosphine showed any evidence of the presence of peaks corresponding to their oxides. Although the possibility that the starting materials might have been contaminated with the oxides may thus be ruled out, in the absence of any other investigations of these reactions, no conclusion may be made on the possible mechanism of formation of the oxides. It must be pointed out that the de-aerating of solvents used in this reaction was only attempted by rapidly passing a stream of dinitrogen through the solvent for 5-10 minutes and it may not have resulted in a complete displacement of dissolved oxygen in the solvent. Hence, the solvent could very well be the source of oxygen required for the reaction. It is possible, but not proved, that catalytic oxidation has occurred(231,233) and if this is so, it may occur before or after the bridge splitting reaction.

It is of interest to note that none of the metallated complexes underwent rupture of the metal-nitrogen bond on treatment with excess of Lewis bases and in this respect, these compounds differ from the well known azobenzene derivatives but are similar to NN-dimethylbenzylamine and 2-methoxy-3-NN-dimethylaminopropyl derivatives(145).

The triphenylphosphineoxide derivatives (e)1 and 2 of the palladium complexes show strong absorptions at 320 and 318 cm^{-1} respectively. On the basis of the higher *trans*-influence of a σ-bonded carbon compared with that of a nitrogen atom, these Pd-Cl stretching frequencies suggest that the chlorine is more probably *trans* to nitrogen than to carbon(145) as shown below

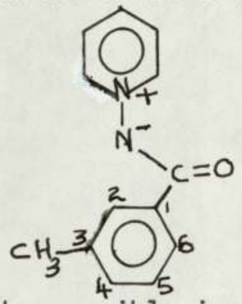


The single ν(PdCl) for compound (a)3 PdL_2Cl_2 suggests a *trans* dichloro-compound(99) and also this vibration at 346 cm^{-1} for compound (a)4 $[Pd(L-H)LCl]2H_2O$ implies the palladium-chlorine bond to be *trans* to nitrogen. Also, in the case of the platinum complex (b)1 $[Pt(L-H)LCl]2H_2O$, ν(PtCl) at 333 cm^{-1} may be indicative of the Pt-Cl bond being *trans* to nitrogen. No analogue of compound (a)1 was prepared in the platinum case. Presumably compound (a)1 arises *via* nucleophilic displacement of the non-metallated ligand from compound(a)4; this reaction is likely to be slow for platinum with the result that the internal metallation of the second ylide molecule may proceed at a rate which is at least comparable to that of the displacement reaction to give a reasonable yield of compound (b)2. 'H *n.m.r.* data indicate that the two metallated ligand molecules of this compound are equivalent and in view of the structure suggested for (b)1, *cis* Pt-C bonds may be present. However, the structure may be distorted from planarity for steric reasons.



Formation of compounds (e)2 and 4 may be envisaged as a nucleophilic displacement of L by triphenylphosphineoxide on structure (a) in the above scheme.

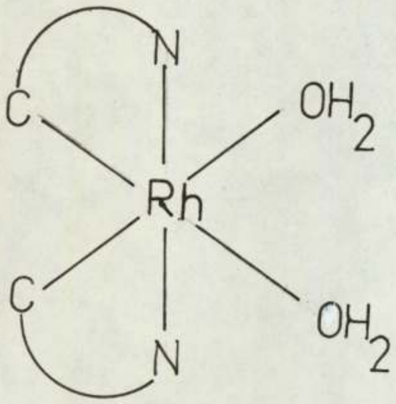
Available data suggest that the palladium compounds of other ylides (Nos.(a)5, 6, 7 and 8) are similar, structurally speaking to (a)1. Their *i.r.* and 'H *n.m.r.* data are given in Table 9 and 11; similar arguments hold in these cases too and therefore they do not merit a special discussion. N-(*m*-toluoylimino)pyridinium betaine (Structure XXXII) could, in principle, undergo metallation at position number 2 or 6.



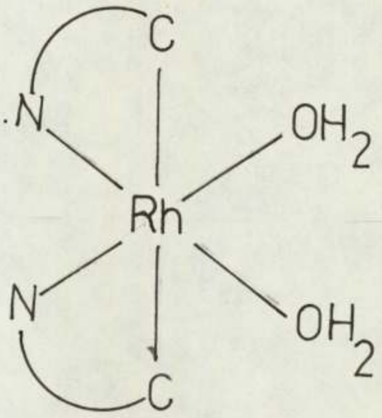
(XXXII)

Thus, two isomers would be possible in this case. However, only one isomer was isolated from the reaction with palladium dichloride and *i.r.* and 'H *n.m.r.* (τ 2.66, singlet, 1H) data indicate that it is the position 6 that has undergone metallation. An attractive explanation would be the steric hindrance at position 2 by the adjoining methyl group.

The evidence that the rhodium complex (c)1, is as formulated in Table 9 may be examined. The compound dissociates as a 1:1 electrolyte in water and the chloride may be replaced by bromide iodide or tetraphenylborate to afford other 1:1 electrolytes. The chloride, bromide and iodide are isomorphous (X-ray powder phorographs) and their *i.r.* spectra are substantially similar from 4000 - 200 cm^{-1}. The far infra-red spectra (400 - 40 cm^{-1}) show no absorptions attributable to ν(Rh-halogen). The near *i.r.* spectra show strong absorption between 3600 cm^{-1} and 3200 cm^{-1} and the absorptions are very broad suggesting extensively hydrogen bonded water molecules. In the case of tetraphenylborate salt, these absorptions become sharp and move slightly towards higher wave number indicating a lowering of the degree of hydrogen bonding. Removal of water in the complexes is impossible without decomposition of the complexes. Further the chloride and bromide give low conductivities in organic solvents. These observations can be reconciled in terms of strong ion-pair formation possibly involving hydrogen bonding which, from ν(OH), is undoubtedly of importance in the solid state. A *cis*-configuration for these complexes {(c)1,2,3 and 4} is likely on steric grounds and the facile reaction with 2,2'-bipyridyl to displace water and give $[Rh(L-H)_2(bipy)]^+Cl^-$ is consistent with this view. Both 'H and ^{13}C *n.m.r.* studies show the metallated ligands of (c)1 and 5 to be equivalent, thus, the Rh-C bonds must be mutually *cis* (XXXIIIA) or mutually *trans* (XXXIIIB).

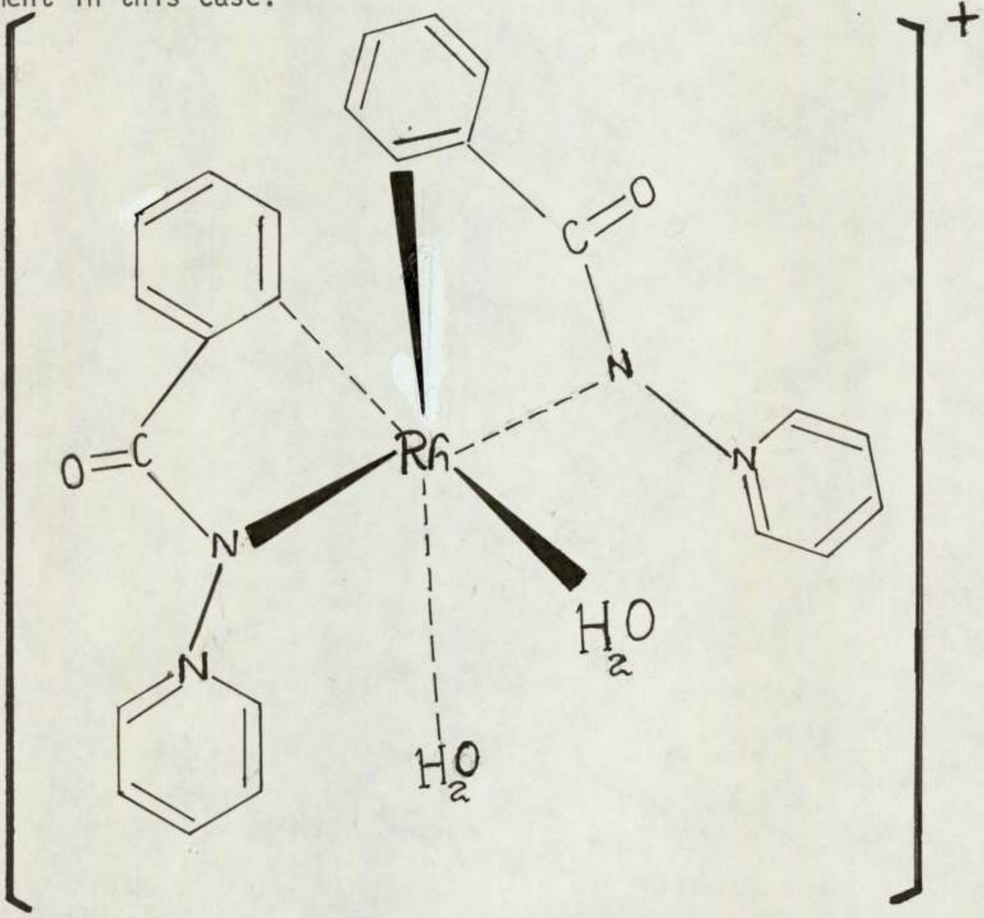


(XXXIIIA)



(XXXIIIB)

A choice between these two geometrical isomers is difficult in the absence of detailed X-ray structure analysis; however, it may be noted that a similar metallated bis-azobenzene complex of rhodium(III)(232) has been shown by X-ray diffraction from single crystals to possess *cis* Rh-C bonds and from the steric viewpoint, this seems a preferable arrangement in this case.

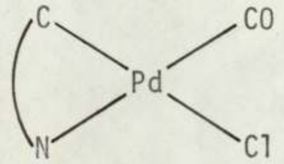


The iridium(III) complex (d) 1 is not isomorphous with the rhodium complex (c)1 and the 'H *n.m.r.* data strongly imply the two ligand molecules to be magnetically inequivalent. Its low conductivity in DMF indicates that it is a non-electrolyte and the *i.r.* band at 341 cm^{-1} may be assigned as ν(IrCl); thus the formulation $[Ir(L-H)_2Cl(H_2O)]3H_2O$ follows. Data available on this compound do not allow the stereochemistry about iridium to be deduced but in this case too *cis* iridium-carbon bonds seem plausible.

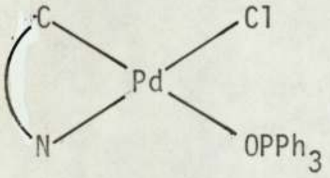
Both rhodium and iridium complexes {(c)1 and (d)1} react with phosphines to give phosphine oxide complexes {(e)5 and 7} in which the phosphine oxides have displaced the co-ordinated water. It is interesting to note that even refluxing these compounds in benzene, with 4-5 fold excess of the phosphine does not lead to displacement of the metallated betaine. It was observed that heating complex (c)1 produced a reversible colour change (to amber) involving a shift of ν(OH) to higher wave numbers in the *i.r.* spectrum in accord with disruption of the hydrogen bonded network of the lattice. The iridium complex {(d)1} also revealed a strong and broad absorption corresponding to ν(OH) from which it was difficult to distinguish between co-ordinated and unco-ordinated water. However, heating the complex to about 200^{o}C produced a red material accompanied by a loss in weight corresponding only to three molecules of water; further heating resulted in the decomposition of the complex. This clearly supports its formulation with only one out of four molecules of water co-ordinated to the metal. The change in colour observed during heating could be a consequence of distortions in the crystal lattice and hence in the symmetry of the molecule; thus facilitating a "charge transfer absorption".

(c) Reaction of the Complexes with Carbon Monoxide

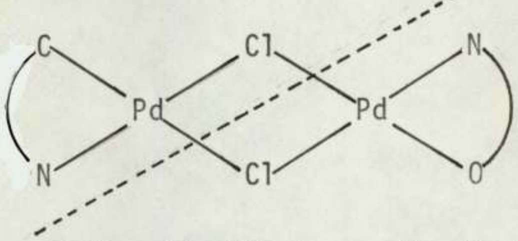
Attempted carbonylation reactions of the complexes to achieve CO insertion across the metal-carbon σ bonds were unsuccessful. However, Pd(II), Pt(II) and Ir(III) complexes react reversibly with carbon monoxide under ambient conditions. These reactions are basically ligand displacement reactions. In the case of the palladium compound side reactions leading to reduction to metallic palladium occur but it is possible to isolate materials of stoichiometry [Pd(L-H)(CO)X](where X = Cl,Br) and the compounds are non-electrolytes. The chloro-compound {(f)1} shows ν(PdCl) at 273 cm^{-1}, a result that implies that the chloride is *trans* to carbon.



This is, in contrast to the product derived from the reaction of Ph_3P with (f)1 which had a chloride ligand *trans* to nitrogen.



In the *di*-μ-chloro complex the ligands *trans* to carbon would be anticipated to be more labile.

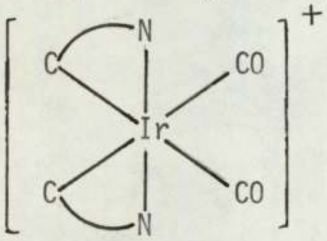


and hence substitution of the chloride *trans* to the Pd-C bond should be preferred. The reaction with triphenyl phosphine seems to be in keeping with this anticipation.

However the reaction with carbon monoxide was not simple since a coloured intermediate which could not be isolated pure was involved (see experimental section). Thus the products such as (f)1 should not be regarded as necessarily arising from a bridge-splitting reaction.

The platinum compound (b)1 reacts very slowly with carbon monoxide to give mixtures of products. Inseparability of products and the minute amount of materials available prevented any further studies. The *i.r.* spectrum showed a characteristic absorption at 2080 cm^{-1} ν(CO) and no sign of any CO-insertion reaction products.

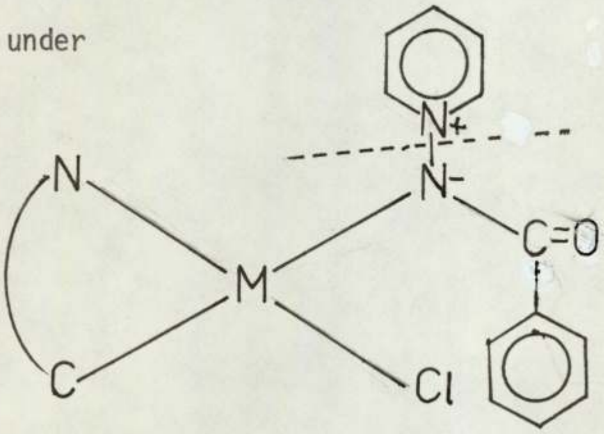
The rhodium complexes were totally unreactive to CO under ambient conditions. These complexes being co-ordinatively saturated, may show inertness due to lack of suitable reaction pathways. By marked contrast the iridium complex (d)1 underwent a smooth and quantitative reaction to afford $[Ir(L-H)_2(CO)_2]^+Cl^-$. Its far infra-red spectra reveal no bands attributable to ν(IrCl) and yet it has an extremely low conductivity in nitromethane in which the compound changes to yellow colour on dissolution. The low conductivity may be due to loss of CO accompanied by re-coordination of the chloride to yield a non-ionic product $[Ir(L-H)_2(CO)_2]^+Cl^-$ shows two ν(CO) absorptions at 2000 and 1985 cm^{-1} and hence a *cis*dicarbonyl arrangement is likely



The starting material (d)1 $[Ir(L-H)_2(H_2O)Cl]3H_2O$ may be regenerated by refluxing (f)3 in water thus showing the reversibility of the reaction with carbon monoxide. It was seen from following the gas uptake (see experimental section) that initially a maximum of approximately 4 moles of CO per mole of starting complex are absorbed and eventually 2 moles are released to give the final product. Consumption of 4 moles of CO may be accompanied by the disruption of the two Ir-N bonds thus making the betaine a mono-dentate ligand. However, this intermediate product could not be isolated pure and hence any comment on its structure is purely speculative. Thus, as in the case of the palladium complex the mechanism of carbon monoxide reaction here too is far from simple.

Although under the mild conditions used, the insertion of CO into the metal-C bond could not be achieved, the feasibility of this reaction is indicated by mass spectroscopic investigations of complexes (a) 4 and (b) 1. In both cases a fragment of stoichiometry $C_8H_5NO_2$ was found and its composition was established by accurate mass determination (m/e observed = 147.03270; m/e calculated = 147.03203). A peak corresponding to this fragment is present neither in the mass spectra of the free ylide(212) nor in the spectra of other complexes of this ylide. This ion is reasonably assumed to be derived from phthalimide which could possibly arise during pyrolysis as follows:

(a) rupture of the N-N bond of the non-metallated ylide in the complex as shown under

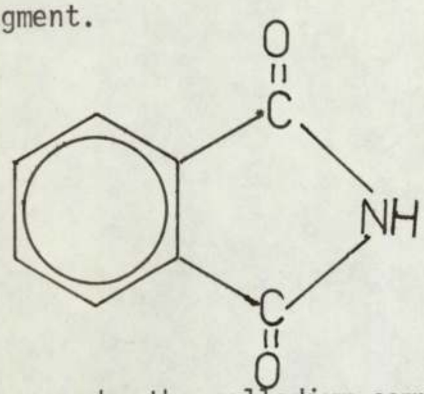


This process is much easier for the co-ordinated than for the free ylide (Chapter V).

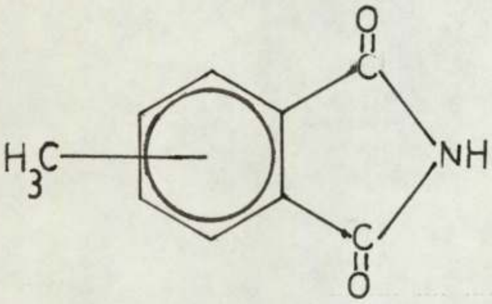
(b) removal of CO from NCOPh formed as above, either before or after re-arrangement to phenylisocyanate (Chapter V).

and

(c) carbonyl insertion across the metal-C bond followed by release of the organic fragment.

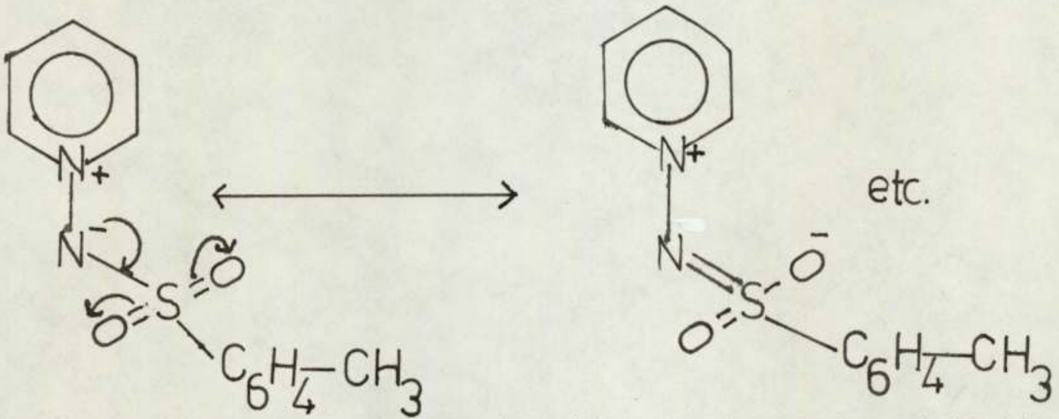


Interestingly enough, the palladium complexes of N-(*m*-toluoylimino) pyridinium {(a)5} and of N-(*p*-toluoylimino)pyridinium betaine {(a)6} also show a corresponding fragment in their mass spectra, at m/e 161. Its accurate mass determination established the composition as $C_9H_7NO_2$ (m/e (observed) = 161.047316; m/e (calculated) = 161.047675). This fragment presumably is methyl substituted phthalimide



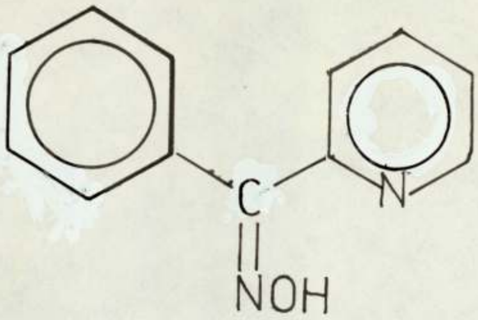
(d) Attempted *ortho*-Metallation Reactions

In view of the facile *ortho*-metallation observed with resonance stabilized carbonyl ylides, it was decided to test the applicability of this reaction to N-phenacylpyridinium betaine and N-(*p*-toluensulphonyl)iminopyridinium betaine, both of which conform to Cope's requirement for *ortho*-metallation. In the case of the former ligand, protonation was observed and in some instances reduction of the metal took place. A comparatively higher basicity of this ylide,pKa 9.7(12) perhaps explains its greater tendency for protonation. The metallation reactions with N-(*p*-toluensulphonyl)iminopyridinium betaine were also unsuccessful In this betaine, the greater delocalization of the negative charge on to the sulphonyl group would be expected to reduce donor ability of the imino nitrogen as compared with the situation in N-benzoyliminopyridinium betaine.

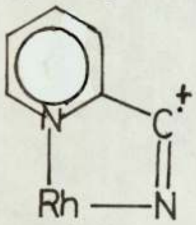


It is known that weak donation by nitrogen makes *ortho*-metallation more likely(111) since electrophilicity of the metal is not much reduced due to preliminary co-ordination *via* nitrogen. Thus, on these arguments this ylide would be expected to undergo *ortho*-metallation even more readily then N-benzoyliminopyridinium betaine. However, -SO_2- group being fairly bulky (compared to >CO group) may present steric hindrance to the reaction. On the other hand it may be that the conditions used in this study are not necessarily the right ones demanded by the reaction.

Phenyl-2-pyridyl ketoxime is isomeric with N-benzoyliminopyridinium betaine.



At the initial stages of the study of *ortho*-metallation reactions with N-benzoyliminopyridinium betaine, it was wondered if in fact, the ylide had isomerized to this ketoxime under the influence of metal salts. Hence it was decided to repeat some of these reactions using this oxime as the ligand. The products obtained were not at all like those from the reaction with N-benzoyliminopyridinium betaine. However, the products were interesting in that, some of them did not show the characteristic OH stretching frequency in the 3310 - 3460 cm^{-1} region in their *i.r.* spectra. In fact, there was no absorption even down to 2700 cm^{-1} assignable to ν(OH).(234). The γ(CH) region also did not show any indication of metallation of the aromatic rings. These compounds were too insoluble for *n.m.r.* examination and are formulated as given in Table 10 on elemental analysis and *i.r.* data. Phenyl-2-pyridyl ketoxime is known(234) to function as a chelating ligand co-ordinating through pyridine and oxime nitrogens either as a neutral molecule or as an anionic ligand by loss of the hydrogen bonded oxime proton. The infra-red data in Table 10 clearly indicate that the ligand is anionic in the case of the chloride and iodide complexes whilst in the case of the bromide, it is present in the neutral as well as anionic forms. The latter behaviour is also known for this oxime and other oximes(234). The 2-substituted pyridine ring should give rise to four ring stretching frequencies between 1640 and 1425 cm^{-1} and a band at 790 - 740 cm^{-1} originating from the four adjacent (ring) hydrogen wagging vibrations. The absorptions at 1587 cm^{-1}, 1558 cm^{-1}, 1471 cm^{-1} and 1431 cm^{-1} have been attributed(234) to the four pyridine ring bands in the free oxime. These bands have slightly moved to higher frequencies as expected due to the coordination of the nitrogen in the pyridine ring. The stretching frequency of -C=N- group has been observed(236) to be lowered by loss of hydrogen of the oxime function. This band which occurs at 1618 cm^{-1} in the free oxime(234) has disappeared in the chloride and iodide complexes and is probably within the pyridine ring bands. It was not possible to distinguish unequivocally ν(-C=N-) in the complexes although the weak absorption at 1630 cm^{-1} in the bromide complex may be attributable to ν(C=N) which is expected(234) to move to higher wave numbers on complexation of the oxime in the neutral form. The strongest absorption at 992 cm^{-1} in the oxime has been assigned to be ν(N-O) and has been found to shift to higher frequency (1073 - 1053 cm^{-1}) on co-ordination of the exocyclic nitrogen or to metals. Thus the most intense band at 1130 cm^{-1} in the *i. r.* spectra of all three complexes may be assigned to the N-O stretching frequency and the position of this band is consistent with the loss of hydroxyl hydrogen and co-ordination of the exocyclic nitrogen(236). The mass spectra of all three complexes showed a strong peak at m/e 207 which is assigned to the following fragment.



This observation too seems to support N-co-ordination. All three compounds (g)1(i)⟶(iii) are non electrolytes and are at least dimeric involving possibly halogen and oxime bridges.

The iodide was prepared by reaction of the chloride with excess of sodium iodide and this product also shows no trace of ν(OH) in its *i.r.* spectrum However, when the preparation of the analogous bromide was attempted using excess of lithium bromide, a different product was obtained which showed ν(OH) at 3640 - 3100 cm^{-1}. Presumably the deprotonated oxime has been reprotonated under the aqueous alcoholic conditions used.

This behaviour of the oxime is in contrast to the findings of Onoue *et al.*(137,237) who observed *ortho*-metallation on the phenyl ring of several aldoximes and ketoximes.

(E) CONCLUSION

It appears that the metallation reaction is general for compounds $\overset{+}{A}\text{-}\overset{-}{B}COAr$ (where A = $C_5H_5\overset{+}{N}$, $(CH_3)_3\overset{+}{N}$, or $Ph_3\overset{+}{P}$ and B = $\overset{-}{CH}$ or $\overset{-}{N}$). However, it does not occur for $C_5H_5\overset{+}{N}\text{-}\overset{-}{C}HCOPh$ and $C_5H_5\overset{+}{N}\text{-}\overset{-}{N}\text{-}SO_2.C_6H_4\text{-}CH_3$. Since reduction of the metal salt occurred in the case of these two ylides, it may be that use of other sources of metal such as $PdX_2(PhCN)_2$ etc., will help to avoid this reduction and further, under different conditions *ortho*-metallation may proceed smoothly. Infra-red and 'H *n.m.r.* have been extremely useful in the structure elucidation of these complexes; in particular, ^{13}C *n.m.r.* spectroscopy offers great potential as a structure tool for the study of metallated complexes.

Although carbon monoxide insertion was not achieved under the ambient conditions used, indications are that it will occur under suitable conditions such as high pressure and temperature. This possibility seems even more likely in view of the correct orientation (CO group being *cis* to M-C bond) of the carbon monoxide in the carbon monoxide adduct. Mechanistic studies in this area might throw light on the mechanism of formation of these complexes. Further, since mass spectra of some of these compounds reveal CO insertion reactions, a study of the thermolysis of these metallated complexes should provide interesting results on the influence of metal salts on the re-arrangement possibilities of the ylides.

CHAPTER FIVE

REACTIONS OF N-IMINOPYRIDINIUM BETAINE WITH SOME FIRST ROW-TRANSITION METAL SALTS, SILVER$^{(I)}$ AND MERCURY$^{(II)}$ SALTS

(A) INTRODUCTION

Until relatively recently the reactivities of organonitrogen compounds having N-N and N=N bonds towards transition metal compounds were largely unexplored. There are a number of scattered reports describing novel complexes produced during reactions of transition metal derivatives with organic azides, azines, azo-compounds, diazonium salts and other organic systems with N-N or N=N chromophores(238, 239). Several compounds involve stabilized nitrene fragments while others have nitrene precursors (240 - 244). The significance of the above reactions for synthetic and mechanistic inorganic chemistry is immense. The cleavage of nitrogen-nitrogen bonds by transition metal derivatives might be mentioned as of specific current interest to the dual problems of dinitrogen co-ordination (245, 246) and atmospheric nitrogen fixation(247).

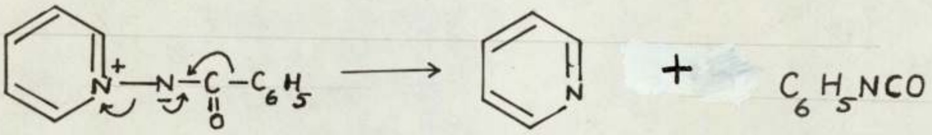
In reactions with transition metal derivatives these organonitrogen compounds may act both as ligands and redox-reagents(239) and in the latter case the fate of the organic substrate is often a mystery. The decomposition of these organonitrogen compounds has been found to be catalyzed by several transition metal derivatives(220b) and the final products from reactions with metal carbonyls have often been isocyanate complexes, e.g. (248)

$$[C_5H_5Fe(CO)_3]^+ + 2N_2H_4 \longrightarrow C_5H_5Fe(CO)_2(NCO) + NH_3 + N_2H_5^+$$

Among the first row transition metals copper is well known(224) to be an effective catalyst for the decomposition of various organonitrogen compounds such as diazoalkanes, diazocarbonyl compounds and sulphonyl azides. Cadogan and Gosney (252) recently claimed that the use of copper led to a lowering of the decomposition points of the nitrene precursors such as ethyl azidoformate, cyanogen azide and toluene-*p*-sulphonyl azide, thus catalyzing the reactions with triphenylarsine to give the little known N-substituted triphenylarsinimines. A copper-nitrene intermediate has often been proposed in these reactions.

Several thermally stable ylides have been investigated for their decomposition in the presence of Lewis acids with filled or partially filled 3*d* shells. Thus dimethylsulphonium phenacyclide has been found (249) to be catalytically decomposed to yield tribenzoylcyclopropane when refluxed in benzene or chloroform with anhydrous cupric sulphate. Here too intermediacy of a copper-complexed carbene($Ph.CO.CH = Cu^{2+}$) is assumed.

Because of the formal similarity to the type of intermediate involved in the Curtius, Schmidt, Hoffmann and Lossen rearrangements, thermolysis of acylimines has been the subject of several investigations. Thus, trimethylamine-benzimide which is stable upto its melting point (169 - 170°C) has been shown (190,209,250) to undergo decomposition at temperatures slightly higher (185 - 200°C) than its melting point, with evolution of trimethylamine and phenyl isocyanate, the latter trimerising to triphenyl isocyanurate. By carrying out the thermolysis in the presence of *p*-bromoaniline, phenyl isocyanate has been "trapped" in the form of NN'-di-*p*-bromophenylurea. Similarly, pyrolysis of trimethylamine methacrylimide $CH_2 = CCH_3CO\overset{-}{N}-\overset{+}{N}(CH_3)_3$ either at atmospheric pressure or at reduced pressure but at elevated temperatures (above the m.p.) has yielded (191) isopropenyl isocyanate. Whether these carbon to nitrogen re-arrangements proceed in a concerted fashion or by a nitrene intermediate has not been established firmly although Wadsworth(251) has presented evidence for a concerted path in the pyrolysis of a cyclic aminimide. Ikeda *et al*(212) in their discussion of the mass spectral fragmentation of N-benzoyliminopyridinium betaine refer to some unpublished results where they claim that pyrolysis of this betaine at 190 to 200°C gave pyridine and phenyl isocyanate, the latter of which was "trapped" as diphenylurea. By analogy to the Curtius re-arrangement, the mechanism of this thermolysis is assumed to proceed through an N-N bond cleavage with concomitant migration of a phenyl group as shown under.



The yields of isocyanate prepared by thermolysis of aminimides are generally very high (50 - 100%)(13). Thus, these reactions offer a convenient synthesis of organic isocyanates and hence have attracted the attention of chemists, both academic and industrial. These reactions pose fundamental problems and they have striking commercial potentialities.

The first-row transition metals are characterized by their ability to form a wide range of co-ordination complexes in which co-ordination numbers 4, 5 and 6 predominate. The copper$^{(II)}$ ion is a typical transition metal ion in respect of the formation of co-ordination complexes, but less typical in its reluctance to take up a regular octahedral or tetrahedral stereochemistry. The $3d^9$ outer electron configuration of the copper$^{(II)}$ ion lacks cubic symmetry and hence yields distorted forms of the basic stereochemistries. The range of stereochemistries which have now been characterized for the first row-transition metal complexes is wide.

The properties of a metal complex are dependent on the nature of the metal ion and also of the ligands. The variation in metal ions is considerable; on the other hand, the variation in ligands is virtually limitless because of the extent of organic chemistry available for the synthesis of suitable molecules. Many types of ligands are known(213) and the properties of their derived metal complexes have been investigated. The description of the metal-ligand bonding in transition metal complexes presents a continuing problem for inorganic chemists. Theoretical work in this area has progressed from the valence bond approach of Pauling through crystal field theory to the current molecular orbital appraoch. Our qualitative understanding of bonding in these complexes can now be described as quite good.

While the foundation of modern coordination chemistry has often been attributed to Werner(214) the elucidation of the stereochemistry and the structural determination of many complexes has only been accomplished during the past 10 to 15 years. The use of modern techniques such as X-ray crystallography, magnetic susceptibility measurements, vibrational and electronic spectroscopy have made this possible. Of major importance in a transition metal coordination complex is the presence of an incomplete *d*-shell in which the energies of the *d*-orbitals are split, the magnitude of splitting being determined by the ligand field strength and the stereochemistry of the complex. These properties are reflected in their electronic absorption spectra and magnetic moments and these two alone have proved invaluable tools in the elucidation of the stereochemistry of inorganic complexes. Apart from any possible effects that first row-transition metal salts might have on the decomposition and rearrangements of N-benzoyliminopyridinium betaine, it was equally tempting to explore the co-ordination behaviour of this ylide towards some of the first row-transition metal salts such as $Cu^{(II)}$, $Co^{(II)}$, $Fe^{(II)}$ and $Ni^{(II)}$. Further, in view of the well-known mercuration reactions of aromatic compounds, it was decided to extend this investigation on to mercury$^{(II)}$ and silver$^{(I)}$ salts as well, in the hope that these salts might bring about substitution reactions on the aromatic rings. Indeed, such a substitution leading to an *ortho*-metallated product has recently been achieved(253) with a mercury$^{(II)}$ salt on azobenzene.

(B) EXPERIMENTAL

Reactions of N-benzoyliminopyridinium betaine with metal salts

(1) With Copper$^{(II)}$ Salts

(a) Reaction with anhydrous copper chloride

Copper chloride dihydrate$^{(II)}$ (0.085g, 0.5m Mol) was dried in the oven at 135°C for 2 hours, until the last trace of green colour disappeared. Anhydrous copper chloride thus prepared was then covered with dry nitromethane (20 ml) containing the ylide (0.620g, 3m Mol) and the mixture was refluxed under N_2 and anhydrous conditions for 1 hour. On cooling an amber coloured product separated out (0.32g) and was filtered and washed thoroughly with hot chloroform and cold diethyl ether. All attempts to recrystallize the product from various solvents failed due to the rapid decomposition in solution.

i.r.(KBr disc) spectrum: 2175 cm^{-1}(doublet), ν(NCO); 1615 cm^{-1} (v.s.br) ν(> CO); 1335 cm^{-1} (v.s.br) ν(N$\underline{-----}$N); 720 cm^{-1} and 695 cm^{-1} γ(CH)Ph; 775 cm^{-1} and 675 cm^{-1} γ(CH)Py.

Repetition of the above reaction using anhydrous cuprous chloride (CuCl) also produced a similar impure complex whose *i.r.* spectrum too revealed a doublet centered at 2170 cm^{-1} besides the absorptions characteristic of the ylide. The reaction of anhydrous cupric chloride when carried out under similar conditions in ethanol produced a similar complex showing a doublet absorption at 2170 cm^{-1} in its *i.r.* spectrum. However, in ethanol the reaction was not reproducible.

After isolation of the copper complex, the filtrate from the first reaction described above, was concentrated to yield a brownish residue which was washed with water (15-20 ml) to remove any copper compounds and then recrystallized from ethanol to yield colourless solid (∼0.2g) which had m.p. 282 - 283^{o}C. This compound was identical (mixed m.p. and infrared spectrum) with an authentic sample of triphenyl isocyanurate (1,3, 5-triphenyl-s-triazine 2,4,6 trione) ν(CO) (Nujol mull) = 1711 cm^{-1}(v.s.) {Lit: (209) m.p. 281 - 283^{o}C}

N-(*m*-toluoyl)iminopyridinium betaine and trimethylamine benzimide also produce impure copper complexes when reacted with $CuCl_2$ in CH_3NO_2

under analogous conditions and their *i.r.* spectra (KBr disc) revealed doublets corresponding to ν(NCO) at 2180 cm^{-1} and 2190 cm^{-1} respectively.

(b) *Thermolysis of N-benzoyliminopyridinium betaine in the Presence of p-Bromoaniline*

N-benzoyliminopyridinium betaine (0.67g, 3.4m Mol) and *p*-bromoaniline (0.58g, 3.4m Mol) were intimately mixed and heated to 200°C (bath temperature) in a stream of dry nitrogen. The melt evolved pyridine vapour which was passed into a solution of concentrated hydrochloric acid. The temperature was maintained at 200°C for a further 15 minutes during which the melt solidified. The mixture was then cooled in a stream of nitrogen. Trituration of the residue with cold ethanol (6 ml) yielded a solid (0.45g) which crystallized from acetic acid as plates;

m.p. 315°C(d.) {Lit:(209) 315°C(d.) for NN'-di-*p*-bromophenylurea}

i.r. (KBr disc): ν(NH) 3300 cm^{-1} (m-br); ν(CO) 1635 cm^{-1} (v.s.).

Found: C,42.32%; H,2.83%; N,7.61%; Br,43.67%.

$C_{13}H_{10}Br_2N_2O$

Requires: C,42.18%; H,2.70%; N,7.57%; Br,43.22%.

Evaporation of the HCl solution yielded pyridinium chloride identified by m.p. and *i.r.* spectrum.

(c) Reaction of N-benzoyliminopyridinium betaine with anhydrous cupric chloride in the presence of p-bromoaniline

A mixture of N-benzoyliminopyridinium betaine (1.98g, 10m Mol) *p*-bromoaniline (3.44g, 20m Mol) and cupric chloride dihydrate (0.85g, 5m Mol) (dried as before) in nitromethane (50 ml) was refluxed for 1.5 hours under dinitrogen and anhydrous conditions. On cooling to room temperature a blackish-brown residue and a dark green solution were obtained. After filtration to separate the blackish-brown residue the filtrate was concentrated and on addition of dry benzene yielded a green product which was unstable to moisture. The green product was washed with dry benzene, ether and dried at 40°C in a stream of nitrogen. This compound shall be referred to as "compound(1)."

Found: C,43.09%; H,3.48%; N,8.09%; Cl, 20.91%; Cu,19.36%.

$C_{12}H_{10}Cl_2CuN_2O$ = $[CuLCl_2]$

Requires: C,43.31%; H,3.01%; N,8.42%; Cl,21.32%; Cu,19.11%.

The filtrate, after isolation of "compound(1)" was concentrated to dryness in a rotatory film evaporator to obtain a dark tarry mass which crystallized out on trituration with cold ethanol. This product (0.5g) on recrystallization from acetic acid/animal charcoal gave colourless plates, m.p. 315°C(d.) and its infra-red spectrum was identical with that of NN'-di-*p*-bromophenylurea isolated from the previous reaction.

(d) Reaction with hydrated copper$^{(II)}$ chloride

Copper chloride *di*hydrate (0.34g, 2m Mol) was dissolved in dichloromethane (75 ml) and the solution was refluxed for 1.5 hours after addition of N-benzoyliminopyridinium betaine (2.4g, 12m Mol). On concentration and addition of ether a greenish-yellow precipitate was formed. The precipitate("Compound(2)")was filtered, washed with ether and dried *in vacuo* over P_4O_{10}.

Found: C,51.21%; H,4.01%; N,9.98%; Cl,12.92%; Cu,11.89%;

$C_{24}H_{24}Cl_2CuN_4O_4$ = $CuL_2(H_2O)_2Cl_2$

Requires: C,50.82%; H,4.27%; N,9.88%; Cl,12.51%; Cu,11.30%.

(e) Reaction with copper$^{(II)}$ nitrate

A hot solution of copper nitrate *tri*hydrate, $Cu(NO_3)_2 3H_2O$ (0.242g) 1m Mol) in ethanol (30 ml) was added with stirring to a hot solution of N-benzoyliminopyridinium betaine (1.200g, 6m Mol) in ethanol (40ml) and the resultant mixture was heated under reflux for 1 hour. A green product separated on cooling. The green product("Compound(3)") was filtered, washed with ethanol and dried *in vacuo* over P_4O_{10}.

Found: C,40.07%; H,3.57%; N,13.22%; Cu,11.87%.

$C_{18}H_{21}CuN_5O_{10.5}$ = $CuL_{1.5}3H_2O(NO_3)_2$

Requires: C,40.11%; H,3.90%; N,13.00%; Cu,11.78%.

(f) Reaction with copper$^{(II)}$ perchlorate

Copper$^{(II)}$ perchlorate *hexa*hydrate (0.37g, 1m Mol) was dissolved in ethanol (30 ml) and to the resultant solution, N-benzoyliminopyridinium betaine (1.20g, 6m Mol) was added with vigorous stirring; immediately a greenish-blue product ("Compound(4)") separated out and it did not change on subsequent refluxing for 2 hours. The greenish-blue product was filtered, washed with ethanol, ether and dried *in vacuo* over P_4O_{10}.

Found: C,52.58%; H,3.64%; N,10.12%; Cu,6.68%.

$C_{42}H_{35}Cl_2CuN_7O_{11.5}$ = $CuL_{3.5}(ClO_4)_2$

Requires: C,52.73%; H,3.69%; N,10.25%; Cu,6.64%.

(g) Reaction with copper$^{(II)}$ acetate

N-benzoyliminopyridinium betaine (2.38g, 12m Mol) was added to a clear solution of copper$^{(II)}$ acetate *mono*hydrate (0.80g, 4m Mol) dissolved in hot ethanol (50 ml) and the reaction mixture was heated under reflux for 2 hours. On cooling the reaction mixture to room temperature, a greenish-blue product separated ("Compound(5)") was washed with cold ethanol, ether and dried *in vacuo* over P_4O_{10}.

Found: C,50.81%; H,4.41%; N,7.41%; Cu,17.23%.

$C_{14}H_{16}CuN_2O_5$ = $CuL(CH_3COO)_2$

Requires: C,50.58%; H,4.21%; N,7.38%; Cu,16.74%.

(2) With Cobalt$^{(II)}$ Salts

(a) Reaction with Cobalt$^{(II)}$ perchlorate

N-benzoyliminopyridinium betaine (2.4g, 12m Mol) was added to a clear solution of cobalt$^{(II)}$ perchlorate *hexa*hydrate (0.80g, 22m Mol) dissolved in ethanol (100 ml) with constant stirring. Almost immediately after mixing the reagents, a blue precipitate separated out and it did not change on subsequent refluxing of the reaction mixture for 2 - 3 hours. The blue precipitate ("Compound(6)") was filtered, washed thoroughly with ethanol, ether and finally dried *in vacuo* over P_4O_{10}.

Repetition of the above reaction with a large excess of ligand did not alter the nature of the final product. However, repetition of the reaction in triethylorthoformate (75 ml) using exactly the same amounts of reactants resulted in an intense blue precipitate which had a similar elemental analysis to that precipitated from ethanol and their *i.r.* spectra were identical.

Found: C,54.42%; H,4.18%; N,10.08%; Cl,6.81%; Co,5.07%.

$C_{48}H_{40}Cl_2CoN_8O_{12}$ = $CoL_4(ClO_4)_2$

Requires: C,54.85%; H,3.84%; N,10.66%; Cl,6.75%; Co,5.61%.

(b) Reaction with cobalt$^{(II)}$ chloride

N-benzoyliminopyridinium betaine (1.98g, 10m Mol) dissolved in triethylorthoformate (50 ml) was added to a solution of cobalt$^{(II)}$ chloride *hexa*hydrate (2.38g, 10m Mol) in triethylorthoformate (50 ml) and the resultant mixture was heated under reflux for 2 hours when a blue product separated out. The product ("Compound(7)") was filtered, washed with ether and dried *in vacuo* over P_4O_{10}.

Found: C,54.19%; H,4.03%; N,10.71%; Cl,12.81%; Co,11.30%.

$C_{24}H_{20}Cl_2CoN_4O_2$ = CoL_2Cl_2

Requires: C,54.75%; H,3.80%; N,10.65%; Cl,13.48%; Co,11.20%.

(c) Reaction with cobalt$^{(II)}$ bromide

Aquated cobalt$^{(II)}$ bromide (3.27g, 10m Mol) was dissolved in triethylorthoformate (50 ml) and to this solution, N-benzoyliminopyridinium betaine (1.98g, 10m Mol) dissolved in triethylorthoformate (30 ml) was added with stirring. The reaction mixture was then heated under reflux for 2 hours when a blue precipitate separated out. The product ("Compound(8)") was filtered, washed with ether and dried *in vacuo* over P_4O_{10}.

Found: C,34.02%; H,2.41%; N,6.68%; Br,38.29%; Co,14.32%.

$C_{12}H_{10}Br_2CoN_2O$ = $CoLBr_2$

Requires: C,34.55%; H,2.40%; N,6.72%; Br,38.34%; Co,14.24%.

(d) *Reaction with cobalt$^{(II)}$ iodide*

N-benzoyliminopyridinium betaine (1.98g, 10m Mol) was added to cobalt$^{(II)}$ iodide *di*hydrate (3.49g, 10m Mol) dissolved in triethylorthoformate (100 ml). Almost immediately on mixing of the reactants a greenish product separated out and it did not apparently change in subsequent heating under reflux for 2 hours. The product ("Compound(9)") was filtered, washed with ether and dried *in vacuo* over P_4O_{10}.

Found: C,28.08%; H,2.11%; N,5.46%; I,49.26%; Co,11.59%.

$C_{12}H_{10}CoI_2N_2O$

Requires: C,28.19%; H,1.96%; N,5.48%; I,49.68%; Co,11.54%.

(e) *Reaction of N-(p-toluoyl)iminopyridinium betaine with cobalt$^{(II)}$ bromide*

N-(*p*-toluoyl)iminopyridinium betaine (0.424g, 2m Mol) was added to aquated cobalt$^{(II)}$ bromide (0.654g, 2m Mol) dissolved in triethylorthoformate (50 ml); almost immediately a blue crystalline product separated out. The reaction mixture was then heated under reflux for 2 hours, but there was no apparent change in the separated product. The product ("Compound(10)") was filtered, washed with boiling triethylorthoformate, ether and dried *in vacuo* over P_4O_{10}.

Found: C,36.43%; H,2.91%; N,6.62%; Br,37.31%; Co,13.82%.

$C_{13}H_{12}Br_2CoN_2O = CoL^{IV}Br_2$

Requires: C,36.21%; H,2.79%; N,6.50%; Br,37.10%; Co,13.68%.

(3) With Nickel$^{(II)}$ Salts

(a) Reaction with Nickel$^{(II)}$ perchlorate

Nickel$^{(II)}$ perchlorate *hexa*hydrate (0.37g, 1m Mol) was dissolved in triethylorthoformate (30 ml) and the solution was then heated under reflux for 1 hour. N-benzoyliminopyridinium betaine (1.5g, 7.6m Mol) dissolved in triethylorthoformate (30 ml) was then added to the hot nickel perchlorate solution and the reaction mixture was refluxed for a further 1 hour when a blue-violet precipitate separated out. The product("Compound(11)")was filtered, washed with ether and dried *in vacuo* over P_4O_{10}.

Found: C,51.39%; H,4.14%; N,9.76%; Cl,5.93%; Ni,5.42%.

$$C_{48}H_{48}Cl_2NiN_8O_{16} = NiL_4(H_2O)_4(ClO_4)_2$$

Requires: C,51.33%; H,4.28%; N,9.98%; Cl,6.32%; Ni,5.23%.

Reactions with aquated nickel$^{(II)}$ chloride, bromide, and acetate under similar conditions resulted only in the co-precipitation of basic nickel salts with the protonated betaine as evident from their *i.r.* spectra.

(4) With Iron$^{(II)}$ Salts

(a) Reaction with Iron$^{(II)}$ chloride

Iron$^{(II)}$ chloride *tetra*hydrate (1.99g, 10m Mol) was dissolved in de-aerated triethylorthoformate (130 ml) and the solution was refluxed for 2 hours under dinitrogen and anhydrous conditions. N-benzoyliminopyridinium betaine (2.0g, 10m Mol) dissolved in de-aerated triethylorthoformate (30 ml) was added to the iron$^{(II)}$ solution and the reaction mixture was heated under reflux for a further 2 hours; a cream coloured product separated out. The product ("Compound(12)") was filtered, washed with ether and dried *in vacuo* over P_4O_{10}.

Found: C,44.20%; H,3.17%; N,8.47%; Cl,22.02%; Fe,17.43%.

$C_{12}H_{10}Cl_2FeN_2O$ = $FeLCl_2$

Requires: C,44.34%; H,3.08%; N,8.62%; Cl,21.83%; Fe,17.20%.

(b) Reaction with iron$^{(II)}$ bromide

The same procedure as above was adopted using aquated iron$^{(II)}$ bromide (3.24g, 10m Mol). On cooling the reaction mixture to room temperature, and addition of ether, an amber coloured product was obtained. The product ("Compound(13)") was filtered, washed with ether and dried *in vacuo* over P_4O_{10}.

Found: C,29.81%; H,2.56%; N,5.84%; Br,31.67%; Fe,11.58%.

$C_{12}H_{18}Br_2FeN_2O_5$ = $FeL(H_2O)_4Br_2$

Requires: C,29.84%; H,3.71%; N,5.76%; Br,32.89%; Fe,11.50%.

Reaction with iron$^{(II)}$ perchlorate *hexa* hydrate under similar conditions resulted in the co-precipitation of basic ferrous salts with the protonated betaine.

(5) With Silver$^{(I)}$ perchlorate Salt

(a) Silver$^{(I)}$ perchlorate (1.04g, 5m Mol) dissolved in triethylorthoformate (30 ml) was added to a hot solution of N-benzoyliminopyridinium betaine (2.0g, 10m Mol) in triethylorthoformate (60 ml) when almost immediately a white precipitate was formed. The reaction mixture was then heated under reflux for 2 hours during which the initial white product completely dissolved and later a cream coloured product separated out. The cream coloured product ("Compound(14)") was filtered, washed with ether and ethanol and finally dried *in vacuo* over P_4O_{10}.

Found: C,43.66%; H,3.22%; N,8.26%; Cl,6.38%.

$C_{18}H_{15}AgCl_4N_3O_{5.5}$ = $AgL_{1.5}(ClO_4)$

Requires: C,42.82%; H,2.97%; N,8.33%; Cl,7.03.

(b) Silver$^{(I)}$ perchlorate (1.04g, 5m Mol) dissolved in triethylorthoformate (30 ml) was added to a hot solution of N-benzoyliminopyridinium betaine (2.0g, 10m Mol) in ethanol (50 ml) and the reaction mixture was heated under reflux for 2 hours. During heating a brownish product separated out, which on cooling to room temperature became white and amorphous. This product appeared to be impure and hence it was recrystallized from ethanol to obtain a colourless powder ("Compound(15)").

Found: C,46.47%; H,3.36%; N,8.98%; Cl,6.00%.

$C_{24}H_{22}AgClN_4O_7$ = $AgL_2(H_2O)(ClO_4)$

Requires: C,46.34%; H,3.54%; N,9.01%; Cl,5.70%.

(6) With Mercury$^{(II)}$ Salts

(a) Reaction with Mercury$^{(II)}$ chloride

Mercury$^{(II)}$ chloride (1.36g, 5m Mol) dissolved in methanol (10 ml) was added to a solution of N-benzoyliminopyridinium betaine (1.98g, 10m Mol) in the same solvent (15 ml). The reaction mixture was then stirred at room temperature for 1 hour during which a white precipitate was formed. The product ("Compound(16)") was filtered, washed with methanol and ether and finally dried *in vacuo* over P_4O_{10}. Concentration of the filtrate afforded a further crop of the product .

Found: C,29.53%; H,2.22%; N,5.86%; Cl,15.20%

$C_{12}H_{10}Cl_2HgN_2O$ = $HgLCl_2$

Requires: C,30.66%; H,2.13%; N,5.96%; Cl,15.10%.

(b) Reaction with Mercury$^{(II)}$ bromide

The same procedure as above was adopted with mercury$^{(II)}$ bromide (1.80g, 5m Mol). The white precipitate formed ("Compound(17)") was washed with methanol and ether and dried *in vacuo* over P_4O_{10}.

Found: C,25.46%; H,1.91%; N,5.25%; Br,28.72%.

$C_{12}H_{10}Br_2HgN_2O$ = $HgLBr_2$

Requires: C,25.78%; H,1.79%; N,5.01%; Br,28.62%.

(C) RESULTS

All the complexes prepared, had mass spectra very similar to those of the free betaine and none of the complexes displayed the parent ion peak corresponding to their molecular weight. The spectra in general were rich with all the characteristic peaks of the betaine thus indicating the presence of unaltered betaine skeleton. Apart from this information, the mass spectra of these complexes have not aided the structure-elucidation of these complexes and hence these data are not presented.

The infra-red spectral data are gathered in Table 12. The *n.m.r.* data were obtained only for diamagnetic complexes and are presented in Table 13. The effective magnetic moments and the electronic absorptions of all the paramagnetic complexes are given in Table 14 whilst conductivity data are shown in Table 15. Figure 13 illustrates the Onsager plot of molar conductivity against $\sqrt{\text{concentration}}$ for cobalt chloride complex assuming a monomeric formulation. Direct examination of ligand-metal and metal-halogen vibrations is, in general, a satisfactory way of determining the structure of complexes of transition metal ions of the first row. Unfortunately, the region in which these vibrations are expected was in general very rich with metal excited ligand vibrations and often their fine structure could not be resolved under the experimental conditions used in this study. Consequently the far infra-red data have been of little use and the assignments of absorption in this region are tentative.

TABLE 12 - Principal absorption in the infra-red spectra (KBr disc)cm^{-1}

Compound	ν(C=O)	ν(N-----N)	γ(CH)Ph	γ(CH)Py	Other
1. $CuLCl_2$	1620(v.s.) 1515(v.s.)	1322(s.br.)	715(v.s.sh) 688(v.s.sh)	765(v.s.sh) 668(s.)	240(br), ν(Cu-Cl) 400(w.br)ν(Cu-N)
2. $CuL_2(H_2O)_2Cl_2$	1620(v.s.) 1520(v.s.)	1370(s.) 1325(v.s.)	718(v.s.sh) 690(s.sh)	770(v.s.sh) 670(s.sh)	480(m.br) ν(Cu-O) 400(w-m,br) ν(Cu-N) 3440(m-s) and 3360(m) ν(O-H)sym & Asym.
3. $CuL_{1.5}(H_2O)_3(NO_3)_2$	1670(v.s.sh)	1312(s)	712(v.s.sh) 690(v.s.)	772(v.s.sh) 670(m.sh)	330(w-m) ν(Cu-N) 1390(v.s.br) $\nu_3(NO_3^-)$ 830(w) $\nu_2(NO_3^-)$ 700(w) $\nu_4(NO_3^-)$ 3520(s) ν_{asy}(OH) 3420(s.)ν_{sy} (OH)
4. $CuL_{3.5}(ClO_4)_2$	1625(m) 1525(v.s.br)	1330(m) 1385(v.s.br)	718(v.s.) 690(v.s.)	775(v.s.sh) 675(m.sh)	1095(v.s.br) $\nu_3(ClO_4^-)$ 625(s.sh) $\nu_4(ClO_4^-)$
5. $CuL(CH_3COO)_2$	1630(v.s.br) ν(C=O)acetate 1545(v.s.br) ν(C=O)betaine + acetate 1425(v.s.br) ν(C=O)	1350(s.) 1331(s)	710(v.s.) 680(v.s.br)	775(v.s.sh) 670(s.br)	2930(w) ν(C-H) CH_3gr 6658(OCO) 621(m) γ(COO)

TABLE 12 continued

Compound	ν(C=O)	ν(N-----N)	γ(CH)Ph	γ(CH)Py	Other
6. $CoL_4(ClO_4)_2$	1515(v.s.br)	1380(v.s.br)	715(v.s.sh) 690(s.sh)	780(v.s.) 675(m.sh)	1085(v.s.br) $\nu_3(ClO_4^-)$ 625(v.s.sh) $\nu_4(ClO_4^-)$
7. CoL_2Cl_2	1530(v.s.)	1380(s)	715(v.s.)	775(v.s.)	316(v.s.) ν(Co-Cl)
			725(shoulder)	765(shoulder)	
			705(shoulder)		340(m) ν(Co-Cl)
	1520(v.s.)	1330(v.s.)	690(v.s.sh)	670(v.s.sh)	279(m) ν(Co-Cl)
8. $CoLBr_2$	1542(v.s.)	1370(v.s.)	718(v.s.sh) 690(s)	775(v.s.sh) 670(s.sh)	345(m) ν(Co-O) 275(s) ν(Co-Br)
9. $CoLI_2$	1540(v.s.)	1370(v.s.)	720(v.s.sh) 690(s)	770(v.s.sh) 670(s.sh)	350(m) ν(Co-O) 243(m) ν(Co-I)
10. $CoL^{IV}Br_2$	1535(v.s.br)	1375(v.s.)	830(s) 750(s.sh)	768(v.s.sh) 672(v.s.sh)	352(m-br)ν(Co-O) 260(s) ν(Co-Br)
11. $NiL_4(H_2O)_4(ClO_4)_2$	1540(v.s.br)	1350(v.s.br)	715(v.s.) 690(s)	768(v.s.) 670(s)	1090(v.s.br)$\nu_3(ClO_4)$ 625(s) $\nu_4(ClO_4)$ 3620-3340(s.br) ν(OH)
12. $FeLCl_2$	1520(v.s.br)	1380(v.s.br)	715(v.s.sh) 685(s.sh)	765(v.s.sh) 668(s.sh)	366(v.s.) ν(fe-Cl) 260(m) ν(fe-Cl)
13. $FeL(H_2O)_4Br_2$	1520(v.s.br)	1370(v.s.br)	710(v.s.br) 686(v.s.)	768(v.s.) 665(s)	3620-3260(v.s.br) ν(OH) 280(s) ν(fe-Br)

TABLE 12 continued

Compound	ν(C=O)	$\nu(N\underline{-----N})$	γ(CH)Ph	γ(CH)Py	Other
14. $AgL_{1.5}(ClO_4)$ (Nujol mull/AgCl and polythene plates)	1540(v.s.br)	1335(v.s.br)	715(v.s.br) 685(s.sh)	768(v.s.) 666(s)	1070(v.s.br) $\nu_3(ClO_4^-)$ 620(v.s.sh) $\nu_4(ClO_4^-)$
15. $AgL_2(H_2O)(ClO_4)$ (Nujol mull/AgCl and polythene plates)	1600(v.s.)	1325(v.s.br)	720(v.s.) 692(s.sh)	770(v.s.sh) 670(s.sh)	1090(v.s.br) $\nu_3(ClO_4^-)$ 622(v.s.sh) $\nu_4(ClO_4^-)$ 3480(w-m) ν_{asym}(OH) 3420(w-m) ν_{sym} (OH)
16. $HgLCl_2$	1645(v.s.sh)	1280(v.s.sh)	715(v.s.sh) 690(s.sh)	768(s.sh) 670(m.sh)	305(m) ν(Hg-Cl) 326(m) ν(Hg-Cl)
17. $HgLBr_2$	1640(v.s.sh)	1280(v.s.sh)	718(v.s.sh) 690(s)	765(s.sh) 670(m.sh)	

TABLE 13 - 'H *n.m.r.* data for Hg(II) and Ag(I) complexes

Compound	τ values (DMSO Solutions)
14. $AgL_{1.5}(ClO_4)$	0.95(d, 2H, H_αPy); 1.50(t, 1H, H_γPy); 1.65-2.00(m, 4H, H_βPy + H_α Ph); 2.20-2.55(m, 3H, H_β + H_γPh)
15. $AgL_2(H_2O)(ClO_4)$	1.00(d, 2H, H_αPy); 1.60(t, 1H, H_γPy); 1.75-2.05(m, 4H, H_βPy + H_αPh); 2.30-2.60(m, 3H, H_β + H_γPh).
16. $HgLCl_2$	1.05(d, 2H, H_αPy); 1.56-2.10(m, 5H, H_β,H_γPy + H_αPh); 2.30-2.65(m,3H, H_β + H_γPh).
17. $HgLBr_2$	0.73(d, 2H, H_αPy); 1.25(t, 1H, H_γPy); 1.65(t, 2H, H_βPy); 1.75-2.00(m, 2H, H_αPh); 2.10-2.47(m, 3H, H_β + H_γPh)

Note: d = doublet, t = triplet, m = multiplet.

Ph = Phenyl ring, Py = Pyridine ring.

The doublet and triplets had J = 6-8 Hz.

TABLE 14 - Solid State data of the Complexes

Compound	μ_{eff} (B.M.)	Band maxima in Diffuse Reflectance Spectra (kK)	
1. $CuLCl_2$	2.01 (293°K)	14.70 (br)	
2. $CuL_2(H_2O)_2Cl_2$	2.13(292°k)	11.00 (s.br);	6.67 (shd)
3. $CuL_{1.5}(H_2O)_3(NO_3)_2$	2.11(295°k)	14.25 (s);	12.85 (w)
4. $CuL_{3.5}(ClO_4)_2$	2.15(294°k)	15.88 (s);	12.32 (s)
5. $CuL(CH_3COO)_2$	2.03(294°k(	12.57 (s.br)	
		$4A_2 \rightarrow 4T_1(P)$ Components of	$4A_2 \rightarrow 4T_1(F)$ Components of
6. $CoL_4(ClO_4)_2$	6.34(293°k)	16.82(s.br); 17.81(w.shd); 15.67, 16.72	7.20, 5.82 7.51 5.92
7. CoL_2Cl_2	4.03(295°k)	15.14, 16.86(shd); 15.15, 16.89	6.64, 6.21, 5.82 6.65 6.20

TABLE 14 continued

Compound	μ_{eff}(B.M.)	Band maxima in Diffuse Reflectance Spectra (kK)		
8. $CoLBr_2$	4.64(296°k)	16.88, 15.88, 14.29 $\underline{16.00}$ $\underline{15.20}$ $\underline{14.00}$	7.56, 6.24, 5.26 $\underline{7.56}$ $\underline{6.12}$	
9. $CoLI_2$	4.98(296°k)	16.22, 15.00, 13.88; $\underline{16.31}$ $\underline{14.21}$	7.36, 6.00, 5.20 $\underline{7.36}$ $\underline{5.12}$	
10. $CoL^{IV}Br_2$	4.66(297°k)	16.50, 14.57; $\underline{16.67}$ $\underline{14.82}$	7.50, 5.64, 4.91 $\underline{7.81}$ $\underline{5.81}$	
		${}^3A_{2g} \longrightarrow {}^3T_{1g}$ ν_3	${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ ν_2	${}^3A_{2g} \longrightarrow {}^3T_{2g}$ ν_1
11. $NiL_4(H_2O)_4(ClO_4)_2$	3.11(296°k)	17.71	15.82 12.91(w);	8.85
12. FeLCl	5.37(296°k)		${}^5T_{2g} \longrightarrow {}^5E_g$	
12 . FeLCl	5.37(296°k)		7.51(m)	
13. $FeL(H_2O)_4Br_2$	5.21(295°k)		8.82(m.br)	

Note: s = strong; w = weak; br = broad; shd = shoulder; m = medium

The values underlined are from the solution spectrum in CH_3NO_2

TABLE 15

Compound	Conductivity (λ_M)ohm^{-1} cm^2 mol^{-1}
1. $CuLCl_2$	20.0
2. $CuL_2(H_2O)_2Cl_2$	50.0
3. $CuL_{1.5}(H_2O)_3(NO_3)_2$	151.0
4. $CuL_{3.5}(ClO_4)_2$	131.0
5. $CuL(CH_3COO)_2$	4.0
6. $CoL_4(ClO_4)_2$	157.0
7. CoL_2Cl_2	92.0
8. $CoLBr_2$	4.8
9. $CoLI_2$	5.0
10. $CoL^{IV}Br_2$	6.0
11. $NiL_4(H_2O)_4(ClO_4)_2$	157.0
12. $FeLCl_2$	5.37
13. $FeL(H_2O)_4Br_2$	87.0
14. $AgL_{1.5}(ClO_4)$	160.0 (dimeric formulation)
15. $AgL_2(H_2O)(ClO_4)$	78.0
16. $HgLCl_2$	5.0
17. $HgLBr_2$	4.0

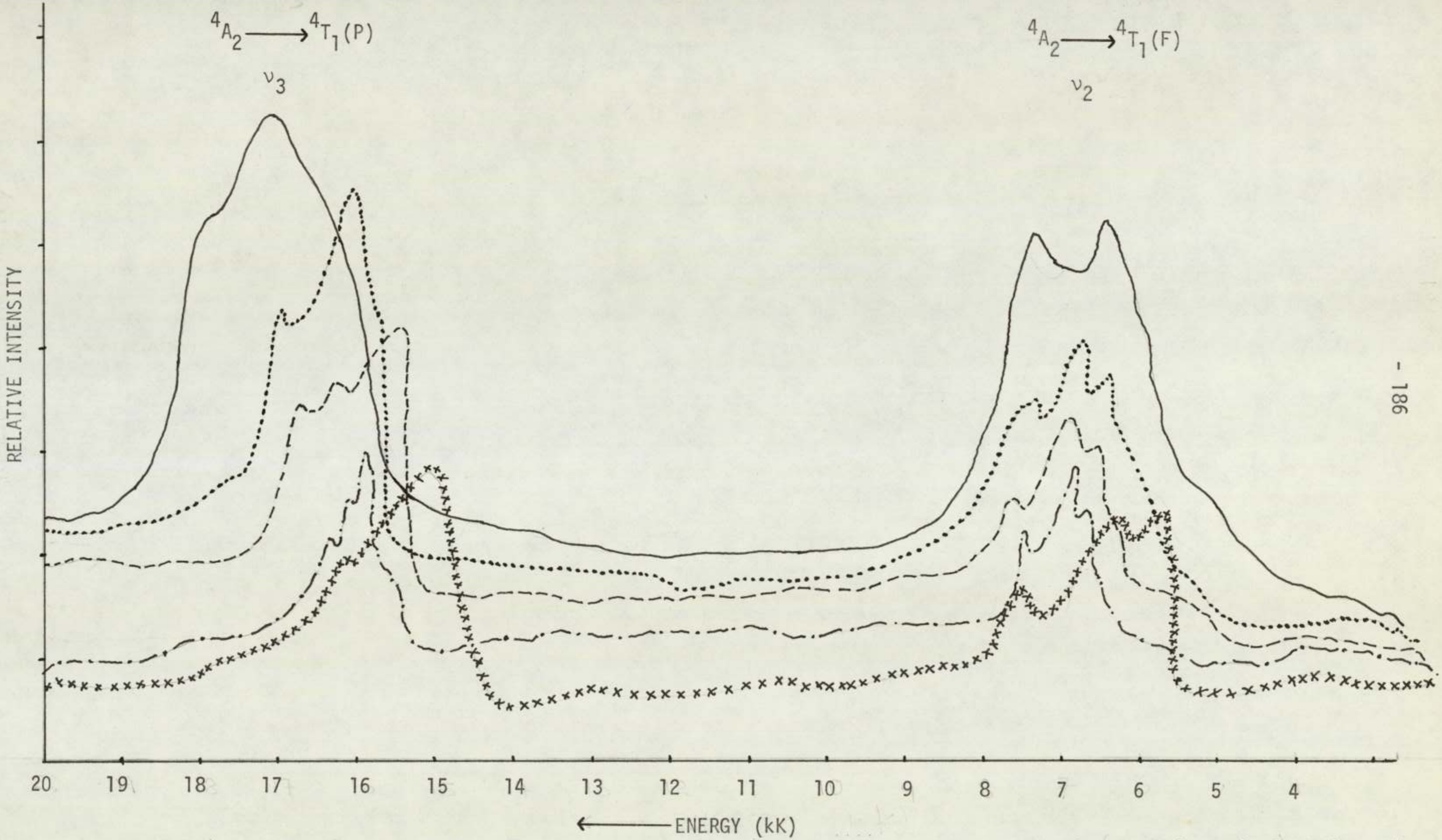


Figure 12. Diffuse Reflectance Spectra of cobalt complexes. $CoL_4(ClO_4)_2$ (——), CoL_2Cl_2(·····), $CoLBr_2$(-----), $CoLI_2$(-•--), $CoL^{IV}Br_2$(xxxxx)

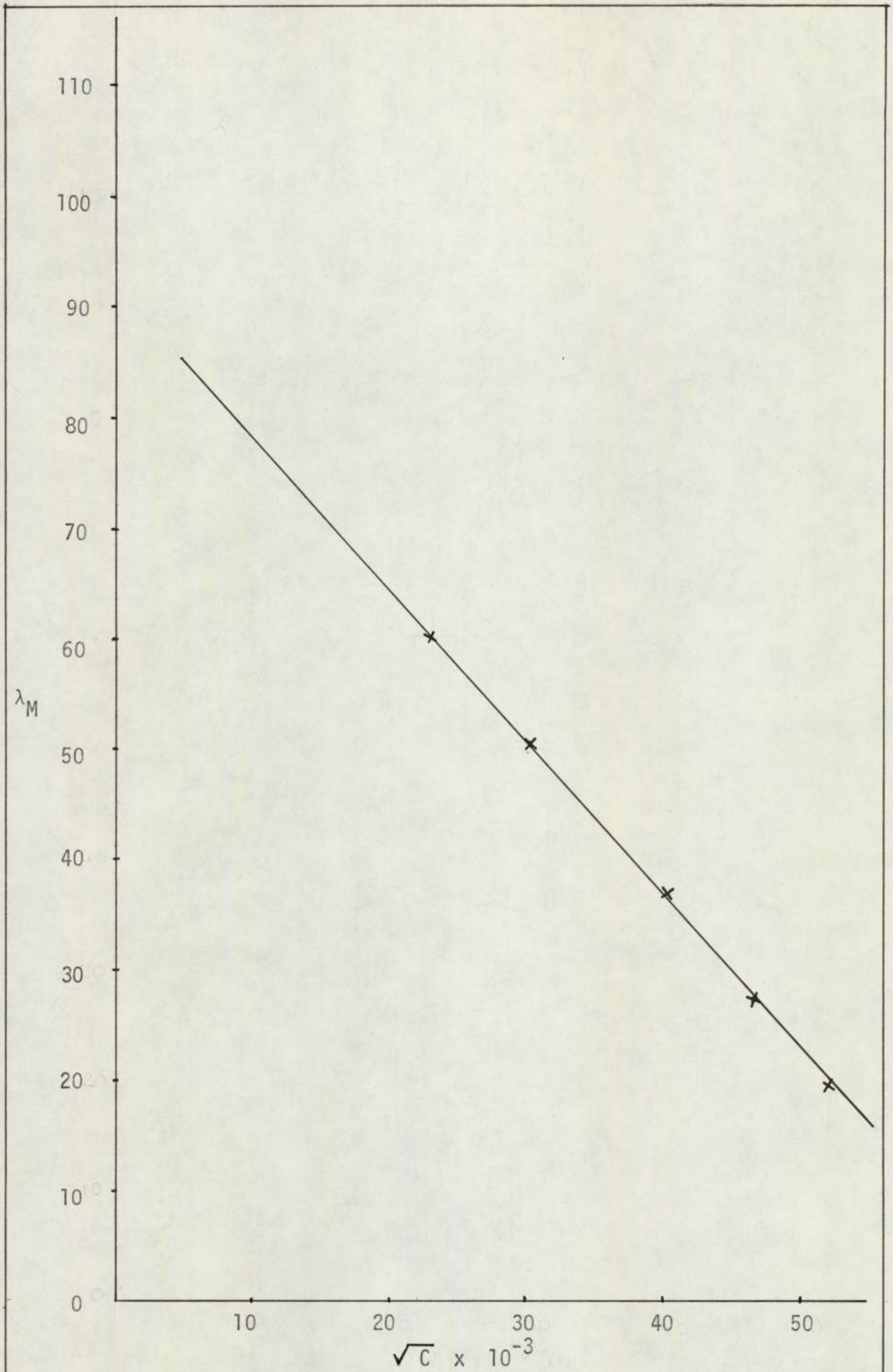


Figure 13. Graph of molar conductance Vs $\sqrt{\text{concentration}}$ for CoL_2Cl_2.

(D) DISCUSSION

The analytical data and infra-red spectra clearly indicate that no metallation of the betaine has taken place with the first row transition metal salts and with silver and mercury salts. The reactions have resulted in the formation of some stable co-ordination compounds with these metal salts. The reaction with copper halides seems to be of a complex nature and under certain conditions leads to the rupture of the N-N bond. In all cases, the betaine functions as a neutral ligand exhibiting three possible modes of co-ordination.

(1) *Decomposition Reactions of the betaine in the presence of copper halide*

N-benzoyliminopyridinium betaine is a stable compound showing no decomposition up to about 180 - 190°C. However, at temperatures above this, it begins to decompose to pyridine and phenylisocyanate which under the experimental conditions trimerizes to phenyl isocyanurate. The isolation of this compound demonstrates that the expected migration of the phenyl group from carbon to nitrogen has occurred, and is consistent with the view that phenyl isocyanate is formed but trimerizes under the somewhat basic reaction conditions(255). Further, when the thermal decomposition was carried out in the presence of *p*-bromoaniline chosen as a selective trapping agent for phenyl isocyanate, NN'-di-*p*-bromophenylurea was isolated- thus confirming the initial formation of phenyl isocyanate. Phenyl isocyanate and *p*-bromoaniline react normally at room temperature to give N-*p*-bromophenyl N'-phenylurea(209). This apparently anomalous result has been explained(209) in terms of the following equilibria;

$$\begin{array}{ll}\mathrm{PhN{=}C{=}O + BrC_6H_4NH_2 \rightleftharpoons PhNH.CO.NH.C_6H_4Br} & \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \upharpoonleft\downharpoonright & \\ \qquad\qquad\qquad\qquad\quad \mathrm{PhNH_2 + O{=}C{=}N.C_6H_4Br} & (1)\end{array}$$

$$\mathrm{BrC_6H_4NH_2 + O{=}N{=}C\text{-}C_6H_4Br \rightleftharpoons BrC_6H_4NH.CO.NHC_6H_4Br} \qquad (2)$$

$$\mathrm{PhNH_2 + O{=}C{=}NPh \rightleftharpoons PhNH.CO.NHPh} \qquad (3)$$

Under the experimental conditions, the set of equilibria seem to be disturbed in favour of the diarylureas in ··(2) and consequently ··(3).

Reaction with anhydrous copper$^{(II)}$ halide has resulted in the rupture of the N-N bond, possibly to yield pyridine and phenylisocyanate which co-ordinates to the metal. The nature of the copper complex could not be established due to the unstable and impure nature of the compound, but the *i.r.* spectrum showed the characteristic absorption frequencies of the co-ordinated ylide and, in addition, a doublet near 2200 $\mathrm{cm^{-1}}$(209). When the reaction was carried out with cuprous chloride (CuCl), under analogous conditions, a cream coloured product was obtained. This product also appeared to be impure and unstable and showed a similar infra-red spectrum with a doublet near 2200 $\mathrm{cm^{-1}}$. Thus, copper in both oxidation states, +1 and +2, is able to bring about the rupture of the N-N bond. Whether it is the copper$^{(I)}$ or $^{(II)}$ species that is really effective in this reaction is unknown. However, the ability of the betaine to exert reducing properties towards copper$^{(II)}$ halides was indicated by some reactions of copper$^{(II)}$ chloride and bromide in toluene with the betaine. In these reactions, diamagnetic substances were obtained and their infra-red spectra were superimposable with that of the free ylide. Further, copper and halogen analysis gave a ratio of 1:1 in each case. Thus, clearly the betaine has been co-precipitated with the cuprous$^{(I)}$ halide. In the light of these observations, copper$^{(I)}$ species may be the active ingredient.

Isolation of similar complexes and observation of doublets around 2200 cm^{-1} in the case of reactions with other ylides {trimethylamine-benzimide and N-(*p*-Toluoylimino)pyridinium betaine} imply a similar influence of copper chloride on the N-N bond of these ylides. Whether the re-arrangement proceeds in a concerted fashion or by a nitrene intermediate is not certain. The important outcome of these observations is that copper in +1 or +2 state is able to lower the decomposition temperature of the ylides by about 90 - 100°C. Out of the first row-transition metals only copper halides could effect this decomposition and this ability may be related to the preference of copper for N-co-ordination of the betaine.

The impure copper complex contains both phenyl isocyanate co-ordinated on to copper and this may, together with the isolation of "compound (1)", suggest that the decomposition of the betaine occurs subsequent to its initial co-ordination.

The reaction with copper$^{(II)}$ chloride in the medium of ethanol was not reproducible and this may be due to the known reaction of ethanol with phenyl isocyanate.

(2) *Complexes of copper$^{(II)}$*

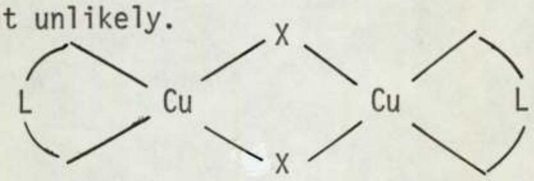
It is well-known that the copper$^{(II)}$ ion exhibits a wide range of stereochemistries and has a tendency to give rise to a large number of structures which involve distortions from otherwise regular structures. Thus, it has generally become a difficult task to correlate the structural information with the electronic properties of the copper$^{(II)}$ion. Further, Ahrland *et al.* (267) have classified copper$^{(II)}$ ion as a borderline case between class a and class b metals.

The characteristic complex behaviour of the copper$^{(II)}$ ion is evident even in the complexes with N-benzoyliminopyridinium betaine. The infrared spectra (Table 12) of these complexes clearly indicate that with the copper$^{(II)}$ ion the betaine exhibits two of the three possible modes of co-ordination namely co-ordination through nitrogen or through both oxygen and nitrogen. Thus, the "compound(1)" shows two strong carbonyl absorptions at 1620 cm^{-1} and 1515 cm^{-1} indicating both N and O co-ordination of the ylide. Similarly, the other copper$^{(II)}$, chloride complex "compound (2)" shows two carbonyl stretching frequencies; one higher than that of the free ylide and the other lower. In this compound, $\underline{\text{N-----N}}$ bond also shows two absorptions and compared to its position in the free ylide, supports both N and O co-ordination. Although it would be difficult to distinguish between the carbonyl absorptions of the co-ordinated ylide and of acetate anion in the case of the copper$^{(II)}$ acetate complex ("compound(5)"), the observations of two strong absorptions at 1350 cm^{-1} and 1331 cm^{-1} assignable to $\nu(\underline{\text{N-----N}})$ cast little doubt as to the occurrence of both N and O co-ordination of the ylide in this case too. However, "compound (3)" reveals only one carbonyl stretching frequency and is in accord with the N co-ordination of the ylide.

The room temperature magnetic moments and the position of d-d absorption bands of all these complexes are listed in Table 14. The envelopes of these d-d bands are generally unsymmetrical, seeming to encompass several overlapping transitions, but definitive resolution into the proper number of sub-bands with correct locations is difficult. Because of the relatively low symmetry of the environments in which Cu^{2+} is characteristically found, detailed interpretations of the spectra and magnetic properties are somewhat complicated, even though the Cu^{2+} ion is the equivalent of a one-electron case.

The values of μ_{eff} of the copper complexes lie within the normal range generally observed for copper$^{(II)}$ complexes(256). The values are consistent with an orbitally nondegenerate ground state for the copper$^{(II)}$ ion, the slight increase above the spin-only value may arise from the mixing in of an orbitally degenerate excited state into the ground state *via* spin-orbit coupling. The latter effect is clearly dependent upon the symmetry of the excited states present and upon their energies, both of which will depend upon the stereochemistry present. However, the total contribution to the magnetic moment by this mechanism is so small, and the accuracy with which μ can be measured is such that no stereochemical information can be obtained from the measurements of the room temperature magnetic moments.

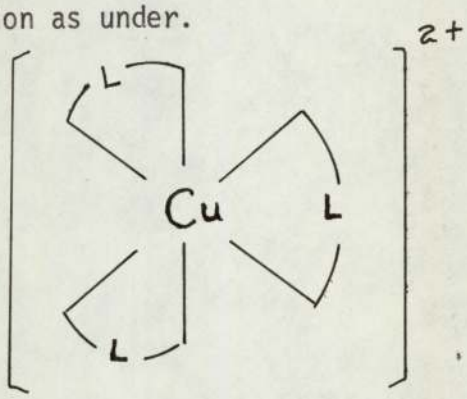
The low conductivity (Table 15) of the "compound(1)" suggests that it is a non-electrolyte and hence a dimeric or polymeric structure with halogen bridges is not unlikely.



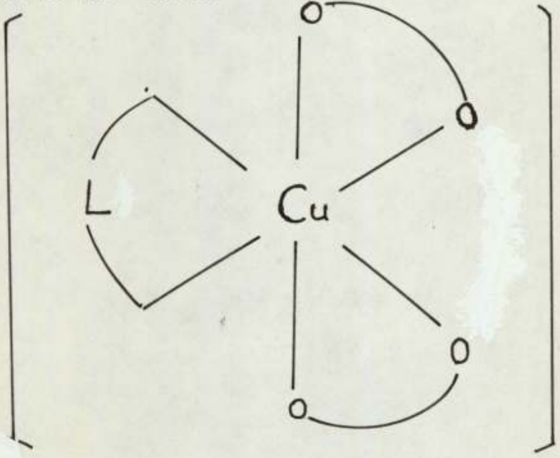
The far infra-red region of this complex shows a strong and broad absorption at 240 cm^{-1} and it may be assigned to ν(Cu-Cl).

The "compound(2)" also has a very similar *i.r.* spectrum and as in the case of "compound(1)" the spectrum indicates that both betaine molecules are in identical environments. The infrared spectrum of this compound further shows a strong absorption at 3440 and 3360 cm^{-1} which may be due to the presence of un-co-ordinated and co-ordinated water molecules. The far infra-red spectrum reveals a strong absorption at 320 cm^{-1} and is assignable to terminal ν(CuCl). The conductivity measurement in nitromethane furnished a value of 50 $ohm^{-1}\ cm^2\ mol^{-1}$, a value approaching a 1:1 electrolyte in this solvent(257). The low value is presumably due to interaction of the anion with the cation *via* hydrogen bonding and this is supported by the broadening of ν(OH) band in the infra-red spectrum. Thus, it is reasonable to formulate "compound(2)" as $[CuL_2(H_2O)Cl]^+\ Cl^-.H_2O$ or as $[CuL_2(H_2O)_2Cl]^+Cl^-$ with one monodentate betaine molecule. The "compound(3)" reproducibly analyzes to the stoichiometry $CuL_{1.5}(H_2O)_3(NO_3)_2$ and its conductivity in CH_3NO_2 assuming this formulation is 151 $ohm^{-1}\ cm^2\ mol^{-1}$, a value within the range expected for 2:1 electrolytes(257). The infra-red spectrum of this complex shows the three characteristic infra-red active bands of ionic nitrate group (D_{3h}). The infra-red spectrum shows no absorption around 1550 cm^{-1} assignable to ν(> C=O) of the free ylide and in view of this it appears that the formula must at least be doubled which makes assignment of a plausible structure most difficult. It is therefore possible to do little more at this stage than to suggest that the electronic spectrum is consistent with a distorted 6-co-ordinate environment for Cu(II) but the details of the structure will only be resolved by an X-ray crystallographic study.

Copper$^{(II)}$ perchlorate complex ("compound(4)") and the acetate complex ("compound(5)") look stoichiometrically dissimilar but structurally they seem to be related to each other. The perchlorate complex is a 1:2 electrolyte and its *i.r.* spectrum shows the characteristic absorption of ionic perchlorate group (Table 12.). Further, the ν(>CO) and ν(N ----N) bands are unusually broad suggesting the possible existence of two types of the ligand molecules, with both N and O co-ordination. The broadening of these characteristic bands may be ascribed to the presence of a "free" ligand molecule in the lattice. The infrared carbonyl absorption at higher frequency (1625 cm^{-1}) is relatively weak and may indicate a weaker interaction through nitrogen as against oxygen. In view of these observations, the "compound(5)" would be reformulated as $[CuL_3](ClO_4)_2 0.5L$, with a basically octahedral environment around the copper$^{(II)}$ion as under.



"Compound(5)" may then, be envisaged as arising by replacement of two of the co-ordinated betaine molecules by two chelating acetate molecules which have a similar "bite"



As might be expected, the acetate complex ("compound 5") is a non-electrolyte in nitromethane and its *i.r.* spectrum shows three strong absorptions at 1425, 1545 and 1630 cm^{-1}; of which, the second absorption (1545 cm^{-1}) is assigned to ν(>CO) betaine suggesting O-co-ordination of the betaine, whilst the first (1425 cm^{-1}) and the third (1630 cm^{-1}) are assigned to ν_s(COO) and ν_{as}(COO) of the acetate group and are very similar to those of $Zn(CH_3COO)_2.2H_2O$(258, 266) for which X-ray analysis has established bidentate co-ordination of the acetate group. Within the broad band at 1630 cm^{-1} also lies the ν(>CO) of the betaine suggesting N-co-ordination as well. This is further indicated by ν(N-----N) absorption at 1330 cm^{-1}.

(3) *Complexes of cobalt$^{(II)}$*

The complexes with cobalt$^{(II)}$ salts were the easiest to prepare and in general the metal-ligand ratio was immaterial. The infra-red spectra of all the complexes ("compound 6-12"), (Table 12) of Co(II) ion show very strong absorptions due to the carbonyl group at values lower than the corresponding value in the free ylides, thus implying a great tendency for O-co-ordination.

The other strong absorption in their *i.r.* spectra, assigned as ν(N-----N) experiences upward shifts in keeping with the lowering of the carbonyl bond strength. A notable exception is the cobalt chloride complex ("compound(7)") whose *i.r.* spectrum reveals two strong absorptions at 1630 cm^{-1} and 1520 cm^{-1} assignable to ν(CO) and two strong absorptions at 1380 cm^{-1} and 1330 cm^{-1} assignable to ν(N-----N) . On the same reasoning as before, this is taken to indicate that the ligand is present both in the N-co-ordinated and O-co-ordinated forms. Further, the *i.r.* spectrum of this compound was more complex than that of any other $Co^{(II)}$ complex prepared in this study and in the γ(CH) region, some of the characteristic absorptions of the betaine showed "shoulders" thus implying that the symmetry of the co-ordinated ligand molecules are different.

All the complexes have a deep clue colour except the iodide ("compound 9") which is green. However, the electronic spectra of all the cobalt compounds indicate a tetrahedral environment for the cobalt ion(260,261). Diffuse reflectance spectra for the cobalt complexes("compounds 6-10") are shown in Figure 12 and the band assignments are given in Table 14.

The band on the low energy side is assigned to the $^4A_2 \longrightarrow {}^4T_1$ transition (ν_2) while the band in the visible region is attributed to the $^4A_2 \longrightarrow {}^4T_1(P)$ transition (ν_3). Assuming these assignments and using the method of Lever(262), the position of ν_1 absorption was calculated. The calculated values of ν_1 agreed remarkably well with the position of a weak absorption in their infra-red spectra (Table 16).

Table 16

Compound	ν_1(cm^{-1}) Observed	ν_1(cm^{-1}) Calculated
CoL_2Cl_2	3640	3679
$CoLBr_2$	3530	3540
$CoLI_2$	3545	3550
$CoL^{IV}Br_2$	3460	3462

This agreement confirms that the weak feature observed in the infra-red spectra is an electronic not a vibrational absorption.

In all the spectra both ν_3 and ν_2 bands exhibit multiple splitting. The spectra of all the three halide complexes are somewhat similar in shape (Figure 12) whilst the perchlorate compound is less complex and may indicate a more symmetric environment around cobalt$^{(II)}$ ion in this case. In fact, Ferguson(259) has discussed the spectra of some solid compounds containing the $CoCl_4^{2-}$ ion and concluded that splitting of the ν_2 transition can best be explained in terms of lower symmetry. Thus "compound(6)" seems to be free from severe distortion and resembles true tetrahedral stereochemistry more closely than the halo complexes. Distortion from regular tetrahedral stereochemistry would be expected to be most moticeable in the ν_1 transition $^4A_2 \longrightarrow {}^4T_2$. However, this transition is seldom observed as it occurs in a very inaccessible low energy region of the spectrum namely the 3-5 kK region and overlaps with vibration overtones.

Using the Lever's method(262), the ligand field parameters $10D_q$ and B(Racah parameter) were calculated from the observed positions of ν_3 and ν_1 absorptions. For these calculations the centre of the near infra-red band was assumed to be the transition $^4A_2 \longrightarrow {}^4T_1$ (F) and that of the visible band was assumed to be the transition $^4A_2 \longrightarrow {}^4T_1$ (P). The calculated values are presented in Table 17.

TABLE 17

The Mean Crystal Field Strength ($10D_q$) and Racah Parameter(B)' for complexes of $Co^{(II)}$. (kK)

Compound	$10D_q$	B
$CoL_4(ClO_4)_2$	3.58	0.822
CoL_2Cl_2	3.72	0.699
$CoLBr_2$	3.19	0.757
$CoLI_2$	3.50	0.730
$CoL^{IV}Br_2$	3.11	0.710

The low value of $10D_q$ indicates that N-benzoyliminopyridinium betaine is relatively a weak ligand. The Racah parameter(B) for the free ion is 1120 cm^{-1} and the lowering of the B value is attributed to increase in covalency due to mixing in of metal *d* functions with ligand functions.

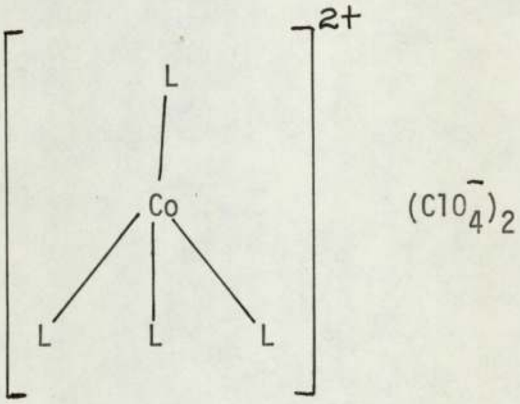
The value of $10D_q$, the ligand field parameter allows N-benzoyliminopyridinium betaine(L) to be placed in a spectrochemical series with respect to $Co^{(II)}$:

$$I^- < Br^- < Cl^- < L < \text{-NCS}$$

Since the ligand exhibits two modes of co-ordination in these complexes, it was interesting to see how the ligand field parameter reflects this behaviour. In the perchlorate complex, the ligand is O-bonded whilst in the chloride complexes, both N or O bonded forms are present. Using Lever's method and the rule of Average Environment, $10D_q$ values for the O-bonded and N-bond ligands were calculated. The value of $10D_q$ for O-bonded betaine is 3.58 kK and that for the N-bonded betaine is 4.90 kK Thus, the N-bonded betaine is a stronger ligand than the O-bonded form and this trend is anyway to be expected in view of the electronegativity difference between nitrogen and oxygen.

(4) Possible structures for the $Co^{(II)}$ complexes

The infra-red spectrum of "compound(6)" clearly indicates the presence of O-co-ordinated betaine and ionic perchlorate group and its conductivity and electronic spectra support a tetrahedral ionic structure.



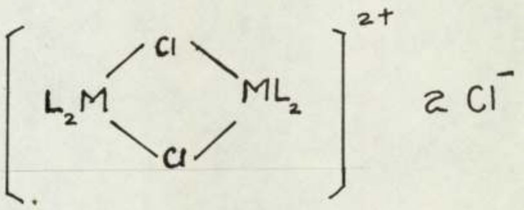
The observed magnetic moment for this complex was 6.34 B.M. at room temperature and is thus considerably in excess of the spin only-value (3.89 B.M.) or even the normal values obtained for other $Co^{(II)}$ complexes: $CoCl_4^{2-}$, 4.59 B.M. $CoBr_4^{2-}$, 4.69 B.M. and CoI_4^{2-}, 4.77 B.M.(263). Furthermore this value is higher than the usual value for octahedral $Co^{(II)}$ complexes 4.7 - 5.2 B.M.(263). The high value may not be attributed to a spin-orbit coupling since for tetrahedral complexes, the ground state $^4A_2$

has no inherent orbital angular momentum. However, it was found that another form of this complex (see experimental section) could be prepared either in triethylorthoformate or by recrystallizing in other solvents. This form has a lower μ_{eff} value (4.61 B.M.) and is thus within the normal range expected for tetrahedral cobalt$^{(II)}$ complexes. These two forms have different X-ray powder photographs and hence are probably different polymorphic forms and thus the high μ_{eff} value seems to be due to a co-operative effect in the lattice.

From the analytical data, the "compound(7)" has the stoichiometry CoL_2Cl_2 and would appear to be a neutral complex. However, in nitromethane it behaves as a strong electrolyte (Figure 13) and further solvolysis or decomposition in solution is unlikely in view of the similarity of the solid state and solution electronic spectra. Thus the monomeric neutral structure $[CoL_2Cl_2]$ may be easily ruled out. Thus suitable ionic formulae must be found for this compound. Two simple possibilities exist when the stoichiometric formula is doubled. $[CoL_2Cl_2]_2$.

$$[ML_4]^{2+}[MCl_4]^{2-}$$

(A)

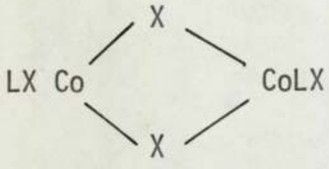


(B)

The doubling of the stoichiometric formula leads to the doubling of conductivity results. i.e. 92 x 2 = 184 $ohm^{-1}\ cm^{2}\ mol^{-1}$, a value quite acceptable for a 2:1 electrolyte in nitromethane. The far infra-red spectrum of this complex was very complex and afforded no evidence for the presence of $[CoCl_4]^{2-}$ species(264).

Further, the infrared spectrum of this compound shows the presence of two types of the betaine molecule and is very different to the spectrum of the perchlorate complex. On the basis of these observations, structure (A) is most unlikely and structure (B) is quite plausible. The *i.r.* spectrum shows evidence for both N co-ordinated and O-co-ordinated ligand molecules and therefore all four ligand molecules present are not in identical environments. The far-infra-red spectrum of this complex shows two absorptions at 316 cm^{-1} and 279 cm^{-1} which may be assigned to bridging ν(CoCl)(265). However the assignments are difficult to make in this region due to numerous absorptions present in this region due to the ligand itself. Further, only broad absorptions with no defined bands were obtained in the far infra-red. Thus, far infra-red spectra of these complexes were of little value in helping to distinguish between *cis and trans* configurations. The observed room temperature magnetic moment (4.03 B.M.) of the "compound (7)" is significantly low and this low value may be due to antiferromagnetic effect operating through the chloride bridges.

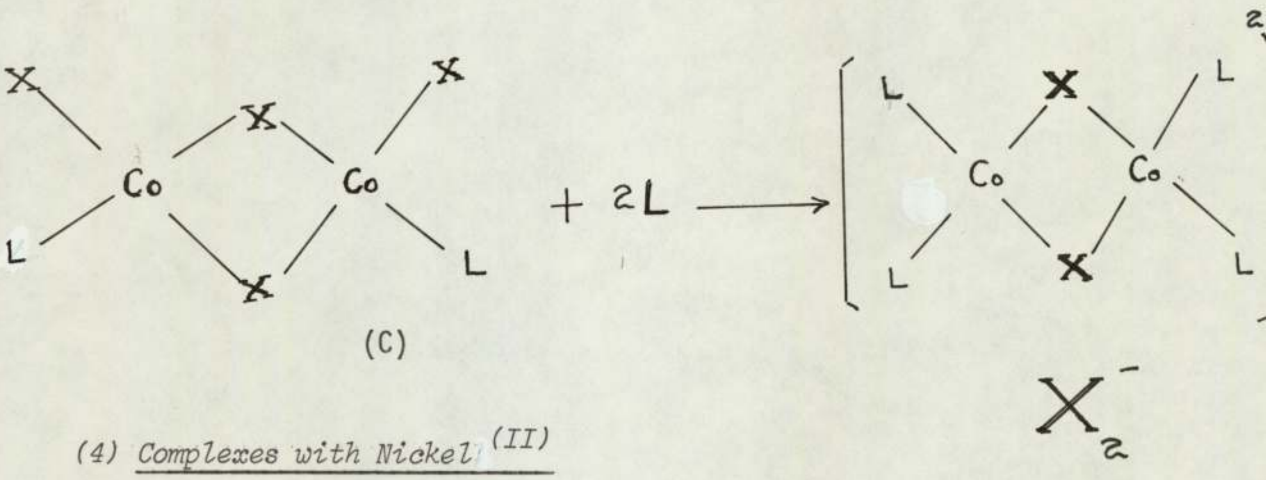
The halo complexes "(8)", "(9)" and "(10)" are non-electrolytes in nitromethane and the *i.r.* spectra indicate only one type of betaine molecule, and shows no sign of N-co-ordination. Therefore it is conceivable that they are dimeric with halogen bridges.



(C)

Again the far infra-red spectra were of little use in distinguishing the isomers possible with such a configuration. The strong absorptions at 275 cm^{-1} ("compound 8") and at 260 cm^{-1} ("compound 10") may be assigned to $\nu(CoBr)$.

It is conceivable that "compound(7)" is formed from a structure such as (C) by a nucleophilic substitution of the terminal halogens by N-donating betaine molecules.



(C)

(4) *Complexes with Nickel* $^{(II)}$

Complexes with the $Ni^{(II)}$ ion were very difficult to prepare. In general, the tendency was for the precipitation of the basic salt with the protonated betaine. This behaviour is in direct contrast to that of the cobalt$^{(II)}$ ion which underwent smooth reactions to give stable co-ordination compounds. The only stable compound isolable with the $Ni^{(II)}$ ion was the perchlorate complex "(compound 11)". The infra-red spectrum of this complex is consistent with the presence of O-co-ordinated unidentate betaine and the presence of co-ordinated water; the perchlorate group is ionic. The observed room temperature magnetic moment and the electronic spectrum are consistent with an octahedral stereochemistry for the $Ni^{(II)}$ ion.

The assignments of absorptions in the electronic spectrum are as follows:

$(\nu_1)\ {}^3A_{2g} \longrightarrow {}^3T_{2g} \quad = \quad 8.85$ kK

$(\nu_2)\ {}^3A_{2g} \longrightarrow {}^3T_{1g}(F) \quad = \quad 15.82$ kK

$(\nu_3)\ {}^3A_{2g} \longrightarrow {}^3T_{1g}(P) \quad = \quad 17.71$ kK

The splitting of the middle band in the electronic spectrum may be due to spin-orbit coupling which mixes the ${}^3T_{1g}$ (F) and 'Eg states which are very close in energy at the $10D_q$ value given by 4L and $2H_2O$ molecules. On the basis of these observations it is reasonable to formulate "compound(11)" as $[NiL_4(H_2O)_2](ClO_4)_2 2H_2O$. In nitromethane it has a conductivity of 157 ohm^{-1} cm^2 mol^{-1} and this agrees with the formulation as a 1:2 electrolyte. On steric grounds a *trans* configuration appears likely for the $[NiL_4(H_2O)_2]$ cation.

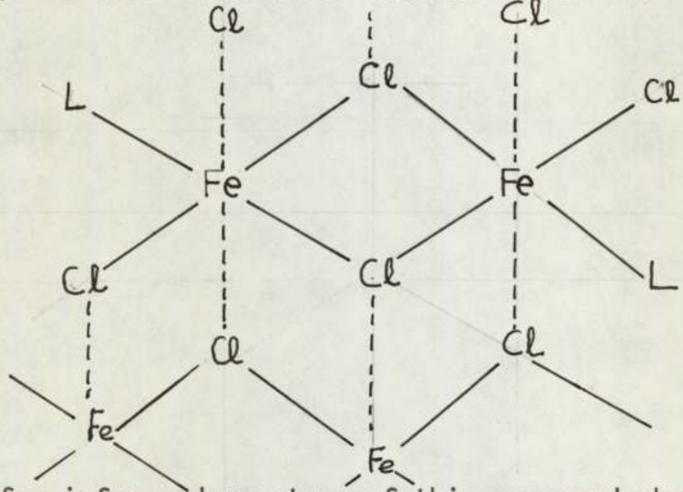
(5) *Complexes with iron$^{(II)}$*

Iron$^{(II)}$ salts also generally had a tendency to precipitate as the basic hydroxide with the protonated betaine. This behaviour is often ascribed to the high Fe-O bond strength which favours loss of a proton from the co-ordinated water molecules in the presence of basic ligands.

The solid state electronic spectra of"compounds (12) and (13)" show single absorptions at 7.51 kK and 8.82 kK respectively. The positions of these absorptions are clearly far above the typical position (~4.00 kK) expected for the single spin-allowed d-d transition for tetrahedral Fe$^{(II)}$ species(263). However, they are close to the normal value for high-spin

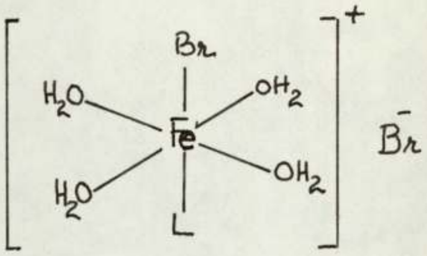
$Fe^{(II)}$ species with relatively weak ligands in octahedral environments, and further the broad nature of the absorptions is also suggestive of octahedral $iron^{(II)}$ species. The observed room temperature magnetic moments also lie outside the normal value for tetrahedral $iron^{(II)}$ species. Thus, clearly the magnetic moments and electronic spectra point to octahedral environments around the $iron^{(II)}$. Hence the observed electronic transition may be assigned to ${}^5T_{2g} \longrightarrow {}^5E_g$.

The infra-red spectra of both the compounds ("12 and 13") are very similar and clearly indicate <u>O</u>-co-ordination of the betaine. In the bromide complex the *i.r.* spectrum also indicates the presence of co-ordinated water molecules. While the compound "(12)" has a low conductivity in nitromethane, the compound "(13)" has a conductivity characteristic of a 1:1 electrolyte. In the light of these observations, the chloride complex may be formulated as a polymeric structure with chlorine bridges to satisfy the octahedral co-ordination of $Fe^{(II)}$.



The far infra-red spectrum of this compound shows strong absorptions at 366 cm^{-1} and 260 cm^{-1} and thus indicates the presence of both terminal and bridging Fe-Cl bonds.

On the other hand a plausible structure for compound "(13)" appears to be $[Fe(H_2O)_4LBr]^+Br^-$ with only one bromine co-ordinated to the metal:



The far infra-red region of this compound has a single absorption at 280 cm^{-1} and may be assigned to ν(FeBr).

(6) Complexes with Silver$^{(I)}$

Reaction of silver$^{(I)}$ perchlorate in triethylorthoformate solution has resulted in the formation of diamagnetic "compound(14)" for which the analysis conforms to the stoichiometry $AgL_{1.5}(ClO_4)$. The *i.r.* spectrum of this compound clearly indicates monodentate O-co-ordinated betaine with an ionic perchlorate group.

Silver$^{(I)}$ ion shows a pronounced tendency to exhibit linear, 2-fold co-ordination; hence a dimeric structure as under is probable

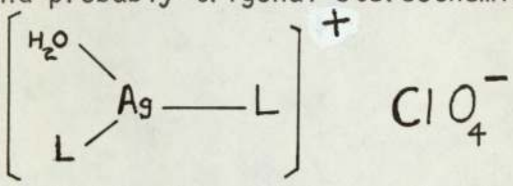
$$[L - Ag - L - Ag - L]^{2+}\ (ClO_4)_2$$

The conductivity in nitromethane, assuming this formulation was 160 $ohm^{-1}\ cm^2\ mol^{-1}$ and is consistent with this formulation. However, the observed *n.m.r.* spectrum (Table 13) of this compound in DMSO appears to suggest the ligand molecules to be equivalent and hence is in apparent conflict with the above structure. Further, if the site of co-ordination is oxygen as strongly indicated by *i.r.* data, the α protons of the pyridine ring would be expected to absorb at a higher τ value than that in the free ylide.

(Table 6). These observations may be rationalized as follows. Dimethyl sulphoxide being a co-ordinating solvent may bring about the solvolysis of the complex in solution and hence the *n.m.r.*, data in this case may not be significant. An equilibrium as follows is likely.

$$[\mathrm{L - Ag - L - Ag - L}]^{2+} + 2n\ (\mathrm{DMSO}) \rightleftharpoons 2\mathrm{Ag(DMSO)}_n + 3\mathrm{L}$$

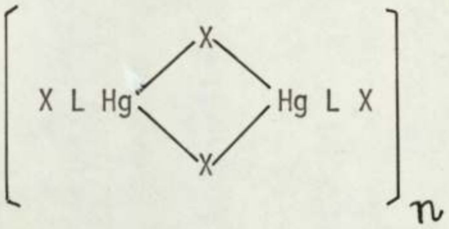
On the other hand, the infra-red spectrum of ("compound(15)") clearly indicates the presence of N-bonded betaine ligand and co-ordinated water. There is no evidence to indicate co-ordinated perchlorate group in this complex. The complex cannot be dehydrated without complete decomposition. These facts, together with the observation of a conductivity of 78 ohm^{-1} cm^{2} mol^{-1} in nitromethane suggest the complex to be $[\mathrm{AgL_2(H_2O)}]^{+}\mathrm{ClO_4^-}$ with tri-co-ordinate and probably trigonal stereochemistry.



The *n.m.r.* spectrum (Table 13) of this complex is similar to the other Ag(I) complex and suggests that in this case too, solvolysis of the compound takes place in DMSO.

(7) Complexes with mercury$^{(II)}$

Both mercury$^{(II)}$ chloride and bromide react with the betaine under similar conditions to yield analogous products. The *i.r.* spectra of both complexes are, indeed, very similar and indicate the presence of monodentate N-co-ordinated betaine liquid. Both these compounds are non-electrolytes in solution and are diamagnetic. Further the *n.m.r.* spectra also indicate that there is only one type of ligand molecule . Hence they must be at least dimeric with probably halogen bridges.



The compound "(16)" exhibits two absorptions at 326 cm^{-1} and 305 cm^{-1} which were absent in the spectrum of the bromide complex and hence may be attributed to ν(HgCl). The far infra-red spectrum, in the case of the compound "(17)" showed several ill-defined bands and hence nothing could be attributed with certainty to ν(Hg-Br).

(E) CONCLUSION

Evidently the interaction of the first row-transition metals, silver$^{(I)}$, and mercury$^{(II)}$, with N-benzoyliminopyridinium betaine has not resulted in *ortho*-metallation reactions. The reactions, instead, have afforded some classical complexes of a less interesting nature. The discussion presented, represents all that can be usefully said about these complexes. Far infra-red spectroscopy has been increasingly used as a technique in inorganic chemistry to assist in stereochemical assignments of new complexes containing metal-halogen bonds. However, the study of complexes of N-benzoyliminopyridinium betaine and its derivatives has shown that a variety of vibrational modes may occur in the same spectral region which make it more difficult to eliminate ligand vibrations confidently. Even in reactions where a large excess of the betaine was used, the maximum number of molecules of the betaine co-ordinated to a metal ion was four and the bulkiness of the betaine may prevent more than four molecules co-ordinating the metal ion. The predominance of O-co-ordination may be due to the greater charge localization on the oxygen atom in the resonance stabilized form of the ylide. The behaviour of copper salts towards the betaine is, as might be expected, different from the other first row-transition metals. The ability of copper salts to lower the decomposition temperature of the betaine is interesting and further studies in this area may be rewarding.

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