

The Chemistry of Ruthenium Schiff Base Complexes,

SCHIFF BASE CHEMISTRY

OF

RUTHENIUM

A thesis submitted

by

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"The great tragedy of Science - the slaying of a beautiful hypothesis by an ugly fact".

T.H. Huxley

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ABBREVIATIONS

A list of the abbreviations used is given here except those of the ligands used which are to be found on the insert inside the back cover.

The abbreviations used, except for the ligands, are those in common usage. However for the ligands a slightly different, more logical nomenclature is used.

For example N,N'-ethylene-bis(salicylideneimine) is usually abbreviated to salenH₂ but in this thesis is abbreviated to sal₂enH₂ as the ligand is formed from 2 moles of salicyl¹aldehyde and 1 mole of ethylenediamine. Similarly N,N'-o-phenylene-bis(salicylideneimine) is usually abbreviated to salophenH₂ or just salphenH₂ when it can be confused with N-phenyl(salicylideneimine). However in the nomenclature used here the latter is salphenH and the former sal₂phenH₂.

Thus to summarise, the first part of the abbreviation refers to the part of the molecule formed from the carbonyl species and the second part of the abbreviation refers to the part of the molecule derived from the amino species. (The diamines considered are 1,2 diamines unless otherwise stated). The subscript between the two sections (omitted if equal to 1) refers to the number of moles of carbonyl compound to each mole of amino compound. The H_n after the abbreviation refers to the number of acidic protons in the molecule.

thf	tetrahydrofuran
Me	methyl

Et	ethyl
Ph	phenyl
n.m.r.	nuclear magnetic resonance
e.s.r	electron spin resonance
nbd	bicyclo(2,2,1)hepta-2,5-diene
COD	cycloocta-1,5-diene
dmsO	dimethylsulphoxide
phent	1,10 phenanthroline
py	pyridine
bipy	bipyridyl
cyoxH ₂	cyclohexan-1,2-dione dioxime
acacH	acetylacetone
ether	diethyl ether
//(A-B)	infra-red spectral absorption due to the vibration of the A-B bond

ABSTRACT

The reactions of $\text{RuCl}_2(\text{PPh}_3)_3$ with the sodium salts of some tetradentate, tridentate and bidentate Schiff bases have been studied and the complexes formed are of the type trans- $\text{Ru}(\text{Schiff base})_n(\text{PPh}_3)_2$ ($n = 1$ or 2). The reactions of the complex trans-bis(triphenylphosphine)- $\text{N,N'$ -ethylene-bis(salicylideneiminato)-ruthenium(II) ($\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$) with carbon monoxide, to yield $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$; nitric oxide, to yield $\text{Ru}(\text{sal}_2\text{en})(\text{ONO})(\text{NO})$ and $[\text{Ru}(\text{sal}_2\text{en})(\text{NO})]_2\text{O}$, and strong non-complexing acids to yield $[\text{Ru}(\text{sal}_2\text{enH})(\text{PPh}_3)] \text{X}$ ($\text{X} = \text{BF}_4^-$, p -toluenesulphonate) are reported.

The preparations of complexes $\text{Ru}(\text{Schiff base})_n\text{Cl}_2$ ($n = 1$ or 2) and $\text{Ru}(\text{CO})_2\text{Cl}_2(\text{Schiff base})$, containing the neutral pyridine-2-alimine Schiff bases, by the reaction with the ruthenium blue solution and $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ are also described.

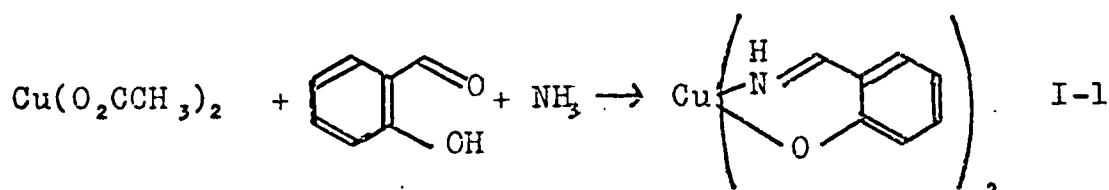
The reactions of several oximes with $\text{RuCl}_2(\text{PPh}_3)_3$ were also studied, the complexes isolated and found to be of the type $\text{Ru}(\text{oxime})_2(\text{PPh}_3)_2$ or $\text{Ru}(\text{oximeH}_n)(\text{PPh}_3)_2\text{Cl}_2$ ($n = 1$ or 2).

The complexes are characterised by i.r., ^1H , ^{31}P and ^{13}C n.m.r. spectra and analytical data.

CHAPTER I

INTRODUCTION

The preparation in 1840 by Ettling ¹ of the first Schiff base complex, bis(salicylideneiminato)copper(II), by the reaction of copper(II)acetate and salicylaldehyde in aqueous ammonia (Equation I-1), and the isolation of



the oxime complex $\text{Ni}(\text{dmgH})_2$ by Chugaev ² by reaction of nickel(II)chloride with dimethylglyoxime, have resulted in the extensive development of the chemistry of these ligands with transition metals.

Interest in this area has been stimulated not only by the desire to form new complexes which may have interesting stereochemistry or different donor atoms, but also in the use of these complexes as biological models for vitamin B_{12} and as reversible oxygen carriers.

However, it is apparent from the literature that while the first row transition metals have been covered in great depth the second and third row elements have been almost neglected. In the case of ruthenium this is particularly surprising considering the amount of interest shown in ruthenium complex chemistry. In fact, only a minimum of work has been carried out using any type of macrocyclic or polydentate ligand and, apart from the complexes $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$, cis- $\text{Ru}(\text{salphen})_2(\text{CO})_2$,

and $\text{Ru}[\text{sal}(\alpha\text{-benzylethyl})]_3$, which will be described in detail later, only a few ruthenium porphyrin complexes have been made ³.

Consequently, the present study was undertaken to react several ruthenium precursors with some of the commoner Schiff bases and oximes in the literature. The reactions carried out here, however are dissimilar from most reports since the complexes prepared are predominantly octahedral 6-co-ordinate with the Schiff base or oxime occupying four or less of the co-ordination sites, and by varying the other ligands present the stereochemistry of the Schiff base or oxime can be altered.

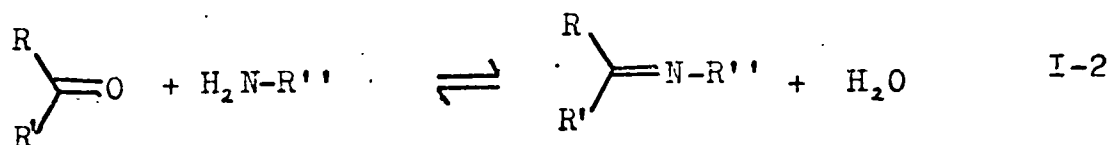
Before discussing the present work it is, however, necessary to place the work in context and so a brief review of Schiff base and oxime complexes follows. This concentrates on the modes of preparation, bonding (in the case of the oximes) and the areas of research which have stimulated most interest. Since the field is so vast it is intended that, while most of the examples cited are from recent work, the earlier reviews pertinent to the subject matter in this thesis will also be quoted where relevant.

A. SCHIFF BASE COMPLEXES

(i) Generalities

A Schiff (or Schiff's) base is defined as the product formed by condensation of an organic carbonyl compound with a primary amine (Equation I-2) to produce a compound .

containing a carbon-nitrogen double bond. The lone pair of electrons on the nitrogen has basic properties which



enables the formation of stable complexes, although it is usual for there also to be present in the molecule a functional group with an acidic proton near enough to the -C=N- group to allow formation of a 5 or 6 membered ring by chelation to the metal atom.

Although the first Schiff base complexes were prepared by Ettling¹ and Schiff⁴ it was not until the 1920's that the first synthetic study of the chemistry of this type of ligand was carried out by Pfeiffer and his co-workers from 1931-1942⁵. They produced a large number of complexes of transition metals with ligands derived from o-aminobenzaldehyde, salicylaldehyde and pyrrole-2-aldehyde.

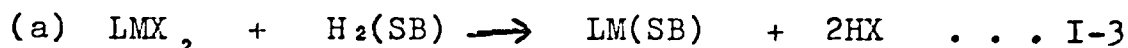
Since then many papers have been published and the last comprehensive review to be published was by Chakravorty, Holm and Everett⁶ which covered the literature to the end of 1964.

(ii) Modes of Formation

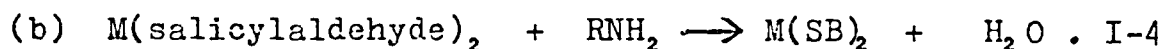
Schiff base complexes have been prepared by a number of methods. Most of these methods have only been applied to salicylideneimine ligands but could be expanded to other Schiff bases with acidic protons. Those Schiff bases derived from pyridine-2-aldehyde are prepared

differently as they contain no acidic protons.

(H₂SB = Schiff Base)

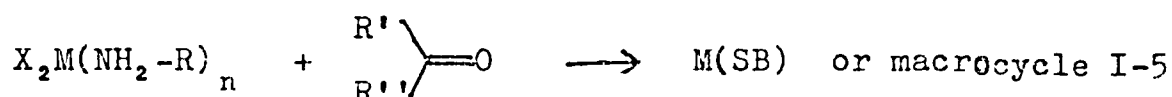


This method is relatively uncommon but has been shown for the reaction of TiX₄ (where X = Cl ⁷, isopropoxy ⁸) with H₂sal₂en and are best formulated $[\text{Ti}(\text{SB})]\text{X}_2$.



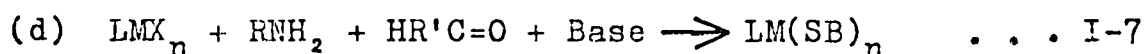
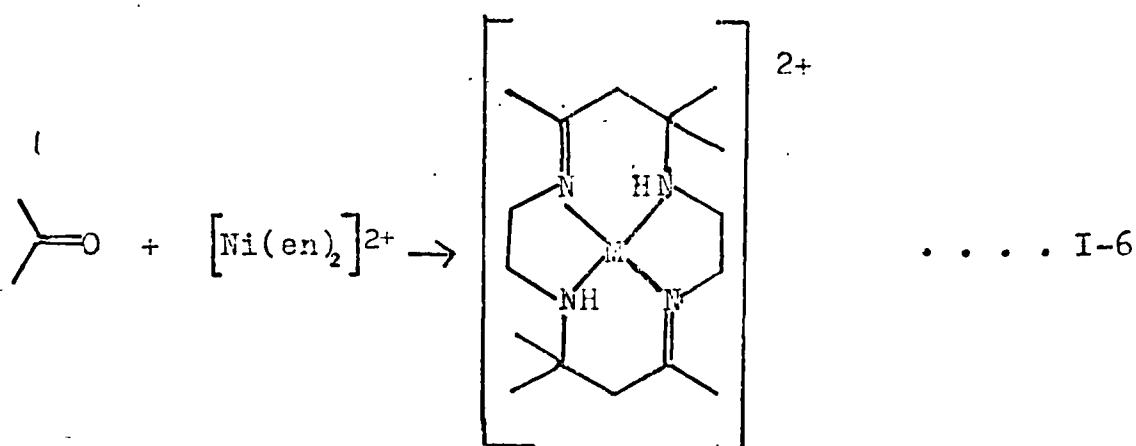
First discovered by Schiff ⁴ this method has found great use primarily among the first row transition metal complexes ⁵ but in some cases unusual products are given. Tris(salicylaldehydato)chromium(III) with primary amines yields the expected product but with ethylenediamine forms the ligand ⁻O-C₆H₄-CH=NCH₂CH₂-NH₂ to give Cr(salen)₂X ⁹.

(c) The converse ¹⁰ reaction has also been shown to be of use

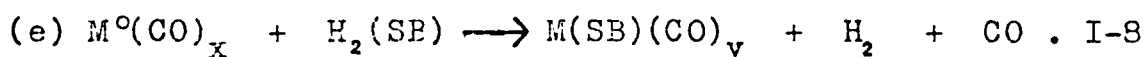


Using M = Ni, Cu a variety of complexes has been prepared. The simple condensation of salicylaldehyde and Ni(en)₂Cl₂ in pyridine yielded the expected product Ni(sal₂en) ¹¹. However a similar reaction using (catechol)(1,3-propanediamine)nickel(II) and salicylaldehyde led to retention of the catechol and co-ordination of the Schiff base formed only through the nitrogens of the -C=N- ¹². Curtis ¹³ has studied the reaction of various amine complexes with acetone and other aliphatic carbonyl

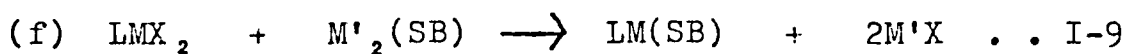
compounds and formed macrocyclic ligands e.g.



The Schiff base is preformed in situ, then equivalent amounts of NaOH, NaOAc, NEt₃ or KOBut are added together with the metal precursor. This is by far the most common method and is particularly useful for ligands which are not readily isolated pure ¹⁴. It is not, however, of use if non-aqueous conditions are required except when NEt₃ has been used as a base.



Under forcing conditions, such as prolonged refluxing in dimethyl formamide, transition metal binary carbonyls react with Schiff bases and oxidation of the metal occurs with formation of the M(SB) complex. For ruthenium $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$ and cis-Ru(salphen)₂(CO)₂ are formed, with M = Fe, Mn only the M(sal₂en) complexes are formed ¹⁵, but with Mo(CO)₆ $[\text{MoO}(\text{sal}_2\text{en})]_2\text{O}$ was formed ¹⁶.

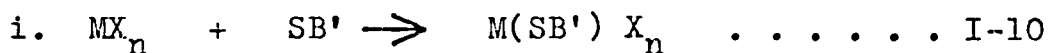


In these reactions the salt of the Schiff base is preformed either by reaction with TlOH ¹⁷, NaH ¹⁸ or.

LiOEt ¹⁹ which can then be isolated pure and used for reactions under anhydrous conditions. Although this method is only relatively new, it would seem to be the best scheme for reaction in non-aqueous media. The reaction of the sodium salts of the Schiff bases is the method employed primarily in this thesis.

The complexes of pyrrole-2-alimine have been prepared generally by reactions of type (d) ²⁰ but in non-aqueous media using potassium tertiary butoxide as the base in thf ²¹.

The complexes prepared from the neutral pyridine-2-alimine ligands have been prepared by three general methods (Schiff base = SB') :-



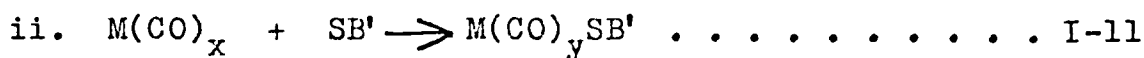
First used by Busch ²² for the preparation of Cu^{II} and Fe^{II} complexes, this is the commonest method. With py_2en , however, the Cu^{II} complexes described as $[\text{Cu}(\text{py}_2\text{en})] \text{X}_2$ ²³ ($\text{X} = \text{Cl}, \text{Br}$) formed via the reaction of CuX and py en in alcohol have been

shown to be a variety of complexes; $\text{Cu}_2\text{py}_2\text{enX}_4$, $[\text{Cu}(\text{py}_2\text{en}+\text{ROH})\text{X}]\text{ClO}_4$ and $[\text{Cu}_2(\text{py}_2\text{en})_3](\text{ClO}_4)_4$ ²⁴.

$\text{Cu}_2\text{py}_2\text{enX}_4$ was postulated as having the py_2en ligand acting as a bridging bis bidentate ligand.

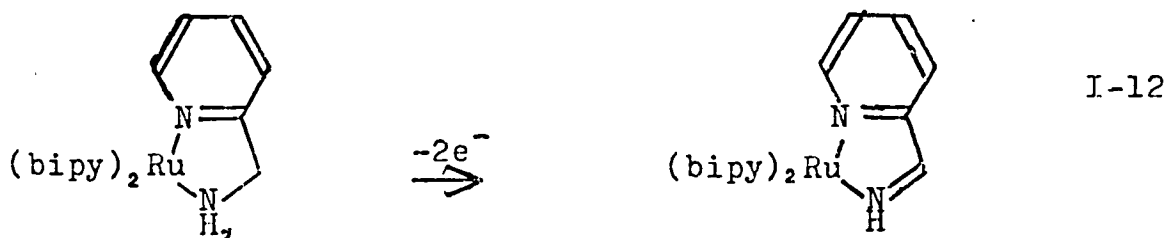
$[\text{Cu}_2(\text{py}_2\text{en})_3](\text{ClO}_4)_4$ was shown by X-ray crystallography to have octahedral Cu^{II} atoms with three bridging py_2en ligands. However, $[\text{Cu}(\text{py}_2\text{en})](\text{ClO}_4)_2$ with Cl^- in alcohol was found to add one mole of alcohol across one $-\text{C}=\text{N}-$ to give a complex of formula $[\text{Cu}(\text{py}_2\text{en}+\text{ROH})\text{X}]\text{ClO}_4$ the structure of which has been established as

5 co-ordinate Cu^{II} 25.



The reactions of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ with bidentate pyridine-2-aldimines yielded $\text{M}(\text{CO})_4(\text{SB}')$. The species with $\text{M} = \text{Mo}$ was also formed by the reaction of $\text{Mo}(\text{CO})_4(\text{nbd})$ and the Schiff base 26. In this respect the Schiff bases form similar complexes to bipyridyl 27,28 and 1,10 phenanthroline 29.

iii. Several ruthenium α, α' diimino complexes which contain pyridine-2-alimine ligands have also been prepared by electrolytic oxidation of 2(aminomethylpyridyl) complexes of ruthenium 30.



More detailed discussion of this type of reaction is to be found later.

(iii) Summary of the Main Areas of Research

By far the greatest interest has been shown in the chemistry of salicylideneimine complexes as compared to other Schiff base ligand types. This is possibly a consequence of the ready synthesis of the deprotonated ligand.

The ability of these complexes to serve as good

models for biological systems, in particular the reversible addition of dioxygen, discovered in 1938, when it was found that $\text{Co}(\text{sal}_2\text{en})$ could act as an oxygen carrier ³¹.

The nature of this dioxygen species has been widely studied ³² and the final species formed has been found to be $[\text{BCo}(\text{sal}_2\text{en})]_2\text{O}_2$ (where B is a base such as dmf or pyridine) where the dioxygen bonds as a μ -peroxo species ³³ and a mechanism has been proposed ³⁴ involving a monomeric $\text{BCo}(\text{sal}_2\text{en})\text{O}_2$ paramagnetic species. Using sterically hindered Schiff bases, the monomeric complexes have been isolated and their structures established by X-ray crystallography ³⁵. The reactions of other $\text{M}(\text{sal}_2\text{en})$ complexes with oxygen have been covered in a general review on these compounds by Hobday and Smith ³⁶ although none have been found to act as reversible oxygen carriers. The general field has very recently been reviewed by Martell and McLendon ³⁷.

Because of the wide range of amines and substituted salicylaldehydes available, much detailed work has been carried out on the stereochemistry of the Schiff base complexes. Calligaris et al. ³⁸ have reviewed the stereochemistry of complexes containing tetradentate Schiff bases and illustrate the various possible conformations of sal_2en in octahedral complexes as either a) planar tetradentate, b) non-planar tetradentate, c) bisbidentate and d) planar tetradentate bridging through the oxygen atoms. The four types are illustrated on the next page (Figure I-i). By far the commonest is type a) with the ligand basically planar, although there are slight conformational changes resulting in either

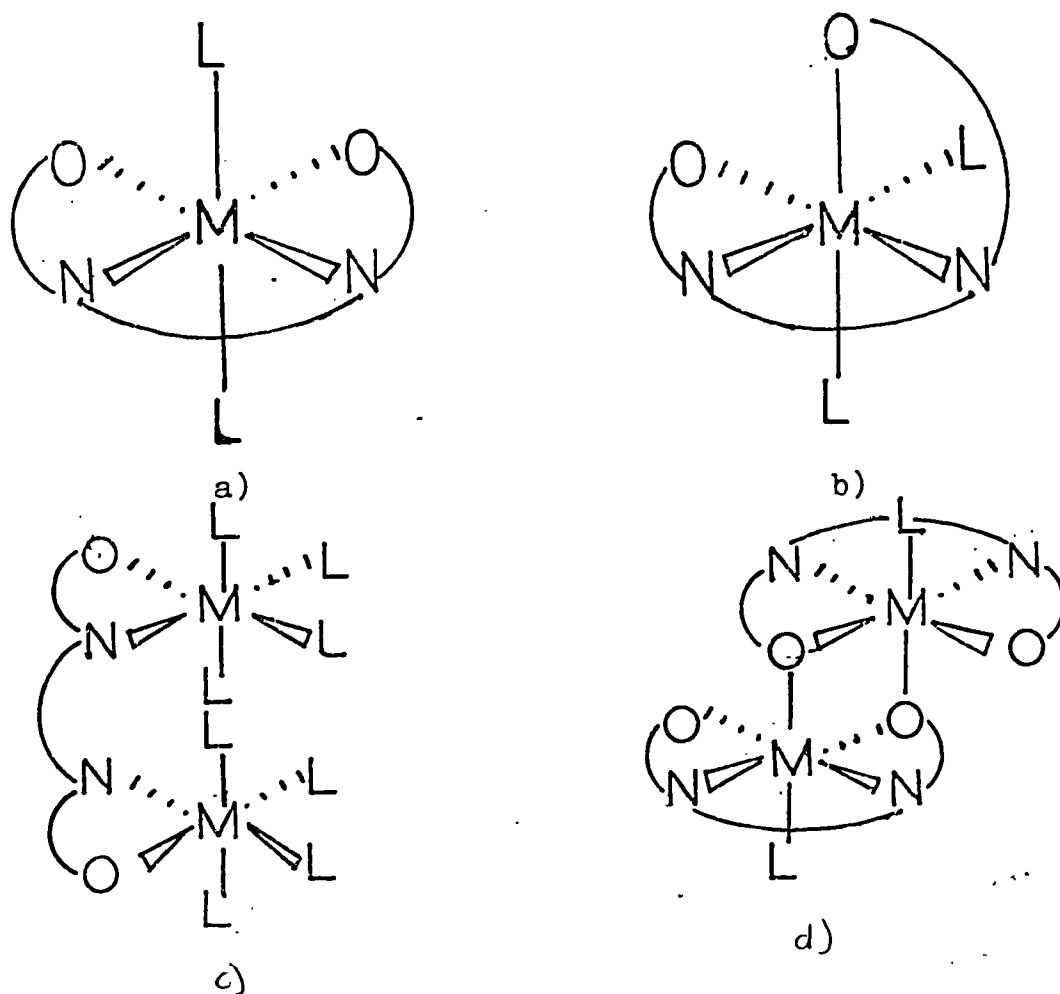
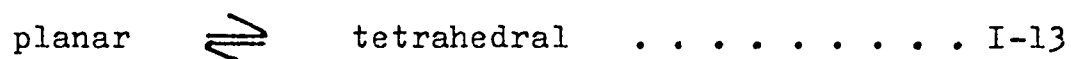


Figure I-i

stepped (see Appendix I) or umbrella forms e.g. $[\text{Co}(\text{sal}_2\text{en})\text{L}_2]^+$ ³⁹, but most complexes of the form $\text{M}(\text{sal}_2\text{en})$ have this monomeric structure, e.g., $\text{M} = \text{Co}$, Fe , Mn , Cu which were all isolated initially by Pfeiffer. Type b) is less common, although an increasing number of examples has been found of the form $\text{M}(\text{sal}_2\text{en})\text{L}_2$. In this thesis $\text{L}_2 = \text{nbd}$, $2(\text{CO})$, while $\text{Co}(\text{sal}_2\text{en})(\text{acac})$ ⁴⁰ $\text{R}_2\text{Sn}(\text{sal}_2\text{en})$ ($\text{R} = \text{Me}, \text{Ph}$) ⁴¹, and $\text{Co}(\text{sal}_2\text{en})(\text{glycine})$ ⁴² were made. Type c) has been shown to exist in $\text{Co}_2[(3\text{-MeOsal})_2\text{en}]_3$ ⁴³ which has both non-planar and bis-bidentate Schiff base ligands. A similar structure has been proposed for $\text{Ln}_2(\text{sal}_2\text{en})_3$ ⁴⁴ ($\text{Ln} = \text{lanthanide}$). Type d) was first recognised in the "inactive" form of $[\text{Co}(\text{sal}_2\text{en})]_2$ ⁴⁵ i.e. that which does not uptake dioxygen, but has

also been found in $[\text{Fe}(\text{sal}_2\text{en})\text{Cl}]_2$ ⁴⁶ and proposed in $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$ ¹⁵.

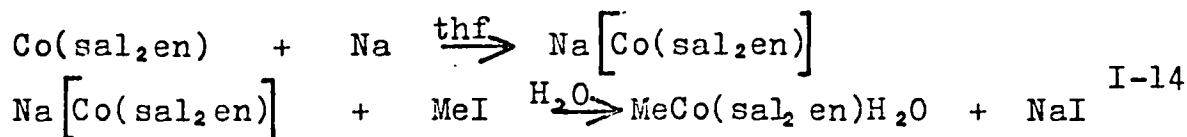
The stereochemistries of the first row transition metal bis-bidentate and quadridentate Schiff base complexes has been extensively studied because of the possibility of structural changes (Equation I-13), with resultant



changes in the magnetic properties of the complex, mainly due to steric effects. Hohm and his co-workers have studied this subject comprehensively⁴⁷ and shown that while Ni^{II} preferentially forms planar complexes, Co^{II} preferentially forms tetrahedral complexes, and so by making the ligand such that the preferred confirmation is no longer the lowest energy state it is then possible to form planar Co^{II} complexes and tetrahedral Ni^{II} complexes, e.g. $\text{Co}(\text{salMe})_2$ and $\text{Ni}(\text{sal-isopropyl})_2$ ⁴⁸, although in a lot of these cases the system is complicated by association to form 5 and 6 co-ordinate species. The resultant stereochemical changes effect perturbations in the magnetic properties of the complexes. This also occurs in sal_2en and pyrrole-2-alimine complexes where increasing the number of methylene groups results in Cu^{II} and Ni^{II} complexes with no structure change, but in Co^{II} increasing the methylene bridge length to 7-10 methylenes results in a change to a tetrahedral structure⁴⁹.

$\text{Co}(\text{sal}_2\text{en})$ complexes have also been widely studied

since the discovery of Co-alkyl bonds in vitamin B₁₂ ⁵⁰, and the subsequent isolation of MeCo(sal₂en)L ⁵¹ (L = H₂O, py) by the reaction below (Equation I-14).



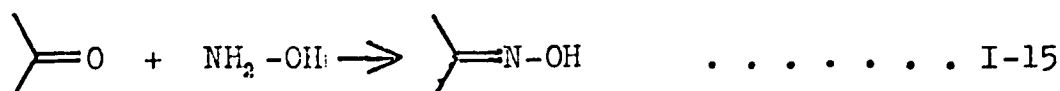
Of course, by substituting functional groups containing acidic protons or basic nitrogens in the amine such that chelation is possible, a large number of complexes have been prepared with not only N and O as donor atoms but also S, P and Se, sometimes resulting in interesting stereochemistries and polymerisation. These areas have been reviewed recently by Bertrand ⁵² and Hodgson ⁵³.

Finally, in industry, Schiff base complexes have been used to stabilise polyolefins ⁵⁴ and as additives in the petroleum industry ⁵⁵, although these appear to be fairly minor uses.

B. OXIME COMPLEXES

(i) Generalities

The name oxime is a contraction of oxy-imine, >C=N-OH. The oxime group is amphiprotic with a slightly basic nitrogen atom and a mildly acidic hydroxyl group. Oximes are generally prepared by the reaction of an organic carbonyl compound with hydroxylamine (Equation I-15).



Since the discovery by Chugaev ² in 1905 of the reaction between Ni^{II} salts and dimethylglyoxime (dmgH_2) to give $\text{Ni}(\text{dmgH})_2$, the reaction of transition metals with oximes has been intensely studied. The early work has been summarised by several authors ^{56,57}.

This brief review of the literature of oxime complexes will concentrate on the structural aspects of the complexes, rather than the use of oximes as analytical reagents though various reviews will be mentioned that concentrate on this aspect.

(ii) Modes of Bonding

The ambidentate nature of the oxime group is illustrated in Figure I-ii.

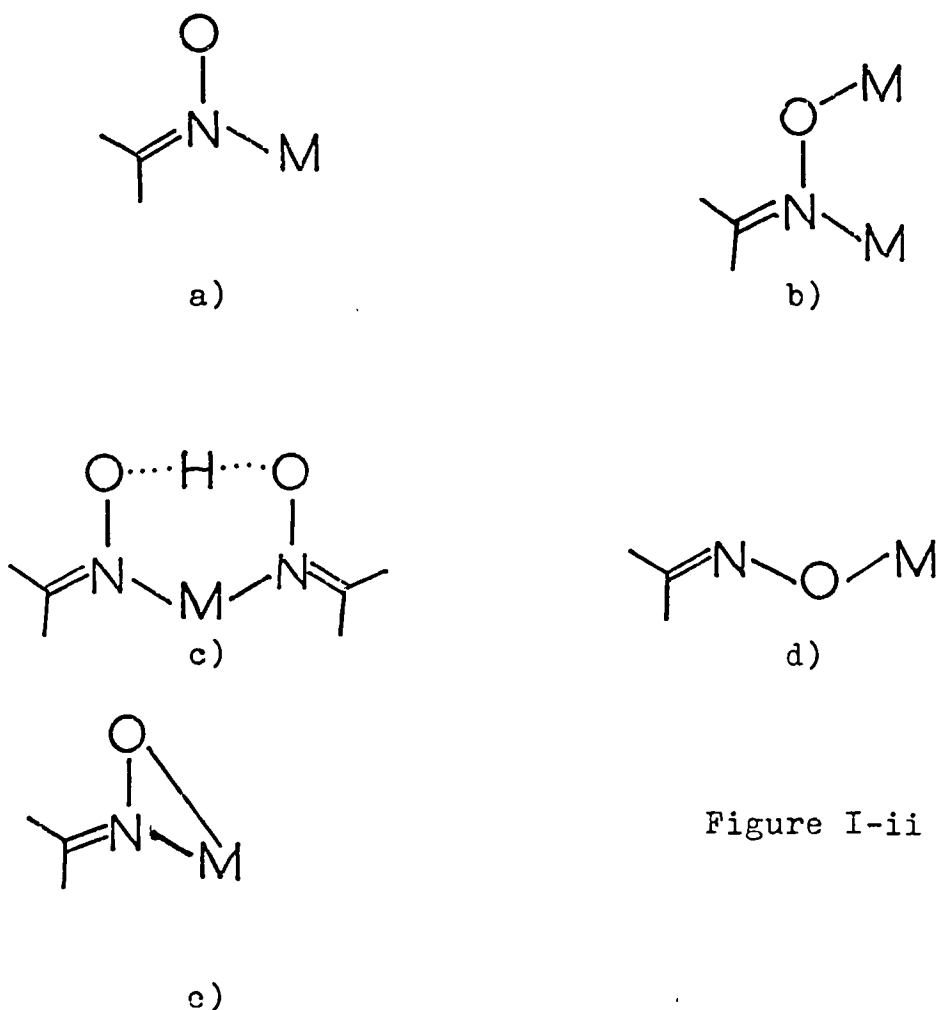
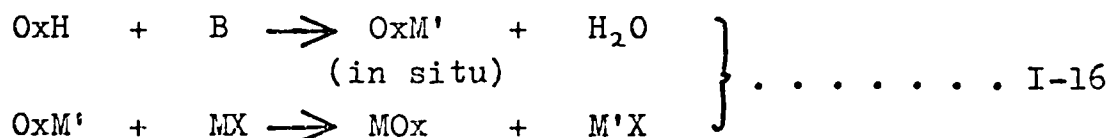


Figure I-ii

The preparation of these oxime complexes is invariably by the reaction (Equation I-16) where OxH = oxime and the base B is usually NaOAc or NaOH. In a very



recent publication lithium and trimethyl tin salts were used for reaction in anhydrous conditions ⁵⁸. In this present work the sodium salts were used.

Of the various types of bonding I-ii is the least common, having been established in one example only; the complex $(\text{ato})\text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ ⁵⁹ (Figure I-iii) prepared by reaction of $\text{NaMo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$ with 2-bromo-2-nitrosopropane or $\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)\text{Cl}$ and the oxime salt ⁵⁸. These

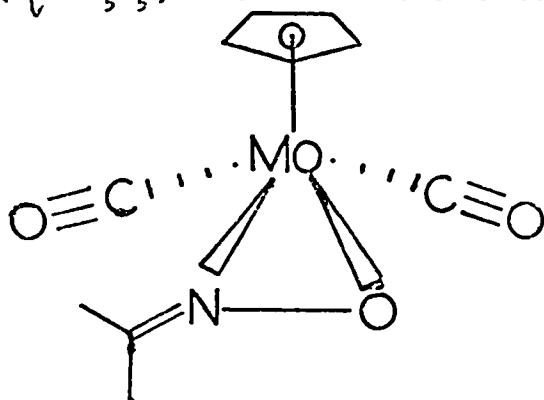


Figure I-iii

complexes will be discussed in detail in chapter IV with relevance to the complex cis- $\text{Ru}(\text{ato})_2(\text{PPh}_3)_2$ which appears to be similar.

The bridging mode shown in I-ii is much more common and, by way of comparison, the ligand atoH reacts with palladium(II)acetate to produce a trimeric complex $[\text{Pd}(\text{OAc})(\text{ato})]_3$ with the three palladium atoms

constituting an equilateral triangle in which each adjacent pair is held by one OAc^- and one ato^- ligand ⁶⁰. Similar acetoxime bridging has been found in the non-transition element complexes $[\text{Z}(\text{ato})\text{Me}_2]_2$ where $\text{Z} = \text{B}, \text{Al}$ or Ge ⁶¹. Recently Bertrand has identified a copper(II) complex, $[\text{Cu}_4\text{L}_4(\text{ClO}_4)_2](\text{ClO}_4)_2$ ⁶² where $\text{L} = 2\text{-2-aminoethylimino-3-butanoneoxime}$ by reaction of $\text{Cu}(\text{ClO}_4)_2$ and the oxime in methanol. Each copper atom is co-ordinated by two oxygens and three nitrogens. Interestingly, the analogous 2-pyridyl complex is only dimeric with the fifth position being taken up by a solvent acetonitrile ligand.

The normal type of bonding in $\text{M}(\text{dmgH})_2$ complexes is type I-iiic with a hydrogen bond between the two oxime ligands resulting in an approximately planar structure. The nature of the hydrogen bonding has been studied with great interest and it has been found that if the $\text{O} \cdots \text{O}$ distance is greater than $2.5\overset{\circ}{\text{A}}$ the hydrogen bond will be assymetric. Thus only $\text{Ni}(\text{dmgH})_2$ ($\text{O} \cdots \text{O} = 2.40\overset{\circ}{\text{A}}$) and similar nickel complexes appear to have symmetric hydrogen bonds ⁶³. The hydrogen atom may be replaced by $-\text{BF}_2-$ by reaction of the complexes $\text{M}(\text{dmgH})_2$ with $\text{BF}_3 \cdot \text{OEt}_2$ in encapsulation reactions. For $\text{M} = \text{Ni}$, $\text{Ni}(\text{dmg})_2(\text{BF}_2)_2$ ⁶⁴ is formed but with $\text{Co}(\text{dmgH})_2$ a bicyclic macrocyclic ligand was formed and a trigonal prismatic complex $\{\text{Co}[(\text{BF}_2)_2(\text{dmg})_3]\}\text{BF}_4$ is formed ⁶⁵.

The infra-red spectra of the $\text{M}(\text{dmgH})_2$ complexes have been studied and it has been determined that the $\text{C}=\text{N}$ stretching vibrations, $\nu(\text{C}=\text{N})$, lie in the range

1550 - 1590 cm^{-1} ^{66,67}; the decrease in frequency $\text{Cu} < \text{Ni} < \text{Cu} < \text{Fe}$ being ascribed to increasing conjugation by increasing the $\text{M} \rightarrow \text{N}=\text{C}$ donor π bond strength. The N-O stretching vibration, $\nu(\text{N}-\text{O})$, is assigned as two bands, one in the range 1190 - 1220 cm^{-1} and the other between 1065 - 1110 cm^{-1} , which are considered to be characteristic of N-bonded dioximes.

A series of compounds has been prepared by Lacey et al. ^{68,69} in which it has been shown that the oxime ligand is both O and N bonded in different isomers (Figure I-iv).

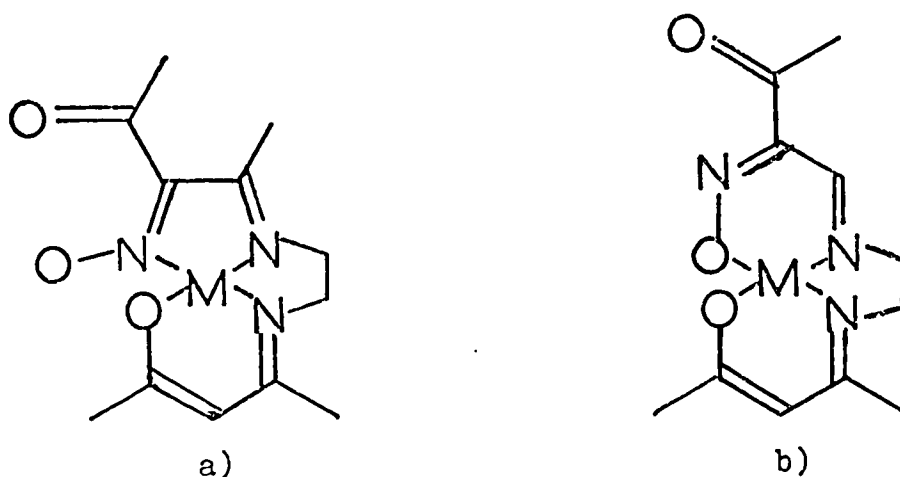


Figure I-iv

The O-bonded oxime I-ivb has a strong band at 1171 cm^{-1} which is assigned to a coupled $\nu(\text{N}-\text{O})$ (44%, by isotopic exchange) O-bonded. In the other isomer I-iva the absence of the strong band at ca. 1200 cm^{-1} is deemed as sufficient evidence for non-oxygen co-ordination ⁷⁰. A recent publication of a mixed oxime complex (Figure I-v) states that in the O-bonded

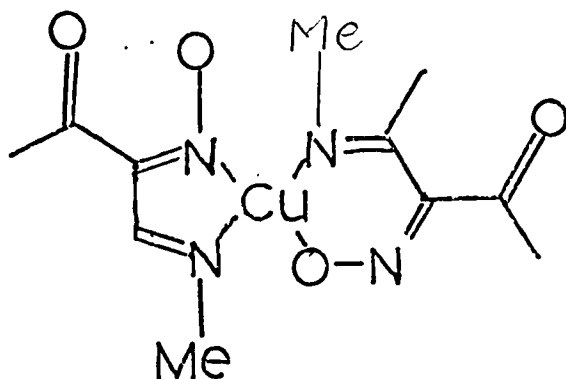


Figure I-v

oxime $\nu(\text{N-O})$ is at 1210 cm^{-1} while that for the N-bonded oxime $\nu(\text{N-O})$ is at 1150 cm^{-1} ⁷¹ with the molecule preferentially forming one five and one six membered chelate ring. It is clear, therefore, that the situation, as to the actual position of N and O bonded oxime $\nu(\text{N-O})$ vibrations is still a little confused, and only by comparison with those complexes of known X-ray structure can the actual mode of bonding be determined (cf. the complex in Figure I-ivb whose structure has been proved by X-ray crystallography ⁷²).

(iii) Primary Areas of Research

Like the $\text{Co}(\text{sal}_2\text{en})$ complexes, the cobalt oxime complexes, abbreviated to cobaloximes, have been used as biological models for vitamin B_{12} ⁷³. The main complexes used have been (Figure I-vi) where $\text{R} = \text{alkyl}$ and $\text{B} = \text{base}$ such as pyridine or imidazole. These are used since they have stable $\sigma\text{Co-alkyl}$ bonds. The complexes are formed in a similar way to $\text{RCo}(\text{sal}_2\text{en})\text{B}$ by reduction to Co^{I} species followed by reaction with alkyl halides. The kinetics of the reactions and

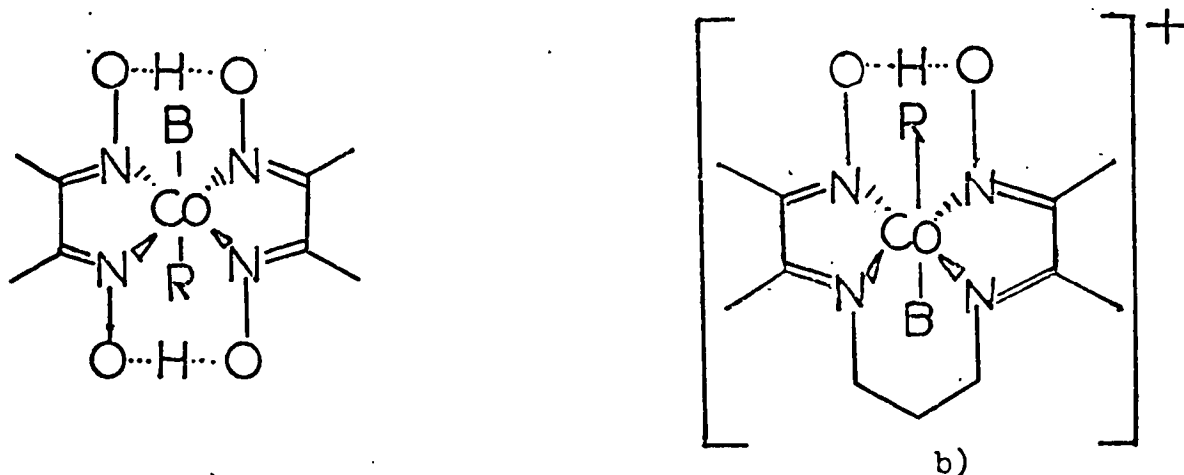


Figure I-vi

the stereochemistries of the reaction products have been extensively studied ⁷⁴ in an attempt to perfect the model systems. Most of the work, however, has been involved with the reactivity of the alkyl fragment. Rhodoximes with σ Rh-C bonds have been prepared but are much less reactive than the corresponding cobalt complexes ⁷⁵.

Apart from the synthetic research which has been described in detail by Chakravorty, the major use of oximes in chemistry is as analytical reagents. Many oximes have been used as either colorimetric reagents ⁷⁶ or as gravimetric reagents. For example, the insolubility of $\text{Ni}(\text{dmgH})_2$ and $\text{Pd}(\text{dmgH})_2$ enables very accurate determination of the nickel and palladium content of a solution. Egneus ⁷⁷ has reviewed the chemistry of dioximes from this aspect rather than a structural viewpoint. The whole field of chelating agents in metal extraction for industry has also recently been reviewed by Ashbrook ⁷⁸. However the gravimetric analysis is only a part of the analytical use, as oximes with transition metals

usually form highly coloured solutions and thus spectrophotometry can be used to determine the heavy metal content in the solution ⁷⁶. Often the exact nature of the metal complex is uncertain, only the metal:ligand ratio being known, and the essence of the problem is to produce selective reagents which can detect the presence of one metal without complexing any others which might be present; an aim which is rarely, if ever, achieved.

The work described in the remainder of this thesis concentrates on the synthesis of novel ruthenium complexes using selected ligands.

In chapter II the reaction of the sodium salts of Schiff bases, derived principally from salicylaldehyde, with various ruthenium precursors are described.

The synthesis of complexes containing neutral Schiff bases required different procedures from those normally used (see above) and these are recorded in chapter III.

Finally in chapter IV the preparation of some ruthenium complexes containing oxime ligands is described.

CHAPTER II

COMPLEXES OF RUTHENIUM (II) WITH SCHIFF BASES DERIVED FROM SALICYLALDEHYDE, PYRROLE-2-ALDEHYDE AND PENTAN-2,4-DIONE

A. INTRODUCTION

In this chapter is described the preparation of complexes of ruthenium(II) using Schiff base ligands which contain acidic protons. Complexes of those Schiff base ligands which do not have acidic protons are discussed in Chapter III.

Although there have been many complexes prepared by the reaction of Schiff bases with transition metals (see Chapter I) there are very few in which a Schiff base ligand has been complexed to ruthenium.

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with sal_2enH_2 has been reported to give a complex of stoichiometry $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$ or $\text{Ru}(\text{sal}_2\text{en})(\text{CO})_2$ ¹⁵. The former is favoured since the complex is insoluble in all common solvents. The proposed structure (Figure II-i) has bridging through the oxygens as has been found for the "inactive" form of $\text{Co}(\text{sal}_2\text{en})$ ⁴⁵ so-called because it does not reversibly complex with O_2 .

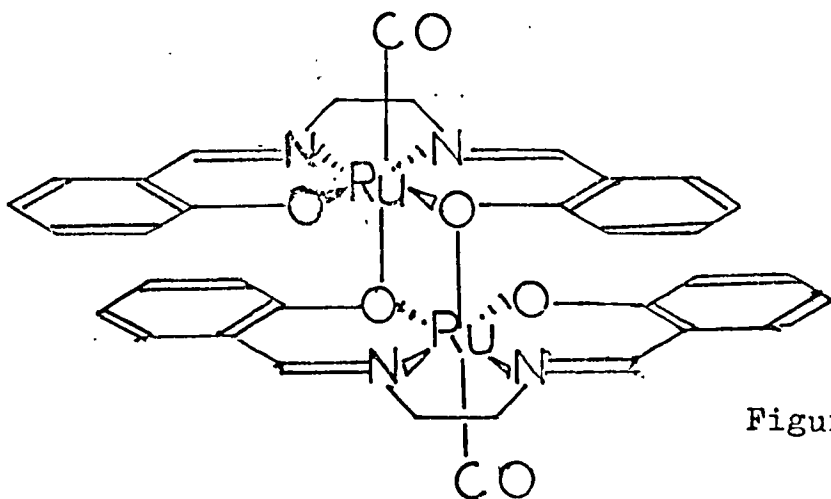


Figure II-i

In this thesis this complex $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$ has been prepared by other methods. The reaction of salphenH and $\text{Ru}_3(\text{CO})_{12}$ gave very small yields (less than 1%) of cis- $\text{Ru}(\text{salphen})_2(\text{CO})_2$. Also the reaction of ruthenium(III)tris(acetylacetonate) with N- α -benzylethylsalicylideneimine in ethyl benzoate gave the chiral tris complex ⁷⁹.

Finally there has been a study of ruthenium Schiff base complexes as potential hydrogenation catalysts ⁸⁰ although no isolation or characterisation of the complexes was described.

B. SCHIFF BASE COMPLEXES CONTAINING TERTIARY PHOSPHINES

A wide range of Schiff base complexes was prepared by the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with the sodium salts of the Schiff bases, which were prepared by stirring the appropriate Schiff base with sodium hydride in diethyl ether ¹⁸ until hydrogen evolution ceased. Although the reactions were carried out with $\text{RuCl}_2(\text{PPh}_3)_3$, the reaction of $\text{RuCl}_2(\text{PPhMe}_2)_4$ appeared to be similar and there is no reason why many different phosphine complexes could not be prepared.

Schiff base complexes containing tertiary phosphines are known only for cobalt and rhodium, the former being prepared by the reaction of $\text{Co}(\text{sal}_2\text{en})$ with PR_3 , followed by acidification with HClO_4 , ⁸¹ to give complexes of the type $[\text{Co}(\text{sal}_2\text{en})(\text{PR}_3)_n]^+$ ($n = 1$ or 2) ⁸². The reactions of $[\text{Rh}(\text{CO})_2]_2(\text{sal}_2\text{en})$ and $\text{Rh}(\text{CO})_2[\text{sal}(\text{p-Mephen})]$ with PPh_3 yielded in benzene $[\text{Rh}(\text{CO})(\text{PPh}_3)]_2(\text{sal}_2\text{en})$

and $\text{Rh}(\text{CO})(\text{PPh}_3)[\text{sal}(\text{p-Mephen})]$ respectively. Similar iridium complexes were also isolated ⁸³.

(i) Quadridentate ligands

On refluxing a suspension of the sodium salt of the Schiff bases and $\text{RuCl}_2(\text{PPh}_3)_3$ in thf, sodium chloride was precipitated and deep red solutions obtained for the ligands derived from salicylaldehyde, and orange-red solutions from pyrrole-2-aldehyde from which were isolated complexes of the type trans- $\text{Ru}(\text{SB})_1(\text{PPh}_3)_2$.

The ^{31}P n.m.r. spectra of the triphenylphosphine complexes have only a singlet in the region +25 - +38 ppm (for $\text{Ru}(\text{sal}_2\text{en})(\text{PPhMe}_2)_2$ a singlet at 16.8 ppm), relative to 85% H_3PO_4 external standard which is in agreement with the complexes having mutually trans phosphines ⁸⁴. Although the isolation of $\text{Ru}[\text{sal}_2(1,3\text{-prop})](\text{PPh}_3)_2$ and $\text{Ru}[\text{sal}_2(1,6\text{-hex})](\text{PPh}_3)_2$ proved very difficult as the complexes appeared oily, there was no evidence for the formation of cis-phosphine complexes with a distorted Schiff base ligand even on increasing the chain length of the methylene groups to six (cf. the change in structure of some cobalt Schiff base complexes ⁴⁹) and the ^{31}P n.m.r. spectra of the two complexes had singlet resonances at +29.81 ppm and +31.58 ppm respectively. This was probably due to the tendency of ruthenium(II) to form octahedral complexes and clearly the least hindered arrangement is with mutually trans-phosphines and the Schiff base planar.

The infra-red spectra of the complexes in the region $1650 - 1500 \text{ cm}^{-1}$ was complicated, with strong bands at ca. 1600 cm^{-1} and others at ca. 1520 cm^{-1} . Initially, the bands at 1520 cm^{-1} were assigned to the C=N stretching vibrations, $\nu(\text{C=N})$, and those at 1600 cm^{-1} to the C-O vibrations of the phenolic groups, $\nu(\text{C-O})$ ⁶. However, it is now generally agreed that the assignments should be reversed. Indeed in the pyrrole-2-alimine complexes no vibrations were observed at 1520 cm^{-1} . The 1600 cm^{-1} region is complicated, in this case, by the vibrations due to the aromatic rings of PPh_3 . The spectra of the complexes did, however, appear similar to other compounds of this type, with $\nu(\text{C=N})$ shifted to lower frequency relative to the unco-ordinated ligand. These shifts in the phosphine containing complexes were, in general, greater than in other complexes prepared due to the π -acceptor properties of the phosphine which increased the Ru-N π bonding, so decreasing the strength of the C=N bond. M-N bonds in sal_2en complexes have been found to be shorter than M-N bonds in amine complexes. For example in $\text{Co}(\text{sal}_2\text{en})$ Co-N are $1.83 \overset{\circ}{\text{\AA}}$ and $1.86 \overset{\circ}{\text{\AA}}$, while in cobalt-bis(L-histadinate) Co-N is $2.07 \overset{\circ}{\text{\AA}} - 2.15 \overset{\circ}{\text{\AA}}$ and in cobalt(peptide) Co-N is $2.12 \overset{\circ}{\text{\AA}} - 2.14 \overset{\circ}{\text{\AA}}$, the difference being ascribed to M-N π bonding³⁸.

In the complex prepared in this work, $\text{Ru}(\text{sal}_2\text{en})(\text{ONO})(\text{NO})$, the average Ru-N(sal_2en) bond length was $2.005 \overset{\circ}{\text{\AA}}$ whereas in $[\text{Ru}(\text{en}) \text{N}_2\text{N}_3] \text{PF}_6$ the Ru-N(en) bond length was found to be $2.13 \overset{\circ}{\text{\AA}}$ ⁸⁵, and in $\text{Ru}_3\text{O}_2(\text{en})_2(\text{NH}_3)_{10}\text{Cl}_6$

the Ru-N(en) bond length was close to $2.13 \text{ \AA}$ ⁸⁶.

The ¹H n.m.r. spectra of these complexes were often difficult to obtain because of low solubility. In the bis-triphenylphosphine complexes the methine resonances were obscured by the phenyl resonances. However, using PPhMe₂ and sal₂enH₂ as the Schiff base the methine resonance of Ru(sal₂en)(PPhMe₂)₂ was observed at 1.96 τ as a 1:2:1 triplet due to long range coupling with the two trans phosphorous atoms. The value $J_{P-H} = 5 \text{ Hz}$ is similar to $[\text{Co}(\text{sal}_2\text{en})(\text{PR}_3)_2]^+$ ⁸², $J_{P-H} = 3.0 - 3.5 \text{ Hz}$. The methylene protons in Ru(sal₂en)(PPh₃)₂ appeared as a broad resonance at 6.2 - 6.4 τ . This broadening was due to the non-equivalence of the four methylene protons on co-ordination. The expected pattern is A₂B₂ or AA'BB' but only a diffused multiplet could be observed. The multiplet is a common feature of M(sal₂en) complexes³⁶. The methylene resonances of Ru(sal₂en)(PPhMe₂)₂ gave a similar pattern but the methyl resonances were observed as two 1:2:1 triplets ($J_{P-H} + J_{P-H'} = 16 \text{ Hz}$) at 8.38 τ , 8.78 τ respectively. This indicates non-equivalence of the methyl groups and loss of symmetry in the plane through the P-Ru-P axis.

The ¹H n.m.r. spectrum of the complex trans-Ru(pyr₂en)(PPh₃)₂ had a broad resonance for the phenyl protons at 2.97 τ and a small shoulder at 2.75 τ due to the methine protons. There was, however, a single resonance at 4.17 τ due to four pyrrole protons (Figure II-ii). Also, unlike the sal₂en complexes the methylene protons resonated as a singlet at 6.36 τ . Ru(pyr₂phen)(PPh₃)₂

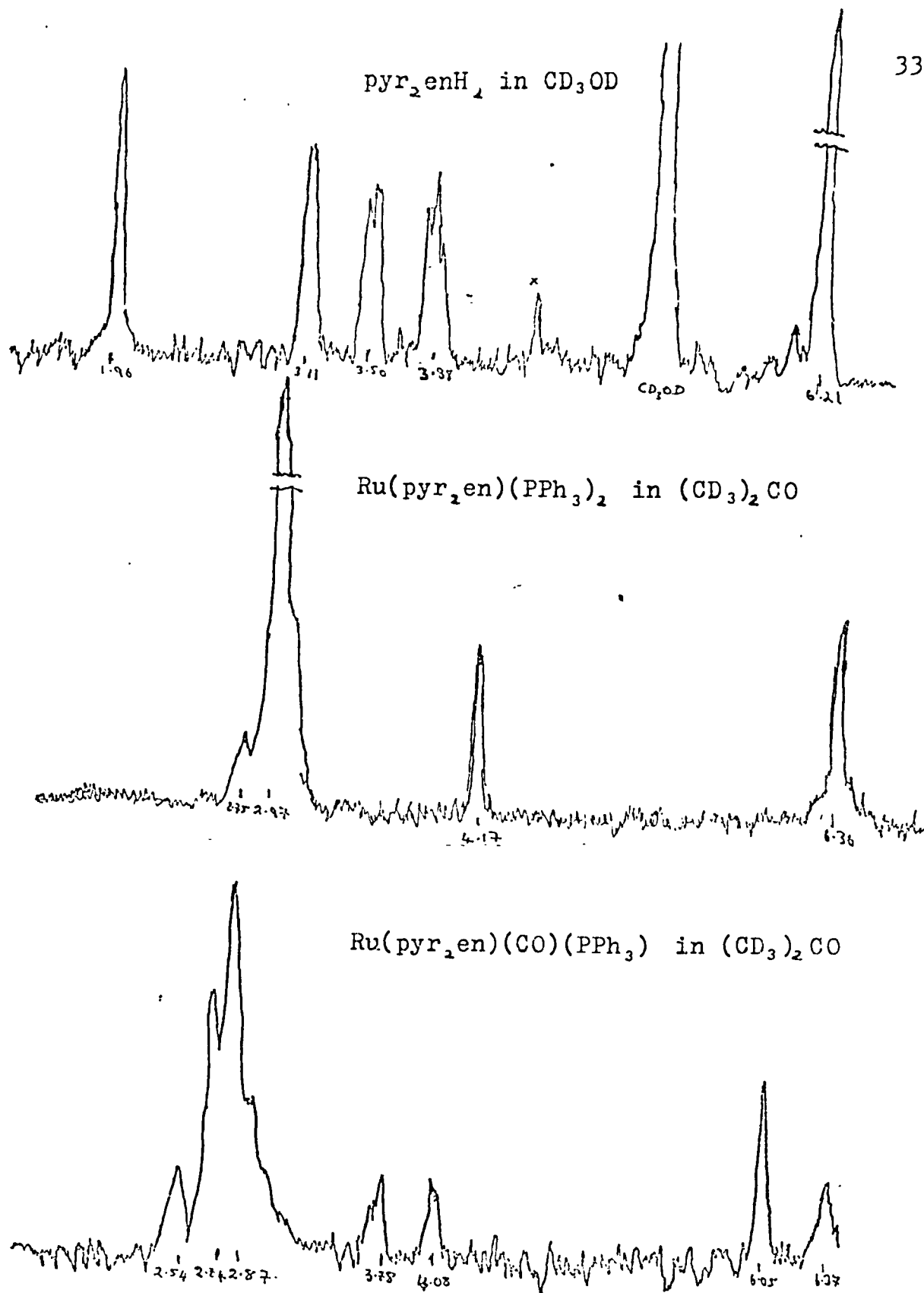
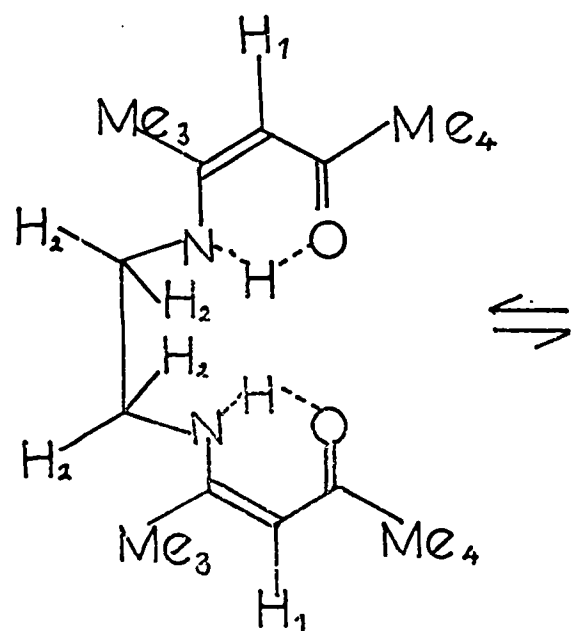


Figure II-ii

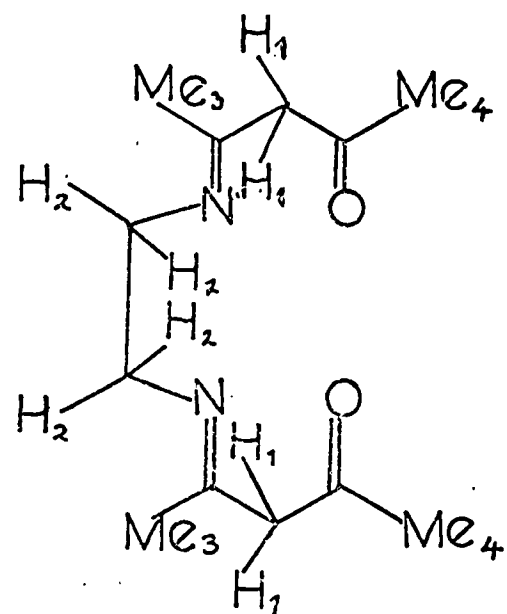
did not have the resonance at 4.17 τ and showed only a broad multiplet assignable to the phenyl and pyrrole protons.

The reaction of $\text{Na}_2(\text{sal}_2\text{en})$ or $\text{Na}_2(\text{sal}_2\text{phen})$ and $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, unlike the reaction in tetrahydrofuran, gave mixtures of the bis-phosphine complex together with a carbonyl containing species ($\nu(\text{C}\equiv\text{O}) = 1900\text{cm}^{-1}$) but separation proved impossible even by chromatography. Using $\text{Na}_2\text{pyr}_2\text{en}$ only the bis-phosphine complex was formed.

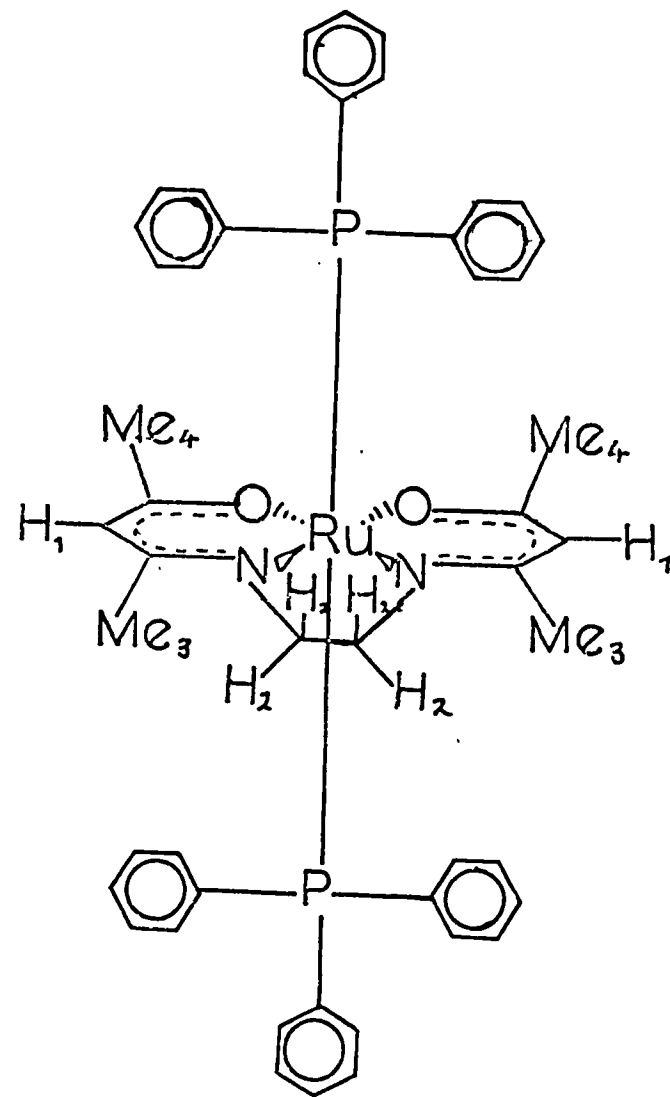
The ligand $\text{acac}_2\text{enH}_2$ and sodium hydride in thf, on treatment with $\text{RuCl}_2(\text{PPh}_3)_3$, gave an orange-red solution from which the red crystalline complex trans- $\text{Ru}(\text{acac}_2\text{en})(\text{PPh}_3)_2$ could be isolated. The ^{31}P n.m.r. spectrum had again only a singlet resonance at +33.24 ppm. The ^1H n.m.r. spectrum was solvent dependent. In CD_2Cl_2 there were four resonances ascribable to the ligand at 6.28 τ (2H), 7.12 τ (4H), 8.60 τ (6H), 8.97 τ (6H). In C_6D_6 the two high field resonances coalesced and the values were 6.14 τ (2H), 7.43 τ (4H) and 8.72 τ (12H). The free ligand has two main tautomeric forms ⁸⁷ (Figure II-iii a, b with hydrogen position labelled) and in most solvents it exists mainly in form a) but in $(\text{CD}_3)_2\text{CO}$ form b) is present to about 30%. The shift of H_1 for a) is ca. 5 τ , varying $\pm 0.2\tau$ with solvent, while in b) H_1 is at 7.2 τ . In the complex $\text{Ru}(\text{acac}_2\text{en})(\text{PPh}_3)_2$, as in other complexes with acac_2en as ligand, the a) form was retained as in Figure II-iiic. The H_1 proton



II-3a



II-3b



II-3c

resonance is shifted considerably because of shielding due to the phenyl ring currents of the PPh_3 in the trans positions. In the presence of P(OMe)_3 , the benzene solution became yellow-green and the H_1 proton resonance was shifted to 5.20τ , while the methyl resonances split into two at 8.09τ , 8.39τ . This change is probably due to the displacement of the trans- PPh_3 ligands by P(OMe)_3 , which reduced the shielding of the H_1 protons.

In the ^1H n.m.r. spectrum of $\text{Ru(acac)}_2\text{en(PPh}_3)_2$ the phenyl protons were a broad single resonance at $2.3 - 3.2\tau$ in CD_2Cl_2 and two broad resonances at 2.40τ 2.92τ in C_6D_6 . The i.r. spectrum had a single band at 1573 cm^{-1} due to the carbonyl stretching mode perturbed by co-ordination resulting in a delocalised environment⁸⁸.

(ii) Bidentate Monofunctional Ligands

The reaction of Na(salbenz) and $\text{RuCl}_2(\text{PPh}_3)_3$ in thf gave red crystals of trans- $\text{Ru(salbenz)}_2(\text{PPh}_3)_2$ for which the ^{31}P n.m.r. resonance occurs at $+28.53\text{ ppm}$ which was indicative of trans-phosphines. This was unlike the reaction with Na(acac) which yielded the orange cis isomer of $\text{Ru(acac)}_2(\text{PPh}_3)_2$ previously prepared by other means⁸⁹ (^{31}P n.m.r. resonance = $+52.30\text{ ppm}$), this must clearly have been due to steric constraints. The methylene protons of the Schiff base are split into a doublet at 5.23τ on co-ordination due to non-equivalence.

A similar reaction occurred with Na(pyrbenz) to yield a yellow microcrystalline solid which appears,

from the physical data, to be trans-Ru(pyrbenz)₁(PPh₃) (³¹P n.m.r. spectrum singlet at +48.30 ppm), but satisfactory analytical data for this complex was not obtained, the analysis being consistently low. No explanation can be offered for this other than that the complexes are not completely combusted in the analyser which has been previously noted in many cases for ruthenium complexes ⁹⁰.

The ligand salpyH which is potentially tridentate also gave the analagous complex trans-Ru(salpy)₂(PPh₃)₂.

(iii) Tridentate Bifunctional Ligands

The interaction of Na₂salnap with RuCl₂(PPh₃)₃ in thf gave a greenish-black solution from which no pure product could be isolated. However, when the reaction was carried out using a large excess of PPh₃, a reddish solution was formed from which dark red-black crystals of stoichiometry Ru(salnap)(PPh₃)₂.2thf were precipitated, these again appeared to have trans-phosphines (³¹P n.m.r. resonance = +23.05 ppm). This complex appeared to be rather unstable when dried, going much greener in colour, and it is probable that the excess phosphine resulted in loose co-ordination to the sixth position, which was not retained on precipitation when this position was occupied by a thf molecule. Reaction of carbon monoxide yielded a readily isolable complex (see below).

C. REACTION OF SCHIFF BASE COMPLEXES OF RUTHENIUM (II)
CONTAINING TERTIARY PHOSPHINES

The reactions of the complexes prepared above with nitric oxide, strong acids and carbon monoxide were studied and found usually to result in retention of the Schiff base with loss of one or both of the phosphines.

(i) Carbon Monoxide

The reaction of these complexes with carbon monoxide gave a variety of isolable complexes.

a. $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$

Bubbling carbon monoxide through a warm solution of $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$ in thf gave immediate precipitation of the complex previously isolated by Calderazzo¹⁵ $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$. The i.r. spectrum of this complex has a single $\text{C}\equiv\text{O}$ stretching vibration, $\nu(\text{C}\equiv\text{O})$, at 1910 cm^{-1} which was diminished in intensity in the Raman spectrum which shows no new absorptions and appears to confirm the dimeric structure (Figure II-i). The $\nu(\text{C}=\text{N})$ region was very complex with four absorptions at 1645, 1627, 1595 and 1550 cm^{-1} . The complex was too insoluble for ^1H n.m.r. studies or molecular weight determinations, while the mass spectrum showed only organic fragments.

However, the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with $\text{Na}_2\text{sal}_2\text{en}$, when carried out under carbon monoxide, did not yield, as the major product $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$, although some of this was formed, but rather a yellow complex $\text{Ru}(\text{sal}_2\text{en})(\text{CO})(\text{PPh}_3)$ which had the carbonyl and

phosphine ligands mutually cis.

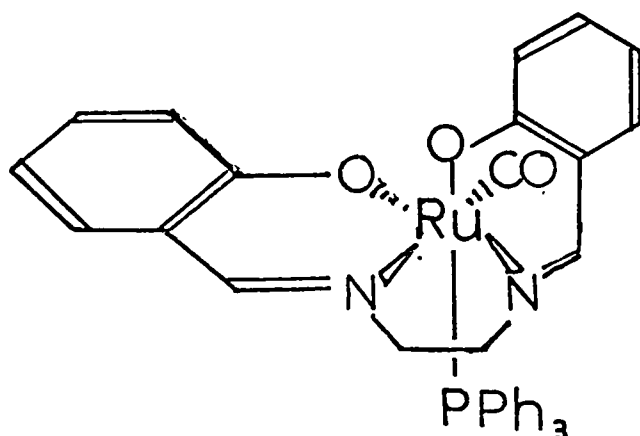


Figure II-iv

The i.r. spectrum of this complex again had only a single $\nu(\text{C}\equiv\text{O})$ but at 1930 cm^{-1} , with $\nu(\text{C}=\text{N})$ at 1622, 1610 cm^{-1} . The ^1H n.m.r. spectrum of the complex had two methine resonances at 1.41 τ and 1.62 τ , indicative of a non-planar sal_2en ligand as in $\text{Co}(\text{sal}_2\text{en})(\text{acac})$ ⁴⁰ where the methine protons resonated at 2.0, 2.2 τ . The methylene protons resonated as a multiplet in the region expected and the ^{31}P n.m.r. spectrum showed merely a singlet resonance at +32.61 ppm and did not offer any information as to the structure of the complex.

b. $\text{Ru}(\text{salbenz})_2(\text{PPh}_3)_2$

Although a longer reaction time was required for the reaction to go to completion under similar conditions to a., the only product which was isolated after chromatography was the orange complex trans- $\text{Ru}(\text{salbenz})_2(\text{CO})_2$. The compound was assigned C_{2h} symmetry (Figure II-v) on the basis of the single $\nu(\text{C}\equiv\text{O})$ at 1930 cm^{-1} in the i.r. spectrum.

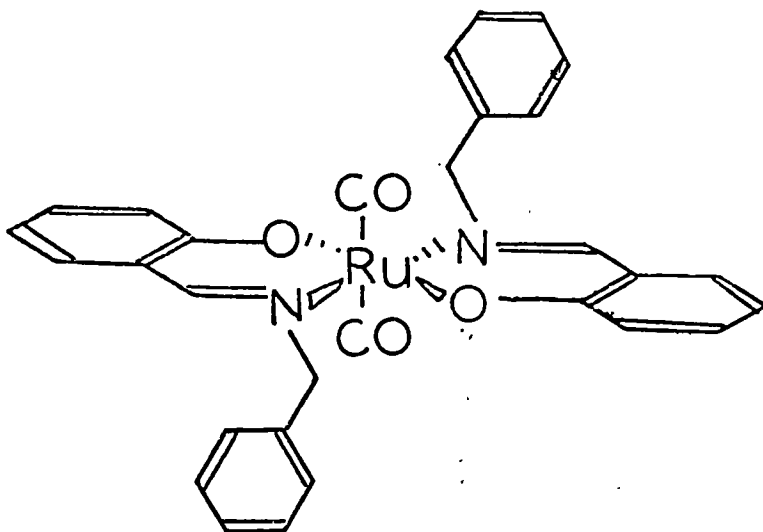


Figure II-v

The alternative trans isomers were not favoured, for steric reasons while the cis carbonyl structures would be expected to have two $\text{C}\equiv\text{O}$ stretching vibrations active in the i.r. spectrum. The ^1H n.m.r. spectrum had a single methine resonance at 1.86τ with the methylene protons split into a doublet at 4.81τ and 4.93τ . Very small amounts of the cis- $\text{Ru}(\text{salbenz})_2(\text{CO})_2$ appeared to be formed ($\nu(\text{C}\equiv\text{O})$ 2041, 1970 cm^{-1}), similar to cis- $\text{Ru}(\text{salphen})_2(\text{CO})_2$ ¹⁵, which was prepared in better yields by an alternative route (see Chapter II-d).

The reaction of $\text{Ru}(\text{pybenz})_2(\text{PPh}_3)_2$ and $\text{Ru}(\text{salpy})_2(\text{PPh}_3)_2$ with carbon monoxide yielded only trace amounts of the complexes which from the i.r. spectra appeared to be trans- $\text{RuL}_2(\text{CO})_2$, $\nu(\text{C}\equiv\text{O}) = 1925, 1930\text{ cm}^{-1}$ respectively.

c. $\text{Ru}(\text{salnap})(\text{PPh}_3)_2$

The complex $\text{Ru}(\text{salnap})(\text{PPh}_3)_2$ was rather difficult to isolate pure, but on refluxing in thf under an atmosphere of carbon monoxide, the yellow crystalline complex $\text{Ru}(\text{salnap})(\text{CO})(\text{PPh}_3)_2$ was formed readily, evidently by replacement of a labile co-ordinating

solvent molecule by carbon monoxide. No phosphine displacement occurred merely by refluxing in thf but it is probable that at high pressures of carbon monoxide such displacement would occur. $\text{Ru}(\text{salnap})(\text{CO})(\text{PPh}_3)_2$ has a single $\nu(\text{C}\equiv\text{O})$ at 1930 cm^{-1} and $\nu(\text{C}=\text{N})$ at 1623, 1610, 1598 and 1585 cm^{-1} . The phosphines resonated as a singlet at +28.51 ppm and were evidently mutually trans so the structure of the complex is probably as Figure II-vi. The ^1H n.m.r.spectrum had a single methine resonance at 2.18τ and the methylene protons resonate at 5.54τ .

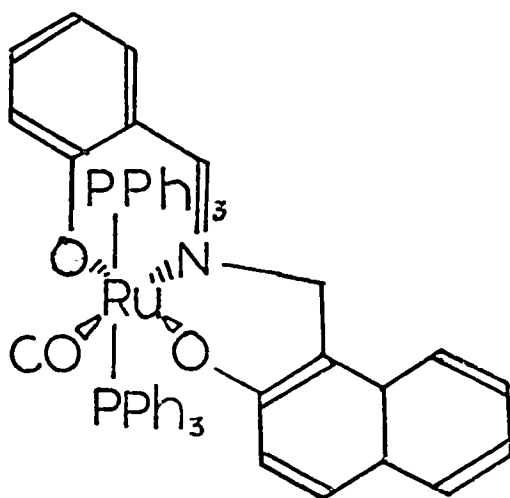


Figure II-vi

d. $\text{Ru}(\text{pyr}_2\text{en})(\text{PPh}_3)_2$

The orange solution of $\text{Ru}(\text{pyr}_2\text{en})(\text{PPh}_3)_2$ in thf changed colour immediately to yellow on exposure to carbon monoxide. Evaporation of the solution yielded yellow crystals of trans- $\text{Ru}(\text{pyr}_2\text{en})(\text{CO})(\text{PPh}_3)_2$. The ^1H n.m.r. spectrum of this complex along with $\text{Ru}(\text{pyr}_2\text{en})(\text{PPh}_3)_2$ and pyr_2enH_2 are shown in Figure II-ii.

Replacement of one phosphine ligand by a carbonyl split the resonance at 4.17 τ into a doublet of doublets at 3.78, 4.08 τ . The i.r. spectrum of Ru(pyr₂en)(CO)(PPh₃) had a single $\nu(\text{C}\equiv\text{O})$ at 1940 cm⁻¹ with vibrations in the region of $\nu(\text{C}=\text{N})$ at 1587 and 1580 cm⁻¹ which were shifted slightly to higher frequency. The ³¹P n.m.r. resonance was shifted from +38.85 ppm in Ru(pyr₂en)(PPh₃)₂ to +22.78 ppm in Ru(pyr₂en)(CO)(PPh₃) .

The reaction of Ru(pyr₂phen)(PPh₃)₂ with carbon monoxide appeared to give a very similar red complex with a single $\nu(\text{C}\equiv\text{O})$ at 1948 cm⁻¹ and ³¹P resonance at +23.4ppm but a satisfactory analysis was not obtained.

e. Ru(sal₂phen)(PPh₃)₂

A solution of Ru(sal₂phen)(PPh₃)₂ in thf reacted instantly with carbon monoxide; the solution colour changing from dark yellow-black to purple. Chromatography of this solution yielded a small amount of a pale orange elutate with thf which was probably cis-Ru(sal₂phen)(CO)₂ (see Chapter II-d) ($\nu(\text{C}\equiv\text{O})$ = 2040, 1965 cm⁻¹) and a red-purple elutate with methanol ($\nu(\text{C}\equiv\text{O})$ = 1940 cm⁻¹), which on evaporation and addition of ether yielded red-purple crystals ($\nu(\text{C}\equiv\text{O})$ = 1925(sh), 1910 cm⁻¹ in nujol), these were insoluble in methanol but soluble in dmsO ($\nu(\text{C}\equiv\text{O})$ = 1908 cm⁻¹). The cryoscopic molecular weight of the crystals in dmsO indicated that the complex was polymeric (Molecular weight = 760, calculated for dimer = 886). The Raman spectra of the above species showed only very weak $\nu(\text{C}\equiv\text{O})$ which appeared not to have shifted from the i.r. frequency, analagous to

$[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$. The species in methanol ($\nu(\text{C}\equiv\text{O}) = 1940 \text{ cm}^{-1}$) may have been the monomeric species which on crystallisation polymerises since it is clear that the species in methanol and the crystalline material obtained were different. The ^1H n.m.r. spectrum of the crystals in deuterated dmsO confirmed that the sal_2phen ligand was planar, with a single methine resonance at 0.59τ , with two groups of phenyl resonances at $1.40 - 3.37\tau$. It is thus probable that the structure of this complex was similar to that proposed for $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$, although the structure may be more polymeric than just a dimer.

(ii) Strong acids

Only with sal_2enH_2 as the Schiff base were the products isolated.

The reaction of $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$ with 40% aqueous fluoroboric acid or p-toluene sulphonic acid (Htos) in thf yielded a red-yellow solution from which red crystals of $[\text{Ru}(\text{sal}_2\text{enH})(\text{PPh}_3)]\text{X}$ were isolated. When however, the initial solution with HBF_4 was heated, other reactions occurred. The red initial solution changed colour and precipitated a red solid which was only stable in the presence of solvent, the removal of which resulted in the formation of a black oil. (This product was also formed if the reaction was carried out in methanol). Addition of solvent to this oil regenerated the red solid which was probably a co-ordinating unsaturated species caused by the loss of

both PPh_3 molecules from the initial $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$. On heating further the red solid redissolved to a green-red solution from which crystallised very small amounts of an unidentified green solid. However, addition of a large excess of water to the solution still resulted in precipitation of $[\text{Ru}(\text{sal}_2\text{enH})(\text{PPh}_3)]\text{BF}_4$.

The complexes $[\text{Ru}(\text{sal}_2\text{enH})(\text{PPh}_3)]\text{X}$ where $\text{X} = \text{BF}_4$, were 1:1 electrolytes in CH_3NO_2 although the conductances were somewhat low, being $\Lambda_{10^{-3}\text{M}} = 49, 41 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for the BF_4 salts respectively. This compares with the usual value for 1:1 electrolytes of $60 - 90 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. The ^{31}P n.m.r. spectra of these salts had a single resonance at +64.22 ppm which is shifted from +34.3 ppm for $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$ suggesting probably a 5-co-ordinate structure (Figure II-vii).

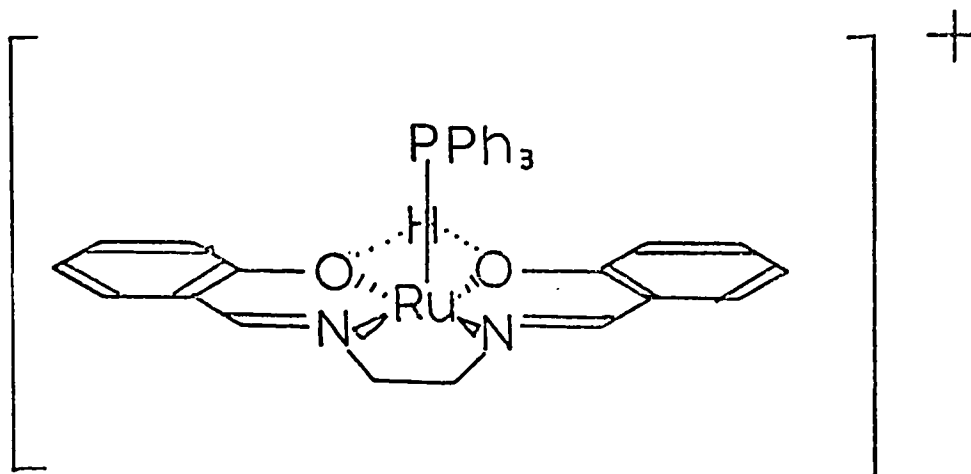


Figure II-vii

The anions are not co-ordinated as both salts have the same ^{31}P n.m.r resonance. This behaviour was unlike that of $\text{Co}(\text{sal}_2\text{en})$ which reacts with PR_3 and HClO_4 to give $[\text{Co}(\text{sal}_2\text{en})(\text{PR}_3)_2]^+ \text{ClO}_4^-$. The complexes prepared

here were diamagnetic. There was, however, no band which could be attributed to O....H - O vibrations in the i.r. spectra of the complexes. Additionally, the ^{31}P n.m.r. spectra were the same in both fully and partially decoupled modes, showing that no ruthenium hydride species was present.

With $\text{Ru}(\text{sal}_2\text{phen})(\text{PPh}_3)_2$ the reaction appeared to be similar, resulting in a purple solid which, although it seemed to be a 1:1 electrolyte in CH_3NO_2 , was less stable than $[\text{Ru}(\text{sal}_2\text{enH})(\text{PPh}_3)]\text{X}$ and could not be isolated pure. The complexes with Schiff bases derived from pyrrole-2-aldehyde did not react in a similar way and only intractable black oils were obtained on reaction with HBF_4 , Htos.

(iii) Nitric Oxide

Very few Schiff base complexes have been reacted with nitric oxide prior to the present work. The reaction of $\text{Co}(\text{sal}_2\text{en})$ with nitric oxide has been shown to yield the complex $\text{Co}(\text{sal}_2\text{en})(\text{NO})$ ⁹² which appeared to have a bent nitrosyl structure (formally bonding as NO^-). Similarly, the reaction of $\text{Fe}(\text{sal}_2\text{en})$ has been shown to give $\text{Fe}(\text{sal}_2\text{en})(\text{NO})$, although oxidation to an oxo bridged Fe^{III} species has been found to occur under different conditions⁹³. The interaction of $\text{Mn}(\text{OAc})_2$ and $(\text{sal}_2\text{enH}_2)$ in the presence of nitric oxide gave the complex $\text{Mn}(\text{OAc})(\text{sal}_2\text{en})$ and an analagous hydroxy complex was formed by the reaction of $\text{Mn}(\text{sal}_2\text{en})$ with nitric oxide⁹⁴. $\text{Mn}(\text{sal}_2\text{en})$ has also been shown to react in dimethyl-sulphoxide with nitric oxide to

yield a complex of stoichiometry $[\text{MnO}(\text{sal}_2\text{en})]_2 \text{O}_2$ ⁹⁵, which has a bridging peroxo and a terminal oxo ligand. Under similar conditions $\text{Ni}(\text{sal}_2\text{en})$ and $\text{Cu}(\text{sal}_2\text{en})$ do not react with nitric oxide in the absence of air, but in the presence of air nitration occurs in the fifth position of the phenyl rings to give $[5,5'\text{-dinitro}(\text{sal}_2\text{en})]$ derivatives of nickel and copper ⁹⁶. Similar reactions have been observed with the reaction of $\text{Cu}(\text{sal}_2\text{en})$ with nitrating agents such as N_2O_4 ⁹⁷. The same authors have shown that in the presence of NaBH_4 several $\text{M}(\text{sal}_2\text{en})$ complexes ($\text{M} = \text{Co}, \text{Fe}$) in dimethyl formamide will reduce nitric oxide to nitrogen ⁹⁸.

The reaction of $\text{Co}(\text{acac}_2\text{en})$ with nitric oxide has been found to form $\text{Co}(\text{acac}_2\text{en})(\text{NO})$ ⁹⁹, but for $\text{M}(\text{acac}_2\text{en})$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Cu}$) ¹⁰⁰ insertion of nitric oxide into the ligand took place to yield an oxime complex, in which there may have been one or two oxime functions (Figure II-viii).

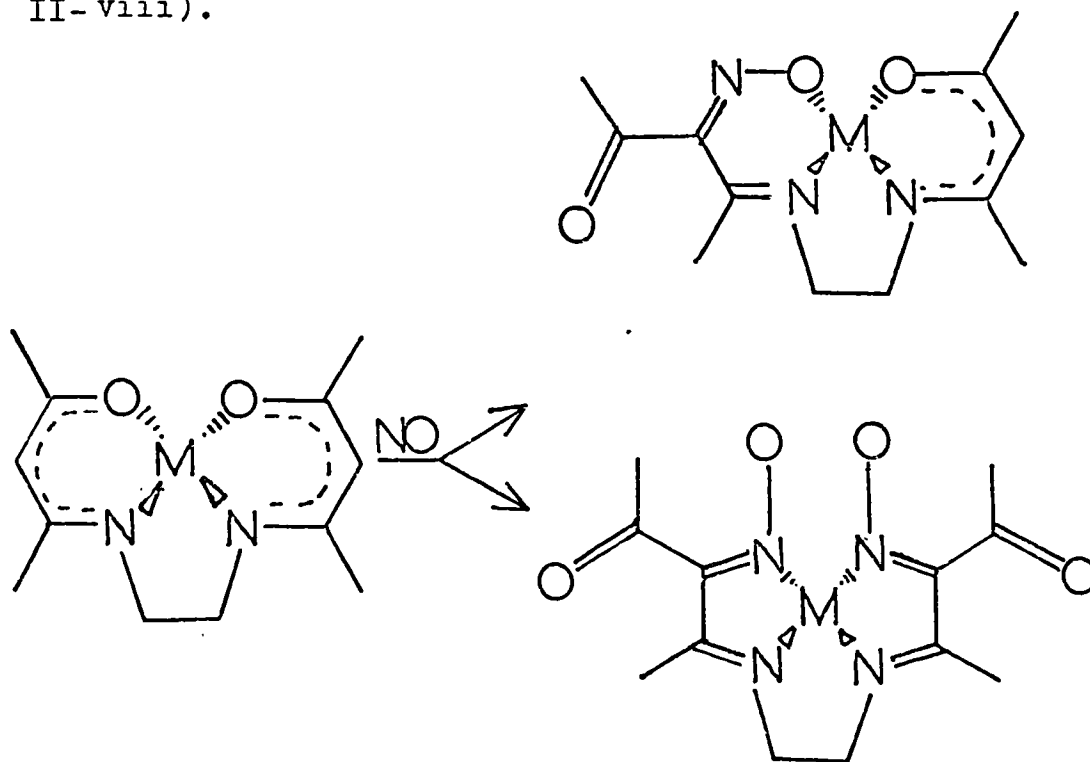


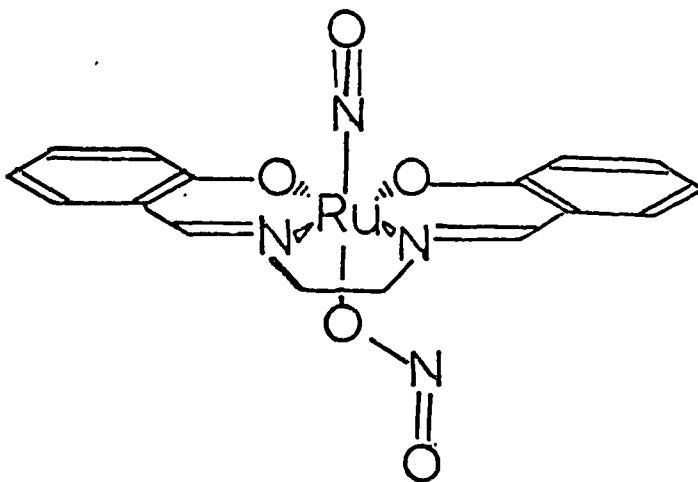
Figure II-viii

In this work only $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$ yielded readily isolable complexes.

Bubbling uncontrolled amounts of nitric oxide through a solution of $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$ in thf resulted in the solution rapidly changing colour from purple-red to yellow-red. The passage of nitric oxide through the solution was continued whilst the solution was warmed, and a red solid precipitated, leaving a red-green solution. After filtration this supernatant yielded burgundy coloured crystals of the complex $\text{Ru}(\text{sal}_2\text{en})(\text{ONO})(\text{NO})$. Evaporation of the initial cold solution yielded the same mixture of complexes (identified by i.r. to be approximately 50% of each), but it appeared that on heating, precipitation of the complex $[\text{Ru}(\text{sal}_2\text{en})(\text{NO})]_2 \cdot \text{O}$ resulted in the yield of the latter increasing relative to the former (80% : 20%). The same complexes were also formed in acetone and toluene, though in the latter the insolubility of both products yielded a 50% mixture of both products. Both products were formed whether the nitric oxide was purified either by passing through 30% KOH and then a CaCl_2 drying tower, by passing through 5A molecular sieves at -78°C or used as purchased.

An X-ray crystallographic structure determination was carried out on the complex $\text{Ru}(\text{sal}_2\text{en})(\text{ONO})(\text{NO})$ ¹⁰¹ and the structure is as shown in Figure II-ix, with a linear nitrosyl and an O-bonded nitrito ligand. The sal_2en ligand is basically planar with the nitrosyl and nitrito ligands mutually trans, a detailed explanation of this structure is given in Appendix I. The i.r.

Figure II-ix



spectrum of this complex had a single N=O stretching vibration, $\nu(\text{N}\equiv\text{O})$ at 1831 cm^{-1} and anti-symmetric N-O vibrations $\nu_{\text{as}}(\text{N-O})$ at $1488, 1507\text{ cm}^{-1}$ as expected from the above structure ¹⁰². The ^1H n.m.r. spectrum of this complex was somewhat similar to that of a usual complex containing a planar sal_2en ligand, with a single methine resonance at 1.77τ and a complex multiplet for the phenyl resonances at $2.53 - 3.3\tau$ but, unexpectedly, a singlet resonance at 5.97τ due to the methylene protons. In the starting material $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$ these protons resonated as a multiplet at $6.2 - 6.4\tau$. A singlet methylene resonance has been ascribed to a bridging sal_2en structure ⁸³ which was clearly not the case in this complex. Busch ¹⁰³ has recently prepared the complex $[\text{Cr}(\text{Me}_6[14]4,11\text{ dieneN})_2(\text{NO}_2)(\text{NO})]\text{PF}_6$ (Figure II-x). The i.r. spectrum of this Cr^{I} species has a single $\nu(\text{N}\equiv\text{O})$ at 1640 cm^{-1} (linear nitrosyl) but did not

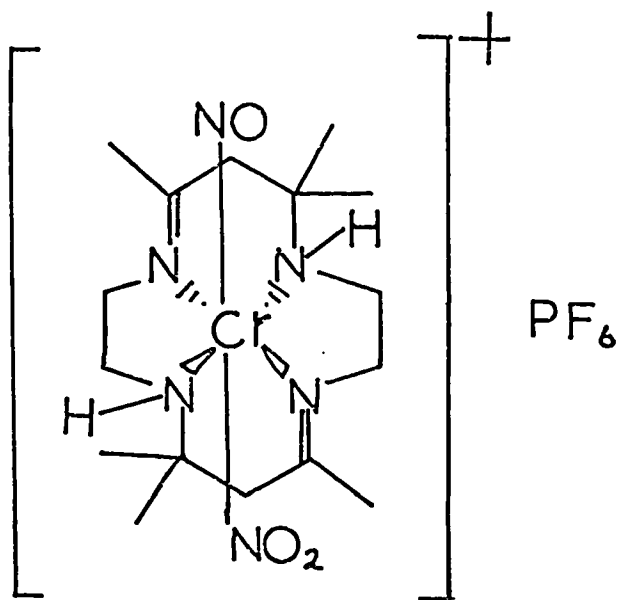


Figure II-x

indicate the frequency of the $\nu_{\text{as}}(\text{N-O})$ vibrations. However the iso-electronic complex cis-Fe[S₂CN(Et)₂]₂(NO₂)(NO)¹⁰⁴ to Ru(sal₂en)(ONO)(NO) has been postulated as having an N-bonded nitro group and has $\nu_{\text{as}}(\text{N-O})$ at 1419, 1470 cm⁻¹ and $\nu(\text{N=O})$ at 1820 cm⁻¹.

Recrystallisation of the other product of this reaction from dichloromethane gave red metallic lustre plates of [Ru(sal₂en)(NO)]₂O. This complex has an i.r. spectrum similar to Ru(sal₂en)(ONO)(NO) except that the bands due to the ONO ligand were absent; the $\nu(\text{N=O})$ was shifted to 1742 cm⁻¹, there was a sharp but very weak vibration at 3490 cm⁻¹, a very strong band at 800 cm⁻¹ and several additional bands in the region 620 - 400 cm⁻¹. Although, initially, the band at 3490 cm⁻¹ seemed to be due to a hydroxy $\nu(\text{O-H})$, carrying out the reaction in deuterated acetone resulted in no shift in frequency or change in intensity of the band. The intensity was much weaker than in the other Ru-OH

species ¹⁰⁵ and no resonance could be assigned to this proton in the ¹H n.m.r. spectrum. Thus the vibration was assigned to an overtone of $\nu(\text{N}\equiv\text{O})$ which could only be proved, of course, by labelling experiments. The vibration at 800 cm^{-1} was comparable with $\nu_{\text{as}}(\text{M}-\text{O}-\text{M})$ vibrations in other sal_2en complexes ($\text{M} = \text{Fe}$, 807 cm^{-1} ¹⁰⁶; Mo , 750 cm^{-1} ; Re , 698 cm^{-1} ¹⁰⁷). The vibration has a strong band in the i.r. spectrum and the new band at 540 cm^{-1} was probably the $\nu_{\text{sym}}(\text{Ru}-\text{O}-\text{Ru})$ indicating that the $\text{Ru}-\text{O}-\text{Ru}$ bond was considerably bent. In $(\text{Ru}_2\text{O}_x)_{10}^{n-}$ and $[\text{Ru}_3\text{O}_2(\text{NH}_3)_{14}]^{6+}$ where the $\text{Ru}-\text{O}-\text{Ru}$ bond is linear the intensity of the vibration in the i.r. spectrum is rather weak ¹⁰⁸. Thus the structure of $[\text{Ru}(\text{sal}_2\text{en})(\text{NO})]_2$ is as shown below in Figure II-xi.

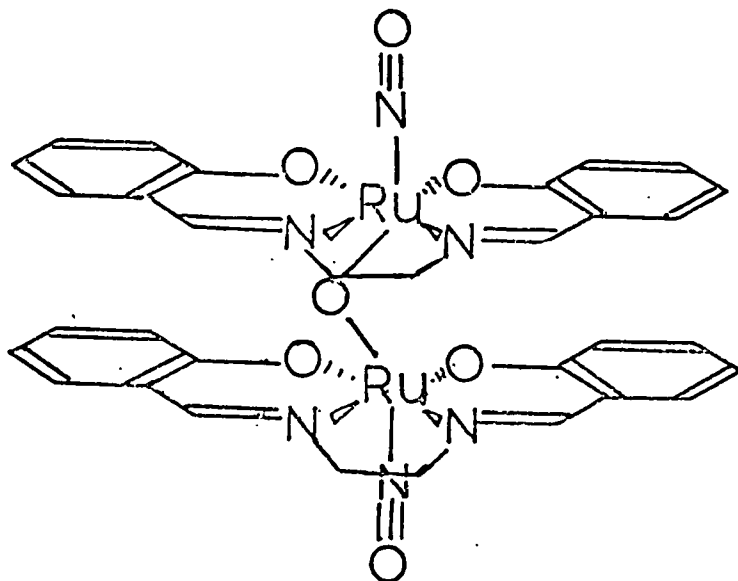
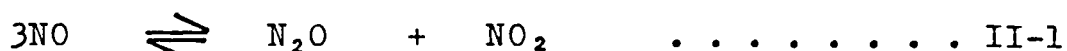


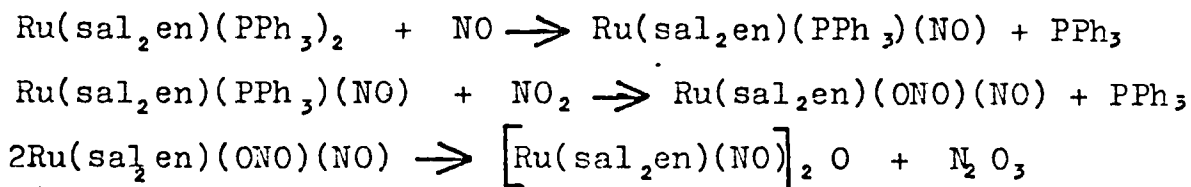
Figure II-xi

The ¹H n.m.r. spectrum of the complex was rather informative with only the expected spectrum giving a single methine resonance at 2.64τ , multiplet phenyl resonances at $2.7 - 3.7\tau$ and two multiplet methylene resonances at $5.64 - 6.04\tau$ and $6.18 - 6.45\tau$.

Although rigorous procedures were taken to exclude NO_2 , the formation of $\text{Ru}(\text{sal}_2\text{en})(\text{ONO})(\text{NO})$ was either formed from NO_2 impurity in the NO used, or from a reaction of the NO (Equation II-1) which is known to occur at 60°C and high pressures ¹⁰⁹.



Reaction of the NO_2 or N_2O formed with O=PPh_3 could have been the driving force required to push the equilibrium to the right. A possible mechanism of formation of the products is outlined in Equation II-2.



Equation II-2

The O=PPh_3 formed may have been due to reaction with either NO , N_2O or NO_2 .

D. SCHIFF BASE COMPLEXES CONTAINING METAL CARBONYLS

As has been shown in the last section the reaction of the bis-phosphine Schiff base complexes yielded principally the trans dicarbonyl products.

However, reaction of $[\text{Ru}(\text{CO})_2\text{Cl}_2]_2$ with the sodium salts of the Schiff bases, salbenzH , sal_2enH_2 , salphenH_2 , yielded principally the cis isomers. On refluxing a mixture of the reactants in thf, a red solution was formed, which after chromatography yielded two solutions, one eluted with thf and the other with methanol.

Evaporation of the methanol elutate was shown to contain a mixture of compounds, but the major products were the trans isomers (identified by their i.r. spectra) previously isolated. In the case of sal_2enH_2 , however, the methanol elutate was a very air-sensitive green-red complex which had a single $\nu(\text{C}\equiv\text{O})$ at 1910 cm^{-1} .

From the thf elutate, only in the case of sal_2enH_2 , has a pure crystalline complex been isolated, but the other reactions from their i.r. spectra appeared to be identical with the cis isomers being formed. The complex cis- $\text{Ru}(\text{sal}_2\text{en})(\text{CO})_2$ was isolated as pale yellow feather-like crystals with $\nu(\text{C}\equiv\text{O})$ at $2038, 1965\text{ cm}^{-1}$ and $\nu(\text{C}=\text{N})$ at $1628, 1598\text{ cm}^{-1}$, although the initial thf solution had four bands at $2038, 2010, 1965$ and 1935 cm^{-1} . However recrystallisation from chloroform yielded the complex cis- $\text{Ru}(\text{sal}_2\text{en})(\text{CO})_2$ with only two $\nu(\text{C}\equiv\text{O})$ absorptions. The expected non-planar structure of this complex was confirmed by the ^1H n.m.r. spectrum which showed two methine resonances at $1.96\tau, 2.16\tau$ and a multiplet methylene resonance at $6.0 - 6.2\tau$. The structure of this complex is similar to that proposed for $\text{Ru}(\text{sal}_2\text{en})(\text{CO})(\text{PPh}_3)$ (see Figure II-iv).

The products from the reactions with Nasalbenz and $\text{Na}_2\text{sal}_2\text{phen}$ were very similar, with $\nu(\text{C}\equiv\text{O})$ at $2041, 1970\text{ cm}^{-1}$ and $2040, 1976\text{ cm}^{-1}$ respectively. The ^1H n.m.r. spectrum of the yellow-orange oil formed by evaporation of the thf solution in the latter case showed that the sal_2phen ligand was non-planar with two methine resonances at 1.58τ and 2.11τ . However for neither of these complexes

has it been possible at present to obtain pure crystalline solids. The complex cis-Ru(sal₂phen)(CO)₂ is the first example of the ligand sal₂phen acting as a non-planar quadridentate ligand.

These complexes are similar to those prepared by the reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_n$ with the thallium salts of bis and tetradentate salicylideneimines to give complexes of the form $\text{Rh}(\text{CO})_2(\text{SB})$ and $[\text{Rh}(\text{CO})_2]_2(\text{SB})$ respectively ⁸³ which also have cis carbonyls and similar infra-red spectra.

E. SCHIFF BASE COMPLEXES CONTAINING BICYCLO(2,2,1)HEPTA-2,5-DIENE(NORBORNADIENE)

The preparation of ruthenium norbornadiene complexes with many different ligands has been shown by the reaction of $[\text{Ru}(\text{nbd})\text{Cl}_2]_n$ with p-toluidine to yield $\text{Ru}(\text{nbd})\text{Cl}_2(\text{p-toluidine})_2$ ¹¹⁰ and with various bidentate ligands ^{111,112} to yield complexes of the form $\text{Ru}(\text{nbd})(\text{L-L})_2$.

However apart from the $[\text{Rh}(\text{COD})]_n(\text{SB})$ ($n = 1$ or 2) prepared by the reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with the thallium salts of various Schiff bases ⁸³, no previous Schiff base complexes containing olefins as the other ligands have been reported.

The reaction of the norbornadiene complex $[\text{Ru}(\text{nbd})\text{Cl}_2]_n$ with the sodium salts of the quadridentate ligands sal₂enH₂ and pyr₂enH₂ resulted in the formation of the complexes $\text{Ru}(\text{sal}_2\text{en})(\text{nbd})$ and $\text{Ru}(\text{pyr}_2\text{en})(\text{nbd})$.

Stirring a suspension of $[\text{Ru}(\text{nbd})\text{Cl}_2]_n$ and Na₂sal₂en

in thf for several days at room temperature resulted in the formation of a deep-red solution and a dark coloured precipitate. Transfer of this mixture to an alumina column followed by chromatography using tetrahydrofuran gave a red-orange elutate from which an orange-red solid, $\text{Ru}(\text{sal}_2\text{en})(\text{nbd})$, was isolated. This complex had the expected i.r. spectrum with a band at 1305 cm^{-1} characteristic of norbornadiene complexes¹¹⁰ with bands due to $\nu(\text{C}=\text{N})$ at around 1600 cm^{-1} . A similar reaction with $\text{Na}_2\text{pyr}_2\text{en}$ yielded a yellow elutate with ether which on evaporation gave the yellow microcrystalline solid $\text{Ru}(\text{pyr}_2\text{en})(\text{nbd})$, this had the characteristic band, at 1302 cm^{-1} , of the co-ordinated norbornadiene and two $\nu(\text{C}=\text{N})$ at 1573 and 1558 cm^{-1} . The complex $\text{Ru}(\text{sal}_2\text{en})(\text{nbd})$ was not soluble enough for molecular weight determinations but in chloroform $\text{Ru}(\text{pyr}_2\text{en})(\text{nbd})$ appeared to be monomeric.

The ^1H n.m.r. spectra of the two complexes were complicated by the methylene resonances of the Schiff bases, which overlapped with the resonances due to the norbornadiene ligand. However in both cases it was possible to tentatively assign some of the resonances. In the spectrum of $\text{Ru}(\text{sal}_2\text{en})(\text{nbd})$ there were two methine resonances at 1.90τ and 2.29τ , indicative of a non-planar sal_2en ligand, and a broad multiplet phenyl resonance in the region $2.8 - 3.7\tau$. $\text{Ru}(\text{pyr}_2\text{en})(\text{nbd})$ had much better resolved resonances in this region, with a number of resonances within $1.93 - 3.90\tau$, including, singlet resonances at 1.93τ , 2.28τ , 2.51τ , and 2.62τ ; a larger doublet resonance at 3.19τ and two doublets of doublets at 3.43τ and 3.90τ . The methine resonances

were tentatively assigned as those resonances at 2.28 τ and 2.51 τ . The remainder of the ^1H n.m.r. spectra of these complexes was rather ill-defined and broad, probably because the complexes have a very low symmetry with the result that all the protons are non-equivalent. This is unlike previous complexes, $\left[(\text{CO})\text{RuCl}_3(\text{nb})\right]^{-113}$ in which several of the olefinic protons are equivalent and as such the fine structure can be observed.

Assuming that $\text{Ru}(\text{sal}_2\text{en})(\text{nb})$ has a structure as in Figure II-xii with the norbornadiene numbered as shown, then the assignments for the norbornadiene are H_2 5.48 τ (doublet, $J_{\text{H}_2-\text{H}_3} = 4 \text{ Hz}$), H_6 5.63 τ (broad singlet), H_3 6.09 τ (doublet $J_{\text{H}_1-\text{H}_3} = 4 \text{ Hz}$), $\text{H}_{1,4}$ 6.35 τ (broad singlet), H_5 6.65 τ (broad singlet), $\text{H}_{7,8}$ 8.75 τ (sharp singlet) with the methylene protons of the sal_2en ligand as a broad underlying resonance at 6.0 - 6.4 τ . The complex $\text{Ru}(\text{pyr}_2\text{en})(\text{nb})$ probably has the same structure, except that the 6-membered chelate rings of $\text{Ru}(\text{sal}_2\text{en})(\text{nb})$ are reduced to 5-membered rings in $\text{Ru}(\text{pyr}_2\text{en})(\text{nb})$ with possibly greater steric constraint. Similarly to the above $\text{H}_{7,8}$ 8.71 τ (broad singlet), $\text{H}_{1,4}$ 6.96 τ (complex multiplet which may be a doublet of doublets) and the remainder of the spectrum was a complex set of resonances 5.07 - 6.62 τ which contains the $\text{H}_{1,3,5,6}$ resonances and the methylene resonances of the Schiff base ligand. Unfortunately decoupling experiments did not clarify the assignments because the decoupler used had too great a band width, which resulted in saturation of more than just the resonance required. Although these assignments

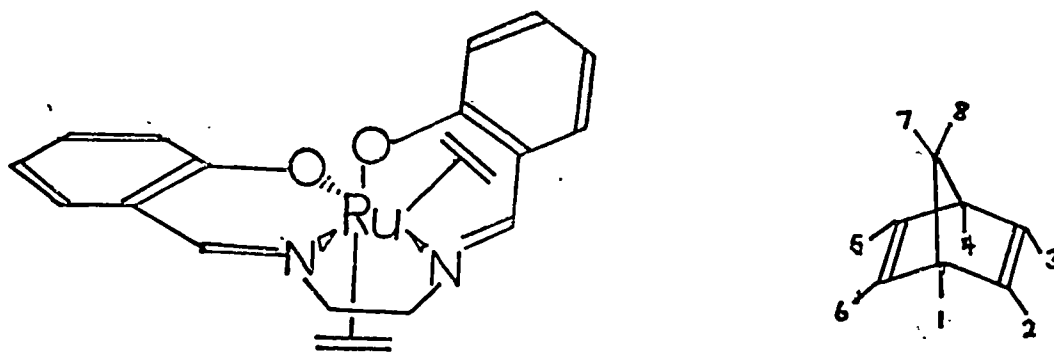


Figure II-xii

are not wholly satisfactory, because of the insolubility of the complexes and the underlying methylene protons of the Schiff base ligand, it was clear that the complexes $\text{Ru}(\text{sal},\text{en})(\text{nbd})$ and $\text{Ru}(\text{pyr},\text{en})(\text{nbd})$ contain non-planar Schiff bases.

F. CATALYSIS

A report that Schiff base complexes of several of the platinum metals, including ruthenium (although no preparative details were given), were effective as hydrogenation catalysts for hex-1-ene⁸⁰, led to investigation of the feasibility of the complexes described above as useful catalysts.

The preliminary study, however, yielded rather disappointing results as it was found that none of the complexes studied acted as hydrogenation catalysts for hex-1-ene. Although the complexes were active as hydroformylation catalysts for the same alkene, with

conversion percentages of up to 90%. This was due to the conversion of the complexes, at the temperatures and pressures used, to other well-known species. The phosphine-containing complexes were converted to $\text{Ru}(\text{CO})_3(\text{PPh}_3)_1$ which was isolated as yellow crystals from the autoclave. This complex has been widely studied and the amount of conversion of alkene appeared to be due only to the relative ease of formation of $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2^{114}$. The oxime-containing complexes do not catalyse hydroformylation of this alkene to any extent under the same conditions.

The non-phosphine containing complexes do hydroformylate alkenes to only a small extent, this being probably due to the production of $\text{Ru}_3(\text{CO})_{12}$ in the course of the reaction.

Conditions used:

Catalyst	10mg
Solvent	Benzene 10ml
Alkene	Hex-1-ene 1ml
Temperature	100°C
Gases	100 at. CO/H ₂ (1:1 ratio) measured at room temperature
Time	15 hours
Gas Chromatograph	Perkin-Elmer F.33
Injection Temperature	175°C
Oven Temperature	120°C
Column used	D.E. 201 Carbowax 1500 (Temp. range = 0 - 160°C)

G UNSUCCESSFUL REACTIONS

Apart from the reactions described above, a large number of unsuccessful reactions were carried out, brief details of which are described below.

The reaction of various ligands with $\text{RuCl}_2(\text{PPh}_3)_3$ did not yield pure complexes. Tetraphenylporphyrin did not react with $\text{RuCl}_2(\text{PPh}_3)_3$ in the presence of NaH in thf and only the free porphyrin was isolated. The reaction of N,N'-bis(salicylideneimine) with $\text{RuCl}_2(\text{PPh}_3)_3$ under similar conditions appeared from the ^{31}P n.m.r. spectrum to give a mixture of complexes in the red solution formed, and no crystalline complex was isolated. This was probably due to steric constraints, which prevented the formation of the chelate complex similar to $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_1$. Also attempts to prepare complexes containing the macrocyclic ligand, formed by the reaction of mesityl oxide and ethylenediamine, failed due to the insolubility of the ligand.

Other ruthenium precursors which were tried were RuCl_2py_4 from which only free ligand could be isolated; $\text{RuCl}_2(\text{MeCN})_4$, which appeared to give Schiff base complexes containing no MeCN ligands, but no pure complexes could be isolated, as was the case for $\text{RuCl}_2(\text{dmsO})_4$. $\text{RuHCl}(\text{PPh}_3)_3$ with the bidentate Schiff bases reacted to give a deep red solution, this contained some $\text{RuL}_2(\text{PPh}_3)_2$ from the ^{31}P n.m.r. spectrum, but did not give $\text{RuH}(\text{L})(\text{PPh}_3)_n$ and no hydride species were prepared. Also, surprisingly, $\text{RuH}_2(\text{PPh}_3)_4$ in toluene did not react with sal_2enH_2 and only the free ligand was obtained.

H. CONCLUSION

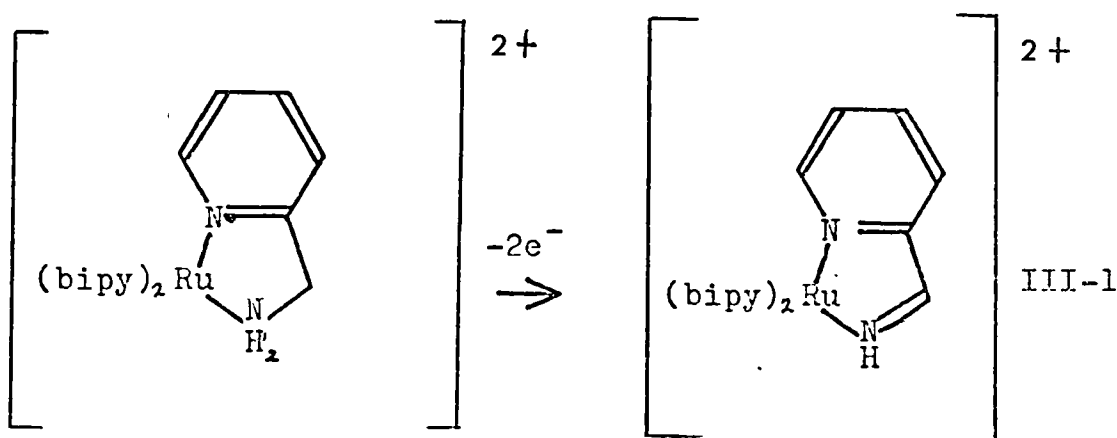
While it has proved possible to prepare many new Schiff base complexes of ruthenium, only for the phosphine containing complexes were the reactions facile. However once prepared these Schiff base phosphine containing complexes proved to be rather reactive, and nitrosyl and carbonyl Schiff base complexes were formed. The other ruthenium sources gave much lower yields as well as mixtures of complexes from which separation of pure compounds was rather difficult.

Finally, it is apparent that this is only an introduction to the chemistry of these types of ruthenium complexes, and inevitably a great many more will be prepared in forthcoming years.

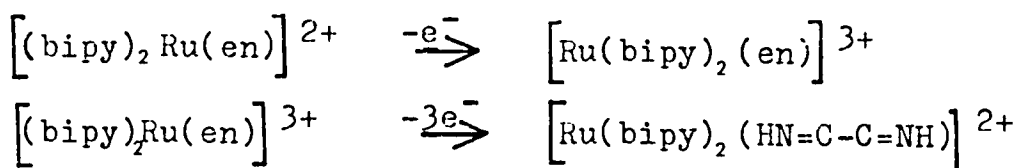
CHAPTER III

PYRIDINE-2-ALDIMINE COMPLEXES OF RUTHENIUMA. INTRODUCTION

While there have been no reports of complexes formed directly by the reaction of pyridine-2-aldimines with ruthenium precursors, Meyer has prepared electrolytically the complex $\{Ru(bipy)_2[N-(pyridine-alimine)]\}^{2+}$ (Equation III-1) ³⁰.



This has proved to be a general method of preparation of α -diimine complexes of ruthenium; $[Ru(en)_3]^{2+}$ ¹¹⁵ underwent a $4e^-$ oxidation to $[Ru(en)_2(HN=C-C=NH)]^{2+}$ and a similar reaction occurred with $[Ru(phent)_2(en)]^{2+}$ ¹¹⁶. The mechanism proposed for the above oxidation is as shown in Equation III-2, with initial oxidation of the metal to Ru^{III} followed by oxidation of the co-ordinated ligand, and reduction of the metal to ruthenium ^{II} .



No assignment for $\nu(\text{C}=\text{N})$ in $\{(\text{bipy})_2\text{Ru} [2-(\text{imino-methylpyridine})] \}^{2+}$ could be given, this was considered as being due to either masking by the bipyridyl vibrations or decreased intensity. Nakamoto ¹¹⁷ has shown that the α -diimine ligand has two resonance forms (see Figure III-i) which shifted the $\nu(\text{C}=\text{N})$ to 1520 cm^{-1} in $[\text{Fe}(\text{CH}_3\text{N}=\text{CH}-\text{CH}=\text{NCH}_3)_3]^{2+}$.

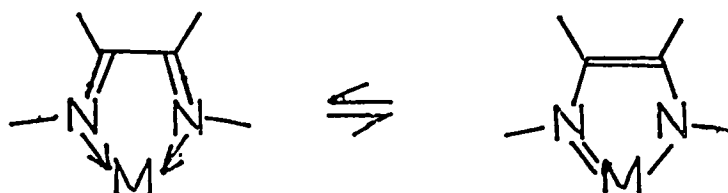


Figure III-i

Since the pyridine-2-alldimine complexes contained this α -diimine group it seemed likely that, using similar methods to those employed for bipyridyl and other heterocyclic aromatics, the relevant ruthenium complexes could be prepared. Using two precursors, the 'blue' solution and $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$, this proved successful.

B. REACTION WITH THE RUTHENIUM BLUE SOLUTION

The blue solutions, formed by reduction of Ru^{III} or Ru^{IV} chloro species either chemically or electrolytically, have been widely studied but the exact nature of the species remains unknown. Wilkinson ¹¹⁸ has proposed that one of the species is $\text{Ru}_5\text{Cl}_{12}^{2-}$ by preparing complexes $(\text{cat})_2\text{Ru}_5\text{Cl}_{12}$ ($\text{cat} = (\text{Ph}_4\text{As})^+$, $[\text{Fe}(\text{bipy})_3]^{2+}$

and others). However, this species is formally Ru^{II} , which is usually diamagnetic, while the solution and the complexes are weakly paramagnetic. Other workers have proposed a mixed valence $\text{Ru}^{\text{II}} - \text{Ru}^{\text{III}}$ species on the basis of electrochemical studies ¹¹⁹.

The blue solution, prepared by the reduction of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in methanol under 2 atmospheres of H_2 in the presence of PtO_2 , has proved to be a useful starting material for Ru^{II} and Ru^{III} species ¹²⁰. Relevant to this work was the preparation of trans- Rupy_4Cl_2 by refluxing the blue solution with pyridine for six hours. Though the reactions of diquinolylpyridine ¹²¹, 2-(2'pyridyl)quinoline and 2,2'-biquinoline ¹²² gave red-brown complexes of the type $(\text{RuL}_2)^{2+}$ which were isolated by the addition of NaClO_4 . The complex $[\text{Ru}(\text{bipy})_3]^{2+}$ has been prepared by directly from the reaction of RuCl_3 and bipy ¹²³.

Consequently several ligands, both bi and tetradentate, were refluxed with the blue solution and formed as above. In all the ligands used, within a short time, the solution became purple-red in colour and, in the case of py_2en and pyphen , precipitated a small amount of crystalline material, analogous to the preparation of trans- Rupy_4Cl_2 ¹²¹ (n.b. $\text{Ru}(\text{bipy})_2\text{Cl}_2$ has been prepared by the reaction of $\text{K}_2(\text{RuCl}_5\text{OH})$, Cl^- and bipy ¹²⁴), $\text{Rupy}_2\text{enCl}_2$ and $\text{Ru}(\text{pyphen})_2\text{Cl}_2$ respectively. The complexes were formed in greatest yields when twice the stoichiometric amount of ligand required to form the complex was added. Adding larger

excesses of the ligand appeared to have no substantial effect on the yield. The bronze coloured crystals of $\text{Ru}(\text{py}_2\text{en})\text{Cl}_2$ and the purple-red crystals of $\text{Ru}(\text{pyphen})_2\text{Cl}_2$ dissolved only slightly in polar solvents to give blue and green solutions respectively.

The deep-red solutions, also formed in the course of the reaction, were chromatographed through an alumina column and, in the case of pyphen and other bidentate ligands, blue or green eluates were separated from the column with thf or ether. These coloured solutions, however, on concentration gave only minute ($\ll 1\%$) amounts of solids which could not be fully characterised, but were probably RuL_2Cl_2 analagous to $\text{Ru}(\text{pyphen})_2\text{Cl}_2$, with the blue solutions being probably the trans isomers and the green solutions the cis isomers.

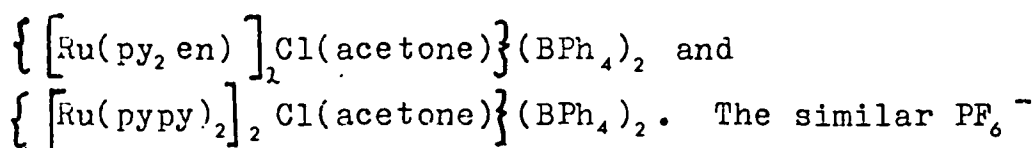
The complexes $\text{Ru}(\text{py}_2\text{en})\text{Cl}_2$ and $\text{Ru}(\text{pyphen})_2\text{Cl}_2$ had the expected i.r. spectra with strong vibrations in the region $1500 - 1600 \text{ cm}^{-1}$ due to the pyridine ring vibrations, and the $\nu(\text{C}=\text{N})$ and $\nu(\text{Ru}-\text{Cl})$ at 295 cm^{-1} (trans- $\text{Ru}(\text{py}_2\text{en})\text{Cl}_2$) and 302 cm^{-1} (cis- $\text{Ru}(\text{pyphen})_2\text{Cl}_2$). These complexes were too insoluble for molecular weight determinations or ^1H n.m.r. spectra to be carried out. They were also remarkably inert, failing to react with carbon monoxide, nitric oxide or sodium metal.

The remainder of the solutions, in each case, was eluted through the alumina column with methanol to yield a deep-red solution. On concentration these red solutions

gave only red oils, although addition of NaBPh_4 to the methanolic solutions yielded red salts. The salts, formed in the reaction with py_2en , were insoluble in methanol and precipitated out immediately, the others however were more soluble. After addition of the NaBPh_4 , the resulting solutions were chromatographed again and this time the main red band was eluted through with acetone (the pyphen salt was eluted through with thf). Addition of ether to the resulting solutions gave red solids.

As yet it has not proved possible to assign a structure to these salts although they appear to resemble the red-brown salts $(\text{RuL}_2)^{2+}$ isolated by Klassen^{122,123}. The ^1H n.m.r. spectra of the salts prepared had only very broad resonances, but using an aliphatic amine with a large number of alkyl protons $[\text{H}_2\text{N}-(\text{CH}_2)_3\text{Si}(\text{OEt})_3]$ to form the pyridine-2-alimine it was possible to show that the ligand framework was still intact after reaction with the blue solution. However, the e.s.r. spectra showed only very weak signals which appeared to be due to impurities.

The i.r. spectra of these complexes was also essentially uninformative apart from the vibrations due to the anions; unlike the complexes $\text{Ru}(\text{py}_2\text{en})\text{Cl}_2$ and $\text{Ru}(\text{pyphen})_2\text{Cl}_2$ which had strong vibrations in their i.r. spectra. The analysis of the py_2en and pypy complexes, however, indicated the formulae



salt of the former was also prepared and a satisfactory analysis obtained. Conductivity measurements of these complexes fitted the above formulae, with the BPh_4^- salts having $\Lambda_{\text{m}}(10^{-3}\text{M}) = 110 - 120 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$, while the PF_6^- salt had the higher conductance $\Lambda_{\text{m}}(10^{-3}\text{M}) = 166 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ as expected ⁹¹. The pyphen BPh_4^- salt, however, when analysed did not contain any chloride. The structure proposed for $\{ [\text{Ru}(\text{py}_2\text{en})]_2 - \text{Cl}(\text{acetone}) \} \text{X}_2$ was a mixed $\text{Ru}^{\text{II}} - \text{Ru}^{\text{I}}$ species which was hitherto unknown. This structure should, however, have had one unpaired electron and so give an e.s.r. signal. As has been explained above the e.s.r. spectra of the complexes appeared to show only small amounts of paramagnetic impurities and no reproducible spectra were obtained. Electrochemical studies were attempted to reduce the ligand but no evidence for either oxidation or reduction of the solutions was observed.

An alternate explanation could have been that hydrolysis of the ligand occurred to yield merely the amine complexes, but the lack of $\nu(\text{N-H})$ in the i.r. spectra and the analytical data were not consistent with this formulation. The lack of i.r. vibrations and broad ^1H n.m.r. spectra has also been noted when similar purple complexes were formed, by the reaction of ReCl_5 and $\text{ReOCl}_3(\text{PPh}_3)_2$ with the ligand py_2en ¹⁰⁷. In the former the complex appeared to be $\text{ReCl}_5 \cdot \text{py}_2\text{en}$.

Thus, although the physical data available for the red salts suggested that the ligand had rearranged in some way, the analytical data suggested

that the ligand was still present, though the structures suggested on the basis of the analytical data appeared unlikely. The colour seemed to resemble the salts of the form $(\text{RuL}_2)^{2+}$ previously prepared, but the analytical data never concurred with this assignment, although the pyphen complex did give analytical data which was reasonably close to that required for $[\text{Ru}(\text{pyphen})_3](\text{BPh}_4)_2$, though even in this case the ruthenium analysis was not as desired.

C. REACTION OF SCHIFF BASES WITH $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$

The reaction of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ with various ligands has been shown to give cis- $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}_2$ where $\text{L}_2 = 2\text{py}$, bipy , diphos , 2AsPh_3 , 2PPh_3 ¹²⁵. Similar complexes have been prepared by the reaction of the red solution, prepared by interaction of carbon monoxide and RuCl_3 , with pyridine, AsPh_3 and PPh_3 ¹²⁶. Also some of the trans isomers are formed.

The reaction of pyphen or pypy in methanol with $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ gave red solutions, from which orange crystals of the cis isomer $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}'$ were produced. The i.r. spectra of the two complexes in chloroform was consistent with this formulation, resembling closely the reaction with pyridine, to give absorptions due to $\nu(\text{C}\equiv\text{O})$ at 2061 and 2003 cm^{-1} , and 2068 and 2012 cm^{-1} respectively (in chloroform cis- $\text{Ru}(\text{CO})_2\text{Cl}_2\text{py}_2$ has similar absorptions at 2074 and 2013 cm^{-1}). The yellow chloroform solutions of $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}'$ ($\text{L}' = \text{pyphen}$, pypy) changed colour on standing in air to deep red. The i.r.

and n.m.r. spectra of the solutions did not appear to change. In thf yellow solutions were formed, from which solids were obtained identical to those isolated from the methanol solutions. The thf solution also changed colour to become red on standing in air.

The reaction of py_2en with $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ in thf yielded initial precipitation of a pale pink coloured solid which was insoluble in thf and had three absorptions due to $\nu(\text{C}\equiv\text{O})$ at 2129(m), 2048(s) and 1972(s, br) cm^{-1} . On leaving the solution in air a further red solid precipitate was formed, this had a similar i.r. spectrum except that the absorption at 2122 cm^{-1} was much stronger, and the absorption below 2000 cm^{-1} was much broader with a shoulder at ca. 1940 cm^{-1} . This solid was dissolved in methanol to give a red solution from which was isolated, by precipitation with ether, a red powder. This powder rapidly became a red oil on drying and had only a weak absorption at 2122 cm^{-1} and three other absorptions due to $\nu(\text{C}\equiv\text{O})$ at 2056(s), 1988(s, br) and 1941(s, br) cm^{-1} .

On carrying out the same reaction in methanol, a red oil was formed on cooling, the i.r. spectrum of which resembled that described above. Rationalisation of this system at this stage is difficult, but it is possible that the methanol solution was a mixture of cis and trans isomers. However separation by normal means was not possible.

The reaction of pyrenH_2 and salpyH in methanol with $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ also gave red solutions which had

the three absorptions due to $\nu(\text{C}\equiv\text{O})$ at 2125, 2040 and 1968 cm^{-1} and 2125, 2060 and 1985 cm^{-1} respectively, although the intensity of the absorption at 2125 cm^{-1} was very variable. These complexes appeared to be of the type cis- $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}$ but no adequate analyses were given.

The same complexes were obtained with $\text{Ru}(\text{CO})_3\text{Cl}_2$ thf.

D. CONCLUSION

It appears from the above work that the pyridine-2-alldimine ligands reacted in a similar fashion to other heteroaromatic bases such as pyridine or bipyridyl, except that because of the lack of good physical data complete characterisation proved difficult.

Other reactions which failed to give even partially characterisable products, included $\text{RuCl}_2(\text{dmsO})_4$, which failed to react and $\text{RuCl}_2(\text{PPh}_3)_3$, which gave a red solution where the ^{31}P n.m.r. spectrum contained a large number of singlet resonances. Chromatography failed to clarify the position.

CHAPTER IV

PREPARATION OF RUTHENIUM(II) COMPLEXES CONTAINING OXIMES

A. INTRODUCTION

Reaction of the ruthenium complexes with oximes has not previously been studied in any detail but, in this chapter, the reactions of $\text{RuCl}_2(\text{PPh}_3)_3$ with both the sodium and protonated forms of a) simple oximes, b) α -carbonyl oximes, c) α -dioximes and d) α -iminooximes are described.

The only reports of ruthenium oxime complexes have been the reaction of ruthenium complexes with violuric acid (VH_3 , Figure IV-i) and the N,N'-dimethyl analogue (Me_2VH). The reaction of $\text{Ru}(\text{NO}_3)_3$ with violuric acid at pH 1, followed by addition of $\text{Ba}(\text{NO}_3)_2$, gave the complex $\text{Ba}[\text{Ru}(\text{VH}_2)_3\text{OH}]_2$ ¹²⁷. The N,N'-dimethyl analogue

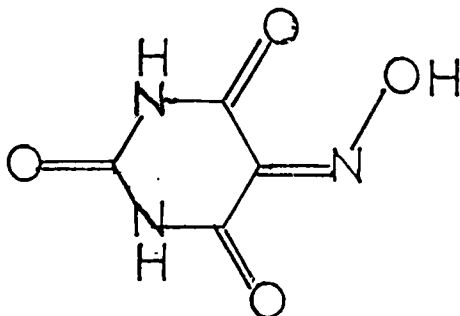
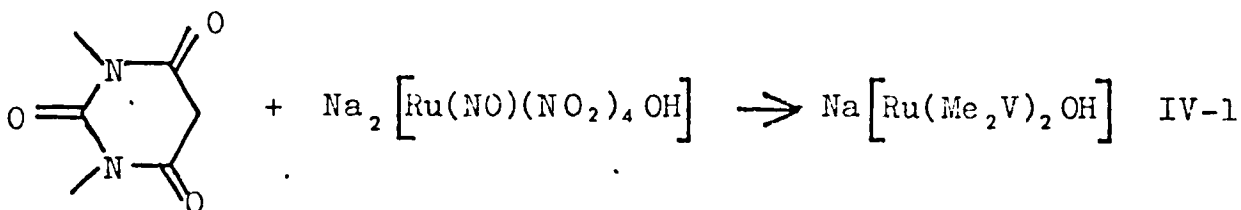


Figure IV-i

with several cations was prepared by the reaction of $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4\text{OH}]$ with N,N'-dimethylbarbituric acid, as below in Equation IV-1.



Replacement of the co-ordinated hydroxyl group by N_3^- and NO_2^- was also carried out and a mechanism proposed for the reaction above ¹²⁸.

However, there have been no previous examples of ruthenium complexes using the ligands described below. Pure complexes were readily obtained with only $\text{RuCl}_2(\text{PPh}_3)_3$ as the ruthenium source.

B. SIMPLE OXIMES

In this reaction a 'simple oxime' is considered as a ligand with only an oxime function available for co-ordination, acetoxime was used as the ligand in this case.

$\text{RuCl}_2(\text{PPh}_3)_3$ did not react with acetoxime other than in the presence of an equivalent of base (NaOH). Under these conditions, stirring the reactants in methanol for several hours gave a yellow solid which, when crystallised from chloroform, gave orange crystals. This material had the stoichiometry $\text{Ru}(\text{ato})_2(\text{PPh}_3)_2$. The ^{31}P n.m.r. spectrum of the complex had a slightly broadened singlet at +66.36 ppm (equivalent mutually cis phosphines), which on cooling partially split into a doublet of doublets (AB pattern) with $J_{\text{P-P}} = 10.3$ Hz, with the two doublets split by only 5.3 Hz. This slight non-equivalence of the two phosphine ligands on cooling was probably due to all four of the methyl groups on the ligands becoming non-equivalent, and not due to the formation of another isomeric form of the molecule. The ^{31}P n.m.r. spectrum of the reaction supernatant, after filtration, had two small resonances

at +31.75 ppm and +36.7 ppm, as well as free triphenylphosphine and trace amounts of the major product cis-Ru(ato)₂(PPh₃)₂. The two extra resonances were probably due to the two possible trans isomers but, as the yield of these was very low (<<1%), these species could not be further identified. The ¹H n.m.r. spectrum of the complex had two non-equivalent methylene resonances at 8.28τ and 8.69τ. At -60°C extra resonance at 8.75τ appeared at the side of the 8.69τ resonance, this concurred with the possible non-equivalence of all four methyl groups at this temperature. Similar complexes (ato)M(CO)₂(η⁵-C₅H₅) (M = Mo, W) ^{129,58} have also been shown to have two non-equivalent methyl groups (2 singlets at 7.90τ and 7.97τ (Mo), 7.84τ and 7.93τ (W)). Acetoxime has a singlet methyl resonance at 8.20τ.

The X-ray crystal structure of (ato)Mo(CO)₂(η⁵-C₅H₅) has shown that the ato ligand was bonded to the metal through both nitrogen and oxygen (Figure I-iii) ⁵⁹. However, if the ligand had been bonded through the nitrogen only, this would also have held; as has been shown by Fischer ¹³⁰ in the similar complex (CO)₅Cr[HN=C(Me)₂] where the cis and trans methyl groups, relative to the chromium, resonated at 8.44τ (singlet) and 8.98τ (doublet, split by the hydrogen atom on the nitrogen) respectively. This complex was formed by the reaction of acetoxime with the carbene complex (CO)₅Cr(OMe)(Me).

The mode of bonding of cis-Ru(ato)₂(PPh₃)₂ is

probably similar to $(\text{ato})\text{Mo}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ (Figure IV-ii) to give an 18 electron ruthenium(II) species, with the ligand acting as a three electron donor, although a 16 electron species, with co-ordination only through the nitrogen, is also a possibility. The ^{13}C n.m.r. spectrum

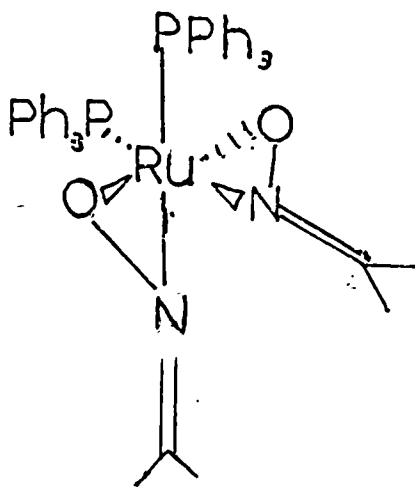


Figure IV-ii

of cis- $\text{Ru}(\text{ato})_2(\text{PPh}_3)_2$ was similar to that of $(\text{ato})\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ (Table IV-1), with two methyl resonances at δ 20.5 and δ 17.6 and the $\text{R}_2\text{C}=\text{N}-\text{O}$ resonance at δ 142.9. The differences in the ^1H n.m.r. resonances and the ^{13}C n.m.r. frequencies of cis- $\text{Ru}(\text{ato})_2(\text{PPh}_3)_2$ and $(\text{ato})\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ were probably due to preferential shielding of one set of methyl groups by the PPh_3 ligands.

The i.r. spectrum of the complex has no $\nu(\text{Ru}-\text{Cl})$ and only a weak absorption at 1626 cm^{-1} which was assigned to $\nu(\text{C}=\text{N})$.

Table IV-1 ^{13}C n.m.r. data*

	atoH	$\text{Ru}(\text{ato})_2(\text{PPh}_3)_2$	$(\text{ato})\text{W}(\text{CO})_2\text{Cp}$	$(\text{ato})\text{Mo}(\text{CO})_2\text{Cp}$
$\text{R}_2\text{C}=\text{N}-\text{O}$	155.2	142.9	148.6	149.0
Me {	21.5	20.5	20.7	20.7
	14.9	17.6	19.4	19.4
Phenyl		137.6 - 127.1		

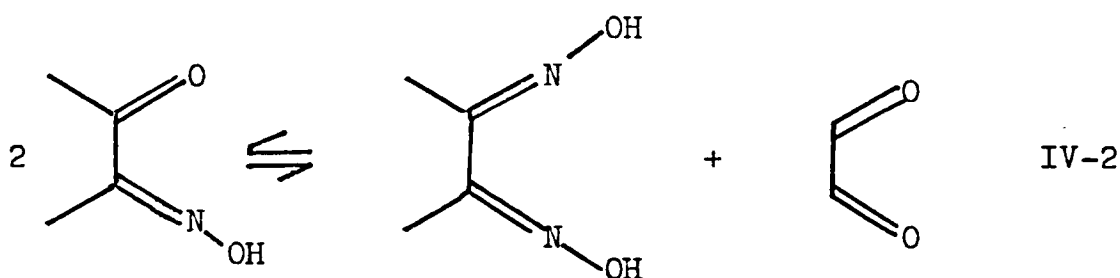
* relative to TMS = $\delta 0$ from CDCl_3 , internal standard = $\delta 76.9$

C. α -CARBONYL OXIMES

The reaction of butan-2,3-dione monoxime with transition metals has been studied only rarely and inconclusive results have generally been given. Taylor and Ewbank¹³¹ in 1926 reported the attempted preparation of metal complexes by the reaction of the M^{II} acetates ($\text{M} = \text{Ni}, \text{Cu}$) with the oxime in aqueous solution in the presence of NaOH , but could isolate only a poorly characterised copper complex. Using a similar procedure, incorporating cobalt(II) chloride, the tris complex has been prepared¹³². Several other workers have noted that the ligand caused a colour change in solution with transition metals¹³³⁻¹³⁵, but have found that even in alkaline solution the ligand bdoH rearranged to dmgH_2 by the reaction below, see Equation IV-2.

The converse has also been shown, whereby the addition of 2N HCl to a solution of sodium molybdate, SnCl_2 and dmgH_2 resulted in the formation of a series of molybdenum

bdo complexes, which were not fully characterised.



However, the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with bdoH, both with and without the addition of base (NaOH), yielded readily isolable complexes with no evidence of formation of dmgH_2 .

On heating a mixture of $\text{RuCl}_2(\text{PPh}_3)_3$ and bdoH in methanol for prolonged periods a brown crystalline complex $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ was precipitated. The ^{31}P n.m.r. spectrum (singlet at +25.31 ppm) indicated that the phosphines were mutually trans. The ^1H n.m.r. spectrum of the complex showed the presence of two methyl resonances (singlets at 8.23 τ , 9.10 τ), a complex phenyl resonance at 2.20 - 2.70 τ and a sharp resonance at -2.39 τ , the latter being due to the hydroxy proton. In the free ligand the methyl resonances occur at 7.60 τ and 8.10 τ , while the hydroxy proton resonates at -0.22 τ as a broad singlet due to isomeric exchange. The ^1H n.m.r. resonances of several $\text{Co}(\text{dmgH})_2\text{L}_2$ complexes have shown that hydrogen bonding causes the hydroxy proton resonance to shift to lower field and resonate at ca. -8.0 τ ¹³⁷. The shift in the hydroxy resonance in $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ was not

concentration dependent in CDCl_3 , and so there was probably little or no intermolecular hydrogen bonding. The i.r. spectrum did not appear to contain an absorption due to the O-H stretch, $\nu(\text{O-H})$. However, the deuterated derivative $\text{Ru}(\text{bdoD})(\text{PPh}_3)_2\text{Cl}_2$ contained a weak absorption at 2315 cm^{-1} which was not present in the original spectrum.

Assuming that the absorption was due to $\nu(\text{O-D})$ then the $\nu(\text{O-H})$ would have occurred at 3253 cm^{-1} . In the free ligand the $\nu(\text{O-H})$ vibration is in this region. However, it was unlikely that the vibration in the spectrum of $\text{Ru}(\text{bdoD})(\text{PPh}_3)_2\text{Cl}_2$ was due to an impurity of the free ligand, since the ^1H n.m.r. spectrum of this complex did not contain a resonance at -2.39τ . Only on addition of one drop of water to the n.m.r. sample was the latter resonance observed. Also, when the sample of $\text{Ru}(\text{bdoD})(\text{PPh}_3)_2\text{Cl}_2$ was exposed to air for several hours the absorption at 2315 cm^{-1} disappeared and in the ^1H n.m.r. spectrum the resonance at -2.39τ reappeared.

The i.r. spectra of the two complexes $\text{Ru}(\text{bdoD})(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ were otherwise very similar. There were no strong absorptions in the region expected for the $\nu(\text{C}\equiv\text{O})$ and $\nu(\text{C}=\text{N})$, which suggested that the ligand was bonding in a bidentate fashion. The complex was thus of structure shown in Figure IV-iii.

Whereas the complex $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ was formed by reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ and bdoH in the absence of added base, the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with bdoH in methanol in the presence of base (NaOH), resulted in a different reaction to that above.

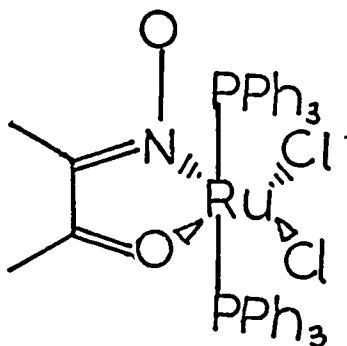


Figure IV-iii

On heating, a deep red solution was formed which precipitated a red solid on further heating. The red solid was recrystallised from thf, acetone and ether to give complexes of stoichiometry $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2 \cdot 2\text{solvent}$, where the amount of solvent present appeared to be dependent on crystal size, varying between 0 - 2 molecules of solvent per ruthenium. The red solution, on cooling, gave a red microcrystalline compound $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_4$. The ^{31}P n.m.r. spectrum of this solution had three singlet resonances at +45.9 ppm, +33.5 ppm and -6.03 ppm. The complex $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ had only a singlet resonance at ca. +45.9 ppm (the value varied slightly with solvent), while the complex $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_4$ had ^{31}P n.m.r. resonances at +45.9 ppm and -6.0 ppm. This was rationalised as being due to $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ and two moles of free PPh_3 and in fact recrystallisation of $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_4$ in thf or acetone yielded only $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$.

Recrystallisation of $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ in hot methanol in the presence of two moles of PPh_3 yielded only $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2 \cdot 2\text{MeOH}$. The resonance at +33.5 ppm, which was only a minor product, was probably due to a different isomer of the complex $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$; probably the isomer with mutually trans phosphines. The resonance at +45.9 ppm was of the cis isomer which was the major product.

The ^1H n.m.r. spectrum of cis- $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ had a singlet broad phenyl resonance at 2.19 τ and two sharp singlet methyl resonances at 8.07 τ and 8.73 τ . There was no hydroxyl resonance below 0 τ observable. The spectrum of $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_4$ was similar to cis- $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ except that there were two extra phenyl resonances at 2.64 τ and 2.79 τ , which were shown to be due to free PPh_3 by addition of PPh_3 to a sample of $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$, which results in the growth of the resonances at 2.64 τ and 2.79 τ .

The i.r. spectra of the complexes $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ were compared with those of bdoH and $\text{RuCl}_2(\text{PPh}_3)_3$, and it was found that the strong absorption at 1012 cm^{-1} in bdoH was probably mainly the $\nu(\text{N-O})$ which had disappeared in both the complexes. The strong absorption at 1665 cm^{-1} had also disappeared. In $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ an additional absorption was observed at 1080 - 1065 cm^{-1} , in this region $\text{RuCl}_2(\text{PPh}_3)_3$ has a single absorption, though in $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ two absorptions were observed. Also

absorptions at 1624 cm^{-1} (medium intensity) and 1508 cm^{-1} (very weak) were found in $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$, which were probably due to $\nu(\text{C}=\text{N})$ or $\nu(\text{C}=\text{O})$, and also an additional strong absorption at 1395 cm^{-1} . In $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ the additional absorptions were at 1520 cm^{-1} (very weak), 1203 cm^{-1} (strong) and 970 cm^{-1} (weak). No unequivocal assignments for these absorptions could be made, except that the absorptions at $1080 - 1065\text{ cm}^{-1}$ in $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ and 1263 cm^{-1} in $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ probably contained some $\nu(\text{N}-\text{O})$ character.

In $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ there was a strong absorption at 259 cm^{-1} and 312 cm^{-1} (shoulder), of these the absorption at 259 cm^{-1} was assigned to $\nu(\text{Ru}-\text{Cl})$ while the other may have been due to $\nu(\text{M}-\text{N})$.

Thus although the oxime in $\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$ was almost certainly N-bonded, little information on the nature of the bonding in $\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ could be obtained from the physical data. By far the commonest arrangement is N-bonded, but without an X-ray single crystal structure it is not possible to separate between the structures shown in Figure IV-iv(a,b).

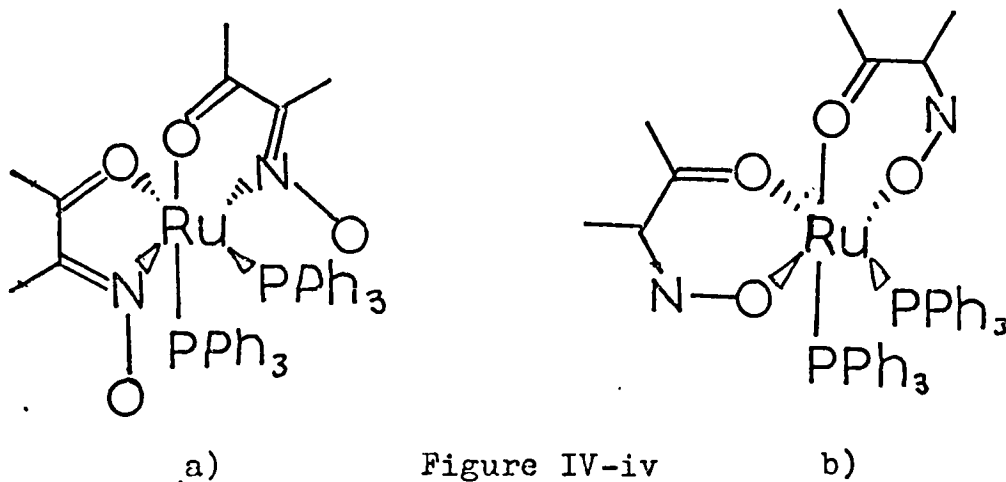


Figure IV-iv

D. L-DIOXIMES

Because of the ability of cobalt dioxime complexes to react in similar fashion to vitamin B₁₂, many complexes containing this ligand have been prepared and their reactions studied in great detail. This study of reactions of Co(dmgh)₂ has led to the preparation of complexes of the type Co(dmgh)₂(PPh₃)₂, [Co(dmgh)₂(PPh₃)]₂¹³⁸ and [Co(dmgh)₂(PR₃)_n]⁺¹³⁹ (n = 1 or 2); while the reaction of RhCl₃ with dmgh₂ and PPh₃ in methanol, in the absence of added base, yielded the complex Rh(dmgh)₂(PPh₃)Cl¹⁴⁰ (which can also be prepared by the reaction of Rh(PPh₃)₃Cl with dmgh₂). The reaction of Rh(dmgh)₂(PPh₃)Cl with NaBH₄ yielded the complex [Rh(dmgh)₂(PPh₃)]₂¹⁴¹, which has been shown by X-ray crystallography to have a Rh-Rh single bond (2.93 Å)¹⁴².

The reaction of RuCl₂(PPh₃)₃ with dmgh₂, without added base, did not result in oxidation of the metal, but merely replacement of one of the phosphine ligands by dmgh₂. On refluxing a mixture of dmgh₂ and RuCl₂(PPh₃)₃ in methanol, a red complex Ru(dmgh₂)(PPh₃)₂Cl₂ was formed which was totally insoluble in all common solvents, thus no ¹H n.m.r. or ³¹P n.m.r. spectra could be obtained. The i.r. spectrum of Ru(dmgh₂)(PPh₃)₂Cl₂ was rather unusual, having a very sharp absorption due to the hydroxy stretching vibration, ν(O-H), at 3440 cm⁻¹ with a much weaker sharp absorption at 3393 cm⁻¹. These peaks were shifted on deuteration to 2540 and 2517 cm⁻¹.

A similar complex was prepared with cyclohexane-1,2-dione dioxime, which had a sharp $\nu(\text{O-H})$ at 3435 cm^{-1} , with the smaller absorption at 3377 cm^{-1} . These absorptions indicated that there was no hydrogen bonding in the complex. In all three complexes the $\nu(\text{Ru-Cl})$ was a single absorption at 323 cm^{-1} indicating that the chlorides were equivalent. It was not possible to determine whether the chlorides were mutually cis (i.e. opposite the nitrogen atoms of the dmgH_2) as in Figure IV-iii or mutually trans, without a ^{31}P n.m.r. spectrum. Weak absorptions at 1542 cm^{-1} in $\text{Ru}(\text{dmgH}_2)(\text{PPh}_3)_2\text{Cl}_2$, 1510 cm^{-1} in $\text{Ru}(\text{dmgD}_2)(\text{PPh}_3)_2\text{Cl}_2$ and 1534 cm^{-1} in $\text{Ru}(\text{cyoxH}_2)(\text{PPh}_3)_2\text{Cl}_2$ were found, and were probably due to coupled $\nu(\text{C=N})$ stretching modes.

The reaction of $\text{Ru}(\text{dmgH}_2)(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Ru}(\text{cyoxH}_2)(\text{PPh}_3)_2\text{Cl}_2$ above, with NaOH in the presence of excess of the oxime ligand, yielded yellow-orange insoluble complexes $\text{Ru}(\text{dmgH})_2(\text{PPh}_3)_2$ and $\text{Ru}(\text{cyoxH})_2(\text{PPh}_3)_2$, respectively. The same complexes were obtained by reacting $\text{RuCl}_2(\text{PPh}_3)_3$ with two equivalents of oxime ligand and NaOH . The complex $\text{Ru}(\text{dmgH})_2(\text{PPh}_3)_2$ was slightly soluble in thf , and a ^{31}P n.m.r. spectrum showed that the phosphine ligands were mutually trans (singlet at $+28.93\text{ ppm}$) the structure of these complexes was probably similar to $\text{Rh}(\text{dmgH})_2(\text{PPh}_3)\text{Cl}$ ¹⁴³ with octahedral co-ordination around the ruthenium (as in Figure I-vi a) and hydrogen bonding between the two oxime groups, although it was not possible to unequivocally assign i.r. absorption due to the $\text{O-H}\cdots\text{O}$ stretching vibration. A polymeric structure is, of course, another possibility.

Deuteration studies proved inconclusive in this case due to contamination of the products with free dmgD_2 ligand. An alternative structure, involving a ruthenium(IV) species of stoichiometry $\text{Ru}(\text{dmg})_2(\text{PPh}_3)_2$ and $\text{Ru}(\text{cyox})_2(\text{PPh}_3)_2$, was unlikely as the complexes were not paramagnetic whereas a ruthenium(IV) species would be expected to have 2 unpaired electrons (d^4), unless spin pairing occurred.

The i.r. spectra of $\text{M}(\text{dmgH})_2$ ($\text{M} = \text{Cu}, \text{Ni}, \text{Pd}, \text{Pt}$) and $\text{Co}(\text{dmgH})_2\text{LL}'$ complexes have been predicted theoretically¹⁴⁵ and it has been found that all the observed absorptions are due to coupling of several vibrations, but those of predominantly $\nu(\text{N-O})$ character were in the range $1190 - 1260 \text{ cm}^{-1}$ and $1070 - 1110 \text{ cm}^{-1}$. This confirmed earlier empirical assignments^{66,67}. In $\text{Ru}(\text{dmgH})_2(\text{PPh}_3)_2$ and $\text{Ru}(\text{cyoxH})_2(\text{PPh}_3)_2$ there were very strong absorptions at 1224 cm^{-1} and 1218 cm^{-1} respectively (in $\text{Rh}(\text{dmgH})_2(\text{PPh}_3)\text{Cl}$ this absorption occurred at 1256 cm^{-1}) which contained certainly some $\nu(\text{N-O})$ character. The other absorption expected was much more difficult to assign due to the PPh_3 absorptions in this region, but it appeared that the absorptions at 1081 cm^{-1} and 1080 cm^{-1} in $\text{Ru}(\text{dmgH})_2(\text{PPh}_3)_2$ and $\text{Ru}(\text{cyoxH})_2(\text{PPh}_3)_2$ respectively were stronger than usually found in PPh_3 complexes. Thus, in conclusion the i.r. spectra appeared to confirm that the complexes were N-bonded.

The complexes $\text{Ru}(\text{dmgH}_2)(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Ru}(\text{cyoxH}_2)(\text{PPh}_3)_2\text{Cl}_2$ did not have a strong absorption at $1210 - 1225 \text{ cm}^{-1}$ since the $\nu(\text{N-O})$ was shifted to lower frequency, as has

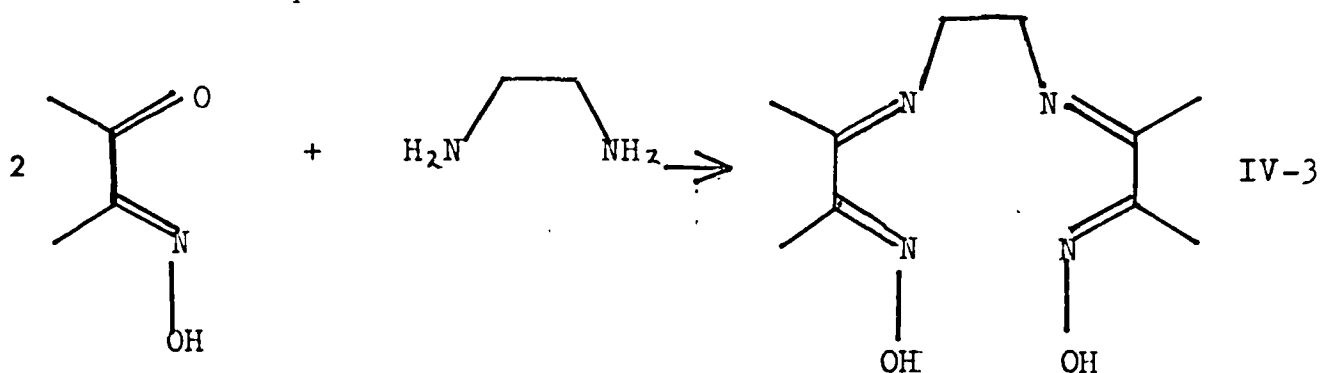
been shown previously with a series of pyridine-2-aldoxime complexes²⁰ due to the non-hydrogen bonded hydroxy group. Comparison of the i.r. spectra of $\text{Ru}(\text{dmgH}_2)(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Ru}(\text{dmgH})_2(\text{PPh}_3)_2$ revealed that, while the strong absorption at 1224 cm^{-1} had disappeared, a weaker absorption at 1152 cm^{-1} appeared. Also a strong absorption appeared centred at 1027 cm^{-1} . In $\text{Ru}(\text{dmgD}_2)(\text{PPh}_3)_2\text{Cl}_2$ the same changes occurred with new absorptions at 1153 cm^{-1} and a very strong absorption at 998 cm^{-1} which almost masked the absorption at ca. 1020 cm^{-1} , the latter appeared merely as a shoulder on the side of this strong absorption. The very strong absorption was possibly due to an O-D vibration, the $\nu(\text{O-H})$ of which in $\text{Ru}(\text{dmgH}_2)(\text{PPh}_3)_2\text{Cl}_2$ vibrated at 1342 cm^{-1} . Comparison of $\text{Ru}(\text{cyoxH}_2)(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Ru}(\text{cyoxH})_2(\text{PPh}_3)_2$ gave similar results, with the new absorptions at 1153 cm^{-1} and 1005 cm^{-1} . Of course, it is not possible to assign these absorptions without doubt to the $\nu(\text{N-O})$, but from the absorptions described above they would seem to be most likely due to $\nu(\text{N-O})$.

E. Δ -IMINO OXIMES

As has been seen in chapter I chelating Δ - imino oximes have been widely studied because of their resemblance to biological systems, in particular vitamin B_{12} ^{73,74}.

The condensation of bdoH and half a mole of ethylenediamine is a rather complicated reaction, since it yields several different compounds, which all appear

to follow Equation IV-3



If the reaction is carried out in water the compound obtained has a melting point of 242°C ¹⁴⁵, in benzene the melting point was $168 - 171^{\circ}\text{C}$ ¹⁴⁶ and in methanol it was $173 - 174^{\circ}\text{C}$. This was due to the formation of different isomers of the starting material, because of the two possible co-ordination sites of the oxygens of the oxime group. The products formed in methanol and benzene contained varying proportions of two isomers which had strong absorptions at 1608 cm^{-1} and 1621 cm^{-1} respectively. The product formed from methanol being much purer containing ca. 90% of the former isomer, while the product for benzene contained 70% : 30% mixtures of the two.

The compound formed by the reaction in water had a totally different i.r. spectrum from the two isomers prepared, with no absorptions at 1600 cm^{-1} , its only features being two strong absorptions at 979 and 905 cm^{-1} , a broad absorption at 3200 cm^{-1} and a weak one at 1678 cm^{-1} . The product also sublimed in the melting point tube as white crystals, and was probably not the required ligand.

Both the isomers formed above, in the presence of added base, reacted with $\text{RuCl}_2(\text{PPh}_3)_3$ in methanol, to give a yellow-red solution from which on cooling red crystals

were isolated. The ^1H n.m.r. spectrum of these crystals showed that the complex contained both triphenylphosphine resonating as a broad singlet resonance at 2.76 τ , methylene protons of the ligand (singlet resonance at 6.30 τ) and two slightly non-equivalent sets of methyl groups resonating as singlet resonances at 8.83 τ and 8.92 τ , with the former in general broader than the latter. Integration of this spectrum gave a complex of stoichiometry $\text{Ru}(\text{bdo}_2\text{en})(\text{PPh}_3)_2$. The ^{31}P n.m.r. spectrum of the complex had only a singlet resonance at +38.24 ppm (trans phosphines).

The i.r. spectrum of the complex $\text{Ru}(\text{bdo}_2\text{en})(\text{PPh}_3)_2$ did not have a strong absorption at 1608 cm^{-1} [$\nu(\text{C}=\text{N})$] or 998 cm^{-1} [$\nu(\text{N}-\text{O})$], but had a very strong broad absorption at 1266 cm^{-1} and an increase in intensity of the absorption at 1130 cm^{-1} (in $\text{Co}[\text{bdo}_2(1,3\text{-prop})\text{H}]\text{Me}_2$ $\nu(\text{N}-\text{O})$ absorbed at 1131 cm^{-1}). The broad absorption at 3130 cm^{-1} had also disappeared, but in the spectrum above 3000 cm^{-1} there were several weak absorptions, at 3640 cm^{-1} , 3300 - 3500 cm^{-1} (very broad) and 3140 cm^{-1} . All three persisted even after several recrystallisations. No resonance in the ^1H n.m.r. spectrum was observed for a hydroxy or N-H proton although the latter may have been hidden under the phenyl resonances. The crystals formed by recrystallisation from thf appeared to have the thf present in variable amounts, and consistent analyses proved difficult to obtain.

The near equivalence of the methyl groups suggested that the ligand was N-bonded (Figure IV-vi) although again unequivocal assignment is impossible.

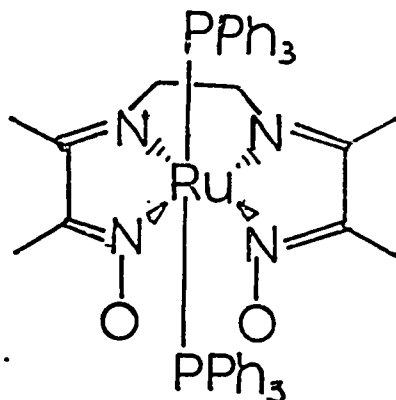


Figure IV-vi

$\text{Bdo}_2(1,3\text{-prop})\text{H}_2$ under similar conditions did not give a crystalline complex, only red oils were obtained.

F. CONCLUSION

The oxime ligands prepared in this chapter were, in general, rather difficult to characterise because of the lack of physical data. They are, however, exceedingly interesting complexes since they are among the first ruthenium oxime complexes prepared.

Further research on this subject should be concentrated on the preparation of further complexes with simple oximes, since they can act as either one, two or three electron donors. Also the reactions of the chlorine containing complexes should facilitate the preparation of a wide range of new complexes, analogous to the reactions of $\text{RuCl}_2(\text{PPh}_3)_3$.

CHAPTER V

EXPERIMENTAL

A. GENERAL

(i) Elemental Analysis

Microanalysis were by the microanalytical laboratories of Imperial College; Butterworth Microanalytical Consultancy and F. Pascher (Bonn). Several ruthenium analyses were carried out using a plasma spectrometer belonging to the Analytical Chemistry department of Imperial College. The results are given in Table 1. For several of the complexes prepared consistent analytical data was difficult to obtain, although the compounds appeared pure by physical tests.

(ii) Instruments

¹H n.m.r. spectra were recorded on Perkin-Elmer R12A (60 MHz) and Varian XL100-12 (100MHz) spectrometers. ³¹P n.m.r. spectra were recorded at 40.505 MHz using the latter spectrometer operating in the Fourier transform mode. Perkin-Elmer 257 and 457 spectrometers were used to record infra-red spectra. G.l.c. measurements were made by a Perkin-Elmer F33 chromatograph and an Infotronics CRS-208 automatic digital integrator. Conductivities were measured using a Mullard conductivity bridge type E7566/3 with a matching conductivity cell.

(iii) Materials and Procedure

All preparations and other operations were normally

carried out under oxygen-free, argon or nitrogen surroundings, using standard Schlenk tube, suba-seal and thin-steel tubing techniques. Tetrahydrofuran, petroleum (b.p. = 40 - 60 °C); diethyl ether and toluene were all dried and distilled from sodium and benzophenone immediately prior to use. Methanol, chloroform, acetone and dichloromethane were all dried by standing over molecular sieves.

The Schiff bases were prepared by refluxing equivalent amounts of the amine and aldehyde in methanol for ten minutes and were recrystallised from ethanol unless otherwise stated. The pyridine-2-alimine ligands were recrystallised from petroleum ^{147,148}.

The sodium salts were prepared by stirring equivalent amounts of sodium hydride and the Schiff bases in diethyl ether until hydrogen evolution ceased ¹⁸.

The nitric oxide used was of reagent grade by Matthesons and was purified by passing through 5A molecular sieves at -78°C ¹⁰⁴ or through 10% KOH solution and then a CaCl₂ drying tower. The carbon monoxide used was of reagent grade and needed no further purification.

The ruthenium complexes employed as precursors were all prepared by existing procedures; RuCl₂(PPh₃)₃ ¹²⁶, [Ru(nbd)Cl₂]_n ¹⁴⁹, RuCl₂(PPhMe₂)₄ ¹⁵⁰, RuCl₂(MeCN)₄ ¹²⁰, RuCl₂(dmsO)₄ ¹⁵¹, [Ru(CO)₃Cl₂]₂ ¹⁵².

On heating all the new complexes formed decomposed without melting, except where otherwise stated. All

yields quoted are the average of several preparations.

B. COMPLEXES PREPARED IN CHAPTER II AND III

(i) Trans-bis(triphenylphosphine)-N,N'-ethylene-bis
(salicylideneiminato)ruthenium(II)

a. $\text{RuCl}_2(\text{PPh}_3)_3$ (1.0g, 1.04 mmole) was added to a suspension of $\text{Na}_2\text{sal}_2\text{en}$ (0.32g, 1.04 mmole) in thf (50 cm^3) and the solution refluxed for two hours. The deep red solution was then filtered and evaporated to small volume to give purple crystals of the complex. These were collected and recrystallised from tetrahydrofuran-petroleum. (Yield 60%).

b. The same complex was prepared using methanol as solvent, but refluxing for several days was required.

(ii) Trans-bis(triphenylphosphine)-N,N'-o-phenylene
bis(salicylideneiminato)ruthenium(II)

Using method a. above but refluxing for five hours a yellow-black solution was formed which on cooling yielded black crystals of the complex. (Yield 70%).

(iii) Trans-bis(triphenylphosphine)-N,N'-ethylene-bis
(pyrrole-2-aldiminato)ruthenium(II)

Similarly except that warming the mixture to ca. 60°C for ten minutes effected complete reaction, an orange solution was formed from which orange crystals of the complex were isolated. (Yield 75%). A similar reaction time was required for the reaction in methanol.

(iv) Trans-bis(triphenylphosphine)-N,N'-o-phenylene-bis(pyrrole-2-aldiminato)

As for (iii) the reaction time was very short and orange crystals of the complex were isolated. (Yield 60%).

(v) Trans-bis(dimethylphenylphosphine)-N,N'-ethylene-bis(salicylideneiminato)ruthenium(II)

This reaction was very similar to (i)a and yielded a red solution, from which red crystals of the complex were isolated. (Yield 50%).

(vi) Trans-bis(triphenylphosphine)-bis-N-benzyl-(salicylideneiminato)ruthenium(II)

Using two moles of the sodium salt for every mole of $\text{RuCl}_2(\text{PPh}_3)_3$ in thf after refluxing a red solution was formed which, after filtration, on cooling gave red crystals of the complex. (Yield 50%).

(vii) Bis(triphenylphosphine)-bis-N-benzyl(pyrrole-2-aldiminato)ruthenium(II)

Under the same conditions as in (vi) a yellow solution was formed which on cooling yielded very air-sensitive crystals of the complex $\text{Ru}(\text{pybenz})_2(\text{PPh}_3)_2$. (Yield 60%).

(viii) Trans-bis(triphenylphosphine)-bis-N-2-pyridyl-(salicylideneiminato)ruthenium(II)

The ligand salpyH was prepared by standard methods and is an orange microcrystalline compound (M.pt. = 64 -

66°C), this was stored at -20°C to prevent decomposition. Method (i)a above gave a red solution from which it proved rather difficult to crystallise large amounts of the complex, however it was prepared in better yield by addition of petroleum to give a red powder. (Yield: of crystals = 10%, of powder = 60%).

(ix) Trans-bis(triphenylphosphine)-N- β -hydroxy- α -naphthylmethyl(salicylideneiminato)ruthenium(II)

The ligand salnapH was prepared by the reaction of β -hydroxy- α -naphthylmethylaniline hydrochloride with salicylaldehyde in methanol in the presence of one equivalent of NaOH. The yellow product was recrystallised from ethanol as yellow crystals (M.pt. = 184 - 185°C).

$\text{RuCl}_2(\text{PPh}_3)_3$ (1.0g, 1.04 mmole) was refluxed in thf (50 cm³) with $\text{Na}_2(\text{salnap})$ (0.33g, 1.04 mmole) and PPh_3 (1.0g, 3.7 mmole) for 12 hours to yield a red-black solution which on cooling yielded red-black crystals of the complex. These crystals rapidly turn green when dry. (Yield 10%).

(x) Trans-bis(triphenylphosphine)-N,N'-ethylene-bis-(pentan-2,4-dione monoiminato)ruthenium(II)

$\text{RuCl}_2(\text{PPh}_3)_3$ (1.0g, 1.04 mmole) was added to a suspension of $\text{Na}_2(\text{acac}_2\text{en})$ (0.27g, 1.04 mmole) in thf (50 cm³) and the mixture refluxed for 1 hour. The resulting red solution was filtered and evaporated to ca. 10 cm³. Petroleum (50 cm³) was then added to precipitate the brown complex, this was recrystallised from acetone

and then tetrahydrofuran to give red needles. (Yield ca. 30%).

(xi) Bis[carbonyl-N,N'-ethylene-bis(salicylideneiminato) ruthenium(II)]

a. Carbon monoxide was bubbled through a warm solution (60°C) of $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$ (0.2g, 0.22 mmole) in thf (20 cm³). Immediate precipitation of the yellow complex $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$ occurred. (Yield ca. 90%).

b. Bubbling carbon monoxide through a warm solution (60°C) of $\text{Ru}(\text{sal}_2\text{en})(\text{nbd})$ (0.2g, 0.43 mmole) also gave immediate precipitation of the yellow complex $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$. (Yield ca. 90%).

(xii) Trans-dicarbonyl-bis-N-benzyl(salicylideneiminato) ruthenium(II)

Refluxing a solution of $\text{Ru}(\text{salbenz})_2(\text{PPh}_3)_2$ (0.5g, 0.4 mmole) in thf under an atmosphere of carbon monoxide gave a change in colour of the solution from red to orange. The resulting solution was transferred to an alumina column and the column eluted with petroleum, thf and methanol. The methanol elutate was collected and on evaporation gave orange crystals of the complex trans-Ru(salbenz)₂(CO)₂. (Yield 40%).

(xiii) Carbonyl-triphenylphosphine-N,N'-ethylene-bis-(pyrrole-2-aldiminato)ruthenium(II)

Bubbling carbon monoxide through a solution of $\text{Ru}(\text{pyr}_2\text{en})(\text{PPh}_3)_2$ (0.2g, 0.2 mmole) in thf (10 cm³) resulted in an immediate colour change from orange to

yellow. After two minutes the flow of carbon monoxide was stopped and the solution evaporated to low volume to give yellow crystals of the complex $\text{Ru}(\text{pyr}_2\text{en})(\text{CO})(\text{PPh}_3)$, this was then recrystallised from thf-petroleum. (Yield ca. 80%).

(xiv) Carbonyl-bis(triphenylphosphine)-N- β -hydroxy- α -naphthylmethyl(salicylideneiminato)ruthenium(II)

A solution of $\text{Ru}(\text{salnap})(\text{PPh}_3)_2$ (0.2g, 0.2 mmole) in thf (20 cm³) was refluxed under a carbon monoxide atmosphere for 3 hours. On cooling a green solution and some yellow solid were given. Evaporation of the green solution to low volume precipitated more of the yellow solid. The combined yellow solid was recrystallised from hot thf (3 times) to give pale yellow crystals of $\text{Ru}(\text{salnap})(\text{CO})(\text{PPh}_3)_2 \cdot 2\text{thf}$. (Yield ca. 60%). The same product was prepared by the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ and Na_2salnap under an atmosphere of carbon monoxide.

(xv) Bis[carbonyl-N,N'-o-phenylene-bis(salicylideneiminato)ruthenium(II)]

Bubbling carbon monoxide through a solution of $\text{Ru}(\text{sal}_2\text{phen})(\text{PPh}_3)_2$ (0.4g, 0.43 mmole) in thf (20 cm³) resulted in an immediate colour change from brown to purple. Work up was as in (xii) and the purple microcrystalline complex, $[\text{Ru}(\text{sal}_2\text{phen})(\text{CO})]_2$, was isolated from the methanolic solution. (Yield 70%).

(xvi) Carbonyl-triphenylphosphine-N,N'-ethylene-bis-(salicylideneiminato)ruthenium(II)

$\text{RuCl}_2(\text{PPh}_3)_3$ (1.0g, 1.04 mmole) was dissolved in thf (30cm^3) under a carbon monoxide atmosphere and $\text{Na}_2(\text{sal}_2\text{en})$ (0.32g, 1.04 mmole) was added. After refluxing the mixture for several hours a red solution and a yellow solid, which contained $[\text{Ru}(\text{sal}_2\text{en})(\text{CO})]_2$ and NaCl , were formed. The red solution was transferred to an alumina column and the red thf elutate collected. Evaporation of this solution yielded the yellow microcrystalline complex $\text{Ru}(\text{sal}_2\text{en})(\text{CO})(\text{PPh}_3)$, which was purified by recrystallisation from thf-petroleum or acetone. (Yield 40%).

(xvii) Triphenylphosphine-N,N'-ethylene-bis(salicylideneiminato)ruthenium(II)-tetrafluoroborate

a. To $\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2$ (0.5g, 0.6 mmole) in thf (25cm^3) was added HBF_4 (15cm^3 of 40% aqueous solution). The solution, which became yellow, was reduced to 10cm^3 and then water (40cm^3) was added. The red precipitate was collected, washed with water, ether and dried in vacuo. Recrystallisation from nitromethane gave orange crystals with a metallic lustre of the salt $[\text{Ru}(\text{sal}_2\text{enH})(\text{PPh}_3)]\text{BF}_4$. (Yield 90%).

b. Using p-toluene sulphonic acid, a similar salt $[\text{Ru}(\text{sal}_2\text{enH})(\text{PPh}_3)](\text{tos})$ was obtained. (Yield 90%).

(xviii) N,N'-ethylene-bis(salicylideneiminato)-nitrito-nitrosyl-ruthenium(II)

Nitric oxide was bubbled through a warm solution (60°C) of Ru(sal₂en)(PPh₃)₂ (0.5g, 0.6 mmole) in thf (20 cm³) until no more red solid formed. The pale green-red solution formed was filtered and evaporation of this solution to low volume yielded burgundy coloured needles of the complex Ru(sal₂en)(ONO)(NO). (Yield 20%).

(xix) μOxo-bis[N,N'-ethylene-bis(salicylideneiminato)-nitrosyl-ruthenium(II)]

The red solid formed in (xviii) was recrystallised from CH₂Cl₂ to give red metallic lustre plates of [Ru(sal₂en)(NO)]₂O. (Yield 70%).

(xx) Cis-dicarbonyl-N,N'-ethylene-bis(salicylideneiminato)ruthenium(II)

[Ru(CO)₃Cl₂]₂ (0.5g, 1.95 mmole) was added to a suspension of Na₂sal₂en (0.60g, 1.95 mmole) in thf (50 cm³) and the suspension refluxed for 1 hour to give a red solution and a yellow-white solid (NaCl plus [Ru(sal₂en)(CO)]₂). The red solution was then transferred onto an alumina column and the product eluted with thf. After evaporation to dryness, the solid was redissolved in chloroform and cooled to -78°C to give pale-yellow feather-like crystals of the complex cis-Ru(sal₂en)(CO)₂, which were then crystallised from hot thf. (Yield 35%).

(xxi) Bicyclo(2,2,1)hepta-2,5-diene-N,N'-ethylene-bis(salicylideneiminato)ruthenium(II)

$[\text{Ru}(\text{nbd})\text{Cl}_2]_n$ (0.30g, 1.14 mmole) was added to a suspension of $\text{Na}_2(\text{sal}_2\text{en})$ (0.35g, 1.14 mmole) in thf (30 cm³) and the mixture stirred for three days. The resulting mixture was transferred to an alumina column. Elution with thf gave a red solution which on evaporation gave the red complex $\text{Ru}(\text{sal}_2\text{en})(\text{nbd})$. (Yield ca. 20%).

(xxii) Bicyclo(2,2,1)hepta-2,5-diene-N,N'-ethylene-bis(pyrrole-2-aldiminato)ruthenium(II)

$[\text{Ru}(\text{nbd})\text{Cl}_2]_n$ (0.30g, 1.14 mmole) was added to a suspension of $\text{Na}_2(\text{pyr}_2\text{en})$ (0.30g, 1.14 mmole) in thf (30 cm³) and the solution heated under reflux until all the $[\text{Ru}(\text{nbd})\text{Cl}_2]_n$ had dissolved. The resulting mixture was transferred to an alumina column, and elution with ether gave a yellow solution from which the yellow microcrystalline complex $\text{Ru}(\text{pyr}_2\text{en})(\text{nbd})$ was isolated. (Yield 30%).

(xxiii) Dichloro-N,N'-ethylene-bis(pyridine-2-aldiminato)-ruthenium(II)

Commercial ' RuCl_3 ' (0.5g, 1.9 mmole) was added to a degassed methanolic solution (50 cm³) in a pressure vessel and PtO_2 (5mg) added. The vessel was then pressurised with two atmospheres of hydrogen and the solution stirred until it became blue. The blue solution was then filtered and py_2en (0.90g, 3.8 mmole) added, and the mixture refluxed for 24 hours. After cooling the deep-red solution was filtered and bronze crystals of

the complex $\text{Ru}(\text{py}_2\text{en})\text{Cl}_2$ washed with methanol (until the washings became blue in colour) and ether, and then dried in vacuo. (Yield ca. 4%).

(xxiv) Dichloro-bis-N'-phenyl(pyridine-2-aldiminato)
ruthenium(II)

This preparation was identical to (xxii) except that 7.6 mmole of the ligand were used to yield purple crystals of $\text{Ru}(\text{pyphen})_2\text{Cl}_2$. These were washed with methanol (until all the washings were green in colour) and ether, and then dried in vacuo. (Yield ca. 4%).

(xxv) Cis-dichloro-dicarbonyl-N-2-pyridyl(pyridine-2-aldiminato)ruthenium(II)

To a suspension of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ (0.30g, 0.59 mmole) in methanol (20cm^3), was added a solution of pypy (0.26g, 1.18 mmole) in methanol (5cm^3) and the solution heated until all the $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ had dissolved. The resulting red solution was transferred onto an alumina column and after elution with ether and thf the main red complex was eluted with methanol. On evaporation to low volume red crystals of cis- $\text{Ru}(\text{CO})_2\text{Cl}_2\cdot\text{pypy}$ were obtained. (Yield 60%).

A similar complex was formed with the ligand pyphen.

C. COMPLEXES PREPARED IN CHAPTER IV(xxvi) Bis(triphenylphosphine)bis(acetoximate)ruthenium(II)

To a solution of acetoxime (0.20g, 2.7 mmole) and NaOH (0.11g, 2.7 mmole) in methanol (50cm³) was added RuCl₂(PPh₃)₃ (1.0g, 1.04 mmole) and the mixture heated at 50°C for ten minutes and then stirred at room temperature for ten hours. The bright yellow precipitate formed was filtered and washed with methanol (30cm³) and then redissolved in hot thf (100cm³) and the red solution filtered. On cooling the yellow complex precipitated from this solution and was collected. The yellow complex was recrystallised from chloroform as orange crystals. (Yield 85%).

(xxvii) Dichloro-bis(triphenylphosphine)-(butan-2,3-dione monoxime)ruthenium(II)

RuCl₂(PPh₃)₃ (1.0g, 1.04 mmole) was added to a solution of butan-2,3-dione monoxime (bdoH) (0.4g, 4.1 mmole) in methanol (30cm³) and the mixture refluxed for 16 hours without stirring, the solution was then left to cool. The resulting brown crystalline complex was filtered off and washed with cold methanol (10cm³), cold thf (10cm³) and then ether (40cm³) and dried in vacuo. Recrystallisation from chloroform or dichloromethane yielded a brown powder. (Yield 60%).

(xxviii) Bis(triphenylphosphine)-bis(butan-2,3-dione monoximinato)ruthenium(II) and tetrakis(triphenylphosphine-bis(butan-2,3-dione monoximato)ruthenium(II)

To a solution of butan-2,3-dione monoxime (0.21g, 2.08 mmole) and NaOH (0.08g, 2.08 mmole) in methanol (30cm³) was added RuCl₂(PPh₃)₃ (1.0g, 1.04 mmole) and the mixture refluxed for several hours. A pale red precipitate was formed and a deep red solution, the latter on evaporation to low volume yielded a red microcrystalline complex Ru(bdo)₂(PPh₃)₄ (Yield 15%)

To the pale red precipitate was added hot thf (20cm³) and the red solution formed filtered from the NaCl remaining. On cooling this red solution yielded red crystals of Ru(bdo)₂(PPh₃)₂·2thf (Yield 50%). The same complex was formed by recrystallisation of Ru(bdo)₂(PPh₃)₄ from thf.

(xxix) Dichloro-bis(triphenylphosphine)-(dimethylglyoxime)ruthenium(II)

RuCl₂(PPh₃)₃ (1.0g, 1.04 mmole) was added to a suspension of dimethylglyoxime (0.20g, 1.73 mmole) in methanol (30cm³) and the suspension refluxed for two hours. The resulting red precipitate was washed with methanol, thf and ether and dried in vacuo. (Yield 70%)

(xxx) Dichloro-bis(triphenylphosphine)-(cyclohexane-1,2-dione dioxime)ruthenium(II)

Under similar conditions to the above reaction $\text{Ru}(\text{cyoxH}_2)(\text{PPh}_3)_2\text{Cl}_2$ was prepared as a red microcrystalline complex. (Yield 70%).

(xxxii) Bis(triphenylphosphine)-bis(dimethylglyoximato)ruthenium(II)

To a solution of dmgH_2 (0.24g, 2.08 mmole) and NaOH (0.08g, 2.08 mmole) in methanol (30 cm^3) was added $\text{RuCl}_2(\text{PPh}_3)_3$ (1.0g, 1.04 mmole) and the mixture heated under reflux for ten hours. The orange complex formed was filtered, washed with water and methanol, and redissolved in hot thf (300 cm^3). On cooling the thf solution precipitated the orange complex. (Yield 80%). Using commercially purchased Na_2dmg the same complex was formed.

This complex was also formed by the reaction of $\text{Ru}(\text{dmgH}_2)(\text{PPh}_3)_2\text{Cl}_2$ with a solution of dmgH_2 and NaOH in methanol.

(xxxii) Bis(triphenylphosphine)-bis(cyclohexane-1,2-dione dioximato)ruthenium(II)

Under similar conditions to those above the orange complex $\text{Ru}(\text{cyoxH})_2(\text{PPh}_3)_2$ was prepared. It was, however, not soluble enough in thf to afford recrystallisation. (Yield 80%).

(xxxiii) Bis(triphenylphosphine)-N,N'-ethylene-bis(butan-2,3-dione-2-oxime-3-iminato)ruthenium(II)

The ligand bdo_2enH_2 was prepared by refluxing bdoH and ethylenediamine (2:1 molar ratio) in methanol for 30 minutes. Evaporation to low volume afforded a cream coloured solid which on recrystallisation from hot ethanol yielded white crystals of the required ligand. (Yield 70%) (Melting point = $173 - 174^\circ\text{C}$)

To a solution of bdo_2enH_2 (0.32g, 1.04 mmole) and NaOH (0.08g, 2.1 mmole) in methanol (30cm^3) was added $\text{RuCl}_2(\text{PPh}_3)_3$ (1.0g, 1.04 mmole) and the mixture heated under reflux until all the $\text{RuCl}_2(\text{PPh}_3)_3$ had reacted (ca. one hour). The dark red solution formed was cooled, filtered to remove NaCl and then evaporated to low volume to yield red crystals of the complex $\text{Ru}(\text{bdo}_2\text{en})(\text{PPh}_3)_2$ these being recrystallised from hot thf . (Yield 40%).

With NEt_3 as base the same reaction occurred, but isolation of the complex proved more difficult.

$\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$ failed to react with ethylene diamine and none of the above complex was formed.

NOTES TO TABLE 1

- a. Analysis results are :- Found (Calculated) %.
- b. Molecular weight determined osmotically in chloroform unless otherwise stated.
- c. By mass spectrometry.
- d. Analysis by Calderazzo ¹⁵, C 50.8, 50.9; H 3.5, 3.4; N 6.45, 6.75.
- e. By cryoscopic measurements in dmso.
- f. Conductivity in CH_3NO_2 at 10^{-3}M conc. $\Lambda_m = 49 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.
- g. Conductivity in CH_3NO_2 at 10^{-3}M conc. $\Lambda_m = 41 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.
- h. By osmometry in dichloromethane.

TABLE 1

ANALYTICAL DATA OF COMPLEXES PREPARED ^a

COMPLEX	COLOUR	C	H	N	P	OTHER	MOL. WT. ^b
Ru(sal ₂ en)(PPh ₃) ₂	purple	68.7(70.1)	5.0(4.9)	3.1(3.1)	7.1(6.9)		643(644) ^c
Ru(sal ₂ en)(PPhMe ₂) ₂	red	59.1(59.7)	5.7(5.6)	3.6(4.3)	9.4(9.6)		
Ru(sal ₂ phen)(PPh ₃) ₂ .2thf	black	71.9(70.8)	5.5(5.5)	2.4(2.6)	5.5(5.7)		
Ru(salbenz) ₂ (PPh ₃) ₂ .2thf	red	72.7(72.9)	5.6(5.6)	2.4(2.4)	5.2(5.2)		
Ru(salpy) ₂ (PPh ₃) ₂ .thf	red	70.3(70.4)	5.5(5.1)	4.6(5.1)	5.8(5.7)		
Ru(salnap)(PPh ₃) ₂ .2thf	green-black	69.8(71.1)	5.6(5.8)	1.3(1.3)	5.9(5.9)		
Ru(pyr ₂ en)(PPh ₃) ₂	orange	68.6(68.8)	5.7(5.6)	6.7(6.7)	7.9(7.4)		
Ru(pyr ₂ phen)(PPh ₃) ₂	red	69.9(70.5)	4.9(4.7)	6.0(6.3)	6.8(7.0)		
Ru(pyrbenz) ₂ (PPh ₃) ₂ .2thf	yellow	69.3(71.9)	5.4(5.3)	4.8(4.9)	5.4(5.4)		
Ru(acac ₂ en)(PPh ₃) ₂ .2thf	red	67.6(68.0)	6.1(5.7)	3.2(3.3)	7.1(7.3)		
[Ru(sal ₂ en)(CO)] ₂ ^d	yellow	51.0(51.6)	4.0(3.6)	6.4(7.1)			716(659) 591(577) 770(886) ^e 929(928)
Ru(sal ₂ en)(CO)(PPh ₃)	yellow	60.6(63.9)	4.6(4.4)	3.8(4.2)	4.6(4.7)	Ru 14.5(15.3)	
<u>trans</u> -Ru(salbenz) ₂ (CO) ₂ .MeOH	orange	60.8(61.1)	5.0(4.6)	4.6(4.6)			
[Ru(sal ₂ phen)(CO)] ₂	purple	53.8(56.9)	3.7(3.2)	5.6(6.3)			
Ru(salnap)(CO)(PPh ₃) .2thf	yellow	69.2(70.1)	5.6(5.5)	1.3(1.3)	5.6(5.8)		
Ru(pyr ₂ en)(CO)(PPh ₃)	yellow	61.6(61.7)	4.8(4.5)	9.3(9.3)	5.0(5.1)		

TABLE 1 (contd.)

COMPLEX	COLOUR	C	H	N	P	OTHER	MOL. WT.
$[\text{Ru}(\text{sal}_2\text{enH})(\text{PPh}_3)]\text{BF}_4$ ^f	orange-red	58.8(57.0)	4.6(4.2)	4.1(3.9)	4.4(4.3)		
$[\text{Ru}(\text{sal}_2\text{enH})(\text{PPh}_3)]\text{tos}$ ^g	orange-red	61.7(61.5)	5.2(5.1)	3.5(3.5)	4.3(3.9)		
$\text{Ru}(\text{sal}_2\text{en})(\text{ONO})(\text{NO})\cdot\text{thf}$	burgundy	46.6(46.6)	3.2(4.2)	11.0(11.0)			486(443)
$[\text{Ru}(\text{sal}_2\text{en})(\text{NO})]_2\text{O}$	orange-red	46.9(47.4)	3.7(3.5)	10.1(10.3)		O 13.7(13.8)	770(810) ^h
<u>cis</u> - $\text{Ru}(\text{sal}_2\text{en})(\text{CO})_2$	pale yellow	50.4(51.1)	4.3(3.3)	5.7(6.6)		Ru21.3(23.4)	454(432)
$\text{Ru}(\text{sal}_2\text{en})(\text{nbd})$	orange-red	58.9(60.1)	4.9(4.8)	5.9(6.1)			
$\text{Ru}(\text{pyr}_2\text{en})(\text{nbd})$	yellow	54.5(56.3)	4.8(4.9)	13.1(13.8)			418(405)
$\text{Ru}(\text{py}_2\text{en})\text{Cl}_2$	bronze	41.0(41.0)	3.5(3.4)	13.3(13.6)		Cl16.7(17.3)	
$\text{Ru}(\text{pyphen})_2\text{Cl}_2$	purple	53.8(53.7)	3.7(3.7)	10.3(10.4)		Cl12.9(13.2)	
$\text{Ru}(\text{CO})_2\text{Cl}_2\cdot\text{pypy}$	orange-red	38.7(37.9)	3.3(2.2)	10.3(10.2)		Cl15.9(17.3)	
$\text{Ru}(\text{ato})_2(\text{PPh}_3)_2$	orange	64.6(65.5)	4.9(5.5)	3.9(3.6)	7.8(8.1)	Cl 0.0(0.0)	817(769)
$\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$	brown	58.6(60.2)	4.6(4.4)	1.8(1.8)		Cl 8.2(8.9)	739(796)
$\text{Ru}(\text{bdo})_2(\text{PPh}_3)_4$	red	71.9(71.1)	5.7(5.6)	2.0(2.1)	9.1(9.1)		
$\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2\cdot 2\text{thf}$	red	63.3(64.3)	6.0(6.0)	2.6(2.9)	6.3(6.4)		
$\text{Ru}(\text{dmgH}_2)(\text{PPh}_3)_2\text{Cl}_2$	red	59.1(59.1)	4.8(4.7)	3.5(3.4)			
$\text{Ru}(\text{cyoxH}_2)(\text{PPh}_3)_2\text{Cl}_2$	red	61.1(60.1)	4.8(4.8)	2.9(3.3)			

TABLE 1 (contd.)

COMPLEX	COLOUR	C	H	N	P	OTHER	MOL. WT.
$\text{Ru}(\text{dmgH})_2(\text{PPh}_3)_2$	orange	60.8(61.7)	5.2(5.1)	6.4(6.5)		Cl 0(0)	
$\text{Ru}(\text{cyoxH})_2(\text{PPh}_3)_2$	orange	60.8(63.4)	5.7(5.2)	5.8(6.1)		Cl 0.7(0)	
$\text{Ru}(\text{bdo}_2\text{en})(\text{PPh}_3)_2$	purple	66.7(65.0)	5.8(5.4)	7.0(6.6)	7.8(7.3)	Cl 0.2(0)	793(849)

NOTES TO TABLES 2 AND 3

- a. All measurements in ppm relative to TMS = 10 τ as internal standard or from solvent resonances.
 - b. All measurements in ppm relative to 85% H₃PO₄ external standard. All resonances are singlets, and resonances to high frequency are termed positive. All spectra were measured in thf/C₆D₆ solution except where stated otherwise.
 - c. Resonance obscured by aromatic proton resonances.
 - d. Solvent CDCl₃.
 - e. Solvent CD₂Cl₂.
 - f. Not observed due to insolubility of complex.
 - g. Solvent (CD₃)₂CO.
 - h. Solvent (CD₃)₂SO.
 - i. Solvent CH₃NO₂/C₆D₆.
 - j. Not assigned due to diverse aromatic resonances.
- + Abbreviations used s = singlet, m = multiplet, t = triplet, d = doublet and br = broad.

TABLE 2

N.M.R. SPECTRA OF COMPLEXES PREPARED IN CHAPTERS II AND III ⁺

COMPLEX	¹ H ^a				³¹ P ^b
	$\tau_{\text{CH=N}}$	τ_{Aromatic}	$\tau_{\text{N-CH}_2}$	OTHER	
$\text{Ru}(\text{sal}_2\text{en})(\text{PPh}_3)_2^{\text{d}}$	c	2.40-4.00(br,m)	6.20-6.40(br,m)		+29.92
$\text{Ru}(\text{sal}_2\text{en})(\text{PPhMe}_2)_2^{\text{e}}$	1.56(t)	2.10-3.80(br,m)	5.90-6.60(br,m)	$\tau_{\text{P-Me}}=8.38(\text{t}), 8.78(\text{t})$	+15.41
$\text{Ru}(\text{sal}_2\text{phen})(\text{PPh}_3)_2^{\text{d}}$	c	2.30-3.20(br,s)			+29.04
$\text{Ru}(\text{salbenz})_2(\text{PPh}_3)_2^{\text{d}}$	c	2.30-3.50(br,m)	5.23(d)		+28.53
$\text{Ru}(\text{salpy})_2(\text{PPh}_3)_2^{\text{d}}$	c	2.10-3.80(br,m)			+30.30
$\text{Ru}(\text{salnap})(\text{PPh}_3)_2^{\text{d}}$	c	2.20-3.40(br,m)	f		+23.05
$\text{Ru}(\text{pyr}_2\text{en})(\text{PPh}_3)_2^{\text{d}}$	2.75(s)	2.80-3.16(br,s)	6.36(s)	4.17(s)	+38.85
$\text{Ru}(\text{pyr}_2\text{phen})(\text{PPh}_3)_2^{\text{d}}$	c	2.70-3.40(br,m)		.	+37.76
$\text{Ru}(\text{pyrbenz})_2(\text{PPh}_3)_2^{\text{d}}$	c	2.60-3.80(br,m)	7.12(br,s)		+48.30
$\text{Ru}(\text{acac}_2\text{en})(\text{PPh}_3)_2^{\text{g}}$		2.30-3.20(br,s)	7.12(s)	6.28(s), 8.60(s), 8.97(s)	+33.24
$\text{Ru}(\text{sal}_2\text{en})(\text{CO})(\text{PPh}_3)_2^{\text{d}}$	1.41(s) 1.62(s)	2.20-3.96(br,m)	5.85-6.20(m)		+32.61
$[\text{Ru}(\text{sal}_2\text{phen})(\text{CO})]_2^{\text{h}}$	0.59(s)	1.40-1.70(m) 2.11-3.37(m)			

COMPLEX	^1H ^a				^{31}P ^b
	$\tau_{\text{CH=N}}$	τ_{Aromatic}	$\tau_{\text{N-CH}_2}$	OTHER	
<u>trans</u> -Ru(salbenz) ₂ (CO) ₂ ^d	1.86(s)	2.43-3.62(br,m)	4.81(s), 4.93(s)		
Ru(salnap)(CO)(PPh ₃) ^g	2.18(s)	2.30-4.00(br,m)	5.54(s)		+28.51
Ru(pyr ₂ en)(CO)(PPh ₃) ^g	2.54(s)	2.75-3.38(br,m)	6.05(s)	3.78(d), 4.08(d)	+22.78
[Ru(sal ₂ enH)(PPh ₃)] BF ₄ ^g	2.26(s)	2.57-3.60(br,m)	6.60-6.80(br,m)		+64.22 ⁱ
[Ru(sal ₂ enH)(PPh ₃)] tof ^g	c	2.40-3.70(br,m)	6.50-6.80(br,m)	7.73(s)	+64.22 ⁱ
Ru(sal ₂ en)(ONO)(NO) ^e	1.77(s)	2.53-3.30(m)	5.97(s)		
[Ru(sal ₂ en)(NO)] ₂ O ^e	2.64(s)	2.70-3.70(m)	5.64-6.04(m) 6.18-6.45(m)		
<u>cis</u> -Ru(sal ₂ en)(CO) ₂ ^d	1.96(s) 2.16(s)	2.87-3.25(m) 3.40-3.60(m)	6.00-6.20(m)		
Ru(sal ₂ en)(nbd) ^e	1.90(s) 2.29(s)	2.80-3.75(br,m)	5.70-6.70(br,m)	5.48(d), 5.63(s) 6.09(d), 6.35(s) 6.65(s), 8.75(s)	
Ru(pyr ₂ en)(nbd) ^d	2.28(s) 2.51(s)	1.93-3.90(m)	5.07-6.62(br,m)	8.71(s), 6.96(m)	
Ru(CO) ₂ Cl ₂ pypy ^d	j	1.12-2.92(br,m)			
Ru(CO) ₂ Cl ₂ pyphen ^d	j	1.12-2.70(m)			

TABLE 3

N.M.R. SPECTRA OF COMPLEXES PREPARED IN CHAPTER IV ⁺

COMPLEX	¹ H ^a			³¹ P ^b
	τ_{Aromatic}	τ_{CH_3}	OTHER	
$\text{Ru(ato)}_2(\text{PPh}_3)_2^{\text{d}}$	2.83(br, s)	8.28(s), 8.69(s)		+66.36
$\text{Ru(bdoH)(PPh}_3)_2\text{Cl}_2^{\text{d}}$	2.20-2.70(m)	8.23(s), 9.10(s)	$\tau_{\text{O-H}} = -2.39$	+25.31
$\text{Ru(bdo)}_2(\text{PPh}_3)_2^{\text{d}}$	2.91(br, s)	8.07(s), 8.73(s)		+45.90
$\text{Ru(bdo)}_2(\text{PPh}_3)_4^{\text{d}}$	2.64(s), 2.79(s), 2.91(s)	8.07(s), 8.73(s)		+45.90, -6.02
$\text{Ru(dmgh)}_2(\text{PPh}_3)_2$				+28.93
$\text{Ru(bdo}_2\text{en)(PPh}_3)_2^{\text{d}}$	2.76(s)	8.83(br, s), 8.92(s)	$\tau_{\text{N-CH}_2} = 6.30(\text{s})$	+38.53

NOTES TO TABLES 4 AND 5

- a. All spectra as nujol mulls using CsI_2 or KBr plates, or KBr discs.
 - b. All values expressed in cm^{-1} .
 - c. See text for details of i.r. spectrum.
 - d. 2200 - 1800 cm^{-1} region in CHCl_3 solution.
 - e. Not assigned.
- + Abbreviations used for intensities: s = strong,
m = medium, w = weak, sh = shoulder, br = broad.

TABLE 4

I.R. SPECTRA OF COMPLEXES PREPARED IN CHAPTERS II AND III ^{a, b +}

COMPLEX	1650-1500 cm ⁻¹	OTHER
Ru(sal ₂ en)(PPh ₃) ₂	1595(s), 1525(m)	
Ru(sal ₂ en)(PPhMe ₂) ₂	1610(w), 1594(s), 1528(m)	
Ru(sal ₂ phen)(PPh ₃) ₂	1598(s), 1568(s), 1509(m)	
Ru(salbenz) ₂ (PPh ₃) ₂	1630(s), 1608(vs), 1594(s), 1528(m)	
Ru(salpy) ₂ (PPh ₃) ₂	1600(s), 1585(s), 1560(m), 1520(m)	
Ru(salnap)(PPh ₃) ₂	1605(m), 1595(sh), 1580(sh), 1530(m), 1500(m)	
Ru(pyr ₂ en)(PPh ₃) ₂	1580(s), 1510(w)	
Ru(pyr ₂ phen)(PPh ₃) ₂	1573(w), 1540(s), 1510(sh)	
Ru(pybenz) ₂ (PPh ₃) ₂	1587(s), 1562(sh)	
Ru(acac ₂ en)(PPh ₃) ₂	1573(m)	
[Ru(sal ₂ en)(CO)] ₂	1645(m), 1627(s), 1595(s), 1550(w), 1528(s)	ν(C≡O)=1910(s), 1865(vw)
Ru(sal ₂ en)(CO)(PPh ₃)	1622(s), 1609(s), 1523(m)	ν(C≡O)=1932(s)
[Ru(sal ₂ phen)(CO)] ₂	1606(s), 1590(m), 1578(s), 1523(m)	ν(C≡O)=1910(s), 1925(sh) ^c
Ru(salnap)(CO)(PPh ₃)	1623(m), 1610(w), 1598(w), 1585(m), 1530(m)	ν(C≡O)=1930(vs), 1887(vw)

COMPLEX	1650-1500	OTHER
<u>trans</u> -Ru(salbenz) ₂ (CO) ₂	1615(s), 1595(s), 1529(m)	ν (C≡O) 1930(s)
Ru(pyr ₂ en)(CO)(PPh ₃)	1587(s), 1580(sh), 1510(m)	ν (C≡O) 1940(s)
[Ru(sal ₂ enH)(PPh ₃)]BF ₄	1595(sh), 1590(s), 1545(m)	
[Ru(sal ₂ enH)(PPh ₃)]tos	1590(s), 1548(m)	
Ru(sal ₂ en)(ONO)(NO)	1628(s), 1599(s), 1529(m)	ν (N-O) 1488(w), 1507(w) ν _{as} (N=O) 1837(s)
[Ru(sal ₂ en)(NO)] ₂ O	1643(s), 1598(s), 1527(s)	ν (N=O) 1742(s) ν _{as} (Ru-O-Ru) 800(s), 3490(vw)
<u>cis</u> -Ru(sal ₂ en)(CO) ₂	1628(s), 1598(s), 1527(s)	ν (C≡O) 2038(s), 1975(sh), 1965(s)
Ru(sal ₂ en)(nbd)	1611(s), 1590(s), 1525(m)	1305(m)
Ru(pyr ₂ en)(nbd)	1573(s), 1558(s)	1302(m)
Ru(py ₂ en)Cl ₂	1591(s), 1559(s), 1538(s)	ν (Ru-Cl) 325(m)
Ru(pyphen) ₂ Cl ₂	1599(s), 1588(s), 1570(s), 1532(s)	ν (Ru-Cl) 348(m), 303(s)
Ru(CO) ₂ Cl ₂ ·pypy	1609(m), 1600(m), 1586(w), 1577(m)	ν (C≡O) 2068(s), 2012(s) ^d ν (Ru-Cl) 328(sh), 320(s)
Ru(CO) ₂ Cl ₂ ·pyphen	1632(s), 1592(m), 1562(w)	ν (C≡O) 2061(s), 2003(s) ^d ν (Ru-Cl) 332(m), 302(m), 1055(vs)

TABLE 5

I.R. SPECTRA OF COMPLEXES PREPARED IN CHAPTER IV^{a, b +}

COMPLEX	1650-1500	$\nu(\text{N-O})$	OTHER
$\text{Ru}(\text{ato})_2(\text{PPh}_3)$	1626(w), 1579(w), 1566(w)	.	
$\text{Ru}(\text{bdoH})(\text{PPh}_3)_2\text{Cl}_2$	1625(w), 1582(w), 1569(w), 1508(vw)	1080-1065(br, s)	$\nu(\text{Ru-Cl})$ 259(s)
$\text{Ru}(\text{bdoD})(\text{PPh}_3)_2\text{Cl}_2$	1608(w), 1581(w), 1568(w), 1540(vw)	e	$\nu(\text{O-D})$ 2315 $\nu(\text{Ru-Cl})$ 259
$\text{Ru}(\text{bdo})_2(\text{PPh}_3)_2$	1580(w), 1569(w), 1520(w)	1263(s)	
$\text{Ru}(\text{bdo})_2(\text{PPh}_3)_1$	1580(w), 1569(w), 1518(wm)	1263(s)	
$\text{Ru}(\text{dmgH}_2)(\text{PPh}_3)_2\text{Cl}_2$	1610(w), 1552(w), 1569(w), 1541(m)	1152(w), 1027(s)	$\nu(\text{O-H})$ 3440(s), 3393(sh) $\nu(\text{Ru-Cl})$ 323(s)
$\text{Ru}(\text{dmgD}_2)(\text{PPh}_3)_2\text{Cl}_2$	1581(w), 1570(w), 1510(w)	1153(w), 1020(sh)	$\nu(\text{O-D})$ 2540(s), 2517(sh) $\nu(\text{Ru-Cl})$ 323(s)
$\text{Ru}(\text{cyoxH}_2)(\text{PPh}_3)_2\text{Cl}_2$	1582(w), 1569(w), 1534(w)	1153(w), 1005(s)	$\nu(\text{O-H})$ 3435(s), 3377(s) $\nu(\text{Ru-Cl})$ 323(s)
$\text{Ru}(\text{dmgH})_2(\text{PPh}_3)_2$	1640(w), 1581(w), 1570(w), 1510(sh)	1224(s), 1081(m)	
$\text{Ru}(\text{cyoxH})_2(\text{PPh}_3)_2$	1620(w), 1581(w), 1569(w)	1218(s), 1080(m)	
$\text{Ru}(\text{bdo}_2\text{en})(\text{PPh}_3)_2$	1635(w), 1583(w), 1569(w)	e	1129(s), 1256(s)

REFERENCES

1. C. Ettling, Annalen, 1840, 35, 241.
2. L. Chugaev, Chem. Ber., 1905, 38, 2520.
3. M. Tsutsui, D. Ostfeld and L.M. Hoffman, J. Amer. Chem. Soc., 1971, 93, 1820.
4. a) H. Schiff, Annalen Supl., 1864, 3, 343.
b) H. Schiff, Annalen, 1869, 150, 193.
c) H. Schiff, Annalen, 1869, 151, 186.
5. For full list of publications by Pfeiffer and co-workers see reference 6.
6. R.H. Holm, G.W. Everett Jr. and A. Chakravorty, Progr. Inorg. Chem., 1966, 7, 83, and references therein.
7. N.S. Biradar and V.H. Kulkarni, J. Inorg. Nuclear Chem., 1971, 23, 3847.
8. S.R. Gupta and J.P. Tandon, Z. Naturforsch B., 1970, 25, 1231.
9. M.J. O'Connor and B.O. West, Austral. J. Chem., 1968, 21, 369.
10. 'Reactions of Co-ordinated Ligands', (R.E. Gould and D.H. Busch, Eds.), Advances in Chemistry Series No. 37, 1963.
11. E.J. Olszewski and D.F. Martin, J. Inorg. Nuclear Chem., 1964, 26, 1577.
12. P.C. Parich and P.K. Battacharya, Indian J. Chem., 1976, 14, 617.
13. N.F. Curtis, Co-ordination Chem. Rev., 1968, 3, 3.
14. S. Yamada, Co-ordination Chem. Rev., 1966, 1, 415.
15. F. Calderazzo, C. Floriani, R. Henzi and F. L'Eplattenier, J. Chem. Soc. (A), 1969, 1378.

16. A. Van den Bergen, K.S. Murray and B.O. West, Austral. J. Chem., 1972, 25, 705.
17. R.J. Cozens, K.S. Murray and B.O. West, Austral. J. Chem., 1970, 23, 683.
18. C. Santini-Sampucci and G. Wilkinson, J.C.S. (Dalton), 1976, 807.
19. J.R. Dilworth, C.A. McAuliffe and B.J. Sayle, J.C.S. (Dalton), 1977, 849.
20. P. Pfeiffer, T. Hesse, H. Pfitzinger, W. Scholl and H. Thielert, J. Prakt. Chem., 1937, 149, 217.
21. R.H. Holm, A. Chakravorty and L.J. Theriot, Inorg. Chem., 1966, 5, 625.
22. D.H. Busch and J.C. Bailar Jnr., J. Amer. Chem. Soc., 1956, 78, 1137.
23. H.A. Goodwin and F. Lions, J. Amer. Chem. Soc., 1960, 82, 5013.
24. C.M. Harris and E.D. McKenzie, J. Chem. Soc. (A), 1969, 749.
25. B.F. Hoskins and F.D. Whillans, J.C.S. Chem. Comm., 1966, 798.
26. H. Brunner and W.A. Hermann, Chem. Ber., 1972, 105, 770.
27. E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., 1959, 2323.
28. M.H.B. Stiddard, J. Chem. Soc., 1962, 4712.
29. D.G. Hendricker and T.E. Reed, Inorg. Chem., 1969, 8, 685.
30. G.M. Brown, T.R. Weaver, F.R. Keene and T.J. Meyer, Inorg. Chem., 1976, 15, 190.
31. T. Tsumaki, Bull. Chem. Soc. Japan, 1938, 13, 252.

32. a) A.E. Martell and M. Calvin, 'Chemistry of Metal-Chelate Compounds', Prentice Hall, 1952.
b) F. Basolo, B.M. Hoffman and J.A. Ibers, Accounts Chem. Res., 1975, 8, 384.
33. C. Floriani and F. Calderazzo, J. Chem. Soc. (A), 1969, 946.
34. E. Cescerotti, M. Guillotti, A. Pasini and R. Ugo, J.C.S. (Dalton), 1977, 757.
35. a) R.S. Gall, J.F. Rogers, W.P. Schaefer and G.G. Christoph, J. Amer. Chem. Soc., 1976, 98, 5135.
b) A. Avdeef and W.P. Schaefer, J. Amer. Chem. Soc., 1976, 98, 5153.
36. M.D. Hobday and M.T. Smith, Co-ordination Chem. Rev., 1972, 9, 311.
37. A.E. Martell and G.E. McLendon, Co-ordination Chem. Rev., 1976, 19, 1.
38. M. Calligaris, G. Nardin and L. Randaccio, Co-ordination Chem. Rev., 1972, 7, 385.
39. a) G.N. Schrauzer, Accounts Chem. Res., 1968, 1, 97.
b) A. Bignotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani and G. Tauzher, Inorg. Chim. Acta. Rev., 1970, 4, 41.
40. M. Calligaris, G. Mangini, G. Nardin and L. Randaccio, J.C.S. (Dalton), 1972, 503.
41. A. Van den Bergen, R.J. Cozens and K.S. Murray, J. Chem. Soc. (A), 1970, 360.
42. A. Syamal and V.D. Ghanekar, Indian J. Chem., 1975, 13, 602.
43. M. Calligaris, G. Nardin and L. Randaccio, J.C.S. Chem. Comm., 1970, 1079.

44. N.K. Dutt and K. Nag, J. Inorg. Nuclear Chem., 1968, 30, 2493 & 2779.
45. a) S. Bruckner, M. Calligaris, G. Nardin and L. Randaccio, Acta. Cryst. (B), 1969, 25, 1671.
b) R. DeIsasi, S.L. Holt and B. Post, Inorg. Chem., 1971, 10, 1498.
46. J.E.Lewis, F.E. Mabbs and A. Richards, Nature, 1965, 207, 855.
47. a) R.H. Holm and M.J. O'Connor, Progr. Inorg. Chem., 1971, 14, 253.
b) G.W. Everett Jnr. and R.H. Holm, Inorg Chem., 1968, 7, 776.
48. D.A. Cruse and M. Gerloch, J.C.S. (Dalton), 1977, 152.
49. M. Hariharan and F.L. Urbach, Inorg. Chem., 1968, 8, 556.
50. D. Crowfoot-Hodgkin, Proc. Roy. Soc. (A), 1965, 288, 294.
51. F. Calderazzo and C. Floriani, J.C.S. Chem. Comm., 1967, 139.
52. J.A. Bertrand and G. Eller, Progr. Inorg. Chem., 1976, 21, 29.
53. D.J. Hodgson, Progr. Inorg. Chem., 1974, 19, 173.
54. B.A.S.F. Ger. Offen., 1, 117, 805 Nov. 23 (1961)
Chem Abs., 1962, 56, P14535a.
55. Ferro. Corporation, Brit. Pat., 1,047,418 Nov. 2 (1966),
Chem. Abs., 1967, 66, P19246u.
56. F.L. Welcher, 'Organic Analytical Reagents', Vol. III,
Van Nostrich, New York, 1947, 157.
57. C.V. Panks, Rec. Chem. Progr., 1964, 25, 85.
58. R.B. King and K.N. Chen, Inorg. Chem., 1977, 16, 1164.

59. G.P. Kare and R.J. Doedans, Inorg. Chem., 1977, 16, 907.
60. A. Mawby and G.E. Pringle, J. Inorg. Nuclear Chem., 1971, 33, 1989.
61. J.R. Jennings and K. Wade, J. Chem Soc. (A), 1967, 1333.
62. J.A. Bertrand, J.H. Smith and D.G. Van der Veer, Inorg. Chem., 1977, 16, 1477.
63. A. Chakravorty, Co-ordination Chem. Rev., 1974, 13, 1.
64. G.N. Schrauzer, Chem. Ber., 1962, 95, 1438.
65. D.R. Boston and N.J. Rose, J. Amer. Chem. Soc., 1965, 90, 6859.
66. K. Burger, I. Ruff and K. Ruff, J. Inorg. Nuclear Chem., 1965, 27, 179.
67. R. Blinč and D. Hadzi, J. Chem. Soc., 1958, 4536.
68. M.J. Lacey, C.G. MacDonald, J.S. Shannon and P.J. Collin, Austral. J. Chem., 1970, 23, 2279.
69. M.J. Lacey, C.G. MacDonald and J.S. Shannon, Austral. J. Chem., 1973, 26, 263.
70. M.J. Lacey, C.G. MacDonald and J.S. Shannon, J.C.S. (Dalton), 1974, 1215.
71. N.S. Dixit, K.S. Bose and C.C. Patel, Indian J. Chem., 1976, 14, 507.
72. M.B. Cingi, A.C. Villa, A.G. Manfredotti, C. Guastini and M. Nardelli, Acta. Cryst. (B), 1972, 28, 1075.
73. G.N. Schrauzer, Angew. Chem. Int. Edn. (English), 1976, 15, 417.
74. J.P. Kitchen, Ph.D. Thesis, London University, 1977.

75. J.H. Weber and G.N. Schrauzer, J. Amer. Chem. Soc., 1970, 92, 726.
76. S. Kuse, S. Motomizi and K. Tâei, Analyt. Chim. Acta., 1974, 70, 65.
77. B. Egneus, Talanta, 1972, 19, 1387.
78. A.W. Ashbrook, Co-ordination Chem. Rev., 1975, 16, 285.
79. K.S. Finney and G.W. Everett Jnr., Inorg. Chim. Acta., 1974, 11, 183.
80. G. Henrici-Olivé and S. Olivé, J. Mol. Cat., 1976, 1, 121.
81. G. Costa, G. Tauzher, G. Mestroni, A. Puxeddu and R. Costanzo, J. Chem. Soc. (A), 1971, 2504.
82. M.C. Baird, G.W. van Loon and C.W. Smith, Canad. J. Chem., 1976, 54, 1875.
83. R.J. Cozens, K.S. Murray and B.O. West, J. Organometallic Chem., 1971, 27, 399.
84. R.G. Caulton and P.R. Hoffman, J. Amer. Chem. Soc., 1975, 97, 4221.
85. B.R. Davies and J.A. Ibers, Inorg. Chem., 1970, 9, 2768.
86. P.M. Smith, T. Fealey, J.E. Earley and J.R. Silverton, Inorg. Chem., 1971, 10, 1943.
87. G.O. Dudek and R.H. Holm, J. Amer. Chem. Soc., 1961, 83, 2099.
88. A.E. Martell and P.J. McCarthy, Inorg. Chem., 1967, 6, 781.
89. J.D. Gilbert and G. Wilkinson, J. Chem. Soc., 1969, 1749.
90. B.R. James, L.D. Markham, B.C. Hui and G.L. Rempel, J.C.S. (Dalton), 1973, 2247.

91. W.J. Geary, Co-ordination Chem. Rev., 1971, 7, 81.
92. A. Earnshaw, E.A. King and L.F. Larkworthy, J. Chem. Soc. (A), 1969, 2459.
93. A. Earnshaw, P.C. Hewlett and L.F. Larkworthy, J. Chem. Soc. (A), 1965, 4718.
94. A. Earnshaw, E.A. King and L.F. Larkworthy, J. Chem. Soc. (A), 1968, 1048.
95. M. Tamaki, I. Masuda and K. Shinra, Chem. Lett., 1972, 165.
96. M. Tamaki, I. Masuda and K. Shinra, Bull. Chem. Soc. Japan, 1972, 45, 1400.
97. B.D. Thaler and P.K. Battarcharya, Bull. Chem. Soc. Japan, 1976, 49, 2845.
98. T. Sakai, Y. Kuroda, S. Goto and Y. Yano, Chem. Lett., 1975, 1085.
99. I. Masuda, M. Tamaki and K. Shinra, Bull. Chem. Soc. Japan, 1969, 42, 2858.
100. I. Masuda, M. Tamaki and K. Shinra, Bull. Chem. Soc. Japan, 1969, 42, 157.
101. M.A.A.F. de C.T. Garrondo, P.R. Rudolf, A.C. Skapski, J.R. Thornback and G. Wilkinson, Inorg. Chim. Acta. in press.
102. F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry' 3rd Edn., John Wiley, London, 1972, 640.
103. D. Webster, R.C. Edwards and D.H. Busch, Inorg. Chem., 1977, 16, 1055.
104. H. Buettner and R.D. Feltham, Inorg. Chem., 1972, 11, 971.
105. B.N. Chaudret, D.J. Cole-Hamilton, R. Nohr and G. Wilkinson, J.C.S. (Dalton), in press.

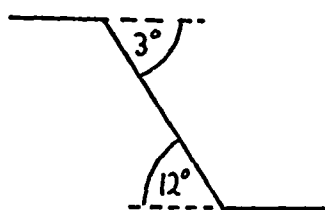
106. W.M. Reiff, G.J. Lang and W.A. Baker Jr., J. Amer. Chem. Soc., 1968, 90, 6347, but also see K.S. Murray, Co-ordination Chem. Rev., 1974, 12, 1, which states $\nu_{as}(\text{Fe-O-Fe}) = 820 - 840 \text{ cm}^{-1}$.
107. A.F. Masters, private communication.
108. W.P. Griffiths, Co-ordination Chem. Rev., 1970, 5, 459 and private communication.
109. F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry' 3rd Edn., John Wiley, London, 1972, 355.
110. E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., 1959, 3178.
111. P. Powell, J. Organometallic Chem., 1974, 65, 89.
112. D.J. Cole-Hamilton, T.A. Stephenson and D.R. Robertson, J.C.S. (Dalton), 1975, 1260.
113. T.A. Stephenson, E.S. Switkes and L. Ruiz-Ramirez, J.C.S. (Dalton), 1973, 2112.
114. a) D. Evans, J.A. Osborn, E.H. Jardine and G. Wilkinson, Nature, 1965, 208, 1203.
b) D. Evans, J.A. Osborn and G. Wilkinson, J. Chem. Soc. (A), 1968, 3133.
c) R.A. Sanchez-Delgado, J.S. Bradley and G. Wilkinson, J.C.S. (Dalton), 1976, 399.
115. B.C. Lane, J.E. Lester and F. Basolo, Chem. Comm., 1971, 1618.
116. D.F. Mahoney and J.K. Beattie, Inorg. Chem., 1973, 2561.
117. K. Nakamoto, 'Infra-red Spectra of Inorganic and Co-ordination Compounds', John Wiley, New York, 1963.
118. D. Rose and G. Wilkinson, J. Chem. Soc. (A), 1970, 1791.

119. P.E. Dumas and E.E. Mercer, Inorg. Chem., 1971, 10, 2755.
120. J.D. Gilbert, D. Rose and G. Wilkinson, J. Chem. Soc. (A), 1970, 2765.
121. D.M. Klassen, C.W. Hudson and E.L. Shaddix, Inorg. Chem., 1975, 14, 2733.
122. D.M. Klassen, Inorg. Chem., 1976, 15, 3166.
123. C. Lui, N. Riu and J.C. Bailar, Inorg. Chem., 1964, 3, 1085.
124. J. Fergusson and G. Harris, J. Chem. Soc. (A), 1966, 1293.
125. M.I. Bruce and F.G.A. Stone, J. Chem. Soc. (A), 1967, 1238.
126. T.A. Stephenson and G. Wilkinson, J. Inorg. Nuclear Chem., 1966, 28, 945.
127. C. Bremard, Bull. Chim. Soc. France, 1975, 953.
128. C. Bremard and S. Sueur, Bull. Chim. Soc. France, 1975, 961.
129. R.B. King and W.M. Douglas, Inorg. Chem., 1974, 13, 1339.
130. E.O. Fischer and L. Knauss, Chem. Ber., 1970, 103, 1262.
131. T.W.J. Taylor and E.K. Ewbank, J. Chem. Soc., 1926, 2818.
132. O.G.B. Nambiar and P.R. Subbaraman, Indian J. Chem., 1971, 9, 1138.
133. A. Okač and M. Simek, Collect. Czech. Chem. Comm., 1950, 445.
134. A. Narayanan and P.R. Subbaraman, Indian J. Chem., 1968, 6, 107.
135. A. Narayanan and P.R. Subbaraman, Indian J. Chem., 1967, 5, 436.
136. M. Attacharaya and P.R. Subbaraman, Indian J. Chem., 1973, 11, 10 5.

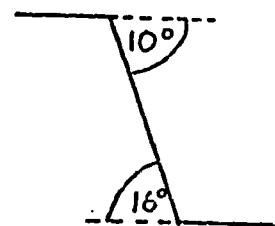
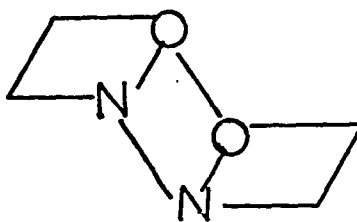
137. R.D. Gillard and G. Wilkinson, J. Chem. Soc., 1963, 6041.
138. G.N. Schrauzer and R.J. Windgassen, Chem. Ber., 1966, 99, 602.
139. G. Costa, G. Tauzher and A. Puxeddu, Inorg. Chim. Acta, 1969, 3, 45.
140. S.A. Ch'chelepinov, E.N. Sal'nikova and M.L. Khidekel, Izv. Akad. Nauk. S.S.S.R. Ser. Khim., 1967, 2057.
141. S.A. Ch'chelepinov, E.N. Sal'nikova and M.L. Khidekel, Izv. Akad. Nauk. S.S.S.R. Ser. Khim., 1967, 2128.
142. F.A. Cotton and K.G. Caulton, J. Amer. Chem. Soc., 1971, 93, 1914.
143. F.A. Cotton and F.G. Norman, J. Amer. Chem. Soc., 1971, 93, 80.
144. A. Bignotto, G. Costa, V. Galasso and G. De Alti, Spectrochim. Acta, 1970, 26A, 1939.
145. N.K. Mathur and G.K. Narang, Talanta, 1964, 11, 647.
146. G. Schrauzer, J.W. Siebert and R.J. Windgassen, J. Amer. Chem. Soc., 1966, 88, 681.
147. H.A. Goodwin and F. Lions, J. Amer. Chem. Soc., 1960, 82, 5013.
148. R.W. Hay and K.B. Nolan, J.C.S. (Dalton), 1976, 548.
149. E.W. Abel and G. Wilkinson, J. Chem. Soc., 1959, 3178.
150. P. W. Armit, A.S.F. Boyd and T.A. Stephenson, J.C.S. (Dalton), 1975, 1663.
151. I.P. Evans, A. Spencer and G. Wilkinson, J.C.S. (Dalton), 1973, 204.
152. M.T. Cleare and W.P. Griffith, J. Chem. Soc. (A), 1969, 372.

APPENDIX ITHE X-RAY STRUCTURE OF N,N'-ETHYLENE-BIS(SALICYLIDENEIMINATO)-
NITRITO-NITROSYL-RUTHENIUM(II)

The X-ray single crystal structure of $\text{Ru}(\text{sal}_2\text{en})(\text{ONO})(\text{NO})$ shows that the NO_2 ligand is O-bonded with an O-N-O bond angle of 118.5° while the nitrosyl is linear having a Ru-N-O angle of 177.8° . The sal_2en ligand is basically planar but is slightly stepped due to the nitrito ligand



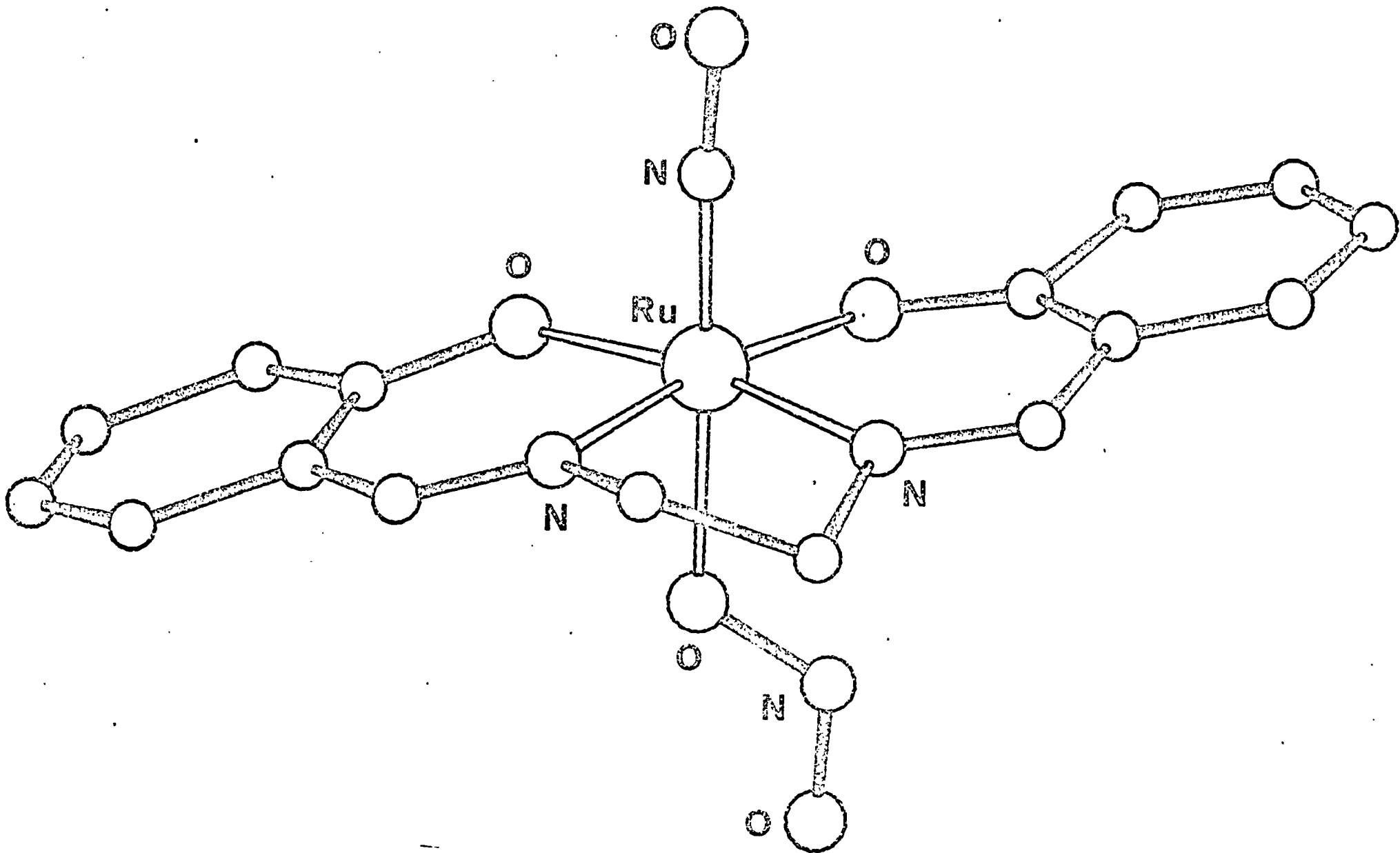
Molecule I



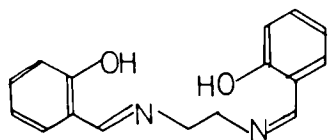
Molecule II

which is bent towards the plane of one of the phenyl rings. Otherwise the sal_2en ligand has bond angles and lengths which are within the limits of reported values ³⁸.

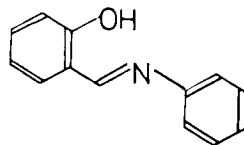
The crystal lattice contains two discrete molecules and the thf of crystallisation appears to be present in only 70% of the positions associated with one molecule of the complex and 100% in the other. This accounts for the variable analysis obtained for this complex, (see following page for diagram of complex).



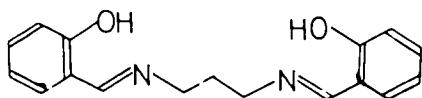
LIGAND ABBREVIATIONS



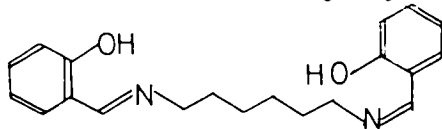
sal₂enH₂



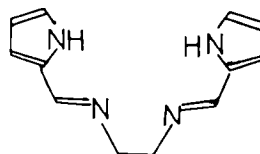
salphenH



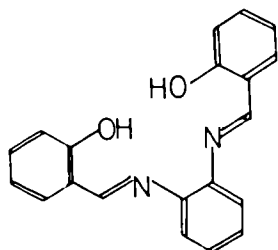
sal₂(1,3-prop)H₂



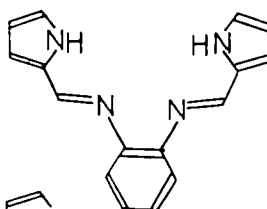
sal₂(1,6-hex)H₂



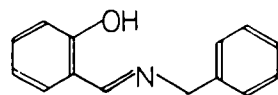
pyr₂enH₂



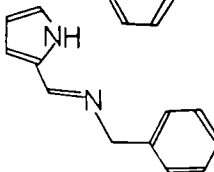
sal₂phenH₂



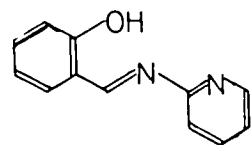
Pyr₂phenH₂



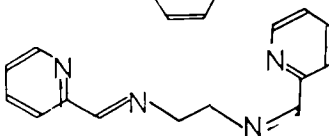
salbenzH



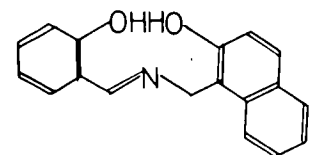
pyrbenzH



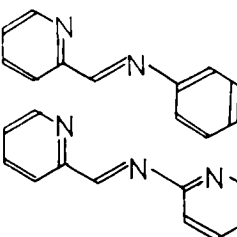
salpyH



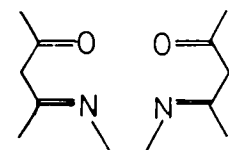
py₂en



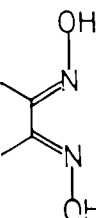
salnapH₂



pyphen



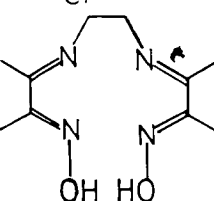
acac₂enH₂



dmgH₂



atoH



bdo₂enH₂

ERRATA

- Page 10, 1.6 - 'dimethylglyoxine' should read 'dimethylglyoxime'.
- " 19, 1.9 - 'Hohm' should read 'Holm'.
- " 19, 1.13 - 'confirmation' should read 'conformation'.
- " 42, last - 'analagous' should read 'analogous'.
line
- " 43, last - 'co-ordinating' should read 'co-ordinatively'.
line
- " 63, 1.13 - 'analagous' should read 'analogous'.