SYNTHETIC STUDIES IN METAL CARBONYLS AND RELATED COMPOUNDS

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BY

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CERTIFICATE

Certified that the work incorporated in the thesis **Synthetic Studies in Metal Carbonyls and Related Compounds** submitted by Mr. I.R. Unny was carried out by the candidate at the Inorganic Chemistry Division, National Chemical Laboratory, Pune 411008, India, under my supervision for the Degree of Doctor of Philosophy in Chemistry, Shivaji University, Kolhapur. This work was not submitted so far for any degree.

(Dr. C. Gopinathan)
Research Guide

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Chapter I : General Introduction to Platinum Group Metal Chemistry

GENERAL INTRODUCTION TO PLATINUM GROUP METAL CHEMISTRY

Ruthenium, rhodium, palladium, osmium, iridium and platinum are the six heaviest members of Group VIII of the Periodic Table. They are rare elements too, platinum being the most common with an abundance of *ca.* 10^{-6}% of earth's crust. These metals occur in the free form, often as alloys such as 'osmiridium'. They are commonly associated with coinage metals - copper, silver and gold, and during processing, the platinum group metals collect in the 'anode sludge' in the electrolysis bath. Subsequent procedure for the separation of metals is complicated and involves classical methods such as complex salt formation, fractional precipitation or crystallization. Thermal decomposition of ammonium salts or electrolytic reduction in acidic solutions afford the metals in a powdery or spongy form.

Ruthenium is more resistant to oxygen than is osmium, but is less so than iridium and rhodium, and a rapid oxidation does not set in below 600°C; there is evidence for the formation of a protective film of the dioxide[1]. In many ways, the chemistry of these transition metals is the chemistry of multiple oxidation states and the associated redox phenomenon. The chemistry of platinum group metals have some common features, but there are neverthless wide variations depending on differing stabilities of oxidation states, stereo-chemistry etc. The principal areas of similarity are[2] :

1) **Binary compounds.** There are a large number of oxides, sulphides, phosphides etc., but the most important are halides.

2) **Aqueous chemistry.** This is almost exclusively of complex compounds. Aqua ions Ru(II), Ru(III), Rh(III), Pd(II) exist, but complex ions are formed in presence of anions other than ClO_4^-, BF_4^-, or p-toluene sulphonate etc. A vast array of complex ions, predominantly with halides or nitrogen donor ligands are water soluble.

3) **Complexes with ligands**

a) Binary carbonyls are formed by all but Pd and Pt, majority of them polynuclear. Substituted polynuclear carbonyls are known for Pd and Pt and all six elements give carbonyl halides and a wide variety of carbonyl complexes containing other ligands and carbonyl anions.

b) Nitric oxide complexes are a feature of ruthenium chemistry.

c) An especially widely studied area is the formation of complexes with trialkyl- and triaryl- phosphines and related phosphites, and to a lesser extent, with R_3As and R_2S. The most important of these are with triphenylphosphine and methyl substituted phosphines. The latter are more soluble in organic solvents than triphenylphosphine complexes and have proved particularly useful for the determination of configuration by NMR. Mixed complexes of PR_3 with CO, alkenes, halides and hydride ligands, in atleast one oxidation state, are common for all elements.

d) All these elements have a strong tendency to form bonds to carbon, especially with alkenes and alkynes.

e) A highly characteristic feature is the formation of hydrido complexes; M-H bonds may be formed when the metal halides in the higher oxidation states are reduced, especially in presence of tertiary phosphines and other ligands; hydrogen abstraction from reaction media such as alcohols or DMF is common.

f) For the d^8 ions Rh(I), Ir(I), Pd(II) and Pt(II), the normal coordination is square (though five coordinate species are fairly common), and oxidative addition reactions are of great importance.

Binary compounds

Hydrated oxides are precipitated when an alkali is added to the aqueous solutions; when freshly precipitated, they are soluble in acids but on aging, tend to become insoluble. They are reduced by hydrogen to metals and tend to dissociate on heating. Direct interaction with other elements such as sulphur, selenium, tellurium, phosphorus, arsenic, bismuth, tin or lead produces semi-metallic solids which may be stoichiometric or not depending upon the conditions of preparation.

All the platinum metals form halides in one or more oxidation states; hydrated halides are also common.

Complexes with π acceptor ligands.

A characterestic feature of the d group transition metals is their ability to form complexes with a variety of neutral molecules such as carbon monoxide, isocyanides, substituted phosphines and arsines, stilbenes, sulphides, nitric oxide,various molecules with delocalized II orbitals such as pyridine and its derivatives, ligands such as 1,2-dithioketones, dithiomalononitrile etc. The most important II acceptor ligand is CO. Although platinum group metals have been known for more than a century, serious attention has been paid to these compounds only recently. Many carbonyl complexes are of importance structurally, industrially and catalytically, and a spate of papers have been published. Carbonyl derivatives of atleast one type are known for all the transition metals. There are two, not very recent, reviews by Tripathy et al[3,4].

Complexes containing phosphines, arsines and sulphides attached to low or zero valent metals in combination with CO are known in thousands. In any carbonyl complex, one or more CO groups can be replaced by these ligands. Greater the electronegativity of the group, the more the ligand can mimic the π acceptor behaviour of carbon monoxide.

In many of these complexes the metal atoms are in low positive, zero or negative formal oxidation states; this property is associated with the fact that these ligands possess vacant π orbitals in addition to lone pairs. These vacant orbitals accept electron density from filled metal orbitals to form a type of π bonding that supplements the bonding arising from lone pair donation. High electron density on the metal atom in low oxidation states can thus be localized on to the ligands. The ability of ligands to accept electron density into low lying empty π orbitals is called π acidity, the word being used in the Lewis sense.

The stoichiometry of many, if not all, of the complexes can be predicted by the use of noble gas formalism or 18 electron rule. This requires that the number of valence eletrons possessed by the metal atom plus the number of pairs of σ electrons contributed by the ligands be equal to the number of electrons in the succeeding noble gas atom, namely 18. This is simply a phenomenological way of formating the tendency of the metal atom to use its valence orbitals $n\ d\ (n+1)\ s$ and $(n + 1)\ p$ as fully as possible in forming bonds to ligands. It is of considerable utility in the design of new compounds, particularly of metal carbonyls, nitrosyls and isocyanides, and their substitution products, but is by no means infallible.

Metal-hydrogen bonded compounds

Complexes of transition metals with M-H bonds are of critical importance in many catalytic reactions, and the formation of such bonds on metal surfaces is clearly essential for the high catalytic activity of metals for hydrogenation, C-H bond cleavage and other reactions. They can be synthesized in many ways. The formation of stable hydrido complexes is generally linked with the presence in the molecule of one or more of certain type of ligands, those most frequently occuring being CO, P or As derivatives and the cyclopentadiene group.

The properties of hydrido complexes vary widely, ranging from those which can be detected only spectroscopically to those showing remarkable chemical stability. Stability generally tends to be at maximum in the compounds of the third transitional series. Furthermore, for a given metal and the type of complex, stability appears to be at its highest when phosphine ligands are present in the molecule.

The most commonly quoted physical data on hydrido complexes are the vibrational spectra and proton magnetic resonance parameters. Hydrido complexes exhibit M-H stretching vibrations in the region 1700-2250 cm^{-1} and M-H bending modes in the region 660-850 cm^{-1}. The absence of absorption in the above regions, however is not to be taken as an indication that the molecule under examination does not contain M-H bonds. Several hydrido complexes are known where M-H bonds were not detectable by IR[5-7]. PMR, on the other hand, is a more generally useful technique. Proton resonances in hydrido complexes have characteristic values ranging from -11 to -42 ppm relative to TMS. The limitation here is introduced by solubility and by fast exchange phenomena.

Hydrido ligands exhibit strong trans effect which appears to operate mainly by labilization of the bond trans to the M-H bond. The labilization generally is associated with a lengthening of the bond which has been labilized, an effect operating mainly by trans influence, caused by selective hybridization of the metal orbitals leading to the M-H bond having a large d and s components. These are most evident in square plannar complexes, but they also appear in some octahedral complexes.

The general reactivity of hydrido complexes is high, and is related mainly to the coordination number of the central metal atom. Thus four and five coordinate complexes usually are more reactive than the corresponding complexes which do not contain M-H bonds. Such reactivity may be induced either by operation of the trans effect, or where possible, by the reductive elimination of a molecule of hydrogen halide with or without the assistance of a base.

The chemical behaviour of M-H bonds varies from that of an active hydride to that of a strong acid. This wide variations in properties, however may be achieved with a relatively small variation of charge distribution. Attempts to correlate chemical shifts and coupling constants with bond distances and electron distribution in M-H bonds have led to the conclusion that such correlations may be valid only when very small changes are made in the ligands[8].

The feverish interest in hydrido complexes has, as its main cause, the tremendous potential in catalytic reactions. In a relatively short span of time, hydrido complexes have been found to play a role in a significant number of catalytic processes[9-12]. Example: oligomerization of olefins, decarboxylation and hydrogenation reactions.

The chemistry of platinum metals in the higher oxidation states.

In general the corresponding oxidation states are less stable in the 4d than the 5d series, differences between the pairs Ru-Os, Rh-Ir, Pd-Pt are much more pronounced than in their normal oxidation states. There is hardly any similarity with the *3d* elements, only in a very few compounds[13]. Thermodynamic data for these high oxidation states are not extensive and has been reviewed. The lower ionization potential for corresponding oxidation states of a *5d* element compared to a *4d* is clearly one factor contributing to the greater stability of the *5d* state.

The factors which influence the stability of oxidation states for the *4d* and *5d* metals have been discussed by several authors. It is also true that states with an even number of *d* electrons are more stable than those with an odd number, and that the odd d^n configurations often have a tendency to disproportionate to d^{n+1} and d^{n-1}. The vast majority of these compounds have octahedral or distorted octahedral coordination around the metal. Five coordination is known in a number of cases, but tetrahedral coordination is rare, being limited to OsO_4, RuO_4 and the $[RuO_4]^{n-}$ (n = 1,2) ions. Seven coordination is only established for Ru and Os.

Osmium and ruthenium resemble each other in a wide range of oxidation states represented in their compounds from

(VIII) to (0) inclusive. For iridium and rhodium all the oxidation states from (VI) to (0) are found, and iridium also forms nitrosyl phosphine complexes in which the formal oxidation states are (-I) and (-II) . Platinum has oxidation states (VI) to (0) though examples of (VI),(V), (III) and (I) are rare. Palladium forms oxidation states (IV) and (0) with (III) and (I) being very rare. The normal oxidation state for each metal, that is, for which the greatest diversity of complexes is formed, is (IV) for osmium and (III) for ruthenium, iridium and rhodium, and (II) for platinum and palladium. The least common states are (VII), (I) and (0) for osmium and ruthenium, (VI), (V) and (II) for iridium and rhodium and (VI), (V), (III) and (I) for platinum and palladium. The role of certain ligands in stabilizing high or low oxidation states is well illustrated by these metals. Small and electronegative ligands such as fluoride and oxide stabilize the complexes of osmium and ruthenium (VIII) to (IV); iridium, rhodium and platinum (VI) to (IV), and palladium (IV). In the case of oxide ligand atleast, these may be associated with strong π donor properties. The highest oxidation states of osmium and ruthenium (VIII) and (VII) are found only in oxy complexes either with or without fluoride or hydroxide ligand, whereas unsubstituted fluoro complexes are found only for oxidation state of (VI) or lower. Conversely, efficient π acceptor ligands such as cyanide, carbon monoxide and phosphines will stabilize lower oxidation states such as osmium and ruthenium (II), (I) and (0), and iridium and rhodium (I) and (0), and platinum and palladium (0). Finally, ligands which are good donors but which have no marked π acceptor or π donor properties (such as water, ammonia and ethylenediamine), are often associated with the normal oxidation states of (IV) for osmium, (III) for ruthenium, iridium and rhodium, and (II) for platinum and palladium.

Tendency of third row elements to exhibit oxidation states higher than their second row analogues is shown by these metals. Thus osmium (VIII) complexes are more common than those of ruthenium (VIII), osmium (VI) than ruthenium (VI) and ruthenium (III) than osmium (III). Similarly there are a number of iridium (IV) complexes, but far fewer than rhodium (IV) and platinum (VI) and (V) more than palladium (VI) or (V). These differences are not so marked between the lower oxidation states.

Catalytic applications of platinum group metals

The platinum group metals have been used as catalysts for the following type of reactions.

1. Hydrogenation of olefins, acetylenes and aromatics.
2. Oxidation of sulphur dioxide in the manufacture of sulphuric acid,although platinum has largely been superseded by vanadium pentoxide for this purpose.
3. Preparation of oxides of nitrogen in the Chamber process for sulphuric acid.
4. Oxidation of ammonia to nitric acid.

5. Reformation of petroleum to branched chain and aromatic

compounds with high octane rating.

6. Electrolytic oxidation of hydrocarbons in fuel cells.

The stability of complexes usually increases from ruthenium to osmium, rhodium to iridium and palladium to platinun. If the same order of stability holds for the transition state complexes in catalytic reactions, it follows that the greater ability of the second row metals to promote isomerization and olefin exchange compared to that of the third row metals, can be attributed to the lower stabilities of the olefin complexes formed by the second row metals. The less stable the complex the more readily will desorption of the reacted olefin occur. Similarly the lower selectivity of the third row metals can be explained if π complex formation is assumed. The selectivity will depend on the readiness of the olefin to desorb than to remain and undergo further hydrogenation to alkane.

Important uses

The industrial applications of platinum metals are based on their high resistance to corrosion and to the catalytic activity of their compounds.

Platinum : The main uses may broadly be classified as (i) chemical engineering, including catalytic applications, (ii) electrical engineering, (iii) jewellery, (iv) dental, medical and laboratory and (v) temeperature measurement .

Platinum and its alloys are used in chemical industry for components subjected to high temperatures and corrosive materials. Platinum has an outstanding resistance to fluorine and its compounds, including hydrofluoric acid. Platinum clad electrodes are finding increasing application. A 3% alloy of platinum with rhodium is used in high temperature laboratory equipment. Perhaps the heaviest use of platinum is in petroleum refining. Alloys containing 5-10% iridium or 5% ruthenium are used for jewellery. Platinum-rhodium thermocouples are used for accurate temperature measurements above 1000°C.

Palladium : Palladium is often used as a substitute for more expensive platinum. Palladium alloys are used for electrical contacts, dental purposes and in jewellery; white gold is an alloy of palladium and gold. Palladium alone is used as catalyst in many applications.

Rhodium : In addition to its use as a constituent of platinum alloys, rhodium finds extensive application as an electro-deposited coating because of its hardness and high reflectivity of the deposit. It is also used for electrical contacts in components of radio frequency circuits.

Iridium : Iridium is used as an additive to harden platinum and palladium, and for extrusion dies for high melting glasses. Iridium is highly resistant to attack by a wide range of molten metals, molten salts and oxides. Iridium crucibles are used in the preparation of single crystals of high melting salts such as barium titanate and calcium tungstate.

Ruthenium : Ruthenium is mainly used to harden palladium and platinum alloys and as additive for osmium alloys. Widely used as a catalyst for many specific reactions.

Osmium : Alloys with 60% osmium content are used where extreme hardness is required such as for instrument pivots.

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Chapter II : Ruthenium

RUTHENIUM

Ruthenium was the last of the six platinum metals to be discovered. In 1826 Gottfried Wilhelm Osann examined with the help of Berzeleius a sample of residues remaining from the treatment of crude platinum from the Urals with aqua regia, and announced the discovery of three new elements which he called pluranium, ruthenium and polinium. Although Berzeleius, the most powerful chemical critic of that time, did not associate himself with this announcement and would not accept the existence of the new elements. Osann's work was later taken up by Karl Karlovitch Klaus (Claus) who like Osann, was at one time professor of chemistry at the University of Dorpat. As a result of his work, he isolated in 1844, the last new element of the platinum group, naming it ruthenium, both in honour of his native Russia (Ruthenia is latin for Russia) and for the pioneering work of Osann. This time Berzeleius accepted the discovery. Klaus's procedure was to take the insoluble residues from the aqua regia treatment of platinum concentrates and ignite them with a potassium nitrate-potash mixture in a silver crucible. The melt was dissolved in water, and then distilled with aqua regia to remove osmium as the tetroxide, on mixing the residue, with ammonium chloride and heating the resulting ammonium hexachlororuthenate(IV) in an inert atmosphere, the metal was isolated.

Ruthenium is a rare-metal. It is as rare as osmium. Its abundance in earth's crust is about 0.0004 ppm. The main source of ruthenium (in admixture with other platinum metals) are the native alloys osmiridium (or siserkite) and nidiosmium (or nevyanskite) laurite (essentially ruthenium, osmium disulphide) and platinum concentrates. The concentration of ruthenium in the minerals is highly variable. However, it is present in much greater amounts in chondite, and especially iron meterites (1-6 $x10^{-4}$%).

Large amounts of short-lived ruthenium isotopes are produced in nuclear reactors during the fission of ^{235}U and ^{239}Pu. According to Fleishman et al[1] thermal neutron fission of ^{235}U yields 11% stable and 4.3% radioactive Ru isotopes. The formation of intermetallic compounds of Ru and other platinum group metals U and Pu is so favourable that reduction of U and Pu oxide and carbide fuels occur in reactors, by reaction with fission products.

Ruthenium is also produced by nuclear explosions. Most of the resulting ruthenium from underground testing is absorbed onto bedrock, but a small percentage of ^{106}Ru has found to migrate as fast as tritium[2].

Natural ruthenium is a mixture of stable isotopes with mass numbers of 96, 98, 99, 100, 101, 102 and 104. Their abundance ranges from 1.9% for ^{98}Ru, to 3.16% for ^{102}Ru. Known radio isotopes have mass numbers 92, 93, 94, 95, 97, 103, 105, 106,107 and 108. Their half lives are relatively short ranging from 50s for ^{93} Ru to 1 year for ^{106}Ru.

Ruthenium has an atomic number of 44, electron configuration [Kr] $4d^{7}5s'$ and an atomic weight of 101.07. It exists in several stable isotopes ^{96}Ru (1=0; 5.5%), ^{98}Ru (1=0; 1.87%), ^{99}Ru (1=3\2; 12.72%), ^{100}Ru (1=0; 12.62%); ^{101}Ru (1= 5\2; 17.07%), ^{102}Ru (1 = 0; 31.61%), ^{104}Ru (1=0; 18.58%) and exists in four allotropes, the stable α-phase being grey-white in colour^{3}.

Chemical properties

Like most of the platinum group metals, ruthenium is fairly resistant to chemical attack. Ruthenium is more resistant to oxygen than is osmium, but is less so than iridium and rhodium, and a rapid reaction does not set in below 600°, when a protective film of the dioxide is formed. At moderate temperatures, ruthenium is unaffected by aqua regia; sulphuric acid, hydrochloric acid, hydrofluoric acid or phosphoric acid solutions. Aqueous chlorine and bromine solutions attack it slowly, whereas aqueous cyanides and mercuric chloride corrode more rapidly. It reacts with chlorine and fluorine above 300° to give a mixture of halides. If potassium chlorate is added to aqua regia, it will oxidise ruthenium explosively. It does not react directly with sulphur, but will do so with arsenic, silicon, phosphorus and boron at high temperatures. Fusion with oxidising alkali (e.g. $KOH-KNO_3$; $NaOH-Na_2O_2$) oxidises ruthenium rapidly and completely.

Most ruthenium compounds decompose to metallic ruthenium when heated sufficiently or when reduced with hydrogen. A common method of preparing the metal is to heat $(NH_4)_2RuCl_6$ in alcohol to form an oxychloride, which is then reduced by hydrogen under pressure. Hydrogen reduction of ruthenocene vapour at 868° gave a very pure film[4]. Ruthenium is nearly insoluble in mercury ($< 10^{-5}$ wt.% at 773°K). Ruthenium metal has a magnesium type hexagonal close packed (HCP) structure.

Estimated boiling points of ruthenium metal vary between 4000-4350 ± 100°K. They are based on long extrapolations of sublimation pressure data. A boiling point of around 4400°K is more consistent with vapour pressure data. Published melting points for ruthenium are 2523 ± 10°K, 2593 ±30°, 2583±20°. The recommended is the average of all but the last; 2546± 36°K. The melting point of a single crystal of 99.98% purity ruthenium has been measured as 2607± 1°K[5]. The reaction of the metal in oxygen begins at 673°K with an activation energy of 55.6 K.cal mol^{-1} forming RuO_3. Oxidation of single crystal is anisotropic, being faster on close packed planes.

Applications

Osmium and ruthenium metals are little used industrially owing chiefly to their expense and also to the very considerable difficulty in working the metals, although it has become easier to do so with modern techniques of rolling and forging. Iridium and ruthenium are sometimes used in alloy with platinum for porcelāin dental restorations. Both osmium and ruthenium tetroxide are used for organic oxidations[6]. One important commercial use is as a coating of RuO_2 on titanium to form dimentionally stable electrodes used in the chlor-alkali process. Under proper conditions electrolysis with these electrodes can be nearly 100% current efficient and over-potentials are lower than for previously used anode materials. RuO_2 coated electrodes have been reviewed in detail[7].

Ru is also used as a hardner for some Pd and Pt alloys used in electrical circuits and RuO_2 is a major constituent of resistive glaze thick film resistors in electrical circuits[8]. A 5% alloy of Ru in Pt is commonly used in jewellery in USA. Ru is also used in various forms as catalyst, but to a lesser extent than most other platinum metals. Chemisorbed Ru^{3+} on n-GaAs considerably enhances its solar energy to electrical energy conversion efficiency[9].

Catalytic applications of ruthenium and its compounds

Complexes of the group VIII metals, particularly platinum metals, have been used as catalysts for a variety of homogeneous reactions, including hydrogenation hydroformylation, oxidation, hydration, polymerization, carbonylation, decarbonylation, isomerization, alkylation and disproportionation. The substrates are commonly olefins and acetylenes but this is not necessarily so. Recently a significant number of reviews and papers related to catalysis by platinum metals individually or collectively have appeared, but very few articles about ruthenium based catalysts are known. A perceptible change in this is noticed recently with the advent of homogeneous catalysis as ruthenium complexes are one of the best known hydrogenation catalysts. Some fields of importance for ruthenium based catalysis are reviewed [10-46]: activation of hydrogen for reduction of inorganic and organic substrates[12,17,19,20,30-36], hydrogen migration reactions[12,16,23,30,37,39,44], hydration, oxidation and polymerization of acetylenes and olefins, arylation and alkylation of olefins, hydroformylation[19,20,31,35] and related carbonylation reactions organic synthesis[11,13,21] activation of nitrogen and oxygen[46], other redox reactions[22]. Ruthenium has been found to be the best catalyst for enantioselective and stereoselective hydrogenation of chiral compounds[10,15,25,32,36,38,45,46]. The catalytic activity of ruthenium carbonyl clusters have been thoroughly reviewed[18,23,24,26,27,29,30,31,40,41,43].

Medical and pharmaceutical applications of ruthenium

After the discovery of the antineoplastic activity of cis$[PtCl_2(NH_3)_2]$ (cis platin) several transition metal complexes have been synthesised and studied for their biological activities. The potential use of ruthenium in anti-cancer pharmaceuticals have been reviewed[47]. Possible applications of Ru complexes in the treatment of cancer have been recognised by workers in diverse areas and the utilization of this metal has been approached from widely different perspectives. Early interest centered on the therapeutic properties of ruthenium complexes with aromatic chelates[48] and then following dormancy efforts became focussed on complexes bearing analogies to cis platin[49,50]. Slightly later, the suggestion was made that ^{97}Ru could provide the basis for a family of radio-diagnostic agents for organ imaging[51]. This suggestion holds the promise that tumors may be specifically imaged, located and diagnosed with the help of tumor localizing Ru containing radio-pharmaceuticals[52,53]. In addition to radio-scintigraphic agents of this type, tumor specificity is a desired (but not required) property of chemotherapeutic pharmaceuticals. A final category of anticancer drugs which has not been addressed with ruthenium containing compounds, is that of radio-therapeutic pharmaceuticals, which would provide a doze of short range radiation directly at the tumor site. These might be possible with the ß-emitting radionucleides, ^{103}Ru or ^{106}Ru provided that a high degree of tumor localization could be obtained[54].

Some rare ruthenium metal complexes seem to possess anti-tumor activity, in particular Ru(III) and Ru(II) complexes fac$[RuCl_3(NH_3)_3]$ shows an activity as good as cis platin, and using imidazole derivatives instead of ammonia, more active complexes are obtained. Cis$[RuCl_2(DMSO)_4]$ also shows good activity. $[RuCl_2(DMSO)_4]$ comparison with cis platin makes the complex interesting and suggests the probability within this class of compounds, there is much room for further investigation on new derivatives[55].

^{97}Ru has a half life of 2.84 days and decays solely by electron capture to ^{97}Tc with the emission of two prominent γ-rays at 216 K eV (86%) and 325 K eV (10%). Though ^{97}Ru is the radionucleide of choice for nuclear medicine applications, many of the preliminary studies involving Ru compounds have been carried out using the longer lived ^{103}Ru or ^{106}Ru which are available commercially.

Chemistry of Ruthenium

The chemistry of transition metals depends mostly on their chemistry of multiple oxidation states, and associated redox phenomena. If a particular element is to be singled out to illustrate this point of view, a model choice would be ruthenium, an element that is directly or indirectly the active centre of a plethora of redox phenomena, encompassing ten different oxidation sites and a diversity of structure and bonding.

Element ruthenium has a $4d^7 5s$ electronic structure. Consequently, it can form compounds with valences upto +8. Ru^{-2} can occur in some solid compounds, with electron donating ligands. Ru forms binuclear, trinuclear and tetranuclear inorganic cluster compounds, resulting in a mixed valence polymers with average formal valences of 4.25, 3.75, 10/3, 11/3, 8/3 etc. Carbonyl compound clusters with 3-6 Ru atoms have recently been reviewed[56]. Clearly ruthenium, like most of the second-row transition metals, has very complicated chemistry both in the solid state and in aqueous solution. Owing to these complexities, much of its chemistry and thermodynamics are still poorly understood.

Osmium and ruthenium resemble each other in a wide range of oxidation states in their compounds from VIII to 0 inclusive. Their chemistry differs from that of iron except in compounds such as sulphides and phosphides and in complexes with ligands such as CO, PR_3, η-C_5H_5. The higher oxidation states VI and VIII are much more readily obtained than for iron, and there is an extensive and important chemistry of the tetroxides (MO_4), oxohalide and oxoanions. There are analogies between the chemistry of Ru, Os, and Re, especially in oxo, nitrogen and nitride complexes. Ruthenium in its normal oxidation state III resembles rhodium and iridium more than osmium.

Ruthenium exhibits a wide range of oxidation states from VIII to II, the most common being III and II for 'classical' type ligands. The least common oxidation states are VII, V, I and -I. The higher oxidation states are stabilized by small donor ligands such as F^-, O^{2-}, N^{3-} (e.g. $[Ru^{VI}\ F_6]$, $[Ru^{VIII}O_4]$, $[Ru^{VI}\ NCl_4]^-$, conversely acceptor ligands such as CO, PR_3, stabilize the lower oxidation states $[Ru^{-11}(CO)_4]^{2-}$, $[Ru(CO)_5]$, $[Ru(CO)_3(PPh_3)_2]$. Ligands which are good σ donors but show no substantial acceptor or donor properties (e.g. H_2, NH_3) are usually associated with Ru^{III} and Ru^{II}.

Ruthenium(0) d^8

The chemistry is primarily one of mononuclear, polynuclear carbonyls and tertiary phosphine complexes; a range of Ru nitrosyls are known.

Ruthenium(I) d^7

Very few monomeric complexes are known with dimerization and polymerization reactions via Ru-Ru metal bond formation being prevalent.

Ruthenium(II) d^6

A wide range of Ru(II) complexes incorporating carbonyl, phosphine, ammine and heterocyclic ligands are known. Virtually all Ru^{II} complexes are octahedral and diamagnetic with a $t\,2g^6$ configuration (unless steric hindrances are present). Catalytic processes utilizing Ru(II) phosphine complexes, kinetic studies on substitution reactions of $[Ru(NH_3)_5L]^{2+}$ and the photophysics and photochemistry of $[Ru(Bipy)_3]^{2+}$ and related systems have been areas of major advance in recent years.

Ruthenium(III) d^5

Ru(III) is often associated with classical type ligands e.g., ammine, water, halides. They are octahedral low spin $t'2g^5$ species with one unpaired electron and generally substitutionally inert. The electronic structure of polynuclear carboxylates and mixed valence Ru(II/III) complexes of the type $[Ru(NH_3)_5]L^{5+}$ has been the subject of much interest particularly with respect to the degree of unpaired electron delocalization within these molecules.

Ruthenium(IV) d^4

These complexes are often octahedral or distorted octahedral with t_{2g}^{4} low spin configuration giving μ_{eff} = 2.7 to2.9 BM which decreases with decreasing temperature. Oxo and nitrido bridged polynuclear complexes of Ru(IV) are of particular interest, while more recently organometallic and hydrido Ru(IV) species have been synthesised.

Ruthenium(V),(VI),(VII),(VIII) (d^3,d^2,d^1,d^o)

These complexes are restricted to halo, oxo, and nitrido species such as $[RuNCl_4]^-$, $[RuNCl_5]^{2-}$ and $[RuO_4]^{-2/-1/0}$. Oxo complexes of ruthenium have been used as oxidation catalysts.

Some important compounds of ruthenium

Halides of ruthenium

Only fluorides are formed in higher oxidation states of ruthenium (VIII to IV). Their applications are rather limited.

The most important halide of ruthenium is the trichloride. It is the starting material for almost all ruthenium compounds from Ru(VIII) to Ru(O). Its main attraction is that though it is stable, it can be oxidized or reduced easily. It is most commonly used in the hydrated form, but for anhydrous or solid state reactions β-$RuCl_3$ is the best source.

Ruthenium trichloride is prepared either by chlorination of the metal at high temperatures or by digestion of higher ruthenium oxides with hydrochloric acid.

The commercial trichloride is prepared by digesting the hydroxo-chloropoly complexes with hydrochloric acid, and purified by recrystallizing from concentrated hydrochloric acid.

The anhydrous salt exists in two modifications: the black α-form is made by chlorination of the metal at 700°[57] or by the prolonged action of sulphuryl chloride under pressure on ruthenium at 300°, and the more reactive β-form is also made similarly but at lower temperatures (350 and 300° respectively)[58].

β-$RuCl_3$ is a bulky dark-brown powder with a low tap-density and a high surface area. It is hygroscopic, but the moisture absorbed can be removed in vacuo at room temperature. However, if heated when moist, some decomposition to RuO_2 occurs. It is soluble in ethanol. Upon heating β-$RuCl_3$ is irreversibly transformed into α-$RuCl_3$.

<u>α-$RuCl_3$</u> Direct reaction between ruthenium and chlorine at 600-700° even with the vigorous exclusion of oxygen provided an impure product contaminated with Ru_2OCl_6 and RuO_2[59]. However, the method developed by Remy and Kohn[60] of heating Ru in a Cl_2/CO mixture at 600-700°, gives pure α-$RuCl_3$. The most reproducible results for preparing pure α-$RuCl_3$ can be obtained by first producing β-$RuCl_3$ and then converting it to the α-modification by heating in argon (< 500°) or chlorine (550-650°).

α-$RuCl_3$ is a black, lustrous, crystalline solid, insoluble in both water and ethanol.

Commercial ruthenium trichloride

Commercial ruthenium(III) chloride, hydrated ruthenium(III) chloride, soluble ruthenium(III) chloride and $RuCl_3xH_2O$ are all synonyms for the same material. It is by far the most common starting material for the synthesis of ruthenium complexes. It is an ill-defined mixture of variable oxidation state, oxochloro, hydroxochloro, monomeric and polymeric ruthenium complexes, frequently containing even nitrosyl derivatives. It would be incorrect to regard these complexes as impurities - they are the principal constituents. It would be also incorrect to regard commercial ruthenium(III) chloride as a source of Ru(III) the average oxidation state of the material is closer to Ru(IV) than it is to Ru(III).

Ruthenium(III) bromide

The first pure samples of $RuBr_3$ were prepared by Shchukarev et al[61] by prolonged reaction between ruthenium and bromine at 450-500° and 20 atm. The black-brown powder is insoluble in water, acid, ethanol and common organic solvents. Upon heating above 500°, it decomposes to give Ru and Br_2, with no evidence of an intermediate decomposition product such as $RuBr_2$.

Ruthenium(III) iodide

The method of preparing $RuCl_3$ is still based upon that reported by Claus[62] in 1854. It is synthesized either by the metathetic reaction between "$RuCl_3$"xH_2O and Kl in aqueous solution[63] or by the action of hydroiodic acid on $[RuO_4]$[64]. It is a black-powder, only very sparingly soluble in water.

Upon heating it reverts to its elements.

Oxides of Ruthenium

Ruthenium(VIII) oxide [RuO_4]

It is an yellow crystal (m.p.25.4°) existing only in one form, and decomposes explosively below its boiling point. Although less toxic than [OsO_4], [RuO_4] should be treated as being extremely poisonous. It has a high vapour pressure at room temperature; creating a strongly irritant effect upon the eyes and respiratory system, it oxidizes tissue leaving a deposit of RuO_2, and should be handled with extreme caution. It has a strong odour similar to that of ozone, and reacts explosively with many common organic solvents. Its preparation is reviewed extensively[65]. It is sparingly soluble in water to give a golden-yellow solution (solubility 1.71 g per 100 g H_2O at 0^{o}, and 2.03 g per 100 g H_2O at $20^{o}C$) and is very soluble in both tetrachloromethane and trichloroethane giving a red orange solution. Its density is 3.28 g/cm^3. [RuO_4] is more powerful oxidizing agent than [OsO_4].

Because of its high vapour pressure, vigour of oxidation and toxicity [RuO_4] ruthenium tetroxide is hardly ever used on its own. However, it is easily generated in an aqueous solution from RuO_2.

$RuCl_3.n\ H_2O$, or $RuO_2.n.\ H_2O$ (a better starting material) with excess aqueous sodium periodate[66], sodium hypochlorite bleach[66] or sodium bromide[67]. In the presence of these co-oxidants, it functions as a catalytic oxidant, [RuO_4] being regenerated after reaction with the organic substrate by the co-oxidant, so that the actual quantity of ruthenium needed is very small. An extensive review of oxidation by transition metal oxides (Ru,Os) is provided by Griffith[44].

Ruthenium(IV) oxide [RuO_2]

RuO_2 is the only stable solid species formed by heating ruthenium metal in oxygen. It has also been prepared by the high temperature oxidation of commercial hydrated ruthenium(III) chloride and anhydrous ruthenium(III) chloride. In pure form it is a blue-back crystal. Recently it has gained importance due to its application in coating of titanium electrodes and other electrode materials.

Ruthenium and osmium are readily recovered and separated by utilizing the high volatility of their tetraoxides, which can be distilled from aqueous solutions. Nitric acid is sufficient to oxidize osmium compounds but for ruthenium more powerful oxidants are required.

RuO_4 is useful in pollution control. With hypochlorite it destroys dioxins[68]. It has capacity to destroy oxidatively industrial pollutants such as organosulphur, polychlorinated biphenyls, chlorinated dioxins and dibenzofurans in the total environment.

Complexes with nitrogen donor atoms

These complexes are largely formed by the metals in the II and III oxidation states, and by and large the ruthenium complexes are far more thoroughly investigated. They can be divided into groups like complexes with NH_3 as donor ligand, with aromatic amines and nitrosyl complexes. Their chemistry is vast, and is expanding rapidly.

Complexes with aromatic amine ligands, which have π-systems, have distinctly different features of interest from the ammine complexes. The most important species are those containing 2,2'-bipyridyl or 1,10-phenanthroline which forms tris-chelates.

The formation of nitric oxide complexes is a marked feature of ruthenium chemistry, those of osmium have been less well studied, but where known, they are even more stable than the ruthenium analogues. The group Ru-NO can occur in both anionic and cationic octahedral complexes in which it is remarkably stable, being able to persist through a variety of substitution and oxidation-reduction reactions. Ruthenium solutions or compounds that have at any time been treated with nitric acid can be suspected of containing nitric oxide bound to the metal. The presence of NO may be detected by IR absorption ca. 1930 to 1845 cm^{-1}. Almost any ligand can be present along with NO-Ru group, but conventional complexes are $[Ru(NO)Cl_5]^{2-}$ $[Ru(NO)(NH_3)_4Cl]^2$ and $[Ru(NO)(SCNMe_2)]_3$.

Tertiary phosphines and related complexes

In common with other platinum metals, an intensively studied area is the chemistry involving trialkyl- and triaryl-phosphines, the corresponding phosphites, and to a lesser extent, the arsines. An extremely wide range of complexes is known, mainly of the (II) state, although compounds in the (O),(III) and less commonly (IV) state are known, other ligands commonly associated with PR_3 are halogens, alkyl and aryl groups, CO, and alkene. A variety of preparative routes for these compounds are known. Only a few selected compounds can be mentioned.

The red brown $RuCl_2(PPh_3)_3$ has an sp structure in which the sixth octahedral position is blocked by an ortho hydrogen atom of one phenyl ring. On treatment with H_2 in presence of base, it is converted to $HRuCl(PPh_3)_3$ which has a tbp structure and is one of the most active catalysts known for homogeneous hydrogenation of alkenes, with remarkable specificity towards 1-alkenes.

Ruthenium forms a series of complexes containing PR_3 and CO as ligands along with nitrate ions or trifluoroacetate ions. Some of the latter, of general formula $Ru(CO)(O_2CCF_3)_2(PR_3)_2$, function as a dehydrogenation catalyst, converting alcohols to aldehydes or ketones; the catalytic cycle includes the intermediate $RuH(CO)(O_2CCF_3)(PR_3)_2$, from which HO_2CCF_3, regenerates the dicarboxylato complex with evolution of hydrogen[69]. The hydrido intermediate can be isolated as a yellow air sensitive material.

β-Diketonate complexes of Ru(II) are obtained by reaction of H(dike) with hydridophosphine or carbonyl phosphine complexes and are of types $Ru(dike)(PR_3)_2$ or $Ru(dike)(PR_3)_2(CO)(X)$
(X = Cl,H)[70].

The dihydrides $RuH_2(PPh_3)_n$ (n = 3 or 4) may be obtained by borohydride reduction. They undergo reversible additions of H_2, CO, N_2 etc. and will act as hydrogenation catalysts for olefins[71], although orthometallated species such as $HRu(C_2H_4)(C_6H_4PPh_3)$ produced by the interaction of the hydrides with alkenes are doubtless involved[72].

Hydride complexes of transition metals contain covalent M-H bonds which have little tendency to ionize or undergo hydrolysis. They are mostly of the type MH_xL_y (L = CO, X^-, cyclopentadienyl or PR_3). It is noteworthy that L must possess a high ligand field strength in order to stabilize the hydride complex of the metal, which is in a low oxidation state, generally (II), for ruthenium. The hydride complexes are usually obtained by reduction or protonation of suitable complexes. The resonance of hydrogen nucleus attached to a transition metal shows a very high positive chemical shift (δ value) in the NMR spectrum as compared to hydrogen atoms attached to non-transition elements. The IR spectra show strong bands due to M-H stretching and bending modes in the regions 2250-1700 cm^{-1} and 850-660 cm^{-1} respectively, although in the carbonyl hydrides the bands are sometimes difficult to identify. The substitution of PPh_3 for CO markedly increases the stability of the hydrides in respect to temperature and oxidation.

Ruthenium carbonyls

$Ru(CO)_5$ and $Ru_3(CO)_{12}$ were first reported in 1936. $Ru(CO)_5$ can be prepared in poor yield (10%) by heating ruthenium powder at 180° under CO at a pressure of 200 atm.

It can also be obtained by heating a mixture of RuI_3 and excess silver powder at 170° for 24 hours with CO at 450 atm. The volatile $Ru(CO)_5$ can be recovered from the gases by trapping it at low temperature. The $Ru_3(CO)_{12}$ formed by this method can be extracted with benzene. An attractive alternative route for $Ru(CO)_5$ via the photochemical degradation of heptane solutions of $[Ru_3(CO)_{12}]$ ($\lambda_{irr} \sim 390$ nm) under carbon monoxide is reported to proceed quantitatively[73]. Dodecacarbonyl $[Ru_3(CO)_{12}]$ can be prepared by treating a solution of $RuCl_3$ in methanol with zinc and CO (10 atm) at 65°, the yield is 75%[74].

$$6RuCl_3 + 9Zn + 24\ CO \longrightarrow 2[Ru_3(CO)_{12}] + 9ZnCl_2$$

An atmospheric pressure synthesis of $[Ru_3(CO)_{12}]$ has been reported[75].

$[Ru_3(CO)_{12}]$ is an air stable, orange, crystalline compound (m.p. 154-55°) which sublimes at 80-100°, and is soluble in most organic solvents, but is insoluble in methanol or water. It does not dimerize. The complexes undergo oxidation reactions with halogen with the loss of [illegible] CO groups to give $[Ru(CO)_2X_2L_2]$ (X = Cl, Br) and L = PPh_3, or CO).

Most of the carbonyl complexes of Ru(II) contain covalently bound halide, however other negatively charged ligands such as dialkyl dithiocarbamate yield carbonyl complexes. Carbonyl chloride complexes are readily formed, usually by the action of CO, followed by the ligand, in alcoholic solutions of commercial $RuCl_3.3H_2O$. In some cases CO can be derived from formic acid, e.g., a 1:1 mixture of hydrochloric and formic acid reacts with Ru(III) chloride to give $[Ru(CO)_2Cl_2]_n$.

The compounds are mostly yellow, although some are colourless while others are orange or brown. Compounds of the type $[Ru(CO)_2X_2]_n$ are polymeric with halogen bridges, the iodo complex reacts with a variety of ligands to give monomeric species $Ru(CO)_2L_2I_2$.

Only a few carbonyl complexes of Ru(III) have been reported e.g., $Ru(CO)Br_3(PPh_3)_2$ or $[Ru(CO)Cl_5]^{2-}$.

Hydridocarbonyl clusters and other types of clusters are prepared either from $[Ru_3(CO)_{12}]$ or arene ruthenium chloro complexes $[ArRuCl_2]_n$[76]. Synthetic methods of ruthenium carbonyl clusters and their derivatives are described in detail in Inorg. Synth.[75].

Mutterties[77] has compared the chemistry of transition metal clusters with that of transition metal surfaces, and is of the view that the study of these metal clusters would provide information about interactions occurring at the surface of heterogeneous catalysts. The clusters also possess intrinsic novel properties which suggest that they might serve as potential catalysts for a range of processes.

Use of carbonyl clusters as homogeneous catalysts have been recently reviewed by Mark[78]. Homogeneous catalysis by carbonyl and other molecular clusters have been reviewed by Mutterties et al.[79]. In a recent series of review reports, Bhaduri[40] has studied the catalysis of CO reactions like water-gas shift reaction, CO hydrogenation, reductive carbonylation of nitrobenzene, hydrogenation; transfer hydrogenation and isomerization reactions, and other non-coreactions like trans alkylation of tertiary amines, oligomerization of silazanes, addition of carboxylic acid into substituted acetylenes, isocyanates to N-formyl urea, spinocyclization of $[HRu_3(CO)_{10}(SiR)_2]$, alkyl isocynates, hydrocondensation of CO_2. H_2 in methanol to give methyl formate, hydrosilylation, silacarbonylation and isomerization of vegetable oils, in their article.

Organometallic chemistry of Ruthenium

The first organometallic compound containing ruthenium was reported in 1910, although the precise nature of the orange solid $[Ru_3(CO)_{12}]$ remained unknown until X-ray studies several decades later. In common with many other transition metal halides, ruthenium trichloride was found to effect the coupling of the organic radical in phenyl magnesium bromide, to give biphenyl in quantitative yield. When interest in organic derivatives in transition metals was reawakened by the discovery of ferrocene, it was natural ruthenium analogue should be one of the first of the host of new compounds to follow.

The subsequent development of the organic chemistry of ruthenium has centred on two major areas. The first is that of the Ru-H bond in a variety of hydridoruthenium complexes containing tertiary phosphine ligands, which although not yet achieving the general utility of their rhodium analogues, have still been shown to catalyze a considerable number of organic reactions. In addition, their reactions have spawned a great variety of novel complexes of interest in their own right. The study of the chemistry of the cluster carbonyl $[Ru_3(CO)_{12}]$, as one of the first readily accessible polynuclear carbonyl derivatives, helped spark the current interest in these complexes, and this compound is the source of a wide range of unusual compounds containing three or more metal atoms. The chemistry of ruthenocene has proved disappointingly similar to that of the much cheaper ferrocene, although investigation of the related complexes containing the $Ru(PR_3)_2(\eta^5 C_5H_5)$ moiety continues to produce many singular molecules.

The organic chemistry of ruthenium revolves around the oxidation state Ru(O) (d^8) and Ru(III) d^5, with a handful of organoruthenium(IV) complexes having been described. Other oxidation states occur rarely. The zerovalent state belong to the carbonyls and their tertiary phosphine and some hydrocarbon derivatives. In molecular complexes the ligand must contribute ten electrons for the metal to achieve the 18 electron configuration commonly resulting in five coordinate stereo chemistry.

The vast majority of complexes containing π acid ligands contain Ru(II) which is easily reached by oxidative addition to Ru(O), often accompanied by ligand elimination. This oxidation state is relatively difficult to reduce.

Usually two anionic ligands (H^-, Cl^-, $\eta^5 C_5H_5^-$) are present together with other ligands which supply a total of 8 electrons. Complexes are generally octahedral, although other stoichiometries and geometries may occur if bulky ligands, such as PPh_3 or PCy_3 are present, preventing coordination of the sixth ligand, as in $[HRuCl(PPh_3)_3]$. However, even in these cases more detailed structural examination may reveal that the sixth coordination position can be occupied by, for example, an ortho hydrogen of an aromatic substituent.

As with many other areas of chemistry, the development of organo-ruthenium chemistry has had to await suitable synthetic routes useful and appropriate precursors. The usual starting point is hydrated ruthenium trichloride, a brown-black highly deliquescent crystalline solid which is soluble in water, the lower alcohols and acetone. Its nature depends on its method of preparation, although species such as $[RuCl_3(OH_2)_3]$ are present, the solid also contains other compounds, some containing ruthenium(IV) others being polynuclear.

The utility of $RuCl_3.xH_2O$ as a precursor for ruthenium complexes of importance is well known. In many cases, relatively mild conditions can be employed, as a result of the solubility of the chloride in organic solvents, which means that organic reactants can be induced to react readily.

Ruthenium carbonyls

There are presently three known neutral binary carbonyls of ruthenium $[Ru(CO)_5]$, $[Ru_2(CO)_9]$ and $[Ru_3(CO)_{12}]$.

Pentacarbonyl ruthenium $[Ru(CO)_5]$

This was first formed by the direct carbonylation of ruthenium metal (180°/200 atm or, a mixture of $[RuI_2(CO)_2]_n$ and silver powder. It is best formed by the reaction of $[Ru(acac)_3]$ with a 2:1 CO/H_2 mixture in heptane (180°/200 atm. 8 h). It is a colourless volatile liquid which readily loses CO to form $[Ru_3(CO)_{12}]$, which occurs either thermally (> 50°) or photochemically.

Nonacarbonyl diruthenium $[Ru_2(CO)_9]$

Although the $[Ru_2(CO)_9]$ described by early workers was later shown to be $[Ru_3(CO)_{12}]$, this dinuclear ruthenium carbonyl was prepared by U.V. irradiation of $[Ru(CO)_5]$ in heptane at -40°, it is stable only at low temperatures readily loosing CO to form $[Ru_3(CO)_{12}]$.

Dodeca carbonyl triruthenium $[Ru_3(CO)_{12}]$

This complex is the most readily prepared binary carbonyl complex of ruthenium and since the discovery of some simple preparative routes some 15 years ago, the development of the chemistry of polynuclear ruthenium complexes has proceeded at a rapid pace. A series of syntheses of $[Ru_3(CO)_{12}]$ of increasing simplicity and efficiency has been described. The direct carbonylation of 125°/50 atm.) methanolic solutions of hydrated $RuCl_3$, is probably simplest of these routes; if an autoclave is not available, carbonylation of $RuCl_3.xH_2O$ in refluxing 2-ethoxyethanol at ambient pressure also gives the carbonyl. It is an air-stable, orange crystal, which is soluble in most organic solvents except light petroleum and alcohols.

Ruthenium carbonyl halides

The first report of carbonyl halides of ruthenium appeared in 1924 when the compounds $[RuX_2(CO)_2]$ were prepared by passing CO over RuX_3. Later accounts described the white crystalline [RuBr(CO)] formed from $RuBr_3$ and CO (180°/400 atm) which sublimed in N_2 to give $[RuBr_2(CO)_2]$ leaving ruthenium behind. The reaction of chlorine with ruthenium metal was reported to be promoted by CO. Red carbonyls containing chlororuthenium solutions were first described in 1964, being obtained by passing CO into ethanolic $RuCl_3$ solutions. An early report of the reactions of $[Ru_3(CO)_{12}]$ described oxidation with halogens to give four types of complexes. However, most preparations commence with hydrated ruthenium chloride.

Hydrido and σ bonded carbon complexes of ruthenium

The first octahedral hydrides of ruthenium(II) of general formula trans$[RuHCl(Chelate)_2]$ were prepared by reduction of cis$[RuCl_2(Chelate)_2]$ with lithium aluminium hydride. They are white or pale yellow solids which are fairly stable to air. Their thermal stability depends on the nature of chelates. Many hydrido-carbonyl complexes of ruthenium are obtained by decarbonylation of oxygen containing solvents (commonly alcohols) a process which often involves formation of a metal-hydride bond. Thus ruthenium(III) halides react with triphenylphosphine or triphenylarsine in the high-boiling alcohols 2-methoxyethanol or ethylene glycol to give $[RuHX(CO)L_3]$ (X = Cl, Br, L = PPh_3, $AsPh_3$). Ruthenium chloride-tetra-phosphine complexes also react with alcohols, particularly in the presence of base to produce very stable hydrido-carbonyl derivatives of ruthenium.

Monocarbonylhydridohalo ruthenium complexes with phosphines $[RuClH(CO)(PR_3)_3]$ (R = aryl, alkyl) have been prepared by reacting the halo phosphine complexes of ruthenium in alcohol in presence of a base, in which the alcohol is reduced to coordinated CO[80].

$$[Ru_2(PEt_2PR)_6Cl_3]Cl + 2KOH + C_2H_5OH \longrightarrow 2\{Ru(CO)(PEt_2PH_3)_3HCl\} + 2CH_4 + 2KCl + 2H_2O.$$

The origin of CO was independently confirmed by treatment of $RuCl_3.x.H_2O$ with PPh_3 in boiling ^{14}C-ethane-1,2,-diol; the product was $[Ru(^{14}CO)(PPh_3)_3(H)Cl]$[81].

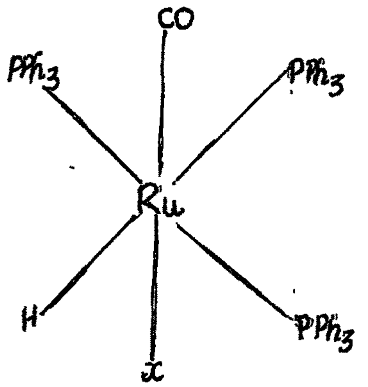
$$RuCl_3 \xrightarrow[\text{2-Methoxy ethanol}]{PPh_3,\ \text{aq. HCHO}} [RuH(CO)Cl(PPh_3)_3]$$

Formaldehyde has also proved a useful carbonylation reagent[82].

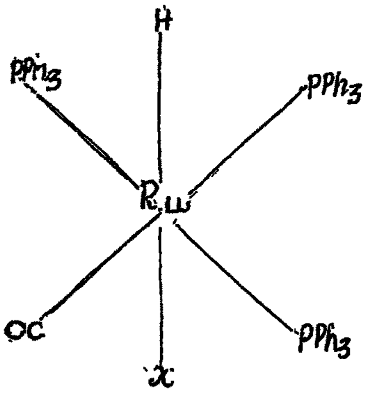
A recent preparative method is to reflux $RuCl_3.x.H_2O$ with excess triphenylphosphine in 2-methoxy ethanol for 48 h. If crystallization did not start after 6 hrs, seeding is recommended. On cooling to room temperature, cream to pale-pink crystals separated[83].

It is a cream coloured or light brown product, stable in air in the solid state. But the solutions slowly decompose in air. It reacts with alcoholic KOH to give the white compound $[RuH_2(CO)(PPh_3)_3]$. In solution it reacts with CO to give $[RuClH(CO)_2(PPh_3)_2]$.

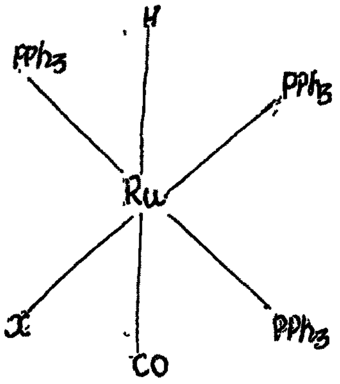
$[RuHCl(CO)(PPh_3)_3]$ is reported to exist in three isomeric forms[85].



Ia



Ib



Ic

In all cases the phosphine ligands adopt a mer-configuration, which is presumably preferred to the fac-isomers on steric grounds.

Most reactions involving $RuH(CO)xL_3$ complexes involve la, the stereochemistry of which is based on the crystal structure of an analogus osmium complex $[OsH(CO)Br(PPh_3)_3]$[85] and the similarity of the IR spectra of the Ru and Os derivatives[86]. The strong trans-labilizing effect of the hydrido ligand in la has been used to effect substitution by a variety of unidentate N, P or As donor ligands[84,86,87].

The most commonly quoted physical data on hydrido complexes are the vibrational spectra and proton magnetic resonance parameters. ν Ru-H stretching in $[RuH(CO)Cl(PPh_3)_3]$ is observed at 2020 cm^{-1} and $\nu(C \equiv O)$ at 1920 and 1900 cm^{-1}. The Ru-H bending mode, expected in the range 660-850 cm^{-1} is not noticed or it is masked by phosphine ligands. Several authors have reported the absence of Ru-H absorptions in the above regions, but assure that it is not an indication that Ru-H bond is not existing in the compound [88]. PMR on the other hand is a more generally useful technique. Ru-H resonance in this complex is seen in the high field spectra at about δ -7.3 relative to TMS.

The hydrido ligand exhibits a very strong trans effect, which appears to operate mainly by labilization of the bond in the trans position to M-H bond. The labilization generally is associated with a lengthening of the bond which has been labilized, an effect operating mainly by trans-influence[89] caused by a selective rehybridization of the metal σ orbitals leading to the M-H bond having a large d and s component. Such effects are most evident in square planar complexes, but they also have been observed in octahedral complexes.

Carbonyldihydridotris(triphenylphosphine)ruthenium(II)
$[RuH_2(CO)(PPh_3)_3]$

The dihydrido complex have been prepared in a variety of ways. Hallman obtained a white mer-cis $[Ru(CO)H_2(PPh_3)_3]$ by reducing a suspension of $[Ru(PPh_3)_3Cl_2]$ in benzene or lower alcohols, by sodium tetrahydroborate, under reflux.[90].

Later, Ahmad et al have shown that $Na[BH_4]$ can be replaced by KOH[82]. The white isomer was also prepared by treating $[Ru(PPh_3)_3\ H_2]$ in benzene with CO[91]. A more recent method of preparing the dihydro compound is by refluxing the carbonyl hydrido-halo complex $[RuH(CO)Cl(PPh_3)_3]$ with sodium hydroxide, in presence of triphenyl phosphine, in 2-methoxy ethanol[83].

It is a white solid with melting point 160-162°. It is stable in air at ambient temperatures, and also thermally stable under vacuum. Benzene solutions react photochemically with the elimination of dihydrogen[93]. It is soluble in organic solvents like benzene, chloromethylenes, etc. but not soluble in alcohols or petroleum ether solvents.

Many hydrides react with halocarbon solvents to yield metal halide derivatives[93].

$$[H_2Ru(PPh_3)_4] + CHCl_3 \longrightarrow [HRuCl(PPh_3)_3] + PPh_3 + CH_2Cl_2$$

The transfer of hydride to another ligand in a complex is one of the key reaction steps in many catalytic cycles.

The IR spectrum shows ν(Ru-H) at 1960 and 1900 cm^{-1} and ν(CO) at 1940 cm^{-1}. ^1H NMR shows Ru-H at -6-9 ppm as multiplet in $CDCl_3$.

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Chapter III : Outline of the Proposed Work

OUTLINE OF THE PROPOSED WORK

In this work we propose to study the coordination chemistry of carbonyl ruthenium(II) complexes. The work is proposed to be done in three different sections. The first section will deal with the preparation and spectral studies of hydrazine dithiocarbazate Schiff bases of aldehydes, ketones, diketones and bis-(ß-diketones), and their reaction with phosphine containing ruthenium carbonyl complexes. The ruthenium precursors proposed for this study are $HRu(CO)Cl(PPh_3)_3$ and $H_2Ru(CO)(PPh_3)_3$. The second section will be devoted to the preparation of bis-(ß-diketones), their spectral characterization and finally their complex formation with ruthenium giving ruthenium(II) carbonyl complexes. The third section will contain the carbonyl complexes of ruthenium(II) with nitrogen heterocyclics and their cationic complexes. The proposed studies include physical properties, infrared absorptions, mass spectra, proton NMR, ^{13}C NMR and ^{31}P NMR resonances.

The Schiff bases will be prepared by the condensation of S-methyldithiocarbazate with various aldehydes and ketones. The carbonyl compounds proposed for the condensation are, aldehydes like pyridine-2-carboxaldehyde, thiophene-2-carboxaldehyde and furfural, ketones like 2-acetylpyridine and 2-acetylthiophene; ß-diketones like acetylacetone and benzoylacetone and bis-(ß-diketones) like 3,5-diacetyl-2,6-heptanedione, 3,5-dibenzoyl-2,6-heptanedione, tetrabenzoylpropane and p-xylylene tetraacetate.

More attention has to be paid to the spectral characterization of the ligands. This is necessary because complete spectral characterization of these ligands is not readily available, especially NMR resonances. We propose to study the characteristics of each ligand by IR, ^{1}H NMR, ^{13}C NMR and mass spectra.

Once the ligands are characterized, the next step will be to prepare their ruthenium(II) complexes. The ruthenium precursors proposed to be used are ruthenium(II) carbonyl chlorohydrido tris-triphenylphosphine and ruthenium carbonyl dihydrido tris-triphenylphosphine, $HRu(CO)Cl(PPh_3)_3$ and $H_2Ru(CO)(PPh_3)_3$ respectively. As these complexes are not readily available, they are to be prepared by reported procedures.

ß-Diketones and metal ß-diketonates are an extensively studied field. They find use in various applications. Tetraketones are, as a class, less studied compounds. Two types of tetraketones, linear and branched, are known. ß-Diketones are the parent compounds of bis-(ß-diketones). Bis-(ß-diketones) are two ß-diketone moities linked directly or through a linking group, usually an alkyl chain. Therefore, bis-(ß-diketones) are expected to follow the pattern of ß-diketones in their properties. They act as dibasic, tetradentate ligands in their reactions. They form a polymeric complex when reacted with bivalent or tervalent metal salts. Most of the reported work has been done with tetraacetylethane and nickel or copper salts. Recently, there are some reports on complexes formed by noble metal compounds.

After a thorough literature survey, we decided to prepare a series of tetraketones of the branched bis diketone variety, that is two ß-diketone moieties linked through the central carbon, with or without a linking group. By reacting these ligands with phosphine containing ruthenium carbonyl complexes in a 1:2 mol ratio, we expect to get monomeric binuclear ruthenium(II) complexes, similar to the mononuclear ruthenium(II) ß-diketone complexes, reported earlier from our laboratory.

We expect to achieve complexation by reacting the ligand with the ruthenium hydrido complex in a solvent in an inert atmosphere. The complexes so formed will be studied by IR, ^{1}H NMR and ^{13}C NMR spectroscopies. These data are expected to yield more insight into the complexation pattern of ruthenium.

Metal hydrides are known to have '*trans* effect', whereby the bond *trans* to hydrogen is weakened. Thus, the *trans* phosphine group in the complex $HRu(CO)Cl(PPh_3)_3$ can be replaced easily by other basic ligands. We are proposing to study the effect of various nitrogen donor heterocyclic bases on the ruthenium complex $HRu(CO)Cl(PPh_3)_3$. The chlorine containing metal complexes are likely to form cationic complexes with sodium tetraphenylborate or sodium hexafluorophosphate. The products will be characterized by IR, ^{1}H NMR and conductivity measurements wherever possible.

During the course of work, any other interesting aspect, if noticed, also will be investigated.

Chapter IV : Schiff Base Ruthenium(II) Complexes

Analysis and Instrumentation

All the analyses reported in this work were carried out in this Laboratory's Analytical Sections. Elemental analyses were carried out using a 'Carlo Erba (Italy) - C H N S automatic analyser, model-1108.

^1H NMR spectra were taken in Bruker MSL 300 (300 MHz), Bruker AC 200 (200 MHz), Bruker WH 90 (90 MHz) and Varian FT 80A (80 MHz) in deuterated chloroform using TMS as internal standard.

^{13}C NMR spectra were recorded on a Bruker MSL 300 (75.5 MHz) and Bruker AC 200 (50 MHz) in $CDCl_3$.

^{31}P NMR spectra were taken in Bruker MSL 300 (121 MHz) using ortho-phosphoric acid as standard.

Mass spectra were recorded on Finnigan Mat 1020 automated GCMS. Infrared spectra were obtained using Perkin-Elmer FT-IR model 1620 in the range 4400-450 cm^{-1}.

Gas chromatographic analyses of liquid samples and starting materials were carried out on a NUCON Gas Chromatograph equipped with a SHIMADZU RC 6A data processor.

SCHIFF BASE COMPLEXES

General

4. S-Containing Schiff basess

Schiff bases are compounds which contain the azomethine group (-RC=N-) and are usually formed by the condensation of a primary amine with an aldehyde or ketone. A five or six-membered chelate is formed if a second group such as phenolic OH is attached ortho to azomethine group. The formation of chelate ring seems essential for the production of a stable complex with ligands containing the >C=N group.

Sulphur atoms in heterocyclic rings have very poor coordinating ability[1], due to the aromatic nature of the ring which has the two-fold effect of causing the lone pairs on the sulphur atom to be less available for donation and the π orbitals to be less capable of accepting electrons from the metal. Towards class (b) and border line metals the coordinating ability of the various types of sulphur donor is $RS^{-}>R^{2}>RC=S>>$ ring sulphur.

What has been stated about complexes of sulphur ligands applies also to complexes of sulphur-nitrogen chelating agents. However, the nitrogen atoms tend to lower the solubility of the complexes in non-aqueous solvents, so that complexes of sulphur-nitrogen ligands are, in general sparingly soluble in non-polar solvents.

The number and diversity of sulphur-nitrogen ligands used to prepare new coordination and organometallic compounds have increased rapidly during the last few years. The pronounced biological activity of the metal complexes of ligands derived from dithiocarbazic acid has created considerable interest in their coordination chemistry. Although complexes of dithiocarbazates with many different transition metal ions have been studied, not much information on their structural aspects is available[2]. Though, a lot of work have been done on dithiocarbazic acid and its derivatives on divalent metals like Cu(II), Co(II), Ni(II), Zn(II) and metals like tin and lead, very few papers are published on complexes of noble metals of group VIII. Most of the work published on ruthenium(II) complexes is from our laboratory[42-46].

Schiff bases derived from dithiocarbazates and their metal complexes

Organic ligands containing N,S as donor atoms have been found to be biologically active. Some copper(II) and platinum complexes of such N,S ligands were also found to have biological activities. One of the simplest N-S ligands is dithiocarbazic acid. A lot of work has been done, studying the characteristics of metal complexes of dithiocarbazic acid. Most of the work has been done on Ni(II) and Cu(II) complexes, though other metals like Co(II),(III), Fe(II), (III), Hg(II), Zn(II), Pt(II) etc.

have also been studied. It was felt that by changing the substituents on the ß-N-atom of the dithiocarbazate and using different metals, the biological activities of the complexes can be modified. As a result of such thought, dithiocarbazic acid and their alkyl or aryl esters were condensed with aldehydes and ketones, to provide a new class of Schiff bases. Sandstrom[3] has prepared the acetone Schiff base of dithiocarbazic acid and its ester. This was followed by a series of papers on the preparation, complexation and their characterization, by Livingstone and his school, of a variety of Schiff bases starting from dithiocarbazic derivatives and condensing them with various aldehydes and ketones. A few examples are:

a) Schiff base of S-methyl dithiocarbazate with acetone and pyridine-2-aldehyde and their metal complexes with Mn, Fe(II), Fe(III), Co(II), Ni(II), Pd(II), Pt(II) and Cu(II)[4].

b) α-N-Methyl, S-methyl-ß-N-(2-pyridyl) methylene dithiocarbazate with 3d metal ions[5].

c) α-N-Methyl-S-methyl-ß-N-(2,6-diacetylpyridine) and metal complexes[6].

d) N-(2-Pyridyl) methylene dithiocarbazate S,S-dimethyl ester[7].

e) S-Methyl-dithiocarbazate condensation product with salicylaldehyde and its chloro, bromo, nitro and methoxy derivatives and acetylacetone and their metal complexes of Ni, Co, Pd, Pt and Cu[8] and

f) N-Methyl and S,S-dimethyl salicylaldehyde complexes with Ni, Co, Pd, Pt and Cu[9].

Das and Livinstone[10] have prepared a series of Schiff bases by condensing S-methyl dithiocarbazate with various aldehydes and ketones and studied the characteristics and their metal complexes with Ni, Cu, Zn, Pd and Pt. They, in collaboration with the US National Cancer Institute, have studied their anti-tumour activities. Gagliardi[11] has studied the characteristics of S-methyl-N-(2-pyridyl)methylene dithiocarbazate (PMTC). complexes of transition metals. The fungicidal properties of furfurylidinemethyl dithiocarbazate have been patented[12].

Klayman Daniel et al.[13,14,15] have studied the 2-acetylpyridine thiosemicarbazones, as new class of potential anti-malarial agents. Klayman Daniel's further studies on 2-acetylpyridine thiosemicarbazone include[16-19].

De Milo et al. [20], Albert et al.[21] have studied the repellancy and toxicity of acetylpyridine thiosemicarbazones.

Two US patents[32,33] by Klayman deal with the anti-malarial and anti-leukemic properties of 2-acetylpyridine dithiocarbazate derivatives. Pai[24] has studied and evaluated the anti-microbial properties of acetylthiophene dithiocarbazate derivatives. A Polish patent[25] deals with furfural dithiocarbazate complexes as agrochemical fungicides. Tandon et al.[26] have studied the anti-bacterial activity of organo lead(IV) complexes with S-benzyl or S-methyl dithiocarbazate Schiff base complexes. Majumdar[27] has synthesised and characterized metal chelates of pentadentate (N_3S_2) ligand by condensing S-methyldithiocarbazate with 2,6-diacetylpyridine and studied their fungi toxicities. Recently a spate of papers have appeared on the medicinal uses of the tetradentate Schiff bases derived from S-methyldithiocarbazate and their technetium complexes[28-33].

Iskander et al[34] have studied the electron spectra and proton NMR spectra of Zn(II), Ni(II), Cd(II), Hg(II) and Pd(II) chelates with bidentate Schiff bases derived from hydrazine-S-methyl dithiocarboxylate and thiosemicarbazide. Iskander et al.[35] have also prepared Schiff bases from ß-dicarbonyl compounds and hydrazine-S-methyl dithiocarbazate, and studied their complexes with transition metals. Recently, organotin complexes with hydrazine-S-methylcarbodithioate were characterized by Iskander[36].

Furan derivatives' condensation products with S-methyl and S-benzyl dithiocarbazones were studied by Krutosikova et al.[37]. Chromium and molybdenum hexacarbonyls' complex formations with Schiff bases derived from S-methyl dithiocarbazate condensation products, were studied by Pandey[38].

A review on metal complexes with hydrazine carboxylic and hydrazine dithiocarboxylic acids is reported[39]. Tarafder has synthesized and characterized Ni(II) complexes of S-benzyl-ß-N-(furyl)methylene dithiocarbazate. Guliani[41] has studied the ^1H and ^{13}C NMR of Schiff base complexes.

Tridentate Schiff base complexes of N-methyl-S-methyl dithiocarbazate ligands with rhodium(I) have been reported by Gopinathan[42]. Only a few ruthenium complexes of dithiocarbazate Schiff bases have been reported so far.

The sulphur atoms in dithiocarbazates have the ability to participate in π-bonding in addition to σ donation, and hence these ligands are expected to give stable complexes.

Results and Discussion

4.1 Schiff base complexes of ruthenium(II)

A. Schiff base ligands

Schiff base ligands were prepared by reacting desired aldehydes or ketone, with S-methyl dithiocarbazate. In all ten ligands were prepared and their spectral properties were studied. The ligands prepared and their abbreviations used were:

a) Hydrazine carbodithioic acid [1-(2-pyridyl) methylene]methyl ester [HPyCDTC]

b) Hydrazine carbodithioic acid [1-(2-pyridyl) ethylidine]methyl ester [HAcPyDTC]

c) Hydrazine carbodithioic acid [1-(thienyl)methylene]methyl ester [HThCDTC]

d) Hydrazine carbodithioic acid [1-(2-thienyl)ethylidine] methyl ester [HAcThDTC]

e) Hydrazine carbodithioic acid[1-(2-furanyl) methylene]methyl ester [HFCDTC]

f) 3-Methyl-5-hydroxy-5-methyl-2-pyrazoline-1-carbodithioic methyl ester [HAcacDTC]

g) 3-Phenyl-5-hydroxy-5-methyl-2-pyrazoline-1-carbodithoic methyl ester [HBzacDTC]

h) Methylenebis-[-4,4'-(3,5-dimethyl-5-hydroxy)-2-pyrazoline] -1-carbodithioic methyl ester [H_2DAHDDTC]

i) Methylene bis-[4,4'-(3-phenyl-5-methyl-5-hydroxy)-2-pyrazoline]-1-carbodithioic methyl ester [H_2DBHDDTC]

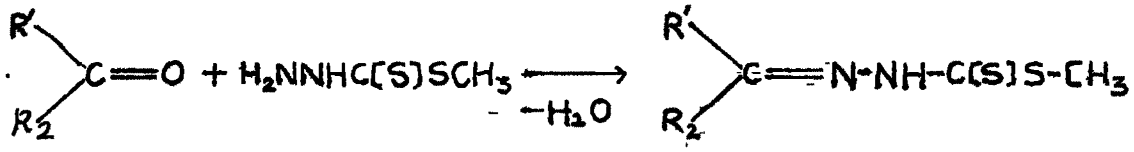
j) Methylene bis-(4,4'-(3,5-diphenyl-5-hydroxy)-2-pyrazoline)-1-carbodithioic methyl ester [H_2TBPDTC]

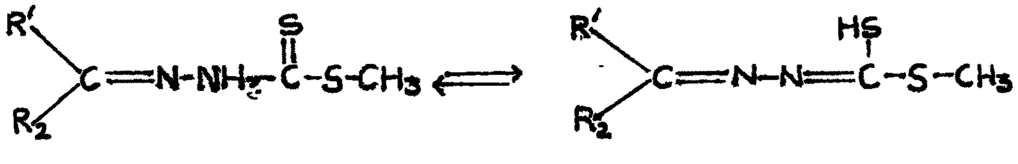
k) p-Xylyline bis-[4,4'-(-3,5-dimethyl-5-hydroxy)-2-pyrazoline]-1-carbodithioic methyl ester [H_2pXyTacDTC]

Ligands (a) to (e) were prepared by mixing the corresponding aldehyde or ketone in alcohol and refluxing for 1-2 h, and recrystallizing the product from alcohol.

Ligands (f) and (g) were prepared by stirring the ß-diketones, acetylacetone or benzoylacetone, with S-methyldithiocarbazate in alcohol, at room temperature for 16 h. The ligands (h) ,(i) and (k) were prepared by refluxing the corresponding bis-(ß-diketone) with S-methyl dithiocarbazate in alcohol for 3 h. The ligand (j) was prepared by refluxing an alcoholic solution of tetrabenzoyl propane (H_2TBP) with S-methyldithiocarbazate containing 2 or 3 drops of concentrated hydrochloric acid for 3 h. [Table 4.6.1].

4.1.1 IR Spectra





THIONOFORM-A THIOLOFORM-B

The Schiff bases can exist as thiono-thiolo tautomer, though the available evidences show the compounds to exist in the thiono form. The IR spectra of the solid compounds do not show any band for the -SH group. This is further supported by ^{1}H NMR spectra as no signal corresponding to -SH is observed. However, Singh [47] has observed that though the solid form Schiff bases derived from β-diketones do not show any band for -SH, their ethanolic solution spectra show a band around 2570 cm^{-1}, indicative of thiolo form. There are those who believe that the Schiff bases may exist in a thiono-thiolo equilibrium, in the solution state[4,11,45].

4.1.1.1 The Schiff base (a) shows peaks at 3092m, 1584s, 1566s, 1530, 1281s, 1046s, 955m, 929m cm^{-1}. The assignments of IR peaks were made by comparison with the reported values for similar compounds. Thus, the band at 3092 was assigned to νNH[4,49,8,51]. The bands at 1584 and 1565, 1530 cm^{-1} can be assigned to ν C=N, ν C=C and pyridine ring vibration[48,50,52-56]. Although the modes of vibration of both C=N and C=C may couple with each other, the bands at 1584 and 1530 cm^{-1} may be safely assigned to the C=N stretching vibrations of the azomethine group, since the frequency of these two bands are lowered by about 10-15 cm^{-1} in the IR spectrum of the metal complex. This is confirmed by the work of Dudek[57] who studied the N^{15} induced shifts in the IR bands of N-aryl Schiff base complexes, and the work of Percy and Thornton[58] who concluded that of the three bands occurring at 1615, 1605 and 1598 cm^{-1} in the IR spectra of N-aryl Schiff bases those at 1615 and 1598 cm^{-1} were due to C=N stretching and that at 1605 cm^{-1} was due to the aromatic C=C vibrations. The bands at 1281 and 955 cm^{-1} may be assigned to ν C-N + ν C-S and ν C-S + ν C-N respectively[48,51]. Akbar Ali has assigned the values at 1235sh and 955s, in the naphthaldehyde thio Schiff bases, to CN+CS and CS+CN respectively[48,51]. The band at 1046 cm^{-1} may be assigned to ν(C=S}. Patel and Shankaranarayana[59] have assigned the band around 1000 cm^{-1} in dithiocarbamates as the assymetric CSS stretching. Mookerjee[60] has assigned the band at 1030 cm^{-1}, in the ß-diketone dithio Schiff bases, to the (C=S), which disappears on complexation with metals. The band seen at 929 cm^{-1} may be assigned to ν(N-N)[52,53].

4.1.1.2 The IR spectrum of Schiff base (b) shows peaks at 3150, 1616s, 1579s, 1563m, 1275s, 1062s, 1044m, 991s and 955 cm^{-1}. These bands may be assigned similarly to those of Schiff base (a). Thus, the band at 3150 cm^{-1} is assigned to

N-H, the three bands at 1616, 1579 and 1563 cm^{-1} to C=N and C=C and pyridine ring vibrations. The bands at 1275 and 991 cm^{-1} may be assigned to ν C-N + νC-S and ν C-S + ν CN respectively. The bands at 1062 and 1044 cm^{-1} may be assigned to CSS vibrations and the one at 955 cm^{-1} to N-N.

4.1.1.3 The IR spectrum of Schiff base (c) shows peaks at 3097s, 1627s, 1592s, 1536s, 1252,1224,1086s, 1041s, 951.5 and 936 cm^{-1}. The band at 3097 cm^{-1} is attributed to NH. The three bands 1627s, 1592, 1536 cm^{-1} are attributed to C=N and C=C. The bands at 1592 and 1536 are affected by complexation and hence assigned ν C=N and the one at 1627 cm^{-1} to ν C=C. The bands at 1252, 1224 and 951 cm^{-1} were attributed to CN+ CS and CS+ CN respectively. The bands at 1086 and 1041 cm^{-1} were assigned to CSS and the band at 936 cm^{-1} to N-N.

4.1.1.4 The IR spectrum of Schiff base (d) shows bands at 3097s, 1653s, 1589m, 1529s, 1232s, 1098s, 1034s, 955s and 930m cm^{-1}. The band at 3097 cm^{-1} was attributed to ν NH, and the ones at 1653 and 1589 cm^{-1} were assigned to ν C=N and the band at 1529 to C=C. The bands at 1223 and 955 cm^{-1} were assigned as the combination bands C-N + C-S and C-S + C-N respectively. The bands at 1098 and 1034 cm^{-1} were assigned to CSS vibrations and the one at 930 to N-N vibration.

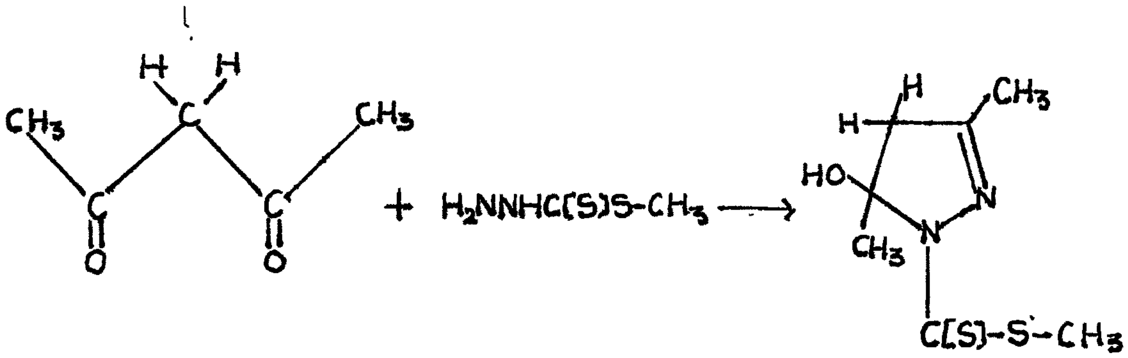
4.1.1.5 The spectrum of Schiff base (e) shows peaks at 3130s, 1612s, 1546m, 1526s, 1325s, 1221s, 1099s, 1074s, 1046s, 1010s, 960s and 945 cm^{-1}. The band at 3130 cm^{-1} was assigned to (NH) and the bands at 1612 and 1526 cm^{-1} were attributed to νC=N, and the one at 1546 cm^{-1} to νC=C. The bands at 1221 and 960 cm^{-1} were assigned as the combination band ν C-N +νC-S and νC-S + νC-N respectively. The bands at 1099 and 1074 cm^{-1} were assigned to-CS vibrations. The band at 1046 cm^{-1} was assigned to ν(C=S) and the one at 1010 cm^{-1} to the (C-O-C) of the furan ring. The band at 945 cm^{-1} was attributed to (N-N) mode.

Tarafder[40] has assigned the values for S-benzyl β-N-(furyl)methylene dithiocarbazate which compare well with our data.

4.1.1.6 Schiff bases of β-diketones

The Schiff base (f) IR spectrum shows peaks at 3404m, 1633s, 1584s, 1247s, 1227s, 1116s, 1091s, 1031s, 1003s, 985s, 961s and 912s cm^{-1}. The band at 3404 cm^{-1} was assigned to OH, attached to a carbon of C-N. The band at 1633 and 1584 cm^{-1} were assigned to νC=N. The bands at 1247, 1227 and 961 cm^{-1} were attributed to combination bands of νC-N + νC+S and νC-S + νC-N. The bands at 1091, 1031 and 1003 cm^{-1} were attributed to CSS modes. The band at 912 cm^{-1} was attributed to ring C=N-N.

These values are entirely different from the values so far reported for unchelated, monosubstituted acetylacetone dithio Schiff base[8,47,52,60-62]. For justifying the different IR values, we are proposing a structure for our product, similar to the one proposed by Iskander[34], with the help of ^{1}H NMR, ^{13}C NMR, mass spectra, microanalysis and X-ray structure for a similar compound.

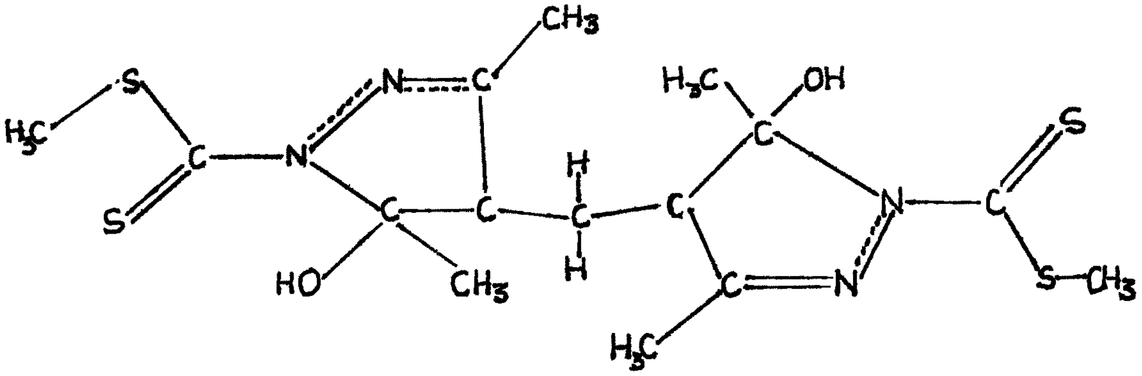


Such a structure is feasible as established by the work of Hedbom et al[63] where they have isolated an intermediate product, with similar structure, from the reactions of acetylacetone with nicotinyl hydrazine and benzoyl hydrazine.

4.1.1.7 The IR spectrum of Schiff base (g), shows peaks at 3648-3464bm, 1628s, 1609sm, 1571s, 1503s, 1283s, 1087s, 1057s,1034s,1013s, 1000.2m, 983s, 969s, 948m and 913m cm^{-1}. The broad band at 3648-3466 is attributable to ν OH, the bands at 1628, 1609 and 1571 cm^{-1} to ν C=N and ν C=C. The bands at 1503 and 1034 cm^{-1} are probably due to ν C-N and C=S[62]. The band at 1283 cm^{-1} is assigned to C-N + C-S and the band at 969 to C-S + C-N. Mookerjee et al.[60] have assigned the band around 1260 cm^{-1} to phenolic C-O stretching. The bands at 1087 and 1013 cm^{-1} can be assigned to C=S, and the band at 948 cm^{-1} to ν (N-N).

In this case also, a 1,3,5,5-tetrasubstituted 2-pyrazoline structure as in the case of Schiff base (f) has been proposed.

4.1.1.8 The Schiff base (h) derived from 3,5-diacetyl-2,6-heptanedione and S-methyl dithiocarbazate, in its IR spectrum, showed bands at 3305, 1633s, 1584s, 1243s, 1091s, 1052m, 1011m, 991s, 958m, and 944 cm^{-1}. The band at 3305 cm^{-1} was attributed to νOH and the bands at 1633 and 1584 cm^{-1} to ν C=N. The band at 1243 cm^{-1} was attributed to C-O[60] and the bands at 1221 and 958 cm^{-1} to (C-N) + C-S and (C-S) + C-N respectively. The bands at 1091 and 1011 cm^{-1} were assigned to ν C=S and the band at 944 cm^{-1} to ν (N-N). The structure proposed is similar to that of Schiff base (f) and has been conclusively proved by X-ray crystal structure.

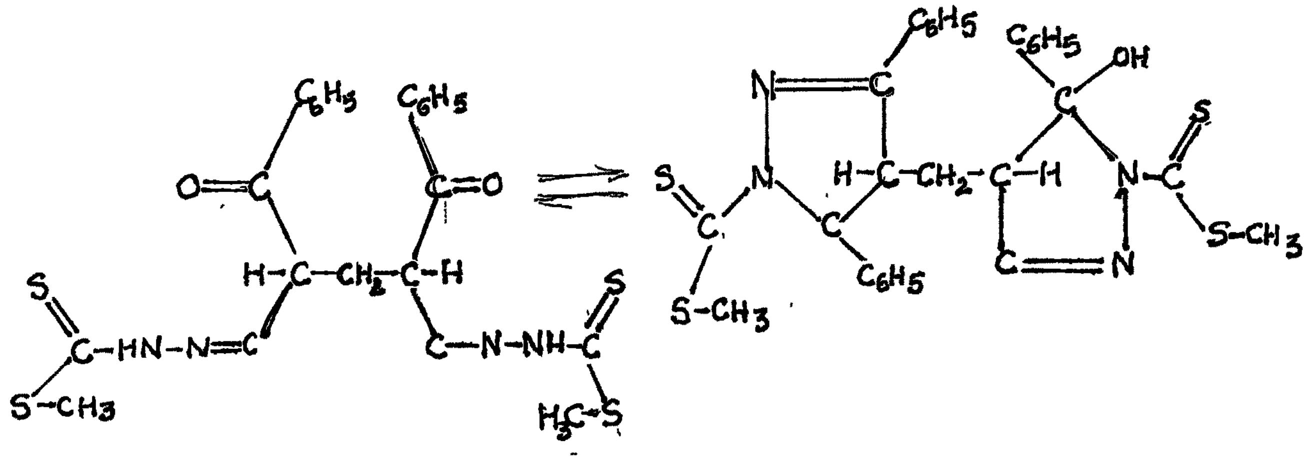


4.1.1.9 The IR spectrum of Schiff base (i) showed peaks at 3291s, 1633s, 1494s, 1259s, 1197s, 1100s, 1055s, 1031s, 988m, 962s and 944m cm^{-1}. The band at 3291 can be assigned to ν (OH), and the one at 1633 to ν (C=N) and the band at 1494 to ν (C=C). The band at 1259 cm^{-1} may be due to

(C-O)[60]. The bands at 1197 and 962 cm^{-1} were attributed to (C-N) + (C+S) and (C-S) + (C-N) respectively. The band at 1055 cm^{-1} may be due to (C-S) and the ones at 1100 and 1031 cm^{-1} due to ν (C=S). The band at 944 cm^{-1} was attributed to ν (N-N).

The structure of the Schiff base, is similar to Schiff base (f).

4.1.1.10. The spectrum of Schiff-base (j) showed bands at 3448s, 1690s, 1670s, 1596s, 1578s, 1290s, 1255s, 1059s, 1020s, 1018s, 999m, 968m, 915s. The band at 3448 cm^{-1} was assigned to ν (OH), and those at 1690 and 1670 cm^{-1} were due to unchelated ketonic C=O, 1596 cm^{-1} to ν (C=N) and the one at 1578 to ν (C=C). The band at 1290 cm^{-1} may be due to (C-O)[60], and the bands at 1255 and 968 to (C-N) + (C-S) and (C-S) + (C-N) respectively. The band at 1059 cm^{-1} was probably due to (C-S), the bands at 1020, 1018 and 999 cm^{-1} were assigned to (C=S). The band at 951 cm^{-1} may be assigned to (N-N). This compound probably exists both as cyclized and uncyclized dithiocarbazate.



4.1.1.11 The IR spectrum of Schiff base (k) showed peaks at 3310-3395s, 1629s, 1516s, 1269s, 1234s, 1198s, 1090s, 1062s, 1032m, 986m, 954s and 915m. The broad band 3310-3395 cm^{-1} was attributed to ν(OH), the one at 1629 cm^{-1} to ν(C=N) and the one at 1516 cm^{-1} to ν(C=C). The band at 1269 cm^{-1} may be due to ν(C-O)[60] and the ones at 1234 and 986 cm^{-1} may be assigned ν(C-N) + ν(C-N) and ν(C-S) + ν(C-N) respectively. The band at 1062 cm^{-1} may be due to ν(C-S) and the bands at 1090 and 1032 cm^{-1} were attributed to ν(C=S).

4.1.2.0 The NMR studies on hydrazine dithiocarbazate Schiff bases are comparatively complicated and less known, and therefore, there are chances of misinterpretation of the available data. In the present work we are attempting a detailed study on some more Schiff base ligands by ^1H and ^{13}C NMR.

^1H NMR

4.1.2.1 The ^1H NMR spectrum of Schiff base (a) showed resonance signals at 8.89(d), 8.84d, 7.62d, 7.54m, 7.41, 2.64 and 10.24 and 15.5δ. The signal at 8.89 was assigned to azomethine H, 7.62 - 7.41 to aromatic protons, and the one at 2.64 was assigned to -S-CH_3. There were two signals downfield at 15.5 and 10.24 attributable to NH. Pardhy et al[42,44] have assigned very similar values for similar dithiocarbazate Schiff-bases. Though Mookerjee et al[60] have observed a signal at 4.43δ corresponding to -SH resonance, we could not observe any signal in that region. [FIG.4.5.1]

4.1.2.2 The ^1H NMR spectrum of Schiff-base (b) showed resonances at 7.5, 7.32, 6.96, 6.90δ all assignable to pyridine ring protons, at 2.58 and 2.23δ attributed to $-S-CH_3$ and $-C-CH_3$ respectively. The resonance corresponding to NH is observed at 9.98 . Klayman[18], Al-Jeng Lin and Daniel Klayman [13] have reported a somewhat similar values for the ligand.

4.1.2.3 The ^{1}HNMR spectrum of Schiff-base (c) showed signals at 8.1s, 7.5-7.4m, 7.27, 7.05, 6.97, 6.92, 10.45 and 2.55δ. The signals at 8.1 was assigned to the azomethine CH, 7.5-6.92 to ring protons and 2.58 to $S-CH_3$. The signal due to N-H is seen at 10.45 .

4.1.2.4 The ^1H NMR spectrum of Schiff base (d) showed signals at 7.6 to 6.92δ for the thiophene ring protons, 2.61 due to $-S-CH_3$, 2.28 for $C-CH_3$ and at 9.86 assignable to NH. Pai[24] has prepared a similar compound and assigned comparable values.

4.1.2.5 The spectrum of Schiff-base (e) showed resonance at 7.74s, 7.6d, 7.48d, 7.01s, 6.75t, 6.5-6.42m, 10.7, 11.92 and 2.63δ . The signal at 7.74 δ is assigned to azomethine CH, 6.42 to 7.60 to furan ring protons and the signal at 2.63δ attributed to $-S-CH_3$. Two signals at 10.7 and 11.92, corresponding to N-H were observed. Tarafder[65] and

Iskander[35] have reported similar results for furanyl Schiff-bases. [Fig. 4.5.4]

Schiff-bases from ß-diketones

4.1.2.6 The ^1H NMR spectrum of the Schiff-base (f) showed signals at 6.26, 3.3-2.72q, 2.51, 2.01 and 1.97δ. As already discussed in the earlier part about IR spectra of ß-diketone Schiff-bases, the values obtained by us did not totally agree with the reported, barring the values of methyl group resonances. [Fig. 4.5.6]

Thus, the signal at 6.26δ is attributed to OH attached to a quarternary carbon. The signal disappeared on D_2O exchange, thus confirming our hypothesis. Such a structure has been reported for the intermediate reaction product of nicotinoyl hydrazone and benzoyl hydrazone, with acetylacetone, by Hedbom et al.[63] They obtained a signal for OH attached to a quarternary carbon at about 5.2 , which disappeared on D_2O treatment. The quartet (Jc 20 Hz) at 3.33 to 2.72δ was assigned to a non-equivalent CH_2 group resonance. The signal at 2.51δ was assigned to methyl groups $-S-CH_3$, the signal at 2.01δ to $(N=C-CH_3)$ and the signal at 1.97δ to $-C-CH_3$ resonance. These assignments were ably supported by the ^{13}C NMR spectrum also.

4.1.2.7 The spectrum of Schiff base (g) showed signals at 7.30, 6.44, 3.55 to 2.83q, 2.46 and 2.1δ. The signal at

7.30 was attributed to aromatic ring protons, the signal at 6.44 to OH, and the quartet at 3.55 to 2.88 (j_H 22Hz) to uneven CH_2. The signal at 2.46 was attributed to $-S-CH_3$ and the one at 2.1 to $N=C-CH_3$.

4.1.2.8 The Schiff-base (h) NMR spectrum showed signals at 6.66 to 6.6, 3.26-3.10q, 2.83q, 2.5, 2.1 and 1.85δ. The signal at 6.66 was assigned to -OH, the quartet at 3.26-3.10 was assigned to the uneven CH of the acetylacetone moiety and the other quartet at 2.53 to the CH_2 linking the two acetylacetone moities. There were three signals for methyl groups, the one at 2.5 being assigned to $-S-CH_3$, the one at 2.1 to $N=C-CH_3$ and the one at 1.85 to $-COH-CH_3$.

4.1.2.9 The spectrum of Schiff base (i) showed resonance peaks at 7.38-6.85, 6.77, 3.55 to 3.40q, 2.85, 2.91, 2.46 and 2.15δ. The signals at 7.38-6.85 were assigned to aromatic protons, the signal at 6.77 to -OH, and the quartet at 3.55 to 3.40 to uneven CH. The linking CH_2 showed major signals at 2.85 and 2.71. The signal at 2.46 was attributed to $-S-CH_3$ and the one at 2.15δ to $N=C-CH_3$.

4.1.2.10 The spectrum of ligand (j) showed resonance at 7.82q, 7.33-6.83, 4.45-4.33q,3.76, 2.46 and 2.45δ. This ligand did not have a deuterium exchangeable hydrogen. The spectrum showed the presence of two types of phenyl rings at

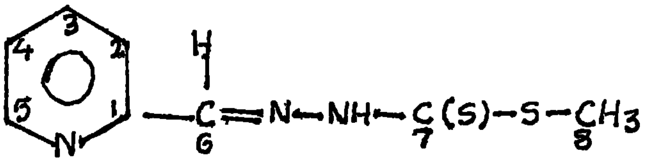
7.82 and 7.33-6.83δ. The signal at 4.45-4.33δ was assigned to an uneven CH, the signal at 3.76δ to linking CH_2 and the signals at 2.45 and 2.46 δ to two different types of methyl groups. This compound probably exists as a mixture of chelated and unchelated hydrazine dithiocarbazate groups.

4.1.2.11 The ligand (k) had signals in its ^1H NMR spectrum at 7.3-7.15, 6.45, 3.66q, and 3.33 to 2.61m, 2.48, 1.83 and 1.75δ. The signals at 7.3 and 7.15 were assigned to the xylene ring protons, the signal at 6.45 to -OH and the quartet at 3.66 to CH. The multiplet at 3.33 to 2.61 may be due to CH_2 of the xylene. There are three different methyl group resonances, the one at 2.48 was assigned to $-S-CH_3$, the one at 1.83 to $N=C-CH_3$ and the one at 1.75δ to $HO-C-CH_3$.

4.1.3.0 ^{13}C NMR

Carbon-13 NMR spectra of the hydrazine dithiocarbazoic acid derivatives are practically unknown. Guiliani[41] has studied the platinum complexes of derivatives of dithiocarbazic acid ligand by ^1H NMR and ^{13}C NMR, mainly complexes of S-methyl dithiocarbazate and S-benzyldithiocarbazate. The values assigned by him for $S-CH_3$ is 17.50, C=S 199.87, (198.15 for S-benzyl), 39.39 for CH_2 of benzyl and aromatics 136.2m 129.14m, 128.74o, and 127.73 for p-carbon atoms of the ring. When dealing with ^{13}C NMR the symbols q and i denotes quarternary and inverted for the carbon signals.

4.1.3.1 Schiff-base (a), in its ^{13}C NMR spectrum showed resonances at 202.2q, 151.6q, 148.5, 137.6, 135.0, 125.7, 124.2 and 17.3δ [Fig. 4.5.2].



The signal at 202.2 was attributed to C=S, at 151.6 to (C_1) of the ring, and the one at 148.5 to (C_5). The signal at 137.6 was assigned to (C_6) the azomethine carbon, and the signals at 135.0, 125.7, 124.2 were assigned to C_2, C_3 and C_4 of the ring respectively. The signal at 17.3 was assigned to the $-S-CH_3$. These assignments were supported by the DEPT spectrum, where the quarternary (without hydrogen) carbon signals disappear, and the carbon having even number of hydrogen atoms attached give inverted peak leaving only the carbon atoms having odd number of hydrogen attached in the original position. In the case of ligand (a) the DEPT spectrum showed signals only at 148.5, 137.6, 135.0, 125.7, 124.2 and 17.3δ. The numbering of the carbon atoms are as shown in the diagram.

4.1.2.2 The ^{13}C NMR spectrum of Schiff base (b) showed signals at 200. 6q, 144.9q, 142.2q, 129.0, 127.8, 127.3, 17.6 and 13.7δ. They were assigned correspondingly to C=S,

C_1, C_6=N, C_5, C_2, $C_{3,4}$ -S-CH_3 and C-CH_3. respectively.

4.1.2.3 The spectrum of Schiff base (c) showed signals at 200.0q, 139.4, 137.5q, 131.3, 129.6, 127.7 and 17.7δ. The signal at 200.0 was assigned to C=S. The signal at 139.4 was attributed to (C_5=N) and the signals at 137.5, 131.3, 129.6 and 127.7 were assigned to C_1, C_4, C_2 and C_3 of the thiophene ring respectively. The signal at 17.7 was attributed to S-CH_3.

4.1.3.4 The spectrum of the ligand (d) showed resonances at 200.7q, 145.0q, 142.2q, 129.0, 127.8, 127.3, 17.6, and 13.7δ. They can be assigned to C=S, C=N, C_1, C_4, C_2 and C_3 of the thiophene ring, -S-CH_3 and C-CH_3 respectively. [Figs.4.5.3a and b].

4.1.3.5 The spectrum of the ligand (e) showed signals at 201.9q, 200.4q, 148.7q, 145.8, 135.2, 128.2, 117.4, 115.4, 112.51 and 17.9δ. The compound appears to be a mixture of isomers. The signals at 201.9 and 200.4 were assigned to C=S. The signal at 148.7 to C_1 of the furan ring, 145.8 to C=N. The signals 135.2 to 112.5 were assigned to C_4, C_3 and C_2 of the furan ring. The signal at 17.9 was assigned to -S-CH_3 [Figs. 4.5.5a and b].

4.1.3.6 Schiff-bases of β-diketones

The ^{13}C spectrum of Schiff-base (f) showed signals at

192.81q, 158.98q, 96.35q, 52.81i (invert), 26.14, 17.75 and 16.486. No signal for carbonyl C=O, about 185-190 was seen, indicating the absence of any free C=O group in the ligand. The signal at 192.81 was assigned to C=S. The signal at 158.98 was assigned to quarternary C=N, carbon. The signal at 96.35 was attributed to quarternary C-OH. There were three signals observed for methyl carbons. The signal at 26.14 was assigned to the CH_3 attached to the carbon containing OH attached, and the signal at 17.75 was assigned to $-S-CH_3$ and the signal at 16.48 to methyl group attached to the carbon containing double bonded nitrogen. The signal at 52.81 was assigned to CH_2 of the ligand, from DEPT spectrum. The DEPT spectrum did not show any signals at 192.81, 158.98 and 96.35 assigned to quarternary carbon atoms. The signal at 52.81 assigned to $-CH_2$ was inverted showing even number of hydrogen atoms attached to it [Figs.4.5.7a &b].

4.1.3.7 The spectrum of Schiff-base (g) showed signals at 193.0q, 157.0q, 142.2q, 128.6, 127.9, 123.8, 97.19q, 54.70i, 17.4 and 16.06. DEPT spectrum did not have signals at 193, 157.9, 142.2 and 97.19, and the signal at 54.70 was inverted. Hence, the assignments were 193.0 (C=S), 157.9 (C=N), 142.2 (C_1 of the phenyl ring) 128.6 (C_2 and C_6 of phenyl ring) 127.9 (ring C_4), 123.8 (ring C_3,C_5), 97.19, C attached to OH, -N, 54.70 (CH_2 of benzoylacetone), 17.4 $-S-CH_3$ and 16.00 $CH_3-C=N$ [Figs. 4.5.8a and b].

4.1.3.8 The spectrum of Schiff base (h) showed signals at

192.6q, 162.4q, 96.30q, 58.2, 27.4, 22.9i, 17.2, and 14.3δ. DEPT spectrum did not show signals at 192.6, 162.4, and 96.3 and showed an inverted signal at 22.9. Based on these results, assignments were made as 192.6 (C=S), 162.4 (C=N), 96.3 (N-C-OH), 58.2 (CH), 27.4 ($HO-C-CH_3$), 22.9 (CH_2 linking), 17.2 ($-S-CH_3$ and 14.3 ($(N=C-CH)_3$) [Figs. 4.5.9a & b].

4.1.3.9 The ^{13}C NMR spectrum of ligand (i) showed signals at 193.2q, 161.6q, 142.9q, 128.7, 128.1, 127.8, 123.8, 123.4, 97.6q, 60.8, 23.1i, 17.3, 15.5 and 14.5δ. DEPT spectrum did not show signals at 193.2, 161.6, 142.9 and 97.6 and showed inverted signal at 23.1.

Based on these results, assignments were made as 193.2 (C=S), 161.6 (C=N), 142.9 (C_1 of ring), 128.7-123.4 (ring carbons), 97.6 (C-OH), 60.8 (CH), 23.1 (CH_2), 17.3 ($-S-CH_3$) and 15.5 and 14.5δ ($N=C-CH_3$) [Figs. 4.5.10a and b].

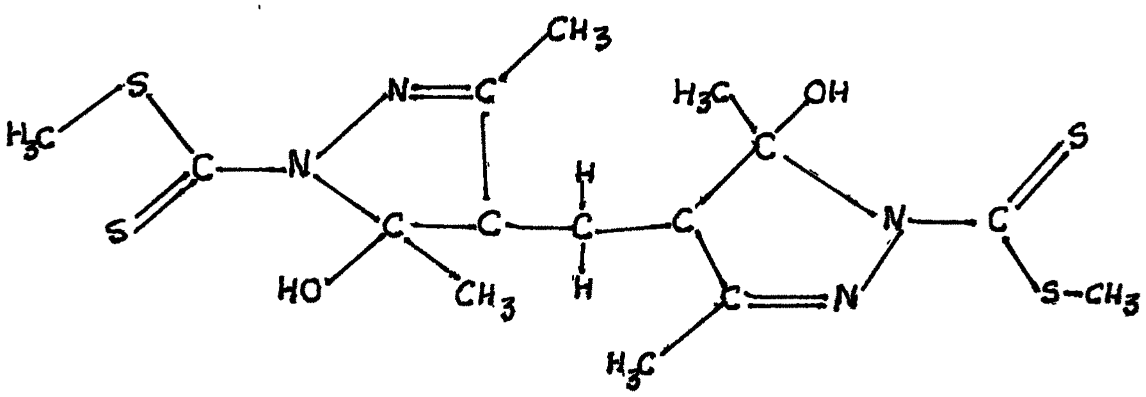
4.1.3.10 The ^{13}C spectrum of Schiff base (j) showed signals at 200.1q, 194.0q, 159.8q, 152.8q, 143.72q, 142.69, 133.25 to 127.37, 123.80, 120.93q, 99.58q, 96.01q, 57.23, 55.31, 27.12i, 23.60q, 19.64, 19.49i, and 17.38δ. DEPT spectrum showed signals only at 133.24 to 127.37, 123.8, 57.23, 55.31, 19.64, 17.38 and inverted signals at 27.12 and 19.49. Because of the multiplicity of signals assigning was very difficult. The spectrum indicates that the compound exists as a mixture of isomers. Attempt has been made to assign only salient signals. The signals may be assigned as

203.7, 194.04 (C=S), 159.59, 152.76 (C=N), 143.72, 142.69 (C_1 of the ring), 133.34 to 123.8 (aromatic C), 99.58 and 96.0 (HO-C-N), 57.23, 55.31 (CH), 27.12, 19.49 (CH_2), 17.38 (S-CH_3).

4.1.3.11 The ^{13}C NMR spectrum of ligand (k) showed signals at 192.76q, 191.91q, 161.95q, 136.76q, 135.6q, 129.19, 128.10, 98.8q, 96.08q, 61.71, 59.25, 31.80i, 31.27i, 26.66, 19.71, 17.20, 15.73 and 15.58δ. The spectrum shows two sets of value, probably of isomers in the approximate ratio of 80:20. The major signals were 192.76q, 161.95q, 136.76q, 96.08q, 61.71, 31.80i, 17.20 and 15.73δ. The DEPT spectrum showed signals at 129.19 - 128.10, 61.71, 26.66, 17.20 and 15.73 and inverted signal at 31.80. The corresponding assignments for the major signals were 192.76 (C=S), 161.95 (>C=N), 136.76 (ring C_1), 129.19 to 128.10 ring carbons, 96.08 (-C-OH), 61.71 (-CH), 31.81 (-CH_2), 26.66 (-C-CH_3) 17.20 (-S-CH_3) and 15.73, (N=C-CH_3).

X-ray crystal structure of the compound methylene bis-(3,5-dimethyl-5-hydroxy-2-pyrazoline-1-carbodithioic methyl ester) $C_{15}H_{24}N_4O_2S_4$.

The compound $C_{15}H_{24}N_4O_2S_4$ belongs to monoclinic space-group P21/c with the unit cell dimensions a = 9.794, b = 12.124, c = 17.992 A and β = 105.26°. The structure was solved by direct methods. The atomic positions are given in Table 4.6.9 . Figure 4.5.17 gives the perspective view of the molecule. Refinement of the structure is in progress.



4.1.3.12 Mass Spectra The mass spectra of the carbodithioate Schiff bases have not been published in detail. We have recorded the spectra of a few Schiff bases. Molecular ions have been found out in all the cases. The ligands seem to dissociate first by the elimination of the $-S-CH_3$ group (m/e 47) as seen from the spectra. Detailed studies on the fragmentation mechanism are in progress and require confirmation before publication. The decomposition pattern of the ligands is given in Table 4.6.10 The spectra of ligands HAcPyDTC, HAcThDTC, HFCDTC, HAcacDTC, HBzacDTC, H_2DAHDDTC are given in figs. 4.5.18 to 4.5.23 .

4.1.4 Schiff base complexes of ruthenium(II)

Schiff base complexes with $H_2Ru(CO)(PPh_3)_3$

The ruthenium(II) complexes were prepared by refluxing the corresponding Schiff base and $H_2Ru(CO)(PPh_3)_3$ in 1:1 molar ratio, in benzene- alcohol mixture.

4.1.4.1 The complex PYCDTC-RuH(CO)$(PPh_3)_2$ showed bands at 1992, 1919.5, 1581.6, 1560, 1522, 1506, 1092, 1028 and 741 cm^{-1} in its IR spectrum. The weak band at 1992 was attributed ν (Ru-H), which is higher than in the starting $H_2Ru(CO)(PPh_3)_3$, but lower than that in $HRu(CO)Cl(PPh_3)_3$. This positive shift may be attributed to stabilization due to chelation. The terminal C≡O of the complex is seen at 1916.5 cm^{-1}, which is less than the value reported for β-diketone complexes[66]. The reduction in frequency is attributed to presence of an azomethine (H-C=N) group trans to the carbonyl ligand. The ligand spectrum showed a band at 3091 attributed to ν(N-H), which disappeared on complex formation. There were no bands around 2550 cm^{-1} indicating the absence of any thiol form. Akbar Ali[8,9,67] suggested that these Schiff bases existed in the solid as thione form, but in solution, they probably remain in equilibrium with the tautomeric thiol form. It has been stated that the thione form is relatively unstable and tends to a stable thiol form if there is at least one hydrogen atom adjacent to the C=S bond[68].

The thiol form deprotonates and coordinates to the metal through the α-nitrogen and thiol sulphur on complexation. This has been confirmed by the lowering of the C=N frequency and the disappearance of the C=S band at about 1060 cm^{-1} on complex formation and a M-S vibration at a lower frequency (30-40 cm^{-1}) in the complex[52]. Therefore the bands at 1585, 1552 and 1508 cm^{-1} were assigned to (C=N) the higher value was accorded to the noncoordinating

(C=N) and the lower frequency to the coordinating C=N. The band at 1560 cm^{-1} was assigned to the pyridine ring vibration. The strong band at 1092 was due to P-C bond which shifts slightly to higher frequency indicating insignificant back-bonding between ruthenium and phosphorus on complexation[70]. The medium to strong bands appearing in the complex at 1028 and 741 cm^{-1} may be attributed to C-S bands, a negative shift of ~20-30 cm^{-1} from the corresponding bands at 1046 and 777 cm^{-1} in the ligand. This changes in the C=S bands of the complex are compatible with the monodentate sulphur coordination of the CS_2 group to the metal[67,69]. A band appearing at 952 cm^{-1} in the complex may be attributed to ν(N-N). These assignments are only tentative as the presence of phosphine groups in the complex makes correct assignments difficult.

The ^1H NMR spectrum of the complex showed resonances at 2.1, 7.6m, 8.44d, and 11.66δ. The S-methyl resonance of the complex was observed at 2.1δ, a shift of about 0.55δ into the high field. This shift may be attributed to the chelate ring formation with coordination of the metal through the thione sulphur atom. The azomethine -CH- was resonating at 8.44. The resonance due to (N-H) was absent in the spectrum. A new resonance in high field at -11.6 was observed. This can be assigned to Ru-H resonance. The absence of NH resonance and the high field shift of S-methyl resonance suggest coordination through the N and S atoms of the ligand to the metal, thus confirming the suggestion from the IR data. The ^{13}C NMR spectrum of the ruthenium(II) complex showed signals 206, 192, 153, 148, 144-121 and 149δ. The signal at 206 was assigned to terminal carbonyl on ruthenium. The signal for C=S has shifted upfield from 202 in the ligand to 192 , indicating its participation in the complex formation. There was a down field shift for both C_1 and C_5 of pyridine ring by about 2-3 ppm on complexation. The signal due to azomethine carbon did not change after complexation and remained at 148δ. The S-methyl carbon shifted to up field and was obsedrved at 14.9 δ. This can be explained as the effect of chelation through the thione sulphur and consequent shielding of the methyl group. Similar shielding is observed in the case of ^{1}H NMR also [Figs.4.5.11a and b].

4.1.4.2 The IR spectrum of the ruthenium complex of Schiff base HAcPYDTC, showed bands at 1989m, 1915s, 1580m, 1511, 1527m, 1480s, 1093s, 1061s, 1029m, 955m, and 743s cm^{-1}. No band corresponding to ν NH or ν SH is observed in the spectrum, indicating their participation in the reaction. The band at 1989 cm^{-1} was assigned to Ru-H and the strong band at 1915 cm^{-1} to terminal carbonyl. The bands at 1580 and 1571, 1527 cm^{-1} can be assigned to ν C=N and pyridine ring vibrations respectively. The strong band at 1480 cm^{-1} may be due to coordinated C=N and phosphine groups. The band at 1093 cm^{-1} was assigned to P-C. The medium band at 1028 and strong band at 743 cm^{-1} may be attributed to coordinated - C-S. The medium band at 955 cm^{-1} may be attributed to -N-N.

The ^{1}H NMR spectrum of the complex showed bands at 1.96 (2s) 6.6-7.5 and -10.57δ. Both the methyl groups, NC-CH_3 and S-CH_3 resonate at 1.96 and upfield shift from 2.25 and 2.6δ, in the ligand respectively. Aromatic proton signals are observed at 7.3-7.5δ. The triplet at -10.57δ upfield were attributed to Ru-H. Very weak signals were observed at -8.16 and -14.1t indicating the compound may be existing as isomers. The same tendency to exist as isomers is noticed in the ^{13}C NMR spectrum of the complex also. The ^{13}C NMR spectrum of the compound showed signals at 205.1, 204.9, 195.7, 154, 152.2, 149.8, 148.5, 140.s, 124-120, 14.8, 14.6, 10.3 and 8.4δ. The signals at 205.1, and 204.9 were attributed to isomeric, terminal carbonyl group. The signal at 195.7 was attributed to C=S and the signal at 154, 152.2 to -C=N. The signal at 149.8 - 140.3 was attributed to C_1 of the pyridine ring. The one at 148 to C_5 and the signals at 124-120 to the other ring carbons. The signals at 14.8 and 14.6 were attributed to isomeric -S-CH_3 carbon while the signals at 21.9 and 11.1 were attributed to -C-CH_3 group isomers. This clearly indicates that the compound exist in isomeric form.

The assignments were made by the help of DEPT spectrum, whereby quarternary carbon signals disappear, carbon attached to even number of hydrogen atoms give inverse signals and only carbon atoms attached to odd number of hydrogen, retain their original vertical position. Thus, signal due to CH_2 inverse and signals due to CH and CH_3 retain their original position.

4.1.4.3 The IR spectrum of ruthenium(II) complex of ligand HThcDTC, showed bands at 1970w, 1918.5s, 1577s, 1541w, 1026s, 999m, 742s and 693s cm^{-1}.

Du Preez[28] has sugested that the oxygen atom in the furan ring and sulphur atom in thiophene ring increase the electron density on the coordinating C=N double bonds in such a way that stronger coordination by the nitrogen atom is possible. The stronger nitrogen coordination will shift the $(C\rightleftarrows N)$ vibration to lower energy.

The band at 1970 cm^{-1} was assigned to ν (Ru-H) and the one at 1918.5 to terminal carbonyl group. The strong band at 1577 and the weak band at 1541 cm^{-1} were assigned to non-coordinating ν(C=N) and coordinating ν(C=N). The bands at 1026, 999 and 742 cm^{-1} were attributed to ν (C=S). The medium band at 952 cm^{-1} was assigned to ν N-N.

The ^1H NMR spectrum of the complex showed signals at 2.0, 6.9 to 7.6(m), 7.8 and -11.66δ, which were assigned to-S-CH_3 aromatic protons, azomethine proton and Ru-H. The ^{13}C NMR spectrum of the compound showed signals at 206, 189, 140, 140-135, and 15δ assignable to $C\equiv O$, C=S, -HC=N, thiophene ring carbons, and -S-methyl carbon, respectively. [Figs. 4.5.12a and b].

4.1.4.4 The IR spectrum of the ruthenium(II) complex with HAcThDTC, showed bands at 2041m, 1942sh, 1923s, 1586w, 1564s, 1258w, 1034s, 999m, 739s and 696s cm^{-1}. They can be assigned to Ru-H, $C\equiv O$, C=N, C=C and C—S, respectively.

The ^1H NMR spectrum of the complex showed signals at

2.0,(2s), 6.9-7.7 and -10.66δ. The signals at 2.0δ were assigned to the two methyl groups of the complex, and the signals at 6.9-7.7 to aromatic protons and the signal at -10.66 upfield to Ru-H.

The ^{13}C NMR spectrum showed signals at 207, 195, 146, 148-124, 14.9 and 9.5δ. The signal at 207 was assigned to $C\equiv O$, and the signal at 195 was assigned to C=S. The signal at 146 was assigned to azomethine carbon. The signals at 148 to 124 were assigned to aromatic carbons. The signal at 14.9 was attributed to $-S-CH_3$ and the one at 9.5 was assigned to $C-CH_3$.

4.1.4.5 The IR spectrum of ruthenium complex FCDTC showed bands at 1966w, 1935s, 1602s, 1586m, 1572m, 1541m, 1065m, 999.7m, 745s and 697s cm^{-1}. The weak signal at 1966 and strong signal at 1935 cm^{-1} were assigned to νRu-H and $\nu C\equiv O$ respectively. The signal at 1602, 1586, 1572 and 1541 cm^{-1} were attributed to ν (C=N) and ν(C=C). The signals at 1065 and 745 were assigned to ν(C=S). The signal at 1016 cm^{-1} was probably due to C-O-C of the furan ring.

The ^{1}H NMR spectrum of the complex showed resonances at 2.0, 6.2-7.5, 8.1 and -11.75δ. The signal at 2.0 was assigned to $-S-CH_3$. The resonances at 6.2-7.5 were due to aromatic protons. The resonance at 8.1 was assigned to the azomethine proton. The high field signal at -11.75 was due to Ru-H. The ^{13}C NMR spectrum of the complex showed signals at 206, 189, 143, 150-112 and 14.8δ. The signals at 206 and 189 were assigned to C≡O and C=S respectively. The resonance at 143 was due to azomethine carbon. The signals at 150-112 were attributed to aromatic carbons. The resonance at 14.8 was assigned to $-S-CH_3$ [Figs. 4.5.13a and b].

4.1.5.0 Schiff base complexes with $HRu(CO)Cl(PPh_3)_3$

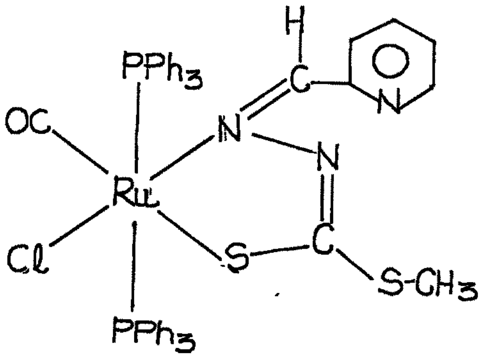
The ruthenium(II) complexes were prepared by refluxing the corresponding Schiff bases with $HRu(CO)Cl(PPh_3)_3$ in 1:1 mol ratio in alcohol-benzene mixture for 3 h.

4.1.5.1 The complex $PyCDTC-ClRu(CO)(PPh_3)_2$, showed bands at 1972s, 1607b,w, 1542w, 1507w, 1090s, 1059m and 984m cm^{-1}, in its IR spectrum. The band at 1972 cm^{-1} was assigned to the terminal carbonyl group. This has shifted to higher wave numbers compared to the starting $HRu(CO)Cl(PPh_3)_3$ ν (C≡O) 1900, 1920), indicating an increased C≡O bond order. This can be explained as due to the presence of electron withdrawing Cl group adjascent on the ruthenium. The reactants showed bands at 3091 (ν -N-H) and 2020 cm^{-1} ν-(Ru-H), both of which were absent in the product, indicating their participation in the reaction. The bands at 1607, 1542 and 1507 could be attributed to the non-coordinated and coordinated C-N groups ν C=C and pyridine ring vibrations. The strong band at 1090 was due to P-C bond. The medium band at 1059 may be attributed to C-S vibrations and the band at 984 to N-N vibration.

The ^1H NMR spectrum of the complex showed signals at 1.85, 7.3 and 7.75δ. The signal at 1.85 ppm was assigned to S-CH_3. Aromatic signals appeared at 7.3 δ and the proton on azomethine carbon at 7.75 ppm. Neither the N-H nor Ru-H signals were observed in the spectrum.

The ^{13}C NMR spectrum showed signals at 203.48, 175.34, 156.93, 153.60, 138.54, 132.89 to 125.76 and 17.9δ. These signals could be attributed to terminal carbonyl, C-S, C_1 of the ring, azomethine carbon, other ring carbons and methyl carbon.

From the above data from IR, ^1H NMR and ^{13}C NMR a structure similar to the hydrido complex is proposed.



4.1.5.2 The IR spectrum of the complex AcPyDTC.ClRu(CO)$(PPh_3)_2$ showed bands at 1958s, 1636m, 1090s, 1031m and 949m cm^{-1}. These can be assigned to terminal carbonyl, -CN, P-C, C-S and N-N vibrations respectively. No band was observed either around 3100 cm^{-1} or around 2000 cm^{-1} indicating the absence of N-H and Ru-H in the compound.

The ^{1}H NMR spectrum of the compound showed signals at 1.81, 1.92 and 7.36 assignable to C-CH_3, S-CH_3 and aromatics. No signal for NH or Ru-H was seen.

The ^{13}C NMR spectrum of the complex showed signals at 203.98, 187.80, 159.34, 154.38,140.09 to 128.43, 17.99 and 15.676. The signal at 203.98 was assigned to C≡O, the signal at 187.8 is due to C-S and the signal at 159.34 may be attributed to C=N. The signal at 154.38 may be due to C_1 carbon of the ring and signals 140.09 to 128.43 due to other aromatic carbons. The signal at 17.99 has been attributed to S-CH_3 and the one at 15.67 to C-CH_3.

4.1.5.3 The IR spectrum of the complex ThCDTC.ClRu(CO)$(PPh_3)_2$ showed bands at 1942s, 1650m, 1570m, 1091s, 1040m, and 959m cm^{-1}. No bands corresponding to νN-H or νRu-H vibrations were found. The band at 1942 was assigned to terminal carbonyl, the bands at 1650 and 1570 were assigned to νC=N and νC=C vibrations and the band at 1091 was assigned to P-C bond. The band at 1040 was assigned to C-S and the one at 959 cm^{-1} to N-N vibrations.

The ^{1}H NMR spectrum showed signals at 2.25, 6.7, 6.9, 7.30 to 7.48 and 7.7 ppm. These could be assigned to -S-methyl, thiophene ring protons, aromatic protons of phenyl ring and azomethine proton [Fig. 4.5.15].

The ^{13}C NMR spectrum of the sample could not be taken due to poor solubility.

4.1.5.4 IR spectrum of the complex AcThDTC.ClRu(CO)$(PPh_3)_2$

showed bands at 1942s, 1652m, 1558, 1531m, 1506m,1089m, 1073m, 1034m, 969m, and 942m cm^{-1}. The spectrum did not show any bands for N-H or Ru-H vibrations. The terminal carbonyl vibration was seen at 1942 and the bands at 1652, 1558, 1531 and 1506 cm^{-1} were assigned to non-coordinated and coordinated C-N and C=C. P-C was seen at 1089 cm^{-1}, the C-S vibrations at 1073, 1036 and 969m, and the N-N vibration was seen at 942 cm^{-1}.

The ^1H NMR spectrum of the compound showed signals at 1.72, 2.00, 6.9, 6.96, 7.1-7.3 and 7.45 ppm. These signals were assigned to C-CH_3, S-CH_3, thiophene ring protons and phenyl ring protons. No signals corresponding to N-H or Ru-H were observed.

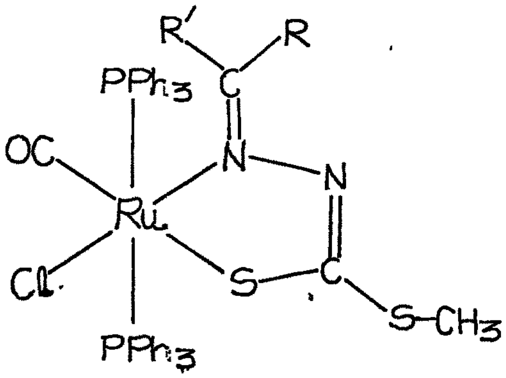
The ^{13}C NMR spectrum of the compound showed signals at 204.28, 179.90, 164.77, 134.91 to 124.91, 23.16 and 16.43 ppm. They can be assigned to terminal carbonyl, C-S, C-N, aromatic carbons, C-CH_3 and S-CH_3 respectively.

4.1.5.5 The IR spectrum of the complex FCDTC.ClRu(CO)$(PPh_3)_2$ showed bands at 1940s, 1652m, 1586m, 1573m, 1540m, 1090s, 1037s, 1010m, 961m and 933m cm^{-1}. The band at 1940 was assigned to the terminal carbonyl, and the bands 1652, 1586, 1573 and 1540 were due to non-coordinated and coordinated C-N, C=C and aromatic rings. The band at 1090 was due to phosphine and the band at 1010 was due to furan ring. The signals at 1037 and 961 were attributed to C-S and the band at 933 to N-N vibration.

The ^{1}H NMR spectrum showed signals at 2.12, 6.24, 6.37, 7.35 and 7.55 ppm. They can be assigned to S-CH_3, furan ring protons, phenyl ring protons and azomethine proton [Fig.4.5.16].

The ^{13}C NMR spectrum showed signals at 204.45, 181.61, 149.38, 145.05, 134.38 to 127.60, 119.28, 111.78 and 17.19 δ. They were assigned to carbonyl CO, C-S, C-N, C_1 of furan ring, phenyl ring carbons, furan ring carbons and S-CH_3 respectively.

Considering all the spectral data the following structure is proposed for the complexes.



Experimental

4.2.2 S-Methyl dithiocarbazate

Potassium hydroxide pellets (22.8 g) were completely dissolved in 9:1 alcohol:water mixture (140 ml) and the solution was cooled in ice. To the cooled solution, hydrazine hydrate (20 g) was added slowly with stirring. A solution of carbon disulphide (30.4 g) in alcohol (25 ml) was then added dropwise from a dropping funnel, with constant stirring over a period of 1 h. The temperature of the mixture was kept below 10° during the addition. The resulting yellow oil was separated by means of a separatory funnel and dissolved in 2:3 alcohol:water mixture (100 ml) and this solution was cooled in ice. Methyl iodide (58 g) was added slowly with vigorous mechanical stirring. After the addition, the mixture was stirred for a further 10 min while a white product appeared. Ice-cold water was then added (100 ml) and the stirring was continued for another 10 min.

The product was separated by filtration, washed with water, and dried in air. The crude product was recrystallized from benzene (150 ml). Yield 18 g (~ 36%), m.p. 83-84°.

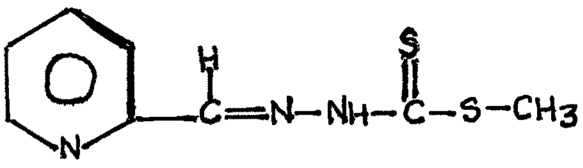
I.R. (KBr disc). 3260.4m, 3219.3m, 3189.9m, 3166.4m, 1618.1s, 15107.4s, 1419.6s, 1149.3s, 1119.2m, 1057.9m, 971.0s, 1002.4s, 943.6s, 705.6, 670.4, 649.8, 468.3 cm^{-1}.

^{1}H NMR δ 2.65 (S-CH$_3$), 4.24 (NH)/(S-H)

Schiff base complexes

4.2.2 Preparation of ligands

4.2.2.1 Hydrazine carbodithioic acid [1-(2-pyridylmethylene) methyl ester] [HPyCDTC]

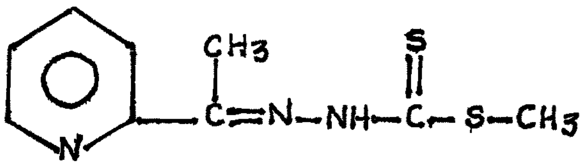


2-Pyridine carboxaldehyde (0.55 g, 0.5 mmol) and S-methyldithiocarbazate, 0.65 g (0.5 mmol) were refluxed in 20 ml absolute alcohol for 1 h. Crystals started separating almost immediately. Cooled, filtered, recrystallized the product from ethanol and dried in vacuo. Yellow crystals. Yield 0.7 g (70 %), m.p. 182-83°.

IR 1648.5m, 1638.2m, 1584.6m, 1565.6m, 1530s, 1312.8s, 1281s, 1146.8s, 1106.4s, 1046.5s, 999.7s cm^{-1}.

^1H NMR δ 2.6 7.39, 7.41 (N=CH) 7.47-8.89 (aro), 10.24, 15.5 (N-H). ^{13}C NMR δ 202.2q (C=S), 137.6 (N=C-), 151.6q, 148.5, 135.7, 125.7 and 124.2 (arom), 17.3 ($S-CH_3$). Mass spec m/e 211(18), 164(24), 136(100), 120(16), 106(34), 91(52), 78(80%).

4.2.2.2 2-Hydrazine carbodithioic acid [1-(2-pyridinyl) ethylidine]methyl ester [HAcPyDTC].



2-Acetylpyridine (0.55 g) in 10 ml ethanol and S-methyl dithiocarbazate (0.54 g) in 20 ml hot alcohol were mixed together and refluxed for 30 min. to get a clear yellow solution. The solution was concentrated to one-fourth volume and cooled to room temperature. The separated yellow crystals were filtered, dried and recrystallized from alcohol. Yield 0.5 g (~ 60%), m.p. 129.130°.

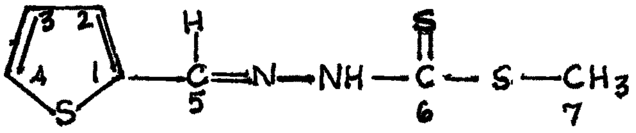
IR 3149.9s, 1579.3m, 1563.1m, 1430.1s, 1144.0m, 1115.6m, 1086.0m, 1062.2s, 1044.4m, 991.7m cm^{-1}.

^{1}H NMR δ 9.9, 7.5, 7.32m, 7.1, 6.96, 6.90, 2.58 and 2.25.

^{13}C NMR δ 200.6, 144.9, 142.2, 129.0, 127.8, 127.3, 17.6 and 13.7.

Mass spec m/e 225(15), 210(4), 178(65), 150(18), 120(36), 106(28), 91(36), 78(100%).

4.2.2.3 Hydrazine carbodithioic acid [1-(2-thienyl)methylene] -methyl ester [HThCDTC].



S-Methyl dithiocarbazate (800 mg; 6.5 mmol) was dissolved in 20 ml hot ethanol and mixed with a solution of thiophene-2-carboxaldehyde (750 mg, ~ 7 mmol) in 10 ml ethanol and refluxed for 1 h. Cooled, and filtered the crystals formed. Recrystallized from ethanol. Yield of yellow-brown crystals 0.65 g (~ 45%), m.p. 166-68°.

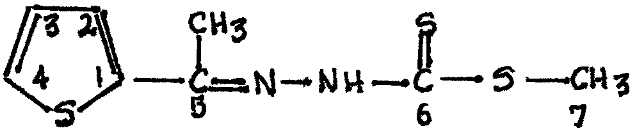
IR 3097s, 1593.9s, 1530.0s, 1507.9s, 1420.8s, 1098.5s, 1087.0s, 1036.6s cm^{-1}.

^{1}H NMR δ 10.45 (NH), 8.1s (-C-H), 7.5-7.47m, 7.27, 7.05, 6.97, 6.92 and 2.55 (S-CH_3).

^{13}C NMR δ 200.0 (C=S), 139.4(C_5), 137.5, 131.3, 129.6, 127.7 and 17.7.

Mass spec m/e. 216(20), 169(27), 110(99), 96(25), 91(77), 83(28), 69(28), 60(32%).

4.2.2.4 Hydrazine carbodithioic acid [1-(2-thienyl)ethylidine] methyl ester [HAcThDTC].



S-Methyl dithiocarbazate (750 mg; ~ 6 mmol) was taken in 20 ml hot ethanol and mixed with 2-acetylthiophene (800 mg, ~ 6.5 mmol) in 10 ml ethanol and the mixture refluxed for 30 min. Cooled and filtered the crystals formed. Recrystallized the product from ethanol to get yellow needles. Yield 0.7 (~ 50%), m.p. 139-140°.

IR 3166.0m, 1734.0m, 1716.8m, 1684.0m, 1653.9m, 1636.1m, 1589.3m, 1558.2m, 1540.1m, 1526.4s, 1506.5m, 1097.7s, 1057.5s, 1034.0s cm^{-1}.

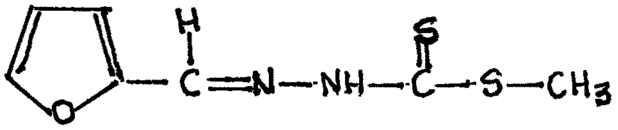
^{1}H NMR δ 9.86 (NH), 7.6, 7.36, 7.35, 7.28d, 7.0, 6.96, 6.92, 2.61 and 2.28.

^{13}C NMR δ 200.7, 145 (-C=N), 142.2 (C_1), 129.0, 127.8, 127.3, 17.6 and 13.7.

Mass spec m/e 230(27), 215(13), 183(100), 139(12), 124(87), 110(75), 97(51), 91(68), 84, 69, 57 (25%).

4.2.2.5 Hydrazine carbodithioic acid [1-(2-furanyl)

methylene]methyl ester [HFCDTC].



Freshly distilled furfuraldehyde (1.2 g, 0.13 mol) was added to a solution of S-methyl dithiocarbazate, 1.3 g (~ 0.11 mol) in 30 ml of ethanol and refluxed for 30 min. Cooled and filtered the crystals formed. Recrystallized the product from alcohol. Yield of yellow needles 1.1 g (~ 50%), m.p. 151-152°.

IR 3130.2s, 1734.6s, 1682.0s, 1612.5s, 1546.4s, 1525.7s, 1099.6s, 1074.4s, 1046.4s, 1009.9s cm^{-1}.

^{1}H NMR δ 10.7, 11.92(NH), 7.74, 7.6d, 7.48d, 7.01s, 6.75t, 6.55-6.42m, and 2.63δ.

^{13}C NMR 201.5, 199.9 (C=S), 148.3, 145.3, 134.8, 127.7, 116.9, 114.9, 112.9, 112.01, and 17.5δ.

Mass spec m/e 200(37), 153(58), 94(94), 91(99), 81(30%).

Schiff bases from β-diketones and bis(β-diketones)

4.2.2.6 Schiff base from acetylacetone

S-Methyl dithiocarbazate (1.1 g) was dissolved in 15 ml of hot ethanol. A solution of acetylacetone (1 g) in 10 ml ethanol was added to the above solution and refluxed the mixture for 5 min. Cooled to about -10°. Fine yellow needle shaped crystals separated. Filtered the product and recrystallized from ethanol. Yield 0.18 g (~ 10%). Yellow needles, m.p. 86-88°.

IR cm^{-1} 3278.2s, 1625.9s, 1434.2s, 1321.5s,1247.4s, 1227.5s, 1116.1s, 1091.0s, 1030.6s, 1003.2s.

^{1}H NMR δ 1.97 ($C-CH_3$), 2.01 ($N=C-CH_3$), 2.51($S-CH_3$), 3.3-2.72q (uneven CH_2) 6.26 (-C-OH).

^{13}C NMR δ 192.81 (C=S), 158.98 (C=N), 96.35 (-C-OH), 52.81 (CH_2), 26.14 ($CH_3C=N$), 17.75($S-CH_3$), 16.48(CH_3-C-N).

Mass spec m/e. 204(100), 189(7), 156(22), 146(27), 114(45), 98(10), 90(26%).

4.2.2.7 Schiff base from benzoyl acetone

S-Methyl dithiocarbazate (400mg, 3.3 mmol) and 540 mg (~3.3 mmol) of benzoylacetone were taken in 2 ml of isopropanol and stirred magnetically at room temperature for 30 min. The reactants dissolved giving a light yellow solution. On further stirring a white precipitate started to separate. Continued stirring for 2 h more, and kept overnight. Filtered the precipitate and washed with pet-ether and dried in vacuo. Recrystallized from ethanol to get white crystals, yield 0.7 g (~ 70%), m.p. 135-37°.

IR cm^{-1}. 3648-3464 bm, 1734w, 1684.0m, 1653.4m, 1608.8m, 1570.5s, 1503.3s, 1444.9s, 1404.4s, 1318.3s, 1283.1s, 1191.6s, 1142.2s, 1087.3s, 1056.5s, 1033.7s, 1013.5s, 1000.2m.

^{1}H NMR δ 2.1 ($C-CH_3$), 2.46 ($S-CH_3$) 3.55-2.88q (uneven CH_2), 6.44 (N-C-OH), 7.30 (ar).

^{13}C NMR δ 193.0 (C=S), 157.9(C=N), 142.2, 128.6, 127.9, 123.8 (ar). 54.7 (CH_2), 17.4 ($S-CH_3$), 16.0 ($C-CH_3$).

Mass spec m/e. 266(78), 251(15), 219(33), 160(18), 117(100), 105(60%).

4.2.2.8 Schiff base with 3,5-diacetyl-2,6-heptanedione (H_2DAHD)

S-Methyldithiocarbazate (1.1 g, ~9 mmol) is dissolved in 15 ml of hot ethanol. A solution of 1 g (~ 5 mmol) H_2DAHD in 10 ml ethanol was added to the above solution and refluxed for 10 min. Cooled and kept at room temperature overnight. Filtered the crystals and washed with pet-ether. Recrystallized from ethanol-benzene mixture, as the solubility in ethanol was slight. Yield of shining colourless crystals 1.2 g (~ 60%), m.p. 166°.

IR cm^{-1}. 1633.3s, 1584.0m,1429.6s, 1359.8s, 1321.3s, 1242.5s, 1221.2s, 1124.4s, 1091.3s, 1052.7m, 1011.3m.

^1H NMR δ 1.85, 2.1, 2.5, 2.83q (CH_2), 3.26-3.10q (uneven CH), 6.66 (C-OH).

^{13}C NMR δ 192.6, 162.4, 96.3 (N-C-OH), 58.2 (CH), 27.4 (NC-CH_3), 22.9 (CH_2), 17.2 (S-CH_3), 14.5 (OHC-CH_3).

Mass spectra m/e 420(40), 402(10), 387(5), 355(7), 299(100), 283(5), 274(10), 256(22), 241(18), 217(16), 204(16), 199(30), 169(20), 157(27), 147(32), 123(12), 109(10), 90(48%).

4.2.2.9 Schiff base with 3,5-dibenzoyl-2,6-heptanedione (H_2DBHD)

S-Methyl dithiocarbazate (0.74 g, ~ 6 mmol) and 1 g H_2DBHD were taken in 30 ml ethanol and refluxed. After about 30 min. the reactants dissolved giving a light yellow solution. On continued refluxing, a pale yellow precipitate formed, and after 4 h, cooled to room temperature and filtered. Washing the precipitate with ethanol gave a white product, which was sparingly soluble in ethanol. Recrystallized from benzene. Yield 0.67 g (~ 55%), m.p. 205-206°.

IR cm^{-1} 1632.3s, 1494s, 1434s, 1303s, 1259s, 1197s, 1151s, 1099.9, 1054.7, 1030.7m, 988.7m, 961.7s, 943.8m, 926.7m.

^{1}H NMR δ 2.15, 2.46,2.71, 2.85, 3.40-3.55q (uneven CH), 6.77 (C-OH), 6.85, 7.13, 7.16, 7.38 (ar).

^{13}C NMR δ 193.2, 161.6 (C=N), 142.9, 128.7,128.1, 127.8, 123.4, 97.6, 60.8 (CH), 23.1 (CH_2), 17.3, 15.5, 14.5.

Mass spec m/e 442(2), 355(10), 337(10), 233(30), 223(15), 208(10), 105(100%).

4.2.2.10 Schiff base from 1,5-diphenyl-1,5-pentanedione-2,4-dibenzoyl (H_2TBP)

S-Methyldithiocarbazate (0.5 g, 4.5 mmol) and 1 g H_2TBP (2.2 mmol) were taken in 30 ml ethanol and refluxed. No change of colour was observed even after 1 h. On addition of 2-3 drops of concentrated hydrochloric acid to the refluxing solution, the colour gradually changed into yellow. Soon a solid started separating. Continued refluxing for 5 hrs. Cooled and filtered, washed with pet.ether and dried in vacuo. Very slightly soluble in alcohol and sparingly soluble in benzene. Soluble in chloroform. Recrystallized from benzene. Yield 1 g (~ 65%). M.p. 209-210°.

IR cm^{-1}. 1596s, 1545s, 1536s, 1429s, 1059m, 1020s, 999m.

^1H NMR δ 2.45, 2.46, 3.76, 4.33-4.45q, 6.83, 7.0, 7.10, 7.16, 7.33, 7.82.

^{13}C NMR δ 200.7, 194.0, 159.6, 152.8, 143.7, 142.7, 135.6-120.9, 99.6, 57.2, 55.3, 27.1(CH_2), 23.6, 19.6, 19.5, 17.4.

Mass spec m/e. 632(2), 586(2), 542(10), 509(2), 495(22), 465(10), 451(25), 441(48), 410(15), 396(10), 381(10), 365(9), 295(25), 263(20), 247(30), 233(60), 220(15), 208(100), 105(45), 91(30%).

4.2.2.11 Schiff base from 2,4-pentanedione,3,3[phenylene bis(methylene) bis [H_2p.XyTAc]

S-Methyldithiocarbazate (50 mg; ~4 mmol) and 65 mg (~ 2 mmol) ligand H_2pXyTAc were mixed in 20 ml ethanol and refluxed for 10 min. A pale yellow, clear solution was obtained. On cooling white crystals separated. Filtered, dried and recrystallized the product from benzene. Yield 70 mg (~ 70%), m.p. 155-156°.

IR cm^{-1}. 3395-3310.9b,s, 1628.5s, 1515.6m, 1433.7s, 1322.9s, 1268.9s, 1233.9m, 1198.3s, 1152.2s, 1090.1s, 1061.7s, 1031.6m.

^1H NMR δ 1.75, 1.83, 2.48, 2.61, 2.66, 2.70, 2.77, 2.85, 2.98, 3.05, 3.10, 3.13, 3.25, 3.33, 3.65, 6.45, 7.15, 7.3, 9.75 (isomeric NH/OH).

^{13}C NMR δ 192.76, 191.91, 161.95, 136.76, 135.60, 129.20, 128.98, 128.44, 128.10, 98.82, 96.08, 61.72, 59.25, 31.80, 31.28 (CH_2), 26.66, 19.71, 17.20, 15.73, 15.58.

Mass spec m/e. 474(7), 459(12), 444(8), 426(13), 411(15), 401(8), 383(20), 369(16), 353(13), 337(11), 311(18), 294, 279, 255, 241 (~ 10), 213(12), 199(21), 185(18), 147(22), 115(10),109(85), 91(100%).

A. Ruthenium(II) Schiff base complexes

4.2.3.1. Reaction with $H_2Ru(CO)(PPh_3)_3$ (dihydrido complex) with HPyDTC: The ligand (a) (pyridine-2-carboxaldehyde S-methyl dithiocarbazate) (65 mg) was dissolved in hot ethanol (10 ml) and added to ruthenium carbonyl dihydridotristriphenyl phosphine (275 mg) in benzene (10 ml) and refluxed in an atmosphere of dry, oxygen free nitrogen for 3 h. The white precipitate formed initially disappeared on heating, and gave a red solution. The solvent was removed under reduced pressure to give a red residue which was washed with n-hexane. The residue was redissolved in minimum benzene and precipitated by the careful addition of n-hexane, filtered the product and dried in vacuo. Yield of dark red crystals, 180 mg (~ 70%).

M.P. 217-18 decomposes.

$C_{45}H_{39}N_3OP_2RuS_2$ requires: C, 62.5, H, 4.5, N, 4.8, S, 7.4 found: C, 61.8, H, 4.6, N, 4.7, S, 7.5.

IR 1991.7m, 1919.3s, 1580.7s, 1560.3s, 1479.2s, 1092s, 1029s, 998, 988m-s, 965,952 cm^{-1}

^1H NMR δ 2.1 ($S-CH_3$), 7.6m (Ring H), 8.44d, (H-C=N), -11.66t, (H-Ru)

^{13}C NMR δ 14.9 ($S-CH_3$), 153-121 (ring c) 148 (C=N), 192, C=S, 206.C≡O.

4.2.3.2 Reaction of HAcPYDTC with $H_2Ru(CO)(PPh_3)_3$

Acetylpyridine dithiocarbazate (110 mg) was dissolved in hot ethanol (10 ml) and added to 450 mg $H_2Ru(CO)(PPh_3)_3$ in 10 ml benzene and refluxed for 2 h. The red solution was processed as in (1). Residue from concentration was redissolved in minimum benzene and slowly added an equal volume of n-hexane and cooled. Filtered the separated product, and washed with n-hexane. The product was dried in vacuo to give a red solid. Yield 180 mg (~42%) m.p. 139-140°. $C_{46}H_{41}N_3OP_2RuS_2$.

C, 62.9, H, 4.7, N, 4.8, S, 7.3 Found C, 63.1, H, 4.91, N, 4.8, S, 8.0.

IR cm^{-1} 1957w, 1922s, 1580s, 1478sh, 1093s, 1061m, 1045, 1028, 999, 990m, 957. ^1H NMR δ 1.96, 1.96, 6.6-7.5m, -10.5t. ^{13}C NMR δ 18 ($C-CH_3$), 21 ($S-CH_3$), 151-120 (ring c), 157 ($C=N$), 196, $C=S$, 205 ($C\equiv O$).

4.2.3.3. Reaction of thiophene-2-carboxaldehyde dithiocarbazate with $H_2Ru(CO)(PPh_3)_3$.

The Schiff base thiophene-2-carboxaldehyde S-methyldithiocarbazate HThCDTC (110 mg) was dissolved in hot ethanol (10 ml) and added to $H_2Ru(CO)(PPh_3)_3$ (450 mg) in benzene (10 ml) and refluxed for 2h to get a light yellow solution. Processed as in (1).

Yellow microcrystalline product was obtained. Yield 130 mg (~ 30%). M.p. 220-21°.

Elemental analysis: $C_{44}H_{38}N_2OP_2RuS_3$ needs C=60.5, H = 4.4, N = 3.2 [illegible] S 11.0. Found: C, 62.5, H, 4.2, N, 3.1, S. 10.4.

IR cm^{-1} 1972w, 1916.2s, 1626m, 1579s, 1476, 1089, 1042sh, 1025s, 999m, 951m, 934m.

^1H NMR δ 2.0, 5.9-7.7m (ring H), 7.8, -10.66

^{13}C NMR δ 15, 140-135 (ring C) 140, C=N, 189 (C=S), 206 (C≡O).

4.2.3.4. Reaction of HAcThDTC with $H_2Ru(CO)(PPh_3)_3$

2-Acetylthiophene S-methyldithiocarbazate,HAcThDTC, (120) mg was dissolved in hot ethanol (10 ml) and added to 450 mg of $H_2Ru(CO)(PPh_3)_3$ in benzene (10 ml). Refluxed for 2 h to get an yellow solution. Processed as in (1). Residue, redissolved in benzene and mixed with equal volume of n-hexane and cooled. Filtered the separated product, washed with n-hexane and dried in vacuum. Yield of orange-yellow product 220 mg (~50%), m.p. 192° decompose.

Elemental analysis: $C_{45}H_{40}N_2OP_2RuS_3$ needs, C, 61.2, H, 4.5, N, 3.2, S, 10.9 found C, 61.8, H, 4.4, N, 3.8, S, 9.2.

^1H NMR δ. 2.00, (C-CH_3 and S-CH_3), 6.9-7.4m (ring H), -10.66 (H-Ru). ^{13}C NMR δ 9(C-CH_3), 15 (S-CH_3), 146-124 (ring C), 148 (C=N), 195, C=S and 206 C≡ O.

4.2.3.5. Reaction of HFCDTC with $H_2Ru(CO)(PPh_3)_3$

Furyl-S-methyldithiocarbazate, HFCDTC (45 mg) was dissolved in hot ethanol (8 ml) and added to $H_2Ru(CO)(PPh_3)_3$ (200 mg) in benzene (8 ml). Refluxed for 2 h to get an yellow solution. Processed as in (1).

Yield of the yellow product 80 mg (~ 48%) m.p./dec. at 232°.

Elemental analysis: $C_{44}H_{38}N_2O_2P_2RuS_2$ requires: C, 61.9, H, 4.5, N, 3.3, S, 7.5. Found: C, 62.0, H, 4.8, N, 3.1, S, 7.1%. IR cm^{-1} 1976w, 1935s, 1603m, 1540m, 1090s, 1065m, 1016s, 999.7m, 956m, 935m, ^1H NMR δ 2.0 ($S-CH_3$), 6.2-7.55 (Ar-H), 8.1 (HC=N), -11.75 (H-Ru). ^{13}C NMR δ 14.8 ($S-CH_3$), 150-112, (aro-C), 143, (C=N), 189, C=S, 206, $C\equiv O$.

<u>Reaction with $HRuCl(CO)(PPh_3)_3$</u>

4.2.4.1 The Schiff base HPyCDTC, 75 mg and $HRuCl(CO)(PPh_3)_3$, 300 mg were mixed in 30 ml benzene: alcohol, 2:1 mixture and refluxed for 3 h. The greenish-yellow solution at the beginning turned into a dark-red solution. Cooled and filtered. Filtrate was concentrated under reduced pressure. The residue dissolved in methylene chloride and reprecipitated by careful addition of pet.ether 60-80°. Cooled and filtered the dark-red product. Dried in vacuo. Yield 130 mg (~48%). The compound does not melt but decomposes above 208°.

Elemental analysis: $C_{45}H_{38}ClN_3OP_2RuS_2$ requires C, 60.09, H, 4.23, N, 4.67 and S,7.12. Found C, 59.78, H, 4.10, N, 4.17, S, 7.47. IR cm^{-1} 1972s, 1607w, 1542w, 1507w, 1090s, 1059m, and 984m.

^1H NMR δ ppm 1.85, 7.30 and 7.75.

^{13}C NMR δ ppm 203.48, 175.34, 156.93, 153.60, 138.54, 132.89 to 125.76 and 17.89.

4.2.4.2 The Schiff base HAcPYDTC (50 mg) and $HRuCl(CO)(PPh_3)_3$ (300 mg) were mixed in benzene:alcohol 1:1 mixture, 20 ml and refluxed for 3 h. The yellow solution turned into dark-red within 15 min. Cooled and filtered. The filtrate concentrated under reduced pressure. Redissolved the residue in CH_2Cl_2 and reprecipitated by careful addition of pet. ether 60-80°. Cooled, filtered and dried the product. Dark red product decomposing above 225°. Yield 28%.

Elemental analysis: $C_{46}H_{40}ClN_3OP_2RuS_2$ requires C, 60.50, H, 4.40, N, 4.60, S 7.0. Found C 59.04, H, 4.61, N, 4.42, S, 7.2. IR cm^{-1} 1958s, 1636m, 1090s, 1031m and 949m.

^{1} NMR δ ppm 1.81, 1.92, and 7.3.

^{13}C NMR δ ppm 203.98, 187.80, 159.34, 154.38, 140.09 to 128.43, 17.99 and 15.67.

4.2.4.3 The Schiff base HThDTC (50 mg) and $HRu(CO)Cl(PPh_3)_3$ (190 mg) refluxed in 1:1 benzene:alcohol (20 ml). Red-yellow solution. Processed as in (1); yellow product. Yield 53%, m.p. 245°.

Elemental analysis: $C_{44}H_{37}ClN_2OP_2RuS_3$ requires C, 58.43, H, 4.09, N, 3.09, and S, 10.62. Found C, 56.56, H, 4.14, N, 2.64, S, 10.87.

IR cm^{-1}. 1942s, 1650m, 1570m, 1091s, 1040m and 959m.

^{1}H NMR δ ppm 2.25, 6.70, 6.90, 7.30-7.48 and 7.70.

4.2.4.4 The Schiff base HAcThDTC (50 mg) and $HRu(CO)Cl(PPh_3)_3$ (190 mg) were refluxed in 20 ml benzene:alcohol mixture for 3 h. Processed as in (1). Orange-product. Yield 58%, m.p.210° decomp.

Elemental analysis: $C_{45}H_{39}ClN_2OP_2RuS_3$ requires C, 58.85, H, 4.25, N, 3.05, S, 10.46. Found C, 58.92, H, 4.47, N, 2.38 and 9.11. IR cm^{-1} 1942s, 1652m, 1558m, 1531m, 1506m, 1089m, 1073m, 1034m, 969m and 942m.

^1H NMR δ ppm 1.72, 2.00, 6.90, 6.96, 7.1-7.45.

^{13}C NMR δ ppm 204.28, 179.90, 164.77, 134.91 to 124.91, 23.16 and 16.43.

4.2.4.5 The ligand HFCDTC (45 mg) and $HRu(CO)Cl(PPh_3)_3$ (190 mg) were refluxed in benzene-alcohol mixture for 3 h. Yellow solution. Processed as in (1). Yellow product. Yield 52% decomp. 232, m.p. 252°.

Elemental analysis: $C_{44}H_{37}ClN_2O_2P_2RuS_2$ requires C,59.49, H, 4.16, N, 2.86, S, 7.21. Found C, 60.55, H,4.38,N, 3.15 and S, 6.80.

IR cm^{-1} 1940s, 1652m, 1586m, 1573m, 1540m, 1090s, 1037s, 1010m, 961m and 933.

^1H NMR δ ppm 2.12, 6.24, 6.37, 7.35 and 7.55.

^{13}C NMR δ 204.45, 181.61, 149.38, 145.05, 134.38 to 127.60, 119.28, 111.78 and 17.19.

4.2.4.6 Reaction of ligand $H_2DAHD(DTC)_2$ with $HRu(CO)Cl(PPh_3)_3)$ via sodium salt

The ligand $H_2DAHD(DTC)_2$ (100 mg; ~2 mmol) was reacted with sodium hydride (12 mg) in dry THF at room temperature.

The solution became yellow almost immediately. Continued stirring for another hour. Added 400 mg of $HRu(CO)Cl(PPh_3)_3$ and continued stirring for another 16 hrs. Solvent removed under suction. Residue extracted with benzene and filtered to give a brown solution. The filtrate concentrated to about one-third and kept. Slow precipitation occurred. Filtered and residue dried in vacuo. The compound resembled the hydrido complex $HRu(CO)Cl(PPh_3)_3$.

The filtrate on concentration gave a viscous brown-liquid which did not solidify even on cooling.

^{1}HNMRδ 0.88, 1.26, 1.61, 7.1, 7.16, 7.26, 7.36, 7.51, 7.68.

4.2.4.7 Reaction of ligand $H_2DAHD(DTC)$ with the dihydro complex $H_2Ru(CO)(PPh_3)_3$.

The ligand $H_2DAHD(DTC)_2$, 45 mg (~ 1 mmol) and 200 mg $H_2Ru(CO)(PPh_3)_3$ were refluxed in 20 ml of 1:1 benzene-alcohol mixture, 3 hrs. A brown solution resulted. Solvent was removed under reduced pressure. The residue was dissolved in benzene and reprecipitated by the addition of 60-80^o pet.ether. Yield 40 mg (~ 20%).

IR cm^{-1}. 1962.6m, 1940.7s, 1716.3m, 1584.6m, 1478.0s, 1433.5s, 1308.1m, 1184.4m, 1157.4m, 1088.8s, 1027.6m, 999.1m. ^{1}H NMRδ1.65, 1.77, 2.0, 6.88, 7.0, 7.04, 7.18, 7.44.

4.2.4.8 Reaction with $HRu(CO)Cl(PPh_3)_3$

Reaction of DAHD(DTC) (Schiff base of H_2DAHD with NH_2NHCS_2Me) with chlorocarbonyl hydrido tris(triphenyl phosphine) ruthenium, $HRu(CO)Cl(PPh_3)_3$.

The ligand HDAHD(DTC) 45 mg (~ 1 mmol) and the monohydrido ruthenium complex $HRu(CO)Cl(PPh_3)_3$) were taken in degassed 2-methoxy ethanol and refluxed under nitrogen atmosphere for 3 hrs. The solution became dark-brown during this time. Cooled and solvent removed under suction. The residue redissolved in benzene and reprecipitated by the careful addition of 60-80 pet.ether. Cooled, solvent decanted and residue dried in vacuum. Brown coloured product. Yield 70 mg (~ 30%).

IR cm^{-1}. 2059.1m, 1983.0m, 1940.9s, 1570.8m, 1519.3m, 1481.3s, 1434.1s, 1260.8s, 1180.7s, 1092.2s, 1027.8s.

^{1}H NMR δ 1.25, 1.55, 1.8, 2.01, 3.3, 3.6, 4.3, 4.6, 7.1-7.4.

4.2.4.9 Reaction of Schiff base of benzoylacetone (HBzacDTC). with dihydrorutheniumcarbonyl tris(triphenylphosphine). $H_2Ru(CO)(PPh_3)_3$

The ligand (HBzacDTC) 60 mg (~ 2 mmol) and the dihydro complex 185 mg were taken in 10 ml 2-methoxy ethanol and refluxed for 2 hrs to get a brownish solution. Cooled and solvent removed under suction. Redissolved in benzene and reprecipitated by the careful addition of 60-80 pet.ether. Cooled in refrigerator and filtered. The brown residue was dried in vacuo. Yield 70 mg (33%).

IR cm^{-1} KBR. disc. 3453.5s, 3050w, 2907w, 1940s, 1513.9s, 1480.2s, 1433.8s, 1410.7s, 1092.5s, 1072w, 1031w.

IR cm^{-1} in nujol 1940.3s, 1652.2w, 1558.7w, 1513.3m, 1480sh, 1433.9s, 1410.7m, 1091.6m, 1034.7m,

^{1}H NMR δ 1.65, 1.95, 4.90, 7.1, 7.3, 7.4, 7.44.

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Chapter V : Bis-(β-diketone)ruthenium(II) Complexes

LIGANDS

5.1 Introduction

5.1.1 Bis-(ß-Diketones)

1,3-Diketones like pentane-2,4-dione, benzoylacetone, dibenzoylmethane, etc. constitute a class of very important ligands, which are known for the past century. They and their metal complexes belong to one of the most thoroughly studied category[1-3]. They are very versatile and exhibit a great variety of coordination modes, besides the usual bidentate behaviour of mono anions[4,5]. The earlier chemistry of these compounds has been reviewed giving valuable insight to their coordination behaviour[6-9]. A very recent review on the chemistry of metal ß-diketonates is authored by Mehrotra[10].

Compared to this even though structurally very similar to ß-diketones, the bis-(ß-diketones) are understudied. Although some of these bis (ß-diketones) have been prepared almost a century ago, their physical, chemical and structural properties are not fully studied[11,12]. Martin[13] et al. have investigated the syntheses and spectral properties of some new bis (ß-diketone). These bis-diketones were prepared by the interaction of a ß-diketone $RCOCH_2COR'$ and an aldehyde R"CHO, in the presence of a basic catalyst. However, newer methods of analyses have disproved many of these claims. With the advent of proton magnetic resonance spectroscopy, in the late fifties, the structure elucidation of these compounds became easier. Wilson[14] has prepared 3,5-diacetyl-2,6-heptanedione by condensing acetylacetone and aqueous formaldehyde in alcoholic solution, in the absence of any base. He has identified the earlier reported product, in the presence of a base such as piperidine, to be the cyclic product 4,6-diacetyl-3-hydroxy-3-methyl cyclohexanone.

In 1959 Martin[15] prepared some branched bis (ß-diketones) like 1,1,8,3-tetracetyloctane (3,10-diacetyl-2,11-dodecanedione) and 1,4-bis(2,2'-diacetylethyl)benzene (p-xylylene tetraacetate), (3,3'-[1,4-phenylene bis(methylene) bis-2,4-pentanedione] by reacting the corresponding α,α-dibromo compounds with potassioacetylacetonate in tertiary butanol. Korshak[16] has prepared tetraacetyl diethyl benzene by refluxing p-xylylene dibromide and sodioacetylacetonate in acetylacetone. Morgan[17] prepared tetraacetylbutane by refluxing excess 1,2-dibromoethylene with sodioacetylacetonate. These compounds were characterised only by later-day workers.

Bis-(ß-diketones) being analogous to ß-diketones, it is pertinent in the context of their structural elucidation to have a brief look at some of the important structural features of ß-diketones.

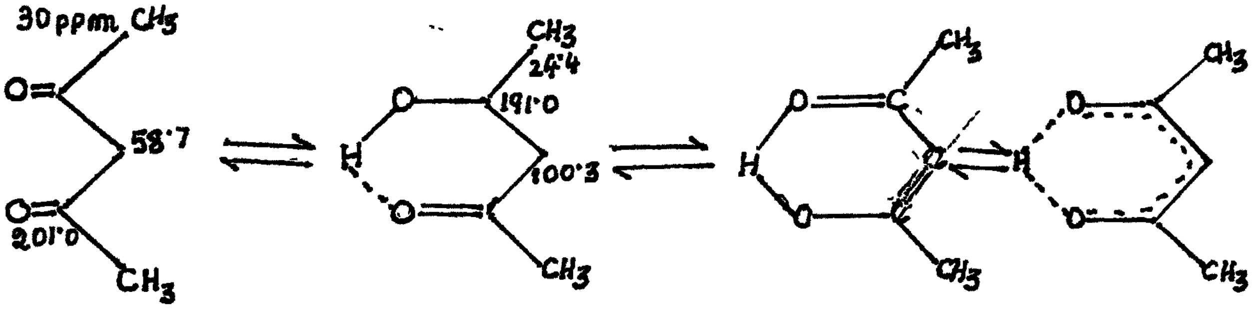
ß-Diketones belong to a class of compounds with interesting structural features, especially in the light of the possibility of their keto-enol tautomerism. It is well known that in the absence of a catalyst, this keto-enol equilibrium is established slowly. The keto-enol equilibrium is very much influenced by a number of sources which are of "internal" as well as "external" in nature. The "internal" sources are the ones arising from the molecule itself, such as, the nature of α- and ß-substituents, and the external sources are the ones due to the nature of the environment, such as, temperature and solvent. For example, acetylacetone (pentane-2,4-dione) has an enol content of 3% in water, whereas, in cyclohexane the enol content is as high as 98%. In many of the cases, the keto-enol tautomerism is sufficiently slow on the NMR time scale and both the keto and enol forms can be observed in the ^{1}H NMR spectrum itself. In the enol form the hydrogen bonded OH proton generally resonate at a very low field (deshielded) typically below 15 ppm and has raised quite a bit of interest especially regarding the nature of hydrogen bond itself[18]. Thus, NMR has been used as a powerful technique in the structure elucidation of ß-diketones.

The advent of pulsed Fourier transformation NMR technique has given a sudden spurt to the study of a rare spin such as ^{13}C, ^{15}N, ^{17}O etc. at the natural abundance itself. The introduction of polarization transfer technique such as INEPT (Insensitive nuclei enhanced by polarization transfer) its analogous and DEPT (Distortion-less enhanced by polarization transfer) made the observation of rare-spin nuclei like ^{13}C and ^{15}N very routine at natural abundance even at very low concentration. ^{13}C NMR has widely been used in the study of keto-enol tautomerism of ß-diketones in solution as well as in solid state.

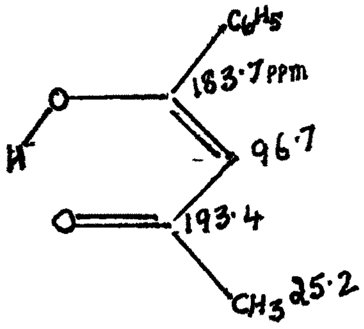
The added advantage of ^{13}C NMR spectroscopy is its spread of chemical shift (~ 250 ppm) compared to that of ^{1}H (~ 15 ppm) and the ability to directly characterize the nature of functional groups like -COOH, -COOR, -CONR, -CO, etc.

It is known that the carbonyl carbons of the keto form are generally deshielded (lower field, high frequency) by about ~ 10 ppm than the corresponding enol carbon[20]. An important factor that has to be kept in mind while dealing with the NMR signals is the fact that the observed chemical shifts are the averages of the intrinsic chemical shifts weighted by corresponding residence time[21].

From the ^{13}C NMR spectrum of acetylacetone in the enol form, only 3 signals are seen viz. at 191.0,100.3 and 24.4 ppm in benzene.



It has been already established that the tendency of enol formation is related to the nature of α-substituent which affect the acidity of the CH proton. Thus, the electron releasing α-substituent tends to decrease the enol percentage by decreasing the acidity of the CH proton, whereas the electron withdrawing groups favour the enol tautomer. In an asymmetric ß-diketone generally, there exist a preference by the enol proton for one of the carbonyls over the other. For example, in CH_3COCH_2COPh, ^{13}C NMR clearly showed that the carbonyl attached to the phenyl group is completely enolyzed in solution.

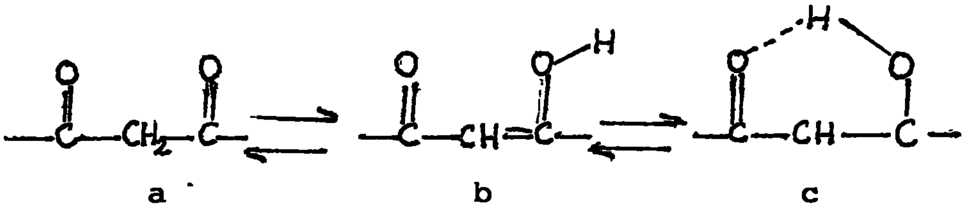


An electron withdrawing substituent on the central carbon has been reported to increase the enol percentage compared to acetyl acetone[22a,b]. An electron releasing alkyl chain should excert an opposite effect, this is consistent with the low enol content found for 3-hexyl-2,4-pentanedione and the branched bis (ß-diketones)[23].

The ^1H and ^{13}C NMR studies on bis (ß-diketones) are comparatively rare. O'Loane[24] has studied the ^1H NMR patterns of 3,5-diacetyl-2,6-heptanedione and related products. ^1H and ^{13}C NMR studies were done by Basetti and Emelina[25,26].

As for infrared spectroscopy, Margareta Avram[27] declares that the so-called pure 1,3-dicarbonyls are not individual compounds, but tautomeric equillibria of keto-enol forms. Because of this, the normal IR spectrum shows characteristic bands for the molecular species present. The tautomeric equillibrium keto $\rightleftharpoons$ enol depends on solvent, dilution and temperature.

In the case of ß-diketones, the spectrum should show three types of bands in the carbonyl region, saturated ketone (a) α,ß-unsaturated ketone (b) and bonded carbonyl (c).



The ß-diketones, examined as pure liquids or in solution usually exhibit two very strong IR absorptions between 1700 and 1500 cm^{-1}. A sharp, often split band near 1700 cm^{-1} is typical of the keto form, whereas, a broader band near 1600 cm^{-1} characterize the enol chelate co-existing at equillibrium[28].

The spectrum of acetylacetone in the liquid state[29,30] shows in the carbonyl region a doublet of medium intensity (1709-1729 cm^{-1}) assigned to the ketonic form (the splitting is attributable to vibrational coupling). The enolic form shows only a broad, a very strong band between 1538 and 1640 cm^{-1}. The bond includes absorption of both functional groups, C=C and C=O, modified by hydrogen bonding. This absorption corresponds to chelate structure (c) resulting from an intramolecular hydrogen-bonding between carbonyl group (acceptor) and the enolic hydroxy group (donor). The

CO frequency in the enolic form (c) is established by deuteration. In the deutero derivative it occurs at 1621 cm^-. The C=C vibration in (c) has a frequency of 1536 cm^{-1} [31]. The band arising from the chelate linkage persists on dilution as an intramolecular hydrogen bonding in hydroxylic compounds.

e f

For chelate structures, a stabilization due to resonance between structures (e) and (f) is assumed.

The IR spectra of the crystalline ß-diketones showed instead the presence of one tautomer only. Several solid mono ß-diketones like benzoylacetone, dibenzoyl methane and solid 2,4-pentane dione at lower temperature exist in the enol form, giving a strong band around 1600 cm^{-1}. It may be concluded in the crystalline state, a ß-diketone generally consists of only one of the two forms present at equillibrium in the liquid phase. This is not surprising since the keto and enol forms have different packing requirements and therefore are not likely to co-crystallize.

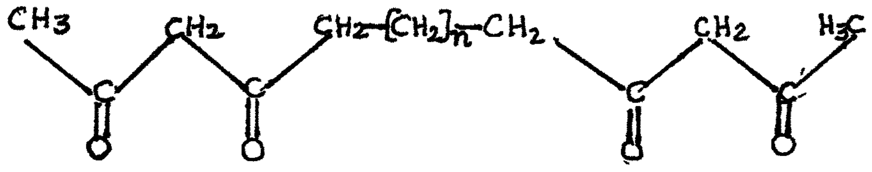
5.1.2 Bis-(ß-Diketones)

Tetraketones or bis-(ß-diketones), LH_2 are the parent compounds of dinegative, tetradentate, bis chelating ligands

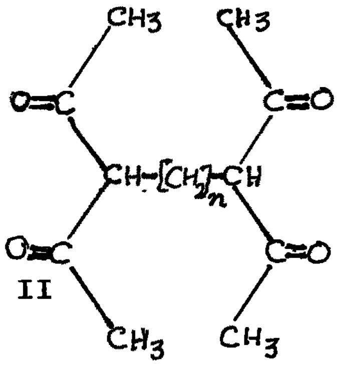
(L^{2-}). Their ability as coordinating agents was first recognized by Kluiber, Bailar and Charles[32-34]. They, like other carbonyl compounds, exhibit high reactivity and can therefore serve as intermediates for the synthesis of aliphatic, aromatic, heterocyclic and high molecular weight compounds.

The interest in tetraketones arose in recent years when existing methods for their preparation were perfected and new methods developed. The greatest number of papers relates to the use of tetraketones, for the synthesis of new compounds, especially those of heterocyclic series, which has attracted the attention of both chemists and investigators in the sciences bordering chemistry. Tetraketones have been used successfully for the synthesis of new class of thermally stable polymers containing macromolecules of hetero cycles in chains, polypyrazoles, polyquinoxalines, polyquinolines and also for obtaining coordination polymers with various metals.

According to their structures bis-(ß-diketones) can be classified into two categories: the linear type $R\text{-}COCH_2COY\text{-}COCH_2\text{-}CO$ (Type 1) and branched type $[(RCO)(R'CO)CH]_2CHR$ and $(RCO)(R'CO)CH\text{-}Y\text{-}CH(RCO)(R'CO)$ (type 2).



TYPE I



TYPE II

Two modes of coordination are possible for ligands of these types.

(1) The two ß-diketonato groups of each ligand may coordinate to separate metal ions, resulting in ligand bridged complexes, which in turn may form either polynuclear chains or oligomeric rings. Polynuclear compounds of the type $[HL]_n$ have been obtained for a number of divalent metal ions with several short chain bis (ß-diketones)[33,34]. Two examples of cyclic dimers $[M_2L_2]$, containing Be(II) at the coordination centers have been described[32] for linear ligands with medium length connecting chains.

(2) The two diketonato groups of each ligand may coordinate to the same metal ion, resulting in a mononuclear 'bifurcate' complex with the connecting alkyl chain spanning across an edge or face of the coordinating polyhedron.

Other factors being equal, the mode of coordination of those bis (ß-diketone) ligands to metal ions may be expected to depend on both length and the point of attachment of the connecting alkyl chain. Short chain branched ligands should strongly favour polynuclear coordination, short chain linear ligands may give rise to either polynuclear chains or cyclic oligomers, linear and branched longer chain ligands may loop to give bifurcate monomeric complexes. Compounds of the latter type should exhibit an increased stability, compared to the analogous complexes of ordinary ß-diketones especially for those 2(+) and 4(+) metal ions in which the preferred coordination number is twice the ionic charge. Bifurcate complexes of bis(ß-diketones) may also be of interest because of the shielding effect and molecular dissymmetry arising from the presence of the spanning alkyl chains.

5.1.3 Metal complexes of ß-diketones

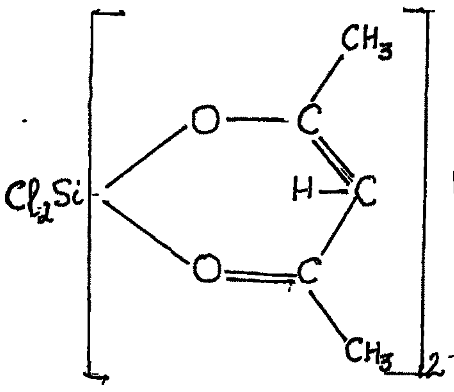
The chemistry of metal ß-diketonates broadly follows the pattern of development in inorganic chemistry as a whole[1]. Beginning with the synthesis of these derivatives for the first time in 1887, the nature of bonding and chelation was elucidated[3] in several prominent schools beginning with those of Werner and Morgan. The suggestion of aromaticity in the ß-diketonate chelate ring[35] in 1945, aroused novel interest in these derivatives.

The strong chelating tendency of these monovalent, bifunctional ligands led to the synthesis of a number of neutral complexes $[M(A)_n]$ (where M = a central element and A = a ß-diketonate ligand) with predominant covalent characteristics i.e., solubility in organic solvents and volatality) at a time when such examples of covalent derivatives of electropositive metals were much less known. These characteristics have been extensively exploited in solvent extraction and chromatographic techniques. Recently, the use of metal ß-diketonates as contact shift reagent in NMR spectroscopy has aroused further interest in them[36].

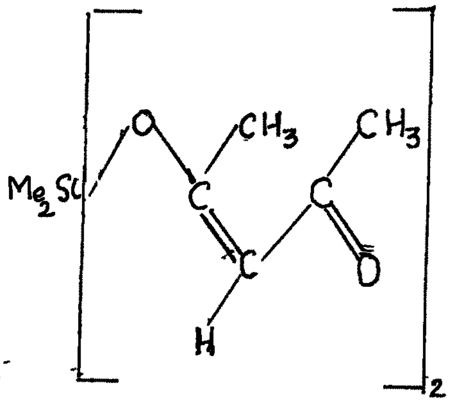
Metal ß-diketonate derivatives may be classified into three broad categories depending upon the mode of bonding of ß-diketonate moieties with the metal atom.

i) Oxygen bonded ß-diketonate complexes

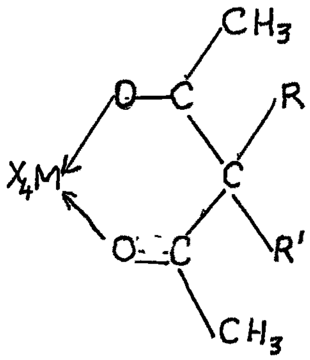
This is the most common mode of bonding with ß-diketonate ligands, acting as a bidentate chelate, which is by far the most common form (A), unidentate (B) and neutral (C) ligand[37].



A



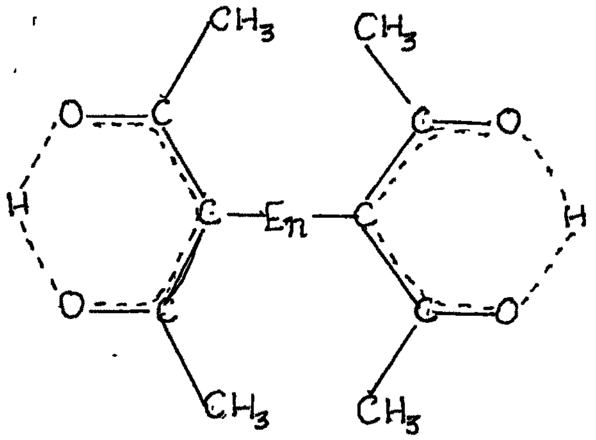
B

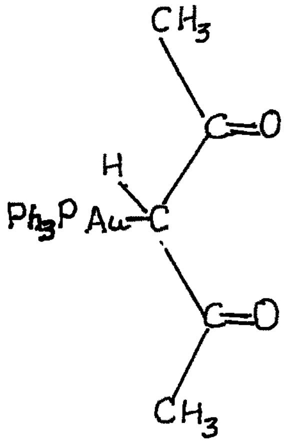


C

ii) Carbon bonded ß-diketonate derivatives

In a number of derivatives of ß-diketones,elements like S, Se, Te, Hg and Au prefer a bonding through the central carbon atom of the ligand rather than the carbonyl oxygen atoms[5,7,38,39,40].





E=S, n=1 or 2, E=Se, n=2

iii) Both oxygen and carbon bonded complexes

Since 1962, a large number of carbon bonded ß-diketonate complexes of later transition metals, like, silver, manganese, nickel and platinum also have been characterized, although in some of these along with C-bonded ß-diketonate ligand another ß-diketonate ligand chelates the metal through the carbonyl oxygens.

Transition metal complexes of ß-diketonate ligands have been studied for many years because of the number and variety of stable complexes that they form and the spectroscopical and chemical properties that these complexes exhibit[1,7]. In these complexes the six membered chelate ring possesses a delocalized electronic structure as suggested by resonance forms, and exhibits partial-aromatic character as evidenced by reaction, chemistry of the acetylacetonate chelating ring.

5.1.3.1 There has been considerable interest in the preparation of metal cocrdination polymers. as possible heat stable materials. Earlier work on this area has been reviewed[41-43].

Bailar[33] has prepared and studied a series of metal ion bis ß-diketone polymers containing Be(II), Cu(II), Ni(II), Zn(II) and Co(II). He has found that polymers containing bis-(diketones) derived from bis(Bzac) and bis(Dbm) are thermally more stable than those derived from bis(Acac). Similarly the polymers derived from bis(diketones) containing no connecting link between the diketone groups are thermally more stable than the polymers derived from the corresponding bis(diketones) which contain a connecting link. The stabilities depend upon this connecting link in the following order:

$$-(CH_2)_n \sim CH_2-CH_2 > -CH_2- > CH.$$

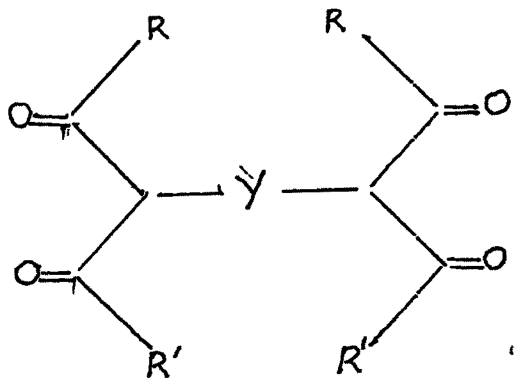
Tetraacetylethane (H_2TAE) and its divalent metallic derivatives have been studied extensively[44-50]. Metal derivatives of other ligands studied are para- and meta-xylylene tetraacetate, 3,5-dibenzoyl-2,6-heptane dione and 3,10-diacetyl-2,11-dodecane dione[51-59].

Very few publications deal with group VIII metal complexes of bis-(ß-diketones) and their derivatives[50,53,54,59]. So far, to the best of our knowledge, no study has been done on ruthenium(II) complexes of these bis (ß-diketones).

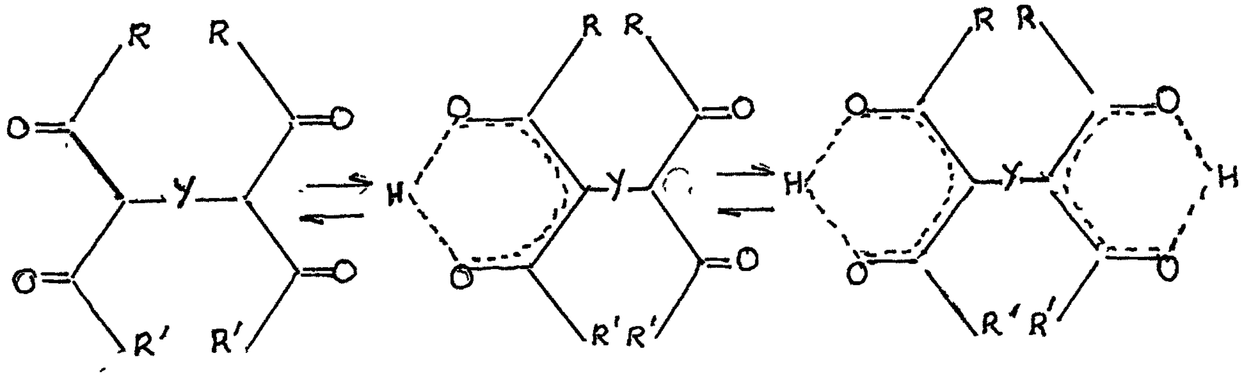
5.2 Results and Discussion

5.2.1 Organic Ligands

A number of bis (ß-diketones) were prepared and were characterized by spectroscopic techniques such as IR, NMR, Mass spectra and by physical constants such as elemental analysis and m.p. (Tables 5.5.1 to 5.5.4). The bis (ß-diketone) ligands prepared have the general structure.



Bis (ß-diketo) compounds are structurally analogous to ß-diketones. The bis (ß-diketone) system can exist in the tetra keto, mono-enol or di-enol forms as depicted below:



TETRA-KETO MONOENOL DIENOL

For the enolic forms only the chelated or the hydrogen bonded structure, where the enolic proton is equally shared by the two oxygen atoms, is shown. In an unsymmetrically substituted bis (ß-diketone) ($R \neq R'$), a structure in which the enolic proton reside only on one oxygen is also, in principle, possible. Apart from these, different rotamers of these structures are also possible. In these compounds the keto-enol tautomerism is established slowly and is very sensitive to (i) the nature of the substituent R,R' and y, and (ii) to temperature and nature of the solvent.

For convenience of discussion the bis(β-diketones) prepared in this study can be broadly classified into three categories, as given below:

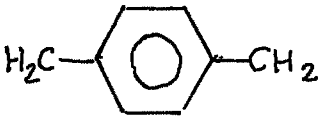
(a) Y = - no substituent (H_2TAE)

(b) Y = $(CH_2)_n$, n = 1-6

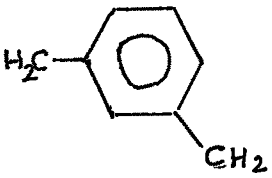
(i)	R = R' = Me	n = 1	(H_2DAHD)
(ii)	R = Me, R' = Ph	n = 1	(H_2DBHD)
(iii)	R = R' = Ph	n = 1	(H_2TBP)
(iv)	R = R' = Me,	n = 2	(H_2DAOD)
(v)	R = R' = Me	n = 3	(H_2DAND)
(vi)	R = R' = Me	n = 4	(H_2HADD)
(vii)	R = R' = Me	n = 5	(H_2DAVD)
(viii)	R = R'= Me	n = 6	(H_2DADDD)

(c) Y = $-CH_2-Ar-CH_2$

(i) Ar (H_2p-XYTAc)



(ii) Ar = (H_2m-XYTAc)



The ligands prepared with their chemical names and abbreviations are

1) R=R'.Me,Y = nothing, 3,4-diacetyl-2,5-hexanedione - H_2TAE

2) R=R'=Me, Y=CH_2,3,5-diacetyl-2,6-heptanedione - H_2DAHD

3) R=Me,R'=Ph, Y=CH_2.3,5-dibenzoyl-2,6-heptanedione - H_2DBHD

4) R=R'=Ph,Y=CH_2.1,5-diphenyl-2,4-dibenzoyl-1,5-pentanedione - H_2TBP

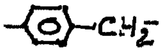
5) R=R'=Me, Y=$(CH_2)_2$.3,6-Diacetyl-2,7-octanedione - H_2DAO

6) R=R'=Me, Y=$(CH_2)_3$.3,7-diacetyl-2,8-nonandedione - H_2DAND

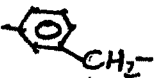
7) R=R'=Me, Y=$(CH_2)_4$.3,8-diacetyl-2,9-decanedione - H_2DADD

8) R=R'=Me, Y=$(CH_2)_5$.3,9-diacetyl-2,10-undecanedione - H_2DADDD

9) R=R'=Me, Y=$(CH_2)_6$.3,10-diacetyl-2,11-dodecanedione - H_2DADDDD

10) R=R'=Me, Y=H_2C 

3,3'-[1,4-phenylene bis methylene bis(2,4-pentanedione)] - H_2pXyTAc

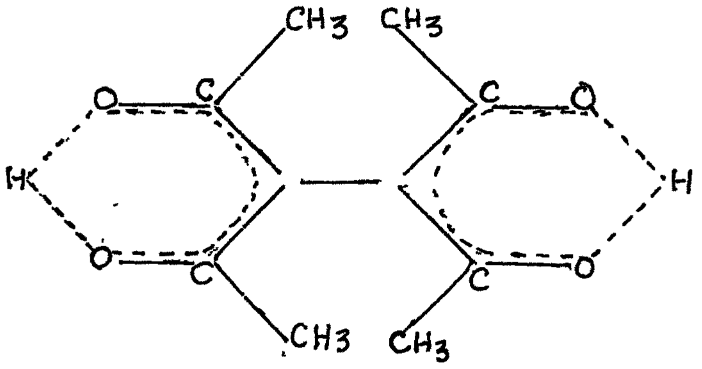
11) R=R'=Me, Y=H_2C 

3,3'[1,3-phenylene bis methylene bis-(2,4-pentanedione)] - H_2mXyTAc

Some of these ß-diketone ligands have been prepared and briefly studied earlier. There has not been any comprehensive study on their structural aspects so far. The most studied of these ligands is 3,4-diacetyl-2,5-hexanedione[45,60,61]. This compound was prepared by treating sodio acetylacetonate with iodine in diethyl ether[62]. This compound showed a sharp melting point at 191°.

The main feature of the IR spectrum of the ligand H_2TAE taken as nujol mull was the presence of a broad and strong band from 1680-1250 cm^{-1} [28-30]. Interestingly, no signal was seen in the region 3600-3200 cm^{-1} which is characteristic of an enolic hydroxyl[27]. The absence of a sharp ketonic band and the hydroxyl band seems to suggest that the compound exists mainly as the hydrogen bonded enol form. This value is in good correspondence with the reported values[47,63,64].

The ^1H NMR spectrum of this ligand, H_2TAE recorded at 200 MHz in $CDCl_3$ gives the values 2 ppm and 16.8 ppm in the ratio 12:2 [Fig. 5.4.1]. The signal at 16.8 ppm is characteristic of an enolic proton[63,64]. The signal at 2 ppm can be easily assigned to the four methyl groups protons, which are equivalent in nature. The simplicity of the ^1H NMR spectrum unambigiously suggests that this compound exists only in the di-enol form. The presence of any mono enol form could have been manifested in the ^1H NMR spectrum as a separate signal for the CH and non-equivalent methyl protons. The ^{13}C NMR spectrum (Fig. 5.4.2) recorded in $CDCl_3$ clearly supports the dienol structure. The ^{13}C spectrum showed only three signals at 192.8, 108.3 and 23.66 ppm which can be assigned to the carbons attached to a hydrogen bonded enolic OH (C_2, C_4), C_3 and C_1, C_5 respectively. Out of these carbons only the carbon at 23.66 ppm showed directly attached proton (confirmed by DEPT experiment, where the carbon atoms containing no hydrogen attached to them, i.e. quarternary carbon, disappear, carbon attached to even number of hydrogen atoms invert in the same position and only carbon attached to odd number of hydrogen atoms, i.e. CH and CH_3, retain their original position) The presence of beta form should have given rise to a characteristic peak at ~ 203 ppm (for carbonyl) and at ~ 60 ppm for (CH). Thus, the structure of H_2TAE can be written as



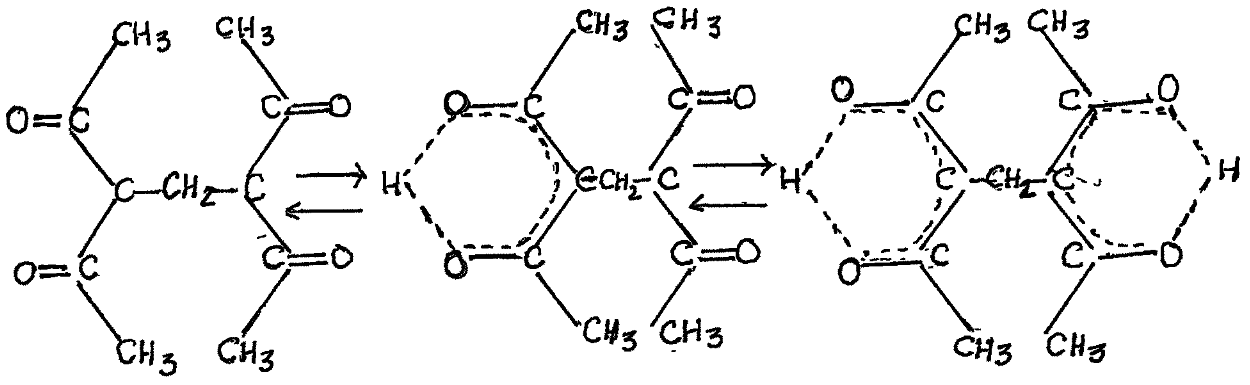
This postulation has been confirmed by the X-ray crystal structure of the compound[60,61,65].

The maximum number of compounds prepared in this study belong to the category (b) where different number of methylene groups were inserted (n = 1-6), between the two acetylacetone moieties.

Ligands H_2DAHD, H_2DBHD and H_2TBP were prepared by treating an ethanolic solution of the corresponding ß-diketone with 40% aqueous formaldehyde at room temperature for 3-5 days and extracting the product with benzene.

The IR spectrum of H_2DAHD (where R = R'=Me, Y = CH_2) as smear showed a broad, strong band in the region 1730 to 1680 cm^{-1}, a broad, weak band at 3300 cm^{-1} and a medium size band at 1500 cm^{-1}. These data seem to indicate the possibility of this compound existing as an equilibrium mixture of the keto and enol tautomer. As the IR spectrum fails to reveal any further details such as the presence of mono enol, dienol or tetra keto forms, ^1H and ^{13}C NMR measurements were carried out in $CDCl_3$ at ambient temperature.

^1H NMR spectrum of H_2DAHD is given in fig. 5.4.3. It is clear from the spectrum that the compound is tautomeric in nature. The major tautomer is the tetraketo form (~ 80%) as evident by the triplets (2H) of CH at ~ 3.4 ppm and 1.8 ppm. The weak signal at 16.55 ppm is characteristic of an enol tautomer. The enol tautomer can exist as the mono enol where only one of the acetylacetone moiety is enolized, or as the dienol form wherein both the acetylacetone moieties are enolized.



A – TETRA-KETO B – MONOENOL C – DIENOL

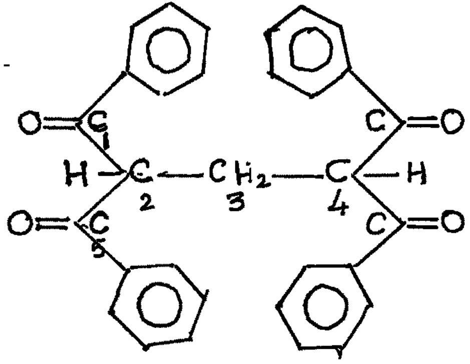
The ^1H NMR spectrum unequivocally shows the presence of only the mono enol forms, of the enol tautomer. It shows a triplet at 3.7 ppm and doublet at 2.5 ppm which are in the ratio 1:2. The former can be assigned to the CH and the latter to the CH_2 in the structure B. If the dienol form were present at a detectable level the CH signal would have been absent and the CH_2 would have been a singlet. These features are not seen in the spectrum. The methyl groups resonate at ~ 2.0 ppm as singlet.

These conclusions are further supported by the ^{13}C NMR (Fig. 5.4.4) data which showed major peaks at 203.2, 64.4, 25.5 and 28.9 ppm assignable to the carbonyl, the CH, the methylene and methyl carbons of the tetra keto form respectively. In the carbonyl region there were two minor signals at 202 and 191.4 ppm arising from the mono enol form. These can be assigned respectively to the keto group of the acetylacetone moiety that has not enolized and chelated carbonyl group of the enolized acetylacetone moiety. A quarternary carbon appear at 106.75 ppm, which is the carbon that is involved in the tautomerization. The nature of carbon signals was determined by a DEPT spectrum. Other assignments are given in table 5.5.2.

Apart from these signals there were very minor signals which could not be assigned to any particular species. To sum up, HDAHD exists as an equilibrium mixture of the tetra keto and mono enol forms and the equilibrium is more shifted to the tetra keto form (~ 80%) as measured from the ratio of the signal area of the peaks at 3.35 (tetra keto) and at 3.75 (mono enol).

The IR spectrum of the compound H_2TBP (where R=R'=Ph, Y = CH_2) showed strong bands at 1695, 1670, 1595 and 1570 cm^{-1} assignable to the carbonyl and C=C stretching. Moreover, this did not show any band in the region of 3400 cm^{-1} which indicated the absence of enolic hydroxyl group.

The ^1H and ^{13}C NMR spectra of H_2TBP are presented in figs. 5.4.5, 5.4.6. The absence of any signal in region 16-17 ppm in the proton spectrum is noteworthy and this data alone is sufficient to postulate a tetra keto structure for this compound. Other features of the spectrum are the 1:1 triplets at 5.63 and 2.65 ppm which can be assigned respectively to the protons on C_2, C_4 which are equivalent and to the methylene group C_3.



The aromatic ortho protons resonate at 8.1 ppm and para and meta protons respectively at 7.6 and 7.4 ppm.

The ^{13}C NMR spectrum showed carbonyl signal at 196.4 ppm. This value being similar to that seen for the carbonyl carbon of the corresponding keto form of the ß-dicarbonyl dibenzoylmethane[20], methine signal at 53.89 ppm and a methylene signal at 28.82 ppm. The aromatic carbons resonate in the region 136 to 128 ppm.

The compound H_2DBHD is quite interesting from the structural point of view as it is asymmetrically substituted at the ß-positions ($R \neq R'$). The IR spectral behaviour is similar to that seen for H_2TBP (strong bands at 1700 and 1600-1580 cm^{-1} and absence of peak around 3400 cm^{-1}), indicating the absence of any enolic tautomer in the compound.

The ^1H NMR spectrum of this compound recorded in $CDCl_3$ did not show the presence of any enolization since the peak ~ 16 ppm was absent. It was interesting to note that all proton signals showed additional resonances which were in the ratio 1:2. For example, the methine protons showed two sets of triplets at 4.60 and 4.52 ppm. The duality of the signals probably be attributed to enantiomeric excess as C_3 is an asymmetric centre, or from rotameric mixtures. The methyl group attached to the asymmetric centre showed expected multiplicity due to the non-equivalence of the methylene protons.

The ^{13}C spectrum also showed the expected duality of resonances, nevertheless it undoubtedly indicated the existence of only the tetra keto form. Therefore, two carbonyl resonances assignable to the acetyl carbonyl at 203.6 ppm and the benzoyl carbonyl at 196.4 ppm. The methine carbon resonated at 59.2, the methyl group at ~ 29 ppm and the methylene group at 27 ppm. (Fig. 5.4.7)

Other samples belonging to category (b) were H_2DAOD (R = R' = Me, Y = $(CH_2)_2$), H_2DAND (R = R' = Me, Y = $(CH_2)_3$), H_2DADD (R = R' = Me, Y = $(CH_2)_4$, H_2DAUD (R = R' = Me, Y = $(CH_2)_5$ and H_2DADDD (R = R'=Me, Y = $(CH_2)_6$). These compounds were prepared by the reaction of potassium salt of acetylacetone with corresponding ω, ω'-dibromohydrocarbons in tertiary butanol for 30 to 48 hours.

The IR and NMR spectral features of these compounds were similar. All of them showed a broad weak band around

3700-3400 cm^{-1} region assignable to the enolic hydroxyl group, strong and broad band between 1730-1680 cm^{-1} region due to the ketonic carbonyl and a strong signal in the region 1585 to 1560 cm^{-1} which can be assigned to C=C and C=O stretching. The IR data indicated the existence of these compounds as keto-enol tautomers.

The ^{1}H NMR spectrum of H_2DAOD showed signals at 2.1(s), 3.55, 4.0(t), 4.3(t), 16.6 and 16.7(s) ppm. The signal at 2.1 could be easily assigned to the acetyl methyl. The signal at 3.55 ppm seemed to arise from the CH_2 group of enolic isomer. The triplets at 4.0 and 4.3 ppm could be assigned to the CH of the keto isomer. The signals at 16.6 and 16.7 ppm were due to hydrogen bonded enolic form.

The ^{13}C NMR spectrum of this compound recorded in benzene also could not give any conclusive evidence for the nature of species present in solution. Nevertheless, the ^{13}C spectral data seem to suggest the possibility of the existence of this compound in the tetra keto, mono enol and dienol forms. The keto C=O seen at 203.5, CH at ~ 65.4 and enolic C-O at 191.6 with quarternary C_3 of enol at 115.4 ppm.

The ^{1}H NMR spectrum of H_2DAND also showed a number of signals at 2.0, 2.21, 2.46, 2.5, 2.66, 4.0(t), 4.35(t), 6.5(d) and 12.5(s) ppm. The methyl group of this ligand could be assigned to the peaks at 2.0 and 2.21 ppm. The methylene groups resonate at 2.44, 2.50 and 2.66 ppm. The triplet signals at 4.0 and 4.35 are due to the methine protons of the tetraketo form. The doublet signal at 6.5

ppm could not be assigned to any proton in the structures under consideration. The origin of the signal is not clear. It is far too downfield for the CH signal of the mono enol form. Another interesting aspect of this compound is the resonance of the enolic OH which is seen at 12.5 ppm, this value being considerably upfield, compared to other bis ß-diketones.

The ^{13}C NMR spectrum in benzene showed keto C=O at 202.7, CH at 65.7 with CH_3 and CH_2 groups overlapping from 28 to 18.8 ppm. The enolic C-O resonates at 190.6 and C_3 quarternary carbon at 109.4. This observation suggests that the compound exists as a keto-enol tautomer.

The ^1H NMR spectrum of H_2DADD showed bands at 1.94, 2.1, 2.66, 3.55, 4.03, 5.5t and 15.0 ppm. The signals at 2.1, 2.66 and 5.5t could be assigned to methyl, methylene and methine groups of the tetra keto form respectively. The signals at 1.94, 4.03, 3.66 and 15.03 could be assigned to the methyl, methine and enolic OH of the mono enol form.

The ^{13}C NMR spectrum showed signals at 203.1 and 67.6, 63.3 ppm assignable to C=O and CH of the tetra keto form respectively with methyl and methylene resonances overlapping in the region 30.9 - 18.9 ppm. The mono enol form resonances could be assigned as C=O, at 190.5 quarternary C_3 at 99.0 and CH, 63.3 ppm respectively.

These data from NMR confirm the supposition that the compound exists as keto-enol tautomers.

The ^1H NMR spectra of H_2DAUD showed signals at 2.09, 2.13, 3.06, 3.35, 3.55t, 4.00 and 16.66 ppm. The signals at

2.13, 3.35 and 3.55t could be assigned to methyl, methylene and methine protons of the tetra keto form respectively. The corresponding resonances for the enol form could be 2.09, 3.06, 4.00 and 16.66 ppm respectively for methyl, methylene, methine and enolic protons.

The ^{13}C NMR spectrum in benzene showed signals at 203.2, 190.5, 110.0, 67.8, 63.8 and 33.5 - 22.2 ppm. The signals at 203.2 and 67.8 could be assigned to the C=O and CH of the keto form respectively with signals in the region 33.5 to 22.1 accounting for methyl and methylene carbon resonances. The signals at 190.5, 109.9, 63.8 could be assigned to C-O, quarternary C_3 and CH of the mono enol form.

The NMR data suggest that this compound also exists in the keto-enol tautomeric forms.

The ^1H NMR spectrum of H_2DADDD showed signals at 1.80, 1.85, 2.0, 2.15, 3.2, 3.85t,4.1t and 16.45 ppm. The signals at 1.85, 2.15, 3.85t and 4.1t could be assigned to the methyl, methylene and methine protons of the tetra keto form respectively. The signals at 1.80, 2.0, 3.2 and 16.45 ppm could be assigned to methyl, methylene, methine and enolic protons of the mono enol form.

The ^{13}C NMR spectrun showed signals at 203.1, 190.5, 110.0, 67.8, 63.8 and 33.5 to 20.1 ppm. The signals at 203.1, 67.8 and 33.5 to 20.1 ppm could be attributed to the C=O, CH and overlapping CH_2, CH_3 carbons of the tetra keto form respectively. The resonances at 190.5, 110.0, 63.8

could be assigned to the C-O, quarternary C_3 and CH of the mono enol form. These values suggest the compound H_2DADDD also exists as keto-enol tautomers.

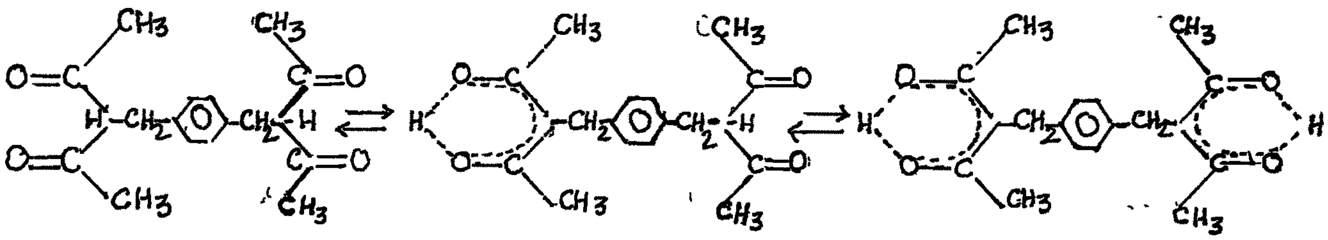
There are two compounds in the category (c) viz. H_2pXYTAc and H_2m-XYTAc. These compounds were prepared by treating 4-methyl bromobenzylbromide or 3-methyl bromobenzyl bromide with the potassium salt of acetylacetone in tertiary butanol for ~ 48 hours.

The IR spectrum of H_2pXYTAc showed peaks at 3380 cm^{-1} which was broad and weak, broad, strong peak at 1730-1680 cm^{-1} and a medium peak at 1500 cm^{-1}, suggesting the existence of keto and enol tautomers.

The ^1H NMR spectrum recorded at 200 MHz in $CDCl_3$ showed a singlet at 2.0 ppm, a doublet at 3.1 ppm and another singlet at 3.6 ppm which was weak in intensity, a triplet at 3.97 ppm and a weak signal at 16.66 ppm. The strong signal at 2.00 was due to the keto methyl group of the tetra keto form the corresponding enolic form signal being at 1.93 ppm of weak intensity. The signals at 3.1 and 3.97 ppm could be easily assigned as due to the CH_2 and CH protons of the tetra keto tautomer respectively. The weak signal at 3.6 could be assigned to CH of the mono enol tautomer. The enolic signal is seen as a weak one at 16.66 ppm, and aromatic protons resonate at 7.2 ppm. It is not obvious from these spectral data whether the enol tautomer exists as the mono enol or the dienol form. But the fact that only one additional signal is there to be assigned and this signal appears as a singlet favours the dienol form. The ^1H NMR data clearly suggest that H_2PXyTAc exists as an equilibrium mixture of keto and enol forms.

The ^{13}C NMR data also showed the expected signals for the keto and enol forms. The signals at 204 and 70, 32.5 and 29.7 ppm could be respectively assigned to the carbonyl, CH, CH_2 and CH_3 carbons of the tera keto form. The corresponding signals of the enol tautomer appeared at 192, 109, 31.8 and 23.0 ppm. The aromatic quarternary carbon appeared at 139 and 137 ppm and aromatic CH at 129.9 and 128.8 ppm (Figs. 5.4.9, 5.4.10).

The ^{13}C NMR spectrum of this compound is quite interesting and a detailed discussion is required. If only one tautomeric form was present the ^{13}C spectrum would have been quite simple. For example, for the tetra keto form the signals would have been at 203 (C=O), 139 (aro.q), 130 (aro.CH), 70(CH), 32.5 (CH_2) and 29.7 (CH_3). For the pure enol form the corresponding signals would have been at 192, 109, 137, 128, 31.8 and 23.0 ppm. A close look at the ^{13}C spectrum showed that each set of these signals for keto and enol forms are further split into two. In other words there were two carbonyl signals at 203.1 and 203.2 ppm arising from keto tautomer. Similarly, there were two very close signals at 108 and 108.1 ppm arising from the enolic tautomer. This clearly indicated the presence of two types of keto forms, tetra keto and diketo mono enol and two types of enol forms (mono and dienol). Thus, the presence of all the three tautomers can be envisaged for this compound.



TETRA-KETO MONOENOL DIENOL

A 300 MHz proton spectrum recorded for H_2PXYTAc is worth mentioning (Fig.5.4.8). It showed the following features: 17.0(s), 7.2(Ar), ~3.85 (1:3:3:1q), 3.49(s), 3.47(s), 2.97 (1:2:1t), 1.99(s), 1.97(s), 1.93(s), and 1.91(s). These signals could be assigned to enolic OH, aromatic protons, CH protons in keto isomer, CH_2, dienol, CH_2 in enol form, CH_2 in keto form and acetylmethyls. The appearance of CH and CH_2 protons of the keto form respectively as 1:3:3:1 quartet and 1:2:1 triplet needs some explanation. The appearance of these two signals is deceptive in nature. Actually the CH proton signal is a super position of two 1:2:1 triplet rather than a 1:3:3:1 quartet. It had the deceptive appearance as the chemical shift difference in hertz is same as the coupling constant (7.4z). Similar argument is applicable for the CH_2 signals also. It is a superposition of two 1:1 doublet rather than a 1:2:1 triplet. The two types of signals are arising from the tetraketo and the mono enol tautomer (signal from the non-enolized acetylacetone moiety). Two singlets at 3.49 and

3.47 can be assigned to the methylene protons in the dienol and mono enol tautomer (from the enolized moiety). Out of the four acetyl methyl signals, the two at low fields (1.99 and 1.97) may be arising from the keto-tautomer and two at higher fields (1.93 and 1.91) may be due to the enol tautomers.

The ^{1}H NMR spectrum of H_2m-XYTAc showed that the compound existed in tetra-keto, mono enol and dienol forms in solution. It showed two enolic hydroxyl signals at 16.7 and 18.7 ppm. The other assignments were as follows: 2.09 (methyl), 2.75 (CH_2, keto), 3.1 (CH_2, enol), 3.6 (CH mono-enol), 3.96 (CH, keto). These values were in agreement with those reported by Maverick et al[58].

The ^{13}C NMR spectrum recorded in benzene showed peaks at 202.4, 68.5, 33.37, and 29.11 ppm which could be respectively assigned to the carbonyl, CH, CH_2 and CH_3 carbons of the keto tautomer. The signals at 191.3, 107.9, 32.06 and 22.23 were due to the enol tautomer.

It is worthwhile mentioning that in all the bis (ß-diketones) studied, the major contribution to the tautomeric mixture, came from the tetra-keto form, accounting more than 50 per cent.

<u>Mass spectra</u>

The mass spectra of H_2TAE, H_2DAHD, H_2DAOD, H_2DAND, H_2DADD, H_2DBHD, H_2TBP, H_2pXyTAc and H_2mXyTAc were obtained. The decomposition patterns of the compounds are quite different from that described for ß-diketones[71,72,73]. With bis-ß-diketones apparently water elimination followed by methyl or acetyl group elimination occurs. The mechanism of the decomposition is under study, and needs confirmation before publication. The fragmentation pattern of the compounds are given in Table 5.5.4. . The spectra of H_2TAE, H_2DADD, H_2DAUD and H_2p.XyTAc are given in Figs. 5.6.1 to 5.6.4 .

2.2 Binuclear ruthenium(II) complexes of bis-(ß-diketones)

Complexes with ruthenium(II) carbonyldihydrido tris(triphenyl phosphine) $H_2Ru(CO)(PPh_3)_3$.

The complexes were prepared by refluxing a 2-methoxy ethanol solution of bis-ß-diketone with $H_2Ru(CO)(PPh_3)_3$ in 1:2 molar ratio for 3 h.

$$\text{Bis-(ß-Dike)} + 2H_2Ru(CO)(PPh_3)_3 \longrightarrow \text{Bis(ß-dike)}[HRu(CO)(PPh_3)_2]_2 + 2PPh_3$$

After removal of the solvent under reduced pressure, the residue was dissolved in benzene and precipitated by the careful addition of 60-80 pet.ether. The precipitated product was filtered and dried in vacuo (Tables 5.5.5 and 5.5.6).

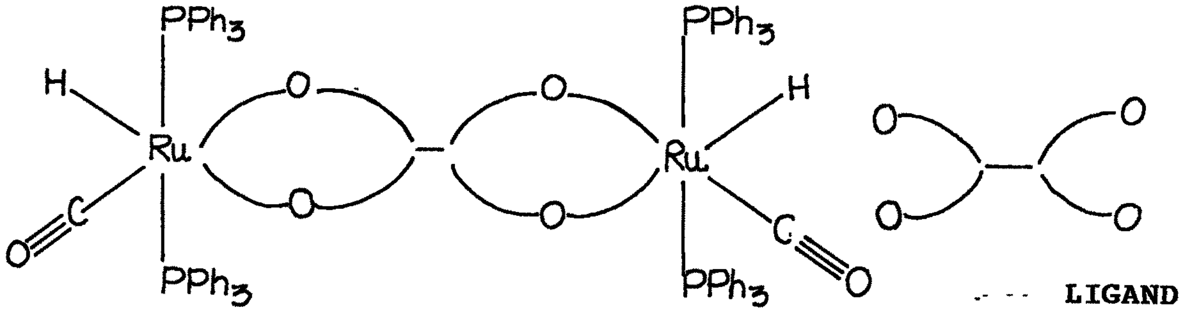
TAE $[HRu(CO)(PPh_3)_2]_2$

The complex showed peaks at 1980, 1910, 1860, 1590, 1560, 1090 and 850 cm^{-1}. The ligand showed a broad strong band at 1650-1280 cm^{-1} due to hydrogen bonded enol. The broad well resolved bands at 1500 and 1560 cm^{-1} indicate that the ligand does not exist in the enol form in the complex. The strong band at 1590 cm^{-1} may be assigned to coordinated CO to the metal with a sharp decrease of 100 cm^{-1}. The band at 1980 cm^{-1} in the complex was attributed to νRu-H. This band is seen about 20 cm^{-1} higher than observed in the starting ruthenium complex. This is attributed to reduced bond order in Ru-H due to the metal coordination to strongly electronegative oxygen atom. This value is also lower by ~ 40 cm^{-1} than the ruthenium carbonyl chlorohydrido tris-triphenyl phosphine, $HRu(CO)Cl(PPh_3)$ in which ν Ru-H is around 2020 cm^{-1}. This may be due to an increase in electron density around ruthenium atom compared to $HRu(CO)Cl(PPh_3)_3$. The band at 1910 cm^{-1} is attributed to ν (C ≡ O), which is about 30 cm^{-1} lower than in the starting material. The negative shift in ν (C ≡ O) in these complexes may be attributed to the presence of strong σ donating hydrido ligand and the chelate ring.

The bands at 1590 and 1560 cm^{-1} were attributed to ν(C=O) and ν (C=C). A band at ~ 618 attributed to Ru–C bond[66] was shifted to around 611 cm^{-1} in the complex suggesting reduced metal-carbon interaction in the complex. The slight positive shift in (P-C) from 1088 cm^{-1} in the $H_2Ru(CO)(PPh_3)_3$ to 1091 in the metal complex indicated the π back-bonding from the metal was not very significant[67].

In the ^1H NMR spectrum signals seen at 0.6 and 0.68, and -14.0 ppm, can be assigned to CH_3 group and Ru-H. The shift to higher field of the methyl resonance could be attributed to the shielding effect due to chelation. The hydrido hydrogen attached to the metal is seen at a higher field at -14 ppm as compared to -6-9 of the starting ruthenium complex. The enolic signal at 16.6 is completely absent in the complex, indicating its participation in the reaction. The methyl groups are not identical as shown by two equal intensity signals. This is attributed to the chelate ring bound trans to an asymmetric ligand pair, H and CO[68]. This indicates coordination through both oxygen atoms, otherwise the methyl groups would have been unequivalent, resonating differently. This suggests chelation of the complex as in the case of ß-diketones.

Considering both IR and NMR data a structure as shown is proposed for the complex.



This is further supported by the ^{31}P NMR spectrum of the compound, where only one signal at ~ 38.8 ppm is observed, indicating that both the phosphine groups are trans to each other[68].

The IR spectra of all other complexes followed the same pattern. There were no bands around 3200-3400 cm^{-1}

assignable to ν(O-H) of the ligands. Similarly, absent were bands around 1700 cm^{-1} attributed to keto carbonyl groups. A broad medium intensity band was observed in the region 1565-1590 cm^{-1} attributed to ν(C-O) and ν (C=O). In the case of aryl ketones, benzoyl and dibenzoyl derivatives, weak to medium bands were also observed around 1510 cm^{-1}, assignable to the phenyl ring of the ketones. The band attributed P-C, and which show a slight positive shift was observed in the region 1090 to 1095 cm^{-1}. Similarly the weak band attributed to Ru-C was seen around 600 cm^{-1}. The other bands could not be assigned properly due to the interference of phosphine bands.

In the case of ^1H NMR data also the general behaviour of the other complexes follow that of the TAE $[HRu(CO)(PPh_3)_2]_2$ (Table 5.5/.6). In general the methyl groups of the ligand, in the complexes were observed around 1 δ, a shift of about 1 δ ppm towards higher field, due to chelation. The linking CH_2 group(s) also show a shift to higher field observed around 1.2 δ. As the number of linking CH_2 groups increases the spectra become more complex. The resonance due to (OH) in the ligand was completely absent in the complexes, indicating its participation in the reaction. The triplet in the high field attributed to Ru-H, was seen in the region -13.5 to -14.0 δ in the other complexes with a $^2J(PH)cis$ = ~ 20 Hz). In the case of the complex of ligand pXYTAc where the linking group was p-xylylene, the NMR spectrum showed signals at 1.1, 1.45,2.74, 6.27 and -13.72 δ The signals at 1.1, 1.45, 2.74 and -13.72 δ were assigned to

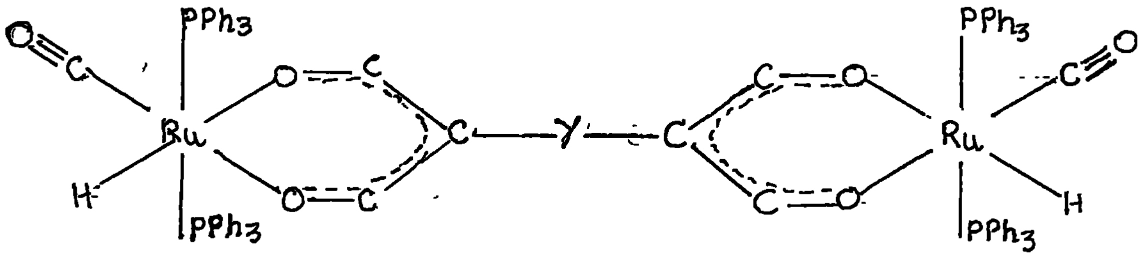
CH_3, CH_2 and Ru-H respectively. The signal at 2.74 δ was assigned $-CH_2-$ of the xylylene group. The signal at 6.27 δ was found to be equal to that of $-CH_2-$ equal to 4H by integration. Therefore this signal is assigned to 4H of the xylene ring. The corresponding CH' in ^{13}C NMR spectrum was observed at ~ 98 ppm which was difficult to assign otherwise. The same phenomenon is observed in the case of m-xylylene, mXYTAc, DBHD and TBP ruthenium complexes also, but to a lesser degree and the integration is also not exactly matching (Fig. 5.4.11).

^{13}C NMR

Efforts were made to study the ^{13}C NMR spectra of the complexes, but due to poor solubility of the complexes the task was difficult. We have taken the spectra of ruthenium(II) complexes of p-XYTAc and DBHD but the signals were weak though we have identified the important groups tentatively. The terminal carbonyl of the complex was assigned to the signal at 213.4 δ. The coordinated CO was assigned a signal at 187. The signal at ~99 in p-XYTAc complex was assigned to the four CH carbons of the xylene ring. The CH_2 of the xylene part was assigned a signal at 61.53 and the methyl carbons around 30 (Fig. 5.4.12). The linking $-CH_2-$ in DBHD was assigned the signal at 31.4 and the methyl carbon was attributed to signal at 14.

^{31}P NMR

The ^{31}P NMR of the dihydrido complex $[H_2Ru(CO)(PPh_3)_3]$ showed signals at 55.1 and 27.3 attributed to the three phosphine groups. In the TAE ruthenium complex the phosphorus signal was seen at 38.8 as a singlet. The ruthenium(II) complex DADDD showed a signal at 30.73. In the p-XYTAc complex the signal was observed at 40.6 and for the m-XYTAc at 42.93. The signal for DBHD complex was seen at 39.65. This singlet in all the complexes indicates two phosphine groups mutually trans to each other, substantiating our projection of the structure for the complexes.



5.2.3. Complexes with ruthenium(II) carbonyl chlorohydrido-tris-(triphenylphosphine) $[HRu(CO)Cl(PPh_3)_3]$

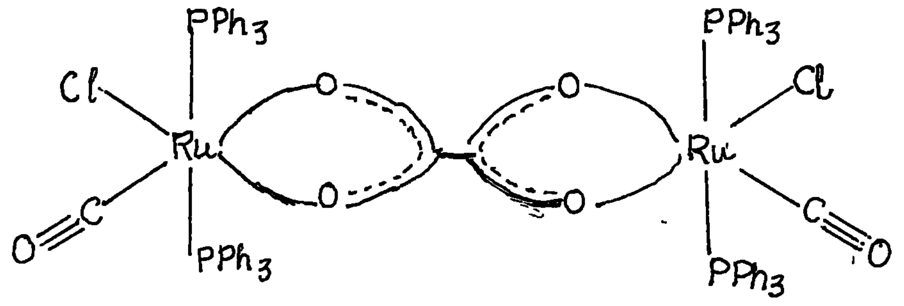
The complexes were prepared by refluxing the respective bis (ß-diketone) with $HRu(CO)Cl(PPh_3)_3$ in 1:2 molar ratio, in 2-methoxyethanol for 3 h. The solvent was removed under suction, and the residue redissolved in minimum volume of benzene and reprecipitated by gradual addition of pet.ether.

$[Ru(CO)Cl(pph_3)_2]_2[TAE]$

The IR spectrum of the complex showed bands at 1940s, 1580-1560t, 1090s cm^{-1} and did not show any bands around 3200-3400 cm^{-1} or 1700 cm^{-1} attributable to enol or keto tautomers. The broad band around 1680-1260 cm^{-1} in the ligand disappeared giving sharper bands at 1580-1560,1485 cm^{-1} indicating participation of the enolic group in the reaction. There was no band around 1960-2020 cm^{-1} indicating the absence of hydrogen attached to ruthenium, which is observed at 2020 cm^{-1} in the starting ruthenium complex. The terminal carbonyl group has shifted to higher wave numbers indicating an increased C≡O bond order. This can be explained as due to the presence of electron withdrawing Cl group adjacent to ruthenium. The broad band at 1560-1580 cm^{-1} was attributed to ν(C-O) and ν(C=O), indicating O,O' coordination to the metal and partial C-O double bond. The phosphorus-carbon bond in the complex is observed at 1090 cm^{-1}.

The ^1H NMR spectrum of the complex does not show any enolic signal in the lower field. Also absent in the spectrum was Ru-H signal, seen around -7 δ in the higher field in the starting ruthenium complex. The methyl group resonance is seen at 0.88 δ and aromatic protons 7-7.44 δ. The shift towards high field, of the methyl resonance was attributed to chelation due to O,O' coordination to the ruthenium atom. The ^{31}P NMR spectrum of the complex showed resonance at 29.64 attributed to mutually trans phosphines.

Considering all these data, we have proposed a structure for the complex as shown



The spectral behaviour of the other complexes follow the same pattern. The methyl resonances of the ligand moieties were observed in the range 1-1.2 δ. In the case of complexes, where the linking group is CH_2, the methylene resonances were observed in the range of 1.5-2.0 δ. Where the linking group was xylylene group, the methylene resonance was observed at a lower field around 2.5 δ. No well defined signals around 6.0 δ due to xylene ring were observed here.

We were unable to produce well defined ^{13}C NMR spectra. The functional groups $C \equiv O$ or C=O were unidentifiable. Same was the case with ^{31}P NMR spectra. The complexes showed a major signal at around 27 δ attributed to mutually trans PPh_3.

In general, the ^{1}H NMR spectra of the complexes tended to be broad and hence assignments were not easy.

5.3 EXPERIMENTAL

5.3.1 Preparation of Organic ligands

1. 2,5-Hexanedione-3,4-diacetyl (H_2TAE)

Sodioacetylacetonate, 25 g, dried under vacuum for 3 hrs at 130° was powdered and suspended in 300 ml diethyl ether, and stirred magnetically in a 2 l Erlenmeyer flask. Iodine, 25.4 g in 300 ml diethyl ether was added slowly during 3 hrs to the stirred solution and kept overnight. Ether was then removed and to the residue, 300 ml water was added and stirring continued for a further 2-3 hrs. Filtered and the crude product was recrystallised from boiling methanol. Colourless, plate-like crystals, m.p. 191°. Yield 11 g (55%)[62].

IR cm^{-1} 1650-1280b,s. ^1H NMR δ 2.0, 16.8, ^{13}C NMR δ 192.79, 108.30, and 23.66.

Mass spec. m/e 198(12%), 180(52%), 165(100%), 123(48%), 113(18%).

2. 3,5-Diacetyl-2,6-heptane dione (H_2DAHD)

Acetylacetone (20 g), and aqueous formaldehyde (40%, 7 ml) in ethanol (10 ml) was kept at room temperature for 5 days. The product was then poured into 100 ml water and extracted with benzene (4x25 ml). The benzene extracts were mixed together and dried over anhydrous sodium sulphate. The solvent and unreacted acetylacetone, if any, were removed under high vacuum. Yield of viscous liquid ~ 17 g. The product was mixed with an equal volume of diethyl ether and cooled below -20°. Colourless crystals separated.

The mother liquor on further cooling and seeding gave additional crystals. Total yield 15 g (~ 75% based on starting materials). The crystals were low melting[14].

IR cm^{-1} 3300b,s, 1730-1680b,s, cm^{-1}. ^{1}H NMR δ 16.6, 3.7t, 3.4t, 2.5d and 2.0.

^{13}C NMR δ 202, 191.4, 106.8, 67, 63, 29.5, 29.3, 29.1 and 27.0. Mass spec. m/e. 194(4%), 169(3%), 151(10%), 127(25%), 113(8%), 110(28%), 100(50%), 85(100%).

3. 3,5-Dibenzoyl-2,6-heptane dione (H_2DBHD)

This was prepared similarly as in the case of H_2DAHD, using benzoylacetone as the ß-diketone instead: benzoylacetone (6 g), 40% aqueous formaldehyde (2 ml). Colourless crystals, recrystallised from benzene. Yield ~ 3 g (75%), m.p. 86-87°.

IR cm^{-1} 1700bs, 1600, 1580s, ^{1}H NMR δ 4.6, 2.6, and 2.15.

^{13}C NMR δ 203, 196, 135, 133, 128, 59, 29, and 27.

Mass spec. m/e: 318(17%), 293(2%), 275(3%), 174(6%), 170(5%), 162(20%), 147(17%), 131(25%), 105(100%), 77(85%).

4. 2,4-Dibenzoyl-1,5-diphenyl-1,5-pentane dione (H_2TBP)

This was prepared by mixing 6.72 g (3 mmol) of dibenzoylmethane and 2 ml (~ 1.5 mmol) of 40% aqueous formaldehyde in 30 ml rectified spirit. Kept for 3 days. Then 10 drops of piperidine were added and kept for one more day when crystals started separating. The mixture was poured into water and extracted with benzene. The benzene

Same as Page 156

The mother liquor on further cooling and seeding gave additional crystals. Total yield 15 g (~ 75% based on starting materials). The crystals were low melting[14].
IR cm^{-1} 3300b,s, 1730-1680b,s, cm^{-1}. ^{1}H NMR δ 16.6, 3.7t, 3.4t, 2.5d and 2.0.
^{13}C NMR δ 202, 191.4, 106.8, 67, 63, 29.5, 29.3, 29.1 and 27.0. Mass spec. m/e. 194(4%), 169(3%), 151(10%), 127(25%), 113(8%), 110(28%), 100(50%), 85(100%).

3. <u>3,5-Dibenzoyl-2,6-heptane dione</u> (H_2DBHD)

This was prepared similarly as in the case of H_2DAHD, using benzoylacetone as the β-diketone instead: benzoylacetone (6 g), 40% aqueous formaldehyde (2 ml). Colourless crystals, recrystallised from benzene. Yield ~ 3 g (75%), m.p. 86-87°.
IR cm^{-1} 1700bs, 1600, 1580s, ^{1}H NMR δ 4.6, 2.6, and 2.15.
^{13}C NMR δ 203, 196, 135, 133, 128, 59, 29, and 27.
Mass spec. m/e: 318(17%), 293(2%), 275(3%), 174(6%), 170(5%), 162(20%), 147(17%), 131(25%), 105(100%), 77(85%).

4. <u>2,4-Dibenzoyl-1,5-diphenyl-1,5-pentane dione</u> (H_2TBP)

This was prepared by mixing 6.72 g (3 mmol) of dibenzoylmethane and 2 ml (~ 1.5 mmol) of 40% aqueous formaldehyde in 30 ml rectified spirit. Kept for 3 days. Then 10 drops of piperidine were added and kept for one more day when crystals started separating. The mixture was poured into water and extracted with benzene. The benzene extract was dried over anhydrous sodium sulphate and filtered. The benzene solution on concentration gave colourless crystals which were filtered, washed with pet.ether and dried in vacuo. Yield 5 g (~ 70%), m.p. 181-82° [14].

IR cm^{-1}. 1695s, 1670s, 1595s, 1570s, ^{1}H NMR δ. 8-7.35 (arom), 5.63 (t, CH), 2.64 (t, CH_2), ^{13}C NMR δ 196, 135, 133, 128.8, 128.4, 53.88, 28.8.

Mass spec. m/e: 442(~0.5), 355(5), 337(7), 233(12), 223(22), 208(8), 147(10), 105(95), 77(55%).

5) <u>3,6-Diacetyl-2,7-octanedione</u> (H_2DAOD)

Sodioacetylacetonate (21 g) and 1,2-dibromoethane were refluxed for 12-14 hrs. Filtered hot, and washed the residue with diethyl ether. The filtrate concentrated under reduced pressure. Ether and unreacted dibromoethane were collected as first fraction. Second fraction was collected as an oily liquid. Yield 1.8 g (~ 10%)[17].

IR cm^{-1} 3600-3400bm,1710-1670bs, 1580-1560bs, ^{1}H NMR δ 16.7, 16.6, 4.3, 4.0, 3.55, 2.20, 2.1.

Mass spec. m/e: 210, 206, 168, 167, 166, 139, 124, 109.

6) <u>3,7-Diacetyl-2,8-nonane-dione</u> (H_2DAND)

Metallic potassium (4 g) was slowly added to 100 ml of absolutely dry, tert-butanol, under nitrogen. After the addition, the solution was refluxed for half an hour. Dry, acetylacetone, 16 ml was added to the solution during 30 min. and refluxed for another half an hour; 10.5 g of 1,3-dibromopropane was then added to the refluxing solution in

20 min. Continued refluxing. After 3 hrs 2 g of potassium iodide was added and refluxed for another 40 hrs. The reaction mixture was poured into water (100 ml) and the mixture was extracted with benzene. The benzene extract was dried over anhydrous sodium sulphate. Filtered and solvent removed under reduced pressure. The residue, a reddish-brown liquid, was used as such. Yield 4 g (~ 25%). IR cm^{-1} 3480bm, 1730m, 1700m, 1670s, 1575bs.

^1H NMR δ 2.0-2.6, 4.0t, 4.3s, 6.5d, 12.5.

Mass spec. m/e: 219(1), 200(9), 189(3), 186(3), 169(7), 166(7), 165(25), 149(45), 140(45), 125(61), 101(42), 100(20), 99(40), 98(52), 97(43%).

7) <u>3,8-Diacetyl-2,9-decanedione</u> (H_2DADD)

This was prepared in a similar manner to that of H_2DAND. Metallic potassium (4 g) acetylacetone (15 g) and 1,4-dibromopropane (11 g) were used. After solvent removal, a reddish liquid was obtained. Yield 7.5 g (~ 60%).

IR cm^{-1} 3700-3500bm, 1685bs, 1610s, 1585s.

^1H NMR δ 15.3, 5.44, 4.03, 3.55, 2.66, 2.01 and 1.94.

Mass spec. m/e: 236, 214, 199, 172(30), 154(35), 149(56), 113(100), 97, 85(70%).

8) <u>3,9-Diacetyl-2,10-undecanedione</u> (H_2DAUD)

The same procedure as above in (6) was used. Potassium metal (4 g), acetylacetone (15 g), and 1,5-dibromopentane (12 g). After the solvent was removed completely a reddish liquid remained, and it was used as such. Yield 8.5 g

(~ 60%). IR cm^{-1}. 3600-3400bm, 1730s, 1700s, 1600bm, 1590-1510bs. ^{1}H NMR δ 16.6, 4.08, 3.52(t), 2.08, 2.13.
Mass spec. m/e: 268(4), 250(2), 225(6), 208(5), 196(5), 183(8), 169(27), 126(26), 113(100) and 100(48%).

9) <u>3,10-Diacetyl-2,11-dodecanedione</u> (H_2DADDD)

Same procedure as above in (6) was followed. Potassium metal (4 g), acetylacetone (15 g), and 1,6-dibromohexane (13 g) were used. The crude product was a red-liquid and was used as such. Yield 10 g (66%)[15].
IR cm^{-1}. 3600-3400bm, 1730-1695bs, 1600-1580bs.
^{1}H NMR δ 16.4, 3.6t, 3.2, 2.1, 2.0, 1.85.

<u>Bis-(p-Bromomethyl)benzene</u> (p-Xylylene dibromide)

Freshly prepared N-bromosuccinimide (110 g), p-xylene (32 g) and benzoyl peroxide (1 g) were taken in carbon tetrachloride (300 ml) and refluxed for 1 hr. Vigorous reaction started within half an hour. Filtered the product while hot, and washed with benzene. When the filtrate was concentrated to about one-third and cooled to room temperature, crystals started separating. Filtered and washed the precipitate with pet.ether. Dried in air. Recrystallized from benzene. Yield of colourless crystals 40 g, m.p.140-41°.

<u>Bis-(m-Bromomethyl)benzene</u> (m-Xylylene dibromide)

This was prepared similarly, as p-xylylene dibromide, using same amounts of reactants. Recrystallized from ethanol. Yield 20 g (~ 25%), m.p. 70-72°.

10) 2,4-Pentanedione-3,3'-[1,4-phenylenebis(methylene)bis

(H_2pXyTAc)

Metallic potassium (4 g) was reacted with t-butyl alcohol (100 ml) and refluxed. After 30 min. acetylacetone (13 g) was added slowly during 10 min. Stirred and refluxed. After another 30 min. p-xylylene dibromide (13.5 g) was added to the refluxing mixture and continued stirring and refluxing. After about 3 hrs potassium iodide (2 g) was added and continued stirring and refluxing for another 40 hrs. After cooling, the reaction mixture was poured into water and extracted with benzene. Benzene extract was dried over anhydrous sodium sulphate. Filtered and the filtrate was concentrated to one-fourth. Crystals of the product separated were filtered, washed with pet.ether and dried. Yield of pale yellow crystals was 12 g (70%). Recrystallized from benzene, m.p. 112-113° [15].

IR cm^{-1}. 3380bw, 1730-1630bs, 1500m, ^{1}H NMR δ 16.66, 3.97, 3.6, 3.1 and 2.00, 1.93. ^{13}C NMR δ 203, 191, 138, 136, 128, 127, 108, 69, 33, 32, 29, 23.

Mass spec. m/e: 302(1), 259(53), 217(22), 202(65), 159(100), 147(32), 141(21), 129(21) and 117(32%).

11) 2,4-Pentanedione-3,3'-[1,3-phenylene bis(methylene)bis

(H_2m.XyTAc).

This was prepared in the same way as that of p.XyTAc. The final product was a reddish-brown liquid, which did not solidify on prolonged cooling in a refrigerator. Yield 10 g (60%). IR cm^{-1}. 3600-3400b,s, 1720sh, 1690s, 1600-1580b,s, ^1H NMR δ 18.7, 16.71, 3.95(t), 3.6, 3.1, 2.75, 2.09. Mass spec. m/e: 301(0.5), 284(7), 266(3), 259(20), 242(10), 223(6), 217(34), 199(21), 181(46), 159(99), 141(76), 117(86) and 91(71%).

Binuclear ruthenium(II) complexes of flexibly bridged bis-(β-diketones)

5.3.2.1 Ruthenium(II) carbonyl chlorohydrido tris-(triphenyl phosphine) $[HRu(CO)Cl(PPh_3)_3]$

Triphenyl phosphine (6.3 g) was refluxed with stirring in 230 ml of 2-methoxy ethanol for 30 min. Ruthenium trichloride hydrate (1 g) dissolved in 90 ml of 2-methoxy ethanol was added to the refluxing solution in one lot. This was followed within 3 min. by 80 ml of 37-40% aqueous solution of formaldehyde. A vigorous reaction took place, and the colour of the reaction mixture turned from dark-red through green to pale yellow. Continued stirring and refluxing for another 10 min. Filtered while hot, and washed the residue with ethanol, diethyl ether and finally by 60-80 pet.ether. Dried under vacuum. Pinkish-cream coloured product, sparingly soluble in common organic solvents like benzene and chloroform, and insoluble in alcohol, diethyl ether or pet. ether. Yield 3 g [69]. IR ν(Ru-H) 2020m, ν-(C≡O) 1922s, 1903sh cm^{-1}.

^1H NMR Ru-H -7.2δ, two triplets.

5.3.2.2 Ruthenium carbonyldihydrido tris-(triphenylphosphine) $[H_2Ru(CO)(PPh_3)_3]$

$[RuHCl(CO)(PPh_3)_3]$ (2 g) and triphenyl phosphine (0.2 g) and sodium hydroxide (0.5 g) were taken in 2-methoxy ethanol (50 ml) and refluxed for 20 min. The mixture was cooled in an ice-bath and the white crystalline solid was collected and washed with ethanol, water and ethanol again. The solid was dissolved in methylene chloride containing 0.1 g triphenyl phosphine and then filtered through a celite pad. Ethanol was then added to the filtrate. Removal of methylene chloride afforded white crystals. Yield 1.6 g (~ 80%), m.p. 160-162° [70].

IR ν(Ru-H) 1960 and 1898m cm^{-1} ν(C$\equiv$O) 1940s cm^{-1}.

^1H NMR Ru-H δ -6.69 to 8.67m.

5.3.3 Binuclear ruthenium complexes of bis (ß-diketones) With ruthenium carbonylchlorohydridotris(triphenylphosphine) $[HRu(CO)Cl(PPh_3)_3]$

1) Reaction of $HRu(CO)Cl(PPh_3)_3$ with H_2TAE

The reaction was carried out by mixing 20 mg (~ 0.1 mmol) of the ligand H_2TAE and 190 mg (0.2 mmol) of the ruthenium hydrido complex in 15 ml of degassed 2-methoxy ethanol and refluxing under oxygen-free nitrogen for 2 hrs. The hydrido ruthenium complex reacted gradually giving a light red solution. The solution was concentrated under reduced pressure leaving an yellow coloured residue. This was redissolved in minimm volume of benzene. The solution was carefully layered with 60-80° pet.ether and kept. Gradually, a precipitate was formed and settled. Filtered and dried in vacuo. Yield of yellow product 150 mg (~ 75%), m.p. 79-80°. IR 1945s, 1590m, 1560m, 600m, 570m and 290w cm^{1}. ^{1}H NMR δ 0.88.

2) R eaction with p.XyTAc

Ligand p.XyTAc (35 mg) and ruthenium complex (190 mg) were reacted similarly as (1) above. An orange coloured solution was obtained. On concentration and purification as above, an orange product was obtained. Yield 130 mg (~65%) m.p. 183-85°. IR 1950s, 1920sh, 1570s cm^{-1}. ^{1} HNMR δ 0.88, 1.2, 2.8, 7.1 to 7.68. ^{13}C NMR δ 20.5, 21.5, 32.4, 60.6, 67.6, 68.2, 127.6-134.4.

3) Reaction with H_2DBHD

The procedure used was the same as above as in reaction (1). Ligand H_2DBHD (35 mg) and ruthenium complex (190 mg) on refluxing gave an yellow solution which on further processing gave an yellow product. Yield 125 mg (60%) m.p. 108-110°. IR 1959.8s, 1583m, 1093m, 898w cm^{-1}.

^{1}H NMR 1.1, 1.28δ.

4) Reaction with H_2TBP

Method of preparation was same as above in (1). Ligand H_2TBP (50 mg) and $HRu(CO)Cl(PPh_3)_3$ (190 mg) on refluxing gave an yellow solution which on further processing gave an yellow product. Yield 170 mg (~ 70%).

IR (Nujol) cm^{-1} 1965.7s, 1923sh, 1577s,

^{1}H NMR δ 1.26.

5) Reaction with H_2DAHD

Similar procedure as in (1) above was used. Ligand H_2DAHD (25 mg) and HRu(CO)Cl$(PPh_3)_3$ (190 mg) on refluxing gave a reddish-brown solution, which on further processing gave a dark red-brown product. Yield 85 mg (40%) m.p. 80-81°.

IR cm^{-1} 1945s, 1925sh, 1580s.

^{1}H NMR δ 0.8, 1.22, 2.1.

6) Reaction with H_2DAOD

The same procedure as in (1) above was adopted. Ligand H_2DAOD (30 mg) and HRu(CO)Cl$(PPh_3)_3$ (190 mg) on refluxing gave a red solution which on further processing gave a dark-brown product.

^{1}H NMR δ 1.25, 1.9.

7) Reaction with H_2DAND

The same reaction conditions as in (1) above were employed. Ligand H_2DAND (30 mg) and HRu(CO)Cl$(PPh_3)_3$ (190 mg) were used. Only a small amount of dark-red product was obtained. Yield 40 mg (~ 15%).

^{1}H NMR δ 1.2, 1.95, 2.3.

8) Reaction with H_2DADD

Same procedure as in (1) above was followed. Ligand H_2DADD (30 mg) and HRu(CO)Cl$(PPh_3)_3$ (190 mg) were used. Dark-brown powder, yield 140 mg (~ 65%) m.p. 82-83°.

IR cm^{-1} 1945s, 1560m and 310w. ^{1}H NMR δ 1.36-2.2.

9) Reaction with H_2DAUD

The same procedure as in (1) above was followed. Ligand H_2DAUD (35 mg) and HRu(CO)Cl(PPh$_3$)$_3$ (190 mg) were used. Red product, yield 70 mg (~ 30%), m.p.78-80.

IR 1945s, 1565m, 1092m, 610m, 315vw cm^{-1}.

^{1}H NMR δ 1.2, 1.6.

10) Reaction with H_2DADDD

The procedure employed was the same as in (1) above. Ligand H_2DADDD (35 mg) and HRu(CO)Cl(PPh$_3$)$_3$ (190 mg) were used. Red-powder, yield 145 mg (~ 65%), m.p. 111-118°.

IR cm^{-1} 1955s, 1570s, and 310w.

^{1}H NMR δ 1.12, 2.00.

Reaction with H_2m-XyTAc

The same procedure as in (1) was followed: m.H_2XyTAc (35 mg) and hydrido complex (190 mg). Red-powder. Yield 105 mg (52%), m.p. 64-65°.

IR cm^{-1} 1950s, 1570s and 310w. cm^{-1} ^{1}H NMR δ 0.84, 1.25 and 2.08.

5.3.4. Reactions of ruthenium carbonyldihydro tris-(triphenyl phosphine) H_2Ru(CO)(PPh$_3$)$_3$ with bis (β-diketones)

The reactions were carried out under oxygen-free nitrogen atmosphere, using Schlenk tube techniques. Solvents were dried before use. 2-Methoxyethanol was degassed before using.

1. Reaction of $H_2Ru(CO)(PPh_3)_3$ with H_2TAE.

The ligand H_2TAE (30 mg, 0.015 mol) and the dihydrido complex $[H_2Ru(CO)(pph_3)_3]$ (235 mg, 0.030 mol) were mixed in 2-methoxyethanol (15 ml) and refluxed under nitrogen for 2 h, forming a pale-yellow solution. The solvent was removed under suction, leaving behind a pale-yellow residue. The residue was redissolved in minimum volume of benzene and then layered with 60-80° pet.ether. On cooling below room-temperature, a nearly colourless product settled at the bottom, and was filtered and dried in vacuo. Yield 170 mg (85%), m.p.164°(d).

IR cm^{-1}. 1980w, 1910s, 1590m, 1560s, 605m, 585m.

^1H NMR δ 0.60, 0.68 and -14.00.

2. Reaction with $H_2p.XyTAc$

The ligand $H_2pXyTAc$ (35 mg) and $H_2Ru(CO)(PPh_3)_3$ (190 mg) were taken in 2-methoxyethanol (15 ml) under nitrogen and refluxed for 2 h. As the reaction proceeded, the reactants dissolved to give a pale-yellow solution and almost immediately an yellow precipitate started to form (about 1 h). Cooled, and concentrated the solution under suction to about one-third, filtered and dried the product. Yield of pale-yellow crystalline product was 90 mg (~ 55%), m.p. 199-200°.

IR cm^{-1} 1970w, 1910s and 1585s.

^{1} H NMR δ 1.16, 2.74, 6.25, 7.1-7.5 and -13.72.

^{13}C NMR δ 213.36, 205.60, 187.02, 184.82, 134.53, 134.28, 133.94, 133.67, 131.92, 131.66, 129.47, 129.13, 127.60, 99.50, 98.48, 61.53, 30.60 and 29.77.

3. Reaction with H_2DBHD

The ligand H_2DBHD (40 mg) and $H_2Ru(CO)(PPh_3)_3$ (190 mg) were mixed in 2-methoxy ethanol (15 ml) and refluxed for 2h. A pale yellow solution was formed. Processed similarly as above in (1). Yield of light yellow product 130 mg (75%), m.p. 93-94°.

IR cm^{-1} 1959m, 1914s, 1592m, 1560s, 1512m, 1093s.

^1H NMR δ 0.9, 1.24 and -13.6.

^{13}C NMR δ 192.4, 134.28, 132.03, 131.89, 131.79, 130.08, 129.17, 129.07, 128.43, 128.28, 127.61, 126.61, 31.45, 22.50, 13.96.

4. Reaction with H_2TBP

The general procedure was the same as above. The ligand (50 mg) and $H_2Ru(CO)(PPh_3)_3$, (190 mg) were employed. After concentrating to about one-third, the solution was kept for cooling. Filtered and dried the product in vacuo. Yield of yellow crystalline product was 160 mg (85%). Decomposed above 201°.

IR cm^{-1} 1970w, 1915s, 1591m, 1551m, 1517m,

^1H NMR δ 1.2, 6.0, 7.1-7.46 and -13.65.

5) Reaction with H_2DAHD

H_2DAHD (35 mg) and $H_2Ru(CO)(PPh_3)_3$ (235 mg) were used. The rest of the procedure was same as in the case of (1). The yield of the light yellow product was 200 mg (~ 80%), m.p. 82-83°. IR cm^{-1} 1970w, 1910s, 1880sh, 1580s.

^1H NMR δ 1.0, 1.2, 2.1 and -14.0.

6) Reaction with H_2DAOD

The ligand H_2DAOD (25 mg) and $H_2Ru(CO)(PPh_3)$ (190 mg) were used. The rest of the procedure was similar to (1). Yield of the dark-brown product was ~ 90 mg (45%), m.p. 132-33°.

IR cm^{-1} 2030w, 1950s, 1570s.

^1H NMR δ 1.2, 1.95, 2.3.

7) Reaction with H_2DAND

The ligand H_2DAND (30 mg) and $H_2Ru(CO)(PPh_3)_3$ (190 mg) were employed. The processing was similar to that in the case of (1). Yield of the dark-brown product was about 90 mg (~ 40%), m.p. 113-15°.

^1H NMR δ 0.9, 1.3, 2.0 and -13.7.

8) Reaction of H_2DADD

The preparation was similar to the one above. Weight of reactants employed were, ligand H_2DADD (30 mg), $H_2Ru(CO)(PPh_3)_3$, (190 mg). Yield of the cream coloured product was 110 mg (~ 55%), m.p. 97-98°.

IR cm^{-1} 2000w, 1900s, 1580s.

^1H NMR δ 1.08, 1.25, 2.08, and -14.0.

9) Reaction of H_2DAUD

The procedure was the same as above. Weight of reactants were ligand H_2DAUD (35 mg) and $H_2Ru(CO)(PPh_3)_3$ (190 mg). Yield of the cream coloured product was 85 mg (~ 40%), m.p. 123-124°.

IR cm^{-1} 1950w, 1900s, 1575s.

^1H NMR δ 1.16, 1.44, 2.08 and -13.86.

10) Reaction with H_2DADDD

The method of preparation was same as in above. Quantities of reactants were, ligand H_2DADDD (35 mg) and the $H_2Ru(CO)(PPh_3)_3$ (190 mg). The yield of the yellow product was 90 mg (45%), m.p. 78-79°.

IR cm^{-1} 2020w, 1940sh, 1910s, 1580s, cm^{-1}.

^{1}H NMR δ 1.24,2.1, and -13.75.

11) Reaction with H_2mXyTAc.

The procedure was similar to the above one. The quantities of reactants were, ligand H_2m.XyTAc (35 mg), and $H_2Ru(CO)(PPh_3)_3$, (190 mg). Yield of the golden yellow product was 130 mg (~ 75%),m.p. 69-70°.

IR cm^{-1} 1980w, 1920s, 1580m.

^{1}H NMR δ 1.1-1.3d, 2.88 and -13.66.

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Chapter VI : Nitrogen Heterocycles Ruthenium(II) Complexes

6.1 Nitrogen Heterocycles Ruthenium(II) Complexes

The chemistry of ruthenium(II) with nitrogen containing ligands has been studied extensively. After Ford[1] prepared ammine complexes containing pyridine and its derivatives $[Ru(NH_3)_5L]^{2+}$ (L = Py or its derivatives), considerable work has been done on ruthenium complexes with nitrogen donor ligands. The high interest in their chemistry may be, probably, due to the intense, visible "metal to ligand charge transfer" (MLCT) band present in these complexes. There has been a considerable amount of work on these compounds, their photochemistry and photophysics. An excellent review on these complexes is given by Ford[2]. The most important part of nitrogen containing complexes with ruthenium is the chemistry of ruthenium bipyridyls and 1,10-phenanthroline and related compounds. Since 1976 these complexes have been the subject of more attention, than any other ruthenium complex. The reason for this is their unique combination of photochemistry, electrochemistry and chemical stability, which has resulted in these complexes being considered as promising candidates for the role of ideal photocatalysts for the visible-light photo-induced decomposition of water into dihydrogen and dioxygen.

The chemistry of nitrogen heterocycles upto 1984 is covered by Seddon[3], in the book 'The Chemistry of Ruthenium'

- 1984. Ruthenium ammine complexes are reviewed frequently[4-5]. The application of ruthenium nitrogen heterocyclic complexes of aromatic chelating heterocycles and their syntheses are thoroughly reviewed by Krause[6]. Bipyridyl and polypyridine complexes of ruthenium have been extensively studied[7-12].

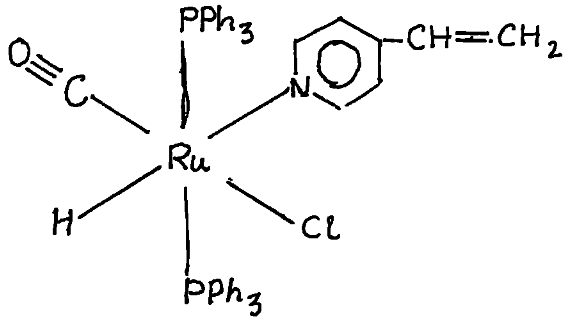
Report on reactions of pyridine and pyridine derivatives, with ruthenium carbonyl chlorohydrido tris(triphenylphosphine) is limited. Only a few papers have been published on this subject, mostly from this Laboratory[6,13-17].

The characteristic *trans*-bond weakening effect of the hydride ligand in $RuH(CO)Cl(PPh_3)_3$ (I) accounts for the ready displacement of trans phosphine by strongly bonding Lewis bases. Hydrogen bound to a transition metal is very effective in causing labilization of the *trans* ligand in substitution reaction[18]. The hydride's high trans influence arises from its ability to direct a large portion of the s-character in the σ bond towards itself, and this weakens the remaining σ bonds, especially the one trans to the hydride. Substitution reaction of (I) using phosphines, phosphites, phosphonites, phosphinates and 4-vinyl pyridine have been studied recently[19-21]. Shah et al.[22] found that no detectable displacement of phosphine was observed when 4-methyl pyridine was added in excess to $RuHCl(CO)(Pr_2PRP)_3$ and suggested the following order of 'coordinating affinities' for group V donors with class 'b' metals:

N <<P>As. We have observed that heterocyclic nitrogen bases can easily replace*trans* phosphine group in the complex (I) giving substitution products in good yields.

6.2 Results and Discussion

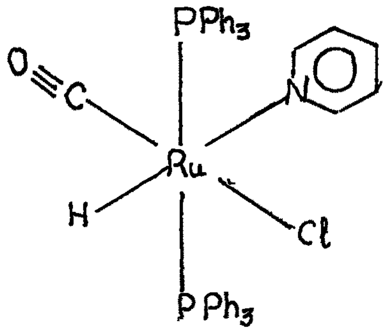
The hydrido complex $RuH(CO)Cl(PPh_3)_3$ (I) reacts with nitrogen donor ligands in benzene or tetrahydrofuran solution at ambient temperature (~25°) to afford the substitution products $RuH(CO)Cl(PPh_3)_2(L)$, as light coloured, air stable solids, soluble in most organic solvents. The ligands used were pyridine, 4-vinyl pyridine, 4-methylpyridine, 3-cyanopyridine, · 2-benzylpyridine, pyridine-2-carbinol, 2-m-xylylpyridine, piperidine, morpholine, 2,2'-bipyridyl, 1,10-phenanthroline, benzo(f)quinoline, isonicotinic acid hydrazide, 4-phenyl-6-chloroquinazoline, and 4-phenyl-6,7-dimethoxyquinazoline. Complexes derived from pyridine, 4-vinyl pyridine, 3-cyanopyridine, piperidine and morpholine were crystalline solids having sharp melting points, while the complexes of other ligands were amorphous solids and they do not melt sharply, due to decomposition on contact with air and moisture. All the complexes are moderately soluble in almost all the common organic solvents. Order of affinities of these ligands for Ru(II) can be given as 4-vinyl pyridine > 4-picoline > 3-cyanopyridine > 2,2'-bipyridine, 1,10-phenanthroline > benzo(f) quinoline > quinazoline. (Table 6.4.1).



6.2.1 The IR spectra of the complexes (Table 6.4.2) $RuH(CO)Cl(PPh_3)_2$ (4-VP), $RuH(CO)Cl(PPh_3)_2$ (4-Mepy) show shift in ν (Ru-H) from 2020 cm^{-1} to 1985 cm^{-1}, suggesting a reduced Ru-H bond order, whereas all the other complexes exhibit medium or weak-band above 2000 cm^{-1}. The ν(C=O) is observed between 1915-1900 cm^{-1} which is 5-15 units lower than the starting hydrido ruthenium(II) complex. This small reduction in ν (C≡O) suggests increased Ru-CO $d\pi - p\pi$ back bonding in these complexes, since the nitrogen donor ligand is a strong σ- donor and a poor π acceptor than triphenyl phosphine. Pyridine and substituted pyridine derivatives show characteristic ν(C=C) + ν(C=N) vibrations around 1600 cm^{-1}. A medium band around 995 cm^{-1} is assigned to the breathing mode of pyridine ring[22,23], which is shifted to higher frequencies (~ 1025 cm^{-1}) suggesting coordination of nitrogen to ruthenium[24].

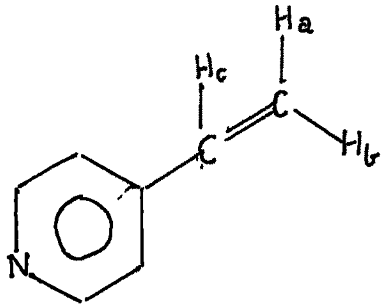
^1H NMR

The high field ^1H NMR spectrum of $RuH(CO)Cl(PPh_3)_2(Py)$ comprises of a triplet centered at δ -13.53 with $^2J(PH)_{cis}$ = ~ 20 Hz, suggesting a trans configuration for the two phosphorus atoms. Hence, a stereochemical structure, as shown, is proposed for the complex.



However, Ru(II) complexes of ring substituted pyridine derivatives like 4-methyl pyridine, 4-vinyl pyridine, 3-cyanopyridine, pyridine-2-carbinol, and isonicotinic acid hydrazide exhibits two triplets of unequal intensity between δ-12.4 to -13.6 and δ-13.4 to 15.10 due to Ru-H resonance, suggesting the existence of two geometrical isomers. Separation of isomers using column chromatography on silica gel using benzene, chloroform and pet.ether (60-80°) as elutants, was attempted without success.

6.2.2 In the ^{1}H NMR spectrum of 4-vinyl pyridine, the three olefinic protons show an ABC type pattern of signals under normal resolution with chemical shifts of H_A = δ 5.4d $[JcHH)_{cis}$=10 Hz], H_B= H_B = δ 5.9d $[J(HH)_{trans}$ = 18 Hz] and H_C = δ 6.6q respectively.



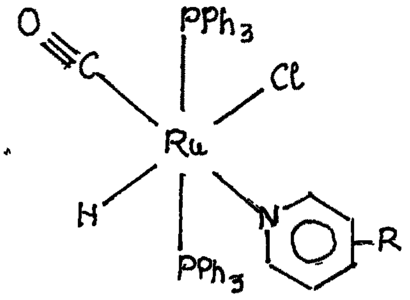
In the ruthenium complex, coordination through nitrogen is accompanied by a small downfield shift of δ 0.1 to 0.3 in resonance attributable to Hc hydrogen atom. The high field proton NMR spectrum of the compound comprises of two triplets of unequal intensity due to coupling of Ru-H proton with two cis phosphorus, suggesting the existence of two isomers. The Ru-H of major isomer resonance is at δ -13.52 with the minor one resonating at δ -12.4.

The resonance due to methyl protons of the 4-methylpyridine complex, $RuH(CO)Cl(PPh_3)_2$ (4-MePy) is observed at a higher magnetic field, δ 2.05 compared to that of the free ligand at δ 2.30. This may be due to diamagnetic anisotropic effect of phosphine phenyl ring in the neighbourhood.

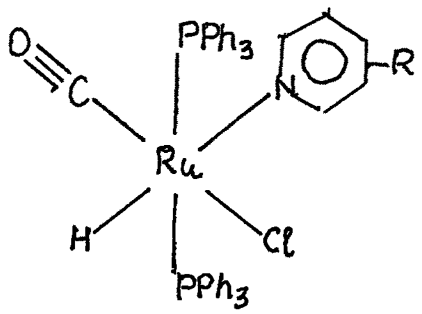
Two triplets due to Ru-H protons are observed suggesting the existence of isomers, with the major isomer contributing the signal at δ -13.55 and the minor one at δ -12.44.

The ratios of the isomers (a and b) calculated from the NMR integration values for 4-methylpyridine, 4-vinylpyridine, 3-cyanopyridine, pyridine-2-carbinol and isonicotinic acid hydrazide ruthenium(II) complexes are 1:7, 1:16, 1:1, 2:1, and 1.1:1 respectively.

From the data, the following stereochemistry is suggested for the isomers a and b.



a



b

Usually 2,2'-bipyridine and 1,10-phenanthroline act as bidentate ligands, but when these ligands react with hydridochlorocarbonyl ruthenium(II) at ambient temperature, they behave as monodentate, forming adducts through one of the nitrogen atoms and the second nitrogen coordinates to one water molecule. This is confirmed by IR, NMR and elemental analysis. IR spectra of the complexes show a broad band centered around 3400 cm^{-1} due to ν OH. A medium band at 1620 cm^{-1} can be assigned as OH deformation mode. The ν(C=N) of the pyridine in the complex is shifted from 1560 to 1575 cm^{-1} which suggests the coordination of nitrogen to ruthenium. The C-H out of plane deformation is found at 780 cm^{-1} instead of at 760 cm^{-1}. Similarly in the case of

1,10-phenanthroline complex, a shift of ν(C=N) from 1500 cm^{-1} is observed.

^1H NMR of these complexes show a downfield shift for Ru-H proton at -11.35 and 11.09δ respectively compared to other monodentate pyridine derivatives of Ru(II). This suggests considerable dπ - pπ back bonding operating in these heterocyclic ligands, compared to that in simple substituted pyridines.

Benzo(f)quinoline and quinazoline derivatives are highly unstable. ^1H NMR of benzo(f) quinoline and quinazoline derivatives did not show any resonance due to Ru-H suggesting decomposition of complex in solution as these ligands are much weaker than pyridine bases.

6.3 Experimental

All the reactions were performed under oxygen-free nitrogen atmosphere using Schlenk tube technique. The solvents were purified and dried using standard procedures, distilled and degassed before use. Nitrogen bases were dried over KOH pellets and were freshly distilled before use in vacuo.

6.3.1 Carbonylchlorohydrido (4-methylpyridine)bis(triphenyl phosphine)ruthenium(II)

Carbonylchlorohydrido tris-(triphenylphosphine)ruthenium [$HRu(CO)Cl(PPh_3)_3$], (0.24 g, 0.25 mmole) was added to benzene (20 ml) containing 4-methylpyridine (0.5 ml) and the mixture was stirred at ambient temperature for 24 h. The solution became green. The solution was concentrated in vacuo and the residual solid was washed with hexane and diethyl ether to get a green microcrystalline solid. Yield of the product melting at 214° is 70%

C, 65.78(65.9), H, 4.78(4.9), N, 1.80(1.8)

IR cm^{-1} ν(Ru-H) 1985, ν(C≡O), 1900,1920, ^{1}HNMR specδ. Ru-H -13.55t, -12.44.

All other compounds were prepared similarly.

6.3.2 Carbonylchlorohydrido(pyridine)bis(triphenylphosphine)ruthenium(II)

$HRu(CO)Cl(PPh_3)_3$ 0.24 g, pyridine 0.5 ml.

Green solid melting at 175°. Yield 65%.

C, 65.51 (65.57), H, 4.59(4.71), N, 1.78(1.82).

IR cm^{-1} ν (Ru-H) 2010; ν (C≡O) 1925, 1915 ^{1}HNMR Ru-H -13.53tδ.

6.3.3 Carbonyl chlorohydrido(4-vinylpyridine) bis(triphenylphosphine)ruthenium(II)

$HRu(CO)Cl(PPh_3)_3$, 0.24 g, 4-vinyl pyridine 0.5 ml.

Colourless solid, m.p. 199°. Yield 78%.

C, 66.51(66.44), H, 4.89(4.81),N, 1.67(1.76).

IR cm^{-1} 1990 ν (Ru-H), ν (C≡O), 1900. ^{1}HNMRδ Ru-H -12.4t, -13.52t.

6.3.4 Carbonylchlorohydrido(3-cyanopyridine)bis(triphenylphosphine)ruthenium(II).

$HRu(CO)Cl(PPh_3)_3$, 0.24 g, (3-cyanopyridine) 50 mg.

Yellow solid m.p. 190°. Yield 70%.

C, 65.08(65.02), H, 4.34(4.44), 3.51(3.52).

IR ν (Ru-H) 2020, ν (C≡O) 1910 and ν (C=N) 2230 cm^{-1}.

^{1}HNMR δ Ru-H -13.60t and 13.46t.

6.3.5 Carbonylchlorohydrido(2-benzylpyridine)bis(triphenylphosphine)ruthenium(II). HRu(CO)Cl(PPh$_3$)$_3$, 0.24 g

2-benzyl pyridine, 0.5 ml.

Brown, low melting solid. Yield 60%.

C, 68.32(68.47), H, 5.14(5.04), N, 1.65(1.63).

IR ν (Ru-H) 2030, ν (C≡O) 1925 cm^{-1}.

6.3.6 Carbonylchlorohydrido(pyridine-2-carbinol)bis(triphenylphosphine)ruthenium(II). HRu(CO)Cl(PPh$_3$)$_3$, 0.24 g,

2-pyridine carbinol, 0.50 ml.

Yellow solid. Does not melt below 250°, Yield 75%.

C, 64.49(64.54), H, 4.80(4.88), N, 1.71((1.75).

IR. ν (Ru-H) 1930, ν (C≡O) 1910 cm^{-1}. ^{1}HNMR (Ru-H) -10.05t, -15.10t, CH$_2$ 4.70 δ.

6.3.7 (2-m-Xylylpyridine)carbonylchlorohydridobis(triphenylphosphine)ruthenium(II).HRu(CO)Cl(PPh$_3$)$_3$ 0.24 g, 2,m-xylylpyridine 0.5 ml.

Grey product melting at 90°. Yield 69%.

C, 68.80(68.74); H, 5.11 (5.04), N, 1.61(1.60).

IR ν (Ru-H) 2030, ν (C≡O), 1920 cm^{-1}, ^{1}HNMR (Ru-H), -4.476t.

6.3.8. (Piperidine)carbonylchlorohydridobis(triphenylphosphine) ruthenium(II). HRu(CO)Cl(PPh$_3$)$_3$ 0.24 g, piperidine 0.5ml.

Pink product, melting at 117°. Yield 60%.

C, 64.95(65.06),H, 5.51(5.42), N, 1.75(1.81).

IR ν (Ru-H) 2020, ν (C≡O) 1915 cm^{-1}, ^{1}HNMR (Ru-H) -13.70t δ.

6.3.9 Morpholine carbonylchlorohydridobis(triphenylphosphine)-ruthenium(II). HRu(CO)Cl(PPh$_3$)$_3$, 0.24 g, morpholine 0.5 ml.

Brown solid melting at 185°. Yield 65%.

C, 63.28(63.35), H, 4.97(5.15), N, 1.71(1.80).

IR ν(Ru-H) 2010, ν(C≡O) 1920 cm^{-1}, ^{1}HNMR (Ru-H) -13.50tδ.

6.3.10 (2,2'-Bipyridyl)carbonylchlorohydridobis(triphenylphosphine)ruthenium(II). $HRu(CO)Cl(PPh_3)_3$ 0.24 g, 2,2 Bipy. 80 mg. Pink product containing one molecule of water attached. M.p. 195°. Yield. 80%.

C, 65.21(65.01), H, 4.76(4.75), N, 3.18(3.24)

IR ν(Ru-H) 1980, ν(C≡O) 1920 cm^{-1} ^{1}HNMR (Ru-H) -11.35tδ.

6.3.11 (1,10-Phenanthroline)carbonylchlorohydridobis(triphenylphosphine ruthenium(II). $HRu(CO)Cl(PPh_3)_3$ 0.24 g, 1,10 Phen. 100 mg.

Yellow product containing one molecule of water. M.p. 179°, yield 75%. C, 66.15(66.23), H, 4.53(4.62), N, 3.06(3.15)

IR ν(Ru-H) 2020, ν (C≡O) 1920 cm^{-1} ^{1}HNMR (Ru-H) -11.09tδ.

6.3.12 (Benzo(f)quinoline)carbonyl chlorohydridobis(triphenylphosphine)ruthenium(II). $HRu(CO)Cl(PPh_3)_3$ 0.24 g, benzo(f) quinoline (90 mg).

Non-melting solid having brown colour. Yield 55%.

IR ν(Ru-H) 2000, ν (C≡O) 1930, 1910 cm^{-1}.

6.3.13 (Isonicotinic acid hydrazide)carbonylchlorohydridobis-(triphenylphosphine)ruthenium(II).

HRu(CO)Cl(($PPh_3)_3$ 0.24 g, isoniaz. 70 mg.

Yellow solid melting at 105°. Yield 80%.

C, 62.75(62.42); H, 4.52(4.63); N, 5.04(5.08).

IR ν (Ru-H)2030, ν (C≡O) 1915cm^{-1} ^{1}HNMRδ(Ru-H), -13.55t,

-14.46t.

6.3.14 (4-Phenyl-6-chloroquinazoline)carbonyl chlorohydrido bis(triphenylphosphine)ruthenium(II).

$HRu(CO)Cl(PPh_3)_3$, 0.24 g, 4-Phenyl(6-chloroquinazoline) 100 mg. Brown product melting at 125. Yield 72%.

C, 65.70(65.81), H, 4.23(4.33), N, 2.93(3.01).

IR ν(Ru-H), 2040, ν($C\equiv O$) 1940 cm^{-1}.

6.3.15 (4-Phenyl-6,7-dimethoxyquinazoline)carbonylchlorohydrido bis(triphenylphosphine)ruthenium(II).

$HRu(CO)Cl(PPh_3)_3$ 0.24 g, 4-Ph,6,7-dimethoxyquinazoline) 100 mg. Brown solid melting at 110°, Yield 60%.

C, 66.62(66.52), H, 4.65(4.71), N, 2.85(2.94).

IR ν(Ru-H) 2040, ν($C\equiv O$) 1935 cm^{-1}.

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Chapter VII : Cationic Ruthenium(II) Complexes

7.1 Cationic complexes of ruthenium(II) with heterocyclic ligands

Cationic ruthenium(II) complexes containing triphenylphosphine, and phosphites have been reported[1-2]. The general method of preparation involves abstraction of a halide ligand in the complex using sodium or silver salts of non-coordinating anions[3-5]. Cationic complexes of the type $[Ru(CO)(PPh_3)_2(L)(RCN)]^+(ClO_4)^-$, derived from acetonitrile and acrylonitrile have been reported[6].

7.2.1 Results and Discussion

Substitution reactions have been carried out in the complex $[Ru\text{-}H(CO)Cl(PPh_3)_3]$ (I) using mono- and bi-dentate nitrogen heterocyclics. Since, the phosphine *trans* to the hydrido hydrogen is labile, substitution takes place at that site, giving a *trans* complex $RuH(CO)Cl(PPh_3)_2$ (L) (II).

$RuHCl(CO)(PPh_3)_3 + L \longrightarrow RuH(CO)Cl(PPh_3)_2(L) + PPh_3$

The monodentate ligands (L) used are pyridine, 4-methylpyridine, 4-vinylpyridine and the bidentate ligands 2,2'-bipyridyl and 1,10-phenanthroline. In the latter complexes one of the nitrogen coordinates to one water molecule. The chloride ion in the complex (II) reacts with $NaBPh_4$ in methanol in presence of an excess of the appropriate ligand involved, to yield cationic complexes of the type $RuH(CO)(PPh_3)_2(L)_2^+\ [BPh_4)^-$ and

$[Ru\text{-}H(CO)(PPh_3)_2(L')][BPh_4]$.

$RuH(CO)Cl(PPh_3)_2(L) + NaBPh_4 + L \longrightarrow [RuH(CO)(PPh_3)_2(L)_2\,[BPh_4]^- + NaCl.$

$RuH(CO)Cl(PPh_3)_2\,(Bipy.H_2O) + NaBPh_4 \longrightarrow$
$[RuH(CO)(PPh_3)_2\,(bipy)]^+\,[BPh_4]^- + NaCl + H_2O.$

These cationic complexes are high melting crystalline solids. They are soluble in chloroform and benzene and insoluble in methanol and hexane.

7.2.2 Ruthenium(II) carbonyl complexes

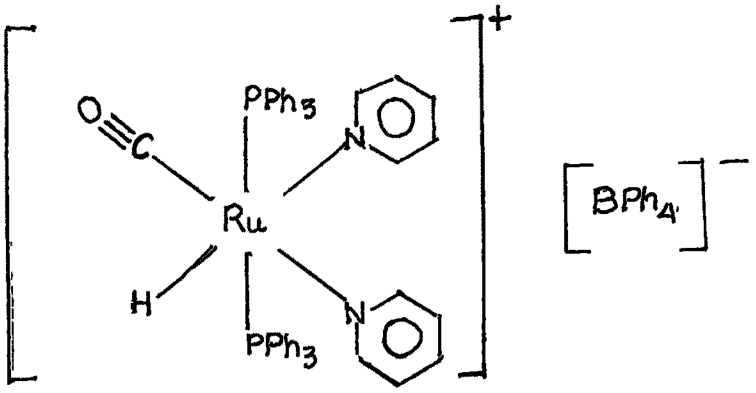
The IR spectra of the complexes in nujol show ν(Ru-H) at ~ 1970 cm^{-1} suggesting reduced Ru-H bond order compared to the starting chloro complexes (II) where it is ~ 1990 cm^{-1}. The terminal carbonyl stretching frequency is observed in the region 1910-1935 cm^{-1}. This shift to the higher frequency side compared to the chloro derivatives (1900-1920 cm^{-1}) is attributed to reduced metal-carbon π -interaction as a resuslt of increased positive charge on ruthenium. Solution spectra in chloroform show an increase of 10 cm^{-1} in their ν(C≡O) as expected. Pyridine and substituted pyridine cationic derivatives show characteristic ν(C=C) and ν(C=N) around 1600 cm^{-1}. A medium band around 995 cm^{-1} is attributed to the pyridine ring breathing.

2,2'-Bipyridyl and 1,10-phenanthroline derivatives show more than one ν(C≡O) bands in nujol, due to solid state splitting, whereas the chloroform solution spectra showed only one band around 1935 cm^{-1}.

7.2.3 The high field ^{1}HNMR spectra of the complexes show a triplet at higher magnetic field at -11.36 to -14.55 ppm with ^{2}J(PH)cis = 20 Hz, suggestive of phosphorus atoms *trans* to each other. The chlororuthenium complexes containing ring substituted pyridines exhibit two triplets for Ru-H proton which confirms the presence of two isomers[9]. The complex $[RuH(CO)(PPh_3)_2\ (4\text{-}MePy)_2]^+\ (BPh_4)^-$, shows signals for aryl, methyl and hydride protons in the ratio 58:6:1. The methyl resonance consisting of two singlets at δ 0.61 and 0.44 suggest them to be magnetically non-equivalent. This high field shift of methyl resonance compared to the chloro complex (δ 2.05) suggests increased steric crowding in this cationic complex.

7.2.3 The conductivity of the cationic complexes has been measured, at a molar concentration of 10^{-3} in nitromethane. These complexes show Λ_M values of 46.57 ohm^{-1} cm^2 mol^{-1}. A 1:1 non-complex electrolyte of the type tetrabutyl ammonium iodide in nitromethane has given the value ~ 91.5 ohm^{-1} cm^2. mol^{-1} [10]. The reference value for $[Bu_4N]^+[BPh_4]^-$ is ~ 60 ohm^{-1} cm^2 mol^{-1}; the lower value may be attributed to low anionic mobilities, and the new cationic complexes exist as 1:1 electrolytes in solution.

Considering IR, ^1H NMR and electronic spectral data, the 4-methylpyridine complex as a sample product, the stereochemistry for the complex is proposed to be



7.3 Experimental

The substituted ruthenium(II) complexes $RuH(CO)Cl(PPh_3)_2(L)$ where the ligand L is pyridine, 4-methylpyridine, 4-vinylpyridine, 2,2'-bipyridyl and 1,10-phenanthroline were used from the earlier preparations.

7.3.1 $[RuH(CO)(PPh_3)_2(4\text{-}MePy)_2]^+[BPh_4]^-$

$[RuH(CO)Cl(PPh_3)_3]$ (0.238 g, 0.25 mmol) was dissolved in benzene (20 ml), mixed with 4-methylpyridine (0.140 g; 1.5 mmol) and stirred for 24 h during which the colour turned yellow green. The contents were concentrated to about 10 ml and $NaBPh_4$ (0.0854 g; 0.25 mmol) dissolved in methanol (20 ml) was added. The resulting green solution was kept for crystallization, at ambient temperature for 12 h. The colourless crystals separated were collected, washed with methanol and dried in vacuo. Yield 0.215 g (77%), m.p.185^{o}C.

C, 75.12(75.32), H, 5.55(5.43), P, 5.46(5.47); IR ν (Ru-H) 1975m cm^{-1}. ν (C≡O)1935s, cm^{-1}. ^{1}HNMR Ru-H δ -13.52t, conductivity 56.98 M ohm^{-1} cm^{2}.

7.3.2 $[Ru\text{-}H(CO)Cl(PPh_3)_2\ (BiPy.H_2O)]$

a) $RuH(CO)Cl(PPh_3)_3$ (0.238 g; 0.25 mmol) was added to a solution of 2,2'-bipyridyl (0.039 g; 0.25 mmol) in benzene (20 ml). The reaction flask was covered with black paper to prevent photochemical decomposition. The contents were stirred for 24 h, the pink brown crystals separated were collected, washed with benzene and dried at room temperature in vacuo. M.p. 195. Yield 0.12 g (55%). The complex with 1,10-phenanthroline was yellow in colour and melted at 175^{o}.

7.3.2 $[Ru\text{-}H(CO)(PPh_3)_2(BiPy)^{+}[BPh_4]^{-}$

b) A methanolic solution of $NaBPh_4$ (0.042 g; 0.125 mmol) was added to $RuH(CO)Cl(PPh_3)_2(BiPy.H_2O)$ (0.1065 g; 0.125 mmol) in methanol (20 ml) and the resulting yellow solution was kept stirring for 4 h. The pale yellow crystals separated were washed with methanol and dried in vacuo.

Yield 0.175 g (61%), m.p. 188^{o}.

C, 75.59(75.45),H, 5.19(5.26), P, 5.44(5.48). I.R. ν (Ru-H) 2000w, ν (C≡O) 1930 m, 1910s,cm^{-1} ^{1}HNMR Ru-H δ -12.96t conductivity 47.71 M ohms^{-1} cm^{1}.

Other complexes were prepared similarly.

7.3.3 $[RuH(CO)(PPh_3)_2(Py)_2]^+[BPh_4]^-$

Colourless crystalline product. Yield 0.215 g (~77%), m.p. 185°.

C, 75.12(75.32), H, 5.55(5.43), P, 5.46(5.47).

IR ν (Ru-H) 1975m, cm^1, ν (C≡O) 1935s cm^{-1}. ^1H NMR, Ru-Hδ -13.52t, conductivity 56.98 M ohm^{-1} cm^2.

7.3.4 $[Ru\text{-}H(CO)(PPh_3)_2(4\text{-}VinPy)_2]^+[BPh_4]^-$

Colourless ~ yield 78%. C, 75.08(76.06), H, 5.47(5.53), P, 5.14(5.23). IR ν (Ru-H) 1975m, cm^{-1}, ν C≡O) 1935s cm^{-1}, ^1H NMR -13.20t. Conductivity 47.81 M ohm^{-1} cm^2.

7.3.5 $[Ru\text{-}H(CO)(PPh_3)_2(Phen)]^+[BPh_4]^-$

Light yellow product, m.p. 230°. Yield 0.190 g (68%).

C, 76.02(75.96), H, 5.17(5.15), P, 5.33(5.36).

IR ν (Ru-H) 1970m cm^{-1}, ν (C≡O) 1910s, 1930m cm^{-1}.

^1H NMR (Ru-H)δ-11.36t. Conductivity 46.20 M ohm^{-1} cm^2.

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