DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

STRUCTURES AND REACTIVITIES OF SOME TRANSITION METAL COMPLEXES CONTAINING SEMICARBAZONE DERIVATIVES

by
Nurdan ÖZTÜRK

February, 2014
İZMİR

STRUCTURES AND REACTIVITIES OF SOME TRANSITION METAL COMPLEXES CONTAINING SEMICARBAZONE DERIVATIVES

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M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"STRUCTURE AND REACTIVITIES OF SOME TRANSITION METAL COMPLEXES CONTAINING SEMICARBAZONE DERIVATIVES"** completed by **NURDAN ÖZTÜRK** under supervision of **PROF.DR. ELİF SUBAŞI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

Prof.Dr. Elif SUBAŞI

Supervisor

Prof. Dr. Suna TİMUR

(Jury Member)

Doç. Dr. Funda DEMİRHAN

(Jury Member)

Prof.Dr. Ayşe OKUR
Director
Graduate School of Natural and Applied Sciences

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Nurdan ÖZTÜRK

STRUCTURE AND REACTIVITIES OF SOME TRANSITION METAL COMPLEXES CONTAINING SEMICARBAZONE DERIVATIVES

ABSTRACT

Thiosemicarbazones are an important class of N, S donor ligands which have considerable interest because of their chemistry and biological activities, such as antitumor, antibacterial, antiviral, antiamoebic and antimalarial activities. The chemistry of complexes of ruthenium with their thiosemicarbazones, which can coordinate with the metal either in neutral thione form or in the anionic thiolate form, has received attention in recent years primarily due to its varied coordination mode, novel electrochemical and electronic properties.

Herein, in connection with our ongoing interest we have explored the chemistry of ruthenium (II) complexes of the thiosemicarbazones, mainly to understand the variable binding mode of these ligands displayed in their complexes. New *complex* 1, *complex* 2, *complex* 3, and *complex* 4 complexes have been synthesized by *[Ru(PPh3)3(CO)(H)Cl]* and thiosemicarbazones ligands TSC1; (*2-hydroxy-3-metoxybenzaldehyde thiosemicarbazone),* TSC2; (*3-hydroxybenzaldehyde thiosemicarbazone),* TSC3; (*3,4-dihydroxybenzaldehyde thiosemicarbazone*), TSC4; *(Thiophene-2-carbaldehyde thiosemicarbazone)* and characterized by analytical and spectroscopic data such as elemental analysis, FTIR, 1H NMR, 31P NMR spectroscopy. The spectroscopic studies showed that first ligand is coordinated to the central metal as a tridendate ligand coordinating *via* the azomethine nitrogen (C=N), phenolic oxygen atom and sulfur atom to the central metal in (1), whereas second, third and fourth ligands are coordinated to the central metal as a bidentate ligand coordinating via azomethine nitrogens (C=N) and sulfur atoms to the central metal in (2), (3) and (4). Antimicrobial activities of the complexes have also been searched for the syntesized complexes.

Keywords: Thiosemicarbazones, biological activities, Ruthenium complexes

SEMİKARBAZON TÜREVLERİ İÇEREN BAZI GEÇİŞ METAL KOMPLEKSLERİNİN YAPILARI VE TEPKİNLİKLERİ

ÖZ

Tiyosemikarbazonlar antitumor, antibakteriyel, antiviral, antiamoebik ve antimalaryal aktiviteleri gibi kimyasal ve biyolojik aktivitelerinden dolayı oldukça ilgi çeken azot, kükürt donor ligandlarının önemli bir sınıfıdır. Metalin ya nötral tiyon formu ya da anyonik tiyolat formu ile koordine olması ile oluşan Rutenyumun tiyosemikarbazonlu komplekslerinin kimyası ilk olarak çeşitli koordinasyon biçimlerinden ve değişik elektrokimyasal ve elektronik özelliklerinden dolayı son yıllarda dikkat çekmektedir.

Burada, devam eden ilgimizle bağlantılı olarak tiyosemikarbazonların Ruthenyum (II) komplekslerinin kimyasını esasen komplekslerindeki değişken bağlanma biçimlerini anlamak için inceledik. Yeni *complex* 1, *complex* 2, *complex* 3 and *complex* 4 kompleksleri, *[Ru(PPh3)3(CO)(H)Cl]* başlangıç maddesi ve bazı tiyosemikarbazon ligandları TSC1; (*2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone),* TSC2; (*3-hydroxybenzaldehyde thiosemicarbazone),* TSC3; (*3,4-dihydroxybenzaldehyde thiosemicarbazone*), TSC4; *(Thiophene-2-carbaldehyde thiosemicarbazone)* ile sentezlendi ve elemental analiz, FTIR, 1H NMR, 31P NMR spektroskopisi gibi analitik ve spektroskopik veriler ile karakterize edildi. Spektroskopik çalışmalar birinci ligandın (1) nolu komplekste merkez atomuna azometin azot atomu (C=N), fenolik oksijen atomu ve sulfur atomu aracılığıyla üç dişli ligand olarak koordine olduğunu gösterirken, ikinci, üçüncü ve dördüncü ligandların merkez atomuna (2), (3) ve (4) nolu komplekslerde azometin azotları (C=N) ve sulfur atomları aracılığıyla iki dişli ligand olarak koordine olduklarını göstermiştir. Ayrıca sentezlenilen komplekslerin antimikrobiyal aktiviteleri incelendi.

Keywords : Tiyosemikarbazonlar, biyolojik aktiviteler, Ruthenyum kompleksler.

CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

CHAPTER ONE
INTRODUCTION

1.1 Thiosemicarbazones

Thiosemicarbazones ($R^1R^2C^2=N^3–N^2(H)–C^1(=S)N^1R^3R^4$) form an considerable class of N, S-donor ligands, and their coordination chemistry was first explored during the early sixties (Gingras, Somorjai, &Bayley, 1961). The synthesis of thiosemicarbazones includes condensation of a ketone, or an aldehyde with a thiosemicarbazide under chillout conditions (Gingras, Hornal, & Bayley, 1960). Akbar Ali and Livingstone in 1974 first reported the chemistry of thiosemicarbazones along with other N, S-donor ligands(Akbar Ali, & Livingstone, 1974) , followed by a report by Campbell in 1975 (Campbell, 1975).

The following developments in metal-thiosemicarbazone chemistry were reported by Padhye and Kauffman in 1985 (Padhye, & Kauffman, 1985), West et al. in 1991–1993 (West, Padhye, & Sonawane, 1991; West, Liberta, Padhye, Chilkate, Sonawane, Kumbhar, & Yerande, 1993), and latest by Casas et al. in 1999–2000 (Casas, Garcia-Tasende, & Sordo, 2000; Casas, Garcia-Tasende, Sordo, 1999). These reports have defined several aspects of thiosemicarbazones such as synthesis of metal complexes, spectroscopic properties, crystal structures, and biological applications (Akbar Ali, & Livingstone, 1974; Campbell, 1975; Padhye, & Kauffman, 1985; West, Padhye, & Sonawane, 1991; West, Liberta, Padhye, Chilkate, Sonawane, Kumbhar, & Yerande, 1993).

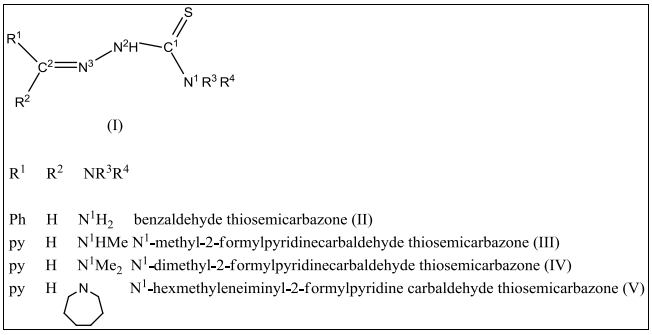


Figure 1.1 Structure of thiosemicarbazones

1.1.1 Types of Ligands

Thiosemicarbazones are essentially Schiff bases gained by the condensation of an aldehyde, or a ketone with a thiosemicarbazide, and are extensively classified as mono thiosemicarbazones and bisthiosemicarbazones.

$$R_2CO + H_2N–NH–C(=S)– NH_2 \rightarrow R_2C\ N–NH–C(=S)–NH_2$$

1.1.1.1 Mono-Thiosemicarbazones

The basic mono-thiosemicarbazone ligand (structure I, Figure 1.1) has different, R^1, R^2, R^3 and R^4 substituents, and depending upon the substituents, different sub-classes of ligands are formed. Thiosemicabazones dependent upon aldehydes have hydrogen atom as one of the substituents (R^2) at C^2 carbon, while second substituent R^1 may be an alkyl, an aryl or a heterocyclic group. Similarly, substituents at N^1 nitrogen may be both hydrogen atoms, or one hydrogen, and second alkyl, or aryl group, and finally N^1may be a part of the cyclic ring. Some examples (II–V) are shown in Figure 1 above. The second category of mono-thiosemicarbazone ligands depends upon the parent ketonic group, and thus both the substituents at C^2 carbon may be same or different alkyl, or aryl groups (VI). Moreover, in type VII, the parent ketone is cyclic and thus C^2 carbon is part of the ring. The pattern of substituents at N^1 nitrogen is alike to the above type of ligands. Some ligands based on ketones are exemplified here.

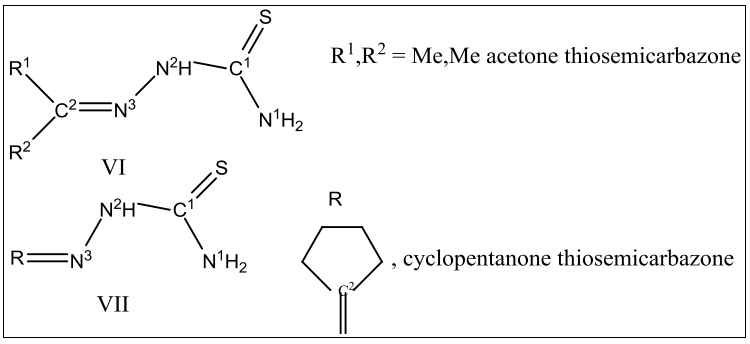


Figure 1.2 Structure of mono-thiosemicarbazones

1.1.1.2 Bis-Thiosemicarbazones

Bis-thiosemicarbazones have two arms combined via a ring, or a C–C bond, as for example, shown in structures VIII and IX below, and for more examples one can refer to the text.

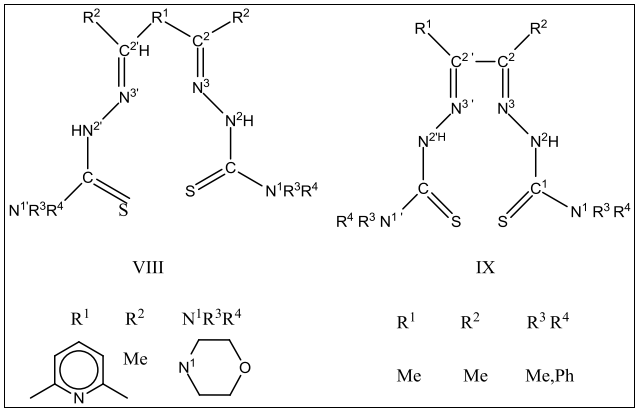


Figure 1.3 Structure of bis-thiosemicarbazones

1.1.1.3 Bonding Modes of Ligands

Thiosemicarbazone ligands exist as thione–thiol tautomers (Xa–Xb), and can bind to a metal center in the neutral (Xa), or the anionic forms (Xc). The anionic form is produced after loss of $–N^2H$ (Xa) or –SH (Xb) hydrogen ions. A number of bonding modes have been observed for the thiosemicarbazones in their neutral or anionic forms.

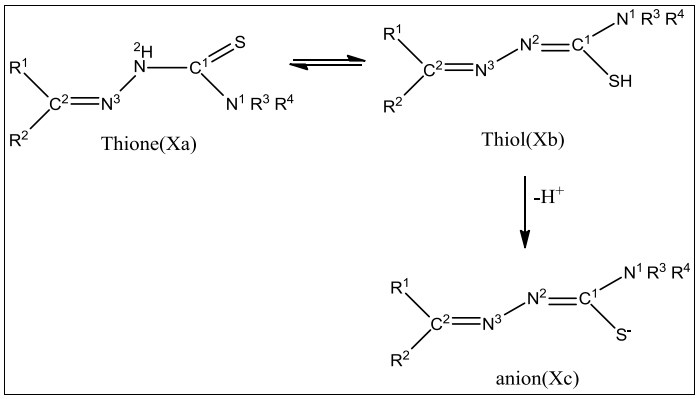


Figure 1.4 Thione and thiol forms of thiosemicarbazones

1.1.1.4 Bonding Modes in Neutral Form

In neutral form, the binding appears via only S atom in η^1-S (XI), μ^2-S (XII), η^2-N^3, S-chelation (XIII), η^3-N^3, S-chelation and S-bridging (XIV) modes. However, if the substituent at C^2 has a donor atom, and engages in bonding, the additional bonding modes observed are, η^3-X, N^3, S-chelation (XV), η^4-X, N^3, S-chelation and S-bridging (XVI), and η^4-X, N^3, S-chelation and X-bridging (XVI) (e.g. X=N, O) (Lobana, Rekha, & Butcher, 2004; Lobana,Rekha, Butcher, Castineiras, Bermejo, & Bharatam, 2006; Lobana, Khanna, Butcher, Hunter, & Zeller, 2007; Lobana, Kumari, & Butcher, 2008; Jouad, Riou, Allain, Khan, & Bouet, 2001; Lhuachan, Siripaisarnpipat, & Chaichit, 2003; Bermejo, Carballo, Castineiras, Dominguez, Maichle-Mossmer, Strahle, & West, 1999; Gomez-Saiz, Garcia-Tojal, Maestro, Mahia, Arniaz, Lezama, & Rojo, 2003; Labisbal, Haslow, Sousa-Pedrares, Valdes-Martinez, Harnandez- Ortega, & West, 2003).

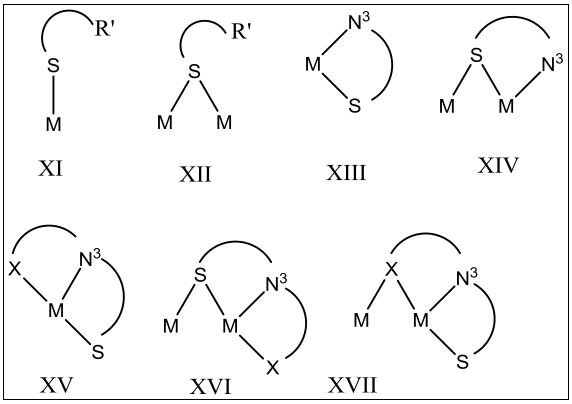


Figure 1.5 Bonding modes in neutral form

1.1.1.5 Bonding Modes in Anionic Form

The modes (XI–XVII) shown by the neutral ligands are also presented by the anionic ligands, viz.η^1-S,μ_2-S,η^2-N^3, S-chelation, η^2-N^3, S-chelation and S- bridging, η^3-X, N^3, S-chelation, η^3-X, N^3, S-chelation-cum-S-bridging, η^3-X, N^3, S-chelation and X-bridging (Kovala-Demertzi, Domopoulou, Demertzis, Valdes-Martinez, Hernandez-Ortega, Espinosa-Perez, West, Salberg, Bain, & Bloom, 1996; Casas, Castellano, Rodriguez-Arguelles, Sanchez, Sordo, & Zukerman-Schpector, 1997;

Garcia-Tojal, Pizarro, Garcia-Orad, Perez-Sanz, Ugalde, Diaz, Serra, Arriortua, & Rojo, 2001; Casas, Castano, Cifuentes, Sanchez, & Sordo, 2002; Lobana, Bawa, Castineiras, & Butcher, 2007; Halder, Peng, Lee, Chatterjee, Mukherjee, Dutta, Sanyal, & Bhattacharya, 2008; Kovala-Demertzi, Kourkoumelis, Demertzis, Miller, Frampton, Swearingen, & West, 2000; Lu, White, Rheingold, & Crabtree, 1993).

Additionally, η^2-N^2, S (XVIII) and N^2, S-bridging and S-bridging modes (XIX) are described (Lobana, Bawa, Butcher, Liaw, & Liu, 2006; Ashfield, Cowley, Dilworth, & Donnelly, 2004).

A rare example of pentacoordination (XX) by a thiosemicarbazone ligand has also been reported (Pal, Basuli, Mak, & Bhattacharya, 2001).

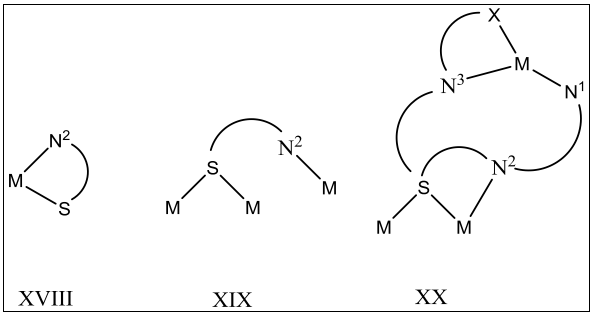


Figure 1.6 Bonding modes in anionic form

1.1.1.6 Bonding Modes of Bis-Thiosemicarbazones

Bis-thiosemicarbazones can bind in neutral as well as anionic forms using their both arms. The common coordination modes are XXI and XXII depending on the participation of the central ring combining the two arms (Gil, Bermejo, Castineiras, Beraldo, & West, 2000; Pedrido, Bermejo, Romero, Vazquez, Gonzalez-Noya, Maneiro, Rodriquez, & Fernandez, 2005; Casas, Castellano, Ellena, Garcia-Tasende, Sanchez, Sordo, Vazquez-Lopez, & Vidarte, 2003).

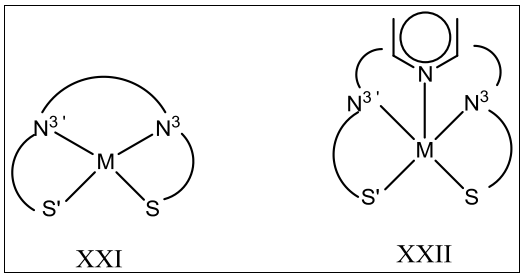


Figure 1.7 Bonding modes of bis-thiosemicarbazones

1.1.2 Thiosemicarbazone-Metal Complexes

Commonly occuring coordination compounds are fundamental to living organisms. Metal complexes play a diversity of important roles in biological systems. Many enzymes, the naturally occuring catalysts that control biological processes, are metal complexes (metalloenzymes); for example, carboxypeptidase, a hydrolytic enzyme important in digestion, have a zinc ion coordinated to several amino acid residues of the protein. Another enzyme, catalase, which is an efficient catalyst for the decomposition of hydrogen peroxide, have iron-porphyrin complexes. In both cases, the coordinated metal ions are probably the sites of catalytic activity. Hemoglobin also have iron-porphyrin complexes, its role as an oxygen carrier being related to the ability of the iron atoms to coordinate oxygen molecules reversibly. Other biologically considerable coordination compounds have chlorophyll (a magnesium-porphyrin complex) and vitamin B_{12}, a complex of cobalt with a macrocyclic ligand known as corrin.

Since Werner's leading work, coordination chemistry has developed in a continued way. Nowadays, coordination compounds are included in an unbelievable wide range of applications in catalysis, optical related applications, medicinal field and hydrometallurgical extraction. There has been important current interest in the chemistry of ruthenium, which is fundamentally due to its attractive redox, photophysical and photochemical properties. As all these properties are directed by the coordination environment around the central metal ion, complexation of ruthenium by ligands of selected types is of heavy importance. (Das, Peng, Lee & Bhattacharya, 2004).

The electronic configuration of ruthenium, $4d^7\ 5s^1$, makes this metal, together with osmium, unique among all the elements in displaying the widest range of oxidation states in their complexes,i.e., from oxidation state -2 in $[Ru(CO)_4]^{2-}$ to +8 in RuO_4 corresponding to d^0 to d^{10}. The coordination chemistry of ruthenium is directed by the oxidation states +2 and +3. Synthetic variability, high oxidation states,easy availability and a robust character of its first coordination sphere are suitable characteristics that make ruthenium complexes perform well as catalysts. As a 4d transition metal, ruthenium is kinetically inert, requiring high temperatures and longer reaction times than unstable 3d metals, such as nickel and copper, for synthetic purposes. As a result, ruthenium complexes are often very stable and ligand exchange can appear with little reorganization. This stability also permits ligands to be modified while coordinated to the metal. (Fanni, Murphy, Killeen & Vos, 2000).

To obtain an suitable balance between the elctronic and steric environment around the metal and in order to control their activity, stability and chemoselectivity, many of these novel ruthenium complexes have been endowed with specific ligands(e.g. hydride, halide, hydrate, carboxylate, phosphane, amine, oxygen or nitrogen chelating groups, Schiff bases, arenes, carbenes, etc.) (Caballero, Carrion, Espino, Jalon & Manzano, 2004; Kinnunen, Haukka, Pesonen & Pakkanen, 2002; Boelrijk, Jorna & Reedijk, 1995; Soler, Moldes, Encarnacion & Ros, 1999; Sellmann, Hille, Rosler, Heinemann & Moll, 2004; Tfouni, Krieger, McGarvey & Franco, 2003; Ooyama, Kobayashi, Shiren & Tanaka, 2003; Clercq & Verpoort, 2002; Ackermann, El Tom & Alois FuErstner, 2000). For several reasons, Schiff bases have been found to be among the most available and fascinating ligands for ruthenium complexes.

The metal complexes with Schiff bases as ligands have been playing an important role in the development of coordination chemistry as a whole. However, it was not until the 1950s that real and rapid advances in this field became evident. Nowadays, the research field coping with Schiff base metal complexes has spread greatly and embraces very broad and different subjects comprising enormous areas of organometallic compounds and various aspects of bioinorganic chemistry (Yamada,

1999; Maurya & Rajput, 2006; Maurya, Pandey, Chaurasia & Martin, 2006; Garcia-Raso, Fiol, Badenas & Munoz, 2001; El-Behery & El-Twigry, 2007).

Because of the following reasons Schiff bases are prefered as ligands. First, steric and electronic effects around the ruthenium core can be calmly tuned by an suitable selection of bulky and/or electron withdrawing or donating substituents incorporated into the Schiff bases. Secondly, the two donor atoms, N and O, of the chelated Schiff base apply two opposite electronic effects: the phenolate oxygen is a hard donor known to stabilize the higher oxidation state of the ruthenium atom whereas the imine nitrogen is a soft donor and, therefore, will stabilize the lower oxidation state of the ruthenium. Thirdly, Schiff bases are currently prepared in high yield through one-step procedures by condensation of common aldehydes with amines, in essentially quantitative yields (Drozdzak, Allaert, Ledoux, Dragutan, Dragutan, & Verpoort, 2005).

Schiff base complexes have remained an important and popular area of research because of their simple synthesis, variability and diverse range of applications. However, it is definitely the range of donor sets (O,N,S) and the coordination geometries afforded to metal centres by these multidentate species which has continued their common interest over the past 150 years (Taylor, Reglinski &Wallace, 2004).

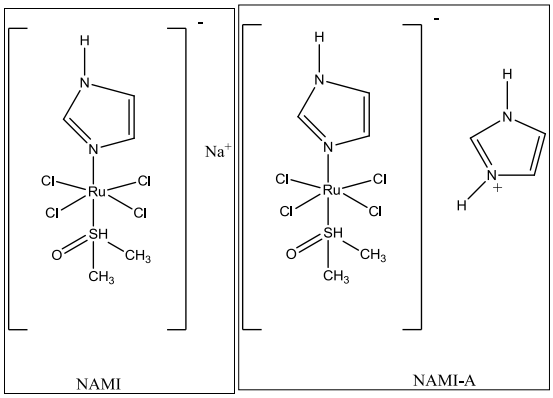
Generally, the tridentate Schiff base ligands with a flexible donor atom, in comparison with the bidentate ligands, can provide the conservational shields for catalytically active metal centers leading to a ‘‘more stable’’ active species by the coordination of the added donor atom. Consequently, the activity of the complex with a tridentate Schiff base ligand is much higher than that of the complex with a bidentate ligand (Li, Yao, Wang, Zhang & Shen, 2008).

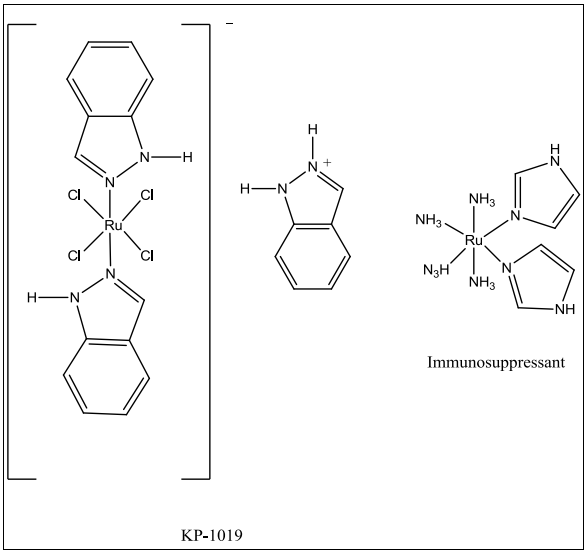
Owing to the wide-ranging efficiency of aldehydes and ketones as an considerable synthetic intermediates, especially for the arrangement of carbon-skeletones (Hudlicky 1990; Sheldon & Kochi, 1981) and preparation of many drugs, vitamins

and compounds (Struss, Barnhart, Velasco, & Bronley-DeLancey, 2006; Lei, Hu, & Wang, 2006; Wang, Kawanami, Dapurkar, Venkataramanan, Chatterjee, Yokoyama & Ikushima, 2008; Vimalaand & Nagendrappa, 2009; Ji, Mizugaki, Ebitani & Kaneda, 2002). Oxidation of alcohols, as a method of the preparation of aldehydes and ketones, is a universal transformation in organic chemistry. The plethora of reagents available to accomplish this key-reaction stands as a clear evidence to its importance. However, the development of newer methods and methodologies is in these days gaining much attention because of the import of these oxidation reactions (Shirinia, Zolfigolb & Shahriari, 2008).

Bioinorganic chemistry has been developing in recent years and the rising success of metal medicines in clinical tests has attracted much interest in the design metal complexes as potential medicines. These compounds are potentially effective in the therapeutic and in diagnostic fields. The synthesis and characterization of biomimetic model complexes can also help in the understanding of biochemical processes in living organisms. Inorganic elements play considerable roles in biological processes and in medicine. It is known that many organic compounds in medicine not only have organic effect, they also interact with metal ions, such as through activation or biotransformation by a metal ion and a direct or indirect impact on metal ion metabolism. Since the perfect antitumour activity of cisplatin, *cis*-$[PtCl_2(NH_3)_2]$, one of the best selling antitumour drugs these days which was discovered in the 1960s by Rosenberg (Rosenberg & Van Camp, 1969), there has been many research efforts on discovering other metal complexes for chemotherapy and other clinical uses. The first ruthenium compound to experience clinical tests is NAMI, (Na)*trans*-$[Ru(Im)(dmso)(Cl)_4]$ (Im= imidazole) (Mestroni, Alessio, Sava, Pacor, Coluccia & Boccarelli, 1994). Several ruthenium complexes have lately been investigated for their antitumour activity. Very lately, two other ruthenium (III) complexes have also efficiently completed phase I clinical trials, (ImH)trans-$[Ru(Im)(dmso)Cl_4]$, namely NAMI-A and KP1019, Indazolium *trans*-$[RuCl_4(1H\text{-indazole})_2]$ (Sava & Bergamo, 2000; Groessl, Reisner, Hartinger, Eichinger, Semenova, Timerbaev, Jakupec, Arion & Keppler, 2007; Beckford, Leblanc, Thessing, Shaloski, Frost, Li & Seeram, 2009).

1.1.2.1 Structure of Some Medicinally Important Ruthenium Complexes





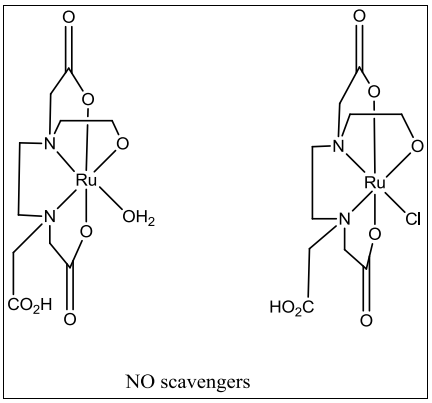


Figure 1.8 Structure of some medicinally important ruthenium complexes

During the past decades, the human population affected with life-treating infectious diseases caused by multidrug-resistant gram-positive and gram-negative pathogen bacteria raised an alarming level around the world. Because of this reason, new classes of antibacterial agents with novel mechanisms are essential need to struggle with the multidrug-resistant infections.

Thiosemicarbazones are of important pharmacological care since a number of derivatives have shown a broad spectrum of chemotherapeutic properties. Thiosemicarbazide and its derivatives as ligands with potential sulphur and nitrogen donors are interesting and have received particular attention not only due to the structural chemistry of their multifunctional coordination modes, but also of their significance in medicinal and pharmaceutical field; they show biological activities containing antibacterial (More, Bhalvankar & Pattar, 2001), antifungal (Singh & Dash, 1988), anticancer (Desai, Desai & Desai, 2001) and herbicidal activities (Samadhiya & Halve, 2001).

The noticeable biological activity of acid hydrazides R–CO–NH–NH_2, a class of Schiff base and their corresponding aroylhydrazones, R–CO–NH–N=CH–R and the dependence of their mode of chelation with transition metal ions present in the living system have been of considerable concern (Savanini, Chiasserini, Gaeta & Pellerano, 2002; Craliz, Rub, Willis & Edger, 1955). The coordination compounds of aroylhydrazones have been reported to behave as enzyme inhibitors (Dilworth, 1976) and are effective owing to their pharmacological applications (Merchant & Clothia, 1970). Aroylhydrazone complexes, however, seem to be a well applicant for catalytic oxidation studies due to their stability to resist oxidation (Monfared, Sadighiana, Kamyabi & Mayer, 2009). Investigation into the iron-binding potential of a range of hydrazone derivatives (Baker, Vitolo & Webb, 1985) as drugs for genetic disorders such as thalassemia, led to the discovery that salicylaldehyde benzoylhydrazone inhibits DNA synthesis and cell growth (Pickart, Goodwin, Burgua, Murphy & Johnson, 1983).

1.1.2.2 Present Status of Metal-Phosphorous and Metal-Arsenic Bonds

Many years ago a kind of alikeness has been noted between carbon monoxide, phosphorous and arsenic donors in their ability to form complexes with transition metals. Based on Pauling's theory of metal carbonyl double bonding, Chatt summarized that phosphorous in ligands such as tertiary phosphines had vacant d-orbitals capable of accepting electrons from filled metal d-orbitals and thus forming dative π-bonds additionally the metal –ligand σ-bond (Chatt & Williams, 1951). The presence of electronegative group bonded to phosphorous would encourage the transfer of electron density from the metal to ligand. Chatt tested the theory by studying the interactions of phosphorous trifluoride with platinum(II) chloride and boron trifluoride where platinum formed stable complexes and boron, which has no electrons accessible for dative π-bond formation, did not have any important interaction with phosphorous trifluoride. Nyholm and co-workers also introduced this proposal of back-bonding or dπ -dπ overlap between the metal and the donor atoms (Nylholm & Short, 1953; Burstall & Nylholm, 1952). Much of the argument about the nature of the bond between phosphorous and metals has centered on the associated importance of a σ or π contribution to the metal-ligand bonding and this topic still remains one of important controversy.

A selection of ruthenium and osmium nitrosyl halide complexes, $[MX_3(NO)(AR_3)_2]$ (M=Ru, Os; X=Cl, Br; A=P; R=alkyl,aryl or mixed alkyl aryl; A=As, R=phenyl) have been prepared by a available single-stage synthesis including addition of ruthenium or osmium halides and *N-methyl-N-nitrosotoluene-p*-sulphonamide or pentyl nitrite to a solution of the suitable tertiary phosphine or arsine in a boiling alcoholic solvent (Robinson & Uttley, 1972).

X-ray emission spectroscopy has been used to prove that phosphorus makes little or no use of its 3d orbitals in bonding in triphenylphosphine or in triphenylphosphine complexes. In comparison, direct evidence is presented for the formation of new bonds between the transition metal d orbitals and the phosphorus-carbon σ-bonds (Bourg, Gamblin & Urch, 1995).

Fractional crystallisation of the mixture, resulting from the direct reaction of mercury(II) bromide with triphenylphosphine (PPh_3) and pyrimidine-2-thione (pmtH), gives crystals of $[HgBr_2(PPh_3)_2]$ and $[HgBr_2(PPh_3)(pmtH)]$. The complexes have been characterised by their elemental analyses, melting points and their FT-IR, far-IR, and UV/Vis spectroscopic data. The crystal structures of both the complexes have been established by single crystal X-ray crystallography at room temperature (Kubicki, Hadjikakou & Xanthopoulou, 2001).

Natarajan and co-workers reported some new Ru(III) and Ru(II) complexes with triphenylarsine oxide. The further investigation on the compound $[RuCl_3(AsPh_3)(OAsPh_3)_2]$ revealed that this compound should be formulated as $[RuCl_3(AsPh_3)_2(OAsPh_3)]$. A new isomer of $[RuCl_3(AsPh_3)_3]$ besides other new complexes is also reported (Natarajan, Poddar & Agarwala, 1976).

1.1.2.3 Survey on Schiff Base Metal Complexes

The synthesis of the new complexes of 1-phenylacetyl-4-phenyl-3-thiosemicarbazide (H_2papts) and 1-phenoxyacetyl-4-phenyl-3-thiosemicarbazide (H_2pxapts); $[Ru(HL)_2(H_2O)_2]$, $[Rh(HL)_3]$, $[Ag(H_2L)(H_2O)_2](NO)_3$, $[UO_2(HL)(bipy)(AcO)(H_2O)_2]$ (H_2L= H_2papts, H_2pxapts; bipy= 2,2'-bipyridyl), $[Ag(H_2papts)(bipy)]^+$ and $[Pd(Hpapts)(bipy)]^+$ is described. Characterization of these complexes by IR, electronic and ^1H NMR spectra, conductometric titrations and thermal analysis is contained. The complexes $[Ru(HL)_2(H_2O)_2]$ were found to be effectual catalysts for the oxidation of primary alcohols to aldehydes and acids, secondary alcohols to ketones and aryl halides to aldehydes and acids in the presence of $NaIO_4$ as co-oxidant (Mostafa & Bekheit, 2000).

Some new metal (II) complexes, ML_2 [M= Mn,Co,Ni,Cu and Zn] of 2-acetylpyridine benzoylhydrazone ligand (HL) including trifunctional NNO-donor system have been synthesized and crystallographically characterized. The complexes consist of two ligands to give six coordinate, which are bonded to the metal atom on a meridional plane through acetylpyridine ring nitrogen, azomethine nitrogen and

benzoyl oxygen atoms, in turn. The coordination geometry for other complexes was described on the basis of the physico-chemical data by elemental analyses, FAB-MS, IR, ^{1}H NMR and electronic spectral measurements (Jang, Lee & Koo, 2005).

The synthesis and characterization of ruthenium (II) complexes, $[RuCl_2(dmso)_2(L)]$ (L= benzoic acid furan-2-ylmethylene-hydrazide, benzoic acid thiophen-2-ylmethylene-hydrazide, benzoic acid (1-furan-2-yl-ethylidene)-hydrazide) and benzoic acid (1-pyridin-2-ylethylidene)-hydrazide) are defined. The ligands, when treated with either cis-$[RuCl_2(dmso)_4]$ or *trans*-(Cl)-$[RuCl_2(dmso)_2(bpy)]$, resulted in the same products. This has been approved by IR spectra and single crystal X-ray diffraction studies. The binding of the complexes to Herring sperm DNA has been studied by absorption titration and cyclic voltammetry. The antibacterial features of the ligands and the complexes have been studied against five pathogenic bacteria (Mahalingam, Chitrapriya, Fronczek & Natarajan, 2008).

Complexes of a new tetradentate Schiff base, 3-[(Z)-2-piperazin-1-yl-ethylimino]-1,3-dihydro indol-2-one with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), UO_2(VI) and Th(IV) have been synthesized and characterized by microanalysis, conductivity, UV/Vis, FT-IR, ^{1}H NMR, TGA and magnetic susceptibility measurements. Octahedral geometry for Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes and a coordination number of 8 for UO_2(VI) and Th(IV) complexes are suggested. The ligand and its metal complexes were screened for antibacterial activity against *Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Pseudomonas aeruginosa* and the complexes are more impressive bactericides than the ligand. The anthelmentic activity of the ligand and its complexes against earthworms was also tested (Rama Krishna Reddy, Suneetha, Karigar, Manjunath & Mahendra, 2008).

Tridentate ligands with [P,N,O] donor sets, prepared either by the condensation of 2-(diphenylphosphino)-benzaldehyde with 1S, 2R-norephedrine or 2-aminophenol or by the condensation of 2-(diphenylphosphino) aniline with salicylaldehyde (sal), 5-(NO_2)sal, 5-(Cl) sal, 5-(Br)sal,5-(MeO)sal or 3-(MeO)sal, reacted with $[RuCl_2(dmso)_4]$ in refluxing. THF solution to yield complexes of the common

formula *cis*-[RuCl(η^3-L^{1-8})$(dmso)_2$]. Use of two equivalents of ligand HL^1 resulted in the formation of *mer*-[Ru(η^3-L^1)$_2$], a reaction not seen for HL^{2-8}. Aerial oxidation of *cis,mer*-[RuCl(η^3-L^3)$(dmso)_2$] in a chloroform solution yielded *cis,fac*-[$RuCl_2$(η^3-L^3)(dmso)], which has undergone an unexpected reform of co-ordination geometry (Bhattacharyya, Loza, Parr & Slawin, 1999).

New hexa-coordinated Ru (II) complexes of the type $[RuCl_2(dmso)_2(diamine)]$ (diamine= o-phenylenediamine and ethylenediamine) have been prepared by reacting cis-$[RuCl_2(dmso)_4]$ with Schiff bases (H_2sal-en, H_2nap-en, H_2sal-o-pdn, H_2nap-o-pdn) in a 1:1 ratio. The ligands, which were expected to behave as tetradentate (N_2O_2) chelates under the normal reaction conditions, were found to undergo hydrolytic cleavage to form the diamine and the related aldehyde. All the complexes have been characterized by analytical and spectroscopic (IR,electronic and ^{1}H NMR) data. Single-crystal X-ray analysis of the complex $[RuCl_2(dmso)_2$-(o-pndn)] revealed that the coordination environment around the ruthenium metal consists of a $N_2S_2Cl_2$ octahedron (Sukanya, Evans, Zeller & Natarajan, 2007).

1.1.2.4 Ruthenium (II) Complexes Containing Triphenylphosphine, Triphenylarsine and Other Ligands

The products gained by reacting ruthenium(II) complexes $[RuHCl(CO)(PPh_3)_2(B)]$ [B= PPh_3, pyridine or piperidine] with tridentate Schiff base ligands determined by condensing salicylaldehyde or o-vanilin with o-aminophenol and o-amino thiophenol, have been characterised by analytical, Iri electronic, ^{1}H and ^{31}P NMR spectral studies and formulated as [Ru(L)(CO)(PPh_3)(B)] (L= bifunctional tridentate Schiff base anion). Some have been tested for the *in vitro* growth inhibitory activity against bacteria *Escherichia coli*, *Bscillus* sp. And *Pseudomonas* sp (Jayabalakrishnan & Natarajan, 2002).

Sixteen neutral mixed ligand thiosemicarbazone complexes of ruthenium having general formula $[Ru(PPh_3)_2L_2]$, where LH= 1-(arylidine)4-aryl thiosemicarbazones, have been synthesized and characterized. The structures of four of the complexes

have been identified by single-crystal X-ray diffraction and they show that thiosemicarbazone ligands coordinate to the ruthenium center through the hydrazinic nitrogen and sulfur forming four membered chelate rings with ruthenium in $N_2S_2P_2$ coordination environment (Mishra, Naskar, Drew & Chattopadhyay, 2006).

Ruthenium(II) carbonyl complexes of the general formula $[Ru(L)(CO)(PPh_3)(Z)]$ (L= Schiff base anion; Z= PPh_3, pyridine or piperidine) have been synthesized by reacting $[RuH_2(CO)(PPh_3)]$ or $[RuHCl(CO)(PPh_3)_2(Z)]$ with tridentate Schiff base ligands determined by condensing salicylaldehyde, *o*-vanillinor *o*-hydroxyacetophenone with *N*(4)phenylsemicarbazide. These complexes have been characterized by analytical, IR, electronic, ^1H NMR and ^{31}P NMR spectral studies. An octahedral structure has been temporarily recommended for the new complexes. Some of the complexes have been tested for *in vitro* growth inhibitory activity against the bacteria *Escherichia coli*, *Bacillus* sp. and *Pseudomonas* sp (Jayabalakrishnan & Natarajan, 2001).

Unsymmetrically-substituted ruthenium (II) Schiff-base complexes, $[Ru(CO)(B)(Lx)]$ [B= PPh_3, $AsPh_3$ or pyridine; Lx= dianion of tetradentate unsymmetrical Schiff-base ligand; x= 4-7, L_4= salen-o-hyac, L_5= valen-o-hyac, L_6= salphen-o-hyac, L_7= valen-2-hacn], were prepared and characterized by analytical, IR, electronic and ^1H NMR spectral studies. The new complexes were tested for their catalytic activity towards the oxidation of benzylalcohol to benzaldehyde (Gowri, Priya, Muthukumar & Viswanathamurthi, 2009).

The reactions of $[RuHCl(CO)(B)(EPh_3)_2]$ (B= EPh_3 or pyridine; E= P or As) and 2-hydroxychalcones in 1:2 ratio led to the formation of $[Ru(CO)(B)(L)_2]$ (L= 2-hydroxychalcones). The new complexes have been characterized by analytical and spectral data. The new complexes were found to catalyze the oxidation of alcohols to aldehydes using NMO as oxidant and are biologically active against bacteria such as *Escherichia coli, Salmonella typhi* and fungi *Aspergillus niger* (Muthukumar, Viswanathamurthi & Natarajan , 2008).

Hexa-coordinated ruthenium(II) complexes of the type [Ru(CO)(PPh_3)(Z)(L)] (Z= PPh_3, pyridine or piperidine; L= anion of the Schiff-base) have been prepared by reacting [RuHCl(CO)(PPh_3)$_2$(Z)] with tridentate Schiff bases determined by condensing anthranilic acid with acetylacetone, salicylaldehyde, *o*-vanilin and *o*-hydroxy acetophenone. The complexes were characterized by analytical and spectral data and were found to be efficient catalysts for oxidising primary alcohols to aldehydes in the presence of NMO as oxidant and were found to be active against the growth of pathogenic fungi *Aspergillus flavus*, *Fusarium oxysporium* and *Rhizoctonia solani* (Jayabalakrishnan, Karvembu & Natarajan, 2002).

A number of *cis*-{$RuCl_2(PPh_3)_2$[4,4'-(X)$_2$-2,2'-bipy]}[*cis*-chlorines; X= -H, -Me, -SMe, and (-Cl, -Me)] complexes have had their structures identified by single crystal X-ray diffraction. The geometry of these complexes, also identified in CH_2Cl_2 solution by $^{31}P\{^1H\}$ NMR spectroscopy, showed that the chemical shifts for the phosphorus atoms are inconsiderably depent on the p*K*a of the 4,4'-(-X)$_2$-2,2'-bipy ligands (Santiago, Batista, de Araujo, Donnici, De, Moreira, Castellano, Ellena, Dos Santos Jr & Queiroz, 2005).

The reaction of [RuHCl(CO)(B)(EPh_3)$_2$] (where E= As, B= $AsPh_3$; E= P, B= PPh_3, pyridine, piperidine, or morpholine) and dehydroacetic acid thiosemicarbazone in benzene under reflux afford a number of new ruthenium(II) carbonyl complexes including dehydroacetic acid thiosemicarbazone of general formula [Ru(dhatsc)(CO)(B)(EPh_3)] (where dhatsc= dibasic tridentate dehydroacetic acid thiosemicarbazone). All the complexes have been characterized by elemental analyses, FT-IR, UV/Vis, and ^1H NMR spectral methods. The thiosemicarbazone of dehydroacetic acid acts as dianionic tridentate O, N, S donor and coordinates to ruthenium via phenolic oxygen of dehydroacetic acid, the imine nitrogen of thiosemicarbazone and thiol sulfur. The free ligand and its ruthenium complexes have been screened for their antibacterial and antifungal activities. The complexes show better activity in inhibiting the growth of bacteria *Staphylococcus aureus* and *Escherichia coli* and fungus *Candida albicans* and *Aspergillus niger* (Kannan, Sivagamasundari, Ramesh & Liu, 2008).

A number of new mixed ligand penta-coordinated square pyramidal ruthenium(II) complexes including benzaldehyde or its substituents and triphenylphosphine or triphenylarsine have been synthesized and characterized. In the electronic spectra, three well-described peaks in the visible region were observed and assigned to d-d transitions in D_4h and low spin axially distortion from *Oh* symmetry. The spectrochemical parameters of the complexes were calculated and placed the ligands in the middle of the spectrochemical series. The mechanism and kinetics of the catalytic oxidation of benzyl alcohol by the complex $[RuCl_2(PPh_3)(C_6H_5CHO)_2]$ in the presence of NMO have also been studied (El-Shahawi & Shoair, 2004).

1.1.2.5 Ruthenium(III) Complexes Containing Triphenylphosphine, Triphenylarsine and Other Ligands

The synthesis and characterization of several hexa-coordinated ruthenium(III) Schiff base complexes of the type $[RuX(EPh_3)_2(L)]$ (E= P or As; X= Cl or Br; L= anion of the Schiff bases derived by the condensation of salicylaldehyde or *o*-hydroxyacetophenone with benzoylhydrazine or *p*-chlorobenzoylhydrazine) are reported. IR, EPR, electronic spectra and cyclic voltammetric data of the complexes are discussed. An octahedral geometry has been tentatively suggested for all of these complexes. The new complexes have been subjected to a catalytic activity study in the aryl-aryl coupling reaction and also to an antibacterial study (Jayabalakrishnan, Karvembu & Natarajan, 2003).

The synthesis and characterization of several hexa-coordinated ruthenium(III) complexes of the type $[RuCl(PPh_3)_2(L)]$ (L= dibasic tridentate ligand determined by the condensation of salicylaldehyde/*o*-vanilin with *o*-aminophenol/*o*-aminothiophenol) are reported. IR, electronic, EPR spectral data and redox attitude of the complexes are discussed. The new complexes were found to be efficient catalysts for the oxidation of benzyl alcohol and cyclohexanol to benzaldehyde and cyclohexanone in turn, using NMO as an oxidant (Priyarega, Prabhakaran, Aranganayagam, Karvembu & Natarajan, 2007).

Ruthenium(III) complexes, $[RuX(EPh_3)_2(L)]$ (X=Cl, Br; E= P, As; L= tridentate Schiff base dianion), have been synthesized by reacting $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$ or $[RuBr_3(AsPh_3)_3]$ with thiosemicarbazones of methyl- and ethylacetoacetates. All of the new complexes have been characterized by elemental analyses, IR, electronic, EPR and cyclic voltammetric data and an octahedral structure has been tentatively suggested. The ruthenium(III) complexes were found to be efficient catalysts for the oxidation of alcohols to the corresponding carbonyl compounds in the presence of NMO as a oxidant. The Schiff bases and the new complexes have been tested for the *in vitro* growth inhibitory activity against the bacteria *E. coli*, *Bacillus* sp. and *Pseudomonas* sp (Jayabalakrishnan, Karvembu & Natarajan, 2002).

New hexa-coordinated ruthenium(III) complexes of the type $[RuX_2(EPh_3)_2(L)]$ (E= P or As; X= Cl or Br; L= monobasic bidentate Schiff base determined from the condensation of benzhydrazide with furfuraldehyde, 2-acetylfuran and 2-acetylthiophene) have been synthesized from the equimolar amounts of $[RuX_3(EPh_3)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ and Schiff bases in benzene. The new complexes have been characterized by analytical, spectral, magnetic moment and cyclic voltammetry. All the complexes have exhibited catalytic activity for the oxidation of alcoholsi in the presence of NMO as oxidant. All the new complexes were found to be active against the bacteria such as *E. coli*,*Pseudomonas sp.*, *Salmonella typhi* and *Staphylococcus aureus.* The activity was compared with standard *Streptomycin* (Balasubramanian, Parameswari, Chinnusamy, Prabhakaran & Natarajan, 2006).

Some reactions of hydrazine with pentachloroaquoruthenite (III) and ammine complexes of ruthenium (II) and ruthenium (III) have been investigated in acid, neutral and alkaline solution. In neutral solution it has been shown that hydrazine monohydrochloride oxidized hexaammineruthenium (II) to hexaammineruthenium (III). In alkaline solution nitrogenpentaammineruthenium (II) was formed and a mechanism for this reaction is assumed (Bottomley, 1970).

New catecholamine ruthenium (III) complexes with potentially interesting biological activity are defined. The complexes were prepared by reacting catecholamine with $[RuCl(NH_3)_5]Cl_2$. The newly prepared species were characterized by elemental analysis, EPR, electronic absorption and FT-IR spectra. They were partially stable in water at room temperature for at least 1 week. *In vitro* tests of antifungal activity showed the ruthenium-catecholamine complexes had strong inhibitory action against the pathogenic yeast *Candida albicans*, *Candida glabrata* and *Candida tropicalis* (de Lima, Lever, Ito & da Silva, 2003).

A number of stable low spin Ru (III) complexes of the tye $[RuX_2(EPh_3)_2(L)]$ (where E= P or As; X= Cl or Br; L= mono basic bidentate Schiff bases) have been synthesized and were characterized by analytical, spectral and electrochemical data. A distorted octahedral geometry has been suggested for all the complexes. These complexes catalyze the oxidation of primary alcohols and secondary alcohols with high yields in the presence of NMO. The ruthenium (III) Schiff base complexes show growth inhibitory activity against the bacteria *Staphylococcus aureus (209p)* and *E. coli ESS (2231)* (Venkatachalam & Ramesh, 2005).

Ruthenium (III) complexes of Schiff bases determined from the condensation of salicylaldehyde or *o*-vanilin with diamines have been prepared and characterized.

A number of new hexa-coordinated ruthenium (III) complexes of the type $[Ru(X)(2\text{-atmp-ba})(EPh_3)]$ (where H_2-2-atmp-ba= N,N'-bis(2-aminothiophenol) benzoylacetone; X= Cl or Br; E= P or As) have been prepared by reacting $[RuX_3(EPh_3)_3]$ (where X= Cl or Br; E= P or As) with tetradentate Schiff base ligand (H_2-2-atmp-ba) in 1:1 molar ratio. The complexes have been characterized by elemental analyses, IR, electronic, EPR spectroscopy, cyclic voltammetry and EXAFS studies. The new complexes were also screened for their antibacterial features (Prabhakaran, Geetha, Thilagavathi, Karvembu, Krishnan, Bertagnolli & Natarajan, 2004).

1.1.3 Trends in Bonding and Structures of Complexes

1.1.3.1 Ruthenium

Figure 1.14 depicts a series of Ru^{II}complexes, namely, **1-9**, with uninegative N^2, S-chelating ligands in $[RuL_2(PPh_3)_2]$ **1-4** (Fig. 1.10, **4**) (Lobana, Bawa, Butcher, Liaw, & Liu, 2006; Basuli, Ruf, Pierpont, & Bhattacharya, 1998; Basuli, Peng, & Bhattacharya, 1997; Mishra, Naskar, Drew, & Chattopadhyay, 2005). $[RuL_2(dppb)]$ **5** *{*dppb = $Ph_2P–(CH_2)_4–PPh_2$*}* (Lobana, Bawa, Butcher, Liaw, & Liu, 2006) (Fig. 1.11, **5**), $[RuL(bpy)_2)](ClO_4)$ **6** (Basuli, Peng, & Bhattacharya, 2000), and uninegative N^3, S-chelating in $[RuL(bpy)_2](ClO4)$ **7** (Basuli, Peng, & Bhattacharya, 2000), and O, N^4, N^3, S tetradentate in $[RuL(PPh_3)_2)](ClO_4)$ **8** (acetyl oxygen at pyridyl ring is also coordinating) (Maji, Ghosh, Chattopadhyay, & Mak, 1997).

The ligands are neutral binding via N^3, S-donor atoms in $[Ru(HL)_2(PPh_3)_2](ClO_4)_2{\cdot}2H_2O$ **9** (Sengupta, Dinda, Ghosh, & Sheldrick, 2003), and N^4, N^3, S-donor atoms in $[RuCl(HL)(PPh_3)_2]Cl{\cdot}CH_2Cl_2$ **4** (Lobana, Bawa, Butcher, Liaw, & Liu, 2006). These bonding modes depend on the substituents at C^2 carbon, and the geometry around each metal center is distorted octahedral. The ^{31}P NMR spectra of complexes **4** and **5** showed single peaks which support that the environment in solution state remain unchanged (Lobana, Bawa, Butcher, Liaw, & Liu, 2006). The sulfur atoms are generally *trans* when two thiosemicarbazones coordinate to the Ru^{II} center.

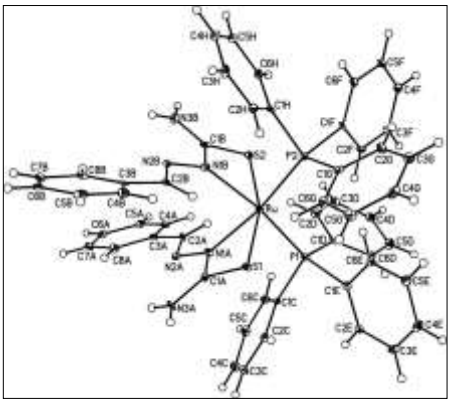


Figure 1.9 Structure of complex $[RuL_2(PPh_3)_2]$ **4** (Lobana, Bawa, Butcher, Liaw, & Liu, 2006).

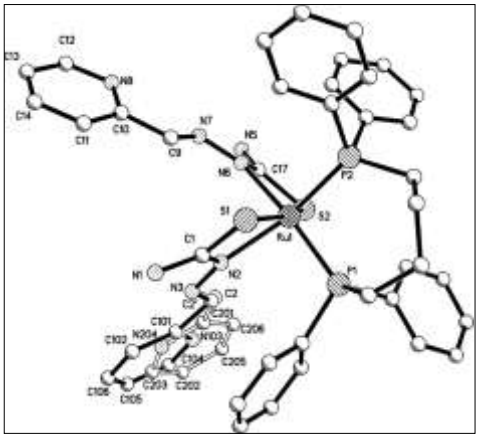


Figure 1.10 Structure of complex [RuL_2(dppb)] **5** (Lobana, Bawa, Butcher, Liaw, & Liu, 2006).

An organometallic dinuclear complex [$Ru_2(HL)_2(CO)_4$] **11** (Yang, Ma, Chen, Huang, & Ma, 2004) includes which metallation of the cyclopentadienyl ring of the ferrocenyl part. The ligand is N^2, S-chelating to Ru (II) in [*{*$Ru(bpy)_2(stsc)$*}*$_4Ni_4$]$(ClO_4)_4$ **12** (Pal, Basuli, Mak, & Bhattacharya, 2001) with four other sites occupied by chelating bipyridine ligands, and the pendant donor atoms, O, N^3, N^1 (as imino moiety N^1H-) *{*after deprotonation of amino group, $-N^1H_2$*}* bind to Ni^{II} centers forming repeat unit, *{*$(bpy)_2Ru(N^2, S)(Ni(O, N^3, N^1)$*}*. Four such repeat units are bridged by coordinate sulfur forming the octanuclear cluster **12**; the ligand is trinegative hexadentate.

Reaction of *trans*-[$Ru(dppm)_2Cl_2$] (dppm) with thiophene-2- carbaldehyde thiosemicarbazone (HL^1) in the presence of Et_3N forms [Ru(η^3-C, N^3, S-L^1)(η^2-P,P-dppm)(η^1-P-dppm)] **13** (Fig. 1.12), with an unprecedented cyclometalation of a heterocyclic ring in Ru^{II}-thiosemicarbazone chemistry. In contrast, the thiophene ring did not undergo cyclometalation in complexes of monotertiary phosphines of stoichiometry [Ru(η^2-N^2,S-HL^1)$_2$(PR')$_3$] (R' = phenyl, **14**; *p*-tolyl, **15**). Benzaldehyde thiosemicarbazone (HL^2) with *trans*-[$Ru(dppm)_2Cl_2$] displayed cyclometalation and yielded an organometallic complex [Ru(η^3-C, N^3, S–L^2)(η^2-P,P-dppm)(η^1-Pdppm)] **16** (Lobana, Bawa, Castineiras, Butcher, & Zeller 2008). The cyclometalation in complexes **13** and **16** is based to the presence of two types of coordination modes of dppm, namely, both η^1-P-dppm and chelating η^2-P,P-dppm in the same complex.

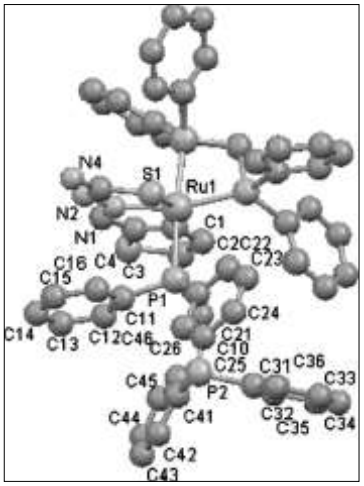


Figure 1.11 Structure of complex [Ru(η^3-C, N^3, S–L^1)(η^2-P,P-dppm)(η^1-P-dppm)] **13** (Lobana, Bawa, & Butcher, 2008).

Pyridine-2 carbaldehyde thiosemicarbazones and its N^1 subtituted thiosemicarbazones with $Ru(PPh3)_3Cl_2$ form mononuclear Ru^{II} precursors [Ru(N^3,S–HL)$_2$(PPh_3)$_2$] **17-19** for the generation of trinuclear complexes with copper(I) halides, [$(Ph_3P)_2Ru^{II}(L)_2Cu^{II}{}_2X_2$] **20-25** (Lobana, Bawa, & Butcher, 2008) (Fig. 1.13, **20**). In complexes **20-25**, the pendant amino group (–N^4H_2) loses one hydrogen atom along with the oxidation of Cu^I to Cu^{II}. Cyclic voltammetry support the Ru^{II}/Ru^{III} redox attitude of this metal in trinuclear complexes.

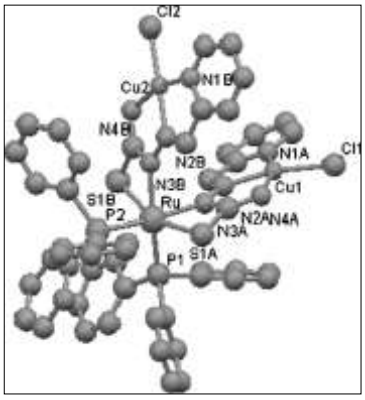


Figure 1.12 Structure of complex [$(Ph_3P)_2Ru^{II}(L)_2Cu^{II}{}_2Cl_2$] **20** (Lobana, Bawa, & Butcher, 2008).

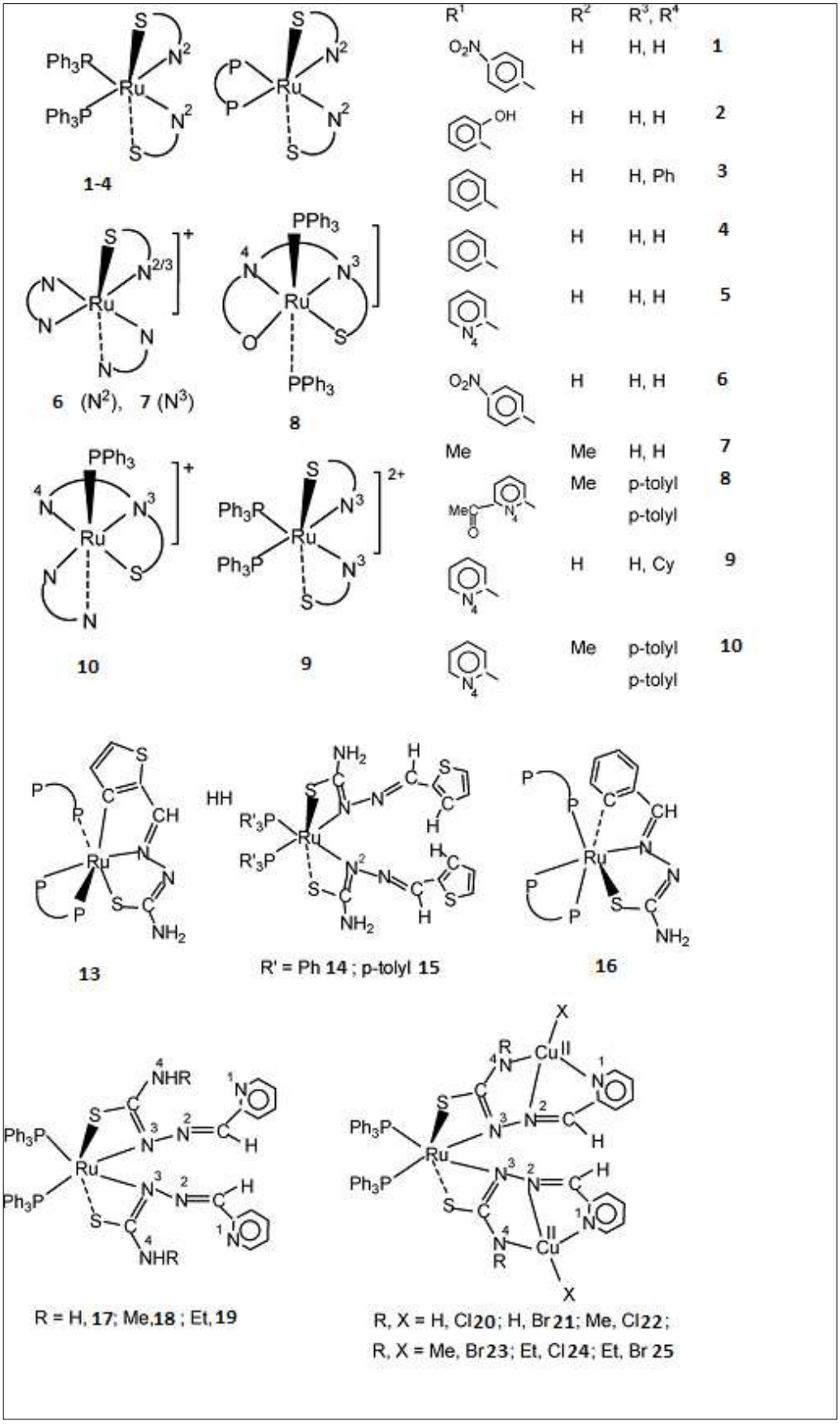


Figure 1.13 Some ruthenium complexes

CHAPTER TWO
MATERIAL AND METHOD

2.1 Instruments

Infrared Spectroscopy: Varian 1000 FT spectrophotometer (Dokuz Eylül University, Faculty of Science and Arts, Chemistry Department)

^{1}H NMR and ^{31}P NMR Spectroscopy: 500 MHz High Performance Digital FT-NMR instrument (Ege University, Science Faculty, Chemistry Department)

UV-Vis Spectroscopy: Shimadzu Model 1800 spectrophotometer (Dokuz Eylül University, Faculty os Science and Arts, Chemistry Department)

Elemental Analysis: LECO-CHNS-O-9320 by Technical and Scientific Research Council of Turkey, TUBITAK.

2.2 Chemicals

Solvents: Toluene, ethanole, petroleum ether, dichloromethane and silica gel were purchased from Merck.

Metal Starting Complex: $RuCl_3$. $3H_2O$ were purchased from Aldrich.

2.2.1 Purification of Solvents

All solvents were dried and degassed using standard techniques and stored under nitrogen until used (Armarego & Perrin, 1980).

2.3 Preparation of Ligands

2.3.1 Preparation of 2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone, (TSC[1])

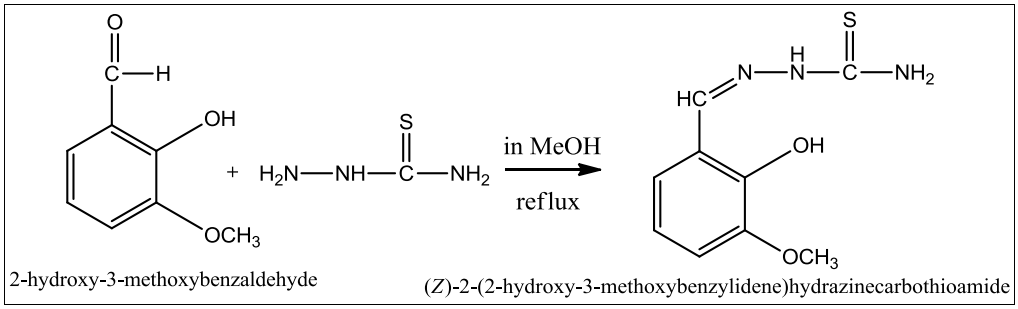


Figure 2.1 Structure of the 2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone, (TSC^1)

The preparative methods for thiosemicarbazones were well described by Klayman et al. (Klayman & Lin, 1984), Scovill (Scovill, 1991) and Blanksma (Blanksma, 1910). In general, a thiosemicarbazide was dissolved in methanol by refluxing for half an hour, however sometimes a few milliliter of distilled water is added to completely dissolve it. After addition of a given aldehyde or ketone, the reaction mixture is refluxed for 8–10 h and evaporation gave crude sample. It is recrystallized from methanol. For the synthesis of thiosemicarbazones, a procedure modification described by Blanksma (Blanksma, 1910) is used.

For (TSC^1) ligand ; Anal. Calcd for $C_9H_{11}N_3O_2S$: C,47.99; H,4.92; N,18.65. Found: C,47.60; H,4.65; N,18.54. FT-IR (KBr, cm^{-1}) : 3151 (s) $\upsilon_{(N–H)}$; 2967 (br) $\upsilon_{(o-OH)}$; 1591 (s) $\upsilon_{(C=N)}$; 819 (m) $\upsilon_{(C=S)}$; 1053 (m) $\upsilon_{(CN, NCN)}$. ^{1}H NMR (500 MHz, DMSO-d^6) : δ (ppm) 11.38 (s,1H,o-OH), 9.16 (s,1H,N–H), 8.18 (s,1H,HC=N), 6.96-7.53 (m,3H,Ar-H). UV-Vis (THF) (nm) (A): λ_1= 324.5 (0.415)

2.3.2 Preparation of 3-hydroxybenzaldehyde thiosemicarbazone, (TSC^2)

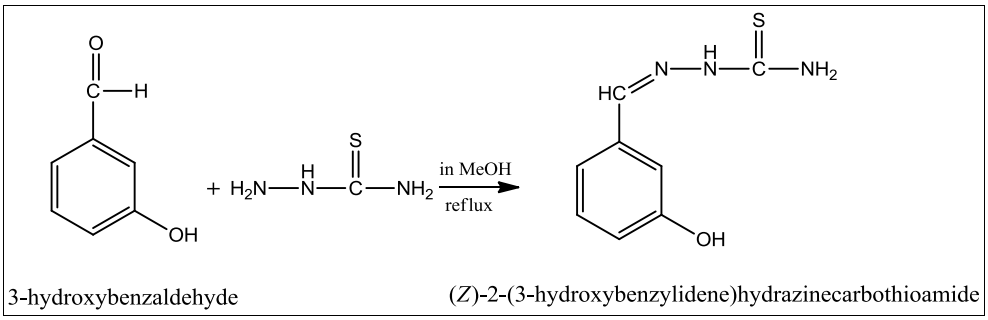


Figure 2.2 Structure of 3-hydroxybenzaldehyde thiosemicarbazone, (TSC^2)

For (TSC^2) ligand ; Anal. Calcd for $C_8H_9N_3OS$: C,49.21; H,4.65; N,21.52. Found: C,49.06; H,4.46; N,21.20. FT-IR (KBr, cm^{-1}) : 3155 (s) $\upsilon_{(N–H)}$; 1593 (s) $\upsilon_{(C=N)}$; 832 (m) $\upsilon_{(C=S)}$; 1060 (m) $\upsilon_{(CN,NCN)}$. ^{1}H NMR (500 MHz, DMSO-d^6) : δ 9.51 (s,1H,N–H), 8.16 (s,1H,HC=N), 6.79-7.95 (m,3H,Ar-H). UV-Vis (THF) (nm) (A) : λ_1= 325.0 (0.393)

2.3.3 Preparation of 3,4-dihydroxybenzaldehyde thiosemicarbazone, (TSC^3)

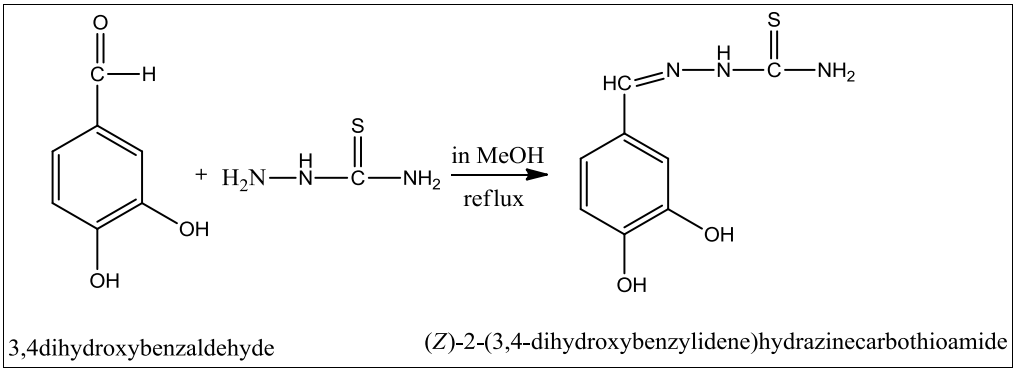


Figure 2.3 Structure of 3,4-dihydroxybenzaldehyde thiosemicarbazone, (TSC^3)

For (TSC^3) ligand ; Anal. Calcd for $C_8H_9N_3O_2S$: C,45.49; H,4.29; N,19.89. Found: C,45.15; H,4.16; N,19.76. FT-IR (KBr, cm^{-1}) : 3181 (s) $\upsilon_{(N–H)}$; 1595 (s) $\upsilon_{(C=N)}$; 838 (m) $\upsilon_{(C=S)}$; 1111 (m) $\upsilon_{(CN,NCN)}$. ^{1}H NMR (500 MHz, DMSO-*d*^{6}) : δ 9.28

(s,1H,N–H), 8.04 (s,1H,HC=N), 6.74-7.87 (m,3H,Ar-H). UV-Vis (THF) (nm) (A): λ_1=333.0 (0.614)

2.3.4 Preparation of Thiophene-2-carbaldehyde thiosemicarbazone, (TSC^4)

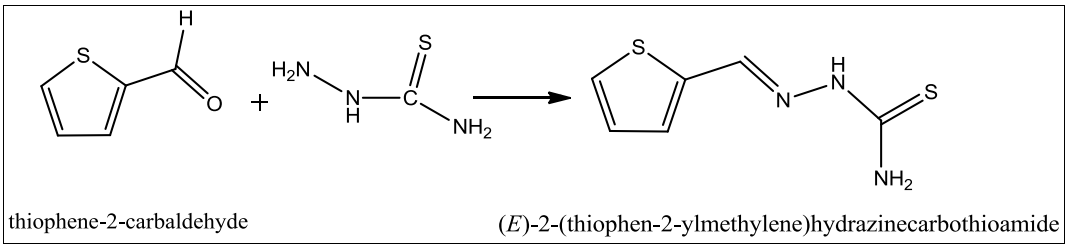


Figure 2.4 Structure of Thiophene-2-carbaldehyde thiosemicarbazone, (TSC^4)

Thiophene-2-carbaldehyde thiosemicarbazone was synthesized by mixing an aqueous solution of thiocarbonylhydrazines (420 mg, 3.0 mmol in 10 mL) and ethanolic solution of thiophene-2-carboxaldehyde (273 mg, 3.0 mmol in 10 mL) at 25 °C for 3 h with continuous stirring. After cooling, the precipitated compound was filtered and recrystallized from an appropriate solvent (Singh, Athar, Maurya, Azam, 2006).

For (TSC^4) ligand; Anal. Calcd for $C_6H_7N_3S_2$: C,38.90; H,3.81; N,22.68. Found: C,38.83; H,3.68; N,22.59. FT-IR (KBr,cm^{-1}) : 3149 (s) $\upsilon_{(N–H)}$; 1586 (s) $\upsilon_{(C=N)}$; 820 (m) $\upsilon_{(C=S)}$; 1058 (m) $\upsilon_{(CN,NCN)}$. ^{1}H NMR (500 MHz, DMSO-d^6) : δ 8.56 (s,1H,N–H), 8.37 (s,1H,HC=N), 6.71-7.73 (m,3H,Ar-H). UV-Vis (THF) (nm) (A): λ_1=329.0 (0.614)

2.4 Preparation of the Starting Complex, [Ru(H)(Cl)(CO)(PPh_3)$_3$]

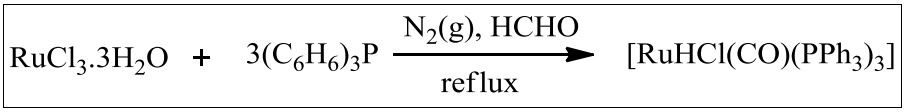


Figure 2.5 Synthesis reaction of the starting complex, [$RuHCl(CO)(PPh_3)_3$]

A solution of 0.26 g (1.0 mmol) of hydrated ruthenium trichloride in 2-methoxyethanol (20 mL) and aqueous formaldehyde (20 mL, 40%) were added rapidly and successively to a vigorously stirred boiling solution of 1.57 g (6 mmol) of triphenylphosphine in 2-methoxyethanol (60 mL). The mixture was heated under reflux for 10 min and allowed to cool. The precipitate formed was separated and washed successively with ethanol, water, ethanol and *n*-hexane and dried in *vacuo*. (Natarajan, Poddar, & Agarwala, 1977).

For starting complex; Yield: 800 mg, 85%. Anal. Calcd for $C_{55}H_{46}ClOP_3Ru$: C,69.36; H,4.87. Found: C,69.30; H,4.79. FT-IR (KBr, cm^{-1}) : 1928 (s) $\upsilon_{(C\equiv O)}$; 2020 (w) $\upsilon_{(Ru-H)}$. ^1H NMR (500 MHz, DMSO-d^6) : 6.99-7.93(m,3H,Ar-H). ^{31}P NMR : 29.26.

2.5 Synthesis of the Complexes (1-4)

Reactions were carried out under an oxygen-free nitrogen atmosphere by the thermal reactions. All glassware was oven-dried at 120˚C.

2.5.1 Synthesis of the [Ru(CO)(PPh$_3$)$_2$(η^3-O,N^3,S-TSC^1)] {TSC^1= 2-hydroxy-3-metoxybenzaldehyde thiosemicarbazone}

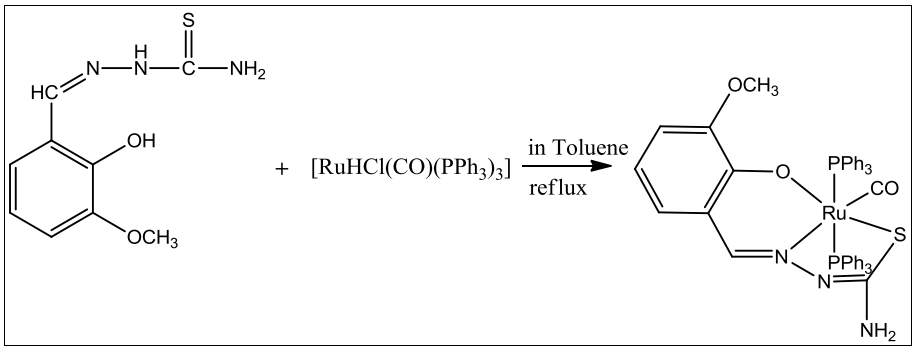


Figure 2.6 Structure of the complex **1** [Ru(CO)(PPh$_3$)$_2$(η^3-O,N^3,S-TSC^1)] {TSC^1= 2-hydroxy-3-metoxybenzaldehyde thiosemicarbazone}

To a solution of $[Ru(H)(Cl)(CO)(PPh_3)_3]$ (950 mg ,1 mmol), in toluene (25 mL) the thiosemicarbazone ligand (TSC^1) (225 mg) was added. The mixture was refluxed for 5h. under nitrogen atmosphere. The resulting solution was concentrated to about 5 mL and the product was separated by the addition of the small amount of petroleum ether. It was filtered and dried in *vacuo*.

For *$[Ru(CO)(PPh_3)_2(\eta^3\text{-}O,N^3,S\text{-}TSC^1)]$*, **1** Yield : 760 mg, 80%. Anal.Calcd for $C_{46}H_{42}N_3O_3P_2RuS$: C,62.79; H,4.81; N,4.78. Found: C,62.75; H,4.75; N,4.71. FT-IR (KBr,cm^{-1}) : 3148 (s) $\upsilon_{(N-H)}$; 1586 (m) $\upsilon_{(C=N)}$; 719 (w) $\upsilon_{(C-S)}$; 1093 (w) $\upsilon_{(CN,NCN)}$; 1944 (s) $\upsilon_{(C\equiv O)}$. 1H NMR (500 MHz, DMSO-d^6): δ (ppm) 8.54 (s,1H,N–H), 8.38 (s,1H,HC=N), 6.74-8.08 (m,3H,Ar-H). ^{31}P NMR : 27.61 UV-vis (THF) (nm) (A): λ_1: 281.0(0.212).

2.5.2 Synthesis of the $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^2)]$ {TSC^2= 3-hydroxybenzaldehyde thiosemicarbazone}

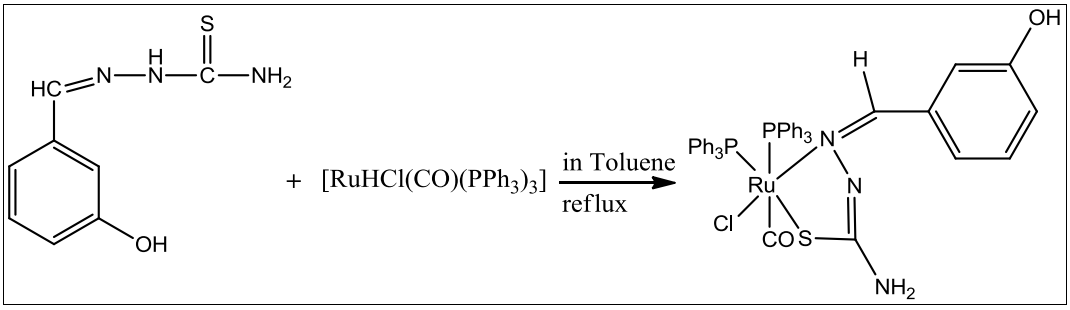


Figure 2.7 Structure of the complex **2** $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^2)]$ {TSC^2= 3-hydroxybenzaldehyde thiosemicarbazone}

To a solution of $[Ru(H)(Cl)(CO)(PPh_3)_3]$ (950 mg ,1 mmol), in toluene (25 mL) the thiosemicarbazone ligand (TSC^2) (195 mg) was added. The mixture was refluxed for 5h. under nitrogen atmosphere. The resulting solution was concentrated to about 5 mL and the product was separated by the addition of the small amount of petroleum ether. It was filtered and dried in vacuo.

For *[Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^2)]*, **2** Yield: 712 mg, 75%. Anal. Calcd for $C_{45}H_{39}ClN_3O_2P_2RuS$: C,61.12; H,4.45; N,4.75. Found: C,61.02; H,4.26; N,4.70. FT-IR (KBr, cm^{-1}): 1587 (m) υ $_{(C=N)}$; 744 (m) υ $_{(C–S)}$; 1092 (w) υ $_{(CN,NCN)}$; 1955 (s) υ $_{(C\equiv O)}$. ^{1}H NMR (500 MHz, DMSO-*d*^{6}): δ (ppm) 8.37 (s,1H,HC=N), 6.79-7.96 (m,3H,Ar-H). ^{31}P NMR: 55.01, 43.52 UV-Vis (THF) (nm) (A) : λ_1: 284.0(0.138).

2.5.3 Synthesis of the [Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^3)] {TSC^3= 3,4-dihydroxybenzaldehyde thiosemicarbazone}

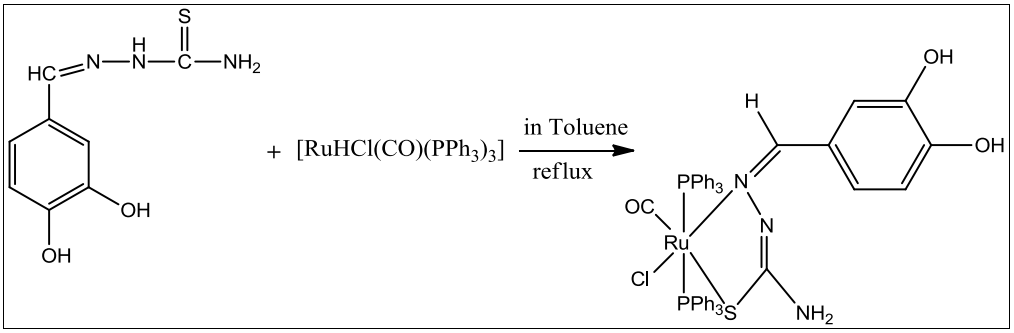


Figure 2.8 Structure of the complex **3** [Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^3)] {TSC^3= 3,4-dihydroxybenzaldehyde thiosemicarbazone}

To a solution of [Ru(H)(Cl)(CO)(PPh$_3$)$_3$] (950 mg ,1 mmol), in toluene (25 mL) the thiosemicarbazone ligand (TSC^3) (211 mg) was added. The mixture was refluxed for 5h. under nitrogen atmosphere. The resulting solution was concentrated to about 5 mL and the product was separated by the addition of the small amount of petroleum ether. It was filtered and dried in vacuo.

For *[Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^3)]*, **3** Yield: 750 mg, 79%. Anal. Calcd for $C_{45}H_{39}ClN_3O_3P_2RuS$: C,60.03; H,4.37; N,4.67. Found: C,60.01; H,4.35; N,4.60. FT-IR (KBr,cm^{-1}): 1592 (m) υ $_{(C=N)}$; 742 (w) υ $_{(C–S)}$; 1113 (w) υ $_{(CN,NCN)}$; 1935 (s) υ $_{(C\equiv O)}$. ^{1}H NMR (500 MHz, DMSO-d^6): δ (ppm) 8.30 (s,1H,HC=N), 6.74-7.17(m,3H,Ar-H). ^{31}P NMR : 36.73 UV-Vis (THF) (nm) (A): λ_1: 267.0 (0.299)

2.5.4 Synthesis of the [Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^4)] {TSC^4= Thiophene-2-carbaldehyde thiosemicarbazone}

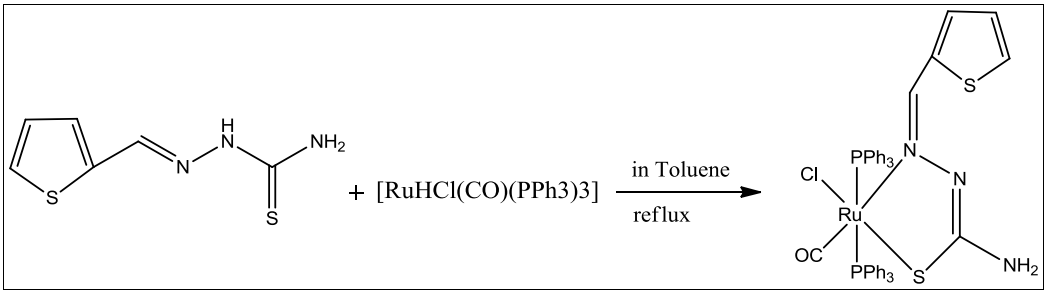


Figure 2.9 Structure of the complex **4** [Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^4)], {TSC^4= Thiophene-2-carbaldehyde thiosemicarbazone}

A solution of appropriate TSC $^{N-S}$ (18.5 mg, 0.1 mmol) in benzene (10 mL) was added drop wise into a stirred suspension of [RuH(CO)Cl(PPh$_3$)$_3$] (95 mg, 0.1 mmol) in benzene (20mL). The contents were refluxed under argon atmosphere for 5h. Then, left to cool to room temperature and the mixture was evaporated in a vacuum. The yellow precipitate washed with dichloromethane/petroleum ether (1:3) and product dried.

For *[Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^4)]*, **4** Yield : 76 mg, 80%. Anal. Calcd for $C_{43}H_{36}ClN_3OP_2RuS_2$: C, 59.14; H, 4.15; N, 4.81. Found: C, 59.43; H, 4.01; N, 4.93. FT-IR (KBr, cm^{-1}): υ (NH2) 3343 (m); υ (N-N) 1078 (m); υ (CO)1938 (s); υ (C=N)1582 (s), 1542 (s); υ (PPh3) 1417-1456 (m),1091-1093 (m), 736-796 (m), 516-518 (m); υ (C-S) 747 (m); υ (C-S-C)thiophen ring 844 (m); υ (C-S)sym thiophen ring 765 (m); υ (C-S)asym thiophen ring 676 (m); υ (Ru-N) 522 (m). ^{1}H NMR (500 MHz, DMSO-*d*^{6}) δ (ppm) = 8.37 (1H, s, -CH=N); 8.56 (2H, br, NH2); 5.60-8.20 (m, PPh3 ring protons); 7.06-7.59 (3H, m, (C_4H_3S)thiophen ring). ^{31}P NMR (500 MHz, DMSO-*d*^{6}) δ= 36.94. UV-Vis (THF) (nm) (A) : λ_1: 281.5 (0.0344).

CHAPTER THREE
RESULTS AND DISCUSSIONS

3.1 Results and Discussions

Ruthenium (II) complexes of the general formula $[Ru(CO)(PPh_3)_2(\eta^3\text{-}O,N^3,S\text{-}TSC^1)]$, **1**; $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^2)]$, **2**; $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^3)]$, **3**; and $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^4)]$, **4** have been prepared by reacting $[Ru(H)(Cl)(CO)(PPh_3)_3]$ with the respective thiosemicarbazone ligands TSC^1 (*2-hydroxy-3-metoxybenzaldehyde thiosemicarbazone*, TSC^2 (*3-hydroxybenzaldehyde thiosemicarbazone)*, TSC^3 (*3,4-dihydroxybenzaldehyde thiosemicarbazone)* and TSC^4 *(Thiophene-2-carbaldehyde thiosemicarbazone)* in a 1:1 molar ratio in toluene and benzene. For the structural characterization of ligands TSC^n (n=1-4) with their Ru(II) complexes (**1-4**) FT-IR spectra, UV–Vis spectra and ^1H NMR ,^{31}P NMR spectra were used and the corresponding data are given in experimental section.

All the complexes were isolated in moderate yields and are quite stable in air and light. The analytical data given in Table 3.1 for the complexes are in good agreement with the formula proposed. The complexes are soluble in common organic solvents such as dimethyl sulphoxide, dichloro methane and chloroform. Various attempts have been made to obtain the single crystals of the complexes but it has been unsuccessful.

Based on elemental analysis and spectroscopic data it was proposed that the complexes are best formulated as $[Ru(CO)(PPh_3)_2(\eta^3\text{-}O,N^3,S\text{-}TSC^1)]$, **1**; $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^2)]$, **2**; $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^3)]$, **3** and $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^4)]$ **4** (**Figure 2.6, Figure 2.7, Figure 2.8** and **Figure 2.9).** The spectroscopic data reasonably support the formula of the compounds.

3.1.1 Analytical Data

The analytical data for novel complexes **1-4** are summarized in Table 3.1. The stochiometry of the ligands and their complexes have been confirmed by their elemental analyses. The spectroscopic data confirm that TSC^1; *2-hydroxy-3-metoxybenzaldehyde thiosemicarbazone*, TSC^2; *3-hydroxybenzaldehyde thiosemicarbazone*, TSC^3; *3,4-dihydroxybenzaldehyde thiosemicarbazone* and TSC^4; *Thiophene-2-carbaldehyde thiosemicarbazone* coordinate to metal as thiosemicarbazone derivatives.

Table 3.1. Elemental analysis results and physical properties for the complexes (1-4) and the thiosemicarbazone ligands (TSC^1, TSC^2, TSC^3, TSC^4)

Complex	Yield	Colour	Found (Calcd.) %		
	(%)		C	H	N
(1)	80	orange	62.75(62.79)	4.75(4.81)	4.71(4.78)
(2)	75	orange	61.02(61.12)	4.26(4.45)	4.70(4.75)
(3)	79	orange	60.01(60.03)	4.35(4.37)	4.60(4.67)
(4)	80	orange	59.01(59.07)	4.20(4.27)	4.76(4.81)

3.1.2 Infrared Spectra

Thiosemicarbazone ligands can coordinate in a number of different manners. Most commonly they bind as either of two tautomeric forms; a neutral thione form or the anion from the thiol form. Infrared spectrophotometry was used to confirm coordination as the thiol form all of the complexes **(1-4)**. The FT-IR spectra of the free ligands were compared with that of the new complexes in order to confirm the coordination of the ligand to the ruthenium metal. The main stretching frequencies of the FT-IR spectra of ligands TSC^n (n=1-4) and Ru(II) complexes **1-4** are given in the experimental section.

The highest frequency bands present around 3337 cm^{-1} in the spectrum of the ligands are assigned to υ_{asym} and υ_{sym} vibration of the terminal NH_2 group. These

bands are present in the spectra of the complexes as well, indicating the non-involvement of this group in coordination.

The coordination via the azomethine nitrogen is inferred by the following observations. The absorption due to C=N group of the free ligand present around 1591 cm^{-1} **(TSC^1)**, 1593 cm^{-1} **(TSC^2)**, 1595 cm^{-1} **(TSC^3)** and 1586 cm^{-1} **(TSC^4)** region in the spectra of the complexes indicating the coordination of azomethine nitrogen to the metal. Co-ordination of the thiosemicarbazone ligands to the ruthenium ion through azomethine nitrogen atom is expected to change the electron density in the azomethine link and thus alters the $\upsilon_{(C=N)}$ absorption frequency in the region 1596 cm^{-1} **(1)**, 1589 cm^{-1} **(2)** , 1596 cm^{-1} **(3)** and **(4)** 1582 cm^{-1} after complexation indicating the co-ordination of azomethine nitrogen to ruthenium ion.

The $\upsilon_{(N–N)}$ bands of the ligands are present around 1053 cm^{-1} **(TSC^1)**, 1062 cm^{-1} **(TSC^2)**, 1111 cm^{-1} **(TSC^3)** and 1058 cm^{-1} **(TSC^4)** . The changing in frequency of these bands 1093 cm^{-1} **(1)**, 1093 cm^{-1} **(2)**, 1090 cm^{-1} **(3)** and 1078 cm^{-1}**(TSC^4)** in the spectra of the complexes provides evidence for the co-ordination via the azomethine nitrogen (A.Manimaran, & C.Jayabalakrishnan, 2012). A strong band at 3151 cm^{-1} **(1)**, 3155 cm^{-1} **(2)** , 3181 cm^{-1} **(3)** and 3149 cm^{-1} **(TSC^4)** attributed to $\upsilon_{(N–H)}$ group of –NH-N=C found in the spectra of free ligands is not present in the spectra of metal complexes. (Sampath, Sathiyaraj, Raja & Jayabalakrishnan, 2013).

The free ligands display $\upsilon_{(C=S)}$ absorption at 819 cm^{-1} **(TSC^1)**, 831 cm^{-1} (**TSC^2**), 838 cm^{-1} **(TSC^3)** and 820 cm^{-1} **(TSC^4)** . This band is also not present in the spectra of the complexes. However, new bands are present around 1541 cm^{-1} (**1**), 1542 cm^{-1} (**2**), 1548 cm^{-1} (**3**), 1540 cm^{-1} (**4**); 1020-1036 cm^{-1} (**1**) and 727 cm^{-1} (**1**), 750 cm^{-1} (**2**) and 742 cm^{-1} (**3**) and 747 cm^{-1} **(4)** which are assigned to the new azomethine group –C=N-, -C-O and –C-S respectively. The disappearance of $\upsilon_{(C=S)}$ and $\upsilon_{(N–H)}$ in all the complexes confirm that the TSC ligands coordinate to the ruthenium metal in the thiol form. Bands due to –SH are not present in the spectra of the complexes (**1-4)**. These observations indicate the thiolisation of the –NH-C=S groups and subsequent deprotonation before coordination to the metal. A strong band was obtained at 1254

cm^{-1} in the free TSC^1 ligand which has been assigned to phenolic –C-O absorption. On complexation, this band was shifted to a higher frequency at 1286 cm^{-1}, indicating the other coordination of TSC^1 ligand through the phenolic oxygen atom. (Natarajan, Poddar, & Agarwala, 1977). This is further confirmed by the disappearance of the $\upsilon_{(ph\text{-}C\text{-}OH)}$ broad band $\upsilon_{(OH)}$ around 2967 cm^{-1} in the $[Ru(CO)(PPh_3)_2(\eta^3\text{-}O,N^3,S\text{-}TSC^1)]$, **1** complex indicates deprotonation of the phenolic proton prior to coordination through the deprotonated oxygen atom. $\upsilon_{(OH)}$ vibration of the phenolic group in the ligand spectra, dissappear in the spectrum of the complexes **1** and an increase in frequency of phenolic C-O vibration from ligand (1261-1278 cm^{-1}) to metal complex (1313-1319 cm^{-1}) is observed. These results suggest that the other coordinating atom is phenolic oxygen.

In all of the complexes, a strong band in the region 1944 cm^{-1} (**1**), 1955 cm^{-1} (**2**), 1935 cm^{-1} (**3**) and 1938 cm^{-1} **(4)** is due to the terminally coordinated carbonyl group and is observed at higher frequency than in the precursor complexes $[RuHCl(CO)(PPh_3)_3]$ 1928 cm^{-1}. In addition the characteristic absorption bands due to triphenyl phosphine were also observed for the complexes in their expected regions. The characteristic bands due to PPh_3 are also present around 1433-1438 cm^{-1}, 1090-1093 cm^{-1}, 750-794 cm^{-1} and 518-526 cm^{-1}. The replacement of the hydride ion in the starting complexes by the ligands have been confirmed by the absence of a band around 2020 cm^{-1} in all the complexes (Sivagamasundari, & Ramesh, 2007).

The spectra of the complexes show that first thiosemicarbazone ligand is coordinated to the central metal as a tridentate ligand coordinating via the azomethine nitrogen (C=N), phenolic oxygen and sulfur atoms, TSC^2, TSC^3 and TSC^4 thiosemicarbazone ligands are coordinated to the central ruthenium metal as a bidentate ligand coordinating via the azomethine nitrogens (C=N) and sulfur atoms. C=N/SH vibrations have been changed difference wave number in the FT-IR spectra of the complexes $[Ru(CO)(PPh_3)_2(\eta^3\text{-}O,N^3,S\text{-}TSC^1)]$, **1**, $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^2)]$, **2**, $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^3)]$, **3** and $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^4)]$ **4** respectively.

Bands are assigned to the $\upsilon_{(M-N)}$ vibration which further supports the coordination of the azomethine nitrogen. In the complexes the medium intensity band in the region 518-526 cm^{-1} is attributed the Ru-N (Manivannan, Prabhakaran, Balasubramanian, Dhanabal, Karvembu, Chinnusamy & Natarajan, 2007). In the low frequency region 439 cm^{-1} is attributed to Ru-O (Nakamoto, 1971).

Table 3.2 Characteristic FTIR bands (cm^{-1}) of TSC^1, TSC^2, TSC^3,TSC^4 ligands and complexes **(1-4)**.

Complexes	$\upsilon_{(NH2)}$	$\upsilon_{(C=N)}$	$\upsilon_{(N-N)}$	$\upsilon_{(N-H)}$	$\upsilon_{ph(C-OH)}$	$\upsilon_{(C=S)}$	$\upsilon_{(C-S)}$	$\upsilon_{(C\equiv O)}$	$\upsilon_{(Ru-N)}$	$\upsilon_{(Ru-O)}$	$\upsilon_{(PPh3)}$
$[RuHCl(CO)(PPh_3)_3]$	-	-	-	-	-	-	-	1928(s)	-	-	1431(s)-1088(s)-794(s)-516(s)
TSC^1	3337(m)	1591(s)	1053(m)	3151(m)	2967(w)	819(s)	-	-	-	-	-
(1)	3288(w)	1596(m) 1541(w)	1093(w)	-	-	-	727(m)	1944(s)	518(m)	439(w)	1435(m)-1093(w)-794(w)-518(m)
TSC^2	3276(m)	1593(s)	1062(m)	3155(m)	-	831(s)	-	-	-	-	-
(2)	3277(w)	1589(m) 1542(w)	1093(w)	-	-	-	750(m)	1955(s)	526(m)	-	1438(w)-1093(w)-750(w)-526(m)
TSC^3	3326(m)	1595(s)	1111(m)	3181(m)	-	838(s)	-	-	-	-	-
(3)	3335(w)	1596(m) 1548(w)	1090(w)	-	-	-	742(m)	1935(s)	518(m)	-	1433(s)-1090(m)-789(w)-518(s)
TSC^4	3229(m)	1586(s)	1058(m)	3149(m)	-	820(s)	-	-	-	-	-
(4)	3336(w)	1582(m) 1540(w)	1078(w)	-	-	-	747(m)	1938(s)	519(m)	-	1433(w)-1091(m)-786(m)-518(m)

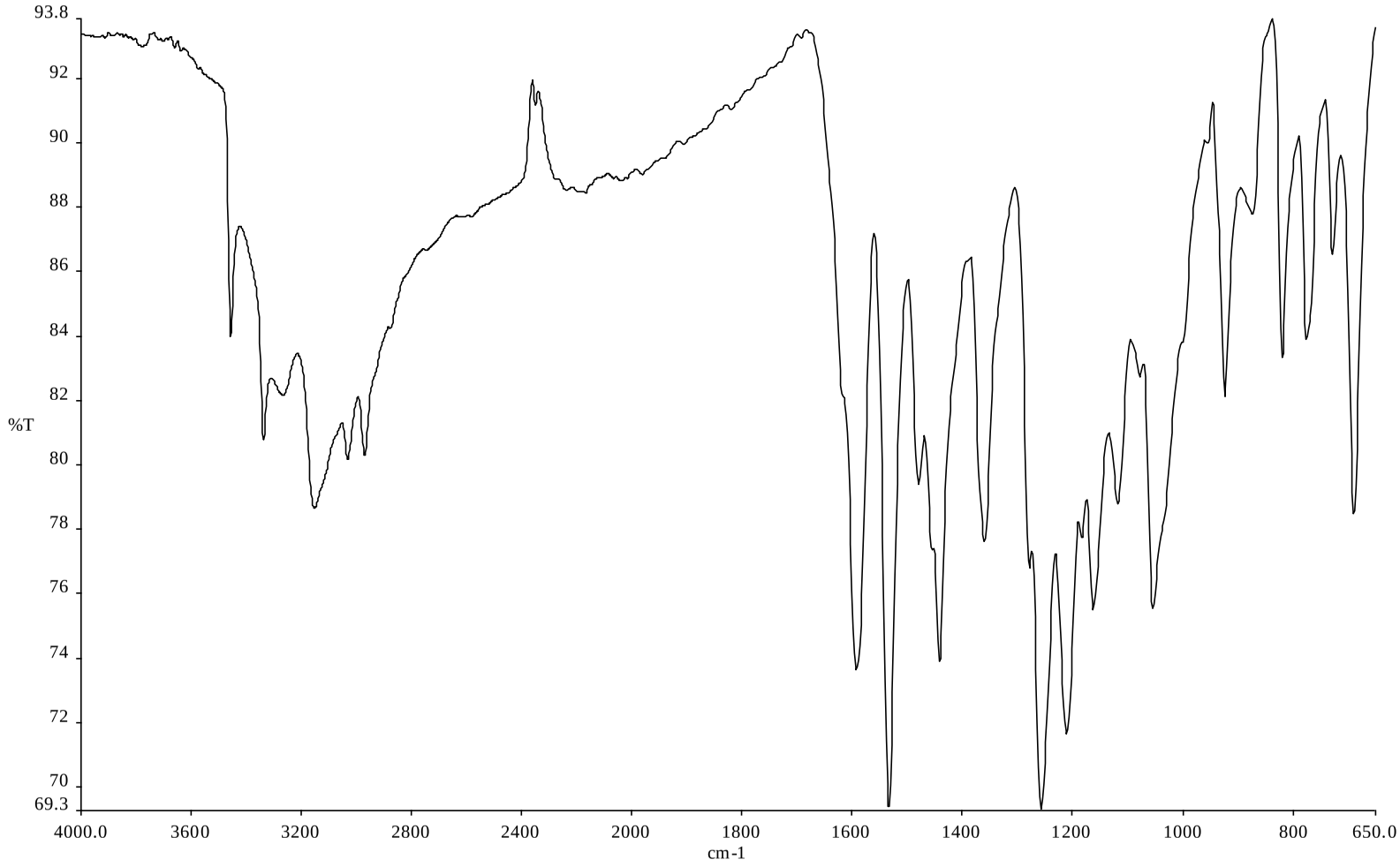


Figure 3.1 The infrared spectrum of **TSC[1]** ligand

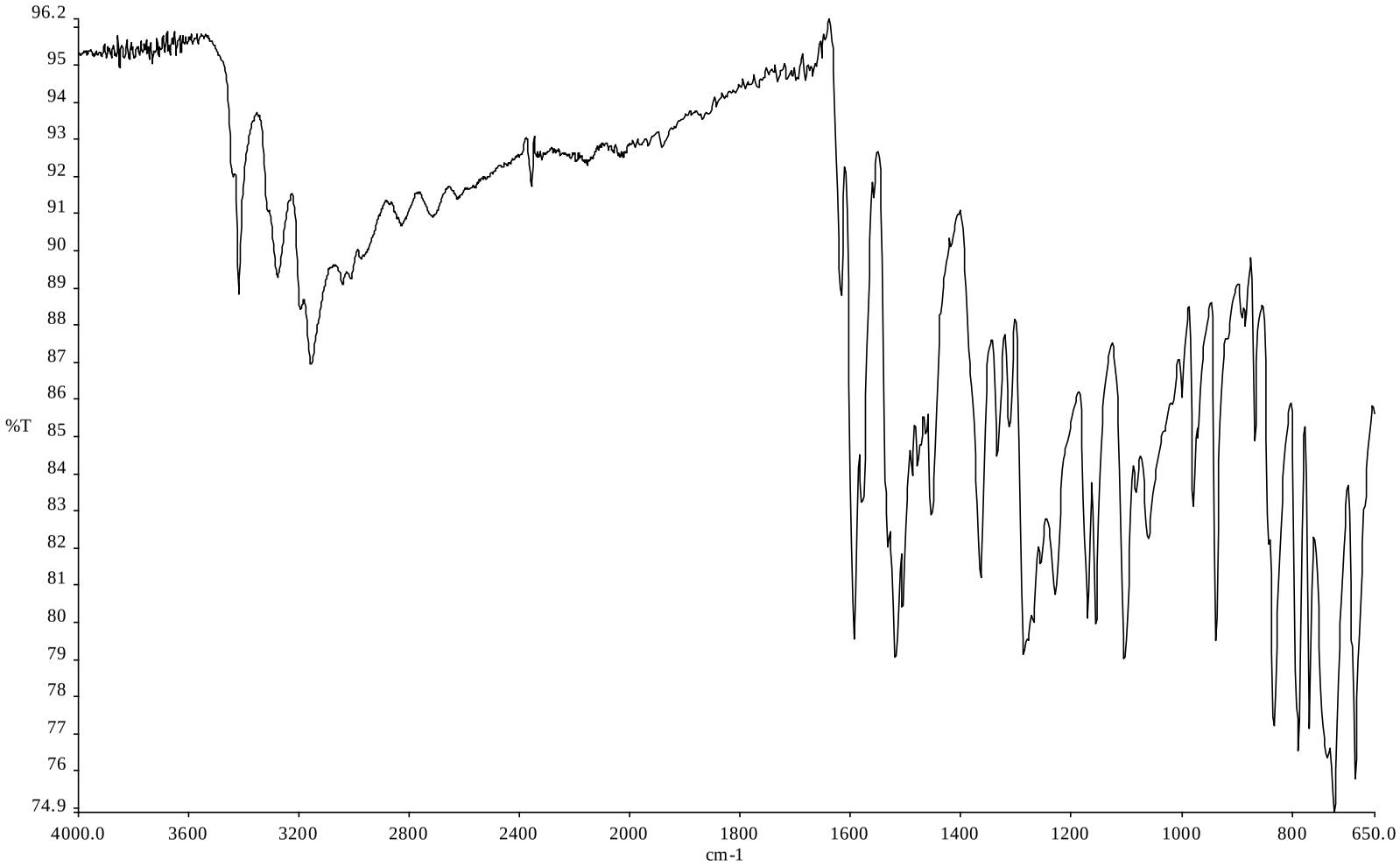


Figure 3.2 The infrared spectrum of **TSC**^{2} ligand

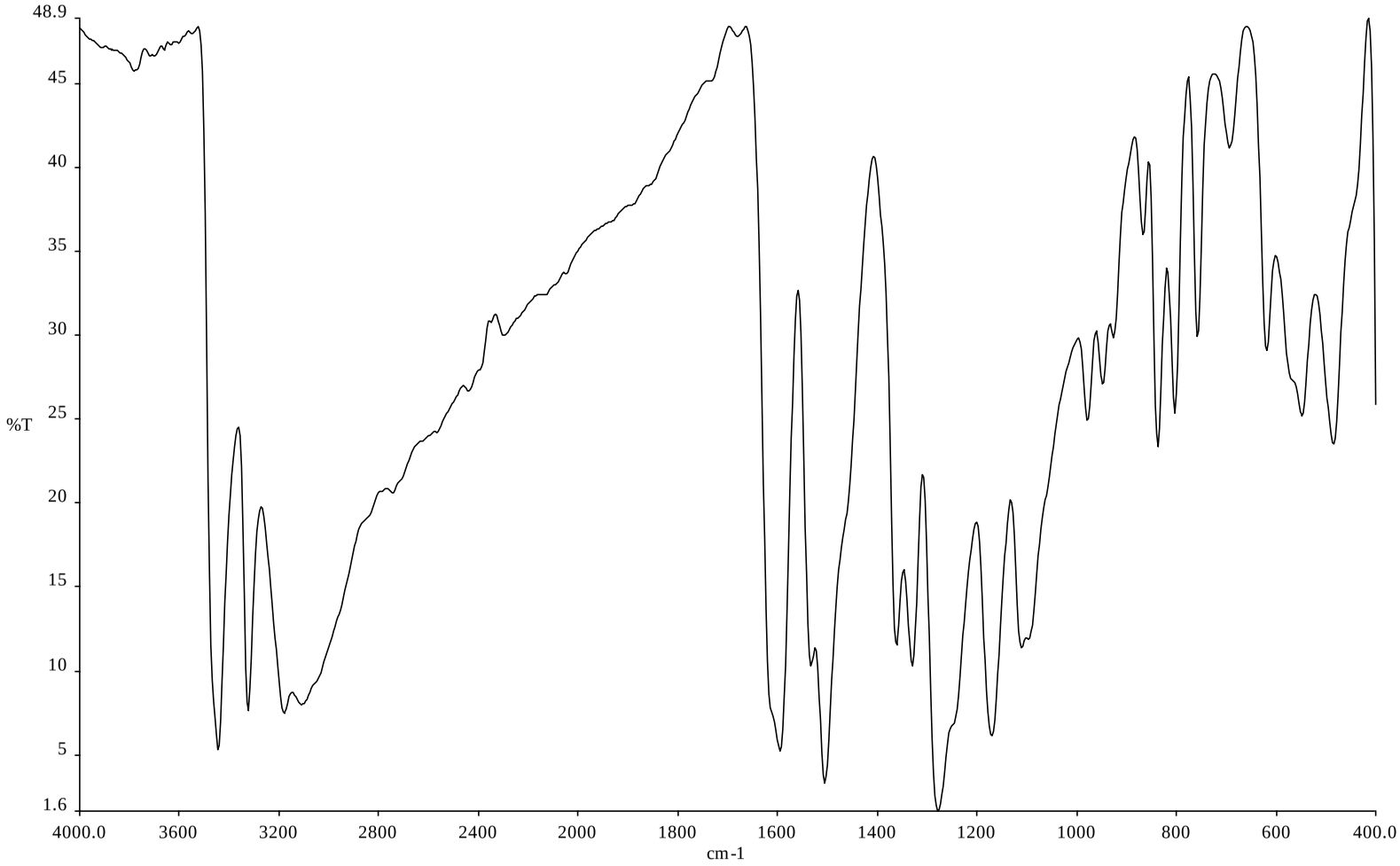


Figure 3.3 The infrared spectrum of **TSC**^{3} ligand

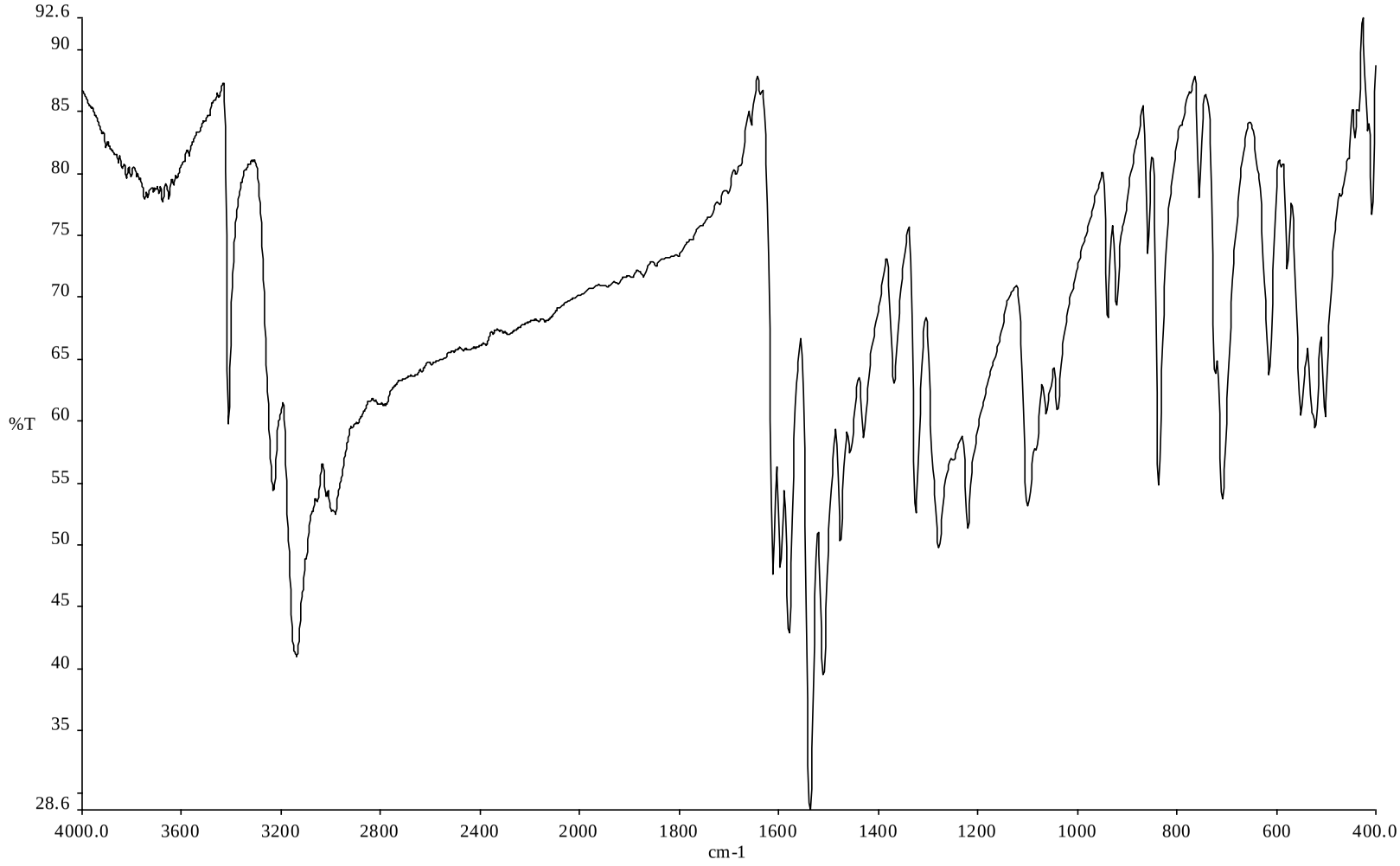


Figure 3.4 The infrared spectrum of **TSC**^{4} ligand

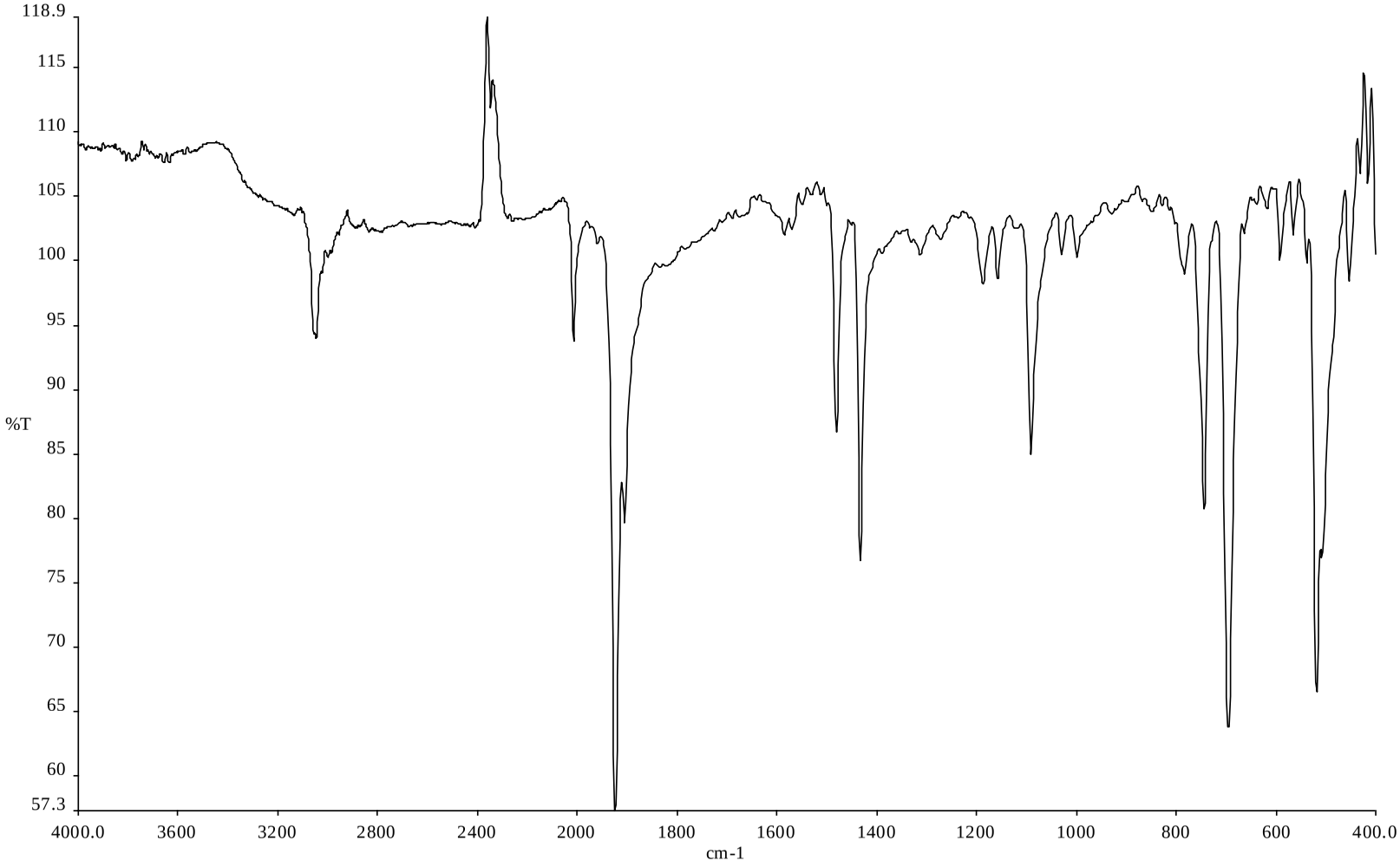


Figure 3.5 The infrared spectrum of starting complex **[RuH(Cl)(CO)(PPh_3)$_3$]**

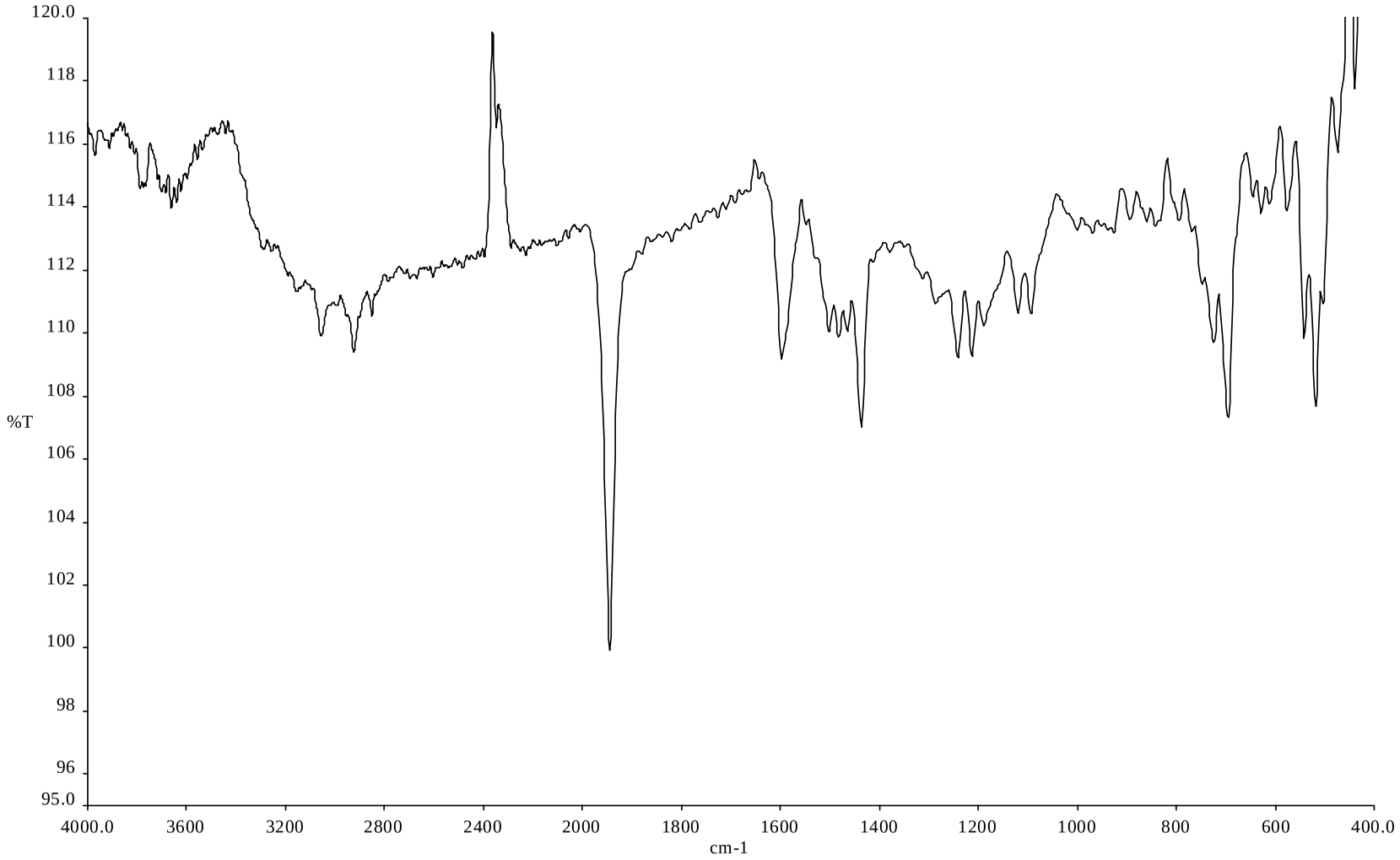


Figure 3.6 The infrared spectrum of complex **1**

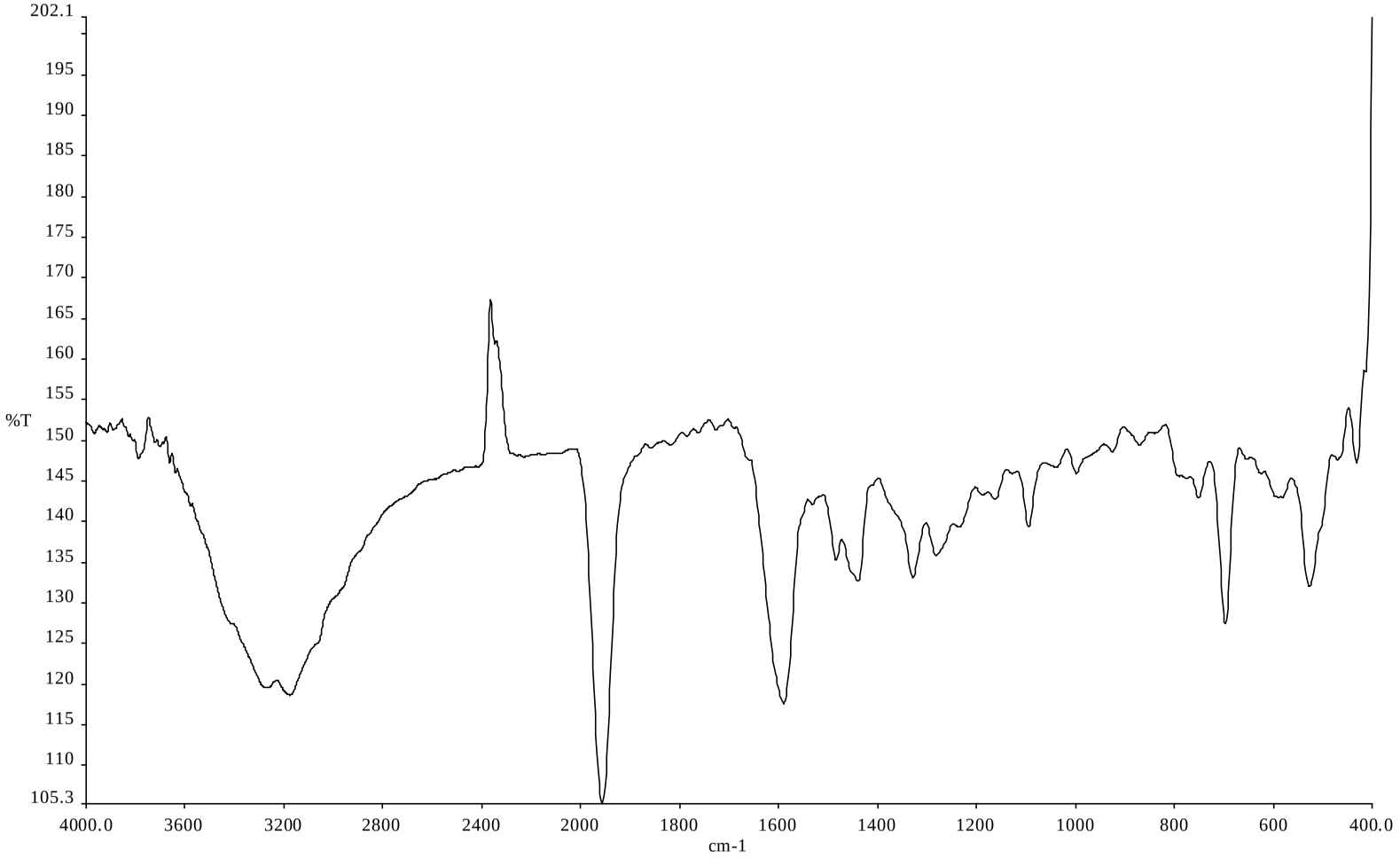


Figure 3.7 The spectrum of complex **2**

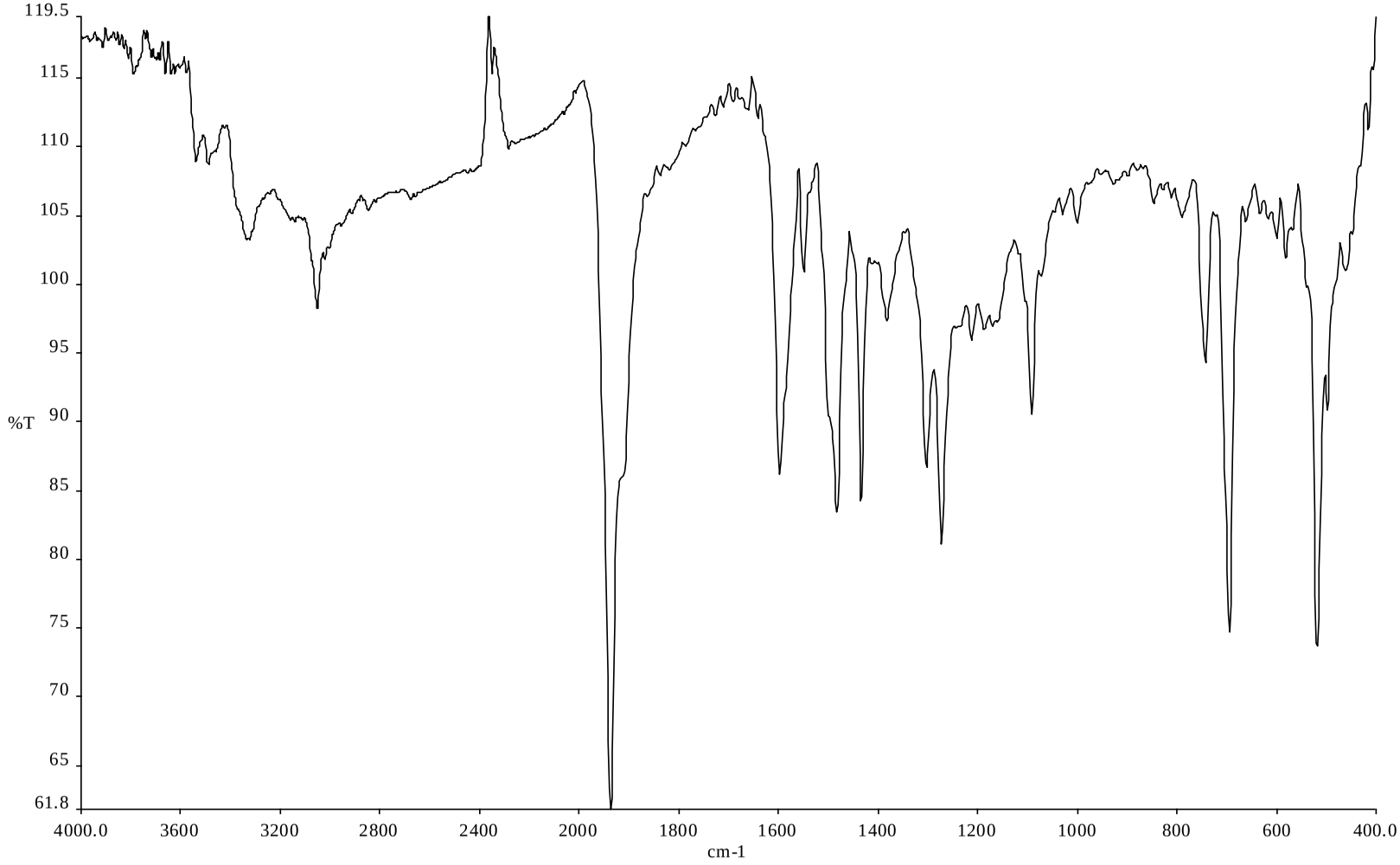


Figure 3.8 The infrared spectrum of complex **3**

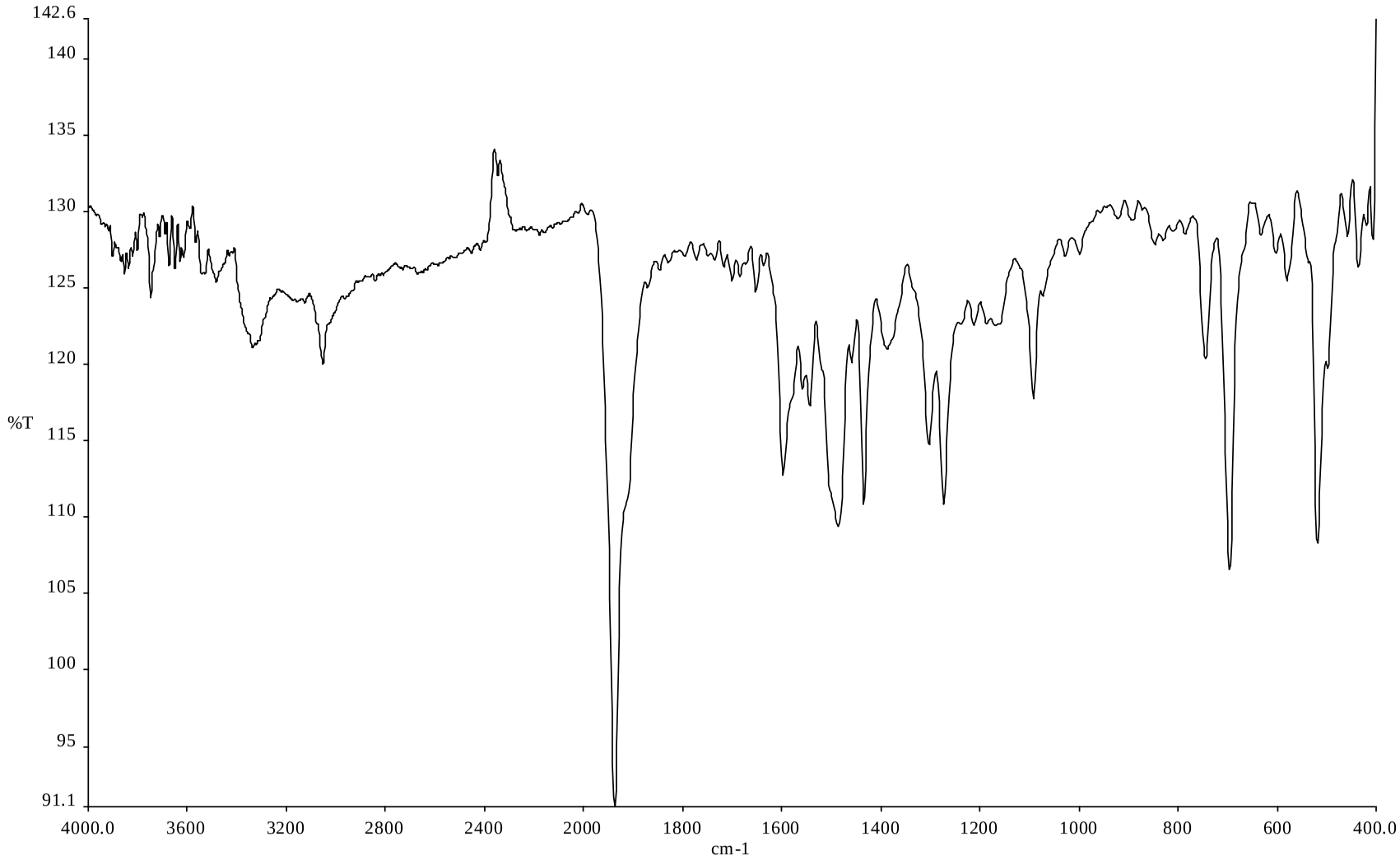


Figure 3.9 The infrared spectrum of complex **4**

3.1.3 ^{1}H and ^{31}P NMR Spectra

The ligand to metal bonding is further supported by ^{1}H and ^{31}P NMR spectra.The TSC ligands and the complexes are very soluble in DMSO and so their NMR spectra were obtained in DMSO-d^6. The NMR spectrum of the thiosemicarbazone ligands and ruthenium (II) compounds confirm the complex formation. The ^{1}H NMR spectral results obtained for TSC^{n} (n=1-4) ligands and Ru(II) complexes $[Ru(CO)(PPh_3)_2(\eta^3\text{-}O,N^3,S\text{-}TSC^1)]$, **1**; $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^2)]$, **2**; $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^3)]$, **3**; $[Ru(Cl)(CO)(PPh_3)_2(\eta^2\text{-}N^3,S\text{-}TSC^4)]$**, 4** in DMSO-$d^6$ with their assignments, are given in the experimental section.

Signals of phenolic proton appear at 11.38 ppm (**TSC^1**), and NH protons at 9.16 ppm (**TSC^1**), 9.51 ppm (**TSC^2**), 9.28 ppm (**TSC^3**) and 8.56 ppm **(TSC^4)** in the ^{1}H NMR spectrum of the ligands. These signals are not present in the spectra of the complexes indicating the deprotonation of these groups. The proton resonance appearing as singlet at δ = 11.38 ppm in the spectra (TSC^1) due to the –OH proton dissappeared in the first complex spectra. The absence of resonance for OH proton in the first complex indicate deprotonation of the phenolic group of the thiosemicarbazone ligand on complexation and coordination to ruthenium through phenolic oxygen atom. In the spectra of all the complexes a sharp singlet appeared at 8.38 ppm (**1**), 8.37 ppm (**2**), 8.30 ppm (**3**) and 8.37 ppm (**4**) has been assigned to azomethine proton (–HC=N). The positions of azomethine signal in the complexes are lower field compared to that of the free ligands observed at 8.18 ppm (**TSC^1**), 8.16 ppm (**TSC^2**), 8.04 ppm (**TSC^3**), and 11.39 ppm **(TSC^4)** indicating coordination through the azomethine nitrogen atom. In the spectra of all the complexes, a multiplet observed around 6.74-8.08 ppm (**1**), 6.79-7.96 ppm (**2**) and 6.74-7.17 ppm (**3**) and 7.07-7.61 ppm (**4**) is assigned to aromatic protons and the phenyl group of triphenylphosphine.

Resonance of terminal NH_2 protons in the complexes are seen in the same positions as in ligand spectrum 3.29-3.34 ppm confirming the non-involvement of this group in coordination with the metal. The terminal $–NH_2$ protons in the

complexes are seen in the positions with slight deviation as in the ligands spectra confirming the non-involvement of this group in coordination with the metal. The resonance for the methoxy protons appeared as a singlet at 3.8 ppm in **TSC^{1}** ligand and in [Ru(CO)(PPh_3)$_2$(η^3-O,N^3,S-TSC^1)], **1,** complex no significant change was observed.

In the ^{1}H NMR spectra of the complexes all indications are that the TSC ligands remain anionic form (as evidenced by the absence of the –NH– protons). Enolization of thiocarbonyl group is indicated by the singlet present at 10.4 ppm in the spectra of the ligand, which are attributed to –C–SH protons of thioamide group of the TSC ligands. The absence of thionyl group in the complexes indicates deprotonation of this group of the TSC ligands on complexation and coordination to ruthenium through thionyl sulfur. The absence of signals that can be ascribed to –SH is consistent with the idea that in solution, as in the solid state, the ligand exists as the deprotonated thiol tautomer. (Das, Sinha, Britto, Somasundaram, & Samuelson, 2010).

The ^{31}P NMR spectra showed one peak in the [Ru(CO)(PPh_3)$_2$(η^3-O,N^3,S-TSC^1)], **1** [Ru(Cl)(CO)(PPh_3)$_2$(η^2-N^3,S-TSC^3)], **3** and [Ru(Cl)(CO)(PPh_3)$_2$(η^2-N^3,S-TSC^4)], **4 c**omplexes at 27.61 ppm, 36.73 ppm and 36.94, respectively. It indicates that the triphenylphoshine groups are trans to each other in these complexes. (Rodrigues, Batista, Aucelio, Teixeira, Visentin & Beraldo, 2008). On the other hand, it is observed two peaks at 55.01 ppm and 43.52 ppm in the [Ru(Cl)(CO)(PPh_3)$_2$(η^2-N^3,S-TSC^2)], **2** complex. It indicates that the triphenylphosphine groups are in cis position in this complex.

Table 3.3 ^{1}H NMR data for TSC^{1}, TSC^{2}, TSC^{3}, TSC^{4} and complexes (1-4) (in DMSO-d^{6} solution)

Complexes	ph(o-OH)ppm	-N-N-H ppm	-HC=N ppm	-NH_2 ppm	-OCH_3 ppm	Ar-H ppm	^{31}P NMR
TSC^{1}	11.38,s,1H	9.16,s,1H	8.18,s,1H	3.29,s,2H	3.8,s.3H	6.96,d,1H, 6.76,t,1H, 7.53,d,1H	-
TSC^{2}	-	9.51,s,1H	8.16,s,1H	3.32,s,1H	-	6.79,m,1H, 7.88,s,1H, 7.95,s,1H	-
TSC^{3}	-	9.28,s,1H	8.04,s,1H	3.34,s,2H	-	6.74,d,1H, 7.16,d,1H, 7.87,s,1H	-
TSC^{4}	-	8.56,s,1H	11.39,s,1H	7.49,s,1H 8.13,s,1H	-	7.07,d,1H, 7.41,d,1H, 7.61,s,1H	-
(1)	-	-	8.38,s,1H	3.76,s,2H	3.9,s,3H	6.74,t,1H, 7.85,s,1H, 8.08,s,1H	27.61
(2)	-	-	8.37,s,1H	3.34,s,2H	-	6.79,m,1H, 7.13,s,1H, 7.96,d,1H	55.01,43.52
(3)	-	-	8.30,s,1H	3.35,s,2H	-	6.74,d,1H, 7.00,d,d,1H, 7.17,d,1H	36.73
(4)	-	-	8.37,s,1H	3.50,s,2H	-	6.71,d,1H, 7.45,d,1H, 7.73,d,1H	36.94
[RuHClCO(PPh_3)$_3$	-	-	-	-	-	6.99,m,1H, 7.48,s,1H, 7.93,s,1H	29.26

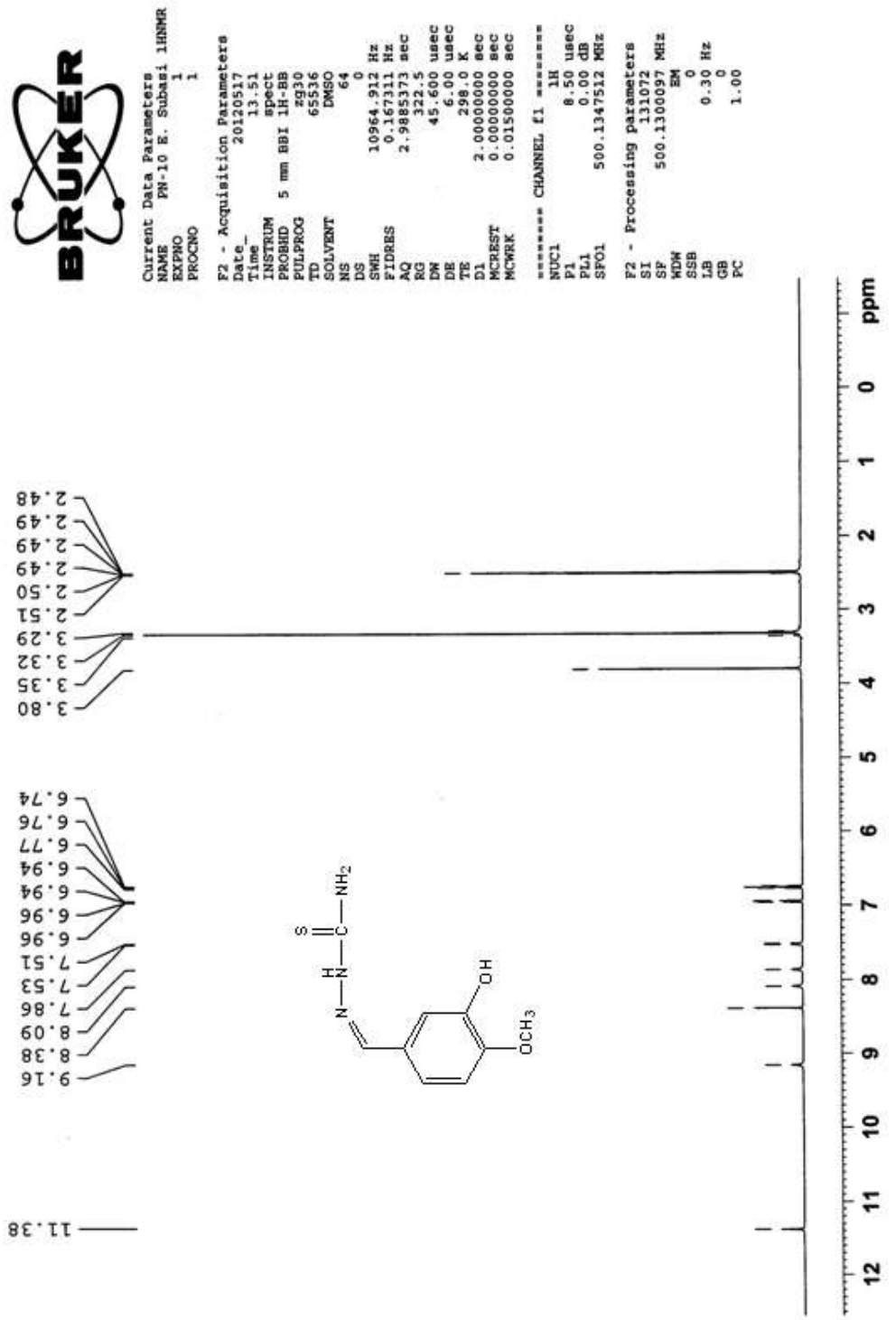


Figure 3.10 The ^{1}H NMR spectrum of TSC^{1} ligand

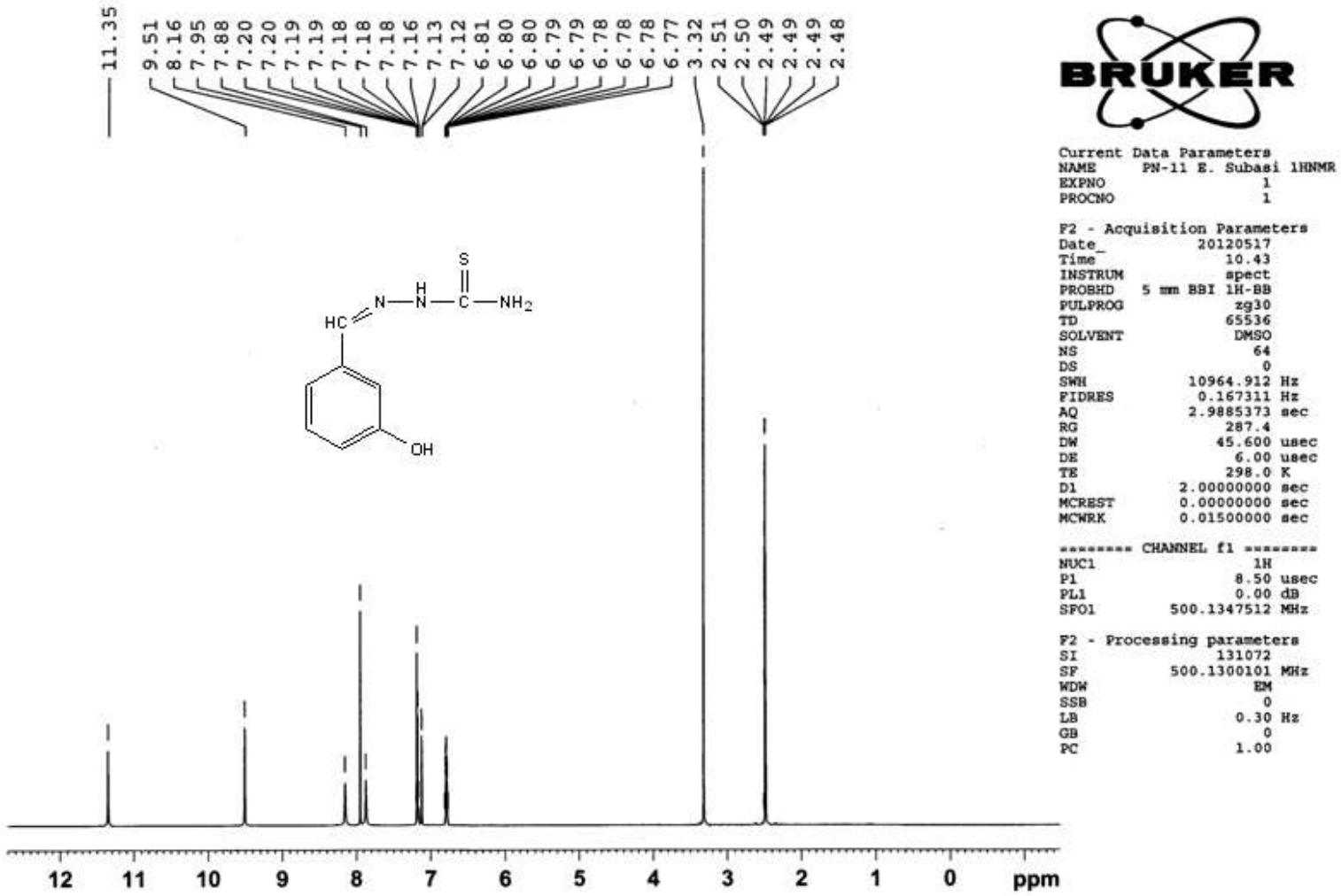


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Figure 3.11 The ^{1}H NMR spectrum of TSC^{2} ligand

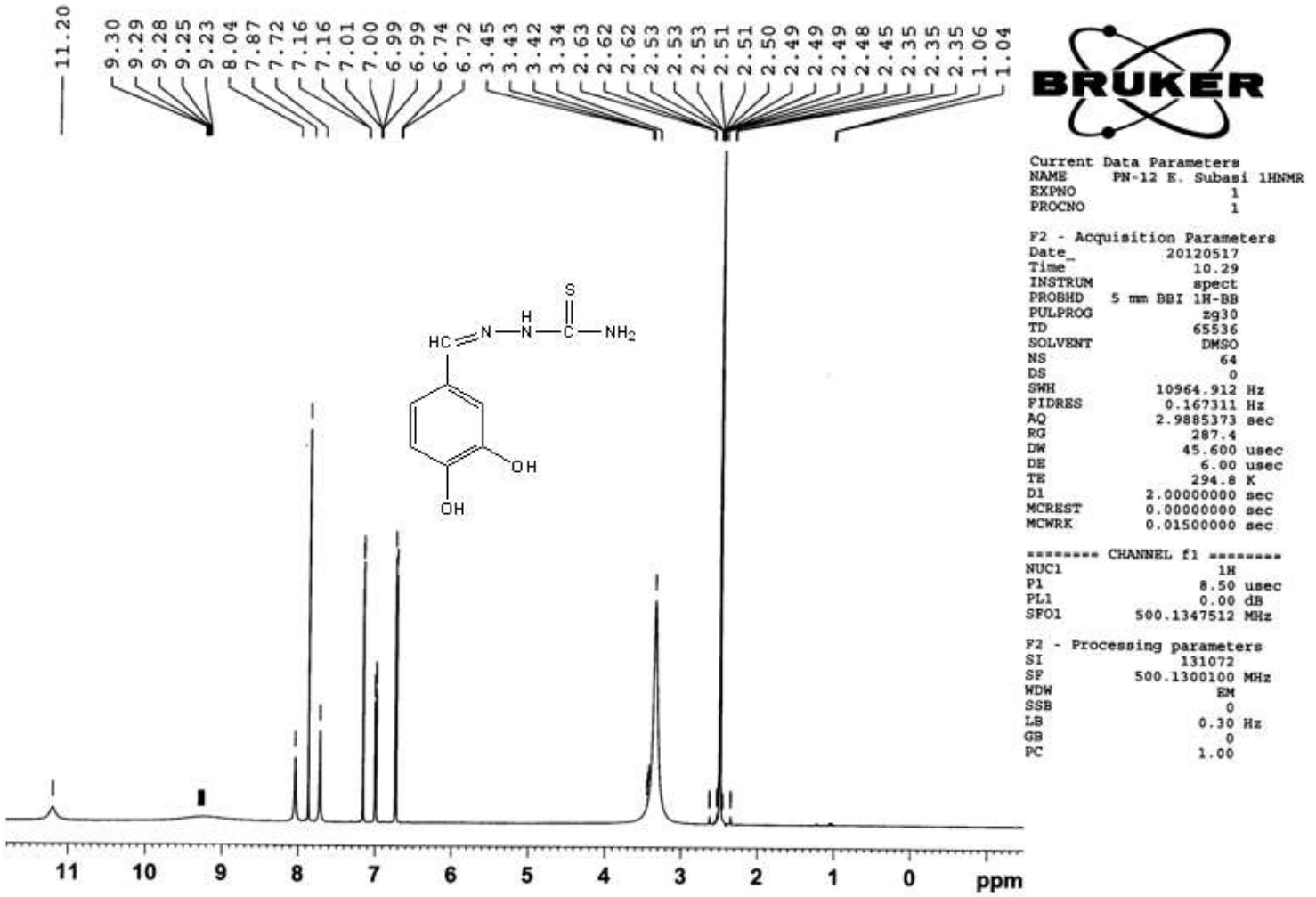

Figure 3.12 The ^{1}H NMR spectrum of TSC^{3} ligand

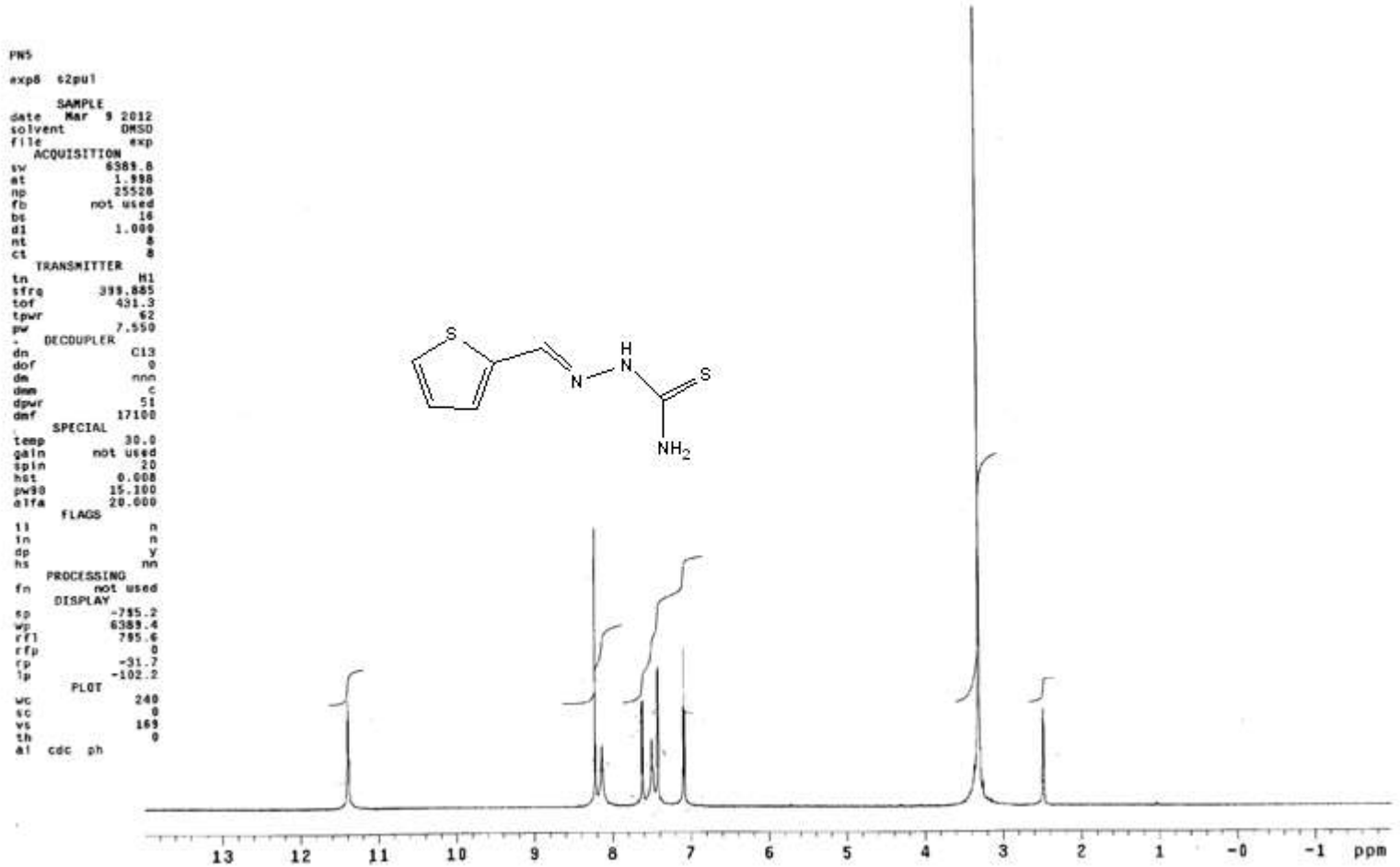

Figure 3.13 The ^{1}H NMR spectrum of TSC^{4} ligand

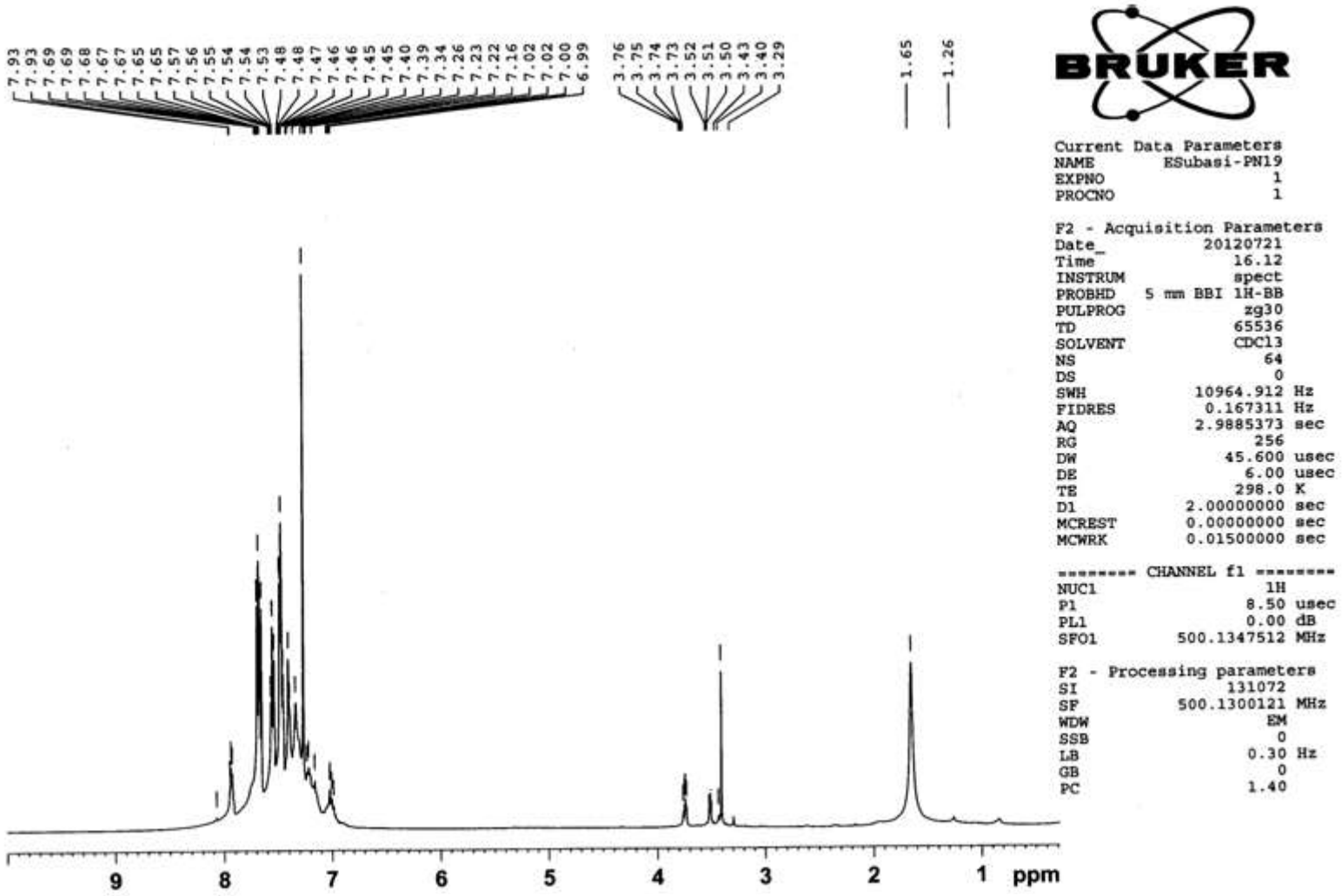

Figure 3.14 The ^{1}H NMR spectrum of starting complex $[RuH(Cl)(CO)(PPh_3)_3]$

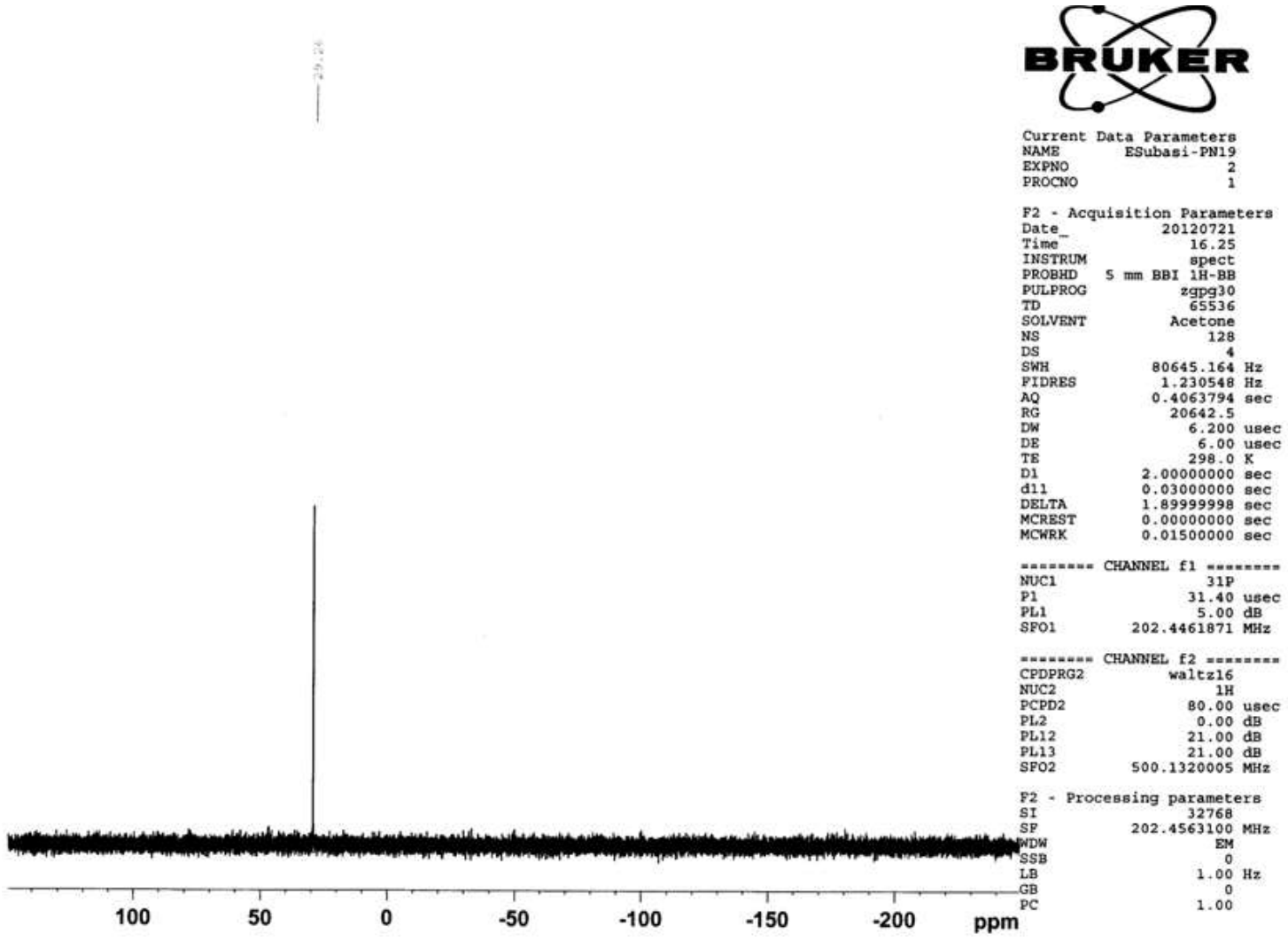

Figure 3.15 The ^{31}P NMR spectrum of starting complex $[RuH(Cl)(CO)(PPh_3)_3]$

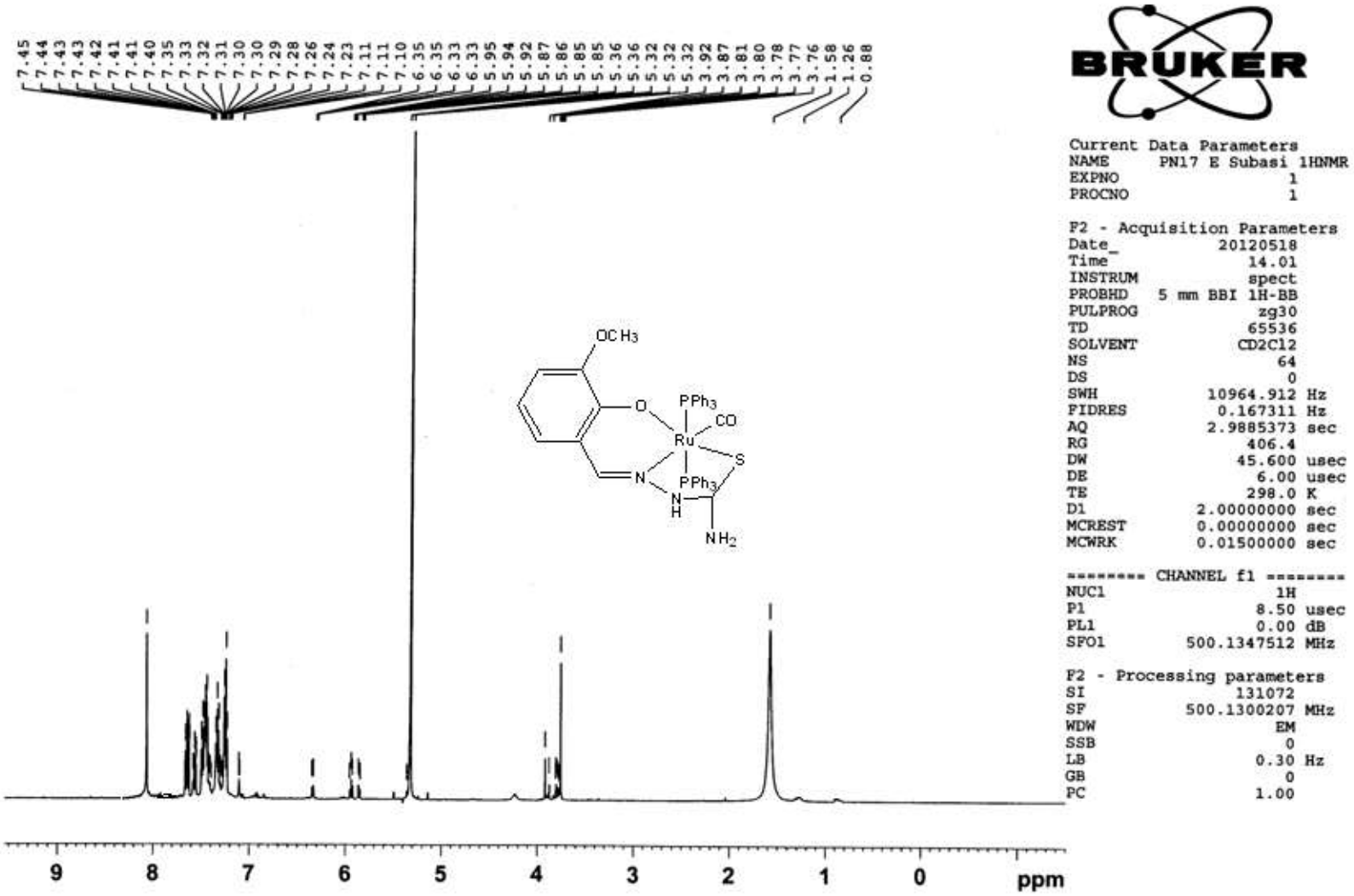

Figure 3.16 The ^{1}H NMR spectrum of complex **1**

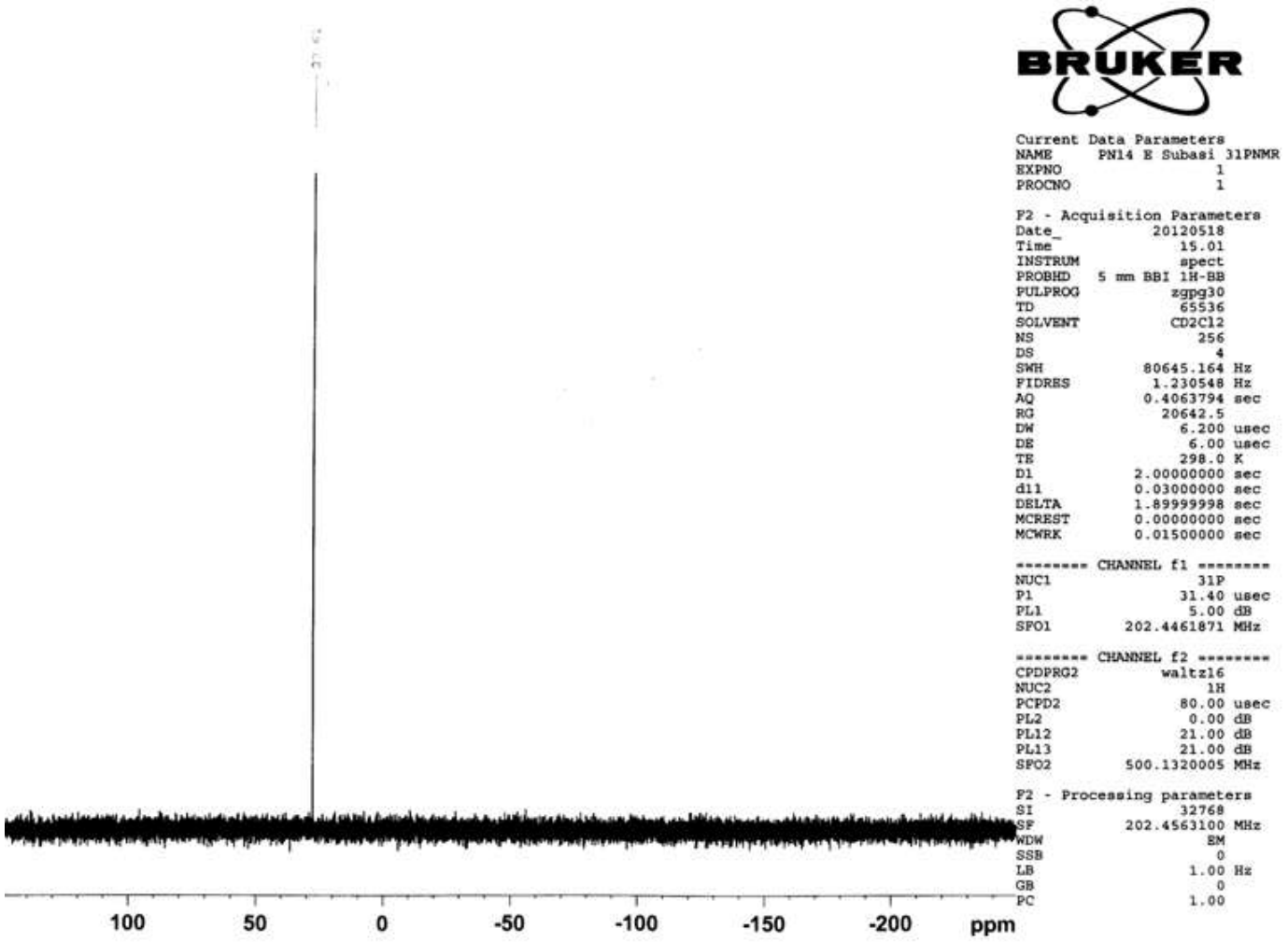

Figure 3.17 The ^{31}P NMR spectrum of complex **1**

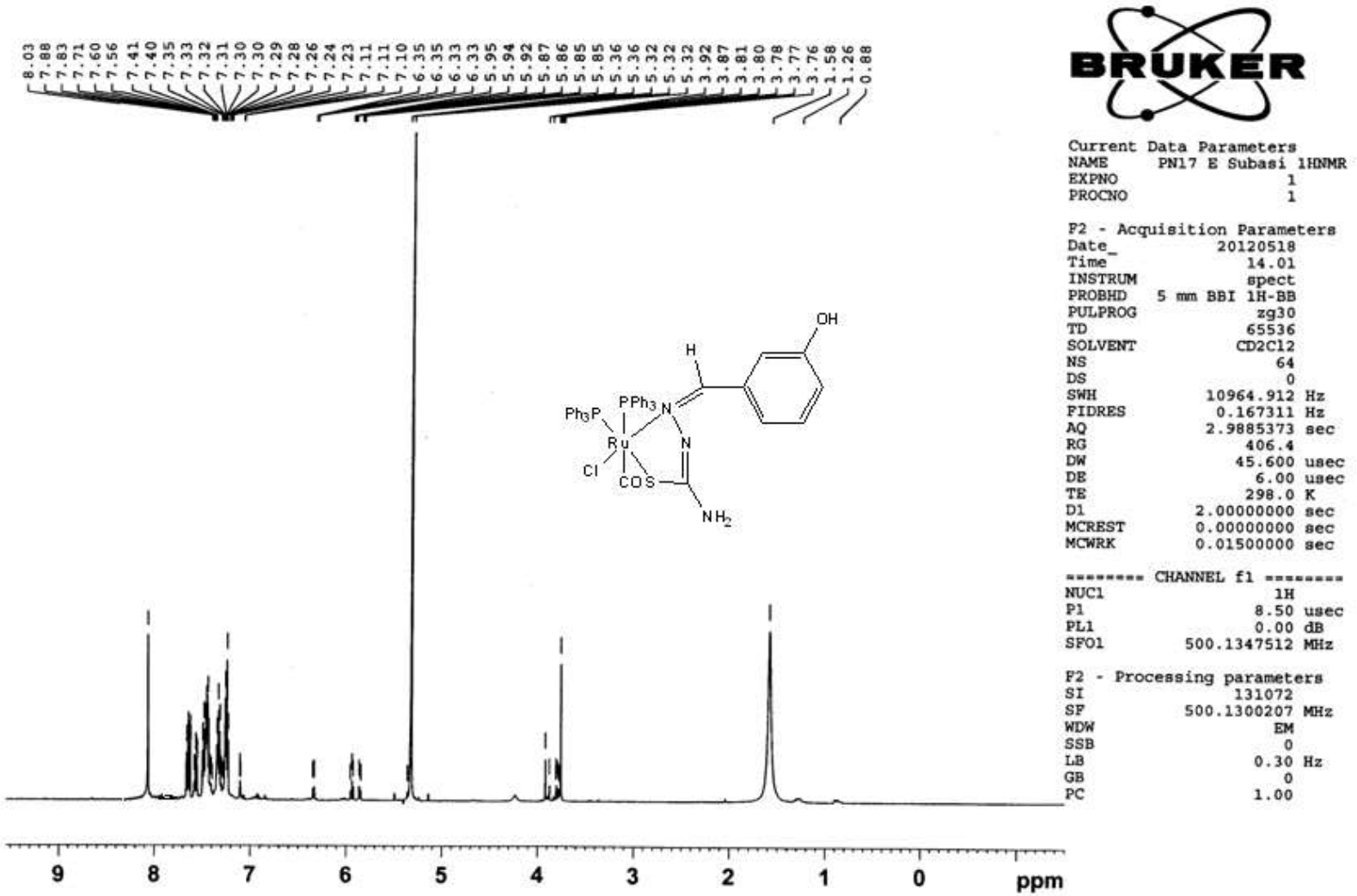

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Figure 3.18 The ^{1}H NMR spectrum of complex **2**

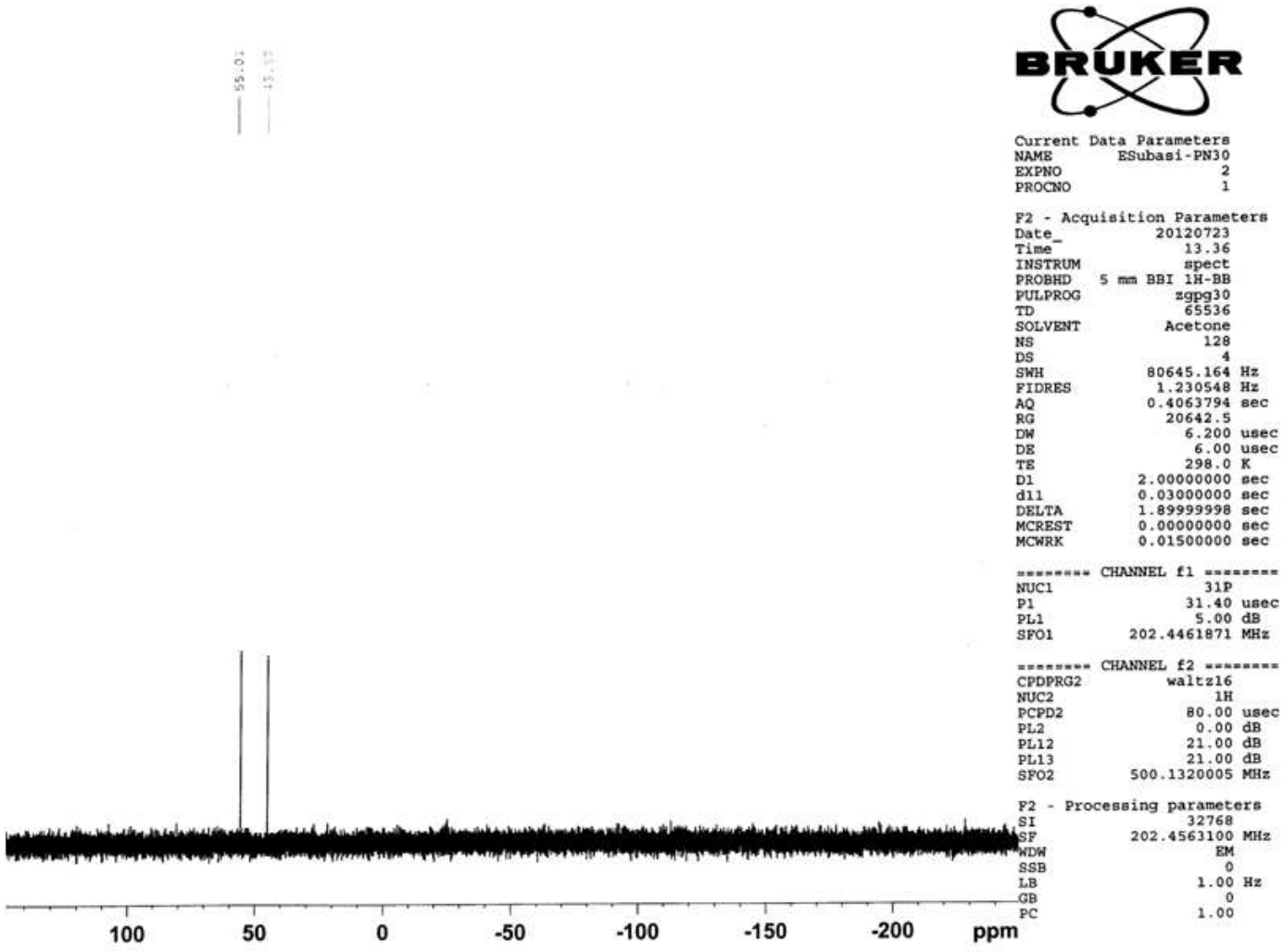

Figure 3.19 The ^{31}P NMR spectrum of complex **2**

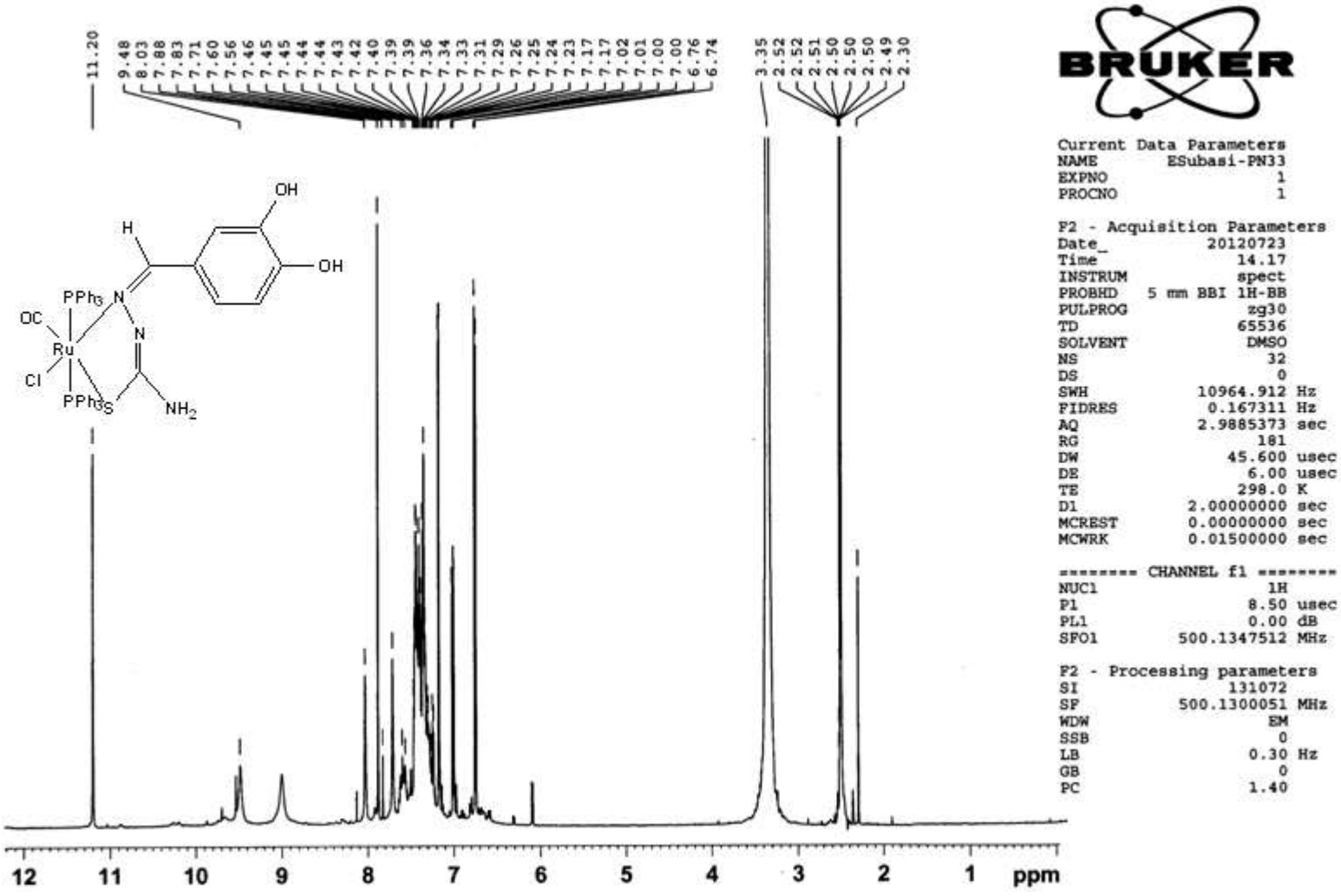

Figure 3.20 The ^{1}H NMR spectrum of complex **3**

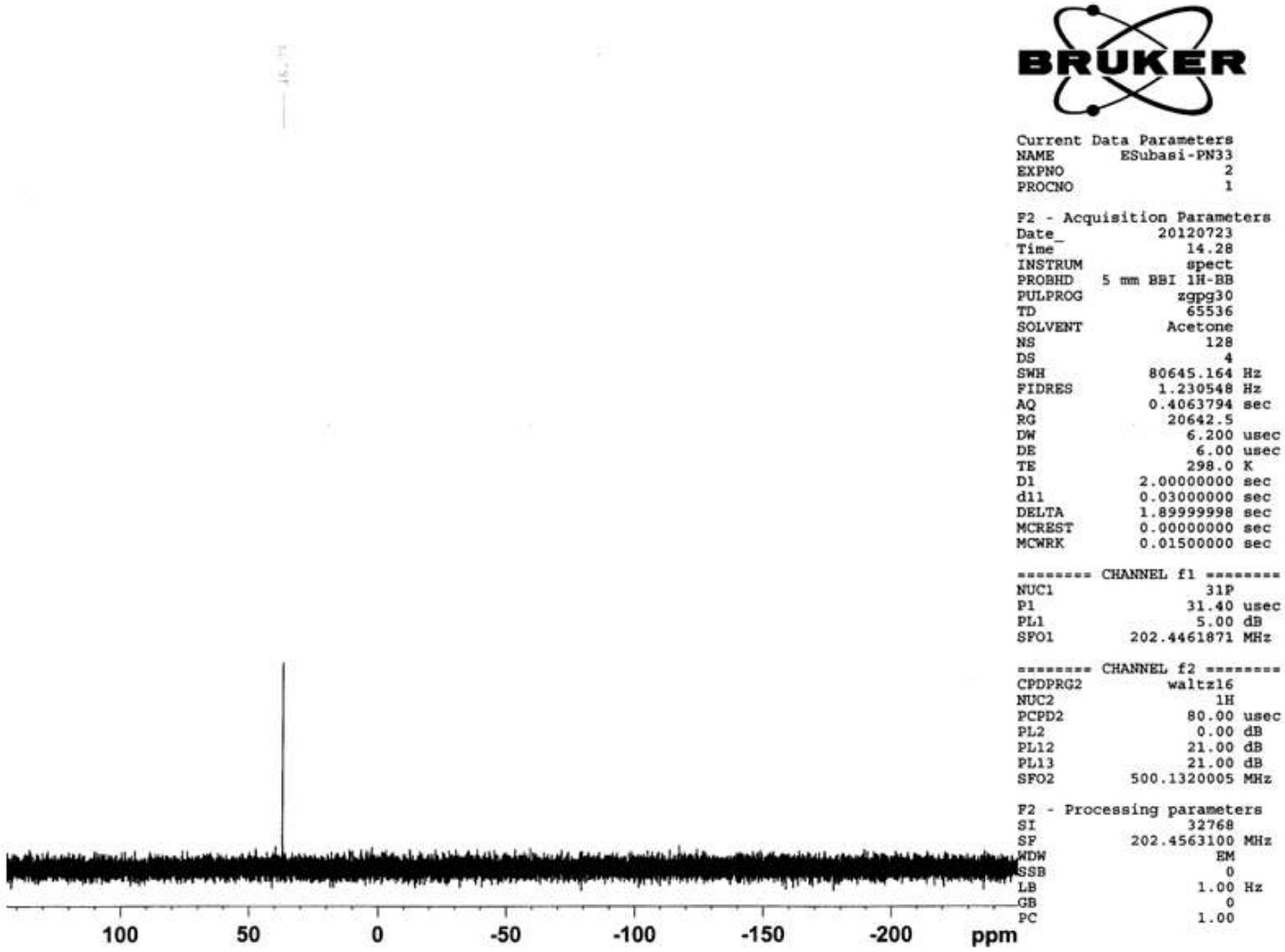

Figure 3.21 The ^{31}P NMR spectrum of complex **3**

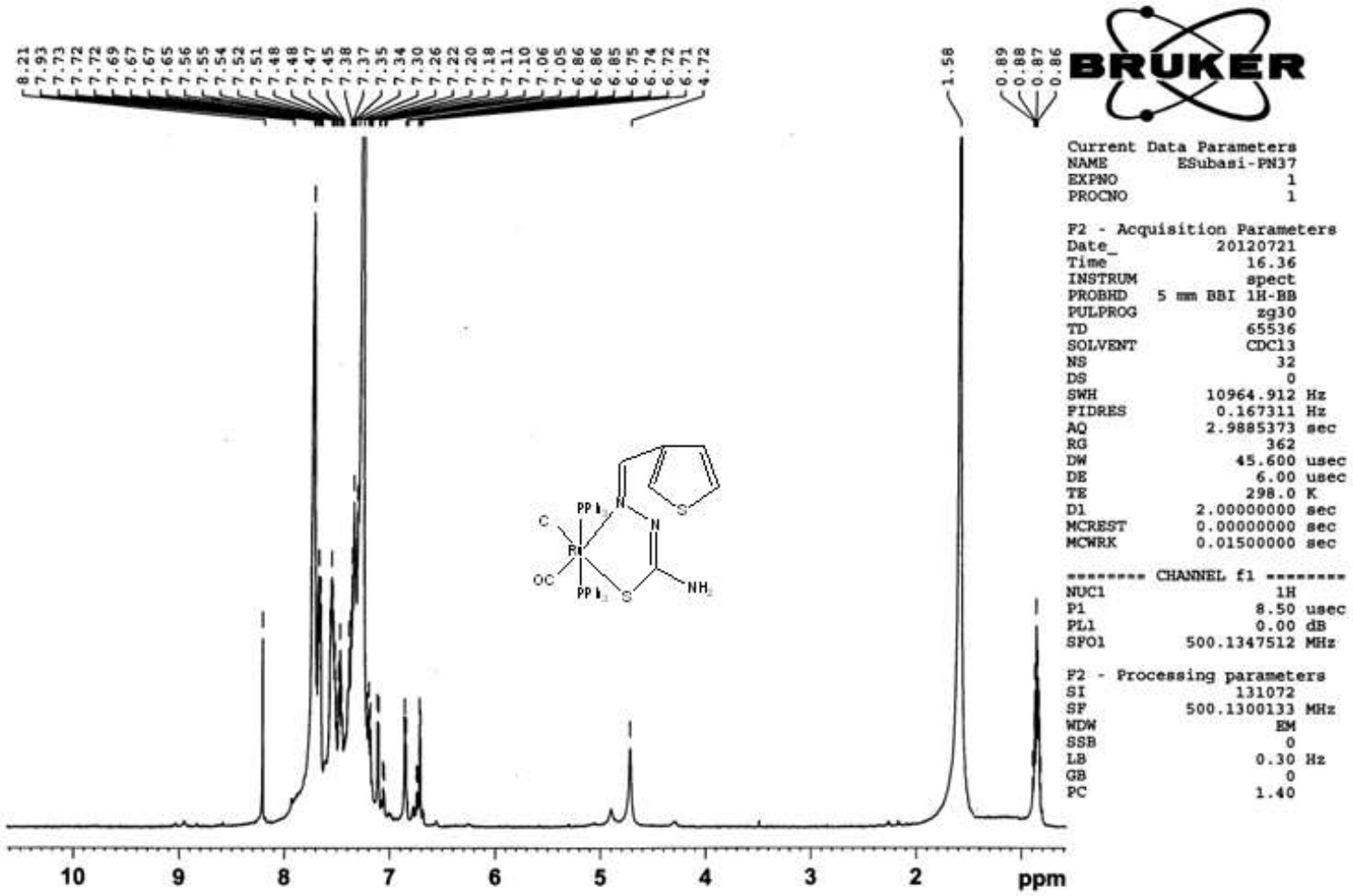

Figure 3.22 The ^{1}H NMR spectrum of complex **4**

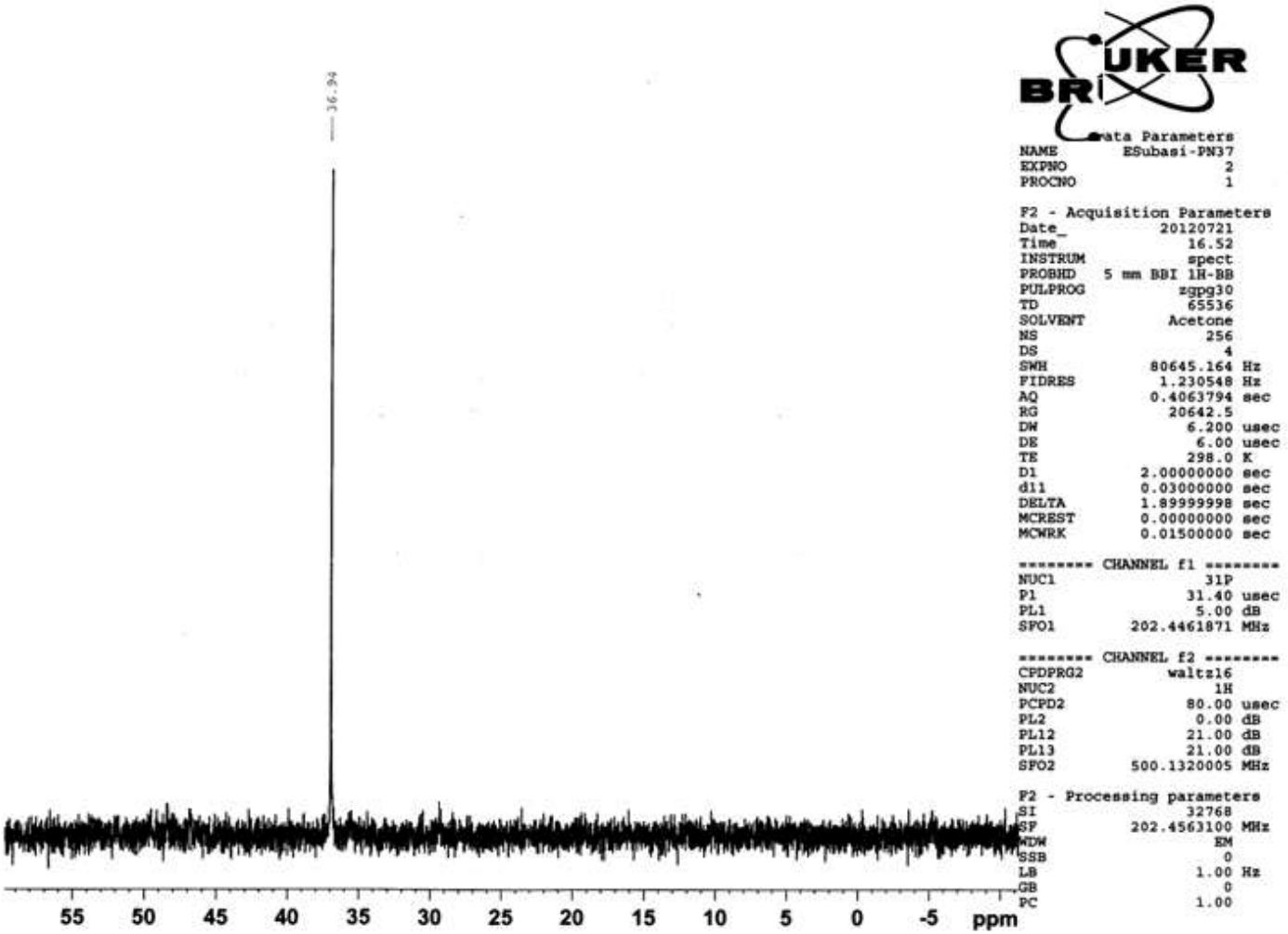

Figure 3.23 The ^{31}P NMR spectrum of complex **4**

3.1.4 Electronic Spectra

Table 3.4 The electronic spectra datas for **TSC[1]**, **TSC[2]**, **TSC[3]**, **TSC[4]** ligands

	λ_{max}(nm), A , c, ε
TSC^1	324.5 (0.415), 10^{-7}, ($4.15^{x}10^{6}$)
TSC^2	325.0 (0.393), 10^{-7}, ($3.93^{x}10^{6}$)
TSC^3	333.0 (0.614), 10^{-7}, ($6.14^{x}10^{6}$)
TSC^4	329.0 (0.064), 10^{-6}, ($6.40^{x}10^{4}$)

Table 3.5 The electronic spectra datas for the complexes **(1-4)**

	λ_{max}(nm), A , c, ε
TSC^1+ [$RuHClCO(PPh_3)_3$]	281.0 (0.212),10^{-7}, ($2.12^{x}10^{6}$)
TSC^2+ [$RuHClCO(PPh_3)_3$]	267.0 (0.299),10^{-7}, ($2.99^{x}10^{6}$)
TSC^3+ [$RuHClCO(PPh_3)_3$]	284.0 (0.138),10^{-7}, ($1.38^{x}10^{6}$)
TSC^4+ [$RuHClCO(PPh_3)_3$]	281.5 (0.034),10^{-6}, ($3.4^{x}10^{4}$)

The electronic spectral assignments of the complexes are given in Table 3.4 and Table 3.5. The electronic spectra of the complexes in THF showed two and three bands in the region 333-324 nm. The ground state of ruthenium (II) is $^1A_{1g}$, arising from the t^6_{2g} configuration in an octahedral enviroment. Excited state corresponding to the $t^5_{2g}e^1_g$ configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence four bands, corresponding to the transitions $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible, in order of increasing energy. The electronic spectra of the complexes show several absorptions in the ultraviolet region.

The bands in the 281-284 nm region present in all the complexes may be assigned to the Ru ($4d\pi$) $\rightarrow \pi^*$ (imine) (MLCT) transition. The other lower wavelength bands below 275 nm are due to intra ligand transitions occuring within ligand orbitals. These bands are seen in the spectra of the ligands also but at a slightly lower wavelength indicating the coordination of the ligands to ruthenium metal. The pattern of the electronic spectra of all the complexes indicate the presence of an octahedral geometry around ruthenium (II) ion.(Sivagamasundari & Ramesh, 2007).

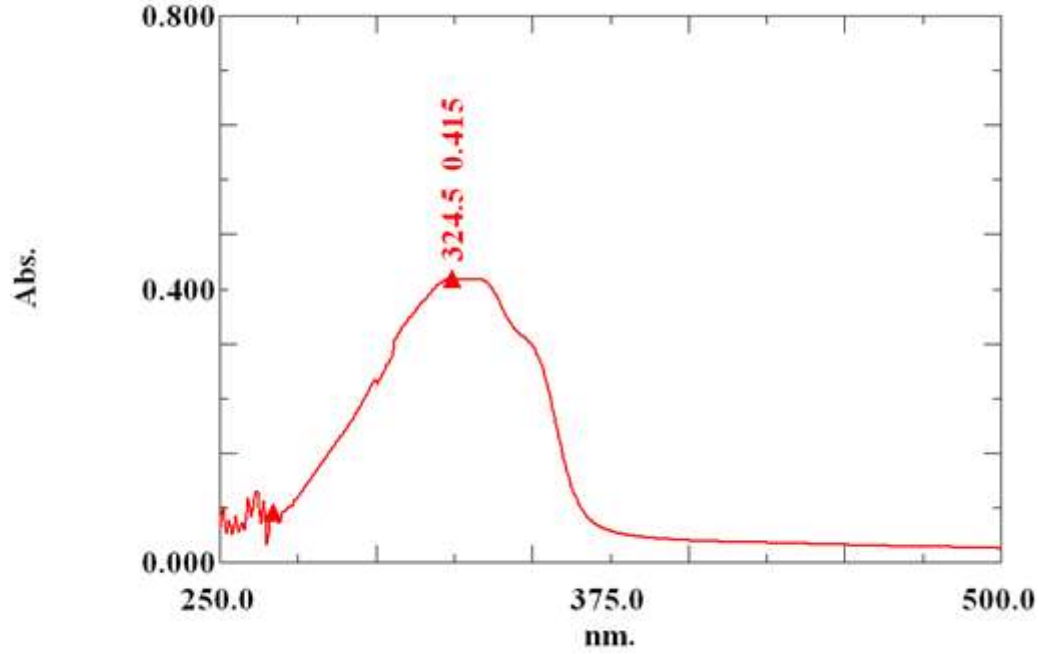

Figure 3.24 The UV-Vis spectrum of **TSC[1]** ligand

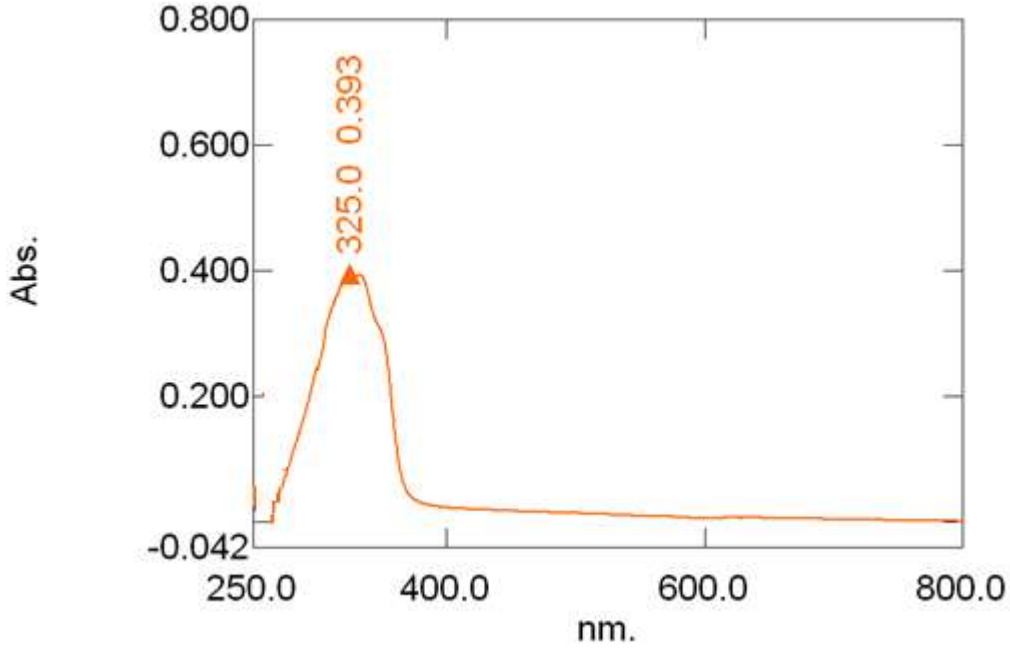

Figure 3.25 The UV-Vis spectrum of **TSC[2]** ligand

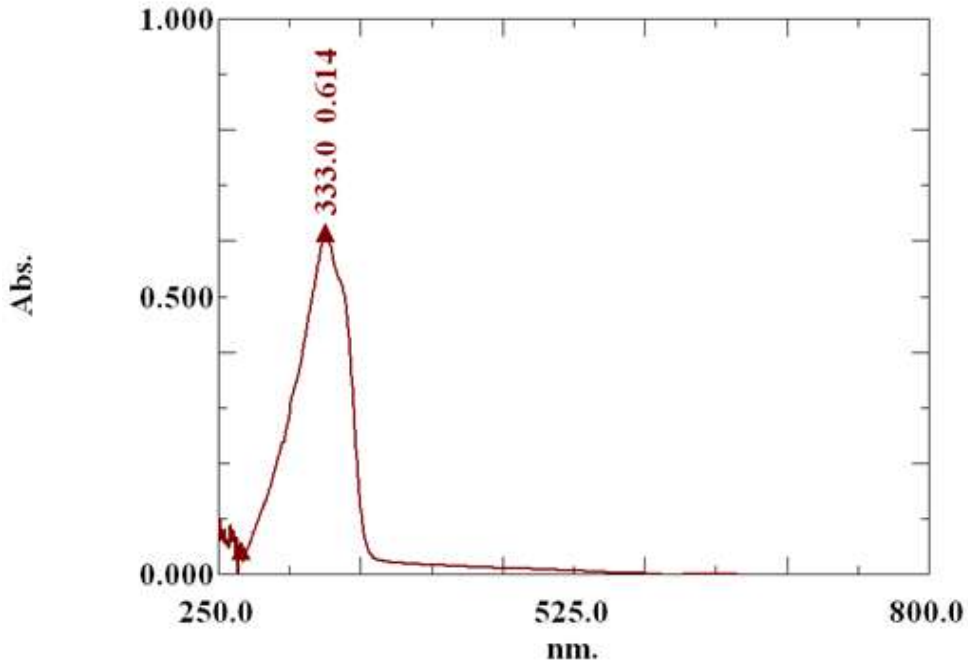

Figure 3.26 The UV-Vis spectrum of **TSC**[3] ligand

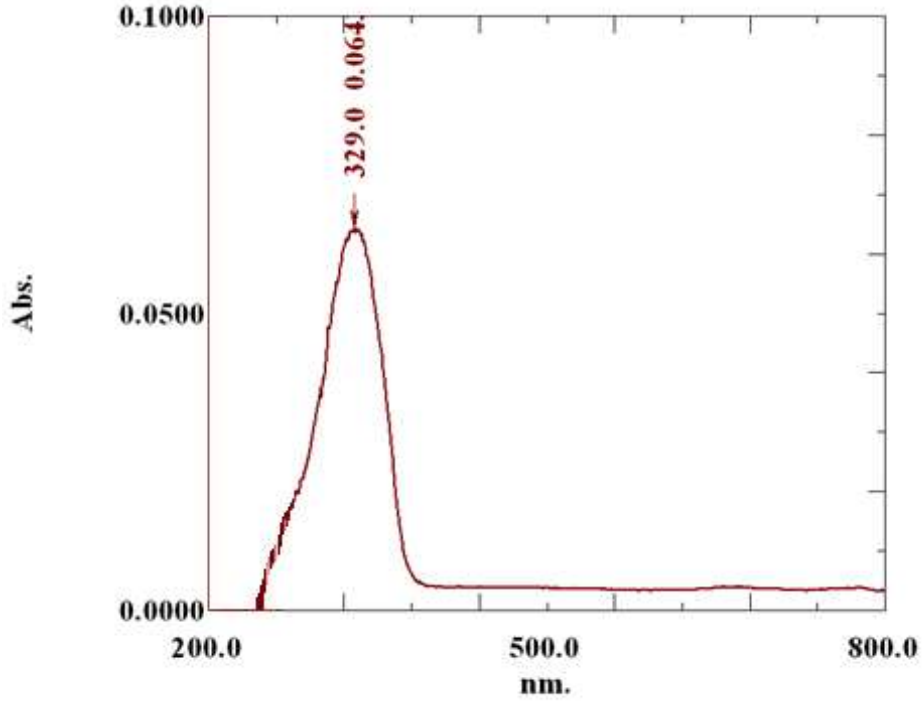

Figure 3.27 The UV-Vis spectrum of **TSC**[4] ligand

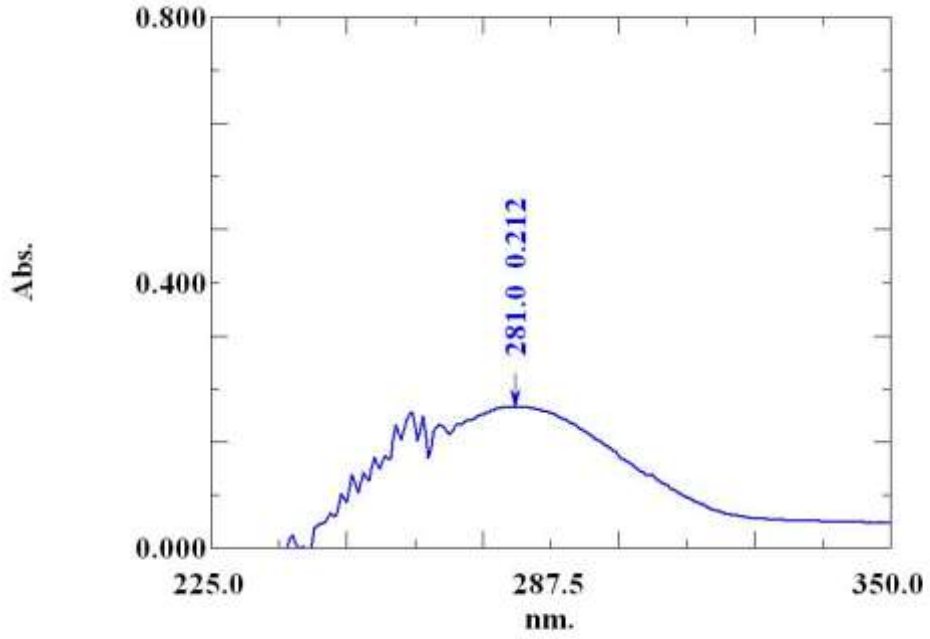

Figure 3.28 The UV-Vis spectrum of complex **1**

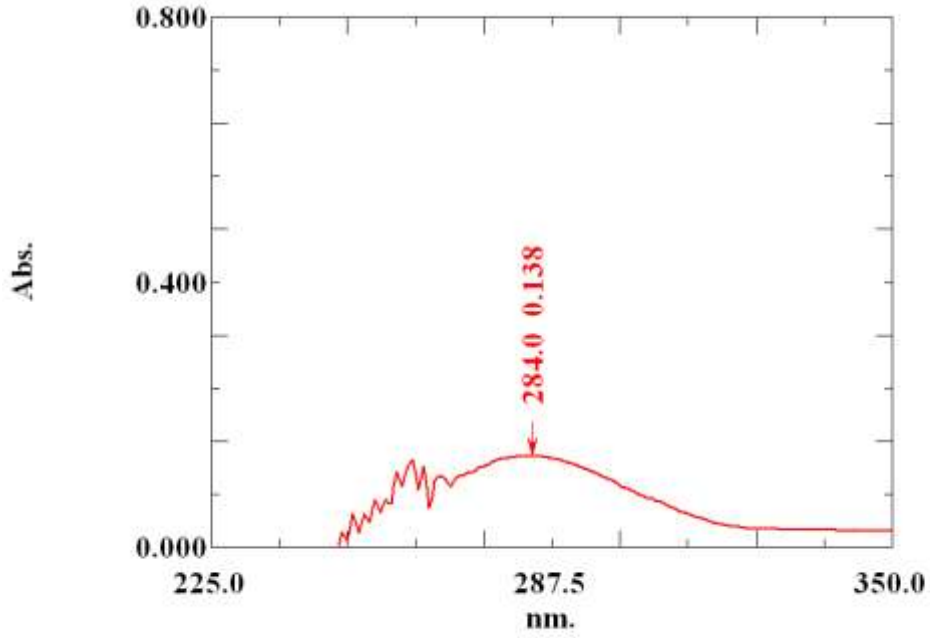

Figure 3.29 The UV-Vis spectrum of complex **2**

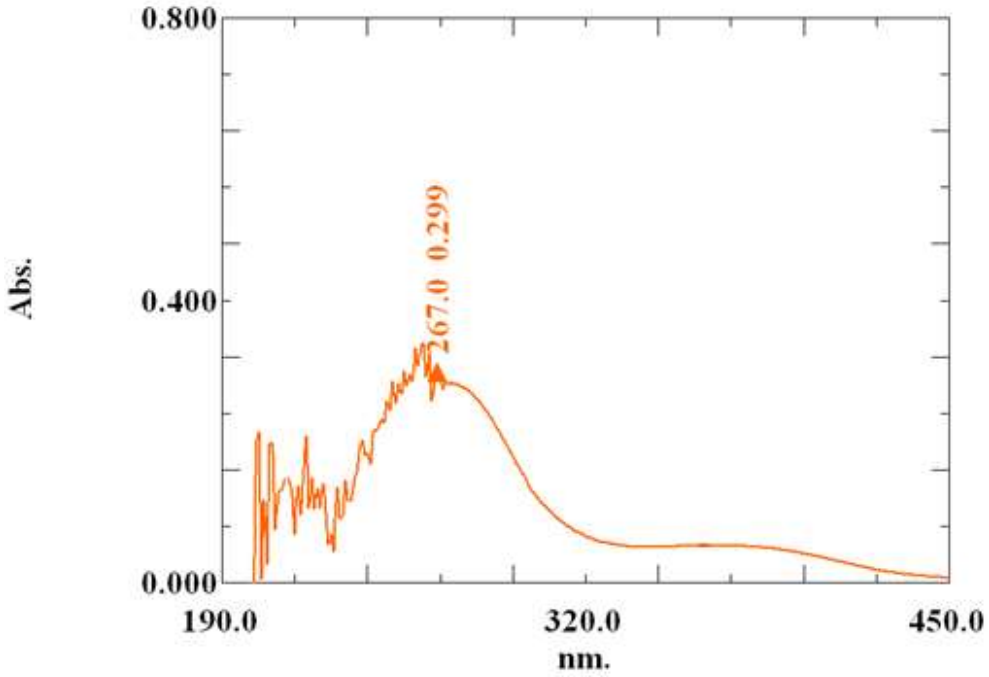

Figure 3.30 The UV-Vis spectrum of complex **3**

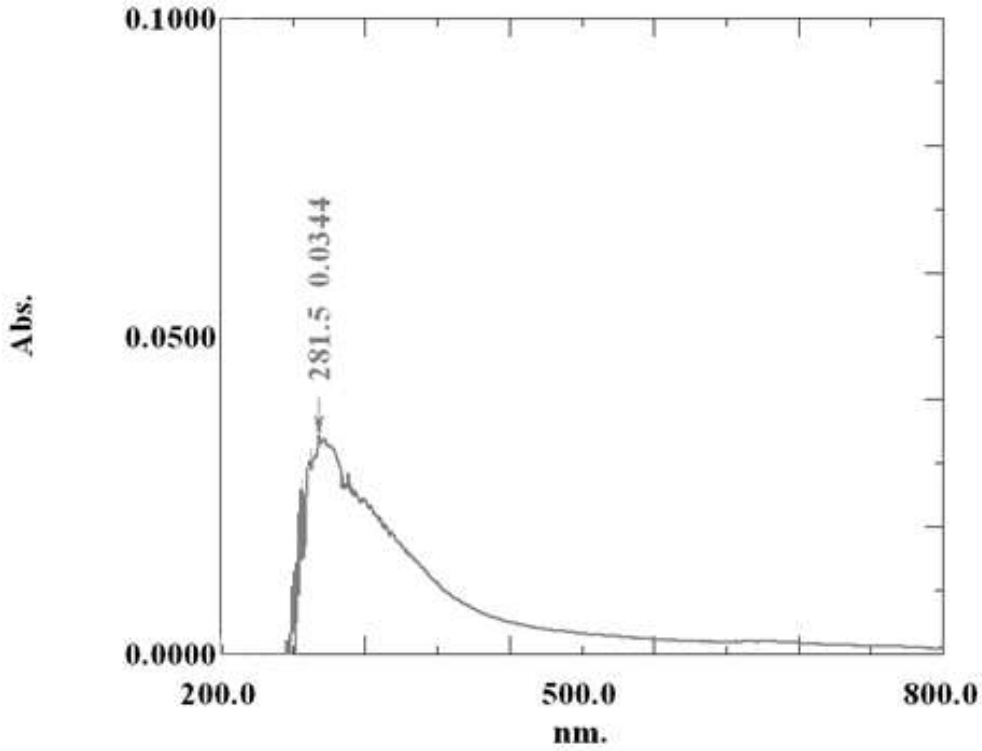

Figure 3.31 The UV-Vis spectrum of complex **4**

3.1.5 Microbiological Activities

The *in vitro* antimicrobial activities of ruthenium complexes *[Ru(CO)(PPh$_3$)$_2$(η^3-O,N^3,S-TSC^1)]*, **1**; *[Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^2)]*, **2**; *[Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^3)]*, **3** and *[Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^4)]* **4** were investigated against nine bacterial strains and one fungus by the disk diffusion test method. No activity was observed against the Gram-negative strains and fungus.

3.1.5.1 Test Microorganisms

The *in vitro* antimicrobial activities of ruthenium complexes *[Ru(CO)(PPh$_3$)$_2$(η^3-O,N^3,S-TSC^1)]*, **1**; *[Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^2)]*, **2**; *[Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^3)]*, **3**; *[Ru(Cl)(CO)(PPh$_3$)$_2$(η^2-N^3,S-TSC^4)]* **4***;* were tested against laboratory control strains belonging to the American Type Culture Collection (LGC Standarts GmbH, Wesel, Germany): *Escherichia coli* ATCC 25922, *Enterobacter cloacae* ATCC 23355,*Pseudomonas aeruginosa* ATCC 27853, *Bacillus subtilis* ATCC 11774, *Staphylococcus aureus* ATCC 25923, *Streptococcus pyogenes* ATCC 19615 andone fungus*Candida albicans* ATCC 10231. Clinical isolate *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Streptococcus agalactiae*were kindly supplied from the Microbiology Department, Faculty of Medicine at the Dicle University (Diyarbakır, Turkey).

3.1.5.2 Evaluation of Antimicrobial Activity

Antimicrobial activities of ruthenium complexes were investigated by the disk diffusion susceptibility test according to the recommendations of the National Committee for Clinical Laboratory Standards (NCCLS) (Clark et al. 1998). It was performed on Nutrient Agar (NA, Oxoid) plates. Plates were dried at approximately 36 ºC for about 30 min in an incubator before inoculation. Three to five freshly grown colonies of bacterial strains were inoculated into 25 mL of Nutrient Broth (NB, Oxoid) medium in a rotary shaker at 200 rpm for 4 to 6 h until a turbidity of 0.5 McFarland (1×10^8 CFU/mL) was reached. Final inocula were adjusted to 5×10^5

CFU/mL. Three to five colonies of *C. albicans*ATCC 10231 were inoculated into 25 mL of SabouraudDextrose Broth (SDB, Oxoid) in a rotary shaker at 200 rpm for 8 to 10 h until a turbidity of 0.5 McFarland was reached. The final inocula were adjusted to 5×10^5 CFU/mL using a spectrophotometer (Kirkpatrick et al. 1998). 50 µL of inoculum from the final inocula was applied to each of agar plates and were uniformly spread with a sterilized cotton spreader over the surface. Absorption of excess moisture was allowed to occur for 30 min before application of sterile filter-paper discs (Oxoid, England, 6 mm in diameter). The discs were impregnated with 10, 15 and 20 µL of the sample solutions in dichloromethane/methanol (DCM/MeOH, 8:2), 5 mg per 1 mL of DCM/MeOH and placed on inoculated plates. These plates were incubated at 37 ºC for 24 h for bacteria and 48 h for fungi. Standard antibiotic discs (all from Oxoid accept for nystatin) of ofloxacin (OFX, 5 µg/disc), Amoxycillin/clavulanic acid (2:1) (AMC, 30 mg/disc), imipenem (IMP, 10 mg/disc),erythromycin (E, 15 µg/disc) and nystatin (Sigma) (N, 60 µg/disc) were individually used as positive controls, while the discs imbued with 20 µL of DCM/MeOH (8:2) solvent system were accepted as negative control. The diameters of the inhibition zones were measured in millimetersusing an inhibition zone ruler.

All most of the ruthenium complexes did not show any activity against Gram-negative bacteria and fungus at the concentration evaluated in this work. Our data revealed that standard ATCC strains of Gram-positive bacteria were more sensitive than Gram-negative ones towards antimicrobial activities studied. This is likely because Gram-positive bacteria lack the outer membrane of Gramnegative ones, which acts as a barrier for penetration of numerous molecules (Walsh, Maillard, Russel, Catrenich,. Charbonneau, & Bartolo, 2003).

The variation of susceptibility of the tested microorganisms could be attributed to their intrinsic properties that are related to the permeability of their cell surface to the ruthenium complexes.

Table 3.6 Antimicrobial activities of standard antibiotics

Tested microorganisms	Zones of inhibition (mm)[a]				
	OFX (5)	AMC (30)	IPM (10)	E (15)	N (60)
Escherichia coli ATCC 25922	26	16	20	10	NT
Enterobacter cloacae ATCC 23355	28	18	22	R	NT
*Pseudomonas aeruginosa*ATCC 27853	14	R	22	R	NT
Pseudomonas aeruginosa[b]	22	R	24	R	NT
*Bacillus subtilis*ATCC 11774	26	28	>30	>30	NT
*Staphylococcus aureus*ATCC 25923	22	30	>30	20	NT
Staphylococcus aureus[b]	22	16	>30	20	NT
*Streptococcus pyogenes*ATCC 19615	16	24	28	24	NT
Streptococcus agalactiae[b]	22	>30	>30	28	NT
*Candida albicans*ATCC 10231	NT	NT	NT	NT	22

OFX: ofloxacin; AMC: amoxycillin/clavulanic acid (2:1); IPM: imipenem; E: erythromycin; N: nystatin; NT: not tested; R: resistance; (–) not active.

[a]µg/6 mm paper disc; .[b]Clinical isolates.

Table 3.7 Antimicrobial activities of ruthenium complexes

Tested microorganisms	µg/ 6 mm paper disc	Zones of inhibition (mm)			
		(1)	**(2)**	**(3)**	**(4)**
Escherichia coli ATCC 25922	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–
Enterobacter cloacae ATCC 23355	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–
Pseudomonas aeruginosa ATCC 27853	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–
Pseudomonas aeruginosa[b]	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–
Bacillus subtilis ATCC 11774	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–
Staphylococcus aureus ATCC 25923	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–
Staphylococcus aureus[b]	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–
Streptococcus pyogenes ATCC 19615	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–
Streptococcus agalactiae[b]	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–
Candida albicans ATCC 10231	50	–	–	–	–
	75	–	–	–	–
	100	–	–	–	–

[b]Clinical isolates; (–) not active.

CHAPTER FOUR
CONCLUSIONS

This thesis describes the synthesis, structural and spectral characterization of four thiosemicarbazones of 2-hydroxy-3-methoxybenzaldehyde, 3-hydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, Thiophene-2-carbaldehyde and their ruthenium complexes and some reactivities of these complexes.

Chapter 1 gives a prologue of the bonding and stereochemistry of the thiosemicarbazones. The different analytical and spectroscopic techniques used for the analysis of the ligands and metal complexes are discussed.

Chapter 2 deals with the synthesis of four thiosemicarbazone ligands and their ruthenium complexes. The ligands synthesized are:

- 2-hydroxy-3-methoxybenzaldehyde thiosemicarbazone,
- 3-hydroxybenzaldehyde thiosemicarbazone,
- 3,4-dihydroxybenzaldehyde thiosemicarbazone,
- Thiophene-2-carbaldehyde thiosemicarbazone.

Thiosemicarbazones are synthesized by adapting a procedure reported elsewhere. The ligands are characterized by elemental analyses, FT-IR, UV-Vis and ^{1}H NMR techniques.

The complexes synthesized are:

- $[RuCO(PPh_3)_2(TSC^1)]$ {TSC^1= 2-hydroxy-3-metoxybenzaldehyde thiosemicarbazone}
- $[Ru(Cl)(CO)(PPh_3)_2(TSC^2)]$ {TSC^2= 3-hydroxybenzaldehyde thiosemicarbazone}
- $[Ru(Cl)(CO)(PPh_3)_2(TSC^3)]$ {TSC^3= 3,4-dihydroxybenzaldehyde thiosemicarbazone}

- $[Ru(Cl)(CO)(PPh_3)_2(TSC^4)]$ {TSC^4= Thiophene-2-carbaldehyde thiosemicarbazone}

These complexes are synthesized by adapting reported procedure in the literature. The complexes are characterized by elemental analyses, FT-IR, UV-Vis, ^1H NMR and ^{31}P NMR techniques.

Chapter 3 represents the structural and spectral characterization of the ligands and their ruthenium complexes. Addititonally, in this chapter is given reactivities of the synthesized ruthenium (II) complexes.

The spectroscopic studies showed that first ligand is coordinated to the central metal as a tridendate ligand coordinating *via* the azomethine nitrogen (C=N), phenolic oxygen atom and sulfur atom to the central metal in **(1)**, whereas second, third and fourth ligands are coordinated to the central metal as a bidentate ligand coordinating via azomethine nitrogens (C=N) and sulfur atoms to the central metal in **(2), (3)** and **(4)** complexes.

All most of the ruthenium complexes did not show any activity against Gram-negative bacteria and fungus at the concentration evaluated in this work. Our data revealed that standard ATCC strains of Gram-positive bacteria were more sensitive than Gram-negative ones towards antimicrobial activities studied. This is likely because Gram-positive bacteria lack the outer membrane of Gramnegative ones, which acts as a barrier for penetration of numerous molecules (Walsh, Maillard, Russel, Catrenich,. Charbonneau, & Bartolo, 2003).

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