Synthesis, Characterization and Reactivity Studies of Some Mixed Ligand Complexes of Ruthenium (II) and Rhodium (III)

and

Novel Synthesis and Crystal Structure of Hydrotris(3,5-Dimethylpyrazolyl)Borate 1-Iminomethyl-3,5-Dimethylpyrazole Copper (II) Perchlorate

Prashanta Sarkhel
DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

A Thesis

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Doctor of Philosophy

To

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TO

MY PARENTS AND

BELOVED PALLAVI SARKHEL

DECLARATION

North-Eastern Hill University

December,2000

I **Prashanta Sarkhel**, hereby declare that the subject matter of this thesis is the record of work done by me, that the contents of this thesis did not form the basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University / Institute.

This is being submitted to the North-Eastern Hill University for the degree of **Doctor of Philosophy** in Chemistry.

Prashanta Sarkhel
14.12.2000
Prashanta Sarkhel
Research Scholar

Countersigned
14/12/2k
Head,
Department of Chemistry

Countersigned
14/12/2k
Dr Raj K. Poddar
Supervisor

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Prashanta Sarkhel

CONTENTS

ABSTRACT

SYNTHESIS, CHARACTERIZATION AND REACTIVITY STUDIES OF SOME MIXED LIGAND COMPLEXES OF RUTHENIUM(II) AND RHODIUM(III)
AND
NOVEL SYNTHESIS AND CRYSTAL STRUCTURE OF HYDRO TRIS(3,5-DIMETHYLPYRAZOLYL)BORATE 1-IMINOMETHYL-3,5-DIMETHYLPYRAZOLE COPPER(II) PERCHLORATE

The thesis presents the results of investigations involving the synthesis, characterization and reactivity studies of (i) some mono and binuclear ruthenium(II) trifluoroacetato/arene complexes containing mono or bidentate co-ligands (ii) rhodium(III) complexes containing acetylacetonate and mono or bidentate ligands and (iii) novel synthesis, characterization and crystal structure of copper (II) amidine complex. The content of the thesis have been distributed over seven chapters.

Chapter 1 presents a brief introduction pertaining to the work described in the thesis. It describes in general, the rapid growth and diversification of interest in the study of chemistry of ruthenium and rhodium. The importance of ruthenium(II) complexes containing trifluoroacetato or arenes and other mono or bidentate ligands have been emphasized in this chapter.

The interest in β-diketonato complex due to the variety in bonding modes, their reactivity and catalytic activity and applications in various industrial processes is also described in Chapter 1. Apart from these, various complexes of copper with hydrotris(pyrazolyl)borate have been discussed with regards to their different synthetic methodologies, reactivity studies and structural aspects. Need to develop method to synthesize copper(II) amidine complex have been justified.

Chapter 2 describes the details of the methods of elemental analyses as well as the particulars of the instruments/equipments used for the characterization and structural assessment of the compounds which are described in chapter 3 to 7. The instruments/equipments used are : Infra-red, UV-visible spectrophotometers, ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR and ESR spectrometers, Conductivity meter, Vibrating Sample Magnetometer, Cyclic Voltameter and single crystal X-ray diffractrometer.

Chapter 3 of the thesis addresses to the simple and efficient methods for the synthesis of some mono and binuclear ruthenium(II) trifluoroacetato complexes containing nitrogen donor co-ligands of the type $[Ru_2(\mu\text{-}O_2CCF_3)_4L_2]$ and $[Ru(O_2CCF_3)_2L_4]$ (L = pyridine, 2-methylpyridine or 3-methylpyridine) and $[Ru(L\text{-}L)_3](O_2CCF_3)_2$ (L-L = 2,2'-bipyridine or 1,10-phenanthroline). The characterization and structural assignments of the above complexes have been described, by making use of the elemental analyses and various physical measurements, as described in chapter 2. The IR spectra of the complexes containing trifluoroacetate show a strong absorption in the region 1630-1640 cm^{-1} for bridging, 1675-1690 cm^{-1} for unidentate and 1660-1670 cm^{-1} for ionic $\nu_{(OCO)asym}$ mode of vibration of the trifluoroacetato group(s). ^1H and ^{13}C NMR spectra of these complexes show signals in the aromatic region due to pyridine and substituted pyridines and ^{19}F NMR spectra of the complexes show signals due to fluorine in the region δ -76.00 to -77.00. The electrochemical studies show quasi reversible oxidation at $E°_{1/2} = 0.15$ to 0.19 V for the mononuclear and at $E°_{1/2} = 0.80$ to 0.90 V for the binuclear ruthenium(II) trifluoroacetato complexes, which is in conformity with the metal to ligand charge transfer bands observed in the electronic absorption spectra of the two systems.

Chapter 4 continues with ruthenium(II) trifluroacetato complexes with some of the co-ligands. The complexes are of the type $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$, $[Ru(O_2CCF_3)_2(CO)(EPh_3)_3]$ (E = P or As) , $[Ru(O_2CCF_3)_2(Me_2SO)_3]$ and $[Ru(O_2CCF_3)_2(Me_2SO)(EPh_3)_2]$ (E = P or As). The bonding modes of trifluoroacetate(s) have been diagnosed with the help of IR and ^{19}F NMR spectral studies. Except $[Ru(O_2CCF_3)(PPh_3)_4](O_2CCF_3)$ in all other complexes trifluoroacetate is bonded to the metal in a unidentate fashion. The dimethylsulphoxide groups in $[Ru(O_2CCF_3)_2(Me_2SO)_3]$ and $[Ru(O_2CCF_3)_2(Me_2SO)(EPh_3)_2]$ (E = P or As) are found to be S-bonded as interpreted from the infrared and ^1H NMR data of the complexes.

In **Chapter 5** is described, the reactivity studies $[(p\text{-cymene})RuCl_2]_2$ and $[(p\text{-cymene})RuCl_2(EPh_3)]$ (E = P or As) with 4,4'bipyridine , which resulted in the formation of bridging binuclear complexes of the type $[\{(p\text{-cymene})RuCl_2\}_2(\mu\text{-}4,4'bipy)]$ and $[\{(p\text{-cymene})RuCl(EPh_3)\}_2(\mu\text{-}4,4'bipy)](BF_4)_2$ (E = P or As). Reaction of $[(p\text{-cymene})RuCl_2(PPh_3)]$ with imidazole yielded $[(p\text{-cymene})RuCl(PPh_3)(Im)](BF_4)$ (Im = Imidazole). All the complexes have been characterized with the help of elemental analysis and various physical methods described in chapter 2. The ^1H NMR studies confirm the presence of bridging 4,4'-bipyridine in the binuclear complexes.

Chapter 6 of the thesis presents the synthesis and characterization of $[RhCl_2(acac)(py)_2]$, $[RhBr_2(acac)(L)_2]$ (L = PPh_3, $AsPh_3$ or py) and $[RhBr_2(acac)(L\text{-}L)]$ (L-L = bipy or phen). The bromo acetylacetonato complexes of rhodium (III) were synthesized by a metathetic reaction of $[RhCl_2(acac)(acacH)]$ with LiBr *in situ,* followed by the addition of neutral monodentate / bidentate ligands. All the complexes were characterized with the help of analytical data and various physical methods as mentioned above. $[RhBr_2(acac)(L\text{-}L)]$ (L-L = bipy or phen) are found to have *cis*-geometry which was characterized by well resolved ^1H NMR spectra of the complexes.

Chapter 7 deals with the synthesis of a new copper(II) amidine complex *viz.* [Tp*CuL]ClO_4 (Tp* = Hydrotris(3,5-dimethylpyrazolyl)borate and L = 1-Methylcarbaldimino-3,5-dimethylpyrazole). The Ligand(L) has been generated *in situ* by a condensation reaction of acetonitrile with 3,5-dimethylpyrazole activated by Cu(II). The X-ray crystal structure shows that the complex is monoclinic, space group Pc, a = 10.2879(7) A°, b = 7.8877(7) A°, c = 17.1301(14) A°, β = 96.896(6)°, V= 1380.01A^{o3}, Z = 2, R = 0.388 and Rw = 0.1041. The three nitrogen atoms of Tp* and two nitrogen atoms of L are coordinating with Cu making a distorted square pyramidal geometry around the metal center. The compound has also been characterized by IR, UV-vis, ESR spectroscopies and Cyclic Voltametry.

The results of studies described in chapters 3,4,5,6 and 7 have been published, while a part of the work described in chapter 4 and 5 has been communicated for publication.