

**SYNTHESIS OF BINUCLEAR IRON COMPLEX WHICH MAY SERVE AS
POSSIBLE STARTING MATERIAL FOR THE FORMATION OF A
DINITROGEN COMPLEX.**

BY

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I56/12518/04

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*Synthesis of
binuclear iron*



2013/422246


**A thesis submitted in partial fulfillment of the requirements for the award of the
degree of Master of Science (Chemistry) in the School of Pure and Applied Sciences
of Kenyatta University**

SEPTEMBER, 2012

DECLARATION

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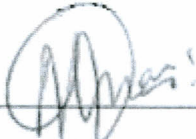
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DEDICATION.

To my lovely parents, Michael Machau Githinji and Ruth Nyawira Machau, who believed in the power of education in individual, family and national development and to my loving and dedicated wife Regina Wairimu, who is a model of perfection.

I wish to thank the Members of the Department of Chemistry of JKUAT led in particular by Mr. John Machau, Mr. Kung'u and Mrs. Elizabeth Wairimu for their technical assistance in analyzing the samples using the IR spectroscopic equipments.

I cannot forget to thank my colleagues, Mr. Soli who taught me the virtue of patience and power of a group in problem solving, Mr. Silvanus Mwirere and Mrs. Cecilia Njoroge who were always ready to help, Mr. James Mwangi who did not mind sharing his time with me, Mr. Joseph Mwangi who was always ready to help, Mr. Joseph Mwangi who was always ready to help, Mr. Joseph Mwangi who was always ready to help.

I would like to thank my friends, Mr. Joseph Mwangi who was always ready to help, Mr. Joseph Mwangi who was always ready to help, Mr. Joseph Mwangi who was always ready to help.

My thanks go to my family, Mr. Joseph Mwangi who was always ready to help, Mr. Joseph Mwangi who was always ready to help, Mr. Joseph Mwangi who was always ready to help.

ACKNOWLEDGEMENT.

I wish to start by thanking the almighty God, the origin of all living and non-living and who this study and all that is ahead depends on.

My special thanks goes to my supervisors, Prof. Naftali Muriithi of Kenyatta University, (KU), and Dr. Martin Opiyo Onani of University of Western Cape, South Africa, for their role of guidance, counsel and direction in this research work. My sincere gratitude also goes to all the staff of the Department of Chemistry of Kenyatta University for their encouraging words, guidance and advice that made my stay at KU smooth. Further I wish to express my sincere gratitude to Dr. Changamu and Dr. Mbuvi for their technical assistance that gave me a better understanding of inorganic synthetic work and Mr. Elias Maina, the Chief Technician, Department of Chemistry of Kenyatta University for his assistance in glass blowing, provision and advice on use of the required chemicals and solvents and constant encouragement.

I wish to thank the Members of the Department of Chemistry of JKUAT and in particular Mr. Tom Odera, Mr. Kung'u and Mrs. Elizabeth Waithira for their technical assistance in analyzing the samples using the IR spectroscopic equipments.

I cannot forget to thank my colleagues; Mr. Soi who taught me the virtue of patience and power of a group in problem solving, Mr. Silvester Mwove and Mrs. Eunice Nyawade who were colleagues in synthetic work, Mr. James Muithya who didn't mind sharing his many reference textbooks and Mr. Irungu who was a symbol of a family, and the entire class for their academic unity and encouraging words that made us through the first year with a smile.

I also wish to commend my family; parents, brothers, sisters, uncles, aunt, wife and sons for their encouragement and support through out this study.

My special thanks also goes to my employer, the Teachers Service Commission (TSC) for granting me a paid study leave to enable me enhance my professional growth.

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ABBREVIATIONS AND ACRONYMS

ATP	Adenosine Triphosphine
ADP	Adenosine diphosphine
BNF	Biological Nitrogen Fixation
Diglyme	Diethylenglykol-dimet+hylether
IR	Infra-red
NMR	Nuclear Magnetic Resonance
N ₂	Dinitrogen
N ₂ -ase	Nitrogenase
dppe	1, 2-bis (diphenylphoshino) ethane
DNA	deoxyribonucleic acid
RNA	ribonucleic acid
TMS	Tetramethylsilane
Cys	Cysteine
Redox Reaction	Reduction-oxidation reaction

ABSTRACT.

The aim of this study was to synthesize a binuclear iron complex which may serve as possible starting material for the formation of a dinitrogen complex at ordinary conditions of temperature and pressure. Dinitrogen complexes are important as they are seen as possible substitutes for the Haber process in the synthesis of ammonia gas as some dinitrogen complex undergo a proton induced reduction to ammonia. The following complexes were synthesized; $\text{FeH}_2(\text{dppe})_2$, $\text{FeH}(\text{SOCl})(\text{dppe})_2$ and the binuclear iron complex $(\text{dppe})_2\text{HFeSOFeH}(\text{dppe})_2$. The complex $\text{FeH}_2(\text{dppe})_2$ was obtained by reacting anhydrous iron (II) chloride and 1,2-bis(diphenylphosphino)ethane in equal molar amounts using acetone as a solvent. Sodium tetrahydroborate was used to reduce the chlorides in the complex formed. The complex $\text{FeH}(\text{SOCl})(\text{dppe})_2$ was obtained by reacting $\text{FeH}_2(\text{dppe})_2$ complex with thionyl chloride in equal molar amounts while the complex $(\text{dppe})_2\text{HFeSOFeH}(\text{dppe})_2$ was obtained by reacting equal molar amounts of complexes $\text{FeH}_2(\text{dppe})_2$ and $\text{FeH}(\text{SOCl})(\text{dppe})_2$ using acetone as a solvent. All preparative work was done in a dry and oxygen-free nitrogen atmosphere as the complexes were thought to be susceptible to destruction by oxygen. The results so far obtained confirms that the binuclear iron complex were synthesized, which contain a sulphur bridge unlike most of the synthesized complexes which contain phosphine ligands. The conclusion made is supported by elemental analysis data that were used to deduce the formula of the complexes, IR spectroscopy and ^{13}C and ^1H NMR spectroscopy for all synthesized complexes as recorded and used to determine the structural information of the complexes. Recommendation for further research are proposed and which include; attempt to crystallize the synthesized binuclear complex and carry out its X-Ray structural determination, and investigate the reaction between the complex $\text{FeH}(\text{SOCl})(\text{dppe})_2$ with the known molybdenum hydrides complexes which may forms an even better binuclear complex of iron and molybdenum joined by a sulphur ligand.

CHAPTER 1

INTRODUCTION

1.1 Background.

The chemistry of iron together with that of molybdenum are of special interest because these elements are components of nitrogenase enzyme which is responsible for converting atmospheric nitrogen to ammonia (Silver, 1993; Porterfield, 1993). Iron is the only transition metal present in all nitrogenases (Eady *et al.*, 1994). In addition to nitrogenase, there are heterogenous iron systems that catalytically reduce dinitrogen (Jennings, 1991). Some solution of Fe-N₂ systems have been reported to give hydrazine or ammonia on protonation. The majority of iron compounds are coordination compounds in which an iron atom has several, but in most cases, those with co-ordination numbers four or six are common (Silver, 1993).

Whereas nitrogen is needed by all living things to synthesize nitrogen - containing substances such as proteins, DNA, RNA, and ATP only a few organisms can use N₂ gas directly (Alton *et al.*, 1998). The rate at which nitrogen is converted to ammonia by nitrogenase enzyme is on the scale of approximately 10⁸ tons per year, which is approximately the same as that produced in the Haber - Bosch process (Jennings, 1991). In the Haber - Bosch process, a mixture of nitrogen from liquid air and hydrogen from natural gas is passed over an enriched iron catalyst and at pressure of 150 – 200 atmospheres at 350 – 450°C. This is an expensive process. Under optimum reaction conditions the conversion rate is only 15% and 85% gas mixture must be re-cycled (Hager, 2008). It consumes more than 1% of all the energy consumed by humans and

requires specialized equipment (Schrock, 2006). The continued recycling of nitrogen and hydrogen would make the overall conversion is about 98% (Greenwood, 1997). The natural processes of nitrogen fixation have not met the increasing demands of growing human population. The Haber - Bosch process requires huge capital investment and is expensive to operate. Thus there is a need to develop a catalytic process that would convert dinitrogen to ammonia at ambient condition of temperature and pressure.

The discovery of the first dinitrogen complex, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ (figure 1) as reported by Allen and Senoff at the University of Toronto (Allen and Senoff, 1965) raised scientists' hope that they might eventually understand how to activate and reduce dinitrogen to ammonia using dinitrogen complexes under mild conditions.

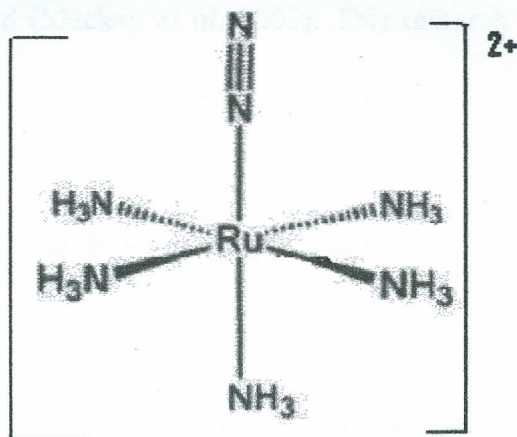


Figure 1: The structure of $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$

Today, many dinitrogen complexes are known (Fryzuk *et al*, 2000). These illustrate how N_2 might bind to metal(s) in nitrogenase. The principles of reduction of dinitrogen to ammonia by $\text{Mo}(0)$ and $\text{W}(0)$ dinitrogen complexes were established in studies that began in the mid 1960s by Chatt and Hidai (Hidai *et al*, 1995). The study proved that dinitrogen can be bound and reduced to ammonia at a single metal center.

The exact mechanism of catalysis of nitrogenase is unknown due to the difficulty in obtaining crystals of nitrogen - bound to nitrogenase (Leigh *et al.*, 2002). The mechanism of operation of nitrogenase is of interest because it holds the promise to a cheaper technology process for nitrogen fixation unlike the industrial process which is not economical and requires heavy capital investment (Greenwood, 1997). There is a need to develop a catalytic process that would convert dinitrogen to ammonia at ambient condition of temperature and pressure. Unfortunately most of dinitrogen complexes are stabilized by tertiarily phosphine ligands yet nitrogenase does not contain phosphorous-donor atoms but sulphur. This makes these complexes unrealistic models of nitrogenase. The discovery of vanadium-containing nitrogenase, and even of all-iron species, show there is a long way to go before the exact mode of action between N_2 and nitrogenase is understood (Mackay *et al.*, 2002). This research was aimed at synthesizing a binuclear iron complex with at least a sulphur ligand.

1.2 Problem statement and justification

Demand for ammonia increases proportionally with the increase in the world population. The most common method for ammonia production is the Haber-Bosch process. Today, the typical modern ammonia-producing plant first converts natural gas or liquefied petroleum or petroleum naphtha into gaseous hydrogen, a gas that is then catalytically reacted with nitrogen to form anhydrous liquid ammonia. The Haber process requires high pressures and high temperatures, routine conditions for industrial catalysis. At the same time, crude oil and natural gas which are the major source of hydrogen used in Haber-Bosch process are getting depleted making ammonia production expensive and

unaffordable. The fertilizer generated from ammonia is responsible for sustaining one-third of the Earth's population and the largest source of human-produced fixed nitrogen in the earth's ecosystem (Curley *et al*, 2006). The Haber process consumes more than 1% of all man-made power; the production of ammonia is a significant component of the world energy budget (Max, 2006).

Much research has been conducted on the discovery of catalysts for nitrogen fixation, often with the goal of reducing the energy required for this ammonia production in the Haber-Bosch process. Such research has thus far failed to even approach the efficiency and ease of the Haber process. Some synthesized compounds have been discovered to react with atmospheric nitrogen under ambient conditions and the first example of homolytic cleavage of dinitrogen under mild conditions was published in 1995 (Curley *et al*, 2006). The first system for converting nitrogen to ammonia at room temperature and pressure was discovered in 2003 and is based on a molybdenum compound, a proton source and a strong reducing agent (Curley *et al*, 2006). Unfortunately, this catalytic reduction only fixates a few nitrogen molecules. More research that may lead to new complexes which may serve as possible starting material for the formation of dinitrogen complexes at ambient conditions of temperature and pressure is then justified. This was the main aim of this research and I was aiming at synthesizing low-coordinate binuclear iron complexes as synthetic models of nitrogenase.

1.3 Hypothesis.

The binuclear iron complex, $(dppe)_2HFe-SO-FeH(dppe)_2$ may be synthesized and serve as possible starting material for the formation of a dinitrogen complex.

1.4 Objectives of the study

General objective.

To synthesis a binuclear iron complex $(dppe)_2HFe-SO-FeH(dppe)_2$.

Specific objectives

- i) To synthesis iron hydride complex $FeH_2(dppe)_2$ and iron thiol complex $FeH(SOCl)(dppe)_2$.
- ii) To complex the synthesized complexes $FeH_2(dppe)_2$ and $FeH(SOCl)(dppe)_2$ in (i) above into binuclear iron complex $(dppe)_2HFe-SO-FeH(dppe)_2$.

CHAPTER 2

LITERATURE REVIEW

This chapter provides a review of the literature on; nitrogen, nitrogenase, nitrogen fixation, ammonia, iron, iron and its compounds, dinitrogen complexes, the nitrogen binding mode, the synthesis of dinitrogen complexes, the iron-sulphur proteins, Preparation of 1,2-bis(diphenylphosphino)ethane, Metal halides, and Thionyl chloride.

2.1 Nitrogen

Nitrogen is a chemical element that has the symbol N, atomic number 7 and atomic mass 14.00675. The earth's atmosphere is more than 78% percent nitrogen by volume. Many industrial important compounds, such as ammonia, nitric acid, organic nitrates (propellants and explosives), and cyanides, contain nitrogen. (Curley *et al*, 2006). The extremely strong bond in elemental nitrogen dominates nitrogen chemistry, causing difficult for both organism and industry in breaking the bond to convert N₂ into useful compounds (Fryzuk *et al.*, 2000). Nitrogen is needed by all living things to build proteins, DNA, RNA, and ATP in their cells yet few organisms can use N₂ gas directly (Alton *et al.*, 1998). Nitrogen is in the chemical structure of almost all neurotransmitters, and is a defining component of alkaloids, biological molecules produced by many organisms (Seefeldt *et al.*, 2004). The world cannot do without nitrogen.

Several species of bacteria (Rhizobium, Azobactor and cyanobacteria) have enzyme that convert N₂ gas into ammonia in a process known as *nitrogen fixation*. Ammonia is then converted to nitrite (NO₂⁻) and nitrate (NO₃⁻) which can be used by plants (Eric and

Marylin, 1998). This conversion is accomplished by metalloenzymes on a scale of $\approx 10^8$ tons per year, a scale that is equivalent to that of Haber-Borsch process for making ammonia (Jennings, 1991). Some plants were known to fix nitrogen and in 1930 a metal (molybdenum) was found to be required for efficient dinitrogen fixation in the soil. In the 1960, the Mo nitrogenase was found to be responsible for fixation of dinitrogen (Hardy *et al.*, 1979).

Two reports of the reduction of dinitrogen to ammonia with protons and electrons at room temperature and pressure have been reported. In the first report, the dinitrogen is reduced to a mixture of hydrazine and ammonia ($\approx 10:1$) (Peters *et al.*, 2003). In the above case the dinitrogen reduction is catalytic with respect to molybdenum and the reaction is run in methanol in presence of magnesium hydroxide and a strong reducing agent such as amalgam. The second report was in year 2006 (Yandulov *et al.*, 2006). The catalyst are Mo complexes that contain the $[(\text{HIPTNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ ($[(\text{HIPTN}_3)]^{3-}$) ligand, where HIPT is 3,5-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃ or hexaisopropylterphenyl (Yundulov *et al.*, 2006). A flow diagram for a dinitrogen complex reduction to ammonia and hydrazine is shown in the figure 2 below. The structures in bold have been isolated and fully characterized. (Seefeldt *et al.*, 2004).

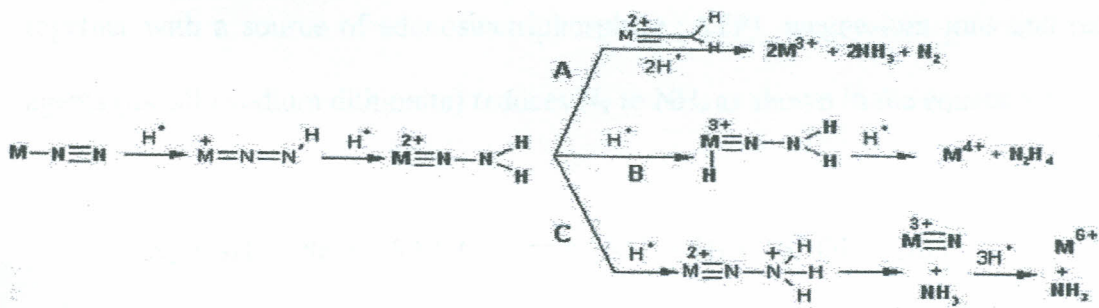


Figure 2: The pathway of protonation of dinitrogen complex to ammonia and hydrazine.

Despite a huge effort being made for over forty years to understand how dinitrogen is being reduced by various nitrogenases, no definitive conclusion has been made concerning the site and mechanism of dinitrogen reduction in nitrogenase (Seefeldt *et al.*, 2004).

2.2 Nitrogenase

All living things require nitrogen. Certain bacteria are able to produce ammonia at room temperature and atmospheric pressure from atmospheric nitrogen. They work their magic using a catalyst called nitrogenase, an enzyme that reduces the activation energy barrier of the reaction (Robson *et al.*, 1986). Nitrogenase obtains energy through the breakdown of a compound called adenosine triphosphate (ATP), a molecule that cells commonly use to store energy. Nitrogenase enzyme consists of two proteins: (1) the molybdenum-iron protein, which holds the FeMo cofactor (FeMoco) and (2) the iron protein, which hydrolyses MgATP and uses the energy obtained to provide the molybdenum-iron protein with electrons (Mackay *et al.*, 2002). It catalyzes the reduction of molecular nitrogen to ammonia at ambient conditions of temperature and pressure (Jolly, 1991). The heterocomplex undergoes cycles of association and dissociation to transfer one electron that supplies enough energy to break one of dinitrogen chemical bonds. These proteins together with a source of adenosinetriphosphate (ATP), magnesium ions and reducing agents (usually sodium dithionite) reduces N_2 to NH_3 as shown in the equation 1.



The exact mechanism of catalysis is unknown due to the difficulty in obtaining crystals of nitrogen bound to nitrogenase (Robson *et al.*, 1986)

Alternative nitrogenases other than the molybdenum (Mo) based nitrogenase are now known, one that contains vanadium (V), (and which function when Mo is absent and V is available) and another that contains only iron (which functions when both Mo and V are absent) (Peters *et al.*, 2006; Smith *et al.*, 2006). It is worth noting that the FeMo-nitrogenase appears to be the most efficient ($\approx 75\%$ in electrons), yielding approximately only one dihydrogen per dinitrogen reduced. The FeMo nitrogenase, which can be purified and crystallized, has been studied for many years and its X-ray studies revealed the now-well known $\text{Fe}_7\text{S}_9\text{Mo}$ core, where dinitrogen is likely to be reduced (Rees *et al.*, 2000). All the three types consist of two components: the catalytic subunit or nitrogenase (MoFe-protein) and nitrogenase iron protein (Fe-protein), or dinitrogenase reductase. All nitrogenases have an iron- and sulphur- containing cofactor that includes a heterometal complex in the active site (e.g. FeMoco) (Seefeldt *et al.*, 2004). Most nitrogenase are irreversibly inhibited by dioxygen except a recently discovered nitrogenase of *Streptomyces thermoautotrophilus*, which is unaffected by the presence of oxygen (Modak, 2002). The discovery of vanadium nitrogenase and even Fe only nitrogenase show there is a long way to go before the exact mode of action of N_2 and nitrogenase is understood (Mackay *et al.*, 2002). The nitrogenase redox cycle is shown in figure 3 below;

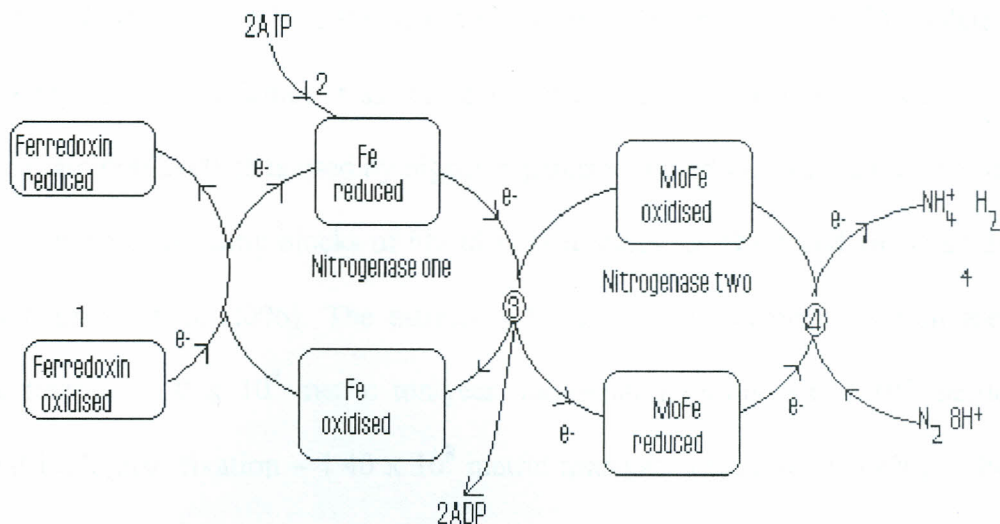


Figure 3: Nitrogenase redox cycle.

2.3 Nitrogen fixation

Nitrogen fixation generally refers to the natural process, either biological or abiotic, by which nitrogen gas (N₂) in the atmosphere is converted to ammonia (Postgate, 1998). Nitrogen fixation also occurs as a result of non-biological processes which include lightning, industrially through Haber-Bosch process and combustion (Eady, 1991). This reaction is necessary for life as we know it because nitrogen fixation is the major route through which nitrogen from the atmosphere becomes available for organisms. Nitrogen reduction is catalyzed in nature by the “iron-molybdenum cofactor” of iron-molybdenum nitrogenase which has six iron atoms that have a usual trigonal pyramidal geometry (Seefeldt *et al.*, 2004).

In the late 1880's, Hellriegel and Wilfarth (Chatt *et al.*, 1978) proved that biological nitrogen fixation took place and in the 1930's Bortels studies revealed the Mo and V dependence of dinitrogen fixation by *Azobactor vinelindii*- a nitrogen reducing bacteria

(Eady *et al.*, 1994). In 1960, Carnahan and others (Greenwood, 1997) isolated nitrogenase enzyme and confirmed it as the factor enabling conversion of atmospheric dinitrogen into ammonia which is used by higher organisms. Fixed nitrogen is required to biosynthesize the basic building blocks of life like nucleotides for DNA and amino acids for proteins (Curley *et al.*, 2006). The estimates for the above nitrogen fixation are: atmospheric fixation- 1.0×10^7 metric ton/year, industrial fixation- 3.6×10^7 metric tons/year and biological fixation – 1.40×10^8 metric tons/year (Silberberg, 1996). The biological fixation process is catalyzed by the enzyme nitrogenase which consists of two kinds of protein components: a reductase, which provides electrons with high reducing power, and a nitrogenase, which uses these electrons to reduce N_2 to NH_4^+ (Richard, 1979). Each component is an Iron-sulphur protein (Prentice, 1996). The biological fixation process which was discovered by a Dutch microbiologist, Martinus Beijerinck (Curley *et al.*, 2006) dwarfs the other two processes and it accounts for greater than 60% of the total annual nitrogen fixation (Eady, 1991). Hence, the biological nitrogen fixation (BNF) is a major contributor to the world's supply of agricultural nitrogen and it holds the key to the long - term solution to global food supply (Kirk-Othmer, 1981). The complexity of the biological system reduces the likelihood of arriving at ambient conditions necessary to replace the Haber - Bosch process in industrial ammonia synthesis (Silberberg, 1996). The BNF is an attractive alternative process to Haber-Bosch process but the wasteful hydrogen gas (H_2) need to be eliminated (Kirk-Othmer, 1981). Conversion of N_2 to NH_3 is a complicated, multi-step process as shown in the flow cycle below;

Nitrogen (N_2) in the atmosphere \rightarrow nitrogen fixing bacteria \rightarrow Ammonia (NH_3) $\xrightarrow{+H}$ ammonium (NH_4^+) \rightarrow nitrifying bacteria \rightarrow nitrate (NO_3^-) \rightarrow denitrifying bacteria \rightarrow nitrogen (N_2) to atmosphere (Neil, 1992).

The natural processes of nitrogen fixation have not met the increasing demands of growing human population. Man made methods of fixation have been introduced of which the Haber- Bosch process is the best. The said complication in nitrogen fixation to ammonia is as a result of dinitrogen being relatively inert due to a very strong triple bond ($N\equiv N$). The bond is very difficult to cleave or oxidize as it has dissociation energy of 941kJ/Mol and an ionization potential of 15.6eV (Kirk-Othmer, 1981; Portefields, 1993). Other multiple-bond enthalpies in kJ/Mol are shown in table 1 below (Brown, 1985).

Table 1: Multiple-bond enthalpies in kJ/Mol

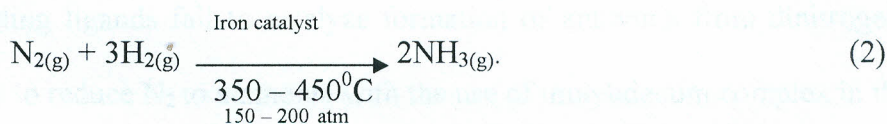
C=C	N=N	O=O	C=O	C \equiv C	N \equiv N
611	410	497	749	835	941
			C \equiv O	C \equiv N	P \equiv P
			1071	890	488

Nitrogen occurs in all oxidation states ranging from -3 through +5. Most nitrogen compounds are relatively unstable and tending to decompose to N_2 (Smooth *et al.*, 1993). Though nitrogen is a poor ligand, it is able to indirectly displace a wide range of neutral and π -donor ligands (White, 1999).

2.4 Ammonia

Ammonia (NH₃) is a compound of nitrogen and hydrogen. The gas contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to foodstuffs and fertilizers. Its use is both caustic and hazardous (Smith, 2001). In the year 2006 the ammonia worldwide production was estimated at 146.5 million tons up from 109 million metric tones in year 2004 (Max, 2006). The People's Republic of China produced 28.4% of the worldwide ammonia. Other producers are; India-8.6%, Russia-8.4%, and United States with 8.2% (Max, 2006). More than 80% of the ammonia produced is used for fertilizer in agriculture either as a salt or as a solution. Today, the typical modern ammonia-producing plant first converts natural gas or liquefied petroleum or petroleum naphtha into gaseous hydrogen, a gas that is then catalytically reacted with nitrogen to form anhydrous liquid ammonia (Greenwood, 1997). More than 1% of all man-made power is consumed in the production of ammonia (Max, 2006).

In certain organisms, ammonia is produced from atmospheric N₂ by enzymes called nitrogenase in a process called nitrogen fixation (Alton *et al.*, 1998). More ammonia is formed through the Haber - Bosch process following equation 2 below.



Intense effort is directed towards understanding the mechanism of BNF and motivated by the usual structure of the active site of nitrogenase enzyme, which consists of a Fe₇MoS₉ ensemble (Modak, 2002), figure 4 below;

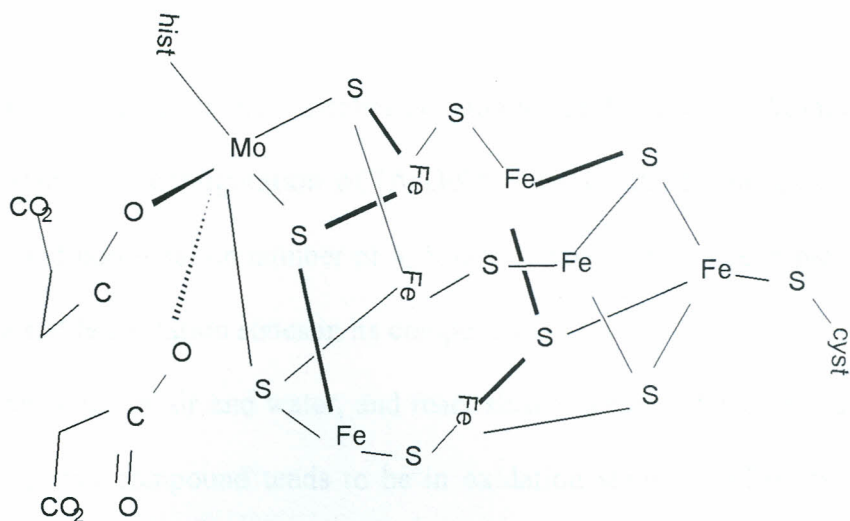


Figure 4: The structure of MoFe-cofactor:

In 1965, the “Nitrogenpentaammineruthenium(II) Complex”, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, was reported and this proved that molecular nitrogen was coordinated to the ruthenium (II) ion (Allen and Senoff, 1965). This made the principle of coordination N_2 , an inert gas, to metals at ambient conditions acceptable. The field that this discovery opened continues to provide surprises in the quest to understand BNF and to find new catalysts that convert N_2 to ammonia or nitrogen-containing organics under mild conditions (Senoff, 1990). The structure of Mo-Fe nitrogenase was solved in 1992 and work continues today to determine the exact site of coordination of N_2 gas (Greenwood, 1997). Some dinitrogen complexes produces ammonia, however, complexes that contain sterically less demanding ligands fail to catalyze formation of ammonia from dinitrogen. A catalytic process to reduce N_2 to ammonia with the use of molybdenum complex in the presence of proton source was established in 2005 (Schrock, 2005).

2.5 Iron

Iron is a metallic chemical element symbol Fe, atomic number 26, and Atomic Weight of 55.847, and electronic configuration of $[\text{Ar}]3d^64s^2$. Its Oxidation States usually range from -2 to +6 and coordination number of 4, 5, or 6 (Knox, 1985). Iron typically displays two relatively stable oxidation states in its compounds (+2 and +3) and it is susceptible to oxidation in presence of air and water, and react slowly forming ferric oxide (rust). The most occurring iron compound tends to be in oxidation states +3 (Greenwood, 1997). Iron is required for the synthesis of chlorophyll necessary in plants for conversion of sunlight energy into chemical energy. Iron is also essential for the synthesizing a myriad of iron-containing enzymes, such as cytochromes. The important enzyme, nitrogenase, which is required for conversion of N_2 to ammonia, contains about 30 atoms of iron for each molecule of enzyme (Emery, 1991).

Iron is the sixth most abundant element in the universe and the fourth most abundant element in the earth's crust, making up 5% of the Earth's crust and is second in abundance to aluminium among the metals and fourth in abundance behind oxygen, silicon and aluminium among the elements (John and Edwards, 1980). Naturally - occurring iron consists of four stable isotopes: iron-56 (91.66%), iron-54 (5.82%), iron-57 (2.19%) and iron-58 (0.33%). Pure iron is a white lustrous metal, m.p. 1536°C , which is extremely reactive with all halogens, sulphur, boron, carbon and silicon (Greenwood, 1997). As seen above iron in pure states is allotropic, existing as a solid in two different crystal forms. These forms and their occurrence are: from subzero to 700°C , iron is identified as alpha (α) iron which is magnetic; from 700°C to 928°C , iron changes from

alpha to beta (β) and loses its magnetism; from 928°C to 1530°C, iron changes to gamma (γ) iron; and from 1530°C upwards, iron is identified as delta (δ) iron (Emery, 1991). Alpha iron, also known as ferrite, is the most stable form of iron at normal temperature. It is fairly soft metal that can dissolve only a small concentration of carbon (John, 2007).

The anhydrous FeCl_2 or FeCl_3 , ferrocene and $\text{Fe}(\text{CO})_5$ are the most common starting materials in the synthesis of iron compounds (Knox, 1985). In living systems, iron is an essential constituent of numerous bio molecules. The body of a health human adult contains about 4g of iron, 65% of which is present in the oxygen- carrying protein hemoglobin, 1% in the various enzymes that control intracellular oxidation and most of the rest stored in the body (Smith *et al.*, 2006) Iron has the following uses; as the primary constituent of ferrous metals/ alloys and steel, in electronics, manufacturing, magnets, heavy construction and building, automotive, fabricated metal products, industrial machinery, transport equipments, instruments, toys and sport goods, carbonyl iron $\{\text{Fe}(\text{CO})_5\}$ powder used for magnetic core for high frequency equipments and for medical applications, ferrocene or dicyclopentadienyl iron $(\text{C}_5\text{H}_5)_2\text{Fe}$, is used as combustion control additive in fuels, as a heat stabilizer in lubricants and plastics and for radiation resistance, iron carbide is used in high wear applications such as mine processing equipments (Jeremy *et al.*, 2003). Industrially, iron is produced starting from iron ores, principally hematite (Fe_2O_3) and magnetite (Fe_3O_4) by a carbothermic reaction in a blast furnace at temperatures of about 2000°C (McMurry, 1995). Iron and iron alloys (Steels) are by far the most common metals and the most common ferromagnetic materials in everyday use. It is the most widely used of all the metals, accounting for 95%

of worldwide metal production (Theodore *et al.*, 2000). The world iron production exceeds 700 million tons per year. In 2005, approximately 1,544 million metric tons of iron was produced worldwide. According to the British Geological Survey, China was the top producer of iron with at least one quarter world share, followed by Brazil, Australia and India (Wagner, 2005).

A study in 2006 of iron-dinitrogen complexes showed that the N-N bond is significantly weakened upon complexation with iron atoms with low coordination number thus it is suspected that Fe in a low-coordination environment is a key factor to the fixation of nitrogen by nitrogenase enzyme (Smith *et al.*, 2006)

2.6 Iron and its compounds

Understanding the interaction of N_2 with iron is relevant to the iron catalyst used in the Haber process and to the possible roles of the FeMoco active site of nitrogenase. Synthetic complexes in which two reactive iron atoms are bridged by a sulfide; the Fe-S-Fe unit has been created which is reminiscent of the di-iron units of the FeMoco. Two iron atoms cooperatively break the N-N bond of certain hydrazines (Jeremy *et al.*, 2003). The first low-coordinate iron and cobalt hydrides have been made which contains protons and electrons for reduction of multiple bond completely cleaving the N=N bond of diazenes and also capable of binding N_2 (Patrick, 2005). Reaction of laser-ablated iron atoms with dinitrogen in excess neon produces the iron dinitrogen complexes $Fe(N(2))$, $Fe(NN)(x)$ ($x= 1-5$), and $Fe(NN)(3)(-)$ through capture of the ablated electrons (Lu *et al.*, 2010).

Irradiation of $\text{FeH}_2(\text{dmpe})_2$ [$\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$] in a solution of methane in liquefied xenon at -107°C affords a mixture of *cis*- $\text{FeH}(\text{dmpe})_2\text{Me}$ and *trans*- $\text{FeH}(\text{dmpe})_2\text{Me}$. The *cis* and *trans* isomers equilibrate photochemically at -100°C but decompose thermally with elimination of methane at a temperature above 0°C following solvent exchange with toluene (Leslie *et al.*, 1991). Ethyl diazoacetate and diphenyldiazomethane are found to react with the $\text{FeCl}_2(\text{PMe}_2\text{Ph})_2$ to form $\text{FeCl}_2[\text{N}(\text{PMe}_2\text{Ph})\text{NC}(\text{H})\text{CO}_2\text{Et}]_2$ and $\text{FeCl}_2[\text{N}(\text{PMe}_2\text{Ph})\text{NCPH}_2]$ (Janis and Robert, 2001). The anhydrous FeCl_2 crystals used in the project was synthesized by a method described in section 4.2. The equation of reaction is as in equation 3;



Other methods for preparing anhydrous iron (II) chloride includes; reducing iron (III) chloride with hydrogen, dehydrating one of the hydrates of iron (II) chloride and the reaction of FeCl_3 with chlorobenzene as in equation 3 below (Kovacic *et al.*, 1960);



Hydrated iron (II) chlorides may also be prepared by dissolving pure iron in hydrochloric acid solution followed by crystallizing (Gayer *et al.*, 1958). The apparatus in figure 5 can be used.

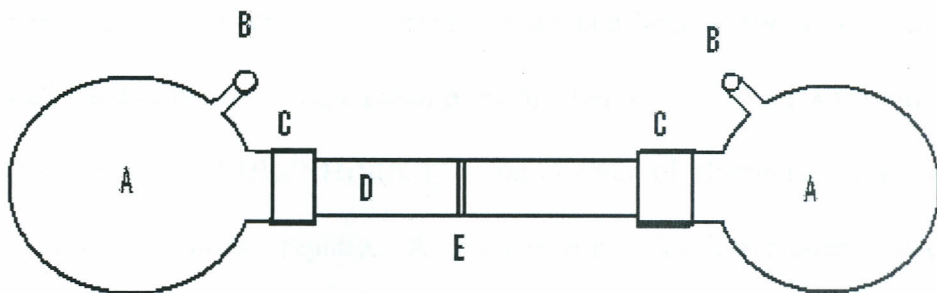


Figure 5: Apparatus for the preparation of iron (II) chloride 2-hydrate.

The reaction takes place in one of the flask A. The excess iron is filtered by turning the apparatus upside down to filter the mixture through frit labeled E. The excess metal is separated through part C and the apparatus assembled again. Crystallization of the filtrate then takes place in the other flask A. The crystals formed are filtered by inverting the apparatus to allow the 'mother liquor' to flow into the first flask A. Crystals are dried by use of nitrogen gas pressure through region B while the other outlet B is connected to a suction pipe. Hydrated forms of ferrous chloride can also be generated by treatment of wastes from steel production with hydrochloric acid (Wildermuth *et al.*, 2005). Ferrous chloride is conveniently prepared using a methanol solution of concentrated hydrochloric acid. The reaction gives the methanol solvate, which on heating in a vacuum at 160°C gives anhydrous FeCl₂ (Winter, 1973).

2.7 Dinitrogen complexes

A dinitrogen complex is a coordination compound that contains molecular dinitrogen, N₂, as a ligand (Fryzuk and Johnson, 2000). The atomic and diatomic forms of nitrogen ligand are distinguished as nitrogen and dinitrogen respectively. Metal complexes of N₂ have been studied since 1965 when the first complex, [Ru(NH₃)₅(N₂)]²⁺ was reported by

Allen and Senoff at the University of Toronto (Allen and Senoff, 1965). The dinitrogen ligand can be bound either to a single metal or bridge two (or more) metals. Immediately following the discovery of $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, the number of elements known to form dinitrogen complexes grew rapidly. A bis(pentamethylcyclopentadienyl)zirconium complex provided the first well-characterized example of a complex with both bridging and terminally bound dinitrogen ligands. The bis(dinitrogen) complexes of molybdenum and tungsten proved invaluable precursors for the synthesis of derivatives with N-H or N-C bonds. Osmium provided the first example of a metal porphyrin dinitrogen complex while the ruthenium pentaammine dinitrogen system continues to be studied and now have very different routes available for its synthesis (Chatt *et al.*, 1978). Interest in such complexes arises because N_2 makes up 78% of gases in the atmosphere. It is widely accepted that biological nitrogen fixation (BNF) occurs via the binding of N_2 to a metal centre in the enzyme nitrogenase, followed by a series of steps that involve electron transfer and protonation (Kirk- Othmer, 1981). The hydrogenation of N_2 is exothermic, and hence the industrial hydrogenation of nitrogen through the Haber – Borsch process employs high pressure and high temperature (Fryzuk *et al.*, 2000). Dinitrogen complexes are well known in inorganic chemistry but are quite different from the proposed biological structures. In presence of strong acid, the N_2 in some dinitrogen complexes undergoes a proton- induced reduction to ammonium ion. This is shown in the equation 4 below (Shriver, 1998);



The first example of homolytic cleavage of dinitrogen under mild conditions was published in 1995. Two equivalents of a molybdenum complex reacted with one equivalent of dinitrogen, creating a triple bonded Mo≡N complex. Since then, this triple bonded complex has been used to make nitriles (Curley and Cummins, 2006).

2.8 The N₂ Bonding modes

The bonding mode of N₂, CO and acetylene are related as all the three species have triple bonds (Leigh *et al.*, 2002). A variety of N₂ bonding modes have been characterized,

i) End – on.

N₂ usually bonds to metals as an “end – on” ligand, as illustrated by Allen and Senoff’s complex, Ru(NH₃)₅(N₂)²⁺ and other complexes such as [Co(N₂)(PPh₃)₃] and [CoHN₂(PPh₃)] (Yamamoto *et al.*, 1967), IrCl(N₂)(PPh₃)₂ (Collman *et al.*, 2000). Few complexes contain two N₂ ligands, and none with three do far. The dinitrogen ligand in W(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂ can be reduced to produce ammonia (Leigh *et al.*, 2002).

ii) Bridging, end – on.

N₂ also serves as a bridging ligand, as illustrated by {[Ru(NH₃)₅]₂(μ-N₂)}⁴⁺ (Senoff, 1990). A study in 2006 of iron- dinitrogen complexes showed that the N-N bond is significantly weakened upon complexation with iron atoms with a low coordination number while increasing the coordination number of iron by modifying the chelating ligands and adding an additional ligands per iron atom showed an increase in the strength of the N-N bond in the resulting complex (Oliver, 2005). It is suspected that

Fe in a low-coordination environment is a key factor to the fixation of nitrogen by the nitrogenase enzyme, since its Fe-Mo cofactor also features Fe with low coordination numbers (Smith *et al.*, 2006).

iii) Side – on , bringing

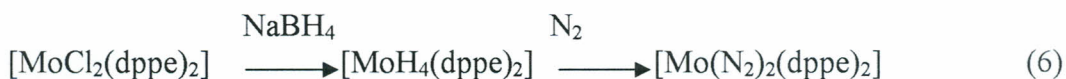
Some bimetallic complexes are known where the N-N vector is perpendicular to the metal-metal vector. One example is $[\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta_2, \eta_2\text{-N}_2)$ (Bernskoetlter *et al.*, 2005).

2.9 The synthesis of dinitrogen complexes

Dinitrogen complexes are substances in which dinitrogen is directly attached as a ligand to a metal. This section outlines the key methods from wide variety of both direct and indirect synthesis routes to dinitrogen complexes. It is possible to form the same complex using different routes. Three broad categories are explained in the following subsections;

2.9.1 Direct reaction with N₂

These routes can either involve the reaction of dinitrogen with a preformed and isolated complex with replacement with neutral or anionic ligands by dinitrogen or a single reaction of a suitable complex with a reductant under dinitrogen (Leslie *et al.*, 1991). The examples are given in equation 5 and equation 6 below.

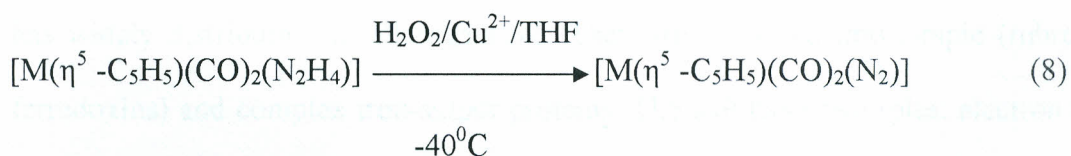




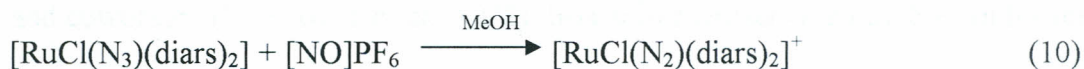
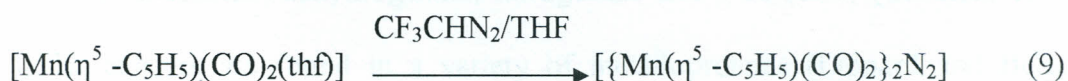
It is always important to select the reducing agent both in terms of suitable reducing potential and convenient in work-up procedures. Generally, reducing agents such as Mg, Zn, Na, nBuLi and Grignard turnings are especially convenient (Chatt and Richards, 1982; Porterfield, 1993).

2.9.2 Indirect Methods

These are a variety of routes to dinitrogen complexes involving generation of the dinitrogen ligand by reaction at a ligating N or N₂ moiety, or oxidation of a hydrazine. Indirect methods of synthesis are often specific for one metal where few have any generality for the synthesis of dinitrogen complexes (Chatt and Richards, 1982). Examples are given in equation 7, 8 and equation 9;

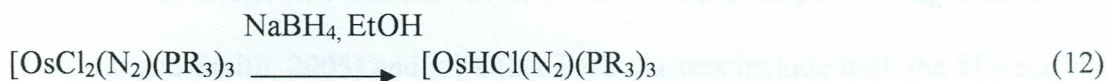


Where M = Mn, Re.



2.9.3 Metathesis

Simple metathesis substitution reaction of the auxiliary ligands in dinitrogen complexes with sufficient stable metal-nitrogen bond allows the preparation of new dinitrogen complexes. The reactions tend to be specific and the high lability of many N₂ complexes particularly those of titanium and the platinum group metals, almost entirely precludes any simple ligand exchange procedure. This is illustrated by equations 10 and 11 (Chatt and Richards, 1982);



2.10 Iron- sulphur proteins, ISP

Iron-sulfur proteins are proteins characterized by the presence of iron-sulfur clusters containing sulphide-linked di-, tri-, and tetrairon centers in variable oxidation states. ISP has widely distribution in all organisms. They are classified into simple (rubredoxins, ferredoxins) and complex iron-sulphur proteins. The ISP have two roles; electron transfer (such as rubredoxins, ferredoxins) and enzymes with both redox and non-redox functions (such as succinate dehydrogenase, nitrogenase and a conitase) (Critcton, 1991). Iron-sulfur clusters are found in a variety of metalloproteins (Lippard and Berg, 1994). Synthetic analogues of the naturally occurring Fe-S clusters were first reported by Holm and coworkers (Herskovitz *et al.*, 1972). Iron-sulfur clusters are best known for their role in the oxidation-reduction reactions and many other functions including catalysis and

generation of radicals. In almost all Fe-S proteins, the Fe centers are tetrahedral and the terminal ligands are thiolato sulfur centers from cysteinyl residues. The core structures of the simple iron-sulphur cluster have been characterized crystallographically (Ibers *et al*, 1980). Three distinct kinds of Fe-S clusters with these features are most common; i) 2Fe-2S clusters- This is constituted by two iron ions bridged by two sulfide ions $[\text{Fe}_2\text{S}_2]$ and coordinated by four cysteinyl ligands, ii) 4Fe-4S clusters- This features a four iron ions and four sulfide ions $[\text{Fe}_4\text{S}_4]$ placed at the vertices of a cubane-type structure. The Fe centers are typically further coordinated by cysteinyl ligands, iii) 3Fe-4S clusters, $[\text{Fe}_3\text{S}_4]$ - These which feature one iron less than the more common $[\text{Fe}_4\text{S}_4]$ cores. Three sulphide ions bridge two iron ions each, while the fourth sulphide bridges three iron ions (Johnson and Smith, 2005) and iv) Other Fe-S clusters include both the 8Fe and the 7Fe clusters in nitrogenase. The biosynthesis of Fe-S cluster has been well studied (Johnston and Smith, 2005). The ISP are shown in the figure 6 as i) one iron one-sulphide centre in the rubredoxins ii) a two-iron two- sulphide centres (2Fe-2S) iii) a three-iron four sulphide cluster (3Fe-4S) and iv) four-iron four-sulphide centre (4Fe-4S) in the ferredoxins (Crichton, 1991) in figure 6 below;

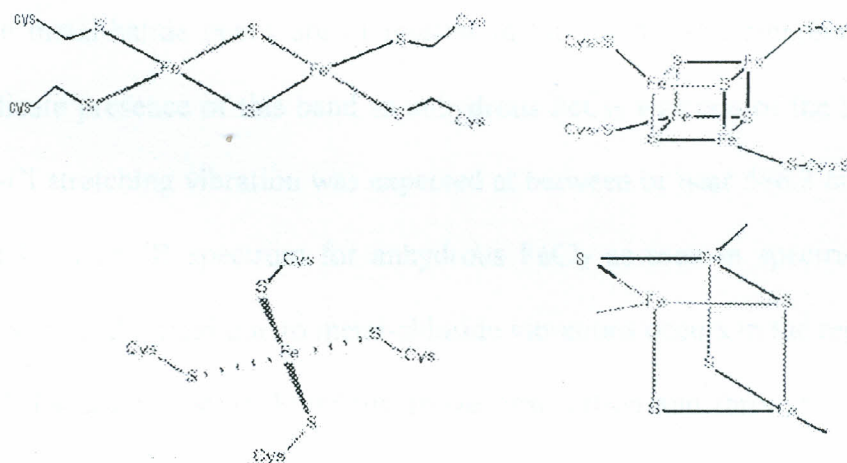


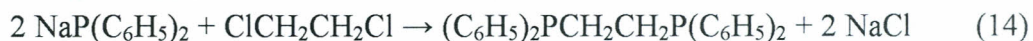
Figure 6: The iron-sulphur cluster structures.

2.11 Preparation of 1,2-bis(diphenylphosphino)ethane, (dppe)

1,2-Bis(diphenylphosphino)ethane (dppe), molecular formula $C_{26}H_{24}P_2$, molar mass 398.42 g/mol and m.p of 140-142°C is a commonly used bidentate ligand in coordination chemistry. dppe is almost invariably chelated, although there are examples of unidentate (e.g., $W(CO)_5(dppe)$) and of bridging behavior (Cotton *et al.*, 1980). The preparation of dppe was conducted via the alkylation of $NaPPh_2$ which was typically prepared from triphenylphosphine ($P(C_6H_5)_3$) following literature method (Hewertson and Watson, 1962). The equations of reaction were as seen in 12 and 13 below.



$NaP(C_6H_5)_2$, which is readily oxidized, is treated with 1,2-dichloroethane ($ClCH_2CH_2Cl$) to give dppe:



2.12 Metal Halides IR spectroscopy peaks.

The metal-halide peaks are of interest in this work. The complexes were expected to indicate presence of this band as anhydrous $FeCl_2$ was one of the starting material. The Fe-Cl stretching vibration was expected at between or near 586.3 cm^{-1} and 493.7 cm^{-1} as got from an IR spectrum for anhydrous $FeCl_2$ as seen in spectrum 3 of appendix II. Generally, the band due to metal-chloride vibrations occurs in the regions 610 cm^{-1} to 220 cm^{-1} (Socrates, 1994). From the above observation and through comparison with dppe

ligand IR spectrum in appendix I, the Fe-Cl stretch is expected at between 610 cm^{-1} and 493 cm^{-1} . Other metal halides vibration occurs in the following regions;

	F	Cl	Br	I
M-X str (cm^{-1})	945-550	610-220	430-200	360- 150
M-X def (cm^{-1})	490-250	200-100	130-50	100-30

The position of a metal halogen absorption band depends mostly on i) the mass of the metal atom and ii) the valence state of the metal atom. The frequency decreases with increase in mass of the metal atom and increase in mass of halogen.

2.13 Thionyl chloride (SOCl_2)

SOCl_2 is a reactive compound that can explosively release dangerous gases upon contact with water and other reagents. SOCl_2 reacts with water to release hydrogen chloride and sulphur dioxide (Pradyot, 2002).



Thionyl chloride is mainly used in the industrial production of organochlorine compounds, which are often intermediates in pharmaceuticals and agrichemicals

CHAPTER 3

EXPERIMENTAL TECHNIQUES.

3.1 Experimental techniques.

Several experimental techniques are discussed in this chapter; Cleaning of apparatus, IR cells preparation, Purification of organic solvents and reagents, Generation of dry oxygen- free nitrogen, Handling of air and moisture - sensitive compounds, analytical techniques and Physical measurements.

3.1.1 Cleaning of apparatus

3.1.1.1 Glassware

There are many different methods of cleaning laboratory glassware. This depends on the kind of compound on it and how stubborn a stain was. The glassware was divided into 'Glassware without grease or stubborn stains' and 'Glassware with grease and stubborn stains'.

i) Glassware without grease or stubborn stains

The glassware without grease or stubborn stains was soaked in a hot detergent solution to remove or loosen most contamination. Then cleaned with tap water and rinsed with distilled water and dried in an electric oven at 120°C. Halogenated solvents such as CH_2Cl_2 or CHCl_3 were sometimes used to dissolve the last traces of dirt. If the glassware were still dirty, more drastic methods were needed. This included soaking the piece in concentrated solution of sodium hydroxide or potassium hydroxide in an alcohol ("base bath"), followed by a dilute solution of hydrochloric acid ("acid bath") to neutralize the

excess base. Concentrated sodium hydroxide cleans glass by dissolving a tiny layer of silica, to give soluble silicates.

ii) Glassware with grease and stubborn stains

Gross contamination and large particles were removed mechanically by scrubbing with a brush or scouring pad. Then solvent known to dissolve the contamination were used to rinse the glassware and remove the last traces of dirt, then rinsed with distilled water and finally dried in an electric oven at 120°C. More aggressive methods involving aqua regia (for removing metals from frits), piranha solution and chromic acid (for removing organics), and hydrofluoric acid baths were generally used. The glassware were finally rinsed with distilled water and dried in the electric furnace at 120°C (McCormick, 2006).

iii) Sintered glass fitted in the fritz apparatus.

Gross contamination and large particles were removed mechanically, by scrubbing with a brush or scouring pad. Then chromic acid and or concentrated nitric acid were first put in the container for thirty minutes. Later normal washing as in i) and ii) were followed. Finally distilled water was added to the apparatus fitted onto a round bottom flask and then distilled water sucked by use of an electric pump to suck out and rinse the sintered glass. The sintered glass was then dried in oven at 130°C.

3.1.1.2 IR cells

The IR cells were rinsed with acetone before use. The stuck compounds were scrubbed off using a long office pin or spatula, and then rinsed in acetone to ensure there is no interference with the samples during the analysis.

3.2 Purification of organic solvents and reagents

3.2.1 Organic Solvents.

The solvents used were dried, freshly distilled following literature methods (Keese *et al.*, 1982, Armarego and Chai, 2003) and purged with dry – free nitrogen before use, a necessary requirement because the prepared complexes were thought to be sensitive to both oxygen and moisture.

i) Acetone

The solvent was shaken in fused calcium oxide and left standing for a day and then distilled under an inert atmosphere at 56°C into a receiving flask that was purged with nitrogen gas.

ii) Diglyme (Diethyleneglycoldimethylether)

Analytical grade diglyme (99%) was used, as bought without further purification. Used diglyme was refluxed over sodium metal in an atmosphere of dry- oxygen free nitrogen gas for 40 minutes, and then distilled in an inert atmosphere. This solvent was used to prepare sodium naphthalide, useful in removing oxygen from nitrogen gas.

iii) Ethanol

The solvent was shaken in fused calcium oxide and left standing for a day and then distilled under an inert atmosphere at 78°C into a receiving flask that was purged with nitrogen gas.

iv) Tetrahydrofuran (THF).

The solvent was refluxed for 40 minutes over sodium metal and then distilled in an inert atmosphere. The middle portion was used.

3.2.2 The dppe ligand

The ligand, 1,2-bis(diphenylphosphino)ethane (dppe) was bought from 'Aldrich Chemicals Company'. It was dried over phosphorous (V) oxide and used without any further purification. More dppe was prepared KU laboratory using the method of Hewert and Watson (Hewertson *et al.*, 1962). The prepared dppe had m.p of 144°C-145°C same to the acquired dppe.

3.3 Reagents

3.3.1 Generation of dry oxygen- free nitrogen

The dry oxygen-free nitrogen was obtained by further purification of high purity 'white spot nitrogen' gas that was obtained from BOC Kenya limited. Commercial available nitrogen is adequate for most purpose. However, for certain applications, it is necessary to further remove water and oxygen. The gas was dried by passing it through concentrated sulphuric acid and then passing it over phosphorus pentoxide suspended on pumice stones. The last traces of oxygen were removed by passing the dried gas over a solution of sodium naphthalide in diglyme as prepared in section 3.3.2 below. The high

purity nitrogen got here was used throughout the synthesis work. The apparatus used for purification of 'white spot nitrogen' gas are seen on figure 7 below.

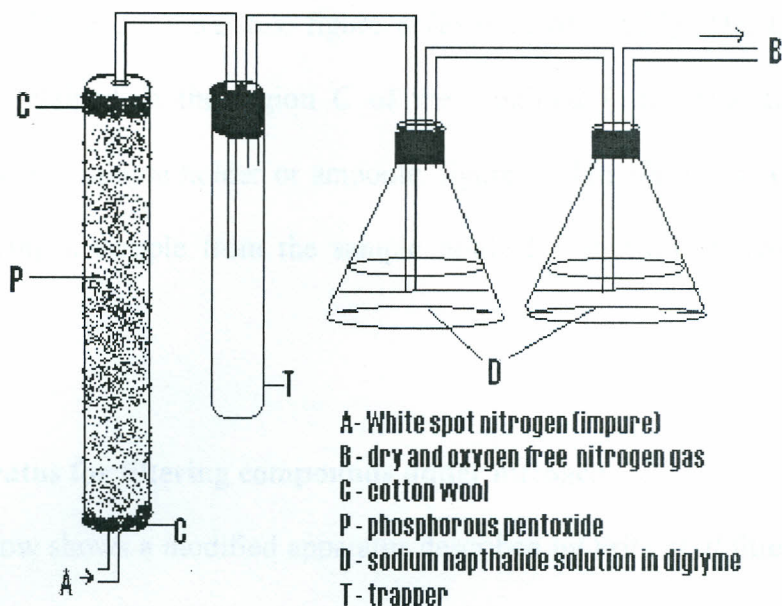


Figure 7: The apparatus for purification of 'white spot nitrogen' gas.

3.3.2 Preparation of sodium Naphthalide solution

Procedure

Naphthalene crystals were dissolved in analytical grade diglyme (99%) to form a clear solution. The solution formed was connected to the source of N_2 gas. Then, very small pieces of sodium metal were added into the above solution. The container was sealed and mixture shaken continuously under nitrogen gas at room temperature. With time, a green solution formed as more and more sodium metal dissolved forming the sodium naphthalide solution. The solution was used in scrubbing oxygen gas from N_2 gas. Fresh sodium naphthalide solution was prepared as soon the green disappeared and a white precipitate of sodium hydroxide is formed.

3.3.3 Handling of air and moisture sensitive complexes

The compounds synthesized in this study were handled in an atmosphere of dry oxygen-free nitrogen. Filtration of air sensitive compounds was done in a nitrogen atmosphere using a modified Fritz apparatus, figure 8 (Fritz *et al.*, 1959). The filtered and dried sample was retained in the region C of the modified Fritz apparatus before it was transferred to the sample holder or ampoule, figure 9, through outlet A. Care was taken when removing a sample from the sample bottle for analysis to avoid hydrolysis or oxidation.

3.3.4 Apparatus for filtering compounds under nitrogen.

Figure 9 below shows a modified apparatus described by Fritz *et al* fitted on a three way flask (Fritz *et al.*, 1959). Reference to filtering apparatus in this thesis will refer to the apparatus in figure 8. The apparatus has four parts; C, a Schlenk tube for holding the dried sample, part A which is the sample outlet to the sample holder or the ampoules, middle part B with a fritted glass disc for filtration and a two way round bottomed flask for holding any filtrate. The samples were filtered free of 'mother liquor' and dried by applying nitrogen pressure or by use of a suction pump connected at point F. The dry samples were then scrubbed off and transferred to sample bottles or ampoules through point A and purged with nitrogen gas then closed or sealed using a blow torch.

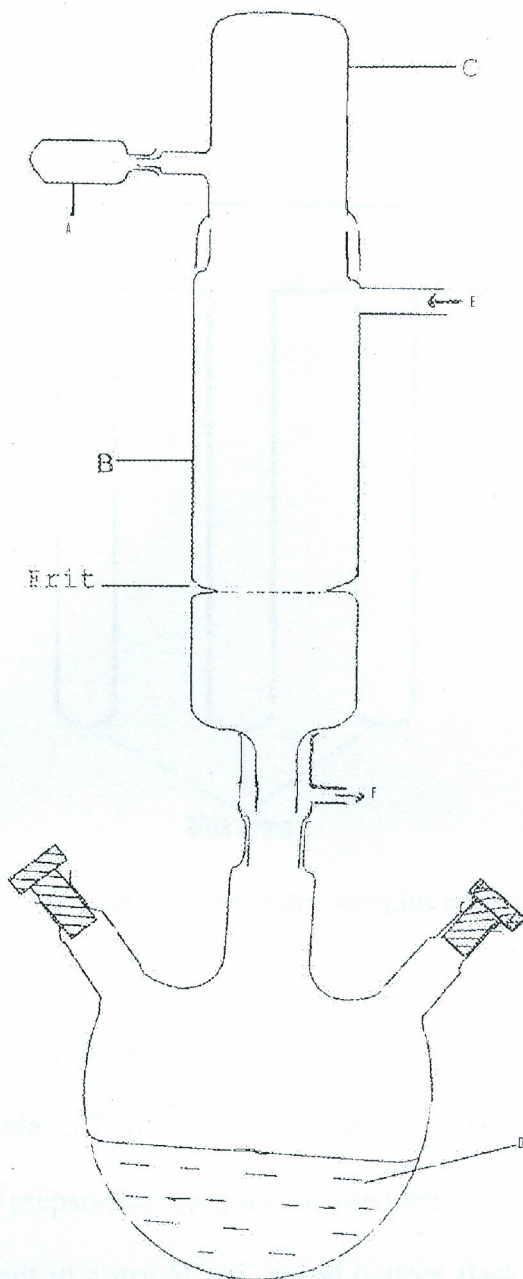


Figure 8: Apparatus for filtering of the synthesized complexes.

3.3.5 Storage and handling of the samples.

Dry samples were transferred from the filtration apparatus to either sample bottles or into ampoules as in figure 9. Drying of solids was brought about by storing them over a

drying agent such as phosphorus pentoxide vacuum or by storing the solid in a glove box that has a dry nitrogen atmosphere.

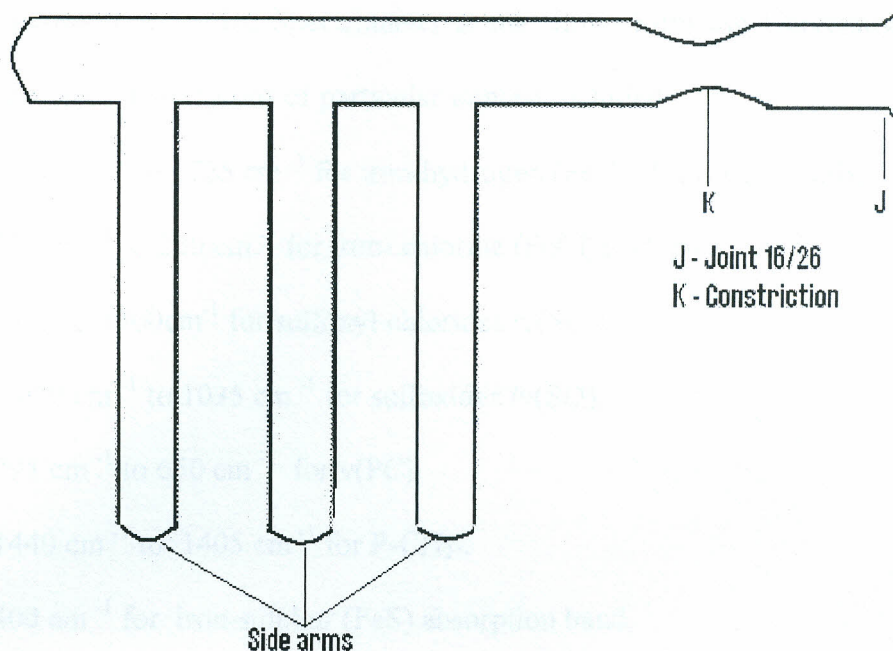


Figure 9: The apparatus for storing dry samples under nitrogen

3.3.6 Preparation of thionyl-acetone solution.

Thionyl chloride (SOCl_2) is very volatile and fumes in air. A safer way of weighing and using it in the preparative work was devised and described here. 10mL of freshly distilled acetone was put in a dry 50 mL round bottom flask. Then 1 mL ($\sim 1.5170\text{g}$) of thionyl chloride (SOCl_2) was added using a micro burette, under a nitrogen environment, drop-by-drop while swaying the round bottom flask in a fume hood. The solution formed was used in section 4.4.

3.4 Physical measurements

3.4.1 Infrared (IR) spectroscopy

The FTIR spectra for all the samples were recorded in the range of 4000 cm^{-1} to 400 cm^{-1} on an FTIR-8400 Shimadzu Spectrometer at the 'Jomo Kenyatta University of Science and Technology'. The regions of particular interest included;

- i) 1900 cm^{-1} to 1725 cm^{-1} for iron-hydrogen (FeH) absorption bands,
- ii) 600 cm^{-1} to 200 cm^{-1} for iron- chlorine (FeCl) absorption band,
- iii) 1375 to 1300 cm^{-1} for sulfonyl chlorides $\nu(\text{SCl})$,
- iv) 1070 cm^{-1} to 1035 cm^{-1} for sulfoxides $\nu(\text{SO})$,
- v) 795 cm^{-1} to 650 cm^{-1} for $\nu(\text{PC})$,
- vi) 1440 cm^{-1} to 1405 cm^{-1} for P-CH₂-,
- vii) 400 cm^{-1} for iron-sulphur (FeS) absorption band,
- viii) 1130 cm^{-1} to 1090 cm^{-1} for P-Ph (Socrates, 1991).
- ix) 1600 cm^{-1} to 1475 cm^{-1} for aromatic C=C stretching
- x) 3050 to 3010 cm^{-1} for aromatic =C-H stretch.

3.4.2 Solid Samples.

The solid samples were prepared by finely grinding 1mg of the sample with a specially purified salt (usually 25mg to 35 mg of KBr). The powder was then mechanically pressed to form a translucent pellet through which the beam of light from the spectrometer the spectrometer can pass (Laurence and Christopher, 2003). The procedure was repeated for all samples.

3.4.3 Determination of the Melting Points.

The melting points (m.p.) of the samples were determined on an Electronic melting point apparatus, Sanyo (UK) in triplicate and the average taken. The samples were heated in a glass capillary tube. These were inserted into the heating block and the preliminary m.p. was recorded in rapid heating. The actual m.p. was determined by a slower rate of heating. This was to ensure the sample and the block was at the thermal equilibrium. The sample average melting points are listed in table 2 below;

Table 2: Melting Points of the Complexes.

Complex formula	Melting point (°C)
$\text{FeH}_2(\text{dppe})_2$	153
$\text{FeH}(\text{SOCl})(\text{dppe})_2$	233
$(\text{dppe})_2\text{Fe-SO-FeH}(\text{dppe})_2$	269

3.4.4 Analytical Techniques

3.4.4.1 Determination of Chloride and phosphates.

The chloride and phosphates content were estimated following literature methods (Arthur, 1980). The process started by fusing the samples as explained in the procedure below.

(i) Sodium Peroxide Fusion of Complexes.

A sample of a known mass was fused using sodium peroxide, (Na_2O_2) in a nickel crucible with about 10 mL combustion spaces. A porcelain lid was used to cover the nickel crucible. The crucible was placed on a tripod stand and held in place using a clamp stand

and heated in a moderately controlled oxygen-butane flame until a chilled melt was formed and cooled in ice cold water. The chilled melt was then dissolved in a known volume of distilled water in a beaker, filtered into a 250cm³ volumetric flask and diluted with distilled water to the mark.

(ii) Gravimetric Determination of Chloride

The chlorine was determined gravimetrically by depositing and weighing it as silver chloride following literature methods (Basset *et al.*, 1978; Arthur, 1980).

Procedure

100 mL of the solution obtained from section 3.4.4.1(i) was transferred into 250 ml volumetric flask. Then 2g of zinc powder were added a little at a time and shaken. This was to reduce any chlorate, ClO_3^- , to chloride ions. The solution was filtered into a 250 ml volumetric flask and the solution made to the mark. 100 ml of the solution was transferred into 250 ml beaker and then 30 ml of 0.1M silver nitrate added drop by drop while stirring until no more precipitate formed (if any). The beaker was wrapped with an aluminium foil and covered with a watch glass. This was to prevent photodecomposition of silver chloride precipitate. The mixture was gently warmed on a hot plate for 30 minutes after which a few drops of 0.1M silver chloride were added to test if there were chloride ions remaining in the solution. When no turbidity was seen the beaker was kept in a dark cupboard to cool and then filtered into a weighed sintered glass crucible. The residue got was washed several times with very dilute nitric acid until the filtrate gave no turbidity with 0.1M hydrochloric acid. The residue was dried in an electric oven at 140°C and weighed. This process of heating, cooling and weighing was repeated until a constant

mass was attained. The chloride determination was done in duplicates from the amount of precipitate obtained to obtain the percentage composition of chloride in the sample.

(iii) The Spectrophotometric Determination of Phosphates

The procedure was adopted from the Vogels (Arthur, 1980). 25 mL of a neutral ash solution from section 3.4.4.1 (i) above was transferred a 50mL flask. Then 5.0mL molybdenum solution and 2.0mL hydrazine sulphate solution were added into the 50mL volumetric flask. The solution was diluted to the mark with dilute water and mixed well. The flask was immersed in boiling water for 10 minutes and then removed and cooled in ice cold water. The absorbance at 830nm was measured against a reagent blank. The phosphate content of the sample was deduced from a calibration graph prepared from a solution of potassium dihydrogen phosphate.

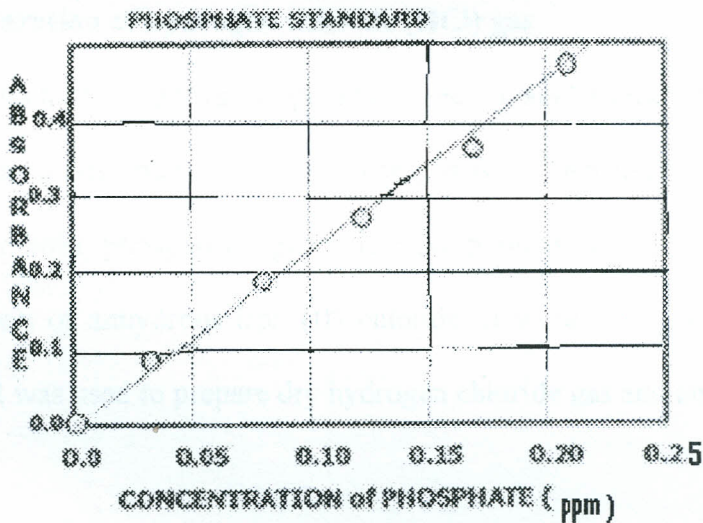


Figure 10: Calibration Curve for Analysis of Phosphate.

3.4.5 Elemental Analysis

The elemental analysis for CHNS were determined using a Perkin Elmer 2400 series II CHNS analyzer at the school of 'Pure and Applied Science, University of Kwa-Zulu Natal', South Africa.

3.4.6 Nuclear Magnetic Resonance (NMR) spectroscopy.

Nuclear Magnetic Resonance (NMR) spectroscopy was obtained using Varian Quadruple 200Mz Mercury VX spectrophotometer using deuterated chloroform, $CDCl_3$ as solvent. Chemical shifts are related to TMS (Tetramethylsilane) which is the reference of choice for proton and carbon NMR. The results of the NMR analysis are discussed in section 5.3.1.

3.5 Preparation of hydrogen chloride (HCl) gas

Hydrogen chloride gas was prepared by reacting analar grade concentrated sulphuric acid and analar grade sodium chloride. The gas was dried over concentrated sulphuric acid and then with phosphorus pentoxide on pumice stones. The gas was used in the preparation of anhydrous iron (II) chloride in section 3.6. The apparatus illustrated in figure 12 was used to prepare dry hydrogen chloride gas and anhydrous iron (II) chloride.

3.6 Preparation of anhydrous iron (II) chloride

Anhydrous iron (II) chloride was prepared following literature method ((Kovacic *et al.*, 1960). Hot iron wires were reacted with dry hydrogen chloride gas in a Pyrex

combustion tube. The combustion tube was continually rotated to facilitate uniform reaction between iron wires and hydrogen chloride gas.

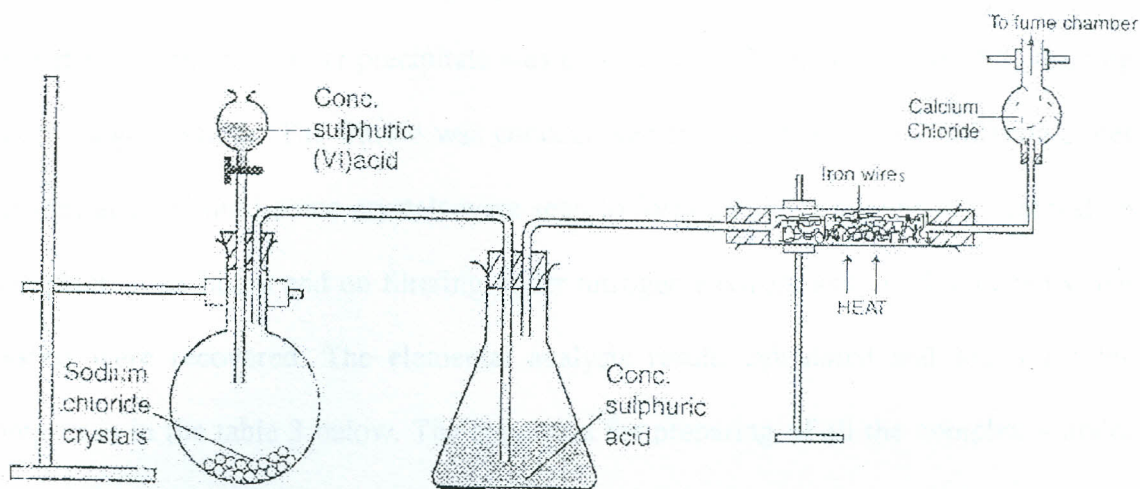


Figure 11: Apparatus for the Preparation of Dry Hydrogen Chloride Gas and Anhydrous Iron (II) Chloride.

3.7 Preparation of $\text{FeH}_2(\text{dppe})_2$.

A 0.7160g anhydrous iron (II) chloride and 45mL of 95% ethanol were placed in a stream of nitrogen gas in a 250mL three - ways round bottom flask containing a magnetic stirring bar. The apparatus was set in a water bath, centrally placed on a hot plate stirrer to help stir the mixture. The mixture was stirred for 20 minutes in a water bath maintained at 60°C by which time FeCl_2 crystals had dissolved. To this solution were added 3.5192g of 1,2-bis(dyphenylphosphino)ethane (dppe) in 40mL ethanol were added. The mixture was stirred at 60°C and a red-brown product formed. Stirring was continued for 16 hours after which time a grey-white solid formed. Then, 0.1780g of sodium tetrahydroborate, NaBH_4 , dissolved in 20mL of ethanol was added to the above mixture.

A red-violet solid formed. The mixture was stirred for one and a half hours at 55°C in a water bath. The red-violet solid remained. On filtering, using the modified Fritz apparatus (figure 9) under nitrogen pressure and with help of an electric suction pump (Model 'Charles Austin' Pumps Ltd), a bright yellow filtrate and a red violet precipitate were recovered. All the red violet precipitate was dissolved in 120ml acetone at 55°C forming a red-orange solution. The filtrate was concentrated through fractional distillation under nitrogen at 55°C until some crystals were seen to form on slight cooling. Crystallization took place in 21 hours and on filtering under nitrogen environment, 3.785g of red-violet crystals were recovered. The elemental analysis result, calculated and found for the complex is in the table 3 below. The apparatus for preparing of all the complexes under nitrogen atmosphere is illustrated in figure 12;

Table 3: Elemental Analysis for $\text{FeH}_2(\text{dppe})_2$.

Element	% calculated	% found
C	77.68	78.06
H	6.56	6.42
P	14.52	14.30

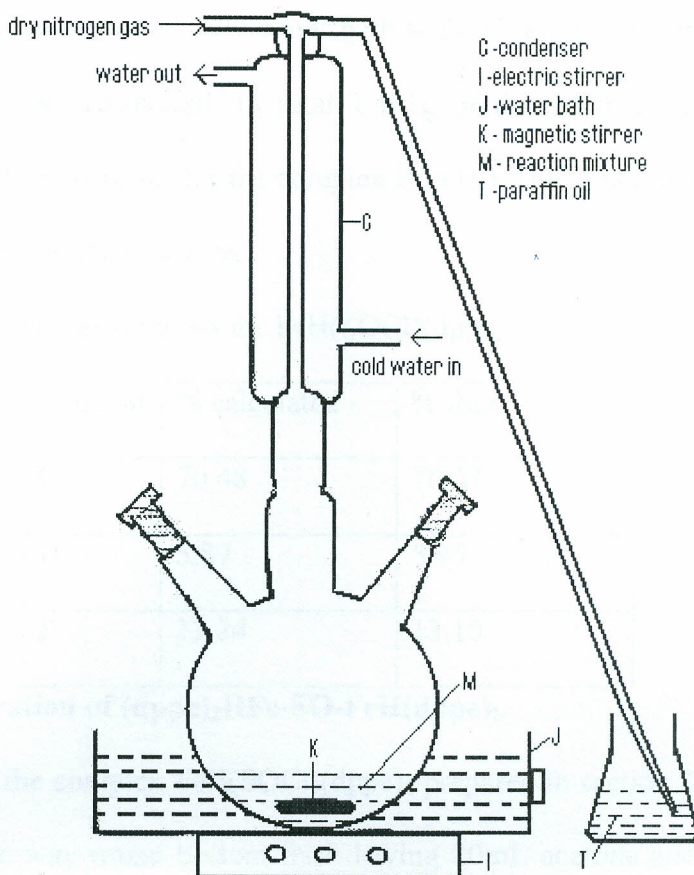


Figure 12: The Apparatus For Preparing Of All The Complexes Under Nitrogen Atmosphere.

3.8 Preparation of $\text{FeH}(\text{SOCl})(\text{dppe})_2$,

A 3.016g of $\text{FeH}_2(\text{dppe})_2$ prepared in section 3.7 was added to 65 mL of freshly distilled acetone in a 250mL three way round bottomed flask containing a magnetic stirrer. The mixture was stirred for 20 minutes by which time the crystals had dissolved. Then 2.663 mL (~0.4040g) mixture of acetone- thionyl chloride solution prepared in section 3.3.6 was added drop by drop to a stirring solution of $\text{FeH}_2(\text{dppe})_2$. A white solution formed immediately. The solution mixture was stirred for 4 hours under nitrogen. On filtering, 0.847g of white residue and a very light green filtrate were recovered. The light green

filtrate was concentrated over water bath at 60°C and set for crystallization. 0.5590g of white solid was recovered. In total 1.401g of the white product was recovered. The elemental analysis result for the complex is in the table 4 below and the apparatus used is illustrated on figure 13 above;

Table 4: Elemental Analysis for $\text{FeH}(\text{SOCl})(\text{dppe})_2$.

Element	% calculated	% found
C	70.48	70.67
H	5.87	5.45
P	13.24	13.10

3.9 Preparation of $(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$.

0.2564g of the complex $\text{FeH}(\text{SOCl})(\text{dppe})_2$ prepared in section 3.8 above was added into 100ml three way round bottom flask having 20mL acetone and a magnetic stirrer. The mixture was stirred for 15 minutes. It did not dissolve. To the suspension of 0.2564g of the $\text{FeH}(\text{SOCl})(\text{dppe})_2$ 0.2300g of $\text{FeH}_2(\text{dppe})_2$ complex dissolved in 5mL acetone was added. The mixture stirred continuously for four hours. On filtering under nitrogen using an electric suction pump, 0.2987g of a white solid was recovered. The elemental analysis results are summarized in table 5 below;

Table 5: Elemental Analysis of $(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$.

Element	% calculated	% found
C	68.87	68.00
H	5.58	5.30
P	13.68	13.89
S	1.77	1.39

CHAPTER 4

RESULTS AND DISCUSSION

This chapter discusses the results of the synthesis of i) $\text{FeH}_2(\text{dppe})_2$, ii) $\text{FeH}(\text{SOCl})(\text{dppe})_2$, and iii) $(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$. Each product is discussed briefly based on the analytical data got for elemental analysis, IR, and NMR. The summary of all important and expected IR bands are given.

4.1 Results and discussion

4.1.1 Results and discussion for $\text{FeH}_2(\text{dppe})_2$.

The calculated and found elemental analysis results for the synthesized complex are identical and are summarized in table 3. These elemental results indicates that the complex has the empirical formula $\text{FeC}_{52}\text{H}_{50}\text{P}_4$, with chemical formula $\text{FeH}_2(\text{dppe})_2$. The IR spectrum of $\text{FeH}_2(\text{dppe})_2$, spectrum 4 on appendix III gave an absorption band at 1886.3 cm^{-1} which is due to the Fe-H stretching vibrations. The Metal-Hydrogen (M-H) stretching vibration is normally expected between 1900 cm^{-1} to 1725 cm^{-1} for Fe-H absorption band (Socrates, 1994). These results are further supported by a study by Oliver *et al* where the Fe-H stretch was observed at 1868 cm^{-1} (Oliver *et al*, 2006).

The gravimetric determination of chloride as silver chloride using 0.1M silver nitrate solution as explained in section 3.4.4. (ii) was negative. No precipitate was observed on adding drops of 0.1M silver chloride. This ruled out the presence of Fe-Cl bond in the synthesized complex. This confirms that all the chloride ions in anhydrous FeCl_2 used in the initial reaction was reduced by the NaBH_4 added. The reduction of all the chloride

ions was further supported by the IR analysis data for the complex. The Fe-Cl stretching vibration that was expected at between or near 586.3 cm^{-1} and 493.7 cm^{-1} as seen on an IR spectrum for anhydrous FeCl_2 spectrum 3 appendixes II was absent in the spectrum for the complex. Generally, the band due to metal-chloride vibrations occurs in the regions 610cm^{-1} to 220cm^{-1} (Socrates, 1994). The above observation are further supported by the comparison between the IR spectrum of dppe spectrum in appendix I and that of the IR spectrum of $\text{FeH}_2(\text{dppe})_2$ complex, spectrum 4 appendix III. The two spectra look similar at the region between 610 cm^{-1} to 220 cm^{-1} , the region where metal-chloride vibrations were expected to occur. The conclusion made above supports the following as the equation of reaction;



The NMR data discussed in section 4.3.1 gave further support to the synthesis of the complex $\text{FeH}_2(\text{dppe})_2$.

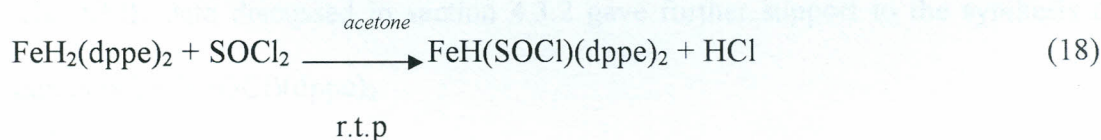
4.1.2 Results and Discussion for $\text{FeH}(\text{SOCl})(\text{dppe})_2$.

The elemental analysis result for the complex is summarized in table 4. All the calculated and found elemental percentages are identical. The elemental analysis for sulphur differs slightly. The elemental analyzer is not very sensitive to sulphur. The chloride analysis for the complex was done following the procedure for 'Gravimetric determination of chlorine' as silver chloride by use of 0.1M silver nitrate solution 'as explained in section 3.4.4 (ii) where a white precipitate was formed on adding drops of 0.1M silver chloride.

This was confirming that there were chloride ions in the solution. The elemental analysis results (Table 4) suggest that the product has the empirical formula $\text{FeC}_{52}\text{H}_{49}\text{P}_4\text{SOCl}$ and a molecular formula $\text{FeH}(\text{SOCl})(\text{dppe})_2$. The phosphorous analysis was done as explained in section 3.4.4 (iii).

The above conclusion is supported by the IR analysis. The IR spectrum of the complex shown as spectrum 5 in appendix III. From the IR spectrum the expected Fe-H appears at 1907.5 cm^{-1} . The Metal-Hydrogen (M-H) stretching vibration is normally expected between 1900 cm^{-1} to 1725 cm^{-1} for $\nu\text{Fe-H}$ stretch (Socrates, 1994). The expected Fe-Cl stretch in the region 610 cm^{-1} to 220 cm^{-1} was missing (Socrates, 1994). The gravimetric determination of chlorine (section 3.4.4) as silver chloride was positive. The detected chloride ions were thought to be linked to sulphur in the thionyl chloride molecule. The IR stretching vibration for the $-\text{SO}-\text{Cl}$ was recorded at 1180 cm^{-1} . The band was absent in the IR spectrum of complex $\text{FeH}_2(\text{dppe})_2$ and $(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$. The literature value for the Alkyl sulphinyl chlorides, R-SO-Cl is 1135 cm^{-1} , this supports the selected band (Socrates, 1994). A band at 408.9 cm^{-1} in KBr disc, which is absent in dppe and in the IR spectrum of complex $\text{FeH}_2(\text{dppe})_2$, is probably due to the $\nu(\text{FeS})$. This is the range expected for such modes (Nakamoto, 1986; Ikram and Powel, 1972).

The proposed equation of reaction is;



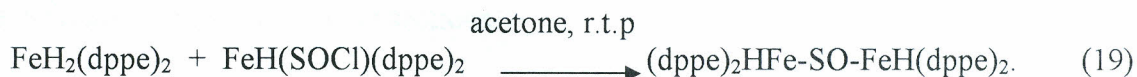
The IR spectrum of the complex $\text{FeH}(\text{SOCl})(\text{dppe})_2$, shown as spectrum 5 in appendix III had additional bands when compared to the spectrum of complex $\text{FeH}_2(\text{dppe})_2$. These bands are in the region of Fe-H stretch, SOCl, and S=O. The additional band at 1909.4cm^{-1} is assigned to the Fe-H stretch. The metal-Hydrogen stretching bands are wide and falling in the range 2270 cm^{-1} to 1700 cm^{-1} and the stretching band for Fe-H falling in the range 1900 cm^{-1} and 1725 cm^{-1} but dihydrides are usually at lower end of the range (Socrates, 1994; Oliver *et al*, 2006). Additional bands at 1284.5 cm^{-1} may be assigned to $\nu(\text{S}=\text{O})$ stretch since these bands are absent in both the phosphine ligand and the hydride complex and are in the range expected for such modes (Nakamoto, 1986). In non-polar solvent the S=O group has a strong absorption at $1070\text{-}1035\text{ cm}^{-1}$. The band may appear $10\text{-}20\text{ cm}^{-1}$ lower than given in solid phase, sometimes consisting of a number of peaks (Socrates, 1994). Electronegative constituents tend to raise the frequency since they tend to stabilize the form S=O bond. The stretching vibration for the sulphinyl chloride, -SO-Cl is expected to increase compared to that of S=O. Thus the IR band at 1334.6 cm^{-1} is assigned to the -SO-Cl stretching vibration. The literature value for the Alkyl sulphinyl chlorides, R-SO-Cl is 1135 cm^{-1} (Socrates, 1994). If coordination to a metal atom occurs through the sulphur atom, there may be an increase in the SO stretching frequency to 1160cm^{-1} to 1115 cm^{-1} . Then, the band 1188.1 cm^{-1} that was absent in the hydride complex and in the phosphine ligand is assigned to the Fe-SO-Cl stretching vibration. The NMR data discussed in section 4.3.2 gave further support to the synthesis of the complex $\text{FeH}(\text{SOCl})(\text{dppe})_2$.

4.1.3 Results and Discussion for $(dppe)_2HFe-SO-FeH(dppe)_2$.

The elemental analysis for the complex $(dppe)_2HFe-SO-FeH(dppe)_2$ are summarized in the table 5. The theoretical and practical elemental percentages for all elements are identical except that of sulphur that differs slightly. The complex gravimetric determination of chloride as silver chloride by use of 0.1M silver nitrate analysis was done following the procedure in section 3.4.4 (ii). The result was negative, an indication that all chloride ions were replaced during the reaction. The absence of chloride ions in the complex were supported by absence of the $-SO-Cl$ stretching vibration, expected at 1135 cm^{-1} (Socrates, 1994) and the $Fe-Cl$ stretching vibration that was expected to occur between 610 cm^{-1} to 493 cm^{-1} . The IR spectrum of the complex is shown as spectrum 6 in appendix III. The band at 1120.6 cm^{-1} , that is found in the IR spectrum of complex $FeH(SOCl)(dppe)_2$ and absent in the $FeH_2(dppe)_2$ complex is assigned to the $Fe-SO$ stretching vibration. The infrared band at 1334.6 cm^{-1} that was assigned to the $-SO-Cl$ stretching vibration in complex $FeH(SOCl)(dppe)_2$ was absent in the spectrum of complex $(dppe)_2HFe-SO-FeH(dppe)_2$ suggesting that the chloride ion was replaced during the reaction. The literature value for the Alkyl sulphonyl chlorides, $R-SO-Cl$ is 1135 cm^{-1} (Socrates, 1994).

A band at 410.8 cm^{-1} in KBr disc that is absent in $dppe$ spectrum and in the IR spectrum of sample $FeH_2(dppe)_2$ is probably due to the $\nu(FeS)$. This is the range expected for such modes (Nakamoto, 1986; Ikram *et al.*, 1972). From the IR spectrum, the expected $Fe-H$ is at 1909.4 cm^{-1} . The literature value is between 1900 cm^{-1} and 1725 cm^{-1} (Socrates, 1994). The elemental analysis results (Table 4) and the IR data indicate that the product had an

empirical formula $\text{Fe}_2\text{C}_{104}\text{H}_{98}\text{P}_8\text{SO}$ and molecular formula $\text{Fe}_2\text{H}_2\text{SO}(\text{dppe})_2$ or $(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$. The proposed equation for the reaction is;



If coordination to a metal atom occurs through the sulphur atom, the SO stretching frequency occurs between 1160 cm^{-1} to 1115 cm^{-1} . The increase may be more when sulphur is coordinated to two metal centre and thus, the band 1176.5 cm^{-1} that was absent in the $\text{FeH}_2(\text{dppe})_2$ complex and in the phosphine ligand, is assigned to the -Fe-SO-Fe-stretching vibration. The phosphorous analysis was done as explained in section 3.4.4 (iii).

4.2 Summary for the Important IR Bands for the Synthesized Complexes.

The summary of all important and expected IR bands for the synthesized complexes are given in table 6 below;

Table 6: The IR bands (cm^{-1}) for various groups and their literature values (in bold)

Complex	$\nu(\text{FeH})$	$\nu(\text{FeS})$	(P-Ph)	P-CH ₂ -	$\nu(\text{SO})$	$\nu(\text{SCL})$	P-C
Literature values	(1900-1725)	(~400)	(1130-1090)	(1440-1404)	---	---	(765-650)
$\text{FeH}_2(\text{dppe})_2$:	1886.3		1097.4	1443.0			727.1
$\text{FeH}(\text{SOCl})(\text{dppe})_2$	1907.5	408.5	1120.6	1436.9	1070.4	1135	731.0
$(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$	1909.4	410.8	1122.5	1421.4	1028.0	----	731.0

4.3 Nuclear Magnetic Resonance (NMR) Spectral Analysis.

The results of the carbon and proton NMR spectroscopy for the complexes synthesized are discussed in the following sections.

4.3.1 The ^{13}C and ^1H NMR spectral data for $\text{FeH}_2(\text{dppe})_2$.

The carbon-13 (^{13}C) and proton (^1H) data for the complex $\text{FeC}_{52}\text{H}_{50}\text{P}_4$ are discussed in the section below. A typical spectrum for the complex is shown as spectrum 6 in appendix IV and spectrum 10 in appendix V. The ^{13}C NMR spectrum of the $\text{FeH}_2(\text{dppe})_2$ complex showed four different types of carbon atoms that give four signals i.e. (a) a signal at 29ppm was assigned to methylene ($-\text{CH}_2\text{CH}_2-$) carbons of the dppe ligand, (b) a signal at around 23.809ppm assigned to carbon atoms in the acetone solvent used in the synthesis of the complex, (c) a signal at around 77ppm assigned to the carbon atoms in the CDCl_3 solvent used to dissolve the sample during the NMR analysis, and (d) signals ranging between 128ppm to 138ppm which are assigned to phenyl carbons atoms of the complex. The signals are related to the position of carbon atom in the phenyl ring as follows; i) The signal at around 138ppm is for α (ipso) carbon, ii) The signal at around 132ppm is for β (ortho) carbon, iii) The signal at around 130ppm is for γ (meta) carbon, and iv) The signal at around 128ppm is for δ (para) carbon. The α (ipso) carbon is most deshielded by the electron withdrawing phosphorous and thus appear more down field. The carbons atoms described in b) and c) are not part of the complex but from the solvents used. These carbon atom positions on the aromatic phenyl ring in relation to the phosphorous are as in figure13 below;

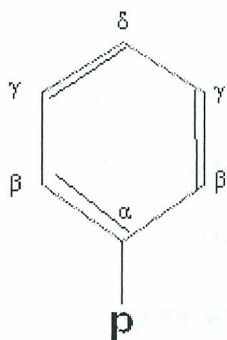


Figure 13: The ^{13}C NMR assignment for the aromatic phenyl ring.

Table 7: ^{13}C NMR chemical shifts (ppm) for all synthesized complexes.

Complex	α	β	γ	δ
$\text{FeH}_2(\text{dppe})_2$	138	132	130	128
$\text{FeH}(\text{SOCl})(\text{dppe})_2$	132	131	130	128
$(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$	132	130	128	128
Literature value for dppe ligand	139	133	132	130

These signals are found to be at a lower field than those of pure dppe ligand indicating that dppe ligand was complexed to the iron metal centre. This is true to all other complexes discussed in this section.

The ^1H NMR spectral data for $\text{FeH}_2(\text{dppe})_2$ are shown in table 8 and discussed based on spectrum 10 of appendix V. The spectrum of the complex showed two different types proton signals that are assigned to hydrogen atoms at different locations in the complex as follows; i) the hydrogen atoms signal at around 7.2ppm is assigned to the aromatic phenyl hydrogen atoms, ii) the signal at around 2ppm is assigned to the hydrogen atoms in the methylene ($-\text{CH}_2\text{CH}_2-$) groups of the dppe ligand. A multiplex is seen here due to the spin-spin coupling of the neighboring protons in the methylene group following the $n+1$ rule. The protons in the methylene group are equivalent and give a triplet at the average chemical shift 2.049ppm. Similarly the aromatic phenyl ring protons couples

with each other. The integration ratio for phenyl protons to the methylene protons gave a ratio of 5:1. This integration is similar to the ratio of phenyl protons (40 protons) and methylene protons (8 protons) of the dppe ligand. This integration ratio was true for the other synthesized complexes. The literature value for methylene hydrogen before complexation is at $\delta = 2.3\text{ppm}$ while the hydrogen atoms of the benzene ring, while equivalent, have a signal at $\delta = 7\text{ppm}$. The NMR spectral results for ^1H are summarized in table 8 below;

Table 8: ^1H NMR spectral data for $\text{FeH}_2(\text{dppe})_2$.

Important ^1H NMR (ppm)	The ^1H NMR band assignment
2.230 to 2.049	For the methylene ^1H atoms
7.207 to 7.260	For the phenyl ^1H atoms at different positions in the ring.

4.3.2 The NMR spectroscopy results and discussion for $\text{FeH}(\text{SOCl})(\text{dppe})_2$.

The carbon-13 (^{13}C) NMR and proton (^1H) NMR for the complex $\text{FeC}_{52}\text{H}_{49}\text{P}_4\text{SOCl}$ are discussed below. A typical ^{13}C NMR spectrum of the $\text{FeH}(\text{SOCl})(\text{dppe})_2$ complex, is shown as in spectrum 7 in appendix IV. It show three different types of carbon atoms that gives three signals i.e. a) a signal at around 25ppm assigned to methylene ($-\text{CH}_2\text{CH}_2-$) carbons of the dppe ligand, b) a signal at around 77ppm assigned to the carbon atoms in the CDCl_3 solvent, and c) signals ranging between 128ppm to 132ppm which are assigned to the aromatic phenyl carbons. The position of carbon atoms in the phenyl ring is as expressed in section 4.3.1 above. A multiple carbon signals were registered between 20.531ppm to 25.187ppm. These multiple bands were due to presence of carbonations

from acetone solvent and those of methylene carbons. These were expanded and gave a spectrum labeled spectrum 8 in appendix IV. The ^{13}C NMR chemical shifts for $\text{FeH}(\text{SOCl})(\text{dppe})_2$ are summarized in table 9 below;

Table 9: ^{13}C spectral data for $\text{FeH}(\text{SOCl})(\text{dppe})_2$.

Important ^{13}C NMR (ppm)	The ^{13}C NMR band assignment
25.187	For the methylene solvent ^{13}C atoms
128 to 132	For the phenyl ^{13}C atoms at different position of the ring

The ^1H NMR spectral analysis based on spectrum 11 in appendix V for $\text{FeH}(\text{SOCl})(\text{dppe})_2$ is described below. The spectrum of the complex (spectrum 11) has two different types proton signal in CDCl_3 . These signals are assigned to hydrogen atoms at different locations in the complex and are discussed here; i) the hydrogen atoms signal between 7.260ppm to 7.390ppm is assigned to aromatic phenyl hydrogen atoms on the phenyl ring, ii) signals between 2.725ppm to 1.778ppm are assigned to the methylene protons. The multiplex is due to spin-spin splitting of adjacent protons according to n+1 rule. The adjacent protons in the phenyl ring are not magnetically equivalent and thus split each other in accordance to n+1 rule. The NMR results for ^1H are summarized in table 10 below;

Table 10: The ^1H NMR analysis for $\text{FeH}(\text{SOCl})(\text{dppe})_2$.

Important ^1H NMR (ppm)	The ^1H NMR band assignment
2.725 to 1.778	For the methylene ^1H atoms
7.846 to 7.260	For the aromatic phenyl ^1H atoms at different position of the ring.

4.3.3 The NMR analysis result discussion for $(dppe)_2HFe-SO-FeH(dppe)_2$.

The NMR ^{13}C spectrum of the complex (spectrum 9 of appendix IV) show three different types of signals; a) The signal around 130ppm assigned to the aromatic phenyl carbons, b) the signal around 77ppm assigned to the $CDCl_3$ solvent and c) a signal at around 21ppm assigned to the methylene carbons. The signals around 130ppm are assigned to phenyl ring carbon atoms and are differentiated here; (i) The signal at 132ppm is assigned to α carbon atom in the phenyl ring of the dppe ligand, ii) the signal at 130ppm assigned to β carbon atom in the phenyl ring of the dppe, iii) the signal at 128ppm is assigned to γ and δ carbon atoms atom in the phenyl ring of the dppe. The triplet signal at around 21ppm is assigned to the methylene carbon atoms in the dppe ligand, and the signal at 77ppm is assigned to the carbon atoms in the $CDCl_3$ solvent used to dissolve the sample during NMR analysis. The above results summarized in table 11 below;

Table 11: NMR analysis for $(dppe)_2HFe-SO-FeH(dppe)_2$.

Important ^{13}C NMR signals (ppm)	The ^{13}C NMR band assignment
22.330 - 21.026	For the methylene ^{13}C atoms
128.712 – 132.851	For the phenyl ^{13}C atoms at different positions

CHAPTER 5

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

The main objectives of this study was to synthesis a dinuclear iron complex from a reaction of iron hydride complex, $\text{FeH}_2(\text{dppe})_2$, and iron thiol complex, $\text{FeH}(\text{SOCl})(\text{dppe})_2$, both of which were synthesized in this study.

5.2 Conclusion

The results obtained so far confirms that the dinuclear iron complex, $(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$ were synthesized. The complex synthesized contains a sulphur bridge and two iron centers unlike the most synthesized complexes which contain one metal centre and phosphine ligands. The conclusion made is supported by elemental analysis, IR spectroscopy and NMR spectroscopy as discussed in earlier chapters. From the study presented in this thesis, the following conclusions were made;

- i) The $(\text{dppe})_2\text{H}_2\text{Fe}$ complex was synthesized by reacting anhydrous FeCl_2 with dppe at a ratio of 1:2 followed by reduction of chloride ions with slightly excess, NaBH_4 , (at ratio 1:1.5)
- ii) The resulting iron hydride complex reacted with thionyl chloride in 1:1 ratio under mild conditions to give $(\text{dppe})_2\text{HFe-SO-Cl}$,
- iii) The complexes in (i) and (ii) above reacted at mild conditions in the ratio of 1:1 to form $(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$.

5.3 Recommendations

The following areas need further research;

- i) Attempt to crystallize the dinuclear iron complex synthesized and carry out its' X-Ray Structure determination,
- ii) Investigate whether the oxygen on sulphur may be reduced and then replace hydrogen in the complex to give co-ordinatively unsaturated centers at both Fe sites which may activate molecular nitrogen to form a dinitrogen complex.
- iii) Investigate if $(dppe)_2FeH(SOCl)$ may react with known molybdenum hydride complexes to give a species of the type $(dppe)_2HFe-SO-MoH(dppe)_2$, which may serve as possible starting material for dinitrogen complexes.

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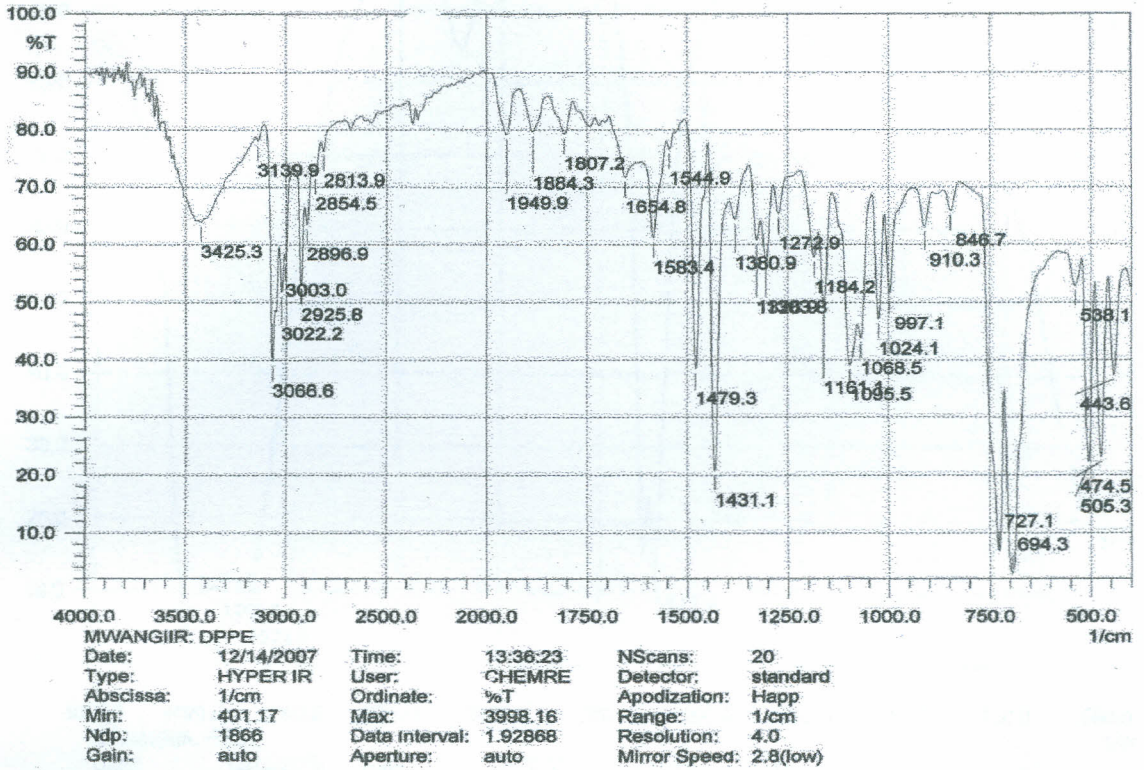
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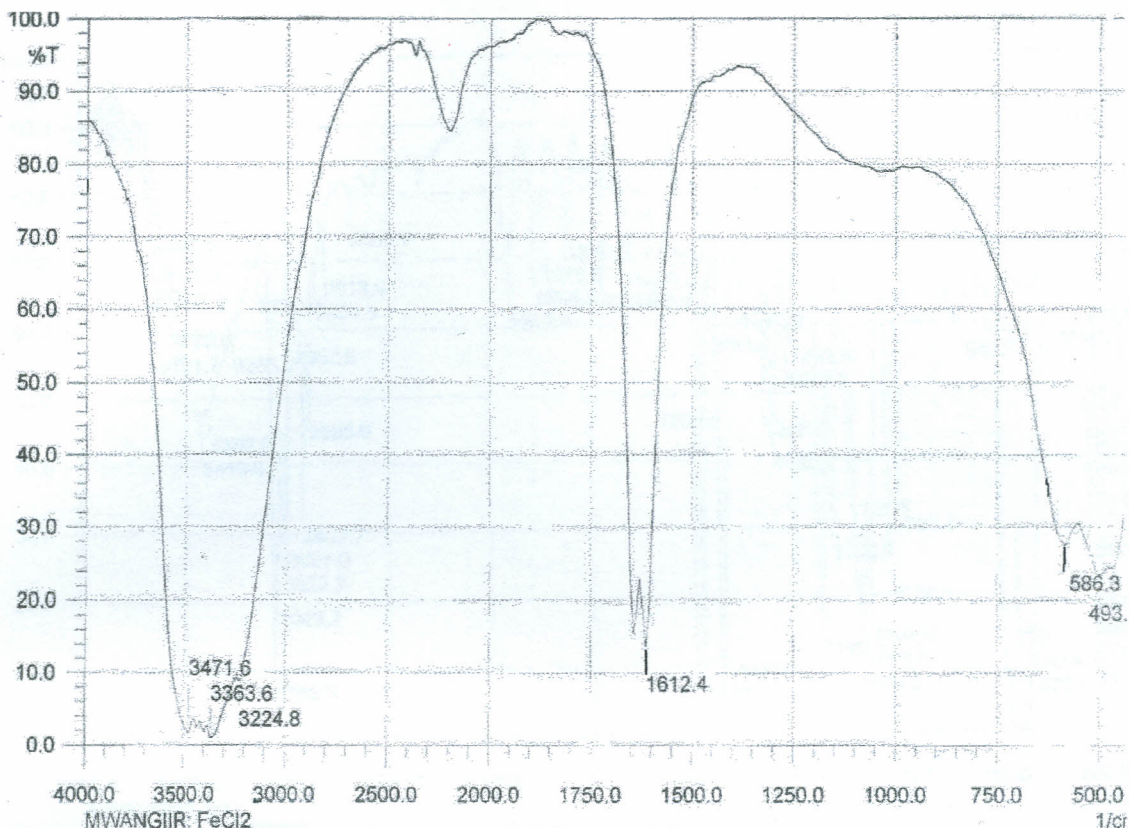
APPENDICES

Appendix I: IR spectrum for dppe



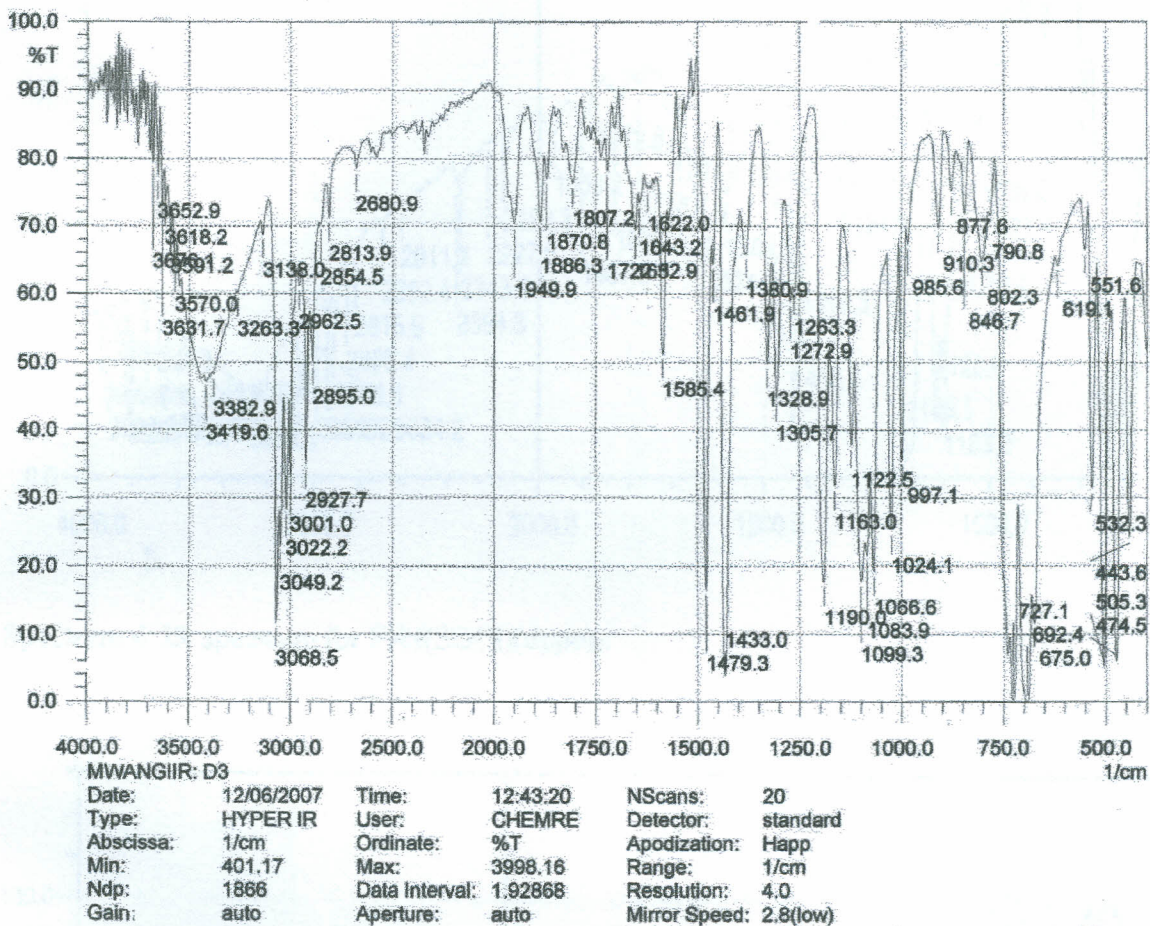
Spectrum 1: IR spectrum for dppe.

Appendix II: IR spectrum of anhydrous FeCl₂.

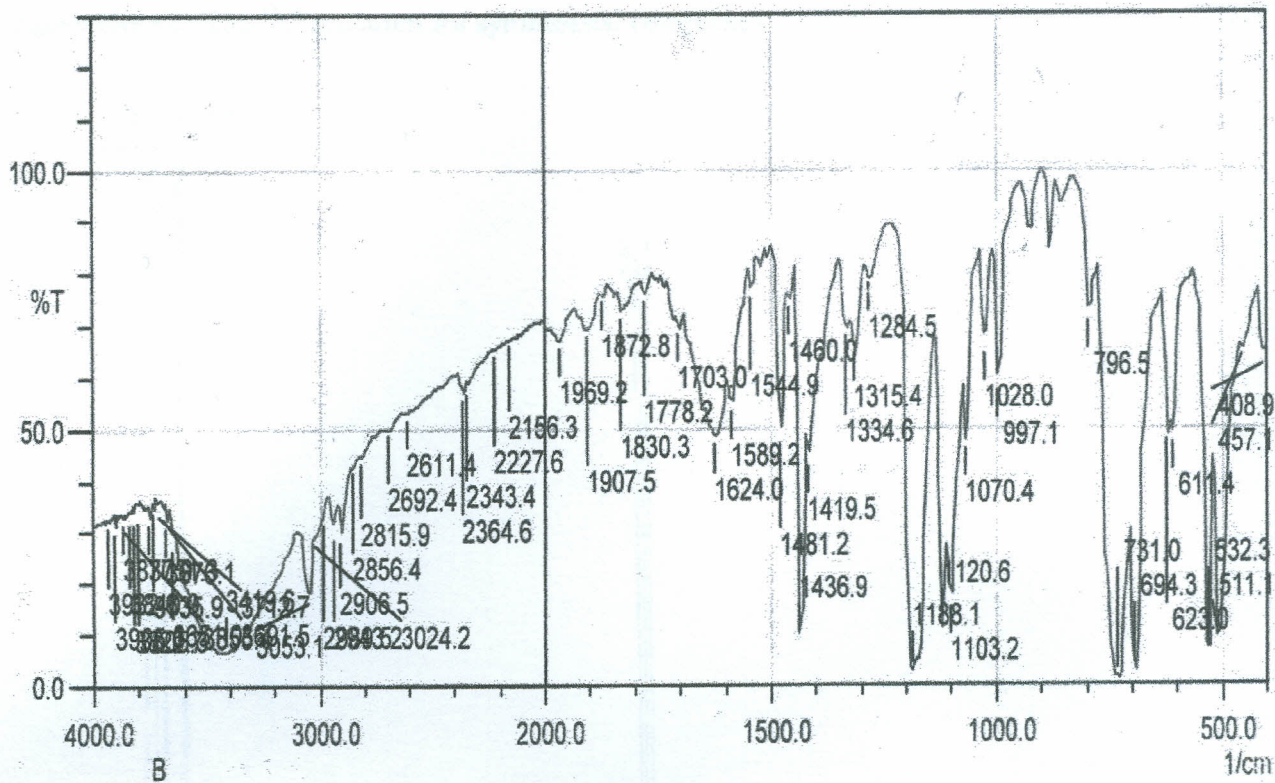


Spectrum 2: IR spectrum for anhydrous FeCl₂.

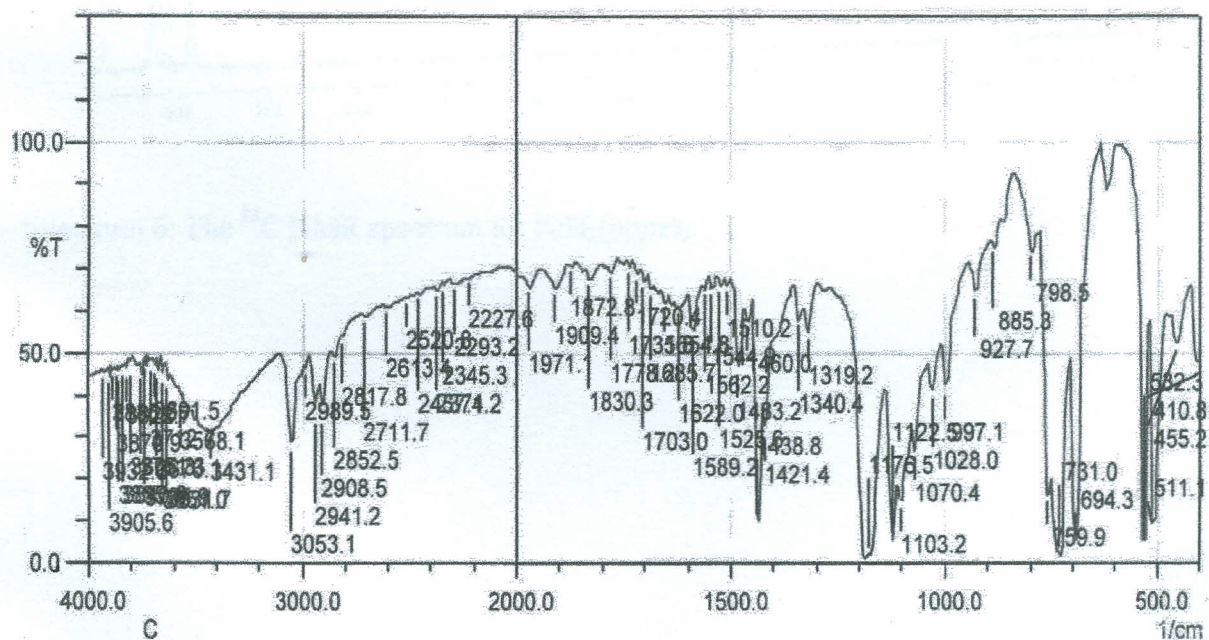
Appendix III: The IR spectra for synthesized complexes.



Spectrum 3: The IR spectrum for FeH₂(dppe)₂.

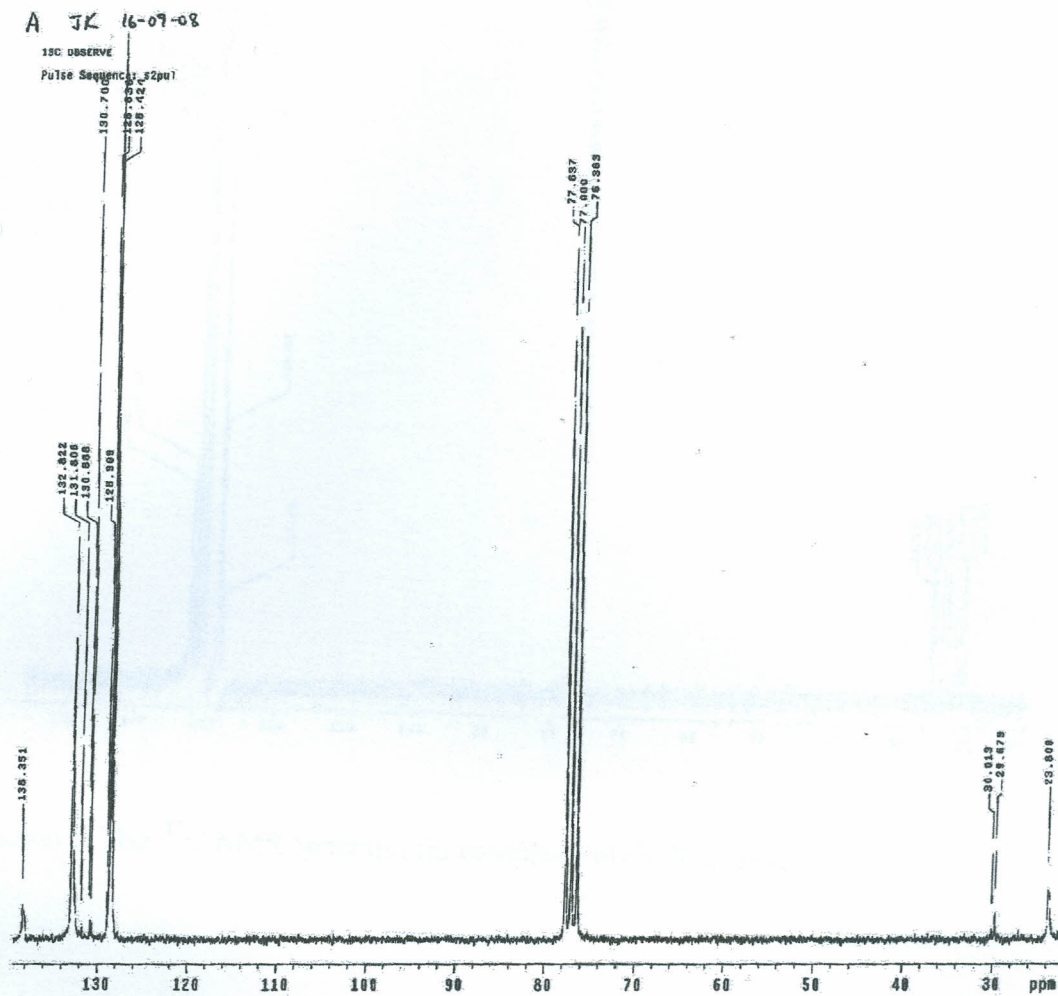


Spectrum 4: IR spectrum for $\text{FeH}(\text{SOCl})(\text{dppe})_2$.



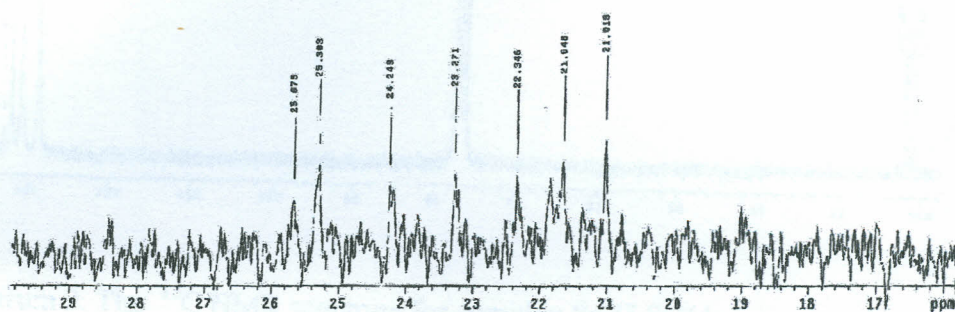
Spectrum 5: IR spectrum for $(\text{dppe})_2\text{HFe-SO-FeH}(\text{dppe})_2$.

Appendix IV: The ^{13}C spectrum for synthesized complexes.



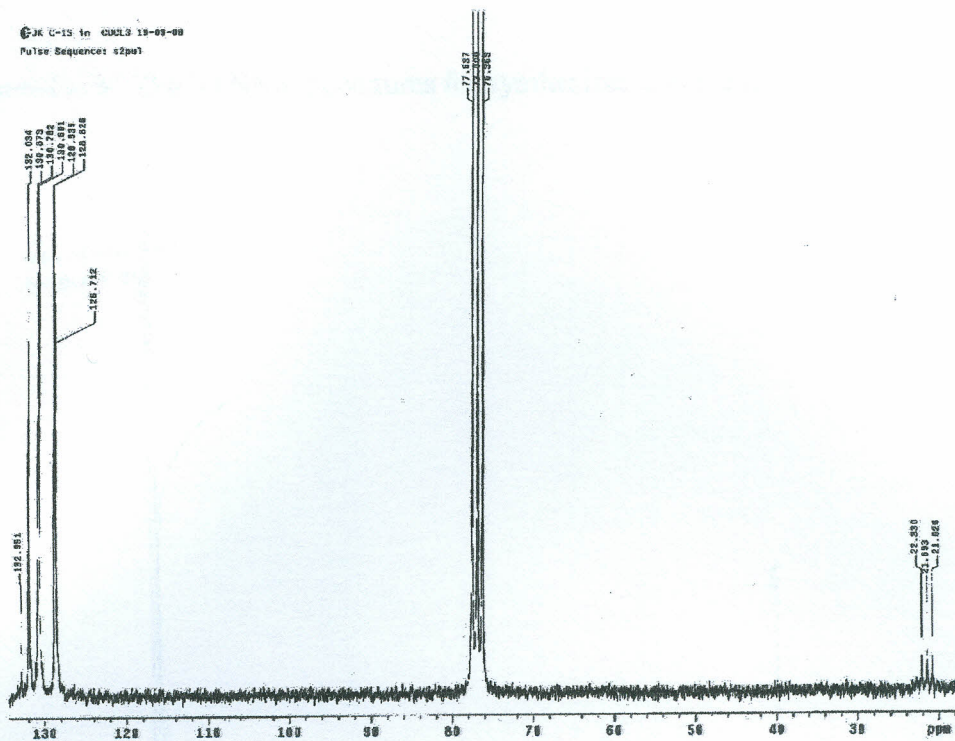
Spectrum 6: The ^{13}C NMR spectrum for $\text{FeH}_2(\text{dppe})_2$.

h-jk c-13 for 66618
Pulse sequence: zgpg30



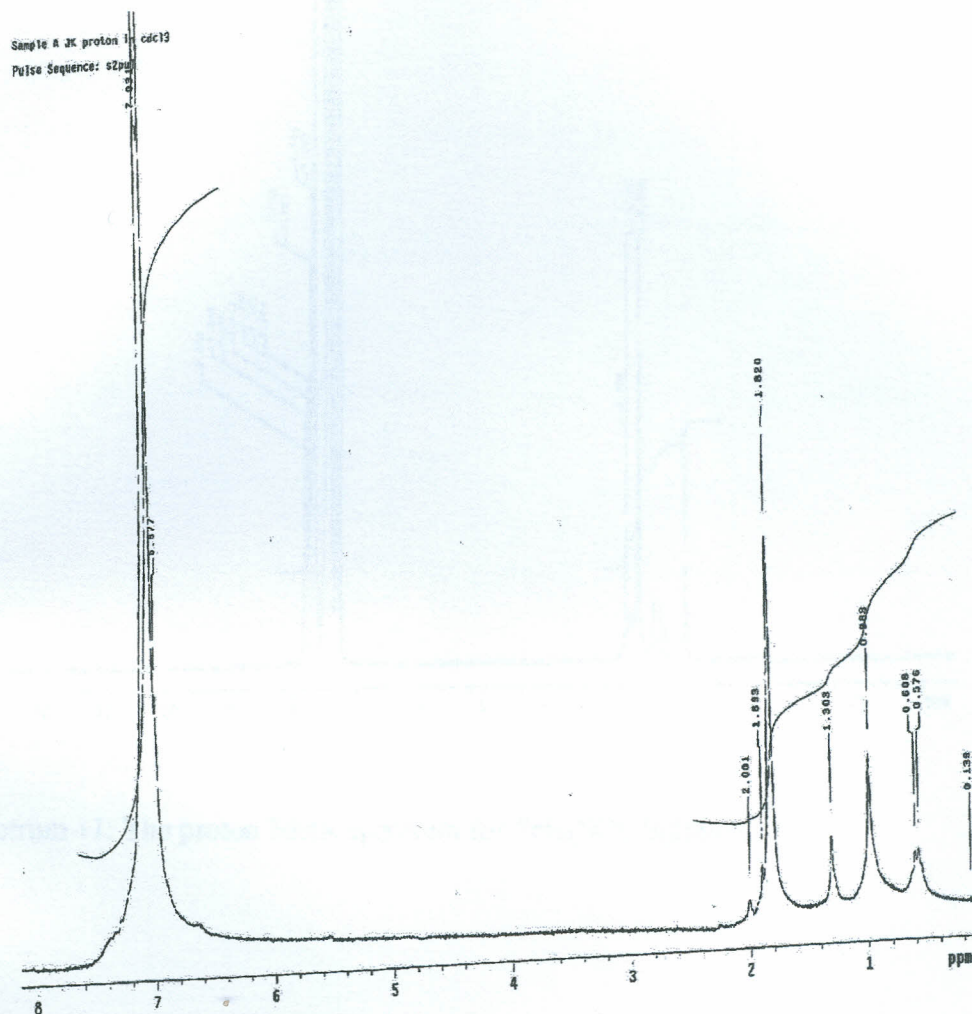
Spectrum 8: The ^{13}C NMR spectrum band expansion for $\text{FeH}(\text{SOCl})(\text{dppe})_2$.

JK C-15 1n GML9 19-09-08
Pulse Sequence: s2pa1



Spectrum 9: The ^{13}C NMR spectrum for complex $\text{Fe}_2\text{H}_2\text{SO}(\text{dppe})_4$.

Appendix V: The ^1H NMR spectra for synthesized complexes.



Spectrum 10: The complex $\text{FeH}_2(\text{dppe})_2$ proton NMR spectrum.

Appendix VI: Charts for the IR band position for metal and non-metal hydrides.

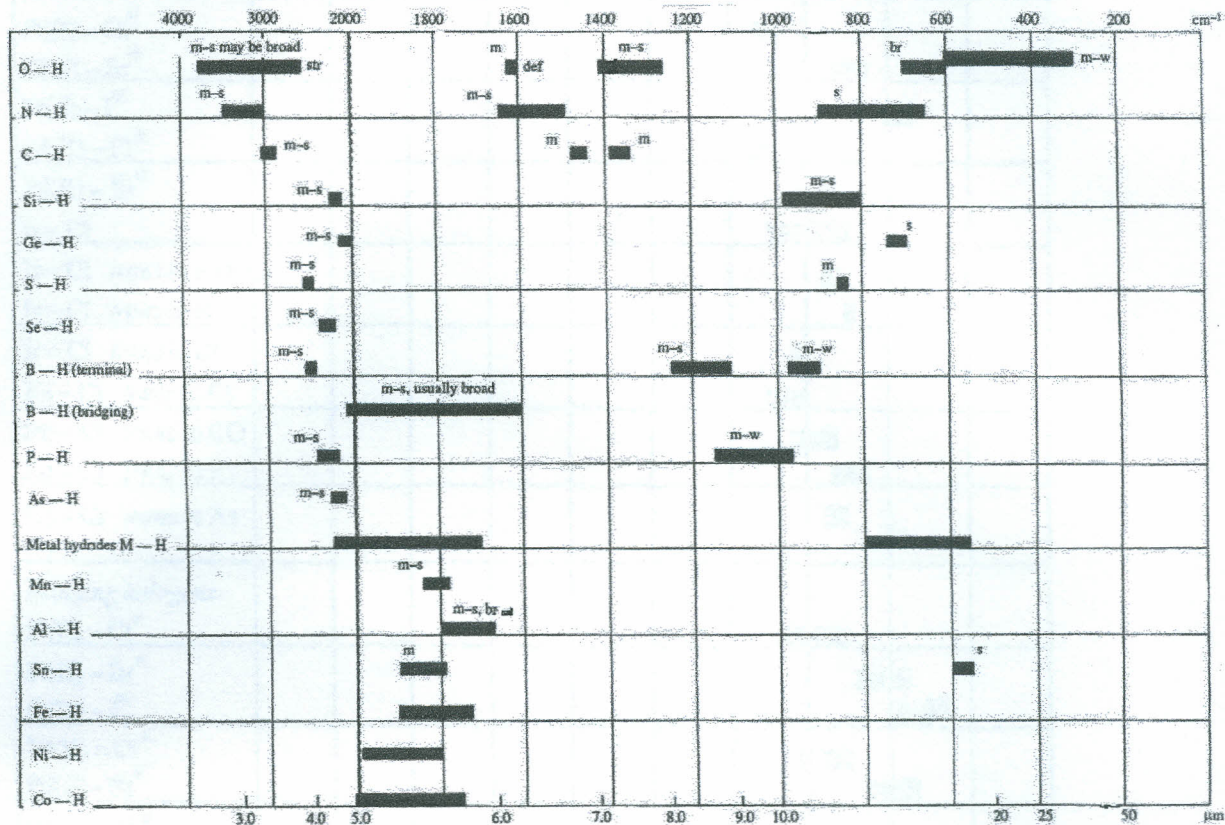
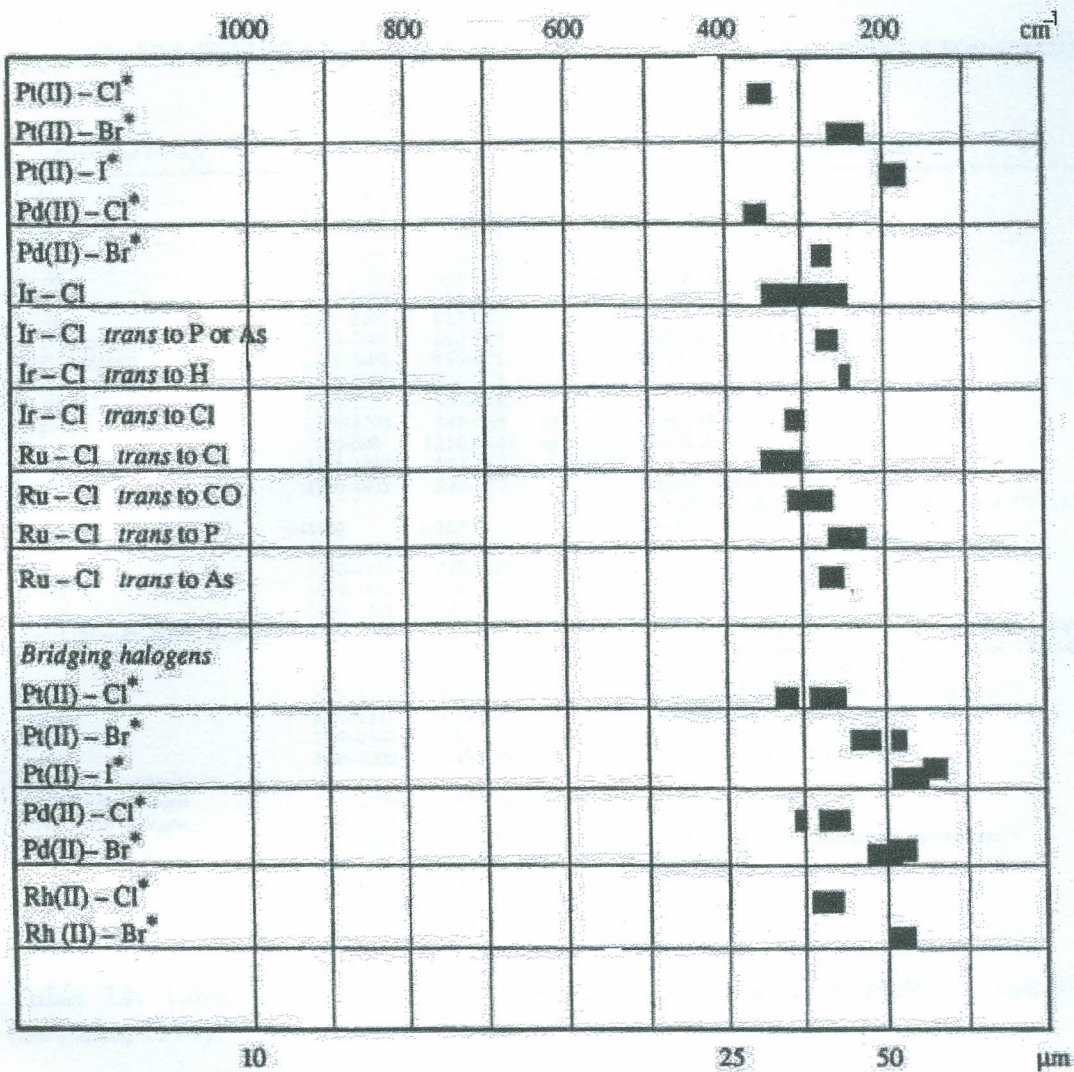


Chart 1: IR bands position for metal and non-metal hydrides (Socrates, 1994).



* Phosphine complexes

Chart 2: Transition metal hydrides stretching vibrations (all band of medium to strong intensity) (Socrates, 1994).

Appendix VII: Table for hydrides A-H stretching vibrations (A = metal or non-metal)

Functional Groups	Region		Intensity	Comments
	cm ⁻¹	μm		
O—H	3800–3000	2.63–3.33		
N—H	3500–3000	2.86–3.33		
C—H	3050–2850	3.28–3.51		
Si—H	2250–2100	4.44–4.76		
Ge—H	2160–2010	4.63–4.98		Strong band ~ 720 cm ⁻¹ def
S—H	2580–2450	3.88–4.08		
Se—H	2400–2200	4.17–4.55		
B—H (terminal)	2565–2440	3.90–4.10		Medium-to-strong intensity
B—H (bridging)	2100–1600	4.76–6.25		Weak to medium intensity
P—H	2450–2200	4.08–4.55		
As—H	2300–2100	4.35–4.76		
Metal-H	2270–1700	4.41–5.88	m	Sharp, M—H str
M—H	800–600	12.50–16.67	m	M—H def
M—H	1845–1780	5.42–5.62		
Al—H	1910–1675	5.24–5.97		Usually br strong band Bridging hydrogens may give band as low as 1550 cm ⁻¹ Bend ~ 700 cm ⁻¹
Ga—H	~ 1980	~ 5.05		
Sn—H	1900–1790	5.26–5.59		Usually broad, strong band ~ 570 cm ⁻¹ def
Fe—H	1900–1725	5.26–5.80		Dihydrides usually lower end of range
Ni—H	1985–1800	5.08–5.56		
Co—H	2050–1755	4.88–5.70		
M—H (M = Pt, Ir, Ru, Os, Re)	2200–1890	4.55–5.29		Strong band. Highest frequency for Pt, lowest for Re; for H <i>trans</i> to a halogen, frequency ~ 100 cm ⁻¹ higher than when <i>trans</i> to a phosphine
Ru—H	2020–1750	4.95–5.71		Strong band. Dihydrides as low as 1615 cm ⁻¹
Os—H	2105–1845	4.75–5.42		Dihydrides as low as 1720 cm ⁻¹
Rh—H	2140–1880	4.67–5.35		
Ir—H	2245–2000	4.45–5.00		Dihydrides as low as 1740 cm ⁻¹
Ir-H <i>trans</i> to phosphorus, arsenic or carbonyl	2100–2000	4.67–5.00		
Ir-H <i>trans</i> to halogen	2240–2195	4.46–4.56		
Pt—H	2265–2005	4.42–4.99		Pt(II)—H str, dihydrides as low as 1670 cm ⁻¹
	870–810	11.49–12.35		Pt—H def
Pd—H	2025–1990	4.94–5.03		Pd(II)—H str
	740–710	13.51–14.08		Pd—H def
U—H	~ 2200	~ 4.55		
Re—H	1980–1760	5.05–5.68		

Table 12: Table for hydrides A-H stretching vibrations (A = metal or non-metal) (Socrates, 1994).

Appendix VIII: Table for organic sulphoxides

Organic sulphoxides, $>S=O$		Region		Intensity	Comments
Functional Groups		cm^{-1}	μm		
Sulphoxides, $>S=O$ (in dilute CCl_4 solution)		1070-1030	9.35-9.70	vs	$S=O$ str, halogen or oxygen atom bonded to S atom increases frequency
Sulphoxides		730-690	13.70-14.49	v	
		395-335	25.32-29.85	v	sym C-S-O def
Cyclic sulphoxides (six- and seven-membered rings) (in CCl_4 solution)		~ 1060	~ 9.43	s	$S=O$ str
Cyclic sulphoxides (four-membered rings) (in CCl_4 solution)		~ 1090	~ 9.17	s	$S=O$ str
Aryl sulphoxides (in CCl_4 solution)		~ 1060	~ 9.43	s	$CHCl_3$
Methyl aryl sulphoxides $Ar-SO-CH_3$		535-495	18.69-20.20	s	C-S=O in-plane def
Thiosulphoxides, $G_1-S-SO-G_2$: $G_1, G_2 = CH_3$ and/or Ar $G_1, G_2 = R$ and Ar $G_1, G_2 = Ar$		1110-1095 1090-1075 1115-1100	9.01-9.13 9.17-9.30 8.97-9.09	s s s	
Compounds of the type $R-S-O-S-R'$		345-255 160-125	28.99-39.22 62.50-80.00		sym S-O-S str, S-O-S bending
Dialkyl sulphites, $(RO)_2SO$		1220-1170 1050-850 750-690	8.20-8.55 9.52-11.76 13.33-14.49	s s m-s	S=O str Due to S-O- CH_2 group S-O str, two bands
Chloroalkyl sulphites		~ 1215	~ 8.23	s	S=O str
Sulphinic acid esters, $-SO-O-$		1140-1125	8.77-8.89	s	$S=O$ str
Sulphinic acids, $-SO-OH$		2790-2340 1090-990 870-810	3.58-4.27 9.17-10.10 11.49-12.35	w vs m-s	O-H str (solid phase value) $S=O$ str S-O str
Aryl sulphinic acids, $Ar-SO-OH$		~ 1100	~ 9.09	s	S=O str
Sulphinic anhydrides, $R-SO_2-SO-R$		~ 1100	~ 9.09	s	S=O str
Sulphinic acid salts, $RSO_2^- M^+$		~ 1030 ~ 980	~ 9.71 ~ 10.20	s s	asym $S^{=O}$ str, stronger of the two bands sym $S^{=O}$ str
Alkyl sulphinyl chlorides, $R-SO-Cl$		~ 1135	~ 8.81	s	$S=O$ str
Thionylamines, $-N=S=O$		1300-1230 1180-1110	7.69-8.13 8.48-9.01	s s	asym N=S=O str, sym N=S=O str
Cyclic sulphites (five-, six-, and seven-membered rings)		1220-1210	8.20-8.26	s	S=O str

Table 13: Table for organic sulphoxides (Socrates, 1994).