SYNTHESIS, STRUCTURE DETERMINATION AND CHARACTERIZATION OF NOVEL ORGANOMETALLIC CHROMIUM HEXACARBONYL DERIVATIVES *VIA* TERTIARY PHOSPHORUS LIGAND (L) SUBSTITUION, WHERE L = DICYCLOPHENYLPHOSPHENE, TRIS-(4-FLUOROPHENYL)PHOSPHENE, TRIS-(3-CHLOROPHENYL)PHOSPHENE, DIPHENYLPENTAFLUOROPHENYLPHOSPHENE, TRIS-(4-FLUOROPHENYLPHOSPHINO)ETHANE

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ABSTRACT

The objective of the research study is to synthesize novel compounds through substitution process. The carbonyl ligand on chromium complexes is replaced by different tertiary phosphine ligands in order to produce a novel organometallic monocrystal compound. The crystal is characterized in terms of its structure, followed by the physical and chemical properties. Derivatives of Chromium Carbonyl are prepared by reaction with a number of tertiary phosphine ligands which have the potential to result in novel organometallic compounds. There are five attempt substitutions being done using Dicyclophenylphosphene, Tris-(4-fluorophenyl)phosphene, Tris-(3-chlorophenyl)phosphine, Diphenylpentafluoro-phenylphosphene and 1,2bis(dicyclohexylphosphino)ethane. From these, the substitution reaction using Tris-(4-fluorophenyl)phosphene resulted in the formation of a fine bright yellow crystal. From the monocrystal x-ray diffraction analysis, the resulting novel crystal structure is determined as Trans-bis[tris(4-flourophenyl)phosphane]tetracarbonylchromium(0) with molecular formula $C_{40}H_{24}CrF_6O_4P_2$. Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR) further compliment the X-ray diffraction results. For the novel structure, the Cr atom is octahedrally coordinated by four carbonyl ligands and two monodentate phosphorus ligands, which are bonded in a *trans* position to each other. The compound crystalizes in the monoclinic system, space group C2/c with an average Cr-P bond length of 2.3331 Å and average Cr-CO bond length of 1.8808 Å.

ABSTRAK

Objektif penyelidikan ini ialah untuk mensintesis sebatian baru melalui proses gantian ligan karbonil yang terdapat pada kromium hexakarbonil dengan pelbagai ligan fosfena untuk menghasilkan kristal sebatian organometalik yang baru. Struktur kristal sebatian baru ini akan ditentukan dengan terperinci melalui pembelauan sinar-X pada monokristal. Ia akan juga melalui pencirian kimia dan fizikal. Sebatian tersebut disediakan melalui sintesis penukargantian ligan karbonil daripada kromium hexacarbonil dengan beberapa ligan phophine. Terdapat lima percubaan gantian yang dilakukan menggunakan Dicyclophenylphosphene, Tris (4-fluorophenyl) phosphene, Tris (3-chlorophenyl) phosphine, Diphenylpentafluorophenylphesphene dan 1,2-bis (dicyclohexylphosphino) etana. Daripada lima percubaan penukargantian yang dilaksanakan, sintesis penukargantian yang menggunakan ligan Tris-(4-fluorophenyl)phosphene berjaya menghasilkan satu kristal yang berwarna kuning terang. Sebatian baru yang berjaya mencapai kestabilan dan membentuk kristal dinamakan Trans-bis [tris (4-flourophenyl) phosphane] tetracarbonylchromium(0) yang mempunyai formula molekul $C_{40}H_{24}CrF_6O_4P_2$. Kompleks baru yang diperolehi telah dikenal pasti ciri-cirinya melalui pancaran sinar-X, Nuclear Magnetic Resonance (NMR) Karbon-13, proton NMR (1H), P31 NMR dan juga menggunakan Spektroskopi Inframerah (IR). Untuk kompaun novel yang terhasil, kedudukan atom Cr terletak oktahedaral antara empat kumpulan karbonil ligan dan juga dua ligan monodentat fosforus dimana kedua ligan fosforus itu berkedudukan *trans*. Kompaun ini terkandung di dalam sistem monoklinik, iaitu kumpulan ruang C2/2, dengan purata panjang ikatan Cr-P 2.3331 Å dan purata panjang ikatan Cr-CO 1.8808 Å.

TABLE OF CONTENTS

	Page
SUPERVISOR'S DECLARATION	ii
STUDENT'S DECLARATION	iii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
ABSTRAK	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF PICTURES	xiii
LIST OF SYMBOLS	xiv
LIST OF ABBREVIATIONS	xv

CHAPTER 1 INTRODUCTION

1.1	Introduction	1
1.2	Background	1
1.3	Problem Statement	3
1.4	Objective	3
1.5	Scope Of Study	3
1.6	Conclusion	4

CHAPTER 2 LITERATURE REVIEW

2.1	Introduction	5
2.3	Brief History Of Organometallic Chemistry	6
2.3	Application of Organometallic Compound In Industry	9
2.4	Research On Organometallic Compound	15
2.5	Metal Carbonyl	18
	2.5.1 Structure and Properties	19
2.6	Chromium Hexacarbonyl	20

2.7 Tertiary Phosphine Ligand 21
2.8 Conclusion 23

CHAPTER 3 METHODOLOGY

3.1 Introduction 25
3.2 Synthesis 27
  3.2.1 The Schlenk Technique 28
  3.2.2 Thin Layer Chrmatography 29
  3.2.3 Column Chromatography 31
  3.2.4 Crystalization Technique 32
3.3 Characterization 33
  3.3.1 Monocrystal X-ray Diffractions 33
  3.3.2 Nuclear Magnetic Resonance Spectroscopy 35
  3.3.3 Infrared (IR) Spectroscopy 37
3.4 Conclusion 39

CHAPTER 4 RESULTS

4.1 Introduction 40
4.2 Synthesis 41
  4.2.1 Substitution of Chromium Hexacarbonyl with Dicyclophenylphosphene Ligand 41
  4.2.2 Substitution of Chromium Hexacarbonyl with Tris-(4-fluorophenyl) Phosphine Ligand 42
  4.2.3 Substitution of Chromium Hexacarbonyl with Tris-(3- Chlorophenyl) Phosphine Ligand 45
  4.2.4 Substitution of Chromium Hexacarbonyl with Diphnenylpentafluorophenylphesphene Ligand 46
  4.2.5 Substitution of Chromium Hexcarbonyl with 1,2-bis(dicyclohexylphosphino) Ethane Ligand 48
4.3 Characterization 50
  4.3.1 X-ray Diffraction Analysis 50
  4.3.2 IR Spectroscopy Analysis 55
  4.3.3 NMR Analysis 57
  4.3.4 Melting Point 62
4.4 Conclusion 62

CHAPTER 5 DISCUSSION

5.1 Introduction 64
5.2 Stability 65
5.3 Properties 66
5.4 Challenges 68

CHAPTER 6 CONCLUSION 68

REFERENCES 71

APPENDICES

A1 International Publication 73

LIST OF TABLES

Table No.		Page
2.1	Trend of patenting metallocenes from 1994-2003	12
2.2	Trend of patenting late transition metal catalyst from 1994-2003	13
2.3	contains a brief listing of additional metal-containing drugs	14
4.1	Crystal data of Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0), $C_{40}H_{24}CrF_6O_4P_2$	50
4.1	Crystal data of Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0), $C_{40}H_{24}CrF_6O_4P_2$ (Cont.)	51
4.2	X-ray diffraction result for Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0), $C_{40}H_{24}CrF_6O_4P_2$ - Bond Distances (Angstrom)	51
4.2	X-ray diffraction result for Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0), $C_{40}H_{24}CrF_6O_4P_2$ - Bond Distances (Angstrom)(Cont.)	52
4.3	X-ray diffraction result for Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0), $C_{40}H_{24}CrF_6O_4P_2$ - Bond Angles (Degrees)	52
4.4	Peak list data for ^{13}C NMR for Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0), $C_{40}H_{24}CrF_6O_4P_2$	58
4.5	Peak list data for ^{1}H NMR for Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0), $C_{40}H_{24}CrF_6O_4P_2$	58
4.6	Peak list data ^{31}P NMR for Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0), $C_{40}H_{24}CrF_6O_4P_2$	58

LIST OF FIGURES

Figure No.		Page
2.1	Total World Reserve Oil	11
2.2	The chemical structure trans-Tetracarbonyl-bis(triethylphosphine)-chromium	17
2.3	The chemical structure of trans-Tetracarbonyl-bis(triphenylphosphine)-chromium(0)	17
2.4	carbonyl Structure of chromium hexacarbonyl	18
2.5	The pi back bonding for metal	19
3.1	Research methodology flow chart	26
3.2	Ways of calculating Rf value	30
3.3	Thin layer Chromatography	31
3.4	The process flow of column chromatography	32
3.5	Crystallization process	32
3.6	Example of NMR spectrum	36
3.7	^{13}C chemical shift reference	36
3.8	IR spectrum for ethyl ethanoate	37
3.9	Theoritical IR spectrum	38
4.1	TLC result for attempt substitution using chromium hexacarbonyl with dicyclophenylphosphene	42
4.2	TLC result for attempt substitution using chromium hexacarbonyl with Tris-(4-fluorophenyl)phosphene	43
4.3	TLC result for attempt substitution using chromium hexacarbonyl with Tris-(3-chlorophenyl)phosphine	46
4.4	TLC result for attempt substitution using chromium hexacarbonyl with Diphenylpentafluorophenylphesphene	47
4.5	TLC result for attempt substitution using chromium hexacarbonyl with 1,2-bis(dicyclohexylphosphino)ethane	49
4.6	The structure of the crystal compound.of Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0),	54

$C_{40}H_{24}CrF_6O_4P_2$

4.7 IR spectrum of Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium 56

4.8 ^{13}C NMR spectra for Tris-(4-fluorophenyl)phosphene substitution 59

4.9 ^{1}H NMR spectra for Tris-(4-fluorophenyl)phosphene substitution 60

4.10 ^{31}P NMR spectra for Tris-(4-fluorophenyl)phosphene substitution 61

4.11 Structure of Trans-bis[tris(4flourophenyl)phosphane]tetracarbonylchromium(0), $C_{40}H_{24}CrF_6O_4P_2$ 63

LIST OF PICTURES

Picture No.		Page
3.1	The Schlenk line	29
3.2	The product compound undergoes reflux process	29
3.3	X-ray diffractormeter Bruker SMART APEXII CCD	34
3.4	NMR 500 was conducted	37
4.1	Image of crystal via substitution with Tris-(4 fluorophenyl)phosphene	44

LIST OF SYMBOLS

π	Pi orbital
C_{4v}	Square Pyramidal coordination complex
R_f	Retention factor
H_0	Static magnetic field
Å	Angstrom
°	Degree
λ	Lamda

LIST OF ABBRIVIATIONS

RF	Radio frequency
TLC	Thin layer chromatography
XRD	X-ray diffraction
IR	Infrared
FTIR	Fourier Transform infrared
NMR	Nuclear magnetic resonance
UV	Ultra violet
DCM	Dichloromethane
ppm	Parts per million
MP	Melting point
USM	Universiti Sains Malaysia
IUCr	International Union of Crystallography

CHAPTER 1

INTRODUCTION

1.1. INTRODUCTION

The research project consists of the synthesis of novel organometallic compounds using chromium hexacarbonyl as parent compound substituted by various tertiary phosphine ligands. Experimentation was conducted at the Laboratory of Organometallic Synthesis and Characterisation, School of Distance Learning, Universiti Sains Malaysia, Penang under the supervision of Dr Wan Norlidah Al Qadri Binti Mohamed Noor in collaboration with Professor Datuk Dr Hj. Omar Shawkataly. The final year project thesis is submitted in partial fulfilment of the requirements for the Degree of Bachelor of Science, University Malaysia Pahang.

1.2. BACKGROUND

The past 50 years have seen enormous growth in transition-metal organometallic chemistry, both as a scientific discipline and as a subject for research in industry. Since 1950, in view of its importance in the underlying science for homogeneous catalysis and the coordination polymerization of olefins, organometallic chemistry grew to become a significant industrial discipline.[1] In the 1980s, the industrial processes based on organometallic chemistry and homogeneous catalysis contributed to almost 23 billion dollars to the U.S. economy.[1] The business emphasis on large scale polymers and commodity chemical products has since decreased. Most major chemical companies went through a period of reassessment of their businesses about 1980. The consensus was that their traditional areas of business, polymers and bulk chemicals, offered little opportunity for improvement of earnings. The consensus further saw the best opportunities for growth and profitability in fine chemicals, speciality polymers, and health care industries. This paved the way for novel disciplines underlying research such as molecular genetics and nonlinear optics in industry. The enterprising organometallic chemist is expected to become the catalyst and major contributor in the development of this and other related industry.

Sustained research in homogeneous catalysis would reside on, perhaps, three rationales: improvement of existing processes; development of processes for new products characterized by small volume and high value; and long-range research on processes based on cheap, abundant feedstocks.

It is this solid state approach that interests our research team: the stoichiometric use of organometallic precursors rather than as catalysts. Furthermore, of major scientific opportunity is the study of organometallic compounds in the crystalline or amorphous states. The physical properties of organometallic solids have received far less attention than those of pure inorganic or even organic compounds. In general, most studies of organometallic solids have barely gone beyond determination of molecular structure in the crystal. Properties such as conductivity, magnetism, and optical effects would present interesting areas of research. It is these underexplored areas that we believe can offer fascinating science.

Thus exploratory chemistry in the form of this study is done in order to discover novel compounds with the aspiration that the novel compound could perhaps lead to an advanced material with interesting properties. Within the framework of this research study, the starting material used is an organometallic compound namely chromium hexacarbonyl, substituted with group 15 tertiary phosphine ligand.

1.3. PROBLEM STATEMENT

In any research undertaking, a problem does not necessarily mean there is a situation or malfunction that needs to be rectified because it has deviated from the acceptable norm. It could simply indicate an interest within an issue where finding the right answer may improve the situation or that it may lead to discovery of a new product. In the context of this study, laboratory research on organometallic transition metal can be tailored through a proper process of restructuring the chemical content of the base compound and as a result of this laboratory experiment we may discover application for the new compound resulting from the process.

The challenge of this research project lies in being able to attempt the synthesis of the novel chromium hexacarbonyl derivatives through substitution with various ligands, in view that the ligands for substitution are bulky and thus present a steric effect, also with an electronic effect that should influence the stability or in most cases the instability. The next challenge is to obtain single crystals suitable for structural characterisation using X-ray diffraction.

1.4. OBJECTIVE

The objective of this research project is to synthesize novel organometallic monocrystal compounds through the substitution of the carbonyl ligand with a tertiary phosphine ligand. This is followed by the structural characterisation of the novel compound using X-ray diffraction complimented by Infra Red Spectroscopy and Nuclear Magnetic Resonance.

1.5. SCOPE OF STUDY

Organanometallic research constitutes a unique chemistry study whereby the metal element is attached to the carbon compound. It is unique due to a combination of two different areas which combine inorganic chemistry and organic chemistry. The authoris interested to exploring the organometallic chemistry to discover new compound that will perhaps have the potential to become an advanced material for application in the industry.

Based on the research objectives, the scope of this study have been identified to consist of three main parts. The first scope will be the synthesis of chromium hexacarbonyl derivatives by substituting the carbonyl ligand with a tertiary phosphine complex ligand. Five ligands were used: Dicyclophenylphosphene, Tris-(4-fluorophenyl)phosphene , Tris-(3-chlorophenyl)phosphine, Diphenylpentafluorophenylphesphene and 1,2-bis(dicyclohexylphosphino)ethane. The second scope of study is the structure analysis of the novel derived compounds. This scope is important in order to determine the exact crystal structure of the compounds that will ultimately determine its physical and chemical properties. In this research, the main characterization technique used is X-ray diffraction, namely to collect the crystal data properties of the monocrystal compound. The third scope is to characterize using IR Spectroscopy to identify the existence of the carbonyl group in the structure and NMR specifically NMR ^{13}C, NMR ^{1}H and NMR ^{31}P used to identify carbon, photon and phosphorus that exist in the structure of the novel compound.

1.6. CONCLUSION

This research thesis is about exploring the chemistry of novel chromium hexacarbonyl derivatives in order to discover compounds may in the future become advanced materials in the industry. The research undertaken adopts an intellectual approach to the design of solid organometallic compounds through synthesis of novel materials with structures that are tailored to specific properties and thus functions.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This research study explores organo-metallic chemistry with the goal of discovering a novel compound that could present novel properties and perhaps interesting applications as an advanced material. Within the framework of this research project, the carbonyl ligand of the parent compound, chromium hexacarbonyl, shall be substituted with group 15 ligands. Substitution is attempted using tertiary phosphine ligands.

In order to fully understand the impact and significance of this research work, it is important to first review aspects pertaining to organometallic chemistry, their applications, fundamentals surrounding the parent compound and fundamentals surrounding the ligands involved. We also carry out a brief review on research conducted with regard to these compounds.

Throughout this chapter on literature review, we put an emphasis on how fundamental knowledge, its exploration and research directly impact the chemistry industrial landscape. We further highlight that knowledge is an important contributor to productivity and economic growth.

2.2. BRIEF HISTORY OF ORGANOMETALLIC CHEMISTRY

Organometallic chemistry grew out of an exchange between inorganic and organic chemistry.[2-3] By associating a metal centre and an organic fragment into a single molecule, the properties of both components proved to be profoundly modified. The part which involves inorganic chemistry refers to the metal atom or complex that is bonded to organic functional group. In particularly, organolithium, organomagnesium, organozinc, and organoaluminium compounds have undergone a revolutionary impact in organic chemistry by providing stabilize but highly reactive carbanions that were able to react as nucleophiles or strong bases. The classical organometallic compound that has been widely used in industry is the metal carbonyl.

Organometallic chemistry is a subfield of coordination chemistry in which the complex contains an M-C or M-H bond for example $[Mo(CO)_6]$. Organometallic species tend to be more covalent, and the metal often more reduced, than in other coordination compounds. Typical ligands that usually bind to metals in their lower oxidation state are CO, alkenes and arenes. For example $Mo(CO)_6$, $(C_6H_6)Cr(CO)_3$ or $Pt(C_2H_4)^{3-}$.

Many organometallic compounds are readily oxidized in air but may keep indefinitely under an inert atmosphere. The environment is therefore critical in determining whether or not a compound can be isolated or studied. Not only thermodynamic, but also kinetic factors must always be taken into account.[4]

In later developments, transition metal organometallic chemistry had different types of impact in the organic chemistry area. Main groups of organometallics which are groups from the s block (group 1-2) and the p block (group 13-18) in the periodic table are normally stoichiometric reagents but the metal organometallic is typically a catalyst.[5] The application of it has several advantages which is not only to enhance selectivity for known reactions but also can open up entirely novel synthetic pathways that can be applied to complex molecule synthesis. Catalyst is usually needed in small amounts thus it avoids the waste formation associated with main group reagent and thus contribute to green chemistry.[5]

Inorganic chemistry has been influence by organometallic chemistry in several ways. Material synthesis for example thin films and nanoparticles often starts from organometallic precursors. Soon to be commercialized for cell phone display panels where light emitting diodes containing luminescent organometallic compound.

The first discovery on organometallic chemistry was made by Louis Claude Cadet. He developed the synthesis of the metal arsenic compound. It was in 1760 where he attempted to make invisible ink. He used cobalt minerals which contain arsine salts. Unintentionally he produced a vile smelling liquid which was later to be named dicacodyl.[6] The equation of the synthesis as in the equation 2.1 below:

$$As_2O_3 + 4CH_3COOK \rightarrow [(CH_3)As]2C \qquad (2.1)$$

In 1827 Zeise's salt became the first platinum or olefin complex ever produced. Further investigation of cacodyls by R.W. Bunsen in 1848 was to mark the beginning of the era of organometallic chemistry. He continued to investigate what he called alkarsines and produced many deravatives of $R_2As\text{-}AsR_2$ such as $(CH_3)2AsCN$. Following this, Bunsen's student by the name of Edward Frankland, became founder of organometallic as a branch of chemistry. Edward synthesized organo zinc compounds by treating organo halides with metal zinc. He was actually attempting to prepare an ethyl radical but instead he prepared diethylzinc.[6] The equation of the synthesis of diethyl zinc is as in equation 2.2 below:

$$2\,EtI + 2Zn \rightarrow Et_2Zn + ZnI_2 \qquad (2.2)$$

He produced metal alkyl complexes such as $ZnEt_2$ in 1849 after which he produced $HgEt_2$ in 1852. He also produced $SnEt_4$ and BMe_3 in 1960, the mercury and zinc complexes being immediately used to synthesize many other group organometallic complexes. Later, Charles Friedel and James Crafts prepared several organochlorosilanes $RnSiCl_{4-n}$ from the reactions of $SiCl_4$ with ZnR_2 in 1863.[6]

Shortly afterwards Schutzenberger, an Alsatian chemist, synthesized the first metal carbonyl derivatives $[Pt(CO)_2Cl_2]$ and $[Pt(CO)Cl_2]_2$ between 1868 and 1970. Twenty years later, the first binary metal carbonyl compounds appeared by Mond et akl in 1890 and also in 1891: $[Ni(CO)_4]$ and $[Fe(CO)_5]$.

Grignard reaction is an organometallic chemical reaction in which alkyl or aryl-magnesium halides are added to a carbonyl group in an aldehyde or ketone.[7] This reaction is the crucial reaction for the formation of carbon carbon bonding.[8] Grignard reaction and reagent were discovered by and named after the French chemist, Francis Auguste Victor Grignard, a chemist in University of Nancy, France. He was awarded the 1912 Nobel Prize in chemistry for this work.

In 1951 Ferrocene was discovered. Ferrocene is an organometallic compound with formula $Fe(C_5H_5)_2$. It is the prototype of metallocene an organometallic chemical compound consisting of two cyclopentadienyl rings bound on opposite sides of a central metal atom. It is also known as a sandwich compound [9]. The rapid growth of organometallic chemistry is often attributed to the excitement arising from the discovery of forrocene and its many analogues.

In 1963, the Nobel Prize was attributed to Karl Ziegler and Gulio Natta for the Ziegler-Natta catalyst. The Ziegler-Natta catalyst is a catalyst that is used in the synthesis of polymers of 1-alkenes. It is used to polymerize terminal 1-alkenes. The equation for ethylene and alkenes with the vinyl double bond is as in equation 2.3 below:

$$n\,CH_2{=}CHR \rightarrow \text{-}[CH_2\text{-}CHR]_n\text{-} \qquad (2.3)$$

This catalyst has been used in the commercial manufacture of various polymeric materials since 1956. In 2010, the total volume of plastics, elastiomers and rubbers produced from alkenes, with these catalysts, worldwide exceeded 100 million metric tons. This clearly indicated that these polymers represent the largest volume commodity plastics as well as the largest volume commodity chemicals in the world. We shall see in the following sections other industrial sectors that are heavily dependent on organometallic catalysts.

2.3. APPLICATION OF ORGANOMETALLIC COMPOUNDS IN INDUSTRY

For the past decade, organometallic compounds have only been applied as catalysts, that is, as substances that increase the rate of reaction but are not themselves consumed. The first industrial applications of organometallic complexes for catalysing chemical reactions were realized in the field of relatively simple, high volume chemical intermediates and polymers. This area of use is still growing and almost every year, new processes are introduced into production. There are also applications of homogeneous catalysts for the synthesis and production of multifunctional, more complex molecules such as agrochemicals and pharmaceuticals. There are several reasons why organometallic complexes are able to catalyse reactions and accelerate the breaking and forming of chemical bonds without being consumed in the process. First of all, almost any molecule with a functional group can coordinate to a specific metal centre. Upon coordination the reactivity of this functional group may change dramatically. Secondly, highly reactive species can be stabilized and react further in a controlled and productive way. Thirdly, two molecules can coordinate to the same metal centre leading, through proximity, to an enhanced probability of reaction. Last, but not least, the ligand present can exert some sort of control over the occurring reactions, leading to selective transformations. The biggest role of organometallic complexes is that it can serve as a catalyst in the polymerization process and also in the petrochemical process where both industries are important to the world now.

The **petroleum industry** includes the global processes of exploration, extraction, refining, transporting (often by oil tankers and pipelines), and marketing petroleum products. The largest volume products of the industry are fuel oil and gasoline (petrol). Petroleum is also the raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics. The industry is usually divided into three major components: upstream, midstream and downstream. Midstream operations are usually included in the downstream category.

Petroleum is vital to many industries, and is of importance to the maintenance of industrial civilization itself, and thus is a critical concern for many nations. Oil accounts for a large percentage of the world's energy consumption, ranging from a low of 32% for Europe and Asia, up to a high of 53% for the Middle East. Other geographic regions' consumption patterns are as follows: South and Central America (44%), Africa (41%), and North America (40%).[10]

Petroleum is the single most popular source of energy available to mankind. Utilizing it for the purpose of fuel needs refining which can only be accomplished through petroleum refining industry. The petroleum refining industry presently uses the latest technological innovations in the field of engineering. This involves the use of chemical reactors and extensive-complicated pipeline systems for converting crude petroleum to the derivative petroleum products like gasoline, asphalt, natural gas, etc.

Refining is the processing of one complex mixture of hydrocarbons into a number of other complex mixtures of hydrocarbons. A refinery breaks crude oil down into its various components, which then are selectively changed into new products. This process takes place inside a maze of pipes and vessels. The refinery is operated from a highly automated control room. All refineries perform three basic steps separation (fractional distillation), conversion (cracking and rearranging the molecules) and treatment.

One of the processes that uses organometallic compounds as catalysts is catalytic olefin condensation. In general, this is the reaction of one molecule of an olefin with one or more molecules of the same olefin or of other olefins to yield heavier olefinic compounds. The term "condensation" reflects the fact that liquid products are obtained from gaseous olefins. It can be carried out in many ways and over a diversity of catalysts. [10]

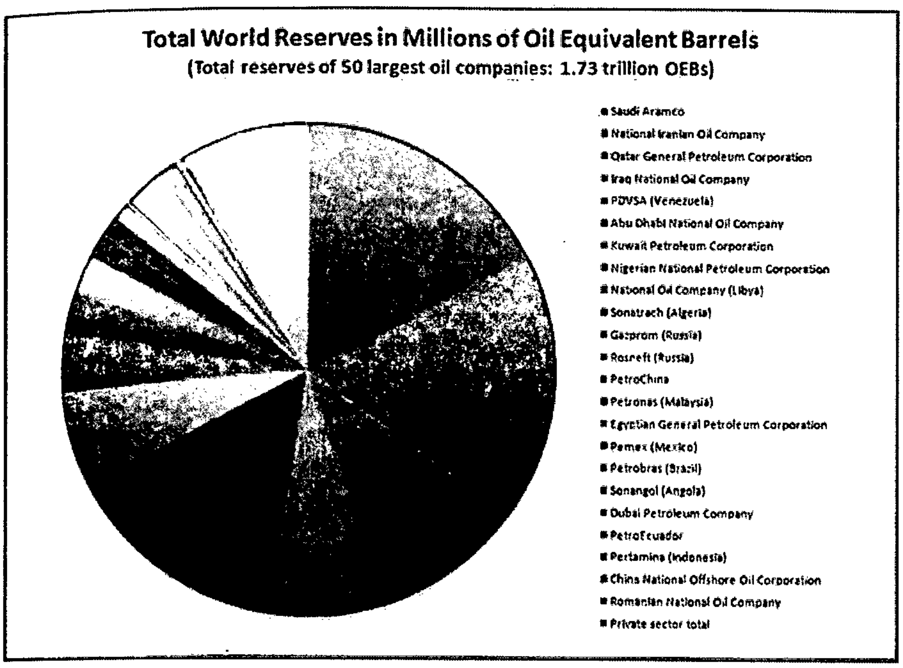

Figure 2.1: Total World Reserve Oil[10]

In the **polymer industrial** sector, in the 1950's, olefin polymerization depended on the use of Ziegler-Natta catalysts. Ziegler-Natta catalysts are based on a mixture of a transition metal, commonly a titanium compound, and an alkali metal, most commonly aluminium oxide. Whilst these systems have extremely high activity, their products have variable physical properties. To this day, the systems are little understood, but the monomers (polymer starting materials) react through a number of reaction sites on the catalyst. Unfortunately, this means the polymer can grow from many sites and at different rates, leading to a very wide distribution in the molecular weight, based on the polymer chain length. As the need to control the chain lengths of polymers has grown, the need for a new type of catalyst has also grown. Modern life has demanded more of the humble polymer: polymers that are stronger than steel, lighter than aluminium, and can be dyed any colour imaginable. The Ziegler-Natta system, with its waxy, variable results, could not reliably supply these attributes. This has given rise to a new breed of catalysts: the metallocene. Metallocene catalysts are, in fact, just as old as the Ziegler-Natta systems but the first systems using them were found to have low activity. It wasn't until 1980, when they were put together with a methyl aluminoxane cocatalyst, that their full potential was realised. Metallocenes are positively charged metal ions, most commonly Titanium or Zirconium, sandwiched between two negatively charged cyclopentadienyl rings. Their big advantage over the Ziegler-Natta systems is that they catalyse the reaction of olefins through only one reactive site. Due to this "single site" reaction, the polymerization continues in a far more controllable fashion, leading to polymers with narrow ranges of molecular weight and, more importantly, predictable and desirable properties. Also, it has been found that changing the ligands (functional groups attached to the metal) upon the metallocene molecule can controllably affect the properties of the polymer. This is very attractive to chemical companies trying to keep up with the demand for engineered plastics.

Patenting in the area has been plentiful, with most of the big chemical and oil companies having at least some patents. The list of patenting metallocenes from 1994 to 2003 in table 2.0 and the top patenting companies that patenting late transition metal catalyst from 1884 to 2003 as shown in table 2.1 clearly indicate this.

Table 2.1: Trend of patenting metallocenes from 1994-2003.[11]

Top Ten Companies Patenting metallocenes from 1994-2003	
Company	**No of Patent**
Mitsui Chemicals	446
Exxon Mobile	338
Basell	219
Mitsubishi Chemicals	172
Dow	161
Tosoh	148
Hoechst	135
Sumitomo Chemicals	134
AtoFinaElf	128
Phillips	115