SYNTHESIS, CHARACTERIZATION AND STRUCTURE DETERMINATION OF NOVEL CHROMIUM HEXACARBONYL DERIVATIVES *VIA* SUBSTITUTION WITH VARIOUS GROUP 15 COMPLEX LIGANDS (L) WHERE L = ETHYLENEBIS DIPHENYL-ARSINE, P-BROMOPHENYL DIPHENYLPHOSPHANE, BIS(DIPHENYLPHOSPHINO) HEXANE, BIS(DIPHENYLPHOSPHINO)PENTANE, AND TRIPHENYLARSINE

MUHAMMAD AZHAR BIN MOHD YUNUS

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Faculty of Industrial Sciences & Technology
UNIVERSITI MALAYSIA PAHANG

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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 ligands in order to produce a novel organometallic monocrystal compound. The crystal is characterized in terms of its structure, physical and chemical properties. Derivatives of chromium carbonyl are prepared by reaction with a number of group 15 complex ligands which have the potential to result in novel organometallic compounds. Five different ligands were used to produce novel organometallic monocrystal compounds namely Ethylenebis diphenyl-arsine, P-bromophenyldiphenylphosphane, Bis(diphenylphosphino)hexane, Bis(diphenylphosphino)pentane, and Triphenylarsine. From these, the substitution reaction using Ethylenebis diphenyl-arsine and P-bromophenyldiphenylphosphane both resulted in the formation of sticky light pale yellow crystals, and a fine bright yellow crystal respectively. From the monocrystal X-ray diffraction analysis, the resulting novel crystal structure is determined as [cis-1,2-bis(diphenylarsinyl)ethane] tetracarbonylchromium with molecular formula $Cr(CO)4(C_{26}H_{24}As_2)$ denoted as A1 and trans-bis [(4-bromophenyldiphenyl) phosphane] tetracarbonylchromium with molecular formula $Cr(CO)_4(P_2C_{36}H_{28}Br_2)$ denoted as A2. Infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) further compliment the X-ray diffraction results. For the A1 novel structure, the Cr atom is octahedrally coordinated by four carbonyl ligands and single bidentate arsenic ligand, which are bonded in a *trans* position to each other. The compound crystallizes in the orthorhombic system with an average Cr-As bond length of 2.44865Å and average Cr-CO bond length of 1.86975Å. For the A2 novel structure, the Cr atom is octahedrally coordinated by four carbonyl ligands and two monodentate tertiary phosphine ligand, which are bonded in a *cis* position to each other. The compound crystallizes in the triclinic system with an average Cr-P bond length of 2.3509Å and average Cr-CO bond length of 1.8895Å. Melting point test is also used to determine the melting point of both crystals with A1 at 185°C and A2 at 182°C.

ABSTRAK

Objektif kajian ini ialah untuk mensintesis sebatian baru menerusi proses penukargantian. Ligan karbonil pada complex kromium karbonyl akan digantikan dengan yang ligan yang berbeza dan ini akan menghasilkan sebatian monokristal organologam yang baru. Struktur kristal sebatian baru ini akan ditentukan diikuti dengan sifat fizikal dan kimianya. Derivatif Kromium karbonil akan disediakan menerusi tindak balas dengan beberapa ligan kompleks kumpulan 15 yang mempunyai potensi untuk menghasilkan sebatian organologam baru. Lima ligan yang digunakan ialah: Etilenabis difenil-arsina; P-bromofenildfenilfosfena; Bis(difenilfosfino)heksana; Bis(difenilfosfino)pentana; dan Trifenilarsina. Tindakbalas penggantian menggunakan Etilenabis difenil-arsina dan P-bromofenildfenillfosfena masing-masing menghasilkan pembentukan kristal melekit berwarna kuning pucat, dan kristal halus berwarna kuning cerah. Spektroskopi inframerah dan resonans magnetik nuklear (NMR) melengkapkan lagi keputusan analisis pembelauan X-Ray monokristal yang memberi struktur kristal baru yang dihasilkan sebagai [cis-1,2-bis (difenilarsenil)etana] tetrakarbonilkhromium dengan formula molekul $Cr_4(C_{26}H_{24}As_2)$, diberi anotasi A1 dan trans-bis[(4-bromofenildifenil)fosfena]tetrakarbonilkhromium dengan formula molekul $Cr(CO)_4(P_2C_{36}H_{28}Br_2)$ yang diberi anotasi A2. Bagi struktur kristal A1, atom Cr dikoordinasikan dalam susunan oktahedral oleh empat ligan karbonil dan satu ligan arsenik bidentate tunggal, yang terikat dalam kedudukan yang *trans* antara satu sama lain. Sebatian kristal terbentuk dalam system ortorombik dengan purata panjang ikatan Cr-As bernilai 2.44865Å dan purata panjang ikatan Cr-CO bernilai 1.86975Å. Bagi struktur kristal A2, atom Cr dikoordinasikan dalam susunan oktahedral oleh empat ligan karbonil dan dua ligan fosfina tertiari monodentate, yang terikat dalam kedudukan yang *cis* antara satu sama lain. Sebatian kristal ini terbentuk dalam sistem triklinik dengan purata panjang ikatan Cr-P bernilai 2.3509Å dan purata panjang ikatan Cr-CO bernilai 1.8895Å. Ujian takat didih juga dijalankan untuk menentukan takat didih kristal A1 iaitu 185°C dan kristal A2 iaitu 182°C.

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LIST OF SYMBOLS

π	Pi orbital
Oh	Octahedral coordination complex
D2h	Rhombic coordination complex
D3h	Trigonal coordination complex
D4h	Tetragonal coordination complex
T_d	Tetrahedron coordination complex
C_{4v}	Square Pyramidal coordination complex
R_f	Retention factor
H_0	Static magnetic field
Å	Angstrom
°	Degree
λ	Lamda

LIST OF ABBRIVIATIONS

DCM	Dichloromethane
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
FTIR	Fourier Transform infrared
IUCr	International Union of Crystallography
IR	Infrared
MAO	Methyllaluminoxane
MP	Melting point
NMR	Nuclear magnetic resonance
ppm	Parts per million
RF	Radio frequency
TLC	Thin layer chromatography
TOA	Thermo-optical analysis
USM	Universiti Sains Malaysia
UV	Ultra violet
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

This research project is conducted within the framework of a final year project. The completion of this project is compulsory in graduating with a Bachelors Degree in Industrial Chemistry from University Malaysia Pahang.

The title of this research is “Synthesis, Characterization and Structure Determination of Novel Chromium Hexacarbonyl Derivatives *via* Substitution With Various Group 15 Complex Ligands (L) where L = Ethylenebis diphenyl-arsine, P-bromophenyldiphenylphosphane, Bis(diphenylphosphino)hexane, Bis(diphenylphosphino)pentane, and Triphenylarsine”. It comprises of three main parts which is the synthesis process of obtaining a stable novel crystals through substitution of group 15 complex ligands with carbonyl ligands of chromium hexacarbonyl; characterization, determining the properties of the crystals using various analysis like infrared spectroscopy, nuclear magnetic resonance spectroscopy and melting point test; and structure determination, using X-ray diffraction analysis to determine the structure of the crystals obtained.

1.2 BACKGROUND

Transition-metal organometallic chemistry has seen enormous growth, in both coordination chemistry scientific discipline and as a subject for research in industry since the past 50 years. Since 1950, the discovery of organometallic with a single-centre transition metal compound like Zeise's salt, Grignard reagent, and Ziegler Natta catalyst provides the importance in the underlying science for homogeneous catalysis and the coordination polymerization of olefins, hence organometallic chemistry has grew to become a significant industrial discipline.

In the 1980's, transition-metal organometallic chemistry contributed to almost 23 billion dollars to the U.S. economy in terms of industrial processes based on organometallic chemistry and homogeneous catalysis (Parshall and Putscher, 1986). 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 products for the electronics and health care industries. This paved the way for novel disciplines underlying research such as molecular genetics and nonlinear optics in industry.

We have witnessed that as the industry diversifies, its boundaries with the electronics and pharmaceutical industries have become indistinct. The enterprising organometallic chemist shall find rewarding opportunities to contribute in these areas. For example, the electronics industry makes extensive use of organometallics in vapour deposition of semiconductor materials. Most of the major chemical companies are now developing materials for use in the electronics industry as well as in other industries. Much current research deals with materials that have specific electronic, biological, or chemical properties. The synthesis of these functional materials presents many interesting challenges to the organometallic chemist.

Given its contribution towards catalytic activity, the solid state approach further amplifies the interests of our research theme: 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. Although the solid state application is the highlight of this research, sustained research in homogeneous catalysis that would reside on 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 would also perform as a benefit of fundamental science in organometallic chemistry field.

Thus, in conclusion, 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. The abnormalities and the fact that such structures are not commonly found can be related microscopically to the combination of metal and carbon within the structure. There is a repositioning of molecules to stabilize and overcome stearic effects and π-backbonding. All this relates to the expanding of materials diversity and given its abnormalities, become possible benchmark of the special future materials.

1.3 PROBLEM STATEMENT

The synthesis process is conducted *via* ligand substitution. The question arises from the ability of various ligands to substitute and stabilize as chromium hexacarbonyl derivatives.

Other than that, the chromium hexacarbonyl precursor presents certain properties that give its specific function. The issue at present is will the synthesized novel derivatives present different properties, and will these properties lead toward a better or more interesting function in both solid state application and also intermediate product for industry. However, within the content of this research project, the quest is narrowed to the determination of the crystal structure and this greater thought will be reserved as a future research.

1.4 SCOPE OF STUDY

The objectives of this study includes: to synthesize a novel organometallic monocrystal compound; to describe the physical and chemical properties of the novel compound; and to conduct structure determination of the novel compound. Based on the objectives, the scopes of this study have been identified to consist of three main parts. The first scope will be on the synthesis of chromium hexacarbonyl derivatives through substitution of carbonyl ligand with group 15 complex ligands. The aspired final product is a novel compound that will be published in an international level journal. Total of five ligands used in this experiment are Ethylenebis diphenyl-arsine, P-bromophenyldiphenylphosphane, Bis (diphenylphosphino) hexane, Bis (diphenylphosphino) pentane, and Triphenyl arsine. This particular ligand was chosen as the substitution would lead to the discovery of novel compound, and those ligands are the most likely to be able to stabilize.

The second scope includes investigating the physical and chemical properties of the novel compounds using infrared spectroscopy, nuclear magnetic resonance spectroscopy and melting point test. This would give the information on the physical and chemical properties of the crystals and may provide important data to establish the idea on the level of stability achieved by each crystal.

The last scope of study is on the structure determination of novel derived compounds using X-ray diffraction (XRD). This scope is important as it is a qualitative analysis in order to determine the intended crystal structures of the compounds are achieved.

The structure of this thesis is comprised of six main parts. Part 1 presents the introduction, background of study, problem statement and scope of study. Part 2 highlights the literature review, background information from closely related report that leads to conducting this research. Part 3 comprise of the methodology used and Part 4 explains the results and observations of the research. Part 5 includes the overall discussion of the research that is targeted to answer all the objectives and research questions pertaining to this research. Lastly Part 6 concludes and gives a summary as regards to this research.

CHAPTER 2

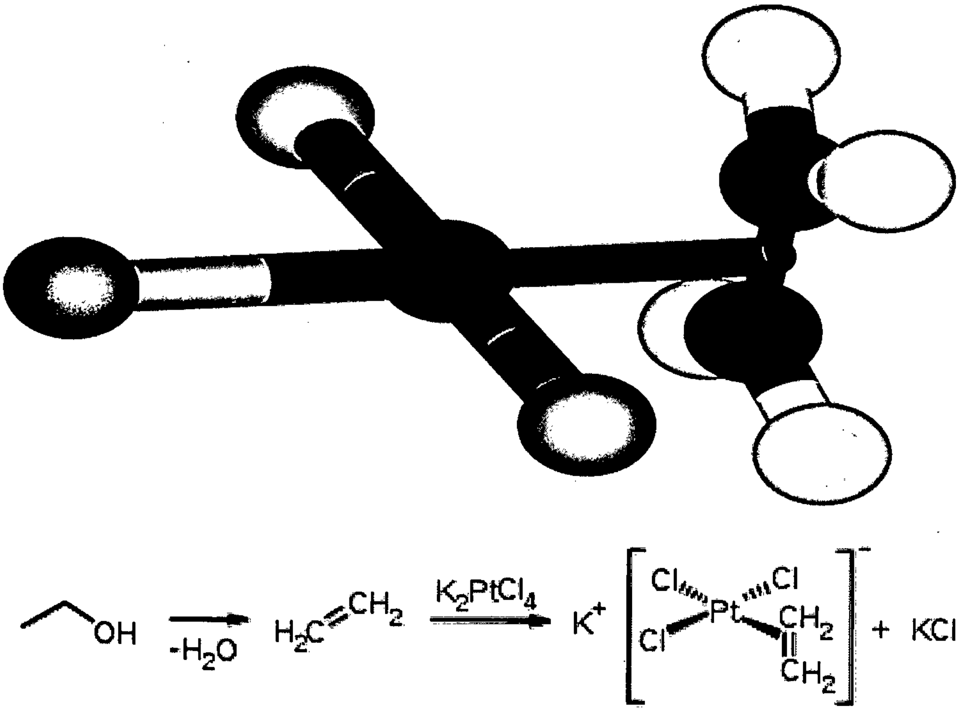
LITERATURE REVIEW

2.1 ORGANOMETALLIC

Organometallic chemistry is the study of chemical compounds containing bonds between carbon and a metal. Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry (Toreki, 2003; Crabtree, 2005). However, several differences in these aspects have made the study in this area more exciting. For example, the atomistic coordination of these compounds is based in general on the inorganic part of chemistry yet the physical property resembles many organic compounds.

The organotransition metal, which is a subset of this study, is a more specific area of organometallic chemistry. It involves at least one bonding of a transition metal and a carbon atom. This area emphasizes more to take advantage of the properties of the transition metal which has the ability to change oxidation state or, in the case of the metals, to adsorb other substances on to theirs. Other aspects that would determine the properties of an organometallic are the type of carbon-metal bonds. The main type of bonding includes; covalent bonds, in which pairs of electrons are shared between atoms; multicentre covalent bonds (cluster compound), in which the bonding involves more than two atoms; and ionic bonds, in which the bonding electron pair is donated by only one atom.

Along the road from the discovery to its prominence, the study of organometallics has exposed several incredible milestones especially in terms of its application. In 1760, in a Parisian military pharmacy, a French chemist L.C. Cadet attempted to make invisible ink. He used cobalt minerals which contained arsine salts. Unintentionally he produced a vile smelling liquid which was later to be named dicacodyl. This discovery sparks the birth of organometallics that was later on made famous by the first synthetic organometallic compound, $K[PtCl_3(C_2H_4)]$ as shown in Figure 2.1, prepared by the Danish pharmacist William C. Zeise in 1827 and nowadays is often referred to as Zeise's salt (Zeise, 1831).



(2.1)

Figure 2.1: Lewis structure and synthesis equation of Zeise’s salt

During 1894, Edward Frankland was responsible in the making of organometallics as a proper branch of chemistry when he first synthesized organozinc compounds by treating organohalides with zinc metal. He was actually attempting to prepare ethyl radical but instead prepared diethylzinc (Seyferth, 2001) as illustrated in Figure 2.2.

$$2EtI + Zn \longrightarrow ZnI_2 + 2Et\cdot \qquad (2.2)$$

Did not work instead it was

$$2EtI + 2Zn \longrightarrow Et_2Zn + ZnI_2 \qquad (2.3)$$

Figure 2.2: Edward Frankland attempts to prepare ethyl radical

Later on, organometallics have seen tremendous milestones in research, such as the new discovery by Charles Friedel and James Crafts in the preparation of organochlorosilanes; Ludwig Mond who discovers $Ni(CO)_4$ (first organometallic carbonyl compound); the modern ideas of coordination chemistry by Alfred Werner and many more (Erin and Paula, 2001). Of all the interesting discoveries, the most significant finding was the discovery of Grignard Reagent, an important tool for the formation of carbon–carbon bonds inorganic compound synthesis by Victor Grignard and Paul Sabatier (Huryn, 1991). Then there is the Ziegler and Natta development in olefin polymerization at low pressure using mixed metal catalysts (transition metal halides / AlR_3) (Kissin, 2008). The importance in corresponding applications of these organometallic compounds was so immense that both discoverers were awarded with a Noble Prize.

2.2 METAL CARBONYL

Metal carbonyls are a subset of organometallic compounds that are formed through coordination complexes of transition metals with carbon monoxide ligands.

Simple substances of transition metals have properties characteristic of metals, *i.e.* they are hard, good conductors of heat and electricity, and melt and evaporate at high temperatures. Transition metals have incomplete *d* or *f* shells in the neutral or cationic states. This lets the transition metal adopt multiple oxidation states, the basis that enables it to form complexes, and coordinate with more than a single ligand. The concept of the formation of a coordinate bond between ligands and a central metal was proposed by A. Werner which became the basis for the development of the chemistry of complexes (Bowman-James, 2005).

In relation to the development of transition metal carbonyls through organometallic chemistry, although an ethylene complex of platinum called Zeise's salt, $K[PtCl_3(C_2H_4)]$, tetracarbonylnickel, $Ni(CO)_4$, and pentacarbonyliron, $Fe(CO)_5$ were prepared in the 19th century, their bonding and structures were unknown. The research of W. Hieber and others on metal carbonyl compounds was important in the 1930s, but the results of these studies were limited because of the underdeveloped techniques of structural analyses available at the time. Hence, the discovery of ferrocene, $Fe(C_5H_5)_2$, in 1951 was epoch-making for the chemistry of this field (Kealy and Pauson, 1951). The very unique bonding mode of this complex became clear by means of single crystal X-ray structural analysis, NMR spectra, infrared spectra, *etc.*, and served as a starting point for subsequent developments in the field. It was a major discovery that ferrocene exhibited very high thermal stability in spite of the general view that the transition metal-carbon bonds were very unstable, hence organotransition metal compounds such as oxides, sulfides, and halides of transition metals are used in the most active research areas in modern inorganic chemistry.

Metal carbonyl complexes may be homoleptic, that is containing only CO ligands, such as nickel carbonyl $Ni(CO)_4$, but more commonly metal carbonyls contain a mix of ligands (Elschenbroich, 2006). Binary metal carbonyl compounds that consist only of a metal and CO ligands are usually prepared by the direct reaction of the powder of a highly reactive metal and carbon monoxide, or by the reduction of a metal salt to zero valance followed by reaction with high-pressure carbon monoxide. However, tetracarbonylnickel, first discovered at the end of the 19th century, formed by the reaction of nickel metal and carbon monoxide under atmospheric pressure and at room temperature. Mond, the founder of ICI was the person that produced a colourless liquid with CO and Nickel. The isolated substance was heavy, colourless, boiled at 34 °C and easily decomposed when heated leaving pure nickel. Experimentally it was found that there were 4 CO atoms per Nickel atom. Hence the first metal carbonyl compound formed was notably $Ni(CO)_4$ (Mond, Langer and Quincke, 1890). Such a reaction was to prove a gold mine for Mond as the process could be used to make high purity Nickel.

2.2.1 CHROMIUM CARBONYL

Chromium carbonyl, also known as chromium hexacarbonyl, is the chemical compound with the formula $Cr(CO)_6$. At room temperature the solid is stable to air, although it does have a high vapor pressure and sublimes readily. $Cr(CO)_6$ is zerovalent, meaning that Cr has a formal charge of zero, and it is called a homoleptic complex, which means that all the ligands are the same. Chromium hexacarbonyl is a mononuclear metal carbonyl compounds that takes a highly symmetric octahedral coordination structures, similar molybdenum, and tungsten hexacarbonyl, $M(CO)_6$ (Whitaker and Jeffery, 1967). The carbon atoms of carbonyl ligands coordinate to the metal, and the CO moieties are oriented along the direction of the metal-carbon axis as shown in Figure 2.3 below.

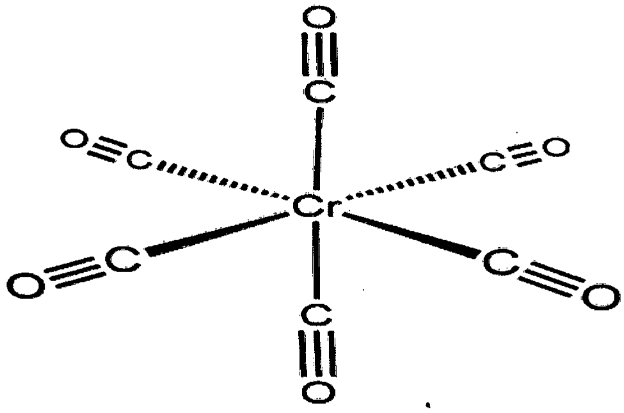


Figure 2.3: Structure of Chromium Hexacarbonyl

The carbon monoxide ligand in chromium hexacarbonyl is coordinated to a zero valent metal. For a long time, it had been unclear why such bonding was possible, let alone stable at all. The belief that normal coordination bonds were formed by the donation of electrons from highly basic ligands to a metal formed the basis of the coordination theory by A. Werner (Bowman-James, 2005). Stability of metal carbonyl compounds was sought based on the knowledge that the basicity of carbon monoxide is very low and transition metal-carbon bonds are generally not very stable. If the shape and symmetry of the metal *d* orbital and of the CO π (antibonding) orbital for the carbon-oxygen bond are suitable for overlap, a bonding interaction between the metal and carbon is expected. The bonding scheme shown in below was proposed from this point of view. The mechanism by which electrons are donated to the vacant carbon monoxide π^*-orbital from the filled metal *d* orbital is called back-bonding. Since accumulation of superfluous electrons on a low oxidation state metal atom is prevented, back-bonding leads to the stabilization of the M-C bond.

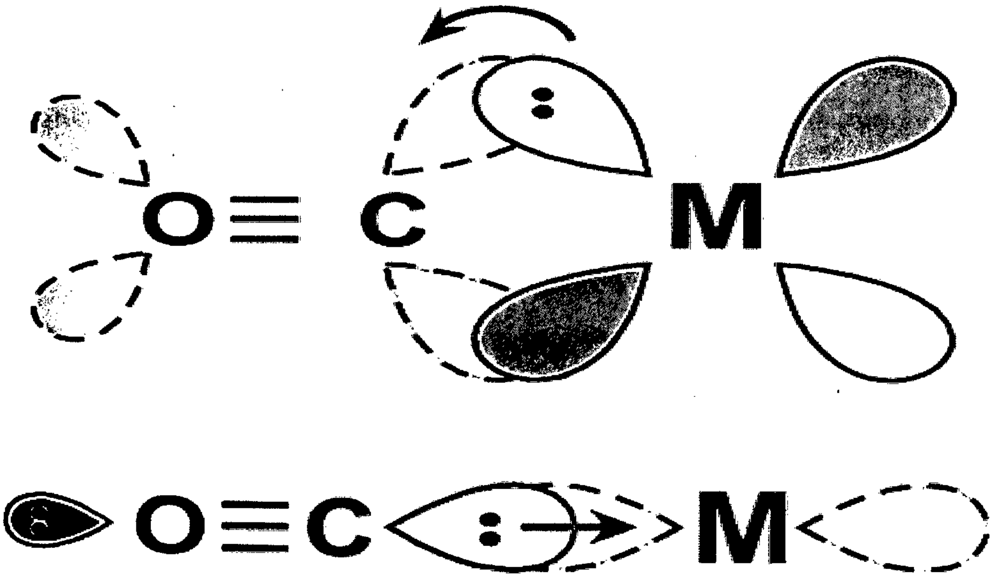


Figure 2.4: Illustration of metal to carbon bonding in $Cr(CO)_6$

Adapted from: Stanley (2008)

In 1926, the first technique used to synthesized chromium hexacarbonyl was developed by Job and Cassal. A small amount of chromium hexacarbonyl is prepared from phenylmagnesium bromide and chromic chloride in the presence of carbon monoxide at atmospheric pressure (Job and Cassal 1926). They obtained yields of 14 % or less, and this unsatisfactory conversion was confirmed by others (Windsor and Blanchaid, 1934). In 1940, the same reaction was carried out by K.N.Anissimov and A.N. Nesmeyanov, at 115 atm and reported yields as high as 22 % (Anissimov and Nesmeyanov, 1940). This conversion was still considered to be unsatisfactory. Hence, B.B Owen et al. directed an effort toward increasing the yields obtained in 1947 by actually using the same method but with the given name of "Grignard method". It produces yields of 67 % at 50 atm, and 24 % at 1 atm (Owen, James English, Cassidy and Dundon, 1947). The success of this trial was rather unexceptional because it was conducted through a known method rather than toward discovering new reactions or investigating the mechanism of old ones.

On 6th June 1957, G. Natta, R. Ercoli and F. Calderazzo reported a new synthesis of chromium hexacarbonyl starting from easily available chromium compounds which appeared to have been converted for the first time, into the hexacarbonyl. Based on their observation, chromic acetylacetonate, chromic and chromous salts of organic acids such as acetic and 2-ethylhexanoic could be reduced easily and converted into the hexacarbonyl under high pressure of carbon monoxide if pyridine or related bases are employed as a reaction medium. Hence a method was devised by dissolving (or suspending) any one of the above compounds in pyridine, containing catalytic amounts of halogens or halogenated substances. The mixture is then treated at 80-170 °C with an excess of powdered magnesium or zinc and 100-300 atm. of carbon monoxide. When soluble chromium compounds are employed the yields are as high as 80-90 %. Interest in the satisfactory method in synthesis of chromium carbonyl at that time arose from an immediate need for a supply of chromium carbonyl for research purposes. This purpose was later on proved to be fruitful as chromium carbonyl and its derivatives serves a major role in catalytic activity in industries nowadays.