



SYNTHESIS AND CHARACTERIZATION OF NOVEL ORGANOMETALLIC
CHROMIUM HEXACARBONYL DERIVATIVES VIA LIGAND (L)
SUBSTITUTION, WHERE L = TRIS(3-METHYLPHENYL)ARSINE,
TRIS(M-FLUOROPHENYL)PHOSPHINE AND
TRIS[3,5-BIS(TRIFLUOROMETHYL)PHENYL]PHOSPHINE

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ABSTRACT

The aim of the research study is to substitute the carbonyl ligand on chromium complexes in order to result in novel organometallic monocrystal compounds for crystal structure elucidation followed by physical and chemical characterization. Derivatives of Chromium Carbonyl are prepared by reaction with a number of tertiary phosphines and arsenic ligands which have the potential to result in novel organometallic compounds. Three different ligands were used to produce novel organometallic monocrystal compounds which are Tris(3-methylphenyl)Arsine, Tris(m-fluorophenyl)Phosphine, and Tris[3,5-bis(trifluoromethyl)phenyl]Phosphine. Of these, the substitution reaction using Tris(m-fluorophenyl)Phosphine resulted in the formation of crystals with pale yellow colour. Monocrystal x-ray diffraction on a resulted in the novel crystal structure determined as trans-Tetracarbonylbis[tris(3-fluorophenyl)phosphane]chromium(0) with molecular formula $\text{Cr}(\text{C}_{18}\text{H}_{12}\text{F}_3\text{P})_2(\text{CO})_4$. Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR) further compliment the X-ray diffraction results. In this novel structure, the Cr atom is octahedrally coordinated by four carbonyl ligands and two tertiary phosphanes, which are located *trans* to each other with a fluorine atom in the meta-position on each phenyl ring. The compound crystallises in the monoclinic system with space group $\text{P2}_1/\text{c}$ and with an average Cr-P bond length of 2.3327 Å and average Cr-CO bond length of 1.8869 Å. This final year project meets international standards and led to an International Union of Crystallography (IUCr) journal publication, specifically in Acta Crystallographica Section E; (2011) with the title trans-Tetracarbonylbis[tris(3-fluorophenyl) phosphane]chromium(0).

ABSTRAK

Tujuan kajian adalah untuk menggantikan ligan karbonil pada kompleks kromium karbonil untuk menghasilkan sebatian organologam yang baru dengan perincian struktur kristal dan diikuti dengan pencirian secara fizikal dan kimia. Derivatif kromium karbonil disediakan melalui tindakbalas dengan beberapa jenis ligan fosfina dan arsenik yang mempunyai potensi untuk menghasilkan sebatian organologam yang baru. Tiga jenis ligan yang berbeza telah digunakan untuk cubaan menghasilkan sebatian organologam yang baru iaitu Tris(3-metilfenil)Arsina, Tris(m-fluorofenil)Fosfina, dan Tris[3,5-bis(trifluorometil)fenil]Fosfina. Hasil percubaan ini, tindakbalas penggantian menggunakan Tris(m-fluorofenil)Fosfina menghasilkan pembentukan kristal dengan warna kuning pucat. Melalui pembelauan sinar-x, sebatian kristal yang baru dikenalpasti sebagai trans-Tetrakarbonilbis[tris(3-fluorofenil)fosfena]kromium(0) dengan formula molekul $\text{Cr}(\text{C}_{18}\text{H}_{12}\text{F}_3\text{P})_2(\text{CO})_4$. Keputusan yang diperoleh dari Spektroskopi Inframerah (IR) dan Resonan Magnet Nuklear (NMR) menyokong keputusan oleh pembelauan sinar-x. Dalam struktur baru ini, atom Cr mempunyai koordinasi enam iaitu terletak di tengah polihidren berbentuk oktahedral dikelilingi oleh empat ligan karbonil dan dua ligan fosfena, yang berkedudukan *trans* antara satu sama lain dengan atom fluorin dalam kedudukan *meta*-pada setiap fenil. Sistem kristal adalah monoklinik, kumpulan ruang $P2_1/c$ dengan purata panjang ikatan Cr-P 2.3327 Å dan purata panjang ikatan Cr-CO 1.8869 Å. Projek tahun akhir ini bertaraf antarabangsa yang membawa kepada penerbitan jurnal Kesatuan Antarabangsa Kristalografi (IUCr), Akta Kristalografi Seksyen E (2011) dengan tajuk trans-Tetrakarbonilbis[tris(3-fluorofenil)fosfena]kromium(0).

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LIST OF SYMBOLS

Π	Pi
R_f	Retention Factor
\AA	Angstrom
$V_{(CO)}$	Vibrational Frequency

LIST OF ABBREVIATIONS

TLC	Thin Layer Chromatography
IR	Infrared Spectroscopy
FTIR	Fourier transform infrared
NMR	Nuclear Magnetic Resonance
XRD	X-ray Diffractometer
UV	Ultra Violet
DCM	Dichlorormethane
Ppm	Part per million
IUC	The International Union of Crystallography
mg	Milligram
mL	Millilitre
ppm	part per million

CHAPTER 1

INTRODUCTION

1.1 Introduction

This thesis is submitted in partial fulfilment of the requirements for the award of the Degree of Bachelor of Applied Science (Honour) in Industrial Chemistry. The title of this thesis is Synthesis and Characterization of Novel Organometallic Chromium Carbonyl Derivatives *via* Ligand (L) Substitution, where L= Tris (3-methylphenyl) Arsine, Tris (m-fluorophenyl) Phosphine, and Tris [3, 5-bis (trifluoromethyl)-phenyl] Phosphine. All substitution of chromium carbonyl were carried out using various ligands that are chosen based on the potential to result in a novel organometallic monocrystal compound. A novel compound obtained is then put through a characterization process in order to determine its crystal structure and parameters, physical and chemical properties.

1.2 Background of Study

The synthesis and structure determination of organometallic compounds with various ligands, usually transition metal complexes, has been an active field of research in the past 50 years due to the practical uses in catalytic processes [1]. For the understanding of reaction mechanisms, we can refer to [2]-[3] and for their potential functionality as magnetic, catalytic, gas absorptive and luminescent materials, we can refer to [4]-[6]. In the 1980s, the industrial processes based on organometallic chemistry and homogeneous catalysis contributed to almost 23 billion dollars to the U.S. economy. 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 [7].

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 feedstock. We note that the type of ligand also influences the compound characteristics as a catalyst [7]. Among the various ligands, tertiary phosphines, PR_3 , that substitute the metal carbonyl complexes are generally very well known [8] and among the most utilized group of ligands in transition metal chemistry, due to the ease with which the steric and electronic properties of phosphine ligands are controlled [9]. On the other hand, diphosphane ligands are an important class of ligands in organometallic chemistry and have found wide applications, especially in catalytic reactions [10]-[13]. Thus, co-ordination chemistry of such ligands (phospine) proves an interesting area of study.

We have witnessed that as the industry has diversified 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 developing materials for use in the electronics industry as well as in other applications in which a specific function imparts high value to a product. 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. Here, the amount of material required for a specific application may be minute, but the value-in-use may be highly extreme. [7]

In the case of ceramics, for example, silicon carbide, silicon nitride, and aluminum nitride are potentially superior in various applications but have proven extraordinarily difficult to fabricate. A promising approach to the production of shaped objects of these materials is the production of preceramic polymers. These materials such as polycarbosilanes which contain $[\text{Si}(\text{H})(\text{CH}_3)\text{CH}_2]_n$ units, can be fabricated by conventional polymer-forming methods but are subsequently pyrolyzed to ceramic objects that retain the shape of the preceramic polymer. [7]

It is this solid state approach that interests the author: 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 [7].

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.

1.3 Problem Statement

There have been extensive studies about transition metal carbonyl group 15 ligands. Metal carbonyls are coordination complexes of transition metals with carbon monoxide ligands [14]. These complexes may be homoleptic. Homoleptic is a metal compound with all ligands identical [15], such in this case Cr containing only CO ligands, $\text{Cr}(\text{CO})_6$. Bond between carbon monoxide to transition metal is π backbonding [14]. π backbonding is a when electrons move from an atomic orbital on one atom to a π^* anti-bonding orbital on another atom or ligand [16].

The bonding in metal carbonyl has three components, giving rise to a partial triple bond. A sigma bond arises from overlap of non-bonding electron pair on carbon with a blend of d-, s-, and p-orbitals on the metal. A pair of π bonds arises from overlap of filled d-orbitals on the metal with a pair of π -antibonding orbital projecting from the carbon of the CO. [14]

The ability of the ligands on a metal to donate electron density to the central metal has considerable effect on the absolute amount of electron density on that metal. By using different ligands, this in turn naturally affects the stretching frequencies in metal carbonyl. The single crystal X-ray studies will give substantial information on the structural geometry (bond angle, bond length) and should enable us to make a more extensive comparison on the changes in the molecular geometries resulting from substitution of CO by different ligands.

Thus, by taking all these into consideration, and also π backbonding, we should see how these will affect the formation of novel organometallic compound in aspect of stability of ligand and stabilization of chromium carbonyl after ligand substitution. This novel organometallic compound should, it is aspired, lead to a material with interesting novel properties that may perhaps present potential application.

1.4 Objective of Study

Since the last 20 decades, there has been extensive research in the field of transition metal organometallics that have contributed to many applications in various industries. However, there lacks substantial explanations regarding observations of compounds in this field compared to other fields in chemistry. Small amount of reference prove there is still a lot room for research and new knowledge discovery. Thus, the main objective in this research study is the exploration of possible novel organometallic compounds, specifically chromium hexacarbonyl derivatives and their possible properties as potential industrial applications.

Within the framework of this objective, there are three sub-objectives in this research study. Firstly is to synthesize a novel organometallic monocrystal compound. This is important as the second and third sub-objectives of this research study can only be achieved if the first is successful. Secondly is to characterize using X-ray diffraction in order to elucidate the structure of the novel organometallic monocrystal compound. Thirdly is to characterize the physical and chemical properties of the novel compound.

Thus through these three objectives, hopefully this work will contribute to an extension of knowledge in this field of study. Furthermore this field of organometallic chemistry has great potential in application and should continue to contribute to various industries. A good example is when Louis Claude Cadet de Gassicourt, a French chemist who synthesized the first organometallic compound, investigated ink based on cobalt salts and instead isolated Cacodyl (IUPAC name, tetramethyldiarsine) from cobalt mineral containing arsenic in 1760. [1]

1.5 Scope of Study

1.5.1 Compounds

The main compound that I am dealing with within the framework of this research project is Chromium Hexacarbonyl, $\text{Cr}(\text{CO})_6$. This shall be the parent compound for the substitution reactions. It is solid at room temperature and stable in air, has a high vapor pressure and sublimates readily. This makes this compound easy

to handle. Other factors are $\text{Cr}(\text{CO})_6$ has a zero formal charge and all the carbonyl ligands surrounding the central chromium atom are identical [35]. Thus, this increases the possibility of substitution reaction occur.

Three different ligands were chosen to undergo substitution reaction based on the apparent possibility to result in a novel organometallic compound. There are two phosphine ligands and one arsenic ligand that been used in this research project which are Tris (3-methylphenyl) Arsine, Tris (m-fluorophenyl) Phosphine and Tris [3, 5-bis (trifluoromethyl)-phenyl] Phosphine. Other factors that are considered in order to synthesize a novel organometallic monocrystal compound include their density, electronic effect and cone angle (size/bulk).

1.5.2 Thesis Structure

The scope of this thesis covers three main parts which are literature review, research work and results and discussion. The first part of this thesis will focus on an introduction to the study and a overview of some related literature. This is the ground work where all the information related is revised and explored in order to master the research project.

Second part of this thesis is the laboratory research work, namely the experimentation covering all synthesis and characterisation. This comprises experimental attempts to synthesize a novel organometallic monocrystal compound via ligand substitution. The synthesis process comprises several techniques such as use of the Schlenk Line, Thin Layer Chromatography (TLC), Column Chromatography, and Recrystallization Technique. Characterization processes need to be carried out only on chromium hexacarbonyl derivatives which show positive synthesis, namely successful substitution of the carbonyl group by another ligand. The successful product from the synthesis process will be characterized using IR Spectroscopy (IR), Nuclear Magnetic Resonance (NMR) and single crystal X-Ray Diffractometer (XRD).

The third part of this thesis covers the results and discussion. This part presents all the results from the synthesis and characterization process. In this section, all graphs, diagrams and data from IR, NMR and XRD shall be presented. Each result will be the subject of discussion and some elaboration on observations.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Since this research project deals with organo-transition-metal compounds, this section presents all related subject matter including several findings in the past decades and scientists who have contributed in this area of study. At the end of this chapter, trends related to studies in this area are summarized and presented thus allowing the author to also present the direction and approach that the author adopts in the exploration of these chromium hexacarbonyl derivatives.

2.2 Organometallic and Organometallic Transition Metal

2.2.1 Organometallic

Organometallics grew out of exchange between organic and inorganic chemistry. These chemical compounds contain bonds between carbon and a metal centre [1]. Generally, the character of the metal-carbon bond in organometallic compounds is intermediate between ionic and covalent and this is very important to the industry due to its relatively stability in solution and relative ionic character

which allows it to undergo numerous reactions for example organolithium and Grignard Reagents [1].

The 18-electron rule is an important concept in organometallic chemistry. The 18-electron rule is useful in predicting formulas and the stabilities of metal complexes [1]. It is said to have achieved the same electron configuration as the noble gas, when a metal complex has 18 valence electrons. The 18-electron rule is similar to the application of the octet rule [18]. The total number of valence electron results can be calculated by adding up the total number of electrons donated from all ligands to the formal d electron configuration [19].

Cadet's fuming liquid was the first organometallic compound synthesized by the French chemist, Louis Claude Cadet de Gassicourt in 1760. It is there that Cadet worked on ink related research on cobalt salt solutions and he used cobalt minerals that contained arsenic for the preparation [20].

In 1849, Sir Edward Frankland discovered 'ethyl radical' or diethylzinc. He is the pioneer and inventor of the term 'organometallic' and concept of valency 'combining power'. He also prepared the important alkylmercury. Alkyl-transfer reaction with R_2Hg and R_2Zn serve in the synthesis of numerous main-group organometallic compounds in the following years. [21]

Main group organometallics are normally dealt largely with stoichiometric reagents. Case in point, tetraethyllead was well-established as an antiknock agent/gasoline additive, tin compounds were used as stabilizers for polyvinyl chloride, and arsenic derivatives were used in medical and agricultural applications [7].

2.2.2 Organometallic Transition Metal

The Organometallic Transition Metal area is a sub-study to organometallic chemistry. Organometallic Transition Metal science is related to compounds which have an organic bond through metal carbon bond [19]. Hence, organometallic transition metals are also called metal carbonyls. Metal carbonyl is also described as coordination complexes of transition metals with carbon monoxide as ligands [14]. These complexes may be homoleptic. Homoleptic is a metal compound with all ligands identical [15], such as, Cr containing only CO ligands, $Cr(CO)_6$.

Since the organotransition metal area is a sub-study to the organometal area, the concepts used in organometallics are also used in metal carbonyl, for example the 18-electron rule concept. Stable, diamagnetic, mononuclear organotransition metal complexes always have nine valence orbitals and contain 18 or fewer valence electron. The number of valence electron can be used to predict the geometry of organometallic complexes. [19]

Other concepts used include the *pi* backbonding. *Pi* backbonding (figure 2.1) is a description of the bonding of π -conjugated ligands to a transition metal which involves a donation of electrons from the filled π -orbital or lone electron pair orbital of the ligand into an empty orbital of the metal, together with release (back donation) of electrons from an *nd* orbital of the metal into the empty π^* -antibonding orbital of the ligand [22]. Bond order will be affected by this phenomenon and will lead to vibrational frequency of the bond [23].

In 1868, the first metal-carbonyl complex was synthesized by Paul Schützenberger. The synthesis of heteroleptic metal carbonyl complex was performed by passing chlorine and carbon monoxide over platinum black resulted in the formation of Dicarbonyl dichloro platinum ($\text{Pt}(\text{CO})_2\text{Cl}_2$) [21].

Nickel Tetracarbonyl ($\text{Ni}(\text{CO})_4$) was the first binary metal carbonyl complex, discovered by Ludwig Mond and his co-workers in 1890. It is the first pure homoleptic metal carbonyl and used in a commercial process for refining nickel [21].

Organometallics are normally stoichiometric reagents and it is different with organometallic transition metals which have various types of applications, typically as a catalyst [24]. Having laid the basis for superior homogeneous catalytic processes with these novel organometallic catalysts, the American chemical industry grew in 1950s [7].

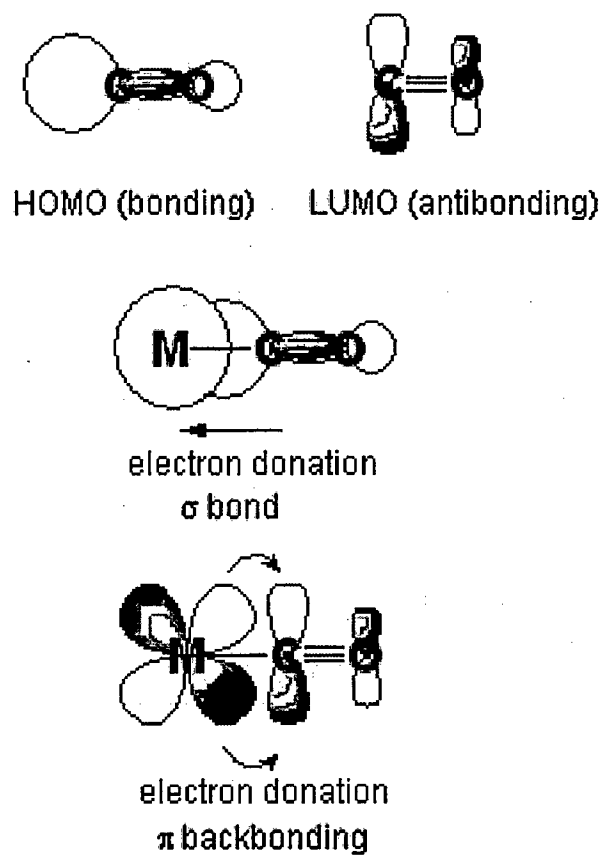


Figure 2.1: Description of pi backbonding

2.3 Chromium Carbonyl, Ligands and Substitution Reactions

2.3.1 Chromium Carbonyl

As has been stated before, metal carbonyls are coordination complexes of transition metals with carbon monoxide ligands [14] and organometallics that deal with chromium to carbon bond and their reaction state as an organochromium [25]. With chromium carbonyl as parent compound in this research study, this work has been classified within the framework of organochromium and metal carbonyl.

Chromium carbonyl, also known as chromium hexacarbonyl, is the chemical compound with the formula $\text{Cr}(\text{CO})_6$ (figure 2.2). At room temperature the solid is stable in air, has a high vapour pressure and sublimes readily. $\text{Cr}(\text{CO})_6$ 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 identical. Distances Cr-C and C-O are 1.91 Å and 1.14 Å with an octahedral geometrical coordination. Safety measures need to be practiced since chromium hexacarbonyl is toxic and thought to be carcinogenic. The vapour pressure is relatively high for a metal complex, 1 mm Hg (36 °C). [35]

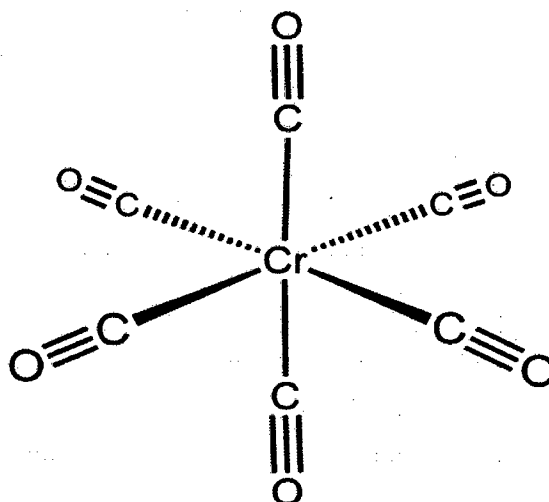


Figure 2.2: Chromium Hexacarbonyl, $\text{Cr}(\text{CO})_6$

In 1926, Job and Cassal [26] were among the first who published a practical synthesis for chromium hexacarbonyl. They described a method for chromium hexacarbonyl synthesis by preparation from phenylmagnesium bromide and chromic chloride in the presence of carbon monoxide at atmospheric pressure. They obtained yields of 14% or less. Later, the yield was substantially improved by Owen and co-workers [27]. Owen and co-workers procedure led to a 60% yield of chromium hexacarbonyl by the action of carbon monoxide on phenylmagnesium bromide and chromic chloride.

2.3.2 Ligand

A ligand is an ion or molecule that binds to a central metal atom to form a coordination complex. Formal donation of one or more of the ligand's electron pairs creates the bonding between metal and ligand, and the bonding can range from covalent to ionic. Generally ligands are Lewis bases and thus typically neutral or ionic, rarely cases are known as cationic ligands. Ligands can be classified in many ways, such as based on their charge, their size (the bulkiness, it indicated by its cone angle), the identity of the coordinating atoms and the number of electrons donated to the metal (denticity or hapticity). [28]

Transition metals exhibit a pronounced tendency to form complexes with trivalent compounds of phosphorus and arsenic [19]. Tertiary phosphines are the most commonly encountered ancillary associated with organotransition-compounds. Phosphines, PR_3 , are important types of ligand because they constitute one of the few series of ligands in which electronic and steric properties can be altered in a systematic and predictable way over a very wide range by varying R, for example triphenylphosphane. The stability of phosphines is of interest to the organometallic chemist in view of their phosphine complexes $(R_3P)_nM-L$, compared to wide variety of other ligands. Phosphines are more commonly spectator than actor ligands. Ability to promote catalytic reactions is the most important property that makes this ligand as favourite. The reason may be that, as ligands of intermediate hardness and pi-acceptor power, they are able to stabilize a broad range of oxidation states. [24]