SYNTHESIS AND CHARACTERIZATION OF ORGANOTUNGSTEN COMPLEX WITH MIXED P/S LIGAND

By

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A project submitted to the Department of Chemical Science

Faculty of Science

Universiti Tunku Abdul Rahman

in partial fulfilment of the requirement for the degree of

Bachelor of Science (Hons) Chemistry

Oct 2015

ABSTRACT

The reaction is carried out between equimolar ratio of tungsten tricarbonyl complex, (mes)W(CO)$_3$ **(1)** and mixed P/S ligand, P(*o*-C$_6$H$_4$SCH$_3$)$_2$Ph, whereby they are refluxed in toluene for 18 hours under nitrogen gas flow. The reaction had led to the isolation of a chelate complex with tridentate bonding through P and S atoms, {P(*o*-C$_6$H$_4$SCH$_3$)$_2$Ph}W(CO)$_3$ **(2)**, with a percentage yield of 68%. The product is purified through column chromatography and gives light yellow crystalline solids. Complex is characterized by IR spectroscopy, ^{1}H-, ^{13}C-, and ^{31}P- NMR spectroscopy.

ABSTRAK

Tindakbalas antara (mes)W$(CO)_3$ **(1)** dengan ligan $P(o\text{-}C_6H_4SCH_3)_2Ph$ dalam nisbah setara, telah direflukskan dalam toluena selama 18 jam di bawah aliran gas nitrogen. Tindakbalas ini telah menghasilkan komplex kelat melalui ikatan dengan atom P and S, $\{P(o\text{-}C_6H_4SCH_3)_2Ph\}W(CO)_3$ **(2)**, dan mempunyai hasil peratusan sebanyak 68%. Produk ini akan ditukarkan menggunakan kromatografi turus dan memberikan pepejal berwarna kuning muda yang mempunyai ciri-ciri habur. Spektroskopi IR, ^{1}H-, ^{13}C-, dan ^{31}P- RMN akan dijalankan ke atas produk ini untuk menentukan ciri-cirinya.

ACKNOWLEDGEMENT

Firstly, I would like to take this opportunity to thank my supervisor, Dr. Ooi Mei Lee, who gave me a lot of help, advice and guidance on the research. Besides that, I would like to express my gratitude her on the time that she had spent in having frequent discussions and brain storming sessions throughout the research.

Apart from that, I sincerely thank my university, Universiti Tunku Abdul Rahman for providing the necessary instruments and a conducive environment to conduct my research. Furthermore, I am grateful towards the assistance of the lab officers of Department of Chemical Science for providing me with the necessities and advice whenever I need them.

Moreover, I would like to thank Prof. Richard Wong from Universiti Malaya for his assistance in the instrumental analysis and useful guidance in the characterisation of the complex. In addition, I would like to thank all my lab mates from D005 for their support and enlightenment along my research.

Lastly, I would like to thank my family members for their moral and physical support throughout my three years in Universiti Tunku Abdul Rahman.

DECLARATION

I hereby declare that the project report is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

TEOH LING WEI

APPROVAL SHEET

This project entitled "**SYNTHESIS AND CHARACTERIZATION OF ORGANOTUNGSTEN COMPLEX WITH MIXED P/S LIGAND**" was prepared by TEOH LING WEI and submitted in partial fulfillment of the requirements for the degree of Bachelor of Science (Hons) in Chemistry at Universiti Tunku Abdul Rahman.

Approved by:

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(Dr. Ooi Mei Lee) Date: …………………….

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PERMISSION SHEET

It is hereby certified that **TEOH LING WEI** (ID No: **12ADB06633**) has completed this final year project entitled "**SYNTHESIS AND CHARACTERIZATION OF ORGANOTUNGSTEN COMPLEX WITH MIXED P/S LIGAND**" under the supervision of Dr. Ooi Mei Lee from the Department of Chemical Science, Faculty of Science.

I hereby to give permission to the University to upload the softcopy of my final year project in pdf format into the UTAR Institutional Repository, which may be made accessible to the UTAR community and public.

Yours truly,

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(TEOH LING WEI)

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v	Stretching frequencies (cm^{-1})
δ	Bending frequencies (cm^{-1})
σ	sigma
π	pi
AR	Analytical Reagent
ATR	Attenuated Total Reflectance
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
Cr	Chromium
DIPAMP	Ethylenebis(2-methoxyphenylphenylphosphine)
fac	facial
FAB	Fast Atom Bombardment
FTIR	Fourier Transform Infrared
HSAB	Hard Soft Acid Base
M	Molar
Mn	Manganese
Mo	Molybdenum
MS	Mass Spectrometry
mer	meridian

mes	Mesitylene
NMR	Nuclear Magnetic Resonance
P	Phosphorus
Ph	Phenyl
ppm	Parts per million
PS	[*o*-(thiomethyl)phenyl]phenylphosphine
PSS	*bis*-[*o*-(thiomethyl)phenyl]phenylphosphine
Py	Pyridine
S	Sulphur
UV	Ultraviolet
W	Tungsten
Xe	Xenon

CHAPTER 1

INTRODUCTION

1.1 Organometallic chemistry: a brief history

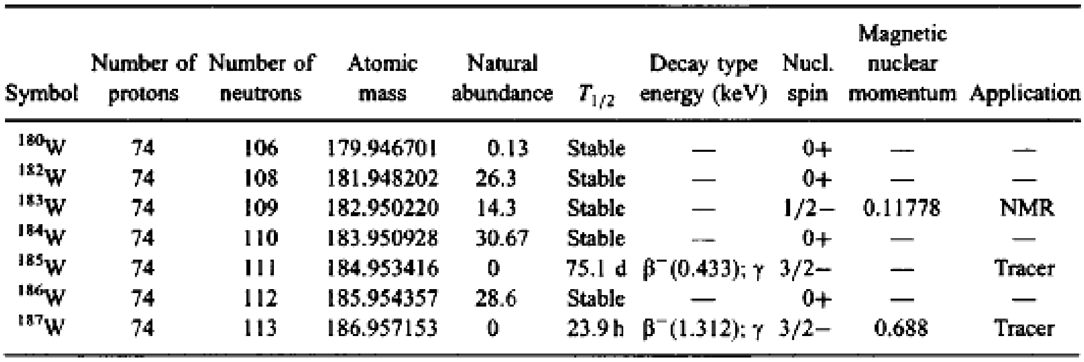
The term “Organometallic” is invented by Sir Edward Frankland in 1849, which is usually being defined as the study of chemical compounds consists of bonding between organic and metallic atoms (or compound). It all started in 1760 in a Paris military pharmacy, where the military personnel works on invisible ink prepared from cobalt minerals containing arsenic, hence giving rise to the first organometallic compound in the process. Along the years, there have been quite a number of breakthroughs and findings in this division which has its own purpose such as the medicine field (Salvarsan for treatment of syphilis), in catalysis (as catalyst) and so on. (Elschenbroich, 2006)

1.2 About the metal: tungsten

Tungsten is a metallic transition element (Lassner and Schubert, 1999) and belongs to Group 6 (VIB), located after chromium (Cr) and molybdenum (Mo). It has an atomic number of 74, and an atomic mass of $183.85 \pm 0.003 gmol^{-1}$. The symbol for tungsten is “W”, an abbreviation of wolframite, which is an important tungsten mineral ore from which tungsten is originally found. The electron configuration for a tungsten atom at its ground state is [Xe]$4f^{14}5d^{4}6s^{2}$.

Apart from that, there are thirty five known isotopes of tungsten (including isomers), but only five of them are naturally occurring ones, while others being formed artificially and are very unstable. Below is Table 1.1 (Lassner and Schubert, 1999) showing a table of information regarding some of the significant isotopes of tungsten (four naturally occurring isotopes and two artificial isotopes).

Table 1.1: Isotopes of tungsten



Symbol	Number of protons	Number of neutrons	Atomic mass	Natural abundance	$T_{1/2}$	Decay type energy (keV)	Nucl. spin	Magnetic nuclear momentum	Application
^{180}W	74	106	179.946701	0.13	Stable	—	0+	—	—
^{182}W	74	108	181.948202	26.3	Stable	—	0+	—	—
^{183}W	74	109	182.950220	14.3	Stable	—	1/2−	0.11778	NMR
^{184}W	74	110	183.950928	30.67	Stable	—	0+	—	—
^{185}W	74	111	184.953416	0	75.1 d	β^-(0.433); γ	3/2−	—	Tracer
^{186}W	74	112	185.954357	28.6	Stable	—	0+	—	—
^{187}W	74	113	186.957153	0	23.9 h	β^-(1.312); γ	3/2−	0.688	Tracer

(Lassner and Schubert, 1999. p. 2)

Like other members of transition metal, tungsten displays various oxidation states from -2 to +6, with +6 being its most common oxidation state such as in WO_3, a compound formed when tungsten metal reacts with oxygen. In general, tungsten metal can react with non-metal [1], metal [2], non-metal compounds [3], metal compounds [4], aqueous solutions [5] and so on. Some of the examples are shown in table 1.2 (Lassner and Schubert, 1999).

Table 1.2 Reaction of Tungsten metal with non-metal [1], metal [2], non-metal compounds [3], metal compounds [4], and aqueous solutions [5]

Reacting element/compound	Product(s)
Arsenic [1]	WAs_2
Beryllium [2]	WBe_{12}, WBe_{22}
Water [3]	$W(O)_2(OH)_2$
Sodium carbonate [4]	Na_2WO_4
Hydrogen peroxide solution [5]	$H_2W_3O_{12}$

1.3 Ligands and bonding

Ligand is an ion or molecule that bonds to one or more central metal atom (s) to form a complex via a coordination bond. In the field of organometallic chemistry, ligands are generally classified into two groups judging by either on the charge of the ligand or the number of electron(s) that a ligand is contributing to the metal-ligand bond (Hartwig, 2010).

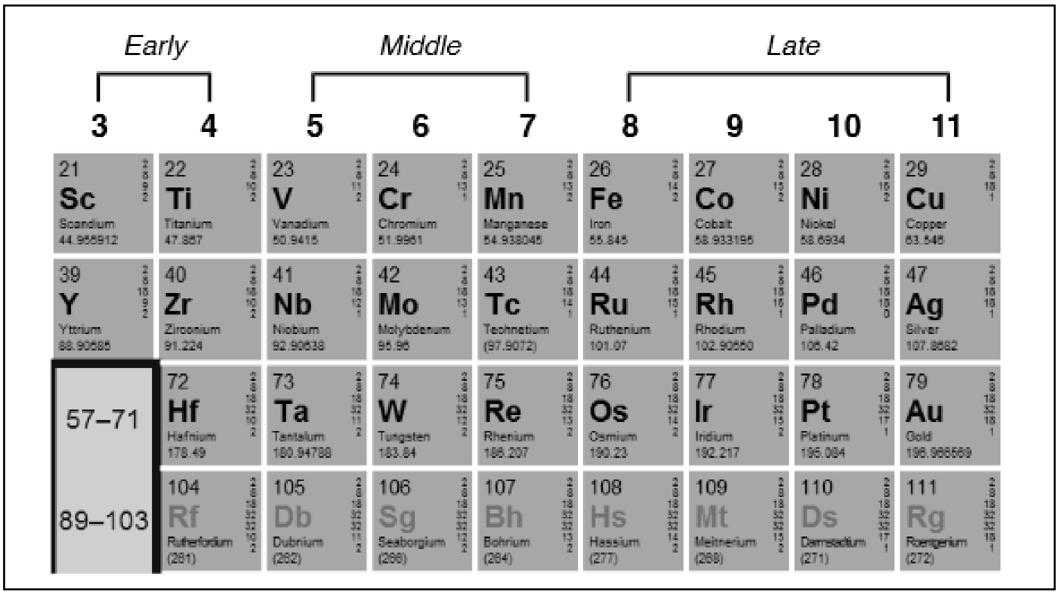
Ligands can be named and described using different terms for the same class of ligands. For example, covalent ligand is the type of ligand which forms a bond with the metal by sharing one of its electrons while the other one electron is shared from the metal. By the former method stated above, the ligand is considered to be charged (usually a negative charge would be assigned if it is the case). At the same time, judging by the number of electron that the ligand donated to the central metal atom (the second method mentioned above), the ligand can be classified as X type ligand, assuming that the ligand is neutral (Hartwig, 2010)..

On the contrary, dative ligand shares two of its electrons in the metal-ligand bond, thus it can be named as L type ligand (by the second method). Under these circumstances, the ligand is usually neutral and does not contain any charge, judging from the perspective of both methods. In addition, the types of ligand that does not fall into the above two categories (donates more than two electrons) are named as LX ligand (three-electron donors), L_2 ligand (four-electron donor) and L_2X ligand (five-electron donor) and so on (Hartwig, 2010).

1.3.1 Phosphine ligands

A phosphine ligand is one of the examples of a neutral ligand; it is bonded to the central metal atom via a dative bond using its lone pair electrons. It has a general formula of PR_3, with R being alkyl, aryl, H, halide, and so on. Since the interaction between metal center and ligand is treated as Lewis acid and Lewis base interaction, phosphine ligand (tertiary phosphine) is viewed and classified as a soft base based on the HSAB (Hard Soft Acid Base) theory introduced by Ralph Pearson, and also its affinity to form complexes with soft "acids" (metal center) especially the late transition metals. Below is a diagram showing the early, middle and late transition metals of d-block elements.

Figure 1.1: Early, Middle and Late transition metals of d-block elements



If compared to other neutral ligand such as amine, phosphine ligand is more susceptible to oxidation as it is stable to oxidation in P(V) form. Hence, less electron rich phosphine such as arylphosphine and phosphite are more air stable than the electron rich alkylphosphine.

Like most dative ligands, phosphine ligands also exhibit the properties of forming a chelating ligand by combining other donor atoms (may of same element or different) within its structure which can bind to the metal as well. If the other donor atom used is phosphorus, the ligand will be named as biphosphine, triphosphine and so on with respect to the number of phosphorus donor atom being attached within the structure. Otherwise, it will be named according to the substituent group (including donor atom) present. The resulting ligands can be bidentate, tridentate, or polydentate depending on the number of donor atoms in one ligand. Figure 1.2 shows two examples of chelating phosphine.

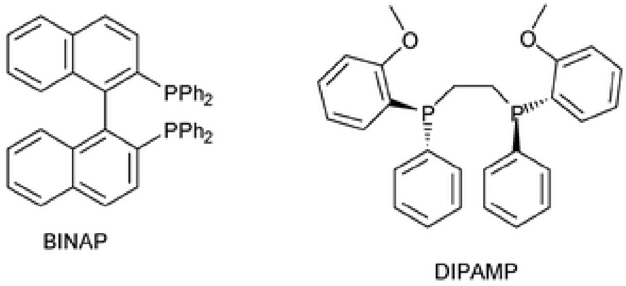


Figure 1.2: Chelating phosphine ligand

In addition, due to the higher barrier to inversion for phosphorus compared to ligand such as amine, an optically active form of phosphine will be produced for most phosphines using three different substituent R group, hence a chiral phosphine can be produced in this manner which can later be used in asymmetric synthesis or reaction. For example, MeP(cyclohexyl)(o-anisyl) was the first ligand used for asymmetric hydrogenation.

The electronic and steric properties of the phosphine ligand can be designed and altered in a predictable manner by varying the R groups on the ligand itself. These two properties, being altered, will have a significant effect on its reactivity and geometry of the complexes formed. Bulkier phosphine ligand will have a greater cone angle (excluding phosphite), increasing the extent of ligand dissociation at the same time. On the other hand, the bulkier the phosphine ligand, the higher the tendency of it binding trans to one another. In addition, having too much bulky phosphine in a complex will tend to distort the idealized coordination geometry.

Apart from the electron donating properties of phosphine ligand (σ-donor) which vary depending on their substituent groups, tertiary phosphines can also serve as π-acceptors depending on the same factor. Most recent studies on the potential of phosphines as π-acceptors showed that the acceptor orbital of PR_3 is the σ^* orbital on P-R bonds, which is stabilized when the R group becomes more electronegative. On the other hand, there will be an increased contribution of phosphorus to the σ^* orbital that increases the size of the σ^* orbital lobe towards the central metal atom. This enhances the role of PR_3 as electron acceptor from the central metal atom as the empty σ^* orbital is more accessible for back donation.

1.4 Starting material: group VIB complexes (M=Cr, Mo,W)

Group VIB belongs to d-block elements and consists of three elements: chromium (Cr), molybdenum (Mo), and tungsten (W). Although they have different atomic number and number of electrons, these three elements contain six valence electrons in their outermost shell. Thus, they are able to form metal complexes with ligands, with 6-coordinated complex being the most commonly found among the complexes formed by these elements.

1.4.1 Metal carbonyls and $W(CO)_6$

Transition metal carbonyls, for one such as tungsten hexacarbonyl ($W(CO)_6$) are one of the most ancient classes of organometallic compounds known in the history of organometallic chemistry. They are common starting materials for almost all syntheses, especially those involving low-valent metal complexes as a product. With the presence of CO (carbon monoxide) ligand in the complex, a large number of other types of ligands (arenes, olefins, Lewis base) can be substituted into the complex, replacing the CO ligand (s) while providing the complex a certain degree of stability against oxidation or thermal decomposition during the reaction. The resulting product of the substitution reaction – metal carbonyl derivatives can later serve their role as an important intermediate in homogenous catalysis. (Elschenbroich, 2006)

There are a few methods in preparing these metal carbonyls. For $W(CO)_6$, the preparation method can be as follows:

Equation 1.1 Preparation of $W(CO)_6$

$$\boxed{WCl_6 + Et_3Al + 6CO \rightarrow W(CO)_6 + 3C_4H_{10}}$$

*reaction condition: C_6H_6, 50 ℃, 70 bar

$W(CO)_6$ exist in the form of white solids at room temperature. As it is being refluxed (temperature gradually increases), it would undergo sublimation and the vapor is not recoverable.

1.4.2 $W(CO)_3(CH_3CN)_3$

$W(CO)_3(CH_3CN)_3$ is a derivative metal carbonyl which can be produced by replacing three CO ligands on $W(CO)_6$ with three molecules of acetonitrile. Furthermore, it is used as an intermediate to obtain (mes)$W(CO)_3$. According to King and Fronzaglia (1966), it is a readily available substitution product of tungsten carbonyl. This is because, if compared to chromium and molybdenum hexacarbonyl, tungsten hexacarbonyl is more inert hence less suitable to be used in the preparation of olefin or other complexes of similar class.

Other than that, the study on this complex by King and Fronzaglia (1966) has stated that acetonitrile is more readily displaced by various olefins due to very little pπ-dπ bonding ability from which this ability provides double bond character to the metal-carbon bond (back-bonding occurred in metal-carbon bond) – makes the displacement reaction more directed as the incoming ligand can be influenced to displace a certain ligand (acetonitrile) only.

1.4.3 (mes)$W(CO)_3$

Mesitylene tungsten tricarbonyl is categorized as arene metal carbonyl. Arene metal carbonyl can be synthesised and obtained through substitution reactions, stated as follows:

(a) Carbonyl substitution of metal carbonyl (maximum of three CO ligands can be substituted)
(b) Reaction between metal carbonyl halide with arene and $AlCl_3$
(c) Ligand exchange reaction

The stability of tungsten hexacarbonyl which is stated in the previous section makes reaction (a) less favourable to be carried out. Therefore, this complex is prepared via reaction (c) as suggested in the studies carried out by King and Fronzaglia (1966), which will be described in detail in Chapter 3.

Complexation of an arene to the metal carbonyl complex alters its reactivity in several ways, one of it being the enhancement of nucleophilic substitution of the complex. Attack of σ-donor or π-acceptor ligand such as phosphine ligand (Section 1.3.1) on the complex may cause the displacement of arene ligand. \

1.5 Problem Statement

The study on the synthesis and coordination chemistry of mixed P/S-phosphine ligand ($P(o\text{-}C_6H_4SCH_3)_2Ph$) with metal carbonyl complexes has been carried out by researchers occasionally throughout the years. However, most of the studies, up to now, have only been using metal hexacarbonyl (for group VIB) as the precursor of the reaction, with only tetracarbonyl species being successfully synthesised even though there were three potential electron donors in the ligand. Hence, this project is carried out by using metal tricarbonyl complex as the precursor of the reaction in order to find out the differences (if any) in terms of reactivity and coordination of the ligand towards tungsten tricarbonyl complex, in the hope of discovering an example of a new tungsten tricarbonyl complex from this project.

1.6 Objectives

The main objectives of this project are as follows:

(a) To synthesize a P/S chelate complex from mesitylene tricarbonyl tungsten complex and heterodonor phosphine ligand

(b) To characterize the chelate complex with infrared (IR) spectroscopy, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy

(c) To study the reactivity of tungsten tricarbonyl complexes

CHAPTER 2

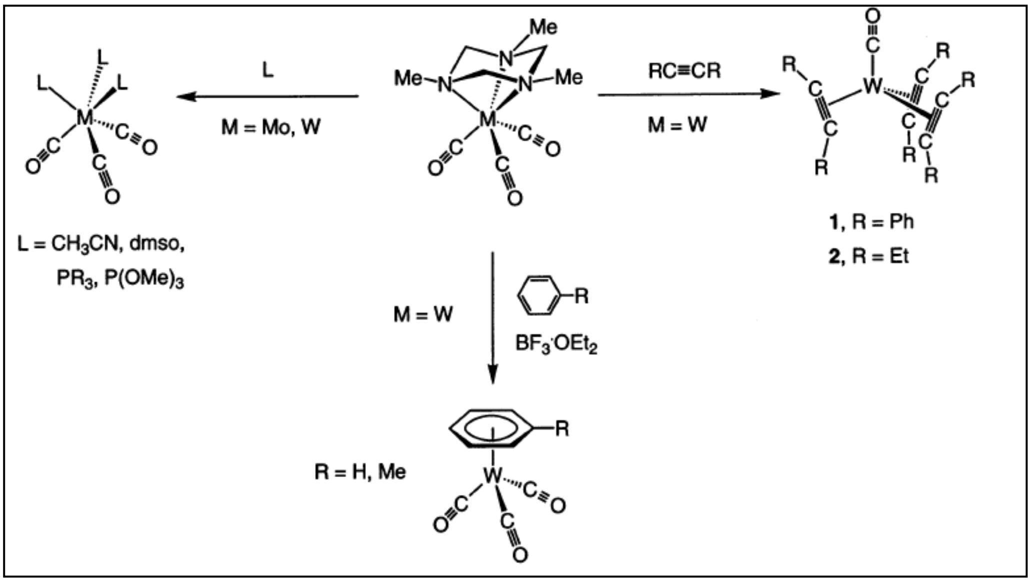
LITERATURE REVIEW

2.1 1, 3, 5-trimethyl-1, 3, 5-triazacyclohexane tricarbonyl complexes of W as sources of fac-W(CO)$_3$ fragment and its reaction with monophosphine ligands

The study is conducted and reported by Baker and North (1997) by using W(CO)$_3$(Me$_3$tach) as the starting material for the reaction. According to the reported study, this complex can be synthesised via two methods - either a direct synthesis from tungsten hexacarbonyl and commercially available Me$_3$tach in dry xylene, or by using W(CO)$_3$(CH$_3$CN)$_3$ synthesised from W(CO)$_6$ in acetonitrile as an intermediate.

The lability of Me$_3$tach ligand in the complex allows its complexes to be used as reactive intermediates in the preparation of other molybdenum and tungsten carbonyl complexes. Some of the examples are given as shown as follows:

Scheme 2.1 Preparation of molybdenum and tungsten carbonyl complexes using Me_3tach complexes of Mo or W



(Baker and North, 1997. p. 226)

The synthesised $W(CO)_3(Me_3tach)$ is reacted with three types of phosphine ligand: PMe_2Ph, PPh_3, P^iPr_3 respectively in attempt to synthesise *fac*-$W(CO)_3$ complexes. Based on their findings, only PMe_2Ph and PPh_3 ligands reacted successfully to form *fac*-$W(CO)_3$ complexes and displaced Me_3tach ligand readily at room temperature while in the case of P^iPr_3, a *trans* complex, *trans*-$[W(CO)_4(P^iPr_3)_2]$ was formed. Moreover, the synthesis of this complex was found to be slower than the reaction of other complexes and required higher temperature during reflux.

The results were confirmed using ^{31}P NMR spectra and carbonyl absorbance characteristics of *fac*-stereochemistry in IR spectra. Besides that, the study showed improvement of yield (96 %) and time consumed (1 h reflux) in synthesis of *fac*-[$W(CO)_3(PPh_3)_3$] compared to another previous study of synthesis using $W(CO)_3(\eta^6$-mesitlylene) as the starting material (32 % yield, 36 h reflux).

2.2 A comparison of the ligating properties of the mixed P/O- and P/S-donor ligands with group 6 and 7 carbonyls

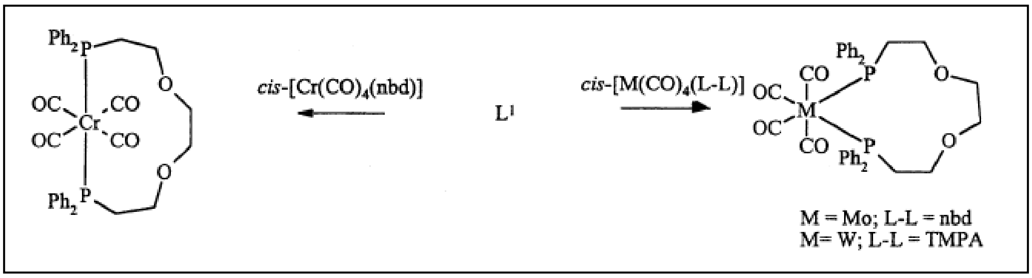
Heuer and co-workers (2002) expressed their interest in mixed phosphine ligands for their ability to bond to a wide range of metal ions, and the presence of two different donor atom types leads to coordination flexibility for these ligands. The mixed phosphines chosen for this study are $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$ (L^1) and $Ph_2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2$ (L^2), and the metal ions chosen are group 6 carbonyls (chromium (Cr), molybdenum (Mo), tungsten (W)) and manganese (Mn). (Heuer, Reid and Ripley, 2002)

2.2.1 Reaction of L^1 ligand ($Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$) with group 6 and group 7 complexes

cis-[M($CO)_4$ (nbd)] (M=Cr or Mo; nbd= 2,5-norbornadiene), *cis*-[W($CO)_4$ (TMPA)] (TMPA=N,N, N',N' - tetramethyl-propyldiamine), and [Mn(Cl)($CO)_5$] are reacted with the ligand in 1:1 molar ratio in toluene (chloroform for W and Mn). These complexes were isolated later and tested using electrospray ionization mass spectrometry, ^{1}H-NMR, and IR spectroscopy and so on. The mass spectra and ^{1}H-NMR data obtained for Mo and W complexes were consistent with the formulation of $[Mo(CO)_4(L^1)]$ and $[W(CO)_4(L^1)]$. Furthermore, the solution IR data also showed peaks associated with ν(CO) which confirms the geometry of *cis*-tetracarbonyl arrangement of these complexes. Moreover, the $^{13}C\{^{1}H\}$-NMR spectra of Mo and W showed resonances of coordinated L^1 indicating CO trans CO (triplets) and CO trans P (doublet of doublets), both in which are poorly resolved peaks. (Heuer, Reid and Ripley, 2002)

On the other hand, the mass spectrum on Cr complex provides no useful information on the formulation of product obtained. However, the IR spectrum and $^{13}C\{^{1}H\}$-NMR spectrum of Cr species show a single and strong ν(CO) absorption at 1877 cm^{-1} and a poorly resolved triplet in CO region respectively, indicating that the Cr complex formed is *trans*-$[Cr(CO)_4(L^1)]$ isomer only. For all three group 6 complexes, $^{31}P\{^{1}H\}$-NMR spectra showed a singlet at +56.5 ppm for Cr species; a singlet at 17.8 ppm and 3.9 ppm respectively for Mo and W species. Thus, a decreasing trend in $\delta(^{31}P)$ can be observed for group 6 complexes (Heuer, Reid and Ripley, 2002). A summary of chemical equations which also shows the geometry of Cr, Mo, and W complexes obtained are shown as follows:

Scheme 2.2 Complexes of L^1 $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$ formed from their respective starting materials (group 6 carbonyl complexes only)



(Heuer, Reid and Ripley, 2002)

Besides that, the reaction of this ligand (mixed P/O ligand) with Mn complex was monitored by solution IR to observe the disappearance of starting material peaks. The four distinct bands of ν(CO) at 2095, 2026, 2010, and 1958 cm^{-1} indicated the presence of more than one geometric isomer, in which they may be of either any of *fac*, *mer-cis*, or *mer-trans* configuration as only P-coordination is considered in the study. The later analyses (IR spectroscopy, NMR spectroscopy, and electrospray ionization mass spectrometry) carried out on the Mn complexes obtained further confirmed a mixture of *fac* and *mer-trans* isomers of Mn is produced, and it is confirmed by using another repeated reflux of prolonged period, in which the *mer-trans* isomer is isolated out for the same analyses (refer above). The Mn geometric isomers produced is shown as follows:

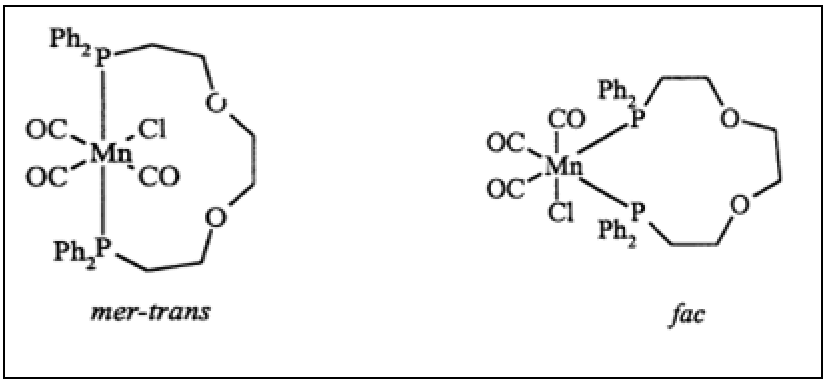


Figure 2.1 Geometric isomers produced from Mn carbonyl complex

The same procedures are also carried out on [ReBr(CO)$_5$], another group 7 complex in which a similar analytical result is obtained for the product, only with prolonged period of reflux due to the lesser reactivity of this complex.

2.2.2 Reaction of L^2 Ph$_2$P(CH$_2$)$_2$S(CH$_2$)$_2$S(CH$_2$)$_2$PPh$_2$ ligand with group 6 and group 7 complexes

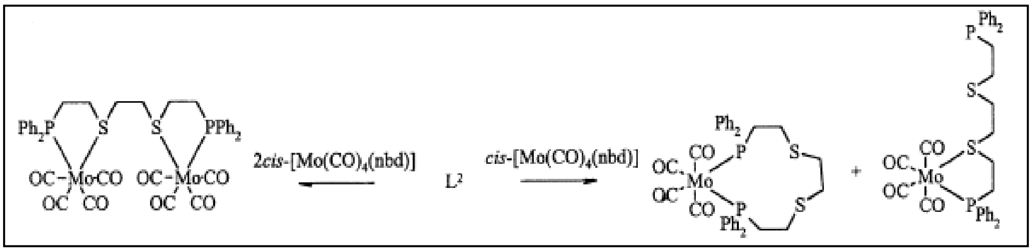
The complexes involved in the reaction are Mo(0) and Mn(I) carbonyls from group 6 and 7 respectively. [Mo(CO)$_4$(nbd)] are used in separate reactions of 1 M and 2 M equivalent of L^2, both reactions in which gives a different outcome. A mixture of two products is obtained for the former while a single product is obtained for the latter.

Based on the results obtained from IR spectroscopy and ^{13}C{^{1}H}-NMR, the mixture of two products produced from 1 M and L^2 ligand appear to be *cis*-

tetracarbonyl species because according to the $^{13}C\{^1H\}$-NMR spectrum, two groups of resonances are present in the spectrum, one of it shows three doublets in 1:1:2 ratio that suggests P,S-chelation while the other one shows doublets of doublets and triplet, which is P_2-chelation of L^2 ligand to the metal centre. The deduction is further supported with the $^{31}P\{^1H\}$-NMR spectrum that found three singlet resonances as follows: two out of three resonances with 1:1 ratio at 52.9 ppm and -16.6 ppm which suggests coordination of bidentate P,S ligand to the Mo carbonyl complex as the higher frequency resonance (52.9 ppm) indicates that the P atom is coordinated to the central metal atom while the lower frequency resonance (-16.6 ppm) indicates that another P atom on the ligand is uncoordinated in the complex. On the other hand, the third resonance which is of higher intensity compared to the pair is found at 26.1 ppm, shows that both P on the ligand is coordinated to the central Mo atom. (Heuer, Reid and Ripley, 2002)

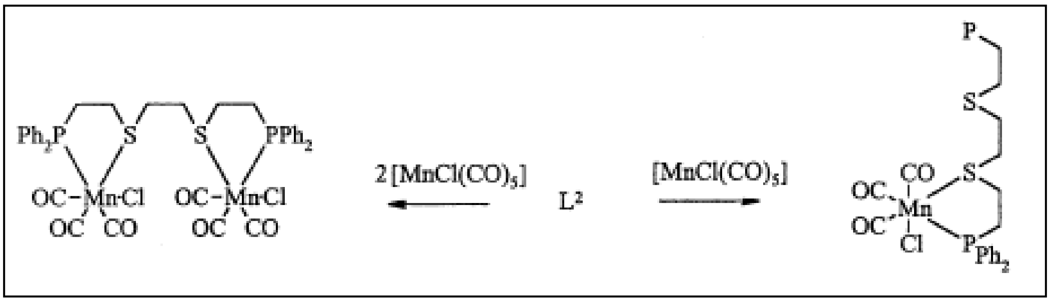
In contrast, reaction with 2 M equivalent of the ligand with Mo(0) complex gives a single product which is characterized later based on the spectroscopic data obtained (will be explained after this) as a *cis* binuclear complex. The $^{31}P\{^1H\}$-NMR spectrum reveals a single resonance at 53.0 ppm which is similar with the P,S-chelated complex obtained from the Mo-L^2 species in the previous reaction mentioned. Furthermore, $^{13}C\{^1H\}$-NMR spectrum of this product shows three doublet resonances corresponding to CO trans CO, CO trans S and CO trans P. Below shows the summary of reaction of Mo(I) complex with the ligand.

Scheme 2.3 Complexes of L^2 ($Ph2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2$) formed with different molar equivalents of the ligand (Mo complex)



The reaction of Mn(I) carbonyls using same molar equivalent (1 M and 2 M) of L^2 ligand both give a single product but of different coordination modes. Reaction with 1 M equivalent of the ligand gives a P,S-chelating complex similar with Mo species, while reaction with 2 M equivalents gives same coordination of ligand with Mo species (fac-binuclear complex). Both reactions are illustrated as shown below.

Scheme 2.4 Complexes of L^2 ($Ph2P(CH_2)_2S(CH_2)_2S(CH_2)_2PPh_2$) formed with different molar equivalents of the ligand (Mn complex)



Based on the study, Heuer and co-workers (2002) concluded that in low valent complexes the ethers in L^1 ligand acts as spacers although it has the potential of electron donor, thus explained its behaviour as a long chain diphosphine ligand. On the other hand L^2 ligand readily forms mono- and bi-nuclear complexes due to the better compatibility of both phosphines and thioethers to coordinate to the metal ion because they are soft ligands (phosphines and thioethers) compared to ethers which is a hard ligand. (Heuer, Reid and Ripley, 2002)

2.3 Synthesis and characterization of group 6 complexes (Cr, Mo, W) with primary and secondary phosphines

Campbell and co-workers (1999) have conducted some prior investigation on the coordination chemistry of primary (PRH_2) and secondary phosphines (PR_2H) on a range of middle and late transition metal ions from Group VIIb to VIIIb. From the results of their previous finding, they have managed to generate a range of species in which phosphines act as neutral ligands.

In this study, Campbell et al. (1999) reported the synthesis and spectroscopic characterization of a series of di- and tri-substituted complexes of group VIb transition metals. The range of complexes covers *fac*-$[M(CO)_3L_3]$ (M=Mo or W; L=PPh_2H or $PPhH_2$), *cis*-$[M(CO)_4L_2]$ (M= Cr, Mo, W; L=PPh_2H, PCy_2H or $PPhH_2$) and *cis*-$[Mo(CO)_4(L\text{-}L)]$ (L-L=$PhHPCH_2CH_2PHPh$, $PhHPCH_2CH_2CH_2PHPh$, *o*-$C_6H_4(PH_2)_2$).

The starting material for the reaction is $M(CO)_6$ (M=Cr, Mo, W) , and its reaction with excess phosphine (4.5 molar equivalents) in ethanolic $NaBH_4$ produces the *fac* or the *cis* species stated in the above paragraph, depending on the nature of the phosphine ligand itself. The above preparation method by using PPh_2H or $PPhH_2$ gives pale yellow solids of *fac*-$[M(CO)_3L_3]$ in average yield (Campbell et al., 1999). The displacement of CO ligands by the phosphine ligands were monitored by solution IR spectroscopy while the isolated products at the end of the reaction were confirmed by fast-atom bombardment mass spectrometry (FAB MS), NMR spectroscopy and micro-analytical data.

However, the reaction of PCy_3 phosphine ligand does not yield *fac* species, but gave *cis*-species of the formula of *cis*-$[M(CO)_3(PCy_2H)_2]$. According to Campbell and co-workers (2002), the reason behind the outcome is less likely to be explained using steric constraints alone because they claimed to have synthesized *fac*-$[Mo(CO)_3(PCy_2H)_3]^+$ previously and the spectroscopic data were consistent with those reported.

On the other hand, *cis*-$[M(CO)_4(nbd)]$ (M=Cr,Mo;nbd=norbornadiene) and *cis*-$[W(CO)_4(TMPA)]$ (TMPA=$Me_2N(CH_2)_3NMe_2$) were used by Campbell and co-workers to obtain the *cis*-disubstituted species in CH_2Cl_2 solution with 2 M equivalents of L ligand stated as follows: *cis*-$[M(CO)_4L_2]$ (M= Cr, Mo, W; L=PPh_2H, PCy_2H or $PPhH_2$) and *cis*-$[Mo(CO)_4(L\text{-}L)]$ (L-L=$PhHPCH_2CH_2PHPh$, $PhHPCH_2CH_2CH_2PHPh$, *o*-$C_6H_4(PH_2)_2$). Another preparation pathway of using *cis*-[M(CO)$_4$(piperidine)$_2$] (M=Mo or W) to synthesize the above desired species were tried by Campbell and co-workers, but the yields obtained were lower hence less preferable. The figure below showed the examples of monophosphines and diphosphines used in the study by Campbell and co-workers.

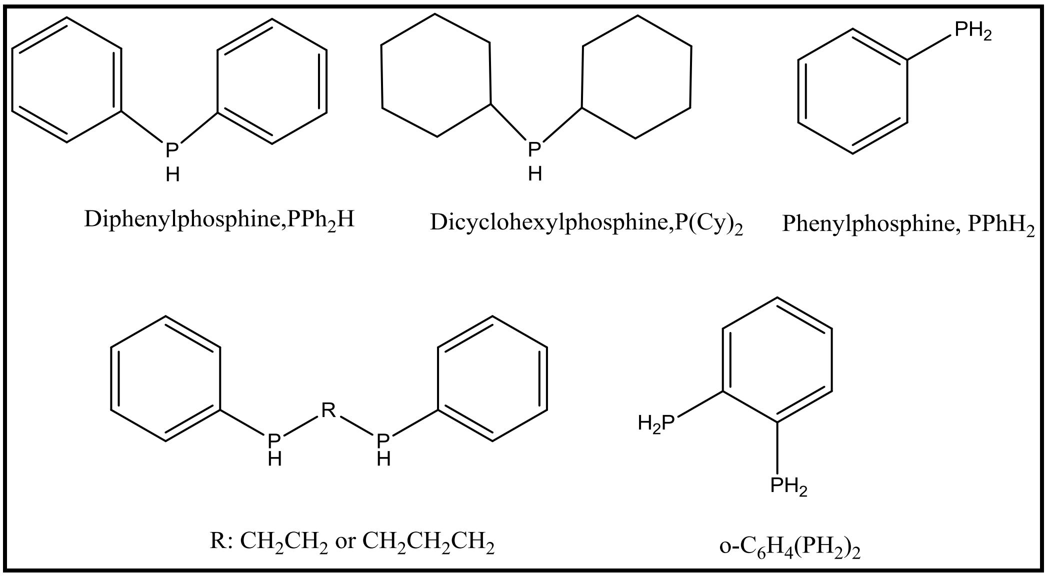


Figure 2.2 Monophosphines and diphosphines ligands

Based on the spectroscopic findings conducted, mass spectra showed peaks consistent with their deduction. Moreover, solution IR revealed four ν(CO) stretching bands that is consistent with the literature data on cis-disubstituted species, while evidences were found on IR spectroscopy (KBr disc) that could further prove the coordination of L and P-H to the complex. Furthermore, the presence of primary and secondary phosphines was confirmed by ^{1}H NMR spectroscopy (broad multiplet around 5-6ppm).

Other than the spectroscopic data above, ^{31}P coupling with CO resonances were observed by Campbell and co-workers. They found out that for the fac species δ(CO) appears as doublet of triplets due to bonding to non-equivalent phosphines in different chemical environments. Apart from that, the ^{13}C-^{31}P coupling for the *cis* species showed a triplet and doublet of doublets which corresponded to cis-bonding of CO to phosphines and trans-bonding of CO to phosphines respectively, with *cis* couplings appearing at lower frequency than *trans* couplings.

Besides that, $^{31}P\{^{1}H\}$-NMR spectra show a singlet (see Table 2.1) except for disecondary phosphine complex. In addition, there is an increase in δ(^{31}P) (to higher frequency) for increasing degree of substitution for the complexes and decrease in shift (to lower frequency) down the group VIb complexes.

$^{31}P\{^{1}H\}$-NMR spectroscopy will be able to show the stereoisomerism property in metal complexes especially disecondary phosphine complexes such as $[Mo(CO)_4(PhHPCH_2CH_2PHPh)]$ and $[Mo(CO)_4(PhHPCH_2CH_2CH_2PHPh)]$. These complexes have the possibility of forming two stereoisomers (*meso* and *DL*). In spite of that, Table 2.1 revealed that only $[Mo(CO-)_4(PhHPCH_2CH_2PHPh)]$ showed two resonances (18.5 ppm and 21.0 ppm) of the same ratio in $^{31}P\{^{1}H\}$-NMR spectrum, which is in contrast to the single resonance observed for $[Mo(CO)_4(PhHPCH_2CH_2CH_2PHPh)]$. This is because in the case of $[Mo(CO)_4(PhHPCH_2CH_2CH_2PHPh)]$, the *meso*-isomer dominates over the other (>95 %) and made the other stereoisomer's (*DL*) resonance too insignificant to be noticed. Lastly, the above assumptions regarding the geometry of the complexes formed were confirmed by Campbell and co-workers via single-crystal X-ray structure analyses

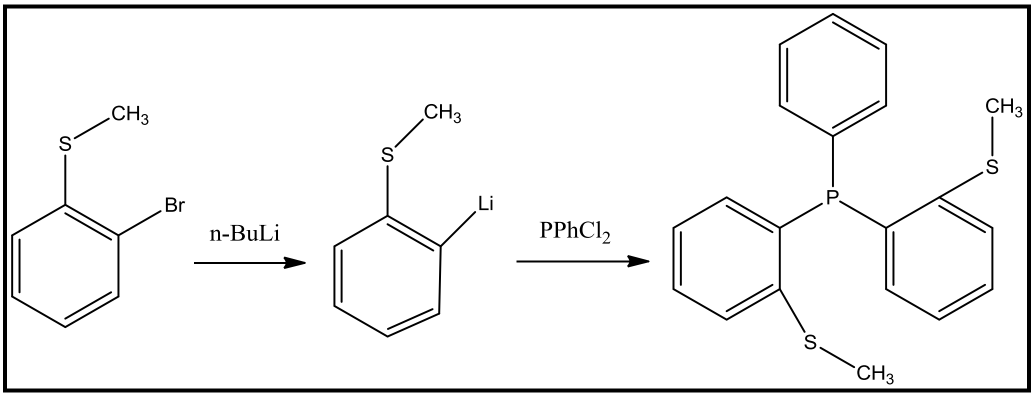
Table 2.1 $^{31}P\{^1H\}$-NMR spectroscopic data of all products

Complex	^{31}P (ppm)
cis-$[Cr(CO)_4(PPh_2H)_2]$	+42.3
cis-$[Cr(CO)_4(PPhH_2)_2]$	-27.5
cis-$[Cr(CO)_4(PCy_2H)_2]$	+53.4
fac-$[Mo(CO)_3(PPh_2H)_3]$	+22.0
fac-$[Mo(CO)_3(PPhH_2)_3]$	-53.5
cis-$[Mo(CO)_4(PPh_2H)_2]$	+14.5
cis-$[Mo(CO)_4(PPhH_2)_2]$	-60.5
cis-$[Mo(CO)_4(PCy_2H)_2]$	+25.0
cis-$[Mo(CO)_4(PhHPCH_2CH_2PHPh)]$	18.5,21.0
cis-$[Mo(CO)_4(PhHPCH_2CH_2CH_2PHPh)]$	-6.9
cis-$[Mo(CO)_4\{o\text{-}C_6H_4(Ph_2)_2\}]$	-44.1
fac-$[W(CO)_3(PPh_2H)_3]$	+4.3
fac-$[W(CO)_3(PPhH_2)_3]$	-72.0
cis-$[W(CO)_4(PPh_2H)_2]$	-4.6
cis-$[W(CO)_4(PPhH_2)_2]$	-80.9
cis-$[W(CO)_4(PCy_2H)_2]$	+8.6

2.4 Preparation and characterization of group 6 metal carbonyl derivatives with heterodonor phosphines: bis[*o*-(methylthio)phenyl]phenylphosphine (PSS)

Heterodonor ligands form one important field in the development of new homologous catalysts (Hirsivaara et.al, 1999). Hirsivaara and co-workers have reported the coordination chemistry of these ligands with group 6 hexacarbonyls (Cr, Mo, and W), and the characterization of the complexes successfully formed from the study as well. Bis[o-(methylthio)phenyl]phenylphosphine is an *ortho*-substituted phosphine by which its structure consists of one phosphine atom in the center of three benzene rings while having two methanethiol (S-CH_3) groups bonded each on ortho position of two of the benzene rings. The ligand used in the synthesis is reproduced according to the work reported by Meek, Dyer and Workman (refer Scheme 2.4.1). The ligand is prepared using *o*-bromothioanisole and phenylphosphonous dichloride from a lithium reagent (Meek, Dyer and Workman, 1976). The ligand produced is white and needle-like (if purified), and soluble in common organic solvents (Meek, Dyer and Workman, 1976).

Scheme 2.5 Preparation of bis[*o*-(methylthio)phenyl]phenylphosphine ligand



According to Hirsivaara and co-workers, the ligand is reacted with metal carbonyls and trimethylamine *N*-oxide dihydrate (Hirsivaara et.al, 1999) in the ratio of 1:1:3 in dichloromethane at room temperature for 3 hours. The isolation and purification of product was done using column chromatography. At the end of the reaction, yellow crystals were obtained via slow evaporation at room temperature in dichloromethane-hexane mixtures.

The reaction of PSS ligand with group 6 metal carbonyls all produced crystalline bidentate complex, $[M(CO)_4(ligand)]$ (M=Cr, Mo, W). However, in terms of reactivity, $Mo(CO)_6$ and $W(CO)_6$ is more reactive than $Cr(CO)_6$ as these two metal carbonyls has higher yield of bidentate complex successfully isolated out from the reaction mixture. Furthermore, some monodentate product is detected through ^1H NMR spectroscopy in the reaction mixture of chromium, but only the bidentate complex is successfully isolated. This indicates that the reaction was incomplete in the case of PSS derivative of

$Cr(CO)_6$, and thus the less readiness in reaction of $Cr(CO)_6$ with PSS ligand, which can be explained in terms of atomic radius or kinetic effects. On the other hand, the crystal structure of each bidentate complex was futher confirmed by single-crystal X-ray diffraction study (Hirsivaara et.al, 1999). The below figure shows the crystal structure of $[Mo(CO)_4(PSS)]$ in which the similar structure can be observed in the case of Cr and W.

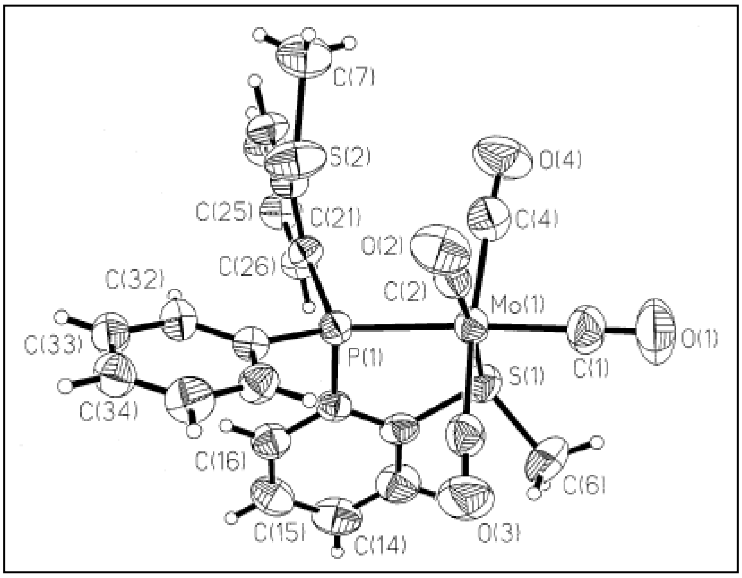


Figure 2.3 Crystal structure of $[Mo(CO)_4(PSS)]$ (Hirsivaara et.al, 1999)

In the end of the study conducted by Hirsivaara and co-workers, there were no tridentate complex formed by any of the metal carbonyls (Cr, Mo, W) above although it has three electron donors present on the ligand. In addition, Hirsivaara and co-workers had performed similar reactions with the potentially tetradentate ligand tris[*o*-(methylthio)phenyl]phosphine, but the attempts were proved to be unsuccessful (Hirsivaara et.al, 1999).

2.5 Reaction of dithiafulvenylphosphine (P-DTF) with group 6 and group 7 metal carbonyls: a comparative study

Dithiafulvenyldiphenylphosphine (P-DTF) is a ligand with redox-active properties, and a derivative of tetrathiafulvalene (TTF). Due to the presence of more than one potential electron donor (P and S) that is contained within its chemical structure, it can act as a mono- or bi-dentate ligand. According to Guerro et.al in two separate studies (2005 and 2008), the coordinating ability of P-DTF is being studied in $M(CO)_4$ fragments (M=Mo, W), $Mo(CO)_6$, and $BrMn(CO)_5$. A comparison can be made based on these two studies. Figure below shows the chemical structure of P-DTF.

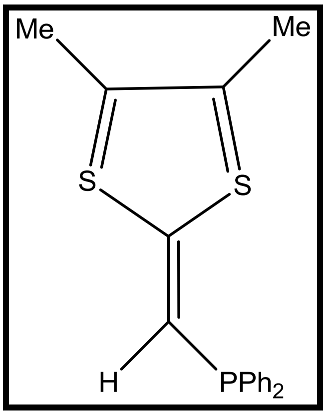
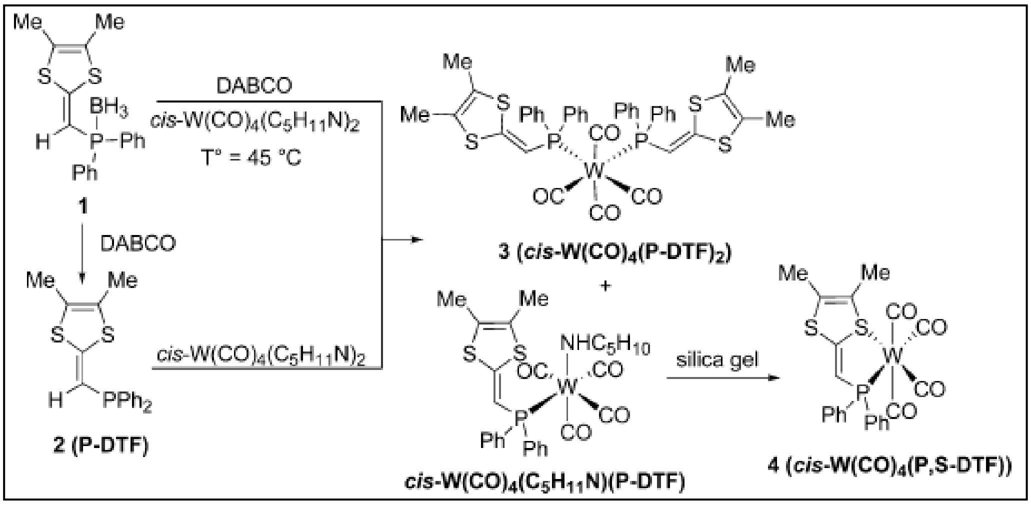


Figure 2.4 Chemical structure of dithiafulvenyldiphenylphosphine (P-DTF) ligand

2.5.1 Reaction of dithiafulvenylphosphine (P-DTF) with $M(CO)_4$ fragments

In the study, the $M(CO)_4$ fragment (M= Mo, W) is prepared from $M(CO)_6$ and reacted with piperidine to yield a *cis*-product of general formula $M(CO)_4L_2$ (L= piperidine in this case) (Darensbourg and Kump, 1978). Furthermore, the *cis*-fragment synthesized is either reacted with stable vinylphosphine 2 (after being decomplexed with DABCO (1,4-diazabicyclo[2.2.2]octane) from phosphine borane which is shown in Scheme 2.6) or directly used by adding in situ 0.5 equivalent of *cis*-$W(CO)_4$(piperidine)$_2$ complex and heating at 45 ℃ for 4 hours under inert atmosphere (Guerro et.al, 2005). The overall synthesis is described in Scheme 2.6 as shown below.

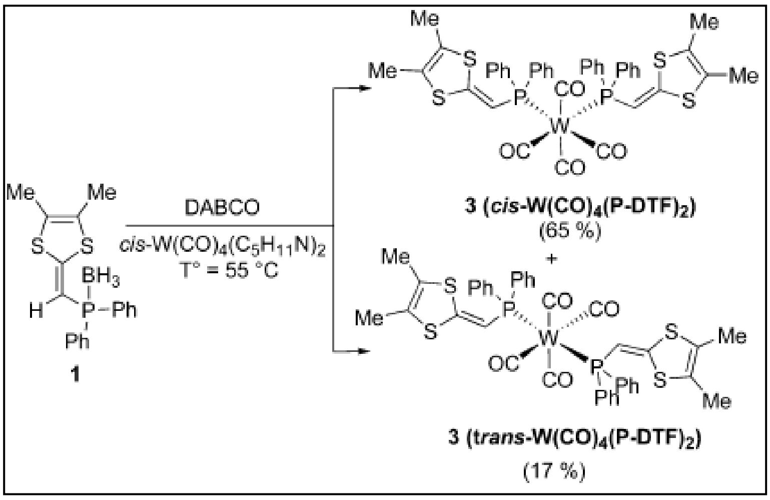
Scheme 2.6 Reaction of P-DTF ligand with *cis*-$W(CO)_4$(piperidine)$_2$



As shown in the above scheme, a mixture of products is obtained at the end of the synthesis via both routes. Under direct synthesis, product 3 (*cis*-$W(CO)_4(P\text{-}DTF)_2$) is obtained with a percentage yield of 63 % in the case of tungsten complex, while some product of monosubstituted tungsten fragment, *cis*-$W(CO)_4$(piperidine)(P-DTF) is isolated out as well. However, upon purification of the monosubstituted fragment with coloumn chromatography, a yellow crystalline solid which is identified as product 4, *cis*-$W(CO)_4$(P,S-DTF) is obtained. Apart from that, Guerro and co-workers also noticed that the ligand reacted more readily as monodentate P ligand if the ligand is already coordinated dithiafulvalene 2, while the bidentate P,S coordination to the tungsten complex can only be obtained after the departure of second piperidino ligand. On the other hand, under the same procedures using *cis*-$Mo(CO)_4(\text{piperidine})_2$ complex, 92 % yield was obtained for *cis*-$Mo(CO)_4(P\text{-}DTF)_2$.

Besides that, Guerro and co-workers intend to increase the yield of *cis*-$W(CO)_4(P\text{-}DTF)_2$ by increasing the temperature to 55 °C instead of 45 °C, whereby the yield of $W(CO)_4(P\text{-}DTF)_2$ did increase to 82 %. However, it is discovered via ^{31}P NMR that isomerisation of $W(CO)_4(P\text{-}DTF)_2$ occurred as both geometrical isomers : *cis*- and *trans*- $W(CO)_4(P\text{-}DTF)_2$ was obtained in the percentage yield of 65 % and 17 % respectively. The reaction is summarized as shown in Scheme 2.7.

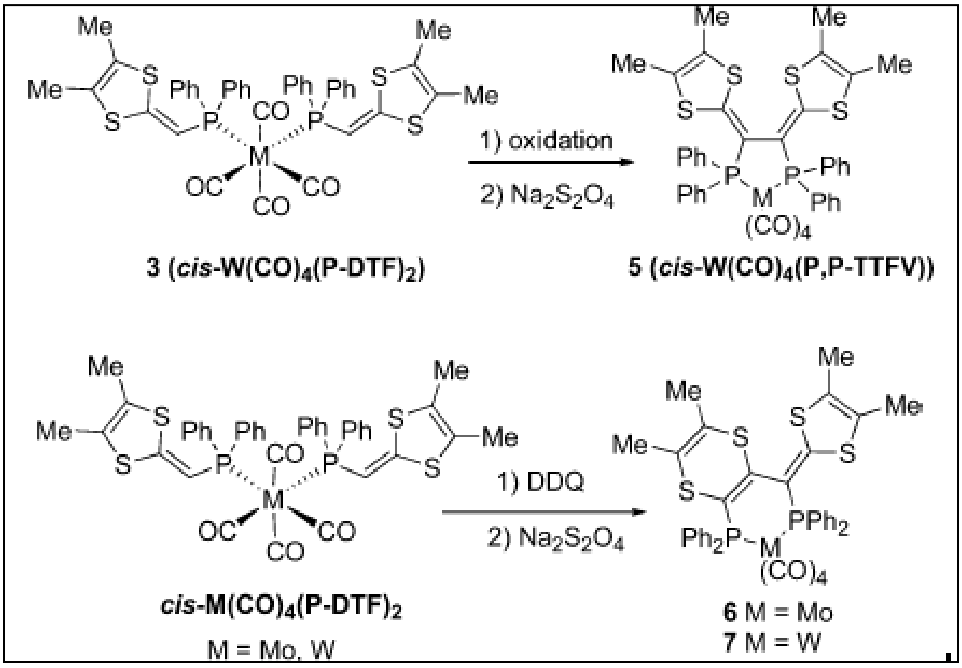
Scheme 2.7 Isomerization reaction of *cis*-W(CO)$_4$(piperidine)$_2$ with P-DTF ligand under modified reaction temperature



2.5.2 Oxidative studies of *cis*-M(CO)$_4$(P-DTF)$_2$ (M=Mo, W) complexes

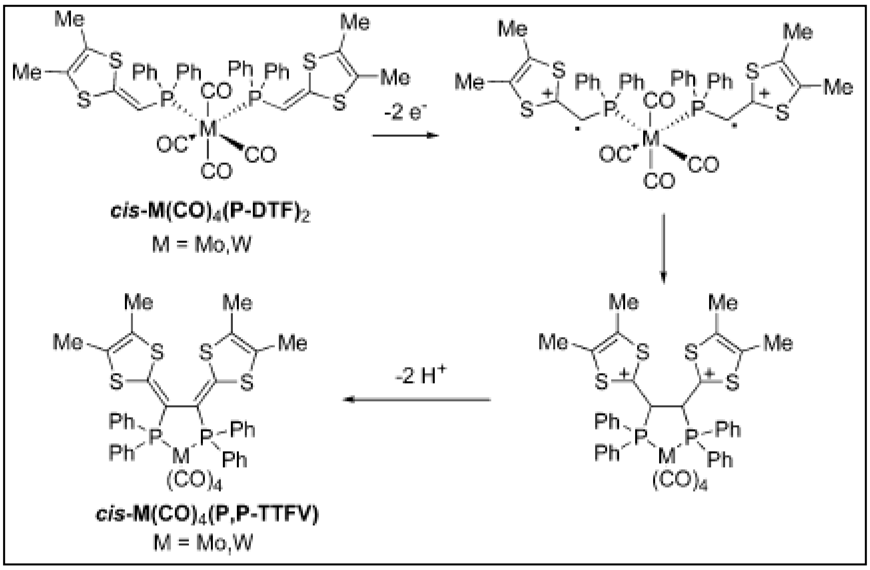
Although the *trans*-W(CO)$_4$(P-DTF)$_2$ is obtained as described in Scheme 2.7 above, it is reported by Guerro and co-workers that only the *cis* isomer can lead to coupling reaction upon oxidation within the coordination sphere of M(CO)$_4$ fragment (Guerro et.al, 2005). Hence, only *cis*-M(CO)$_4$(P-DTF)$_2$ (M=Mo, W) complexes was involved in the oxidative studies in the presence of a few oxidizing agents such as tris(4-bromophenyl)aminium hexachloroantimonate, (BrC$_6$H$_4$)$_3$NSbCl$_6$, AgBF$_4$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Oxidative coupling would occur in cis-M(CO)$_4$(P-DTF)$_2$ (M=Mo, W) which induced the formation of bidentate diphosphine complex with a redox-active vinylogous tetrathiafulvalene (TTF) backbone in the form of five-membered metallacyclic ring cis-W(CO)$_4$(P,P-TTFV) (for (BrC$_6$H$_4$)$_3$NSbCl$_6$ and increase in yield for AgBF$_4$), except for the case in which DDQ was used a six-membered metallacyclic ring of the same molecular formula was obtained. Both metallacycles are formed by the formation of intramolecular C-C bond between the two dithiafulvalene (DTF) rings. Both reaction pathways are summarized as shown in the scheme below.

Scheme 2.8 Oxidative studies of *cis*-$M(CO)_4(P\text{-}DTF)_2$ (M=Mo, W) using different oxidizing agents (oxidation=$(BrC_6H_4)_3NSbCl_6$, $AgBF_4$)



As described in the above scheme, the reaction takes place by a similar mechanism consisting of three steps: (i) oxidation of *cis*-$M(CO)_4(P\text{-}DTF)_2$ by the oxidizing agent into *bis* radical cation; (ii) coupling reaction of bis radical cation; (iii) deprotonation of the intermediate to afford the vinylogous TTF core before being reduced by sodium hydrosulfite, $Na_2S_2O_4$ to gain products 5, 6, and 7 from the above scheme. The mechanism is illustrated in the below scheme.

Scheme 2.9 Mechanism of oxidative coupling reaction

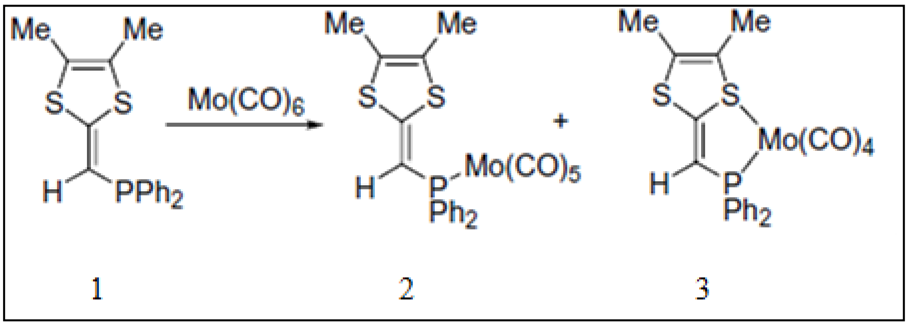


Besides that, it is found out that the strength of oxidizing agent, $(BrC_6H_4)_3NSbCl_6$> DDQ> $AgBF_4$ does not appear to be the pertinent parameter for the formation of either five-or six-membered metallacycle , and the cause of this behaviour is not found by Guerro and co-workers (Guerro et.al, 2005).

2.5.3 Reaction of dithiafulvenylphosphine (P-DTF) with $Mo(CO)_6$ and $[Mn(Br)(CO)_5]$

According to the study carried out by Guerro and co-workers, the reaction of P-DTF ligand with $Mo(CO)_6$ was carried out under two different reaction conditions: (1) formation of monosubstituted metal carbonyl via reaction with one equivalent of $Mo(CO)_6$ with one vinyl phosphine ligand in decalin (150 °C) for 30 minutes, followed by another three hours reflux using different solvents and temperature under inert atmosphere; (2) formation of bisubstituted metal carbonyl via reaction of $Mo(CO)_6$ with one equivalent of vinyl phosphine and two equivalents of $Me_3NO.2H_2O$ in dichloromethane (Guerro et.al, 2008). The reaction with first part of reaction (1) is shown in the scheme below.

Scheme 2.10 Reaction of $Mo(CO)_6$ with one equivalent of vinyl phosphine ligand

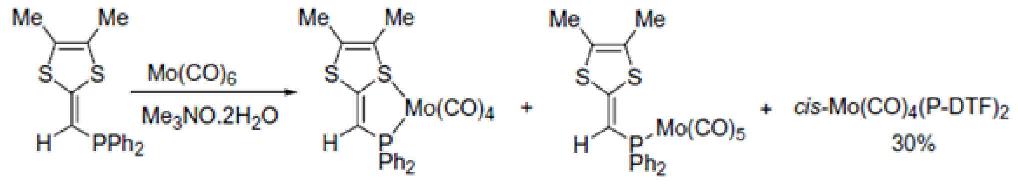


Note: Percentage yield of 2 and 3 : 45% and 5% for 30 minutes reaction time

In the second part of the reaction, the reaction mixture is further refluxed in dichloromethane for three hours, whereby a small amount of $[Mo(CO)_4$(P,S-DTF)] is detected by ^{31}P NMR signal at 62.4 ppm. The reaction time is then lengthened to five days by Guerro and co-workers, as they successfully convert 25 % of $[Mo(CO)_5$(P-DTF)] to $[Mo(CO)_4$(P,S-DTF)]. Besides that, reaction of solution of 2 in toluene with increased temperature did not succeed as the decoordination of phosphine ligand occurred in the place of CO ligand (Guerro et.al, 2008).

Apart from that, reaction (2) was carried out by Guerro and co-workers, in which they succeeded in increasing the yield of complex **3** to 40 %, along with formation of complex **2** and bi-substituted complex cis-[Mo(CO)$_4$(P-DTF)$_2$] in 20 % yield and 30 % yield respectively. The overall reaction is described as shown in the scheme below.

Scheme 2.11 Reaction of Mo(CO)$_6$ with vinyl phosphine ligand in the presence of two equivalents of Me$_3$NO.2H$_2$O in dichloromethane

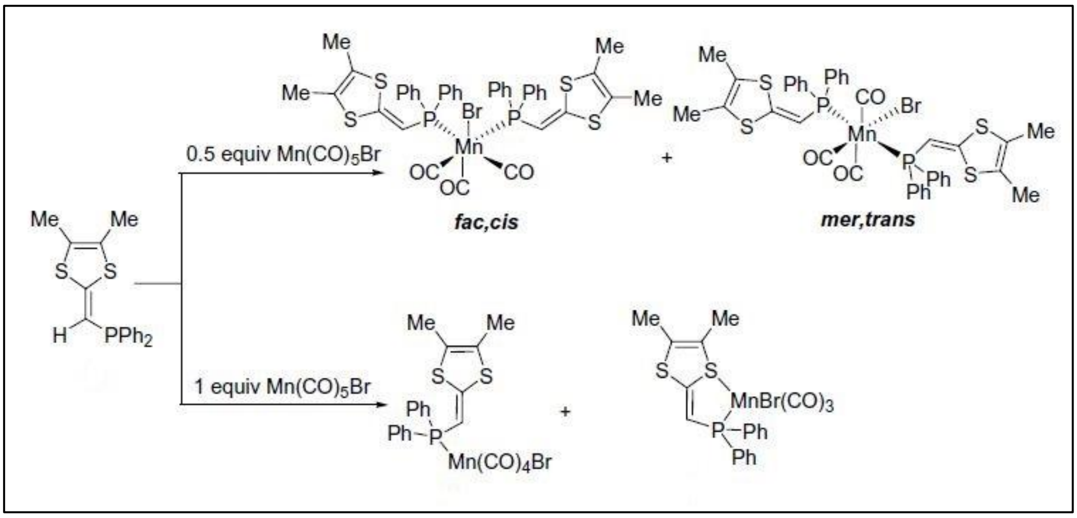


1 3(40%) 4(20%)

On the other hand, reaction of half equivalent of group 7 carbonyl complex, [Mn(Br)(CO)$_5$] with P-DTF ligand occurred as predicted by Guerro and co-workers as two CO ligands are substituted out of the complex with the bi-substituted manganese complex, [MnBr(CO)$_3$(P-DTF)$_2$] being obtained in 40 % yield after it is refluxed in dichloromethane for seven hours and purified by column chromatography. However, the presence of two isomers is detected by ^{31}P NMR as there were two signals present at 41.6 ppm and 21.3 ppm. The two isomers were then identified by Guerro and co-workers in accordance of the work by Beckett et.al as *mer-trans*-P-Mn-P isomer (41.6 ppm) and *fac-cis*-P-Mn-P isomer (21.3 ppm). Later on, a similar reaction (2) is carried out by using one equivalent of [Mn(Br)(CO)$_5$] for three hours yielded mainly

$[MnBr(CO)_4(P\text{-}DTF)$ in 56 % yield. Another complex, $[MnBr(CO)_3(P,S\text{-}DTF)]$ was formed in the reaction as well with unknown yield as it is not isolated out from the column chromatography (but able to be identified in ^{31}P NMR) due to the cleavage of the weaker link of the chelate ring, the Mn-S bond. Both reactions using group 7 carbonyl complex are summarized as shown below.

Scheme 2.12 Reaction of $[MnBr(CO)_5]$ with vinyl phosphine ligand



CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The materials used in this project were of AR grade. The organic solvents used in this project were all dried by activated molecular sieves (4 Å). The table below lists all the materials and their respective sources.

Table 3.1 Materials used and their sources

Materials/Chemicals	**Source**
Acetonitrile	Systherm
Celite	R&M Marketing
Chloroform	QRëC
Dichloromethane	Merck
Diethyl ether	Merck
Decalin	Merck
HCl	Sigma Aldrich
Hexane	GENE
Mesitylene	Merck
Molecular sieves (4 Å)	Fluka
n-butyl lithium	Sigma Aldrich

o-bromoanisole	Sigma Aldrich
Phenyl phosphorous dichloride	Merck
Toluene	GENE
Tungsten hexacarbonyl	Merck

3.2 Methods

3.2.1 General Procedures

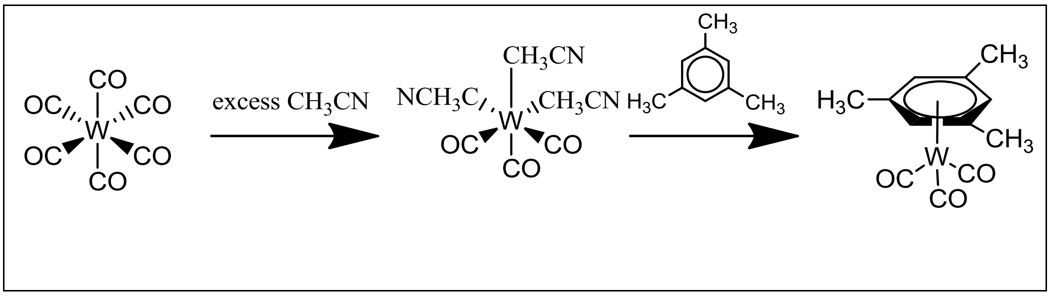
The syntheses carried out along the project were all subjected to nitrogen gas flow *via* Schlenk techniques. As mentioned in Section 3.1, the organic solvents were all desiccated using activated molecular sieves (4 Å). Other than that, the organic solvents were degassed using ultrasonicator prior synthesis process. On the other hand, the celite and silica gel (60 Å, 230-400 mesh (40-63 μm)) were dried thoroughly in oven at 140 °C overnight before use. All the apparatus used in the synthesis process were dried in the oven overnight (110 ℃) and cooled to room temperature before the synthesis process. The above general procedures were applied to all processes unless stated otherwise.

3.2.2 Preparation of starting material, (mes)W(CO)$_3$

The preparation of mesitylene tungsten tricarbonyl, (mes)W(CO)$_3$ (**1**) in this project could be divided into two separate phases, in which an intermediate was synthesized as the precursor for the reaction (refer Section 1.4.2). Phase one of the reaction was carried out according to the experimental methods described by Tate, Knipple and Augl (1961). Initially, tungsten hexacarbonyl (1.0 g, 0.0028 mol) was added to an empty Schlenk flask (100 mL) and flushed with nitrogen gas which flowed along the Schlenk line for 20 minutes. Next, excess acetonitrile (10 mL) and magnetic stir bar were added to the flask as well. The flask with its content were then fitted to a reflux condenser and flushed again with nitrogen gas for approximately 20 to 30 minutes prior the reaction. This step was to ensure that the atmospheric gases were completely expelled from the flask. After that, the flask was lowered down to the oil bath (90 °C) and refluxed for 45 hours, with the formation of a pale yellow solution. Next, the flask was lifted up from the oil bath and cooled to room temperature. The excess acetonitrile was removed from the flask by evaporating it to dryness under vacuo and a yellow-greenish solid, $W(CO)_3(CH_3CN)_3$ was obtained.

Phase two of the reaction was carried out according to the work of King and Fronzaglia (1966). Mesitylene and decalin (5 mL each) were added into the flask containing $W(CO)_3(CH_3CN)_3$ solid. The flask, together with its contents was then purged again with nitrogen gas before it was refluxed for three hours in oil bath (170 ℃). The black solution was filtered through Buchner funnel to obtain yellow solids of (mes)$W(CO)_3$ with some solid impurities. The solids were then redissolved in dichloromethane, CH_2Cl_2 and passed through celite disc (approx. 4 cm thick) in order to remove the solid impurities. A yellow solution was obtained which was then evaporated to dryness under vacuo to obtain crystalline lemon yellow solids of (mes)$W(CO)_3$ (0.4494 g, 41.7 %) and stored in vacuum desiccator for further reaction. The reaction scheme below showed the chemical equation of the preparation of (mes)$W(CO)_3$.

Scheme 3.1 Preparation of (mes)$W(CO)_3$



3.2.3 Preparation of mixed P/S ligand, {$P(o\text{-}C_6H_4SCH_3)_2Ph$}

The synthesis of the mixed phosphine ligand was prepared according to the work of Meek, Dyer, and Workman (1976). Firstly, *o*-bromothioanisole (2.5 g, 0.0123 mol) was placed in a dry 100mL three necked round bottom flask. Next, sodium dried ether (13 mL) was added into the flask. The entire system was then purged with nitrogen gas for 30 minutes while being cooled to around 5 ℃. On the other hand, *n*-butyllithium which was dissolved in hexane (1.6 M, 8 mL) was added dropwise to the liquid *o*-bromothioanisole along a period of 2 hours at a temperature of 0 ℃, under nitrogen atmosphere with vigorous stirring using a mechanical stirrer. Furthermore, it was observed that some white solid began to form when one-half of the *n*-butyllithium was added.

After the addition of *n*-butyllithium in hexane was complete, the resultant mixture was continuously stirred for another 1 hour or so before phenyl phosphorus dichloride, $PPhCl_2$ (1.10 g, 0.0031 mol) which was dissolved in ether (7 mL), was added dropwise to the mixture with stirring. At this point, the temperature of the mixture was found out to increase to a slightly warm temperature. The mixture was stirred at room temperature for another 2 hours.

In order to remove the excess lithium reagent in the mixture, 5 mL of distilled water and 8 mL of 0.2 N hydrochloric acid was consecutively added to hydrolyse it. The white solids formed during the addition of *n*-butyllithium in hexane was filtered, washed with minimum amount of cold ethanol and dried. Subsequently, the organic layer (ether-hexane) was separated from the aqueous layer and the remaining water (if any) was dried over anhydrous sodium sulphate. The organic layer was then left to evaporate to dryness to collect the remaining white solid (total yield: 1.00 g, 90.32 %), which could be further purified with recrystallization to give needle-like crystals.

3.2.4 Reaction of (mes)W(CO)$_3$ and {P(*o*-$C_6H_4SCH_3$)$_2$Ph}

(mes)W(CO)$_3$ (**1**) (200 mg, 0.0052 mol) and *o*-PPh(C_6H_4SMe)$_2$ (182.8 mg, 0.0052 mol), with a ratio of 1:1, were weighed and placed into an empty 50 mL Schlenk flask. The entire flask was flushed with nitrogen gas for approximately 20 minutes. Degassed toluene (~15 mL to 20 mL) was added to the flask and the flask was fitted with reflux condenser before it underwent another flushing process of 20 minutes. Next, the flask was lowered down into the oil bath and refluxed for 18 hours. The colour of the solution turned from greenish yellow to brown at the end of the reflux process. The flask was then lifted up from the oil bath and cooled to room temperature. Subsequently, a TLC test was performed at this point to check the completeness of the reaction and the purity of product synthesised (refer Section 4.2 for further description).

The crude product is then filtered through a celite disc (approx. 2 cm thick) and evaporated to dryness under vacuo. The dried crude product is purged again with nitrogen gas and redissolved in 1.5 mL of dichloromethane. On the other hand, a chromatography column (1.5 cm in diameter) is packed with silica gel (11 cm) using n-hexane as the solvent. The crude product is then purified via column chromatography in which a mixture of unreacted (mes)W(CO)$_3$ (32%) and pure product (68%) is obtained. The product is then recrystallized to form a light yellow crystalline solids (refer Table 4.1 for further descriptions). The light yellow crystalline solid obtained (312.3 mg, 68 %) is then characterized using ATR FTIR and NMR spectroscopies.

3.2.5 Instrumental Analyses

Infrared spectra were generated by a Perkin Almer ATR- FTIR instrument in the range of 450-4000 cm^{-1}. ^1H, ^{13}C and ^{31}P NMR spectra were generated by a JEOL ECX FT NMR 400MHz Spectrometer. The chemical shifts were referred to $CHCl_3$ in chloroform-d_1 for ^1H and ^{13}C NMR spectra, and H_3PO_4 acid is the external reference in ^{31}P NMR spectrum of the product.

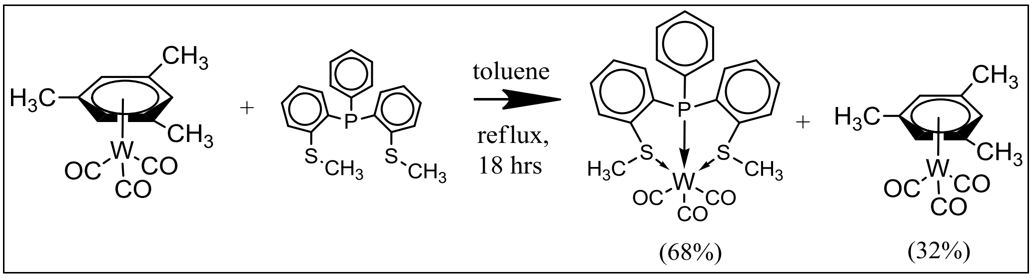
CHAPTER 4

RESULT AND DISCUSSION

4.1 Reaction of (mes)W(CO)$_3$ with {P(*o*-C$_6$H$_4$SCH$_3$)$_2$Ph}

The reaction between mesitylene tungsten tricarbonyl (**1**) and the mixed P/S ligand (P(*o*-C$_6$H$_4$SCH$_3$)$_2$Ph) in equivalent ratio initially gave a brown solution which is then purified and produced light yellow crystalline tridentate complex of {P(*o*-C$_6$H$_4$SCH$_3$)$_2$Ph}W(CO)$_3$ (**2**) with a percentage yield of 68 %, while 32% of it is mes(W)(CO)$_3$ (**1**). The characterisation of the complex was then determined and confirmed using instrumental analyses. The reaction was summarized in the scheme shown below.

Scheme 4.1 Reaction between (1) and {P(*o*-C$_6$H$_4$SCH$_3$)$_2$Ph}ligand



4.2 Thin Layer Chromatography (TLC) and Column Chromatography

As mentioned in Section 3.2.4 earlier, a TLC test was performed on the product obtained at the end of the reaction using hexane: chloroform: toluene (2: 1: 3). It was then found out that the product obtained is not entirely pure as it contained minute amount of **1** which is only visible under short wave (254 nm) UV light. The R_f value for both starting material and pure product (dissolved in dichloromethane) were found out to be 0.5312 and 0.1375 respectively. Figure below shows a rough sketch of TLC test result obtained.

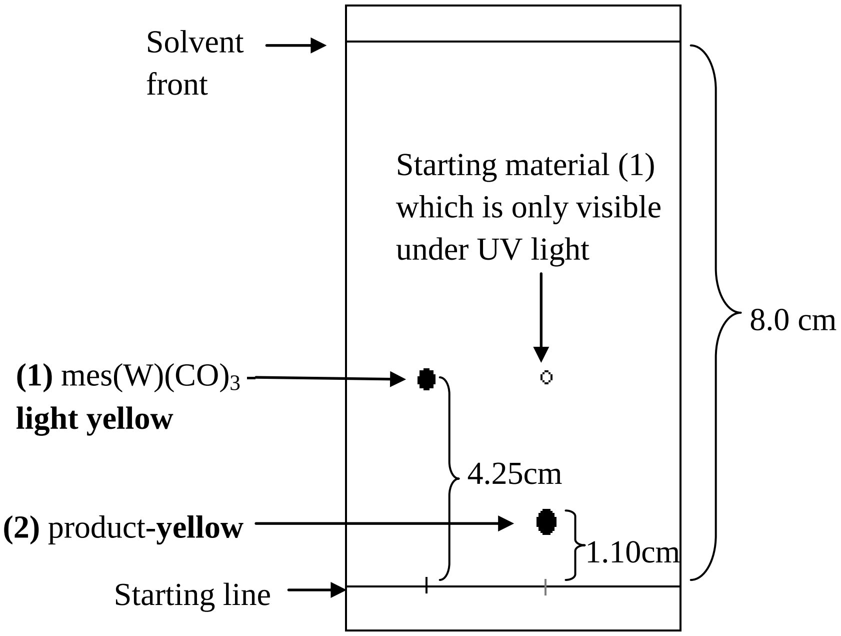


Figure 4.1 Rough sketch of TLC plate (5X10cm)

Hence, column chromatography was performed in order to obtain a pure product. As expected, two separate fractions were successfully eluted out from the column, while some black solids, which were most likely the oxidised materials from the reaction, were left on top of the column. The first fraction, eluted with toluene: diethyl ether (2:1; 15 mL) was identified as (mes)W(CO)$_3$ (**1) (33 mg)**, formed a bright yellow precipitate when it is dried via evaporation. On the contrary, the second fraction, which was eluted with diethyl ether (20 mL), was identified as {P(*o*-$C_6H_4SCH_3)_2$Ph}W(CO)$_3$ (**2**) **(312.3 mg)**, formed a light yellow crystalline solid. The table below showed the column chromatography result on the crude product.

Table 4.1 Purification of product using column chromatography

Fraction	Solvent(s) used; Volume	Observation	Weight /Percentage yield after dried(mg)
(mes)W(CO)$_3$	Toluene: diethyl ether (2:1); 15 mL	Bright yellow solution, formed bright yellow precipitate upon evaporation	33 (32%)
{P(*o*-$C_6H_4SCH_3)_2$Ph} W(CO)$_3$	Diethyl ether; 20 mL	Dark brown yellowish solution, formed light yellow solid upon evaporation	312.3 (68%)

4.3 Fourier Transform Infrared (FTIR) Spectroscopy

IR spectroscopy was carried out on both starting material, (mes)W$(CO)_3$ and the purified product, {P(*o*-$C_6H_4SCH_3)_2$Ph}W$(CO)_3$ (2) in ATR cell. ATR (Attenuated Total Reflectance) spectroscopy is one of the reflectance methods in FTIR spectroscopy which applied the principle of total internal reflection on the sample which is usually in crystal (solid) form. This method does not require any medium (solid, liquid, or gas) during its measurement and only requires an ATR cell in close contact with the sample (Stuart, 2005).

4.3.1 A comparison of (mes)W$(CO)_3$ (1) to the literature source

The significant functional groups found in **1** were listed out as shown in Table 4.2 below. For **1**, there were a few peaks that were missing from the experimental peaks obtained, such as two peaks for aromatic C-H stretch (2987 cm^{-1} and 2970 cm^{-1}), and one peak each for methyl C-H stretch, aromatic C=C stretch, and M-C stretch and so on. However, the IR frequencies measured experimentally and those from literature source were either the same or very close to the wavenumber value provided by the literature source (refer Table 4.2 and Figure 4.2). Thus, it can be concluded that the (mes)W$(CO)_3$ synthesised in this project was pure.

Table 4.2 IR frequencies for (mes)W(CO)$_3$

Complex	Significant Functional Group	Types of frequency	IR frequencies (cm^{-1})	
			Experimental **ATR-FTIR**	Literature * **KBr pellet** (Armstrong, et al., 1990)
(mes)W(CO)$_3$ (**1**)	Aromatic C-H	ν	3077 (w)	3077, 2987, 2970
	Methyl C-H	ν	2926 (w)	2925, 2862
		δ	1379(m)	1380
	Terminal CO	ν	1940 (s), 1865 (vs)	1956, 1945, 1879, 1854
	Aromatic C=C	ν	1513 (w), 1441 (m), 1006 (w), 988 (m)	1633, 1512, 1444, 1004, 989
	Aromatic C-Me	ν	1299 (m)	1299
	M-CO	δ	597 (s)	600
		δ_{oop}	578 (s)	579
		δ_{ip}	504 (m)	505
	M-C	ν	474 (m)	482, 476

*The peak intensities were not mentioned in the literature source.

Note: ν: stretching frequency; δ: bending; oop:out of plane; ip: in plane

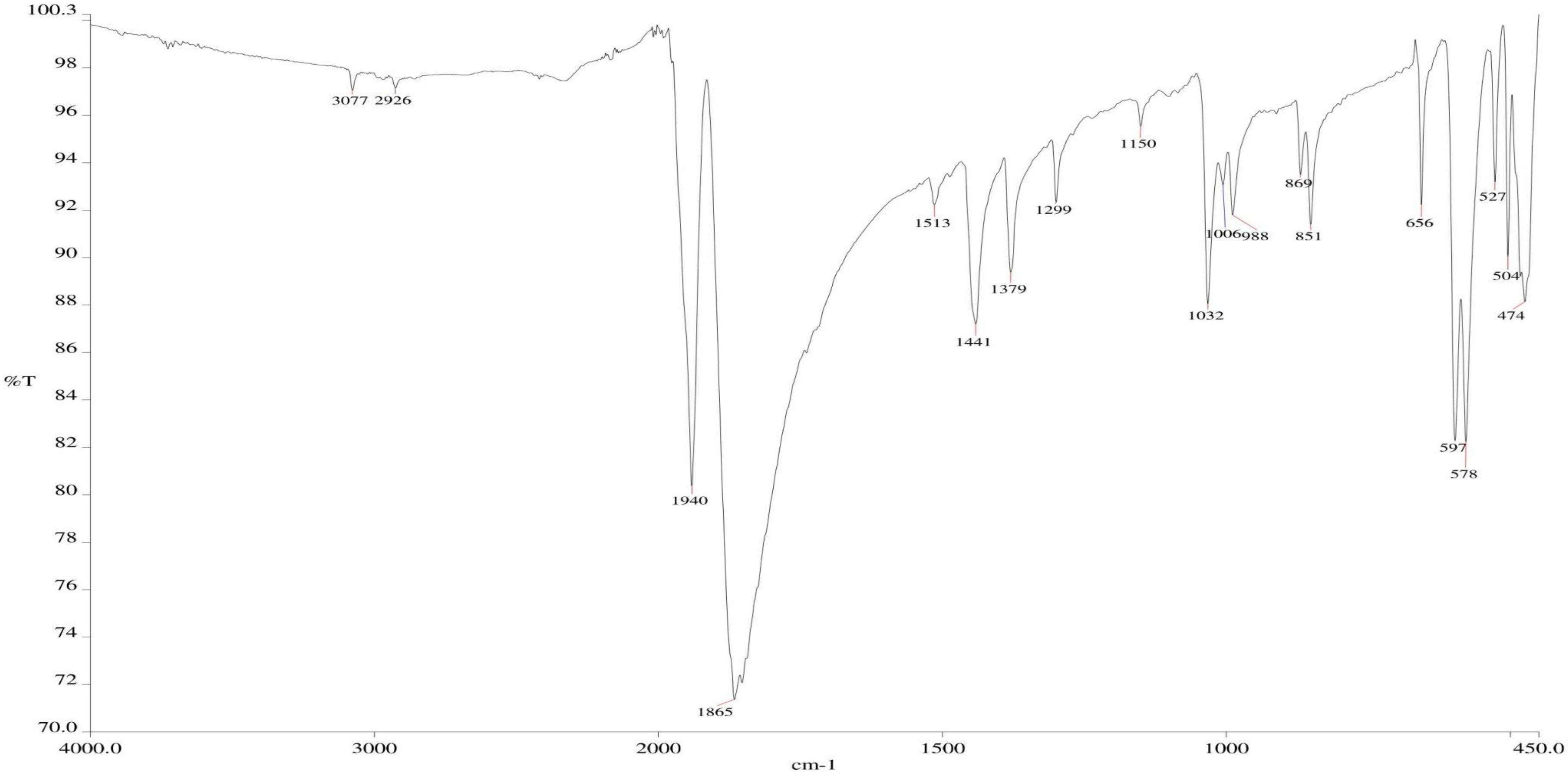


Figure 4.2 IR spectrum of mes(W)(CO)$_3$ (1)

4.3.2 A comparison between mes(W)(CO)$_3$ (1), {P(*o*-C$_6$H$_4$SCH$_3$)$_2$Ph}W(CO)$_3$ (2) and {P(*o*- C$_6$H$_4$SCH$_3$)$_2$Ph} from the literature source

The product, {P(*o*-C$_6$H$_4$SCH$_3$)$_2$Ph}W(CO)$_3$ (**2**) had only very few functional groups that could be identified from the spectrum obtained, such as terminal CO stretch, aromatic C=C stretch, C-P stretch and C-S stretch. If compared to **1**, the stretching frequencies of terminal CO is lower in **2** than **1,** which indicated that the CO bond strength had been weakened from triple bond to double bond thus shifted the wavenumber to lower frequency. This is due to the presence of electron donating P and S which would increased the π-basicity of the metal, which in turn would further stabilized the π-back bonding effect on the M-C bond, raising the number of M-C bond from one bond to two bonds.

Besides that, there were only three stretching frequencies identified as the terminal CO stretch, indicating that there may be only three terminal CO ligands bonded to the tungsten complex, unlike the reported tetracarbonyl species of tungsten in which a fourth terminal CO stretch can be observed at 2022 cm^{-1}. Furthermore, one of the stretching frequencies of terminal CO is lower than any of the reported value, indicated that there were more electron rich species bonded to the centre metal atom which increased the π-back bonding effect on the CO ligand compared to the tetracarbonyl complex reported.

Table 4.3 Stretching frequencies of {*o*-PPh($C_6H_4SMe)_2$}W$(CO)_3$ (2)

Complex	Significant Functional Group	Stretching frequencies (cm^{-1})	
		Experimental **ATR-FTIR**	Literature **In CH_2Cl_2** (Hirsivaara, et al., 1999) **{P(*o*-$C_6H_4SCH_3)_2$Ph} W$(CO)_4$**
{P(*o*-$C_6H_4SCH_3)_2$Ph} W$(CO)_3$ (**2**)	Terminal CO	1922 (s), 1835 (sh), 1798 (vs)	2022 (s), 1918 (sh), 1904 (vs), 1877 (s)
	Aromatic C=C	1494 (vw), 1453(w), 1426(m)	-
	C-P	741 (m), 730 (m)	-
	C-S	693 (m)	-

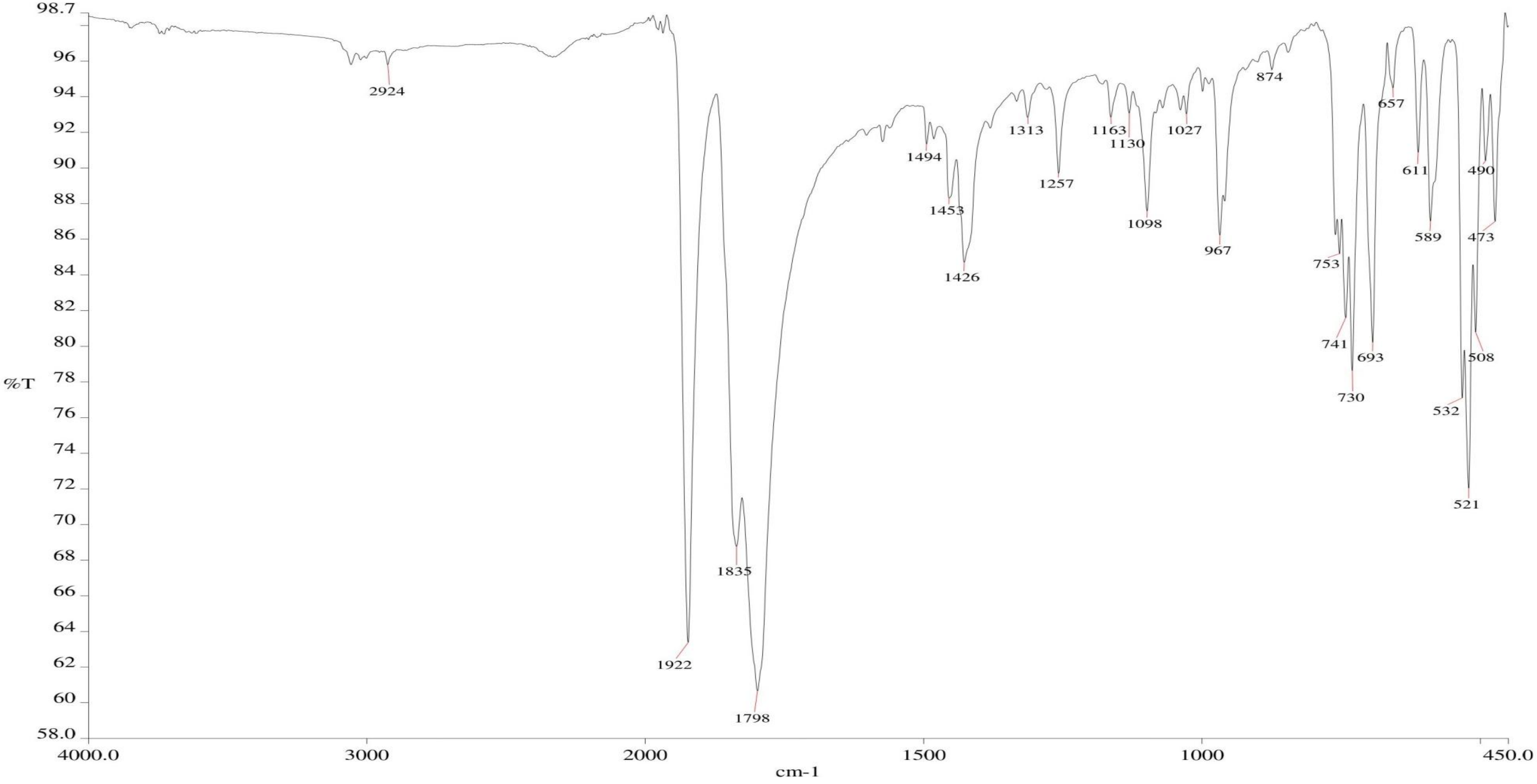


Figure 4.3 IR spectrum of $\{P(o\text{-}C_6H_4SCH_3)_2Ph\}W(CO)_3$ (2)

4.4 Nuclear Magnetic Resonance (NMR) Spectroscopy

4.4.1 ^{1}H NMR

The proton chemical shifts for both (mes)W$(CO)_3$ (**1**) and {P(*o*-$C_6H_4SCH_3)_2$Ph}W$(CO)_3$ (**2**) were referenced to residual $CHCl_3$ in $CDCl_3$ (chloroform-d_1), with a reference peak shown at 7.26 ppm. This included the (mes)W$(CO)_3$ from the literature source as well.

There were two major peaks that can be found in its proton NMR spectrum (refer Table 4.4 and Figure 4.4). These peaks belonged to the protons in methyl group at 2.44 ppm, and the aromatic proton at 5.12 ppm. The proton of the methyl group would be more shielded and appeared as a tall singlet compared to aryl proton. Aromatic protons, on the other hand, is more deshielded and could be found downfield (larger ppm value) due to the anisotropic effect caused by the π-electrons in the double bond.

Furthermore, it is relatively easier to identify both types of protons as the total number of protons in the methyl group is higher (9 H) than that of the total number of protons attached directly to the benzene ring (3 H).

Table 4.4 ^{1}H NMR chemical shifts for (mes)W(CO)$_3$ (1)

Complex	Types of Proton	Chemical shift (ppm)*	
		Experimental	Literature (Kolehmainen, et al., 1992)
(mes)W(CO)$_3$ (**1**)	CH_3	2.44	2.42
	Aromatic H	5.12	5.18

*reference: residual $CHCl_3$ in $CDCl_3$

There were two groups of major peaks that can be found in **2** as well, which is all located in the mixed P/S ligand: protons from *o*-SCH_3 group and phenyl groups respectively. The protons found in *o*-SCH_3 group were more shielded than the protons found in aromatic ring as they were found at 2.34 ppm and 3.05 ppm respectively.

Referring to the NMR spectrum of **2**, the peaks of the aromatic protons could not be identified further as there were three aromatic rings contained within the structure with closely similar chemical environments. However, it is still possible to tell from the spectrum of the position of the aromatic protons as they are usually found in a region ranging from 6.50 ppm to 8.00 ppm.

In comparison with the reported tetracarbonyl species (refer literature values in Table 4.5), the chemical shifts of proton from *o*-SCH_3 group are slightly different. This observation applied to the chemical shifts of aromatic proton of both experimental and literature source as well. Hence, there is a possibility that the tungsten complex synthesized in this project have a different geometry or coordination than that of the reported structure.

Table 4.5 ^{1}H chemical shifts for {P(*o*-$C_6H_4SCH_3)_2$Ph}W(CO)$_3$ (2)

Complex	Types of Proton	Chemical shift (ppm)	
		Experimental	Literature (Hirsivaara, 2001) **{P(*o*-$C_6H_4SCH_3)_2$Ph} W(CO)$_4$**
{P(*o*-$C_6H_4SCH_3)_2$Ph}W(CO)$_3$ (**2**)	*o*-SCH_3	2.34, 3.05	2.45, 2.92
	Aromatic H	7.17, 7.18, 7.24, 7.26, 7.32, 7.39, 7.45, 7.46, 7.83	6.25, 7.01, 7.28-7.78

*reference: residual $CHCl_3$ in $CDCl_3$

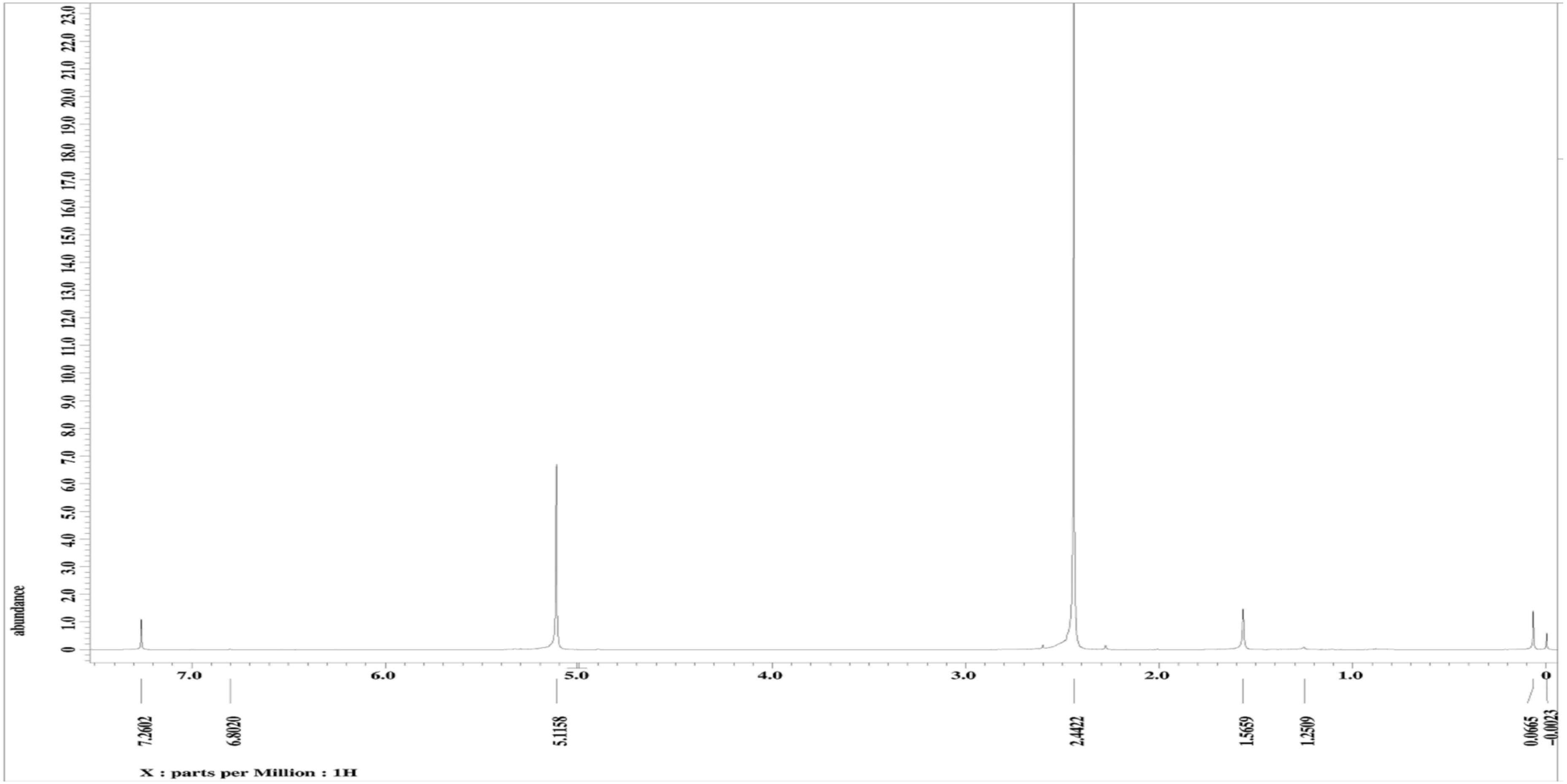


Figure 4.4 ^{1}**H NMR spectrum of (mes)W(CO)$_3$ (1)**

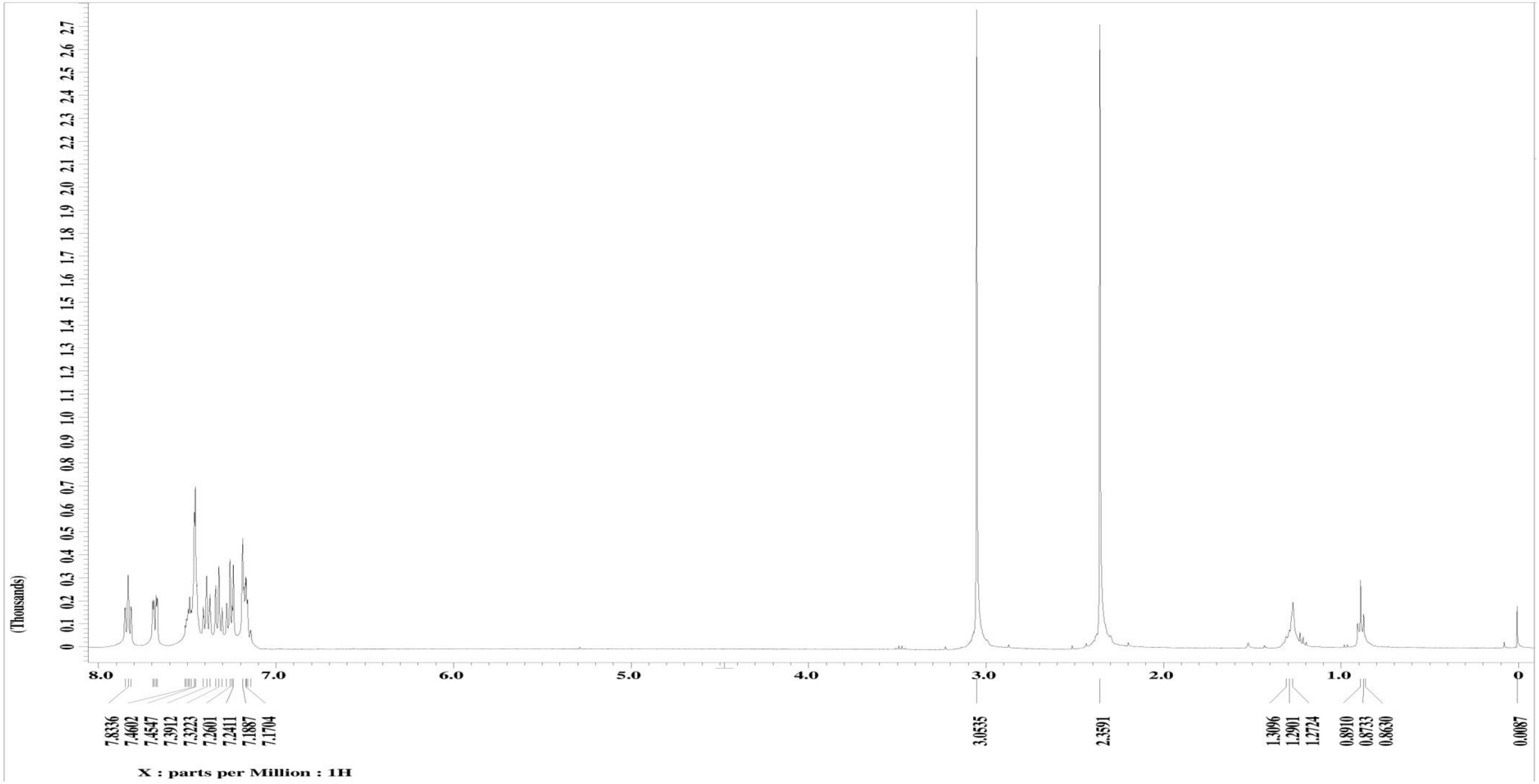


Figure 4.5 ^{1}H NMR spectrum of $\{P(o\text{-}C_6H_4SCH_3)_2Ph\}W(CO)_3$ (2)

4.4.2 ^{13}C NMR

The same deuterated solvent, $CDCl_3$ were used in measuring the chemical shifts of **1** and **2**, while the reference signal were found at 77.1 ppm and 77.2 ppm in reference of the residual $CHCl_3$ in the solvent. Furthermore the other peaks which were not mentioned in the table below were most probably the solvent residues signals which are NMR active.

Carbon-13 NMR of **1** showed 5 distinct peaks which belonged to four chemically non-equivalent carbons (refer Table 4.6). In comparison with the literature values, the chemical shift values are slightly lower. Furthermore, there was an additional peak shown for carbon from CO group which suggested that there were two chemical non-equivalent carbons among the three CO ligands bonded to tungsten, and also a possibility of another $(mes)W(CO)_3$ of a different geometry may be synthesised from that of the reported structure. Nonetheless, it was confirmed from the chemical shifts that the $(mes)W(CO)_3$ is successfully synthesised from the reaction.

Table 4.6 ^{13}C chemical shifts of mes(W)(CO)$_3$ (1)

Complex	Types of Carbon	Chemical shift (ppm)*	
		Experimental	Literature (Kolehmainen, et al., 1992)
(mes)W(CO)$_3$ (**1**)	CH_3	20.7	21.0
	Aromatic C-H	90.2	91.4
	Aromatic C-CH_3	110.1	111.5
	CO	191.4, 212.3	213.3

*reference: residual $CHCl_3$ in $CDCl_3$

For complex **2**, the carbon chemical shifts of *o*-SCH_3 group were found at 21.7 ppm and 31.6 ppm respectively. Moreover, the experimental values were relatively different from the literature values and were closer to each other, indicated that the carbons from *o*-SCH_3 group were having similar bonding, as both S were bonded to the tungsten which would decreases the electron density of S as electrons were withdrawn from its nucleus (to the metal centre).

There were a total of 15 peaks observed in the ^{13}C NMR spectrum of **2** for the complex synthesized (refer Table 4.7 and Figure 4.8), while there were a total of 16 peaks observed for the reported tetracarbonyl species using the same ligand. Other than that, there were only three CO peaks that could be observed from the spectrum in comparison to the four CO peaks from the literature source. In addition, the chemical shift for CO is higher than that of the CO in starting material due to the phosphine ligand acting as σ-donor that enhanced the back donating effect of metal to the CO ligand.

Table 4.7 ^{13}C chemical shifts of {P(*o*-$C_6H_4SCH_3)_2$Ph}W(CO)$_3$ (2)

Complex	Types of Carbon	Chemical shift (ppm)**	
		Experimental	Literature (Hirsivaara, 2001) **{P(*o*-$C_6H_4SCH_3)_2$Ph} W(CO)$_4$**
{P(*o*-$C_6H_4SCH_3)_2$Ph} W(CO)$_3$ (**2**)	*o*-SCH_3	21.7, 31.6	18.82, 33.02
	Aromatic carbon*	125.5, 128.4, 128.7 (d), 129.0 (d), 129.2, 130.1, 130.7, 130.9, 131.0, 131.5 (131.7) , 132.4, 133.4 (133.9), 138.1, 139.1 (139.5), 145.6 (146.0)	125.20 (d), 129.07, 129.15 (d), 129.42, 130.4-131.0, 131.04 (d), 131.05, 132.31 (d), 133.46 (d), 134.07, 136.90 (d), 138.88 (d), 143.26 (d), 146.01 (d)
	CO	215.1, 217.9, 218.2	200.1, 202.0, 207.8, 208.8

*(d) - doublets arise due to J_{CP} coupling constants; those in parentheses are those doublets that can be identified

**reference: residual $CHCl_3$ in $CDCl_3$

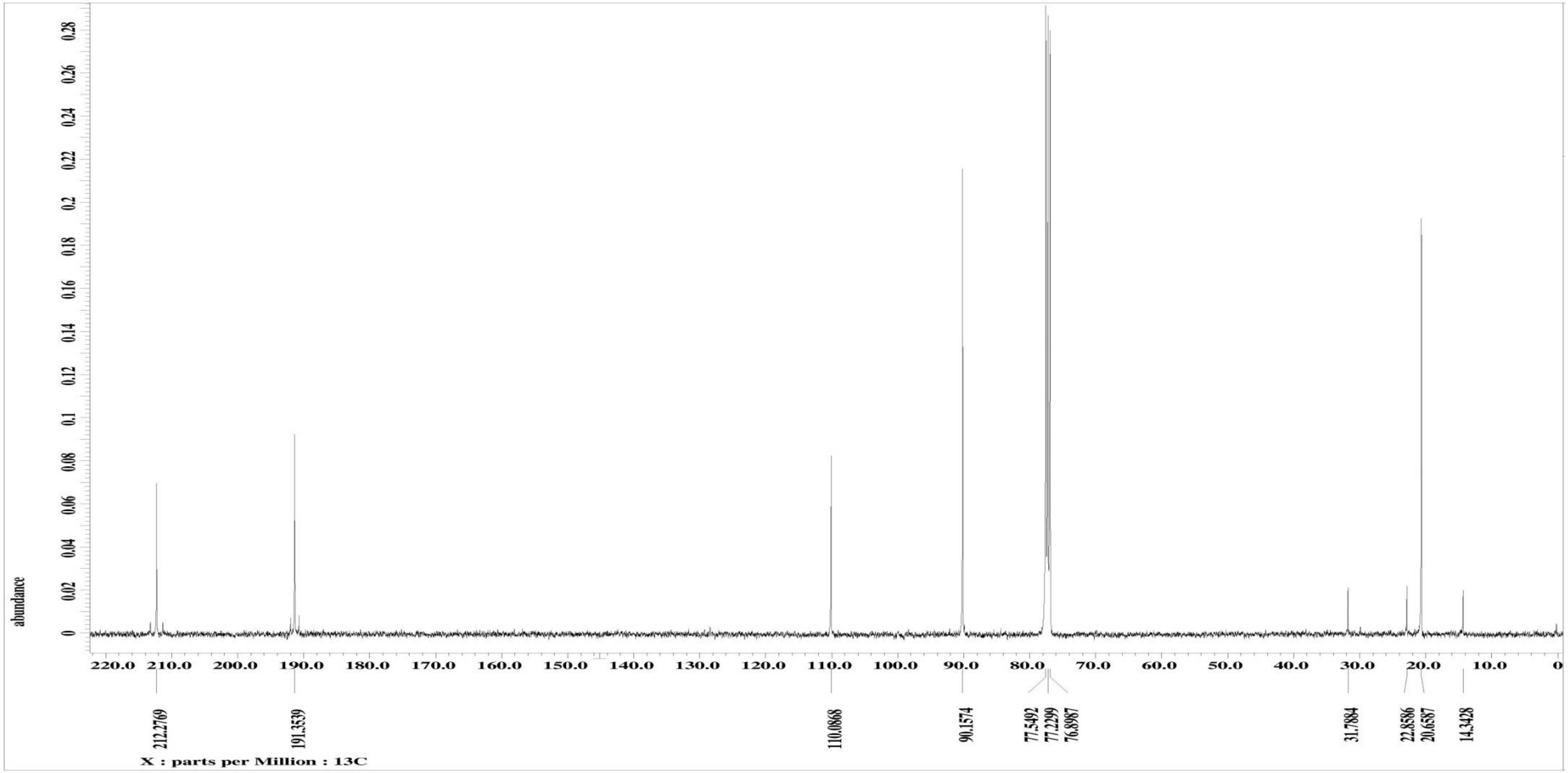


Figure 4.6 ^{13}C NMR spectrum of (mes)W(CO)$_3$ (1)

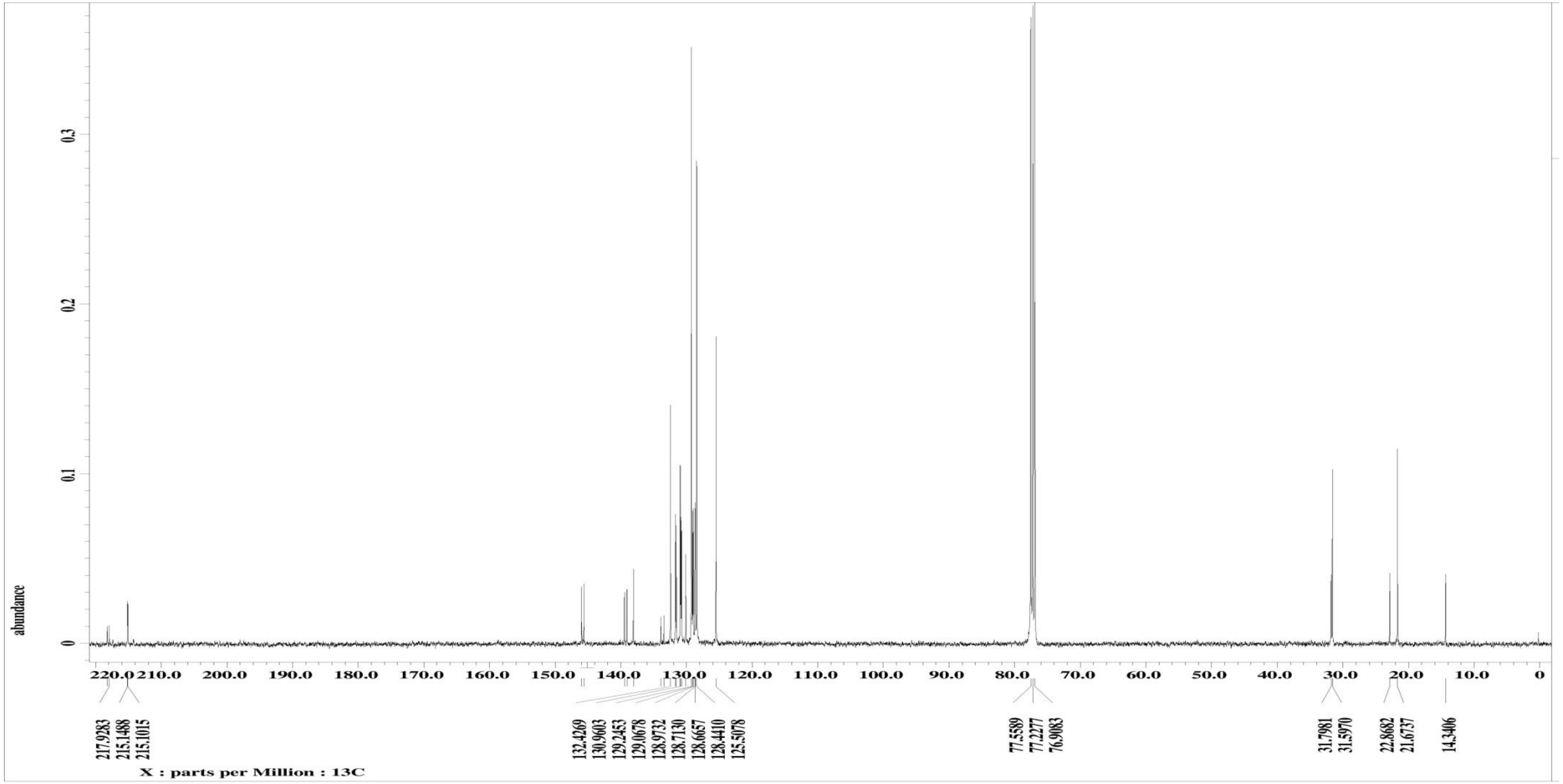


Figure 4.7 ^{13}C NMR spectrum of {P(*o*-$C_6H_4SCH_3)_2$Ph}W(CO)$_3$ (2)

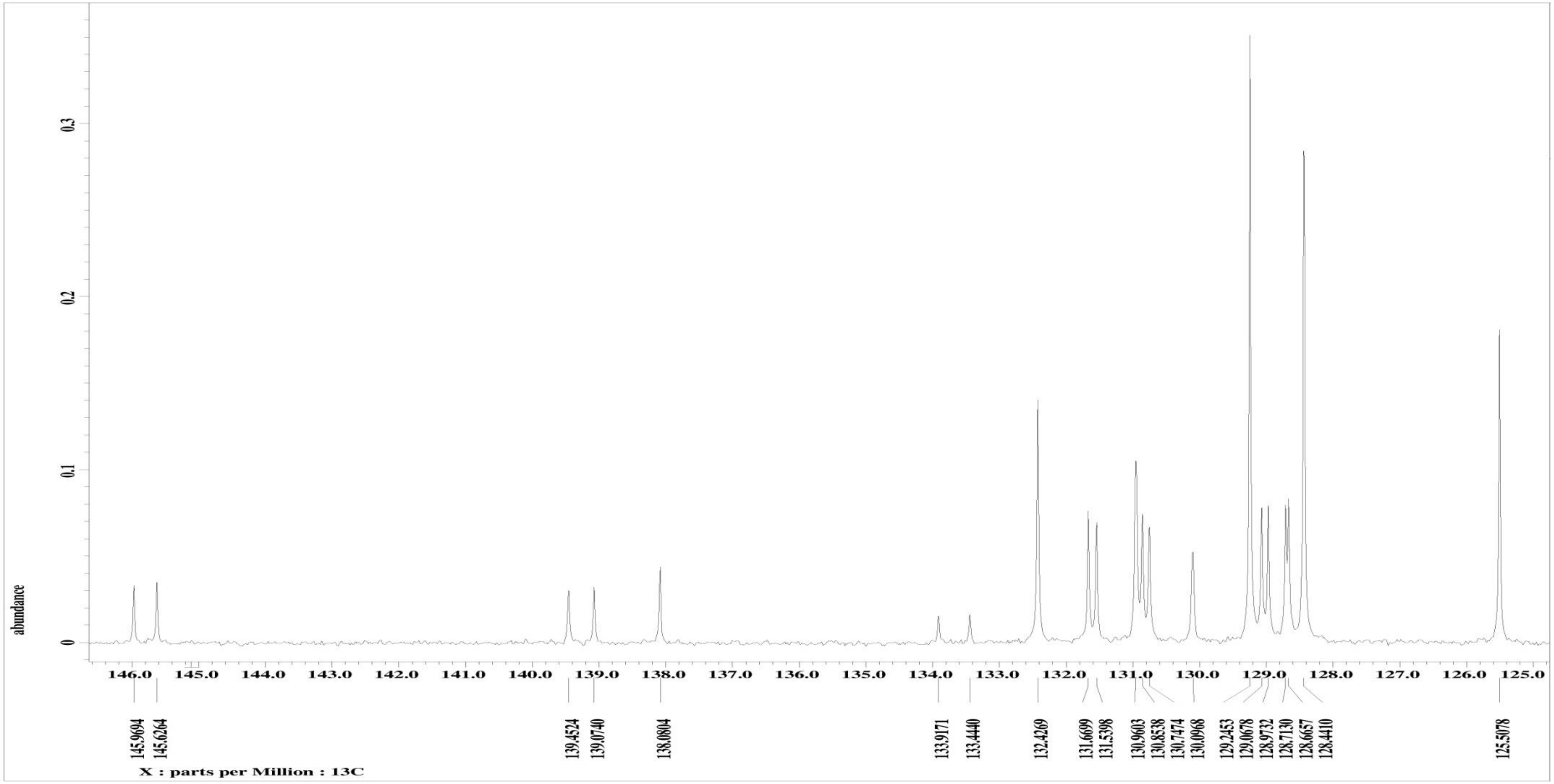


Figure 4.8 ^{13}C **NMR spectrum of {P(*o*-$C_6H_4SCH_3$)$_2$Ph}W(CO)$_3$ (2) – Aromatic carbon region**

4.4.3 ^{31}P NMR

The phosphorus in ^{31}P NMR spectrum was both referenced to phosphoric acid, H_3PO_4 as the external reference, which had a NMR signal at 0 ppm. The phosphine ligand showed a chemical shift at -22.0 ppm in its free ligand form. In the contrary, once it is bonded to a metal complex such as tungsten carbonyl complex, a downfield shift can be observed as it shifted to 77.9 ppm as shown experimentally in the table below.

A similar downfield shift can be observed for the literature value provided in the table below but in different magnitude. In comparison with the tetracarbonyl species below (Table 4.8), the chemical shift of **2** is higher, most probably due to the presence of an extra five-membered chelate ring (refer Figure 4.9) whereby the delocalisation of electrons occurred.

Furthermore, phosphorus which is incorporated into a five-membered chelate ring would cause deshielding effect, not to mention there were two five-membered chelate rings found in **2**. Hence, the chemical shift of phosphorus is higher in the experimental compared to that of the tetracarbonyl species with only one five-membered chelate ring from the literature source.

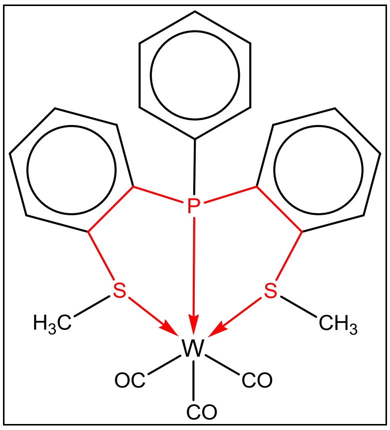


Figure 4.9 Proposed structure with two five-membered chelate rings (highlighted in red)

Table 4.8 ^{31}P chemical shifts of free phosphine ligand and bonded phosphine ligand

Complex	Types of Phosphorus	Chemical shift (ppm)*	
		Experimental	Literature (Hirsivaara, *et al*., 1999) **{P(*o*-$C_6H_4SCH_3)_2$-Ph}W(CO)$_4$**
{P(*o*-$C_6H_4SCH_3)_2$-Ph}W(CO)$_3$ (**2**)	P on free phosphine ligand	-22.0	-22.0
	P on phosphine ligand after bonded to W	77.9	45.7

*external reference: phosphoric acid, H_3PO_4

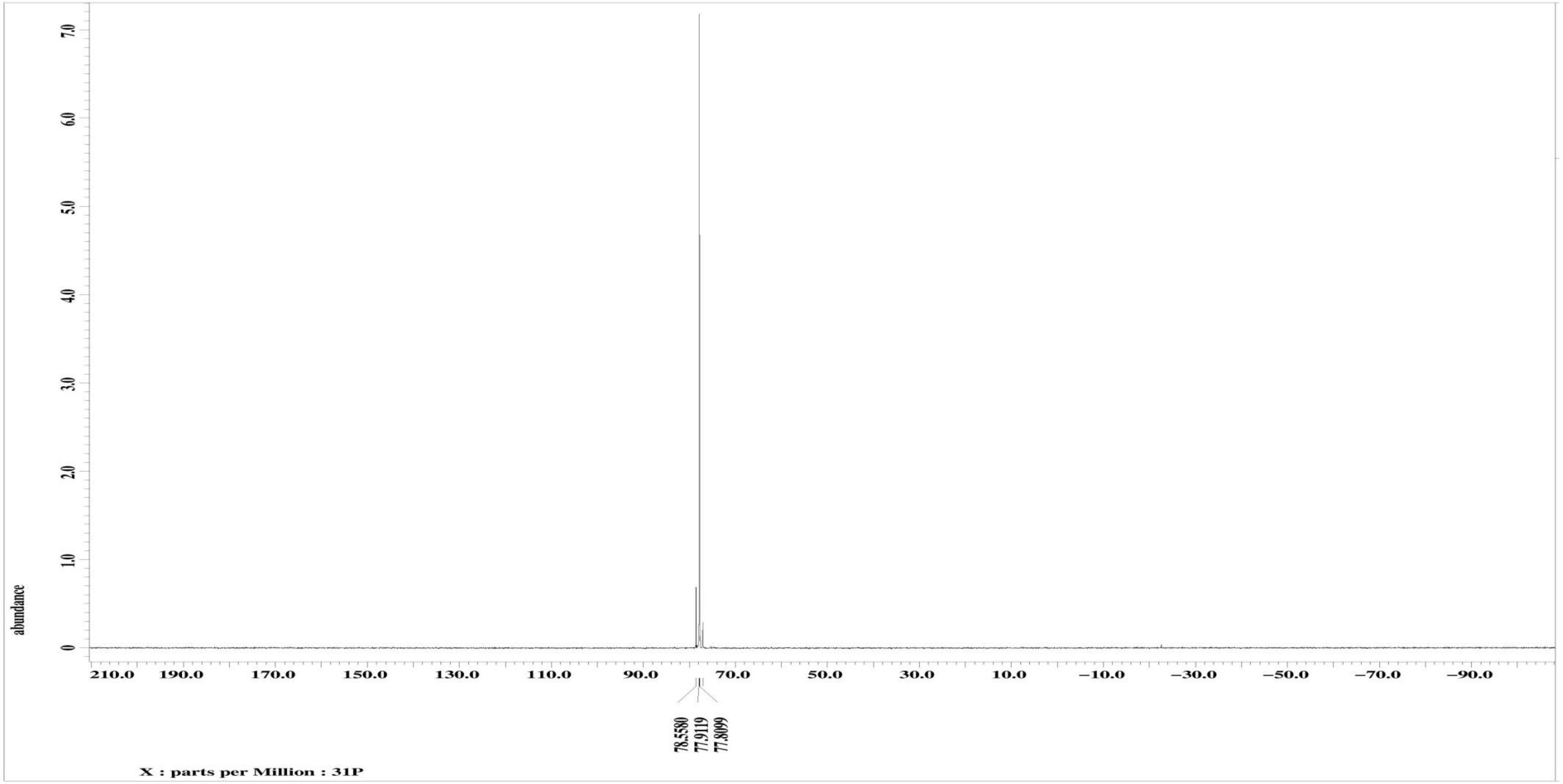


Figure 4.10 ^{31}P NMR spectrum of {P(o-$C_6H_4SCH_3)_2$Ph}W$(CO)_3$ (2)

4.5 Proposed structure: comparison and explanation

Based on the comparison between experimental and literature values obtained from both IR and NMR spectroscopy, it is possible that a tungsten tricarbonyl species bonded tridentate to the mixed P/S ligand had been synthesized. This deduction could be valid as the precursor used in the reaction is a tricarbonyl species and not hexacarbonyl species as used in the literature source.

In addition, the reaction is conducted under inert atmosphere (nitrogen gas) and under strong flow of nitrogen gas. As the system is a closed system, it is even less likely that there will be contact with atmospheric gases (especially CO_2). Moreover, this system would minimized the availability of free CO ligands to be bonded again to the metal complex as they are mostly removed from the solvent and trapped in the oil bubbler (paraffin oil).

Table 4.9 showed the evidence in comparison between the proposed structure (experimental) and reported structure (literature), while Figure 4.10 showed the proposed structure of the complex synthesised from this project based on the evidences provided, which is a tricarbonyl complex which has not been reported by any published journals previously.

Table 4.9 Supporting evidence for proposed stucture

	Proposed structure	Reported structure	Difference
ν(CO)	1798 cm^{-1}, 1835 cm^{-1}, 1922 cm^{-1}	1873 cm^{-1}, 1894 cm^{-1}, 1911 cm^{-1},2018 cm^{-1}	One CO stretch missing
^{13}C-NMR	Three CO peaks	Four CO peaks	One CO carbon peak missing
^{31}P-NMR	77.9ppm	46.0ppm	Larger magnitude of chemical shift

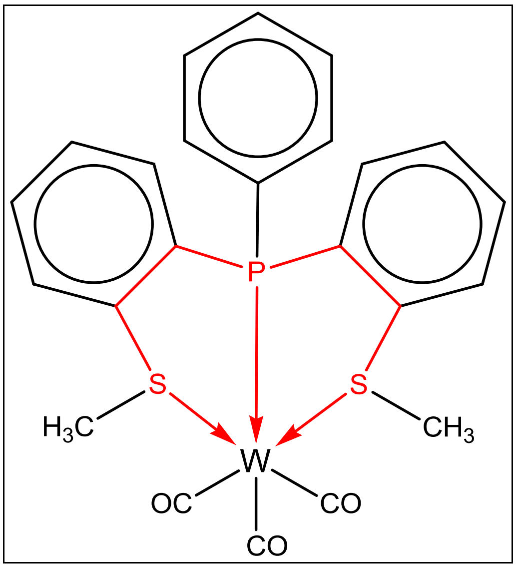
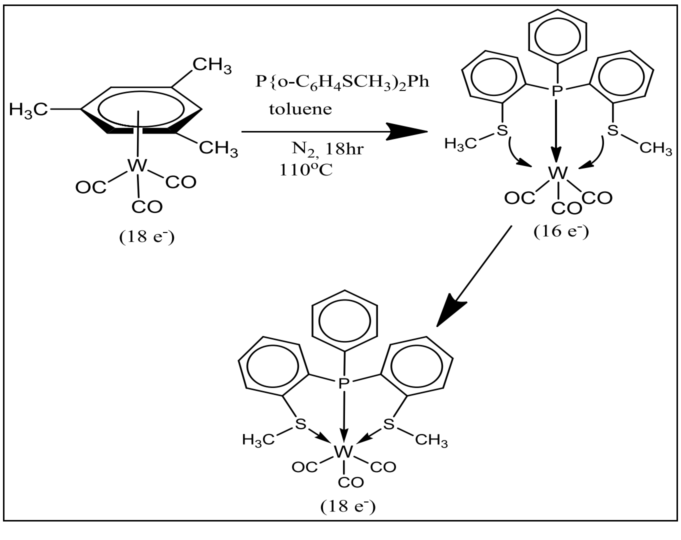


Figure 4.11 Proposed structure

4.6 Proposed synthetic route for {P(*o*-$C_6H_4SCH_3)_2$Ph}W(CO)$_3$ (2)

The starting material of the reaction, (mes)W(CO)$_3$ (**1**) is a stable metal complex as it fulfilled the 18 ē rule proposed by Irving Langmuir (Crabtree, 2009). Hence, the most likely mechanism that the product, {P(*o*-$C_6H_4SCH_3)_2$Ph}W(CO)$_3$ (**2**) may undergo is the dissociative ligand substitution reaction, which is shown in Scheme 4.2 below. As CO ligands are bonded more strongly to the metal atom, mesitylene ligand would be the one leaving the complex, taking along with it the 6 electrons that it used to donate to the metal atom. Thus, the metal atom would require 6 electrons in order to stabilize the complex, and this task could be done by the incoming tridentate ligand, P(*o*-$C_6H_4SCH_3)_2$Ph whereby P and two S-CH$_3$ could donate two electrons each to the metal center and gave a stable 18 ē complex with two five-membered chelate rings.

Scheme 4.2 Proposed synthetic pathway for {P(*o*-$C_6H_4SCH_3)_2$Ph}W(CO)$_3$

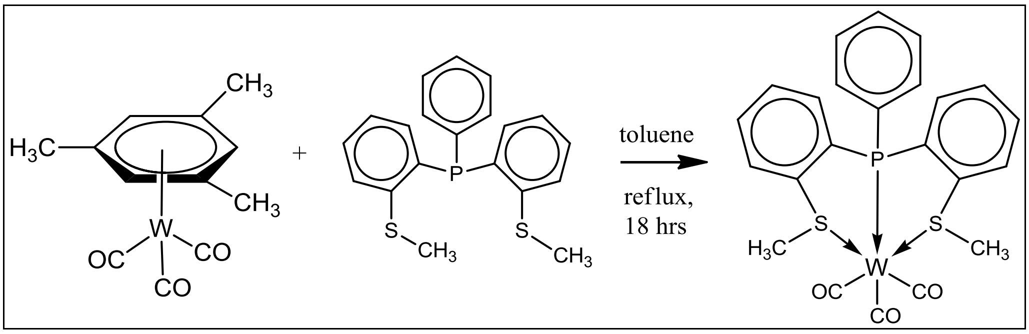


CHAPTER 5

CONCLUSION

Arene tungsten tricarbonyl species, (mes)W$(CO)_3$ would react with mixed P/S ligand, P(*o*-$C_6H_4SCH_3)_2$Ph of equimolar ratio in toluene for 18 hours to give a tridentate *bis*(*o*-methylthiobenzene)phenyl phosphine tungsten tricarbonyl complex with two five-membered P,S chelate rings, which is a *fac* isomer. The percentage yield of the reaction is 68 % and not of higher yield due to decomposition reaction. However, the reaction proved that tridentate product could be synthesised by using a tricarbonyl complex as a precursor in place of a hexacarbonyl complex, which have not been reported by any journals previously. Scheme 5.1 below illustrates the reaction taking place between (mes)W$(CO)_3$ and P(*o*-$C_6H_4SCH_3)_2$Ph ligand to yield {P(*o*-$C_6H_4SCH_3)_2$Ph}W$(CO)_3$.

Scheme 5.1 Reaction between (mes)W$(CO)_3$ and P(*o*-$C_6H_4SCH_3)_2$Ph ligand



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