

**SYNTHESIS, CHARACTERIZATION, AND REACTIVITY STUDIES OF**  
 **$\eta^5$ -CYCLOPENTADIENYLIRON DICARBONYL 4-**  
**(DIMETHYLAMINO)PHENYLDIPHENYLPHOSPHINE IODIDE AND**  
**DI( $\mu_2$ -CHLORO)( $\eta^5$ -CYCLOPENTADIENYL)4-**  
**(DIMETHYLAMINO)PHENYLDIPHENYLPHOSPHINE IRON-**  
**PALLADIUM IODIDE**

By

**TONG YONG YAO**

A project report submitted to the Department of Chemical Science

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## ABSTRACT

**SYNTHESIS, CHARACTERIZATION, AND REACTIVITY STUDIES OF  
 $\eta^5$ -CYCLOPENTADIENYLIRON DICARBONYL 4-  
(DIMETHYLAMINO)PHENYLDIPHENYLPHOSPHINE IODIDE AND  
DI( $\mu_2$ -CHLORO)( $\eta^5$ -CYCLOPENTADIENYL)4-  
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PALLADIUM IODIDE**

**TONG YONG YAO**

A study on synthesis of new organometallic complexes,  $[\text{CpFe}(\text{CO})_2(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))]\text{I}$  (**2**) from the reactions of  $\text{CpFe}(\text{CO})_2\text{I}$  (**1**) with 4-(dimethylamino)phenyldiphenylphosphine *via* microwave-assisted reaction in toluene at 110 °C for 30 minutes. Besides, another new bimetallic complexes,  $[\text{CpFe}(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)(\mu\text{-Cl})_2\text{Pd})]\text{I}_4$  (**3**) was synthesized from the microwave-assisted reaction of complex **2** with palladium chloride in acetonitrile at 60 °C for 3 hours. The progress of the reaction was monitored by Thin Layer Chromatography (TLC) and the compounds were isolated *via* silica gel column chromatography then further purified by recrystallization at -20 °C. These new complexes were characterized by Fourier Transform Infrared Spectroscopy (FTIR),  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  Nuclear Magnetic Resonance (NMR) Spectroscopy, UV-Visible Spectrophotometry,

Elemental Analysis, Electrospray-Ionization Mass Spectrometry (ESI-MS). The molecular structures of the complexes along with their synthetic pathways were proposed based on various spectroscopy results and the NMR tube reactions, C,H,N elemental analysis and fragmentation patterns of complexes **2** and **3** from the ESI-MS. Furthermore, antioxidant properties of the complex **2** was studied using 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay.

## ABSTRAK

### KAJIAN SINTESIS, CIRI-CIRI DAN REAKTIVITI $\eta^5$ - CYCLOPENTADIENYLIRON DICARBONYL 4- (DIMETHYLAMINO)PHENYLDIPHENYLPHOSPHINE IODIDE DAN DI( $\mu^2$ -CHLORO)( $\eta^5$ -CYCLOPENTADIENYL) 4-(DIMETHYLAMINO) PHENYLDIPHENYLPHOSPHINE IRON-PALLADIUM IODIDE

TONG YONG YAO

Kajian tentang sintesis kompleks organologam baharu,  $[\text{CpFe}(\text{CO})_2(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))]\text{I}$  (**2**) daripada tindak balas  $\text{CpFe}(\text{CO})_2\text{I}$  (**1**) dengan 4-(dimethylamino)fenildifenilfosfin melalui gelombang mikro- tindak balas berbantu dalam toluena pada  $110\text{ }^\circ\text{C}$  selama 30 minit. Selain itu, satu lagi kompleks dwilogam baharu,  $[\text{CpFe}(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)(\mu\text{-Cl})_2\text{Pd})]\text{I}_4$  (**3**) telah disintesis daripada tindak balas dibantu gelombang mikro kompleks **2** dengan paladium klorida dalam asetonitril pada  $60\text{ }^\circ\text{C}$  selama 3 jam. Kemajuan tindak balas dipantau oleh Kromatografi Lapisan Nipis (TLC) dan diasingkan melalui kromatografi lajur gel silika kemudian disucikan lagi dengan penghabluran semula pada  $-20\text{ }^\circ\text{C}$ . Kompleks baharu ini dicirikan oleh Spektroskopi Inframerah Transformasi Fourier (FTIR),  $^1\text{H}$ ,  $^{13}\text{C}$  dan  $^{31}\text{P}$  Spektroskopi Resonans Magnetik Nuklear (NMR), Spektrofotometri UV-Visible, Analisis Unsur, Spektroskopi Jisim Electrospray-Ionization (ESI-MS).

Struktur molekul kompleks bersama dengan laluan sintetikanya telah dicadangkan berdasarkan pelbagai keputusan spektroskopi dan tindak balas tiub NMR, analisis unsur C, H, N dan corak pemecahan kompleks **2** dan **3** daripada ESI-MS. Tambahan pula, sifat antioksidan kompleks **2** telah dikaji menggunakan ujian 2,2-diphenyl-1-picrylhydrazyl (DPPH).

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Lastly, I would also like to give a special thanks to National University of Singapore (NUS) for helping in providing Element Analysis and Electrospray-Ionization Mass Spectroscopy (ESI-MS) analysis.

## DECLARATION

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



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(TONG YONG YAO)

## APPROVAL SHEET

This project report entitled “**SYNTHESIS, CHARACTERIZATION, AND REACTIVITY STUDIES OF  $\eta^5$ -CYCLOPENTADIENYLIRON DICARBONYL 4-(DIMETHYLAMINO)PHENYLDIPHENYLPHOSPHINE IODIDE AND  $DI(\mu_2\text{-CHLORO})(\eta^5\text{-CYCLOPENTADIENYL})4\text{-}(\text{DIMETHYLAMINO})\text{PHENYLDIPHENYLPHOSPHINE IRON-PALLADIUM IODIDE}$ ” was prepared by TONG YONG YAO and submitted as partial fulfillment of the requirements for the degree of Bachelor of Science (Hons) Chemistry at Universiti Tunku Abdul Rahman.**

Approved by:



Date: 18.10.2023

( Asst. Prof. Dr. Ooi Mei Lee)

Supervisor

Department of Chemical Science

Faculty of Science

Universiti Tunku Abdul Rahman

**FACULTY OF SCIENCE**  
**UNIVERSITI TUNKU ABDUL RAHMAN**

Date: \_\_\_\_\_18.10.2023\_\_\_\_\_

**PERMISSION SHEET**

It is hereby certified that **TONG YONG YAO** (ID No: **20ADB05440**) has completed this final year project entitled “**SYNTHESIS, CHARACTERIZATION, AND REACTIVITY STUDIES OF  $\eta^5$ -CYCLOPENTADIENYLIRON DICARBONYL 4-(DIMETHYLAMINO)PHENYLDIPHENYLPHOSPHINE IODIDE AND  $DI(\mu_2\text{-CHLORO})(\eta^5\text{-CYCLOPENTADIENYL})4\text{-}(\text{DIMETHYLAMINO})\text{PHENYLDIPHENYLPHOSPHINE IRON-PALLADIUM IODIDE}$ ” supervised by Dr. Ooi Mei Lee from the Department of Chemical Science, Faculty of Science.**

I hereby 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,



\_\_\_\_\_  
(TONG YONG YAO)

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## LIST OF ABBREVIATION

~	approximately
°C	Degree Celsius
μ	Bridging
Bu	Butyl
C	Carbon
Cl	Chloride
CO	Carbonyl
Cp	Cyclopentadiene ring
CpFe(CO) <sub>2</sub> I	Cyclopentadienyliron dicarbonyl iodide
dba	Dibenzylideneacetone
Decomp.	Decompose
DPPH	2,2-diphenyl-1-picrylhydrazyl
ESI-MS	Electrospray Ionization Mass Spectrometry
etc.	And so on
Fe	Iron
FTIR	Fourier Transform Infrared Spectroscopy
H	Hydrogen
I	Iodide
<i>m</i>	Meta
Me	Methyl group (CH <sub>3</sub> )
MeCN	Acetonitrile
N	Nitrogen

Net <sub>3</sub>	Triethylamine
NMR	Nuclear Magnetic Resonance Spectroscopy
<i>o</i>	Ortho
O	Oxygen
<i>p</i>	Para
P	Phosphorus
Pd	Palladium
Ph	Phenyl
PPh <sub>2</sub> ( <i>p</i> -C <sub>6</sub> H <sub>4</sub> NMe <sub>2</sub> )	4-(dimethylamino)phenyldiphenylphosphine
ppm	Parts per million
PR <sub>3</sub>	Tertiary Phosphine
R	Organic substituent
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
Tol	Tolyl group
UV-Vis	Ultraviolet Visible Spectrophotometry
X	Halogen
η	Hapto
π	Pi
σ	Sigma

## CHAPTER 1

### INTRODUCTION

#### 1.1 Organometallic chemistry

The origin of the first reported organometallic complex, Zeise's salt, with the formula  $K[PtCl_3(C_2H_4)] \cdot H_2O$ , which discovered by William Christopher Zeise in 1827 has been pivotal continues to advance until now (Thayer, 1969). Organometallic compounds defined as the chemical compound that having at least one metal-carbon bonding which often comes with organic groups or ligands bonded to a centre metal atom. According to Nakazawa and Koe (2011), organometallic chemistry is an interdisciplinary field that encompasses fundamental aspects of both organic and inorganic chemistry which exhibits remarkably unique and distinctive chemistry due to their structures, bonding modes, and reactivity which extending beyond the boundaries of traditional chemistry fields (Nakazawa and Koe, 2011).

Ligands as mentioned above, known as the species, ions, or groups which able to function as Lewis base and promoting their lone pairs to a metal atom (which serves as a Lewis acid), leading to the formation of coordination or organometallic complexes. Various bonding modes can be exhibited in organometallics complexes

*via* both  $\sigma$  and  $\pi$  bonding to the central metal atom. The behavior of the ligands can be diverge significantly depending on their size, shape, and chemical properties which possesses great impacts on determination of structure, stability and reactivity of the organometallic compounds formed. The classification of the ligands according to donor atoms present in their structure which can be termed as monodentate, bidentate, polydentate, ambidentate, chelating, heterocyclic, bridging, and other type of ligand (Crabtree, 2005).

One of the most successful applications of organometallic chemistry is homogenous catalysis, which is highly demands in a wide range of major needs from industry to minor scale of reagent for synthetic chemistry in laboratory. Examples include the alkene isomerization using transition metal organometallic complexes as a homogenous catalyst which provide an alternative pathway with lower activation energy thus the reactants can form the product in a smoother reaction condition (in lower pressure or temperature), faster and higher efficiency. Organometallic complexes are also playing an important role in material science which act as the precursors in the synthesis of advanced materials such as metal-organic frameworks and conducting polymers (Aslam and Verma, 2023). Moreover, some of the organometallic compounds have been reported could exhibit biological activities and can be applied in medicinal field such as antitumor, examples like cyclopentadienyliron dicarbonyl halides, antibacterial examples like ruthenium (II) complexes function as an agent for monitoring protein-protein interactions (Coogan *et al.*, 2012; Devagi *et al.*, 2018).

Recently iron carbonyl complexes are in the limelight of research due to their rich redox chemistry properties and therapeutic application (Long *et al.*, 2013; Gao *et al.* 2018; Romanski *et al.* 2011). Therefore, we are interested to synthesis and characterise the new iron complexes and explore their potential in the biochemistry reaction.

## 1.2 Problem statement

The reactivity of  $\text{CpFe(CO)}_2\text{I}$  (**1**) with various phosphine ligands has been reported for many times by various methods. The ligand used in the project, 4-(dimethylamino)phenyldiphenylphosphine,  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$ , which consist of a soft phosphorus donor atom and a hard nitrogen donor atom in its structure where complex **1** act as the intermediate acid due to oxidation state in iron (II). It is interesting to be study their interaction. Besides, palladium chloride one of the non-toxic and well-known catalyst in organometallic chemistry was used to study with the new synthesized iron complex to form a bimetallic compound as both metals are non-toxic towards the human body. Moreover, organoiron complexes was reported have the potential in the biological activity. Hence, in this project, DPPH assay will be carried out to determine antioxidant properties of the synthesized organoiron complexes.

### 1.3 Objectives

Cyclopentadienyliron dicarbonyl iodides have been found to exhibit varying reactivity toward different types of ligands and have been reported in several methods. The aim of this project is to synthesize a new organoiron-phosphine complex from cyclopentadienyliron dicarbonyl iodide,  $[\text{CpFe}(\text{CO})_2\text{I}]$  (**1**) and 4-(dimethylamino)phenyldiphenylphosphine,  $\text{PPh}_3(p\text{-C}_6\text{H}_4\text{N}(\text{CH}_3)_2)$  via microwave irradiation method under mild condition. To characterize the new organoiron-phosphine complex with Fourier Transform Infrared Spectroscopy (FTIR),  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy, UV-Vis spectroscopy, Elemental analysis, and Electrospray ionization mass spectrometry (ESI-MS). To carry out reactivity studies on the synthesized organoiron-phosphine complex. Furthermore, to synthesize bimetallic compound from the organoiron-phosphine complex formed with palladium chloride. To propose the molecular structure and synthetic pathways of both complexes formed. To determine the antioxidant activity of the new synthesized complexes.

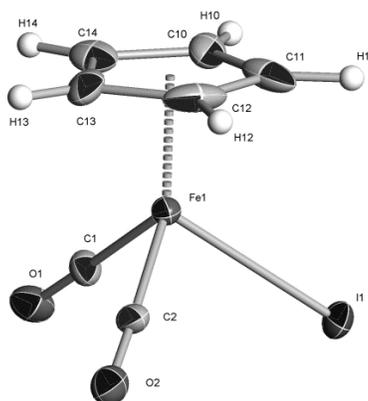
## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Brief review of starting material: Cyclopentadienyliron dicarbonyl iodide, $\text{CpFe}(\text{CO})_2\text{I}$ (**1**)

Cyclopentadienyliron dicarbonyl iodide with the formula of  $\text{CpFe}(\text{CO})_2\text{I}$  (**1**) was first reported by Hallam and Pauson (1956) in the study of ferrocene. It is one of the halides derivatives from the dimeric complex, cyclopentadienyliron dicarbonyl dimer with the formula of  $[\text{CpFe}(\text{CO})_2]_2$  which synthesized through undergo oxidative cleavage by halogens,  $\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) (King *et al.*, 1963). The structure of the  $\text{CpFe}(\text{CO})_2\text{I}$  (**1**) consist of an iron atom coordinated to a cyclopentadienyl ligand in pentahapto ( $\eta^5$ -) mode of bonding along with different monodentate ligands of two carbonyl (CO) ligand and an iodide (I<sup>-</sup>) ligand to give an 18 electron species of organometallic complex which exhibit as a three-legged piano stool geometry (Zeller *et al.*, 2003). It appears as dark-brown crystals, air sensitive which slowly decompose to oxide once exposed to air, high soluble in organic solvent such as toluene and chloroform. Over the past half-century,  $\text{CpFe}(\text{CO})_2\text{I}$  have been used as the precursor for the preparation of other organoiron derivatives such as heteroferraborane complexes (Geetharani *et al.*, 2011) and replacement of ligands by tertiary phosphines, alkyl and ambidentate ligands (such

as  $\text{NCS}^-$ ). Recently, some of the derivatives of the cyclopentadienyliron carbonyl derivatives had also been reported showing some biological properties such as anticancer and might be able to be used in medicinal field (Poh et al., 2016). Figure 2.1 showed the molecular structure of the  $\text{CpFe}(\text{CO})_2\text{I}$  (**1**).



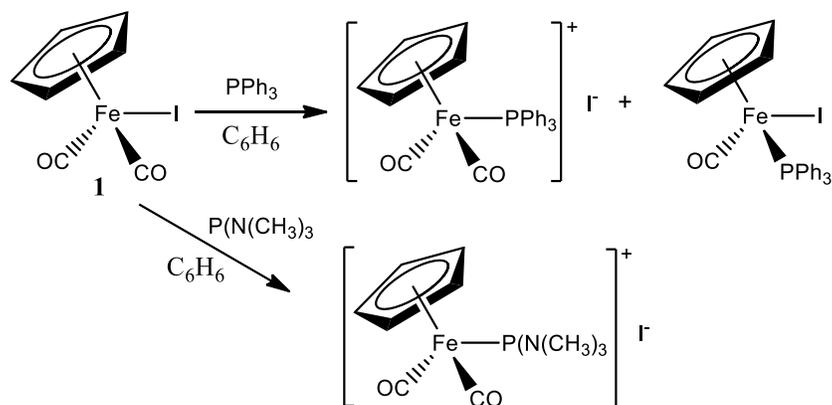
**Figure 2.1: Molecular structure of  $\text{CpFe}(\text{CO})_2\text{I}$  (**1**) (Zeller *et al.*, 2003)**

## **2.2 Overview on the synthesis and reactivity studies of phosphine derivatives of cyclopentadienyliron dicarbonyl iodide, $\text{CpFe}(\text{CO})_2\text{I}$ (**1**)**

Since the 1960s, the reactivity studies of  $\text{CpFe}(\text{CO})_2\text{I}$  (**1**) with phosphines have been discussed and gain significant interest among organometallic chemists. King (1963) has reported the reaction of the  $\text{CpFe}(\text{CO})_2\text{I}$  (**1**) with *tris*(dimethylamino)phosphine,  $\text{P}(\text{NMe}_2)_3$  with the aim to investigate its ability in displacement of monodentate ligands (CO or halides) or monoanionic ligand (Cp) in the metal carbonyl halides

derivatives. According to the studies above, King isolated pale-yellow crystals of  $[\text{CpFe}(\text{CO})_2(\text{P}(\text{NMe}_2)_3)]\text{I}$  after 6 hours of reflux in benzene. The product showed conductivity property due to its salt form characteristics.

After a lapse of three years, Treichel *et al.* (1966) also reported a new discovery of the triphenylphosphine can be substituted to iron carbonyl halides complexes either through replacement of CO or I<sup>-</sup> by reflux in benzene for 18 hours to isolate out yellow ionic product of  $[\text{CpFe}(\text{CO})_2(\text{PPh}_3)]\text{I}$  and  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$  in neutral form. They claim that the triphenylphosphine favor the formation of ionic product (50.2 % yield) rather than its neutral form (33.7 % yield) without giving any explanation. The reaction scheme of the above two literatures was illustrated in the Scheme 2.1 below.



**Scheme 2.1: Reaction of  $\text{CpFe}(\text{CO})_2\text{I}$  (1) towards different phosphine ligand via conventional heating method (King., 1963; Treichel et al., 1966)**

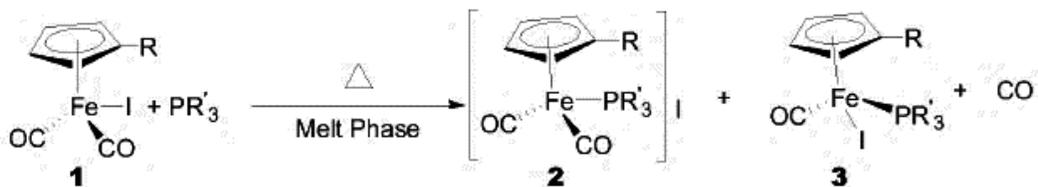
No further investigation on the triphenylphosphine of the studies above until Pandey (1977) examined the effect of reaction time on the formation of the major products. According to Pandey's report that in the shorter reaction time by reflux (8 to 12 hours) the neutral complex of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$  was isolated as the major product while a longer time of reflux had yielded  $[\text{CpFe}(\text{CO})_2(\text{PPh}_3)]\text{I}$  as the dominant product. This researcher had pointed out that by alternating the reaction period would improve the selectivity of the product either in ionic form or as a neutral complex. Table 2.1 showed the results of the reaction of  $\text{CpFe}(\text{CO})_2\text{I}$  (1) with triphenylphosphine within a shorter reaction time reported by Pandey (1977)

**Table 2.1: Results of the reaction of  $\text{CpFe}(\text{CO})_2\text{I}$  (1) with triphenylphosphine within a shorter reaction time (Pandey., 1977)**

Products	Colour	Yield	M.P.	$\nu(\text{CO}) \text{ cm}^{-1}$
1) $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{Ph}_3\text{P})\text{I}$	Green	60%	140 °C	1935 vs
2) $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{Ph}_3\text{P})]\text{I}$	Yellow	25%	172 °C	2055s,2010s
3) $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ (unreacted portion)	Black	15%	120 °C	2044s,2000s

Moving on to the era which emphasized the greener method in the chemical synthesis due to environmental concerns. A study on the solventless reaction of cyclopentadienyliron dicarbonyl halides complexes,  $\text{RCpFe}(\text{CO})_2\text{I}$  ( $\text{R} = \text{H}$  (1) or Me) with various tertiary phosphines in solid state was first reported by Munyaneze, Bala, and Covaille (2007). Mixture of the iron complexes with tertiary phosphines was grinded using pestle and mortar into a fine homogenous powder and transferred into

a flask then placed in the oil bath for direct heating to give ionic products with the formula of  $[\text{RCpFe}(\text{CO})_2(\text{PR}'_3)]\text{I}$  and neutral complex of  $\text{RCpFe}(\text{CO})(\text{PPh}_3)\text{I}$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ;  $\text{R}' = \text{Ph}$ , *m*-Tol, *p*- $\text{C}_6\text{H}_4\text{OMe}_2$ , *p*- $\text{C}_6\text{H}_4\text{Cl}$ , or *p*- $\text{C}_6\text{H}_4\text{F}$ ). The reaction scheme was shown in Scheme 2.2 below.



**Scheme 2.2: Solventless melt-phase reaction of cyclopentadienyliron dicarbonyl halides complexes,  $\text{RCpFe}(\text{CO})_2\text{I}$  ( $\text{R} = \text{H}$  (1) or  $\text{Me}$ ) with various tertiary phosphines in solid state (Munyanze, Bala and Coville, 2007)**

In this studies, Munyanze, Bala, and Covaille (2007) had further investigated the catalyst properties of the cyclopentadienyliron dicarbonyl dimer,  $[\text{CpFe}(\text{CO})_2]_2$  in the reaction of cyclopentadienyliron dicarbonyl halides complexes,  $\text{RCpFe}(\text{CO})_2\text{I}$  ( $\text{R} = \text{H}$  (1) or  $\text{Me}$ ) with various tertiary phosphines, in solid state which possessed an excellent impact towards in an increasement in rate of reaction in forming the iron carbonyl phosphine halide complexes at different temperature. Table 2.2 showed that conversion of the product in the reaction of  $\text{CpFe}(\text{CO})_2\text{I}$  (1) with various phosphine ligands with or without catalyst at  $100\text{ }^\circ\text{C}$ .

**Table 2.2: The conversion of the product in the reaction of RCpFe(CO)<sub>2</sub>I with various phosphine ligands at 100 °C with/without catalyst (Munyaneza, Bala and Coville, 2007)**

Ligand PR' <sub>3</sub> R'	Time (min)	Products of reaction with metal complex RCpFe(CO) <sub>2</sub> I (%)							
		R = H				R = Me			
		Uncatalysed		Catalysed		Uncatalysed		Catalysed	
		<b>2</b>	<b>3</b>	<b>2</b>	<b>3</b>	<b>2</b>	<b>3</b>	<b>2</b>	<b>3</b>
Ph	5	70	24	81	19	31	0	61	39
	15	72	28	76	24	61	0	42	58
<i>m</i> -Tol	5	39	57	61	32	26	0	0	100
	15	40	57	20	80	43	0	0	100
<i>p</i> -C <sub>6</sub> H <sub>4</sub> OMe	5	80	20	76	16	57	0	84	0
	15	85	15	71	29	75	0	100	0
<i>p</i> -C <sub>6</sub> H <sub>4</sub> F	5	36	53	0	87	10	0	44	56
	15	0	95	0	98	15	0	0	100
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	5	0	76	0	84	8	0	0	100
	15	0	88	0	93	12	0	0	100

From the reaction as mentioned above, they claimed that when the reaction was carried out at 100 °C, the phosphine consists of electron withdrawing group will give neutral complexes rather than ionic while in oppositely electron donating phosphines tends to form ionic product in more rapid reaction. However, when same reaction was repeated at 60 and 70 °C for 4 hours, the formation of the products can be extremely different which does not affect by the factor of electron donating or withdrawing effect. Table 2.3 and 2.4 showed the different temperature in conversion of product in the reaction of RCpFe(CO)<sub>2</sub>I with various phosphine ligands with or without catalyst.

**Table 2.3: The conversion of the product in the reaction of RCpFe(CO)<sub>2</sub>I with various phosphine ligands at 60 °C with/without catalyst (Munyaneza, Bala and Coville, 2007)**

Ligand PR' <sub>3</sub> R'	Time (min)	Products of reaction with metal complex RCpFe(CO) <sub>2</sub> I (%)							
		R = H				R = Me			
		Uncatalysed		Catalysed		Uncatalysed		Catalysed	
		2	3	2	3	2	3	2	3
Ph	0.5	52	3	100	0	39	0	100	0
	4	90	1	100	0	76	0	100	0
<i>m</i> -Tol	0.5	0	0	69	0	70	0	100	0
	4	58	6	86	0	82	0	100	0
<i>p</i> -C <sub>6</sub> H <sub>4</sub> OMe	0.5	37	0	55	0	60	0	100	0
	4	59	0	78	0	70	0	100	0
<i>p</i> -C <sub>6</sub> H <sub>4</sub> F	0.5	40	10	90	3	10	0	100	0
	4	64	20	75	25	40	0	100	0
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	0.5	0	7	28	5	0	0	60	0
	4	0	21	43	21	21	0	72	0

**Table 2.4: The conversion of the product in the reaction of RCpFe(CO)<sub>2</sub>I with various phosphine ligands at 70 °C with/without catalyst (Munyaneza, Bala and Coville, 2007)**

Ligand PR' <sub>3</sub> R'	Time (min)	Products of reaction with metal complex RCpFe(CO) <sub>2</sub> I (%)							
		R = H				R = Me			
		Uncatalysed		Catalysed		Uncatalysed		Catalysed	
		2	3	2	3	2	3	2	3
Ph	0.5	52	3	100	0	39	0	100	0
	4	90	1	100	0	76	0	100	0
<i>m</i> -Tol	0.5	0	0	69	0	70	0	100	0
	4	58	6	86	0	82	0	100	0
<i>p</i> -C <sub>6</sub> H <sub>4</sub> OMe	0.5	37	0	55	0	60	0	100	0
	4	59	0	78	0	70	0	100	0
<i>p</i> -C <sub>6</sub> H <sub>4</sub> F	0.5	40	10	90	3	10	0	100	0
	4	64	20	75	25	40	0	100	0
<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	0.5	0	7	28	5	0	0	60	0
	4	0	21	43	21	21	0	72	0

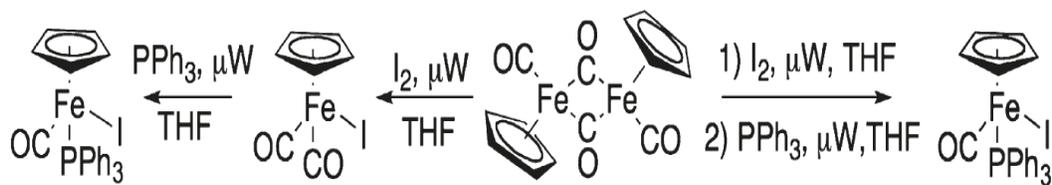
Munyaneze, Bala, and Coville (2007) has proven that the solventless reaction having higher yields of the salt product than conventional heating method from the comparative study of reaction CpFe(CO)<sub>2</sub>I (**1**) with tertiary phosphine in benzene and a solvent-free reaction at 70 °C. Table 2.5 showed the conversion of the product

in the reaction of  $\text{CpFe(CO)}_2\text{I}$  (1) with phosphine ligands *via* reflux and melt-phase reaction.

**Table 2.5: The conversion of the product in the reaction of  $\text{CpFe(CO)}_2\text{I}$  (1) with phosphine ligands *via* reflux and melt-phase reaction (Munyaneza, Bala and Coville, 2007)**

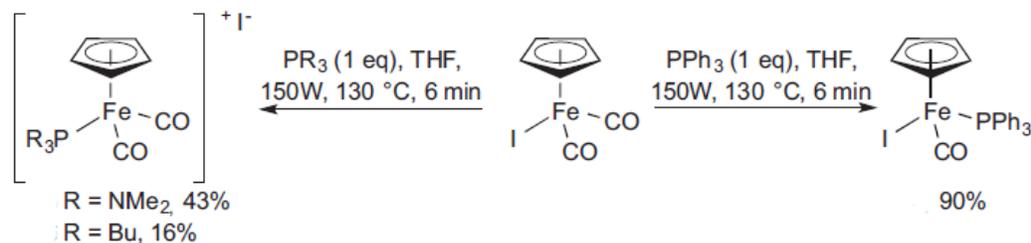
Ligand $\text{PR}'_3$ $\text{R}'$	Reaction time (min)	Relative conversion to products under similar catalysed conditions	
		benzene (15 mL)	solvent-free
$p\text{-C}_6\text{H}_4\text{F}$	30	28 % (3)	90 % (2) 3 % (3)
Ph	60	42% (3)	99% (2)

Two years later, Garringer *et al.* (2009) had reported the same reaction on the synthesis of  $\text{CpFe(CO)(PPh}_3\text{)I}$  *via* microwave-assisted method instead of conventional method which has been previously reported by Treichel *et al.* (1966). In this study, Garringer *et al.* (2009) managed to isolate the high yield of the monosubstituted product of  $\text{CpFe(CO)(PPh}_3\text{)I}$  (76% yield) as green crystals in a very short reaction time (< 30 minutes) at 90 °C *via* microwave-assisted method which showed a great improvement on the reaction time and yield for the same product that was reported by Treichel *et al.* (1966) and Pandey (1977) using conventional heating method. (Refer to Section 2.1.1). The reaction scheme of the microwave-assisted method in the synthesis of  $\text{CpFe(CO)(PPh}_3\text{)I}$  was shown in Scheme 2.3.



**Scheme 2.3: Synthesis of CpFe(CO)(PPh<sub>3</sub>)I via microwave heating method at 90 °C for ~30 minutes reaction (Geetharani et al., 2011)**

The convenient of the microwave-assisted method was further explored by Pagnoux-OZherelyeya *et al.* (2014) on the synthesis of piano-stool iron phosphine complexes by using CpFe(CO)<sub>2</sub>I (**1**) and tertiary phosphines. According to Pagnoux-OZherelyeya, they had successfully isolated the product in salt formation of [CpFe(CO)<sub>2</sub>(PR<sub>3</sub>)I] (R= NMe<sub>2</sub> or Bu) as grey powder and green powder respectively and neutral complex of CpFe(CO)(PPh<sub>3</sub>)I as green crystals by microwave-assisted reaction which using THF as the solvent and took only 6 minutes to complete the reaction. Based on the obtained results, which evidenced that microwave-assisted method is significantly more efficient and time-saving in the synthesis of iron complexes. A notable example is the synthesis of [CpFe(CO)<sub>2</sub>(P(NMe<sub>2</sub>)<sub>3</sub>)I], as reported by King in 1963. Using the conventional heating method, this synthesis takes approximately 6 hours to complete the reaction (as discussed in Section 2.1.1). In contrast, the microwave-assisted method achieves the same reaction in 60 times faster than the time required for refluxing reaction. The reaction of the CpFe(CO)<sub>2</sub>I (**1**) with tertiary phosphines *via* microwave synthesizer was illustrated in Scheme 2.4.

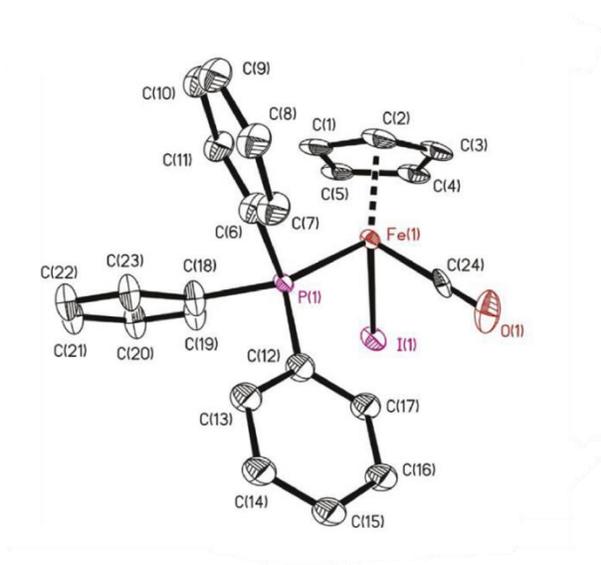


**Scheme 2.4: Reaction of the CpFe(CO)<sub>2</sub>I (1) with tertiary phosphines via microwave synthesizer (Pagnoux-Ozherelyeva et al., 2014)**

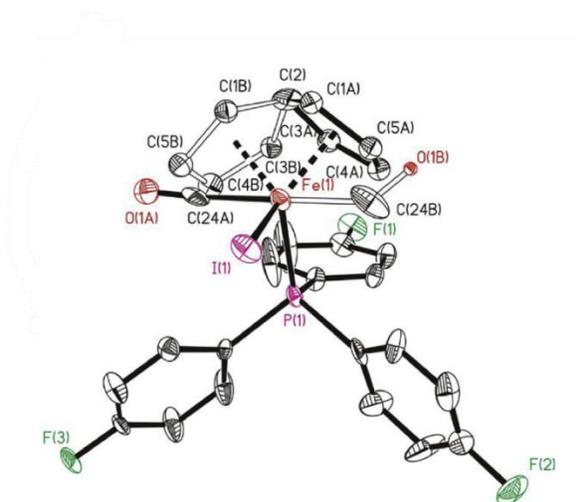
A conclusion was given by Pagnoux-Ozherelyeva *et al.* (2014) on the formation of the product which stated that the tertiary phosphines with electron donating groups like P(NMe<sub>2</sub>)<sub>3</sub> or PBu<sub>3</sub> tends to give salt formation of product which might be due to the present of the carbon monoxide that being liberated by the complexes but still remaining in the microwave pressure tube.

UV irradiation have been employed since 1970s which reported by Pandey (1977) in the synthesis of cyclopentadienyliron carbonyl phosphine complexes. From the studies above, a mixture of CpFe(CO)<sub>2</sub>I (1) and PPh<sub>3</sub> in benzene under ultraviolet irradiation for 18 hours which resulted CpFe(CO)(PPh<sub>3</sub>)I as the major product and [CpFe(CO)<sub>2</sub>(PPh<sub>3</sub>)I] as the minor product while irradiation period up to 60 hours which only yielded salt product only. This observation further substantial that reaction period does affect the formation of the products although using alternative reaction method.

More recently, Pilon *et al.* (2017) had contributed a lot of precise information on the reactivity studies of organophosphorus and cyclopentadienyliron *via* UV-irradiation method. Pilon *et al.* (2017) had carried out the reaction of  $\text{CpFe}(\text{CO})_2\text{I}$  (**1**) with various tertiary phosphine,  $\text{PR}_3$  ( $\text{R} = \text{Ph}, \text{Ph}_2(\text{C}_6\text{H}_4\text{COOH}), p\text{-C}_6\text{H}_4\text{F}$ ) by UV light irradiation (125W) for 3 to 5 hours. Dark green  $\text{CpFe}(\text{CO})(\text{PR}_3)\text{I}$  ( $\text{R} = \text{Ph}, \text{Ph}_2(\text{C}_6\text{H}_4\text{COOH}), p\text{-C}_6\text{H}_4\text{F}$ ) complexes were obtained. The X-ray structure of the  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$  and  $\text{CpFe}(\text{CO})(\text{P}(p\text{-C}_6\text{H}_4\text{F})_3)\text{I}$  were shown in Figure 2.2 and Figure 2.3.



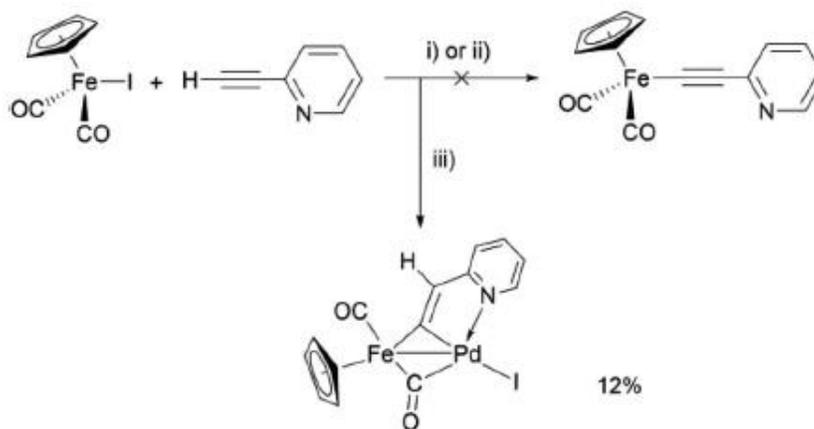
**Figure 2.2: Molecular Structure of  $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{I}$  (Pilon *et al.*, 2017)**



**Figure 2.3: Molecular Structure of  $\text{CpFe}(\text{CO})(\text{P}(p\text{-C}_6\text{H}_4\text{F})_3)\text{I}$  (Pilon *et al.*, 2017)**

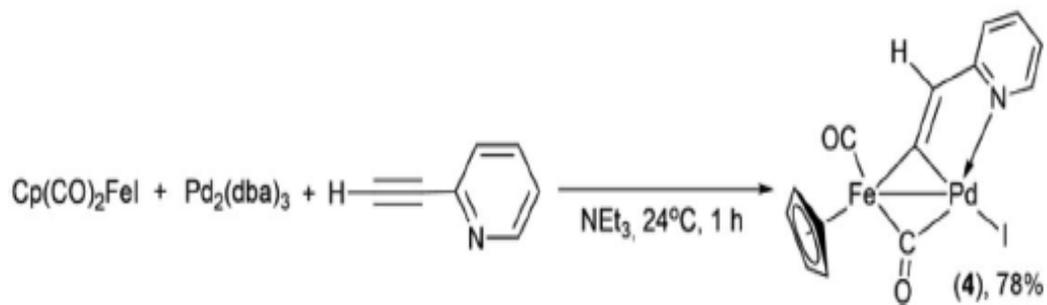
### **2.3 Reactivity and synthesis of bimetallic iron-palladium complex from cyclopentadienyliron dicarbonyl iodide, $\text{CpFe}(\text{CO})_2\text{I}$ (1)**

Verpekin *et al.* (2020) had reported the synthesis of  $\sigma$ -(pyridylethynyl) cyclopentadienyliron dicarbonyl complexes under Pd/Cu-catalysed condition which resulted an unexpected product of a bimetallic iron-palladium  $\mu$ -pyridylvinylidene complex with the formula of  $\text{Cp}(\text{CO})_2\text{Fe}[\mu\text{-C}]\text{CH}(2\text{-C}_5\text{H}_4\text{N})\text{PdI}$  (Refer to Scheme 2.4). According to their studies, the reaction of equivalent amount of  $\text{CpFe}(\text{CO})_2\text{I}$  (1),  $\text{PdCl}_2$  and 2-ethynylpyridine mixture in acetonitrile and refluxed for an hour lead to the formation of an iron-palladium bimetallic complex in 12 % yield which showed in Scheme 2.5

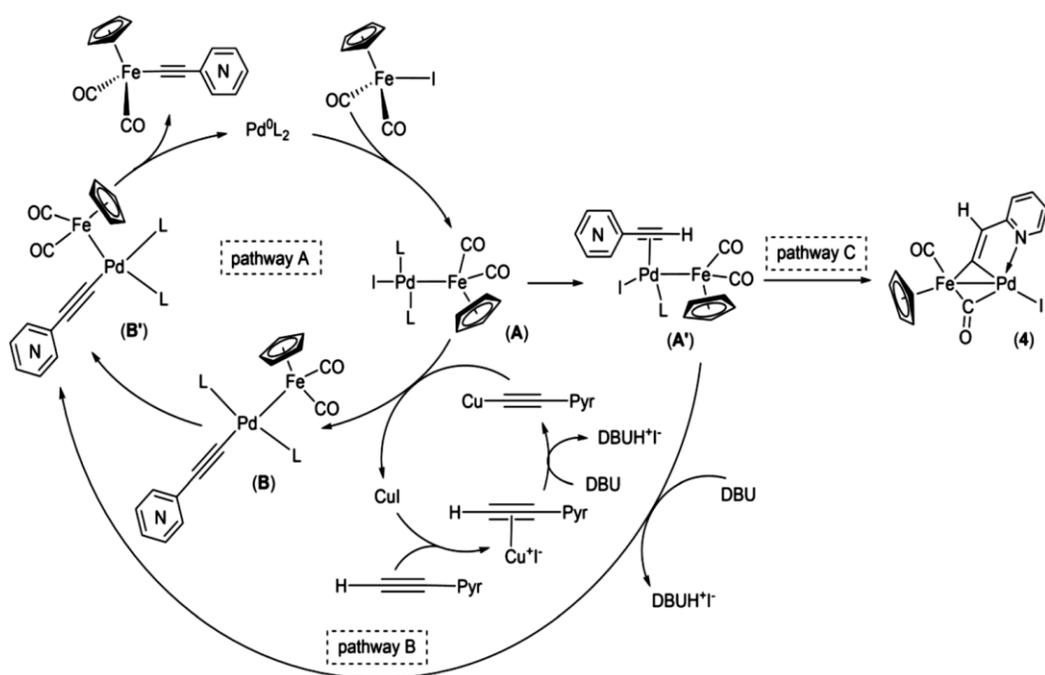


**Scheme 2.5: Synthetic pathway of the reaction of equivalent amount of CpFe(CO)<sub>2</sub>I (1), PdCl<sub>2</sub> and 2-ethynylpyridine refluxed in acetonitrile for 1 hours (Verpekin *et al.*, 2020)**

Later, they had carried out another reaction to improve the yields of the iron-palladium bimetallic complex by reacting CpFe(CO)<sub>2</sub>I (1) with Pd<sub>2</sub>(dba)<sub>3</sub>.CHCl<sub>3</sub> in the triethylamine with vigorous stirring together with the addition of the 2-ethynylpyridine for 1 hours. After evaporated to dryness and purification by column chromatography, a red-brown microcrystals of Cp(CO)<sub>2</sub>Fe[μ-C]CH(2-C<sub>5</sub>H<sub>4</sub>N)]PdI was isolated and further purified with recrystallization in chloroform/*n*-hexane. The reaction as mentioned above is shown in Scheme 2.6 and its mechanism was shown in Scheme 2.7.



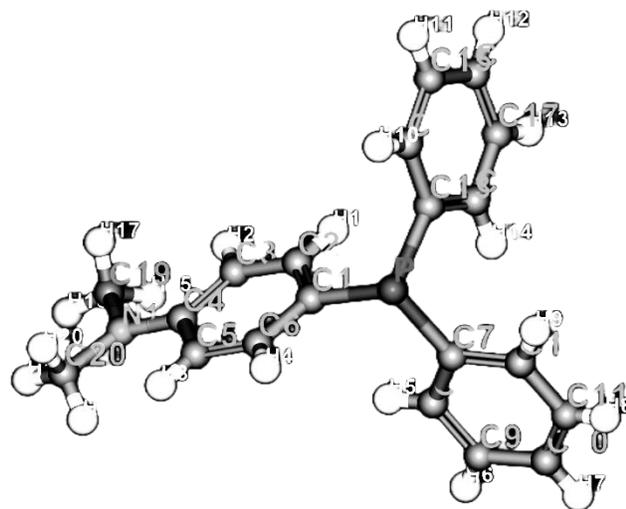
**Scheme 2.6:** Another pathway proposed for the synthesis of  $\text{Cp}(\text{CO})_2\text{Fe}[\mu\text{-C}]\text{CH}(2\text{-C}_5\text{H}_4\text{N})\text{PdI}$  (Verpekin *et al.*, 2020)



**Scheme 2.7:** Proposed Mechanism of the synthesis  $\text{Cp}(\text{CO})_2\text{Fe}[\mu\text{-C}]\text{CH}(2\text{-C}_5\text{H}_4\text{N})\text{PdI}$  under Pd/Cu- and Pd-catalysed coupling reactions (Verpekin *et al.*, 2020)

## 2.4 Brief review of starting material: 4-(dimethylamino)phenyldiphenylphosphine, $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$

4-(dimethylamino)phenyldiphenylphosphine, with the formula,  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  is a tertiary phosphine ligand consists of hetero-donor atoms (P-N) present in the structure. P-N mixed ambidentate ligand often gain high interest among the organometallic chemists as the phosphine atom is a soft donor while nitrogen atom is a hard donor which allows them to investigate the possibility in the synthesis of hetero-bimetallic complex based on the hard soft acid base (HSAB) theory where soft-soft and hard-hard interaction is more favored by most of the compounds.  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  is a white crystalline powder which decomposes rapidly under air and soluble in common organic solvents. This ligand was involved in the alkylation with benzyl bromide in chloroform as reported by Cairns and McEwen (1990) and Mitsunobu reaction which is an organic reaction that transforms primary or secondary alcohol into ether, esters, and various other compounds as reported by Von Itzstein and Mocerino (1990), respectively. Figure 2.4 showed the molecular structure of the  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$ .

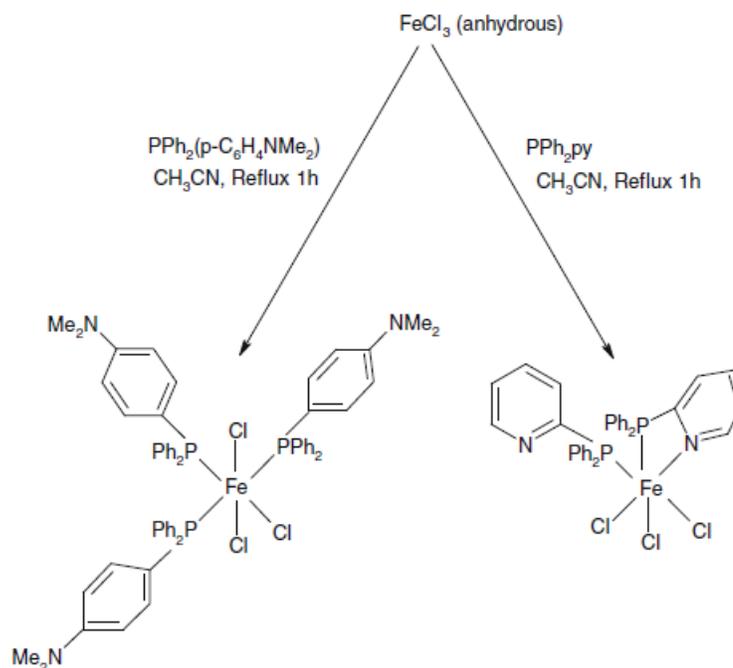


**Figure 2.4: Molecular structure of PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) (Lynch et al., 2003)**

### **2.5 Overview on the reactivity of 4-(dimethylamino)phenyldiphenylphosphine, PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) towards various metal complexes**

Das *et al.* (2009) had reported on the reaction of 4-(dimethylamino)phenyldiphenylphosphine, PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) with anhydrous iron (III) chloride, FeCl<sub>3</sub>. The reaction mixture was refluxed under nitrogen atmosphere for 1 hour and it was observed that the colour of the solution turned from yellow to dark brown colour. After evaporation of the solvent and washing with ether and hexane followed by drying under pressure lead to the formation of a dark-brown complex, FeCl<sub>3</sub>(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>3</sub>) (86% yield). Similar procedures were applied to the reaction involved another P-N ambidentate ligand, diphenyl(2-pyridyl)phosphine, PPh<sub>2</sub>py where a yellowish-brown complex of FeCl<sub>3</sub>(PPh<sub>2</sub>py-

$P)(PPh_2py-P,N)_2$  (85% yield) was obtained. The synthetic pathways of the  $FeCl_3(PPh_2(p-C_6H_4NMe_2)_3)$  and  $FeCl_3(PPh_2py-P)(PPh_2py-P,N)_2$  were illustrated in Scheme 2.8.



**Scheme 2.8: Synthesis of monocuclear iron(III) complexes (Das et al., 2009)**

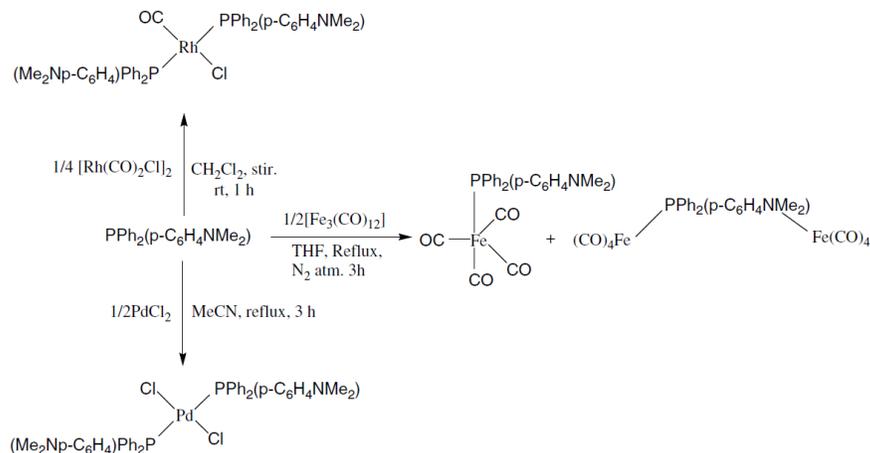
Sarmah *et al.* (2011) also reported on the reaction of 4-(dimethylamino)phenyldiphenylphosphine,  $PPh_2(p-C_6H_4NMe_2)$  with various metal carbonyl complexes,  $Fe_3(CO)_{12}$ ,  $Rh(CO)_2Cl_2$  and palladium chloride,  $PdCl_2$ . According to the studies mentioned above, they managed to isolate a total of three different mononuclear complexes through the reaction as shown below:

- (i)  $PPh_2(p-C_6H_4NMe_2)$  was added to the  $Fe_3(CO)_{12}$  in tetrahydrofuran solution and reflux under nitrogen for 3 hours. The colour of the solution changed

from green to dark brown. After evaporation of the solvent, and purified through column chromatography, a dark brown solid of  $[\text{Fe}(\text{CO})_4(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))\text{-P}]$  (52 % yield) and a small amount of yellow solid of binuclear non-metal-metal bonded complex,  $[\text{Fe}_2(\text{CO})_8(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)\text{-P,N})]$  (12 % yield) were isolated.

- (ii) Dropwise of the  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  solution in dichloromethane to the  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  for about 10 minutes. The reaction mixture was stirred under nitrogen atmosphere at room temperature for 1 hour which resulted a bright yellow solid after evaporated to dryness by *vacuo*. Bright yellow solid was characterized as  $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)_2)\text{-P}]$  (96% yield)
- (iii) A mixture of  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  and  $\text{PdCl}_2$  in acetonitrile was refluxed under nitrogen atmosphere for 3 hours. A yellowish precipitate was formed, and further purification was done which resulted a bright yellow solid of  $[\text{PdCl}_2(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)_2\text{-P})]$  (86 % yield).

The three reactions involved the  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  as listed in (i), (ii) and (iii) were illustrated in the Scheme 2.9.



**Scheme 2.9: Synthesis of the complexes of involved PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)**

**(Sarmah *et al.*, 2011)**

For the complex formed from the PdCl<sub>2</sub>, apparently it is a catalyst for Suzuki-Miyaura cross-coupling reaction. The reaction was carried out using different reactants combination for cross-coupling reaction at room temperature:

- (a) 4-bromonitrobenzene with phenylboronic acid
- (b) aryl bromides with arylboronic acids
- (c) aryl chlorides with phenylboronic acid

The above catalytic studies showed that [PdCl<sub>2</sub>(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub>-P)] is suitable for the cross-coupling reaction of reaction of (a) and (b) where higher yield of products was obtained. However, it is not effective for the reaction (c) as low yield was obtained as aryl chlorides was used as the starting material in the reaction due to its low reactivity. The details of the yield for reaction (a), (b) and (c) were shown in Table 2.6, 2.7 and 2.8, respectively.

**Table 2.6: Catalytic study of Pd complex [PdCl<sub>2</sub>(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub>-P)] on Suzuki–Miyaura cross-coupling reactions of (a) (Sarmah et al., 2011)**

Entry	Catalyst (mol%)	Time (h)	Yield (%) <sup>b,c</sup>
1	0.50	10	99
2	0.25	13	99
3	0.12	16	99
4	0.06	24	99
5	0.02	36	65
6	0.01	48	40

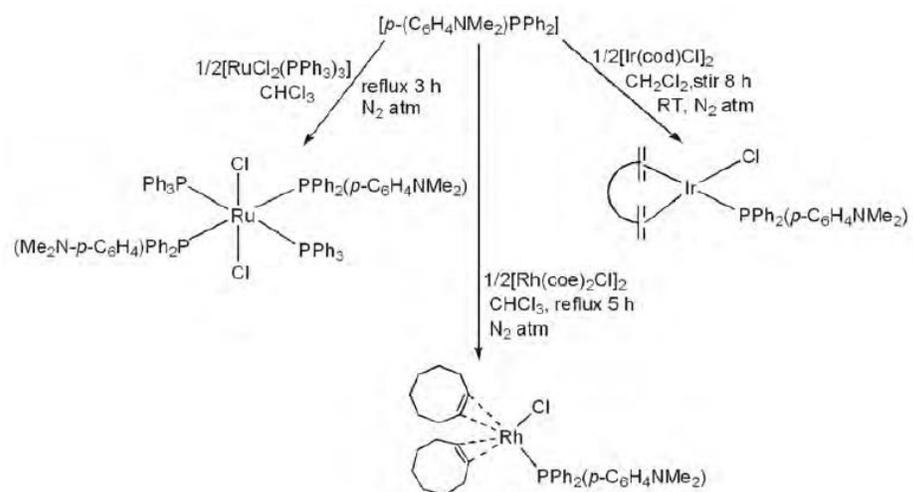
**Table 2.7: Catalytic study of Pd complex [PdCl<sub>2</sub>(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub>-P)] on Suzuki–Miyaura cross-coupling reactions of (b) (Sarmah et al., 2011)**

Entry	R	R'	Time (h)	Yield (%) <sup>b,c</sup>
1	4-NO <sub>2</sub>	H	24	99
2	4-COMe	H	30	98
3	4-COOH	H	30	96
4	4-CHO	H	30	94
5	4-NO <sub>2</sub>	4-Cl	24	96
6	4-NO <sub>2</sub>	4-Me	24	90
7	4-NO <sub>2</sub>	3-NO <sub>2</sub>	24	10
8	H	H	30	91
9	4-Me	H	30	94
10	4-OMe	H	30	93
11	2-Me	H	42	78
12	2-OMe	H	42	82

**Table 2.8: Catalytic study of Pd complex [PdCl<sub>2</sub>(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)<sub>2</sub>-P)] on Suzuki–Miyaura cross-coupling reactions of (c) (Sarmah et al., 2011)**

Entry	R	Catalyst (mol%)	Solvent	Time	Yield (%) <sup>b,c</sup>
1	4-NO <sub>2</sub>	0.06	<sup>i</sup> PrOH–H <sub>2</sub> O (1 : 1)	30	10
2	4-NO <sub>2</sub>	0.5	<sup>i</sup> PrOH–H <sub>2</sub> O (1 : 1)	30	17
3	4-NO <sub>2</sub>	0.5	<sup>i</sup> PrOH	24	58
4	4-COMe	0.5	<sup>i</sup> PrOH	30	43
5	4-CHO	0.5	<sup>i</sup> PrOH	30	46
6	4-H	0.5	<sup>i</sup> PrOH	30	36
7	4-Me	0.5	<sup>i</sup> PrOH	36	26

Borah and Boruah (2013) had also reported on the synthesis of various metal complexes with  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  ligand (refer to Scheme 2.10). From their studies, metal complexes of  $\text{RuCl}_2(\text{PPh}_3)_3$ ,  $[\text{Rh}(\text{coe})_2\text{Cl}]_2$  and  $[\text{Ir}(\text{cod})\text{Cl}]_2$  reacted with  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  to give mononuclear complexes with the soft donor atom of phosphorus coordinated to the metal centre. For the reaction of  $\text{RuCl}_2(\text{PPh}_3)_3$  and  $[\text{Rh}(\text{coe})_2\text{Cl}]_2$ , when an equivalent molar of the metal complex precursor was added to  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  solution in dichloromethane and refluxed for 3 hours and 5 hours under nitrogen atmosphere respectively which resulted in green solids of  $[\text{RuCl}_2(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))_2]$  (85% yield) and  $[\text{Rh}(\text{coe})_2\text{Cl}(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))]$  as an orange-brown solids (90% yield). For the reaction of  $[\text{Ir}(\text{cod})\text{Cl}]_2$ , it was carried out in a similar condition for 8 hours and lead to the isolation of a brown solids,  $[\text{Ir}(\text{cod})\text{Cl}(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))]$  (83% yield). From their studies, it was noticed that the  $[\text{Rh}(\text{coe})_2\text{Cl}(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))]$  can act as the catalyst for the carbonylation of methanol to acetic acid and methyl ester in the percentage of total conversion 48.2 – 72.2% which is comparable with the commercial species,  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$  which give 24.1 – 52.1% under same conditions.



**Scheme 2.10: Reaction of  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  towards various metal complexes (Borah and Boruah, 2013)**

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Materials**

All the solvents and reagents used in this project were of analytical reagent (A.R.) grade and high purity. Table 3.1 showed the chemicals used in this project.

**Table 3.1: Sources of materials used in this project**

Materials	Source
Cyclopentadienyliron dicarbonyl iodide (97%)	Sigma Aldrich
4-(dimethylamino)phenyldiphenylphosphine (95 %)	Sigma Aldrich
Palladium Chloride (A.R. Grade)	R&M Chemical
<i>n</i> -hexane (A.R. Grade)	Merck
Toluene (A.R. Grade)	Merck
Diethyl ether (A.R. Grade)	Merck
Chloroform (A.R. Grade)	Merck
Dichloromethane (A.R. Grade)	Merck
Tetrahydrofuran (A.R. Grade)	Merck
Acetonitrile (A.R. Grade)	Merck
Ethanol (A.R. Grade)	Merck
Methanol (A.R. Grade)	Merck
Celite 545	R&M Chemical
Silica gel 60 (0.040-0.062 mm)	Merck
Molecular sieves 4Å	Fluka
TLC plate – Silica gel 60	Merck
Benzene-D <sub>6</sub> (D, 99.6%)	Merck
Chloroform-D (D, 99.8%)	Merck
Toluene-D <sub>8</sub> (99%)	Merck

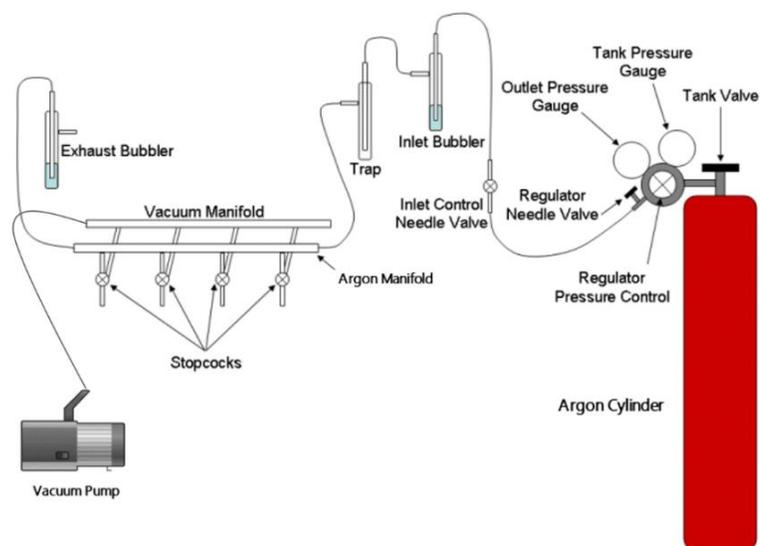
### 3.1.1 Pre-treatment of materials and apparatus

All the solvents used in this study were pre-dried with the pre-activated molecular sieves (4 Å) in the oven at 140 °C overnight and purging with argon gas or degassed *via* an ultrasonicator bath before use. Chromatographic materials were Silica gel 60 (Merck), Celite (Fluka AG) and TLC plate (Merck Silica gel 60 F<sub>254</sub>) were dried at

110 °C overnight before chromatographic use. All the glassware used in this project were washed with water and soap and rinsed with acetone then dried in the oven at 110 °C overnight before used. Any unknown contaminant stuck to the wall of glassware will be either soaked in base bath or washed with chromic acid or using ultrasonicator to remove the contaminants.

### 3.2 General Procedures

All the reactions in this project were carried out through microwave-assisted method under an ambient atmosphere. The reactions were carried out using CEM Discover-SP with Activent microwave synthesizer in dynamic mode with the parameter of 300 psi for pressure under 150 W of power. 20 minutes for the ramping time while the temperature and hold time was subjected to change for different reactions. The decomposition precipitate was removed by celite-filtration and the product mixture from the reaction were evaporated to dryness under *vacuo* using Edward 5 rotary vane pump and the evaporated organic solvent were collected into a cold trap which soaked in liquid nitrogen. The isolation of the products was performed by column chromatography *via* Schlenk technique and purified through recrystallization under an argon atmosphere at -20 °C before characterization.



**Figure 3.1:** Schlenk line setup

### 3.3 Physical Measurements

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were measured on a JEOL JNM-ECZL S series 400 MHz spectrometer. The chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to the residual  $\text{C}_6\text{H}_6$  in benzene- $d_6$ ,  $\text{CHCl}_3$  in chloroform- $d$ , and  $\text{C}_6\text{H}_5\text{CH}_3$  in toluene- $d_8$  while  $^{31}\text{P}$  NMR spectra were reference to the external standard 85%  $\text{H}_3\text{PO}_4$ . IR spectra in Nujol mulls applied in between KBr salt plate were measured in the range of  $4000\text{-}400\text{ cm}^{-1}$  via Perkin Elmer Spectrum RX1 FT-IR instrument. Electronic absorption spectra were obtained at room temperature on a Thermo Fischer Scientific Genesys 50 Ultraviolet-Visible spectrophotometer for solution concentration of  $0.5 \times 10^{-3}\text{ M}$  in quartz cuvettes (1 cm optical path). Elemental analyses measurements were performed by National University of Singapore (NUS).

Mass spectrometric measurements were performed using Electrospray Ionization mode (ESI) by National University of Singapore (NUS).

### **3.4 Reactivity study of CpFe(CO)<sub>2</sub>I (1) with equivalent molar of PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) at 110 °C *via* microwave synthesizer**

200 mg (0.658 mmol) of **1** and 201 mg (0.658 mmol) of PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) were weighed and transferred into a dry 50 mL microwave reaction vessel. Then, 12 mL of toluene which acted as the solvent was added to the reaction mixture. The reaction mixture was degassed by ultrasonicator for 30 seconds and sealed with a Teflon cap before proceeding to the reaction in the microwave synthesizer at 110 °C under an ambient atmosphere. Thin Layer Chromatography (TLC) was performed to monitor the completion of the reaction. Once the reaction was completed after 30 minutes which evidenced by absence of the spots of starting materials on the TLC plate and a deep green solution was obtained along with some decomposition stain at the wall of microwave reaction vessel. The reaction mixture was cooled down and filtered through a celite disc in approximately 1 cm thickness using sintered-glass funnel to remove the decomposition substances and the filtrate was collected in a two-neck round bottom flask. The green filtrate was concentrated to approximately 3 – 4 mL *via vacuo* and purified by column chromatography *via* Schlenk technique in a packed silica gel column in *n*-hexane (length: 10.0 cm × diameter: 2.0 cm). Two fractions were isolated:

- (i) A bright yellow solution was collected in the solvent mixture of *n*-hexane: toluene (2:1, 25 mL) in a one-neck round bottom flask and a yellowish precipitate was obtained after dried *via vacuo*. This product was remained uncharacterized due to a very low yield percentage (only 5.2 mg)
- (ii) A deep green solution was eluted in toluene (55 mL) and collected in a one-neck round bottom flask. The solvent was evaporated to dryness *via vacuo* which gave a dark greenish oily precipitate. Further purification was carried out through recrystallization in tetrahydrofuran/diethyl ether under argon atmosphere at -20 °C for 3 – 4 days which yielded needle-like green crystalline solids of [CpFe(CO)<sub>2</sub>(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>))]I (**2**) (133.2 mg, 0.219 mmol, 33.28 % yield)

Noted that there was some brownish-black precipitate remained on top of the silica gel in the column which resulting the low yields of the products as some of the products could be oxidized to decomposition under ambient atmospheric condition.

### **3.5 Reactivity study of [CpFe(CO)<sub>2</sub>(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>))]I (**2**) with equimolar amount of PdCl<sub>2</sub> at 60 °C *via* microwave synthesizer**

**2** (200 mg, 0.328 mmol) and equimolar of PdCl<sub>2</sub> (58.2 mg, 0.328 mmol) were weighed and transferred into a dry microwave reaction vessel. Approximately 12 mL acetonitrile was added into the mixture and act as the solvent. The reaction mixture was degassed for 30 seconds by ultrasonicator bath. The microwave

reaction vessel with the reaction mixture was sealed with cap and placed in the microwave synthesizer for reaction at 60 °C. Thin Layer Chromatography (TLC) was used to monitor the progress of the reaction until completion. After 3 hours, the reaction was completed which showed no spots of starting materials on the TLC plate and a deep red solution was obtained along with some decomposition precipitates was observed at the bottom of microwave reaction vessel. The solution was allowed to cool and filtered through a celite disc (~1 cm thickness) using sintered-glass funnel to remove the decomposition precipitates and the red filtrate was collected in a one-neck round bottom flask. The red filtrate was concentrated to approximately 3 – 4 mL left by *vacuo* and then purified by column chromatography *via* Schlenk technique in a packed silica gel column in solvent combination of *n*-hexane: toluene (2: 1) (length: 11.0 cm × diameter: 2.0 cm). Total of three fractions were isolated:

- (i) A deep red solution was eluted out with dichloromethane (40 mL) and collected in a one-neck round bottom flask. A dark red precipitate was obtained after dried under *vacuo*. Further purification was done by recrystallization in chloroform/*n*-hexane under argon atmosphere at -20 °C for 3 – 4 days which yielded dark red crystalline solids of [CpFe(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>)(μ-Cl)<sub>2</sub>Pd)]<sub>4</sub> (**3**) (28.5 mg, 0.025 mmol, 7.82 % yield)
- (ii) A light red-orange solution was collected in chloroform (35 mL) in a one-neck round bottom flask. The solvent was evaporated to dryness by *vacuo* which gave a reddish-orange precipitate and uncharacterized due to time constraint (25.3 mg)

- (iii) A yellowish solution was collected in acetonitrile (30 mL) in a one-neck round bottom flask. The solvent was evaporated to dryness by *vacuo* which resulted in a brownish-yellow precipitate and uncharacterized due to time constraint (12.5 mg)

Noted that the brownish decomposition precipitates left on top of the silica gel in the column which leads to the yields of the product in a small amount. Some orange residue was observed at the top rim the column which cannot be eluted by acetonitrile.

### 3.6 NMR Tube Reactions

#### 3.6.1 Thermolysis studies of $[\text{CpFe}(\text{CO})_2(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))]\text{I}$ (**2**) at 110 °C

A green solution of  $[\text{CpFe}(\text{CO})_2(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))]\text{I}$  (**2**) (10 mg, 0.016 mol) in  $\text{C}_6\text{D}_5\text{CD}_3$  (~0.5 mL) in a 5 mm NMR tube, was thermolyzed at 110 °C. The reaction was monitored at regular intervals *via*  $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR spectra.

### **3.6.2 Co-Thermolysis of [CpFe(CO)<sub>2</sub>(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>))]I (2) with equimolar of PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) at 110 °C**

10 mg (0.016 mmol) of [CpFe(CO)<sub>2</sub>(PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>))]I (2) together with an equimolar of PPh<sub>2</sub>(*p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) (4.9 mg, 0.016 mmol) was dissolved in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> (~0.5 mL) in a 5 mm NMR tube. The reaction mixture was thermolyzed at 110 °C. The reaction was monitored at regular intervals *via* <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra.

### **3.7 Antioxidant Study: 2,2-diphenyl-1-picrylhydrazyl (DPPH) Radical Scavenging Activity**

The free radical scavenging activity of the compounds, based on the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity was determined by the method described by Devagi *et al.* (2018) with minor modification.

The stock solution of the compounds was dissolved in ethanol at the concentration of 0.2 mg/mL and the stock solution was sonicated for 5 minutes to ensure the compounds were fully dissolved in the ethanol and kept in the refrigerator under 4 °C in the dark before use. Followed by the preparation of the DPPH solution at 0.1 mM concentration in methanol and also sonicated for complete dissolution and kept in the dark condition in the fridge at 4 °C as it is very light-sensitive. Different

concentrations of the compounds (0.04 to 0.2 mg/mL) were prepared from the stock solution by diluting them in ethanol using micropipette. 0.5 mL of the compound from the final concentration of the solution was added with 0.5 mL of 0.1 mM DPPH solution which total of 1mL in a sample vial. The vials were closed immediately with its cap after addition of reagent and compound solution to prevent evaporation and followed by incubation in the dark environment at room temperature for 30 minutes. After 30 minutes, the absorbances of the mixtures in each vial were measured using UV-Vis spectroscopy at 517 nm in the dark as DPPH reagent is light-sensitive. The percentage of the DPPH free radical scavenging activity was calculated according to the formula below:

$$\text{DPPH free radical scavenging activity} = \frac{A_0 - A_1}{A_0} \times 100 \%$$

....**Equation 1.1**

Where  $A_0$  = absorbance of the control,  $A_1$  = absorbance of the sample

In this study, ascorbic acid was used as the positive control and ethanol used as the negative control. Determination of each compound was conducted for 3 times to obtain the mean value of the  $EC_{50}$  by plotting a graph of DPPH scavenging activity (%) against concentration of samples (mg/mL)

## CHAPTER 5

### CONCLUSION

#### 5.1 Conclusion

In this project, two new organometallics complexes of  $[\text{CpFe}(\text{CO})_2(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))]\text{I}$  (**2**) (33.8% yield) and  $[\text{CpFePdCl}_2(\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2))]\text{I}_4$  (**3**) (7.82% yield) were successfully synthesized *via* microwave-assisted method under ambient atmosphere at 110 °C (toluene, 30 minutes) and at 60 °C ( $\text{CH}_3\text{CN}$ , 3 hours), respectively. Complexes **2** and **3** were characterised *via*  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR, FTIR, C, H, N elemental analysis and ESI-MS analysis. The molecular structure for complexes **2** and **3** were successfully proposed based on the results and observation obtained from various spectroscopy and chemical analyses. The synthetic pathways for both complexes **2** and **3** were proposed by referring to their ESI-MS fragmentation patterns and the time-dependent NMR tube thermolysis of complex **2** and co-thermolysis of complex **2** with  $\text{PPh}_2(p\text{-C}_6\text{H}_4\text{NMe}_2)$  at 110 °C. The antioxidant properties study of complex **2** showed that it consists of antioxidant activity. However, the antioxidant activity of complex **2** was found lower than the conventional standard antioxidant, ascorbic acid.

## 5.2 Further studies

Complex **2** and **3** can be further characterized by the single crystal X-ray diffraction analysis to determine their actual molecular structures. Furthermore, antioxidant activity of complex **3** also can be studied by DPPH assay. Other than that, catalytic properties of complexes **2** and **3** in olefin epoxidation can be carried out as well.

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