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Solventless substitution chemistry of iron and ruthenium metal carbonyl complexes

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CHAPTER 4. SOLVENTLESS REACTIONS OF CYCLOPENTADIENYLIRON DICARBONYL IODIDE AND SOME SOLID PHOSPHINE LIGANDS.

4.1 INTRODUCTION

4.1.1 The Cyclopentadiene ligand

Cyclopentadiene (figure 4.1) is a simple organic compound found initially in the volatile parts of coal tar [1]. At room temperature, it dimerizes after many hours to give dicyclopentadiene through a Diels-Alder reaction. Metals can bind to the cyclopentadiene (Cp) group. Based on the type of bonding between a metal and a Cp moiety, cyclopentadienyl complexes are classified in three categories namely p-complexes, s-complexes and ionic complexes.

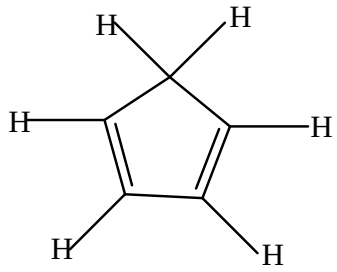


Figure 4. 1. The Cyclopentadiene molecule

Since the discovery of ferrocene in 1951 [2, 3], which is regarded as the first highly stable organometallic compound synthesized that contained the Cp ligand, the use of cyclopentadiene in chemistry has become very successful [4, 5].

The popularity of the use of the Cp ligand in chemistry is due to some interesting features associated with this ligand:

- The Cp ligand can bind to the metal through one to five carbon atoms (η^1- η^5) [6];
- The Cp ligand can stabilize both low and high oxidation state metals [7];
- By changing the functionality (all H atoms can be replaced) on the Cp ligands, the resulting compounds possess different physical and chemical properties from the normal Cp such as stability, solubility, electron donor character etc [8].

The cyclopentadiene ligand reacts with transitional metals to form cyclopentadienyl metal complexes.

4.1.2. Synthesis of substituted cyclopentadienylmetal complexes

The methods of synthesizing substituted cyclopentadienyl metal complexes are very diverse, but they can be classified into two major groups:

a) Starting from a modified Cp ring: the substituent is attached to a Cp ring prior to binding to the metal [9] (equation 2-1).

$$HCp + NaH \xrightarrow{0^oC} CpNa + H_2 \xrightarrow{RX} RCp + NaX \quad (2\text{-}1)$$

This RCp ligand can now react with a metal to give a “RCpM” containing complex.

b) Modification of a cyclopentadienylmetal complex [10, 11].

In this approach, the unsubstituted Cp ligand reacts first with the metal to form a cyclopentadienylmetal complex. Therefore, some or all of the hydrogens on the Cp ring are replaced. The synthesis can proceed by metallation of the Cp ring or by the internal ligand migration from the metal to the Cp ring (equations 2 – 2 and 2 – 3).

$$2\ HCpMLn + 2\ R \longrightarrow 2\ RCpMLn + H_2 \qquad (2 - 2)$$

$$2\ HCpM\text{-}R + 2\ L' \longrightarrow 2\ RCpM\text{-}L' + H_2 \qquad (2 - 3)$$

4.1.3. Carbon monoxide substitution reactions

Generally, a reaction in which a coordinated ligand is replaced by another ligand from the coordinating sphere is called a "substitution reaction" (equation 2 - 4).

$$ML_x + nL' \rightleftharpoons ML_{x-n}L'_n + nL \qquad (2 - 4)$$

The ligand substitution process can occur either via an associative mechanism classically symbolized by S_N2 or via a dissociative mechanism, S_N1 [12]. In organometallic chemistry, the substitution reaction plays a key role in generating materials that can be used as catalysts. A common substitution reaction that has been studied in detail is the metal carbonyl substitution reaction in which a CO ligand is replaced by another two electron donor ligand [13, 14, 15, 16]. It has been also found that a variety of procedures can be used to enhance this CO substitution.

4.1.3.1 Reagent induced CO substitution reactions.

In this class of reactions a decarbonylating reagent is used to promote CO substitution from the metal centre. For example, Me_3NO, is a very useful reagent used in the decarbonylation of $M(CO)_n$ complexes [17] (equation 2 – 5).

$$M(CO)_n + L + Me_3NO \longrightarrow M(CO)_{n-1}L + Me_3N + CO_2 \qquad (2 - 5)$$

The CO substitution in group 6 hexacarbonyls by a range of ligands (tertiary alkyl, tertiary amines, arsines etc.) can also be induced by sodium borohydride in ethanol [18].

4.1.3.2 Catalytic induced CO substitution reactions

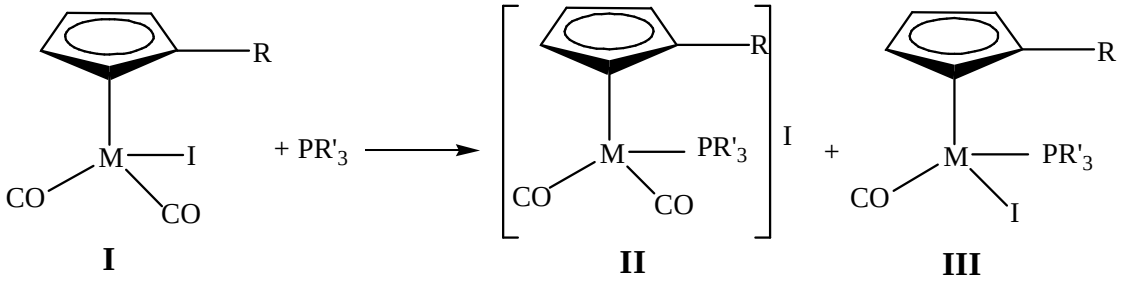
The use of a catalyst to induce CO substitution from a metal centre has been widely explored [16, 19, 20]. Webb and Mitchell [21] in 1959 were the first to report a catalytic CO substitution of a metal carbonyl complex.

A range of metal and metal oxides were tested and the order of activity was found to be Pt > Ni >> $Fe_3(CO)_4$ > Cu > Fe > Al_2O_3 > Fe_2O_3 for the exchange of ^{14}CO with CO in $Fe(CO)_5$ at 0^oC.

The salts of transition metals ($CoCl_2$, $NiCl_2$ etc.) have also been found to be effective catalysts for the displacement of CO from $Fe(CO)_5$ by isonitriles [22] as shown in equation 2- 6.

$$Fe(CO)_5 + nRNC \xrightarrow{CoCl_2} Fe(CO)_{5-n}(CNR)n \qquad (2 - 6)$$

Cyclopentadienyl metal dimers, $[CpFe(CO)_2]_2$, $[MeCpFe(CO)_2]_2$, $[CpMo(CO)_3]_2$ etc. have also been shown to be catalysts for the substitution of CO from $RCpM(CO)_nI$ systems. In particular, $[CpFe(CO)_2]_2$ is an efficient catalyst for the reaction of $CpFe(CO)_2I$ with PR_3 or RNC to yield $CpFe(CO)(PR_3)I$ or $[CpFe(CO)_2(PR_3)]I$ in refluxing benzene [23]. $[CpMo(CO)_3]_2$ has also been shown to be a catalyst for CO replacement in $CpMo(CO)_3I$ by PR_3 ligands [24]. The general scheme for these reactions is represented in figure 4.2.



I **II** **III**

Figure 4.2. Reaction between $RCpM(CO)_2I$ and phosphine ligands

The outcome of the reaction in solution has been shown to be a salt product (**II**) or a non salt product (**III**) depending on the nature of L (basic or acidic), X (halide = I, Br, Cl) and the time of the reaction [25].

The following chapter is devoted to the solventless reactions between $CpFe(CO)_2I$ and some phosphine ligands. As discussed in this introduction, these reactions are known to occur in solution (benzene) at a temperature around 80^oC.

The product formed mainly involves the substitution of one CO ligand by a phosphine ligand. Our aim in this chapter is to study the same systems in the absence of the solvent and establish the chemistry involved in the solventless reactions. Will the reaction occur in the absence of solvent? If yes, do we have the same type of products as those produced in the solution procedure? How are the kinetics of the reaction affected by the non - use of a solvent?

4. 2 EXPERIMENTAL

4.2.1. Synthesis of the starting material

All operations involving the handling of air sensitive materials were carried out under dry nitrogen using standard Schlenk techniques. Solvents were dried by conventional methods and distilled under nitrogen prior to use. Cyclopentadienyliron dicarbonyl dimer and all the phosphines were used as supplied (Strem Chemicals). The starting material $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ was prepared from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and I_2 in dichloromethane [15, 26]. The starting material was characterized by FTIR and NMR spectroscopy. Results were in accordance with the literature values.

4.2.2 Experimental procedure for solventless reactions

The reaction between $CpFe(CO)_2I$ and PR_3 has been performed in the absence of solvent. One of the following two procedures can be used but for our experiments, mainly procedure 2 has been used. Typical procedures using PPh_3 are presented below.

Procedure 1

$CpFe(CO)_2I$ (0.08 mM, 22 mg) and PPh_3 (0.08 mM, 21 mg) were mixed in a 50 ml round bottomed flask. A minimum volume of CH_2Cl_2 (2-3 ml), enough to dissolve the material, has been added and quickly removed to afford a powdered material. Portions of this material (5-10 mg) were then loaded into NMR tubes and flushed with nitrogen gas and well sealed. The NMR tubes were then placed in an oil bath pre-heated at 70^oC. After a pre-determined time, a tube was removed from the oil bath and analysed by ^1H NMR spectroscopy in $CDCl_3$ [27].

Procedure 2

$CpFe(CO)_2I$ (0.08 mM, 22 mg) and PPh_3 (0.08 mM, 21 mg) were ground together in an agate mortar using a pestle. After making a fine homogeneous powder, portions of this material (5-10 mg) were placed into NMR tubes. The rest of the procedure is the same as that used in procedure 1. When a catalyst was used, 10 % mole of $[CpFe(CO)_2]_2$ were added to $CpFe(CO)_2I/PPh_3$ mixture and the three solids ground together.

4.2.3 Optical microscope studies

A homemade glass heating device was pre-calibrated with crystals of known melting points. An optical microscope fitted with a JVC Digital Camera was used to monitor the reaction. Crystals or fine powders of the reactants were placed on the glass surface. The heating device was then adjusted to heat at a certain rate to a preset temperature, while changes in the reactants were monitored and recorded on a PC monitor attached to a camera [28].

4.3 RESULTS AND DISCUSSIONS

4.3.1 Solventless reactions between $CpFe(CO)_2I$ and PPh_3

4.3.1.1 Reactions in the absence of catalyst

A preliminary study between $CpFe(CO)_2I$ and PPh_3 was carried out in 1: 1 mole ratio at 70^oC and the reaction followed by ^1H NMR spectroscopy to assess if the reaction in the absence of solvent would occur. ^1H NMR spectra allowed us to calculate the conversion of the starting material into product. The ^1H NMR spectrum of the starting material in $CDCl_3$ exhibits a singlet at 5.04 ppm representing the five hydrogens of the Cp ring while the peak at 7.26 ppm represents the solvent $CDCl_3$ used to record the spectrum (figure 4.3). After mixing the reactants, a ^1H NMR spectrum of the mixture before heating was recorded and this revealed that minimal reaction occurred at room temperature,
(figure 4.4).

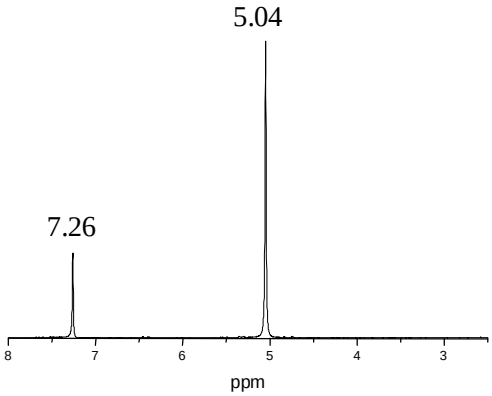


Figure 4.3. ^1H NMR spectrum of $CpFe(CO)_2I$

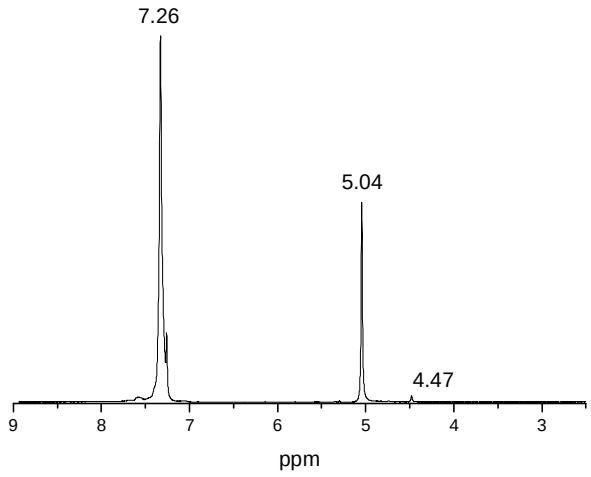


Figure 4.4. ^{1}H NMR spectrum of $CpFe(CO)_2I$ + PPh_3 1: 1 ratio before heating

A small new peak in the Cp region at 4.47 ppm in about 3% abundance compared to the original starting material was observed. The NMR tubes were then placed into the oil bath pre-set at 70^{o}C. A spectrum was recorded after 30 minutes and 180 minutes. As it can be seen (figure 4.5, 4.6) a new resonance at 5.51 grew with time while the resonance at 5.04 decreased. The peak at 4.47 did not change in intensity.

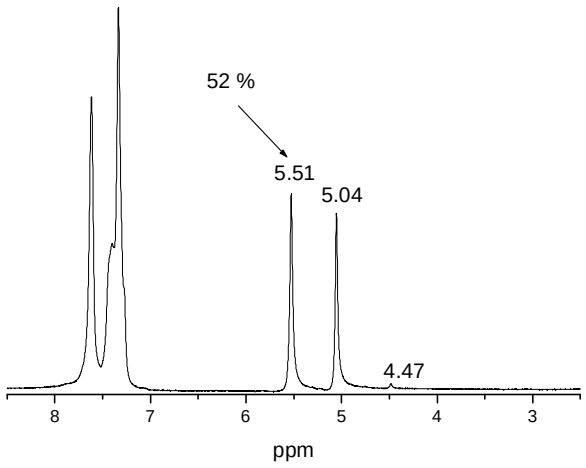


Figure 4.5. ^{1}H NMR spectrum of $CpFe(CO)_2I$ + PPh_3 1: 1 ratio after 30 minutes at 70^{o}C

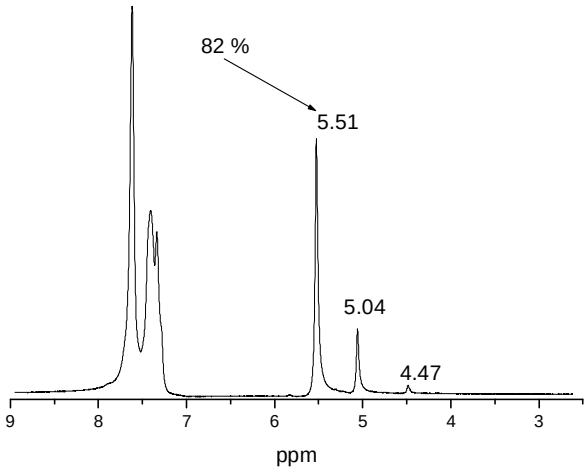


Figure4. 6. ^{1}H NMR spectrum of $CpFe(CO)_2I$ + PPh_3 1: 1 ratio after 3 hours at 70^{o}C

Comparison of the NMR spectral data with that of the known complexes: non-salt product, $CpFe(CO)(PPh_3)I$, and salt product, $[CpFe(CO)_2PPh_3]I$, reveals that the peak at 5.51 corresponds to the salt product and peak at 4.47 to the non-salt product [15, 25].

A DSC profile of the 1: 1 $CpFe(CO)_2I/PPh_3$ mixture was recorded (figure 4.7). The data reveal that this mixture has an endotherm at ~ 71^oC corresponding to the eutectic melting point of the mixture (mp PPh_3 = 78 - 80^oC, mp $CpFe(CO)_2I$ = 114^oC) and possibly a chemical reaction.

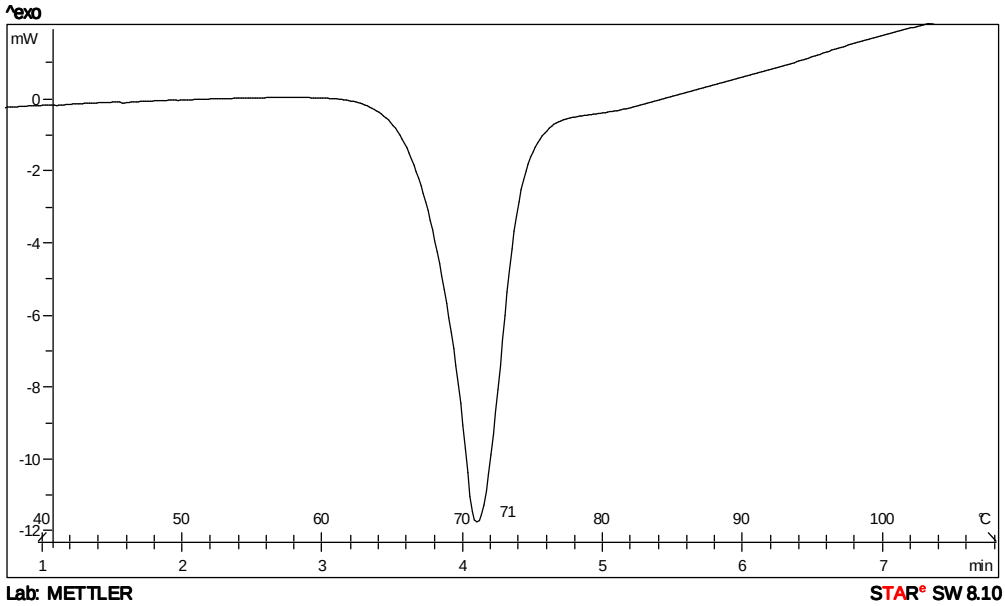


Figure 4. 7. DSC profile for $CpFe(CO)_2I$ + PPh_3 1: 1 mole ratio

As can be seen from the DSC profile the exotherm commences at around 62^oC and suggests that temperatures lower than 70^oC could be used to carry out the reaction. An optical microscope investigation of the reaction mixture was also conducted (figure 4.8).

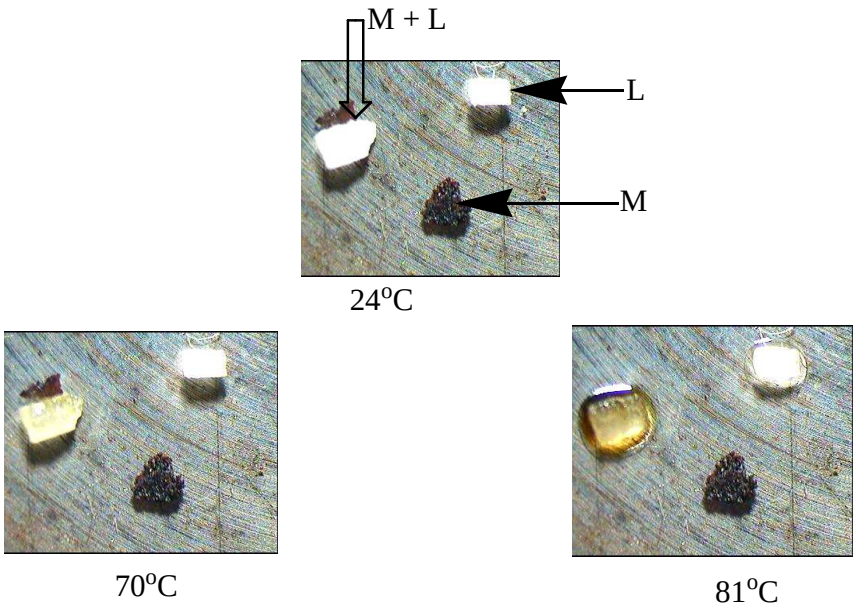


Figure 4.8. Microscopic pictures of $CpFe(CO)_2I + PPh_3$

M= $CpFe(CO)_2I$ L = PPh_3

Three samples were placed on a microscope plate: PPh_3, $CpFe(CO)_2I$ and a continuation of PPh_3 and $CpFe(CO)_2I$ in which the studied materials were pushed in contact with each other. The process clearly shows the commencement of the melt process at 70°C for the touching materials while separated samples do not melt. After this preliminary study, the reaction was followed systematically by collecting ^1H NMR spectra after regular intervals at 70°C (0 min, 30 min., 1 h, 2 h, 3 h, 4 h) and the conversion of the starting material into products calculated by area integration. Results are shown in table 4.1. From this table, it is clear that the salt product (labeled **II** throughout the thesis) is the only product of the reaction, the small amount of non-salt product (labeled **III** throughout the thesis) observed in the reaction relates to the grinding process and not to the melt reaction.

Furthermore, it is clear the heating process did not have any influence on the amount of the non salt product formation even after 4 hours of heating at 70°C.

Table 4.1. $CpFe(CO)_2I + PPh_3$ at different ratios at 70^0C without catalyst

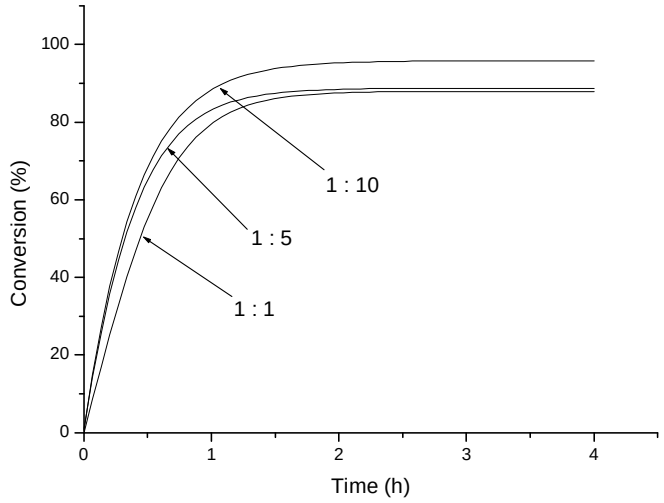
Time (h)	**Mole ratio**	**Conversion (%)**	
	1 : 1	**II**	**III**
0.5		52	3
1		76	4
2		81	4
3		83	4
4		90	1
0.5	1 : 5	59	7
1		74	7
2		77	7
3		83	8
4		83	9
0.5	1 : 10	61	11
1		69	13
2		78	13
3		93	6
4		86	14

Although the solventless procedure gives the same products as the procedure using a solvent, the ratio between the two products is significantly different: in solvent (refluxing benzene) [23], the non-salt compound is the major product, with the salt product being the minor component while in the solventless procedure, the salt is the major product and the non-salt product is the minor product of the reaction.

The effect of the starting material to ligand mole ratio was also explored. Ratios of 1: 5 and 1: 10 mole were studied. Results are shown in table 4.1 and graph 4.1.

As can be seen, the mole ratio plays an important role in the early stages of the reaction. Thus, after 30 minutes, the 1: 1 ratio gives 55% conversion, the 1: 5 ratio gives 66% conversion and the 1: 10 ratio gives 72 % conversion of the starting material into the products. As the reaction progresses, the effect of the mole ratio is not important. For instance, after 1h of reaction, all three mole ratios give more or less the same conversion (~80% see table 4.1). However, in the later stages of the reaction, the reaction mixture with the higher mole ratio more rapidly goes to 100 % completion while reactions with lower mole ratios seem to stabilize around 90 %.

Thus, it is clear from these data that diffusion of reactant to reach each other is not determining the overall state of the reaction. In the melt, reactants readily form the product(s).



Graph 4.1. $CpFe(CO)_2I + PPh_3$ at 70°C and different mole ratios.

The products were isolated from a silica gel column made up with hexane. Hexane was used to elute the excess of the ligand. Benzene was then used to elute the non-salt fraction and acetone eluted the salt product. It has to be noted that the solvent is used in the purification of the product not in the synthesis process. The pure salt compound was characterized by NMR (figure 4.9) and IR (figure 4.10) spectroscopy as well as by MS (figure 4.12). The melting point was determined by DSC (figure 4.11).

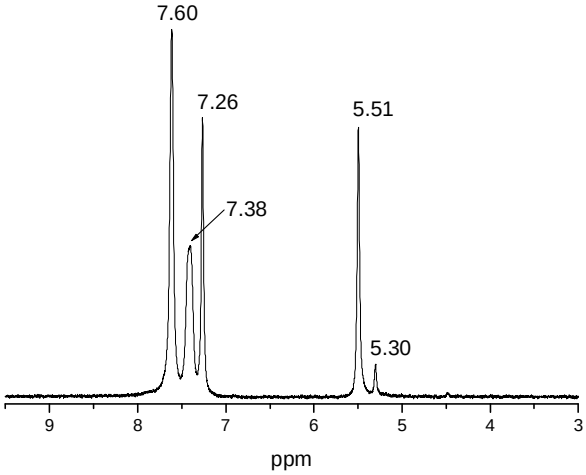


Figure 4.9. ^{1}H NMR spectrum of $[CpFe(CO)_2PPh_3]I$

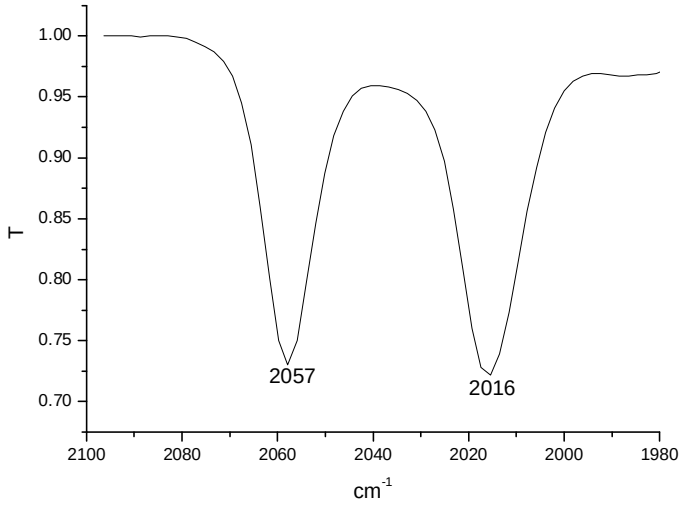


Figure 4.10. IR spectrum of $[CpFe(CO)_3PPh_3]I$

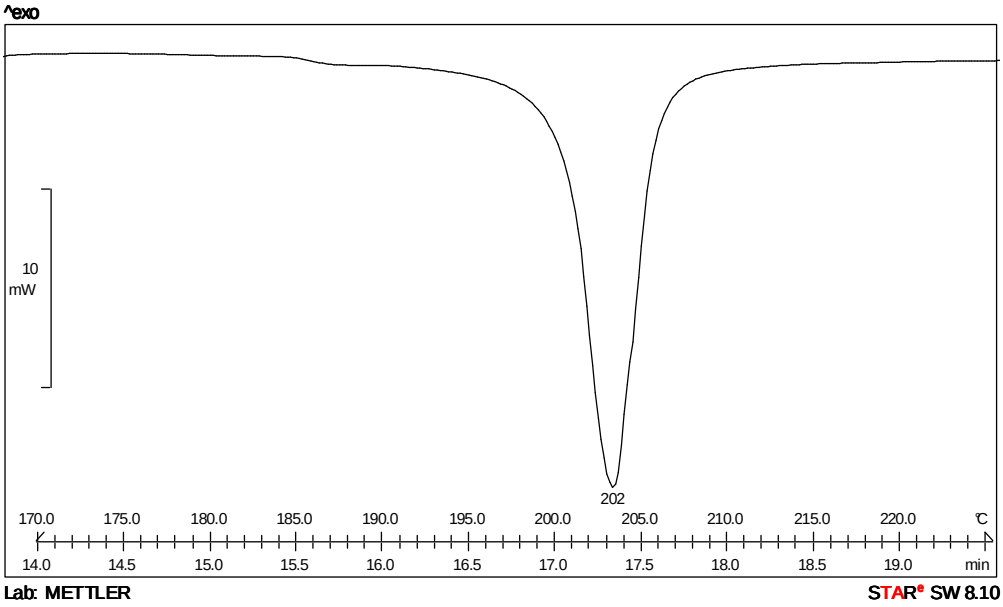


Figure 4.11. DSC profile for $[CpFe(CO)_2PPh_3]I$

To determine the product formed in the initial stages of the melt phase, reactions were carried out at 60°C.

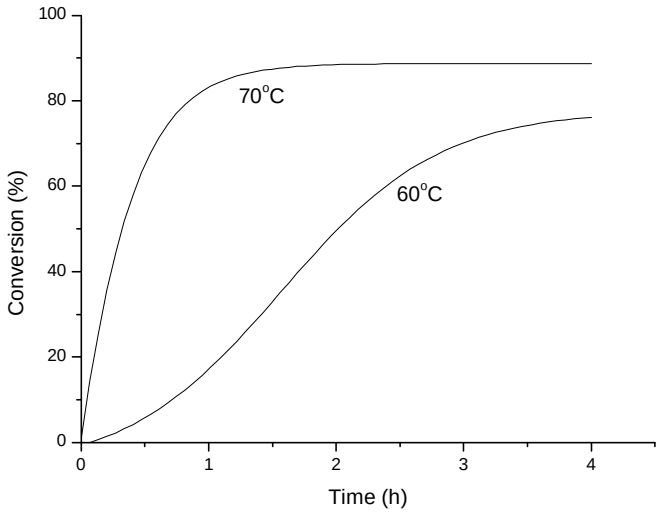
As expected, the results show that the reaction is slower at 60°C than at 70°C (see table 4. 2 and graph 4.2). After 30 minutes we have 7% overall conversion against 55% overall conversion at 70°C, but after 4 hours, a conversion of 80% can be reached when working at 60°C. The main product formed is a salt.

Table 4.2. Solventless reactions between $CpFe(CO)_2I$ and PPh_3 at 60°C 1: 1 mole ratio

Time (h)	**Conversion (%)**		
	II	**III**	**Overall**
0.5	0	7	7
1	5	8	13
2	48	7	55
3	56	6	62
4	75	6	81

II: Salt product

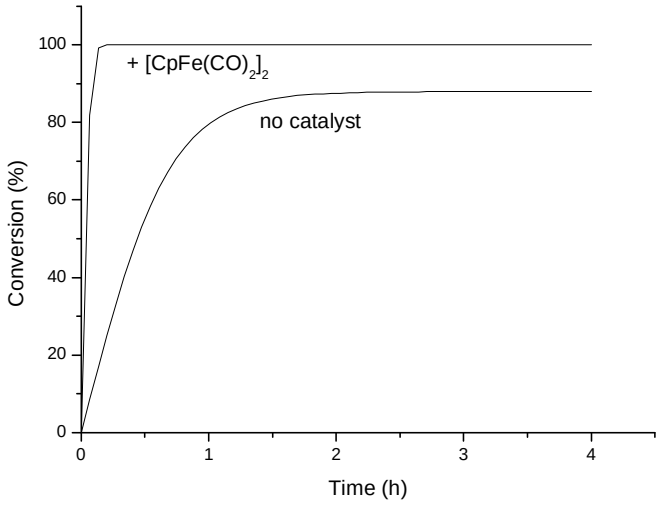
III: Non-salt product



Graph 4.2. $CpFe(CO)_2I$ + PPh_3 1: 1 ratio at 60 and 70°C

4.3.1.2 Effect of $[CpFe(CO)_2]_2$ as a catalyst on the reaction between $CpFe(CO)_2I$ and PPh_3

The dicyclopentadienyliron dicarbonyl dimer, $[CpFe(CO)_2]_2$, has been shown in previous solution studies to be a good catalyst for the CO substitution reactions of $CpFe(CO)_2I$ systems [15]. Our investigations have been also oriented in that direction to find out whether the same capability will also be manifest under solvent free conditions. The procedure used is described in the experimental section. After 30 minutes at 70°C, 100% product was formed compared to 55 % of product obtained in the absence of catalyst in the same conditions (graph 4.3).

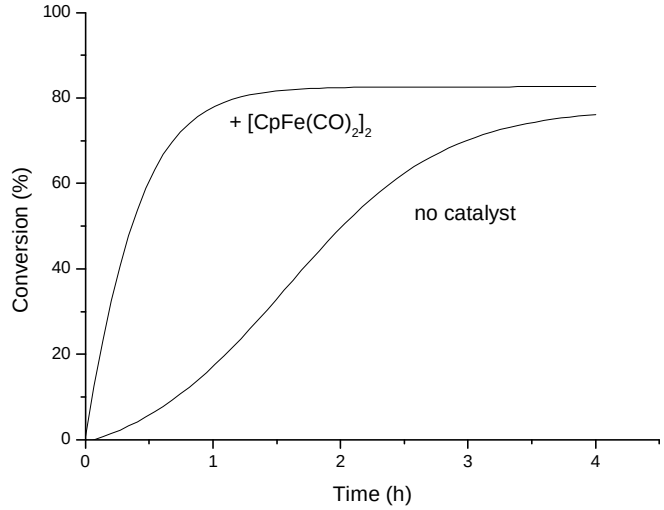


Graph 4.3. $CpFe(CO)_2I$ + PPh_3 at 70°C with/without catalyst

The effect of the catalyst on the reaction has been also observed at 60°C (table 4.3 and graph 4.4). $[CpFe(CO)_2]_2$ enhances considerably the rate of the reaction.

Table 4.3. Solventless reactions between $CpFe(CO)_2I$ and PPh_3 at 60°C in presence of $[CpFe(CO)_2]_2$ as a catalyst.

Time (h)	**Conversion (%)**		
	II	**III**	**Overall**
0.5	46	15	61
1	66	11	77
2	64	13	77
3	73	9	82
4	77	12	89



Graph 4. 4. $CpFe(CO)_2I + PPh_3$ at 60°C with/without catalyst

4.3.2 Solventless reactions between $CpFe(CO)_2I$ and solid PR_3 ligands

4.3.2.1 Reactions in the absence of the catalyst

After this model study using PPh_3, a range of solid phosphine ligands [P(*p*-$OCH_3C_6H_4)_3$, P(*m*-$CH_3C_6H_4)_3$, P(*p*-$FC_6H_4)_3$, P(*p*-$ClC_6H_4)_3$] were explored in order to find out the effect of variation of the ligand on the reaction. All these ligands have the same cone angle (145°) except P(*m*-$CH_3C_6H_4)_3$ (165°) [29, 30]. Therefore, the steric effect of para-substituted ligands is expected to be the same; the major difference among them being the electronic effect. Considering the electron donating ability of all the ligands used, based on the CO stretching frequency studies, the ligands can be ranked in decreasing order of electron donating ability as follows: P(*p*-$OCH_3C_6H_4)_3$ > P(*m*-$CH_3C_6H_4)_3$ > PPh_3 > P(*p*-$FC_6H_4)_3$ >P(*p*-$ClC_6H_4)_3$ [31, 32, 33]. DSC studies were conducted on the $CpFe(CO)_2I$ + PR_3 mixtures and results are condensed in table 4.4. All the 1: 1 mixtures give their DSC endotherm between 70 - 90°C, similar to that seen in figure 4.8 for $CpFe(CO)_2I/PPh_3$ mixture.

Thus, choice of the reaction temperature could aid in discriminating between the reaction rates, an effect that could influence steric and electronic effects.

Table 4. 4. Melting points of $CpFe(CO)_2I + PR_3$ mixtures (1: 1 molar ratio)

Mixture	**Melting points (^oC)**
$CpFe(CO)_2I + PPh_3$	70
$CpFe(CO)_2I + P(p\text{-}OCH_3C_6H_4)_3$	91
$CpFe(CO)_2I + P(m\text{-}CH_3C_6H_4)_3$	89
$CpFe(CO)_2I + P(p\text{-}FC_6H_4)_3$	71
$CpFe(CO)_2I + P(p\text{-}ClC_6H_4)_3$	88

The reaction between $CpFe(CO)_2I$ and PR_3 ligands were initially conducted at 100^oC, temperature at which all mixtures are in melt. Results are recorded in table 4.5. At this temperature, reactions are very rapid for all ligands. Salt and non-salt products are formed in different ratios. The salt and non- salt products have been isolated using the same method as that used for PPh_3 compounds (page 59) and characterized by a combination of IR, NMR (tables 4.6, 4.7), melting points (table 4.8) and MS analysis (table 4.9).

Table 4.5. Reactions of $CpFe(CO)_2I$ and PR_3 ligands at 100^0C without catalyst (1: 5 mole ratio).

Ligand	**Time(min)**	**Conversion (%)**		
		II	**III**	**Overall**
PPh_3	5	70	24	94
	15	72	28	100
$P(m\text{-}CH_3C_6H_4)_3$	5	39	57	96
	15	40	57	97
$P(p\text{-}OCH_3C_6H_4)_3$	5	80	20	100
	15	85	15	100
$P(p\text{-}FC_6H_4)_3$	5	36	53	89
	15	0	95	95
$P(p\text{-}ClC_6H_4)_3$	5	0	76	76
	15	0	88	88

Table 4.6. Spectroscopic data for $[CpFe(CO)_2PPh_3]I$ complexes

	^{1}H NMR(ppm)				**^{31}P NMR (ppm)**		**IR**
Complex	**Cp**	**CH_3**	**OCH_3**	**Phenyl**	**Product**	**Free ligand**	**νCO(cm^{-1})**
$[CpFe(CO)_2P(Ph)_3]I$	5.50	-	-	7.60; 7.39	61.78	-4.71	2057; 2016
$[CpFe(CO)_2P(p\text{-}OCH_3C_6H_4)_3]I$	5.44	-	3.88	7.09	56.96	-9.47	2054; 2012
$[CpFe(CO)_2P(m\text{-}CH_3C_6H_4)_3]I$	5.47	2.40	-	7.52; 7.34	61.21	-4.53	2056; 2014
$[CpFe(CO)_2P(p\text{-}ClC_6H_4)_3]I$	5.59	-	-	7.61; 7.35	61.98	-7.78	2060; 2018

Table 4.7. Spectroscopic data for $CpFe(CO)(PR_3)I$ complexes.

Complex	**^{1}H NMR (ppm)**			**^{31}P NMR (ppm)**	**IR (cm^{-1})**
	Cp	CH_3	OCH_3		
$CpFe(CO)(PPh_3)I$	4.47	-	-	68.01	1951
$CpFe(CO)P(p\text{-}OCH_3C_6H_4)I$	4.46	-	3.82	62.62	1947
$CpFe(CO)P(m\text{-}CH_3C_6H_4)_3I$	4.45	2.36	-	67.07	1950
$CpFe(CO)P(p\text{-}FC_6H_4)_3I$	4.48	-	-	66.79	1955
$CpFe(CO)P(p\text{-}ClC_6H_4)_3I$	4.49	-	-	68.29	1956

Table 4. 8. Melting points of $[CpFe(CO)_2PR_3]I$ complexes

Complexes	**Melting points (^{0}C)**
$[CpFe(CO)_2PPh_3]I$	202
$[CpFe(CO)_2P(p\text{-}OCH_3C_6H_4)_3]I$	171
$[CpFe(CO)_2P(m\text{-}CH_3C_6H_4)_3]I$	168
$[CpFe(CO)_2P(p\text{-}FC_6H_4)_3]I$	174
$[CpFe(CO)_2P(p\text{-}ClC_6H_4)_3]I$	181

The mass spectra for the salt compounds were recorded on a VG70-SEQ instrument using the Fast Atomic Bombardment (FAB) method. In general, these results shown that iodine is the first particle to get out of the molecule for all the complexes. The next step was the loss of the two carbon monoxide ligands and the rest of the fragmentation was dependent on the phosphine ligand present until the whole PR_3 fragment was removed to afford $(C_5H_5)Fe$. As illustration, the mass spectrum of $[CpFe(CO)_2PPh_3]I$ is shown in figure 4.12 and its fragmentation patterns in figure 4.13.

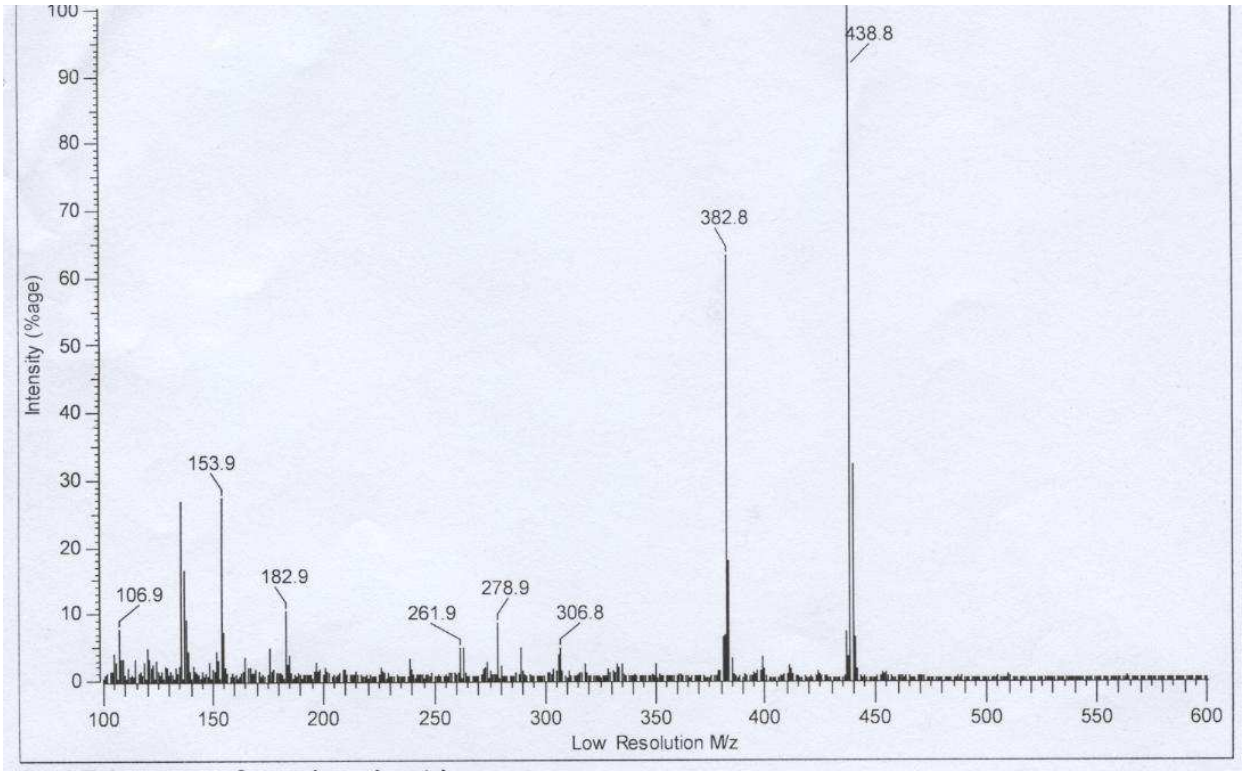


Figure 4.12: Mass spectrum for $[CpFe(CO)_2PPh_3]I$

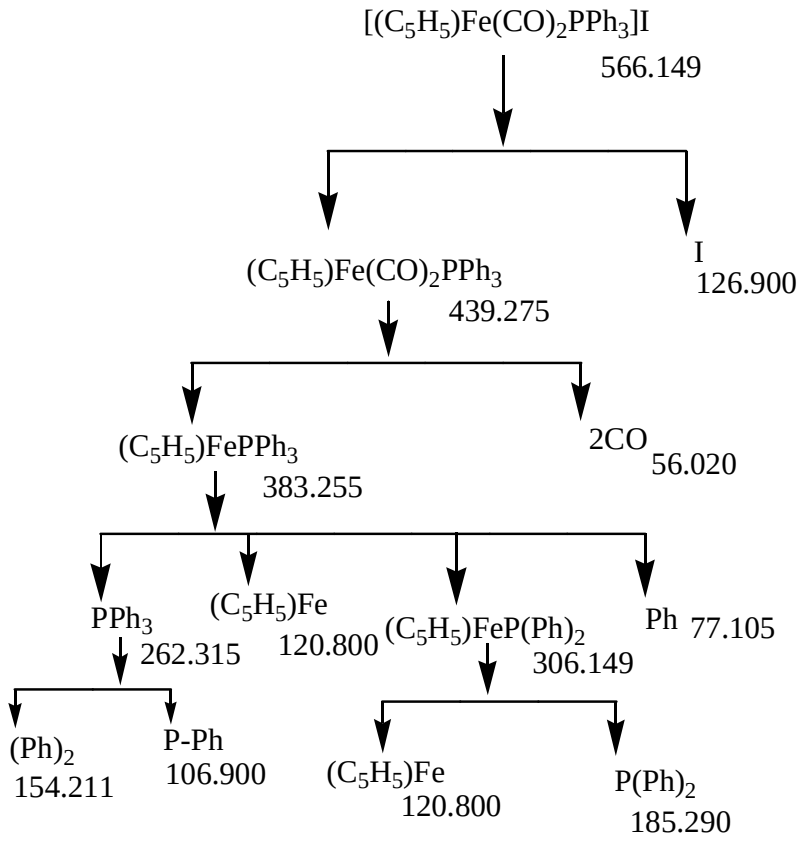


Figure 4.13: Fragmentation patterns for $[CpFe(CO)_2PPh)_3]I$

The mass spectral data for $[CpFe(CO)_2PR_3]I$ are shown in table 4.9.

Table 4.9. Mass spectral data for $[CpFe(CO)_2PR_3]I$ products.

Ligand	S-I	S-I-2CO	S-I-2CO-PR_3
PPh_3	438.8 (100.00)	382.8 (63.50)	120.8 (5.00)
P(*p*-$OCH_3C_6H_4)_3$	529.2 (98.98)	473.2 (69.36)	120.8 (15.29)
P(*m*-$CH_3C_6H_4)_3$	481.1 (100.00)	425.1 (57.67)	120.8 (8.39)
P(*p*-$FC_6H_4)_3$	493.1 (41.09)	437.2 (21.72)	120.8 (14.47)
P(*p*-$ClC_6H_4)_3$	541.1 (17.40)	487.1 (7.96)	120.8 (14.50)

S = $[CpFe(CO)_2PR_3]I$

Contrarily to the salt products, in the non salt products, the CO molecule leaves before the iodine atom.

The data in table 4.5 reveal that the product produced is determined by the incoming ligand. Three trends are to be noted after 5 minutes of reaction:

- Overall conversion: P(*p*-$OCH_3C_6H_4)_3$ > P(*m*-$CH_3C_6H_4)_3$ > PPh_3 > P(*p*-$FC_6H_4)_3$ >P(*p*-$ClC_6H_4)_3$.
- Conversion into **II**: P(*p*-$OCH_3C_6H_4)_3$ > PPh_3 > P(*m*-$CH_3C_6H_4)_3$ > P(*p*-$FC_6H_4)_3$ > P(*p*-$ClC_6H_4)_3$
- Conversion into **III**: P(*p*-$ClC_6H_4)_3$ > P(*m*-$CH_3C_6H_4)_3$ >P(*p*-$FC_6H_4)_3$ > PPh_3 > P(*p*-$OCH_3C_6H_4)_3$

The overall reaction rate reveals that electron donating ligands more rapidly generate products than the electron withdrawing ligands. Thus in the melt phase, the reaction is well behaved in terms of reaction rates. However, three other issues related to the data are to be noted:

The first is that the ratio of **III/II** at 100^{o}C is higher than at lower temperature (see table 4. 5) as exemplified by the PPh_3 data at 60^{o}C and 70^{o}C. Thus more non-salt product is present at higher temperature. This could be due in part to the conversion of **II** into **III** by decarbonylation reaction.

The second issue relates to the slow conversion of **II** to **III** with time for the electron donating groups on the phosphines. When the products have been formed, little reaction occurs. This fact was established in an experiment heating pure $[CpFe(CO)_2PPh_3]I$ at 145 ^{o}C. After 15 minutes, only 3 % of $CpFe(CO)(PPh_3)I$ was obtained.

The third issue relates to the phosphorus that contains electron withdrawing groups [P(p-$FC_6H_4)_3$, P(p-$ClC_6H_4)_3$]. These ligands gave (eventually) exclusively non-salt products and further for P(p-$FC_6H_4)_3$ the salt product converts to the non-salt product with time (table 4.5). Reactions were also performed at lower temperatures (60^{o}C, 70^{o}C) to obtain further information on the reaction (table 4.10 and 4.11).

Table 4.10: Reactions of $CpFe(CO)_2I$ and PR_3 ligands at 60^0C
Without catalyst.

Ligand	**Time (h)**	**Conversion (%)**		
		II	**III**	**Overall**
PPh_3	0.5	0	7	7
	4	75	6	81
$P(m\text{-}CH_3C_6H_4)_3$	0.5	0	6	6
	4	0	14	14
$P(p\text{-}OCH_3C_6H_4)_3$	0.5	0	5	5
	4	0	12	12
$P(p\text{-}FC_6H_4)_3$	0.5	0	7	7
	4	0	14	14
$P(p\text{-}ClC_6H_4)_3$	0.5	0	6	6
	4	0	15	15

At 60^oC in the absence of catalyst (table 4.10), only PPh_3 reacts to any significant extent. After 4 hours, little product is formed in most of reactions.
Data at 70^oC in the absence of catalyst reveals faster reactions for all ligands (table 4.11). Intermediate data collected between 0.5 hour and 4 hours shown also that the conversion of starting material into product is a direct function of time.

Table 4.11: Reactions of $CpFe(CO)_2I$ and PR_3 ligands at 70^0C without catalyst.

Ligand	**Time (h)**	**Conversion (%)**		
		II	**III**	**Overall**
PPh_3	0.5	52	3	55
	4	90	1	91
P(*m*-$CH_3C_6H_4)_3$	0.5	0	0	0
	4	58	6	64
P(*p*-$OCH_3C_6H_4)_3$	0.5	37	0	37
	4	59	0	59
P(*p*-$FC_6H_4)_3$	0.5	40	10	50
	4	64	20	84
P(*p*-$ClC_6H_4)_3$	0.5	0	7	7
	4	0	21	21

Rate: PPh_3 > P(*p*-$FC_6H_4)_3$ > P(*p*-$OCH_3C_6H_4)_3$ > P(*m*-$CH_3C_6H_4)_3$ >P(*p*-$ClC_6H_4)_3$.

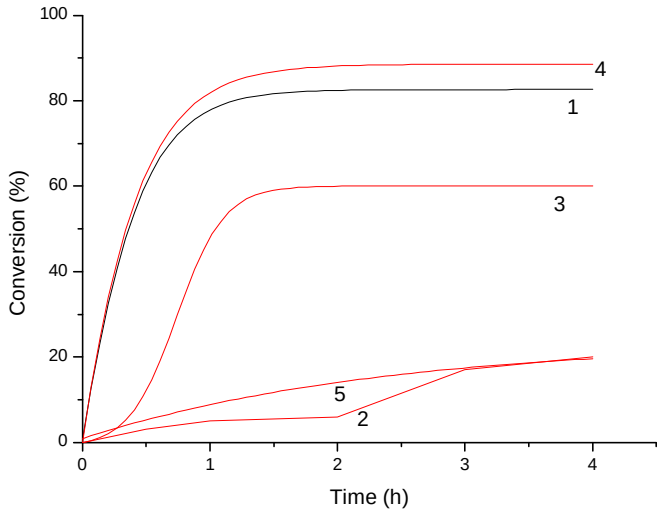
This order of the ligands reactivity show that the reaction is favourable to the electron donor ligands. However, P(*p*-$FC_6H_4)_3$ is making an exception as its reactivity is even better than that of electron donor ligands. This could be due to the melt issue. In fact, at 70^oC only PPh_3 and P(*p*-$FC_6H_4)_3$ mixtures are in complete melt phase (DSC data table 4.4).

4.3.2.2. Effect of $[CpFe(CO)_2]_2$ as a catalyst on the reactions between $CpFe(CO)_2I$ and PR_3 ligands

The effect of $[CpFe(CO)_2]_2$ as a catalyst was also explored for different PR_3 ligands at 60^oC (table 4.12 and graph 4.5) and 70^oC (table 4.13 and graph 4.6).

Table 4.12: Reactions of $CpFe(CO)_2I$ and PR_3 ligands at 60^0C with catalyst.

Ligand	Time (h)	Conversion (%)		
		II	**III**	**Overall**
PPh_3	0.5	46	15	61
	4	77	11	88
$P(m\text{-}CH_3C_6H_4)_3$	0.5	8	4	12
	4	58	6	64
$P(p\text{-}OCH_3C_6H_4)_3$	0.5	0	3	3
	4	17	3	20
$P(p\text{-}FC_6H_4)_3$	0.5	55	7	62
	4	83	7	90
$P(p\text{-}ClC_6H_4)_3$	0.5	0	8	8
	4	13	9	22

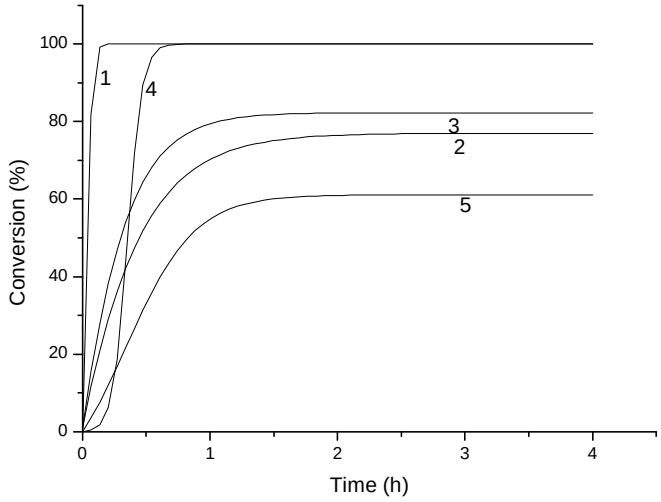


Graph 4.5. $CpFe(CO)_2I + PR_3$ at 60°C with catalyst

1. PPh_3 2. $P(p\text{-}OCH_3C_6H_4)_3$ 3. $P(m\text{-}CH_3C_6H_4)_3$ 4. $P(p\text{-}FC_6H_4)_3$ 5. $P(p\text{-}ClC_6H_4)_3$

Table 4.13: Reactions of $CpFe(CO)_2I$ and PR_3 ligands at 70^0C with catalyst

Ligand	**Time (h)**	**Conversion (%)**		
		II	**III**	**Overall**
PPh_3	0.5	100	0	100
	4	100	0	100
P(*m*-$CH_3C_6H_4)_3$	0.5	69	0	69
	4	86	0	86
P(*p*-$OCH_3C_6H_4)_3$	0.5	55	0	55
	4	78	0	78
P(*p*-$FC_6H_4)_3$	0.5	90	3	93
	4	75	25	100
P(*p*-$ClC_6H_4)_3$	0.5	28	5	33
	4	43	21	64



Graph 4.6. $CpFe(CO)_2I + PR_3$ at 70^oC with catalyst

1. PPh_3 2. $P(p\text{-}OCH_3C_6H_4)_3$ 3. $P(m\text{-}CH_3C_6H_4)_3$ 4. $P(p\text{-}FC_6H_4)_3$ 5. $P(p\text{-}ClC_6H_4)_3$

The use of catalyst also influences the reaction with regard to the type of product formed (salt or non-salt) product. For instance, $P(p\text{-}FC_6H_4)_3$ at 60^0C without catalyst gives only a non-salt product (table 4.10), while at the same temperature in the presence of catalyst, we have mainly a salt product and little of the non - salt formed (see table 4.12).

The catalysed reaction in solution has been proposed to occur via a free radical mechanism [24]. The mechanism proposed involves generation of a 17 electron radical species either from $CpFe(CO)_2I$ (i.e. $CpFe(CO)_2^{\bullet} + I^{\bullet}$) or from a metal dimer $[CpFe(CO)_2]_2$ ($2CpFe(CO)_2^{\bullet}$). It is this 17 electron species that was proposed to create a catalytic cycle to lead to product formation (scheme 4.1).

Scheme 4.1. Mechanism of non salt product formation via a radical chain

$[CpFe(CO)_2]_2 \leftrightarrow 2\ [CpFe(CO)_2]^{\bullet}$

$[CpFe(CO)_2]^{\bullet} + PR_3 \rightarrow [CpFe(CO)PR_3]^{\bullet} + CO$

$[CpFe(CO)PR_3]^{\bullet} + CpFe(CO)_2I \rightarrow \mathbf{CpFe(CO)(PR_3)I} + [CpFe(CO)_2]^{\bullet}$

The last step implicates the exchange between CO from the starting material and PR_3 from the radical catalyst. This mechanism does not however explain how $[CpFe(CO)_2]_2$ can be a catalyst in a reaction that will produce a salt product.
An alternative mechanism can however be proposed to explain the salt product formation. This involves generation of a 19 electron intermediate (scheme 4.2).

Scheme 4.2. Mechanism of Salt product formation via a radical chain

$[CpFe(CO)_2]_2 \leftrightarrow 2\ [CpFe(CO)_2]^{\bullet}$

$[CpFe(CO)_2]^{\bullet} + PR_3 \rightarrow [CpFe(CO)_2PR_3]^{\bullet}$

$[CpFe(CO)_2PR_3]^{\bullet} + CpFe(CO)_2I \rightarrow \mathbf{[CpFe(CO)_2PR_3]I} + [CpFe(CO)_2]^{\bullet}$

The last step is the migration of the ligand from the catalyst to the starting material.
Evidence for this mechanism was provided by replacing $CpFe(CO)_2I$ by another reactant for example $MeCpFe(CO)_2I$ (see chapter 5) with the same catalyst.

The catalyst is playing an important role in enhancing the rate of the reaction for all ligands. This has been also observed earlier in solvent procedure studies [19, 20, 23, 34, 35].

4. 3.3 Solvent free procedure versus solvent procedure.

A significant difference between the solvent free and the solvent procedure is observed (table 4.14).

- The product: using exactly the same conditions the only difference being the presence or not of the solvent, the solvent procedure gives mainly a non-salt product while the solvent free method gives mainly a salt product. Examples are shown for the $P(p\text{-}FC_6H_4)_3$ and PPh_3 yields.
- The rate of the reaction: Solvent free procedure gives a very high percentage of conversion into product compared to the solvent procedure. In 1: 5 mole ratio at 70^0C in the presence of 10% mole $[CpFe(CO)_2]_2$ as a catalyst and benzene as a solvent, the reaction between $CpFe(CO)_2I$ and PPh_3 or $P(p\text{-}FC_6H_4)_3$ yielded lower percentage conversion compared with the solvent free method (table 4.14).

Table 4.14. Solvent free procedure versus solvent procedure for PPh_3 and $P(p\text{-}FC_6H_4)_3$

Ligand	**Time (min)**	**Solvent procedure**	**Solvent free procedure**
$P(p\text{-}FC_6H_4)_3$	30	Only non salt product in 28% conversion	90% salt product and 3% non-salt product
PPh_3	60	Non salt product in 42% conversion	100% salt product , no non-salt product observed

These results show that in solution medium, the reactions follow the mechanism of non-salt product formation (scheme 4.1) whereas in solvent free medium, the mechanism followed is that of the formation of salt product (scheme 4.2).

4.4 CONCLUSION

The solvent free reactions between $CpFe(CO)_2I$ and some solid phosphines [PPh_3, P(*p*-$OCH_3C_6H_4)_3$, P(*m*-$CH_3C_6H_4)_3$, P(*p*-$FC_6H_4)_3$, P(*p*-$ClC_6H_4)_3$] have been shown to occur at temperatures ranging from 60^0C to 100^0C. The lower the temperature, the lower the conversion of the starting material into product. The product of the reaction could be a neutral (non-salt) or ionic (salt) product. Electron donating phosphines show higher reactivity compared to electron withdrawing ligands and they tend to give higher yields of ionic than neutral products. The conversion of salt product into non salt product has been observed at high temperature.

The complex, $[CpFe(CO)_2]_2$, has a very significant catalytic activity on the reaction by enhancing the reaction rate. Solvent free procedures for the studied reactions gave higher yields when compared to the solvent procedure results.

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