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Solventless substitution chemistry of iron and ruthenium metal carbonyl complexes

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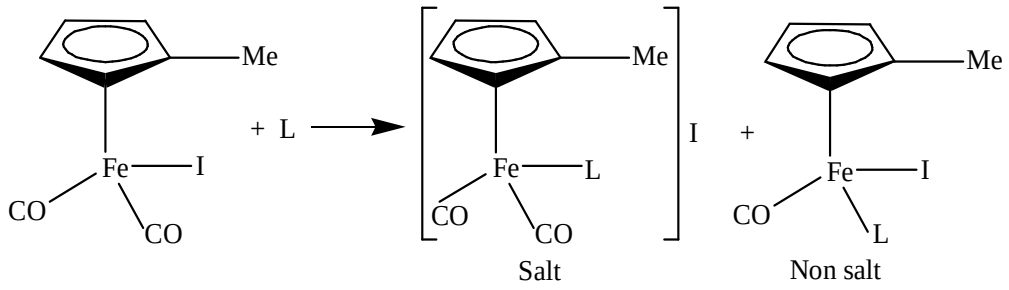
Chapter 5. Solventless reactions between $CH_3CpFe(CO)_2I$ and solid phosphine ligands

5.1 INTRODUCTION

The reaction between $CpFe(CO)_2I$ and electron donor ligands (phosphines, phosphites, isonitriles) have been established in solvent medium [1]. When a substituent is attached to the Cp ring, the resulting substituted complexes present a reactivity different from that of the unsubstituted complexes. Steric and electronic parameters of the incoming ligand are believed to have a significant effect on the rate of the reaction of $RCpFe(CO)_2I$ and electron donor ligands [2, 3]. The aim of this chapter is to study solventless reactions between $CH_3CpFe(CO)_2I$ and phosphine ligands in order to establish the effect of the absence of solvent to the reaction as well as the effect of the Me substituent presence on the Cp ring.

5.2 EXPERIMENTAL

Experimental procedures used to study the solventless reactions between MeCpFe(CO)$_2$I and some solid phosphine ligands are similar to those employed when following the reaction between CpFe(CO)$_2$I and phosphine ligands (4.2.2). Solution studies of CH$_3$CpFe(CO)$_2$I and phosphine ligands revealed the possibility of the formation of two products: salt, [CH$_3$CpFe(CO)$_2$PPh$_3$]I and non salt products, CH$_3$CpFe(CO)(PPh$_3$)I (scheme 5.1).



Scheme 5.1. Reaction between MeCpFe(CO)$_2$I and electron donor ligands.

5.3. RESULTS AND DISCUSSIONS

5.3.1. Reaction between $CH_3CpFe(CO)_2I$ and PPh_3

5.3.1.1 Uncatalyzed reactions

Triphenylphosphine was used as a model ligand. The solventless reactions between $CH_3CpFe(CO)_2I$ was then studied in detail before proceeding to a large set of phosphine ligands. After that preliminary study, the reactivity of other ligands followed. ^1H NMR was used to calculate the conversion of the starting material into product.

^1H NMR of the starting material $CH_3CpFe(CO)_2I$ was first recorded (figure 5.1) and shows two signals at 4.82 and 4.89 ppm for Cp protons and a singlet at 2.17 ppm for the Me protons.

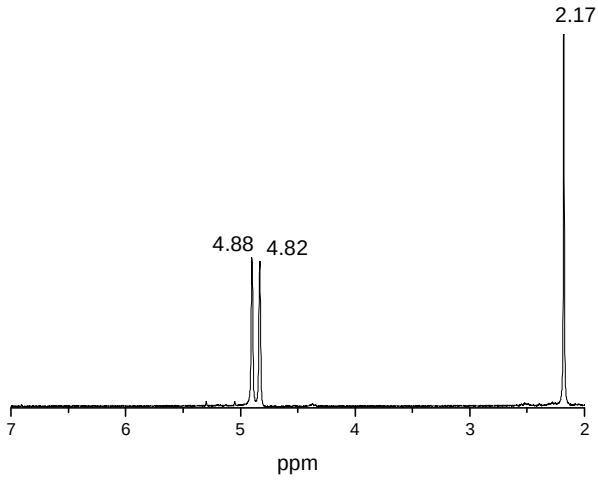


Figure 5.1. ^1H NMR spetrum of $CH_3CpFe(CO)_2I$

$MeCpFe(CO)_2I$ and PPh_3 were then mixed in 1: 1 mole ratio. ^1H NMR spectrum of the mixture was recorded (figure 5.2) and a DSC profile run (figure5.3).

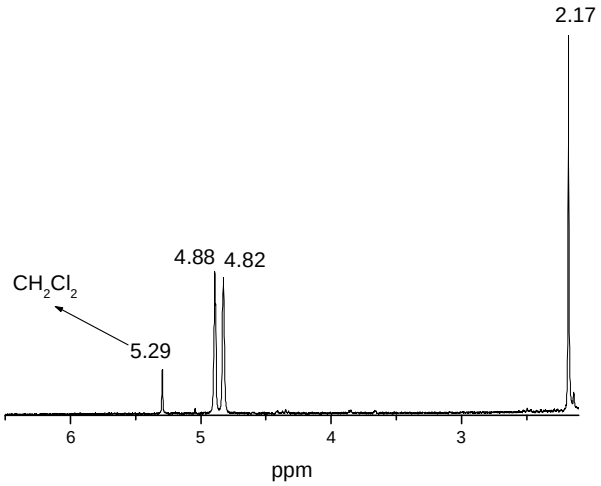


Figure 5.2. ^{1}H NMR spectrum of $CH_3CpFe(CO)_2I$ + PPh_3 before heating

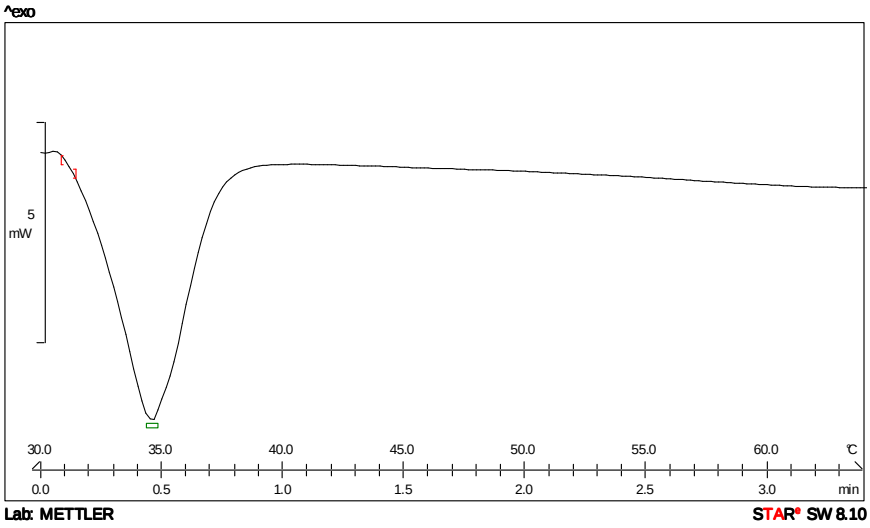


Figure 5.3. DSC profile for $CH_3CpFe(CO)_2I$ + PPh_3 1: 1 ratio

From the ^{1}H NMR spectrum we could see that no change happened to our starting material meaning that mixing does not produce any reaction for these systems.

The DSC profile shows an exotherm at 34°C for the eutectic melting of the mixture (mp of $CH_3CpFe(CO)_2I$ = 40°C, mp of PPh_3 = 80°C). As the mixture was melting at a relatively low temperature, we decided to start our screening at a low temperature and 40°C was used. At that temperature, the mixture starting material/ligand was in melt phase.

The reaction was followed by taking a ^1H NMR spectrum after regular intervals from 30 minutes to 4 hours. No reaction was observed under these conditions even after 4 hours.

We decided to increase the temperature of the reaction and 60°C was the next step. The reaction was then carried out at 60°C in the same procedure. Signals at 5.58 and 5.68 ppm were growing with time while those at 4.82 and 4.88 ppm were decreasing in intensity (figure 5.4).

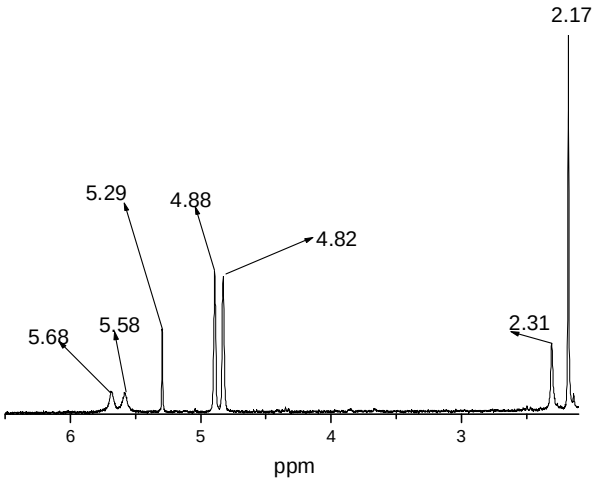


Figure 5.4. ^1H NMR spectrum of $CH_3CpFe(CO)_2I + PPh_3$ at 60°C after 3 hours

From the previous solution studies [4] and the characterization data of a pure material we isolated by column chromatography, the new signals correspond to the salt product $[CH_3CpFe(CO)_2PPh_3]I$. Results showing the formation of salt product as a function of time are assembled in table 5.1.

Table 5. 1. Solventless reactions between $CH_3CpFe(CO)_2I$ and PPh_3 at 60°C to form $[CH_3CpFe(CO)_2PPh_3]I$

Time (h)	**Conversion (%)**
0.5	6
1	13
2	22
3	29
4	38

From table 5.1 we can see that the reaction progresses quite slowly as only 38% of the product could be obtained after 4 hours of reaction. Then we judged it necessary to increase again the temperature of the reaction to 70°C hoping to improve the rate of the reaction and results are condensed in table 5.2. It is clear that the reaction goes better at 70°C than at 60°C.

Table 5.2. Solventless reactions between $CH_3CpFe(CO)_2I$ and PPh_3 at 70°C to form $[CH_3CpFe(CO)_2PPh_3]I$

Time (h)	**Conversion (%)**
0.5	39
1	55
2	65
3	69
4	76

We became then curious to see the behaviour of these systems at quite high temperature and the reaction was then followed at 100°C. After 5 minutes of reaction, the conversion into salt product was 31% and after 15 minutes, the salt product formed was in 61% abundance. No non-salt product was formed.

As can be seen, the temperature is the key for these systems because as the temperature increases, the rate of the reaction also increases all other factors remaining the same: 40°C < 60°C < 70°C < 100°C.

5.3.1.2 Catalyzed reactions

Previous solution studies demonstrated that $[CpFe(CO)_2]_2$ have a good catalytic activity for these systems. Our next step was then to find out whether that activity will also be shown in the absence of solvent. The procedure followed is the same as that used for the solventless catalysed reactions between $CpFe(CO)_2I$ and phosphine ligands (4.2.2). The catalyst did not show any effect on the reaction at 40°C but at 60°C, the effect of the catalyst by increasing the rate of the reaction is clearly recognizable. Results are shown in table 5. 3.

Table 5.3. Solventless reactions between $CH_3CpFe(CO)_2I$ and PPh_3 at 60°C in the presence of the catalyst to form $[CH_3CpFe(CO)_2PPh_3]I$

Time (h)	Conversion (%)
0.5	61
1	85
2	90
3	96
4	100

At 70°C in the presence of 10% of $[CpFe(CO)_2]_2$ as a catalyst, the reaction goes to completion before 30 minutes of reaction.

5.3.2. Reactions between $CH_3CpFe(CO)_2I$ and PR_3 ligands.

5.3.2.1 Uncatalyzed reactions

After these preliminary studies with PPh_3, a range of phosphine ligands was studied. Phosphines used are PPh_3, $P(p\text{-}OCH_3C_6H_4)_3$, $P(m\text{-}CH_3C_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$.
DSC studies were conducted on 1: 1 Starting material/ligand mixtures to find out their melting points and results are shown in table 5.4.

Table 5. 4 DSC results for $CH_3CpFe(CO)_2I + PR_3$ mixtures

Starting material	**mp for the pure material (°C)**	**mp for the mixture (°C)**
$CH_3CpFe(CO)_2I$	40	-
PPh_3	80	34
$P(m\text{-}CH_3C_6H_4)_3$	100	36
$P(p\text{-}OCH_3C_6H_4)_3$	131	37
$P(p\text{-}FC_6H_4)_3$	79	33
$P(p\text{-}ClC_6H_4)_3$	99	37

From table 5.4, it is clear that all the mixtures have quite low melting points (< 40°C)
At 70°C in the absence of catalyst, the solventless reactions between $CH_3CpFe(CO)_2I$ and all phosphines studied occurred but the rate of the reaction is different from one ligand to another (table 5.5)

Table 5.5: Reactions of $CH_3CpFe(CO)_2I$ and PR_3 ligands at 70^0C without catalyst

Ligand	**Time (h)**	**Conversion (%)**	
		II	**III**
PPh_3	0.5	39	0
	4	76	0
P(*m*-$CH_3C_6H_4)_3$	0.5	70	0
	4	82	0
P(*p*-$OCH_3C_6H_4)_3$	0.5	60	0
	4	70	0
P(*p*-$FC_6H_4)_3$	0.5	10	0
	4	40	0
P(*p*-$ClC_6H_4)_3$	0.5	0	0
	4	21	0

At 70^0C without catalyst, the order of reactivity between $CH_3CpFe(CO)_2I$ and PR_3 appears as follows:

After 30 minutes:

- Overall conversion : P(*m*-$CH_3C_6H_4)_3$ > PPh_3 > P(*p*-$OCH_3C_6H_4)_3$ > P(*p*-$FC_6H_4)_3$ > P(*p*-$ClC_6H_4)_3$
- Conversion into **II** : the same order is observed since no **III** is formed

Electron withdrawing groups (fluoro and chloro) are significantly less reactive compared to electron donating groups.

The reaction was also carried out at 100^oC in the absence of catalyst. After 15 minutes of the reaction, the ligands shown different reactivity and results are presented in table 5.6.

Table 5.6 Reactions of $CH_3CpFe(CO)_2I$ and PR_3 ligands at 100^0C without catalyst.

Ligand	**Time (min)**	**Conversion (%)**
PPh_3	5	31
	15	61
P(*m*-$CH_3C_6H_4)_3$	5	26
	15	43
P(*p*-$OCH_3C_6H_4)_3$	5	57
	15	75
P(*p*-$FC_6H_4)_3$	5	10
	15	15
P(*p*-$ClC_6H_4)_3$	5	8
	15	12

The order of ligands reactivity is the following: P(*p*-$OCH_3C_6H_4)_3$ > PPh_3 > P(*m*-$CH_3C_6H_4)_3$ > P(*p*-$FC_6H_4)_3$ > P(*p*-$ClC_6H_4)_3$.

5.3.2.2. Catalyzed reactions

The reaction was then carried out in the presence of catalyst at 70°C and the rate was significantly improved (table 5.7).

Table 5.7: Reactions of $CH_3CpFe(CO)_2I$ and PR_3 ligands at 70°C with catalyst.

Ligand	**Time (h)**	**Conversion (%)**	
		II	**III**
PPh_3	0.5	100	0
	4	100	0
P(*m*-$CH_3C_6H_4)_3$	0.5	100	0
	4	100	0
P(*p*-$OCH_3C_6H_4)_3$	0.5	100	0
	4	100	0
P(*p*-$FC_6H_4)_3$	0.5	100	0
	4	100	0
P(*p*-$ClC_6H_4)_3$	0.5	60	0
	4	72	0

When using a catalyst, all ligands give 100% after 30 minutes except $P(p\text{-}ClC_6H_4)_3$.

The solution studies have proposed that these catalyzed reactions go through a radical chain mechanism. A solventless experiment carried out between $CH_3CpFe(CO)_2I$ and PPh_3 in the presence of a stoichiometric amount of $[CpFe(CO)_2]_2$ revealed the presence of $[CpFe(CO)_2PPh_3]I$. Considering the reactants present, this unsubstituted salt product may come only from the 19 electron intermediate $[CpFe(CO)_2PPh_3]^{\cdot}$. However, an electron transfer chain mechanism (ETC) for these systems have been also proposed [7, 8].

Products were isolated by column chromatography built up using silica gel and hexane. Acetone was used to elute the required salt products. Characterization of the pure materials was achieved by IR and NMR spectroscopy (table 5.8) and MS (table 5.9). Melting points were determined by DSC (figure 5. 6).
Attempts to crystallize the salt products were unsuccessful as powders were obtained during the process. The same difficulties was also experienced in other studies [6].

Table 5.8. Spectroscopic results for $CH_3CpFe(CO)_2PR_3]I$ complexes

	^{1}H NMR(ppm)				**^{31}P NMR (ppm)**	**IR(cm^{-1})**
Complex	**Cp**	**$CpCH_3$**	**CH_3**	**OCH_3**		
$[CH_3CpFe(CO)_2PPh_3]I$	5.43; 5.29	2.16	-	-	62.53	2053; 2010
$[CH_3CpFe(CO)_2P(p\text{-}OCH_3C_6H_4)_3]I$	5.42; 5.37	2.17	-	3.89	57.37	2048; 2006
$[CH_3CpFe(CO)_2P(m\text{-}CH_3C_6H_4)_3]I$	5.38; 5.22	2.18	2.40	-	61.75	2052; 2008
$[CH_3CpFe(CO)_2P(p\text{-}ClC_6H_4)_3]I$	5.64; 5.58	2.27	-	-	63.60	2054; 2012
$[CH_3CpFe(CO)_2P(p\text{-}FC_6H_4)_3]I$	5.59; 5.47	2.20	-	-	62.56	2054; 2010

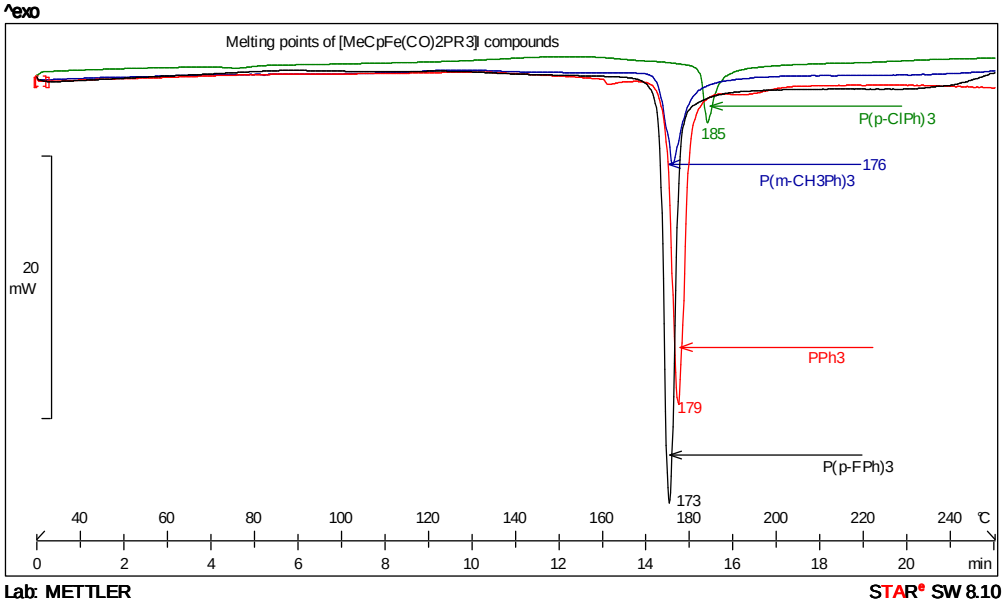
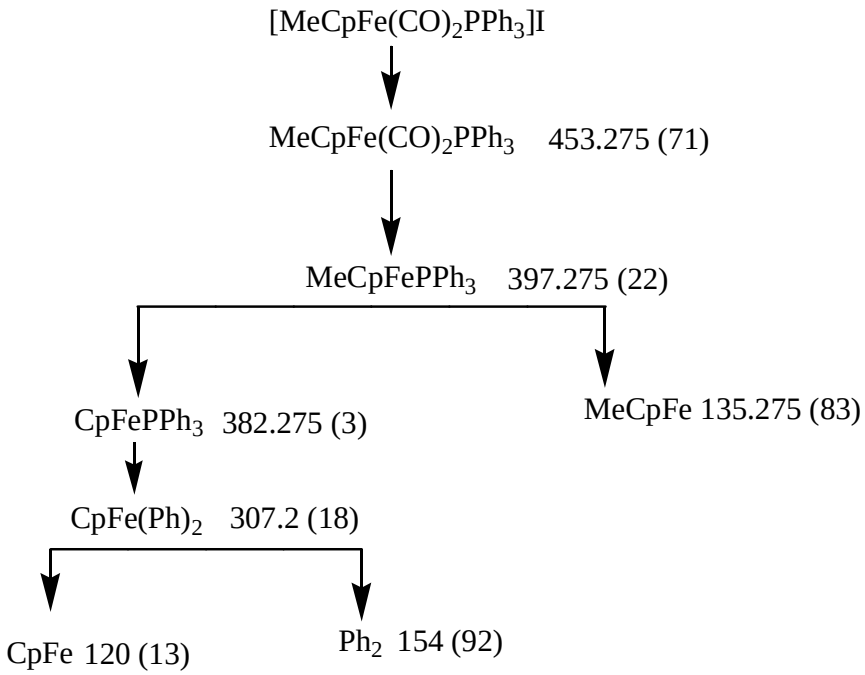


Figure 5.5. DSC profiles for [$CH_3CpFe(CO)_2PR_3$]I compounds

Mass spectrometry results

As it was observed in chapter four with unsubstituted salt compounds, iodine is the first particle to be removed from [$CH_3CpFe(CO)_2PR_3$]I complexes, followed by the loss of the two CO ligands. The rest of fragmentation depends on the particular ligand present in the complex. As an example, the fragmentation patterns for [$CH_3CpFe(CO)_2PPh_3]_2$ are presented in figure 5.7.



Scheme 5.2 Fragmentation patterns for $[CH_3CpFe(CO)_2PPh_3]I$

The mass spectrometry results for other salt products are presented in table 5.9.

Table 5.9. Mass spectrometry data for $[CH_3CpFe(CO)_2PR_3]I$

Ligand	**R-I**	**R-I-2CO**	**R-I-2CO-PR_3**
PPh_3	453.275 (71)	397.275 (22)	136.0 (83)
P(*p*-$OCH_3C_6H_4)_3$	543.1 (36)	487.1 (19)	136.0 (90)
P(*m*-$CH_3C_6H_4)_3$	495.382 (90)	439.382 (54)	136.0 (38)
P(*p*-$FC_6H_4)_3$	507.272 (57)	451.2 (28)	136.0 (90)
P(*p*-$ClC_6H_4)_3$	556.637 (35)	500.637 (20)	136.0 (90)

R = $[CH_3CpFe(CO)_2PR_3]I$

Contrarily to the salt compounds, in the non-salt compounds, it has been observed that the CO molecule leaves the complex before the I atom.

Some issues can be discussed from the solventless reactions between $CH_3CpFe(CO)_2I$ and PR_3 ligands.

- At 40°C, all the starting material/ligand mixtures are in melt phase but no reaction occurred even in the presence of the catalyst; by increasing the temperature to 60°C, 70°C, the reaction occurred and the higher the temperature the higher the conversion into product. From these results one could say that the melt state in not the only condition for the reaction to occur but also some factors are involved such as energy required for the reaction.
- The fact that no decarbonylated product is formed when $CH_3CpFe(CO)_2I$ reacts with PR_3 is consistent with results obtained previously [5, 6]. As stipulated in Gmelin [6], the combination effect of R donating group attached to Cp and L, a basic ligand, results in the strengthening of Fe-CO bond allowing Fe-I bond to break. Therefore, the product to be formed will be mainly a salt compound. Thus for $CpFe(CO)_2I$**,** donating ligands should be favoured to salt formation and withdrawing group to decarbonylated product formation. This has been observed throughout our results.
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5.3.3 Effect of the Me substituent on the Cp ring

The comparison between the reactivity of $CpFe(CO)_2I$ and $CH_3CpFe(CO)_2I$ towards the same ligands can be made: The CH_3 substituent affects somehow the reactivity of the complex with the solid phosphine used. Table 5.10 shows a summary of the results of both substrates at 70°C in the presence or absence of the catalyst with regard to the salt product formation.

Table 5. 10. Comparison between $CpFe(CO)_2I$ and $CH_3CpFe(CO)_2I$ reactivity towards solid phosphine ligands at 70°C with regard to salt product formation.

Ligand	Time (h)	$CpFe(CO)_2I$		$CH_3CpFe(CO)_2I$	
		Uncatalyzed (%)	Catalysed (%)	Uncatalyzed (%)	Catalysed (%)
PPh_3	0.5	52	100	39	100
	4	90	100	76	100
P(*p*-$OCH_3C_6H_4)_3$	0.5	37	55	60	100
	4	59	78	70	100
P(*m*-$CH_3C_6H_4)_3$	0.5	0	69	70	100
	4	58	86	82	100
P(*p*-$FC_6H_4)_3$	0.5	40	90	10	100
	4	64	75	40	100
P(*p*-$ClC_6H_4)_3$	0.5	0	28	0	60
	4	0	43	21	72

From these data, some ligands are favourable to $CpFe(CO)_2I$ than $CH_3CpFe(CO)_2I$, others favourable for $CH_3CpFe(CO)_2I$ than $CpFe(CO)_2I$. Considering the first 30 minutes of the reaction in the absence of catalyst we find that PPh_3 and P(p-$FC_6H_4)_3$ are better ligands in the case of $CpFe(CO)_2I$ than $CH_3CpFe(CO)_2I$ while P(*p*-$OCH_3C_6H_4)_3$ and P(*m*-$CH_3Ph)_3$ are reacting better towards $CH_3CpFe(CO)_2I$ than $CpFe(CO)_2I$. An anticipated conclusion would say that the Me substituent on Cp ring favours the reaction with electron donating ligands.

The reactions at 100°C in the absence of the catalyst show clearly that $CpFe(CO)_2I$ is more reactive than $CH_3CpFe(CO)_2I$ in respect with the studied ligands.

After only 15 minutes of the reaction $CpFe(CO)_2I$ gave more than 90% for all the ligands while $CH_3CpFe(CO)_2I$ gave a high conversion of 75%.

Some reactions have been conducted to explore the competitivity of $CpFe(CO)_2I$ and $CH_3CpFe(CO)_2I$ towards one ligand. In this regard, a 1: 1 mole mixture of $CH_3CpFe(CO)_2I$ and $CpFe(CO)_2I$ was prepared. To this mixture, PPh_3 has been added in the ratio of 1: 5 compared to the previous mixture. The final mixture was heated at 70^oC in the absence of catalyst and followed within 15 minutes. Results are shown in table 5. 11.

Table 5. 11. Competition reactions between $CpFe(CO)_2I$ and $CH_3CpFe(CO)_2I$ towards PPh_3 in the absence of catalyst at 70^oC.

Time (min.)	**$CpFe(CO)_2I$**			**$CH_3CpFe(CO)_2I$**		
	Salt (%)	Non salt (%)	Overall	Salt (%)	Non salt (%)	Overall
5	17	10	27	0	0	0
10	20	10	30	0	0	0
15	23	9	32	0	0	0

From these data, it is clear that in the presence of PPh_3, $CpFe(CO)_2I$ is more competitive, more reacting than $CH_3CpFe(CO)_2I$ in the absence of catalyst.

The catalyst was then added to the mixture and results are condensed in table 5.12.

Table 5. 12. Competition reactions between $CpFe(CO)_2I$ and $CH_3CpFe(CO)_2I$ towards PPh_3 in the presence of catalyst at 70^oC.

Time (min.)	**$CpFe(CO)_2I$**			**$CH_3CpFe(CO)_2I$**		
	Salt (%)	Non salt (%)	Overall	Salt (%)	Non salt (%)	Overall
5	84	6	90	86	0	86
10	81	9	90	100	0	100
15	76	16	92	100	0	100

In the presence of the catalyst, $CH_3CpFe(CO)_2I$ becomes much more active and it is even slightly more reactive than $CpFe(CO)_2I$.

5.4. CONCLUSION

The solventless reactions between $CH_3CpFe(CO)_2I$ and a range of solid phosphine ligands: 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 studied at different temperatures (40^oC-100^oC). Only salt products were obtained from these reactions due to the presence of an electron donor group Me on the Cp ring which strengthen the Fe-CO bond to the detriment of Fe-I bond. The complex, $[CpFe(CO)_2]_2$, was found to be a good catalyst for these systems. Generally, $CH_3CpFe(CO)_2I$ was found to be more reactive than $CpFe(CO)_2I$ towards all the phosphine ligands studied with regard to the catalyzed salt products formation.

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