

# Solvent-free Substitution Reactions of Solid Phosphines with $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$ ( $\text{R} = \text{H, Me}$ ) Complexes

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*Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65<sup>th</sup> birthday – friend and colleague over many decades*

Reactions of  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$  ( $\text{R} = \text{H, Me}$ ) complexes with phosphine ligands  $\text{PR}'_3$  ( $\text{R}' = \text{Ph, } m\text{-Tol, } p\text{-C}_6\text{H}_4\text{OMe, } p\text{-C}_6\text{H}_4\text{Cl, } p\text{-C}_6\text{H}_4\text{F}$ ) have been performed under solvent-free conditions in the melt phase and generally yielded the ionic products  $[(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{PR}'_3]\text{I}$  rather than the CO substituted products  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})(\text{PR}'_3)\text{I}$ . The complexes have been characterised by IR, NMR and MS techniques. By contrast, the same reactions studied in benzene solution have yielded mainly the CO substitution products. Factors that affect the solvent-free reaction include variation in  $\text{R}$  and  $\text{R}'$ , reaction temperature and the addition of  $[\text{CpFe}(\text{CO})_2]_2$  as a catalyst. The mechanism of the reaction for the formation of the ionic complex is proposed to go *via* a 19 electron intermediate. This is in contrast to the reaction in benzene that occurs *via* a 17 electron intermediate, clearly indicating the role of the melt phase in the reaction.

**Key words:** Melt Phase, Solvent-free Reaction, Iron Cyclopentadienyl Complex, Metal Dimer Catalyst, Green Chemistry

## Introduction

Over the last 2 decades an increased awareness of environmental issues associated with chemical synthesis has led to the recognition of ‘green chemistry’ as an active field of chemical research [1–2]. The simplest approach to environmentally benign chemical synthesis is to perform reactions in the absence of solvents. The solvent-free technique has been utilised in the synthesis of organic compounds [3], the processing of materials [4] and more recently to a study of organometallic reactions and transformations [5]. From the reported studies several advantages of solvent-free techniques have been documented, notably the possibility of synthesising novel products not readily produced by solution procedures [6].

To further evaluate the possibilities inherent in the solventless approach in syntheses we have commenced an investigation of this procedure by studying well documented reactions. For example, the substitution reaction of  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{X}$  complexes ( $\text{R} = \text{organic substituent, } \text{X} = \text{halide}$ ) with electron donating ligands (isonitriles, phosphites and phosphines) is

well-established in the literature [7–8]. The reaction has been studied in non-coordinating solvents and in the absence and presence of catalysts (transition metal oxides and cyclopentadienyl metal dimers) [9–10]. The reactions produced predominantly the neutral CO substituted products  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})(\text{PR}'_3)\text{I}$  under the reaction conditions used [11–13].

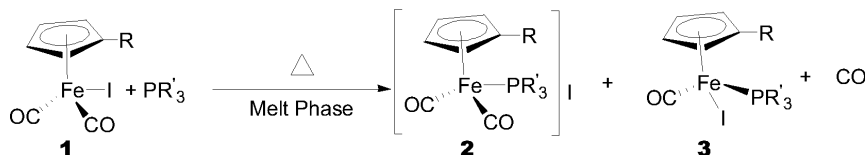
In the present study we report that in contrast to the above solution studies, the reaction between  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$  ( $\text{R} = \text{H, Me}$ ) and a series of solid phosphine ligands ( $\text{PR}'_3$ ,  $\text{R}' = \text{Ph, } m\text{-Tol, } p\text{-C}_6\text{H}_4\text{OMe, } p\text{-C}_6\text{H}_4\text{Cl, } p\text{-C}_6\text{H}_4\text{F}$ ) in the absence of solvents generate preferentially the ionic products  $[(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{PR}'_3]\text{I}$ , but also the neutral complexes  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})(\text{PR}'_3)\text{I}$ , by way of a *melt reaction*.

## Results and Discussion

### *Synthesis and characterisation*

The solvent-free reaction between  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$  and solid phosphine ligands  $\text{PR}'_3$ , is schematically represented in Scheme 1.

| Ligand $\text{PR}'_3$<br>$\text{R}'$        | Time<br>(min) | Products of reaction with metal complex $\text{RCpFe}(\text{CO})_2\text{I}$ (%)                        |                       |                         |                       |                         |                       |
|---|---------------|--|-----------------------|-------------------------|-----------------------|-------------------------|-----------------------|
|   |               | $2 = [\text{RCpFe}(\text{CO})_2\text{PR}'_3]\text{I}; 3 = \text{RCpFe}(\text{CO})\text{PR}'_3\text{I}$ |                       |                         |                       |                         |                       |
|   |               | $\text{R} = \text{H}$  |                       | $\text{R} = \text{Me}$  |                       |                         |                       |
|   |               | Uncatalysed<br><b>2</b>  | Catalysed<br><b>3</b> | Uncatalysed<br><b>2</b> | Catalysed<br><b>3</b> | Uncatalysed<br><b>2</b> | Catalysed<br><b>3</b> |
| Ph  | 5             | 70   | 24                    | 81                      | 19                    | 31                      | 0                     |
|   | 15            | 72   | 28                    | 76                      | 24                    | 61                      | 0                     |
| <i>m</i> -Tol                               | 5             | 39   | 57                    | 61                      | 32                    | 26                      | 0                     |
|   | 15            | 40   | 57                    | 20                      | 80                    | 43                      | 0                     |
| <i>p</i> -C <sub>6</sub> H <sub>4</sub> OMe | 5             | 80   | 20                    | 76                      | 16                    | 57                      | 0                     |
|   | 15            | 85   | 15                    | 71                      | 29                    | 75                      | 0                     |
| <i>p</i> -C <sub>6</sub> H <sub>4</sub> F   | 5             | 36   | 53                    | 0                       | 87                    | 10                      | 0                     |
|   | 15            | 0  | 95                    | 0                       | 98                    | 15                      | 0                     |
| <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl  | 5             | 0  | 76                    | 0                       | 84                    | 8                       | 0                     |
|   | 15            | 0  | 88                    | 0                       | 93                    | 12                      | 0                     |

Table 1. Melt reaction of  $\text{RCpFe}(\text{CO})_2\text{I} + \text{PR}'_3$  at 100 °C.Scheme 1. Solvent-free melt phase reaction between  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$  ( $\text{R} = \text{H, Me}$ ) and  $\text{PR}'_3$  ( $\text{R}' = \text{Ph, } m\text{-Tol, } p\text{-C}_6\text{H}_4\text{OMe, } p\text{-C}_6\text{H}_4\text{Cl, } p\text{-C}_6\text{H}_4\text{F}$ ).

The reaction was carried out with a 1 : 5 complex to ligand mole ratio at various temperatures. The reactions were monitored by  $^1\text{H}$  NMR spectroscopy as described in the experimental section and at the end of the reaction the reaction mixture was cooled, and the products separated and isolated. Analysis of the reaction mixtures revealed the formation of typically two products,  $[(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2(\text{PR}'_3)]\text{I}$  and  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})(\text{PR}'_3)\text{I}$ .

The products were characterised by FTIR and NMR spectroscopy and mass spectrometry. In particular:

- The  $^1\text{H}$  NMR spectra are consistent with the presence of the Cp and  $\text{PR}'_3$  ligands.
- The  $^{31}\text{P}$  NMR spectra of all the complexes confirmed the presence of a bound phosphine ligand by a singlet peak. The NMR peaks for the ionic products **2** range from 57.4 ppm for  $\text{R}' = \text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3$  to 61.8 ppm for  $\text{PPh}_3$ , while the peaks for the neutral products **3** are observed slightly downfield ( $\delta = 62.6$  to 68.3 ppm).
- The IR spectra exhibit two well separated absorption peaks ( $\Delta\nu$  40  $\text{cm}^{-1}$ ) for the two CO ligands at  $> 2000 \text{ cm}^{-1}$  for all the salt complexes, and one CO absorption at *ca.* 1950  $\text{cm}^{-1}$  for the neutral complexes.
- The mass spectra of **2** typically exhibit a loss of iodine from the parent ions as the principal peak.

Reactions were initially carried out at 100 °C and at this temperature a melt could be clearly observed in

all the reactions. The amount of the products formed (**2** and **3**) was routinely deduced by integration of  $^1\text{H}$  NMR peaks (in solution) on analysis of the reaction mixture after various time intervals. Data for the solvent-free reaction of  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$  with the various phosphine ligands  $\text{PR}'_3$  at 100 °C is shown in Table 1. The results which are discussed in detail below clearly show that (i) all reactions with  $\text{R} = \text{H}$  go to near completion within 15 min, (ii) the electron withdrawing phosphines give neutral complexes while the other ligands give predominantly ionic products for  $\text{R} = \text{H}$ , and (iii) the electron donating ligands give a more rapid reaction than the electron withdrawing ones (compare data in Table 1).

The effect of the electron donating Cp-methyl substituent on the reaction was studied in the melt at 100 °C. The result is presented in Table 1 and a comparison of the data in the corresponding columns for the  $\text{R} = \text{H}$  and  $\text{R} = \text{Me}$  complexes indicate that (i) the un-catalysed reaction is slower for  $\text{R} = \text{Me}$  and (ii) reaction product ratios for **2** and **3** are different. The increased electron density on the Fe atom due to the presence of a Me group on the Cp ring favours iodine substitution by the phosphine ligands.

#### Ligand effects on the solvent-free CO substitution reaction

For the two metal complexes  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$  ( $\text{R} = \text{H, Me}$ ), the reactions with the solid phosphines

| Ligand $\text{PR}'_3$<br>$\text{R}'$        | Time<br>(min) | Products of reaction with metal complex $\text{RCpFe}(\text{CO})_2\text{I}$ (%)                        |    |           |    |             |   |           |   |
|---|---------------|--|----|-----------|----|-------------|---|-----------|---|
|   |               | $2 = [\text{RCpFe}(\text{CO})_2\text{PR}'_3]\text{I}; 3 = \text{RCpFe}(\text{CO})\text{PR}'_3\text{I}$ |    |           |    |             |   |           |   |
|   |               | 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. Melt reaction of  $\text{RCpFe}(\text{CO})_2\text{I} + \text{PR}'_3$  at 70 °C.

| Ligand $\text{PR}'_3$<br>$\text{R}'$        | Time<br>(min) | Products of reaction with metal complex $\text{RCpFe}(\text{CO})_2\text{I}$ (%)                        |    |           |    |             |   |           |   |
|---|---------------|--|----|-----------|----|-------------|---|-----------|---|
|   |               | $2 = [\text{RCpFe}(\text{CO})_2\text{PR}'_3]\text{I}; 3 = \text{RCpFe}(\text{CO})\text{PR}'_3\text{I}$ |    |           |    |             |   |           |   |
|   |               | R = H  |    |           |    | R = Me      |   |           |   |
|   |               | Uncatalysed  |    | Catalysed |    | Uncatalysed |   | Catalysed |   |
|   |               | 2  | 3  | 2         | 3  | 2           | 3 | 2         | 3 |
| Ph  | 0.5           | 0  | 7  | 46        | 15 | 6           | 0 | 61        | 0 |
|   | 4             | 75   | 6  | 77        | 11 | 38          | 0 | 100       | 0 |
| <i>m</i> -Tol                               | 0.5           | 0  | 6  | 8         | 4  | 10          | 0 | 63        | 0 |
|   | 4             | 0  | 14 | 58        | 6  | 17          | 0 | 78        | 0 |
| <i>p</i> -C <sub>6</sub> H <sub>4</sub> OMe | 0.5           | 0  | 5  | 0         | 3  | 20          | 0 | 46        | 0 |
|   | 4             | 0  | 12 | 17        | 3  | 38          | 0 | 71        | 0 |
| <i>p</i> -C <sub>6</sub> H <sub>4</sub> F   | 0.5           | 0  | 7  | 55        | 7  | 0           | 0 | 82        | 0 |
|   | 4             | 0  | 14 | 83        | 7  | 0           | 0 | 100       | 0 |
| <i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl  | 0.5           | 0  | 6  | 0         | 8  | 0           | 0 | 46        | 0 |
|   | 4             | 0  | 15 | 13        | 9  | 0           | 0 | 61        | 0 |

Table 3. Melt reaction of  $\text{RCpFe}(\text{CO})_2\text{I} + \text{PR}'_3$  at 60 °C.

were then performed at lower temperatures (60 and 70 °C) and the data (Tables 2 and 3, respectively) permitted a better separation of the ligand effects on the reaction.

By choosing substituted phosphines (same Tolman cone angle = 145° [14]), the steric influence of the ligands in the reaction is kept constant. Hence, electronic factors will account for the changes in reactivity of the metal complexes with the various phosphine ligands [except  $\text{P}(m\text{-Tol})_3$ ]. Since ionic product formation followed a trend in reactivity  $\text{R}'$ :  $\text{Ph} \gg m\text{-Tol} \approx p\text{-C}_6\text{H}_4\text{OMe} > p\text{-C}_6\text{H}_4\text{F} \gg p\text{-C}_6\text{H}_4\text{Cl}$  it is clear that the donor ability of the ligand differentiates between CO or I replacement in the reaction – the better the donor ability the more the salt formed.

For the R = Me complex, the effect of the ligand  $\text{PR}'_3$  on the reaction is clear. Electron donating phosphines give more rapid reaction than electron withdrawing ones and the sequence in terms of the reactivity of the  $\text{PR}'_3$  ligand after 15 min is thus  $\text{R}'$ :  $p\text{-C}_6\text{H}_4\text{OMe} > \text{Ph} > m\text{-Tol} \gg p\text{-C}_6\text{H}_4\text{F} \approx p\text{-C}_6\text{H}_4\text{Cl}$ .

#### Effect of catalyst $[\text{CpFe}(\text{CO})_2]_2$ addition

Earlier studies in our group have shown that various organometallic complexes, transition metal carbonyl dimers and oxides, can be used as catalysts for CO substitution reactions of metal carbonyl complexes in solution [10, 13]. The study of the effect of the catalyst  $[\text{CpFe}(\text{CO})_2]_2$  on the solvent free reactions of  $(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$  was thus undertaken for a melt reaction. The results of the study at 60, 70 and 100 °C, using various ligands  $\text{PR}'_3$ , are presented in Tables 1 to 3, respectively. A comparison of the data in each table for the catalysed and un-catalysed reactions under similar conditions shows that the catalyst  $[\text{CpFe}(\text{CO})_2]_2$  increases the rate of the reaction and affects the product ratios found in the reactions studied.

#### Melt-phase reaction

In order to understand the effect of the metal to ligand ratio on the melt reaction a study was conducted of the reaction of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$  with  $\text{PPh}_3$  at 70 °C in which the relative concentration of Fe : P was varied from 1 : 1 to 1 : 10. The melting points of both reagents

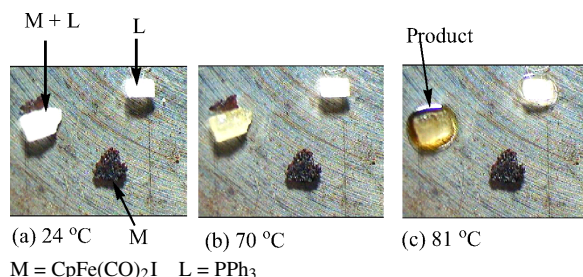


Fig. 1. Solvent-free reaction of  $\text{CpFe}(\text{CO})_2\text{I}$  and  $\text{PPh}_3$ . Formation of a eutectic melt where the two reactants are in contact is noticeable.

( $\text{PPh}_3 = 78\text{ }^\circ\text{C}$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I} = 117\text{ }^\circ\text{C}$ ) are *higher* than the reaction temperature. In every case however, a melt was observed at  $70\text{ }^\circ\text{C}$  either in the reaction tubes or under an optical microscope (Fig. 1). This was also consistent with DSC data which indicated a melt had formed at  $70\text{ }^\circ\text{C}$ . The following conclusions may be drawn from the study:

- (i) The rate of the solvent-free reaction shows a small dependence on the Fe : P ratio. The initial rate of reaction is faster at higher ligand concentrations.
- (ii) After 4 h reaction, the total combined reactant conversion to products (**2** and **3**) was similar indicating that the excess ligand merely serves as 'solvent' for Fe : P contact that eventually drives the reaction to completion.
- (iii) A small amount of **3** was detected at the beginning of the reaction. It was independently established that its presence was due to the grinding/mixing of the reactants in the mortar.
- (iv) The amount of **3** formed generally did not grow with time and this indicates that little conversion from **2** to **3** occurs in the melt reaction. This however does not hold for the catalysed reaction (see data for  $\text{R}' = p\text{-C}_6\text{H}_4\text{Cl}$ ,  $p\text{-C}_6\text{H}_4\text{F}$  in Table 2).

Indeed remarkable effects in terms of the product ratio (**2** and **3**) are observed. For example, reaction of  $\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$  with  $\text{CpFe}(\text{CO})_2\text{I}$  ( $60\text{ }^\circ\text{C}$ , 5 : 1 ratio) yields exclusively the neutral product **3** in the absence of  $[\text{CpFe}(\text{CO})_2]_2$  as a catalyst. In the presence of the catalyst however, the ionic product **2** is mainly formed (90 %; 30 min). After an extended reaction time at  $70\text{ }^\circ\text{C}$  some of the **2** is converted to **3** *via* the loss of one CO molecule. The conversion of **2**  $\rightarrow$  **3** has previously been shown to occur in the presence of the decarbonylating agent  $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$  [15].

In the presence of  $[\text{CpFe}(\text{CO})_2]_2$  the observed preference for the ionic product **2** in the melt can readily be explained by a radical reaction mechanism (see below). This was further confirmed by conducting a set of reactions with  $\text{MeCpFe}(\text{CO})_2\text{I}$  and the various phosphines under similar conditions as above, with and without the catalyst  $[\text{CpFe}(\text{CO})_2]_2$  (Table 2). The substituted complex  $\text{MeCpFe}(\text{CO})_2\text{I}$  has a lower melting point and forms a eutectic melt with the phosphine ligands at a lower temperature than  $\text{CpFe}(\text{CO})_2\text{I}$ . A comparison of the data in Table 2 reveals that the reactions with  $\text{MeCpFe}(\text{CO})_2\text{I}$  now occur faster than with  $\text{CpFe}(\text{CO})_2\text{I}$  clearly indicating that the ease of formation of a melt phase is responsible for the inverted reaction sequence,  $\text{MeCpFe}(\text{CO})_2\text{I} > \text{CpFe}(\text{CO})_2\text{I}$ .

As described above, the reactions with the different phosphines that occur at  $100\text{ }^\circ\text{C}$  (Table 1) follow the expected order of reactivity that relates to the electron donating ability of the phosphines. At lower temperatures, this sequence is modified, *e. g.* for the  $\text{CpFe}(\text{CO})_2\text{I}$  complex at  $70\text{ }^\circ\text{C}$  (Table 2), the order of  $\text{PR}'_3$ ,  $\text{R}' = \text{Ph} > p\text{-C}_6\text{H}_4\text{F} > p\text{-C}_6\text{H}_4\text{OMe} > m\text{-Tol} > p\text{-C}_6\text{H}_4\text{Cl}$ . A similar inversion in the order of reactivity is observed for the above reaction when conducted in the presence of  $[\text{CpFe}(\text{CO})_2]_2$  as a catalyst. This effect is due to the presence or absence of a melt phase. At  $70\text{ }^\circ\text{C}$  some of the reactants combine to form a eutectic melt; while for others the temperature is still below their threshold for the formation of a eutectic melt. Thus, the rate of the reaction is clearly determined by diffusion of the reactants and this in fact does allow for rate information *not* related to the electron donating/withdrawing capability of the various ligands.

#### Solution studies in benzene

The required amounts of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$  (0.04 mmol) and  $\text{PPh}_3$  or  $\text{P}(p\text{-C}_6\text{H}_4\text{F})_3$  (0.20 mmol) and a catalytic amount of  $[\text{CpFe}(\text{CO})_2]_2$  were placed in a Schlenk flask and dissolved in 15 mL of benzene. The flask was placed in an oil bath preset at  $70\text{ }^\circ\text{C}$  and heated for 60 min. The reaction was stopped and all volatiles were removed by rotary evaporation. The resulting solid product was analysed by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$ . A comparison of the solvent-free technique and the reactions in benzene as a solvent under similar conditions ( $70\text{ }^\circ\text{C}$ ; Fe : P = 1 : 5) is presented in Table 4. From the data the following observations are noted:

Table 4. A comparative study of the reaction ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)-Fe(CO)<sub>2</sub>I + PR'<sub>3</sub> in benzene as a solvent and a solvent-free reaction at 70 °C; Fe : P = 1 : 5.

| Ligand PR' <sub>3</sub><br>R'             | Reaction time<br>(min) | Relative conversion to products<br>under similar catalysed conditions |                     |
|---|------------------------|---|---------------------|
|   |                        | benzene (15 mL)   | solvent-free        |
| <i>p</i> -C <sub>6</sub> H <sub>4</sub> F | 30                     | 28 % (3)  | 90 % (2)<br>3 % (3) |
| Ph  | 60                     | 42% (3)   | 99% (2)             |

- (i) Reaction in benzene gives CO substituted compounds as the main products while the solvent-free method results in ligand inserted products *via* iodide substitution.
- (ii) As expected, the higher relative concentration of reactants in the solvent-free procedure gives a more rapid overall conversion to products.

#### Reaction mechanism

The reaction between ( $\eta^5$ -RC<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>I and PR'<sub>3</sub> was initially believed to be a dissociative process entailing loss of CO followed by addition of PR'<sub>3</sub> [9]. However, later studies have shown that the reaction is more complex, and that in the presence of a catalyst, a free radical process can be used to explain the data [13]. Importantly, the earlier data were obtained in the presence of benzene and the products detected were mainly the CO substituted products. The mechanism proposed, using [CpFe(CO)<sub>2</sub>]<sub>2</sub> as catalyst, was consistent with a chain carrier involving a 17 electron intermediate [10].

Formation of the substitution product by way of a 17 electron intermediate can occur as shown in Scheme 2.

However, the above mechanism does *not* explain the formation of salt products as observed in the melt phase reaction. The formation of salt products in the reaction can be explained by a modification of step (ii) above in which addition of PR'<sub>3</sub> takes place prior to CO loss. Thus the modified reaction entails formation of a 19 electron intermediate either *via* an electron transfer chain catalysed reaction [16] or as shown in Scheme 3.

The data rationalise the following observations:

- (i) A high concentration of PR'<sub>3</sub>, as found in the melt phase, favours the reaction.
- (ii) Electron donating ligands favour the formation of ionic products, as observed.

Further evidence in support of the mechanism was obtained by carrying out a “competing” reaction in which the metal complex and the usual catalyst are both in stoichiometric quantities. The reac-

- i [CpFe(CO)<sub>2</sub>]<sub>2</sub> ↔ 2 [CpFe(CO)<sub>2</sub>]<sub>·</sub>  
 ii [CpFe(CO)<sub>2</sub>]<sub>·</sub> + PR'<sub>3</sub> → [CpFe(CO)PR'<sub>3</sub>]<sub>·</sub> + CO  
 iii [CpFe(CO)PR'<sub>3</sub>]<sub>·</sub> + CpFe(CO)<sub>2</sub>I → CpFe(CO)(PR'<sub>3</sub>)I (3)  
 + [CpFe(CO)<sub>2</sub>]<sub>·</sub>

*etc.*

Scheme 2. 17 Electron radical mechanism for the formation of the substitution product 3.

- i [CpFe(CO)<sub>2</sub>]<sub>2</sub> ↔ 2 [CpFe(CO)<sub>2</sub>]<sub>·</sub>  
 ii [CpFe(CO)<sub>2</sub>]<sub>·</sub> + PR'<sub>3</sub> → [CpFe(CO)<sub>2</sub>PR'<sub>3</sub>]<sub>·</sub>  
 iii [CpFe(CO)<sub>2</sub>PR'<sub>3</sub>]<sub>·</sub> + CpFe(CO)<sub>2</sub>I → [CpFe(CO)<sub>2</sub>(PR'<sub>3</sub>)I] (3)  
 + [CpFe(CO)<sub>2</sub>]<sub>·</sub>

*etc.*

Scheme 3. 19 Electron radical mechanism for the formation of the ionic product 2.

tion between ( $\eta^5$ -MeC<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>I with PPh<sub>3</sub> was carried out at 70 °C for 10 min in the presence of a stoichiometric quantity of [CpFe(CO)<sub>2</sub>]<sub>2</sub>. At the end of the reaction the products were analysed by solution NMR spectroscopy. The expected salt product [( $\eta^5$ -MeC<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>(PPh<sub>3</sub>)]I was formed *as well as* a significant amount (15 %) of [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>(PPh<sub>3</sub>)]I. This is expected as this salt would form in step iii (Scheme 3).

#### Conclusions

The solvent-free reactions between ( $\eta^5$ -RC<sub>5</sub>H<sub>4</sub>)Fe(CO)<sub>2</sub>I (R = H, Me) with a range of phosphine ligands PR'<sub>3</sub> (R' = Ph, *m*-Tol, *p*-C<sub>6</sub>H<sub>4</sub>OMe, *p*-C<sub>6</sub>H<sub>4</sub>Cl, *p*-C<sub>6</sub>H<sub>4</sub>F) has been studied. The reaction has been conducted at various temperatures (60–100 °C) and was found to give the same two products at all the temperatures studied. The methyl substituent on the cyclopentadienyl moiety has the effect of preferentially increasing the rate of formation of the ionic product. Electron donating phosphines exhibit higher reactivity as compared to electron withdrawing ones.

The catalyst [CpFe(CO)<sub>2</sub>]<sub>2</sub> had an impact on the reaction by enhancing the reaction rate, and in general the solvent-free methodology has yielded higher conversions to the salt product as compared to similar reactions in solvents. A mechanism entailing a 19 electron intermediate is consistent with the product distribution obtained.

This represents one of the few studies in which the melt phase has been shown to generate data different from those found in the solution phase. We have no doubt that other examples exist and current efforts are underway to extend the melt studies to other well documented solution reactions.

## Experimental Section

Solution IR spectra were recorded in dichloromethane on a Bruker Vector 27 FTIR spectrometer.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded in deuterated chloroform on a Bruker AC 300 spectrometer at 300 and 121.5 MHz, respectively. Melting points were determined on a Mettler Toledo DSC822e device. The positive ion mode fast atom bombardment mass spectra were recorded on a Micromass VG70SEQ instrument at a resolution of 1000.

$[\text{CpFe}(\text{CO})_2]_2$ ,  $[(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2]_2$  and all the phosphines were used as supplied (Strem Chemicals). The starting materials  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$  [11] and  $(\eta^5\text{-MeC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{I}$  [17] were prepared by the adaptation of published procedures.

### Solvent-free reactions monitored by $^1\text{H}$ NMR spectroscopy

The catalysed and un-catalysed thermally initiated reactions were carried out using a similar method for all the ligands and starting metal complexes employed. Initial exploratory tests were conducted in NMR tubes to establish the optimum conditions for the reactions.

A typical example, the reaction between  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$  and  $\text{PPh}_3$  is described. The required amounts of  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$  (0.04 mmol) and  $\text{PPh}_3$  (0.20 mmol) were placed in an agate mortar and gently ground to a fine homogeneous mixture using a pestle. This mixture was initially checked for mechanically induced reaction, and minimal product formation was recorded. The mixture (5–10 mg) was transferred into nitrogen-flushed NMR tubes. The tubes were then placed in a pre-heated oil bath set at a known temperature and after a predetermined time, a tube was removed from the bath and chilled in ice.  $\text{CDCl}_3$  was added and NMR analyses performed *in solution*. For the catalysed reaction  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  (0.004 mmol) was added as a catalyst to the mixture prior to grinding.

### Macroscopic synthesis of $[(\eta^5\text{-RC}_5\text{H}_4)\text{Fe}(\text{CO})_2\text{L}]\text{I}$

A typical example is described. The ionic compounds were synthesised following the procedure described above, but typically using 0.1 mol of Fe complex and 0.5 mol of ligand. Both catalysed and un-catalysed reactions were conducted at 70 °C for 4 h in a 50 mL round bottom flask. The purified compounds were isolated in yields of 70–90 % from a silica gel column made up in hexane. Hexane was used to first elute the excess ligand, then benzene was used to elute the non-salt fraction **3**, and finally acetone eluted the salt product **2**. The compounds were characterised by NMR and FTIR spectroscopy and mass spectrometry.

The  $\text{PPh}_3$  based products  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{PPh}_3]\text{I}$  **2a** [13] and  $[\text{MeC}_5\text{H}_4\text{Fe}(\text{CO})_2\text{PPh}_3]\text{I}$  **2b** [18] have previously been reported.

*Physical and spectroscopic data of the new salt products:*  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{P}(m\text{-Tol})_3]\text{I}$ , **2c**. M. p. 168 °C. – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2056, 2014 \text{ cm}^{-1}$ . –  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 5.47$  (s, 5H,  $\text{C}_5\text{H}_5$ ), 2.40 (s, 3H, OMe). –  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 61.21$ . – MS (FAB):  $m/z$  (%) = 529.2 (99)  $[\text{M-I}]^+$ .

$[\text{MeC}_5\text{H}_4\text{Fe}(\text{CO})_2\text{P}(m\text{-Tol})_3]\text{I}$ , **2d**. M. p. 176 °C. – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2052, 2008 \text{ cm}^{-1}$ . –  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 5.38$  (t, 2H, CpH), 5.22 (t, 2H, CpH), 2.40 (s, 3H, PhMe), 2.18 (s, 3H, CpMe). –  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 61.75$ . – MS (FAB):  $m/z$  (%) = 543.1 (41)  $[\text{M-I}]^+$ .

$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3]\text{I}$ , **2e**. M. p. 171 °C. – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2054, 2012 \text{ cm}^{-1}$ . –  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 5.44$  (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.88 (s, 3H, OMe). –  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 56.96$ . – MS (FAB):  $m/z$  (%) = 481.1 (100)  $[\text{M-I}]^+$ .

$[\text{MeC}_5\text{H}_4\text{Fe}(\text{CO})_2\text{P}(p\text{-C}_6\text{H}_4\text{OMe})_3]\text{I}$ , **2f**. M. p. 184 °C. – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2048, 2006 \text{ cm}^{-1}$ . –  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 5.42$  (t, 2H, CpH), 5.37 (t, 2H, CpH), 3.89 (s, 3H, OMe), 2.17 (s, 3H, CpMe). –  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 57.37$ . – MS (FAB):  $m/z$  (%) = 495.2 (93)  $[\text{M-I}]^+$ .

$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3]\text{I}$ , **2g**. M. p. 174 °C. – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2058, 2017 \text{ cm}^{-1}$ . –  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 5.56$  (s, 5H,  $\text{C}_5\text{H}_5$ ). –  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 61.92$ . – MS (FAB):  $m/z$  (%) = 493.2 (41)  $[\text{M-I}]^+$ .

$[\text{MeC}_5\text{H}_4\text{Fe}(\text{CO})_2\text{P}(p\text{-C}_6\text{H}_4\text{Cl})_3]\text{I}$ , **2h**. M. p. 173 °C. – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2054, 2010 \text{ cm}^{-1}$ . –  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 5.59$  (t, 2H, CpH), 5.47 (t, 2H, CpH), 2.20 (s, 3H, CpMe). –  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 62.56$ . – MS (FAB):  $m/z$  (%) = 507.2 (61)  $[\text{M-I}]^+$ .

$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{P}(p\text{-C}_6\text{H}_4\text{F})_3]\text{I}$ , **2i**. M. p. 181 °C. – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2060, 2018 \text{ cm}^{-1}$ . –  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 5.59$  (s, 5H,  $\text{C}_5\text{H}_5$ ). –  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 61.98$ . – MS (FAB):  $m/z$  (%) = 541.1 (17)  $[\text{M-I}]^+$ .

$[\text{MeC}_5\text{H}_4\text{Fe}(\text{CO})_2\text{P}(p\text{-C}_6\text{H}_4\text{F})_3]\text{I}$ , **2j**. M. p. 185 °C. – IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{CO}} = 2054, 2012 \text{ cm}^{-1}$ . –  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 5.64$  (t, 2H, CpH), 5.58 (t, 2H, CpH), 2.27 (s, 3H, CpMe). –  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25 °C, TMS):  $\delta = 63.60$ . – MS (FAB):  $m/z$  (%) = 556.6 (35)  $[\text{M-I}]^+$ .

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