Research Article

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Solventless Substitution Reaction of Solid Phosphine Ligands with $Ru(C_5H_4R)(CO)_2I$ (R = H, Me)

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ABSTRACT

The solventless reaction between $Ru(C_5H_4R)(CO)_2I$ (R = H, Me) and solid phosphine ligands [PPh_3, P(*p*-$MeOC_6H_4)_3$, P(*m*-$MeC_6H_4)_3$, P(*p*-$FC_6H_4)_3$, P(*p*-$ClC_6H_4)_3$] was undertaken at various temperatures with all the reactions occurring in the melt phase. The reaction rates and type of products isolated are dependent on the electronic properties of the Cp-substituent and the *para*-substituent on the phosphine ligands. For the C_5H_4R moiety, when R = H the ligand substitution product $Ru(C_5H_5)(CO)(PR_3)I$ was obtained, and the ligand addition product $[Ru(C_5H_4Me)(CO)_2(PR_3)]I$ was predominantly obtained when R = Me. The reaction rates are enhanced by *para*-substituted electron-donating phosphines. These results are similar to those obtained from studies utilizing benzene and xylene as solvents. The products have been characterized by FTIR and NMR spectroscopy and by MS. The complex $Fe_2(C_5H_5)_2(CO)_4$ was found to act as a catalyst in all the melt reactions.

KEYWORDS

Solvent-free, ruthenium, cyclopentadienyl complexes, phosphines.

1. Introduction

The reactions of half-sandwich cyclopentadienyl complexes have been extensively reported in the literature.[1–4] In particular, the preparation of cyclopentadienyl ruthenium complexes[5,6] and their reactions with electron donor ligands such as phosphines, phosphites and isonitriles in benzene or toluene as solvent have been documented.[7,8] Brown and co-workers[9] have studied the kinetics of CO substitution reactions of $Ru(C_5H_5)(CO)_2X$ (X = Cl, Br, I) with phosphine and phosphite ligands in different solvents. The reactivity follows the expected trend for the halogens, with the Cl complex being the most reactive. Furthermore, the polarity of the solvent was found to be important in determining the rate of the reaction. It has been established that the CO substitution reaction was favoured in non-polar solvents compared with polar solvents.[9] The effect of catalysts on the CO substitution reactions has also been studied and it was found that the rates of reaction were dramatically enhanced by the presence of transition metal dimers such as $Fe_2(C_5H_5)_2(CO)_4$.[7,10]

As an extension of our interest in green chemistry using solventless reactions we herein report on the reactions between $Ru(C_5H_4R)(CO)_2I$ (R = H, Me) and a range of phosphine ligands: PPh_3, P(*p*-$MeOC_6H_4)_3$, P(*m*-$MeC_6H_4)_3$, P(*p*-$FC_6H_4)_3$, P(*p*-$ClC_6H_4)_3$, in the absence of a solvent. This study furthers our understanding of the influence of reaction conditions on the rates of stoichiometric reactions of organometallic compounds that are key steps in catalytic applications of the complexes.

2. Results and Discussion

2.1. Solventless Reactions between $Ru(C_5H_5)(CO)_2I$ and Phosphine Ligands

The thermally-initiated solventless reactions of $Ru(C_5H_5)(CO)_2I$ and solid phosphine ligands [PPh_3, P(*p*-$MeOC_6H_4)_3$, P(*m*-$MeC_6H_4)_3$, P(*p*-$FC_6H_4)_3$, P(*p*-$ClC_6H_4)_3$] were conducted and a typical result using PPh_3 is first discussed; then the data discussion is expanded to the other ligands.

The reaction between $Ru(C_5H_5)(CO)_2I$ and PPh_3 led to two possible products: a salt product **2** formed *via* ligand addition and a neutral product **3** formed through a CO substitution reaction (Scheme 1). As expected, IR spectral analysis of the two products showed IR absorption bands for the CO ligand at 1957 cm^{-1} for **3** and 2020 and 2066 cm^{-1} for **2**. Furthermore, the ^1H NMR spectra showed resonances for the cyclopentadienyl protons at δ 5.78 ppm for **2** and δ 4.91 ppm for **3**, respectively.

In order to understand the factors that drive the reaction an initial study was conducted at 70 °C (Table 1). The conversion of the starting material into products at this temperature showed that the salt is the predominant product formed (50 % conversion after 4 h), while the non-salt product was produced in lesser quantities (9 % conversion after 4 h). As the total conversion to products after 4 h was only 59 %, the effect of raising the reaction temperature to 100 °C, while keeping all other experimental variables constant was explored. As expected, for a thermally driven solventless reaction, a significant improvement in the reaction rate was observed as 42 % total conversion was obtained after only 30 min (at 70 °C, no reaction occurred after the same period of time).

Since the reaction between $Ru(C_5H_5)(CO)_2I$ and PPh_3 has been shown to be enhanced by the action of catalysts,[7] a study was conducted to determine the effect of a catalytic amount of $Fe_2(C_5H_5)_2(CO)_4$ on this reaction. At 70 °C, the catalyzed solventless reaction was also found to proceed at a more rapid rate (89 % conversion to both salt and non-salt products after 4 h) compared with the non-catalyzed reaction.

Importantly, optical microscopy and DSC studies revealed that both the catalyzed and non-catalyzed reactions occurred in the melt phase (Figs. 1 and 2).

After this preliminary study with PPh_3, a range of other solid phosphine ligands was studied. A DSC study of a 1:1 mixture

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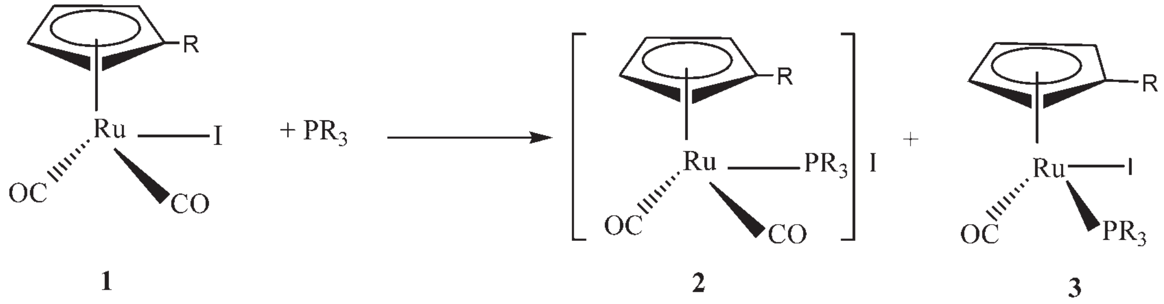


Scheme 1
Reaction between $Ru(C_5H_5)(CO)_2I$ and phosphine ligands.

$Ru(C_5H_5)(CO)_2I/PR_3$ was first undertaken in order to determine the physical state of the mixture as a function of temperature. It was found that the melting points of the mixtures ranged between 70 and 97 °C (Supplementary Material, Table S1).

The reactions were then carried out at 70 °C (metal complex mixtures with PPh_3 and $P(p\text{-}FC_6H_4)_3$ are visually observed in the melt phase at this temperature) and at 100 °C (all the metal complex/ligand mixtures are in the melt phase). The reactions were also conducted in the presence of $Fe_2(C_5H_5)_2(CO)_4$ as a catalyst.

At 70 °C in the absence of catalyst (Table 1), only PPh_3 led to the formation of a product while all other ligands failed to react with the $Ru(C_5H_5)(CO)_2I$. However, the addition of $Fe_2(C_5H_5)_2(CO)_4$ as a catalyst gave a set of ligand-dependent product yields. Generally, the salt was the major product formed when electron donor ligands [PPh_3, $P(p\text{-}MeOC_6H_4)_3$, $P(m\text{-}MeC_6H_4)_3$] were used, while the non-salt product was predominantly formed when the electron-withdrawing ligands [$P(p\text{-}FC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$] were used. The reactivity with respect to the total conversion of the reactants into (salt + non-salt) products was found to follow the order: $PPh_3 > P(p\text{-}MeOC_6H_4)_3 > P(p\text{-}FC_6H_4)_3$ $P(p\text{-}ClC_6H_4)_3 > P(m\text{-}MeC_6H_4)_3$.

At 100 °C in the absence of the catalyst (Supplementary Material, Table S2), the reaction rate, as expected, was significantly improved when compared with the reaction carried out at 70 °C. This could be attributed to increased mobility in the melt, since all the reactants are in the molten phase at this temperature. After 30 min of reaction, the order of the ligand reactivity was: $P(p\text{-}FC_6H_4)_3 > PPh_3 > P(p\text{-}MeOC_6H_4)_3 > P(m\text{-}MeC_6H_4)_3 > P(p\text{-}ClC_6H_4)_3$. In the presence of the iron dimer as a catalyst, all the ligands gave 100 % conversion after a period of 4 h and the non-salt product was the major product of the reaction for all the ligands.

Table 1 Reactions of $Ru(C_5H_5)(CO)_2I$ and L at 70 °C in the presence or absence of the catalyst.

Ligand (L)	Time/h	Uncatalyzed		Catalyzed	
		2	3	2	3
PPh_3	0.5	0	0	64	16
	4	50	9	70	19
$P(p\text{-}MeOC_6H_4)_3$	0.5	0	0	0	0
	4	0	0	24	9
$P(m\text{-}MeC_6H_4)_3$	0.5	0	0	0	3
	4	0	0	34	10
$P(p\text{-}FC_6H_4)_3$	0.5	0	0	51	35
	4	0	0	32	68
$P(p\text{-}ClC_6H_4)_3$	0.5	0	0	0	0
	4	0	0	0	13

From the results described above, the following observations can be made:

(i) Compared with the Fe analogues,[11] Ru compounds are much less reactive in the melt phase. For example, when $Fe(C_5H_5)(CO)_2I$ was reacted with PR_3 ligands at 70 °C in the absence of a catalyst, a reaction was observed to take place for all the ligands studied, while only PPh_3 reacted with $Ru(C_5H_5)(CO)_2I$. $Fe(C_5H_5)(CO)_2I$ gave ~100 % conversion for all the ligands after just 15 min of reaction at 100 °C in the absence of catalyst, while for $Ru(C_5H_5)(CO)_2I$, <50 % product was obtained for all the ligands after 30 min reaction (Supplementary Material, Table S2).

(ii) $Fe(C_5H_5)(CO)_2I$ gives mainly the salt product, together with a small amount of the covalent product. At 100 °C, $Ru(C_5H_5)(CO)_2I$ preferentially forms the non-salt material as

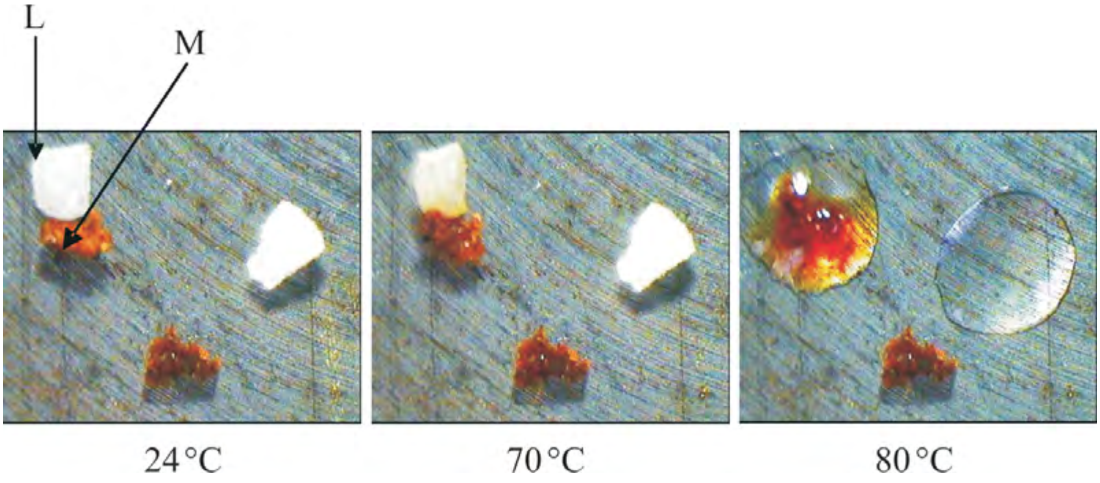


Figure 1 Microscopic pictures of $Ru(C_5H_5)(CO)_2I + PPh_3$ (M = Ru complex; L = PPh_3).

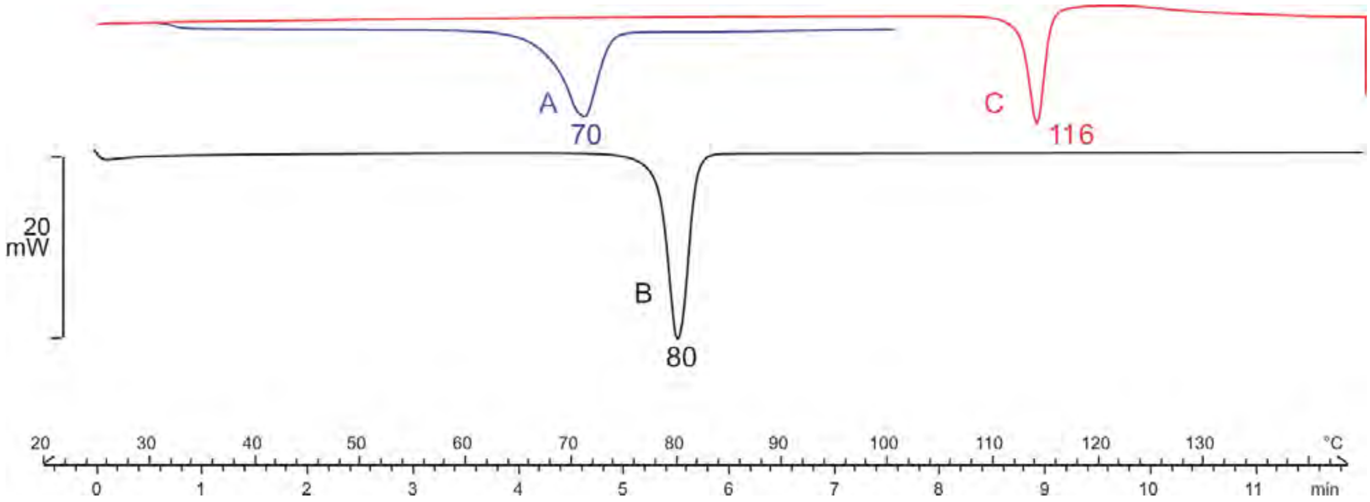


Figure 2 DSC profile for Ru(C_5H_5)(CO)$_2$I + PPh$_3$ 1:1 ratio.

the major product in the presence of the catalyst (see Supplementary Material Table S2) with the salt as the minor product of the reaction. This is probably due to a difference in the mechanisms of the two reactions. The Fe complexes are believed to react *via* an associative mechanism while the Ru complexes react *via* a dissociative mechanism.[12]

(iii) The lower reactivity of the Ru complexes compared with the Fe analogues has also been established when similar reactions were conducted in solvents.[13–15] In addition, the Ru complexes formed no ionic product in the solution studies (xylene, toluene),[7,9] while Fe complexes afforded a significant amount of the ionic product under the same conditions. Hence we can conclude that melt phase and solution phase reactivity of the metal complexes follows the group trends.

(iv) The CO substitution reaction of Ru(C_5H_5)(CO)$_2$I with phosphine ligands is generally observed to be enhanced by electron-withdrawing phosphine ligands.

2.2. Solventless Reactions between Ru(C_5H_4Me)(CO)$_2$I and Phosphine Ligands

The effect of substituents on the Cp ring has been studied and it was established that the electronic properties of the substituent affects the reaction rates. Rerek and Basolo[16] have shown that the presence of an electron-donating group on the Cp ring results in a slower CO substitution reaction and this is consistent with a nucleophilic attack mechanism.[17] However, Tabatabaian and White[18] have demonstrated the opposite effect by comparing the kinetic data for the CO substitution reactions of Ru(C_5Me_4Et)(CO)$_2$Br and Ru(C_5H_5)(CO)$_2$Br with phosphine and phosphite ligands. They found that the ethyltetramethylcyclopentadienyl complex underwent CO substitution much easier (18 times faster) than the unsubstituted cyclopentadienyl complex. The authors suggested that the effect was due to the more favourable enthalpy term associated with the substituted complex as well as the stabilization of the transition state by the electron donor alkyl groups.

To study the effect of a ring substituent on the reaction, a 1:1 Ru(C_5H_4Me)(CO)$_2$I/PPh$_3$ mixture was prepared as described under the experimental procedure.

A ^{1}H NMR spectrum recorded after mixing of the reactants revealed that no reaction had taken place. A DSC and microscopic study of the mixture showed that a melt phase forms at 36 °C (Fig. 3 and Supplementary Material Table S3).

The reaction was then carried out at 45 °C to ensure that all

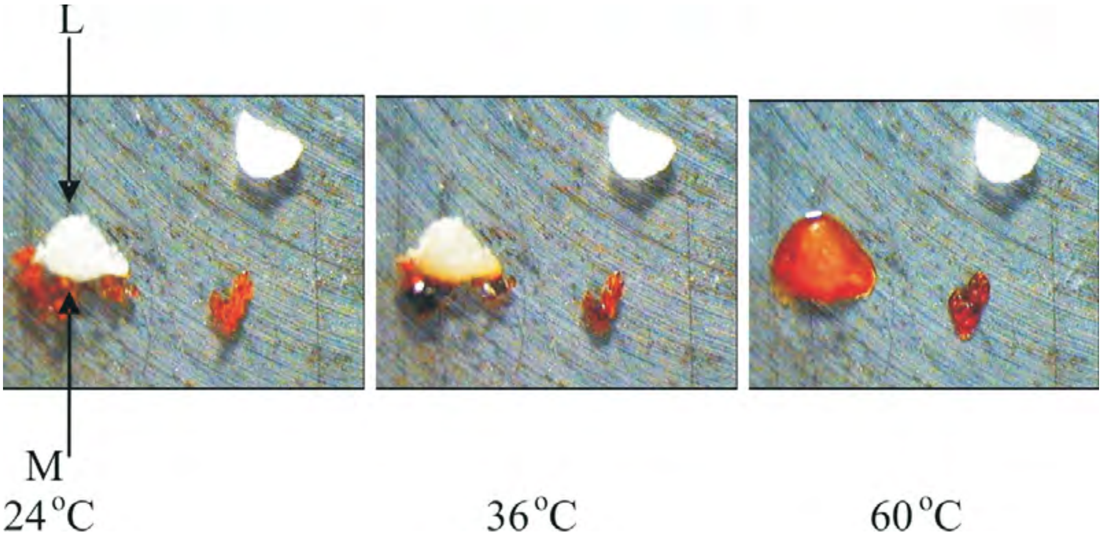


Figure 3 Microscopic pictures of Ru(C_5H_4Me)(CO)$_2$I + PPh$_3$ (M = Ru complex; L = PPh$_3$).

reactants were in the melt phase. No reaction occurred after a period of 4 h and increasing the reaction temperature to 60 and 70 °C did not lead to reaction. The reaction was then conducted at 100 °C and after 4 h both salt product (39 %) and non-salt product (36 %) were detected by ^{1}H NMR spectroscopy.[19]

The metal dimer $Fe_2(C_5H_5)_2(CO)_4$ was then used as a catalyst for the reaction of $Ru(C_5H_4Me)(CO)_2I$ with PPh_3. At 70 °C, an increase in the reaction rate was observed as 30 % of the salt product was formed after 30 min of reaction and 100 % conversion into salt product was achieved after 4 h. No non-salt product was observed in these catalyzed reactions. At 100 °C, complete conversion was obtained after only 30 min with 72 % salt product and 28 % non-salt product formed, suggesting the conversion of salt to non-salt product (decarbonylation) at high temperature.

After this preliminary study with PPh_3, the same range of phosphine ligands as used earlier with $Ru(C_5H_5)(CO)_2I$ was studied. DSC studies performed on 1:1 $Ru(C_5H_4Me)(CO)_2I/PR_3$ mixtures revealed that their melting points ranged from 36 to 42 °C (Supplementary Material Table S3), depending on the ligand. The reactions were carried out at 70 °C and 100 °C both in the presence and absence of $Fe_2(C_5H_5)_2(CO)_4$ as a catalyst.

At 70 °C, in the absence of the catalyst, no reaction was observed for any of the ligands studied. In the presence of the catalyst, little improvement in the reactivity was observed for $P(p\text{-}MeOC_6H_4)_3$ and $P(m\text{-}MeC_6H_4)_3$, while no reaction was observed for $P(p\text{-}FC_6H_4)_3$ and $P(p\text{-}ClC_6H_4)_3$ (Supplementary Material Table S4). However, the PPh_3 reactivity was dramatically improved. In summary, the order of reactivity was: $PPh_3 >> P(m\text{-}MeC_6H_4)_3 > P(p\text{-}MeOC_6H_4)_3 > P(p\text{-}FC_6H_4)_3 = P(p\text{-}ClC_6H_4)_3$.

At 100 °C, improvement was observed when compared with the results obtained at 70 °C in the absence of the catalyst (Table 2). PPh_3 and $P(m\text{-}MeC_6H_4)_3$ gave salt and non-salt products in a 1:1 ratio while $P(p\text{-}MeOC_6H_4)_3$ gave only a salt product. Only the non-salt product was formed in the reaction with $P(p\text{-}FC_6H_4)_3$ and $P(p\text{-}ClC_6H_4)_3$. In the presence of $Fe_2(C_5H_5)_2(CO)_4$ as a catalyst at 100 °C, the reaction rates were dramatically improved as the reactions with all the ligands gave >80 % conversion in the first 30 min, the salt being the major product of the reaction (Table 2).

From the results of the solventless reactions between $Ru(C_5H_4Me)(CO)_2I$ and phosphine ligands, the following conclusions can be drawn:

(i) In the absence or presence of $Fe_2(C_5H_5)_2(CO)_4$ as catalyst the reactivity order towards phosphine ligands is the following: $Fe(C_5H_5)(CO)_2I > Fe(C_5H_4Me)(CO)_2I > Ru(C_5H_5)(CO)_2I > Ru(C_5H_4Me)(CO)_2I$.

(ii) The salt product is the major product formed in the solventless reaction between $Ru(C_5H_4Me)(CO)_2I$ and phosphine ligands at 100 °C in the presence of $Fe_2(C_5H_5)_2(CO)_4$ as a catalyst.

(iii) As a general observation, the electron-donating ligands [PPh_3, $P(p\text{-}MeOPh)_3$, $P(m\text{-}MePh)_3$] have been shown to be more reactive than the electron-withdrawing ligands [$P(p\text{-}FPh)_3$, $P(p\text{-}ClPh)_3$] for all the compounds studied.

(iv) The use of $Fe_2(C_5H_5)_2(CO)_4$ as a catalyst significantly promoted formation of the salt product. This is clearly observable in the solventless reactions of either $Ru(C_5H_5)(CO)_2I$ or $Ru(C_5H_4Me)(CO)_2I$ at 100 °C. A proposed mechanism for the non-salt product formation from $Ru(C_5H_5)(CO)_2I$ in the presence of $Fe_2(C_5H_5)_2(CO)_4$ is shown in Scheme 2.

Table 2 Reactions of $Ru(C_5H_5Me)(CO)_2I$ and ligands, L, at 100 °C in the presence or absence of the catalyst.

Ligand (L)	Time/h	Uncatalyzed		Catalyzed	
		2	3	2	3
PPh_3	0.5	0	0	72	28
	4	39	36	40	60
$P(p\text{-}MeOC_6H_4)_3$	0.5	0	0	90	0
	4	39	0	100	0
$P(m\text{-}MeC_6H_4)_3$	0.5	15	0	96	0
	4	22	21	100	0
$P(p\text{-}FC_6H_4)_3$	0.5	0	0	100	0
	4	0	19	100	0
$P(p\text{-}ClC_6H_4)_3$	0.5	0	0	88	0
	4	0	12	100	0

In all the reactions a melt phase was identified by optical microscopic studies and DSC analysis. For example, the mixture of $Ru(C_5H_5)(CO)_2I$ and PR_3 melted at 70 °C (Fig. 1 and Supplementary Material Table S1) while the $Ru(C_5H_4Me)(CO)_2I$ and PR_3 mixture was observed to melt at 36 °C (Fig. 3 and Supplementary Material Table S3). The reactants thus provide the 'solution medium' for the reaction. This is consistent with studies by others,[20,21] in which solid state reactions seemingly occur in the melt phase and not in the solid phase.[22]

Although formation of the melt phase is important for the solventless reaction, it is not an absolute condition for reactivity. This can be seen by comparing the reactivities of $Ru(C_5H_5)(CO)_2I$ and $Ru(C_5H_4Me)(CO)_2I$.

2.3. Mechanism of the Catalyzed Reaction between $Ru(C_5H_4R)(CO)_2I$ and Phosphine Ligands

In the present study $Fe_2(C_5H_5)_2(CO)_4$ has been shown to be a catalyst for the reaction between $Ru(C_5H_4R)(CO)_2I$ and phosphine ligands.

The mechanism for the Ru complexes, e.g. $Ru(C_5H_5)(CO)_2I$ has been proposed to occur *via* 17-electron intermediates as the non-salt material is the predominant product formed in the reaction.

$$Fe[(C_5H_5)(CO)_2]_2 \rightleftharpoons 2\,Fe(C_5H_5)(CO)_2^{\bullet} \tag{1}$$

$$Fe(C_5H_5)(CO)_2^{\bullet} + PR'_3 \longrightarrow [Fe(C_5H_5)(CO)(PR'_3)]^{\bullet} + CO \tag{2}$$

$$[Fe(C_5H_5)(CO)(PR'_3)]^{\bullet} + Ru(C_5H_5)(CO)_2I \longrightarrow Fe(C_5H_5)(CO)(PR'_3)I + [Ru(C_5H_5)(CO)_2]^{\bullet} \tag{3}$$

$$[Ru(C_5H_5)(CO)_2]^{\bullet} + PR'_3 \longrightarrow [Ru(C_5H_5)(CO)(PR'_3)]^{\bullet} + CO \tag{4}$$

$$[Ru(C_5H_5)(CO)(PR'_3)]^{\bullet} + Ru(C_5H_5)(CO)_2I \longrightarrow \mathbf{Ru(C_5H_5)(CO)(PR'_3)I} + [Ru(C_5H_5)(CO)_2]^{\bullet} \tag{5}$$

Scheme 2
Catalyzed non-salt product formation from $Ru(C_5H_5)(CO)_2I$.

$$\mathrm{Fe[(C_5H_5)(CO)_2]_2 \rightleftharpoons 2\,Fe(C_5H_5)(CO)_2{}^{\bullet}} \tag{1}$$

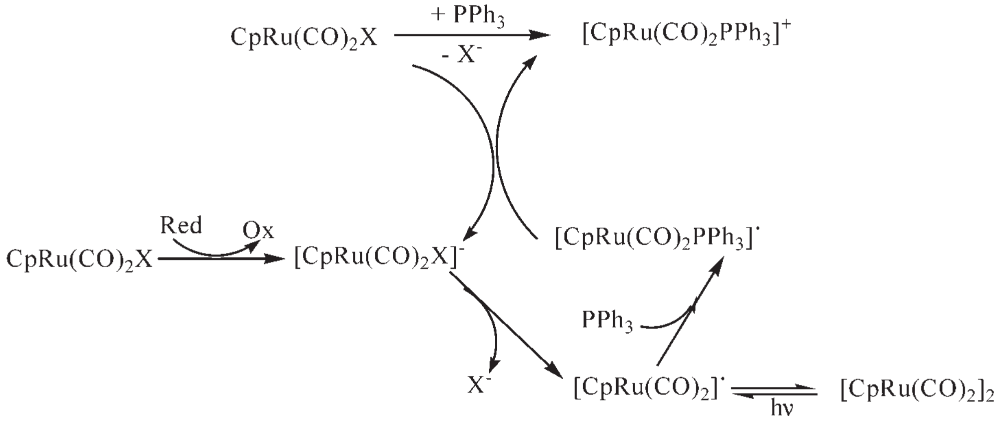
$$\mathrm{Fe(C_5H_5)(CO)_2{}^{\bullet} + PR'_3 \longrightarrow [Fe(C_5H_5)(CO)_2(PR'_3)]^{\bullet}} \tag{2}$$

$$\mathrm{[Fe(C_5H_5)(CO)_2(PR'_3)]^{\bullet} + Ru(C_5H_5)(CO)_2I \longrightarrow [\,Fe(C_5H_5)(CO)_2(PR'_3)]I + [Ru(C_5H_5)(CO)_2]^{\bullet}} \tag{3}$$

$$\mathrm{[Ru(C_5H_5)(CO)_2]^{\bullet} + PR'_3 \longrightarrow [Ru(C_5H_5)(CO)_2(PR'_3)]^{\bullet}} \tag{4}$$

$$\mathrm{[Ru(C_5H_5)(CO)_2(PR'_3)]^{\bullet} + Ru(C_5H_5)(CO)_2I \longrightarrow \mathbf{[\,Ru(C_5H_5)(CO)_2(PR'_3)]I} + [Ru(C_5H_5)(CO)_2]^{\bullet}} \tag{5}$$

Scheme 3
Catalyzed salt product formation from $Ru(C_5H_5)(CO)_2I$.



Scheme 4
Electron transfer mechanism for the salt product formation.

The formation of the catalyzed salt product can be explained by the following mechanism in Scheme 3.

However, Gipson and co-workers[23] have demonstrated that an electron transfer chain (ETC) mechanism induced by the presence of a reducing agent is also possible for these catalyzed reactions as shown in Scheme 4.

3. Experimental

Solution IR spectra were recorded in dichloromethane on a Bruker Vector 27 FTIR spectrometer (Bruker SA, Johannesburg, SA).

^1H and ^{31}P NMR spectra were recorded in chloroform-*d* on a Bruker AC 300 spectrometer (Bruker Biospin, Karlsruhe, Germany) at 300 and 121.5 MHz respectively. Melting points were determined on a Mettler Toledo (Johannesburg, SA) DSC822e device. The positive ion mode FAB MS spectra were recorded on a Micromass (Manchester, England) VG70SEQ instrument at a resolution of 1000.

3.1. Synthesis and Characterization of the Starting Materials

Ruthenium carbonyl, $[Ru_3(CO)_{12}]$ (0.4 g) was refluxed overnight in 10 mL of either dicyclopentadiene or methylcyclopentadiene dimer–heptane (2:3) mixture, producing the dimer $Ru_2(C_5H_4R)_2(CO)_4$ (R = H,Me, respectively) in quantitative yields. The monomeric complexes, $Ru(\eta^5\text{-}C_5H_4R)(CO)_2I$, were readily obtained by reacting the dimer (0.3 g) with iodine (0.2 g) in tetrahydrofuran (10 mL) for 1 h at room temperature.[24] After removing all volatiles, the product was dissolved in dichloromethane and an aqueous solution of sodium thiosulphate was used to extract out any excess iodine. The organic phase was dried to afford the required products, R = H (**1a**) and R = Me (**1b**). The starting materials were characterized by IR (CH_2Cl_2) and ^1H NMR ($CDCl_3$).

$Ru(C_5H_5)(CO)_2I$, 1a: Cp: δ 5.46 ppm (s); ν_{CO}: 2049, 1998 cm^{-1}

$Ru(C_5H_4Me)(CO)_2I$, 1b: Cp: δ 5.29, 5.20 ppm (d); ν_{CO}: 2045, 1994 cm^{-1}

3.2. Monitoring of the Reaction by ^1H NMR Spectroscopy

$Ru(C_5H_4R)(CO)_2I$ (0.08 mmol) and phosphine ligands (0.08 mmol) were ground together in an agate mortar using a pestle. After making a fine powder, portions of this material (5–10 mg) were placed into NMR tubes, flushed with nitrogen gas and sealed. The NMR tubes were then placed in an oil bath pre-heated to a predetermined temperature. After a predetermined time, a tube was removed from the oil bath and analyzed by ^1H NMR spectroscopy in $CDCl_3$.[25]

For catalyzed reactions a 10 mol percentage of $Fe_2(C_5H_5)_2(CO)_4$ was added to the complex/ligand mixture and ground together as described above.

3.3. Optical Microscopic Studies

A homemade glass heating device was calibrated with crystals of known melting points. An optical microscope fitted with a JVC digital camera (Micro Met Scientific, Johannesburg, SA) 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 *via* a PC monitor attached to a digital camera.[26]

3.4. Macroscopic Synthesis of $Ru(C_5H_5)(CO)(PR_3)I$ and $[Ru(C_5H_4Me)(CO)_2(PR_3)]I$ Compounds

The salt and the non-salt compounds were synthesized by grinding in a mortar and pestle as described above. Typically 0.1 mol of reactants were used at a standard temperature of 100 °C for 4 h in a 50 mL round-bottomed flask.

The purified compounds were isolated in yields of 60–80 % using a silica gel column made up in hexane. Toluene was used to elute the non-salt fractions **2a–e**, and acetone was used to elute the salt products **3a–e**.

Compounds were characterized by NMR and FTIR for **3a–e** and in addition by FAB-MS for **2a–e**. Due to non-volatility it was not possible to characterize the salt products by MS.

3.5. Characterization of $Ru(C_5H_5)(CO)(PR_3)I$ Compounds

$Ru(C_5H_5)(CO)(PPh_3)I$, 2a: IR (CH_2Cl_2): ν_{CO} = 1957 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.91 (s, 5H, CpH) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 49.53 ppm. MS (FAB): m/z (%): 584.9 (62): M; 555.9 (30): $[M\text{-}CO]^+$; 429.0 (12): $[M\text{-}CO\text{-}I]^+$.

$Ru(C_5H_5)(CO)[P(p\text{-}MeOC_6H_4)_3]I$, 2b: IR ($CH_2Cl_2$): ν_{CO} = 1953 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.91 (s, 5H, CpH); 3.82 (s, 3H, OCH_3) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 44.30 ppm. MS (FAB): m/z (%): 673.8 (33): M; 645.8 (12): $[M\text{-}CO]^+$; 519.0 (45): $[M\text{-}CO\text{-}I]^+$.

$Ru(C_5H_5)(CO)[P(m\text{-}MeC_6H_4)_3]I$, 2c: ν_{CO} = 1955 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.89 (s, 5H, CpH), 2.32 (s, 3H, CH_3) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 48.96 ppm. MS (FAB): m/z (%): 626.0 (13): M; 598.0 (5): $[M\text{-}CO]^+$; 471.1 (20): $[M\text{-}CO\text{-}I]^+$.

$Ru(C_5H_5)(CO)[P(p\text{-}FC_6H_4)_3]I$, 2d: IR ($CH_2Cl_2$): ν_{CO} = 1960 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.93 (s, 5H, CpH) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 48.90 ppm. MS (FAB): m/z (%): 637.6 (16): M; 609.6 (10): $[M\text{-}CO]^+$; 482.8 (22): $[M\text{-}CO\text{-}I]^+$.

$Ru(C_5H_5)(CO)[P(p\text{-}ClC_6H_4)_3]I$, 2e: IR ($CH_2Cl_2$): ν_{CO} = 1962 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 4.93 (s, 5H, CpH) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 48.84 ppm. MS (FAB): m/z (%): 688.1 (23): M; 657.0 (15): $[M\text{-}CO]^+$; 530.0 (19): $[M\text{-}CO\text{-}I]^+$.

3.6. Characterization of $[Ru(C_6H_4Me)(CO)_2PR_3]I$ Compounds

$[Ru(C_6H_4Me)(CO)_2PPh_3]I$, 3a: IR ($CH_2Cl_2$): ν_{CO} = 2017, 2064 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.69 (s, 2H, CpH), 5.60 (s, 2H, CpH), 2.14 (s, 3H, CH_3Cp) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 43.55 ppm.

$[Ru(C_6H_4Me)(CO)_2P(p\text{-}MeOC_6H_4)_3]I$, 3b: IR ($CH_2Cl_2$): ν_{CO} = 2015, 2062 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.62 (s, 2H, CpH), 5.59 (s, 2H, CpH), 3.89 (s, 3H, OCH_3), 2.13 (s, 3H, CH_3Cp) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 38.56 ppm.

$[Ru(C_6H_4Me)(CO)_2P(m\text{-}MeC_6H_4)_3]I$, 3c: IR ($CH_2Cl_2$): ν_{CO} = 2017, 2064 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.62 (s, 2H, CpH), 5.52 (s, 2H, CpH), 2.39 (s, 3H, $CH_3C_6H_4$), 2.15 (s, 3H, CH_3Cp) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 43.10 ppm.

$[Ru(C_6H_4Me)(CO)_2P(p\text{-}FC_6H_4)_3]I$, 3d: IR ($CH_2Cl_2$): ν_{CO} = 2019, 2066 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.80 (s, 2H, CpH), 5.70 (s, 2H, CpH), 2.18 (s, 3H, CH_3Cp) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 41.79 ppm.

$[Ru(C_6H_4Me)(CO)_2P(p\text{-}ClC_6H_4)_3]I$, 3e: IR ($CH_2Cl_2$): ν_{CO} = 2020, 2068 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.83 (s, 2H, CpH), 5.75 (s, 2H, CpH), 2.20 (s, 3H, CH_3Cp) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C, TMS): δ = 42.15 ppm.

4. Conclusions

Solventless reactions between $Ru(C_5H_4R)(CO)_2I$ (R = H, Me) and solid phosphine ligands [PPh_3, $P(p\text{-}MeOC_6H_4)_3$, $P(m\text{-}MeC_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$] have been conducted at different temperatures in the presence or absence of $Fe_2(C_5H_5)_2(CO)_4$ as a catalyst. The optimal conditions for the reactions are 100 °C and the presence of a catalytic amount of $Fe_2(C_5H_5)_2(CO)_4$.

A product dependency on the nature of the Cp substituent is observed, typically with formation of the ionic (salt) product when R = Me and a neutral ligand substitution (non-salt) product when R = H.

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Table S1 Melting temperatures for $CpRu(CO)_2I + PR_3$ (1:1) mixtures.

Mixture	Melting point/°C
$CpRu(CO)_2I + PPh_3$	70
$CpRu(CO)_2I + P(p\text{-}OCH_3C_6H_4)_3$	97
$CpRu(CO)_2I + P(m\text{-}CH_3C_6H_4)_3$	88
$CpRu(CO)_2I + P(p\text{-}FC_6H_4)_3$	70
$CpRu(CO)_2I + P(p\text{-}ClC_6H_4)_3$	87

Table S2 Reactions of $CpRu(CO)_2I$ and PR_3 ligands at 100 °C.

Ligand (L)	Time/h	Uncatalyzed		Catalyzed	
		2	3	2	3
PPh_3	0.5	29	13	58	34
	4	50	19	35	65
$P(p\text{-}OCH_3C_6H_4)_3$	0.5	18	0	66	22
	4	44	8	0	100
$P(m\text{-}CH_3C_6H_4)_3$	0.5	0	0	5	95
	4	27	8	0	100
$P(p\text{-}FC_6H_4)_3$	0.5	0	15	0	100
	4	0	100	0	100
$P(p\text{-}ClC_6H_4)_3$	0.5	0	9	31	69
	4	10	17	0	100

Table S3 Melting temperatures of $MeCpRu(CO)_2I + PR_3$ mixtures (1:1 ratio).

Mixture	Melting point/°C
$CH_3CpRu(CO)_2I + PPh_3$	36
$CH_3CpRu(CO)_2I + P(p\text{-}MeC_6H_4)_3$	42
$CH_3CpRu(CO)_2I + P(m\text{-}MeC_6H_4)_3$	38
$CH_3CpRu(CO)_2I + P(p\text{-}FC_6H_4)_3$	36
$CH_3CpRu(CO)_2I + P(p\text{-}ClC_6H_4)_3$	40

Table S4 Reactions of $MeCpRu(CO)_2I$ and PR_3 ligands at 70 °C.

Ligand (L)	Time/h	Uncatalyzed		Catalyzed	
		2	3	2	3
PPh_3	0.5	0	0	30	0
	4	0	0	100	0
$P(p\text{-}OCH_3C_6H_4)_3$	0.5	0	0	0	0
	4	0	0	10	0
$P(m\text{-}CH_3C_6H_4)_3$	0.5	0	0	0	0
	4	0	0	19	0
$P(p\text{-}FC_6H_4)_3$	0.5	0	0	0	0
	4	0	0	0	0
$P(p\text{-}ClC_6H_4)_3$	0.5	0	0	0	0
	4	0	0	0	0