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SOLVENTLESS MIGRATORY-INSERTION REACTIONS OF SUBSTITUTED CYCLOPENTADIENYL IRON COMPLEXES INDUCED BY ELECTRON DONOR LIGANDS

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ABSTRACT. Reaction between solid $(C_5H_5)Fe(CO)_2CH_3$ and a range of solid phosphine ligands, L (L = PPh_3, P(*m*-$CH_3C_6H_4)_3$, P(*p*-$CH_3C_6H_4)_3$, P(*p*-$FC_6H_4)_3$, P(*p*-$ClC_6H_4)_3$, PCy_3) occurred in the absence of solvent in the melt phase to give the migratory-insertion products, $(C_5H_5)Fe(CO)(COCH_3)(L)$. The reaction was more rapid with small electron withdrawing ligands. Insertion reaction between $(RC_5H_4)Fe(CO)_2R'$ (R = H, CH_3; R' = CH_3, CH_2Ph) and gaseous ligands such as SO_2 and CO were also studied. The insertion of SO_2 occurred readily for all the substrates investigated, but CO insertion did not occur (< 1 %) using the solventless reaction condition.

KEY WORDS: Melt phase, Solventless chemistry, Cyclopentadiene, Iron complexes, Migratory-insertion

INTRODUCTION

An insertion reaction occurs when an incoming ligand is incorporated into an existing complex without releasing any of the previously coordinated groups [1]. Generally, small molecules such as CO, SO_2, carbenes, etc. are known to lead to insertion products but incoming phosphine and phosphite ligands can also yield substitution products [2].

Over the last three decades, solution insertion reactions of carbon monoxide into metal carbonyl complexes have been extensively studied [3]. For example the insertion reaction of CO into the manganese complex, $Mn(CO)_5CH_3$, can occur via initial migration of a metal attached CO to the methyl ligand or via methyl migration to a metal attached CO, but the latter was shown to be the correct mechanism [4].

The product formed by reaction of an alkyl or aryl cyclopentadienyl metal carbonyl complex of the type $(C_5H_5)M(CO)_xR$ (R = aryl or alkyl), and phosphine ligands are acetyl complexes, formed by R group migration and phosphine coordination [5]. In particular, the reaction of $(C_5H_5)Fe(CO)_2CH_3$ and ligands L, such as PPh_3, P(*n*-$C_4H_9)_3$, P(*n*-$OC_4H_9)_3$ in THF to give acetyl complexes, $(C_5H_5)Fe(CO)(L)COCH_3$, was studied by Butler and co-workers [6]. The rate of reaction was found to be influenced by the chain length of the alkyl group [1, 7]. However, the reaction of $(C_5H_5)Fe(CO)_2CH_3$ with phosphine ligands does not always lead to an acetyl complex formation. For example, under ultraviolet irradiation, the reaction of $(C_5H_5)Fe(CO)_2CH_3$ with PPh_3 produced $(C_5H_5)Fe(CO)(PPh_3)CH_3$ together with the acetyl product [8]. Also, the reaction of $(C_5H_5)Fe(CO)_2CH_3$ with CO has been found to produce the expected insertion product, $(C_5H_5)Fe(CO)_2(COCH_3)$ as well as a significant amount of the dimer, $[(C_5H_5)Fe(CO)_2]_2$ [9, 10]. The chemistry of η^5-cyclopentadienyl dicarbonyl iron anion has been also recently reviewed [11].

Insertion reactions of molybdenum complexes such as $(C_5H_5)Mo(CO)_3CH_3$ have been also reported [6, 12].

A slightly different type of insertion reaction has been observed when sulfur dioxide is the incoming ligand [13]. SO_2 insertion into alkyl or aryl complexes does not result in ligand

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*Corresponding author. E-mail: neil.coville@chem.wits.ac.za migration as found for phosphines, phosphites and CO. Instead, a S-sulfinate derivative forms by external insertion of the SO_2 ligand into the Fe–C bond. Thus, SO_2 insertion into $(C_5H_5)Fe(CO)_2R$ affords $(C_5H_5)Fe(CO)_2SO_2R$ [14]. These reactions have been studied under various conditions including the absence of a solvent [15-17].

In a continuation of our study on solid state and solventless reactions, we wish to report on the solventless reactions between $(RC_5H_4)Fe(CO)_2R'$ and a range of solid and gaseous two electron donor ligands. A preliminary investigation of the insertion reaction between $(C_5H_5)Fe(CO)_2CH_3$ and PPh_3 as well as CO ligands in the absence of solvent was reported by us [18].

In this study we report on the influence of steric and electronic effects of the incoming ligand on the insertion reaction and evaluate a green chemistry approach in which the traditional synthetic routes are replaced by alternative methodologies with the objective of preventing waste and enhancing the environment and human health [19-24].

EXPERIMENTAL

The starting materials, $(C_5H_5)Fe(CO)_2CH_3$, $(CH_3C_5H_4)Fe(CO)_2CH_3$, $(C_5H_5)Fe(CO)_2CH_2C_6H_5$ and $(HCO_2C_5H_4)Fe(CO)_2CH_3$ were prepared by the standard procedures [25, 26]. All reactions were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by conventional methods, distilled under nitrogen, and used immediately. Melting points were recorded on a Mettler Toledo DSC 822e device. Solution infrared spectra were measured on a Bruker Vector 22 FTIR spectrometer, in KBr cells. NMR spectra were recorded on a Bruker AC300 spectrometer operating at 300 MHz with $CDCl_3$ as a solvent.

Experimental procedure for solid phosphine ligands reaction

Solventless reactions were conducted between $(C_5H_5)Fe(CO)_2CH_3$ and a range of solid phosphine ligands. A typical experimental procedure described below was used: $(C_5H_5)Fe(CO)_2CH_3$ and the ligand in 1:1 mole ratio were mixed with 2-3 mL of CH_2Cl_2 to dissolve the material. The solvent was then removed under vacuum. The solid material left was distributed into NMR tubes (approximately 5-10 mg per tube). The tubes were then flushed with nitrogen, stoppered with a rubber septum and placed in an oil bath heated at a pre-set temperature.

After a pre-determined time, the tube was removed from the oil bath, cooled and ^1H NMR spectra of the mixture recorded in $CDCl_3$ [18].

Experimental procedure for gaseous ligands

Reactions between SO_2 or CO and $(C_5H_5)Fe(CO)_2CH_3$, $(C_5H_5)Fe(CO)_2CH_2C_6H_5$, $(CH_3C_5H_4)Fe(CO)_2CH_3$ and $(HCO_2C_5H_4)Fe(CO)_2CH_3$ were carried out in the absence of solvent. The reaction was carried out in a steel autoclave.

The starting material was weighed out (0.08 mmol) and placed into a sample vial. The latter was placed in an autoclave which was flushed with nitrogen, evacuated and the process repeated three times. The gaseous ligand was introduced to the evacuated autoclave from a cylinder at a required pressure. Thereafter, the autoclave was placed in an oil bath heated at a pre-set temperature (if heating was required) or kept at room temperature to allow the reaction to proceed. After a pre-determined time, the autoclave was removed from the oil bath, the sample removed from the autoclave and the ^1H NMR spectrum of the sample recorded [18].

Microscopic study

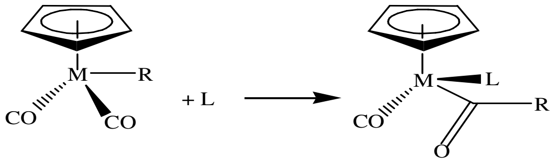
Optical microscopy studies were conducted between $(C_5H_5)Fe(CO)_2CH_3$ and PPh_3.

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, performed under nitrogen. 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 pre-set temperature, while changes in the reactants were monitored and recorded on a PC monitor attached to the camera [27].

RESULTS AND DISCUSSION

Solventless reactions between (C_5H_5)Fe(CO)$_2$CH$_3$ and solid phosphine ligands

The reactions between $(C_5H_5)Fe(CO)_2CH_3$ and a range of phosphine ligands have been carried out in the absence of solvent (1:1 and 1:5 metal/ligand mole ratios at temperatures ranging from 50 °C to 80 °C) to evaluate acetyl complex formation via a migratory-insertion reaction in the absence of solvent (Scheme 1).



Scheme 1. Migratory-insertion reactions.

Solventless reactions of (C_5H_5)Fe(CO)$_2$CH$_3$ and PPh$_3$

$(C_5H_5)Fe(CO)_2CH_3$ and PPh_3 were mixed as described in the experimental procedure. The ^1H NMR spectrum in $CDCl_3$, after mixing, did not reveal any product formation. The mixture was then heated at 80 °C for various times. The insertion was monitored by measurement of the ratio of acyl to (acyl + methyl) peaks in the ^1H NMR spectrum. The conversion of alkyl to the acyl complex as a function of time is shown in Figure 1.

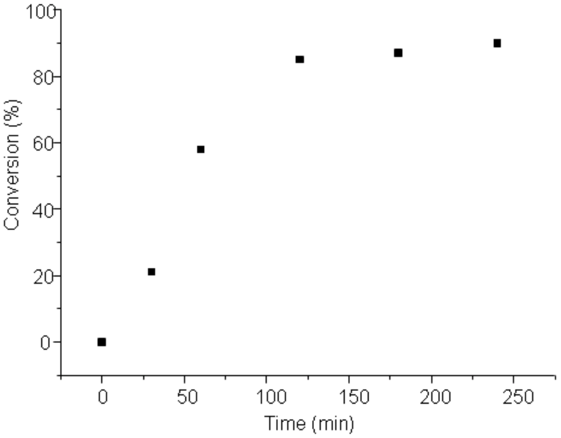
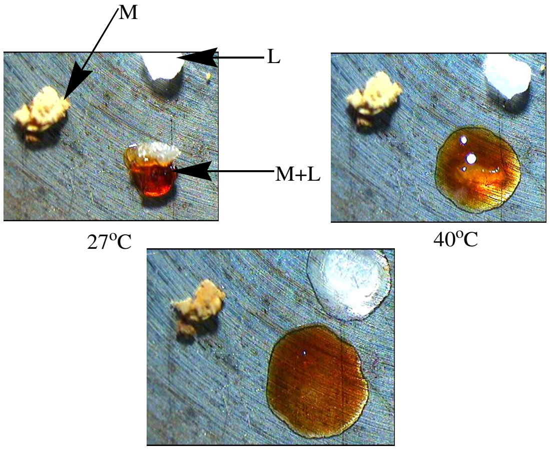


Figure 1. Solventless reaction between $(C_5H_5)Fe(CO)_2CH_3$ and in 1:1 mole ratio to yield $(C_5H_5)Fe(CO)(PPh_3)(COCH_3$.

A microscopic study of the $(C_5H_5)Fe(CO)_2CH_3/PPh_3$ reaction was also undertaken. As can be seen from Figure 2, a melt phase had formed by 40 °C for the case in which $(C_5H_5)Fe(CO)_2CH_3$ (M) and PPh_3 (L) were in contact. It is to be noted that the $(C_5H_5)Fe(CO)_2CH_3$ and PPh_3 melt, respectively at 80 and 78 °C [28, 29]. Therefore, it is clear (as also observed from the NMR tube experiments) that the solventless reaction between $(C_5H_5)Fe(CO)_2CH_3$ and PPh_3 is a melt phase reaction at a temperature above 40 °C [22].



27°C 40°C

80°C

Figure 2. Microscopic pictures of the reaction between $(C_5H_5)Fe(CO)_2CH_3$ and PPh_3. M = $(C_5H_5)Fe(CO)_2CH_3$. L = PPh_3.

The metal/ligand mole ratio was then changed from 1:1 to 1:5 and the solventless reaction carried out at 50 °C, 60 °C and 70 °C for a maximum period of 4 h.

Results are shown in Figure 3. As can be seen from Figure 3, the reaction rate in the melt phase is well behaved since the conversion of reactant into product occurred smoothly with time and temperature.

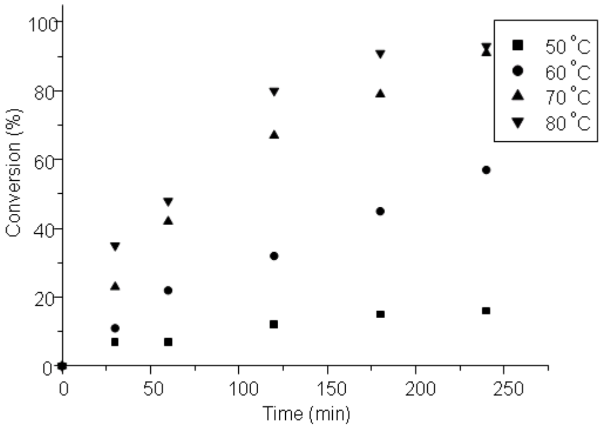


Figure 3. Solventless reaction between $(C_5H_5)F(CO)_2CH_3$ and PPh_3 1:5 mole ratio at different temperatures.

Solventless reactions between (C_5H_5)Fe(CO)$_2$CH$_3$ and a range of phosphine ligands

After the preliminary study using PPh$_3$ as a reference ligand, the solventless reactions of (C_5H_5)Fe(CO)$_2$CH$_3$ were extended to a range of phosphine ligands L (L = PPh$_3$, P(*m*-CH$_3$C$_6$H$_4$)$_3$, P(*p*-CH$_3$C$_6$H$_4$)$_3$, P(*p*-FC$_6$H$_4$)$_3$, P(*p*-ClC$_6$H$_4$)$_3$, PCy$_3$). Some properties of these ligands are presented in Table 1. All the complexes (C_5H_5)Fe(CO)(L)(COCH$_3$) (L = PPh$_3$, P(*m*-CH$_3$C$_6$H$_4$)$_3$, P(*p*-CH$_3$C$_6$H$_4$)$_3$, P(*p*-FC$_6$H$_4$)$_3$, P(*p*-ClC$_6$H$_4$)$_3$, PCy$_3$) have been synthesized and characterized by well established infrared and proton NMR criteria. Further, these complexes have been previously synthesized by solution procedures and our spectroscopic data are in agreement with these other studies [30, 31].

Table 1. Properties of the phosphine ligands used in the study.

Ligand	Melting point (^{o}C))	Electronic effect: ν (cm^{-1}) ^{a}	Steric effect: θ (deg) ^{a}	pK$_a$^{b}
PPh$_3$	78	2068.9	145	2.73
P(*p*-FC$_6$H$_4$)$_3$	80-82	2071.3	145	1.97
P(*p*-ClC$_6$H$_4$)$_3$	100-102	2072.8	145	1.03
P(*p*-CH$_3$C$_6$H$_4$)$_3$	148-150	2066.7	145	3.84
P(*m*-CH$_3$C$_6$H$_4$)$_3$	100-102	2067.2	165	3.30
PCy$_3$	81-82	2056.4	170	9.70

^{a}See ref [32]. ^{b}See ref [31].

The NMR spectra of the complexes clearly show the formation of acetyl complexes with a downfield resonance between 2.36-3.83 ppm for the acetyl protons. Strong metal carbonyl IR absorption at 1906-1921 cm^{-1} was observed for the complexes. The spectroscopic data for the (C_5H_5)Fe(CO)(PR$_3$)(COCH$_3$) products are shown in Table 2.

Table 2. Spectroscopic data for (C_5H_5)Fe(CO)(PR$_3$)COCH$_3$ complexes.

Complexes	^{1}H NMR CDCl$_3$ (δ)			IR (cm^{-1})	
	C$_5$H$_5$	OCH$_3$	CH$_3$CO	νCO	νCOMe
(C_5H_5)Fe(CO)PPh$_3$COCH$_3$ ^{a}	4.41	-	2.31	1915	1595
(C_5H_5)Fe(CO)[P(*p*-FPh)$_3$]COCH$_3$ ^{a,b}	4.41	-	2.34	1918	1605
(C_5H_5)Fe(CO)[P(*p*-ClPh)$_3$]COCH$_3$ ^{a}	4.41	-	2.35	1921	1603
(C_5H_5)Fe(CO)[P(*p*-CH$_3$Ph)$_3$]COCH$_3$ ^{a,b}	4.39	2.39	2.33	1915	1602
(C_5H_5)Fe(CO)[P(*m*-CH$_3$Ph)$_3$]COCH$_3$ ^{a}	4.39	2.36	2.30	1914	1603
(C_5H_5)Fe(CO)(PCy$_3$)COCH$_3$ ^{a}	4.54	-	2.5	1906	1604
(C_5H_5)Fe(CO)$_2$CH$_3$ ^{c}	4.74	0.16	-	2006; 1945	-

^{a}See ref 31. ^{b}see ref 30. ^{c}see ref 25.

A series of solventless reactions were conducted as a function of time using a 1:1 reactants mole ratio at 80 ^{o}C for a maximum period of 4 h. Results at 80 ^{o}C are shown in Table 3.

The results reveal the order of ligand reactivity after a period of 4 h is as follows:

P(*m*-CH$_3$C$_6$H$_4$)$_3$ > P(*p*-FC$_6$H$_4$)$_3$ ~ PPh$_3$ > P(*p*-ClC$_6$H$_4$)$_3$ > P(*p*-CH$_3$C$_6$H$_4$)$_3$ $\geq$ PCy$_3$.

In terms of electronic effects, it appears that these reactions are favored by electron withdrawing ligands. A measure of the electronic effect is the ν_{CO} stretching frequency of the product (C_5H_5)Fe(CO)(L)(COCH$_3$) (Table 2).

For example when the Tolman cone angle, θ is kept constant by changing the substituents only in the *para* position in the PPh$_3$ ligands, the rate of insertion is P(*p*-FC$_6$H$_4$)$_3$ > P(*p*-CH$_3$C$_6$H$_4$)$_3$.

Table 3. Solventless reactions between $(C_5H_5)Fe(CO)_2CH_3$ and PR_3 ligands at 80 °C (1:1 mole ratio).

Ligand	Time (h)	Conversion (%)
PPh_3	0.5	21
	2	85
	4	90
$P(p\text{-}FC_6H_4)_3$	0.5	24
	2	76
	4	91
$P(p\text{-}ClC_6H_4)_3$	0.5	37
	2	82
	4	85
$P(p\text{-}CH_3C_6H_4)_3$	0.5	28
	2	63
	4	70
$P(m\text{-}CH_3C_6H_4)_3$	0.5	38
	2	89
	4	100
PCy_3	0.5	11
	2	47
	4	69

It is clear that these reactions are also influenced by steric properties [30-33]. Hence the ligands with large cone angle, PCy_3 ($\theta = 170^o$) have low reactivity compared to the ligands with small cone angle ($\theta = 145^o$) (Table 1). But $P(m\text{-}CH_3C_6H_4)_3$ with $\theta = 165^o$ is an exception. However, the combined effect of steric and electronic changes show that $(C_5H_5)Fe(CO)_2CH_3$ and the phosphine ligand could react through an electron donor-acceptor interaction, where $(C_5H_5)Fe(CO)_2CH_3$ behaves as donor and phosphine as acceptor [34]. Phosphines with lower pK_a have been found to be more reactive. For instance, $P(m\text{-}CH_3C_6H_4)_3$ (pKa = 3.30) is more reactive than $P(p\text{-}CH_3C_6H_4)_3$ ($pK_a = 3.84$) (Table 1) [34].

By comparing the solventless migratory-insertion reactions for the same reactions carried out in the presence of the solvent, we found that the solventless reactions proceed more rapidly than the solution reactions. For instance Bibler and Wojcicki [15], reported that no reaction occurred between $(C_5H_5)Fe(CO)_2CH_3$ and PPh_3 in refluxing hexane (~70 °C) after a period of 48 h while in refluxing THF (~65 °C), the reaction went to completion after 48 h. Using solventless conditions, we obtained 91 % conversion to product after 4 h at 70 °C (Figure 3) and 57 % conversion after 4 h at 60 °C.

Solventless reactions between substituted cyclopentadienyl iron dicarbonyl complexes and gaseous ligands

Solventless reactions with sulfur dioxide. The solventless reactions between $(RC_5H_4)Fe(CO)_2R'$ (R = H, CH_3, HCO_2; R' = CH_3, $CH_2C_6H_5$) and SO_2 were carried out in an autoclave as described in the experimental section. The pressure of SO_2 was varied from 1 to 3 bar. The conversion of the starting material into product was followed as a function of time.

The starting materials were tested for SO_2 insertion at room temperature and found to give the expected insertion products. As already stated in the introduction, the SO_2 inserted product is the S-sulfinate derivative in which the S atom inserts between the metal and the alkyl or aryl group [13].

Table 4 shows the ^1H NMR data for the SO_2 inserted products. The table shows clearly the effect of the SO_2 group on the protons of the R group attached to the iron center. The chemical shifts for the methyl and benzyl protons in the complexes are moved to lower field than in the parent complexes.

Table 4. ^{1}H NMR data for $R(C_5H_4)Fe(CO)_2SO_2R'$.

Complex	Cp	CH_3Cp	CH_3	CH_2
$(C_5H_5)Fe(CO)_2CH_3$ [a]	4.74	-	0.16	-
$(C_5H_5)Fe(CO)_2SO_2CH_3$ [b, c]	5.19	-	3.09	-
$(C_5H_5)Fe(CO)_2CH_2C_6H_5$ [b, c]	4.64	-	-	2.68
$(C_5H_5)Fe(CO)_2SO_2CH_2C_6H_5$ [b, c]	4.91	-	-	4.23
$CH_3(C_5H_4)Fe(CO)_2CH_3$	4.62; 4.50	1.86	0.11	-
$CH_3(C_5H_4)Fe(CO)_2SO_2CH_3$	4.90; 4.82	2.18	2.17	-

[a] See ref [25]. [b] see ref [15]. [c] see ref [35].

The results of the insertion reactions between $(RC_5H_4)Fe(CO)_2R'$ (R = H, CH_3, HCO_2; R' = CH_3, $CH_2C_6H_5$) and SO_2 are summarized in Table 5. The methyl group attached to iron favors the SO_2 insertion reaction compared with the case in which the benzyl group is attached to iron; this can be explained by the bulkiness of the benzyl group which does not allow facile SO_2 insertion to occur.

Table 5. SO_2 solventless insertion reactions into different substrate at room temperature.

Substrate	Pressure (bars)	Time (h)	Conversion (%)
$(C_5H_5)Fe(CO)_2CH_3$	3	5 min	95
		10 min	100
	1	0.5	3
		1	33
		2	63
		3	80
		4	100
	0.1	10	No reaction
$(C_5H_5)Fe(CO)_2CH_2C_6H_5$	2	0.25	10
		1	47
		2	71
		3	83
		4	93
$CH_3(C_5H_4)Fe(CO)_2CH_3$	1	0.15	100
$HCO_2(C_5H_4)Fe(CO)_2CH_3$	1	6	No reaction

The data in Table 5 reveal the following: SO_2 insertion is concentration dependent, hence the rate of the reaction increases with increase of pressure. The reactivity of the substrate is as follows: $(CH_3C_5H_4)Fe(CO)_2CH_3$ > $(C_5H_5)Fe(CO)_2CH_3$ > $(C_5H_5)Fe(CO)_2CH_2C_6H_5$ > $(HCO_2C_5H_4)Fe(CO)_2CH_3$. These results show that an electron donating group (CH_3) attached to the ring promotes the SO_2 insertion reaction while the electron withdrawing (carboxylic acid CO_2H) inhibits the reaction. This observation is consistent with the proposed mechanism for SO_2 insertion into the alkyl complexes which occurs via an electrophilic process [35]. A backside attack of SO_2 on the α-carbon is proposed to lead to a heterolytic cleavage of the Fe–R' bond to form $[(C_5H_5)Fe(CO)_2O_2S]^+R'^-$. Therefore, it is clear that an electron donating group attached to the ring will enhance the electron releasing ability of the R' group by making the metal less positive thus favoring SO_2 insertion. In contrast an electron withdrawing group on the ring will increase the positive charge on the metal and hence reduce the electron releasing ability of R' which results in a slowing down of the SO_2 insertion reaction rate.

Carbon monoxide insertion reactions

The carbon monoxide insertion reactions in the absence of solvent were also attempted on $(C_5H_5)Fe(CO)_2CH_3$ and $(C_5H_5)Fe(CO)_2CH_2C_6H_5$.

The procedure used is described in the experimental section. The room temperature carbon monoxide insertion at various pressures (5, 10, 20 bar) into $(C_5H_5)Fe(CO)_2CH_3$ did not take place even after a long reaction time (8 h) and at high pressure (P = 30 bar) of the CO. At 80 ^{o}C, only traces (< 1 %) of the products could be observed.

Instead a significant amount of the dimer $[(C_5H_5)Fe(CO)_2]_2$ was formed (30-35 % after 15 h at 20 bar).

The poor carbon monoxide insertion into $(C_5H_5)Fe(CO)_2CH_3$ metal complexes has also been observed in procedures employing solvent [3]. Nevertheless, a relatively easy carbon monoxide insertion into a monocarbonyl complex in which CO was replaced by a stronger base ligand has been reported [3].

CONCLUSIONS

The migratory-insertion reactions between $(C_5H_5)Fe(CO)_2CH_3$ and a range of solid phosphine ligands L (L = PPh_3, $P(m\text{-}CH_3C_6H_4)_3$, $P(p\text{-}CH_3C_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}ClC_6H_4)_3$, PCy_3) have been carried out in the absence of solvent. The rate of the reaction appears to depend on a number of factors, the most important being the steric and the electronic properties of the incoming ligand, i.e. small and electron withdrawing ligands favor the reaction. Compared to the procedures using solvents as a reaction medium, the solventless procedure presents the advantage of giving higher reaction rates.

The solventless insertion reaction of gaseous ligands such as SO_2 and CO into $(C_5H_5)Fe(CO)_2CH_3$, $(CH_3C_5H_4)Fe(CO)_2CH_3$, $(C_5H_5)Fe(CO)_2CH_2C_6H_5$ and $(HCO_2C_5H_4)Fe(CO)_2CH_3$ were explored. The SO_2 insertion reaction appeared to proceed relatively easily and the results could be explained in terms of electronic effects.

From these results, it is clear that the SO_2 insertion is faster than CO insertion.

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