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Metal dimers as catalysts

IX *. The catalysed reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and group 15 donor ligands

Neil J. Coville*, **Elisabeth A. Darling, Andrew W. Hearn and Peter Johnston**

Department of Chemistry, University of the Witwatersrand, Johannesburg 2000 (Republic of South Africa)

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Abstract

The reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ (I) and 1 equivalent of L (group 15 donor ligand) in the presence of catalysts (e.g. $Pd/CaCO_3$, PdO, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (II)) yields $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$ (phosphines, diphosphines, phosphites), $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]I$ (phosphines) and $[(\eta^5\text{-}C_5H_5)Fe(CO)(L\text{–}L)]I$ (diphosphines). $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]I$ can be converted into $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$ in the presence of II. The reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)(PMePh_2)I]$ or $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PMePh_2)]I$ and $PMePh_2$ is also catalysed by II and yields in both instances $[(\eta^5\text{-}C_5H_5)Fe(CO)(PMePh_2)_2]I$. In the series of catalysed reactions the displacement sequence was found to be $PMePh_2 > I^- > CO$.

Introduction

The thermal and photochemical reactions between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2X]$ (X = Cl, Br, I) and group 15 ** donor ligands, L, have been well documented and yield $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)X]$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L)]X$ in varying amounts [1]. Under more forcing conditions the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2X]$ with more than 1 equivalent of L leads to multiply substituted products [2a,2b]. It has been mentioned that occasionally difficulties have been experienced in obtaining reproducible results in the above reactions [3,4], but the factors responsible for these observations have not been established. It should also be mentioned that the room temperature reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and PPh_3 in the presence of equimolar amounts of $[Ni(Et)(PPh_3)(acac)]$ readily yields $[(\eta^5\text{-}C_5H_5)Fe(CO)_2PPh_3]I$ [5].

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* For Part VIII see ref. 22.

** New IUPAC nomenclature.

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In our continuing investigation of the effect of catalysts on the substitution reactions of transition metal carbonyl complexes [6] we wish to report on the reactions between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ (I) and L in the presence of catalysts. A brief mention of the effect of the catalyst $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (II) on the above reaction has been made in the literature [7] and herein we wish to report more fully on the catalysed reactions.

Experimental

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemicals as were most of the group 15 donor ligands. $NMe_3O \cdot 2H_2O$ was obtained from Aldrich Chemicals. $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ [8], $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$ [8], $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3[P(O^iPr)_3]]$ [9] and $AsMe_2Ph$ [10] were synthesized by literature procedures. All reactions were performed in dried, degassed, solvents under nitrogen.

IR and NMR spectra were recorded on a Jasco IRA 1 and a Bruker WP80 spectrophotometer respectively. Mass spectra were recorded on a Varian MAT CH5 spectrometer (operating at 70 eV). Melting point determinations were performed on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratories, CSIR, Pretoria.

Preparation of $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$ ($L = PMe_2Ph$, $PMePh_2$, PPh_3, $P(OMe)_3$, $P(OEt)_3$, $P(O^iPr)_3$, $P(OPh)_3$, $P(Bz)_3$, $PHPh_2$, $AsMe_2Ph$)

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ (310 mg, 1 mmol) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg, 0.03 mmol) were added to benzene (15 ml) and the solution brought to reflux. The ligand (1.1 mmol) was added to this solution and the reaction monitored by changes in the IR spectrum and by thin layer chromatography (silica gel, benzene/hexane mixtures as eluent). At the end of the reaction the solution was cooled, filtered through a cellulose column, concentrated and purified by column chromatography (silica gel packed with hexane, eluent benzene). This procedure separated the required product from starting material and catalyst. Recrystallization of $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$ was achieved from CH_2Cl_2/hexane mixtures. The yellow precipitate which collected on the cellulose column was eluted with CH_2Cl_2, crystallised from CH_2Cl_2/hexane mixtures and characterized as $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]I$. Extended reaction times gave higher yields of the non-salt products. Further experimental details as well as chemical and spectroscopic properties of the iron complexes are given in Tables 1 and 2. Similar reactions were also performed in propionitrile for $L = PMePh_2$ and $P(O^iPr)_3$.

Preparation of $[(\eta^5\text{-}C_5H_5)Fe(CO)(L\text{–}L)]I$ ($L\text{–}L = Ph_2P(CH_2)_nPPh_2$, $n = 1\text{–}4$)

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ (310 mg, 1 mmol) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg, 0.03 mmol) were added to propionitrile (15 ml) and the solution brought to reflux. The diphosphine (1.1 mmol) was added to this solution and the reaction monitored by IR spectroscopy. On completion of the reaction, the solution was cooled, solvent evaporated and the product isolated by column chromatography (silica gel; benzene eluent). Recrystallisation from CH_2Cl_2/hexane yielded the required product.

Preparation of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PMePh_2)_2]I$ from $[(\eta^5\text{-}C_5H_5)Fe(CO)(PMePh_2)I]$ and $PMePh_2$

$[(\eta^5\text{-}C_5H_5)Fe(CO)(PMePh_2)I]$ (510 mg, 1 mmol), $PMePh_2$ (210 mg, 1.1 mmol)

Table 1

Experimental and analytical data for the iron complexes

Complex	Reaction time (min)	Yield (%)	M.p. (°C)	Analyses (Found (calc.) (%))		
				C	H	I
$[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$ L =						
PMe_2Ph	30	70	103–105	40.11	3.80	29.10
				(40.62)	(3.90)	(30.65)
$PMePh_2$	20	80	142–144	47.34	3.68	24.39
				(47.94)	(3.81)	(26.65)
PPh_3	60	80	173–175	53.41	3.82	23.04
				(53.56)	(3.75)	(23.58)
$P(OMe)_3$	5	60	120–124	27.29	3.51	33.36
				(27.03)	(3.53)	(31.73)
$P(OEt)_3$	15	60	36–38			
$P(O^iPr)_3$	10	70	121–123			
$P(OPh)_3$	30	80	145–147	49.42	3.39	23.25
				(49.18)	(3.44)	(21.65)
$P(Bz)_3$	25	60	173–175			
$PHPh_2$	5	70	–			
$AsMe_2Ph$	420	40	86–87	36.87	3.50	26.67
				(36.72)	(3.52)	(27.71)
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]I$ L =						
PMe_2Ph	10	75	145–147	42.10	3.98	
				(40.76)	(3.65)	
$PMePh_2$	10	60	191–193	47.78	3.50	25.10
				(47.66)	(3.60)	(25.17)
PPh_3	120	40	205	52.75	3.41	
				(53.04)	(3.57)	
$AsMe_2Ph$	180	20	105–106	35.90	3.32	26.98
				(37.07)	(3.32)	(26.11)
$[(\eta^5\text{-}C_5H_5)Fe(CO)(L)_2]I$ L =						
$PMePh_2$	40	80	228–230	55.20	4.31	
				(56.83)	(4.62)	
$AsMe_2Ph$	450	20	155–157	40.21	4.07	
				(41.29)	(4.25)	
$\frac{1}{2}$1,1-diphos	30	60	130–135	56.01	4.01	
				(56.39)	(4.12)	
$\frac{1}{2}$1,2-diphos	10	70	134–140	55.91	4.23	19.64
				(57.00)	(4.34)	(18.82)
$\frac{1}{2}$1,3-diphos	20	60	dec.	56.82	4.30	
				(57.58)	(4.54)	
$\frac{1}{2}$1,4-diphos	30	60	dec.	57.11	4.23	
				(58.15)	(4.74)	

and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) were added to benzene (15 ml) and the solution brought to reflux. Over a period of 20 min the solution lost its green colour and a heavy yellow precipitate formed. The solution was cooled, filtered through cellulose and crystallised from CH_2Cl_2/hexane to give the required product (80% yield).

Table 2

IR and ^{1}H NMR data for the iron complexes

Complex	IR (ν(CO); cm^{-1}) [a]	NMR (δ, ppm; J in Hz) [b,c,d]	
		C_5H_5	CH_3 or CH_2
[(η^5-C_5H_5)Fe(CO)(L)I] L =			
PMe_2Ph	1950	4.38(1.6)	d 2.17(10.0); d 1.77(9.5)
$PMePh_2$	1952	4.45(1.4)	d 2.17(9.3)
PPh_3	1957	4.47(1.4)	–
$P(OMe)_3$	1967	4.71(0.9)	d 3.73(11.1)
$P(OEt)_3$	1961	4.68(0.8)	q 4.10(7.0); t 1.31(7.0)
$P(O^iPr)_3$	1960	4.64(1.0)	d 1.31(6.1), d 1.30(6.1) [e]
$P(OPh)_3$	1984	4.18(0.9)	–
$P(Bz)_3$	1949	3.76(0.9)	d of q: 3.57(J(HH) 14, J(PH) 7.4)3.30(J(HH) 14.6, J(PH) 10.2)
$PHPh_2$	1957	4.12 [k]	d 7.10(J(PH) 369)
$AsMe_2Ph$	1952	4.45	1.93; 1.60
$AsPh_3$	1956	3.96	–
[(η^5-C_5H_5)Fe(CO)$_2$L]I L =			
PMe_2Ph	2052,2008	5.53(1.6)	d 2.30(10.9)
$PMePh_2$	2050,2004	5.53(1.6)	d 2.64(10.2)
PPh_3	2045,2005	5.50(1.4)	–
$AsMe_2Ph$	2050,2000	5.58	2.24
1,2-diphos	2049,1998	5.31(1.1)	1.78
[(η^5-C_5H_5)Fe(CO)(L)$_2$]I L =			
$PMePh_2$	1964	5.01(1.6) [f]	1.57 [g]
$AsMePh_2$	1962	4.96	1.78; 1.63
$\frac{1}{2}$1,1-diphos	1982	4.96(1.4) [f]	d of t at 5.61, 4.17 [h]
$\frac{1}{2}$1,2-diphos	1980	4.87(1.2) [f]	~ 2.7
$\frac{1}{2}$1,3-diphos	1966	4.80(1.3) [f]	2.88, t 2.14 (J ~ 12), 1.73 [i]
$\frac{1}{2}$1,4-diphos	1967	4.56(1.3) [f]	2.86, 2.47, 1.81 [j]

[a] Recorded in $CHCl_3$. [b] Recorded in $CDCl_3$ (relative to TMS); J(PH) in brackets unless otherwise stated. [c] d = doublet, t = triplet, q = quartet. [d] Phenyl absorbtions broad and complex at ±7.5. [e] CH: doublet of septets 4.75 (J(HH) 6.0, J(PH) 8.9 Hz). [f] C_5H_5 couples to both P atoms to give a resonance triplet. [g] Virtual triplet; ref. 32. [h] 5.61 (J(PH) 16.2, J(HH) 10.6 and 12.1 Hz); 4.17 (J(HH) 16.2, J(PH) 12.1 Hz). [i] Broad resonances, ratio 1/1/1. [j] Broad resonances, ratio 1/1/2. [k] Recorded in C_6D_6.

Preparation of [(η^5-C_5H_5)Fe(CO)($PMePh_2$)$_2$]I from [(η^5-C_5H_5)Fe(CO)$_2$($PMePh_2$)]I and $PMePh_2$

[(η^5-C_5H_5)Fe(CO)$_2$($PMePh_2$)]I (510 mg, 1 mmol), $PMePh_2$ (215 mg, 1.1 mmol) and [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ (10 mg) were added to benzene (15 ml) and the solution brought to reflux. The reaction was monitored by IR spectroscopy. This was achieved by recording the IR spectra of the material in CH_2Cl_2 after benzene evaporation of small aliquots of the heterogeneous solution. After 40 min the reaction was complete and recrystallisation from CH_2Cl_2/hexane gave the yellow salt in 70% yield.

Table 3

Crossover experiments involving $P(O^iPr)_3$ [a]

Reactants	Products	Comments
$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3[P(O^iPr)_3]]$ $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I]$	$[(\eta^5\text{-}C_5H_5)Fe(CO)[P(O^iPr)_3]I]$ $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2(\eta^5\text{-}C_5H_5)Fe(CO)_2]$	5 min
$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3[P(O^iPr)_3]]$ $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$	$[(\eta^5\text{-}C_5H_5)Fe(CO)[P(O^iPr)_3]I]$ $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	5 min
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ $[(\eta^5\text{-}C_5H_4Me)Fe(CO)[P(O^iPr)_3]I]$ [b]	-	no reaction 12 h
$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2$ $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(O^iPr)_3]I]$	-	no reaction 12 h

[a] Reaction conditions: Reactants (0.3 mmol), benzene (15 ml reflux). [b] For synthesis see ref. 33.

Catalysed conversion of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PMePh_2)]I$ to $[(\eta^5\text{-}C_5H_5)Fe(CO)(PMePh_2)I]$

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PMePh_2)]I$ (510 mg, 1 mmol) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (10 mg) were added to benzene (15 ml) and the solution brought to reflux. The solution turned green and the yellow precipitate dissolved. After 2 h the reaction was stopped, and the two products isolated as described above for the direct reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and $PMePh_2$. 85% conversion was achieved.

NMe_3O induced conversion of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PMePh_2)]I$ to $[(\eta^5\text{-}C_5H_5)Fe(CO)(PMePh_2)I]$

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PMe_2Ph)]I$ (510 mg, 1 mmol) was dissolved in CH_2Cl_2 (15 ml) and to this was added $NMe_3O \cdot 2H_2O$ (250 mg, 2.3 mmol). The reaction solution rapidly turned green. After 5 min the reaction was quenched with water, the solution then dried with $MgSO_4$ and the product isolated as described previously (60% yield).

Crossover experiments

Dimer (0.3 mmol) and monomer (0.3 mmol) (Table 3), were added to benzene (15 ml) and the solution was heated to 85 °C. The reactions were monitored by IR spectroscopy and by thin layer chromatography (silica gel; benzene/hexane mixtures as eluent). At the end of the reaction, the products were separated by column chromatography and product characterization was achieved by IR and NMR spectroscopy.

Discussion

Reaction with phosphines

The thermal reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ (I) and L has been reported to yield both $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L)]I$ in varying yields [1]. We have repeated the above reaction in benzene with a range of L (e.g. $L = PPh_3$, $PMePh_2$, $P(Bz)_3$, $PHPh_2$, $AsPh_3$) and confirm that a reaction does occur in which a green solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I]$ and a yellow precipitate of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L)]I$ are formed. The products can readily be separated by filtration through a cellulose column.

Attempts were then made to catalyse the above reactions using transition metals or their complexes. The reaction

$$\underset{\text{(I)}}{[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]} + PMePh_2 \rightarrow \underset{\text{(III)}}{[(\eta^5\text{-}C_5H_5)Fe(CO)(PMePh_2)I]}$$
$$+ \underset{\text{(IV)}}{[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PMePh_2)]I}$$

was chosen as a standard reaction (benzene as solvent) to screen potential catalysts. Catalysis of the above reaction was observed for a range of supported transition metals. These included Pd/$CaCO_3$ (5%), Pd/Al_2O_3 (5%) and Pd/$BaSO_4$ (5%). PdO was also found to catalyse the reaction. In every instance a rapid reaction occurred to give ±30% III and ±70% IV. Catalysis using iron dimers (e.g. II or $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2$) was also observed. Consideration of the data suggested that II would be suitable for further study and consequently was used to catalyse the reaction between I and a range of phosphines'(and $AsMe_2Ph$). The results of this study are shown in Table 1. No catalysis using II was observed for the reaction between I and $AsPh_3$ (8 h). Also, no reaction was observed between $SbPh_3$ or PPh_2Cl and I (24 h, refluxing benzene).

The products from the catalysed reaction were characterized by elemental analyses, mass spectra, IR and NMR spectroscopy. The IR and NMR spectra of these types of complexes have been commented on previously and need no further discussion [11,12]. In all instances the spectroscopic data recorded on products from the catalysed and uncatalysed reactions were identical.

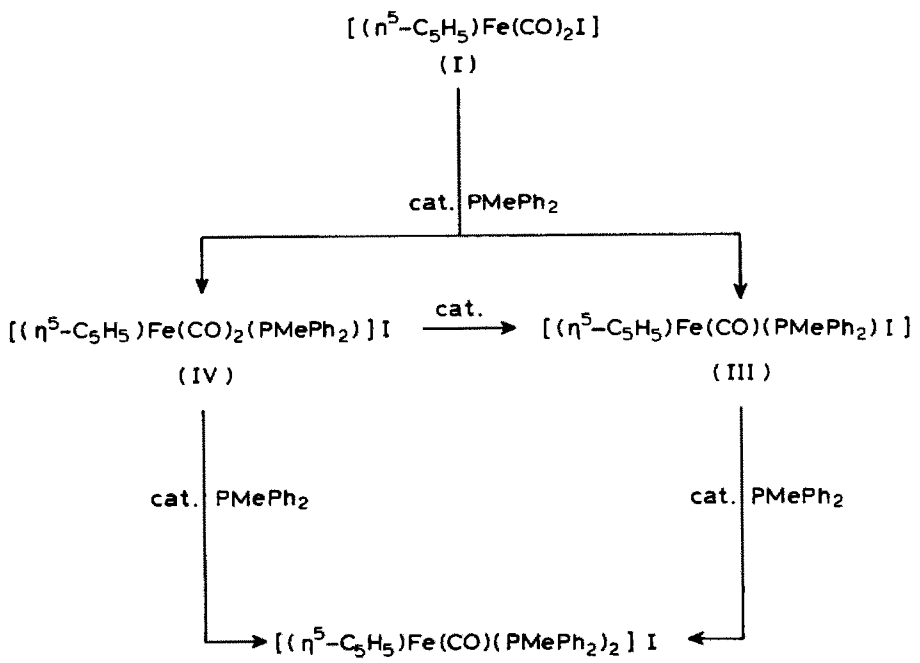
Extended reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and $PMePh_2$, in the presence of II, was found to change the product ratio such that after 2 h the ratio of III to IV was found in an 85 to 15 ratio. In an independent reaction, IV and catalytic amounts of II were heated together (benzene, 80 ° C, dark) and excellent conversion to III (80%, 60 min) was observed. The qualitative rate data suggest that *both* II and IV are primary products in the catalysed reaction [13]. No reaction occurred in the absence of catalyst. A slow reaction did however occur in daylight (absence of catalyst) and is consistent with a report on related reactions of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2X]$ with PMe_3 [25]. We have also observed that IV slowly converts to III in the solid state if IV is exposed to sunlight. Unless strict precautions are taken to control these two effects variable ratios of III and IV are always obtained and these effects could explain the irreproducible results previously reported for these reactions [3,4].

An alternative and more rapid method for converting IV to III is via an NMe_3O-CO oxidation route in CH_2Cl_2 [6,14]. Thus a rapid conversion of IV to III was observed (solution colour changes; IR spectroscopy) in the presence of NMe_3O, similar to results described previously for related reactions [15,16].

The reaction between either III or IV and $PMePh_2$ was also catalysed by II (benzene, 80 ° C). In both reactions the final product was found to be $[(\eta^5\text{-}C_5H_5)Fe(CO)(PMePh_2)_2]I$ which was characterized by IR and NMR spectroscopy.

The catalysed reactions between I and $PMePh_2$ are summarized in Scheme 1.

This series of catalysed reactions indicates that the reaction product depends on the attacking ligand with displacement sequence $PMePh_2 > I^- > CO$. The nucleophilic properties of the ligand cannot be the only factor determining the



Scheme 1

reaction sequence as the reaction between I and amines [17] was not found to be catalysed by II.

Since the catalysed reaction between I and phosphine, in benzene, produced salt products (e.g. IV) difficulties were experienced in monitoring the progress of the reaction. Consequently propionitrile (or the lower boiling acetonitrile) was used as a solvent in the catalysed reaction between I and $PMePh_2$ to establish whether any advantages could be derived from working with a homogeneous reaction mixture. (The salts were insoluble in THF). The reactions between I, III or IV and $PMePh_2$ were found to be catalysed by II (but not by $Pd/CaCO_3$). The conversion of IV to III was not however catalysed to any great extent ($< 10\%$) by II (not at all by $Pd/CaCO_3$). Thus, although the reaction is more readily monitored in a polar solvent, not all the reactions are catalysed in propionitrile. The reaction in propionitrile does however provide further information on the formation of two non-interconverting primary products in the above reaction.

Reaction with phosphites

The reaction between I and phosphites has also been investigated in some detail and both thermal and photochemical routes have been used to synthesize a wide range of iron substituted derivatives [2a,2c]. We have carried out the reaction between I and the phosphites $P(OMe)_3$, $P(OEt)_3$, $P(O^iPr)_3$ and $P(OPh)_3$ in both the absence and the presence of potential catalysts. Some of our results are reported in Table 4 and indicate that a rapid reaction occurs between the reactants in the presence of Pd or iron dimer complexes. The results are summarized below:

(*i*) No disubstituted products were detected by IR spectroscopy even on extended heating in the presence of excess phosphite e.g. $P(O^iPr)_3$.

Table 4

Effect of catalysts on the synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)[P(OR)_3]I]$ [a]

Phosphite	Catalyst	Reaction time (min) [b]	Phosphite	Catalyst	Reaction time (min) [b]
$P(O^iPr)_3$	–	180 (5(%) [c]	$P(OMe)_3$	–	45 (< 5%) [e]
	$Pd/CaCO_3$ (5%)	5		$Pd/CaCo_3$ (5%)	8
	Pd/Al_2O_3 (5%)	5		II	<10
	PdO	5	$P(OEt)_3$	II	15
	$Mn_2(CO)_{10}$	– [d]	$P(OPh)_3$	II	30
	II	10		$[(C_5Me_5)Fe(CO)_2]_2$	– [d,f]
	$[(C_5Me_5)Fe(CO)_2]_2$	20			

[a] Reaction conditions: I (0.5 mmol), phosphite (0.52 mmol), benzene (10 ml), reflux; catalyst (10 mg). [b] Reaction monitored by IR spectroscopy. The reaction was stopped either when gas evolution had ceased or when the ν(CO) bands in the IR spectrum remained constant. [c] < 5% reaction. [d] No catalysis. [e] Ref. 13, 24 h (75%). [f] Reaction in refluxing toluene.

(*ii*) No salt formation was observed.

(*iii*) The phosphite derivatives were characterized by elemental analyses and IR and NMR spectroscopy. All data are in agreement with the product formulation and previously reported data on these complexes, and do not suggest the formation of complexes, formed via ligand breakdown [13,18].

(*iv*) The results (product yield, reaction rate) [19] for the synthesis of the phosphite derivatives compare favourably with the alternative synthetic routes reported to date.

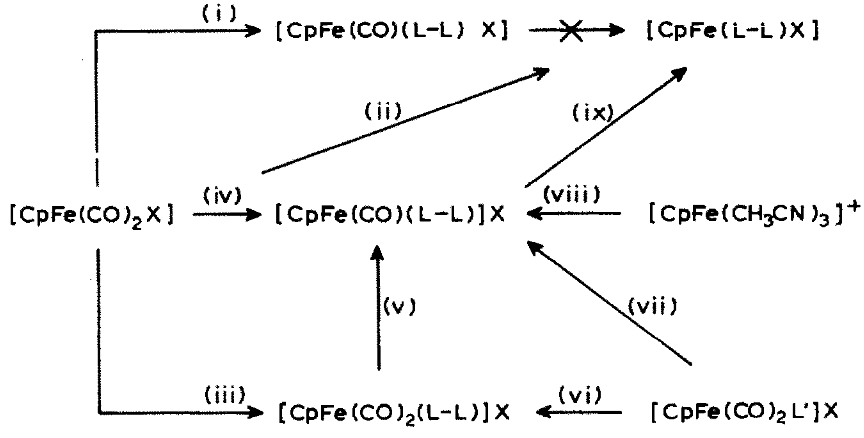
Crossover experiments were performed to obtain information on the relative rates of ligand transfer (Table 3). $P(O^iPr)_3$ was chosen as the ligand for this study since no salts are formed in the reactions and the substituted iron dimer $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3[P(O^iPr)_3]]$ is stable at 80 °C [9]. These reactions indicate that rapid scrambling between reactants occurs in which the driving force is the production of a substituted monomer and an unsubstituted dimer. This reaction confirms the presence of the radicals $[(\eta^5\text{-}C_5H_5)Fe(CO)(L)]^{\cdot}$ ($L = CO$, $P(O^iPr)_3$) being present in solution [20]. However, the synthesis of the substituted dimer $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3[P(O^iPr)_3]]$ is extremely slow in refluxing benzene (5% reaction 1 h; 70% 24 h) [9] and implies that substitution of a radical viz.:

$$\left[(\eta^5\text{-}C_5H_5)Fe(CO)_2\right]^{\cdot} + P(O^iPr)_3 \rightarrow \left[(\eta^5\text{-}C_5H_5)Fe(CO)P(O^iPr)_3\right]^{\cdot} + CO$$

would be rate-limiting for a reaction involving phosphite transfer between a dimer and a monomer, as implied by the data in Table 3. It is still however unclear as to whether the reaction occurs via an alternative radical mechanism or an electron transfer process [6,21].

Reaction with diphosphines

The reaction between I and diphosphines has been well documented and a range of monometallic and bridged species can be formed under suitable conditions [1]. It appears that salts, $[(\eta^5\text{-}C_5H_5)Fe(CO)(L\text{–}L)]^+$ (L–L = diphosphine), are almost exclusively formed from the reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2X]$ and L–L, and not unexpectedly, routes starting from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2L']^+$ (L′ = readily displaced ligand) also yield the same products [16,27b]. A summary of routes, to the



Scheme 2. Cp = cyclopentadiene, L–L = diphosphine, L′ = readily displaced ligand. (i) this work, [23]; (ii) [24]; (iii) [28,29]; (iv) [9,25,26,28,29]; (v) [27a]; (vi) [16,27b]; (vii) [16,27b]; (viii) [30]; (ix) [31].

unbridged iron-diphosphine complexes, which have been reported in the literature, are shown in Scheme 2.

We have carried out an investigation of the use of catalysts on the reaction between I and diphosphines to establish whether increased yields can be obtained for some of the pathways indicated in Scheme 2. A number of metals and metal complexes were screened for catalysis and the results of this study, using $Ph_2PCH_2CH_2PPh_2$ as ligand are indicated in Table 5. It can be seen that the thermal (blank) reaction gives the iron substituted product slowly under the reaction conditions whereas in the presence of either Pd supported catalysts or II the disubstituted products are rapidly formed. II was found to catalyse the reaction between I and a range of diphosphines of the type $Ph_2P(CH_2)_nPPh_2$ ($n = 1–4$) and details of the reactions are shown in Table 6.

The reaction between the diphosphines was monitored by IR spectroscopy and in every reaction the appearance of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L–L)]I$ was readily identified in the IR spectrum (ν(CO) 2050, 2000 cm^{-1}). This complex was isolated in low yield from a reaction between I and L–L = 1,2-diphos (CH_3CN, reflux, 5 min, II as

Table 5

The reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and $Ph_2PCH_2CH_2PPh_2(L–L)$ [a]

Catalyst	Reaction time (min)	Comments
–	210	90% $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L–L)]I$
II	15	$[(\eta^5\text{-}C_5H_5)Fe(CO)(L–L)]I$
II	10 [b]	$[(\eta^5\text{-}C_5H_5)Fe(CO)(L–L)]I$
$Pd/CaCO_3$ (5%)	10	$[(\eta^5\text{-}C_5H_5)Fe(CO)(L–L)]I$
Pd/C (5%)	60	$[(\eta^5\text{-}C_5H_5)Fe(CO)(L–L)]I$
Pt/C (5%)	200	no catalysis
$CoCl_2$	200	no catalysis

[a] Reaction conditions: 1,2-diphos (1 mmol), I (1 mmol), CH_3CH_2CN (15 ml), catalyst (10 mg), temperature (reflux). [b] Solvent = benzene.

Table 6

The reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2I]$ and diphosphine ligands [a]

diphos [c]	Reaction time (min) [b]	
	blank	cat.
1,1-diphos	210 (25%)	20
1,2-diphos	210 (40%)	10
1,3-diphos	120 (5%)	10
1,4-diphos	200 (25%)	30

[a] Reaction conditions as in Table 5. [b] % reaction as estimated by IR spectroscopy shown in brackets. [c] diphos = $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ to 4).

catalyst) and spectroscopic properties for this complex are given in Table 2. However, at the end of the reaction a strong $\nu(CO)$ absorption at 1950 cm^{-1} was observed, which corresponds to $[(\eta^5\text{-}C_5H_5)Fe(CO)(L\text{-}L)]I$. The products were purified by column chromatography. Small amounts of starting material, unreacted catalyst and a green complex were also obtained during the purification procedure. The green complex was not obtained pure but its IR spectrum ($\nu(CO)$ 1950 cm^{-1}) suggested it to be either $[(\eta^5\text{-}C_5H_5)Fe(CO)(L\text{-}L)I]$ or $[(\eta^5\text{-}C_5H_5)Fe(CO)I]_2(L\text{-}L)]$ [9]. The yellow diphosphine salts were characterized by IR and NMR spectroscopy and data are consistent with the product formulation $[(\eta^5\text{-}C_5H_5)Fe(CO)(L\text{-}L)I$ [1].

The catalysed reaction between I and 1,2-diphos in benzene gave a 1/3 ratio of mono- to di-substituted product which precipitated from solution. Further reactions to convert the monosubstituted product to the disubstituted product in the presence of catalyst was slow. This would suggest that in benzene as solvent a competing reaction involving displacement of CO or I^- is taking place; consistent with the reactivity pattern established with the phosphines.

Alternative procedures to obtain pure $[(\eta^5\text{-}C_5H_5)Fe(CO)(L\text{-}L)]I$ from the above mixture in benzene were attempted and found to be successful viz.:
(*i*) Thermal catalysed reaction of the mixture in propionitrile.
(*ii*) Addition of NMe_3O to a CH_2Cl_2 solution of the mixture.

Under the mild reaction conditions $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(L\text{-}L)]I$ reacted with NMe_3O to give $[(\eta^5\text{-}C_5H_5)Fe(CO)(L\text{-}L)I]$ and so a facile separation of the salt from the green non-salt product was feasible [16]. This method indirectly provides a source of the difficult to obtain "dangling phosphine" complex $[(\eta^5\text{-}C_5H_5)Fe(CO)(L\text{-}L)I]$ albeit in low yield.

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