Journal of Organometallic Chemistry, 232 (1982) 261—266
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

METAL DIMERS AS CATALYSTS

III *. THE REACTION BETWEEN $Fe(CO)_5$ AND GROUP V DONOR LIGANDS IN THE PRESENCE OF $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ (R = H, Me) AND $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ AS CATALYST *

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(Received January 19th, 1982)

Summary

The reaction between $Fe(CO)_5$ and Group V donor ligands L, (L = PPh_3, $AsPh_3$, $SbPh_3$, $PMePh_2$, PMe_2Ph, $AsMe_2Ph$, $P(C_6H_{11})_3$, $P(n\text{-}Bu)_3$, $P(i\text{-}Bu)_3$, $P(OPh)_3$, $P(OEt)_3$, $P(OMe)_3$) in the presence of $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ (R = H, Me) or $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ as catalyst in refluxing toluene, rapidly gives the complexes $Fe(CO)_4L$ in yields >85%. The reaction rate is essentially independent of the nature of L for $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ as catalyst. For the other catalysts, the rate is influenced predominantly by the steric properties of L. These results are interpreted in terms of the interaction between the catalyst and the ligand L to give derivatives of the type $(\eta^5\text{-}C_5H_4R)_2Fe_2(CO)_3(L)$. These derivatives were also found to catalyse the reaction between $Fe(CO)_5$ and L. The complexes $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ (R = H, Me) and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ also catalyse the reaction between $Mn_2(CO)_{10}$ and PPh_3 to give $Mn_2(CO)_8(PPh_3)_2$ in >80% yield.

Introduction

Recently we reported that the reaction between $Fe(CO)_5$ and Group V donor ligands, L, to give $Fe(CO)_4L$ is catalysed by CoX_2 (X = Cl, Br, I) [3]. Although excellent yields were obtained for L = PPh_3, $AsPh_3$ and $SbPh_3$, we

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* For Parts I and II see refs. 1 and 2, respectively.

0022-328X/82/0000—0000/$02.75

found that for certain ligands e.g. $P(OMe)_3$, little or no product formation was observed under our reaction conditions. The possibility of using $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and related ring substituted derivatives as catalysts for the synthesis of $Fe(CO)_4L$ complexes was suggested by our recent finding that $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ catalyses the synthesis of $Fe(CO)_4RNC$ (RNC = isonitrile) from $Fe(CO)_5$ and RNC [2]. Herein we report our results on the facile, high yield synthesis of $Fe(CO)_4L$ derivatives, with a range of phosphine and phosphite ligands L, using cyclopentadienyliron dicarbonyl dimers as catalysts.

Experimental

$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2$ and $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ were prepared by published procedures [4]. The complex $[(\eta^5\text{-}C_5H_4CO_2Me)Fe(CO)_2]_2$ was similarly synthesised from $Fe(CO)_5$ and $C_5H_5CO_2Me$ in octane under reflux. The Group V donor ligands were obtained from various sources. $Fe(CO)_5$ (Strem Chemicals) was used as purchased. Toluene was distilled from sodium under a blanket of nitrogen before use, and all reactions were carried out in an inert atmosphere. IR spectra were recorded on a Pye Unicam SP300 spectrophotometer, and mass spectra were obtained using a Varian Mat CH5 spectrometer (operating at 70 eV).

Reaction between $Fe(CO)_5$ and L

$Fe(CO)_5$ (1.96 g, 10 mmol) and catalyst (0.1 mmol) were added to a 2-necked reaction flask containing toluene (10 ml). The solution was heated to reflux and L (5 mmol) added to the reaction mixture. The reaction was monitored by IR spectroscopy and heating continued until the reaction had gone to completion. Solvent was removed in vacuo together with excess $Fe(CO)_5$, to give near quantitative yields of the product, $Fe(CO)_4L$ (Table 1). The $Fe(CO)_4L$ complexes were purified by column chromatography [3] followed by recrystallisation (where applicable).

Preparation of $Mn_2(CO)_8(PPh_3)_2$

$Mn_2(CO)_{10}$ (3 mmol), PPh_3 (6.0 mmol) and catalyst $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ (R = H, Me) or $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ (0.1 mmol) were heated together in toluene (10 ml) under reflux. The course of the reaction was monitored by IR spectroscopy until complete conversion of $Mn_2(CO)_{10}$ to $Mn_2(CO)_8(PPh_3)_2$ had occurred. At the end of the reaction, the solvent was removed in vacuo, and column chromatography, followed by recrystallisation (benzene/hexane mixtures), gave the required product in >80% yield.

Results and discussion

Addition of catalytic amounts of $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ (R = H, Me) or $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ to $Fe(CO)_5$ and a Group V donor ligand in refluxing toluene results in the rapid formation of $Fe(CO)_4L$. The results are recorded in Table 1. The complexes were all characterized by IR spectroscopy and mass spectrometry and the data for the three complexes, not reported in our previous publication [3], are given in Table 2.

TABLE 1

EXPERIMENTAL DATA FOR THE REACTION BETWEEN $Fe(CO)_5$ AND GROUP V DONOR LIGANDS IN THE PRESENCE OF IRON DIMER AS CATALYST

	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$		$[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2$		$[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$	
	Yield (%)	Time (h) [a]	Yield (%)	Time (h) [a]	Yield (%)	Time (h) [a]
$Fe(CO)_4PPh_3$	90	5.0	87	5.0	97	1.25
$Fe(CO)_4AsPh_3$	88	5.0	88	3.0	94	1.25
$Fe(CO)_4SbPh_3$	92	2.75	96	2.0	97	1.25
$Fe(CO)_4PMePh_2$	98	1.75	98	1.25	96	1.25
$Fe(CO)_4PMe_2Ph$	93	0.5	96	0.5	91	1.25
$Fe(CO)_4AsMe_2Ph$	97	2.5	95	2.25	98	1.25
$Fe(CO)_4P(C_6H_{11})_3$	69	5.0	93	3.5	90	1.50
$Fe(CO)_4P(n\text{-}Bu)_3$	98	1.0	98	2.0	93	1.25
$Fe(CO)_4P(i\text{-}Bu)_3$	93	3.75	97	3.25	87	1.25
$Fe(CO)_4P(OPh)_3$	93	4.0	95	4.0	94	1.50
$Fe(CO)_4P(OEt)_3$	93	1.5	93	0.5	90	1.25
$Fe(CO)_4P(OMe)_3$	83	0.75	92	0.5	86	1.50

[a] Determined by IR spectroscopy.

The complexes, as formed, are all discoloured by the small amount (~2%) catalyst used in the reaction. This contaminant may be removed by repeated crystallisation or by column chromatography.

A comparison of the data in Table 1 with our previously reported results for cobalt(II) halide catalysts [3], indicate that the latter are superior catalysts for the synthesis of $Fe(CO)_4L$ (L = PPh_3, $AsPh_3$, $SbPh_3$, $PMePh_2$, $P(OPh)_3$). However, the dimeric iron catalysts readily give $Fe(CO)_4L$ (L = $P(n\text{-}Bu)_3$, $P(OMe)_3$, $P(OEt)_3$] in excellent yield, thus complementing the use of cobalt(II) halides as catalysts for the replacement of CO by Group V donor ligands on $Fe(CO)_5$.

From Table 1 it can be seen that the catalysed CO substitution of $Fe(CO)_5$ by L, in the presence of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ as catalyst, is qualitatively ligand independent whereas for the catalysts $[(\eta^5\text{-}C_5H_4R)Fe(CO)_2]_2$ (R = H, Me) a marked ligand dependence is observed. These ligand dependent reactions could arise from either an associate mechanism or through a prior catalyst—ligand interaction.

The nature of the catalyst—ligand interaction probably takes the form of a ligand substitution reaction on the catalyst. Indeed, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ is known to react with Group V donor ligands, L, in benzene at 80°C to yield

TABLE 2

IR AND MASS SPECTRAL DATA FOR $Fe(CO)_4L$ (L = $AsMePh_2$, $P(i\text{-}Bu)_3$, $P(OMe)_3$)

	IR (cm^{-1}) [a]			Mol. mass [b,c]
$Fe(CO)_4AsMe_2Ph$	2039	1970	1937	350 (349.99)
$Fe(CO)_4P(i\text{-}Bu)_3$	2037	1970	1934	370 (370.22)
$Fe(CO)_4P(OMe)_3$ [d]	2053	1986	1949	292 (291.97)

[a] Recorded in $CHCl_3$. [b] Determined by mass spectrometry. [c] Found, calculated in parentheses. [d] Ref. 11.

$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(L)$, but quantitative data have as yet not been reported for this reaction [5]. Thus, for instance, the poor results obtained for the catalysed synthesis of $Fe(CO)_4PPh_3$ may arise from the facile synthesis and subsequent decomposition of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3PPh_3$ in refluxing toluene. This substituted dimer decomposes at ~50°C and is normally synthesized via photochemical techniques at room temperature [5].

Investigation of the catalyst during the reaction between $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, $P(OMe)_3$ and $Fe(CO)_5$ has revealed the presence of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3P(OMe)_3$ in the reaction mixture. This complex, prepared independently from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $P(OMe)_3$ [5], was also shown to catalyse the reaction between $Fe(CO)_5$ and $P(OMe)_3$. Thus, the addition of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3P(OMe)_3$ (0.1 mmol) as catalyst to $Fe(CO)_5$ (10 mmol) and $P(OMe)_3$ (5 mmol) in refluxing toluene (10 ml) gives an identical product yield and reaction time as that observed for the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ catalysed reaction. Similar results have been observed for other phosphine and phosphite ligands.

From a consideration of ligand cone angles [6] and ligand electronic parameters [6] it is apparent that for the catalyst $[(\eta^5\text{-}C_5H_5R)Fe(CO)_2]_2$ (R = H, Me), an approximate correspondence between the reaction time for the CO substitution of $Fe(CO)_5$ and the ordering of the ligands according to their cone angles exists. Thus, for $[(\eta^5\text{-}C_5H_4Me)Fe(CO)_2]_2$ as catalyst, the reaction rate varies with L, $P(OMe)_3 \sim P(OEt)_3 \sim PMe_2Ph > PMePh_2 > SbPh_3 \sim P(n\text{-}Bu)_3 > AsMe_2Ph > AsPh_3 > P(i\text{-}Bu)_3 > P(C_6H_{11})_3 > P(OPh)_3 > PPh_3$. This ordering suggests that, in general, the smaller the ligand cone angle the faster the substitution reaction.

The above observed effect could arise from the attack of L at $Fe(CO)_5$ (an associative mechanism), the interaction of L with the catalyst, or both factors. On the other hand, the ligand independence observed for $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ as catalyst suggests that the catalyst is not modified in the reaction i.e. via CO substitution. However, the results do not serve to distinguish between an associative * or dissociative mechanism (Fig. 1). (Quantitative data on the reaction are, as yet, not available and thus do not allow us to decide between the two possibilities).

The reaction rate for the CO substitution reaction of $Fe(CO)_5$ is also affected by the nature of the substituents attached to the cyclopentadiene ring. The general trend (Table 1) is that electron donating methyl groups increase the reaction rate. Electron-withdrawing groups on the ring retard the reaction. This is evidenced by the use of $[(\eta^5\text{-}C_5H_4CO_2Me)Fe(CO)_2]_2$ as a catalyst for the substitution of CO by PPh_3 and $AsPh_3$ on $Fe(CO)_5$ (toluene, 100°C). Thus, reaction times of 5.5 and 7.0 h were observed respectively (cf. Table 1), with recorded yields of $Fe(CO)_4L$, generally 80—90%.

The actual nature of the catalytic species in solution could be the appropriate dimeric complex (substituted or unsubstituted) or free radicals derived from the

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* The rate law for an associative mechanism in which the slow reaction step is attack of $Fe(CO)_5$. catalyst by L (Fig. 1) is given by:

$$\text{Rate} = \frac{k_1 k_3 [Fe(CO)_5][\text{catalyst}][L]}{k_2 + k_3[L]} \text{ and if } k_3[L] >> k_2\text{: } \text{Rate} = k_1 [Fe(CO)_5][\text{catalyst}].$$

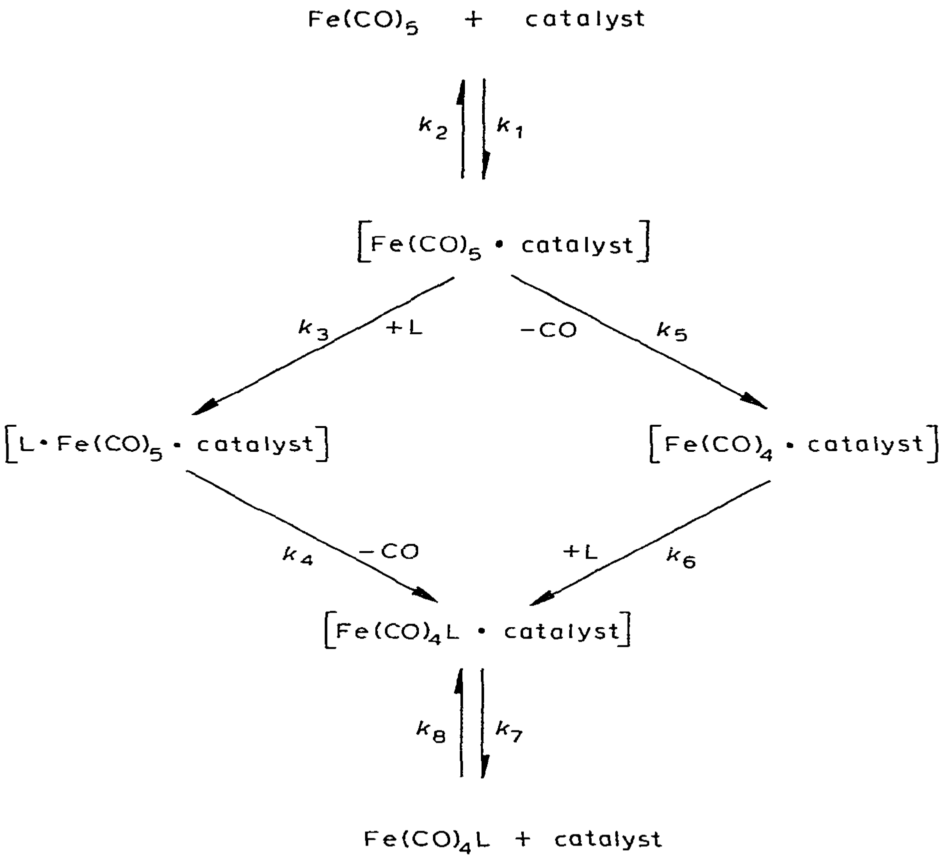
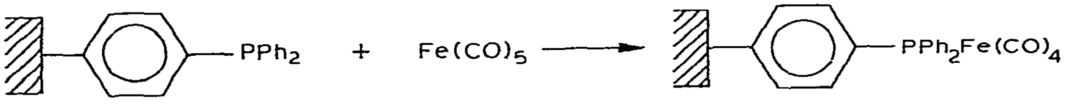


Fig. 1. Possible mechanism for the catalysed reaction $Fe(CO)_5 + L \xrightarrow{cat} Fe(CO)_4L$ (L = group V donor ligand).

iron dimer. Visible light (500 W) was found to cause an ~40—50% rate increase for the reaction $Fe(CO)_5 + P(OMe)_3 \xrightarrow{cat} Fe(CO)_4P(OMe)_3$ (cat = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$) although the addition of the radical inhibitors galvinoxyl and hydroquinone (10 mole % relative to catalyst) had little or no effect on the reaction. The results are thus not inconsistent with radical participation in the catalytic substitution reaction.

We have extended the use of catalysts to the synthesis of polymer supported metal carbonyl complexes. For instance, reaction of a polymer support functionalized with phosphine, I, with $Fe(CO)_5$ in the presence of $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$ as catalyst, readily gives the mono-substituted derivative II.



(I) (II)