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# Effect of the ligand L on the transesterification processes of bismethoxycarbonyl iron complexes: *cis* $Fe(CO_2Me)_2(CO)_3L$, L = CO, $PMe_3$, $PPh_3$, $P(OEt)_3$

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**Abstract**

The synthesis of the new *mer* or *fac* $Fe(CO_2Me)_2(CO)_3$ (L) (L = $PMe_3$: **2a**; L = $PPh_3$: **2b**; L = $P(Cy)_3$: **2c**; L = $P(OEt)_3$: **2d**) complexes of various electron densities has been realized in order to study the transesterification reactions between these methoxycarbonyl complexes and alcohols. The easy formation of $[Fe(CO_2Me)(CO)_4(L)]$ $[BF_4]$ by removing a methoxy group from these complexes clearly indicates that their methoxy group and particularly the one *trans* to the phosphane ligand are mobile. However whereas the unsubstituted complex $Fe(CO_2Me)_2(CO)_4$ (**1**) presents fast exchange reactions with ethanol, **2a** and **2b** are found unreactive towards the same reagent and **2d** (L = $P(OEt)_3$) only undergoes slow transesterification reactions at 28°C. It is proposed an associative mechanism for this transesterification process probably induced by a preliminary nucleophilic addition of an alcohol molecule at a terminal carbonyl ligand prior to the elimination of the methoxy group of a methoxycarbonyl. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Iron; Alkoxycarbonyl; Transesterification; Phosphane

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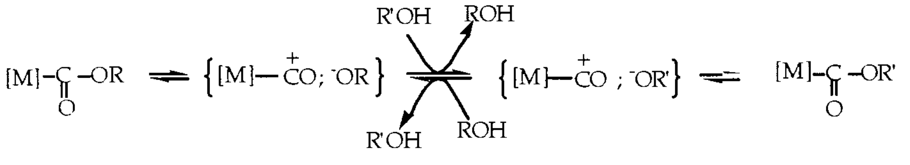
## 1. Introduction

Carbonylation reactions via nucleophilic activation of carbon monoxyde mediated by transition metals have been the subject of considerable attention. Alkoxycarbonyl or related carbamoyl complexes have often been put forward as possible intermediates in such catalytic or stoichiometric carbonylation processes and, for this reason, have been studied for many years [1,2]. An important feature of the alkoxycarbonyl complexes is their great ability to give rapid exchanges of their alkoxy group by reaction with alcohols [3]. These facile exchange reactions strongly contrast with the transesterifications of organic esters wich require acid or base catalysis.

This process has been observed for a wide range of alkoxycarbonyl complexes: Pt [4], Re [5], Ir [6], Mn [7], Ru [8], and Fe [7,9–11]. However the mechanism of the reaction seems to depend on the nature of the metal centre of the complex, on the electronic effects of the ancillary ligands and to proceed according to two different pathways.



$$[M]{-}C({=}O){-}OR \rightleftharpoons \{[M]{-}\overset{+}{C}O;\ {}^{-}OR\} \rightleftharpoons \{[M]{-}\overset{+}{C}O;\ {}^{-}OR'\} \rightleftharpoons [M]{-}C({=}O){-}OR' \quad (1)$$

Thus a dissociative mechanism (Eq. 1) has been postulated for the exchange processes observed on rhenium: $(ReCp(NO)(CO_2Me)(CO)$; $ReCp(NO)(CO_2Me)$-

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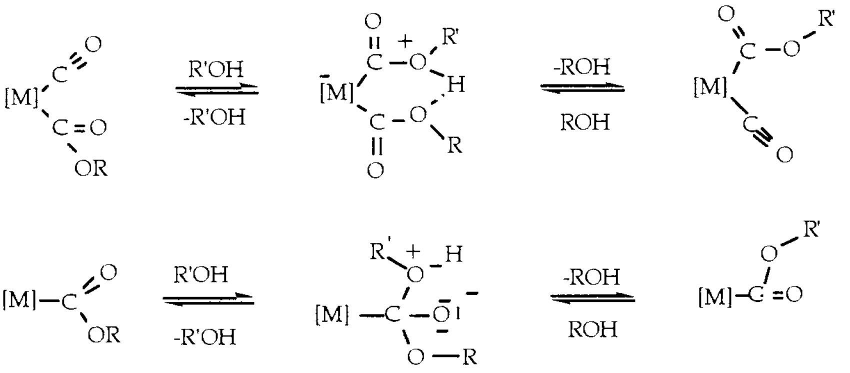
(PPh$_3$)) [5] or on iron complexes: (FeCp(CO$_2$Menthyl)(CO)(PPh$_3$)) [7] whose homologues: FeCp(COR)(CO)(PPh$_3$) (R = OMe, OPh, SMe, SPh) exhibit spontaneous ionizations in polar solvents [9,10].

An associative route is also conceivable for this transesterification reaction; it has been proposed for MnCp(NO)(CO$_2$Menthyl)(PPh$_3$) [7] or Ru(CO$_2$Me)$_2$(CO)$_2$(dppe)[1] [8]. However it is still unclear wether the nucleophilic attack of the alcohol occurs on a terminal CO or on the alkoxycarbonyl itself (Eq. 2).



(2)

It is well known that nucleophilic additions of R$^-$, OR$^-$ or R$_2$N$^-$ on terminal carbonyls give rise to the formation of acyl, aryl, alkoxycarbonyl or carbamoyl complexes [12–17]. However, it has also been described that the addition of MeLi [18] or RONa [7] to alkoxycarbonyl complexes bearing no carbonyl occurs on the alkoxycarbonyl itself inducing the formation of new acyl or alkoxycarbonyl ligands. When acetyl and carbonyl ligands are present on the same complex, addition of nucleophiles such as organolithium reagents occurs on a terminal CO rather than at the acyl [15]. However as alkoxycarbonyl are more electrophilic than acyl ligands, a nucleophilic addition on their carbonyl cannot be dismissed. To our knowledge only one example of nucleophilic attack of alcoholate on a polyfonctional organometallic complex bearing both CO and CO$_2$R ligands has been described. Indeed complex Co(CO$_2$Me)(CO)$_4$ by reaction with MeO$^-$ affords the anion [Co(CO$_2$Me)$_2$(CO)$_3$]$^-$ formally formed by addition of MeO$^-$ on a terminal CO [17]. However, due to the same nature of the alcoholate and the alkoxy group of the complex, a rapid exchange alkoxy-alcohol resulting from an attack of the alcoholate on the carbonyl of the alkoxycarbonyl ligand cannot be precluded.

We recently showed that *cis* Fe(CO$_2$R)$_2$(CO)$_4$ complexes (**1**) undergo rapid exchanges of their alkoxy group with alcohols, oxalates or other bis(alkoxycarbonyl)iron compounds [11].

Since an increase of the electron density of the metal centre is expected to favour a dissociative pathway (or to disfavour an associative process) of the transesterification reactions of alkoxycarbonyl complexes, we have realized the preparation of alkoxycarbonyl complexes of higher electron density than **1** by substituting one CO ligand of this compound by different phosphanes.

In the present paper we describe the synthesis of bis(alkoxycarbonyl)Iron complexes: Fe(CO$_2$Me)$_2$CO)$_3$L (L = PMe$_3$, PPh$_3$, PCy$_3$[2] P(OEt)$_3$) and the influence of the ligand L on the transesterification reactions of these compounds.

## 2. Results

### 2.1. Preparation of Fe(CO$_2$Me)$_2$(CO)$_3$(PR$_3$) (R = Me, Ph, Cy, OEt)

When heated for 24 h at 28°C in CH$_2$Cl$_2$, *cis* Fe(CO$_2$Me)$_2$(CO)$_4$: **1** and 1.1 equivalent of phosphane give rise to the formation of the new complexes Fe(CO$_2$Me)$_2$(CO)$_3$(PR$_3$): (**2**) R = Me: **2a;** Ph: **2b;** Cy: **2c;** OEt: **2d** obtained in ca 40% yield after recrystallization. The coordination of a phosphorous ligand on these complexes induces in IR spectroscopy a shift of their $\nu$ CO stretching bands towards low frequencies (see Table 1). This shift is consistent with an increase in the $\pi$ back-bonding to the carbonyl ligands induced by a higher electron density of the metal centre [19]. An analogous effect is observed in $^{13}$C-NMR where the presence of the phosphane on the complex, indicated by a coupling between the phosphorus and the CO linked to the metal, induces a deshielding of the carbonyl resonances of the remaining CO ligands [20].

The substitution of one terminal carbonyl of **1** by a phosphorous ligand may form three possible isomers of **2** (Eq. 3).

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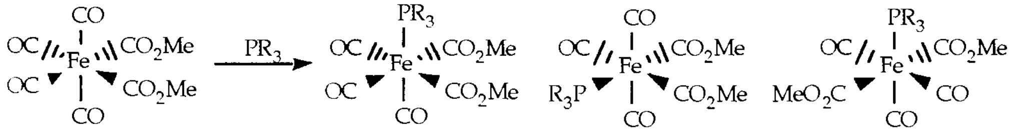
[1] dppe = 1,2-bis diphenylphosphinoethane.

[2] Cy = cyclohexcyl.

Table 1
Spectroscopic data for complexes **1**, **2** and **3**

| Complex | IR hexane ($cm^{-1}$) | | NMR ($CD_2Cl_2$ $-20°C$) $\delta$ (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $^{13}C$ | | | | | $^{1}H$ | $^{31}P$ |
| | $\nu_{C\equiv O}$ | $\nu_{C=O}$ | C≡O | $J_{C-P}$ (Hz) | $CO_2Me$ | $J_{C-P}$ (Hz) | Me | OMe | |
| **1** | 2138(s) | 1665(m,br) | 199.7:2 | | 192.2:2 | | 53.5 | 3.69(s) | |
| | 2080(sh) | | 199.3:2 | | | | | | |
| | 2052(vs) | | | | | | | | |
| | 2075(vs) | | | | | | | | |
| **2a**[a] | 2080(w) | 1640(w,br) | 205.1:2(d) | 18.9 | 201.6:2(d) | 29.7 | 51.9(s) | 3.47(s) | 15.0 |
| | 2030(s) | | 205.7:1(d) | 37.0 | | | | | |
| **2b** | 2100(w) | 1645(w,br) | 205.8:2(d) | 16.0 | 201.8:1(d) | 19.0 | 52.2(s) | 3.66(s) | 45.1 |
| | 2035(s) | 1630(w,br) | 205.6:1(d) | 9.5 | 197.0:1(d) | 30.5 | 51.2(s) | 3.26(s) | |
| | 2010(s) | | | | | | | | |
| **2c** | 2090(w) | 1625(w,br) | 209.3:2(d) | 14.5 | 203.2:1(d) | 18.7 | 52.5(s) | 3.61(s) | 50.6 |
| | 2020(s) | 1595(w,br) | 207.3:1(d) | 10.6 | 198.5:1(d) | 25.3 | 51.3(s) | 3.49(s) | |
| | 2010(sh) | | | | | | | | |
| **2d** | 2095(w) | 1670(w,br) | 204.3:2(d) | 27.4 | 199.9:1(d) | 30.4 | 51.5(s) | 3.51(s) | 150.0 |
| | 2050(s) | 1645(w,br) | 203.8:1(d) | 15.9 | 198.5:1(d) | 56.4 | 51.0(s) | 3.47(s) | |
| | 2030(s) | | | | | | | | |
| **3a** | 2155(m) | 1670(m) | 198.7:2(d) | 27.5 | 189.9:1(d) | 23.0 | 55.9(s) | 3.34(s) | 37.3 |
| | 2115(sh) | | 197.2:1(d) | 24.2 | | | | | |
| | 2090(s) | | 196.0:1(d) | 12.7 | | | | | |
| | 2075(sh) | | | | | | | | |
| **3b** | 2160(w) | 1685(m) | 197.8:2(d) | 25.6 | 188.4:1(d) | 23.0 | 55.9(s) | 3.34(s) | 37.3 |
| | 2120(w) | | 195.9:1(d) | 26.4 | | | | | |
| | 2100(s) | | 195.3:1(d) | 12.9 | | | | | |
| | 2080(sh) | | | | | | | | |
| **3d** | 2160(w) | 1685(m) | 195.8:2(d) | 42.8 | 186.1:1(d) | 32.1 | 56.2(s) | 3.17(s) | 107.8 |
| | 2120(sh) | | 193.7:1(d) | 43.8 | | | | | |
| | 2100(s) | | 192.4:1(d) | 22.3 | | | | | |
| | 2085(sh) | | | | | | | | |

[a] As the *mer* isomer **2a**′ has never been isolated, some of its characteristics are missing. NMR $^{13}C$: C≡O: 205.7(d) (18.7 Hz); $CO_2Me$ 207.7:1(d) (22.3 Hz); 199.1(d) (27.4 Hz); Me 51.4(s). $^{1}H$: OMe: 3.59(s) 3.49(s). $^{31}P$: 7.5.



**1** A B C

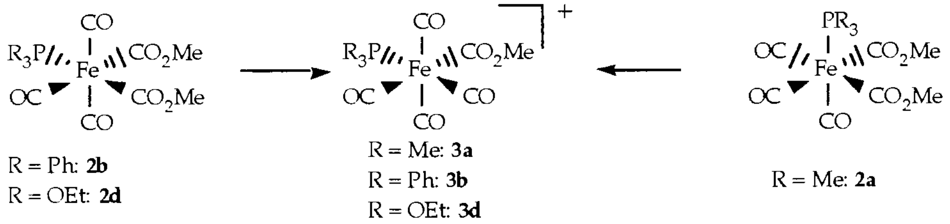
(3)

The IR spectra of complexes **2b**, **2c** and **2d** clearly indicate that these compounds display the same geometry. The presence of two $\upsilon$ C=O bands in the 1625–1670 $cm^{-1}$ area of their IR spectra suggests that the two methoxycarbonyl ligands of these complexes are not equivalent. This result is confirmed by their $^{13}C$-NMR spectra which exhibit two doublets between 203 and 209 ppm for the resonances of the CO of the alkoxycarbonyl ligands and two singlets about 52 ppm for their methoxy groups and by the $^{1}H$-NMR which shows two singlets for the same methoxy groups. The nonequivalence of the two methoxycarbonyl ligands is consistent with the *mer* geometry B (Eq. 3) of the complexes **2b**, **2c** and **2d.**

The other $^{13}C$-NMR signals observed for these complexes are in good accordance with the proposed structure. These spectra display a *trans* $J_{C-P}$ (from 25 to 56 Hz) and a *cis* $J_{C-P}$ (from 18 to 30 Hz) coupling constants for the signals of the CO of the methoxycarbonyl ligands. The resonances of the terminal CO present only *cis* couplings (from 9 to 27 Hz) with the phosphorus. The weakness of the coupling constants between the phosphorus and the CO *trans* to the alkoxycarbonyl ligand is noteworthy, it probably results from a reduced back bonding toward this CO *trans* to an electron-withdrawing ligand.

As generally observed the magnitude of $^{2}J_{C-P}$ couplings is significantly larger for the complex **2d** bearing the phosphite ligand (from 15.9 to 56.4 Hz).

The spectroscopic data obtained for **2a** formed by reaction of **1** with $PMe_3$ are quite different from those observed for **2b**, **2c** and **2d**. The IR spectrum of this compound exhibits only one $\upsilon$C=O stretching band at 1640 $cm^{-1}$ for the CO of the two methoxycarbonyl



(4)

ligands. The equivalence of these two ligands is confirmed by the presence of only one doublet at 201.6 ppm ($CO_2Me$) and one singlet at 51.9 ppm ($CH_3$) in $^{13}$C-NMR and by one singlet at 3.47 ppm in $^{1}$H-NMR.

Both isomers A and C (Eq. 3) present this equivalence. However, as the starting material **1** bears its two methoxycarbonyl ligands in *cis* position and as, probably due to a strong *trans* influence of these ligands, *trans* bisalkoxycarbonyl octahedral complexes have never been observed, the structure C is highly improbable. The $J_{C-P}$ values observed in the $^{13}$C-NMR spectrum of **2a** of geometry *mer* (A) indicate that $PMe_3$ is *cis* to both methoxycarbonyl ligands ($J_{C-P} = 29.6$ Hz) and to two terminal CO ($J_{C-P} = 18.9$ Hz). A higher value of the $J_{C-P}$ coupling constant (37.0 Hz) is observed for the carbonyl *trans* to the phosphine.

**2a** is not the only complex obtained by reaction of $PMe_3$ with **1**.The formation of a second compound **2a′** which represents ca. 7% of the reaction products is also observed. The similarity of the $^{13}$C- and $^{1}$H-NMR spectra of this complex **2a′** (see Table 1) with those observed for **2b**, **2c** or **2d** strongly suggests that **2a′** is the *mer* isomer B of **2a.**

An organic carbonylated ligand is supposed to induce a dissociative loss of CO from the position *cis* to itself [21] therefore the primary product of the reaction of substitution of one CO of $Fe(CO_2Me)_2(CO)_4$ by a phosphane is expected to be the *fac* compound.

However, careful monitorings realized by $^{31}$P-NMR at the early stages of these reactions of substitution have not revealed the transitory formation of other isomers of **2b**, **2c** and **2d** and any change in the relative proportions of complexes **2a** and **2′a**. These results lead us to assume that, at the temperature of reaction (28°C), rapid isomerizations of the *fac* compounds into their *mer* isomers could occur. These processes are possibly realized via alkoxy hopping from one CO to another as proposed by Gladfelter and colleagues [8].

### 2.2. Preparation of the cationic complexes $[Fe(CO_2Me)(CO)_4(PR_3)]$ $[BF_4]$: 3

The increase in the electron density of the metal induced by the phosphorous ligand in complexes **2a**,**2b**, and **2d** should favour their ionization into $[Fe(CO_2Me)(CO)_4(PR_3]^+[OMe]^-$ [3,9].

Though complexes **2a**,**2b**, and **2d** do not afford spontaneous dissociations in polar solvents such as DMF, they are easily transformed into the cationic species $[Fe(CO_2Me)(CO)_4(PR_3)]^+$ **(3)** by reaction with a strong acid ($HBF_4$) [22] (Eq. 4).

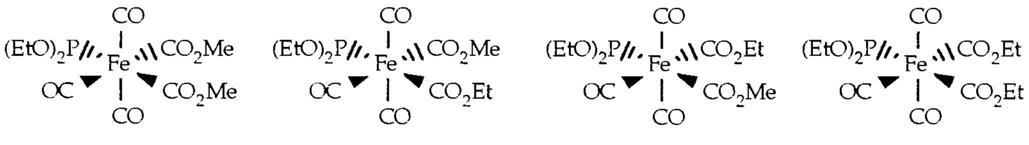
The cationic character of the compounds formed by reaction of the complexes **2a**, **2b**, and **2d** with $HBF_4$ in THF is indicated in IR by high $\upsilon C{\equiv}O$ stretching frequencies and in $^{13}$C-NMR by a shift of the carbonyl resonances towards the highest fields (see Table 1). The spectroscopic data of **3a**, **3b** and **3d** clearly indicate that these cations formed by reaction of either *fac* or *mer* isomers of **2** with $HBF_4$ present the same geometry. Their $^{13}$C-NMR which display three doublets (intensity 2.1.1) for the resonances of the terminal CO clearly demonstrate that this geometry is *cis*.

Starting from **2b** or **2d** the observed process indicates that the phosphane ligand of these *mer* complexes induces specifically the dissociation of the methoxycarbonyl *trans* to itself. This enhanced mobility probably results from the reduced $\pi$ accepting ability of the phosphanes compared with CO which allows the dxy orbital to participate to a greater extend in back bonding with the alkoxycarbonyl *trans*. These results clearly show that an increase in the electron density of the described complexes makes easier the dissociation of the alkoxy groups of their alkoxycarbonyl ligands and therefore should favour a transesterification process realized via a dissociative mechanism.

### 2.3. Reactions of transesterification of complexes 2a, 2b and 2d

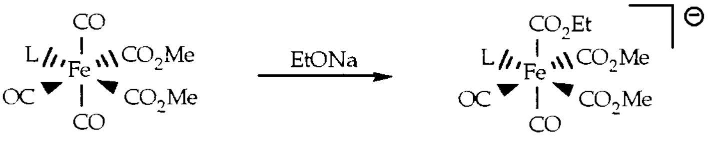
Contrary to the unsubstituted complex **1** which reacts with ethanol in dichloromethane to give a fast exchange (3 h at + 10°C) of its methoxy groups, **2a** or **2b** are found unreactive even at higher temperatures and after longer reaction times. Only **2d** (L = $P(OEt)_3$) undergoes a slow transesterification reaction. This process, as shown by $^{13}$C-NMR, is achieved after 25 h at 30°C. When the reaction is realized with a large excess of EtOH it affords only **2‴d**; on the other hand, when two equivalents of EtOH are added to **2d** the $^{13}$C-NMR spectrum of the reactional mixture shows numerous resonances in the CO region (190–215 ppm). The assigment of these signals is consistent with the possible presence of the four complexes described in Scheme 1.

$^{13}$C-NMR spectra realized at the very first stages of the reaction have not allowed us to establish whether **2′d** is formed prior to **2″d** and **2‴d**. According to the observed



**2d** **2'd** **2"d** **2'''d**

Scheme 1.



1: L = CO; 2d: L = P(OEt)$_3$

(5)

carbonyl resonances these spectra suggest that the three complexes **2′d**, **2″d** and **2‴d** are rapidly formed under the reaction conditions.

## 3. Discussion

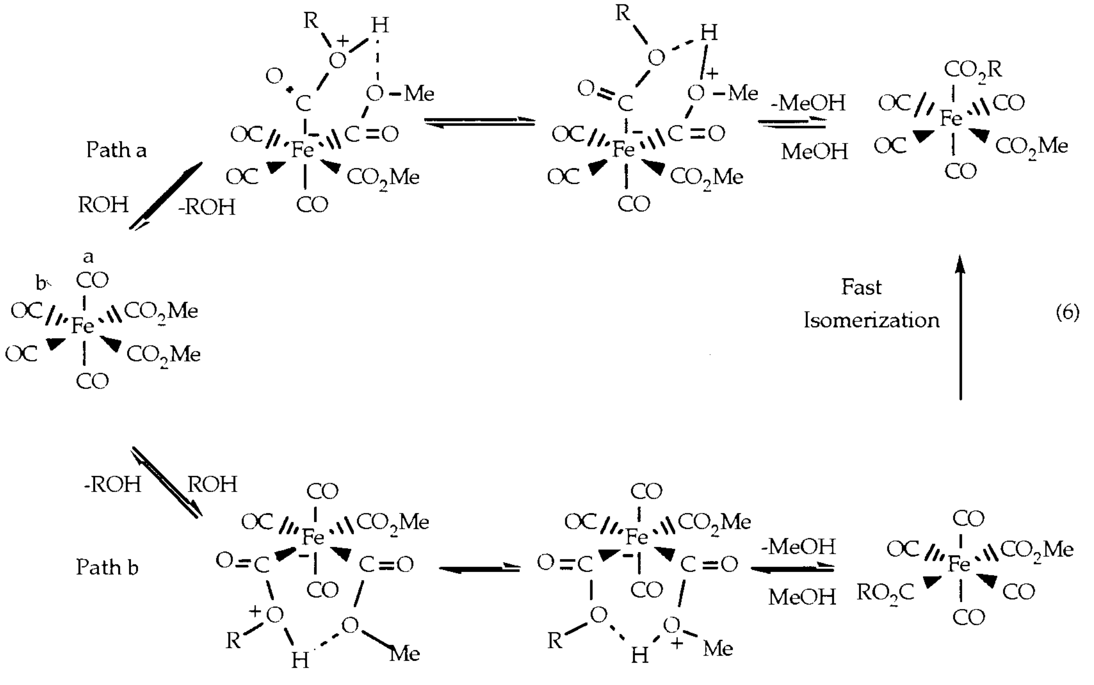
The lack of reaction observed for **2a** or **2b** and the low reactivity of **2d** strongly suggest that the transesterification processes observed for **1** occur via an associative mechanism. These conclusions agree with the results obtained by Gladfelter and colleagues [8] on bis(alkoxycarbonyl) ruthenium complexes. However, as shown in Eq. 2, this associative mechanism involves prior to the exchange a nucleophilic attack of ethanol either at a carbonyl group or at the methoxycarbonyl ligand of complex **1**.

A study that we realized recently provides an answer to this question [23]. This work established that EtONa reacted with complex **1** (L = CO) to induce specifically the formation of the *fac* tris(alkoxycarbonyl) anion resulting from a nucleophilic attack on a terminal carbonyl ligand (Eq. 5).

This addition occurs also on complex **2d** (L = P(OEt)$_3$) but, probably because of the reduced electrophilic character of their CO ligands **2a** (L = PPh$_3$) or **2b** (L = PMe$_3$) are found unreactive. It is noteworthy that exchange reactions are only observed for complexes which undergo nucleophilic additions of alcoholates on a CO ligand.

These results lead us to suggest the following mechanism for the transesterification reactions observed for **1** **(Eq. 6)**.

This mechanism is of associative type; it includes an addition of alcohol on a terminal CO prior to the elimination of the methoxy group of one methoxycarbonyl ligand of the original complex. The nucleophilic addition of alcohol can occur on an axial CO (a) and after elimination of methanol the reaction is supposed to induce the formation of the observed *cis* bis(alkoxycarbonyl) complex (path a). According to a similar process, the



(6)

addition of alcohol on an equatorial CO (b) (path b) should lead to the formation of a *trans* bis(alkoxycarbonyl) complex. This second reactional pathway cannot be ruled out since equatorial CO *trans* to electron withdrawing alkoxycarbonyl ligands are considered more electrophilic than the axial ones. As careful monitorings of the reaction has never allowed us to establish the transient formation of the *trans* bis(alkoxycarbonyl) complex, path b would involved a very fast isomerization of this *trans* compound into its *cis* isomer.

The transesterification reactions observed for **2d:** *mer* ($Fe(CO_2Me)_2(CO)_3P(OEt)_3$) probably occur via similar processes. However due to the relatively high temperature required to realize the exchanges, fast isomerizations may explain the rapid formation of **2′d**, **2″d** and **2‴d.**

## 4. Experimental section

All operations involving organometallics were carried out under argon atmosphere. All solvents were distilled under an inert atmosphere from an appropriate drying agent [24]. Infrared spectra were recorded in hexane on a Perkin-Elmer 1430 spectrometer. $^1$H- (300 MHz) and $^{13}$C- (75.47 MHz) NMR spectra were obtained on a Brucker AC 300 spectrometer with chemical shifts reported in $\delta$ values relative to residual solvent ($^1$H) or to the solvent resonance ($^{13}$C). The $^{31}$P (40.32MHz) spectra were recorded on a Jeol FX 100 spectrometer using 87% $H_3PO_4$ as an external standard. Elemental analyses were performed by the Service central d'analyses du CNRS.

Complex **1**: $Fe(CO_2Me)_2(CO)_4$ was prepared as described in Ref. [11]. Other reagents: $PPh_3$, $PMe_3$, $PCy_3$, $P(OEt)_3$, $HBF_4 \cdot OMe_2$ were obtained from commercial sources and used without purification.

### *4.1. General procedure for the preparation of phosphorous complexes: Fe(CO$_2$Me)$_2$(CO)$_3$L: **(2)** L = PMe$_3$: **2a**; L = PPh$_3$: **2b**; L = PCy$_3$: **2c**; L = P(OEt)$_3$: **2d***

A 5.5 mmol volume of phosphane were added to a solution of $Fe(CO_2Me)_2(CO)_4$ (**1**) (1.43 g, 5 mmol.) in 30 ml of $CH_2Cl_2$ at 28°C. After the reactional mixture was stirred for 24 h, the IR [13] and the $^{31}$P-NMR [25] spectra of the resulting solution revealed together with $Fe(CO_2Me)_2(CO)_3(L)$: (**2**) the presence of small amounts of $Fe(CO)_3(L)_2$ (10%). The solvent was evaporated at r.t.. The oily residue was washed with two portions of 15 ml of hexane to remove the excess of phosphane (L = $PPh_3$, $PCy_3$, $P(OEt)_3$). The residue which crystallizes as a cream coloured powder was redissolved into a small amount of a hexane/dichloromethane mixture (5/1). After filtration the solution was slowly concentrated at −60°C. Complexes **2** which precipitated were obtained after filtration and drying as pale yellow powders. As separations of **2** and $Fe(CO)_3(L)_2$ by fractionnal crystallizations were rather tricky, yields of pure **2** were relatively low.

**2a**: L = $PMe_3$ yield, 30% (500 mg) Anal. Found: C, 36.05; H, 4.47; P, 9.37. $C_{10}H_{15}FeO_7P$ Calc.: C, 35.96; H, 4.53; P, 9.21%.

**2b**: L = $PPh_3$ Yield, 20% (520 mg) Anal. Found: C, 57.71; H, 4.00; P, 5.82. $C_{25}H_{21}FeO_7P$ Calc.: C, 57.72; H, 4.07; P, 5.95%.

**2c**: L = $PCy_3$ Yield, 40% (1.10 g) Anal. Found: C, 55.85; H, 7.48; P, 5.69. $C_{25}H_{39}FeO_7P$ Calc.: C, 55.77; H, 7.30; P, 5.75%.

**2d**:L = $P(OEt)_3$ Yield, 40% (840 mg) Anal. Found: C, 36.61; H, 5.03; P, 7.15. $C_{13}H_{21}FeO_{10}P$ Calc.: C, 36.82; H, 4.99; P, 7.30%.

### *4.2. Preparation of cationic complexes: [Fe(CO$_2$Me)(CO)$_4$(L)] [BF$_4$]: **3a**: L = PMe$_3$, **3b**: L = PPh$_3$, **3d**: L = P(OEt)$_3$*

A 0.426 ml (3.5 mmol) volume of $HBF_4$,$OMe_2$ were added dropwise via syringe to a stirred solution of 1.4 mmol of $Fe(CO_2Me)_2(CO)_3(L)$ (**2**) in THF (15 ml) at −20°C. A cream coloured precipitate formed rapidly. The reaction mixture was stirred for 1 h. After filtration the residue was washed with two portions of cold THF (5 ml, −40°C) and dried in vacuo to afford complexes **3** as white powders.

**3a**: L = $PMe_3$ yield, 70% (380mg) Anal. Found: C, 27.68; H, 3.15; B, 2.81; F, 19.56. $BC_9F_4FeH_{12}O_6P$ Calc.: C, 27.73; H, 3.10; B, 2.77; F, 19.49%.

**3b**: L = $PPh_3$ Yield, 65% (525 mg) Anal. Found: C, 49.98; H, 3.21; B, 1.92; F, 13.27. $BC_{24}F_4FeH_{18}O_6P$ Calc.: C, 50.04; H, 3.15; B, 1.88; F, 13.19%.

**3d**: L = $P(OEt)_3$ Yield, 60% (400 mg) Anal. Found: C, 30.01; H, 3.84; B, 2.35; F, 15.91. $BC_{12}F_4FeH_{18}O_9P$ Calc.: C, 30.03; H, 3.78; B, 2.25; F, 15.84%

### *4.3. Reactions of transesterification realized from **2a**, **2b** and **2c***

A 0.4 mmol volume of ethanol (0.022 m) were added to a solution of $Fe(CO_2Me)_2(CO)_3(L)$ (**2**) (0.2 mmol) in 0.7 ml of $CD_2Cl_2$ in an NMR tube at −20°C. The solution was warmed to 30°C and $^{13}$C-NMR spectra were recorded periodically.

Complexes **2a**: (L = $PMe_3$) and **2b** (L = $PPh_3$): The $^{13}$C-NMR spectra remained unchanged after 20 h at 30°C.

Complex **2d** (L = $P(OEt)_3$): The $^{13}$C-NMR spectra realized at $t = 0.5$, 1, 1.5, 2, 3.5, 7.5, 10, 15, and 20 h revealed the formation of numerous signals in the 190–215 ppm area. No further evolution of these spectra was observed after 20 h of reaction.

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