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Synthesis, reactivity of the $[(\text{CO})_3(\text{L})\text{Fe}(\text{CO}_2\text{R})_2]$ dialkoxycarbonyl carbonyl iron complexes ($\text{L} = \text{CO}$ or PPh_3 ; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$), and an easy access to $[(\text{CO})_5\text{Fe}(\text{CO}_2\text{Me})]^+$

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Abstract

The *cis*-dialkylcarboxytetracarbonyliron complexes $[(\text{CO})_4\text{Fe}(\text{CO}_2\text{R})_2]$ were readily obtained from reaction of oxalyl chloride with the corresponding tetracarbonylcarboxyiron anion $[(\text{CO})_4\text{Fe}(\text{CO}_2\text{R})]^-$ ($\text{R} = \text{Me}$, **1a**; $\text{R} = \text{Et}$, **1b**). **1a** underwent a clean ligand exchange with triphenylphosphine to give $[\text{Fe}(\text{CO})_3(\text{PPh}_3)(\text{CO}_2\text{Me})_2]$ (**2**). Neither **1a** nor **2** yielded dimethyl oxalate after thermolysis; rather, a mixture of methanol and methyl carbonate was obtained. The mobility of the alkoxy groups on **1** was shown by several exchange experiments. A clean reaction of the tetrafluoroboric acid ether with **1a** gave $[(\text{CO})_5\text{Fe}(\text{CO}_2\text{Me})]^+$ which was isolated and characterized by IR, ^1H , and ^{13}C NMR spectroscopy.

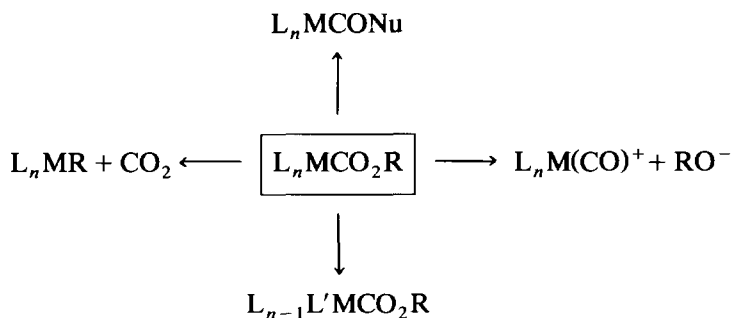
Introduction

Monoalkylcarboxy transition metal complexes $[\text{M}](\text{CO}_2\text{R})$ have been extensively studied because of their pivotal role in the nucleophilic activation of carbon monoxide [1]. They also are believed to play an important role as alternatives to the acyl complex $[\text{M}](\text{COR})$ in several catalytic processes of carbonylation [2–4]. Their hydrido derivatives $[\text{M}](\text{H})(\text{CO}_2\text{R})$ may be significant intermediates in the activation of methyl formate [5,6]. The closely related carboxy complexes $[\text{M}](\text{CO}_2\text{H})$ are key intermediates in the water–gas shift reaction [1,7,8].

The essential reactivity of these complexes is summarized in Scheme 1. The chemistry of the $[\text{FeCp}(\text{CO})(\text{L})\text{CO}_2\text{R}]$ complexes is typical and the reader is referred to a recent review [9].

In contrast, bis(carboxy) complexes $[\text{M}](\text{CO}_2\text{R})_2$ are much rarer and very little is known about their chemistry. Examples have been described for the following metals: Co [10], Rh [11], Pd [12,13], Pt [14–16] and Ru [17].

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Scheme 1.

A bis(carboxy)palladium complex has been invoked as an intermediate in the carbonylation of methanol to methyl oxalate [12]. It has been claimed that traces of oxalate could be detected after its thermolysis, although no yield was reported [12,13]. This raises the question of the feasibility of a carbon-carbon coupling between the two alkylcarboxy ligands to give an oxalate ester. It must be stressed that there is, so far, no clear-cut evidence for such a coupling in a thermal process. However, oxalate has been detected after oxidation of a bis(carboxy)rhodium complex [11].

To our knowledge, no bis(carboxy) complexes are reported in the literature with iron as the metallic centre. Here we report an easy and unexpected synthesis of such iron complexes $[Fe(CO)_3(L)(CO_2R)_2]$ and a study of their reactivity.

Results and discussion

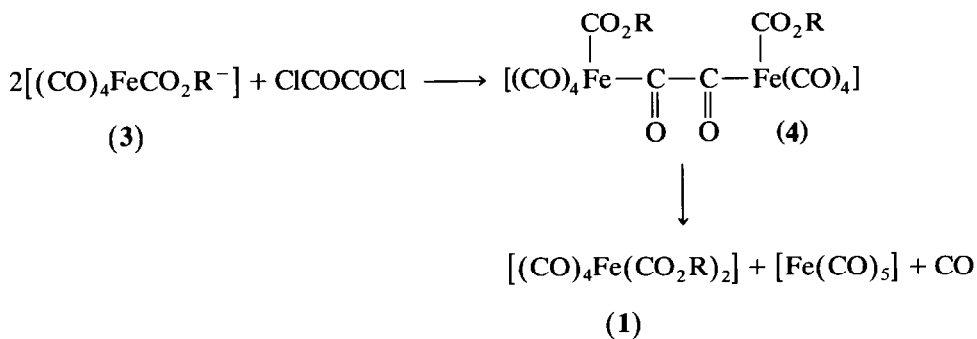
Syntheses and spectroscopic characterization of the $[Fe(CO)_3L(CO_2R)_2]$ complexes 1 ($L = CO$) and 2 ($L = P(C_6H_5)_3$)

Complexes **1** (**1a**, $R = CH_3$; **1b**, $R = C_2H_5$) were readily obtained by reaction of oxalyl chloride with the tetracarbonyl (carboxy)-iron anions **3** (1:2 molar ratio) in dry THF (overall yield 70%). The reaction was carefully monitored by ^{13}C NMR spectroscopy in THF- d_8 at low temperature (Table 1). At $-90^\circ C$, anion **3** completely disappeared to give a neutral complex to which we ascribe formula **4**. The

Table 1

^{13}C NMR observations for the reaction of oxalyl chloride with anion **3b** ($R = C_2H_5$)

Conditions and observations	^{13}C NMR (THF- d_8) δ (ppm)			Attribution to complexes	
	$Fe(CO)_2Fe$	$C\equiv O$	CO_2 CH_2CH_3		
$-90^\circ C$, before addition of oxalyl chloride		221.0	216.7	58.2	3b
				15.3	
$-90^\circ C$, after addition of oxalyl chloride	259.1	201.7	192.3	61.8	4b
		201.2		15.0	
$-40^\circ C$, after decarbonylation		201.4	191.5	61.6	1b
		200.9		14.9	



Scheme 2.

observed signal at 259.1 ppm is particularly significant. A similar resonance was observed for the MCOCOM group of the structurally well defined $[(\text{CO})_5\text{MC-OCOM}(\text{CO})_5]$ complexes (256 ppm for $\text{M} = \text{Mn}$ and 253 ppm for $\text{M} = \text{Re}$) [18]. At -50°C , this complex thermolysed into complex 1, pentacarbonyl iron and carbon monoxide (Scheme 2). (Complexes 1 could not be obtained after reaction of alkyl chloroformate ClCO_2R on anions 3.)

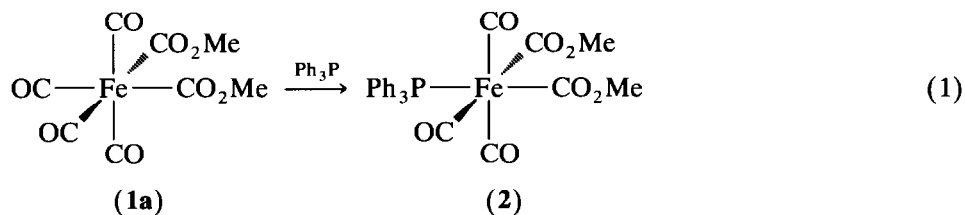
Although crystals of 1 ($\text{R} = \text{CH}_3$ or C_2H_5) were not found suitable for an X-ray structural investigation, the spectroscopic data in Table 2 are in full agreement with the proposed formulas.

The four IR bands in the $2050\text{--}2140\text{ cm}^{-1}$ region are consistent with an $\text{M}(\text{CO})_4$ fragment of C_{2v} symmetry. The other band at 1665 cm^{-1} is assigned to the ester group.

The ^{13}C NMR spectra, consistent with this symmetry, show two kinds of signal of equal intensity around 200 ppm for the four terminal CO ligands. The other signal, near 192 ppm is assigned to the metal-bonded carbon atom of the carboxy ligands.

The mass spectra of complexes 1 suggest two parallel pathways of decomposition of the molecular cation radical: one involves a prior loss of carbon monoxide, and the other a prior loss of the alkoxy group (Scheme 3).

On heating 1a at 28°C with 1 equiv. of triphenylphosphine in a dichloromethane solution, one equatorial carbon monoxide ligand exchanged with triphenylphosphine to give complex 2 (reaction 1).

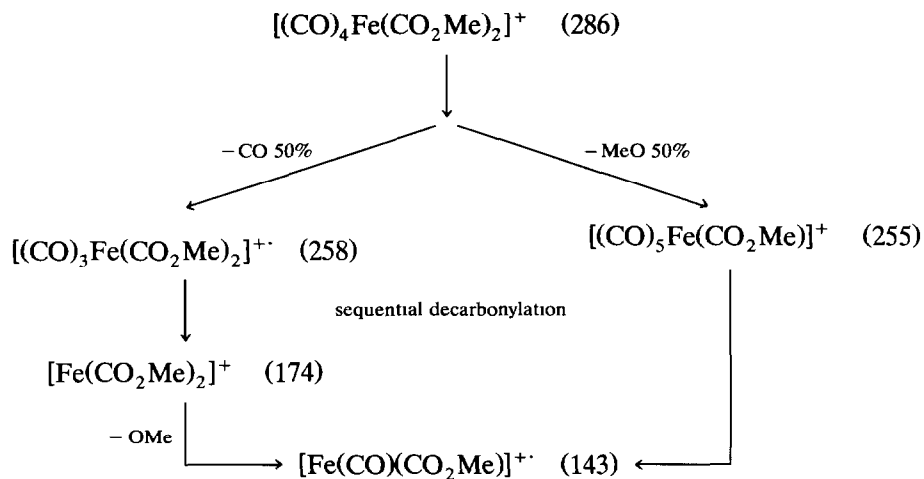


The IR and NMR data in Table 2 agree with the proposed formula 2 and its geometry. Three IR bands between 2000 and 2100 cm^{-1} are consistent with the $\text{M}(\text{CO})_3$ fragment; the two different carboxyl groups give two bands (1630 and

Table 2
Selected spectroscopic data for complexes **1**, **2** and **5**

Complex	IR (hexane) (cm^{-1})		NMR (CD_2Cl_2 , -20°C) δ (ppm)		^1H
	$\nu(\text{C}\equiv\text{O})$	$\nu(\text{C}=\text{O})$	^{13}C	C=O	
1a	2138m	1665m,br			
	2080vs,sh		198.8(1)	192.6	53.7
	2075vs		198.7(1)		
	2052vs				
1b	2131m	1665m,br			
	2072s,sh		199.8(1)	191.7	62.2
	2069vs		199.4(1)		14.4
	2046s				
1c			200.1(2)	192.2(1)	62.6
			199.8(1)	191.3(1)	53.6
			199.6(1)		14.8
			205.8(2, d, $J(\text{C}-\text{P}) = 16$ Hz)	201.8(d, $J(\text{C}-\text{P}) = 19$ Hz)	52.2 ^b
2 R = Et	2100m ^a	1645w	205.6(1, d, $J(\text{C}-\text{P}) = 9.5$ Hz)	197.0(d, $J(\text{C}-\text{P}) = 30.5$ Hz)	51.2
	2035s	1630w			
5 R = Me	2010s,sh				
	2195m ^c	1680m,br	191.7(4) ^d	180.0	57.7
	2145s		184.4(1)		
	2130s				

^a ^{31}P NMR for **2**: $\delta = 47.0$ ppm. ^b ^{13}C NMR for ar: $\delta = 134-128$ (m) ppm; ¹H NMR for ar: δ 7.5-7.6 (m) ppm. ^c Nujol. ^d CD_3CN .



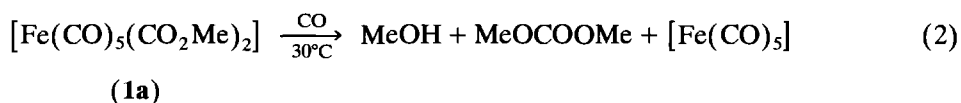
Scheme 3.

1645 cm^{-1}), the lower frequency being attributed to that which is *trans* to the phosphine ligand.

The ^{13}C NMR spectrum of **2** shows two doublets (intensity ratio 2:1) near 205 ppm for the CO ligands coupled to phosphorus. Two signals are observed for the iron-bonded carbon atoms of the two carboxymethyl ligands, also coupled to phosphorus, the resonance at lower field (201.8 ppm) being ascribed to that *trans* to phosphorus. Two singlets are observed for the carbon atoms of the methyl groups.

Thermolysis of complexes **1** and **2**

The thermolysis of alkylcarboxy complexes into an oxalate ester is not clearly established. After 48 h of smooth thermolysis of complexes **1** at 30°C under pressure of carbon monoxide (25 bars), no traces of methyl oxalate were detected (GC); instead, a mixture of alcohol, dialkyl carbonate and pentacarbonyl-iron was obtained (reaction 2). A similar reaction was observed after thermolysis of **2**, bis(triphenylphosphine)(tricarbonyl)iron being produced in the place of pentacarbonyliron.

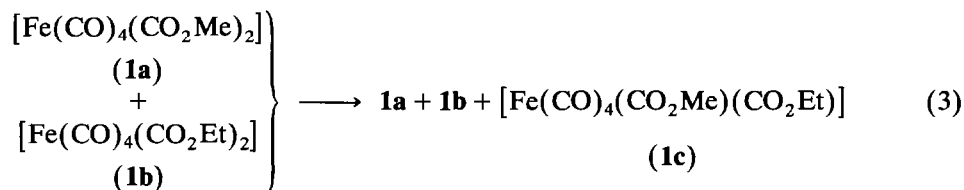


Mobility of the alkoxy groups of complexes **1**

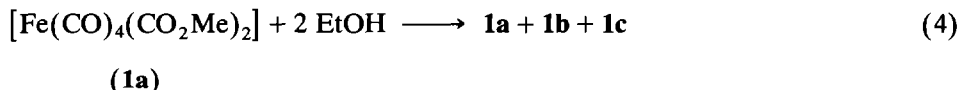
An important feature in the chemistry of complexes **1** is the great mobility of the alkoxy groups. This was well illustrated by the following exchange experiments.

A solution of a 1:1 mixture of complexes **1a** and **1b** in deuterated dichloromethane was monitored by ^{13}C NMR spectroscopy at +10°C. After 3 h, a

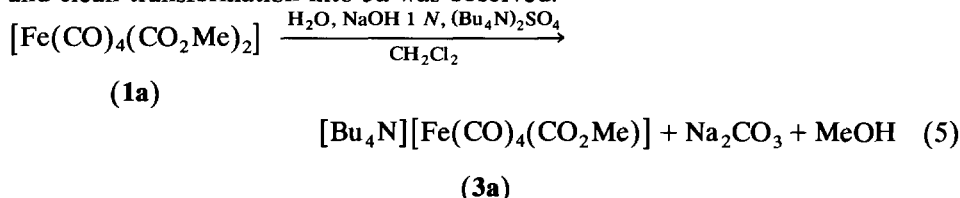
statistical mixture of **1a**, **1b** and **1c** was observed (reaction 3, 25% **1a**; 25% **1b**; 50% **1c**)



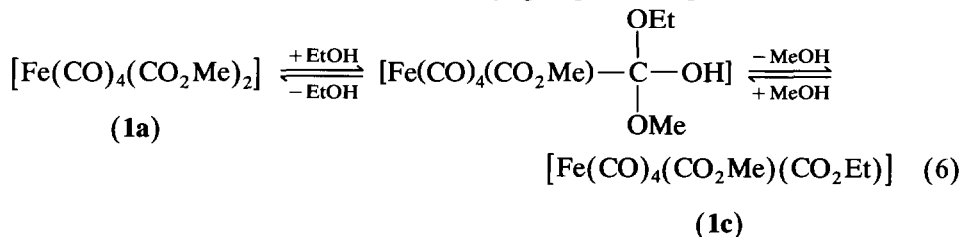
Similar results were obtained after reaction of a stoichiometric quantity of ethanol with **1a** at +10°C (reaction 4). However, such an exchange was not observed with complex **2**.



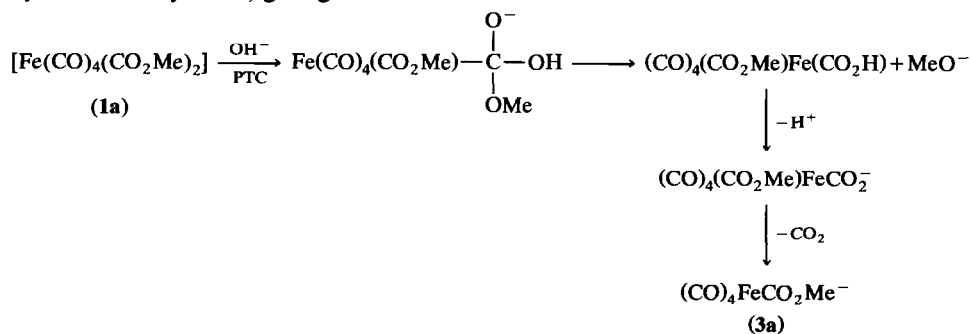
The mobility of the methoxy group of complex **1a** under basic conditions was also shown by the phase-transfer experiment summarized in reaction 5. A rapid and clean transformation into **3a** was observed.



Reaction 4 is explained by supposing a reversible nucleophilic attack of ethanol on the methoxycarbonyl group of complex **1a** (reaction 6). This addition cannot occur on the electron-rich methoxycarbonyl groups of complexes **2**.

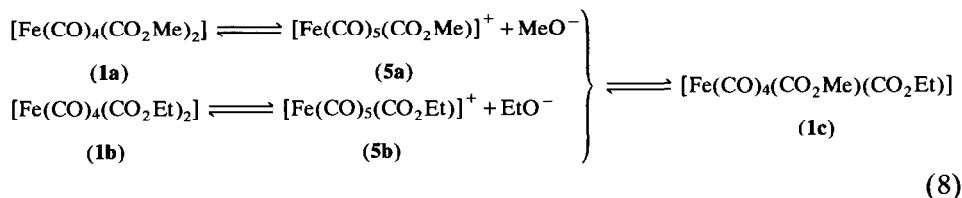


The first step of the phase transfer reaction 5 is interpreted similarly; further deprotonation of the hydroxycarbonyl intermediate would be followed immediately by a decarboxylation, giving rise to the anion **3a**.



(7)

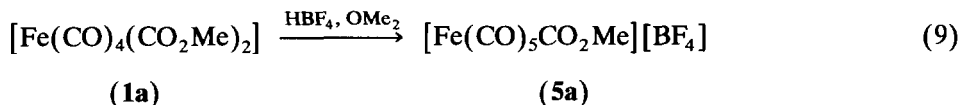
These associative mechanisms do not account for the uncatalysed exchange of the alkoxy groups between complexes **1a** and **1b** (reaction 3); this raises the possibility of dissociation of complexes **1** into cations **5** and the corresponding alcoholate anions (reaction 8).



Although we were not able to provide direct experimental evidence for such an equilibrium by spectroscopic examination of **1a** in several solvents of different polarities, we were able to prepare cation **5a** in a separate experiment (see below).

*Synthesis and characterization of the $[(\text{CO})_5\text{FeCO}_2\text{CH}_3]^+$ cation **5a***

Two equivalents of tetrafluoroboric acid dimethyl ether were added to a solution of complex **1a** in dry THF at -20°C . The reaction was complete within 48 h and cation **5a** precipitated as the tetrafluoroborate salt (reaction 9)



The IR spectrum (Table 2) showed a strong band at 1680 cm^{-1} ascribable to the alkoxy-carbonyl group, and a set of three bands ($2195, 2145, 2130\text{ cm}^{-1}$) consistent with a C_{4v} symmetry for the five CO ligands in a cation. The ^{13}C NMR spectrum (in CD_3CN , Table 2) confirmed the presence of two kinds of terminal CO ligands (191.7 and 189.4 ppm, intensity ratio 4:1, upfield of the neutral complex **1a**) and one metal-carbon bonded carboxyalkyl group (180.0 ppm).

This cation **5a** was found to be very sensitive towards hydrolysis. Reaction with water, rapidly gives pentacarbonyl-iron, methanol and carbon dioxide as judged by ^{13}C NMR spectroscopy.

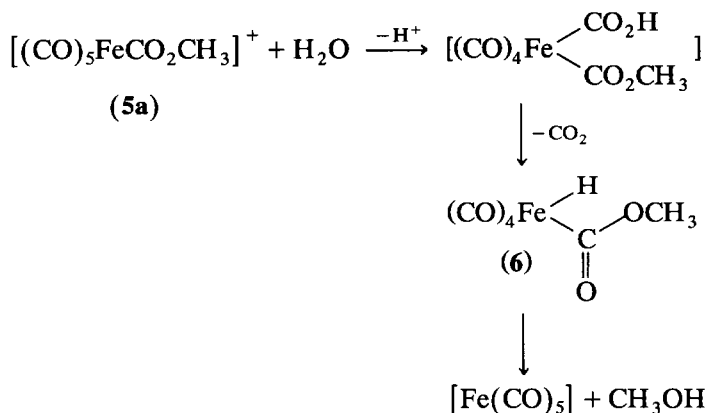
The first step of this reaction is evidently a nucleophilic attack of water on the cation, most likely at CO. A decarboxylation could then occur, giving pentacarbonyl-iron, methanol and carbon dioxide possibly through the intermediate of the (so far unknown) hydridocarboxyalkyl complex **6** (Scheme 4).

Such a thermal expulsion of methanol has indeed been observed with two well characterized hydridocarboxyalkyl complexes [4,5].

Experimental section

All experiments were conducted under an inert atmosphere (nitrogen or argon) by means of standard Schlenk techniques.

^1H (300 MHz) and ^{13}C (75.47 MHz) NMR spectra were recorded on a Bruker AC 300 spectrometer. Chemical shifts were measured relative to residual protonated solvent for ^1H NMR spectra and to the solvent resonance for ^{13}C NMR spectra. ^{31}P NMR spectra (40.27 MHz) were recorded on a JEOL FX 100



Scheme 4.

spectrometer and chemical shifts are downfield from 87% H_3PO_4 as the external reference. The solvent was CD_2Cl_2 , unless otherwise specified.

IR spectra were obtained on a Perkin-Elmer 1430 spectrometer. Mass spectroscopic analyses were recorded on a Hewlett Packard GCMS 5995 (70 eV).

Solvents were freshly distilled under nitrogen from an appropriate desiccant (sodium/benzophenone for THF, LiAlH_4 for hexane, calcium hydride for CH_2Cl_2) and degassed before use.

Synthesis of $[\text{Fe}(\text{CO})_4(\text{CO}_2\text{R})_2]$ (1) ($R = \text{Me}$, a; or $R = \text{Et}$, b)

To a suspension of NaRO (10 mmol, $R = \text{Me}$, 540 mg; $R = \text{Et}$, 680 mg) in 20 ml of THF at 0°C , $[\text{Fe}(\text{CO})_5]$ (15 mmol, 2 ml) was added according to the procedure used for the preparation of anion **3** [19]. After 0.5 h, when the alcoholate was dissolved and the solution had turned orange, the temperature was lowered to -20°C and ClCOCOC (5 mmol, 0.436 ml) was added. The solution instantly turned brown. The solvent was removed after 15 min stirring and the residue was extracted with a mixture of CH_2Cl_2 /hexane (1:1) for **1a** or with hexane for **1b**. After filtration, the solution was maintained overnight at -30°C yielding pale yellow microcrystals (**1a**: 2.0 g, 70% yield *vs.* ClCOCOC ; **1b**: 2.1 g, 67% yield *vs.* ClCOCOC). **1a**: Anal. Found: C, 33.34; H, 2.27; Fe, 19.40. $\text{C}_8\text{H}_6\text{FeO}_8$ calc.: C, 33.60; H, 2.12; Fe, 19.53%. **1b**: MS (70 eV): m/e 314 (M^+).

*^{13}C NMR monitoring of the reaction of $[\text{Fe}(\text{CO})_4\text{CO}_2\text{Et}]^-$ (**3b**) with oxalyl chloride*

ClCOCOC (0.015 ml, 0.175 mmol) was introduced under nitrogen into an NMR tube containing a solution of $\text{Na}[\text{Fe}(\text{CO})_4\text{CO}_2\text{Et}]$ (0.35 mmol, 92 mg) in 0.7 ml of $\text{THF-}d_8$ cooled to -90°C . ^{13}C NMR spectra were recorded every hour at -90°C , -70°C , -50°C and -40°C . At -90°C the orange solution turned green and signals of complex **4** were detected together with those of anion **3**. When the temperature reached -70°C , gas evolution was observed together with the appearance of a red colour. At a temperature higher than -50°C , the mixture became brown and signals attributed to **1b**, $[\text{Fe}(\text{CO})_5]$ and CO appeared.

Reaction of 1a with PPh₃: synthesis of [Fe(CO)₃(PPh₃)(CO₂Me)₂] (2)

The following reagents were successively introduced into a Schlenk tube: [Fe(CO)₄(CO₂Me)₂] (0.427 mmol, 122 mg), PPh₃ (0.512 mmol, 134 mg) and 15 ml of CH₂Cl₂. The solution was maintained overnight at 28°C under 1 atm of CO. The solution became yellow-brown. The solvent was removed, leaving a brown oil. The ³¹P NMR spectra of this crude product indicated the presence of 20% of [Fe(CO)₃(PPh₃)₂] [19] together with complex **2**. After two extractions with hexane (2 × 20 ml) to remove the excess of PPh₃, the residue crystallized. [Fe(CO)₃(PPh₃)₂] was precipitated by fractional crystallization in CH₂Cl₂ and CH₂Cl₂/hexane (1:1). Finally the supernatant solution was shown to contain **2**, isolated in 20% yield (44 mg) *vs.* **1a**. **2**: Anal. Found: C, 57.71; H, 4.00; Fe, 10.39; P, 5.81. C₂₅H₂₁FeO₇ calc.: C, 57.71; H, 4.07; Fe, 10.73; P, 5.95%. MS (70 eV): *m/e* 520 (*M*⁺).

Thermolysis of [Fe(CO)₄(CO₂Me)₂] (1a) under 25 bar of CO

A solution of **1a** (0.2 mmol, 56 mg) in CH₂Cl₂ (15 ml) was introduced into an autoclave thermostated at +30°C under a CO atmosphere. Then the pressure was raised to 25 bar and the reaction was monitored by IR spectroscopy for 48 h. The methanol, methyl carbonate and [Fe(CO)₅] formed were analysed by gas chromatography (capillary column CP SIL, 25 m).

This reaction under dinitrogen gave a paramagnetic solution, as shown by ¹³C NMR monitoring.

Thermolysis of [Fe(CO)₃(PPh₃)(CO₂Me)₂] (2)

Compound **2** (52 mg, 0.1 mmol) in solution in 0.7 ml of CD₂Cl₂ was introduced into two NMR tubes. One equivalent of PPh₃ (0.1 mmol, 26 mg) was added to the first sample. The two samples were maintained at +30°C and the reactions were monitored by ¹³C and ³¹P NMR. The [Fe(CO)₃(PPh₃)₂] formed was identified by comparison with the data in the literature [20]; methanol and methyl carbonate were analysed by GC (see above).

¹³C NMR monitoring of the exchange of the alkoxy groups between 1a and 1b

A solution of **1a** (0.1 mmol, 28 mg) and **1b** (0.1 mmol, 30 mg) in 0.7 ml of CD₂Cl₂ was maintained at +10°C in an NMR tube. ¹³C NMR spectra recorded every hour, showed the rapid appearance of **1c** together with the starting materials in the proportion 2:1:1. Because of the great mobility of the alkoxy groups, fractional crystallization to isolate pure **1c** failed.

Reaction of 1a with EtOH

A solution of **1a** (0.2 mmol, 60 mg) in 0.7 ml of CD₂Cl₂ was introduced into an NMR tube; 2.7 × 10⁻² ml of EtOH (0.4 mmol) were added at +10°C. The solution was maintained at this temperature and the ¹³C NMR spectra were recorded every 10 min. Equilibrium was reached after 1 h.

Phase transfer transformation of [Fe(CO)₄(CO₂Me)₂] (1a) into anion [Fe(CO)₄CO₂Me]⁻ (3a)

The following phase transfer system was introduced under nitrogen into a Schlenk tube containing **1a** (1 mmol, 286 mg): NaOH (10 mmol, 40 mg), [Bu₄N][H₂SO₄] (1.5 mmol, 510 mg), H₂O (10 ml) and CH₂Cl₂ (10 ml). After 15

min stirring at +10°C, an IR spectrum of the organic layer showed complete disappearance of **1a** and a new set of bands belonging to the tetrabutylammonium salt of anion **3a** $[\text{Fe}(\text{CO})_4\text{CO}_2\text{Me}]^-$. The carbonate anion was quantified with a Toepler pump after acidification (HCl) of the aqueous phase (21 ml of CO_2 produced 0.95 mmol).

*Synthesis of $[\text{Fe}(\text{CO})_5\text{CO}_2\text{Me}]\text{BF}_4$ (**5**)*

To a solution of **1a** (400 mg, 1.4 mmol) in THF (15 ml) were added, at -20°C, $\text{HBF}_4 \cdot \text{OMe}_2$ (0.275 ml, ~ 3 mmol). The solution was left at -30°C for 2 days. The precipitate was filtered off and washed with two 5-ml portions of THF to give **5** (335 mg, 70% yield) as a very water sensitive (see below) white powder. **5**: Anal. Found: C, 24.44; H, 0.96; Fe, 16.15. $\text{C}_7\text{H}_3\text{BF}_4\text{FeO}_8$ calc.: C, 24.60; H, 0.82; Fe, 16.34%.

*^{13}C monitoring of the reaction of **5** with water*

In an NMR tube containing **5** (55 mg, 0.16 mmol) in CD_3CN (0.4 ml) was added, at -40°C, a solution of H_2O (5.8×10^{-2} ml, 0.32 mmol) in CD_3CN (0.3 ml). ^{13}C NMR monitoring showed that the reaction was instantaneous and allowed us to detect as the final products $\text{Fe}(\text{CO})_5$ (211.3 ppm), MeOH (52.2 ppm) and CO_2 (125.4 ppm).

Acknowledgement

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