Synthesis and reactivity of bis(alkyloxalyl) and alkoxycarbonyl alkyloxalyl iron complexes $[Fe(COCO_2R)_2(CO)_4]$ and $[Fe(CO_2R)(COCO_2R')(CO)_4]$ (R, R′ = Me or Et): evidence for reductive elimination of oxalate

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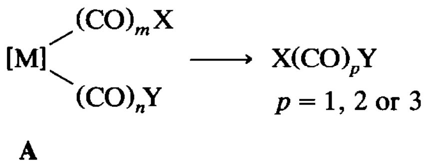
Abstract

The new complexes cis-$[Fe(COCO_2R)_2(CO)_4]$ (R = Me or Et) and *cis*-$[Fe(COCO_2R)(CO_2R')(CO)_4]$ (R, R′ = Me, Et or ^iPr) have been synthesized. The bis-(alkyloxalyl) complexes decarbonylate at +12°C to their alkoxycarbonyl alkyloxalyl homologues. The latter decompose at +28°C by to two pathways: further decarbonylation to give the known compound $[Fe(CO_2R)_2(CO)_4]$ or via reductive elimination to give oxalates $[RO_2CCO_2R]$ and $[Fe(CO)_5]$. Bulky and the more electron-donating R or R′ groups favour the last pathway, and this is the only route observed when the CO *trans* to the alkyloxalyl is replaced by PPh_3. The alkoxy group of the alkoxycarbonyl is easily removed; thus the reaction of HBF_4 with $[Fe(CO_2Me)(COCO_2Me)(CO)_4]$ gives the new cation $[Fe(COCO_2Me)(CO)_5]^+$.

Key words: Iron; Alkyloxalyl; Alkoxycarbonyl

1. Introduction

The following carbonylating carbon–carbon coupling process is a key step in important carbonylation reactions [1]:



$$[M]\begin{array}{l}(CO)_mX\\ (CO)_nY\end{array} \longrightarrow \underset{p = 1, 2 \text{ or } 3}{X(CO)_pY} \qquad (1)$$

A
$m = 1$
$n = 0, 1$ or 2

Reaction (1) is deceptively simple since it describes different situations and a number of mechanisms which are more or less understood. Only a few metals (generally in a low oxidation state and belonging to Groups 8, 9 and 10) are efficient in this reaction.

The two organic ligands should be in the favourable *cis* disposition on complexes **A**, and it has been shown that a transient decoordination of an ancillary ligand (which can be CO itself) often favours carbonylation [2,3]. The nature of the two organic ligands involved in this carbon–carbon coupling is also of importance, as shown below.

Monocarbonylation (reaction (1) with $p = 1$) generally involves one alkyl ligand and one ligand linked to the metal through a carbonyl carbon atom (**A** with $m = 1$ and $n = 0$). The C–C coupling reaction on acyl alkyl complexes [M](COR)(R′) is generally fast and gives rise to ketones [2]. Indeed its ease has often hindered the characterization of organometallic models for this carbonylation step. Acyl alkyl complexes have been described for M = Re [4] and M = Pt [5]. For our part, we have characterized the moderately stable complex *cis*-$[Fe(CH_2CO_2Me)(COMe)(CO)_4]$ and have shown that it cleanly thermolyses to give methyl acetyl acetate [6].

Alkoxycarbonyl alkyl complexes $[M](CO_2R)(R')$ have been described for Fe [7,8] and Pt [9]. They readily give

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TABLE 1. Spectroscopic data for complexes 1–7

Complex	IR (hexane) (cm^{-1})		NMR (CD$_2$Cl$_2$, −20°C) δ (ppm)					
	ν(C≡O)	ν(C=O)	^{13}C					^{1}H
			C=O acyl	C≡O	CO$_2$R	COCO$_2$R	R	
1a	2120m	1730m	239.8	200.0(1)		162.3	53.7	3.71(s)
	2072s	1670m, br		199.4(1)				
	2062vs							
	2053s, sh							
1b	2121m	1725m	240.0	199.7(1)		162.6	63.6	4.21(q, 2H, J(H–H) = 7 Hz)
	2069s	1670m, br		198.4(1)			13.8	1.29(t, 3H, J(H–H) = 7 Hz)
	2060vs							
	2051s, sh							
2a	2128m	1735m	239.2	200.1(2)	192.7	164.7	53.8	3.78(s)
	2075s	1675m		198.5(1)			53.5	3.61(s)
	2064vs	1665m, sh		198.3(1)				
	2058s							
2b	2125m	1732m	239.5	200.2(2)	191.9	163.8	63.2	4.20(q, 2H, J(H–H) = 7 Hz)
	2070s, sh	1679m		198.4(1)			62.8	4.07(q, 2H, J(H–H) = 7 Hz)
	2061s	1666m		198.2(1)			14.3	1.29(t, 3H, J(H–H) = 7 Hz)
	2052s, sh						13.9	1.17(t, 3H, J(H–H) = 7 Hz)
2c	2125m	1725m	239.5	200.5(1)	191.3	163.5	71.4	5.06–4.96(m, 1H)
	2072s	1675m		198.8(1)			70.0	1.27(d, 3H, J(H–H) = 6.2 Hz)
	2062vs	1660m					21.9	1.15(d, 3H, J(H–H) = 6.2 Hz)
	2055s						21.5	
2d	2128m	1730m	239.0	200.1(2)	192.5	164.0	63.3	4.27(q, 2H, J(H–H) = 7 Hz)
	2075s	1675m		198.5(1)			53.8	3.64(s, 3H)
	2068vs	1665m, sh		198.3(1)			14.0	1.33(t, 3H, J(H–H) = 7 Hz)
	2058s							
2e	2128m	1735m	239.5	200.2(2)	192.0	164.5	62.9	4.07(q, 2H, J(H–H) = 7 Hz)
	2075s	1675m		198.3(1)			53.6	3.77(s, 3H)
	2065vs	1662m		198.2(1)			14.3	1.17(t, 3H, J(H–H) = 7 Hz)
	2058s							

3a [18]	2138m 2080vs, sh 2075vs 2052vs	1665m, br		198.8(1) 198.7(1)	192.6		53.7	3.69(s)
3b [18]	2131m 2072s, sh 2069vs 2046s	1665m, br		199.8(1) 199.4(1)	191.7		62.2 14.4	4.11(q, 2H, *J*(H–H) = 7 Hz) 1.20(t, 3H, *J*(H–H) = 7 Hz)
3c	2135m 2076s, sh 2070vs 2048vs	1658m, br		200.0(1) 199.6(1)	191.2		69.1 21.9	5.05(sept, 1H, *J*(H–H) = 6.2 Hz) 1.16(d, 6H, *J*(H–H) = 6.2 Hz)
3d [18]				200.1(2) 199.8(1) 199.6(1)	192.2(1) 191.3(1)		62.6 53.6 14.8	4.09(q, 2H, *J*(H–H) = 7 Hz) 3.61(s, 3H) 1.34(t, 3H, *J*(H–H) = 7 Hz)
4 [a]			247.1(d, *J*(C–P) = 22 Hz)	206.7(2)(d, *J*(C–P) = 17 Hz) 205.2(1)(d, *J*(C–P) = 8 Hz)	199.7(d, *J*(C–P) = 17 Hz)	164.7(d, *J*(C–P) = 18 Hz)	53.8 53.6	7.4–7.2(m, 15H) 3.72(s, 3H) 3.61(s, 3H)
5 [18] [b]	2100m 2035vs 2020s, sh	1645m, br 1630m, br		205.9(2)(d, *J*(C–P) = 16 Hz) 205.7(1)(d, *J*(C–P) = 9.5 Hz)	201.7(1)(d, *J*(C–P) = 19.5 Hz 197.0(1)(d, *J*(C–P) = 30 Hz)		52.4 51.4	7.6–7.4(m, 15H) 3.63(s, 3H) 3.23(s, 3H)
6	2195m [c] 2150s 2135s	1740m 1685m	225.3 [d]	199.9(4) 189.9(1)		159.2	55.9	3.87(s)
7 [18]	2195m [c] 2145s 2130s	1680m, br	[d]	191.7(4) 184.4(1)	180.0		57.7	3.78(s)

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[a] ^{31}P NMR for **4**: $\delta = 45.1$ ppm.

[b] ^{31}P NMR for **5**: $\delta = 42.6$ ppm.

[c] Nujol.

[d] CD_3CN, -30°C.

organic esters. It is worth recalling that the hydroxycarbonyl analogues (R = H) undergo preferential carbon dioxide elimination [10].

A second type of coupling, involving an intermediate with two organic ligands linked to the metal through a carbonyl carbon atom (**A** with $m = 1$ and $n = 1$), should account for the "double carbonylation" (reaction (1) with $p = 2$) and here too several cases are known.

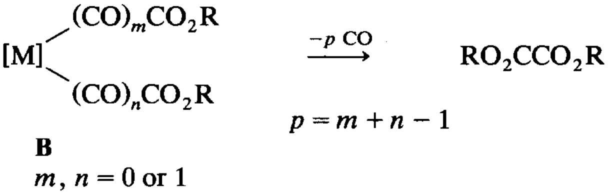
For example, there is a coupling between two acyl ligands to give diketones. Most of the bis(acyl) complexes [M](COR)(COR′) described in the literature, either anionic M = Mn [11] and M = Re [12], or neutral M = Pt [5] and M = Fe [13], undergo decarbonylation to acyl alkyl complexes which give rise to monocarbonylation reaction. However, *cis*-[Pt(COMe)(COEt)(PPh$_3$)$_2$] affords 33% of the diketone MeCOCOEt together with 66% of MeCOEt [14]. This provided the first clear-cut example of carbon–carbon coupling between two acyl ligands to give α-diketones.

The catalytic double carbonylation of several organic halides to give α-ketoamides or ketoesters is now well recognized, with either Co or Pd as catalyst (see for example [15]). However, no organometallic model system exists for M = Co, and those for M = Pd have their two organic ligands *trans*. Whilst *trans*-[Pd(COPh){CON(CH$_2$)$_4$}/(PMe$_3$)$_2$] thermolyses to α-ketoamide, the *trans* geometry suggests that the process is somewhat complicated [16]. A carbamoyl group favours carbon–carbon coupling, as shown by the thermolysis of *cis*-[Pt(COPh)(CONEt$_2$)(PPh$_3$)$_2$] to PhCOCONEt$_2$ (17%) whereas its alkoxycarbonyl analogue only produced traces of PhCOCO$_2$Me [17].

A final model for double-carbonylation reactions are bis-(alkoxycarbonyl) complexes [M](CO$_2$R)$_2$. There is as yet no clear-cut evidence for their coupling into oxalate. We addressed this problem in a recent paper dealing with complexes [Fe(CO$_2$R)$_2$(CO)$_4$] [18].

A few models have been designed to explore the possibility of the still undetected "triple carbonylation" (reaction (1) with $m = 1$, $n = 2$ and $p = 3$). Some recent models with M = Pt have the unfavourable *trans* geometry [19]. The complex *cis*-[Pt(COCOPh)(CONEt$_2$)(PPh$_3$)$_2$] has been characterized but no thermal decomposition was reported [20].

Such direct coupling is very unlikely, owing to the facile decarbonylation of α-ketoacyl, ester or carbamoyl ligands [19,21–23]. Nevertheless, we hoped that the transient destabilization provided by such a process could produce oxalate (reaction (2) with $m = 1$ and $n = 0$ or 1), which has never been detected after thermolysis of dialkoxycarbonyl complex (reaction (2) giving **B** with m, $n = 0$):



$$[\mathrm{M}]\begin{cases}(\mathrm{CO})_m\mathrm{CO_2R}\\(\mathrm{CO})_n\mathrm{CO_2R}\end{cases}\xrightarrow{-p\,\mathrm{CO}}\mathrm{RO_2CCO_2R}\qquad p = m + n - 1$$

B

$m, n = 0$ or 1

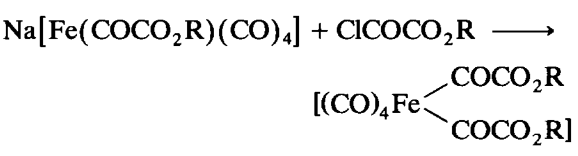
(2)

We report here the synthesis of an unusual series of complexes **B** with [M] = Fe(CO)$_4$, $m = 1$, $n = 0$ or 1 and their subsequent thermolysis into oxalate esters.

2. Results and discussion

2.1. Synthesis and thermolysis of bis(alkyloxalyl) complexes [Fe(COCO$_2$R)$_2$(CO)$_4$](1)

The *cis* bis(alkyloxalyl) complexes [Fe(COCO$_2$R)$_2$(CO)$_4$] (R = Me (**1a**), Et (**1b**)) were prepared with a 40% yield from Na[Fe(COCO$_2$R)(CO)$_4$] [24] and ClCOCO$_2$R in tetrahydrofuran (THF) at −40°C



$$\mathrm{Na[Fe(COCO_2R)(CO)_4] + ClCOCO_2R}\longrightarrow[(\mathrm{CO})_4\mathrm{Fe}\begin{cases}\mathrm{COCO_2R}\\\mathrm{COCO_2R}]\end{cases}\qquad(3)$$

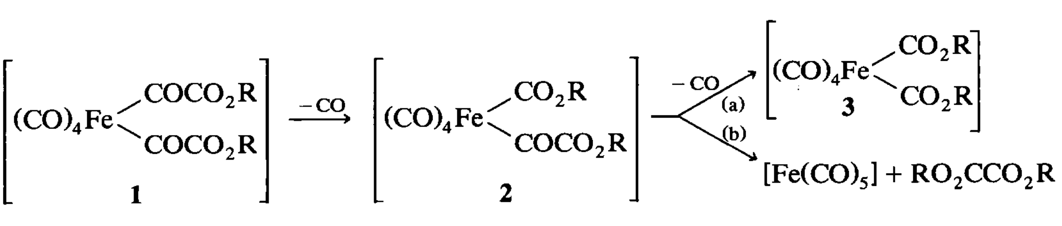
1

1a: R = Me

1b: R = Et

(reaction (3)). They were purified by low-temperature recrystallization from hexane, as pale-yellow microcrystals.

Their spectra (Table 1) are fully consistent with the proposed formulae. The four IR bands observed in the metal carbonyl stretching region are consistent with a C_{2v} symmetry for the Fe(CO)$_4$ group. A band at 1730



Scheme 1.

cm^{-1} was assigned to the ester group of the alkyloxalyl which has ν(CO)(acyl) at 1670 cm^{-1}.

The two resonances in the ^{13}C NMR spectrum of **1a** or **1b** for the four terminal carbonyl groups are also consistent with a *cis* disposition of the two alkyloxalyl ligands. The resonance to higher fields was assigned to the two carbonyl groups *trans* to the electron-withdrawing alkyloxalyl ligands.

To our knowledge, **1a** and **1b** are the first complexes bearing two ligands of the type COCOX. These *cis* ligands are susceptible to intramolecular carbon–carbon coupling via a thermally induced reductive elimination reaction.

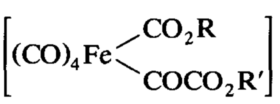
Complexes **1a** or **1b** were found to be stable in solution at a low temperature. When the temperature of the solution was raised to 12°C, carbon monoxide evolution was observed, giving a single organometallic compound **2** without any organic compound (Scheme 1). The reaction reached completion within 14 h at 12°C. Further reaction of **2** is described in the next section.

The structure *cis*-[Fe(CO$_2$R)(COCO$_2$R)(CO)$_4$] (R = Me (**2a**) or Et (**2b**)) was attributed to these new compounds on the basis of their spectroscopic features (Table 1), which were quite similar to those obtained for complexes **1**. ν(CO) for the alkoxycarbonyl bound to the metal was observed at 1665 cm^{-1}. The ^{13}C NMR spectra confirm the *cis* alkoxycarbonyl and alkyloxalyl, with three signals (2 : 1 : 1) for the terminal CO ligands.

2.2. *Synthesis and thermolysis of (alkoxycarbonyl)(alkyloxalyl) complexes [Fe(CO$_2$R)(COCO$_2$R')(CO)$_4$] (2)*

To confirm the structure of complexes **2a** and **2b**, direct synthesis of these compounds was undertaken by reaction of Na[Fe(CO$_2$R)(CO)$_4$] [25] with one equivalent of ClCOCO$_2$R' in THF at −20°C (reaction (4)):

$$\mathrm{Na[Fe(CO_2R)(CO)_4] + ClCOCO_2R' \longrightarrow}$$



$$\left[(\mathrm{CO})_4\mathrm{Fe}\begin{matrix}\nearrow \mathrm{CO_2R}\\ \searrow \mathrm{COCO_2R'}\end{matrix}\right] \qquad (4)$$

2
2a: R = R' = Me
2b: R = R' = Et
2c: R = R' = ^{i}Pr
2d: R = Me, R' = Et
2e: R = Et, R' = Me

Complexes **2** (R = R' = Me (**2a**), Et (**2b**) or ^{i}Pr (**2c**) and R ≠ R', R = Me, R' = Et (**2d**) or R = Et, R' = Me (**2e**)) were obtained as pale-yellow powders (about 25% yields after recrystallization). Their spectra were identical with those of complexes obtained by decarbonylation of **1** (Table 1).

TABLE 2. Influence of the nature of R on the thermolysis of 2

R = R'	Decarbonylation reaction (a)	C–C coupling reaction (b)
Me (**2a**)	85%	15%
Et (**2b**)	70%	30%
^{i}Pr (**2c**)	50%	50%

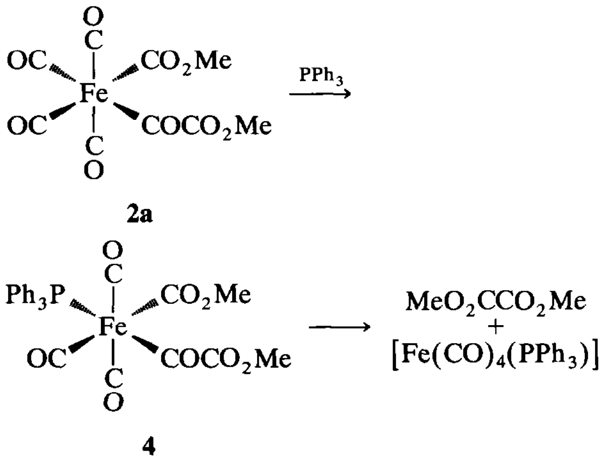
The complexes **2**, which are stable in solution at low temperatures, decompose slowly at +28°C. Two different processes were detected by (Scheme 1) ^{13}C NMR when R = R'. The first was decarbonylation into [Fe(CO$_2$R)$_2$(CO)$_4$] (reaction (a)). This was concomitant with carbon–carbon coupling with loss of CO, giving [Fe(CO)$_5$] and oxalates (reaction (b)). The bis(alkoxycarbonyl) complexes **3** were identified by comparison with ^{13}C NMR data of authentic samples (see Table 1) [18]. Oxalates are not released from complexes **3** which appear quite reluctant to give C–C coupling, even after heating for several hours at 70°C [18]. No ketomalonate (ROCOCOCO$_2$R') was detected in solution, even when the reaction was performed under CO pressure, and this rules out direct carbon–carbon coupling on complexes **2**.

Several factors influence the balance between the two pathways for the thermolysis of **2**.

(1) *The nature of R and R'.* Table 2 shows that bulkier and more electron-donating ligand R seemed to favour carbon–carbon coupling.

(2) *The carbon monoxide pressure.* The reactions were run under dinitrogen in an autoclave at +34°C. After 2.5 h, 75% of **2a** had disappeared. This amount lessened dramatically under a low carbon monoxide pressure (50% at 2 bar), but increasing the pressure of CO to 5 bar brought little change (45% at 10 bar). These results might suggest two different paths, only one of them requiring initial decoordination of a terminal carbonyl ligand and inhibited by free carbon monoxide. However, as the ratio of the two observed reactions (the decarbonylation and the carbon–carbon coupling) is not modified by the variation in CO pressure, the existence of these two pathways seems unlikely.

(3) *The presence of PPh$_3$.* The thermolysis of **2a** in the presence of two equivalents of triphenylphosphine was monitored by ^{13}C NMR spectroscopy at 28°C under a dinitrogen atmosphere. Prior substitution of one equatorial CO by PPh$_3$ was observed, affording complex **4** as a single isomer, which rapidly decomposed *in situ* into methyl oxalate and [Fe(CO)$_4$PPh$_3$] (reaction (5)):



(5)

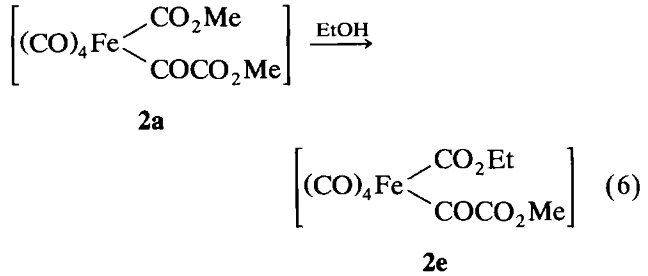
It is worth noting that no $[Fe(CO_2Me)_2(CO)_3PPh_3]$ was detected; this last complex, which is stable under these conditions [18], cannot give rise to oxalate. However, the ^{13}C NMR characteristics (Table 1) of this intermediate and the comparison with those of the known $[Fe(CO_2Me)_2(CO)_3(PPh_3)]$ [18] suggested a *mer* structure (two axial equivalent terminal carbonyl groups). Judged by the value of J(C–P) the phosphine was probably *trans* to the alkyloxalyl ligand. The electronic effect of the phosphine was indicated by a shift of about 8 ppm toward a lower field.

To our knowledge, **2** and **4** are the first compounds whose decomposition gives oxalate with a high yield. This carbon–carbon coupling reaction is favoured by the strong electron-donating substituents of the esters and by increasing the electronic density at the metal *.

2.3. Mobility of the alkoxy group on complexes 2

The lability of the alkoxy group on $[M](CO_2R)$ complexes is well known [28]. The reaction exchange with an alcohol generally does not require any catalyst. Whatever the mechanism (associative [29] or dissociative [30]) this is undoubtedly due to coordination.

Reaction of **2a** with one equivalent of ethanol was monitored at 10°C in CD_2Cl_2 by ^{13}C NMR spectroscopy. The formation of 25% of **2e** was observed after 30 min. A 50:50 equilibrium of the two compounds was reached after 2 h. No exchange was observed with the methyloxalyl ligand. With an excess of ethanol, the only product of the reaction was the single *cis* isomer of **2e** (reaction (6)):



(6)

Under the same conditions, complexes **1** were found to be unreactive; again no exchange of alkoxy on alkyloxalyl ligands was observed.

A cross-over experiment was run with complexes **2a** and **2b** in solution in CD_2Cl_2 at 10°C. After 2 h an equilibrium between the four complexes **2a** (25%), **2b** (25%), **2d** (25%) and **2e** (25%) was reached.

Exchanges with alcohol have been best explained by association, as no isomerization was observed and as the liberation of RO^- would probably lead to some alkyloxalyl exchange [23a]. However, such an associative mechanism is unlikely in the exchanges between two complexes and a dissociative process cannot be dismissed. This process might occur through the $[Fe(COCO_2Me)(CO)_5]^+$ cation, but this was unobserved *in situ* even in high dielectric constant solvents such as formamide. However, this cation was subsequently synthesized as described below.

2.4. Preparation of [Fe(COCO2Me)(CO)5][BF4] (6)

The complex **2a** in solution in THF at −20°C reacts rapidly with two equivalents of $HBF_4 \cdot OMe_2$. The new cation **6** is precipitated as its tetrafluoroborate salt (reaction (7)):

$$\underset{\mathbf{2a}}{[Fe(CO)_2Me\,)\,(COCO_2Me)(CO)_4]} \xrightarrow[-MeOH]{HBF_4\cdot Me_2O} \underset{\mathbf{6}}{[Fe(COCO_2Me)(CO)_5][BF_4]} \quad (7)$$

The spectroscopic characteristics of **6** are very similar to those of the known compound $[Fe(CO_2Me)(CO)_5][BF_4]$ (**7**) (Table 1).

Its IR spectrum is consistent with a C_{4v} symmetry of the five carbonyls, with two additional bands for the methyloxalyl ligand. The high values observed for these frequencies are indicative of a cationic form.

The complex **6** was soluble only in acetonitrile and acetone, and in these solvents it did not show any tendancy to decarbonylate. This is consistent with the results obtained with platinum α-ketoacyl cations which decarbonylate rapidly only in the absence of a potential ligand [23c,31].

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* Oxidatively induced reductive elimination is a well-known process and double carbonylation had been observed upon reaction of diacyl or dialkoxycarbonyl complexes with I_2 or Br_2 [26,27]. When complexes **1** or **2** were allowed to react with Ce^{IV} salts or with I_2 at a low temperature, the only organic products formed were oxalates. No trace of ketomalonates or diketosuccinates, products of tricarbonylations and tetracarbonylations, were detected.

Complex **6** reacted instantaneously at −35°C in CD_3CN with one equivalent of MeONa to give **2a** quantitatively. Careful monitoring of the reaction showed no evidence for a *trans* isomer. This is consistent with a possible dissociative mechanism in the alkoxy exchange on alkoxycarbonyls.

3. Experimental section

All manipulations were carried out under an inert atmosphere using standard Schlenck techniques. The solvents were purified under dinitrogen and used freshly distilled from a desiccant before use: sodium–benzophenone for THF; $LiAlH_4$ for hexane; CaH_2 for dichloromethane; P_2O_5 for acetonitrile. Deuterated dichloromethane, acetonitrile or acetone were stored over molecular sieves under argon. Anhydrous ethanol or methanol or iso-propanol were obtained by distillation from $Mg(OR)_2$ under dinitrogen. Alkoxides were prepared by reacting the appropriate alcohol with sodium under argon. $Na_2[Fe(CO)_4]$ was prepared as previously reported [32]. The salts $Na[Fe(CO_2R)(CO)_4]$ were obtained according to the procedure of McLean [25] for the synthesis of $Na[Fe(CO_2Me)(CO)_4]$. $Na[Fe(COCO_2R)(CO)_4]$ was prepared as described in ref. 24.

MeOCOCOCl, EtOCOCOCl and all other reagents were used as supplied by Aldrich. ^1H (300 MHz) and ^{13}C (75.47 MHz) NMR spectra were recorded on a Bruker AC300 spectrometer. Chemical shifts were measured relative to residual protonated solvents for ^1H NMR spectra and to the solvent resonance for ^{13}C NMR spectra. A JEOL FX100 instrument was used to obtain the ^{31}P spectra (40.27 MHz) and chemical shifts are given relative to 87% H_3PO_4. Values upfield of the standard were defined as negative. The solvent was CD_2Cl_2 unless otherwise specified. The IR spectra were run on a Perkin-Elmer 1430 spectrometer. Mass spectroscopy analyses were obtained on a Hewlett–Packard GCMS 5995 instrument (70 eV). Gas chromatography (GC) studies were performed on a Hewlett–Packard 5890 instrument using a CP SIL 25 m capillary column. Microanalyses were carried out either by the Centre de Microanalyses du CNRS de Lyon or by the Analytische Laboratorien Dr Malissa and Reuter, Germany.

3.1. General procedure for the synthesis of bis(alkyloxalyl)tetracarbonyliron (1)

The anion $[Fe(COCO_2R)(CO)_4]^-$ was prepared *in situ* in solution in THF at 0°C by reaction of 10 mmol of $ClCOCO_2R$ with 10 mmol of $Na_2[Fe(CO)_4]$-1.5 dioxane [32] according to ref. 24. After 0.5 h the solution was cooled to −20°C and 10 mmol of $ClCOCO_2R$ was added. The mixture was stirred at this temperature for 1 h as the dark-orange colour of the solution turned green. After removal of the solvent under vacuum at a low temperature the residue was extracted with two portions of cold hexane (R = Et (**1b**)) or of 80% hexane–20% dichloromethane (R = Me (**1a**)). The products **1** precipitated as pale-yellow needles upon partial removal (40%) of the solvent *in vacuo* at −60°C. Removal of the remaining solution and washing with 2 ml of cold hexane gave complexes **1**. They are very temperature sensitive and repeated attempts at obtaining satisfactory elemental analyses were unsuccessful.

1a: yield, 45%. *m/z*: 314 (M^+ − CO).

1b: yield, 40%. *m/z*: 342 (M^+ − CO).

3.2. General procedure for the preparation of (alkyloxalyl)(alkoxycarbonyl)tetracarbonyliron (2)

The anions $[Fe(CO_2R)(CO)_4]^-$ were prepared by adding 15 mmol of $[Fe(CO)_5]$ to a suspension of NaOR (10 mmol) in 20 ml of THF at 0°C [25]. The alcoholate dissolved gradually as the solution turned orange. After 30 min the solution was cooled to −20°C, and 10 mmol of the appropriate alkyloxalylchloride ($ClCOCO_2R$) were added dropwise by syringe. The solution turned green. THF was removed at a low temperature and the residue extracted with a suitable solvent: 80% hexane–20% dichloromethane for **2a**; hexane for **2b** and **2c**; 90% hexane–10% dichloromethane for **2d** and **2e**. Compounds **2** were then obtained as described for **1** as pale-yellow powders.

2a $[Fe(CO_2Me)(COCO_2Me)(CO)_4]$: yield, 28%. *m/z*: 314 (M^+). Anal. Found: C, 34.71; H, 1.97; Fe, 17.61. $C_9H_6FeO_9$ calc.: C, 34.43; H, 1.91; Fe, 17.78%.

2b $[Fe(CO_2Et)(COCO_2Et)(CO)_4]$: yield, 25%. *m/z*: 342 (M^+). Anal. Found: C, 38.75; H, 2.95; Fe, 16.17. $C_{11}H_{10}FeO_9$ calc.: C, 38.63; H, 2.92; Fe, 16.32%.

2c $[Fe(CO_2{}^iPr)(COCO_2{}^iPr)(CO)_4]$: yield, 23%. *m/z*: 370 (M^+). Anal. Found: C, 42.45; H, 3.85; Fe, 14.92. $C_{13}H_{14}FeO_9$ calc.: C, 42.20; H, 3.78; Fe, 15.09%.

2d $[Fe(CO_2Me)(COCO_2Et)(CO)_4]$: yield, 25%. *m/z*: 328 (M^+). Anal. Found: C, 36.71; H, 2.51; Fe, 16.95. $C_{10}H_8FeO_9$ calc.: C, 36.62; H, 2.44; Fe, 17.03%.

2e $[Fe(CO_2Et)(COCO_2Me)(CO)_4]$: yield, 21%. *m/z*: 328 (M^+). Anal. Found: C, 36.62; H, 2.45; Fe, 17.00. $C_{10}H_8FeO_9$ calc.: C, 36.62; H, 2.44; Fe, 17.03%.

3.3. General procedure for the thermolysis of compounds 1 and 2: monitored by ^{13}C nuclear magnetic resonance

A solution of 0.1 mmol of **1** or **2** in 0.7 ml of CD_2Cl_2 at 0°C was introduced into an NMR tube. The temperature of the NMR probe was maintained at 12°C (**1**) or at 28°C (**2**), and ^{13}C spectra were recorded every 30 min. The products **2** and **3** formed were identified by comparison with the ^{13}C data of authentic samples. Free CO and [Fe(CO)$_5$] were detected as singlets at 184 ppm and 211 ppm respectively. [Fe(CO)$_5$], ROCOCO$_2$R, ROCO$_2$R and ROH were detected by gas chromatography.

3.4. Influence of CO pressure on the thermolysis of ***2a***

A solution of 0.3 mmol (94 mg) of [Fe(CO$_2$Me)(CO-CO$_2$Me)(CO)$_4$] (**2a**) in 15 ml of CH$_2$Cl$_2$ was introduced into an autoclave thermostatted at 34°C. The desired CO pressure was applied to the solution which was stirred for 2.5 h. MeOCOCO$_2$Me, MeOCO$_2$Me, MeOH and [Fe(CO)$_5$] were detected as above. The solution was then cooled and the solvent was removed under vacuum. The residue was redissolved in 0.7 ml of CD$_2$Cl$_2$ and its composition determined by ^{13}C NMR spectroscopy as described above.

3.5. Thermolysis of ***2a*** *in the presence of two equivalents of triphenylphosphine*

A mixture of 0.1 mmol (31 mg) of **2a** and of 0.2 mmol (53 mg) of PPh$_3$ in solution in 0.7 ml of CD$_2$Cl$_2$ was introduced into an NMR tube. The reaction was monitored by ^{13}C or ^{31}P NMR spectroscopy at 28°C. Complex **4** was detected (Table 1), but its rapid decomposition at 28°C did not allowed its isolation. The decomposition of **4** was also monitored by ^{13}C NMR spectroscopy. [Fe(CO)$_4$(PPh$_3$)] [33] was identified by comparison with the data of authentic samples. The composition of the different organic products in the final mixture was determined by GC.

3.6. ^{13}C monitoring of the alkoxy group exchanges on complexe ***2a***

*3.6.1. Reaction between [Fe(CO$_2$Me)(COCO$_2$Me)-(CO)$_4$] (**2a**) and EtOH*

A solution of 0.2 mmol (63 mg) of **2a** and 0.2 mmol (0.012 ml) of ethanol (equimolecular reaction) or 2 mmol (0.12 ml) of ethanol (in an excess) was maintained at 10°C in an NMR tube. ^{13}C NMR spectra recorded every 15 min showed the appearance of **2e**. This complex was identified by comparison with an authentic sample (see above).

3.6.2. Alkoxy exchanges on ***2a*** *and* ***2b***

The ^{13}C monitoring of this reaction was carried out as described above using 0.2 mmol (63 mg) of **2a** and 0.2 mmol (69 mg) of **2b**. The new complexes formed during the reaction (**2d** and **2e**) were identified in the usual way.

*3.7. Preparation of [Fe(COCO$_2$Me)(CO)$_5$][BF$_4$] (**6**)*

A cold solution of **2a** (0.64 mmol, 200 mg) in 10 ml of THF was treated dropwise with two equivalents of HBF$_4$ · OMe$_2$ (1.28 mmol, 0.117 ml). **6** precipitated very rapidly as a white powder. Removal of the solvent via a cannula, washing with cold THF (2 × 5 ml) and drying under vacuum gave **6**. This complex was soluble in only acetone or acetonitrile and is extremely sensitive to moisture.

6: yield, 60% (140 mg). Anal. Found: C, 26.15; H, 0.95; Fe, 15.02. C$_8$H$_3$BF$_4$FeO$_8$ calc.: C, 25.99; H, 0.81; Fe, 15.11%.

3.8. Reaction of ***6*** *with NaOMe*

To a solution of 50 mg (0.135 mmol) of **6** in 0.6 ml of CD$_3$CN maintained at −40°C in an NMR tube was added a suspension of 0.135 mmol (7.3 mg) of NaOMe in 0.3 ml of CD$_3$CN at the same temperature. The reaction was immediate and the only product was **2a**, identified by comparison with an authentic sample.

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