

Thermal properties and reactions towards nucleophiles of an iron complex displaying an acetyl and a pyruvoyl ligands

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Abstract

Thermal evolution at 4 °C of the structurally characterized *cis*-(CO)₄Fe[C(O)C(O)CH₃][C(O)CH₃] (**1**(**2**)) gives rise to the *cis*-(CO)₄Fe-[C(O)CH₃]₂ (**1**(**3**)) which, probably owing to synthetic problems, has never been described in the literature. By reaction with anionic nucleophiles (Nu⁻), **1**(**2**) affords anionic trifunctionalized metallalactones {(CO)₃Fe[C(O)CH₃][C(O)C(CH₃)(Nu)OC⁷(O);(Fe-C⁷)]⁻ (**3**) formed by addition of the nucleophile reagent on the β carbon of the pyruvoyl moiety followed by the cyclization of this ligand on a terminal carbonyl of the complex. Anions **3** are characterized by ¹H and ¹³C NMR and by X-ray diffraction for the complex with Nu = C(H)(CO₂C₂H₅)₂. Complexes **3** are also prepared by reaction of CH₃Li with the neutral metallalactones (CO)₄Fe[C(O)C(CH₃)-(Nu)OC⁷(O);Fe-C⁷] (**2**). The results of this study shed light on the reaction of cyclization of a pyruvoyl ligand as they clearly show that the presence of a second ligand (for example CO₂R) with a labile OR group is not required to perform the formation of the metallalactone ring and then that the observed reaction has no connection with organic chain-ring transformations.
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1. Introduction

The carbonylated organic ligands of transition metal complexes have been long known to play an important role in many catalytic carbonylation reactions [1]. However, their complexation to metals atoms efficient in catalytic carbonylation processes, gives rise to unstable species making the properties of these compounds difficult to evaluate. To appraise the possible intervention of complexes substituted by one or two of these organic carbonylated ligands in mono or poly carbonylation processes, the study of similar more stable complexes of Pt, Mn, Co, Fe have been performed [2,3]. In the course of our study of tricarbonylation reactions induced by iron models of the type *cis*-(CO)₄Fe[C(O)C(O)R][C(O)R'], we did not observe, for R = CH₃ and R' = OCH₃ (**1**(**1**)), the expected car-

bon-carbon coupling process. At 15 °C this compound displayed a spontaneous isomerisation into the metallalactone **2**(**1**) (Scheme 1a) [4].

This process looks very similar to the well known ring-chain isomerism observed for organic γ-keto-esters [5] and, as complex **1**(**1**) can be considered as a γ-keto-ester with a metal inserted into its organic chain, it was attractive to establish a parallel between organic and organometallic reactions. However, unlike the organic isomerism, the metallalactone formation does not require acid or base catalysis and is not reversible. The cyclisation of **1**(**1**) performed in the presence of pronucleophile reagents (NuH) such as C₂H₅OH, CH₃SH, HP(C₆H₅)₂, or HP(C₆H₁₁)₂ gave rise to Nu substituted metallalactones **2** (Scheme 1b) [6]. The observed reactions are indicative of regioselective additions of the nucleophile reagents at the β-carbonyl of the pyruvoyl ligand of **1**(**1**). We recently performed the same reaction with anionic nucleophiles (C₂H₅O⁻, CH₃S⁻, (C₆H₅)₂P⁻, (C₆H₁₁)P⁻ or carbanions: CH₃⁻[C₂H₅OC(O)]₂-

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CH^- , $[\text{CH}_3\text{C}(\text{O})]_2\text{CH}^-$, $(\text{CN})_2\text{CH}^-$ etc) and observed the formation of anionic trifunctionalised metallalactones **3** (Scheme 1c) [7,8]. As shown in Scheme 2, two reaction paths can explain the formation of **3**. After addition of the nucleophile on the β -carbonyl of the pyruvoyl moiety, the first path (a) considers the formation of the metallalactone ring by addition of the oxygen of this carbonyl on the alkoxy carbonyl ligand with release of CH_3O^- which, by a further addition on a terminal carbonyl, would afford **3**. In the second path (b) the cyclization of the pyruvoyl moiety occurs on a terminal carbonyl ligand giving directly **3**.

The formation of **3** in very low yield by reaction of the neutral lactones **2** with CH_3O^- suggested the mechanism 2b as the most probable pathway of the reaction. This assumption was reinforced by the description, in the literature, of an hydride induced cyclisation of a phenylglyoxyl ligand on a terminal carbonyl of a manganese complex [9]. To confirm the possible formation of a metallalactone ring by addition of the pyruvoyl ligand on a terminal carbonyl, it seemed appropriate to perform the reaction on (pyruvoyl)(carbonyl)iron complexes which did not display ligands with labile groups. The present paper describes

the synthesis, the properties and the reactions with nucleophiles of such a compound: the *cis*-(CO)₄Fe[C(O)-C(O)CH₃][C(O)CH₃] (**1(2)**) a complex closely related to **1(1)**.

2. Results and discussion

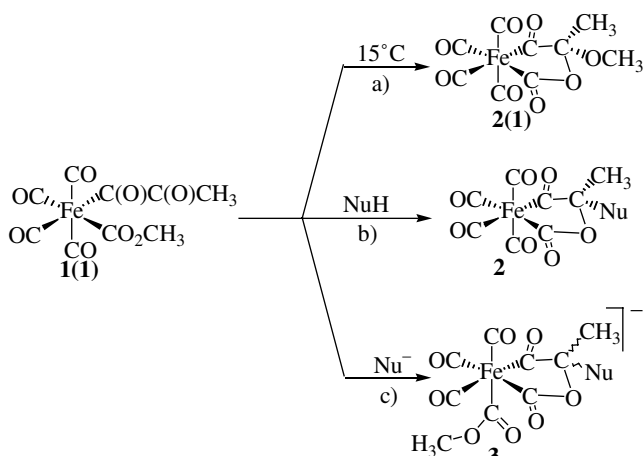
2.1. Preparation and properties of complex **1(2)**

1(2) is obtained as a pale yellow powder (45% yield) by reaction at -70°C of one equivalent of pyruvoyl chloride [10] with the anionic complex $\{\text{Fe}(\text{CO})_4[\text{C}(\text{O})\text{CH}_3]\}^-$ itself prepared *in situ* by addition at 0°C of CH_3Li on $\text{Fe}(\text{CO})_5$ [11]. Its IR spectrum displays four $\nu(\text{C}=\text{O})$ bands between 2115 and 2040 cm^{-1} while its ^{13}C NMR spectrum exhibits three signals at 201.8 (2 C), 201.1 and 198.9 ppm for the terminal $\text{C}=\text{O}$, two singlets at 245.2 and 198.6 ppm for the $\text{C}=\text{O}$ of the pyruvoyl moiety and one peak at 246.7 ppm for the carbonyl of the acetyl ligand. These spectra are indicative of the presence of an acetyl and of a pyruvoyl ligands in *cis* position on the carbonylated complex.

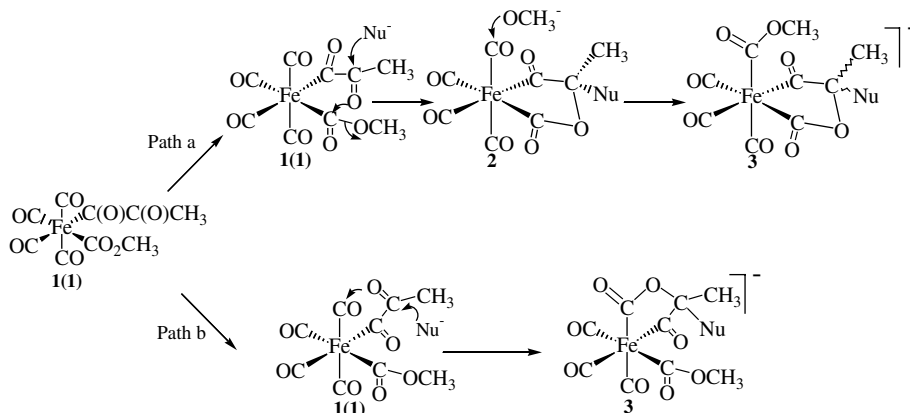
Crystals suitable for an X-ray diffraction study are obtained from an hexane solution at -30°C . This study confirms the structure attributed to complex **1(2)**. The ORTEP drawing of the molecule is displayed on Fig. 1; selected bond lengths and bond angles are listed in Table 1 and crystallographic data are mentioned in Table 4.

The ligands around the Fe (II) metal are disposed in a slightly distorted octahedron geometry.

The angle between the acetyl and the pyruvoyl ligands ($\text{C}(5)\text{--Fe--C}(7) = 85.7 (1)^\circ$) has a value intermediate between those generally observed for complexes displaying two organic carbonylated ligands in *cis* position on the metal ($88.93 (8)^\circ$ for a pyruvoyl-alkoxycarbonyl [7] or $88.5 (2)^\circ$ for a bis alkoxycarbonyl [12]) and those, smaller, measured for five membered iron metallacycle (from 79.3 to 82.6°) [4,6–8,13]. As usually observed for *cis* disubstituted iron complexes, the two axial terminal carbonyls are bent towards the plane which contains the two carbonylated organic ligands ($\text{C}(5)\text{--Fe--C}(7)$ plane). This is



Scheme 1.



Scheme 2.

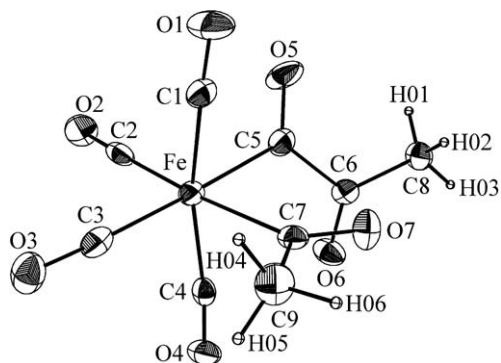


Fig. 1. ORTEP perspective view of the molecular structure of **1(2)** (50% ellipsoids).

Table 1
Bond lengths (Å) and bond angles (°) for compound **1(2)**

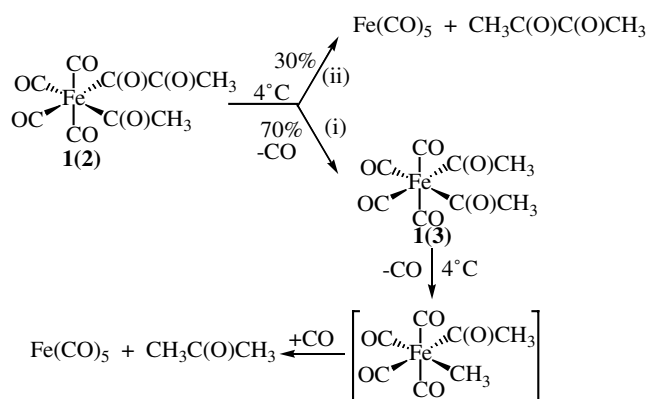
Fe–C(1)	1.802(3)	C(3)–O(3)	1.142(4)
Fe–C(2)	1.848(4)	C(4)–O(4)	1.135(4)
Fe–C(3)	1.840(4)	C(5)–O(5)	1.205(4)
Fe–C(4)	1.840(3)	C(5)–C(6)	1.547(5)
Fe–C(5)	2.038(4)	C(6)–O(6)	1.208(4)
Fe–C(7)	2.055(4)	C(6)–C(8)	1.483(5)
C(1)–O(1)	1.142(4)	C(7)–O(7)	1.205(4)
C(2)–O(2)	1.138(4)	C(7)–C(9)	1.491(5)
C(1)–Fe–C(2)	96.6(2)	C(5)–Fe–C(7)	85.7(1)
C(1)–Fe–C(3)	94.0(2)	Fe–C(1)–O(1)	177.9(3)
C(1)–Fe–C(4)	167.8(2)	Fe–C(2)–O(2)	178.3(3)
C(1)–Fe–C(5)	83.1(1)	Fe–C(3)–O(3)	177.2(3)
C(1)–Fe–C(7)	83.8(1)	Fe–C(4)–O(4)	172.4(3)
C(2)–Fe–C(3)	93.3(2)	Fe–C(5)–O(5)	124.2(3)
C(2)–Fe–C(4)	94.6(1)	Fe–C(5)–C(6)	120.5(2)
C(2)–Fe–C(5)	87.2(1)	O(5)–C(5)–C(6)	115.3(3)
C(2)–Fe–C(7)	172.8(1)	C(5)–C(6)–O(6)	119.6(3)
C(3)–Fe–C(4)	90.2(1)	C(5)–C(6)–C(8)	116.6(3)
C(3)–Fe–C(5)	177.1(1)	O(6)–C(6)–C(8)	123.5(3)
C(3)–Fe–C(7)	93.8(1)	Fe–C(7)–O(7)	121.0(3)
C(4)–Fe–C(5)	92.6(1)	Fe–C(7)–C(9)	119.0(3)
C(4)–Fe–C(7)	84.5(1)	O(7)–C(7)–C(9)	119.9(3)

well shown by the value of the C(1)–Fe–C(4) angle: 167.8 (2)°. The two carbonyls of the pyruvoyl ligand adopt an almost *s-trans* geometry with a torsion angle of 138.6 (3)° between these two groups. This value is similar to that measured for the pyruvoyl moiety of the close complex **1(1)**: 141.7 (2)° [7] but is smaller than those usually observed for α -keto acyl complexes (from 157° to 177°) [14]. It is also worth noting that smaller values have been observed for the homologues angles of α -keto acyl ligands of manganese (112° [15]) or platinum (127° [16]) complexes. To minimize the repulsions between the acetyl and the pyruvoyl moieties, these two ligands adopt staggered positions; the acetyl plane (Fe–C(7)–O(7)) is very close to the median plane of the complex (C(5)–Fe–C(7)) as these two planes exhibit a dihedral angle of 10°82 whereas the plane containing the metal and the α -acetyl of the pyruvoyl ligand (Fe–C(5)–O(5)) displays a dihedral angle of 56.91° with the C(5)–Fe–C(7) median plane. The two oxygen atoms of the α -C=O groups O(5) and O(7) are located from both sides of this plane. The carbon–carbon and the carbon–oxygen

distances of the pyruvoyl and of the acetyl ligands are normal. The relatively long Fe-terminal carbonyls bonds (1.84 Å) probably result from a reduced back donation towards these ligands induced by the electron-withdrawing effects of the two organic ligands. However, it is worth noting that the distance between the metal and one axial terminal carbonyl (Fe–C(1) = 1.802(3)) is shorter than the others and falls within the normal values found for this type of bonds.

2.2. Thermolysis of **1(2)**

Complex **1(2)**, in solution in hexanes or CH₂Cl₂, is found to evolve at 4 °C into Fe(CO)₅, acetone (70%) and butanedione (30%) with no trace of metallalactone complex formation. A ¹³C monitoring of the reaction shows, at the first stage of the process, together with the formation of butanedione and Fe(CO)₅ (30% of conversion) the appearance of a new organometallic compound (70%). As this complex displays only one resonance at 243.4 ppm for the C=O linked to the metal, two signals of equal intensities at 202.5 and 200.3 ppm for the terminal carbonyls and one peak at 49.2 ppm corresponding to a CH₃ acetyl, it very probably displays two similar ligands (acetyls) in *cis* position on the metal and is very likely the *cis*-(CO)₄Fe[C(O)CH₃]₂ (**1(3)**) formed by a selective decarbonylation of the pyruvoyl ligand of **1(2)**. Such a decarbonylation of a ligand displaying a double C=O chain has already been observed for the ethyloxalyl ligand of the close complex: *cis*-(CO)₄Fe[C(O)CO₂C₂H₅](CO₂C₂H₅) [17]. We were unable to isolate and to get a better characterization of **1(3)** as it very rapidly evolves thermally at 4 °C to afford Fe(CO)₅ and acetone. No additional formation of butanedione was observed at this stage of the reaction. The thermal evolution of **1(2)** can be described as two concurrent reactions: (i) a decarbonylation of the pyruvoyl ligand affording **1(3)** (70%) and (ii) a decarbonylating carbon–carbon coupling process giving rise to butanedione and Fe(CO)₅ (Scheme 3). The evolution of **1(3)** into acetone and Fe(CO)₅ can occur either by a second decarbonylating carbon–carbon coupling or by a decarbonylation



Scheme 3.

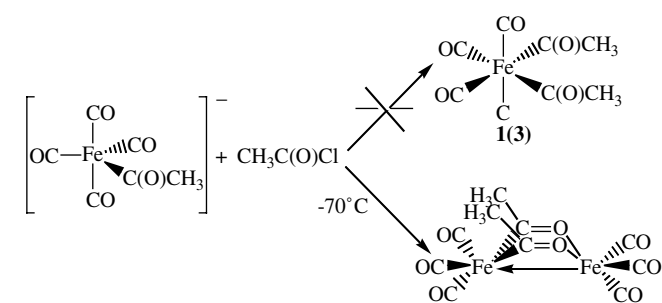
giving rise to the intermediate $(\text{CO})_4\text{Fe}(\text{CH}_3)[\text{C}(\text{O})\text{CH}_3]$ which is supposed to evolve rapidly, even at low temperature, to give acetone by an easy $\text{sp}^2\text{--sp}^3$ carbon–carbon coupling.

The formation of **1(3)** is of importance as bis-acyl iron monomer complexes described in the literature are scarce. They either present a cyclic structure [13,18] or display electron-withdrawing perfluorinated carbonylated ligands [19]. The observation of the bis-acyl complex **1(3)** by decarbonylation of **1(2)** suggests that a synthetic problem could explain the lack of achievement of such complexes. Indeed our attempts to prepare **1(3)** by reaction of $\text{CH}_3\text{C}(\text{O})\text{Cl}$ with $[(\text{CO})_4\text{Fe}\{\text{C}(\text{O})\text{CH}_3\}]^-$ failed as the only product of this reaction, even performed at -70°C , was a bimetallic complex displaying two acetyl ligands in bridging position (Scheme 4). This complex is identified by comparison with an authentic sample as we already obtained it by reaction of $[(\text{CO})_4\text{Fe}\{\text{C}(\text{O})\text{CH}_3\}]^-$ with oxalyl chloride [20].

Though known for over than 30 years, the number of this type of iron dimers is very limited. Most of them are prepared by oxidation of anions $[(\text{CO})_4\text{Fe}\{\text{C}(\text{O})\text{R}\}]^-$ with one electron oxidants ($\text{R} = \text{CH}_3$, C_6H_5 [11a,20,21]; C_9H_{19} [21c,21d]; $\text{N}(\text{C}_2\text{H}_5)_2$ [22] N^{i-}Pr_2 [20,23]. In the present process, as observed for the reaction of $[(\text{CO})_4\text{Fe}\{\text{C}(\text{O})\text{CH}_3\}]^-$ with oxalyl chloride [20], or when $[(\text{CO})_4\text{Fe}\{\text{C}(\text{O})\text{N}^{i-}\text{Pr}_2\}]^-$ is allowed to react with $\text{ClC}(\text{O})\text{N}^{i-}\text{Pr}_2$ [20] or HgCl_2 [23] the organic chloride can play the part of the oxidant.

2.3. Reaction of **1(2)** with nucleophiles

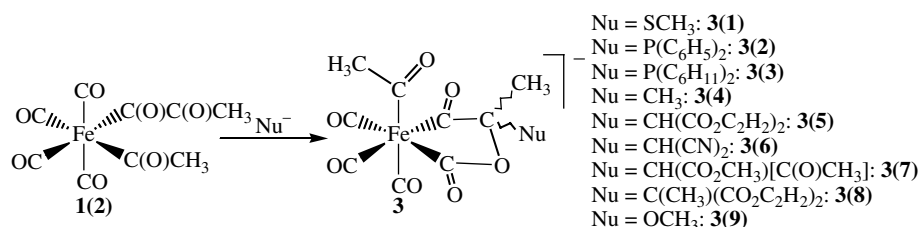
As its thermolysis did not give rise to a metallalactone complex we tried to induce this metallalactone formation by reacting **1(2)** with various nucleophiles.



Scheme 4.

Contrary to $(\text{CO})_4\text{Fe}[\text{C}(\text{O})\text{C}(\text{O})\text{CH}_3][\text{CO}_2\text{CH}_3]$ (**1(1)**) which, in the presence of pronucleophiles such as CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CH_3SH , $\text{HP}(\text{C}_6\text{H}_5)_3$ or $\text{HP}(\text{C}_6\text{H}_{11})_3$ at -70°C , affords very rapidly Nu substituted neutral metallalactones, thermolysis of **1(2)** at 4°C in the presence of these reagents, only gives rise to the same products than those already obtained when the thermolysis was performed without nucleophile. **1(2)** is also found unreactive towards anionic nucleophiles such as CH_3O^- or $[\text{CH}_3\text{C}(\text{O})]_2\text{CH}^-$. On the other hand, IR monitorings of its reaction at -70°C with CH_3SNa , $(\text{C}_6\text{H}_5)_2\text{PLi}$, $(\text{C}_6\text{H}_{11})_2\text{PLi}$, CH_3Li , $[\text{C}_2\text{H}_5\text{OC}(\text{O})]_2\text{CHNa}$, $(\text{CN})_2\text{CHNa}$, $[\text{CH}_3\text{C}(\text{O})][\text{CH}_3\text{OC}(\text{O})]\text{CHNa}$ or $[\text{C}_2\text{H}_5\text{OC}(\text{O})]_2(\text{CH}_3)\text{CNa}$ show rapid formation of new complexes displaying $\nu\text{C}\equiv\text{O}$ bands between 2070 and 1983 cm^{-1} . The values of these frequencies which fall between those observed for monofunctionalized anionic compounds (1910 cm^{-1} [24]) and those displayed by neutral difunctionalized iron complexes (from 2115 to 2040 cm^{-1} for complexes **1(1)** or **1(2)**) suggested, as observed for analogous reactions performed with **1(1)** [7,8], the possible formation of anionic *fac* trifunctionalized complexes **3** (Scheme 5).

The observation of three $\nu\text{C}\equiv\text{O}$ bands instead of the two bands formally required by a *fac* $\text{L}_3\text{Fe}(\text{CO})_3$ geometry could result as previously mentioned [7,8], from the presence of a metallacycle on these complexes. These products are obtained as gray powders which are, for most of them, poorly soluble in organic solvents. Their NMR spectra are in good agreement with the proposed metallalactone trifunctionalized anionic structure. The anionic character of these complexes is shown in ^{13}C NMR by a shift of ~ 10 ppm toward the lower fields of the resonances of the carbonyls linked to the metal. Thus, the signals of the carbonyl of the acetyl groups linked to the metal are found between 256.2 and 285.4 ppm those of the cyclic $\text{C}(\text{O})\text{O}$ between 219.2 and 237.9 ppm while the resonances of the terminal carbonyl ligands are located between 200.5 and 213.1 ppm. The formation of a metallalactone ring is shown by the presence of a resonance between 92.9 and 97.7 ppm corresponding to that of a cyclic quaternary carbon. The presence of two different substituents on the quaternary carbon of **3(1)** ($\text{Nu} = \text{SCH}_3$) together with the *fac* trisubstitution of the metal, explain the observation of two isomers for this complex. They are obtained as a 55/45% mixture. The formation of these two isomers is shown by the splitting in two of most of the ^{13}C NMR resonances



Scheme 5.

of **3(1)**. Thus four resonances are observed at 285.4, 265.7, 262.7 and 259.9 ppm for the two acetyl groups linked to the metal and two signals for the cyclic C(O)O at 226.2 and 221.1 ppm; for the cyclic quaternary carbon at 96.2 and 94.6 ppm; for the acetyl CH₃ at 54.4 and 47.6 ppm; for the CH₃ of the cycle at 23.6 and 22.6 ppm and for the SCH₃ at 12.4 and 11.6 ppm. Probably due to the overlap of two signals, the three terminal carbonyls are observed as five resonances at 211.7, 210.6, 209.7(2), 209.2, and 208.6 ppm. In the same way, **3(2)** (Nu = P(C₆H₅)₂) is also obtained as a mixture of two isomers (70/30%). Its ¹³C NMR spectrum is not very different from that observed for **3(1)** (see experimental section). It is worth noting that, probably due to a poor resolution of this ¹³C NMR spectrum the coupling between the phosphorus atom and the cyclic quaternary carbon cannot be observed. The formation of two isomers is confirmed by the presence of two resonances at 10.38 and 9.16 ppm in the ³¹P NMR spectrum of **3(2)**. Complex **3(3)** which displays a bulky Nu group (P(C₆H₁₁)₂) is formed as a single isomer shown by a lack of splitting of its ¹³C NMR signals and by the presence of a single signal at 13.45 ppm in its ³¹P NMR spectrum. Again no interaction is observed between the cyclic quaternary carbon and the phosphorus of this complex. The bulkiness of P(C₆H₁₁)₂ suggests the formation of the isomer displaying its acetyl ligand and the P(C₆H₁₁)₂ group on both side of the metallacycle plane. Complex **3(4)** (Nu = CH₃) which presents two methyl substituents on its cyclic quaternary carbon is formed as one isomer. Its ¹³C NMR spectrum (see experimental section) then displays one resonance for each carbon of the molecule. The *fac* geometry around the metal center induces the inequivalency of the two methyl groups on the cyclic quaternary carbon shown by the presence of two signals at 24.5 and 15.75 ppm in ¹³C NMR. The bulky ⁻C(H)(CO₂C₂H₅)₂ used as nucleophile induces the formation of only one isomer of the corresponding metallalactone (**3(5)**). The presence of a single isomer in the reaction mixture is shown, in ¹³C NMR, by the observance of one signal for each carbon of the molecule. The resonances of the two acetyl linked to the metal are observed at 269.8 and 265.3 ppm, those of the cyclic C(O)O group at 230.65, of the cyclic quaternary carbon at 92.1 ppm and of the two methyl groups at 22.05 and 46.15 (acetyl) ppm. The asymmetry of the metallalactone ring induces a diastereotopy of the central carbon of the malonyl group shown by the presence of a single signal at 55.1 ppm for this carbon whereas the two CO₂C₂H₅ substituents are non equivalent (signals of equal intensities at 169.0 and 167.5; at 62.8 and 62.4 and at 13.75 and 13.55 ppm). The same diastereotopy is observed for **3(6)** the anionic metallalactone obtained by reaction of **1(2)** with ⁻C(H)(C≡N)₂. However, this complex (see experimental part) is obtained as a 70/30% mixture of two isomers. Four resonances at 113.4, 113.05, 112.6 and 112.0 ppm are therefore observed for the C≡N of the malonyl group whereas two signals corresponding to the central atom of this substituent are found at 30.8

and 30.6 ppm. Complex **3(7)** (Nu = C(H)[C(O)CH₃]- (CO₂CH₃)) is also obtained as two isomers (80/20%) and moreover displays a non symmetric aceto-acetyl substituent on the quaternary carbon of its non symmetrical metallacycle. For this reason, two diastereoisomers of the above mentioned isomers are formed and the ¹³C NMR spectrum of **3(7)** displays, for each of its carbon, two major signals and two minor resonances (see experimental section). Complex **3(8)** (Nu = (CH₃)C(CO₂C₂H₅)₂), substituted by a bulky group, is obtained as one isomer. However, as observed for **3(5)** and **3(6)**, the two CO₂C₂H₅ groups of (CH₃)C(CO₂C₂H₅)₂ are not equivalent. Two signals are then observed for their carbon atoms whereas one resonance is observed for the central carbon of this malonyl group and for its methyl substituent (see Section 4).

2.4. Crystallographic study of complex **3(5)** (Nu = C(H)(CO₂C₂H₅)₂)

Single crystals of **3(5)** are obtained from an hexanes/dichloromethane (80:20) mixture at -40 °C. The ORTEP diagram of the structure is displayed in Fig. 2, selected bond lengths and angles are mentioned in Tables 2 and 3, and crystallographic data can be found in Table 4.

The crystallographic study confirms for **3(5)** the already proposed anionic *fac* trisubstituted {(CO)₃Fe[C(O)CH₃]-{C(O)C(CH₃)[C(H)(CO₂C₂H₅)₂]OC7(O);Fe-C7}}⁻ structure. In the solid state, the study shows the presence of four essentially equivalent entities named **a**, **b**, **c** and **d** which only exhibit slight variations in their bond lengths and angle values probably due to the relatively low precision of the crystallographic data. The coordination about the central Fe atom of these entities can be described as a distorted octahedron. Each metal center is substituted by three terminal carbonyl ligands (in *fac* positions), by an acetyl moiety and by a metallalactone ring with a diethylmalonyl substituent on the quaternary carbon (C(6)) of this ligand. The malonyl group and the acetyl ligand are located on each side of the lactone plane. The crystallized isomer is very probably the same compound than that already observed in solution by NMR spectroscopy. Recall that a close geometry has already been observed by us for the alkoxycarbonyl homologue of **3(5)** [8]. The presence on the metal of a five membered ring induces, as generally observed for such metallacycles [4,6–8,13], a value of the bite angle smaller than that required by a regular octahedron: C(7)–Fe–C(5) from 83.1(6) to 84.0(6)°. Its opposite angle on the metal center: C(2)–Fe–C(3) then displays a higher value: from 97.1(9) to 100.7(8)°. As Shown by the angles C(4)–Fe–C(5) (from 80.8(6) to 82.3(7)°) and C(4)–Fe–C(7) (from 83.1(6) to 84.0(6)°) the acetyl ligand is bent toward the metallacycle. The reduced dihedral angles observed between the median plane C(5)–Fe–C(7) and Fe–C(7)–O(6) (4.29°) or between C(5)–Fe–C(7) and Fe–C(5)–C(6) (3.22°) show the quasi planeness of the lactone ring of the molecule. O(6) and C(6) only deviate from this median plane by -0.0930 Å and -0.0829 Å respectively

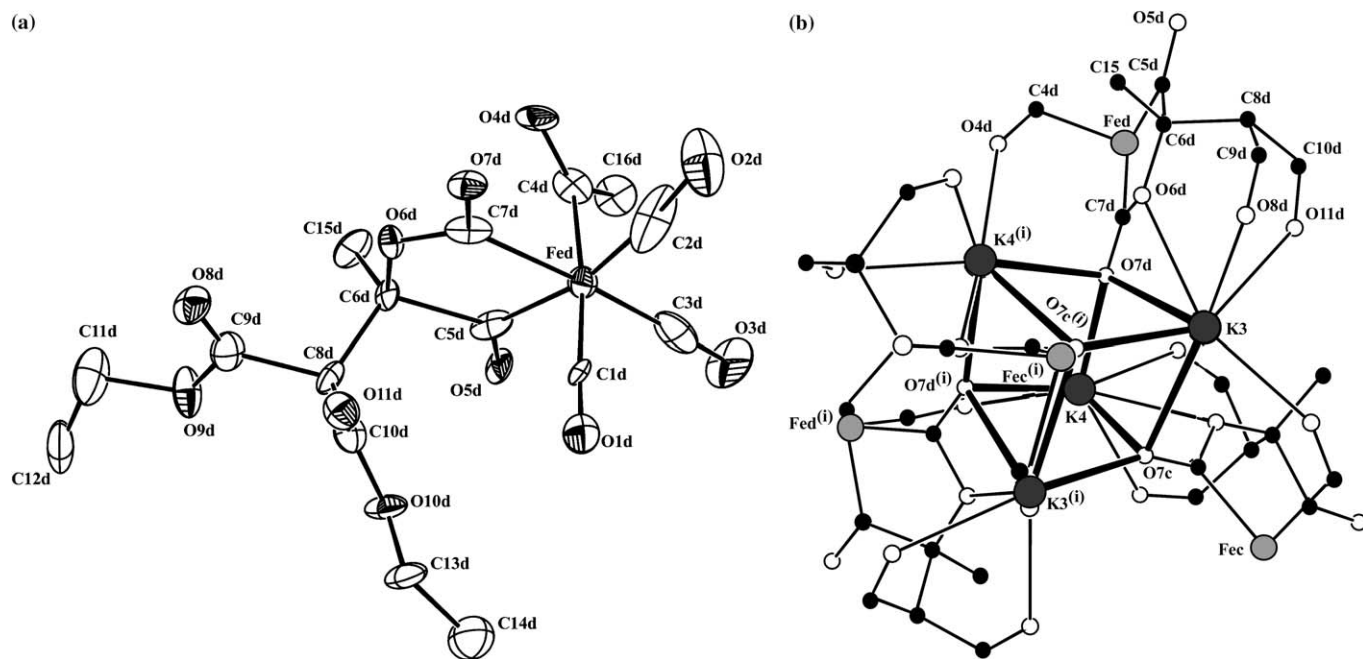


Fig. 2. Structure of **3(5)d**. (a) ORTEP view of one anionic entity (50% ellipsoids), the similar views of **a**, **b** and **c** anions are not shown. (b) Perspective view showing the K3 and K4 ions surrounded by two **c** and two **d** forms of **3(5)**, the similar view involving K1, K2, Fea and Feb is not shown. (i): $(-x + 1, y, -z + 3/2)$.

Table 2

Bond lengths (Å) and bond angles (°) observed for the four anionic forms (**a**, **b**, **c**, and **d**) of **3(5)**

	a	b	c	d
Fe–C(1)	1.786(19)	1.76(2)	1.798(17)	1.788(16)
Fe–C(2)	1.86(2)	1.80(2)	1.786(17)	1.80(2)
Fe–C(3)	1.81(2)	1.827(19)	1.830(18)	1.808(16)
Fe–C(4)	2.056(16)	2.017(16)	2.042(14)	2.016(14)
Fe–C(5)	1.84(2)	1.974(1)	1.966(16)	1.958(15)
Fe–C(7)	1.985(15)	1.943(14)	1.934(14)	1.962(15)
O(4)–C(4)	1.188(19)	1.244(18)	1.214(16)	1.223(17)
O(5)–C(5)	1.249(19)	1.194(17)	1.210(17)	1.192(16)
O(7)–C(7)	1.187(15)	1.209(16)	1.208(15)	1.193(15)
O(6)–C(6)	1.417(18)	1.459(15)	1.436(15)	1.403(15)
O(6)–C(7)	1.362(16)	1.389(17)	1.402(16)	1.382(16)
O(8)–C(9)	1.206(19)	1.195(18)	1.197(17)	1.142(18)
O(11)–C(10)	1.174(17)	1.222(18)	1.246(16)	1.186(16)
C(5)–C(6)	1.67(3)	1.589(19)	1.55(2)	1.61(2)
C(2)–Fe–C(3)	97.1(9)	100.7(8)	98.9(7)	98.1(7)
C(2)–Fe–C(1)	95.1(8)	95.6(8)	95.3(7)	97.1(8)
C(2)–Fe–C(4)	86.5(7)	85.6(7)	85.3(7)	85.7(8)
C(2)–Fe–C(7)	89.7(6)	86.1(7)	87.9(6)	86.6(6)
C(2)–Fe–C(5)	166.4(7)	164.6(7)	163.9(7)	163.9(7)
C(1)–Fe–C(5)	96.5(8)	96.3(7)	97.7(7)	95.1(6)
C(1)–Fe–C(7)	89.9(6)	90.9(6)	88.3(6)	89.1(6)
C(4)–Fe–C(5)	81.4(7)	82.3(7)	80.8(6)	81.5(6)
C(4)–Fe–C(7)	85.5(6)	87.6(6)	86.2(6)	87.8(5)
C(4)–Fe–C(1)	175.1(8)	178.1(7)	174.1(7)	175.6(6)
C(5)–Fe–C(7)	83.4(7)	84.0(6)	83.1(6)	83.2(6)
C(7)–O(6)–C(6)	118.1(12)	116.8(10)	115.3(10)	119.8(10)
Fe–C(7)–O(7)	128.7(11)	132.4(11)	131.2(11)	130.3(11)
Fe–C(7)–O(6)	116.7(9)	117.3(10)	117.6(9)	115.8(9)
O(7)–C(7)–O(6)	114.6(13)	1103.0(12)	111.2(11)	113.9(13)
Fe–C(5)–O(5)	135.0(17)	130.2(11)	129.5(11)	130.9(11)
Fe–C(5)–C(6)	115.9(9)	112.5(10)	113.3(10)	113.3(9)
O(5)–C(5)–C(6)	109.1(19)	117.3(13)	117.3(13)	115.7(12)
O(6)–C(6)–C(5)	105.8(13)	109.2(11)	110.7(11)	107.8(10)

Table 3
K–O distances (Å) and angles between K1–4 and O7a–c (°) observed for **3(5)**

K(1)–O(4b)	2.658(11)	K(2)–O(4a)	2.669(12)	K(3)–O(4c)	2.690(10)	K(4)–O(4d)	2.626(12)
K(1)–O(6a)	2.859(10)	K(2) ⁱⁱ –O(6b)	2.770(9)	K(3)–O(6d)	2.808(9)	K(4)–O(6c)	2.767(8)
K(1)–O(7a)	2.863(9)	K(2) ⁱⁱ –O(7a)	2.646(9)	K(3) ⁱ –O(7c)	2.651(9)	K(4)–O(7c)	2.933(9)
K(1) ⁱⁱ –O(7b)	2.684(10)	K(2)–O(7a)	2.987(10)	K(3)–O(7c)	2.862(9)	K(4)–O(7d)	2.655(9)
K(1)–O(7b)	2.879(9)	K(2) ⁱⁱ –O(7b)	2.944(10)	K(3)–O(7d)	2.905(9)	K(4) ⁱ –O(7d)	2.884(9)
K(1)–O(8a)	2.775(12)	K(2)–O(8b)	2.687(11)	K(3)–O(8d)	2.802(11)	K(4)–O(8c)	2.754(11)
O(7b) ⁱⁱ –K(1)–O(7a)	86.6(3)	O(7a) ⁱⁱ –K(2)–O(7b) ⁱⁱ	80.7(3)	O(7c) ⁱ –K(3)–O(7c)	76.8(3)	O(7d)–K(4)–O(7d) ⁱ	75.1(3)
O(7b) ⁱⁱ –K(1)–O(7b)	75.9(3)	O(7a) ⁱⁱ –K(2)–O(7a)	74.0(3)	O(7c) ⁱ –K(3)–O(7d)	80.3(3)	O(7d)–K(4)–O(7c)	80.6(3)
O(7a)–K(1)–O(7b)	78.3(3)	O(7b) ⁱⁱ –K(2)–O(7a)	79.9(3)	O(7c)–K(3)–O(7d)	77.8(3)	O(7d) ⁱ –K(4)–O(7c)	76.2(3)

Atoms are labeled as mentioned in Fig. 2b. Symmetry transformations used to generate equivalent atoms (i) $-x + 1, y, -z + 3/2$ and (ii) $-x + 2, y, -z + 3/2$.

Table 4
Crystal data for compounds **1(2)** and **3(5)**

Compound	1(2)	3(5)
Empirical formula	C ₉ H ₆ O ₇ Fe	C ₆₆ H ₆₅ O ₄₄ Fe ₄ K ₄
Molecular weight	281.99	2083.78
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	8.960(1)	24.262(2)
<i>b</i> [Å]	9.725(1)	32.278(2)
<i>c</i> [Å]	13.022(1)	27.503(2)
β [°]	99.136(8)	113.596(6)
<i>V</i> [Å ³]	1120.2(4)	19738(2)
<i>Z</i>	4	8
ρ_{calcd} [g cm ⁻³]	1.67	1.40
Temperature	100(2)	100(2)
μ [cm ⁻¹]	13.62	9.36
<i>F</i> (000)	568	8488
Refl. measured	3544	51030
2 θ range	5.00–44.04	5.84–47.48
Refl. Unique/ <i>R</i> _{int}	1200/0.03	11059/0.0654
Refl. with <i>I</i> > 2 σ (<i>I</i>)	975	8605
<i>N</i> _r	178	1094
<i>R</i> ^a	0.026	0.1284
<i>R</i> _w ^{b,c}	0.029 (<i>F</i> _o)	0.3244 (<i>F</i> _o ²)
Goof ^d	0.999	1.030
$\Delta\rho_{\text{max,min}}/e\text{\AA}^{-3}$	+0.291, -0.262	1.551, -0.58

^a $R = \sum ||F_o| - |F_c|| / \sum F_o$.

^b $R_w(F_o) = \{ \sum [w(F_o - F_c)^2] / \sum [w(F_o)^2] \}^{1/2}$

^c $R_w(F_o) = wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

^d $\text{Goof} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / N_{\text{obs}} - N_{\text{var}} \}^{1/2}$

and are located on the same side of this plane. The methyl substituent of C(6) is also located on the same side of the median plane (distance between C(15) and the C(7)–Fe–C(5) plane = -1.32 Å). It adopts a slightly more axial position than that of the second substituent of C(6): the malonyl group, which is found in a pseudo equatorial position shown by a distance of 1.15 Å. between C(8) (the central atom of the malonyl group) and the C(7)–Fe–C(5) plane. We mentioned above that, in the solid state, **3(5)** can be described as four slightly different anionic entities named **a**, **b**, **c**, and **d**. The perspective view of the potassium cations environments shows that two **a** and two **b** anions are linked to four potassium ions (two equivalent K(1) and two equivalent K(2)). In the same way, two **c** and two **d** anionic entities are linked to two equivalent K(3) and two equivalent K(4) ions. Lets consider this last case drawn in Fig. 2. It

comes to light that the four K(3), K(4), K(3)ⁱ and K(4)ⁱ ions and the four carbonyl oxygen atoms of the cyclic C(O)O groups of the two **c** anions and the two **d** anions (O(7c), O(7d), O(7c)ⁱ and O(7d)ⁱ) are alternately located at the corners of a distorted cube. This cuboïd structure displays small O–K–O angles (from 75.1(3)° to 80.6(3)°) and larger K–O–K angles (from 96.2(3)° to 104.2(3)°). Edges of different lengths are also observed. Short edges are measured between K(4) and O(7d), K(3)ⁱ and O(7d) and between their symmetric atoms. These distances: 2.655(9) Å and 2.651(9) Å respectively are by far shorter than those measured for the eight other edges of the cube (average of 2.90 Å). They correspond to an interaction between the oxygen of the carbonyl of a cyclic C(O)O group (O(7)) and a potassium ion which is not linked by other oxygen atoms to the same entity. In the crystal, each potassium is surrounded by seven oxygen atoms; four of them belong to the same molecule: for example K(3) is linked to **d** by the carbonyl oxygen of the cyclic C(O)O group (O(7d)), by the ether oxygen of the same function (O(6d)) and by the two carbonyl oxygen atoms of the malonyl substituent (O(8d) and O(11d)). K3 is also linked to **c** via O(4c) the oxygen of the acetyl ligand and via O(7c) the carbonyl oxygen of the cyclic C(O)O function of this entity. At last, K(3) is connected to **c**ⁱ (symmetric of **c**) by O(7c)ⁱ the carbonyl oxygen of the cyclic C(O)O of this anion. Considering a $\{(\text{CO})_3\text{Fe}[\text{C}(\text{O})\text{CH}_3]\{\text{C}(\text{O})\text{C}(\text{CH}_3)[\text{C}(\text{H})(\text{CO}_2\text{C}_2\text{H}_5)_2]\text{OC}(\text{O})\}^-\}$ pattern, for example **d**, as mentioned above, this anion is linked to K(3) by the two oxygen atoms of its cyclic C(O)O function (O(7d) and O(6d)) and by the two carbonyl oxygens of its malonyl group (O(8d) and O(11d)). **d** is also connected to K(4)⁽ⁱ⁾ by O(7d) the carbonyl oxygen of its C(O)O group and by O(4d) the oxygen of its acetyl ligand and **d** is also linked to K(4) via the same O(7d) atom (the oxygen carbonyl of the cyclic C(O)O). It is worth noting that O(5d) the oxygen of the cyclic carbonyl does not interact with any potassium. The interaction of O(7) the oxygen of the cyclic C(O)O group with three potassium cations does not induce a significant lengthening of the C(7)=O(7) double bond (from 1.187(15) to 1.209(16) Å compared to an average of 1.20 Å measured for neutral lactones [4,8]. On the other hand, the interaction of the two oxygen atoms (O(7) and O(6)) of the C(O)O cyclic function

of a molecule with the same potassium ion induces the presence of small O(7)–C(7)–O(6) angles (from 110.3(12) to 114.6(13)°) and of large O(7)–C(7)–Fe angles (from 128.7(11) to 132.4(11)°). The homologues angles of neutral lactones are respectively of 118° and 127° [4,8].

2.5. Preparation of anionic complexes **3** by reaction of neutral lactones **2** with CH₃Li

We briefly mentioned, in the introductory part the achievement of neutral lactones **2** by reaction of complex **1(1)** with pronucleophiles. These compounds **2**, by reaction with CH₃Li, are supposed to afford anionic metallalactones **3** by addition of [−]CH₃ on one of their terminal carbonyl ligands. Indeed, **2(2)** (Nu = CH₃), the neutral lactone substituted by two methyl groups, affords rapidly, at −70 °C a complex displaying the same IR and ¹³C NMR spectra than **3(4)**. However, the yield of formation of **3(4)** by this method remains lower (15%) than the yield of formation of the same product by reaction of **1(2)** with CH₃Li (65%). An analogous reaction affords **3(1)** (Nu = SCH₃) by addition of CH₃Li with the appropriate neutral lactone. The process is slow (one hour at −70 °C) and the yield remains low (20%). It is noteworthy that **3(1)** is formed in the same proportion of isomers (55/45%) than that obtained by reaction of **1(2)** with CH₃SNa. As described above, the reaction of **1(2)** with CH₃ONa failed to afford the anionic trifunctionalized lactone substituted by a methyl and a methoxy groups. This complex (**3(9)**) is still obtained in 20% yield by reacting CH₃Li with the neutral metallalactone substituted by a methyl and a methoxy groups. Recall that this lactone was prepared by thermolysis of **1(1)** in methanol. Complex **3(9)** is formed as a mixture of isomers (40/60%); its ¹³C NMR spectrum is in good agreement with the spectra of analogous compounds **3** except that, a shift toward the lower fields of the resonances of the cyclic quaternary carbon substituted by the methoxy group (two peaks at 114.8 and 117.8 ppm), is observed in ¹³C NMR.

3. Conclusion

This work shows that spontaneous metallalactones formation previously observed on a complex displaying a pyruvoyl and an alkoxy carbonyl ligands does not occur on pyruvoyl complexes which do not present a ligand with a labile group. A decarbonylation of the pyruvoyl ligand together with a carbon–carbon coupling are then observed by thermolysis. This study also confirms that on a complex bearing a pyruvoyl, an acetyl and terminal carbonyl ligands, the pyruvoyl β-carbonyl carbon is the most electrophilic site of the molecule. The formation of anionic trifunctionalized metallalactones by reaction of this complex with anionic nucleophiles confirms unambiguously the cyclization of the pyruvoyl ligand to occur by an attack of the nucleophile reagent on the carbon of

the β-carbonyl followed by an addition of the oxygen of this carbonyl on a terminal carbonyl ligand. The difference of reactivity observed between **1(1)** which displays an alkoxy carbonyl co-ligand and **1(2)** whose metal center bear an acetyl, could result from the difference between the electronic effects of these two ligands. The electron-withdrawing effect of the alkoxy carbonyl ligand of **1(1)** can explain the enhanced reactivity of this complex toward anionic nucleophiles whereas the lability of the alkoxy group of the same ligand the formation of metallalactones by reaction with pronucleophiles. Further experiments are at present under progress to extend this reaction to all complexes bearing terminal carbonyls and a ligand with a double C(O) chain.

4. Experimental

4.1. Materials

All reactions were performed under argon using standard Schlenk techniques. All solvents were purified by preliminary distillation from an appropriate drying agent [25]. Deuterated dichloromethane or THF were stored under argon over molecular sieves before use. NMR spectra were recorded at 0 °C on a Bruker AC 300, a Bruker AMX 3-400 or a Bruker DRX 500 spectrometers with chemical shifts reported in δ values relative to residual protonated solvents for ¹H NMR spectra and to the solvent for ¹³C NMR spectra. ³¹P NMR spectra were externally referenced to H₃PO₄ (85%). Infrared spectra were recorded in the range 2300–1600 cm^{−1} in solution in hexane, dichloromethane or tetrahydrofuran with a FT-IR NEXUS NICOLET spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 instrument using a CP SIL 25 m column. Elemental analyses were performed by the Service Central d'Analyses du CNRS. All reagents were purchased from commercial sources and used as received. {(CO)₄Fe[C(O)CH₃]}[−] [11], CH₃SNa [26], (C₆H₁₁)₂PLi and (C₆H₆)₂PLi [27] and stabilized carbanions (NaC(H)(CO₂C₂H₅)₂, NaC(H)(C≡N)₂, NaC(H)[C(O)CH₃](CO₂CH₃), and NaC(CH₃)(CO₂C₂H₅)₂) [8,28,29] were prepared *in situ* as previously described. ClC(O)C(O)CH₃ [10] was obtained after distillation as a mixture with HC(O)OCH₃. The percentages of these two compounds were measured by ¹H NMR.

4.2. Preparation of Fe(CO)₄[C(O)CH₃][C(O)C(O)CH₃] (**1(2)**)

Reaction at −10 °C of 15 mmol of Fe(CO)₅ (1.97 ml) dissolved in 50 ml of THF with 10 mmol of CH₃Li (6.25 ml of a 1.6 N solution in diethyl ether) afforded, as shown by IR monitoring, {Fe(CO)₄[C(O)C(O)CH₃]}[−] [11]. After one hour the temperature of the solution was lowered to −30 °C and 10 mmol (1.065 g) of ClC(O)C(O)CH₃ [10], in solution in 5 ml of THF, was slowly added under stirring. After two hours at this temperature,

the solvent was evaporated to dryness at 0 °C. The yellow residue was washed with two portions of 5 ml of hexanes at –70 °C and extracted with three fractions of a CH₂Cl₂/hexanes (10/90%) mixture at –10 °C. These fractions were joined and the volume of the resulting solution slowly reduced under vacuum at –40 °C. The pale yellow solid which precipitated was filtered off and washed with hexanes at –70 °C (2 × 3 ml) to afford, after recrystallization in an hexanes/CH₂Cl₂ (95/5%) mixture at –40 °C, 1.27 g; (45% yield) of complex **1(2)**. IR (hexanes, cm⁻¹): ν(C≡O) 2115 (w), 2065 (w,sh), 2055 (w, sh), 2040 (s); ν(C=O) 1780 (w, br), 1740 (w, br), 1680 (w,br). ¹H NMR (CD₂Cl₂, 273 K, δ ppm): 2.7 (s, 3H, CH₃ acetyl), 2.4 (s, 3H, CH₃ pyruvoyl). ¹³C {¹H} NMR (CD₂Cl₂, 273K, δ ppm): 246.7, 245.2 (C=O bound to the metal), 201.8 (2), 201.1, 198.9, 198.6 (terminal C=O and organic C=O), 51.2 (CH₃ acetyl), 23.2 (CH₃ pyruvoyl). Anal. Calc. for C₉FeH₆O₇: C, 38.33; Fe, 19.80; H, 2.14. Found: C, 38.25; Fe, 19.89; H, 2.17.

4.3. Thermal evolution of **1(2)**

A portion of 0.282 g (1 mmol) of **1(2)** in 15 ml of CH₂Cl₂ was stirred at 4 °C for one hour. The formation of acetone (70%) and 2,3 butanedione (30%) was detected by gas chromatographic analyses of the solution by comparison with authentic samples.

¹³C NMR monitoring of the reaction: 60 mg of **1(2)** in solution in cold CD₂Cl₂ was introduced into an NMR tube. The reaction was monitored at –3 °C, each spectrum being drawn over a period of 30 min. The thermal evolution of **1(2)** was shown by the appearance of the resonances of the butanedione at 23 and 197 ppm, of Fe(CO)₅ at 211 ppm and by the presence of four signals of equal intensities at 243.4, 202.5, 200.3 and 49.2 ppm corresponding to **1(3)**. The presence of free CO in solution was shown by a signal at 184 ppm. The peaks of **1(3)** then slowly disappeared and the formation of acetone was shown by the resonances at 206.0 and 29.8 ppm.

4.4. Reaction of **1(2)** with anionic nucleophiles

4.4.1. General procedure for the preparation of anionic trifunctionalized metallalactones **3**

A cold solution of 1.5 mmol of the anionic nucleophile reagent was added under stirring to a solution of 1.5 mmol of **1(2)** (423 mg) in 30 ml of THF at –70 °C. IR monitoring showed the reaction to be generally fast. After 1 h at –70 °C, the temperature was raised to 0 °C and the solvent evaporated to dryness. The residue was washed with hexanes at 0 °C to afford a grey powder. With the exception of **3(5)** (Nu = C(H)(CO₂C₂H₅)₂) and **3(8)** (Nu = C(CH₃)-(CO₂C₂H₅)₂), these anions **3** were found only sparingly soluble in most organic solvents. **3(5)** and **3(8)** were crystallized from a hexanes/CH₂Cl₂ (70/30%) mixture at –40 °C. It was not possible to obtain correct elemental analyses for **3** since these complexes are very unstable.

4.4.2. Reaction of **1(2)** with NaOCH₃ or NaC(H)[C(O)CH₃]₂

As shown by IR monitoring, when **1(2)** (1.5 mmol, 423 mg) was reacted, according to the general procedure described for this process, with one of these two nucleophiles no reaction was observed even if the temperature of the solution was brought up to 0 °C.

4.4.3. Reaction of **1(2)** with NaSCH₃, preparation of **3(1)**

The reaction of **1(2)** (1.5 mmol, 423 mg) with 1.5 mmol of NaSCH₃ (105 mg) was found to give rise to **3(1)** obtained as a white powder (400 mg, 75% yield). IR (THF, cm⁻¹): ν(C≡O) 2056 (s), 1997 (br, s); ν(C=O) 1652 (sh), 1637 (m), 1595 (w). ¹H NMR (400 MHz, [D₈] THF, 273 K, δ ppm): 2.3 [s, 3H, C(O)CH₃], 1.75 (s, 3H, SCH₃), 1.36 (s, 3H, CH₃). ¹³C {¹H} NMR [400 MHz, [D₈] THF, 273 K, δ ppm] two isomers (55:45): 285.4, 265.7, 262.7, 259.9 [C(O)CH₃ and cyclic C(O)], 226.2, 221.1 [cyclic C(O)O], 211.7, 210.6, 209.7 (2), 209.2, 208.6 (terminal CO), 96.2, 94.6 (quaternary carbon), 54.4, 47.6 [C(O)CH₃], 23.6, 22.6 (CH₃), 12.4, 11.6 (SCH₃).

4.4.4. Reaction of **1(2)** with LiP(C₆H₅)₂, preparation of **3(2)**

Complex **1(2)** (1.5 mmol, 423 mg) was treated with 1.5 mmol of LiP(C₆H₅)₂ to give 390 mg (55% yield) of **3(2)** obtained as a grey powder. IR (THF, cm⁻¹): ν(C≡O) 2058 (s), 1995 (s) 1985 (s); ν(C=O) 1646 (sh), 1618 (s), 1576 (sh). ¹H NMR (400 MHz, [D₈] THF, 273 K, δ ppm) two isomers (70:30): 7.8–7.05 (m, 10H, C₆H₅), 2.36 [s, 2.1H, C(O)CH₃], 2.06 [s, 0.9 H, C(O)CH₃], 1.35 (s, 0.9H, CH₃), 1.18 (s, 2.1H, CH₃). ¹³C {¹H} NMR [400 MHz, [D₈] THF, 273 K, δ ppm] two isomers (70:30): 270.3, 270.7, 261.5, 267.4 [C(O)CH₃ and cyclic C(O)], 227.0, 227.7 [cyclic C(O)O], 213.1, 209.7, 209.5, 206.9, 207.3 (terminal CO), from 137.7 to 128.6 numerous signals (aromatics), 97.7, 97.3 (s, quaternary carbon), 47.5, 46.2 [C(O)CH₃], 23.6, 23.0 (CH₃). ³¹P NMR ([D₈] THF, 273 K, δ ppm) two isomers (70:30) 10.38 (70%), 9.16 (30%).

4.4.5. Reaction of **1(2)** with LiP(C₅H₁₁)₂, preparation of **3(3)**

According to the general procedure, complex **1(2)** (1.5 mmol, 423 mg) was reacted with 1.5 mmol of LiP(C₅H₁₁)₂ to give 330 mg (45% yield) of **3(3)** (one isomer) obtained as a white powder. IR (THF, cm⁻¹): ν(C≡O) 2058 (s), 1991 (s); ν(C=O) 1640 (sh), 1616 (m), 1560 (sh). ¹H NMR (400 MHz, [D₈] THF, 273 K, δ ppm) numerous signals between 2.1 and 1.1. ¹³C {¹H} NMR (400 MHz, [D₈] THF, 273 K, δ ppm) one isomer: 282.9, 270.7 [C(O)CH₃ and cyclic C(O)], 230.5, [cyclic C(O)O], 209.9, 209.1, 208.2 (terminal CO), 97.7 (s, quaternary carbon), 46.6 [C(O)CH₃], from 32.0 to 30.1 10 peaks (cyclohexyl), 24.8 (CH₃). ³¹P NMR ([D₈] THF, 273 K, δ ppm) one isomer 13.45.

4.4.6. Reaction of **1(2)** with LiCH_3 , preparation of **3(4)**

As above, 1.5 mmol of **1(2)** (423 mg) was reacted with 1.5 mmol of CH_3Li (950 μL of a 1.6 M solution in diethyl ether). After treatment of the reaction, 300 mg (65% yield) of **3(4)** was obtained as a grey powder. IR (THF, cm^{-1}): $\nu(\text{C}\equiv\text{O})$ 2069 (m), 2003 (s) 1987 (s); $\nu(\text{C}=\text{O})$ 1746 (s), 1731 (sh), 1620 (s). ^1H NMR (400 MHz, $[\text{D}_8]$ THF, 273 K, δ ppm): 2.16 [s, 3H, $\text{C}(\text{O})\text{CH}_3$], 1.40 (s, 3H, CH_3), 1.32 (s, 3H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (400 MHz, $[\text{D}_8]$ THF, 273 K, δ ppm): 271.45, 261.2 [$\text{C}(\text{O})\text{CH}_3$ and cyclic $\text{C}(\text{O})$], 226.15 [cyclic $\text{C}(\text{O})\text{O}$], 209.8, 209.5, 208.4 (terminal CO), 94.05 (quaternary carbon), 47.4 [$\text{C}(\text{O})\text{CH}_3$], 24.5, 15.75 (CH_3).

4.4.7. Reaction of **1(2)** with $\text{NaC}(\text{H})(\text{CO}_2\text{C}_2\text{H}_5)_2$, preparation of **3(5)**

Reaction of complex **1(2)** (1.5 mmol, 423 mg) with 1.5 mmol of $\text{NaC}(\text{H})(\text{CO}_2\text{C}_2\text{H}_5)_2$ was found to afford a white residue after evaporation of the solvent. This white powder was washed with three portions of hexanes at -40°C and then extracted with a hexanes/ CH_2Cl_2 mixture (3×10 ml) at -10°C . These fractions were joined and the volume of the resulting solution was reduced under vacuum at -40°C to afford a white precipitate of **3(5)** (520 mg, 75% yield). IR (THF, cm^{-1}): $\nu(\text{C}\equiv\text{O})$ 2069 (m), 2003 (s), 1987 (s); $\nu(\text{C}=\text{O})$ 1746 (s), 1731 (sh), 1620 (s). ^1H NMR (400 MHz, CD_2Cl_2 , 273 K, δ ppm): 4.26 (br q $J = 7$ Hz, 4H, OCH_2), 3.72 (s, 1H, CH) 2.40 [s, 3H, $\text{C}(\text{O})\text{CH}_3$], 1.21 (br t $J = 7$ Hz, 6H, CH_3) 1.01 (s, 3H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR [400 MHz, CD_2Cl_2 , 273 K, δ ppm] one isomer: 269.8, 265.3 [$\text{C}(\text{O})\text{CH}_3$ and cyclic $\text{C}(\text{O})$], 230.65 [cyclic $\text{C}(\text{O})\text{O}$], 208.5, 206.8, 205.3 (terminal CO), 169.0, 167.5 [organic $\text{C}(\text{O})$ ester], 92.1 (quaternary carbon), 62.8, 62.4 (OCH_2), 55.1 (CH), 49.15 [$\text{C}(\text{O})\text{CH}_3$], 22.05 (CH_3), 13.75, 13.55 (CH_2CH_3).

4.4.8. Reaction of **1(2)** with $\text{NaC}(\text{H})(\text{CN})_2$, preparation of **3(6)**

The reaction of **1(2)** (1.5 mmol, 423 mg) with 1.5 mmol of $\text{NaC}(\text{H})(\text{C}\equiv\text{N})_2$ was found to give rise to **3(6)** obtained as a white powder (220 mg, 40% yield). IR (THF, cm^{-1}): $\nu(\text{C}\equiv\text{N})$ 2194 (w), 2174 (w); $\nu(\text{C}\equiv\text{O})$ 2062 (s), 1997 (s), 1983 (sh); $\nu(\text{C}=\text{O})$ 1666 (m), 1644 (s), 1611 (m). ^1H NMR (400 MHz, $[\text{D}_8]$ THF, 273 K, δ ppm) two isomers 70/30%: 4.81 (br s, 0.7H, CH), 4.63 (br s, 0.3H, CH), 2.40 [br s, 2.1H, $\text{CH}_3\text{C}(\text{O})$], 2.19 [br s, 0.9H, $\text{CH}_3\text{C}(\text{O})$], 1.25 (br s, 0.9H, CH_3), 1.02 (br s, 2.1H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (400 MHz, $[\text{D}_8]$ THF, 273 K, δ ppm): 270.0, 268.7, 262.4, 259.4 [$\text{C}(\text{O})\text{CH}_3$ and cyclic $\text{C}(\text{O})$], 219.9, 219.2 [cyclic $\text{C}(\text{O})\text{O}$], 209.3, 209.1, 208.4, 208.0, 206.5, 201.9 (terminal CO), 113.4, 113.05, 112.6, 112.0 ($\text{C}\equiv\text{N}$), 89.8, 89.6 (quaternary carbon), 47.3, 47.0 [$\text{C}(\text{O})\text{CH}_3$], 30.8, 30.6 (CH), 21.7, 21.5 (CH_3).

4.4.9. Reaction of **1(2)** with $\text{NaC}(\text{H})[\text{C}(\text{O})\text{CH}_3](\text{CO}_2\text{CH}_3)$ preparation of **3(7)**

Complex **1(2)** (1.5 mmol, 423 mg) reacted with 1.5 mmol of $\text{NaC}(\text{H})[\text{C}(\text{O})\text{CH}_3](\text{CO}_2\text{CH}_3)$ to give 315 mg (50% yield)

of **3(7)** as a grey powder. IR (THF, cm^{-1}): $\nu(\text{C}\equiv\text{O})$ 2067 (s), 2004 (s), 1990 (sh); $\nu(\text{C}=\text{O})$ 1624 (s), 1599 (sh), 1575 (sh), 1523 (m). ^1H NMR (400 MHz, $[\text{D}_8]$ THF, 273 K, δ ppm) two isomers 80/20%: 3.78 (br s, 1H, CH), 3.56 (br s, 3H, OCH_3) 2.32 [br s, 3H, $\text{CH}_3\text{C}(\text{O})$], 2.11 [br s, 3H, $\text{CH}_3\text{C}(\text{O})$], 1.23 (br s, 2.4H, CH_3), 1.11 (br s, 0.6H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (400 MHz, $[\text{D}_8]$ THF, 273 K, δ ppm) two “*cis-trans*” isomers 80/20% and two diastereoisomers: 269.9, 269.5, 268.6, 268.4, 261.1, 259.95, 256.3, 256.2 [$\text{C}(\text{O})\text{CH}_3$ and cyclic $\text{C}(\text{O})$], 222.9, 222.8, 222.3, 222.1 [cyclic $\text{C}(\text{O})\text{O}$], 209.35, 209.3, 209.2, 209.1, 208.4, 208.15, 208.1, 203.3, 203.1 202.1, 201.9, 200.5 (terminal CO), 169.3, 169.1, 168.4, 168.15 [organic $\text{C}(\text{O})\text{O}$], 93.5, 92.9, 92.8, 92.6 (quaternary carbon), 62.3, (2) 62.0, 59.7(CH) 52.7, 52.5 (2), 52.2 (OCH_3), 47.6, 47.2, 46.6, 46.4 [$\text{C}(\text{O})\text{CH}_3$], 33.7, 32.9, 32.6, 29.9 [$\text{C}(\text{O})\text{CH}_3$], 23.0, 22.4, 21.8, 20.8 (CH_3).

4.4.10. Reaction of **1(2)** with $\text{NaC}(\text{CH}_3)(\text{CO}_2\text{C}_2\text{H}_5)_2$ preparation of **3(8)**

Complex **1(2)** (1.5 mmol, 423 mg) reacted with 1.5 mmol of $\text{NaC}(\text{CH}_3)(\text{CO}_2\text{C}_2\text{H}_5)_2$. After evaporation of the solvent a white residue was obtained. This white powder was washed with three portions of hexanes at -40°C and extracted with a hexanes/ CH_2Cl_2 mixture (3×10 ml) at -10°C . These fractions were joined and the volume of the resulting solution was reduced under vacuum at -40°C to afford a white precipitate of **3(8)** (320 mg, 45% yield). IR (THF, cm^{-1}): $\nu(\text{C}\equiv\text{O})$ 2071 (s), 2005 (s), 1995 (sh); $\nu(\text{C}=\text{O})$ 1733 (sh), 1721 (sh), 1652 (m), 1612 (s), 1576 (sh). ^1H NMR (400 MHz, CD_2Cl_2 , 273 K, δ ppm): 4.12 (br m, 4H, OCH_2), 2.51 [br s, 3H, $\text{C}(\text{O})\text{CH}_3$], 1.20 (br m, 12H, other CH_3). ^{13}C $\{^1\text{H}\}$ NMR (400 MHz, CD_2Cl_2 , 273 K, δ ppm), one isomer: 269.05, 267.9 [$\text{C}(\text{O})\text{CH}_3$ and cyclic $\text{C}(\text{O})$], 237.9, [cyclic $\text{C}(\text{O})\text{O}$], 207.1, 206.2, 205.8 (terminal CO), 175.6, 168.2 [organic $\text{C}(\text{O})$ ester], 96.1, (quaternary carbon), 62.9, (CH), 61.5, 58.4 (OCH_2), 46.5 [$\text{C}(\text{O})\text{CH}_3$], 21.6 (CH_3), 19.1 (CH_3), 13.7, 13.4 (CH_2CH_3).

4.5. Preparation of anionic complexes **3** by reaction of neutral lactones **2** with CH_3Li

4.5.1. General procedure

One mmol of CH_3Li (0.625 μL of a 1.6 M solution in ether) was added to a solution of one mmol of the neutral lactone **2** in 20 ml of THF at -70°C . The reaction was monitored by IR (substitution of the $\nu(\text{C}\equiv\text{O})$ of **2** at 2120, 2075, 2065 and 2050 cm^{-1} by their homologues of the trifunctionalized anionic complex **3** at 2060, 2000, and 1985 cm^{-1} . After evaporation of the solvent, the residue was washed with three portions (5 ml) of CH_2Cl_2 at -40°C to afford **3** as a gray powder.

4.5.2. Preparation of **3(4)**

Two hundred and eighty-two milligrams of **2(2)** ($\text{Nu} = \text{CH}_3$) were found to afford 45 mg (15% yield) of **3(4)** identified by comparison with the spectroscopic properties of an authentic sample.

4.5.3. Preparation of **3(1)**

315 mg of **2(3)** (Nu = SCH₃) gave rise to 67 mg (20% yield) of **3(1)**.

4.5.4. Preparation of **3(9)**

After reaction of 300 mg of **2(1)** (Nu = OCH₃) with CH₃Li, 64 mg of **3(9)** were obtained as a white powder. IR (THF, cm⁻¹): ν(C≡O) 2060 (s), 1998 (s); ν(C=O) 1652 (m), 1625 (s), 1576 (m). ¹H NMR (400 MHz, CD₂Cl₂, 273 K, δ ppm): 3.5 (br s, 3H, OCH₃), 2.3 [br s, 3H, C(O)CH₃], 1.1 (br s, 3H, CH₃). ¹³C {¹H} NMR (400 MHz, CD₂Cl₂, 273 K, δ ppm), two isomers (60/40%): 272.6, 269.6, 268.5, 265.7 [C(O)CH₃ and cyclic C(O)], 221.0, 219.7 [cyclic C(O)O], 210.3, 210.2, 209.2, 208.2 (terminal CO), 117.8, 114.8 (quaternary carbon), 53.40, 52.9 (OCH₃), 50.45, 49.7 [C(O)CH₃], 20.5, 19.2 (CH₃).

4.6. X-ray crystallography

Data for compounds **1(2)** and **3(5)** were collected on a Xcalibur 2 diffractometer (Oxford Diffraction) at 100 K. Structure of **1(2)** was solved by direct methods and successive Fourier difference syntheses, and was refined, on *F*, by weighted anisotropic full-matrix least-squares methods [30a]. All the hydrogen atoms were located by difference Fourier and were refined isotropically. The very low stability of compound **3(5)** made difficult a correct X-ray data collection. In this case we had only a few seconds to select a single crystal which was very quickly mounted on a goniometer head of the diffractometer at 100 K. After several attempts we found a single crystal of **3(5)** covered by a crystalline powder and giving, after data collection, a relatively high cell parameters and then a very high parameter number (see Table 4) was obtained.

After locating all the non-hydrogen atoms, the structure was refined, on *F*², first using isotropic and finally anisotropic thermal displacement parameters for all non-hydrogen atoms [30b]; the hydrogen atoms were then calculated and included as isotropic fixed contributors to *F*_c. It is noteworthy that despite the high values of *R* and *R*_w (0.128 and 0.324 respectively) due to the bad quality of the single crystal, the bond lengths and bond angles are relatively correct as they fall within the normal range of the corresponding values observed in parent compounds. Two other data collections were also performed using slightly better single crystals, but their low diffracting power due to their low dimensions did not afford better crystallographic data. Scattering factors and corrections for anomalous dispersion were taken from the International Tables for X-ray Crystallography [31]. The thermal ellipsoid drawings were made with the ORTEP program [32]. Selected bond distances and bond angles are listed in Tables 1–3. Pertinent crystal data are mentioned in Table 4.

5. Supplementary material

Complete crystallographic details are included in the supporting information. CCDC reference numbers 293145 and 603315 for **1(2)** and **3(5)** respectively contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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