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Formation of Anionic Trifunctionalized Metallalactones by Nucleophilic Addition at the β-Carbonyl of a Pyruvoyl Ligand

P. Cabon, R. Rumin, J. Y. Salaün,* S. Triki, and H. des Abbayes

Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, UMR CNRS 6521,
Université de Bretagne Occidentale, UFR Sciences et Techniques, 6 Avenue le Gorgeu,
CS 93837, 29238 Brest Cédex, France

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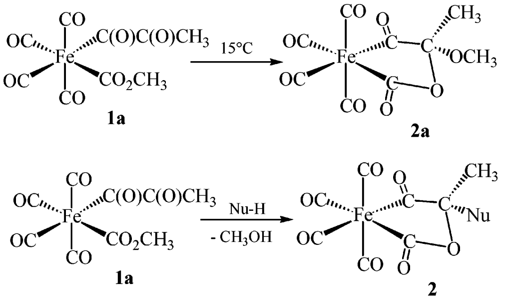
Anionic nucleophilic reagents $Nu^- = CH_3O^-$, $C_2H_5O^-$, t-BuO$^-$, CH_3S^-, and $P(C_6H_5)_2^-$ were found to react with $(CO)_4Fe(CO_2CH_3)[C(O)C(O)CH_3]$ to afford two isomers of anionic trifunctionalized metallalactones, $\{(CO)_3Fe[C(O)C(CH_3)(Nu)OC(O)](CO_2CH_3)\}^-$, whose formation resulted from an addition of the nucleophile to the β carbonyl of the pyruvoyl ligand. In this reaction, the metallacycle formation was found to occur by a further addition of the oxygen of the same β carbonyl on a terminal carbonyl. In acidic medium, these anionic complexes evolved into neutral metallalactones $(CO)_4Fe[C(O)C(CH_3)(Nu)OC(O)]$ already obtained by performing the same reaction with pronucleophiles (Nu-H type reagents). Achievement of $(CO)_4Fe[C(O)C(=CH_2)OC(O)]$ when the reaction was performed with t-BuO$^-$ could result from an intermediate formation of the enolate form of the pyruvoyl ligand [Fe]-C(O)-C(=CH$_2$)-O$^-$ under basic conditions.

Introduction

For their possible involvement in double-carbonylation catalytic processes, a wide variety of organometallic complexes bearing two carbonylated ligands in *cis* position have been described.[1] Possible models for tricarbonylation displaying the [M][C(O)R][C(O)C(O)-R′] pattern are more scarce;[1] they have generally been found to be thermally subjected to an exclusive decarbonylation giving rise to diacyl, acyl-alkoxycarbonyl, or bis-alkoxycarbonyl complexes. However, together with this decarbonylation, a carbon−carbon coupling process giving rise to organic diketones, keto-esters, or diesters has sometimes been observed.[2]

To our knowledge, the thermal behavior of *cis*-$(CO)_4Fe[C(O)C(O)CH_3](CO_2CH_3)$ (**1a**) is the only exception to these observations. This complex, which can be considered as a model for the so far elusive tricarbonylation reactions, has been found to evolve thermally into a metallalactone, **2a** (Scheme 1), formed by a cyclization process occurring between its two carbonylated ligands. **2a** was formally obtained by a C−O coupling between the oxygen of the β carbonyl of the pyruvoyl and the carbon of the alkoxycarbonyl ligand and by a migration of the alkoxy group of this last ligand toward the carbon of the β carbonyl of the pyruvoyl.[3] This process looked very similar to the ring-chain isomerism observed for organic γ-keto-esters.[4] The similarity between the two mechanisms seemed plausible, as **1a** can be considered as a γ-keto-ester with a metal inserted into its organic chain. However, the reaction performed from **1a** was irreversible and did not require acid or basic catalysis as it does for γ-keto-esters.

Scheme 1



Nu-H = CH_3OH, C_2H_5OH, CH_3SH, $HP(C_6H_5)_2$, $HP(C_6H_{11})_2$.

The achievement of a similar reaction in the presence of a series of Nu-H type nucleophiles (pronucleophiles) allowed us to show the β-carbonyl of the pyruvoyl to be the more electrophilic site of **1a**. Under these conditions it was presumed that metallalactone **2** formation could occur by an attack of the nucleophile reagent at the β carbonyl of the pyruvoyl and that a further addition of the oxygen of this group on the carbonyl of the alkoxycarbonyl that could induce the elimination of methanol. These reactions were found to afford quantitatively and under mild conditions Nu-substituted metallalactones **2** with Nu = O-CH_3, O-C_2H_5, S-CH_3, $P(C_6H_5)_2$, or $P(C_6H_{11})_2$ (Scheme 1).[5]

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* To whom correspondence should be addressed. E-mail: Jean-Yves.Salaun@univ-brest.fr.

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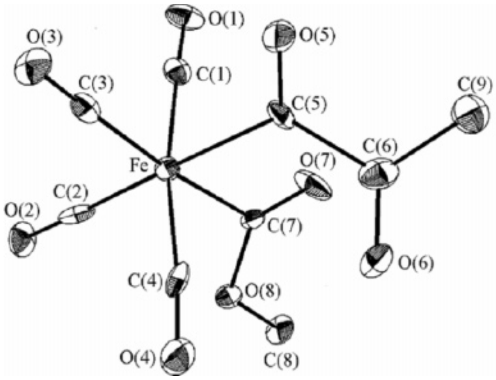

Figure 1. Molecular structure of **1a** with probability ellipsoids drawn at the 50% level. Hydrogen atoms have been omitted for clarity.

However, achievement of an analogous metallalactone $\{(CO)_4\overline{Mn[C(O)C(H)(C_6H_5))OC}(O)]\}^-$ by reaction of $Mn(CO)_5[C(O)C(O)C_6H_5]$ with $Li(C_2H_5)_3BH$ suggested that, for this complex, the formation of the lactonic ring initiated by H^- could be performed by a cyclization of the phenylglyoxyl ligand on a terminal CO.[6] To check that the presence of an alkoxycarbonyl ligand with a mobile alkoxy group is essential for the achievement of metallalactones by cyclization of a pyruvoyl ligand, we reinvestigated the mechanism of formation of these metallalactones by inducing the reactions with anionic nucleophiles. The results of this study will be the topic of this paper.

Results and Discussion

Preparation and Properties of Complex 1a. *cis*-$Fe(CO)_4(CO_2CH_3)[C(O)C(O)CH_3]$ (**1a**) was prepared, as previously described,[5] by reacting, at −80 °C, $[Fe(CO)_4(CO_2CH_3)]^-$ [7] with pyruvoyl chloride.[8] The complex, isolated as a pale yellow powder, was found to be stable below 20 °C. Suitable crystals for an X-ray diffraction study were only recently obtained from a hexane/dichloromethane (90/10) mixture, at −30 °C. Figure 1 displays the ORTEP drawing of the molecule; selected bonds and angles are listed in Table 1 and crystallographic data gathered in Table 3.

Table 1. Bond Lengths (Å) and Bond Angles (deg) for 1a

Fe−C(1)	1.827(2)	C(4)−O(4)	1.125(3)
Fe−C(2)	1.848(2)	C(5)−O(5)	1.203(2)
Fe−C(3)	1.853(2)	C(5)−C(6)	1.563(3)
Fe−C(4)	1.833(2)	C(6)−O(6)	1.197(3)
Fe−C(5)	2.023(2)	C(6)−C(9)	1.497(2)
Fe−C(7)	2.001(2)	C(7)−O(7)	1.206(2)
C(1)−O(1)	1.127(3)	C(7)−O(8)	1.353(2)
C(2)−O(2)	1.126(2)	C(8)−O(8)	1.455(3)
C(3)−O(3)	1.119(3)		
C(1)−Fe−C(2)	94.50(8)	C(4)−Fe−C(7)	87.37(9)
C(1)−Fe−C(3)	93.38(9)	C(5)−Fe−C(7)	88.93(8)
C(1)−Fe−C(4)	170.21(9)	Fe−C(5)−O(5)	124.3(1)
C(1)−Fe−C(5)	85.52(7)	Fe−C(5)−C(6)	119.9(1)
C(1)−Fe−C(7)	84.68(9)	Fe−C(7)−O(7)	126.3(2)
C(2)−Fe−C(3)	93.36(8)	Fe−C(7)−O(8)	112.7(1)
C(2)−Fe−C(4)	91.26(8)	O(5)−C(5)−C(6)	115.7(1)
C(2)−Fe−C(5)	179.28(9)	C(5)−C(6)−O(6)	119.3(2)
C(2)−Fe−C(7)	90.36(8)	C(5)−C(6)−C(9)	116.5(2)
C(3)−Fe−C(4)	94.19(9)	O(6)−C(6)−C(9)	123.9(2)
C(3)−Fe−C(5)	87.36(8)	O(7)−C(7)−O(8)	121.0(2)
C(3)−Fe−C(7)	175.93(7)	C(7)−O(8)−C(8)	115.6(1)
C(4)−Fe−C(5)	88.63(7)		

Table 2. Bond Lengths (Å) and Bond Angles (deg) for 5

Fe−C(1)	1.948(3)	C(3)−O(3)	1.099(3)
Fe−C(2)	1.791(3)	C(4)−O(4)	1.125(4)
Fe−C(3)	1.791(3)	C(5)−O(5)	1.170(4)
Fe−C(4)	1.800(3)	C(5)−C(7)	1.599(4)
Fe−C(5)	1.935(3)	C(6)−O(6)	1.161(4)
Fe−C(6)	2.101(3)	C(6)−O(7)	1.398(3)
C(1)−O(1)	1.192(4)	O(7)−C(7)	1.352(4)
C(2)−O(2)	1.074(3)	C(7)−C(8)	1.291(4)
C(1)−Fe−C(2)	91.5(1)	C(4)−Fe−C(6)	87.3(1)
C(1)−Fe−C(3)	94.8(1)	C(5)−Fe−C(6)	78.3(1)
C(1)−Fe −C(4)	91.8(1)	O(6)−C(6)−O(7)	107.6(3)
C(1)−Fe−C(5)	96.5(1)	Fe−C(5)−O(5)	121.8(2)
C(1)−Fe−C(6)	174.8(1)	Fe−C(5)−C(7)	113.6(2)
C(2)−Fe−C(3)	90.6(1)	O(5)−C(5)−C(7)	124.7(2)
C(2)−Fe−C(4)	99.7(1)	Fe−C(6)−O(6)	131.2(2)
C(2)−Fe−C(5)	171.9(1)	Fe−C(6)−O(7)	121.2(2)
C(2)−Fe−C(6)	93.7(1)	C(6)−O(7)−C(7)	108.5(2)
C(3)−Fe−C(4)	167.6(1)	C(5)−C(7)−O(7)	118.1(2)
C(3)−Fe−C(5)	87.7(1)	C(5)−C(7)−C(8)	127.9(3)
C(3)−Fe−C(6)	85.1(1)	O(7)−C(7)−C(8)	114.0(3)
C(4)−Fe−C(5)	81.1(1)		

To our knowledge, **1a** is the first structurally characterized iron complex with a ligand displaying a double C(O) chain described in the literature. As revealed by this study, the coordination about its metal center can be described as a distorted octahedron with angle values between ligands in *trans* positions from 170.21(9)° (C(1)−Fe−C(4)) to 179.28(9)° (C(2)−Fe−C(5)) and between ligands in *cis* position from 85.52(7)° (C(1)−Fe−C(5)) to 94.50(8)° (C(1)−Fe−C(2)). The relatively long Fe-terminal carbonyl distances (from 1.827(2) to 1.853(2) Å) compared with an average of 1.80 Å observed for similar bonds could result from a reduced back-donation induced by the electron-withdrawing alkoxycarbonyl and pyruvoyl ligands. In the pyruvoyl fragment, the acyl carbonyls are in *s-trans* conformation as seen in most complexes displaying an α-keto acyl ligand.[9−14] The torsion angle O(5)−C(5)−C(6)−O(6) measured between these two carbonyls is 141.7(2)°. This value is smaller than its homologues generally observed for α-keto acyl complexes (157−177°)[9,10,13,15,16] but larger than analogous angles of a manganese[17] and a platinum[12] complex (112° and 127°, respectively). The iron pyruvoyl (Fe−C(5) = 2.023(2) Å) and iron methoxycarbonyl (Fe−C(7) = 2.001(2) Å) distances are normal;[11,18] they can be

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Table 3. Crystallographic Data for Compounds 1a and 5

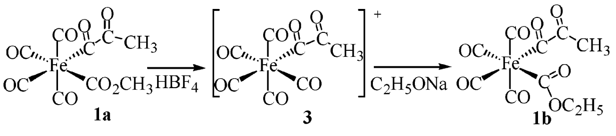
	1a	**5**
formula	$C_9H_6O_8Fe$	$C_8H_2O_7Fe$
fw	297.99	265.95
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	6.3286(7)	11.5836(9)
b (Å)	8.776(1)	6.9549(5)
c (Å)	10.946(1)	12.4252(9)
α (deg)	87.08(1)	90
β (deg)	89.52(1)	105.260(7)
γ (deg)	68.99(1)	90
V (Å^3)	566.7(2)	965.7(2)
Z	2	4
cryst size (mm)	0.21*0.18*0.07	0.15*0.11*0.08
D_{calcd} (g cm^{-3})	1.75	1.83
F(000)	300	528
abs coeff, μ (mm^{-1})	1.356	1.574
T (K)	100	288
2θ limits (deg)	5.0−63.46	5.00−70.12
no. of reflns collected	5303	10 494
no. of reflns unique/R_{int}	3185/0.031	3819/0.051
no. of reflns with $I > 4\sigma(I)/N_v$	2164/187	1653/145
$R(F_o)^a$	0.026	0.032
$R_w(F_o)^b$	0.028	0.035
GOF^c	1.095	1.055
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å^{-3})	0.465/−0.263	+0.477/−0.305
Δ/ρ	0.003	0.000

[a] $R = \sum|F_o - F_c|/F_o$. [b] $R_w = [(\sum wF_o - F_c)^2/w(F_o)^2]^{1/2}$. [c] GOF $= [(\sum w|F_o| - |F_c|)^2/(N_{\mathrm{obs}} - N_{\mathrm{var}})]^{1/2}$. $w = 4F_o^2/(\sigma^2(F_o^2) + (0.02F_o^2)^2)$.

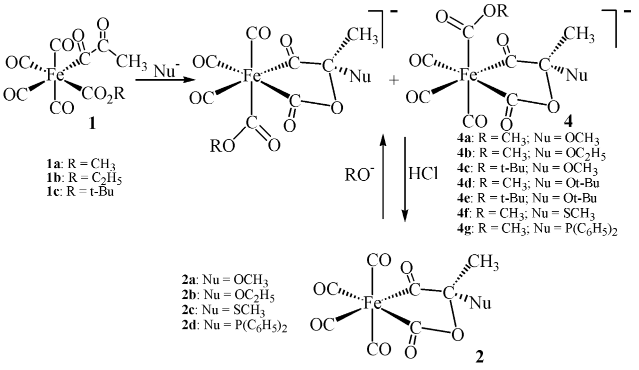
compared to long Fe−C carbene bonds in a variety of iron carbene complexes.[19] The carbon−carbon and carbon−oxygen distances of these two ligands are also normal. Nonbonding repulsions between the pyruvoyl and the methoxycarbonyl linked to $Fe(CO)_4$ are minimized by a staggered relationship between these two ligands. The dihedral angle between the Fe−C(O) pyruvoyl plane (Fe−C(7)−O(7)) and the equatorial plane of the complex (Fe−C(3)−C(2)−C(5)−C(7)) is 29.61°, whereas its homologue between the Fe−C(O) alkoxycarbonyl plane and the same equatorial plane is 41.93°.

To check the possibility of performing the cyclization of a pyruvoyl ligand into a metallalactone on a complex that did not display an alkoxycarbonyl ligand, we made use of the well-known mobility of alkoxy groups of alkoxycarbonyl ligands on iron complexes.[20] This mobility, generally shown by rapid exchanges with alcohols, allowed us, by reacting **1a** with HBF_4,[5] to obtain the ionic complex **3**. The stability of this cation clearly showed that no spontaneous cyclization of the pyruvoyl ligand by a nucleophilic attack of the oxygen of the β carbonyl of this ligand at a terminal carbonyl occurred. Moreover, we showed that by reaction with anionic nucleophiles **3** was not found to afford a metallalactone. Thus, by reaction with C_2H_5ONa, the *cis* complex **1b** (Scheme 2) was formed whose spectroscopic characteristics were very close to those reported for **1a**.[5] The formation of the ethoxycarbonyl ligand was indicative, on this cationic complex, of an enhanced electrophilicity of the terminal carbonyls compared to that of the β acyl of the pyruvoyl.

Scheme 2



Scheme 3



As this result did not answer the question of the possible formation of a metallalactone by cyclization of the pyruvoyl at a terminal carbonyl, we carried on with this study by reacting **1a** with anionic nucleophiles $Nu^- = CH_3O^-$, $C_2H_5O^-$, t-BuO$^-$, CH_3S^-, and $(C_6H_5)_2P^-$.

Reactions of Cyclization of 1a Induced by RO$^-$ Nucleophiles. Although **1a** displayed an alkoxycarbonyl together with the pyruvoyl ligand, its reactions with anionic reagents were found to reveal interesting information about the mechanism of cyclization of the pyruvoyl ligand.

Addition of CH_3ONa to 1a. IR monitoring of the reaction performed at −10 °C showed the formation (3 h) of a new complex characterized by three $\nu C{\equiv}O$ bands at 2069, 2004, and 1987 cm^{-1} and by three $\nu C{=}O$ at 1678, 1639, and 1592 cm^{-1}. This compound, which was isolated as a pale yellow powder, was only sparingly soluble in THF. Its IR and NMR characteristics suggested for this complex the metallalactonic anionic trifunctionalized structure **4a** (R = CH_3; Nu = OCH_3) displayed in Scheme 3. Its IR $\nu C{\equiv}O$ frequencies were halfway between the values observed for the same oscillators of the starting neutral complex **1a** (2130−2050 cm^{-1}) and those measured for the monofunctionalized anionic iron complex $[Fe(CO)_4(CO_2CH_3)]^-$ (1910 cm^{-1}).[7] They were very close to the $\nu C{\equiv}O$ observed for the trifunctionalized anion $[Fe(CO)_3(CO_2R)_3]^-$ (two bands about 2080 and 2015 cm^{-1}), obtained by reaction of RO$^-$ with *cis*-$(CO)_4Fe(CO_2R)_2$.[21] The values measured for the $\nu C{\equiv}O$ of **4a** suggested a strong delocalization of the negative charge of the complex along electron-withdrawing carbonylated organic ligands. The observation of three bands (two $\nu C{\equiv}O$ are expected for a C_{3v} symmetry) could result from the presence on the complex of a metallacycle with an asymmetric carbon. The ^{13}C NMR spectrum of **4a** was also consistent with the proposed structure. The presence on the metallacycle of a quaternary carbon bearing two different substituents together with an alkoxycarbonyl ligand in axial position on the metal brought about the possible formation of two isomers of **4a**. Indeed, the two signals of equal intensities observed for the quaternary carbon of the cycle at 111.0 and 109.7 ppm as well as for the cyclic

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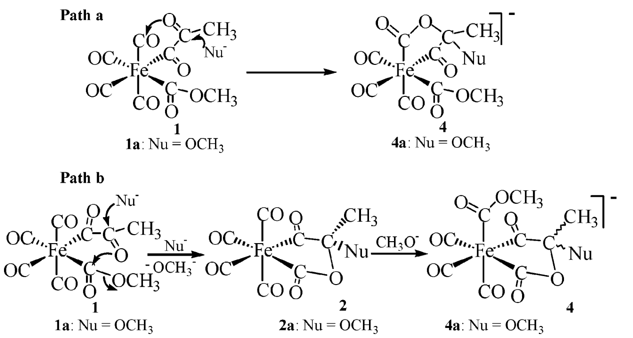
Scheme 4



M−C(O) acyl (271.4 and 265.5 ppm) and for the methyl substituent of this quaternary carbon (21.5 and 20.6 ppm) strongly suggest the formation of an equimolecular mixture of two isomers of **4a**. Four methoxy resonances were also found at 51.1, 50.6, 50.5, and 50.4 ppm, and the signals corresponding to the terminal carbonyls and to the cyclic C(O)O linked to the metal were observed as 10 peaks between 222.1 and 206.4 ppm. Among these signals, the two more deshielded resonances (222.1, 220.0 ppm) were attributed to the M−C(O)O group of the cycle. By comparison with the resonances of analogous neutral complexes, the signals of this anionic compound were shifted by about 10 ppm toward the lower fields.[3,5]

The exclusive formation of the trifunctionalized anion **4a** by reaction of **1a** with CH_3ONa strongly suggested the formation of the metallalactone to occur via a cyclization of the pyruvoyl at a terminal carbonyl (Scheme 4, path a). This result brought up the question of the formation of only **2a** when the isomerization of **1a** was induced by CH_3OH.[5] An answer to this problem was given by the reaction of **4a** with HCl. We already described the instantaneous evolution in acidic media of anionic trifunctionalized complexes $\{(CO)_3Fe[C(O)R]_2(CO_2R')\}^-$ displaying at least one alkoxycarbonyl ligand. Neutral complexes $(CO)_4Fe[C(O)R]_2$ were then quantitatively formed, and elimination of alcohol was observed.[21] In the same way, when the mixture of isomers of **4a** was reacted with HCl at −70 °C, the instantaneous and quantitative formation of the already structurally characterized neutral metallacyclic lactone **2a** (Nu = OCH_3) was observed (Scheme 3). This reaction confirmed the structure attributed to **4a** and also showed that this last complex with H^+ as counterion evolved into **2a** with liberation of CH_3OH. This observation explained the production of only **2a** when the cyclization of **1a** was induced by Nu-H reagents. The formation of the metallalactonic cycle of this process could then be achieved by an attack of the oxygen of the pyruvoyl on a terminal carbonyl (Scheme 4, path a), as the reaction would afford **4a** with H^+ as counterion that would evolve instantaneously into **2a** under the reaction conditions. On the other hand, the formation of **4a** via the addition of the pyruvoyl at the alkoxycarbonyl as displayed by path b of Scheme 4 cannot be completely dismissed.

To check the possible validity of this last assumption, we reacted CH_3ONa with the metallalactone **2a**, which would be the intermediate species of this process. This reaction was found to afford, within 3 h, **4a** as a mixture of isomers (50/50, 60% yield). However, although the rate of this last reaction was similar to that of the process between **1a** and CH_3ONa, careful monitoring of the reaction between **1a** and CH_3ONa never allowed the transient detection of **2a**, whose formation would be required by the cyclization of the pyruvoyl on the alkoxycarbonyl ligand. Furthermore, contrary to the reaction of **1a** with CH_3ONa, the addition of this last reagent to **2a** was not quantitative. These results made the formation of the lactone by cyclization of the pyruvoyl on a terminal carbonyl the more plausible hypothesis.

Reaction of 1a with C_2H_5ONa. This process showed that the mechanism of formation of **4** could be more complex. When performed at 0 °C, the reaction afforded numerous compounds whose IR and ^{13}C NMR spectra were very close to those displayed by **4a**. The ^{13}C NMR spectrum of the crude product of this reaction exhibited six signals between 276 and 265 ppm (M-cyclic C(O)), five resonances for the metallalactonic quaternary carbon between 111.6 and 109.5 ppm, six peaks corresponding to OCH_2- (59.9−57.5 ppm), and only three signals between 51.2 and 50.4 ppm for OCH_3. When reacted with HCl at −70 °C, this mixture of compounds, which were very probably anionic trifunctionalized complexes **4**, afforded quantitatively a mixture of 50% of **2a** and 50% of its ethyl homologue **2b**.[22] These results were clearly indicative of an exchange between the two alkoxy groups that could afford eight isomers of **4**. Such exchanges have already been observed between the alkoxy of alkoxycarbonyl ligands of iron complexes and alcohols;[20] however, they were never performed by reaction of alkoxycarbonyl iron complexes with alcoholates.[21] Careful monitoring of the reaction between **1a** and 1 equiv of C_2H_5ONa or performing the same reaction in the presence of 0.5 equiv of C_2H_5ONa showed the absence of alkoxy−alcoholate exchange on **1a** prior to the formation of the mixture of complexes **4**. The same lack of exchange was noticed between anion **4a** and C_2H_5ONa or C_2H_5OH. In the same way although the neutral lactone **2a** reacted with C_2H_5ONa to afford an analogous mixture of **4**, no exchange prior to the anion formation could be detected. It must also be mentioned that, contrary to the easy exchange reactions observed between alcohols and the alkoxy substituent of organic lactones in acidic media,[23] such a process was not observed between **2a** and C_2H_5OH even in the presence of HCl. Under these last reaction conditions, decomposition of **2a** rapidly occurred. All these results showed that exchange processes were concomitant with the metallalactonic ring formation affording **4**.

Reaction of 1c (R = t-Bu) with MeONa. Surprisingly, although easy exchanges were observed between CO_2t-Bu ligands of $(CO)_4Fe(CO_2t\text{-}Bu)_2$ and methanol,[20] such reactions were not observed when **1c** was reacted with CH_3ONa. Again IR monitoring of the reaction showed the formation of trifunctionalized anions, but the ^{13}C NMR spectrum of the crude product of the reaction clearly showed the formation of only two isomers of the anionic lactone **4c** (R = t-Bu, Nu = OCH_3). The characteristics of these isomers were very close to those displayed by **4a**, and as shown by the relative intensities of the two signals observed at 271.15

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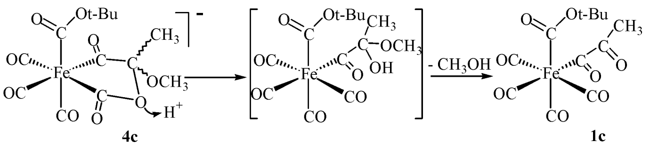
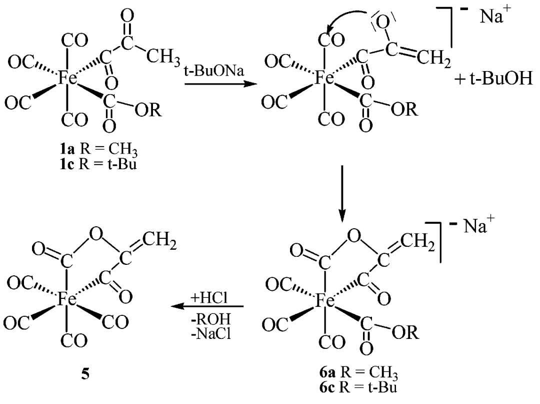
[22] This compound had already been specifically obtained by inducing the cyclisation of **1a** with C_2H_5OH via the intermediate formation of **1b**: $(CO)_4Fe(CO_2C_2H_5)[C(O)C(O)CH_3]$.[5]

[23] des Abbayes, H. *Bull. Soc. Chim. Fr.* **1970**, 3671.

Scheme 5



Scheme 6



and 264.5 (M−C(O)) and at 110.9 and 109.6 ppm (quaternary carbon of the metallacycle), their relative proportions were estimated to be 55/45%. This result was indicative of a low steric effect of the alkoxy group in the course of the reaction. Treatment of these two isomers with HCl at 0 °C afforded the neutral metallalactone **2a** in 80% yield together with 20% of the starting complex **1c**. The absence of formation of O-tBu-substituted neutral metallalactone confirmed the nonoccurrence of any exchange in the course of formation of **4c**. The presence of **1c** as a final product of the reaction can be explained, as already supposed for a Mn metallalactone,[6] by an electrophilic addition of H$^+$ on the lactonic cyclic oxygen followed by a ring opening of the lactone with release of methanol (Scheme 5).

Reaction of 1a or 1c with t-BuONa: Formation of a Methylene-Substituted Metallalactone 5. As shown by IR monitorings, these reactions were again found to induce the formation of trifunctionalized anions. We were unfortunately unable to obtain correct ^{1}H or ^{13}C NMR spectra of these complexes. When treated with HCl at −80 °C, these intermediates respectively evolved into the structurally characterized neutral methylene metallalactone **5** (Scheme 6). This complex was the only product of the reaction performed with the anion resulting from the addition of t-BuONa to **1a** (60% yield), while the anions obtained by reaction of **1c** with t-BuONa, under the same conditions, were found to give rise to 43% **5** and 13% **1c**, whose formation could be explained as above. In the IR, the C=O and C≡O stretching bands of **5** were similar to those displayed by **2a**; however, an additional band (probably a νC=C) was observed at 1618 cm^{-1}. The ^{1}H NMR spectrum of this complex displayed two broad signals at 5.07 and 4.86 ppm, suggesting the presence of a methylene group. In ^{13}C NMR the signals of the carbonyls were similar to those observed for **2a** except the resonance of the cyclic C(O), which, due to its conjugation with the C=CH$_2$ group, was shielded by about 9 ppm at 236.9 ppm. The cyclic carbon bound to the methylene was found at 157.5 ppm and the methylene carbon at 89.7 ppm. ^{13}C−^{1}H NMR HMQC sequences showed ^1J interactions between the two protons and the methylene signal at 89.7 ppm and confirmed the proposed structure. The formation of **5** by reaction of t-BuONa with **1a** or **1c** could occur either by a proton abstraction with elimination of tBuOH from the anionic intermediates of type **4** (**4d** or**4e**, Scheme 3) by a reaction analogous to the process already observed, under basic conditions, for a Pd π allyl lactone[24] or, as described for a malonyl ligand of a rhenium complex,[25] by the intermediate formation, in the presence of t-BuONa, of the enolate of the pyruvoyl ligand of **1a** or **1c**, enolates that could undergo a cyclization on a terminal carbon and then give rise to trifunctionalized methylene metallalactonic anions **6a** or **6c**, which, in the presence of HCl, would afford **5** (Scheme 6).

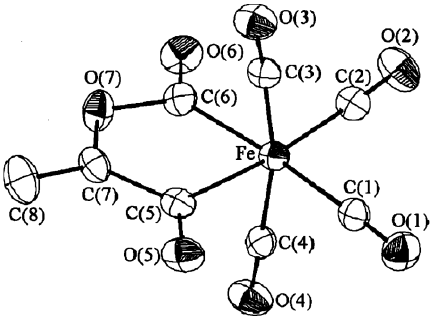


Figure 2. Molecular structure of **5** with probability ellipsoids drawn at the 40% level. Hydrogen atoms have been omitted for clarity.

The molecular structure of **5** was determined by a single-crystal X-ray study. Pale yellow monocrystals of this product were grown from a hexane/dichloromethane (90/10) solution at −30 °C. An ORTEP drawing of the complex is depicted in Figure 2. Selected bond lengths and angles are listed in Table 2, and crystallographic data are gathered in Table 3.

As suggested from Figure 2, the metallacycle of the complex is quasi planar. Both atoms C(7) and O(7) deviate from the plane defined by C(5), Fe, C(6) by only 0.07 Å. The acyl oxygen atoms O(5) and O(6) (0.09 and 0.06 Å) as well as the methylene carbon C(8) (0.25 Å) are also only slightly removed from this plane. The presence in the metallacycle of the sp^2 carbon linked to the methylene group is indicated by a higher value of the C(5)−C(7)−O(7) angle, 118.1(2)°, compared to an average of 109° measured for homologous angles of iron metallalactones with an sp^3 carbon.[3,5] This large angle brings about a small C(6)−O(7)−C(7) angle (108.5(2)° vs 118°) and a large iron−acyl−oxygen angle (Fe−C(6)−O(7)) of 121.2(2)° (vs an average of 115.5°). The geometry around the iron atom shows distortions from idealized octahedral. As generally observed for five-membered iron metallacycles,[3,5,26] the angle between the two acyls of the metallacycle (C(6)−Fe−C(5): 78.3 (1)°) is smaller than their homologues of a noncyclic bis-

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[24] Carfagna, C.; Gatti, G.; Mosca, L.; Paoli P.; Guerri, A. *Organometallics* **2003**, *22*, 3967.

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alkoxycarbonyl iron complex (88.5° is observed for the *cis*-$(CO)_4Fe(CO_2tBu)_2$).[27] The two axial C≡O also present a significant bending toward the metallacyclic ring: C(3)−Fe−C(4) = 167.6(1)°. Surprisingly the molecule displays a very long Fe−terminal CO bond: Fe−C(1) = 1.948(3) Å. The lengthening of this Fe−C≡O bond *trans* from the C(O)O group could result from an electronic delocalization along the metallacycle. Compared to other metallalactones, the presence of the methylene group on the metallacycle of **5** induces significant modifications of interatomic distances. Thus, the Fe−acyl (Fe−C(5) = 1.935(3) Å), C(=CH_2)−O (C(7)−O(7) = 1.352(4) Å), and C(O)−O (C(6)−O(7) = 1.398(3) Å) bonds are shorter than expected, whereas C(O)−C(C=H_2) (C(5)−C(7) = 1.599(4) Å) and Fe−C(O)O (Fe−C(6) = 2.101(3) Å) distances are longer than their homologues of other iron metallalactones.[3,5] The very short value between O(6) and O(7) (2.070(3) Å) is also worth noting; it is associated with a small O(6)−C(6)−O(7) angle: 107.6(3)°.

Generalization of the Reaction of Formation of Metallalactones. To expand the scope of the reaction of cyclization of pyruvoyl iron complexes into metallalactones, we tried to perform the process by using RS^-, PR_2^-, NR_2^-, and H^- as nucleophiles. According to the procedure described for the reaction between **1a** and CH_3ONa, CH_3SNa was found to react in 1.5 h at −30 °C to afford the anionic complex **4f** (Scheme 3), displaying in its IR νCO stretching bands very close to those observed for **4a** (three νC≡O at 2068 (s), 2005 (s), and 1987 (s) cm^{-1} and two νC=O at 1646 (s) and 1593 (m) cm^{-1}). The ^{13}C NMR spectrum of the product of the reaction confirmed the formation of an anionic trifunctionalized metallalactone, as it displayed an acyl carbon at 259.6 ppm, a carbonyl (cyclic CO_2 group) at 222.8 ppm, and an unresolved broad signal between 207.7 and 209.3 ppm for the other CO of the molecule. The resonance of the quaternary carbon of the metallacycle, now substituted by a SCH_3 group, was observed at 95.5 ppm (a shielding of 15 ppm compared to its homologue substituted by a OCH_3 group), whereas the signals of the CH_3 were found at 50.3 (OCH_3), 22.6 (CH_3-C), and 12.5 ppm (SCH_3). The formation of a second isomer of this product (15%) was shown by the presence of minor peaks at 259.7, 223.0; 97.0; 51.0 and 12.2 ppm. When reacted with 1 equiv of HCl at −80 °C, this mixture of complexes afforded quantitatively the SCH_3-substituted neutral metallalactone **2c**, characterized by IR and ^{13}C NMR. These characteristics were very similar to those displayed by **2a** except, in the ^{13}C NMR, the resonance of the quaternary carbon of the cycle substituted by the SCH_3 group, which is shielded by 12.5 ppm compared to its OCH_3 homologue. Again, by reaction with 1 equiv of CH_3ONa, **2c** gave rise to **4f** (as a mixture of 85/15 isomers) in 30% yield. An analogous process was observed when **1a** was reacted with $(C_6H_5)_2PLi$. As shown by the ^{13}C NMR spectrum of the product of the reaction (C=O at 267.5 and 253.3 ppm; $C(CH_3)(PPh_2)$ (broad signals) at 91.35 and 90.2 ppm and CH_3 at 21.2 and 19.6 ppm), an anionic PPh_2-substituted trifunctionalized metallalactone **4g** was formed as a mixture of two isomers (50/50). The formation of these two isomers was confirmed by the presence in the ^{31}P NMR of two signals of equal intensities at 30.2 and 24.6 ppm. When treated with HCl at low temperature, this mixture afforded quantitatively the PPh_2-substituted neutral lactone **2d**. The presence of the $P(C_6H_5)_2$ group on the sp^3 carbon of the metallacycle was shown in the ^{13}C NMR by the large coupling constant observed for the signal of this carbon at 101.1 ppm (J_{C-P} = 35.6 Hz) and by the lower interactions of the phosphorus with the acyl carbon at 252.7 ppm (J_{C-P} = 8.7 Hz) and with the methyl at 23.1 (J_{C-P} = 17.4 Hz). J_3 interactions P−CH_3 were also detected by $^{31}P-^{1}H$ NMR HMBC sequences. In the ^{31}P NMR, **2d** displayed one signal at 10.9 ppm, which was indicative of an uncomplexed large cone angle phosphine.[28] This absence of coordination of the phosphine to the metal was confirmed by the lack of interaction between the phosphorus and the terminal carbonyl carbons.

Two other nucleophiles, NaH and $LiNEt_2$, were also reacted with **1a**; at low temperature they were found unreactive and, at 0 °C, the only products of the reactions were $Fe(CO)_5$ and organic compounds.

Conclusions

This work clearly established that addition of alcoholates to pyruvoyl-substituted cationic iron complexes occurred on a terminal carbonyl, affording an alkoxycarbonyl ligand. On the other hand, on neutral iron complexes, the β carbonyl of the pyruvoyl was shown to be the most electrophilic site of the molecule, as the reactions of **1a** or **1c** with anionic nucleophiles (Nu^-) were found to give rise to anionic trifunctionalized Nu-substituted metallalactones **4** (Nu = OCH_3, OC_2H_5, SCH_3, $P(C_6H_5)_2$) formed by addition of the nucleophile on the β carbonyl of the pyruvoyl followed by the metallalactone formation probably performed by an attack of the oxygen of this β carbonyl on a terminal carbonyl of the complex. These anionic lactones **4** were generally obtained as a mixture of isomers. In acidic medium, they quantitatively afforded neutral metallalactones **2**. This last process was shown to be reversible, as the reaction of RO^- with **2** gave rise to **4** by addition of the reagent on a terminal carbonyl. However, the yield of this last reaction was found to be rather low. When a stronger base (t-BuO^-) was added to **1a** or **1c**, the major product of the process, after reaction with HCl, was a methylene-substituted metallalactone **5**, whose formation could result from the cyclization of the enolized form of the pyruvoyl ligand on a terminal carbonyl of the complex. The original compounds **1a** and **5** were characterized structurally.

Experimental Section

All manipulations were performed under a dry oxygen-free argon atmosphere using standard Schlenk techniques. Hexane and THF were distilled under nitrogen from sodium/benzophenone. CH_2Cl_2 was dried with CaH_2. CD_2Cl_2 and D_8-THF were stored on molecular sieves in a Schlenk storage flask until needed. $Fe(CO)_5$, CH_3ONa, C_2H_5ONa, t-BuONa, HCl (1 M in ether), and BuLi (1.6 M in hexanes) were used as received from Aldrich. CH_3SNa,[29] $(C_6H_5)_2PLi$,[30] and $ClC(O)C(O)CH_3$[8] were prepared by literature methods. $ClC(O)C(O)CH_3$ was obtained

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as a mixture with $HC(O)OCH_3$ and $ClC(O)CH_3$. The respective percentages of these compounds were evaluated by ^{1}H NMR. Infrared spectra were recorded in solution in hexanes, CH_2Cl_2, or THF on a Nicolet Nexus 470 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded (unless otherwise stated) at 0 °C in CD_2Cl_2 (neutral compounds) or in D_8-THF (anionic complexes) on a Bruker AMX-3 300 or on a Bruker DRX 400 spectrometer. NMR HMQC sequences were performed on a Bruker DRX 500. Chemical shifts were measured relative to residual protonated solvents for ^{1}H NMR spectra and to the solvent resonance for ^{13}C NMR spectra. ^{31}P spectra were externally referenced to H_3PO_4 (85%). Elemental analyses were performed by the Service Central D'analyses du CNRS.

Crystallographic Analyses. Crystallographic data of compounds **1a** and **5** were collected ($T = 100$ K for **1a**, $T = 288$ K for **5**) on an Xcalibur 2 diffractometer (Oxford diffraction). The two structures were solved by direct methods and successive Fourier difference syntheses and were refined on F by weighted anisotropic full-matrix least-squares methods.[31] For compound **1a**, the hydrogen atoms were located by difference Fourier maps and refined isotropically, while those of compound **5** were calculated [d(C−H) = 0.95 Å; thermal parameters $U_{\mathrm{iso}} = 1.3U_{\mathrm{eq}}(\mathrm{C})$] and therefore included as isotropic fixed contributors to F_c. Scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography*.[32] The thermal ellipsoid drawings were made with the ORTEP program.[33] All calculations were performed on an Alphastation 255 4/233 computer. Pertinent crystal data, bond distances, and bond angles of both compounds are listed in Tables 1−3. Complete crystallographic data, in CIF format, are included in the Supporting Information.

Preparation of Complexes 1a, 1b, and 1c. Syntheses of complexes **1b** and **1c** were performed by following the method of preparation of **1a**:[5] A solution of pyruvoyl chloride (20 mmol, 2.07 g) in 5 mL of THF was added dropwise to a stirred solution of 20 mmol of $[(CO)_4Fe(CO_2R)]^-$ [7] in THF at −70 °C. $[(CO)_4Fe(CO_2R)]^-$ was obtained by reaction at 0 °C of 20 mmol of the appropriate alcoholate (CH_3ONa: 1.08 g; C_2H_5ONa: 1.36 g; t-BuOK: 2.24 g) with $Fe(CO)_5$ in excess (40 mmol, 7.95 g, 5.33 mL). The orange-brown solution of the anion slowly turned yellow-green as, in IR, the ν(C≡O) bands of the anions at 1915, 1890, and 1870 cm^{-1} were replaced by four bands at 2125, 2075, 2070, and 2060 cm^{-1}. After 2 h at −20 °C, the solvent was evaporated to dryness and the residue washed at −70 °C with two portions (5 mL) of hexanes. Neutral complexes **1** were extracted, at 0 °C, from the residue by three fractions (20 mL) of hexanes/CH_2Cl_2 (95:5) for **1a** or **1b** or hexanes for **1c**. These different fractions were joined, and concentration of the extract to approximately half its volume and cooling to −40 °C resulted in crystallization of pale yellow solid of pure **1a** or **1b**, which were washed twice with a minimum of hexanes at −70 °C and dried under vacuum. **1a**: yield: 60% (3.57 g). IR (hexane, cm^{-1}): ν(C≡O) 2125 (m), 2075 (w, sh), 2070 (m, sh), 2060 (s); ν(C=O) 1740 (br), 1665 (w, sh), 1630 (br). ^{1}H NMR (CD_2Cl_2, 273 K; δ, ppm): 3.56 (s, 3H, OCH_3), 3.22 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K; δ, ppm): 245.7 (C=O); 201.3 (2), 199.2 (1), 198.2 (1) (C≡O); 198.1 (C=O); 193.9 (CO_2CH_3) 50.5 (OCH_3); 23.0 (CH_3). Anal. Calc for $C_9FeH_6O_8$: C, 36.28; Fe, 18.74; H, 2.03. Found: C, 36.42; Fe, 18.65; H, 2.11. **1b**: yield: 55% (3.43 g). IR (hexane, cm^{-1}): ν(C≡O) 2120 (w), 2085 (w, sh), 2075 (m, sh), 2065 (s); ν(C=O) 1730 (br), 1660 (sh), 1625 (br). ^{1}H NMR (CD_2Cl_2, 273 K; δ, ppm): 4.06 (q, J = 7.5 Hz, 2H, CH_2), 2.23 (s, 3H, CH_3), 1.17 (t, J = 7.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K; δ, ppm): 246.0 (C=O); 201.6 (2), 199.4 (1), 198.4 (1) (C≡O); 198.0 (C=O); 193.2 ($CO_2C_2H_5$); 62.8 (OC_2H_5); 23.2 (CH_3); 14.5 (CH_3). Anal. Calc for $C_{10}FeH_8O_8$: C, 38.50; Fe, 17.90; H, 2.59. Found: C, 38.70; Fe, 17.75; H, 2.65. **1c**: We were unable to get crystals of **1c**. However, after evaporation of the solution to dryness, **1c** was obtained as an oily residue in 70% yield (4.76 g). IR (hexane, cm^{-1}): ν(C≡O) 2118 (m), 2070 (w, sh), 2060 (m, sh), 2045 (s); ν(C=O) 1730 (br), 1663 (m, sh), 1618 (br). ^{1}H NMR (CD_2Cl_2, 273 K; δ, ppm): 2.23 (s, 3H, CH_3), 1.36 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K; δ, ppm): 246.8 (C=O); 201.9 (2), 199.4 (1), 198.8 (1) (C≡O); 198.4 (C=O); 191.9 (CO_2t-Bu); 84.6 (Ot-Bu); 28.3 (CH_3); 23.3 (CH_3). Correct analysis of this complex was not obtained.

Preparation of the Cationic Complex 3. To a solution of 100 mg (0.33 mmol) of **1a** in 10 mL of THF was added, at −40 °C, 2.5 equiv (0.825 mmol, 0.110 mL) of HBF_4, $O(CH_3)_2$. The solution was stirred for 1 h at −40 °C. Pale yellow crystals slowly separated. After filtration these crystals were washed with three portions (5 mL) of THF at −50 °C and dried under vacuum to give 46 mg (40%) of **3**. ^{1}H NMR (CD_3CN, 273 K; δ, ppm): 2.80 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN, 273 K; δ, ppm): 231.5 (C=O); 196.1 (4), 190.4 (1) (C≡O); 189.5 (C=O); 24.6 (CH_3). Probably due to its high sensitivity to moisture, we were unable to obtain a correct IR spectrum and microanalysis of this complex.

Reaction of 3 with C_2H_5ONa: Formation of 1b. A solution of 20 mg (0.283 mmol) of C_2H_5ONa in 5 mL of THF was added dropwise to a stirred suspension of 100 mg (0.283 mmol) of **3** in 30 mL of THF at −40 °C. Within 15 min the solid in suspension gradually disappeared and a yellow solution was obtained. The solvent was then removed under vacuum at 0 °C. The remaining residue was washed at −70 °C with two portions of 5 mL of hexanes and extracted with 2 × 15 mL of a hexanes/CH_2Cl_2 (95:5) mixture. After concentration of the so obtained solution to about 10 mL at −50 °C, 53 mg (60% yield) of **1b** was obtained as a pale yellow crystalline solid.

Reactions of Complexes 1 with Anionic Nucleophiles Nu^-: General Procedure for the Preparation of 4. Nu^-M^+ (1 mmol) in solution in 5 mL of THF was added dropwise to 1 mmol of **1** in solution in 20 mL of THF at −30 °C. The reaction, which was monitored by IR, was complete after 1.5 h. The solvent was then removed and the oily residue washed at 0 °C with two portions of 10 mL of hexanes to afford **4** as a pale yellow powder. We were unable to obtain correct analysis of these anionic complexes.

Formation of 4a. Complex **1a** (1 mmol, 300 mg) was reacted with 54 mg (1 mmol) of CH_3ONa to afford 240 mg (yield 80%) of **4a**. IR (THF, cm^{-1}): ν(C≡O) 2069 (s), 2004 (s), 1987 (s); ν(C=O) 1678 (sh), 1639 (m), 1592 (w). ^{1}H NMR (D_8-THF, 273 K; δ, ppm): 3.30 (br s, 3H, OCH_3), 3.11 (br s, 3H, OCH_3), 1.15 (br s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (THF, 273 K; δ, ppm): 271.4, 265.5 (C=O); 222.1, 220.0 (cyclic C(O)O−); 209.15, 209.0, 208.8, 208.5, 208.1, 207.9 207.35, 206.4 (C≡O and C(O)O−); 111.0, 109.7 (cyclic quaternary carbon); 51.1, 50.6, 50.5, 50.4 (OCH_3); 21.5, 20.6 (CH_3).

Reaction of 1a with C_2H_5ONa. **1a** (1 mmol, 300 mg) was reacted with 68 mg (1 mmol) of C_2H_5ONa to give rise to 250 mg of trifunctionalized anionic lactones **4**. IR (THF, cm^{-1}): ν(C≡O) 2068 (s), 2003 (s), 1985 (s); ν(C=O) 1667 (sh), 1638 (m), 1591 (w). ^{1}H NMR (D_8-THF, 273 K; δ, ppm): numerous signals between 3.50 and 0.80. $^{13}C\{^1H\}$ NMR (THF, 273 K; δ, ppm): 276.2, 271.5, 270.0, 265.55, 265.4, 264.9. (C=O); 222.5, 222.3, 222.0, 219.9 (cyclic C(O)O-); 211.6, 209.2, 209.1, 209.0, 208.8, 208.5, 208.4, 208.2, 208.1, 207.9, 207.6, 207.5, 207.4, 207.3, 206.6, 206.5, 206.4 (C≡O and C(O)O−); 111.6, 111.0, 110.9, 109.7 109.5 (cyclic quaternary carbons); 59.9, 59.3, 59.0, 58.9, 58.3, 57.5 (OCH_2) 51.2, 50.5, 50.4, (OCH_3); 22.4, 21.5, 21.1, 20.6, 19.5 (CH_3).

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^{13}C NMR Monitoring of the Reaction. To 7 mg of C_2H_5ONa in an NMR tube was added a cold solution of **1a** (30 mg) in 0.7 mL of D_8-THF. The spectra recorded at −30 °C were not found to display characteristic signals corresponding to **1b**: C=O at 246, CO_2 at 193.2, CH_2 at 62.8, or CH_3 at 14.5 ppm.

Reaction Performed with 0.5 Equiv of C_2H_5ONa. 1a (1 mmol, 300 mg) was reacted with 34 mg (0.5 mmol) of C_2H_5ONa at −30 °C; after the usual treatment, the ^{13}C NMR spectrum of the crude product of the reaction was not found to display any signals corresponding to **1b**.

Reaction of 1c with CH_3ONa. 1c (1 mmol, 340 mg) was allowed to react with 54 mg (1 mmol) of CH_3ONa to afford 300 mg (70% yield) of **4c**. IR (THF, cm^{-1}): ν(C≡O) 2066 (s), 2002 (s), 1981 (s); ν(C=O) 1678 (sh), 1639 (s), 1590 (m). ^{1}H NMR (D_8-THF, 273 K; δ, ppm): 3.30 (br s, 3H, OCH_3), 1.65 (br s, 9H, Ot-Bu), 0.8 (br s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (THF, 273 K; δ, ppm): (two isomers 60/40) 271.15, 264.4 (C=O); 224.1, 219.0 (cyclic C(O)O-); numerous signals between 209.8 and 207.5 (C≡O and C(O)O−); 110.9, 109.6 (cyclic quaternary carbon); 79.25 (C t-Bu); 51.4, 50.4 (OCH_3); 28.5, 30.5 (CH_3 t-Bu); 20.5, 19.8 (CH_3).

Reaction of 1a with t-BuONa. 1a (1 mmol, 300 mg) was reacted with 95 mg (1 mmol) of t-BuONa to form 225 mg (yield: 60%) of an anionic complex which could be **4d**. The presence of paramagnetic impurities in the crude product could explain the very poor resolution of the NMR spectra of this complex, which was only characterized by its IR spectrum: (THF, cm^{-1}) ν(C≡O) 2069 (s), 2007 (s), 1988 (s); ν(C=O) 1678 (sh), 1640 (s), 1612 (m).

Reaction of 1c with t-BuONa. 1c (1 mmol, 340 mg) was reacted with 1 mmol (95 mg) of t-BuONa to give rise to 310 mg (yield: 75%) of an anionic complex which could be **4e**. For the same reason as for the preceding complex, no suitable NMR spectrum was obtained. IR (THF, cm^{-1}): ν(C≡O) 2068 (s), 2005 (s), 1982 (s); ν(C=O) 1673 (sh), 1636 (s), 1585 (m).

Reaction of 1a with CH_3SNa. 1a (1 mmol, 300 mg) was reacted with 1 mmol (70 mg) of CH_3SNa[29] to afford 275 mg (yield: 80%) of **4f**. IR (THF, cm^{-1}): ν(C≡O) 2068 (s), 2005 (s), 1987 (s); ν(C=O) 1646 (s), 1593 (m). ^{1}H NMR (D_8-THF, 273 K; δ, ppm): 3.5 (br s, 3H, OCH_3), 2.1 (br s, 2.55 H, SCH_3), 1.9 (br s, 0.45 H, SCH_3) 1.5 (br s, 2.55 H, CH_3) 1.4 (br s, 0.45 H, CH_3). $^{13}C\{^1H\}$ NMR (THF, 273 K; δ, ppm): (two isomers 85/15) 259.6, (C=O); 222.8, (cyclic C(O)O−); 209.3, 208.4, and 207.7 (C≡O and C(O)O−); 95.5 (cyclic quaternary carbon); 50.3 (OCH_3); 22.6 (CH_3); 12.5(SCH_3). The presence of a second isomer (15%) is shown by the following resonances: 259.7 (C=O); 223.0 (cyclic C(O)O−); 97.0 (cyclic quaternary carbon); 51.0 (OCH_3); 12.2(SCH_3).

Reaction of 1a with $P(C_6H_5)_2Li$. 1a (1 mmol, 300 mg) was reacted with 200 mg (1 mmol) of $P(C_6H_5)_2Li$[30] to form 340 mg (yield: 75%) of **4g**. IR (THF, cm^{-1}): ν(C≡O) 2072 (s), 2012 (s), 1994 (s); ν(C=O) 1637 (s), 1615 (s). ^{1}H NMR (D_8-THF, 273 K; δ, ppm): from 8.1 to 6.9 (broad signal, 10 H, C_6H_5), 3.3 (br s, 3H, OCH_3), 1.5 (br s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (THF, 273 K; δ, ppm): (two isomers 50/50) 267.5, 253.3 (C=O); 226.0, 214.5, 214.1, 207.2, and 205.8 (cyclic C(O)O; C≡O and C(O)O−); 91.35, 90.2 (cyclic quaternary carbon); 50.4 (OCH_3); 21.2 and 19.6 (CH_3). The poor resolution of the spectrum precludes the evaluation of the $^{31}P-^{13}C$ coupling. ^{31}P NMR (D_8-THF, 273 K; δ, ppm): 30.2, 24. 6 (two signals of equal intensities).

Reaction of 1a with $NaNH_2$ or $LiN(C_2H_5)_2$. As shown by IR, 1 mmol of **1a** reacts in 2 h time at −10 °C with 1 mmol of $NaNH_2$ or $LiN(C_2H_5)_2$ to afford $Fe(CO)_5$ and organic products.

Reaction of 1a with NaH. No reaction was observed between these two compounds even at room temperature.

Reactions of the Anionic Trifunctionalized Metallalactones 4 with HCl; Preparation of the Neutral Lactonic Complexes 2: General Procedure. A 1 N solution of HCl in ether (0.5 mL) was added to a suspension of 0.5 mmol of complexes **4** in 50 mL of THF at − 70 °C. As shown by an IR monitoring, the reaction was very fast even at low temperature. After 15 min at −70 °C, the solvent was removed under vacuum and the residue washed with two portions of 5 mL of hexanes at −70 °C. Complexes **2** were extracted from the residue by a hexanes/CH_2Cl_2 (90/10) mixture (2 × 25 mL). The reduction of this solution to ~20 mL under vacuum at −40 °C afforded pale yellow crystals of **2**, which, after filtration, were washed twice with 5 mL of hexane at −70 °C.

Preparation of 2a by Reaction of 4a with HCl. 4a (176 mg) was reacted with 0.5 mL of 1 N HCl in ether to give 97 mg (yield: 65%) of **2a**. IR (hexane, cm^{-1}): ν(C≡O) 2125 (m), 2085 (sh), 2060 (sh), 2050 (s); ν(C=O) 1720 (m), 1685 (sh). ^{1}H NMR (CD_2Cl_2, 273 K; δ, ppm): 3.35 (s, 3H, OCH_3), 1.4 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K; δ, ppm): 245.8 (C=O); 199.7, 199.1, 198.7, 198.0 (terminal C≡O) 196.8 (cyclic C(O)O); 109.8 (cyclic quaternary carbon); 50.5 (OCH_3); 16.1 (CH_3). Anal. Calc for $C_9FeH_6O_8$: C, 36.27; Fe, 18.74; H, 2.03. Found: C, 35.95; Fe, 18.53; H, 2.18.

Reaction of HCl with the Trifunctionalized Lactones 4 Formed by Addition of C_2H_5ONa to 1a. A 175 mg portion of the mixture of the lactones **4** obtained by reaction of **1a** with C_2H_5ONa was reacted with 0.5 mL of 1 N HCl in ether to afford 105 mg of a pale yellow powder composed of a 50/50 mixture of **2a** and **2b**. These two complexes were not separated. IR (hexane, cm^{-1}): ν(C≡O) 2125 (m), 2085 (sh), 2060 (sh), 2050 (s); ν(C=O) 1720 (m), 1685 (sh). ^{1}H NMR: (CD_2Cl_2, 273 K; δ, ppm): 3.63 (q, J = 6.5 Hz, 2H, OCH_2), 3.34 (s, 3H, OCH_3) 1.40 (s, 6H, CH_3) 1.14 (t, J = 6.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K; δ, ppm): The two products were identified by their ^{13}C NMR specific resonances. **2a**: 50.5 (OCH_3) and 16.1 (CH_3) and **2b** 59.1 (OCH_2), 16.6 (CH_3), and 14.9 ppm (CH_3).[5]

Reaction of the Anionic Lactone 4c with HCl. 4c (0.5 mmol, 170 mg) was reacted with 0.5 mL of 1 N HCl in ether to afford 120 mg of a pale yellow powder composed of 80% **2a** and 20% **1c**. The presence of these complexes was shown in ^{13}C NMR by their specific resonances: 245.8, 196.8, 109.8, 50.5, and 16.1 ppm for **2a** and 246.8, 201.9, 191.9, 84.6, 28.3, and 23.3 ppm for **1c**.

Reaction of 4d or 4e with HCl: Formation of 5. 4d or **4e** formed in situ respectively by reaction of 1 mmol (300 mg) of **1a** or 340 mg of **1c** with 100 mg of t-BuONa was reacted with 1 mL of 1 N HCl in ether. **4d** gave rise specifically to **5**, which was obtained as a white powder in 60% yield (160 mg). IR (hexane, cm^{-1}): ν(C≡O) 2134 (m), 2083 (sh), 2074 (m), 2056 (s); ν(C=O) and ν(C=C) 1725 (m), 1688 (m) 1618 (m). ^{1}H NMR (CD_2Cl_2, 273 K; δ, ppm): 5.07 (br s, 1H, CH_2), 4.86 (br s, 1H, CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K; δ, ppm): 236.9 (C=O); 198.6 (2), 199.1, 198.0, 196.9, 196.1 (terminal C≡O and C(O)O), 157.5 (cyclic C=CH_2); 89.7 (CH_2). NMR HMQC sequences showed interactions between the two protons and the carbon at 89.7 ppm. Anal. Calc for $C_8FeH_2O_7$: C, 36.13; Fe, 21.00; H, 0.76. Found: C, 36.75; Fe, 20.72; H, 1.05. Under the same reaction conditions, **4e** afforded 115 mg of **5** (43% yield) and 45 mg of **1c** (13% yield). **1c** was extracted from the crude product by five portions of 5 mL of hexanes at −70 °C, while **5** was purified by crystallization from a CH_2Cl_2/hexanes mixture (5/95) at −30 °C. Both complexes were characterized in ^{13}C NMR by comparison with authentic samples.

Reaction of 4f with HCl. 4f (184 mg 0.5 mmol) was reacted with 0.5 mL of 1 N HCl in ether to give rise to 87 mg (yield: 60%) of **2c**. IR (hexane, cm^{-1}): ν(C≡O) 2127 (s), 2077 (m), 2066 (s), 2049 (s); ν(C=O) 1726 (m), 1706 (sh), 1696 (sh). ^{1}H NMR (CD_2Cl_2, 273 K; δ, ppm): 2.13 (s, 3H, SCH_3), 1.64 (s, 3 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K; δ, ppm): 244.5 (C=O); 199.7 (2), 198.2, 197.0, 196.3 (terminal C≡O) and cyclic C(O)O); 97.4 (cyclic quaternary carbon); 21.6 (CH_3) 12.6 (SCH_3). Anal. Calc for $C_9FeH_6O_7S$: C, 34.42; Fe, 17.78; H, 1.93. Found: C, 34.54; Fe, 17.65; H, 2.05.

Reaction of 4g with HCl. 4g (245 mg, 0.5 mmol) was reacted with 0.5 mL of 1 N HCl in ether to form 125 mg (yield: 55%) of **2d**. IR (hexane, cm^{-1}): ν(C≡O) 2120 (m), 2075 (m, sh), 2065 (m, sh), 2045 (s); ν(C═O) 1710 (m, br), 1695 (sh). ^{1}H NMR (CD_2Cl_2, 273 K; δ, ppm): from 7.9 to 7.3 (m, 10H, C_6H_5), 1.51 (d, J_{P-H} = 11.2 Hz, 3 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 273K; δ, ppm): 10.9. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 273 K; δ, ppm): 252.7 (d, J_{P-C} = 8.7 Hz) (C═O); 200.8, 198.2 (2), 197.4 196.3 (terminal C≡O) and cyclic C(O)O); from 135.2 to 136.1 (m, 4C); 133.9 (d, J_{P-C} = 15 Hz, 1C); 132.7 (d, J_{P-C} = 16.5 Hz, 1C); 130.4 (bs, 1C); 130.1 (bs, 1C); 128.8 (bs, 4C); 101.1 (cyclic quaternary carbon); (d, J_{P-C} = 35.6 Hz); 23.1 (d, J_{P-C} = 17.4 Hz (CH_3). $^{13}C\{^1H,^{31}P\}$ NMR: 135.9 (2C (ortho)); 135.7 (2C (ortho)); 133.9 (1C (α)); 132.7 (1C (α)); 130.4 (1C (para)); 130.1 (1C (para)); 128.9 (2C (meta)); 128.8 (2C (meta)). Anal. Calc for $C_{20}FeH_{13}O_7P$: C, 53.12; Fe, 12.85; H, 2.90; P, 6.85. Found: C, 53.32; Fe, 12.70; H, 2.95; P, 6.91.

Reactions of Metallalactones 2 with RO$^-$: General Procedure. To a solution of 0.5 mmol of lactone **2** in 20 mL of THF at −5 °C was added 1 equiv of solid RO$^-$. The reaction, which was monitored by IR, was complete after 2 h at this temperature. The solvent was then removed and the residue washed with two portions of 10 mL of hexanes at −70 °C. The composition of the so obtained white powder was determined by ^{13}C NMR.

Reaction of 2a with CH_3ONa. 2a (150 mg) was reacted with 30 mg of CH_3ONa to give 97 mg (55% yield) of **4a**, whose ^{13} C NMR spectrum was similar to that obtain by reaction of CH_3ONa with **1a** (mixture of isomers: 50/50)

Reaction of 2a with C_2H_5ONa. (1) **2a** (150 mg, 0.5 mmol) was allowed to react with 0.5 mmol (35 mg) of C_2H_5ONa to afford 82 mg (∼45% yield) of a mixture of **4**. As shown by ^{13}C NMR, the so formed products were similar to those already obtained by reaction of **1a** with C_2H_5ONa (numerous isomers). (2) **2a** (150 mg, 0.5 mmol) was allowed to react with 0.25 mmol of C_2H_5ONa (18 mg). After evaporation of the solvent, the ^{13}C NMR spectrum of the residue showed the formation of the same mixture of complexes **4** together with 50% of unchanged **2a**.

Reaction of 2c with CH_3ONa. 2d (160 mg, 0.5 mmol) was reacted with 0.5 mmol of CH_3ONa (28 mg) to give 92 mg of **4f** (50% yield). As observed for the reaction between **1a** and CH_3SNa, the ^{13}C NMR spectrum of the product of the reaction showed only the formation of two isomers of **4f** (85/15).

Reaction of 2a with C_2H_5OH or C_2H_5OH and HCl. C_2H_5OH (20 equiv, 1.180 mL) was added to a solution of 1 mmol of **2a** in solution in 25 mL of CH_2Cl_2 at 0 °C. The solution was stirred for 5 h at this temperature. The solvent was removed and the ^{13}C NMR spectrum of the residue was found unchanged. If 1 equiv of HCl was added to the solution, as shown by IR, a decomposition of **2a** occurred, affording $Fe(CO)_5$ together with organic compounds.

When C_2H_5ONa (1 mmol, 68 mg) or C_2H_5OH (20 mmol, 1.180 mL) was reacted with **4a** in THF solutions at 0 °C (5 h stirring), no reaction was observed by ^{13}C NMR.

Supporting Information Available: X-ray structural information for complexes **1a** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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