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Ring Closure of Alkoxycarbonyl(tetracarbonyl)pyruvoyliron Complexes into Metallalactones Induced by Nucleophilic Attack of Carbanions

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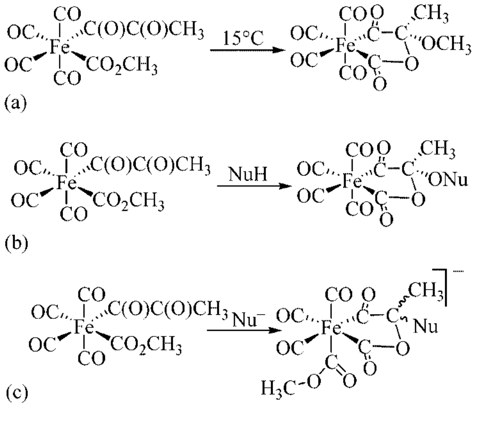
The reaction of carbanions with the pyruvoyl-substituted iron complex $[(CO)_4Fe(CO_2CH_3)\{C(O)C(O)CH_3\}]$ (**1**) affords the anionic trifunctionalized metallalactones $[(CO)_3Fe\{C(O)C(CH_3)(CRR'R'')OC^4(O)(Fe\text{–}C^4)\}(CO_2CH_3)]^-$ (**3**), whose formation results from the addition of the nucleophile to the β carbonyl of the pyruvoyl moiety, followed by attack of the oxygen of this β carbonyl on a terminal carbonyl ligand. These anionic lactones react, at low temperature, with HCl to give rise to the neutral lactones $[(CO)_4Fe\{C(O)C(CH_3)(CRR'R'')OC^4(O)(Fe\text{–}C^4)\}]$ (**2**), which were previously obtained by addition of NuH nucleophiles to **1**. Complex **3(3)**, whose lactonic ring formation has been performed using the diethyl malonate anion ($R = R' = CO_2C_2H_5$; $R'' = H$), and the dimethyl-substituted neutral lactone **2(1)** ($R = R' = R'' = H$) have been characterized by X-ray diffraction studies.

Introduction

Nucleophilic attacks upon organic ligands coordinated to transition metals are important processes in the formation of new reactive organometallic intermediates that are useful in organic synthesis. Although it is possible to assess the reactivity of various ligands toward nucleophiles, it is more difficult to predict the site of nucleophilic attack on polyfunctional complexes. Thus, while nucleophiles react very easily with terminal carbonyls of metal–carbonyl compounds to afford acyl, aroyl, alkoxycarbonyl, or carbamoyl ligands, the same reaction occurs regiospecifically at the α-carbon of a carbene ligand,[1] at the α- and γ-carbons of an allenylidene,[2,3] and at the β-carbon of an allenyl ligand[4] of analogous complexes. It has also been shown that acyl ligands are less electrophilic than terminal carbonyl ligands.[5] In the course of a study of complexes considered as possible models for double or polycarbonylation reactions, we investigated the reactivity of compounds displaying a ligand with a C(O)C(O)R chain toward nucleophilic reagents. Indeed, addition of nucleophiles at C_α of this type of ligand has been proposed to account for the formation of phenylpyruvic esters by dicarbonylation of organic halides catalyzed by $[Co(CO)_4]^-$.[6] The very few nucleophilic additions performed on cationic (Fe[7] Pt[8]) or neutral complexes (Fe[9]) displaying an M–C(O)–C(O)–R chain have been shown to occur at a terminal carbonyl ligand of the molecule. We recently observed the original behavior of the complex *cis*-$[(CO)_4Fe\{C(O)C(O)CH_3\}(CO_2CH_3)]$ (**1**), which afforded its cyclic isomer **2** quantitatively, at 15 °C, in a reaction involving the formation of a metallalactone ring by addition of the oxygen of the β carbonyl of the pyruvoyl to the alkoxycarbonyl ligand and a migration of the methoxy group of this latter ligand to the β carbon of the pyruvoyl (Scheme 1, a).[10]



Scheme 1.

This reaction appeared very similar to the ring-chain isomerism observed for organic γ-keto esters.[11] Indeed, as the alkoxycarbonylpyruvoyliron complex **1** can be considered as a γ-keto ester with a metal inserted into the chain linking its two organic functions, a parallel between the organic reaction and the organometallic process can be drawn. When performed in the presence of an excess of pronucleophilic reagents (Nu–H), the reaction affords Nu-sub-

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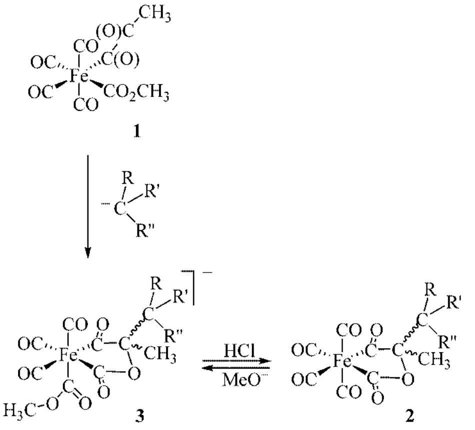
stituted metallalactones (Scheme 1, b) which are formed, under these conditions, by an addition of the nucleophile to the β carbonyl of the pyruvoyl followed by metallalactone ring formation due to attack of the oxygen of this β carbonyl on the alkoxycarbonyl ligand and elimination of the methoxy group of this latter ligand.[7] To the best of our knowledge, prior to our study, only one example of nucleophilic addition at a carbonyl carbon of a ligand displaying a double C(O) chain had been described in the literature. In this paper, hydride was reported to attack the β carbonyl of a ligand of $[(CO)_5Mn\{C(O)C(O)C_6H_5)\}]$ to afford an anionic metallalactone by cyclization of the phenylglyoxyl with a terminal carbonyl.[12] These results prompted us to perform the cyclization of **1** with anionic nucleophiles (RO^-, RS^-, or R_2P^-).[13] These reactions, as they only afford two isomers of the anionic trifunctionalized metallalactone **3** (Scheme 1, c), also suggested that the formation of the metallalactonic ring could indeed proceed by addition to a terminal carbonyl rather than to the alkoxycarbonyl ligand. However, as the structure of these trifunctionalized anions **3** was not firmly established, we tried to perform analogous reactions using C–H nucleophiles and carbanions of various nucleophilicity and of different steric effects. The results of this study will be the topic of this paper.

Results and Discussion

Reaction of 1 with Activated C–H Bonds or Carbanions as Nucleophiles

Although often used as nucleophiles,[14] pronucleophiles displaying activated methylenes, such as diethyl malonate (1 equiv.) or malononitrile (20 equiv.), were found to be unreactive towards **1** at –10 °C. This lack of reactivity is not too surprising as **1** only reacts slowly with CH_3OH, C_2H_5SH, $HP(C_6H_5)_2$, or $HP(C_6H_{11})_2$.[7] On the other hand, as shown by IR monitoring, **1** reacts very rapidly with carbanionic reagents such as MeLi, *n*BuLi, $NaCH(CO_2C_2H_5)_2$, $NaCH(C{\equiv}N)_2$, $NaCH[C(O)CH_3]_2$, $NaCH[C(O)CH_3](CO_2CH_3)$, $NaCH(CO_2C_2H_5)(C{\equiv}N)$, $NaC(CH_3)(CO_2C_2H_5)_2$, or $NaC(CH_2CH{=}CH_2)(CO_2C_2H_5)_2$ to afford instantaneously, even at –70 °C, new complexes displaying a set of three ν(C≡O) bands between 2084 and 1970 cm^{-1}. These frequencies are similar to those observed for the product of the reaction between **1** and RO^-, RS^-, or R_2P^- anions,[13] and are intermediate between the ν(C≡O) of the monofunctionalized anion $[Fe(CO)_4(CO_2R)]^-$ (three bands around 1910 cm^{-1})[15] and those of their homologues of the neutral complex *cis*-$[Fe(CO)_4(CO_2R)_2]$ (four bands between 2130 and 2050 cm^{-1}).[16] They fall within the range of those of trifunctionalized mono anions such as *fac*-$[(CO)_3Fe(CO_2R)_3]^-$ (two bands at 2080 and 2015 cm^{-1}), which are themselves obtained by addition of RO^- to a terminal carbonyl of $[(CO)_4Fe(CO_2R)_2]$.[9] These values measured for ν(C≡O) are therefore consistent with a moderate increase of the electron density on the metal. The observation of three ν(C≡O) bands instead of the two required by C_{3v} symmetry could result from the presence of a metallacycle in the complex. These results suggest the *fac* trifunctionalized metallalactone structure **3** for the products of these reactions (see Scheme 2).



2a or **3a**: R = R' = R'' = H
2b or **3b**: R = R' = H, R'' = C_3H_7
2c or **3c**: R = R' = $CO_2C_2H_5$, R'' = H
3e: R = R' = CN, R'' = H
2f or **3f**: R = CO_2CH_3, R' = $C(O)CH_3$, R'' = H
3g: R = CO_2CH_3, R' = CN, R'' = H
2h or **3h**: R = R' = $CO_2C_2H_5$, R'' = CH_3
2i or **3i**: R = R' = $CO_2C_2H_5$, R'' = $CH_2CH{=}CH_2$

Scheme 2.

This assumption was confirmed by the ^{13}C NMR spectroscopic data of these compounds. Although most of these complexes were found to be sparingly soluble in organic solvents, the ^{13}C NMR spectra of these compounds could be obtained in $[D_8]$THF (see Exp. Sect.). The anionic structure of complexes **3** was indicated by a shift of the signals of the carbonyls linked to the metal toward lower fields relative to their homologues **1** ($\Delta\delta$ = 10 ppm for the terminal carbonyls and 15 ppm for the carbon of the alkoxycarbonyl).[13] However, the negative charge is very probably delocalized over the three carbonylated substituents of the complex as the chemical shifts of the terminal carbonyls of **3** (from δ = 205 to 212 ppm) fall between those observed for **1** (δ = 200 ppm)[13] and those of $[(CO)_4Fe(CO_2R)]^-$ (δ = 220 ppm).[15] The electron density of the metal center of **3** is therefore intermediate between that observed for neutral complexes and for the monofunctionalized anion. The formation of a metallacycle in complexes **3** is shown by the signal of their disubstituted cyclic quaternary carbon atom between δ = 86.5 and 96.9 ppm. This value is not very different from those observed for similar carbons substituted by OR (δ = 111 ppm), SR (δ = 95.5 ppm), or PR_2 (δ = 90 ppm) groups.[13] As **3(1)** displays two methyl substituents on this cyclic quaternary carbon, it only exists as one isomer. The formation of this single isomer is shown in the ^{13}C NMR spectrum by the observation of one signal for each carbon of this complex. The nonequivalency of these two methyls, shown by two signals at δ = 15.8 and 8.4 ppm, results from the *fac* position of the alkoxycarbonyl ligand. Reaction of **1** with *n*BuLi afforded a similar complex. This compound, which has both *n*-butyl and methyl substituents on the quaternary carbon of its metallalactone [R = R′ = H; R′′ = C_3H_7; **3(2)**], was formed as a 50:50 mixture of two isomers. The presence of these two isomers is shown by the observation of two signals of equal intensities at δ = 274.1 and 271.5 ppm for the C=O acyl, at δ = 96.9 and 96.7 ppm for the cyclic sp^3 carbon, and at δ = 60.5 and 59.9 ppm for the OCH_3 group of the alkoxycarbonyl ligand. Surprisingly, the same reaction performed with $NaCH(CO_2C_2H_5)_2$ afforded only one isomer of the anion **3(3)** (R = R′ = $CO_2C_2H_5$; R′′ = H). Indeed, the ^{13}C NMR spectrum of this compound only displays one signal at δ = 269.3 ppm for the acyl C=O, at δ = 94.3 ppm for the cyclic sp^3 carbon, at δ = 50.9 ppm for the methoxy of the methoxycarbonyl ligand, and at δ = 21.7 ppm for the methyl located on the cyclic sp^3 carbon. On the other hand, due to the asymmetry of the metallalactone ring, the two ethoxycarbonyls of the malonyl group are not equivalent and appear as two signals at δ = 168.7 and 167.3 ppm, 62.65 and 62.55 ppm, and 13.6 and 13.7 ppm for the carbonyl, the CH_2, and the CH_3 carbon atoms, respectively, while the central carbon of this malonyl group only displays a single resonance at δ = 55.25 ppm. The solubility of **3(3)** is significantly better than **3(1)** and **3(2)**.

When **1** was treated with the anions obtained from 2,4-pentanedione or malononitrile, **3(4)** [R = R′ = $C(O)CH_3$, R′′ = H] and **3(5)** (R = R′ = CN, R′′ = H) were formed, respectively. As shown by their ^{13}C NMR spectra (see Exp. Sect.), they are obtained as mixtures of two isomers (70:30 and 60:40, respectively). As observed for **3(3)**, the $CH_3C(O)$ and CN groups of each isomer of these complexes are not equivalent. Thus, **3(4)** displays four CH_3 resonances at δ = 32.9, 32.7, 32.3, and 32.1 ppm (the signals for the C=O groups of the terminal carbonyls are not detectable) and **3(5)** four CN resonances at δ = 113.7, 113.45, 112.6, and 112.5 ppm while two peaks are observed for the central carbon of the malononitrile group of **3(5)** at δ = 31.1 and 30.8 ppm [the resonance of the homologue carbon atom of **3(4)** is probably hidden by the signal of the THF]. Asymmetric nucleophiles such as $NaCH[C(O)CH_3](CO_2CH_3)$ or $NaCH(CO_2C_2H_5)(CN)$ also afforded anions of type **3**. The formed complexes **3(6)** (R = CO_2CH_3, R′ = $C(O)CH_3$, R′′ = H) or **3(7)** (R = CO_2CH_3, R′ = CN, R′′ = H) were again obtained as two *cis*/*trans* isomers (50:50) but, due to the asymmetry of their metallacycle and of the central carbon of their nucleophile group, each of these isomers is observed as two diastereoisomers. For this reason, the ^{13}C NMR spectra of **3(6)** and **3(7)** exhibit four signals for each of their carbon atoms. For example, **3(6)** displays four acyl CO signals at δ = 268.5, 267.4, 267.0, and 266.8 ppm, four peaks for the cyclic quaternary carbon at δ = 94.2, 93.1, 92.6, and 92.1 ppm, and four signals for the resonance of the central carbon atom of the nucleophilic group at δ = 62.5, 62.2, 61.9, and 61.2 ppm. In the same way, the ^{13}C NMR spectrum of **3(7)** shows four CO signals at δ = 267.5, 266.8, 266.5, and 266.2 ppm, four CN signals at δ = 118.0, 117.5, 117.3, and 116.8 ppm, four resonances for the cyclic quaternary carbon at δ = 93.0, 92.5, 91.5, and 91.0 ppm, and four signals for the central carbon of the nucleophile at δ = 44.5, 43.5, 42.5, and 42.0 ppm.

As shown by IR monitoring, the reaction of **1** with the bulky nucleophiles $NaC(CH_3)(CO_2C_2H_5)_2$ or $NaC(CH_2CH{=}CH_2)(CO_2C_2H_5)_2$ also affords trifunctionalized anionic metallalactones. However, the ^{13}C NMR spectra of the thus formed compounds **3(8)** (R = R′ = $CO_2C_2H_5$, R′′ = CH_3) and **3(9)** (R = R′ = $CO_2C_2H_5$, R′′ = $CH_2CH{=}CH_2$) are found to display broad signals whose chemical shifts are in good agreement with those expected for anionic metallalactones (see Exp. Sect.). The detection of at least three signals for the resonances of the acyl CO or for their cyclic quaternary carbon suggests the presence of at least three isomers for these two complexes. The broadness of the observed signals probably results from slow interconversion between the observed species. However, no change was observed in the spectra of these compounds when they were recorded at different temperatures (from 20 °C to –50 °C). The only isomer of **3(3)** was obtained as single crystals suitable for an X-ray diffraction study.

Structural Study of Complex 3(3)

Single crystals of **3(3)**, with K^+ as counterion, were grown from a hexanes/dichloromethane mixture (90:10) at –30 °C. An ORTEP diagram of the anion is displayed in Figure 1, crystallographic data are given in the Exp. Sect., and selected bond lengths and angles are gathered in Table 1 and Table 2, respectively.

The crystal structure confirms the proposed anionic, metallacyclic, trifunctionalized geometry for **3(3)**. The structure can be described as being composed of four crystallographically different (Figure 1, a) trifunctionalized entities linked to four potassium ions (Figure 1, b). As these anions exhibit slight differences in their bond lengths and angles, the values measured for each of these entities (a, b, c, and d) will be mentioned in the following discussion. The crystal structure study establishes that the only formed complex is the isomer with the alkoxycarbonyl ligand and the malonyl group *trans* to each other on the metallacycle (Figure 1, a). This complex, which is sterically less hindered than the corresponding *cis* isomer, is probably the species observed in solution. The coordination polyhedron at the metal center is a distorted octahedron built of three terminal carbonyl ligands, an alkoxycarbonyl, and the chelating carbonylated ligand. As observed for neutral metallalactones[7,10,12,13] and for five-membered iron metallacycles,[17] the bite angle of the chelate C(7)–Fe–C(6) [82.3(5)–83.4(5)°] is smaller than the angle measured between the two organic carbonylated ligands of the noncyclic *cis*-bis(alkoxycarbonyl)iron complex [$(CO)_4Fe(CO_2tBu)_2$] [88.5(2)°].[18] Therefore, its opposite angle on the metal [C(1)–Fe–C(2)] displays a larger value than that expected for an octahedral geometry [96.0(6)–100.2(5)°]. The axial alkoxycarbonyl ligand is bent toward the metallacycle [C(4)–Fe–C(6) from 81.3(5)° to 84.6 (5)° and C(4)–Fe–C(7) from 84.8(5)° to 89.0(5)°]. The other angles around the metal are normal,

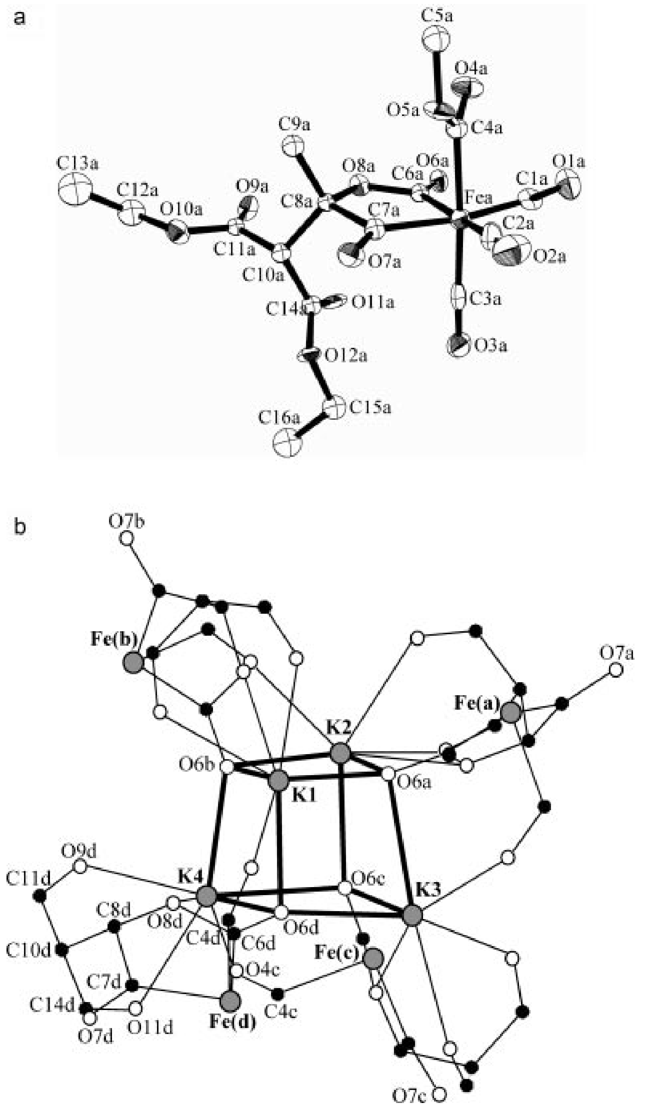


Figure 1. Structure of **3(3)**. Part a: ORTEP view of the anionic complex **a** (50% probability ellipsoids); anions **b**, **c**, and **d** are similar. Part b: Perspective view showing the potassium ions' environment.

Table 1. Bond lengths [Å] and angles [°] measured for the four (**a**, **b**, **c**, and **d**) anionic forms of **3(3)**.

	a	**b**	**c**	**d**
Fe–C1	1.83(1)	1.86(1)	1.79(1)	1.87(1)
Fe–C2	1.78(1)	1.81(1)	1.90(1)	1.85(1)
Fe–C3	1.79(1)	1.79(1)	1.82(1)	1.84(1)
Fe–C4	1.99(1)	2.00(1)	2.05(1)	2.01(1)
Fe–C6	1.93(1)	1.94(1)	1.97(1)	1.94(1)
Fe–C7	1.94(1)	1.96(1)	1.97(1)	1.98(1)
O4–C4	1.24(1)	1.22(2)	1.14(2)	1.22(1)
O6–C6	1.23(1)	1.22(2)	1.21(2)	1.22(1)
O7–C7	1.21(1)	1.22(2)	1.20(2)	1.21(1)
O8–C6	1.38(1)	1.38(1)	1.36(1)	1.41(2)
O8–C8	1.40(1)	1.42(2)	1.43(2)	1.44(1)
O9–C11	1.17(1)	1.20(2)	1.18(2)	1.23(1)
O11–C14	1.20(2)	1.19(2)	1.22(2)	1.21(2)
C7–C8	1.60(1)	1.56(2)	1.58(1)	1.55(2)
C1–Fe–C2	99.3(5)	98.5(6)	100.2(5)	96.0(6)
C1–Fe–C3	97.1(6)	94.8(6)	94.7(6)	95.4(6)
C1–Fe–C4	85.1(6)	87.6(5)	87.1(5)	85.8(6)
C1–Fe–C6	88.4(5)	88.9(6)	87.8(5)	88.7(5)
C1–Fe–C7	89.2(5)	89.4(6)	88.7(5)	91.2(6)
C3–Fe–C6	93.0(5)	91.1(5)	93.5(5)	89.9(5)
C3–Fe–C7	88.3(5)	89.7(5)	88.6(6)	93.3(6)
C4–Fe–C6	83.3(5)	83.4(5)	81.3(5)	84.6(5)
C4–Fe–C7	89.0(5)	87.2(5)	88.9(5)	84.8(5)
C6–Fe–C7	82.3(5)	82.6(5)	82.9(5)	83.4(5)
C6–O8–C8	117.8(9)	117.7(9)	117.2(8)	116.0(8)
Fe–C6–O6	130.1(8)	129.8(8)	129.4(9)	130(1)
Fe–C6–O8	117.6(8)	116.6(9)	116.8(9)	116.7(9)
O6–C6–O8	112.3(9)	113(1)	113.8(9)	112(1)
Fe–C7–O7	131.1(8)	128.5(8)	129.8(8)	130.5(9)
Fe–C7–C8	113.9(8)	114.0(9)	112.1(9)	112.5(8)
O7–C7–C8	115.0(9)	117(1)	118(1)	117(1)
O8–C8–C7	107.6(8)	108.6(9)	110(1)	110(1)

with values close to 90°. The Fe–terminal carbonyl distances [1.79(1)–1.90(1) Å] are similar to those in the homologous trifunctionalized iron monoanion[9] or to the neutral complex $[(CO)_4Fe(CO_2tBu)_2]$[18] but are longer than the Fe–C≡O distance observed in a monofunctionalized iron anion.[19] These data confirm a reduced electron density on the metal due to the delocalization of the negative charge of the complex on the carbonylated organic ligands. The short Fe–cyclic(C=O)O distances [Fe–C(6) from 1.93(1) to 1.97(1) Å] associated with long C(6)–O(6) bonds [from 1.21(1) to 1.23(1) Å] show the enolate character of this group whose C=O oxygen is bound to three potassium ions (see below). Such a lengthening of the C=O double bond is not observed for C(4)=O(4), C(11)=O(9), or C(14)=O(11), whose oxygens are only bound to one potassium, or for C(7)=O(7), which does not interact with this metal. The other bond lengths or angles of the complex are analogous

Table 2. Interionic K–O distances [Å] and angles [°] in the cubane-like structure of **3(3)** (see Figure 1, part b).

K1–O4d	2.688(8)	K2–O4b	2.650(9)	K3–O4a	2.611(8)	K4–O4c	2.675(9)
K1–O6b	2.886(7)	K2–O6b	2.787(8)	K3–O6c	2.839(7)	K4–O6b	2.742(9)
K1–O6d	2.859(9)	K2–O6c	2.709(9)	K3–O6d	2.709(9)	K4–O6c	2.799(8)
K1–O6a	2.721(8)	K2–O6a	2.873(7)	K3–O6a	2.876(9)	K4–O6d	2.868(7)
K1–O8b	2.758(8)	K2–O8a	2.760(8)	K3–O8c	2.708(7)	K4–O8d	2.827(7)
K1–O9b	2.741(9)	K2–O9a	2.697(8)	K3–O9c	2.79(1)	K4–O9d	2.726(9)
K1–O11b	2.81(1)	K2–O11a	2.744(8)	K3–O11	2.804(9)	K4–O11d	2.824(9)
O6b–K1–O6d	75.3(2)	O6b–K2–O6c	83.5(2)	O6c–K3–O6d	73.3(2)	O6b–K4–O6c	82.6(3)
O6b–K1–O6a	75.1(2)	O6b–K2–O6a	74.3(2)	O6c–K3–O6a	75.2(2)	O6b–K4–O6d	77.4(2)
O6d–K1–O6a	79.0(2)	O6c–K2–O6a	77.2(2)	O6d–K3–O6a	78.9(2)	O6c–K4–O6d	71.5(2)
K1–O6b–K2	104.1(3)	K1–O6d–K3	96.8(2)	K1–O6b–K4	104.1(3)	K1–O6d–K4	101.6(3)
K2–O6b–K4	92.0(3)	K3–O6d–K4	108.3(3)	K2–O6c–K3	105.6(2)	K1–O6a–K2	106.2(3)
K2–O6c–K4	92.4(3)	K1–O6a–K3	96.1(2)	K3–O6c–K4	106.6(2)	K2–O6a–K3	100.5(2)

to those measured for neutral metallalactones.[7,10,13] As shown by the deviations of O(8) (+0.13 and +0.18 Å) and C(8) (+0.11 and +0.20 Å) from the plane defined by C(6)–Fe–C(7), the metallalactone ring of **3(3)** is not rigorously planar. It is worth noting that C(8) and O(8) are located on the same side of this plane. The steric effect of the malonyl group induces a pseudo axial position of the methyl substituent of the metallacycle, as shown by deviations of C(9) from the C(6)–Fe–C(7) plane of between 1.42 and 1.53 Å; deviations of between 0.91 and 1.09 Å are observed for C(10), which is the central atom of the malonyl group. As mentioned above, **3(3)** is composed of four slightly different entities in the solid state that display their four potassium ions and four cyclic ester carbonyl oxygens [O(6)] alternately at the corners of a distorted cube (see Figure 1, b). This cube displays small O–K–O angles (71.5–83.5°) and larger K–O–K angles (92.0–108.3°). Each potassium is linked to seven oxygen atoms; for example, K(4) interacts with O(6d) and O(8d), which are the two oxygen atoms of the cyclic ester group of d, with the oxygen atoms [O(9d) and O(11d)] of the two carbonyl oxygens of the malonyl group of d, with the oxygen atoms of the carbonyl of the cyclic esters of molecules b and c [O(6b) and O(6c)], and with the carbonyl oxygen of the alkoxycarbonyl ligand of complex c [O(4c)]. Short K–O(4) distances (2.61–2.68 Å) are observed between the potassium and the oxygen of this latter ligand. Recall that O(6) − the carbonyl oxygen of the cyclic ester group of each anion − interacts with three potassium ions, which induces a lengthening of the C(6)–O(6) bond (1.23 vs. 1.19 Å observed for neutral lactones[7,10,13]) and a shortening of the Fe–C(6) distance (1.93 vs. 1.99 Å). The complexation of O(6) with a potassium ion [K(4)] that is itself bound to O(8), O(9), and O(11) of the same molecule brings about a reduction of the O(6)–C(6)–O(8) sp^2 angle from 112(1)° to 113.8 (9)°. The absence of complexation of the cyclic acyl oxygen O(7) must also be noted.

This crystallographic work confirms without any doubt the structure attributed to this series of anionic trifunctionalized metallalactones **3**. However, a clear relation between the nature of the nucleophile and the *trans*/*cis* ratio observed for the different complexes **3** (from 100% to 50% of the *trans* isomer) has not been established. For example, the steric hindrance of $KCH(CO_2C_2H_5)_2$ cannot justify the specific formation of the *trans* isomer of **3(3)** except if the possible formation of aggregates of the anionic nucleophile is considered. Such a hypothesis has already been taken into account to explain the stereospecific nucleophilic additions on organic ketones. The formation of anionic compounds **3** when the transformation of **1** is induced by anionic nucleophiles raises the question of the specific formation of neutral lactones **2** by reaction of **1** with pronucleophiles Nu–H. An answer to this question is given by the reaction of complexes **3** with anhydrous HCl.

Reaction of Anionic Lactones 3 with HCl

As shown by IR monitoring of the process, the reaction of complexes **3(1)**, **3(2)**, **3(3)**, **3(4)**, **3(6)**, **3(8)**, and **3(9)** with one equivalent of anhydrous HCl at –80 °C instantaneously affords new compounds displaying four ν(C≡O) bands between 2131 and 2041 cm^{-1}. The presence of these four IR bands and their frequencies suggested the formation of neutral *cis* disubstituted complexes. Under the same reaction conditions an analogous process was observed for **3(5)** and **3(7)**, although the formed complexes rapidly evolved into $Fe(CO)_5$ and organic compounds. Complexes **2(1)**, **2(2)**, **2(3)**, **2(4)**, **2(6)**, **2(8)**, and **2(9)**, formed by reaction of **3(1)**, **3(2)**, **3(3)**, **3(4)**, **3(6)**, **3(8)**, and **3(9)** with HCl, respectively, were obtained as pale-yellow crystals from a hexanes/CH_2Cl_2 (95:5) mixture at –30 °C. Their ^{13}C NMR spectra confirm their neutral character as they display terminal C≡O resonances between δ = 202.75 and 196.2 ppm (vs. δ = 212.5–201.0 ppm for the starting complexes). Their other resonances are very close to those exhibited by neutral metallalactones: a C=O cyclic acyl between δ = 249.9 and 254.1 ppm (vs. δ = 274.1 and 262.3 ppm for the anionic lactones) and a cyclic C=O ester indiscernible from the terminal C≡O. The presence of a metallacycle in these complexes is shown by the observation of signals corresponding to cyclic quaternary carbons between δ = 92.3 and 98.4 ppm. All these characteristics are in good agreement with the formation of neutral metallalactones of type **2** (Scheme 2). Complex **2(1)**, whose quaternary cyclic carbon is substituted by two methyl groups, displays a single signal for its two axial terminal carbonyl ligands at δ = 200.2 ppm. This equivalence may result either from the quasi planarity of the metallacycle or from rapid interconversion between different conformations of the metallacycle. Other complexes **2** whose cyclic quaternary carbons are substituted by two different groups exhibit two signals for their axial carbonyl ligands. For example, five peaks are observed for the four terminal C≡O groups and the C=O of the cyclic ester of **2(2)** between δ = 200.5 and 196.5 ppm. Due to the asymmetry of the lactone ring, the two ethoxycarbonyl groups of the malonyl substituent of **2(3)** are not equivalent (two peaks are observed for the C=O at δ = 168.74 and 168.70 ppm, for the CH_2 at δ = 62.2 and 62.15 ppm, and for the CH_3 at δ = 13.9 and 13.75 ppm, whereas a single signal at δ = 58.6 ppm corresponds to the CH). A similar spectrum should be obtained for **2(4)**. However, as its acetyl C=O signals are hidden by those of the terminal C≡O, the presence of two different acetyl groups is only shown by the two peaks of their methyl groups at δ = 31.05 and 30.2 ppm. Complex **3(6)**, which displays an acetomethyl acetate and a methyl group on its cyclic quaternary carbon, affords, upon reaction with HCl, the neutral complex **2(6)**. Owing to the presence of the asymmetric central carbon of the acetoacetate group and to the asymmetry of the metallacycle itself, **2(6)** is obtained as an equimolecular mixture of two diastereoisomers. The presence of these two isomers is shown in the ^{13}C NMR spectrum by two C=O acyl resonances at δ = 251.32 and 251.22 ppm, by numerous signals between δ = 202.06 and 196.29 ppm [terminal carbonyls, cyclic ester group and organic C(O) acetyl], and by the splitting in two of the other signals: the organic C=O ester at δ = 169.9 and 169.4, the cyclic quaternary carbon at δ = 92.78 and

92.32 ppm, the CH at δ = 65.86 and 65.35 ppm, the OCH_3 at δ = 53.30 and 53.08 ppm, the acetyl CH_3 at δ = 30.11 and 29.42 ppm, and the other CH_3 at δ = 22.19 and 22.15 ppm. Recall that anions **3(8)** and **3(9)**, whose metallacycle is substituted by the crowded diethyl methyl- or allylmalonate groups, exhibit broad signals in their ^{13}C NMR spectra. Their reaction with HCl also affords complexes of type **2**, whose formation confirms the structure attributed to these anions. Contrary to their precursors, **2(8)** and **2(9)** give very well resolved ^{13}C NMR spectra. The characteristics of these spectra are very close to those of **2(3)**, which bears an unsubstituted malonyl, as they display two nonequivalent ethoxycarbonyls on their substituted malonyl group. This is shown by a splitting in two of the signals of the carbons of these ethoxycarbonyl groups, whereas the resonances of the third substituent and of the central quaternary carbon of the malonyl are found as singlets (see Exp. Sect.). Among this series of neutral complexes **2**, crystals suitable for a structural study were obtained for **2(1)**.

Crystallographic Study of Complex 2(1)

Single crystals of **2(1)** suitable for an X-ray diffraction study were obtained from a hexanes/dichloromethane mixture (95:5) at –30 °C. Figure 2 displays an ORTEP drawing of the molecule; selected bond lengths and angles are listed in Table 3, and further crystallographic data can be found in the Exp. Sect.

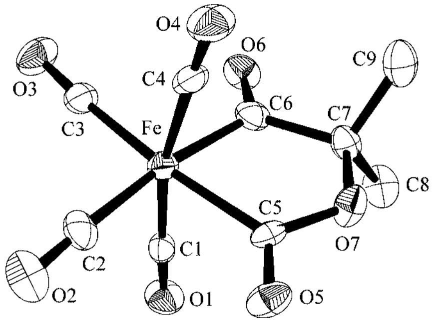


Figure 2. ORTEP view of **2(1)** (50% probability ellipsoids).

As observed for **3(3)**, the coordination around the iron atom in this complex can be described as a distorted octahedron with a reduced metallacyclic angle [C(6)–Fe–C(5) = 82.6(3)°, vs. an average of 82.8° for **3c**] and a larger value for its opposite angle C(3)–Fe–C(2) of 96.8(2)° due to the presence of the metallacycle. As already described by us for other neutral metallalactones,[7,10,13] the two axial terminal carbonyls of **2(1)** are bent toward the metallacycle [C(1)–Fe–C(4) = 167.7(2)°; C(4)–Fe–C(6) = 88.1(2)°; C(4)–Fe–C(5) = 83.8(2)°; C(1)–Fe–C(6) = 84.2(2)°; C(1)–Fe–C(5) = 85.7(2)]°. The Fe–cyclic ester bond [Fe–C(5)] of 1.991(5) Å and the C=O bond of this organic function [C(5)–O(5) = 1.199 (6) Å] are respectively longer and shorter than their homologues in **3(3)** (average of 1.95 Å for the first and 1.22 Å for the second). These bond lengths, which are similar to those measured for neutral metallalactones,[7,10,13] are indicative of an absence of enolate character of this function, whose oxygens are linked to the counterion in **3(3)**. The metallacycle is quasi planar, as shown by the torsion angles C(5)–Fe–C(6)–C(7) [–4.6(4)°] and C(6)–Fe–C(5)–O(7) [+6.2(4)°]. However, contrary to **3(3)**, O(7) and C(7) are no longer located on the same side of the C(6)–Fe–C(5) plane. The rapid evolution of complexes **3** into neutral metallalactones **2** when treated with HCl sheds new light on the direct formation of **2** by reaction of **1** with Nu–H nucleophiles. These observations suggest that the formation of **2** could result from a cyclization of the pyruvoyl and a terminal carbonyl ligand (and not, as considered earlier, the alkoxycarbonyl ligand) that affords an anionic, trifunctionalized metallalactone **3**. This intermediate, which would have H^+ as counterion, would then instantaneously evolve into **2**. The formation of complexes **2** by cyclization of the pyruvoyl and the alkoxycarbonyl ligand is therefore not necessarily involved in the process of anionic lactone formation. The reaction of **2** with NaOMe will confirm that this compound is not an intermediate of the reaction of formation of **3** by cyclization of **1** by anionic reagents.

Table 3. Bond lengths [Å] and angles [°]for compound **2(1)**.

Fe–C4	1.796(7)	O1–C1	1.143(6)
Fe–C1	1.811(7)	O3–C3	1.130(6)
Fe–C2	1.849(8)	O5–C5	1.199(6)
Fe–C3	1.856(6)	O2–C2	1.146(7)
Fe–C6	1.975(6)	O4–C4	1.137(5)
Fe–C5	1.991(5)	C9–C7	1.524(9)
O6–C6	1.205(6)	C7–C8	1.508(8)
O7–C5	1.371(6)	C7–C6	1.539(7)
O7–C7	1.451(6)		
C4–Fe–C1	167.7(2)	O1–C1–Fe	177.3(5)
C4–Fe–C2	93.6(2)	O3–C3–Fe	176.1(5)
C1–Fe–C2	92.8(2)	O5–C5–O7	117.4(5)
C4–Fe–C3	95.1(2)	O5–C5–Fe	127.1(5)
C1–Fe–C3	94.6(2)	O7–C5–Fe	115.4(5)
C2–Fe–C3	96.8(2)	O7–C7–C8	107.2(5)
C4–Fe–C6	88.1(2)	O7–C7–C9	105.7(5)
C1–Fe–C6	84.2(2)	C8–C7–C9	112.8(6)
C2–Fe–C6	172.6(3)	O7–C7–C6	109.5(4)
C3–Fe–C6	90.3(2)	C8–C7–C6	112.0(5)
C4–Fe–C5	83.8(2)	C9–C7–C6	109.3(5)
C1–Fe–C5	85.7(2)	O2–C2–Fe	177.6(6)
C2–Fe–C5	90.4(3)	O4–C4–Fe	176.4(5)
C3–Fe–C5	172.8(3)	O6–C6–C7	117.8(5)
C6–Fe–C5	82.6(3)	O6–C6–Fe	128.2(4)
C5–O7–C7	117.8(5)	C7–C6–Fe	114.0(4)

Reactions of Neutral Lactones 2 with NaOMe

The formation of anionic trifunctionalized metallalactones **3** by nucleophilic addition of CH_3O^- to a terminal carbonyl of complexes **2** was performed with **2(1)** (R = R′ = CH_3; R′′ = H), **2(3)** (R = R′ = $CO_2C_2H_5$; R′′ = H), and **2(8)** (R = R′ = $CO_2C_2H_5$; R′′ = CH_3). As shown by the IR, ^1H, and ^{13}C NMR spectra of the formed complexes, **2(1)** affords **3(1)** while **2(3)** gives rise to **3(3)**, again as a single isomer. The product formed by reaction of **2(8)** with NaOMe also displays the IR spectrum of a trifunctionalized anionic lactone. Its ^{13}C NMR spectrum is similar to that of **3(8)** obtained by cyclization of **1** performed with

$CH(CH_3)(CO_2C_2H_5)_2$ and exhibits broad signals that again reveal the formation of at least three isomers of this compound. Upon reaction with HCl at low temperature this latter compound, which is very probably **3(8)**, was again found to evolve into **2(8)**. The yield of complexes **3(1)**, **3(3)** and **3(8)**, upon addition of NaOMe to a terminal carbonyl of neutral lactones, remains low (from 30 to 35%), and careful IR monitoring of the process showed that their formation is always concomitant with the detection of another product displaying the IR spectrum of a monofunctionalized anion (three bands around 1900 cm^{-1}). Unfortunately, the low stability of this complex did not allow its characterization.

Conclusion

This work has allowed us to show that in complex **1**, which displays an alkoxycarbonyl, a pyruvoyl, and terminal carbonyl ligands, the β carbonyl of the pyruvoyl is the most electrophilic site of the molecule. Addition of various nucleophiles to this site affords anionic trifunctionalized metallalactones **3** whose metallalactone ring is formed by addition of the oxygen of this β carbonyl to a terminal carbonyl. When treated with HCl, the rapid evolution of these complexes **3** into neutral metallalactones **2** explains the direct formation of **2** when the cyclization of **1** is performed with pronucleophiles (Nu–H). Recall that, starting from complex **1**, the formation of **3** could also be performed by the intermediate formation of **2** obtained by cyclization of the pyruvoyl ligand of **1** with the alkoxycarbonyl moiety of the same complex and release of CH_3O^-. The rapid addition of this CH_3O^- to a terminal carbonyl of **2** was then supposed to afford **3**. This work allowed us to dismiss this hypothesis as the reaction of complex **2** with CH_3O^- was only found to afford **3** in very low yield. However, two aspects of this work remain unclear: i) the formation of a single isomer of **3(3)** from the cyclization of **1** with the anion of diethyl malonate, and ii) the broadness of the NMR signals of **3(8)** and **3(9)** associated with the high number of isomers observed for the complexes bearing a diethyl methylmalonate or a diethyl allylmalonate as substituent. Further experiments are under progress to find an answer these questions.

Experimental Section

General Remarks: All reactions were carried out with Schlenk techniques under dry, oxygen-free argon. All solvents were purified by preliminary distillation from an appropriate drying agent.[20] CD_2Cl_2 and $[D_8]$THF were stored over molecular sieves under inert atmosphere until needed. Infrared spectra were recorded in the range 2300–1600 cm^{-1} in solution in hexanes, CH_2Cl_2, or THF with a FT-IR NEXUS NICOLET spectrometer. ^1H and ^{13}C NMR spectra were recorded at 0 °C in CD_2Cl_2 or $[D_8]$THF with a Bruker AMX-3 300 or Bruker DRX 400 spectrometer. NMR HMQC, HMBC, and COSY spectra were recorded with a Bruker DRX 500. Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane. Elemental analyses were performed by the Service Central d'Analyses du CNRS. $Fe(CO)_5$, NaOMe, CH_3Li (1.6 M in diethyl ether), *n*BuLi (1.6 M in hexanes), $CH_2(CO_2C_2H_5)_2$, $CH_2[C(O)CH_3]_2$, $CH_2(CN)_2$, $CH(CH_3)(CO_2C_2H_5)_2$, $CH_2(CO_2C_2H_5)[C(O)CH_3]$, and $CH_2(CO_2C_2H_5)(CN)$ were purchased from commercial sources and used as received. $CH(CH_2CH=CH_2)(CO_2C_2H_5)_2$ was prepared as described in the literature[21] by reaction of $ClCH_2CH=CH_2$ with $NaCH(CO_2C_2H_5)_2$[21–23] and purified by distillation (b.p. 105 °C, 15 Torr). Complex **1** was obtained as described elsewhere[13] by reaction of $ClC(O)C(O)CH_3$[24] with $[(CO)_4Fe(CO_2CH_3)]^-$.[15]

General Procedure for the Preparation of Stabilized Carbanions: These anions were prepared as described in the literature.[21,23] The substrate (1.5 mmol) in solution in THF (5 mL) was added dropwise, over a period of 10 min, to a suspension of NaH (36 mg, 1.5 mmol obtained from a 40% dispersion in mineral oil washed with 5 × 5 mL of hexanes before use) in THF (10 mL) at room temperature. H_2 gas evolution was observed. The solution obtained was stirred for 10 min and used without further purification.

Reaction of $[(CO)_4Fe\{C(O)C(O)CH_3\}(CO_2CH_3)]$ (1) with Carbanions. General Procedure for the Preparation of the Trifunctionalized Anionic Complexes 3: The carbanion (1.5 mmol; 0.94 mL of a 1.6 M solution of CH_3Li in diethyl ether, 0.6 mL of a 2.5 M solution of *n*BuLi in hexanes, or the solution of the stabilized carbanion prepared as described above) was added, with stirring, to a solution of **1** (450 mg, 1.5 mmol) in THF (30 mL) at –70 °C. As shown by IR monitoring, the reaction was very fast as three new bands were rapidly observed in the ν(CO) region. The temperature was then raised to –10 °C and the solvent evaporated to dryness. The residue was washed with hexanes at –20 °C (3 × 5 mL) to afford a white powder, which was generally found to be insoluble in most organic solvents, with the exception of the complexes obtained with $(CO_2C_2H_5)_2C(R)^-$ (R = H, CH_3 or allyl) and $(CO_2C_2H_5)[C(O)CH_3]C(H)^-$, which could be extracted with a hexanes/CH_2Cl_2 mixture (75:25) at 0 °C (3 × 30 mL) and recrystallized from this mixture at –40 °C. We were unable to obtain correct analysis of these rather unstable anionic complexes **3**.

Reaction of 1 with CH_3Li: According to the general procedure for this reaction, **1** (450 mg, 1.5 mmol) was treated with CH_3Li (950 µL of a 1.6 M solution in diethyl ether) to give **3(1)** (385 mg, 80% yield). IR (THF): ν(C≡O) = 2070 (w), 1995 (s), 1970 cm^{-1} (s); ν(C=O) = 1680 (br), 1635 (br), 1605 (br). ^1H NMR (400 MHz, $[D_8]$THF, 273 K): δ = 3.3 (br. s, 3 H, OCH_3), 1.1 (br. s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, THF, 273 K): δ = 262.3 (C=O), 225.4 [cyclic C(O)O-], 209.7, 208.3, 207.2 and 206.3 [CO and C(O)-O-], 94.3 (cyclic quaternary carbon), 50.3 (OCH_3), 15.8 (CH_3), 8.4 ppm (CH_3).

Reaction of 1 with *n*BuLi: The reaction of **1** (1.5 mmol, 450 mg) with *n*BuLi (600 µL of a 2.5 M solution in hexanes) was found to afford white crystals of **3(2)** (270 mg, 50% yield). IR (THF): ν(C≡O) = 2068 (m), 2002 (s), 1982 cm^{-1} (s); ν(C=O) = 1660 (sh), 1636 (m), 1610 (m). ^1H NMR (400 MHz, $[D_8]$THF, 273 K): δ = 3.4 (br. s, 1.5 H, OCH_3), 3.2 (br. s, 1.5 H, OCH_3), 1.7–0.8 (br. m, 12 H, *n*Bu and CH_3) ppm. $^{13}C\{^1H\}$ NMR [400 MHz, THF, 273 K; two isomers (50:50)]: δ = 274.1, 271.5 (C=O), 229.5, 228.8 [cyclic C(O)O-], 212.5–208.0 [numerous signals for CO and C(O)O], 96.9, 96.7 (cyclic quaternary carbon), 60.5, 59.9 (OCH_3), 50.3, 50.1, 38.2, 37.7, 23.1, 22.2 (CH_2), 22.5, 22.1, 14.7, 14.5 ppm (CH_3).

Reaction of 1 with $NaC(H)(CO_2C_2H_5)_2$: Complex **1** (450 mg, 1.5 mmol) was treated at –70 °C with a solution of $NaC(H)(CO_2C_2H_5)_2$ (1.5 mmol, prepared as described above) in THF (10 mL). The product of the reaction, obtained as a white powder, was extracted at –10 °C with a hexanes/CH_2Cl_2 (60:40) mixture

(3 × 30 mL) and recrystallized at –40 °C from this solution to give white crystals of **3(3)** (650 mg, 90% yield). IR (CH_2Cl_2): ν(C≡O) = 2082 (s), 2022 (s), 2000 cm^{-1} (s); ν(C=O) = 1747 (s), 1624 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 4.26 (dq, *J* = 7, *J′* = 3 Hz, 1 H, OCH_2), 4.09 (dq, *J* = 7, *J′* = 3 Hz, 1 H, OCH_2), 3.88 (dq, *J* = 7, *J′* = 3 Hz, 1 H, OCH_2), 3.74 (dq, *J* = 7, *J′* = 3 Hz, 1 H, OCH_2), 3.74 (s, 1 H, CH), 3.24 (s, 3 H, OCH_3), 1.21 (t, *J* = 7 Hz, 3 H, $C\mathit{H}_3CH_2$), 1.09 (t, *J* = 7 Hz, 3 H, $C\mathit{H}_3CH_2$), 1.06 (s, 3 H, $C\mathit{H}_3C$) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 269.3 (C=O), 229.5 [cyclic C(O)O-], 207.1, 206.9, 206.4 and 204.4 [CO and C(O)O], 168.7 (C=O ester),; 167.3 (C=O ester), 92.0 (cyclic quaternary carbon), 62.65 (OCH_2), 62.55 (OCH_2), 55.25 (CH), 50.9 (OCH_3), 21.7 ($C\mathit{C}H_3$), 13.7 ($CH_2\mathit{C}H_3$), 13.6 ($CH_2\mathit{C}H_3$) ppm. The different signals were allocated to each carbon by HMBC and HMQC sequences.

Reaction of 1 with NaC(H)[C(O)CH$_3$]$_2$: As described in the general procedure, **1** (450 mg 1.5 mmol) was added at –70 °C to a suspension of NaC(H)[C(O)CH$_3$]$_2$ (1.5 mmol) in THF (10 mL) to give **3(4)** as a white powder (475 mg, 75% yield) that was found to be insoluble in most organic solvents. IR (THF): ν(C≡O) = 2071 (s), 2011 (s), 1985 cm^{-1} (s); ν(C=O) = 1726 (w), 1697 (w), 1651 (s), 1598 (w). ^{1}H NMR (400 MHz, [D$_8$]THF, 273 K): δ = 3.54 (s, 1 H, CH), 3.39 (s, 3 H, OCH_3), 2.20 (s, 3 H, CCH_3), 2.06 [s, 6 H, C(O)CH$_3$] ppm. $^{13}C\{^1H\}$ NMR [400 MHz, [D$_8$]THF, 273 K; 2 isomers (70:30)]: δ = 268.8 (C=O), 267.5 (C=O), 220.9 [cyclic C(O)O], 207.7, 207.1, 206.3, 205.1, 204.6, 203.5, 203.15, 202.6, and 201.6 [CO, C(O)O, and *C*(O)CH$_3$], 94.0 (cyclic quaternary carbon), 69.2 [*C*{C(O)CH$_3$}$_2$], 51.85, 50.45 (OCH_3), 34.05, 33.88, 33.05,32.05 [C(O)*C*H$_3$], 21.95, 20.3 (CH_3) ppm.

Reaction of 1 with NaC(H)(C≡N)$_2$: As described in the general procedure, **1** (450 mg, 1.5 mmol) was added at –70 °C to a solution of NaC(H)(C≡N)$_2$ (1.5 mmol) in THF (10 mL). The yellow powder of **3(5)** which was obtained (375 mg, 65% yield) was insoluble in most organic solvents. IR (THF): ν(C≡N) = 2253 cm^{-1} (w); ν(C≡O) = 2075 (s), 2015 (s), 1987 (s); ν(C=O) = 1658 (s), 1622 (sh), 1601 (sh). ^{1}H NMR [400 MHz, [D$_8$]THF, 273 K; 2 isomers (60:40)]: δ = 4.98 (s, 0.6 H, CH), 4.61 (s, 0.4 H, CH), 3.34 (s, 1.8 H, OCH_3), 3.30 (s, 1.2 H, OCH_3), 1.39 (s, 1.8 H, CH_3), 1.15 (s, 1.2 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, [D$_8$]THF, 273 K): δ = 267.6 (C=O), 264.5 (C=O), 220.4, 219.25 [cyclic C(O)O], 208.7, 207.8, 207.35, 207.2, 206.9, 206.65 (CO), 206.2, 205.25 [s, C(O)OCH$_3$], 113.7, 113.45, 112.6, 112.5 (C≡N), 90.5, 88.5 (cyclic quaternary carbon), 51.5, 50.65 (OCH_3), 31.1, 30.8 [*C*(C≡N)$_2$], 22.15, 21.0 ($C\mathit{C}H_3$) ppm.

Reaction of 1 with NaC(H)(CO$_2$CH$_3$)[C(O)CH$_3$]: Following the general procedure, **1** (450 mg, 1.5 mmol) was allowed to react with a solution of NaC(H)(CO$_2$CH$_3$)[C(O)CH$_3$] (1.5 mmol) in THF (10 mL) at –70 °C to give **3(6)** as a yellow powder (490 mg, 75% yield) after extraction with a 60:40 hexanes/CH_2Cl_2 mixture (3 × 15 mL) at 0 °C and crystallization from this mixture at –40 °C. IR (CH_2Cl_2): ν(C≡O) = 2071 (s), 2011 (s), 1984 cm^{-1} (s); ν(C=O) = 1744 (s), 1655 (sh), 1621 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K; 4 isomers): δ = 4.2 (s, 1 H, CH), 3.65 (s, 3 H, OCH_3), 3.4 (s, 1.5 H, OCH_3), 3.25 (s, 1.5 H, OCH_3), 2.3 [s, 1.5 H, C(O)CH$_3$], 2.1 (s, 1.5 H, C(O)CH$_3$], 1.2 (s, 1.5 H, CCH_3), 1.1 (s, 1.5 H, CCH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, [D$_8$]THF, 273 K): δ = 268.5, 267.4, 267.1, 267.0 (C=O), 221.9, 221.3, 220.6, 220.4 [cyclic C(O)O], 211.7, 209.6, 208.5, 208.4, 208.3, 208.1, 207.7, 207.2, 207.1, 203.5, 203.3, 202.7, 201.0 [CO, *C*(O)OCH$_3$, and *C*(O)CH$_3$], 169.6, 169.2 (2), 168.7 [organic C(O)OCH$_3$], 93.9, 93.1, 92.6, 92.3 (cyclic quaternary carbon), 62.5, 62.2, 61.9, 61.2 (CH), 52.7, 52.5, 52.2, 50.8 (2), 50.5, 50.3, 49.9 (OCH_3), 32.9, 32.7, 32.3, 32.1 [*C*H$_3$ C(O), 24.1, 23.7, 23.2, 22.9 ($C\mathit{C}H_3$) ppm.

Reaction of 1 with NaC(H)(CO$_2$C$_2$H$_5$)(C≡N): Complex **1** (450 mg, 1.5 mmol) was treated with a solution of NaC(H)(CO$_2$C$_2$H$_5$)(C≡N) (1.5 mmol) in THF (10 mL) at –70 °C. After evaporation of the solvent, the yellow oily residue was washed with hexanes (3 × 15 mL) at 0 °C to afford **3(7)** as a brown powder (350 mg; 59% yield). IR (THF): ν(C≡N) = 2246 cm^{-1} (w); ν(C≡O) = 2073 (s), 2012 (s), 1987 (s), ν(C=O) = 1749 (m), 1652 (s). ^{1}H NMR (400 MHz, [D$_8$]THF, 273 K): δ = 4.45 (s, 1 H, CH), 4.10 (m, 2 H, OCH_2), 3.30 (s, 3 H, OCH_3), 1.10 (m, 3 H, $CH_2C\mathit{H}_3$), 1.05 (s, 3 H, $CC\mathit{H}_3$) ppm.$^{13}C\{^1H\}$ NMR (400 MHz, [D$_8$]THF, 273 K; four isomers): δ = 267.5, 266.8, 266.5, 266.2 (C=O), 222.5–202.0 [numerous peaks for CO, *C*(O)OCH$_3$, and cyclic *C*(O)O], 167.0, 166.2, 165.5, 164.0 [organic *C*(O)OC$_2$H$_5$], 118.0, 117.5, 117.3, 116.8 (C≡N), 93.0, 92.5, 91.5, 91.0 (cyclic quaternary carbon), 60–52 (numerous peaks for OCH_3 and OCH_2), 14–10 (numerous resonances for $C\mathit{C}H_3$ and $CH_2\mathit{C}H_3$) ppm.

Reaction of 1 with Substituted Malonate Anions NaC(R)(CO$_2$C$_2$H$_5$)$_2$ (R = CH$_3$ or allyl): Compound **1** (450 mg 1.5 mmol) was treated at –70 °C with NaC(R)(CO$_2$C$_2$H$_5$)$_2$ [1.5 mmol in solution in THF (10 mL) prepared as described above: 300 mg for R = CH_3 or 330 mg for R = allyl]. The product of the reaction, obtained as a white powder, was extracted at 0 °C with a hexanes/CH_2Cl_2 (60:30) mixture (3 × 30 mL) but, despite several attempts, we were unable to get crystals from these solutions. The solvent was removed to give 550 mg (R = CH_3; 75% yield) or 505 mg (R = allyl; 65% yield) of a white powder which was probably composed of several isomers of **3(8)** (R = CH_3) or **3(9)** (R = allyl).

3(8): IR (CH_2Cl_2): ν(C≡O) = 2084 (s), 2023 (s), 2000 cm^{-1} (s); ν(C=O) = 1721 (s), 1606 (s); (THF): ν(C≡O) = 2069 (s), 2006 (s), 1995 cm^{-1} (s); ν(C=O) = 1735 (s), 1637 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 4.20 (br. m, 4 H, OCH_2), 3.41 (br. s, 3 H, OCH_3), 1.46 (br. s, 3 H, CH_3), 1.40 (br. s, 3 H, CH_3), 1.23 (br. m, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 262.3, 266.2, 265.8 (C=O), 237.8, 236.3 [cyclic C(O)O], 210.9, 210.6, 209.4, 208.9, 206.3, 205.6, 205.2 [CO and C(O)O], 173.7, 168.2 (C=O ester), 96.3, 96.2, 95.4, 95.0 (cyclic quaternary carbon), 62.9, 62.3, 62.2, 62.1, 59.6, 59.2 (OCH_2), 52.0, 51.8, 51.5 [O*C*H$_3$, *C*(CH$_3$)], 22.4, 21.6, 20.2, 19.3, 18.4, 13.9, 13.8 (CH_3) ppm.

3(9): IR (CH_2Cl_2): ν(C≡O) = 2070 (s), 2010 (s), 1983 cm^{-1} (s); ν(C=O) = 1749 (s), 1610 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 5.74 (br. m, 1 H, CH allyl), 5.30 (br. m, 2 H, CH_2 allyl), 4.16, 4.05 (br. m, 4 H, OCH_2), 3.36 (br. s, 3 H, OCH_3), 2.61, 2.19 (br. m, 2 H, CH_2 allyl), 1.36 (br. s, 3 H, CH_3), 1.15 (br. s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 272 (br., C=O), 237.5 [br., cyclic C(O)O], 210.0, 206.7, 206.3 [br., CO and C(O)O], 171.3, 167.6 (C=O ester), 134.4, 133.8, 132.4 (allylic CH), 119.3, 118.2, 117.3 (allylic CH_2), 95.6, 93.9, 92.2 (cyclic quaternary carbon), 64.5 (malonyl quaternary carbon), 62.1, 61.7 (OCH_2), 51.6, 51.3 (OCH_3), 36.5, 35.3, 34.5 (allylic CH_2), 25.5, 22.8 ($C\mathit{C}H_3$), 13.6 (CH_3) ppm.

Reaction of the Anionic Trifunctionalized Metallalactones 3 with HCl. General Procedure for Preparation of Neutral Alkyl-Substituted Lactones 2: A 1 M solution of HCl in diethyl ether (1 mL) was added to a slurry of anionic lactones **3** (1 mmol) in THF (40 mL) at –70 °C. As shown by IR monitoring of the reaction, the reaction was very fast. After 15 min at this temperature the ν(CO) bands of neutral complexes **2** at 2120, 2070, 2060, and 2040 cm^{-1} were found to have totally replaced those of the starting complexes **3** at 2080, 2020, and 2000 cm^{-1}. The temperature was then raised to –10 °C and the solvent removed to dryness. The residue was extracted at –10 °C with a hexanes/CH_2Cl_2 (95:5) mixture (5 × 25 mL). This solution was reduced to 10 mL at –40 °C to afford pure crystals of complexes **2**.

Reaction of 3(1) with HCl: Preparation of 2(1): Following the general procedure, **3(1)** (385 mg, 1.20 mmol) was treated with HCl (1.2 mL of a 1 M solution in diethyl ether) to afford **2(1)** (219 mg 65% yield). IR (hexanes): ν(C≡O) = 2125 (m), 2073 (sh), 2064 (m), 2042 cm^{-1} (s); ν(C=O) = 1780 (m), 1685 (sh). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 1.3 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 254.1 (C=O), 200.2 (2 C, axial C≡O), 198.4, 196.6, 196.3 [CO and cyclic C(O)O], 96.2 (cyclic quaternary carbon), 24.1 (CH_3) ppm. $C_9H_6FeO_7$ (281.95): calcd. C 38.33, H 2.14, Fe 19.80; found C 38.21, H 2.12, Fe 19.73.

Reaction of 3(2) with HCl. Preparation of 2(2): The reaction of **3(2)** (270 mg, 0.75 mmol) with HCl (750 µL of a 1 M solution in diethyl ether) gave rise to **2(2)** (134 mg, 55% yield). IR (hexanes): ν(C≡O) = 2124 (s), 2072 (sh), 2063 (s), 2041 cm^{-1} (s); ν(C=O) = 1738 (w), 1704 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 1.5–1.2 (br. m, 9 H, *n*Bu), 0.85 (br. s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 254.1 (C=O), 200.5, 200.3, 198.4, 196.6, 196.5 [CO and cyclic C(O)O], 98.4 (cyclic quaternary carbon), 36.9, 26.9, 25.6, 23.0, 21.9 (CH_2 and CH_3) ppm. $C_{12}H_{12}FeO_7$ (324.03): calcd. C 44.48, H 3.73, Fe 17.23; found C 44.62, H 3.92, Fe 17.15.

Reaction of 3(3) with HCl. Preparation of 2(3): Complex **3(3)** (480 mg, 1 mmol) and HCl (1 mL of a 1 M solution in diethyl ether) were reacted to afford **2(3)** (255 mg, 60% yield). IR (hexanes): ν(C≡O) = 2131 (s), 2083 (m), 2064 (s), 2047 cm^{-1} (s); ν(C=O) = 1734 (m), 1689 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 4.13 (m, 4 H, OCH_2), 3.70 [s, 1 H, $C(H)(CO_2C_2H_5)_2$], 1.34 (s, 3 H, CCH_3), 1.22 (m, 6 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 251.8 (C=O), 202.0, 199.4, 199.05 (2 C), 196.3 [CO and cyclic C(O)O], 166.3, 166.1 ($CO_2C_2H_5$), 92.6 (cyclic quaternary carbon), 62.2, 62.15 (OCH_2), 58.6 (CH), 22.2 (CCH_3), 13.9, 13.75 ppm (CH_2CH_3). $C_{15}H_{14}FeO_{11}$ (426.12): calcd. C 42.28, H 3.31, Fe 13.11; found C 42.46, H 3.35, Fe 13.05.

Reaction of 3(4) with HCl. Preparation of 2(4): Complex **3(4)** (1 mmol 420 mg) was reacted at –50 °C with HCl (1 mL of a 1 M solution in diethyl ether) to afford **2(4)** (200 mg, 55% yield). IR (hexanes): ν(C≡O) = 2131 (s), 2085 (m), 2064 (s), 2047 cm^{-1} (s); ν(C=O) = 1720 (sh), 1705 (s), 1690 (sh). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 2.15 (s, 3 H, CCH_3), 2.02 [s, 6 H, $C(O)CH_3$] ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 251.65 (C=O), 202.1, 201.8, 201.3, 199.3 (2 C), 197.85, 196.2 [CO, cyclic C(O)O and $C(O)CH_3$], 92.65 (cyclic quaternary carbon), 74.0 (CH), 31.05, 30.2 [$CH_3C(O)$], 22.2 (CCH_3) ppm. $C_{13}H_{10}FeO_9$ (366.064): calcd. C 42.65, H 2.75, Fe 15.26; found C 42.78, H 2.85, Fe 15.22.

Reaction of 3(6) with HCl. Preparation of 2(6): The reaction of **3(6)** (500 mg, 1.15 mmol) with HCl (1.15 mL of a 1 M solution in diethyl ether) at –50 °C was found to afford **2(6)** (285 mg 65% yield). IR (hexanes): ν(C≡O) = 2131 (m), 2085 (m), 2064 (s), 2047 cm^{-1} (s); ν(C=O) = 1755 (w), 1721 (sh), 1703 (m). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K; two isomers: δ = 3.98 (s, 0.6 H, CH), 3.92 (s, 0.4 H, CH), 3.78 (s, 1.8 H, OCH_3), 3.66 (s, 1.2 H, OCH_3), 2.25 [s, 1.2 H, $C(O)CH_3$], 2.12 [s, 1.8 H, $C(O)CH_3$], 1.28 (s, 1.8 H, CCH_3), 1.25 (s, 1.2 H, CCH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 251.32, 251.22 (C=O), 202.06, 201.94, 200.72, 200.01, 198.41, 198.31, 198.15, 198.08, 198.02, 196.29 [CO, cyclic C(O)O and $C(O)CH_3$], 167.70, 167.18 (CO_2CH_3), 92.78, 92.32 (cyclic quaternary carbon), 65.86, 65.35 (CH), 53.30, 53.08 (OCH_3), 30.11, 29.42 [$C(O)CH_3$], 22.19, 22.15 (CCH_3) ppm. $C_{13}H_{10}FeO_{10}$ (382.063): calcd. C 40.87, H 2.64, Fe 14.62; found C 41.05, H 2.63, Fe 14.52.

Reaction of Complexes 3(5) or 3(7) with HCl: The reactions of these complexes, which contain one or two C≡N groups, with 1 equiv. of HCl was found, even at low temperature (–80 °C), to lead to their decomposition into $Fe(CO)_5$ and organic compounds.

Reaction of the Mixture of Isomers of 3(8) or 3(9) Bearing Bulky Substituents with HCl. Preparation of 2(8) and 2(9): The reaction of **3(8)** or **3(9)** [1 mmol, 500 mg for **3(8)** (R = CH_3) or 520 mg for **3(9)** (R = allyl)] with HCl (1 mL of a 1 M solution in diethyl ether) at –50 °C afforded **2(8)** (310 mg, 70% yield) or **2(9)** (233 mg, 50% yield), respectively, as white powders after crystallization from hexanes at –40 °C.

2(8): IR (hexanes): ν(C≡O) = 2131 (s), 2084 (m), 2052 (m), 2050 cm^{-1} (s); ν(C=O) = 1727 (m), 1695 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 4.11 (q, *J* = 7 Hz, 4 H, OCH_2), 1.58 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.20 (t, *J* = 7 Hz, 6 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 249.9 (C=O), 202.6, 199.55 (3 C), 196.35 [CO and cyclic C(O)O], 169.9, 169.4 ($CO_2C_2H_5$), 95.25 (cyclic quaternary carbon), 62.1, 61.8 [quaternary malonic carbon and OCH_2 (2 C)]; 20.1 (CH_3), 18.95 (CH_3), 13.8 [CH_2CH_3 (2 C)] ppm. $C_{16}H_{16}FeO_{11}$ (440.143): calcd. C 43.66, H 3.66, Fe 12.67; found C 43.85, H 3.63, Fe 12.62.

2(9): IR (hexanes): ν(C≡O) = 2128 (s), 2083 (m), 2059 (m), 2041 cm^{-1} (s); ν(C=O) = 1750 (m). 1737 (m), ^{1}H NMR (400 MHz, CD_2Cl_2, 273 K): δ = 5.8 (m, 1 H, =CH), 5.1 (m, 2 H, $=CH_2$), 4.15 (m, 4 H, OCH_2), 2.8 (d, *J* = 5 Hz, 2 H, allylic CH_2), 1.49 (s, 3 H, CH_3), 1.22 (t, *J* = 7 Hz, 6 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, CD_2Cl_2, 273 K): δ = 249.84 (C=O), 202.75, 198.48, 198.34, 197.98, 196.41 [CO and cyclic C(O)O-], 168.74, 168.70 ($CO_2C_2H_5$), 133.94 (=CH), 118.16 ($=CH_2$), 95.60 (cyclic quaternary carbon), 65.71 (quaternary malonic carbon), 62.19, 62.07 (OCH_2), 37.59 (allylic CH_2), 19.90 (CH_3), 13.94, 13.80 (CH_2CH_3) ppm. $C_{18}H_{18}FeO_{11}$ (466.181): calcd. C 46.38, H 3.89, Fe 11.98; found C 46.52, H 3.93, Fe 11.97.

Reaction of 2(1) (R = R′ = R′′ = H), 2(3) (R = R′ = $CO_2C_2H_5$; R′′ = H), and 2(8) (R = R′ = $CO_2C_2H_5$; R′′ = CH_3) with NaOMe. Formation of 3(1), 3(3), and 3(8): Complex **2** [0.5 mmol; 140 mg of **2(1)**, 210 mg of **2(3)**, or 220 mg of **2(8)**] in solution in THF (30 mL) at 0 °C was added to a suspension of 28 mg of NaOMe in THF. The reaction was monitored by IR spectroscopy. After 90 min the solvent was removed to dryness. The residue of the reaction performed with **2(1)** was washed with CH_2Cl_2 (3 × 5 mL) at 0 °C. The residues obtained from **2(3)** and **2(8)** were washed with hexanes (3 × 5 mL) and extracted with a hexanes/CH_2Cl_2 (60:40, 3 × 10 mL) mixture and crystallized from this solution at –40 °C. The ^{13}C NMR spectra of the obtained products were found to be similar to those of **3(1)**, **3(3)**, and **3(8)**, respectively. These reactions were found to afford 60 mg of **3(1)** (35% yield), 70 mg of **3(3)** (30% yield), or 75 mg of **3(8)** (30% yield).

X-ray Crystallographic Studies: Data for compounds **2(1)** and **3(3)** were collected on a Xcalibur 1 diffractometer (Oxford Diffraction) at 150 and 100 K, respectively. The very low stability of compound **3(3)** made a correct X-ray data collection difficult. In this case we had only a few seconds to select a correct single crystal which was very quickly mounted on the goniometer head of the diffractometer at 100 K. After several attempts we succeeded in finding a correct single crystal of **3(3)** suitable for the data collection. Both structures were solved by direct methods and successive Fourier difference syntheses, and were refined by weighted anisotropic full-matrix least-squares methods.[25] The hydrogen atoms of compound **2(1)** were located by difference Fourier techniques and were refined isotropically; while those of compound **3(3)** were calculated [d(C–H) = 0.95 Å]; their thermal parameters were taken as $U_{iso} = 1.3 \cdot U_{equ}(C)$ and therefore included as isotropic fixed contributors to F_c. Scattering factors and corrections for anomalous dispersion

Table 4. Crystal data and structural refinement details for **2(1)** and **3(3)**.

	2(1)	**3(3)**
Empirical formula	$C_9H_6FeO_7$	$C_{67}H_{74}Cl_6Fe_4K_4O_{48}$
Molecular weight	281.99	2239.82
Space group	$P\bar{4}2_1c$	$P\bar{1}$
a [Å]	17.824(2)	14.892(1)
b [Å]	17.824(2)	17.082(1)
c [Å]	7.1894(5)	20.093(2)
α [°]	90	75.553(7)
β [°]	90	84.644(7)
γ [°]	90	77.615(6)
V [Å^3]	2284.0(4)	4830.3(9)
Z	8	2
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.64	1.54
Temperature	150(2)	100
μ [cm^{-1}]	13.30	10.16
$F(000)$	1136	2284
Reflections measured	7474	16359
2θ range	7.22–43.70	5.0–44.10
Reflections unique/R_{int}	952/0.049	7262/0.042
Reflections with $I > 2\sigma(I)$	881	5125
N_v	178	837
R_1,[a] wR_2[b]	0.0262/0.0556	0.065/0.082
$GooF$[c]	1.064	1.619
Flack parameter	–0.01(3)	
$\Delta\rho_{\text{max.,min.}}$ [e Å^{-3}]	+0.209, –0.159	+0.771, –0.223

[a] $R_1 = \Sigma|F_o - F_c|/F_o$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] GooF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{\text{obsd}} - N_{\text{var}})\}^{1/2}$.

were taken from the International Tables for X-ray Crystallography.[26] The thermal ellipsoid drawings were made with the ORTEP program.[27] Pertinent crystal data and selected bond lengths and bond angles of **2(1)** and **3(3)** are listed in Tables 1–4.

CCDC-286043 [for **2(1)**] and -270916 [for **3(3)**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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