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# Cyclization of the Pyruvyl(methoxycarbonyl)tetracarbonyliron Complex *cis*-$(CO)_4Fe[C(O)C(O)CH_3](CO_2CH_3)$ Induced by Pronucleophile Reagents

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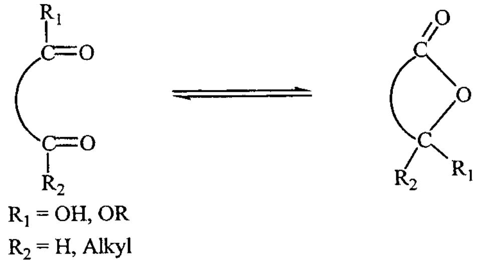
Two iron complexes, *cis*-$(CO)_4Fe[C(O)C(O)CH_3](CO_2CH_3)$ (**1a**) and *cis*-$(CO)_4Fe[C(O)CO_2CH_3][C(O)CH_3]$ (**3**), are reported. Each complex can be considered as a $\gamma$-keto ester with a metal atom inserted into the chain linking its two organic groups. **1a** is the only one found to evolve thermally, similarly to organic $\gamma$-keto esters, into the methoxy metallalactone $(CO)_4\overline{\text{Fe}C(O)C(CH_3)(OCH_3)O\text{C}}(O)$ (**2a**). This reaction is not reversible and does not require any acid or alkaline catalysis. The process does not result from a spontaneous dissociation of the methoxycarbonyl ligand of **1a** but from an associative intra or intermolecular mechanism. A similar process can also be induced by pronucleophile reagents, and it affords a series of substituted metallalactones: $(CO)_4\overline{\text{Fe}C(O)C(CH_3)(Nu)O\text{C}}(O)$ ($Nu = OCH_3$ (**2a**), $OC_2H_5$ (**2b**), $SC_2H_5$ (**2c**), $P(C_6H_5)_2$ (**2d**), $P(C_6H_{11})_2$ (**2e**)). Complex **2e** has been characterized structurally. These substituted lactones are formed by nucleophilic attack of the reagent at the pyruvyl $\beta$-carbonyl followed by carbonylate attack on the alkoxycarbonyl ligand.

## Introduction

Complexes bearing one acyl, aroyl, or alkoxycarbonyl ligand have been widely investigated due to their involvement in catalytic carbonylation processes,[1] and the difference in reactivity of carbonylated ligands and organic ketones or esters has been well-established. On the other hand, complexes displaying two carbonylated ligands are often unstable and thus are less common. For this reason, no comparison between their chemical properties and those of diketones, keto acids, or keto esters has been described. Thus, though studied for more than 30 years, the well-known ring-chain isomerization process, $\gamma$-hydroxy or $\gamma$-alkoxy lactone ⇌ $\gamma$-keto or $\gamma$-aldehydo acids or esters,[2] has no real organometallic counterpart. This reversible organic process, which is of importance in carbohydrate chemistry,[3] proceeds from an intramolecular addition of the oxygen of the ketone group at the carbon of the carbonyl of the acid or ester functions, followed by migration of the alkoxy (or the hydroxy) group (Scheme 1). Except for keto acid compounds, this process requires acid or base catalysis.

### Scheme 1



In organometallic chemistry, only a few iron,[4] nickel,[5] or molybdenum[6,7] complexes present reactions that can be compared to this organic transformation. However, in these processes the organometallic complex acts as the migrating group ($R_1$). Such a cyclization has also been described for a ligand in a tungsten complex whose

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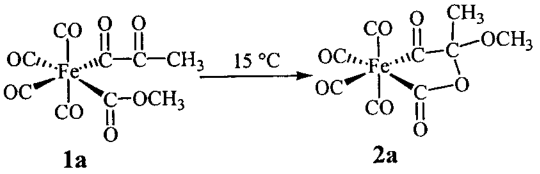
10.1021/om010989d CCC: $22.00

**Scheme 2**



organometallic part, inserted into the $R_2$ group, is not directly involved in the cyclization process and may only increase the polarity of the double bond.[8] To our knowledge, only some platinum complexes are found to display a metal center inserted into the link bridging $\gamma$-positioned keto and ester groups.[9] However, these compounds, when they do not display trans geometries unfavorable for achievement of cyclizations,[9a] are not reported to thermally induce such reactions.[9b]

In a preliminary work[10] we reported the thermal behavior of a complex which can be considered as a $\gamma$-keto ester with a metal inserted into its organic chain. This compound, *cis*-pyruvyl(alkoxycarbonyl)tetracarbonyliron $Fe(CO)_4[C(O)C(O)CH_3](CO_2CH_3)$ (**1a**), affords thermally the alkoxy $\gamma$-metallalactone **2a** (Scheme 2) by a reaction similar to the chain-ring isomerization of organic $\gamma$-keto esters.

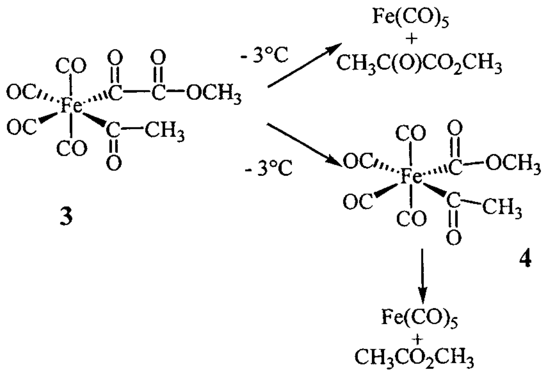
This irreversible process, which requires no catalysis, formally involves the formation of a metallacycle by C−O coupling between the oxygen of the $\beta$-carbonyl of the pyruvyl and the carbon of the alkoxycarbonyl of **1a** and the migration of the methoxy of this last ligand to the pyruvoyl $\beta$-carbonyl. In the present paper we report full results of our investigations concerning the mechanism of formation of substituted metallalactones analogous to **2a** obtained by inducing the reaction with various nucleophiles.

## Results and Discussion

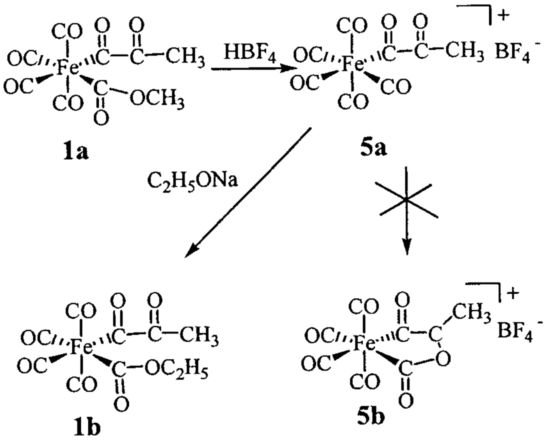
As mentioned above, thermolysis of **1a** affords the methoxy metallalactone **2a** (60% yield). The cis geometry of the complex is established in IR by the presence of four $\nu(C{\equiv}O)$ bands at 2125, 2085, 2060, and 2050 $cm^{-1}$ and in $^{13}C$ NMR (where two different substituents on the $sp^3$ carbon of the metallacycle induce the inequivalency of the two axial carbonyls) by four signals at 199.8, 199.7, 199.2, and 198.7 ppm in the terminal carbonyl resonance area. The resonance of the metallacyclic $sp^3$ carbon is observed at 109.9 ppm. The structure attributed to **2a** is confirmed by an X-ray diffraction study[10] showing the envelope shape of the metallacycle, which displays an out-of-plane $sp^3$ carbon and a methoxy group in a pseudoaxial position.

Thermolysis of the closely related complex $Fe(CO)_4[C(O)CO_2CH_3][C(O)CH_3]$[10] (**3**) shows completely different behavior. The observed reactions are a carbon−carbon coupling, affording methyl pyruvate, and a decarbonylation, giving rise to *cis*-$Fe(CO)_4(CO_2CH_3)[C(O)CH_3]$[10] (**4**) (see Scheme 3). **4** can also be prepared in low yield (15%)[10] by reaction of acetyl chloride with $[Na][Fe(CO)_4(CO_2CH_3)]$.[11]

**Scheme 3**



**Scheme 4**



Like **1a** and **3**, complex **4** displays four IR bands in the $\nu(C{\equiv}O)$ region. In $^{13}C$ NMR, the resonances of the terminal carbonyls are found in 2/1/1 intensities at respectively 201.4, 199.8, and 198.8 ppm; the signal of the acetyl carbonyl is found at 242.3 ppm and that of the alkoxycarbonyl at 195.3 ppm.

The difference in reactivity of complexes **1a** and **3** may result from the difference of mobility observed between the alkoxy groups of alkoxycarbonyl and alkyloxalyl ligands. The high mobility of the alkoxy of alkoxycarbonyl ligands is well-known; it has been shown to occur either by a spontaneous dissociation of the ligand in $Fe(Cp)[C(O)R](CO)[P(Ph)_3]$ ($R = OCH_3, OC_6H_5, SCH_3, SC_6H_5$)[12] or by an associative pathway,[13] via the trifunctionalized intermediate $H[Fe(CO)_3(CO_2R)_3]$ in *cis*-$Fe(CO)_4(CO_2R)_2$.[14]

To probe a potential contribution of a spontaneous dissociation of **1a** to its process of thermal cyclization, we synthesized the cation $\{Fe(CO)_5[C(O)C(O)CH_3]\}^+$ (**5a**) by reacting **1a** with $HBF_4$[15] (Scheme 4). The reaction performed in THF at −50 °C afforded a white

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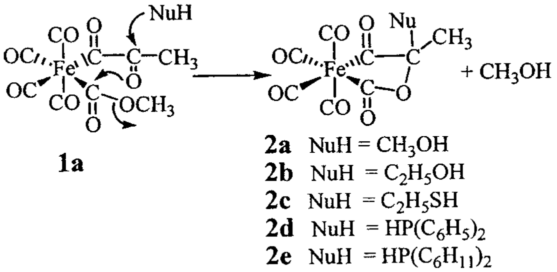
**Scheme 5**



precipitate whose characteristics are in good agreement with the proposed structure (see Experimental Section). The cationic nature of the complex was confirmed in $^{13}$C NMR by a shift of its carbonyl resonances toward higher fields. The two signals of 4/1 intensities at 196.1 and 190.4 ppm in the terminal carbonyl resonance area together with the resonances of the pyruvyl group at 231.5 and 189.5 ppm suggest the presence of a single organic ligand on the metal center (the pyruvyl) and rules out the possible formation of the cyclic isomer **5b**, which would require in $^{13}$C NMR three resonances of 2/1/1 intensities for its terminal carbonyls and an additional signal near 100 ppm.

The stability of **5a** shows that a spontaneous cyclization by a nucleophilic attack of the oxygen of the $\beta$-carbonyl of the pyruvyl on a terminal carbonyl to afford **5b** does not occur. To check the possible formation of **2a** by a nucleophilic addition on **5a** of $MeO^-$, which would be released in solution by a spontaneous dissociation of **1a,** the cationic complex **5a** was allowed to react with 1 equiv of alcoholate ($C_2H_5ONa$). The reaction, performed at low temperature ($-20$ °C), afforded a new complex whose characteristics (see Experimental Section) are very close to those displayed by **1a**. This compound was characterized as *cis*-$Fe(CO)_4(CO_2C_2H_5)[C(O)C(O)CH_3]$ (**1b**) and can also be prepared by reaction of $ClC(O)C(O)CH_3$ with $[Fe(CO)_4(CO_2C_2H_5)]^-$. Its formation results from a nucleophilic addition of $C_2H_5O^-$ on a terminal carbonyl of **5a**. This shows that the more electrophilic sites of this cation are the terminal carbonyls and not the $\beta$-carbonyl of the pyruvyl ligand and rules out the possible intervention of a dissociative mechanism in the process of formation of **2a**.

A second reaction pathway that could account for the formation of the metallacyclic complex **2a** is an inter- or an intramolecular nucleophilic addition of the methoxy group of **1a** on the carbon atom of the $\beta$-carbonyl of the pyruvyl of the same complex (Scheme 5). To check this assumption, we attempted to perform the cyclization of **1a** in the presence of an excess of pronucleophile reagents (NuH = $CH_3OH$, $C_2H_5OH$, $C_2H_5SH$, $HP(C_6H_5)_2$, $HP(C_6H_{11})_2$). In the presence of a large excess of methanol (used as solvent), **1a** was found to afford the metallacyclic complex **2a** in 4 h at 0 °C (compared to 24 h at 15 °C under thermolysis conditions). Performed in the presence of 1 equiv of MeOH, the process requires longer reaction times, however (20 h at 0 °C). Such an enhancement in the cyclization rate lends support to a possible induction of formation of the metallacycle by a nucleophilic addition of methanol at the $\beta$-carbonyl of the pyruvyl ligand. However, this result does not give any information about the intra- or intermolecular nature of the formation of **2a** by thermal evolution of **1a**.

When performed in the presence of 100 equiv of ethanol, the cyclization of **1a** was found to afford in 3 h at 0 °C the ethoxy metallacyclolactone **2b**, whose spectroscopic characteristics (see Experimental Section) are very close to those displayed by **2a**. However, a careful $^{13}$C NMR monitoring of the reaction leading to **2b** revealed the transitory formation of an intermediate species presenting the same characteristics as $Fe(CO)_4(CO_2C_2H_5)[C(O)C(O)CH_3]$ (**1b**) already obtained by reaction of $C_2H_5ONa$ with the cationic complex **5a**. The formation of **1b** from **1a** results from a rapid methoxy/ethanol exchange, which once more makes more obvious the mobility of alkoxy groups of alkoxycarbonyl ligands and shows the more electrophilic sites of **1a** to be the terminal carbonyls and not the $\beta$-carbonyl of the pyruvyl. Indeed, as already mentioned, the alkoxy/alcohol exchange on this complex is thought to occur by an associative pathway via the formation of the trifunctionalized intermediate *fac*-$\{(CO)_3Fe[C(O)C(O)CH_3](CO_2CH_3)(CO_2C_2H_5)\}H$, formed by addition of EtOH on a terminal carbonyl of **1a**.[13,14] The observation of this methoxy/ethanol exchange prior to the cyclization, affording the ethoxy metallalactone **2b**, raises the question of whether the formation of the ethoxycarbonyl complex **1b** is essential for the formation of the ethoxy lactone **2b**.

As we have previously shown that exchanges between alkoxycarbonyl ligands of iron complexes and thiols do not occur,[16] the reaction of **1a** with $C_2H_5SH$ was thought to give an answer to this question. In presence of 80 equiv of ethanethiol **1a** gives rise over 48 h at 0 °C to 90% of the ethylthio metallalactone **2c**. A careful monitoring of the reaction by $^{13}$C NMR confirms that no exchange occurs between the methoxycarbonyl ligand of **1a** and $C_2H_5SH$. Though slow, the reaction of **1a** with $C_2H_5SH$ only produces 5% of the methoxy metallalactone **2a** as a byproduct whose formation probably results from a nucleophilic addition at the pyruvyl $\beta$-carbonyl of **1a** of the methanol released in solution at the first stages of the formation of **2c**. The new complex **2c** displays IR and NMR spectra similar to those of **2a** and **2b** (see Experimental Section). The carbons linked to the sulfur atom, however, exhibit $^{13}$C NMR resonances at higher fields than those observed for their homologues of the ethoxy complex **2b**.

Several attempts to bring about the cyclization of **1a** with an excess of amines (diethylamine, aniline) as pronucleophile reagents failed. These reactions do not afford any metallacyclic lactones; $Fe(CO)_5$ and pyruvamides are the only products observed in the reaction mixtures. As these last compounds are also obtained by reaction of the carbamyl ferrates $Fe[C(O)NR_2](CO)_4^-$ with pyruvyl chloride, their formation may be due to a fast thermal evolution of $Fe(CO)_4[C(O)NR_2][C(O)C(O)CH_3]$ intermediates formed from **1a** by a rapid amine/alkoxy exchange.[17] Fast evolutions of carbamyl pyruvyl intermediates are not unexpected, since iron complexes carrying two carbamyl ligands or a carbamyl ligand and

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a carbonylated organic ligand in cis positions have already been found to be unstable.[18]

Soft nucleophiles such as secondary phosphines are also found to induce the cyclization of **1a**. The reaction performed at 0 °C in the presence of 1 equiv of the reagent affords after 1 h ($HPPh_2$) or 4 h ($HP(C_6H_{11})_2$) two new metallalactonic complexes (**2d**,**e**) displaying the same structure as **2a**−**c** with a $PR_2$ substituent on the $sp^3$ carbon of their metallacycle. Similarly to the metallalactones already synthesized, **2d**,**e** present in their IR spectra four $\nu(C{\equiv}O)$ bands and, in $^{13}C$ NMR, four signals for the resonances of their terminal carbonyls. The signals of the $sp^3$ carbon of their metallacycle are found at 100.1 ppm (**2d**) and 99.2 ppm (**2e**). Due to the presence of a $PR_2$ group ($R = C_6H_5$ (**2d**), $C_6H_{11}$ (**2e**)) on this carbon, large $^{13}C-^{31}P$ coupling constants (35.6 Hz for **2d** and 37.3 Hz for **2e**) are observed. Smaller interactions between the phosphorus and the ketonic carbon of each metallacycle (8.7 Hz, **2d**; 23.2 Hz, **2e**) are also detected. $^{31}P-^{1}H$ NMR HMBC sequences show for both complexes $^3J$ interactions between the protons of the methyl substituent and the phosphorus. In $^{31}P$ NMR, **2d**,**e** each display one signal, respectively, at 10.9 and 14.1 ppm; these values fall within the range of the resonances observed for organic phosphines presenting a large cone angle[19] and do not correspond to phosphines bound to a metal. The absence of interaction between the terminal carbonyls and the phosphorus also confirms the noncoordination of the phosphine to the metal.[13] $^{13}C\{^1H,^{31}P\}$ NMR spectra of the two complexes also reveal the presence of 8 signals in the aromatic carbon resonance area of **2d** and of 12 resonances for the cyclohexyls of **2e** (see Experimental Section). In both complexes, the two phosphorus substituents (phenyls or cyclohexyls) are then not equivalent. The presence of 8 signals for the phenyl carbons of **2d** suggests fast rotations of these groups around the P−C bonds, while the detection of 12 signals for the cyclohexyls of **2e** is indicative of slow rotations of these groups on the scale of NMR detection. This difference of behavior is certainly due to a greater steric hindrance of the cyclohexyl groups.

The molecular structure of **2e** was determined by a single-crystal X-ray study. Monocrystals of **2e** were grown from a hexane/dichloromethane solution at −30 °C. An ORTEP drawing of the complex is depicted in Figure 1, crystallographic data are gathered in Table 1, and selected bond lengths and angles are listed in Table 2. As revealed by this study, the metal center of this complex is part of a five-membered metallacycle. The coordination polyhedron of the iron atom in **2e** is a distorted octahedron built of four terminal carbonyls and the chelating ligand. As generally observed for iron five-membered metallacycles,[10,20] the C(5)−Fe−C(7) bite angle of 81.8° is smaller than 90°. The two axial carbonyls are bent toward the metallacyclic ring (C(4)−Fe−C(1) = 169.7(1)°). As in the structure of **2a**, the five-membered ring is slightly puckered with deviations from the best plane formed by five atoms varying from

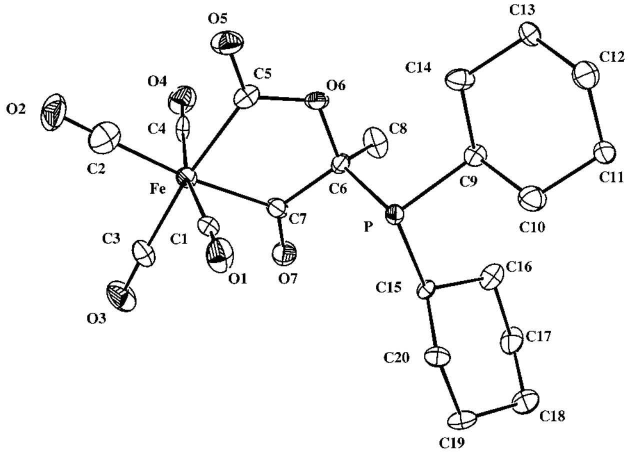

**Figure 1.** ORTEP representation of **2e**. Hydrogens have been omitted for clarity. (the thermal ellipsoids are drawn at the 50% probability level)

**Table 1. Crystal Data and Structure Refinement Details for 2e**

| compd | 2e |
|---|---|
| chem formula | $C_{20}H_{25}FeO_7P$ |
| fw | 464.22 |
| color; dimens, mm | pale orange; 0.30 × 0.30 × 0.17 |
| cryst syst | monoclinic |
| space group | $P2_1/n$ (No. 14) |
| $a$, Å | 10.6941(3) |
| $b$, Å | 10.9020(3) |
| $c$, Å | 18.8707(7) |
| $\beta$, deg | 90.097(1) |
| $V$, Å$^3$ | 2200.08(12) |
| $Z$ | 4 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.402 |
| $F$(000) | 968 |
| radiation, Å | $\lambda$(Mo Kα) 0.710 73 |
| temp, K | 110 |
| $\theta$ range, deg | 2.16−32.03 |
| linear abs coeff $\mu$, mm$^{-1}$ | 0.795 |
| abs cor | none |
| detector to cryst dist, mm | 35 |
| no. of rflns measd | 6156 |
| no. of rflns with $I > 2\sigma(I)$ | 2240 |
| no. of variables | 263 |
| final $R$ indices ($I > 2\sigma(I)$) | R1 = 0.095, wR2 = 0.130 |
| final $R$ indices (all data) | R1 = 0.143, wR2 = 0.140 |
| GOF | 1.005 |
| $\rho_{max}/\rho_{min}$, e Å$^{-3}$ | 1.03/−0.41 |

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2e**

| | | | |
|---|---|---|---|
| Fe−C(1) | 1.855(4) | P−C(6) | 1.905(3) |
| Fe−C(2) | 1.861(5) | O(6)−C(5) | 1.378(4) |
| Fe−C(3) | 1.877(3) | O(6)−C(6) | 1.433(4) |
| Fe−C(4) | 1.812(3) | C(6)−C(7) | 1.545(4) |
| Fe−C(5) | 1.991(3) | C(6)−C(8) | 1.517(4) |
| Fe−C(7) | 1.999(4) | | |
| C(1)−Fe−C(2) | 89.44(16) | C(2)−Fe−C(7) | 172.05(13) |
| C(1)−Fe−C(3) | 94.41(13) | C(3)−Fe−C(4) | 92.67(13) |
| C(1)−Fe−C(4) | 169.67(14) | C(3)−Fe−C(5) | 171.10(15) |
| C(1)−Fe−C(5) | 87.71(12) | C(3)−Fe−C(7) | 89.60(14) |
| C(1)−Fe−C(7) | 88.94(15) | C(4)−F−-C(5) | 84.17(12) |
| C(2)−Fe−C(3) | 98.28(16) | C(4)−Fe−C(7) | 83.59(13) |
| C(2)−Fe−C(4) | 96.98(14) | C(5)−Fe−C(7) | 81.79(12) |
| C(2)−Fe−C(5) | 90.37(15) | | |
| C(5)−O(6)−C(6) | 118.5(2) | O(6)−C(6)−C(7) | 108.7(3) |
| Fe−C(5)−O(6) | 115.80(19) | Fe−C(7)−C(6) | 114.0(2) |

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−0.043(1) Å (C(6)) to +0.058 Å (C(7)). The P(cyclohexyl)$_2$ group linked to C(6) is located in a pseudoaxial position with the two cyclohexyls directed toward the outside of the complex. Bond lengths are close to those reported for **2a**, except for the C(6)−C(7) distance (1.545(4) Å), which, probably due to the proximity of the bulky dicyclohexylphosphine group, is longer than in **2a** (1.49(2) Å).[10]

## Conclusion

This work has permitted a better understanding of the isomerization reaction of $(CO)_4Fe[C(O)C(O)CH_3](CO_2CH_3)$ (**1a**) to $(CO)_4Fe[C(O)C(OCH_3)(CH_3)OC(O)]$ (**2a**). It has been shown that the lactone metallacycle formation is not induced by a spontaneous dissociation of the alkoxy group from the alkoxycarbonyl ligand of **1a**. On the other hand, nucleophilic reagents (NuH = $CH_3OH$, $C_2H_5OH$, $C_2H_5SH$, $HP(C_6H_5)_2$, $HP(C_6H_{11})_2$) were found to react with **1a** to induce the formation of metallacycles and to afford metallalactones substituted by OR, SR, or $PR_2$ groups. The reaction probably proceeds by a nucleophilic addition of NuH at the $\beta$-carbonyl of the pyruvyl of **1a** followed by an attack of the oxygen of this carbonyl at the carbonyl carbon of the alkoxycarbonyl ligand. After a splitting of the Nu−H bond, methanol is released in solution. Although the more electrophilic sites of **1a** are the coordinated terminal carbonyls (rapid alkoxy/alcohol exchanges), a slower nucleophilic addition on the pyruvyl $\beta$-carbonyl is very probably the first step of the reaction. With the exception of nucleophilic additions on terminal carbonyls, such reactions between nucleophiles and carbonylated ligands are scarce. A few examples of these reactions have, however, been described, mainly when no other electrophilic sites are available on the complex. Methylmagnesium bromide has been found to react with the methoxycarbonyl ligand of a rhenium complex to afford an acetyl derivative,[21] and specific additions of nucleophiles to a carbonyl linked to a butadienyl $\eta^4$-coordinated to an iron center have also been noted.[22] To our knowledge, no addition on a ligand with two C(O) groups has been described. The reactivity of the pyruvyl ligand toward nucleophilic reagents appears to be very different from that of carbenes, whose carbon (in an α-position with respect to the metal) electrophilicity is well-documented, and from that observed for allenylidenes[23] or cumulenes,[24] whose electrophilic sites are the α- and $\gamma$-carbons. However, the pyruvyl reactivity can be compared to that of allenyl ligands,[25] which, by addition of amines[25a] or carbanions[25d] on their $\beta$-carbon, have been found to afford $\pi$-allyl complexes.

Additions of phosphines on a carbonyl of an organic ligand (formation of **2d**,**e**) are particularly noteworthy. While additions of phosphines on complexed polyolefins or allenes are numerous, similar reactions on carbonyls are scarce. Such additions have, however, been described for $\eta^2$-acetyl cationic W[26a] and Mo[26b] and neutral Ta,[26c] Ti,[26d] and Zr[26e] complexes, whose acetyl carbons (in α-positions with respect to the metal) exhibit a high electrophilic reactivity. To our knowledge, additions of phosphines on the carbonyls of other organic carbonylated ligands have never been described.

The process of formation of the metallacycles results from a C−O coupling between pyruvyl and alkoxycarbonyl ligands. Reactions involving such C−O couplings between two ligands are scarce. They have, however, been put forward to explain the thermal evolution of bis(carbamyl) neutral iron complexes into metallacyclic carbenes[18,27] and the transformation of anionic tungsten intermediates into amino methylidene complexes.[28] Similar couplings have also been observed between carbamyl[29] or aroyl[30] and carbenic ligands located on the same metal center, but none of them was induced by a previous nucleophilic addition on a carbonyl.

We are currently investigating the syntheses of similar metallalactones from complexes of different structures that are induced by nucleophilic reagents.

## Experimental Section

**General Considerations.** All experiments were performed under argon using standard Schlenk techniques. Solvents were dried and distilled under nitrogen before use: THF and hexane over sodium/benzophenone ketyl, dichloromethane over $CaH_2$, MeOH and EtOH over $Mg(OR)_2$. Deuterated dichloromethane or $CD_3CN$ were stored under argon over molecular sieves before use. Infrared spectra were recorded in solution in hexane on a Perkin-Elmer 1430 spectrometer. $^1H$ (300 MHz), $^{13}C$ (75.47 MHz), and $^{31}P$ (121.49 MHz) NMR spectra were recorded (unless otherwise stated) at 0 °C in $CD_2Cl_2$ solutions on a Bruker AC 300 and Bruker AMX 3-400 spectrometers. NMR HMQC or HMBC sequences were performed on a Bruker DRX 500. Chemical shifts were measured relative to residual protonated solvents for $^1H$ NMR spectra and to the solvent resonance for $^{13}C$ NMR spectra. $^{31}P$ spectra were externally referenced to $H_3PO_4$ (85%). Gas chromatographic analyses

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were performed on a Hewlett-Packard 5890 instrument using a CP SIL 25 m column. Elemental analyses were obtained from the Centre de Microanalyses du CNRS. $[Fe(CO_2CH_3)(CO)_4]^-$,[11] $[Fe[C(O)CH_3](CO)_4]^-$,[31] and $ClC(O)C(O)CH_3$[32] were obtained according to published methods. $ClC(O)C(O)CH_3$ was obtained, after distillation, as a mixture with $HC(O)OCH_3$. The respective percentages of these compounds were evaluated by $^1H$ NMR.

**Preparation of $Fe(CO_2CH_3)[C(O)C(O)CH_3](CO)_4$ (1a).** To a stirred solution (20 mmol) of $[Fe(CO_2CH_3)(CO)_4]^-$ [11] in THF at −70 °C was added dropwise a solution of 20 mmol of pyruvyl chloride in 5 mL of THF. The orange-brown solution slowly turned yellow-green. After 2 h the IR spectrum of the solution showed the disappearance of the $\nu(C\equiv O)$ bands of the starting anion at 1915, 1890, and 1870 $cm^{-1}$. The solvent was then evaporated to dryness and the residue washed at −50 °C with two portions (5 mL) of hexane. Complex **1a** was extracted at −20 °C from the residue by three fractions (20 mL) of a hexane/$CH_2Cl_2$ mixture (95:5). These different fractions were joined, and the resulting solution was reduced under vacuum at −40 °C. The pale yellow solid which precipitated was filtered, washed with two portions of hexane (5 mL, −20 °C), and dried under vacuum to give 0.895 g (yield 60%) of **1a**. IR (hexane, $cm^{-1}$): $\nu(C\equiv O)$ 2125 (m), 2075 (w, sh), 2070 (m, sh), 2060 (s); $\nu(C{=}O)$ 1740 (br), 1665 (w, sh), 1630 (br). $^1H$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 3.56 (s, 3H, $OCH_3$), 3.22 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 201.3 (2), 199.2 (1), 198.2 (1) ($C\equiv O$); 245.7 ($C{=}O$); 198.1 ($C{=}O$); 193.9 ($CO_2CH_3$); 50.5 ($OCH_3$); 23.0 ($CH_3$). Anal. Calcd for $C_9FeH_6O_8$: C, 36.28; Fe, 18.74; H, 2.03. Found: C, 36.42; Fe, 18.65; H, 2.11.

**Thermolysis of $Fe(CO)_4(CO_2CH_3)[C(O)C(O)CH_3]$ (1a).** A 0.300 g (1 mmol) portion of **1a** in solution in 20 mL of $CH_2Cl_2$ was stirred at 15 °C. The monitoring of the reaction by IR showed the slow disappearance of the $\nu(C{=}O)$ band at 1630 $cm^{-1}$ of the starting complex. After 24 h, the solution was evaporated to dryness and the solid residue washed at −50 °C with 2 × 5 mL of hexane. **2a** was extracted at 0 °C from the residue by 30 mL of a hexane/$CH_2Cl_2$ mixture (95:5). After a slow reduction of this solution at −30 °C, colorless crystals of **2a** were obtained. After filtration these crystals were washed at −50 °C with 2 × 5 mL of hexane (yield 60%, 0.180 g). IR (hexane, $cm^{-1}$): $\nu(C\equiv O)$ 2125 (w), 2085 (w, sh), 2060 (w, sh), 2050 (s); $\nu(C{=}O)$ 1720 (br), 1665 (w, sh). $^1H$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 3.34 (s, 3H, $OCH_3$), 1.41 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 199.8, 199.7, 199.2, 198.7 ($C\equiv O$); 245.7 ($C{=}O$); 197.9 ($C{=}O$); 109.9 ($C(CH_3)(OCH_3)$); 50.6 ($OCH_3$); 16.2 ($CH_3$). Anal. Calcd for $C_9FeH_6O_8$: C, 36.28; Fe, 18.74; H, 2.03. Found: C, 36.32; Fe, 18.65; H, 2.15.

**Preparation of $(CO)_4Fe[C(O)CH_3][C(O)CO_2CH_3]$ (3).** This complex was obtained by following the method of preparation of **1a**. When the reaction was performed with 5 mmol of $[Fe[C(O)CH_3](CO)_4]^-$ [31] and 5 mmol of methyloxalyl chloride (0.612 g, 0.460 mL), 0.600 g of **3** was obtained (40% yield). IR (hexane, $cm^{-1}$): $\nu(C\equiv O)$ 2120 (w), 2065 (w, sh), 2055 (w, sh), 2045 (s); $\nu(C{=}O)$ 1740 (m), 1685 (s) 1660 (s). $^1H$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 3.80 (s, 3H, $OCH_3$), 2.70 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 200.9 (2), 200.3 (1), 198.0 (1), ($C\equiv O$); 242.3 ($C{=}O$); 241.5 ($C{=}O$); 164.5 ($CO_2CH_3$); 53.7 ($OCH_3$); 50.0 ($CH_3$). Anal. Calcd for $C_9FeH_6O_8$: C, 36.28; Fe, 18.74; H, 2.03. Found: C, 36.35; Fe, 18.52; H, 2.07.

**Thermolysis of $(CO)_4Fe[C(O)CH_3][C(O)CO_2CH_3]$ (3).** A solution of 1 mmol of **3** (300 mg) in 20 mL of $CH_2Cl_2$ was stirred at −3 °C for 24 h. The solvent was then evaporated to dryness. The oily residue was washed at −30 °C with two portions (5 mL) of hexane. GC analysis of these two fractions showed the presence of methyl pyruvate (retention time 1.58 min) together with traces of methyl acetate (retention time 0.79 min). Further extraction of the residue at −20 °C with 20 mL of a hexane/$CH_2Cl_2$ mixture (95:5) afforded, after filtration and slow concentration of the solution at −40 °C, 0.110 g (yield 40%) of pale yellow crystals of **4**.

**$^{13}C$ NMR Monitoring of the Thermal Evolution of 3.** A 60 mg portion of **3** (0.2 mmol) in solution in 0.8 mL of cold $CD_2Cl_2$ was introduced under argon into an NMR tube. The reaction was monitored at −3 °C. The progress of the reaction was shown by the appearance of new resonances at 242.3, 201.4, 199.8, 198.8, 195.3, 53.1, and 49.6 ppm (complex **4**), 191.9, 161.3, 52.2, and 29.9 ppm (methyl pyruvate), 211.1 ppm ($Fe(CO)_5$), and 184.5 ppm (free CO). The integration of the signals at 49.6 and 29.9 ppm showed the formation of 60% of **4** and 40% of $CH_3C(O)CO_2CH_3$. The reaction was quantitative.

**Synthesis of $Fe[C(O)CH_3](CO_2CH_3)(CO)_4$ (4).** Similarly to **1a** and **3a**, complex **4** was prepared by reacting $[Fe(CO_2CH_3)(CO)_4]^-$ [11] (5 mmol) with 5 mmol of acetyl chloride (0.390 g, 0.350 mL). After the usual workup, the reaction was found to afford in low yield (less than 10%, ~80 mg) yellow crystals of **4**. IR (hexane, $cm^{-1}$): $\nu(C\equiv O)$ 2080 (w), 2050 (w, sh), 2045 (w, sh), 2035 (m); $\nu(C{=}O)$ 1680 (s), 1660 (s). $^1H$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 3.50 (s, 3H, $OCH_3$), 2.60 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 201.4 (2), 199.8 (1), 198.8 (1), ($C\equiv O$); 242.3 ($C{=}O$); 195.3 ($CO_2CH_3$); 53.1 ($OCH_3$); 49.6 ($CH_3$). Anal. Calcd for $C_8FeH_6O_7$: C, 35.59; Fe, 20.69; H, 2.24. Found: C, 35.75; Fe, 20.51; H, 2.32.

**Preparation of the Cationic Complex $[Fe[C(O)C(O)CH_3](CO)_5]^+$ (5a).** 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 $HBF_4{\cdot}O(CH_3)_2$. The solution was stirred for 1 h at −40 °C. Pale yellow crystals slowly separated. After filtration these crystals of **5a** were washed with THF at −50 °C (3 × 5 mL) and dried under vacuum; yield 46 mg (40%). $^1H$ NMR ($CD_3CN$, 273 K; $\delta$, ppm): 2.80 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CD_3CN$, 273 K; $\delta$, ppm): 196.1 (4), 190.4 (1) ($C\equiv O$); 231.5 ($C{=}O$); 189.5 ($C{=}O$); 24.6 ($CH_3$). Probably due to the high sensitivity of **5a** to moisture, we were unable to obtain a correct IR spectrum and microanalysis of this complex.

**Reaction of 5a with EtONa: Achievement of 1b.** To a stirred suspension of **5a** (0.100 g; 0.283 mmol) in 30 mL of THF at −20 °C was added a solution of 1 equiv of EtONa (20 mg) in 5 mL of THF. Within 15 min the solid in suspension gradually disappeared and a yellow solution was obtained. The solvent was then removed under vacuum. The remaining yellow solid was washed at −40 °C with hexane (2 × 5 mL) and extracted at −20 °C with 30 mL of a hexane/$CH_2Cl_2$ mixture (95:5). A total of 53 mg (yield 60%) of **1b** was obtained as a pale yellow crystalline solid after concentration of the solution to 10 mL at −50 °C. IR (hexane, $cm^{-1}$): $\nu(C\equiv O)$ 2120 (w), 2085 (w, sh), 2075 (m, sh), 2065 (s); $\nu(C{=}O)$ 1730 (br), 1660 (sh), 1625 (br). $^1H$ NMR ($CD_2Cl_2$, 273 K; $\delta$, 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; $\delta$, ppm): 201.6 (2), 199.4 (1), 198.4 (1) ($C\equiv O$); 246.0 ($C{=}O$); 198.0 ($C{=}O$); 193.2 ($CO_2C_2H_5$); 62.8 ($OC_2H_5$); 23.2 ($CH_3$); 14.5 ($CH_3$). Anal. Calcd for $C_{10}FeH_8O_8$: C, 38.50; Fe, 17.90; H, 2.58. Found: C, 38.70; Fe, 17.75; H, 2.65.

**Preparation of 1b.** This complex was obtained by following the procedure used to prepare **1a** by reacting 5 mmol of $[Fe(CO)_4(CO_2C_2H_5)]^-$ with 5 mmol of $ClC(O)C(O)CH_3$. The yield of the reaction was 55% (0.860 g).

**Thermal Evolution of 1a in the Presence of MeOH: Achievement of 2a. Reaction Performed in Methanol.** A solution of 100 mg of **1a** (0.33 mmol) in 10 mL of MeOH was stirred for 4 h at 0 °C. As shown by IR (disappearance of the $\nu(C{=}O)$ band at 1630 $cm^{-1}$), the reaction was then complete. The solvent was evaporated to dryness and the solid residue washed with hexane at −50 °C (2 × 5 mL). **2a** was extracted with 30 mL of a hexane/$CH_2Cl_2$ mixture (95:5), and the

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extracts, after concentration at −30 °C, afforded 65 mg (yield 65%) of yellow crystals.

**Reaction Performed in the Presence of 1 Equiv of Methanol.** A 100 mg amount of **1a** was dissolved in 10 mL of $CH_2Cl_2$ at 0 °C. A 0.015 mL portion of methanol was added to the solution, and the mixture was stirred for 20 h. After evaporation of the solvent, the residue was treated as above to afford 50 mg (50%) of **2a**.

**Thermal Evolution of 1a in the Presence of EtOH: Formation of 2b.** As above, 100 mg (0.33 mmol) of **1a** in $CH_2Cl_2$ was reacted at 0 °C with 2 mL (34 mmol, ~100 equiv) of ethanol. The solvent was removed after 3 h of reaction; after the usual workup **2b** was obtained (75 mg, yield 70%) as pale yellow crystals. IR (hexane, $cm^{-1}$): $\nu$(C$\equiv$O) 2120 (w), 2072 (w, sh), 2060 (w, sh), 2050 (s); $\nu$(C=O) 1725 (br), 1712 (w, sh). $^1H$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 3.49 (q, $J$ = 7 Hz, 2H, $OCH_2$), 1.41 (s, 3H, $CH_3$), 1.29 (t, $J$ = 7 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 199.6, 199.3, 198.8, 196.7 (C$\equiv$O); 245.8 (C=O); 198.3 (C=O); 109.8 ($C(CH_3)(OC_2H_5)$); 59.1 ($OCH_2$); 16.6 ($CH_3$), 14.9 ($CH_3$). Anal. Calcd for $C_{10}FeH_8O_8$: C, 38.50; Fe, 17.90; H, 2.58. Found: C, 38.65; Fe, 17.65; H, 2.60.

**$^{13}$C NMR Monitoring of the Thermal Evolution of 1a in the Presence of Ethanol.** A 60 mg amount of **1a** (0.2 mmol) and 37 mg (50 $\mu$L, 0.8 mmol) of ethanol in solution in 0.6 mL of cold $CD_2Cl_2$ were introduced under argon into an NMR tube. The reaction was monitored at 0 °C by $^{13}C$ NMR. Samples were drawn every 30 min. At the first stages of the reaction the spectra clearly showed the appearance of two new signals at 62.5 and 14.5 ppm (complex **1b**). The resonances corresponding to **2b** grew more slowly. After 1 h of reaction, the signals of the starting complex were no longer detected. The two compounds **1b** and **2b** were then formed in equal quantities, and the reaction seemed quantitative. Longer reaction times showed a decrease of the signals of **1b** and an increase of those of **2b**. After 4 h **2b** was the only product of the reaction.

**Thermal Evolution of 1a in the Presence of EtSH: Formation of 2c.** The reaction was performed at 0 °C by reacting 100 mg of **1a** (0.33 mmol) in the presence of 80 equiv (27 mmol, 2 mL, 1.7 g) of ethanethiol. The reaction was complete after 48 h at 0 °C. After evaporation of the solvent, the usual workup of the reaction mixture failed to afford a solid product. As determined by $^{13}C$ NMR, the oily residue thus obtained was found to be composed of 95% of **2c** and 5% of **2a.** Data for compound **2c** are as follows. IR (hexane, $cm^{-1}$): $\nu$(C$\equiv$O) 2120 (w), 2075 (w, sh), 2067 (w, sh), 2050 (s); $\nu$(C=O) 1728 (br), 1705 (w, sh). $^1H$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 2.54 (q, $J$ = 6 Hz, 2H, $SCH_2$), 1.64 (t, $J$ = 6 Hz, 3H, $CH_3$), 1.20 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 199.8, 199.7, 198.2, 196.4 (C$\equiv$O); 245.2 (C=O); 196.9 (C=O); 98.2 ($C(CH_3)(SC_2H_5)$); 23.9 ($SCH_2$); 23.1 ($CH_3$), 14.3 ($CH_3$). The oily residue failed to afford correct analyses corresponding to **2c**. The possible formation of $Fe[C(O)SEt][C(O)C(O)CH_3](CO)_4$ was not evidenced by a monitoring of the reaction by $^{13}C$ NMR.

**Reaction of 1a with $HP(C_6H_5)_2$ or $HP(C_6H_{11})_2$.** To a stirred solution of 0.5 mmol (150 mg) of **1a** in 20 mL of $CH_2Cl_2$ was added at −20 °C 0.5 mmol of phosphine $HP(C_6H_5)_2$ (93 mg, 87 $\mu$L) or $HP(C_6H_{11})_2$ (100 mg, 101 $\mu$L). The reaction was monitored by IR; at this temperature the reaction was complete after 1 h when performed with $HP(C_6H_5)_2$ or after 4 h when the reagent was $HP(C_6H_{11})_2$. The solvent was then removed under reduced pressure. The yellow residue was washed with hexane at −50 °C (2 × 5 mL). **2d** or **2e** was extracted at 0 °C from this residue with two 30 mL portions of a hexane/$CH_2Cl_2$ mixture (95:5). After filtration the solution was concentrated at −50 °C to afford pale yellow crystals of **2d** (135 mg, yield 60%) or **2e** (160 mg, yield 70%). Data for **2d** are as follows. IR (hexane, $cm^{-1}$): $\nu$(C$\equiv$O) 2120 (w), 2075 (w, sh), 2065 (w, sh), 2045 (s); $\nu$(C=O) 1710 (br), 1695 (w, sh). $^1H$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 7.9−7.3 (m, 10H, $C_6H_5$), 1.51 (d, $J_{P-C}$ = 11.2 Hz, 3H, $CH_3$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 10.9. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 200.8 (1), 198.2 (2), 196.3 (1) (C$\equiv$O); 252.7 (d, $J_{P-C}$ = 8.7 Hz) (C=O); 197.4 (C=O); 101.1 (d, $J_{P-C}$ = 35.6 Hz) ($C(CH_3)[P(C_6H_5)_2]$); 23.1 (d, $J_{P-C}$ = 17.4 Hz) ($CH_3$); aromatic resonance area, from 135.2 to 136.1 (m, 4C); 133.9 (d, $J_{PC}$ = 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). $^{13}C\{^1H,^{31}P\}$ 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. Calcd for $C_{20}FeH_{13}O_7P$: C, 53.13; Fe, 12.35; H, 2.90; P, 6.85. Found: C, 53.32; Fe, 12.22; H, 2.95; P, 6.91. Data for **2e** are as follows. IR (hexane, $cm^{-1}$): $\nu$(C$\equiv$O) 2118 (w), 2068 (w, sh), 2060 (w, sh), 2042 (s); $\nu$(C=O) 1715 (br, m), 1690 (w, sh). $^1H$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 1.49 (d, $J_{P-C}$ = 1.6 Hz, 3H, $CH_3$), 2.00−1.10 (m, 22H, $C_6H_{11}$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 14.1. $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 273 K; $\delta$, ppm): 200.3, 200.0, 198.6, 196.8 (C$\equiv$O); 253.1 (d, $J_{P-C}$ = 23.2 Hz) (C=O); 197.7 (C=O); 99.2 (d, $J_{P-C}$ = 37.3 Hz) ($C(CH_3)[P(C_6H_{11})_2]$); 21.2 ($CH_3$); cyclohexane resonance area, 33.2 (d, $J_{P-C}$ = 24.5 Hz, 1C); 32.5 (d, $J_{P-C}$ = 21.6 Hz, 1C); 31.9 (d, $J_{P-C}$ = 21.3 Hz, 1C); 31.3 (d, $J_{P-C}$ = 16.6 Hz, 1C); 30.4 (d, $J_{P-C}$ = 6.9 Hz, 1C); 29.4 (d, $J_{P-C}$ = 5.2 Hz, 1C); from 27.5 to 27.9 (m, 4C); 26.5 (s, 1C); 26.4 (s, 1C). $^{13}C\{^1H,^{31}P\}$ NMR ($\delta$, ppm): 33.2 (1C); 32.5 (1C); 31.9 (1C); 31.3 (1C); 30.4 (1C); 29.4 (1C); 27.9 (2C); 27.8 (1C); 27.7 (1C); 27.6 (1C); 26.5 (1C); 26.4 (1C). Anal. Calcd for $C_{20}FeH_{25}O_7P$: C, 51.75; Fe, 12.03; H, 5.42; P, 6.67. Found: C, 51.92; Fe, 11.93; H, 5.45; P, 6.78.

**Crystal Analysis for 2e.** Crystals suitable for single-crystal X-ray diffraction studies were obtained from a hexane/dichloromethane (95:5) solution at −30 °C. A pale orange crystal of **2e** having the approximate dimensions 0.30 × 0.30 × 0.17 mm was mounted on an Nonius Kappa-CCD diffractometer. The crystal data and details of data collection are given in Table 1. A total of 155 frames of data were collected at 110(2) K with Mo Kα radiation ($\lambda$ = 0.710 73 Å) and with an oscillation range of 1.5°/frame and an exposure time of 30 s/deg.[33] A total of 25 195 reflections were indexed, integrated, and corrected for Lorentz and polarization effects using DENZO-SMN and SCALEPACK.[34] Data reduction together with the suppression of 339 of the most disagreeable reflections yielded 6495 unique reflections, of which 2240 had $I > 2\sigma(I)$.

The structure was solved by a Patterson search program[35] and refined by full-matrix least squares on $F^2$ using SHELXL.[35] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the complex were included in their calculated positions and refined in a riding model with isotropic displacement coefficients. The refinement converged to R1($F$) = 0.095 and wR2($F^2$) = 0.130 for 2240 reflections and R1($F$) = 0.143 and wR2($F^2$) = 0.140 for 6156 unique reflections (Table 1).

**Supporting Information Available:** Tables of crystal data and refinement details, bond lengths, bond angles, and thermal parameters for **2e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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