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Synthesis and Characterization of High-Spin $[(CO)_3Fe^{II}(CO_2R)_3]_2Fe^{II}$ Complexes Formed by Thermolysis of *cis*-$(CO)_4Fe(CO_2R)_2$ (R = Me, t-Bu, Allyl, 1,1′-Dimethylallyl). X-ray Crystal Structure of the Allyl Derivative

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Instead of the expected carbon−carbon coupling into oxalates, thermolysis at 30 °C of the *cis*-bis(alkoxycarbonyl) monomers $(CO)_4Fe(CO_2R)_2$ (**1**) affords the novel trimetallic compounds $[(CO)_3Fe(\mu,\eta^2\text{-}CO_2R)_3]_2Fe$ (R = Me (**2a**), t-Bu (**2b**), allyl (**2c**), 1,1′-dimethylallyl (**2d**)). As shown by ^1H and ^{13}C NMR, these complexes **2,** which can be described as a central Fe(II) surrounded by two $[(CO)_3Fe(CO_2R)_3]^-$ ligands, are paramagnetic. A Mössbauer study of **2a** and **2d** revealed that these complexes display a high-spin configuration of their central iron atom and a low-spin configuration of the two lateral iron atoms. The easy formation of these complexes **2** by reacting *fac*-$[(CO)_3Fe(CO_2R)_3]^-$ anions with $FeCl_2$ suggests that formation of **2** by thermal evolution of **1** could occur via an associative mechanism, giving rise to the $[(CO)_3Fe(CO_2R)_3]$ pattern. Further thermolysis of **2** at 50 °C affords alcohols, $Fe(CO)_5$, carbon monoxide, and bis(alkyl carbonates).

Introduction

The syngas route to ethylene glycol is an important industrial reaction. A crucial step of this process is the production of oxalates, which are subsequently reduced by H_2 to afford ethylene glycol. An alternative method for the preparation of oxalates is the oxidative carbonylation of alcohols. The key intermediate of this reaction, which has only been achieved with palladium-based catalysts,[1−3] is believed to be a bis(alkoxycarbonyl) Pd species that could release oxalate by a reductive carbon−carbon coupling between its two alkoxycarbonyl ligands. However, this mechanism remains doubtful as, among the bis(alkoxycarbonyl) complexes described in the literature,[4] only one has been claimed to induce oxalate formation under thermolysis conditions.[5]

To study the possibility of performing such a reaction with well-characterized complexes, we carried out the synthesis of *cis*-bis(alkoxycarbonyl)iron compounds displaying a metal center known for its low catalytic activity. These syntheses were carried out by reaction, at low temperature, of 0.5 equiv of oxalyl chloride on tetracarbonyl(alkoxycarbonyl)iron anions ($[(CO)_4Fe(CO_2R)]^-$) obtained by nucleophilic addition of alcoholates on $Fe(CO)_5$. Though the mechanism of this reaction remains unclear, the process enabled us to prepare *cis*-$Fe(CO_2R)_2(CO)_4$ complexes specifically in good yields. These compounds (**1a**, R = Me; **1b**, R = t-Bu; **1c**, R = allyl; **1d**, R = 1,1′-dimethylallyl) were

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found to be relatively stable at room temperature and only evolved thermally at 50 °C to afford dialkyl carbonates (low yields), alcohols, and $Fe(CO)_5$.[6] No trace of dialkyloxalates that would result from a carbon−carbon coupling process between the two alkoxycarbonyl ligands of these complexes was detected in the different reaction mixtures. However, a recent reinvestigation of these thermolysis reactions of $Fe(CO_2R)_2(CO)_4$ led us to show the transient formation of a series of complexes, $[Fe(CO)_3(\mu,\eta^2\text{-}CO_2R)_3]_2Fe$ (**2**), never described previously in thermal evolution processes of bis(alkoxycarbonyl) complexes.

In the present paper, we wish to report the synthesis of these new poly(alkoxycarbonyl) trimetallic complexes and their further preparation via a new synthetic method. The structural study of the allyl derivative will be developed, and a possible mechanism that could account for the formation of these complexes by thermal evolution of bis(alkoxycarbonyl) entities will also be suggested.

Results and Discussion

Preparation and X-ray Crystallographic Characterization of Complexes 2. IR monitoring of the thermal evolution of the complexes *cis*-$Fe(CO_2R)_2(CO)_4$ (**1**) performed in CH_2Cl_2 or in THF at 30 °C showed the slow disappearance of the starting set of four bands in the terminal carbonyl ν(CO) area at 2130, 2080, 2070, and 2045 cm^{-1}. The concomitant growth of two new ν(CO) bands at 2080 and 2025 cm^{-1} was indicative of the formation of a series of relatively stable new organometallic compounds. The complexes thus formed, **2** (**2a,** R = Me; **2b,** R = t-Bu; **2c,** R = allyl; **2d,** R = 1,1′-dimethylallyl), were obtained after 15 h of thermolysis and isolated as pale yellow crystals (yields ca. 70% after recrystallization). Crystals suitable for an X-ray crystallographic study were obtained for **2c**. These crystals grown from hexane at −30 °C allowed us to assign to this complex the trimetallic structure $[Fe(CO)_3\text{-}(\mu,\eta^2\text{-}CO_2CH_2CH{=}CH_2)_3]_2Fe$.

The ORTEP plot of the molecule with its atom-numbering scheme is displayed in Figure 1, and the X-ray data conditions are summarized in Table 1, while selected bond distances and bond angles are given in Table 2.

Complex **2c** crystallizes in the trigonal space group $R\bar{3}$. The unit cell contains one molecule. The molecule displays a linear chain composed of three iron atoms, it is centrosymmetric, and the central Fe(1) atom is the center of inversion. The two lateral iron atoms are surrounded by three terminal carbonyls and three bridging alkoxycarbonyl ligands bound to the metal by the carbon of their carbonyl. The central iron is coordinated to six bridging alkoxycarbonyl ligands via the oxygen of their carbonyl. **2c** can also be described as two *fac*-$[Fe(CO_2CH_2CH{=}CH_2)_3(CO)_3]^-$ entities acting as tridentate ligands encapsulating a central Fe^{2+}.

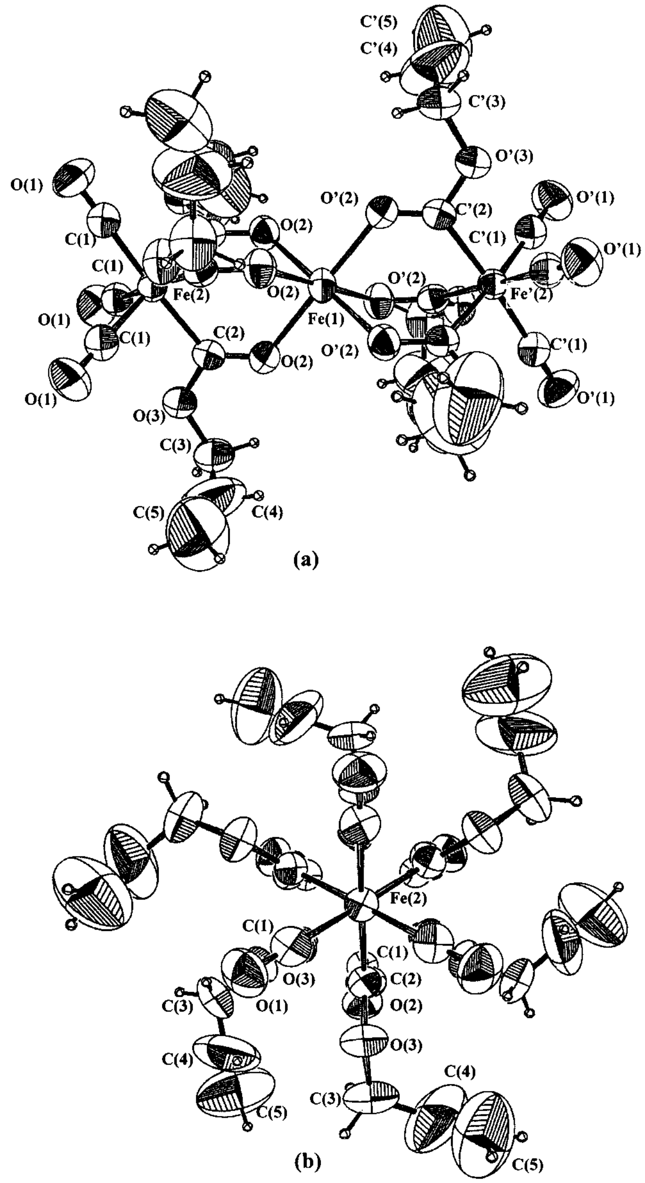

Figure 1. (a) Molecular structure of **2c**, showing 50% probability displacement ellipsoids and the numbering scheme. (b) Crystal structure of **2c** viewed along the Fe−Fe−Fe axis.

Figure 1b shows the alignment of the three metals and the staggered positions of the alkoxycarbonyls and the terminal carbonyls, resulting in a minimization of the interactions between these ligands and inducing a 3-fold axis along the Fe(2)−Fe(1)−Fe′(2) direction. Such a structure makes the six terminal carbonyls and the six bridging alkoxycarbonyls of **2c** respectively equivalent. In the solid state it is noteworthy that analogous equivalencies of the three alkoxycarbonyl or the three acyl ligands are not observed for the related complexes $[(CO)_3Fe(CO_2t\text{-}Bu)_3][K]$[7] and $[(CO)_3Re(\mu,\eta^2\text{-}C(O)Me)_3]\text{-}[BX]$[8] (X = Cl, Br).

The tripodal ligands $[Fe(CO)_3(CO_2R)_3]^-$ formally display two alkoxycarbonyl groups and one carbenic group. However, the equivalence of these groups strongly suggests an electronic delocalization along the whole ligand. This assumption is confirmed by the absence of carbenoid character of these alkoxycarbonyls, which

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Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for 2c

formula	$C_{30}H_{30}Fe_3O_{18}$
fw	846.10
cryst syst	trigonal
space group	$R3$
a, Å	10.112(5)
α, deg	103.85(8)
V, Å^3	925(2)
Z	1
ρ(calcd), g cm^3	1.800
cryst size, mm	0.28 × 0.28 × 0.32
$2\theta_{max}$, deg	50
h,k,l range	0−12; 0−12; −12 to +12
diffractometer	Enraf-Nonius CAD4
radiation	Mo Kα
μ(Mo Kα), cm^{-1}	12.308
monochromator	graphite cryst
T, K	294
F(000)	432
no. of rflns measd	1432
no. of rflns obsd ($I > \sigma(I)$)	912 (3σ)
R_{int} (from merging equiv rflns)	0.014
R(isotropic)	0.09
R(anisotropic)	0.050
N(obs)/N(var)	912/78
final R	0.036
R_w^{a}	0.036
$\sum w$	0.692
max residual, e Å^{-3}; Δ/σ	0.297; 0.04

^{a} $w = 1/\sigma(F_o)^2 - [\sigma^2(I) + 0.04F_o{}^2)^2]^{-1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2c

Bond Lengths			
Fe(1)−O(2)	2.100(2)	C(1)−O(1)	1.121(4)
Fe(2)−C(1)	1.820(4)	C(2)−O(2)	1.221(4)
Fe(2)−C(2)	1.991(3)	C(2)−O(3)	1.349(4)
Bond Angles			
C(1)−Fe(2)−C(1)	94.7(2)	O(2)−Fe(1)−O′(2)	93.50(9)
C(1)−Fe(2)−C(2)	87.5(2)	O(2)−Fe(1)−O′(2)	180.0(1)
C(1)−Fe(2)−C(2)	175.5(1)	C(2)−Fe(2)−C(2)	88.6(1)
O(2)−Fe(1)−O(2)	86.50(9)		

Table 3. Selected Infrared and NMR Data for Complexes 2

	IR (cm^{-1}; in hexane)			NMR (δ (ppm); in CD$_2$Cl$_2$, 298 K)		
				^{13}C		
	$\nu_{C\equiv O}$	ν_{COOR}	$\delta_{C\equiv O}$	δ_{COOR}	δ_R	^{1}H
2a	2089 (m) 2022 (s)	1590	245.1	494.3	86.8	−14.1 (s, 3H)
2b	2078 (m) 2017 (s)	1592	249.9	460.0	89.1 25.1	−18.4 (s, 9H)
2c	2085 (m) 2032 (s)	1596	246.5	503.2	123.9 118.4 101.5	−0.2 (m, 1H) −3.1 (m, 1H) −18.0 (m, 1H) −20.5 (m, 2H)
2d	2080 (m) 2019 (s)	1597	250.2	463.0	127.8 103.7 87.7 16.7	−1.0 (m, 1H) −8.3 (m, 1H) −17.0 (s, 6H) −17.6 (m, 1H)

show C═O (C(2)−O(2)) bond lengths of 1.221(4) Å, very close to the values observed for the same bonds of *fac*-[(CO)$_3$Fe(CO$_2$R)$_3$][K] (average of 1.21(1) Å). These values are well within the range of distances found for C═O of the alkoxycarbonyl group of the neutral complex Fe(CO$_2$-t-Bu)$_2$(CO)$_4$[9] (average of 1.241(9) Å) and much shorter than the C−O bonds observed for iron carbenes substituted by OR groups: 1.394(5) Å for (CO)$_3$Fe(C(NEt$_2$)OC(O)NEt$_2$)[10] and 1.336(3) Å for (CO)$_4$Fe(C(NEt$_2$)OC$_2$H$_5$).[11] Since the covalent radius of iron is 1.43 Å,[12] the Fe(1)−Fe(2) distance of 3.680(2) Å observed for **2c** rules out any direct metal−metal interaction.

The ligand arrangement around the two lateral Fe(2) atoms is that of a slightly distorted octahedral environment, as the C(1)−Fe(2)−C(1), C(1)−Fe(2)−C(2), and C(2)−Fe(2)−C(2) angles are respectively 94.7, 87.5, and 88.6°. These angles compare well with the same data determined for [(CO)$_3$Fe(CO$_2$-t-Bu)$_3$][K][7] (95.1, 88.6, and 87.5°, respectively), whose alkoxycarbonyls, in the solid state, are not bound to the same counterion and suggest that coordination of the tripodal group Fe(CO$_2$CH$_2$CH═CH$_2$)$_3$ to the central iron does not induce significant deformations of the (CO)$_3$Fe(CO$_2$CH$_2$CH═CH$_2$)$_3$ pattern.

The geometry about the central Fe(1) atom can also be described as a distorted octahedron with angles of 86.50(9)° for O(2)−Fe(1)−O(2) (between two alkoxycarbonyl ligands bound by their carbon to the same Fe(2)) and 93.50(9)° for O(2)−Fe(1)−O′(2) observed between two alkoxycarbonyls linked by their carbon to two different lateral Fe(2) atoms. The Fe(1)−O(2) (or Fe(1)−O′(2)) bond length, 2.100(2) Å, is longer than those observed for the bimetallic complexes Fe$_2$(μ,η^2-C(O)-C$_6$H$_5$)$_2$(CO)$_6$ (1.967(5) Å)[13] and Fe$_2$(μ,η^2-CO$_2$t-Bu)$_2$(CO)$_5$-(PPh$_3$) (2.009(2) Å).[9]

To our knowledge, only a few examples of compounds displaying structures related to **2c** have been described in the literature. We have already mentioned the complexes [Fe(CO$_2$-t-Bu)$_3$(CO)$_3$][K][7] and [Re(μ,η^2-C(O)-Me)$_3$(CO)$_3$][BX] (X = Cl, Br),[8] which display the tripodal ligand M(CO)$_3$[C(O)R]$_3$ linked to a second metal by the oxygen of the carbonyl of their organic ligands. The complexes [Fe(μ,η^2-SC$_6$H$_5$)$_3$(CO)$_3$]$_2$Fe[14,15] and [Fe(μ,η^2-SeC$_6$H$_5$)$_3$(CO)$_3$]$_2$M (M = Zn, Cd, Ni, Fe),[16] which exhibit a three-metal linear arrangement similar to that observed for **2c**, must also be mentioned. These molecules are centrosymmetric and display the same 3-fold axis as **2c**. They are respectively prepared by reaction of Fe(CO)$_5$ with C$_6$H$_5$SSC$_6$H$_5$ or by addition of the anion [Fe(SeC$_6$H$_5$)$_3$(CO)$_3$]$^-$ to MX$_2$ (X = BF$_4$ (Zn), NO$_3$ (Cd, Ni), ClO$_4$ (Fe)). A series of complexes of the general formula L$_2$M (L = CpCo[P(O)(OR)$_2$]$_3$; M = Co, Ni, Cu, Fe) has also been described.[17] These last compounds, like complexes **2**, present two organometallic tripodal ligands linked by their oxygens to a central metal atom.

In the IR spectra of complexes **2** (see Table 3) the presence of two bands in the terminal carbonyl stretching region confirms the existence in the molecule of

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fac-$FeX_3(CO)_3$ groups of C_{3v} symmetry. The values measured for the frequencies of these ν(CO) bands (2090 and 2015 cm^{-1}), very close to those displayed by the anions $[Fe(CO_2R)_3(CO)_3]^-$ (2070, 2005 cm^{-1}),[7] suggest that complexes **2** are better described as two $[Fe(CO_2R)_3(CO)_3]^-$ anions linked to a central Fe^{2+} atom rather than the bis(carbene) $[(CO)_3Fe(\mu,\eta^2\text{-}CO_2R)_2(\mu,\eta^2{=}C(OR)O)]_2Fe$. These conclusions are in good agreement with those of the structural study of **2c**, whose alkoxycarbonyl ligands do not display any carbenic character.

Complexes **2** are found to exhibit unusual ^1H and ^{13}C NMR spectra with resonances well removed from the diamagnetic region (see Table 3); such spectra suggest the presence of a paramagnetic center in the molecule. Performed at 298 K, the ^1H NMR spectrum of **2d** (R = 1,1′-dimethylallyl) displays broad signals at high fields.

A resonance at −17.0 ppm ($\omega_{1/2}$ = 80 Hz) is assigned to the protons of the methyl groups, whereas the signal of the internal allylic protons is observed at −17.6 ppm ($\omega_{1/2}$ = 110 Hz). As shown by a $^1H-^{13}C$ heteronuclear correlation (HMQC), the signals of the methylenic protons are found at −8.3 ppm ($\omega_{1/2}$ = 55 Hz) and −1.0 ppm ($\omega_{1/2}$ = 35 Hz). The large difference (~7 ppm) between the shifts of these two protons could be induced by a great difference in through-space interactions with the electronic spins. It is noteworthy that the protons closest to the metals present the broadest and the most shifted NMR signals.

In contrast to the ^1H signals, the ^{13}C NMR resonances observed for **2d** are shifted toward lower fields. At 298 K the carbonyl resonance of the alkoxycarbonyl ligands is observed at 463.0 ppm (212 ppm for the diamagnetic homologues[7]) and that of the terminal C≡O at 250.2 ppm (210 ppm for C≡O of a related diamagnetic complex[7]). The signals observed for the carbons of the 1,1′-dimethylallyl groups are similar to those quoted for the carbons of the same ligand on diamagnetic entities.

The ^{13}C NMR resonances observed for the carbonyls of complexes **2** are then very different from those observed for the series of related complexes $[Fe(CO_2R)_3(CO)_3]M$ (R = Me, M = Na; R = t-Bu, M = K;[7] signals at 212 ppm for C=O and at 209 ppm for the terminal C=O), from which complexes **2** can be considered to differ by the nature of the counterion. These observations suggest that the paramagnetic center of **2** is the central Fe^{II}, atom which could display a high-spin configuration. Such an electronic structure with unpaired electrons has already been reported for the related complexes $(CO)_3Fe(\mu\text{-}SPh)_3Fe(\mu\text{-}SPh)_3Fe(CO)_3$,[14,15] $(CO)_3Fe(\mu\text{-}SePh)_3Fe(\mu\text{-}SePh)_3Fe(CO)_3$,[16] and $\{CpCo[P(O)(OR)_2]_3\}_2Fe$,[17] whose central irons are respectively surrounded by six sulfide, selenium, and oxygen atoms.

As expected for paramagnetic complexes, **2d** shows, at low temperature, broader and more greatly contact shifted resonances. In ^1H NMR, low temperatures induce a shielding of the signals; thus, at 253 K one methylenic proton of **2d** is found at −5.1 ppm ($\omega_{1/2}$ = 96 Hz) and the second at −16.1 ppm ($\omega_{1/2}$ = 80 Hz), the methyl group protons display a broad resonance at −27.0 ppm ($\omega_{1/2}$ = 128 Hz), and the last ethylenic hydrogen shows a broad signal at −30.8 ppm ($\omega_{1/2}$ = 144 Hz). However, as displayed in Figure 2, the variations of these chemical shifts versus T^{-1} are not rigorously linear and show that the behavior of **2d** does not exactly fit the Curie−Weiss law.

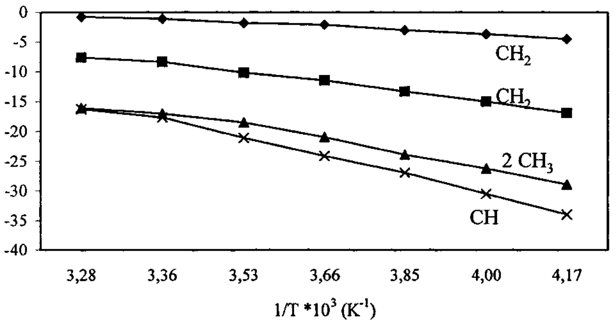

Figure 2. Plot of ^1H NMR chemical shifts obtained for **2d** as a function of T^{-1}.

Table 4. ^{13}C NMR Resonances (δ (ppm)) of 2d at Various Temperatures

	temp (K)				
	298	283	268	265	253
C(O)OR	463.0	486.6	514.5	526.0	548.2
C≡O	250.2	256.0	262.9	267.3	271.3
*C*H=	127.8	125.5	123.0	125.0	119.8
CH_2	103.7	102.4	100.9	102.5	99.2
C$(CH_3)_2$	87.7	87.6	87.5	89.6	87.3
CH_3	16.7	15.1	13.1	14.5	10.7

In the same way, the ^{13}C NMR spectra of **2d** are found to be temperature dependent. As the temperature is lowered, the signals of the carbonyls are shifted toward lower field (see Table 4). The resonance of the carbonyls of the alkoxycarbonyl ligands is found at 548.2 ppm at 253 K (a difference of 85 ppm from the signal of the same carbon observed at 298 K) and that of terminal carbons at 271.3 ppm (vs 250.2 ppm at 298 K).

Though they are ESR silent in frozen solutions, complexes **2** are found to display solid-state effective magnetic moments. The values of this parameter are determined as μ_{eff} = 5.30 (**2a**), 5.20 (**2b**), 5.41 (**2c**), 5.45 μ_B (**2d**) at 298 K. As regular octahedral iron complexes are supposed to show either $S = 0$ or $S = 2$ electronic configurations, it is noteworthy that these values are higher than that required for four unpaired electrons (4.90 μ_B). The same observations are also made for the magnetic moments determined in solution by the Evans' method:[18] **2a**, 5.0 μ_B; **2b**, 5.20 μ_B; **2c**, 5.80 μ_B; **2d**, 6.90 μ_B. The occurrence of such high μ_{eff} values may be explained either by an orbital angular momentum contribution or by a distorted-octahedral complexation around the central Fe^{II}.

As it is well-known that Mössbauer spectroscopy is a very useful tool to identify Fe^{II} high- or low-spin configurations in organometallic complexes, we have undertaken such a study on **2a** and **2d**.

Mössbauer Study of Complexes 2a and 2d. At all temperatures, the spectra of **2a** and **2d** can be resolved into two subspectra: one single line and one quadrupolar doublet which are, according to the typical values of the hyperfine parameters,[19] attributed to Fe^{II} in the low-spin (LS) and high-spin (HS) states, respectively.

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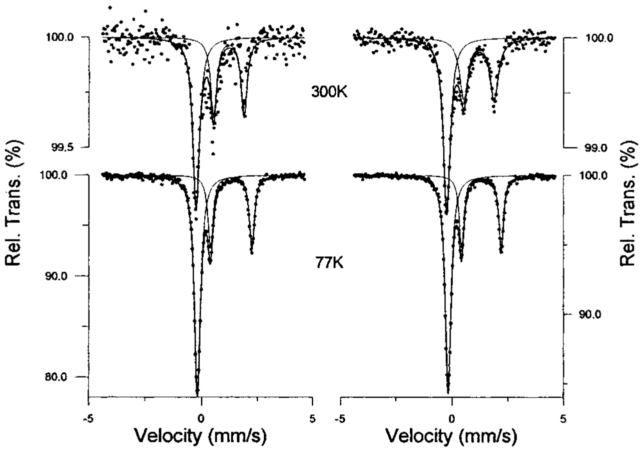

2d **2a**

Figure 3. Selected Mössbauer spectra of **2d** and **2a** with least-squares fitted Lorentzian lines.

Selected spectra are shown in Figure 3. The poor statistics of the room-temperature spectra result from the particularly low values of the *f*(*T*) factor (at 300 K, the Mössbauer lines of **2d** are 20 times smaller than at 77 K).

The relative proportions of the spectral contributions were determined at low temperature (77−200 K) as 39(1) and 37(1)% HS in compounds **2d** and **2a**, respectively. This determination of the low-temperature atomic proportions enabled us to unambiguously assign the HS state to the central iron. The two lateral iron atoms are then low-spin. Such an assignment is similar to those given for other trimetallic iron compounds displaying a related structure.[15,16] The central Fe^{II} atom is linked to six oxygen atoms, which provide a weak ligand field consistent with an HS state, while the lateral Fe^{II} atoms are bound to six carbons (CO groups) which provide a stronger ligand field, due to the presence of the LS state.[20] It is worth noting that the Mössbauer parameters of these lateral iron atoms coordinated to six CO groups are very close to those observed in the 4-fold coordinated Na$_2$Fe(CO)$_4$.[21] At higher temperature (above 200 K), despite the smaller *f* factor of the HS species and a decrease of the total area, an increase of the HS percentage area is observed (47% for **2a** and 46% for **2d** at 300 K), suggesting, for both complexes, a gradual but incomplete LS−HS spin transition. However, as no sizable change is observed in the magnetic properties of **2a** and **2d** in the temperature range suggested by the Mössbauer data, the occurrence of such a spin conversion can be ruled out.

Oxidative Electrochemistry of 2d. The electrochemical behavior of complex **2d** was investigated by cyclic voltammetric and potential step experiments in THF−[NBu$_4$][PF$_6$] at room temperature. In this electrolyte, the trimetallic complex undergoes a single one-electron oxidation ($E_{1/2} = -0.02$ V) in the potential range extending from −3.0 to ca. 1.2 V (see Figure 4). That this oxidation is a quasi-reversible step is shown by the increase of the anodic-to-cathodic peak separation (ΔE_p) with increasing scan rates. In a typical experiment[22a] ΔE_p increased from 96 mV at $v = 0.025$ V/s to 223 mV at $v = 1$ V/s (under similar conditions ΔE_p for the reversible oxidation of ferrocene increased from 68 mV ($v = 0.05$ V/s) to 91 mV ($v = 0.5$ V/s), showing the effect of some uncompensated solution resistance). The rate constant of the heterogeneous electron transfer, $k_s = (3.0 \pm 0.5) \times 10^{-3}$ cm/s, was calculated by measurements of ΔE_p at different scan rates and use of the equation[22b,23]

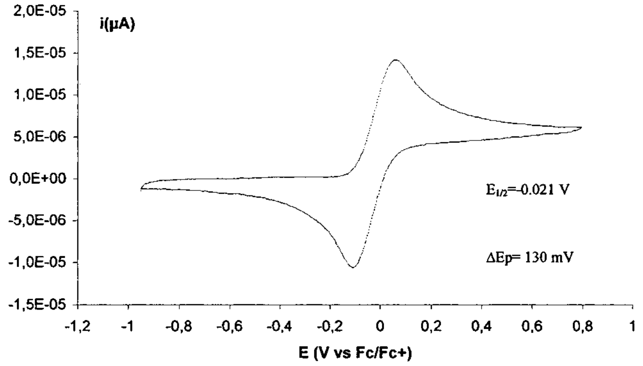

Figure 4. Cyclic voltammogram of **2d** in THF−[Bu$_4$N]-[PF$_6$] (glassy-carbon electrode, $v = 0.05$ V/s, $T = 25$ °C).

$$k_s = \psi(\pi a D)^{1/2}$$

where D is the diffusion coefficient of **2d**, $a = Fv/RT$, and ψ is a dimensionless parameter related to ΔE_p. For ΔE_p values outside the range reported by Nicholson,[23] ψ was calculated using the fact that ΔE_p vs log ψ is linear for ΔE_p values larger than ca. 170 mV.[23−25]

Mechanism of Formation of Complexes 2. The mechanism of formation of complexes **2** by thermal evolution of *cis*-(CO)$_4$Fe(CO$_2$R)$_2$ (**1**) remains unclear. The formation of the two "(CO)$_3$Fe(CO$_2$R)$_3$" patterns of **2** could, however, result from the particular mobility of the alkoxy groups of the alkoxycarbonyl ligands of **1**. This great mobility is evidenced by rapid exchanges between the alkoxy groups of **1** and alcohols.[6] We have already shown in a previous study that, for complexes **1**, these exchanges take place via an associative mechanism, which includes a nucleophilic addition of an alcohol on a terminal carbonyl of **1**, giving rise to trifunctionalized *fac*-[(CO)$_3$Fe(CO$_2$R)$_2$(CO$_2$R′)][H] intermediates which, after elimination of ROH, afford *cis*-(CO)$_4$Fe(CO$_2$R)(CO$_2$R′).[26] The same exchange occurs also between the alkoxy groups of different bis(alkoxycarbonyl)iron complexes. The formation of these *fac*-tris(alkoxycarbonyl) intermediates could then occur during

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(20) (a) Greatrex, R.; Greenwood, N. N. *Discuss. Faraday Soc.* **1969**, *47*, 126. (b) Greenwood, N. N.; Gibb, T. C. *Mössbauer Spectroscopy*; Chapman and Hall: London, 1971; p 223.

(21) Greenwood, N. N.; Gibb, T. C. *Mössbauer Spectroscopy*; Chapman and Hall: London, 1971; p 169.

(22) (a) The shape of the cyclic voltammograms (peak currents and peaks separation) was found to be critically dependent on the surface state of the vitreous carbon disk used throughout. Reproducible results were obtained, provided the disk was polished with a wet felt tissue before each individual CV scan. (b) The diffusion coefficients of the neutral and oxidized forms of the trimetallic compounds were assumed to be identical; the diffusion coefficient of the neutral species was obtained from potential-step experiments in which the potential was stepped at a value far beyond the anodic peak potential ($E_p{}^a = +500$ mV).

(23) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

(24) Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275.

(25) Tulyathan, B.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5960.

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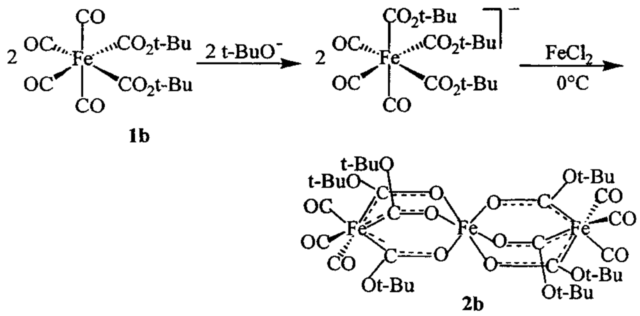
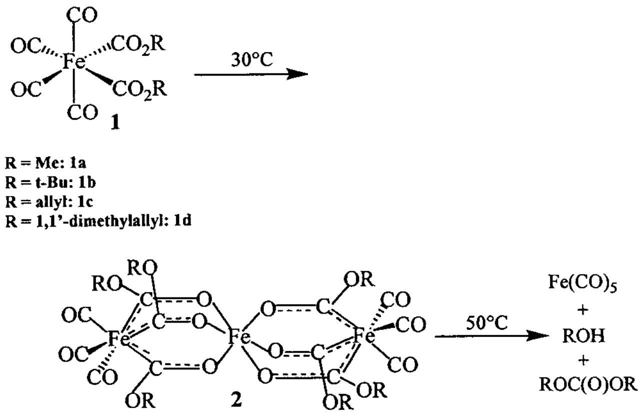
Scheme 1



Scheme 2



the thermolysis of **1** either by an intermolecular addition of an alkoxy group of a first molecule on a terminal carbonyl of a second molecule of **1** or by a partial decomposition of the complex, releasing RO^-, which could attack a terminal carbonyl of **1** still present in solution. Formation of **2** could result from a further reaction of these trifunctionalized intermediates with unidentified iron fragments. With the aim of clarifying the mechanism of formation of **2**, we performed the synthesis of the *fac*-tris(*tert*-butoxycarbonyl)tricarbonyliron anions by reacting complex **1b** (R = t-Bu) with t-BuOK.[7] The $[(CO)_3Fe(CO_2t\text{-}Bu)_3]^-$ anion thus formed was found to be stable as a potassium salt. It reacted rapidly at 0 °C with $^1/_2$ equiv of $FeCl_2$ to afford complex **2b** in good yield (74%) (see Scheme 1). This process, performed at low temperature, confirms the possible intervention of tris(alkoxycarbonyl) intermediates in the process of formation of **2** by thermal evolution of **1**.

The easy preparation of **2** also shows the potentiality of the anion $(CO)_3Fe(CO_2R)_3^-$, which has an isolobal analogy with $C_5H_5^-$.

Thermal Evolution of Complexes 2. As shown by IR monitoring, when they are thermolyzed at 50 °C in THF, complexes **2** undergo rapid evolutions. Analysis of the resulting reaction mixtures by IR, ^{13}C and ^1H NMR, and GC shows in each case the formation of $Fe(CO)_5$ (quantitative), alcohols (90%), and dialkyl carbonates (5%). No formation of oxalates, which would result from direct carbon−carbon couplings between two alkoxycarbonyl ligands, is observed, confirming that thermally induced carbon−carbon couplings between two ligands linked to a metal center by two sp^2 carbonyl carbons do not occur easily.[27] The nature of the alkoxy groups seems to have no influence on the course of the reaction. These results, similar to those already observed by thermolysis of the bis(alkoxycarbonyl) monomers **1**,[6] confirm that the thermal evolution of these latter complexes into alcohols and dialkyl carbonates occurs via the intermediate formation of complexes **2**, as shown in Scheme 2.

Conclusion

For the first time, thermolysis of *cis*-bis(alkoxycarbonyl) complexes has been found to give rise to the series of poly(alkoxycarbonyl) complexes $[(CO)_3Fe(\mu,\eta^2\text{-}CO_2R)_3]_2Fe$. These compounds display three metal centers and can be described as a central iron linked to two $(CO)_3Fe(CO_2R)_3$ groups by the oxygens of the carbonyls of the six alkoxycarbonyl groups of these ligands. As shown by ^1H and ^{13}C NMR, the new trimetallic complexes are paramagnetic and a Mössbauer study evidenced, at low temperature, a central high-spin iron atom and two low-spin lateral irons.

However, the mechanism of formation of these trimetallic complexes is not obvious. The $[(CO)_3Fe(CO_2R)_3]$ pattern of complexes **2** could be formed from $(CO)_4Fe(CO_2R)_2$ by an intermolecular nucleophilic addition of an alkoxy group of a first molecule of **1** on the terminal carbonyl of a second molecule of the same compound. This reaction, leading to **2**, would then display an associative mechanism analogous to that proposed to justify the alkoxy exchanges observed between *cis*-$(CO)_4Fe(CO_2R)_2$ complexes bearing different alkoxy groups.[27] The easy formation of **2** by reaction of $[(CO)_3Fe(CO_2R)_3][M]$ (M = Na, K) with $FeCl_2$ is also in good agreement with the possible intervention of trifunctionalized intermediates in the course of formation of **2** by thermal evolution of **1**. This study also shows that thermolysis of complexes **2** does not afford dialkyloxalates by a carbon−carbon coupling process between two of their alkoxycarbonyl ligands. Again, these results confirm the difficulty of performing the synthesis of double carbonyl chaining by carbon−carbon coupling between two carbonylated ligands and even bring up the question of the real intervention of bis(alkoxycarbonyl) intermediates in the course of catalytic processes, affording dialkyloxalates. Further experiments are in progress to obtain an answer to this question.

Experimental Section

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques, and all solvents were purified by distillation under an inert atmosphere from an appropriate drying agent.[28] Infrared spectra were obtained with a Perkin-Elmer 1430 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker AC 300 and AMX 3-400 spectrometers. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane in dichloromethane (external reference) (^1H) or from the solvent resonance as external reference (^{13}C). Gas chromatography studies were performed on a Hewlett-Packard 5890 instrument using a CP SIL 25 m capillary column. Magnetic measurements were carried out with a Gouy balance at room temperature. Magnetic moments were calculated following standard methods,[29]

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and corrections for underlying diamagnetism were applied to the data.[30] Elemental analyses were performed at the Centre de Microanalyses du CNRS at Lyon-Solaize, France. Complexes **1** were prepared as described in the literature.[6]

Preparation of the Complexes (CO)$_3$Fe(μ,η^2-CO$_2$R)$_3$Fe(μ,η^2-CO$_2$R)$_3$Fe(CO)$_3$ (2). General Procedure. Complexes **1** (4 mmol) dissolved in 25 mL of THF were stirred under argon at 30 °C. The reactions were monitored by IR. After disappearance of the ν(CO) bands of the starting complexes (ca. 15 h), the solvent was removed under reduced pressure. The remaining brown residue was extracted with two 25 mL portions of hexane (R = t-Bu (**2b**), allyl (**2c**), 1,1′-dimethylallyl (**2d**)) or with a 5/1 mixture of hexane and dichloromethane (2 × 25 mL) (R = Me, **2a**). After filtration and concentration of the solution, complexes **2** were obtained as pale yellow crystals after one night at −30 °C. IR and room-temperature ^{1}H and ^{13}C NMR data of **2a**−**d** are collected in Table 3.

2a (R = Me). Yield: 63% (1.74 g). Anal. Calcd for $C_{18}H_{18}Fe_3O_{18}$ (689.55): C, 31.32; H, 2.61. Found: C, 31.25; H, 2.67.

2b (R = t-Bu). Yield: 69% (2.60 g). Anal. Calcd for $C_{36}H_{54}Fe_3O_{18}$ (941.55): C, 45.88; H, 5.73. Found: C, 45.95; H, 5.79.

2c (R = Allyl). Yield: 73% (2.47 g). Anal. Calcd for $C_{30}H_{30}Fe_3O_{18}$ (846.10): C, 42.58; H, 3.55. Found: C, 42.51; H, 3.63.

2d (R = 1,1′-Dimethylallyl). Yield: 72% (2.91 g). Anal. Calcd for $C_{42}H_{54}Fe_3O_{18}$ (1013.55): C, 49.73; H, 5.33. Found: C, 49.65; H, 5.42.

NMR Studies of Complexes 2. We only report the details of the spectra obtained at different temperatures for **2d**. The resonances observed for this complex vs the temperature are reported in Figure 2 (^{1}H) or collected in Table 4 (^{13}C).

Determination of the Unpaired Electron Numbers. An average of 10 mg of complexes **2** in solution in 0.35 mL of CD_2Cl_2 + 5% of TMS was introduced under argon into an NMR tube together with a capillary tube containing a solution of CD_2Cl_2 and 5% of TMS. The difference (Δf in Hz) between the two ^{1}H TMS signals allowed the determination of the magnetic moment of the molecule by the Evans method. The chemical shift of the ^{1}H and ^{13}C signals of complexes **2** were obtained by the same method. They were measured using the resonance of the TMS in solution in CD_2Cl_2 contained in a capillary tube as external reference. For the ^{13}C resonances the use of TMS as internal reference did not induce an error exceeding 1.5 ppm.

X-ray Crystallography for 2c. Crystals suitable for X-ray diffraction studies were obtained from hexane at −30 °C. The data were collected on a CAD-4 Enraf-Nonius diffractometer. Calculations were performed on a Hewlett-Packard 9000-710 instrument for structure determination and on a digital Microwax 3100 computer with the MolEN package[31] for refinement and Ortep calculations. Crystal data collection and refinement parameters are collected in Table 1. The cell parameters were obtained by least-squares fitting of a set of 25 high-θ reflections. After Lorentz and polarization corrections, the structure was solved by direct methods with the program SHELX-86,[32] which located all the non-hydrogen atoms of the compound. After isotropic (R = 0.09) and then anisotropic refinement (R = 0.05), all the hydrogen atoms were set in theoretical positions. The whole structure was refined by full-matrix least-squares techniques (use of F magnitude; x, y, z, and β_{ij} for Fe, C, and O atoms and x, y, z fixed for H atoms; 78 variables and 912 observations). Atom scattering factors were obtained from ref 33.

Mössbauer Investigations Carried Out on 2a and 2d. The Mössbauer spectra were recorded on a constant-acceleration spectrometer, with a 50 mCi ^{57}Co source, giving a typical instrumental line width of 0.215 mm/s. Thin absorbers were prepared (~20 mg/cm^2), and the spectra were fitted by doublets of Lorentzian lines. Isomer shift data were referred to metallic iron at room temperature (also used for velocity calibration).

Magnetic Investigations. Using a MPS5 Design SQUID magnetometer, we investigated the temperature dependence of the magnetic properties of compounds **2a** and **2d**, a few milligrams of which were taken from the Mössbauer samples.

Electrochemistry. Electrochemical experiments were performed in deaerated solutions under an inert atmosphere (N_2 or Ar) using a Tacussel-Radiometer PJT 120 potentiostat connected via an IMT102 interface (Tacussel-Radiometer) to a PC computer running the VM2 software (Tacussel-Radiometer). The electrodes used were a vitreous carbon disk (working electrode) and either a carbon rod or a stainless steel wire as the secondary electrode. The reference electrode was a Ag/Ag$^+$ electrode. The potentials are referred to the Fc$^+$/Fc couple.

Preparation of 2b by Reaction of *fac*-[(CO)$_3$Fe(CO$_2$-t-Bu)$_3$][K] with FeCl$_2$. *fac*-[(CO)$_3$Fe(CO$_2$-t-Bu)$_3$][K] was prepared as described elsewhere[7] by nucleophilic addition of t-BuOK on a terminal carbonyl of **1b**.

Synthesis of 2b. To 0.5 mmol of *fac*-[(CO)$_3$Fe(CO$_2$-t-Bu)$_3$][K] (241 mg) in solution at 0 °C in 20 mL of THF was added 0.25 mmol of $FeCl_2$ (32 mg). The solution was left for 2 h at 0 °C with agitation before the solvent was removed. The residue was extracted with two 20 mL portions of of a hexane−dichloromethane mixture (4/1). After filtration the solution was kept for 15 h at −30 °C. The brown precipitate that formed was isolated by filtration (0.174 g; 74% yield).

Thermolysis of Complexes 2. General Method. A solution of 2 mmol of complex **2** in 30 mL of THF was heated with stirring for 6 h at 50 °C. The reaction mixture was then cooled to room temperature, and its composition was determined by gas chromatography analysis (CP SYL capillary column), by IR (Fe(CO)$_5$), and by ^{1}H and ^{13}C NMR (dialkyl carbonates).

Complex **2a** (R = Me; 1.4 g) was found to give rise to 2% of MeOC(O)OMe, 70% of MeOH, and 85% of Fe(CO)$_5$.

Compounds formed by thermolysis of **2b** (R = t-Bu; 1.9 g): t-BuOC(O)O-t-Bu, 5%; t-BuOH, 80%; Fe(CO)$_5$, 70%.

Compounds formed by thermolysis of **2c** (R = allyl; 1.7 g): $(CH_2{=}CHCH_2O)_2C(O)$, 3%; $CH_2{=}CH{-}CH_2{-}OH$, 70%; Fe(CO)$_5$, 65%.

Compounds formed by thermolysis of **2d** (R = 1,1′-dimethylallyl; 2 g): $(CH_2{=}CHC(CH_3)_2O)_2C(O)$, 3%; $CH_2{=}CHC(CH_3)_2{-}OH$, 70%; Fe(CO)$_5$, 75%.

Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, and bond distances and angles for complex **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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