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Study of the Nucleophilic Addition of Alcoholates on *cis*-Fe(R)(R′)(CO)$_3$L (R, R′ = Alkyl, Alkoxycarbonyl, Alkyloxalyl; L = CO, P(OEt)$_3$) and the First Characterization of a Tris(alkoxycarbonyl) Complex: K[Fe(CO$_2$tBu)$_3$(CO)$_3$]

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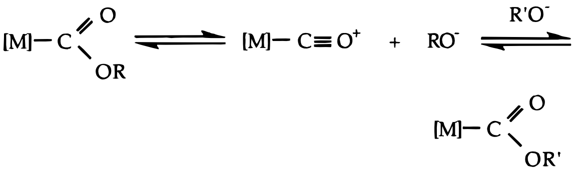
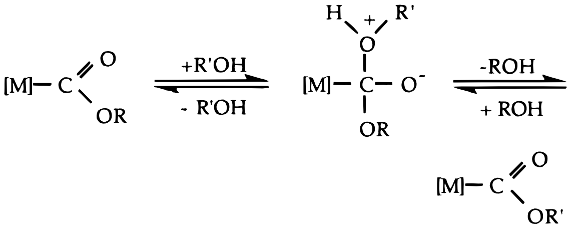
The nucleophilic additions of alcoholates (MeONa or tBuOK) on the complexes *cis*-Fe(R)(R′)(CO)$_3$L (R, R′ = CO$_2$Me, CO$_2$tBu, CH$_2$CO$_2$Me, COCO$_2$Me; L = CO, P(OEt)$_3$) occur at one terminal carbonyl ligand to give the new [Fe(R)(R′)(CO$_2$R″)(CO)$_2$L]$^-$ anions. No transesterification (*via* addition at an alkoxycarbonyl ligand) is observed. An X-ray diffraction study gives the space group $P2_1/c$ for K[Fe(CO$_2$tBu)$_3$(CO)$_3$] (resulting from the addition of KOtBu on Fe(CO$_2$tBu)$_2$(CO)$_4$), which is better described as the dimer K$_2$Fe$_2$(CO$_2$tBu)$_6$(CO)$_6$·H$_2$O·THF.

Introduction

Mono(alkoxycarbonyl) complexes, [M](CO$_2$R), have been extensively studied, since they are proposed as intermediates in several catalytic processes of carbonylation[1−3] and play an important role in the nucleophilic activation of carbon monoxide.[4] Bis(alkoxycarbonyl) complexes, [M](CO$_2$R)$_2$, are more scarce,[5−9] and hence their properties have been less studied. Intermediates of this type have been put forward in the catalytic process of carbonylation of alcohols into oxalates (M = Pd),[7] although no clear-cut thermal carbon-carbon coupling to give the oxalate has been observed so far from a well-characterized bis(alkoxycarbonyl) complex; however, this coupling may be induced by the action of oxidizing agents.[6,8a] So far, there is no known example of the tris(alkoxycarbonyl) complex [M](CO$_2$R)$_3$.



(1)



(2)

A common chemical feature of alkoxycarbonyl complexes is the great mobility of the alkoxy groups. Two mechanistic pathways, dissociative (eq 1) or associative (eq 2), may be considered, although in many cases it is not clear which of them is at work. The spontaneous dissociation of [M]−CO$_2$R into [M]−CO$^+$ and RO$^-$ has only been reported for solutions of FeCp(CO$_2$Me)(CO)PPh$_3$ in polar solvents,[10] and a dissociative mechanism has also been put forward for rhenium complexes.[11] However, other results are not in agreement with this mechanism and an addition−elimination route has been used to explain either the configurations of final products[12] or kinetic data.[13] Our own results obtained on the complexes Fe(CO$_2$R)$_2$(CO)$_3$L (L = CO, PR$_3$)[14] also strongly suggest an associative mechanism to account for the mobility of the alkoxy groups of their alkoxycarbonyl ligands: they are very labile in complexes with L = CO and are reluctant to any transesterification in their homologues with L = PR$_3$. Consequently, the

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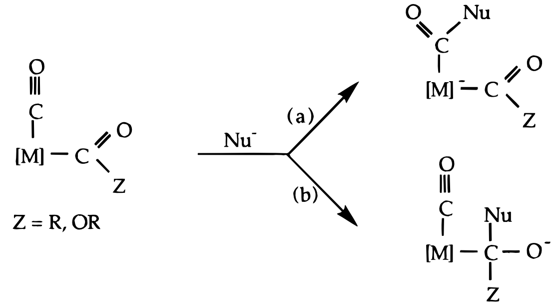
Scheme 1



addition of alcohol may occur before the departure of the alkoxy group.

If a complex bears both alkoxycarbonyl (or acyl) and terminal carbonyl ligands, the addition of a nucleophile may occur at any of the two ligands (Scheme 1). For COZ being acyl (Z = R), pathway (a) is observed in the example of reaction 3.[15,16] For COZ being alkoxycarbonyl (Z = OR), the unique following example shows a nucleophilic attack apparently according to pathway (a) (eq 4).[5b] When no terminal carbonyl is present, the nucleophilic attack on the COZ group (pathway (b)) has been observed (eq 5).[17]

$$M(COR)_x(CO)_yL_z + R'Li \rightarrow Li[M(COR)_x(COR')(CO)_{y-1}L_z] \quad (3)$$

$$Co(CO_2Me)(CO)_4 + CsOMe \rightarrow Cs[Co(CO_2Me)_2(CO)_3] \quad (4)$$

$$Re(CO_2Me)(NO)(indenyl)(PPh_3) \xrightarrow{MeMgBr} Re(COMe)(NO)(indenyl)(PPh_3) \quad (5)$$

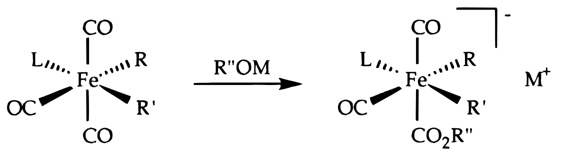
We describe in this paper the study of nucleophilic additions of alcoholates on the unique series of iron complexes *cis*-$Fe(R)(R')(CO)_3L$,[2,14,18] (R, R′ = alkyl, alkoxycarbonyl, alkyloxalyl; L = CO, $P(OEt)_3$) and the full structural characterization of the first tris(alkoxycarbonyl) complex $[M](CO_2R)_3$.

Results and Discussion

Synthesis and Spectroscopic Characterization of Complexes 7−15. The reaction of complexes **1**−**6** in solution in THF at −20 °C with an equimolar amount of alcoholate gives rise to monoanionic complexes **7**−**15** in quantitative yield. The formation of these anions is monitored either by IR or by ^{13}C NMR spectroscopy at low temperature. Their physical characteristics, displayed in Table 1, are very similar, which is indicative of comparable structures for the complexes formed.

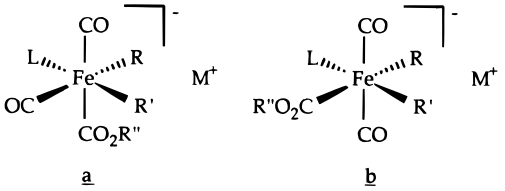
IR spectra of compounds **7**−**14**, which exhibit two bands for the three carbonyl ligands, suggest a C_{3v} symmetry. This geometry corresponds to the *fac* isomer which results from an attack of the alcoholate at a terminal carbonyl according to Scheme 2. The values of the IR frequencies fall between 2070 and 1980 cm^{-1}; they represent an energy decrease of ca. 50 cm^{-1} from the respective oscillators of the starting neutral complexes.[2,14,18] This trend is consistent with an increase of the negative charge on the metal. However, the electron density on iron is lower than that observed for the monosubstituted anionic iron complexes $[Fe(CO_2R)(CO)_4]^-$ (ν(C≡O) ~1910cm^{-1}).[19] This suggests a strong delocalization of the negative charge along the three electronwithdrawing carbonylated ligands of complexes **7**−**15**.

Scheme 2



1 → 7 R = R' = CO_2Me ; L = CO ; R" = Me ; M = Na
2 → 8 R = R' = CO_2tBu ; L = CO ; R" = tBu ; M = K
1 → 9 R = R' = CO_2Me ; L = CO ; R" = tBu ; M = K
2 → 10 R = R' = CO_2tBu ; L = CO ; R" = Me ; M = Na
1 → 11 R = R' = CO_2Me ; L = CO ; R" = Et ; M = Na
3 → 12 R = CO_2Me ; R' = CH_2CO_2Me; L = CO ; R" = Me ; M = Na
4 → 13 R = R' = CH_2CO_2Me ; L = CO ; R" = Me ; M = Na
5 → 14 R = CO_2Me ; R' = $COCO_2Me$; L = CO ; R" = Me ; M = Na
6 → 15 R = R' = CO_2Me ; L = $P(OEt)_3$; R" = Me ; M = Na

Chart 1



12 : R = $CO2Me$, R' = $CH2CO2Me$, R" = Me, L = CO
14 : R = $CO2Me$, R' = $COCO2Me$, R" = Me, L = CO

In ^{13}C NMR spectroscopy, the presence of only two signals in the spectra of **7** and **8** confirms the *fac* structure attributed to these compounds, which possess three equivalent terminal carbonyls and three equivalent alkoxycarbonyl ligands.

There is also no ambiguity for the *fac* structure of complexes **9**−**11** and **13**, prepared by addition of an alcoholate on symmetrical neutral complexes (R = R′), since they exhibit only one signal for R and R′.

Complexes **12** and **14** are obtained by addition of alcoholates on unsymmetrical complexes (R ≠ R′). Two geometries (Chart 1) agree with the ^{13}C NMR spectra of the anions so formed (one signal for the two alkoxycarbonyl ligands and two signals for the terminal carbonyls). However, structure *b* can be ruled out, since it has a C_{2v} symmetry which would require the presence of three ν(C≡O) bands in the IR. Only the geometry a attributed to complex **15** (Chart 1, R = R′ = CO_2Me, R″ = Me, L = $P(OEt)_3$) remains uncertain. However, *b*, which displays two electronwithdrawing ligands in *trans* positions is electronically disadvantaged and its formation is unlikely.

By comparison with the neutral starting compounds, the ^{13}C signals of the anionic complexes are shifted

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Table 1. Spectroscopic Data for Complexes 7−15

			NMR (THF-d_8,[a] −20 °C) δ, ppm			
			^{13}C			
starting complex	anionic complex formed	IR (hexane ν(CO)	CO	$\mathit{C}\mathrm{O_2R}$	$\mathrm{CO_2}\mathit{R}$	^{1}H
$Fe(CO2Me)_2(CO)_4$ (**1**)	$Na[Fe(CO_2Me)_3(CO_3]$ (**7**)	2070 (s) 2000 (s) 1680 (m)	209.6	212.5	49.8	3.42 (s)
$Fe(CO_2tBu)_2(CO)_4$ (**2**)	$K[Fe(CO_2tBu)_3(CO_3]$ (**8**)	2065 (s) 1990 (s) 1670 (s)	209.4	214.25	78.2 28.2	1.34 (s)
$Fe(CO_2Me)_2(CO)_4$ (**1**)	$K[Fe(CO_2Me)_2$-$(CO_2tBu)(CO)_3]$ (**4**)	2060 (m) 1995 (s) 1665 (s)	210.1(2) 209.9(1)	212.9(2) 210.5(1)	78.0 50.0 29.3	1.35 (s, 9H) 3.48 (s, 6H)
$Fe(CO_2tBu)_2(CO)_4$ (**2**)	$Na[Fe(CO_2Me)$-$(CO_2tBu)_2(CO)_3]$ (**10**)	2063 (m) 1990 (s) 1675 (s)	210.8(1) 210.5(2)	212.5(1) 211.4(2)	77.9 49.8 29.3	1.40 (s, 18H) 3.40 (s, 3H)
$Fe(CO_2Me)_2(CO)_4$ (**1**)	$Na[Fe(CO_2Me)_2$-$(CO_2Et)(CO)_3]$ (**11**)	2065 (m) 1995 (s) 1670 (s)	210.3(1) 210.1(2)	210.8(1) 210.2(2)	58.6 50.2 15.3	4.21 (q, $J = 7$ Hz, 2H) 3.45 (s, 6H) 1.45 (t, $J = 7$ Hz, 3H)
$Fe(C)_2Me)(CH_2$-$CO_2Me)(CO)_4$ (**3**)	$Na[Fe(CO_2Me)_2(CH_2$-$CO_2Me)(CO)_3]$ (**12**)	2065 (s) 1980 (s) 1685 (m) 1645 (m)	211.2(2)[b] 210.4(1)	215.7(2) 185.8(1)	50.6(1) 50.5(2)	3.37 (s, 6H) 3.34 (s, 3H) 1.39 (s, 2H)
$Fe(CH_2CO_2$-$Me)_2(CO)_4$ (**4**)	$Na[Fe(CO_2Me)(CH_2$-$CO_2Me)_2(CO)_3]$ (**13**)	2065 (s) 1980 (s) 1665 (br)	212.7(1)[c] 212.2(2)	216.9(1) 185.2(2)	50.6(1) 50.2(2)	3.57 (s, 6H) 3.55 (s, 3H) 1.66 (s, 4H)
$Fe(CO_2Me)(CO$-$CO_2Me)(CO)_4$ (**5**)	$Na[Fe(CO_2Me)_2(CO$-$CO_2Me)(CO)_3]$ (**14**)	2070 (s) 2005 (s) 1660 (br)	209.9(1)[d] 209.0(2)	210.6(2) 168.6(1)	51.2(2) 50.2(1)	3.45 (s, 6H) 3.34 (s, 3H)
$Fe(CO_2Me)_2(CO)_3$-$(P(OEt)_3)$ (**6**)	$Na[Fe(CO_2Me)_3(CO)_2$-$(P(OEt)_3)]$ (**15**)	2085 (m) 2010 (s) 1685 (m) 1645 (br)	213.0 (d, $J = 19.2$ Hz)[e]	220.6 (2, d, $J = 40.3$ Hz) 217.5 (1, d, $J = 68.2$ Hz)	49.7(1) 49.1(2)	3.41 (s, 3H) 3.35 (s, 6H)

[a] When NMR spectra of compounds **7**−**15** are run a solvent other than THF-d_8, the presence of THF and H_2O is detected. ^{1}H NMR integrations show one molecule of THF and one molecule of H_2O per two molecules of complexes **7**−**15**. [b] ^{13}C Fe−$\mathit{C}H_2$: 15.7 ppm. [c] ^{13}C Fe−$\mathit{C}H_2$: 18.6 ppm. [d] ^{13}C Fe−$\mathit{C}OCO_2R$: 259.9 ppm. [e] $P(OEt)_3$: ^{13}C, 61.1 ppm (d, $J = 5.5$ Hz), 16.2 ppm (d, $J = 5.7$ ppm); ^{31}P, 167 ppm; ^{1}H, 4.02 ppm (dq, $J_{P-H} = J_{H-H} = 7$ Hz, 6H), 1.27 ppm (t, $J_{H-H} = 7$ Hz, 9H).

toward the lower fields of about 10 ppm for the terminal CO and 20 ppm for the carbon of the CO_2R ligand. These results, which are consistent with the anionic structure attributed to the compounds **7**−**15**, might reflect, in agreement with the IR results, an increase of the electron density mainly located on the alkoxycarbonyl ligands.

It is noteworthy that the ^{13}C chemical shifts observed for the terminal carbonyls of complexes **7**−**15** fall between the values observed for the neutral starting complexes **1**−**6** (∼200 ppm)[2,14,18] and those of $[Fe(CO_2R)(CO)_4]^-$ (∼220 ppm).[14] Due to the delocalization of the negative charge on their three alkoxycarbonyl ligands, complexes **7**−**15** present electron densities of the metal center intermediate between those observed for neutral and for monosubstituted anionic compounds.

X-ray Crystal Structure of 8. The stucture of $K[Fe(CO_2tBu)_3(CO)_3]$ **8** determined by X-ray crystallography confirms the *fac* geometry attributed to this compound. Suitable crystals for X-ray analyses are obtained by recrystallization from hexane at −30 °C. The structural analyses have been carried out on the basis of the $P2_1/c$ group. Refinement leads to the final values of $R = 0.072$ and $R_w = 0.066$.

The complex can be described as a dimer including two $Fe(CO_2tBu)_3(CO)_3$ entities, two different potassium atoms, one molecule of THF (reaction solvent), and one molecule of water (probably coming from reaction solvents). The presence of these last two molecules has already been confirmed by ^{1}H or ^{13}C NMR spectroscopy (Table 1). As the solvent of crystallization is hexane, THF and H_2O can be considered as real ligands. Relevant bond lengths and bond angles are given in Tables 2 and 3 and Figure 1 shows the ORTEP drawing of the complex.

Table 2. Selected Bond Distances (Å) in Complex 8 (Estimated Standard Deviations in Parentheses)

Fe1−C1	1.77(1)	K1−O6	2.685(9)	C4−O5	1.37(1)
Fe1−C2	1.80(1)	K1−O8	2.67(1)	C9−O6	1.22(1)
Fe1−C3	1.83(2)	K1−O26	2.744(9)	C9−O7	1.37(1)
Fe1−C4	2.00(1)	K1−O28	2.788(9)	C14−O8	1.21(1)
Fe1−C9	1.98(1)	K1−O50	2.75(2)	C14−O9	1.36(1)
Fe1−C14	2.01(1)	K2−O4	2.780(9)	C21−O21	1.16(1)
Fe2−C21	1.79(1)	K2−O6	2.79(1)	C22−O22	1.14(1)
Fe2−C22	1.82(1)	K2−O24	2.66(1)	C23−O23	1.13(2)
Fe2−C23	1.81(2)	K2−O26	2.66(1)	C24−O24	1.23(1)
Fe2−C24	2.01(1)	K2−O30	2.70(2)	C24−O25	1.35(2)
Fe2−C29	1.99(1)	C1−O1	1.16(2)	C29−O26	1.21(1)
Fe2−C34	1.97(1)	C2−O2	1.15(1)	C29−O27	1.39(1)
		C3−O3	1.12(1)	C34−O28	1.24(1)
		C4−O4	1.21(1)	C34−O29	1.37(1)

The crystal structure study reveals that the iron metal atom is surrounded in a distorted-octahedral fashion by three terminal carbonyl and three alkoxycarbonyl ligands. The *fac* structure of the complex is confirmed by the angle values between these ligands (Table 3). The parameters inducing the observed differences between these angles are not obvious. This structure may be compared with that of the triacylmetalate complex of boron $BCl[\mathit{fac}\text{-}Re(COMe)_3(CO)_3]$.[20]

Bond lengths between terminal CO ligands and the metal center (from 1.77 to 1.83 Å) fall within the range

Table 3. Selected Bond Angles (deg) in Complex 8 (Estimated Standard Deviations in Parentheses)

C1–Fe1–C2	99.4(6)	C21–Fe2–C24	90.3(6)	O8–K1–O26	137.2(3)
C1–Fe1–C3	97.6(6)	C21–Fe2–C29	88.0(5)	O8–K1–O28	142.9(3)
C1–Fe1–C4	85.9(5)	C21–Fe2–C34	173.4(6)	O8–K1–O50	90.0(5)
C1–Fe1–C9	87.2(6)	C22–Fe2–C23	98.4(6)	O26–K1–O28	63.1(3)
C1–Fe1–C14	168.4(6)	C22–Fe2–C24	88.5(5)	O26–K1–O50	111.3(4)
C2–Fe1–C3	88.3(6)	C22–Fe2–C29	176.0(5)	O28–K1–O50	112.2(4)
C2–Fe1–C4	89.8(6)	C22–Fe2–C34	88.8(6)	O4–K2–O6	62.8(2)
C2–Fe1–C9	173.4(6)	C23–Fe2–C24	169.2(6)	O4–K2–O24	141.5(3)
C2–Fe1–C14	88.2(5)	C23–Fe2–C29	85.5(6)	O4–K2–O26	103.3(3)
C3–Fe1–C4	176.3(6)	C23–Fe2–C34	88.6(5)	O4–K2–O30	113.2(4)
C3–Fe1–C9	89.8(6)	C24–Fe2–C29	87.8(5)	O6–K2–O24	137.5(3)
C3–Fe1–C14	91.4(6)	C24–Fe2–C34	83.1(5)	O6–K2–O26	71.9(3)
C4–Fe1–C9	91.7(5)	C29–Fe2–C34	92.1(5)	O6–K2–O30	109.3(4)
C4–Fe1–C14	85.4(5)	O6–K1–O8	68.4(3)	O24–K2–O26	68.4(3)
C9–Fe1–C14	85.5(5)	O6–K1–O26	72.2(3)	O24–K2–O30	91.7(4)
C21–Fe2–C22	90.7(6)	O6–K1–O28	103.7(3)	O26–K2–O30	139.3(4)
C21–Fe2–C23	97.9(6)	O6–K1–O50	141.2(5)		

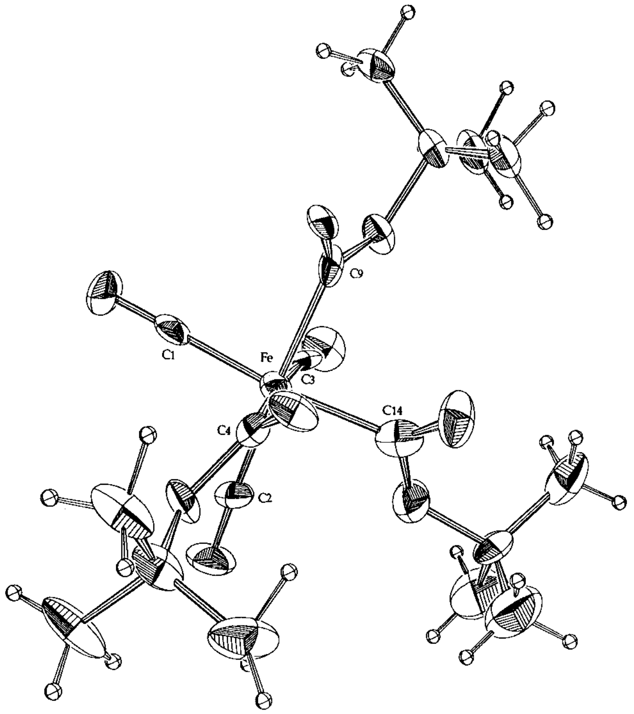

Figure 1. ORTEP drawing of **8** (thermal ellipsoids at the 50% level).

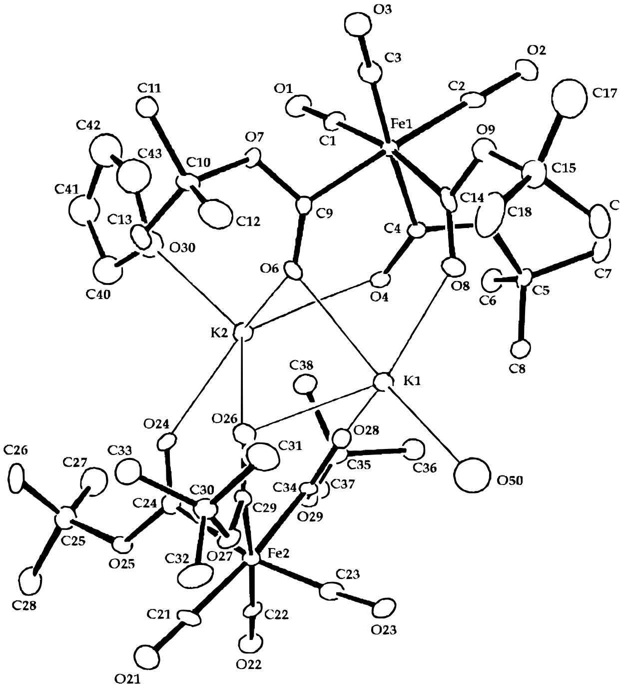

Figure 2. View of $K_2[Fe(CO_2tBu)_3(CO)_3]_2 \cdot H_2O \cdot THF$ showing the atom-labeling scheme. Thermal ellipsoids are scaled to the 50% probability level.

of similar bonds of the neutral bis(alkoxycarbonyl)iron complex $[Fe(CO_2tBu)_2(CO)_4]$[21] but are slightly shorter than the values reported for the iron anion $[Fe(COCOtBu)(CO)_4]^-$.[22] These data again suggest a rather low electron density on the metal. Distances between the metal and its alkoxycarbonyl ligands (2.00 Å) and also the lengths of the C=O bonds of these ligands (1.21 Å) are normal.[21] These results support that the bonding framework is largely σ for Fe–C whereas the C=O bonds have a large additional π component. These alkoxycarbonyl ligands present no carbenoid character, which would be indicated by a lengthening of C–O bonds up to 1.335 Å.[23] Surprisingly, in contrast with the results observed for $Cs[Co(CO_2Me)_2(CO)_3]$,[5b] which presents two different alkoxycarbonyls (one bound to the cesium atom by the oxygen of its carbonyl (C–O distance 1.24 Å) and the second having no interaction with the cation (C–O length 1.21 Å)), the three alkoxycarbonyls of our complex are very similar. The structure displayed on Figure 2 helps in understanding these observations.

As we have already said, the molecule can be described as a dimer including two $[Fe(CO_2tBu)_3(CO)_3]$ entities, two different potassium atoms, one molecule of water, and one molecule of THF. Each potassium is surrounded by five oxygenated ligands: four alkoxycarbonyls and either H_2O (K1) or THF (K2). K1 interacts with two alkoxycarbonyl ligands of Fe1 *via* the oxygens of their carbonyl groups (K–O distances 2.685, 2.67 Å) and in the same way with two alkoxycarbonyls of Fe2 but with slightly longer K–O distances (2.744, 2.788 Å). The reverse situation is observed for K2: stronger interactions with two alkoxycarbonyl ligands linked to Fe2 and weaker ones with these ligands bound to Fe1. In each $[Fe(CO_2tBu)_3(CO)_3]$ entity one alkoxycarbonyl is bound to K1, another is bound to K2, and the last one interacts with both K1 and K2.

Mechanism of Formation of Complexes 7–15. We have shown that the final products of the reaction

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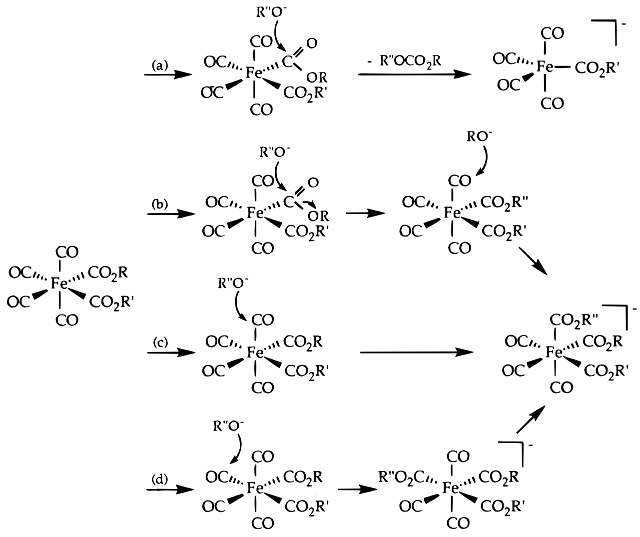
Table 4. Crystal Data and Structure Refinement for 8

formula	$(FeC_{18}H_{27}O_9)2\cdot H_2O\cdot C_4H_8O$
mol wt	1036.83
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	12.318(5)
b, Å	22.273(9)
c, Å	21.670(9)
β, deg	102.47(4)
V, Å^3	5805(3)
Z	4
ρ_{calc} g cm^{-3}	1.189
$F(000)$	2176
μ(Mo Kα), cm^{-1}	6.99
T, (K)	120
cryst size, mm	0.25 × 0.25 × 0.45
radiation	Mo Kα
max 2θ, (deg)	50
range of hkl	0−13; 0−23; −24 to +24
no. of rflns meas	8567
no. of rflns obs ($I > \sigma(I)$)	3602 (3σ)
R_{int} (from merging equiv rflns)	0.022
N(obs)/N(var)	3602/548
R	0.072
R_w^{a}	0.066
S_w	3.8
max residual, e Å^{-3}	0.75
Δ/σ	0.05

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

of alcoholate with *cis*-bis-substituted iron complexes have a *fac* geometry. These complexes result formally from a nucleophilic attack at a terminal CO in an axial position, although a preliminary attack on the alkoxycarbonyl ligand is also conceivable (see Introduction). Scheme 3 shows different pathways for the reaction of an alcoholate with a *cis*-bis(alkoxycarbonyl)tetracarbonyliron complex.

Scheme 3



In reaction paths (a) and (b), the addition of the alcoholate occurs on the carbonyl of one alkoxycarbonyl ligand. According to path (a), this addition is followed by a rapid elimination of dialkyl carbonate and by the formation of $[Fe(CO_2R)(CO)_4]^-$. This assumption is easily dismissed, since the formation of the monoalkoxycarbonylated anion would be immediately detected by IR spectroscopy (ν(CO) 1910 cm^{-1}).[19] In path (b), the nucleophilic addition of R″O$^-$ at one alkoxycarbonyl ligand induces a rapid elimination of RO$^-$, which, after addition on a terminal carbonyl, gives rise to the tris(alkoxycarbonyl)anion. However, when R″ ≠ R′ = R (preparation of **9−11**) this reaction pathway should

Table 5. Atomic Coordinates and B_{eq} Values and Their Estimated Standard Deviations for Complex 8

atom	x	y	z	B_{eq} (Å^2)	atom	x	y	z	B_{eq} (Å^2)
Fe1	0.8994(1)	0.19732(8)	0.42553(8)	2.00(3)	C9	0.9541(9)	0.2113(5)	0.3477(5)	1.9(3)
Fe2	0.4684(1)	0.08992(8)	0.31734(8)	1.96(3)	C10	0.891(1)	0.2559(6)	0.2402(6)	3.2(9)
K1	0.2462(2)	0.2002(1)	0.4182(1)	2.75(6)	C11	0.771(1)	0.2679(8)	0.2044(6)	4.9(4)
K2	0.1125(2)	0.4061(1)	0.8096(1)	2.56(6)	C12	0.952(1)	0.3145(7)	0.2553(7)	5.1(4)
O1	0.7850(7)	0.0917(4)	0.3617(4)	3.5(2)	C13	0.949(1)	0.2131(7)	0.2049(6)	4.4(4)
O2	0.8258(7)	0.1936(5)	0.5465(4)	3.7(2)	C14	0.004(1)	0.2626(6)	0.4635(5)	2.6(3)
O3	0.7190(7)	0.2850(4)	0.3823(4)	3.8(2)	C15	0.006(1)	0.3614(6)	0.5154(7)	3.6(3)
O4	0.0823(6)	0.3862(3)	0.9314(4)	2.2(2)	C16	0.093(1)	0.3430(7)	0.5437(7)	4.5(4)
O5	0.0372(6)	0.3634(4)	1.0235(4)	2.5(2)	C17	−0.084(2)	0.3947(7)	0.5370(9)	7.3(6)
O6	1.0477(6)	0.2089(4)	0.3379(4)	2.7(2)	C18	0.055(2)	0.3966(8)	0.4712(8)	7.1(5)
O7	0.8710(6)	0.2303(4)	0.2988(4)	2.7(2)	C21	0.5389(9)	0.1152(6)	0.2579(6)	2.8(3)
O8	0.1033(7)	0.2649(4)	0.4672(4)	3.5(2)	C22	0.5516(9)	0.0215(5)	0.3284(6)	2.3(3)
O9	−0.0507(7)	0.3085(4)	0.4847(4)	3.4(2)	C23	0.547(1)	0.1326(5)	0.3828(6)	2.6(3)
O21	0.5849(8)	0.1293(5)	0.2189(4)	4.2(2)	C24	0.356(1)	0.45356)	0.7512(6)	2.6(3)
O22	0.6058(7)	−0.0202(4)	0.3325(4)	3.3(2)	C25	0.342(1)	0.5258(6)	0.6636(7)	3.7(3)
O23	0.5905(7)	0.1607(4)	0.4245(4)	3.2(2)	C26	0.261(1)	0.4889(8)	0.6157(7)	4.9(4)
O24	0.2550(6)	0.4549(4)	0.7477(4)	2.7(2)	C27	0.289(1)	0.5731(7)	0.6946(8)	5.4(4)
O25	0.4039(6)	0.4843(4)	0.7106(4)	3.0(2)	C28	0.430(1)	0.5509(8)	0.6333(7)	6.3(4)
O26	0.2748(7)	0.1699(4)	0.2999(4)	2.8(2)	C29	0.3722(9)	0.1625(5)	0.2995(5)	1.9(3)
O27	0.4311(6)	0.2097(4)	0.2806(4)	2.6(2)	C30	0.379(1)	0.2658(6)	0.2524(6)	2.8(3)
O28	0.3131(6)	0.0827(4)	0.4014(4)	2.5(2)	C31	0.320(1)	0.2982(7)	0.2970(8)	5.3(4)
O29	0.3957(6)	−0.0034(3)	0.3845(4)	2.3(2)	C32	0.474(1)	0.3002(8)	0.2391(8)	5.1(4)
O30	1.061(1)	0.5378(7)	0.2655(7)	4.7(3)*	C33	0.297(1)	0.2463(7)	0.1898(7)	4.8(4)
O50	0.4190(2)	0.2300(9)	0.9814(9)	8.4(5)*	C34	0.3797(9)	0.0571(5)	0.3748(5)	1.9(3)
C1	0.8289(9)	0.1336(5)	0.3875(6)	2.3(3)	C35	0.333(1)	−0.0428(5)	0.4176(6)	2.7(3)
C2	0.8540(9)	0.1930(5)	0.4995(6)	2.4(3)	C36	0.354(1)	−0.0269(6)	0.4871(6)	3.3(3)
C3	0.787(1)	0.2519(6)	0.3986(6)	2.9(3)	C37	0.379(1)	−0.1040(6)	0.4089(7)	4.0(3)
C4	0.0236(9)	0.3587(5)	0.9595(5)	1.9(3)	C38	0.208(1)	−0.0386(6)	0.3876(7)	3.4(3)
C5	0.130(1)	0.3981(6)	1.0636(5)	2.6(3)	C40	1.041(2)	0.486(1)	0.298(1)	6.2(6)*
C6	0.116(1)	0.4640(6)	1.0482(6)	3.2(3)	C41	1.149(2)	0.455(1)	0.316(1)	6.9(7)*
C7	0.113(1)	0.3844(7)	1.1292(6)	3.8(3)	C42	1.228(2)	0.495(1)	0.300(1)	8.0(8)*
C8	0.240(1)	0.3722(6)	1.0543(6)	2.7(3)	C43	1.170(2)	0.548(1)	0.281(1)	8.3(8)*

[a] Estimated standard deviation are in parentheses. Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2(B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(1,3)]$.

induce the formation of a complex mixture of products composed of $[Fe(CO_2R)_3(CO)_3]^-$, $[Fe(CO_2R)_2(CO_2R'')(CO)_3]^-$, $[Fe(CO_2R)(CO_2R'')_2(CO)_3]^-$, and $[Fe(CO_2R'')_3(CO)_3]^-$. The formation of $[Fe(CO_2R)_2(CO_2R'')(CO)_3]^-$ as the only product of the reaction makes mechanism (b) highly unlikely.

In paths (c) and (d) the addition of the alcoholate occurs on a terminal carbonyl. Path (c) represents the most likely route, as it induces directly the formation of the *fac* anion. However, path (d) cannot be ruled out, since the equatorial terminal carbonyls *trans* to strongly electronwithdrawing ligands are thought to be more electrophilic than the axial ones. The reaction would require a fast isomerization of the *mer* compound so formed into its *fac* homologue. A careful monitoring of the reaction at low temperature has never allowed us to detect the transient formation of the *mer* isomer. It is, however, noteworthy that for octahedral carbonyl complexes, the isomers which display two electronwithdrawing carbonylated ligands (acyl, alkoxycarbonyl, ...) in *trans* positions have, to our knowledge, never been described.

Formation of the pure $[Fe(CO_2R)_2(CO_2R'')(CO)_3]^-$ complex is indicative of an absence of direct exchanges between the alkoxy groups of our anionic compounds and alcoholates. This property has been checked on well-isolated anions.

Conclusion

We have shown that, whatever the cis R and R′ substituents of $Fe(R)(R')(CO)_4$ complexes are, the nucleophilic additions of an alcoholate selectively occur on a terminal carbonyl ligand to give an original series of *fac*-tris(carbonylated ligand)tricarbonyliron anions, $[Fe(R)(R')(CO_2R'')(CO)_3]^-$. Particularly noteworthy is the full characterization of the first tris(alkoxycarbonyl) complex, $K[Fe(CO_2tBu)_3(CO)_3]$.

Experimental Section

All manipulations were performed under an atmosphere of nitrogen or argon with standard Schlenk techniques, and all solvents were distilled under an inert atmosphere from an appropriate drying agent.[24]

Infrared spectra were recorded in hexane on a Perkin-Elmer 1430 spectrophotometer. The ^1H (300 MHz) and the ^{13}C (75.47 MHz) NMR spectra were obtained on a Bruker AC300 spectrometer with chemical shifts reported in δ values relative to residual protonated solvent (^1H) or to the solvent resonance (^{13}C). The ^{31}P (40.27 MHz) NMR spectra were recorded on a JEOL FX100 spectrometer using 87% H_3PO_4 as an external standard.

Elemental analyses were performed by the Center de Microanalyses du CNRS.

The neutral starting complexes were prepared according to literature procedures: **1**,[14] **2**,[21] **3** and **4**,[2] **5**,[18] and **6**.[25] Other reagents were obtained from commercial sources and used without purification.

General Procedure for the Preparation of Anionic Compounds: $M[Fe(R)(R')(CO_2R'')(CO)_2(L)]$. To 1.50 mmol of $Fe(R)(R')(CO)_3(L)$ dissolved in 20 mL of THF at −20 °C was added dropwise a solution ($R'' = tBu$, $M = K$) or a suspension ($R'' = Me$, Et, $M = Na$) of R″OM in 5 mL of THF. The resulting mixture was stirred for an additional 1 h before being warmed to room temperature. Monitoring of the reaction by IR spectroscopy indicated the quantitative formation of anionic species.

The solvent was removed under reduced pressure, and the residue was taken up with hexane (90%) and CH_2Cl_2 (10%). These anions were recrystallized from this mixture of solvents at −30 °C and obtained as pale yellow microcrystals.

Analyses of compounds **7**−**15** are in good agreement with the presence of one molecule of THF and one molecule of H_2O per two molecules of complex. Yields are given after recrystallization.

7: $[Fe(CO_2Me)_3(CO)_3]Na\cdot{}^1/_2THF\cdot{}^1/_2H_2O$. Anal. Calcd for $C_{11}H_{14}FeNaO_{10}$: C, 34.30; H, 3.64. Found: C, 34.88; H, 3.75. Yield: 75%.

8: $[Fe(CO_2tBu)_3(CO)_3]K\cdot{}^1/_2THF\cdot{}^1/_2H_2O$. Anal. Calcd for $C_{20}H_{32}FeKO_{10}$: C, 45.54; H, 6.07. Found: C, 45.75; H, 6.21. Yield: 70%.

9: $[Fe(CO_2Me)_2(CO_2tBu)(CO)_3]K\cdot{}^1/_2THF\cdot{}^1/_2H_2O$. Anal. Calcd for $C_{14}H_{20}FeKO_{10}$: C, 37.92; H, 4.51. Found: C, 38.33; H, 4.53. Yield: 75%.

10: $[Fe(CO_2Me)(CO_2tBu)_2(CO)_3]Na\cdot{}^1/_2THF\cdot{}^1/_2H_2O$. Anal. Calcd for $C_{17}H_{26}FeNaO_{10}$: C, 43.51; H, 5.54. Found: C, 43.65; H, 5.48. Yield: 70%.

11: $[Fe(CO_2Me)_2(CO_2Et)(CO)_3]Na\cdot{}^1/_2THF\cdot{}^1/_2H_2O$. Anal. Calcd for $C_{12}H_{16}FeNaO_{10}$: C, 36.09; H, 4.01. Found: C, 36.22; H, 4.02. Yield: 65%.

12: $[Fe(CO_2Me)_2(CH_2CO_2Me)(CO)_3]Na\cdot{}^1/_2THF\cdot{}^1/_2H_2O$. Anal. Calcd for $C_{12}H_{16}FeNaO_{10}$: C, 36.09; H, 4.01. Found: C, 36.15; H, 4.22. Yield: 75%.

13: $[Fe(CO_2Me)(CH_2CO_2Me)_2(CO)_3]Na\cdot{}^1/_2THF\cdot{}^1/_2H_2O$. Anal. Calcd for $C_{13}H_{18}FeNaO_{10}$: C, 37.78; H, 4.36. Found: C, 38.12; H, 4.32. Yield: 80%.

14: $[Fe(CO_2Me)_2(COCO_2Me)(CO)_3]Na\cdot{}^1/_2THF\cdot{}^1/_2H_2O$. Anal. Calcd for $C_{12}H_{14}FeNaO_{11}$: C, 34.87; H, 3.39. Found: C, 35.15; H, 3.45. Yield: 60%.

15: $[Fe(CO_2Me)_3(P(OEt)_3)(CO)_2]Na\cdot{}^1/_2THF\cdot{}^1/_2H_2O$. Anal. Calcd for $C_{16}H_{29}FeNaO_{12}P$: C, 36.71; H, 5.54. Found: C, 36.75; H, 5.57. Yield: 55%.

Crystal Structure Analysis for $[Fe(CO_2tBu)_3(CO)_3]K\cdot{}^1/_2THF\cdot{}^1/_2H_2O$ (8). Crystals suitable for single-crystal X-ray diffraction studies were obtained from hexane at −30 °C. The data were collected on a CAD-4 Enraf-Nonius diffractometer with graphite-monochromated MoKα radiation. Tables 4 and 5 give the experimental data for the crystal structure of **8**. The unit cell parameters are determined by least-squares fitting of a set of 25 high-θ reflections. After Lorentz and polarization corrections, the structure was solved with direct methods, scale factor refinement, and Fourier differences. After isotropic ($R = 0.115$) and then anisotropic refinements ($R = 0.09$) the hydrogens were located with a difference Fourier map. The entire structure was refined by full-matrix least-squares techniques. Atomic scattering factors were taken from ref 26. All calculations were performed on a digital Microvax 3100 computer with the MolEN package (Enraf-Nonius, 1990).

Supporting Information Available: Tables of all bond lengths and bond angles, hydrogen atom coordinates, and anisotropic thermal parameters for **8** (16 pages). Ordering information is given on any current masthead page.

OM950255Z

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