Chain–ring isomerism *vs.* carbon–carbon coupling on two (tetracarbonyliron)-γ-ketoesters: *cis*-[Fe(COR)(COCOR′)(CO)$_4$] (R = Me, R′ = OMe; R = OMe, R′ = Me)

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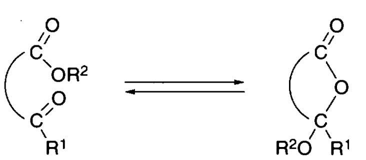
Ferra-γ-ketoesters 1 and 2 induce thermally either a carbon–carbon coupling process or a chain–ring isomerization; the orientation of the reaction likely depends on the proximity of the ester group to the metal centre.

Ring–chain isomeric interconversion of bifunctional organic compounds has attracted considerable interest.[1] In particular, the acid or base catalysed formation of alkoxylactones from γ-ketoesters is well documented (Scheme 1).

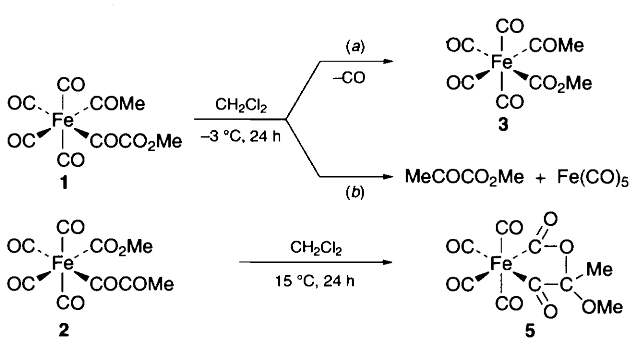
Surprisingly, to our knowledge, this isomerization has no organometallic counterpart since the few metalla-γ-ketoesters which possess a metal inserted in the fragment connecting the two carbonylated groups were not found to induce such a process.[2]

Herein we report the syntheses of two isomeric ferra-γ-ketoesters **1** and **2** and the study of their ability to isomerize into alkoxymetallalactones. **1** and **2** were obtained in 55% yield by treatment of the appropriate ferrate M[Fe(COR)(CO)$_4$][3] with 1 equiv. of ClCOCOR′.† They were fully characterized by IR and ^{13}C NMR spectroscopy.‡ At −3 °C, **1** reacted slowly according to two different processes (Scheme 2).

The first reaction [path (*a*)] produced a new complex, *cis*-[Fe(CO$_2$Me)(COMe)(CO)$_4$] **3**, formed by a decarbonylation of the alkyloxalyl ligand. This compound which was fully identified by IR and NMR‡ was also obtained in low yield (15%) by reaction of 1 equiv. of CH$_3$COCl with Na[Fe(CO$_2$Me)(CO)$_4$]. The second process [path (*b*)] which accounted for 35% of the whole transformation of **1** induced a reductive elimination of methylpyruvate which resulted formally from a coupling between the acetyl ligand and the carbon in the β position on the alkyloxalyl. We already reported analogous reactions for the thermolysis of [Fe(CO-CO$_2$Me)(CO$_2$Me)(CO)$_4$] **4**.[5] Dimethyl oxalate was then formed in 15% yield. The change of substituent from MeO to Me in **4** and **1** respectively, gives a more electrodonating dicarbonylated ligand favouring the reductive elimination process.



Scheme 1



Scheme 2

The reactivity of the (alkoxycarbonyl)(pyruvoyl)tetracaronyliron, **2**, was found to be completely different (Scheme 2). Analogous to the reactions of its organic homologues, the thermolysis of **2** at 15 °C generated the formation of the ferramethoxyketolactonic complex **5** characterized by NMR, IR‡ and by an X-ray structural study.§

The X-ray study of **5** confirms the presence of a five-membered ring which contains an asymmetric carbon. For this reason the solid-state structure consists of a juxtaposition of two enantiomers differing in the configuration of C(6). Isomer (*R*) is shown in Fig. 1. Coordination about the metal centre is pseudooctahedral. The axial terminal carbonyl groups are bent toward the ring, with C(3)–Fe–C(4) 170.7(7) °. As C(5)–Fe–C(7) is reduced by ring contraction [81.1(7) °], the angle between the equatorial carbonyl ligands opens slightly [98.6(8)°]. The ring adopts a distorted envelope conformation with C(6) out of the plane. The preferred axial position of the methoxy on C(6) may be due either to lower interactions between this methoxy and the axial terminal carbonyls on the

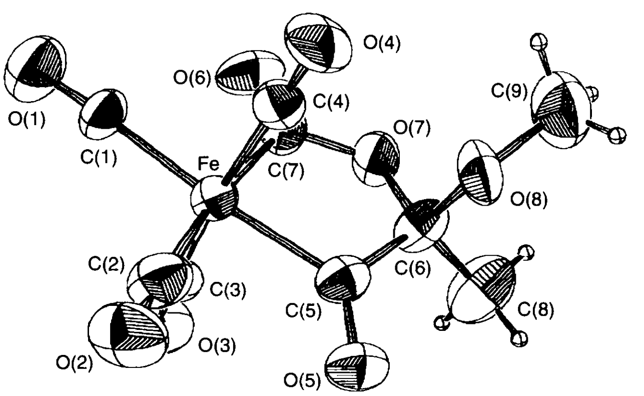


Fig. 1 Crystal structure of **5**(*R*). Selected bond lengths (Å) and angles (°): Fe(1)–C(1) 1.85(2), Fe(1)–C(2) 1.87(2), Fe(1)–C(3) 1.80(2), Fe(1)–C(4) 1.84(2), Fe(1)–C(5) 1.98(2), Fe(1)–C(7) 2.02(2), O(5)–C(5) 1.21(2), O(6)–C(7) 1.20(2), O(7)–C(6) 1.43(2), O(7)–C(7) 1.37(2), O(8)–C(6) 1.41(2), C(5)–C(6) 1.49(2), C(6)–C(8) 1.49(2); C(1)–Fe(1)–C(2) 98.6(8), C(3)–Fe(1)–C(4) 170.7(7), C(4)–Fe(1)–C(5) 88.0(6), Fe(1)–C(5)–O(5) 126(1), Fe(1)–C(5)–C(6) 113(1), O(5)–C(5)–C(6) 122(1), Fe(1)–C(7)–O(6) 127(1), Fe(1)–C(7)–O(7) 115(1), O(6)–C(7)–O(7) 118(1). Half of the molecules [**5**(*R*) and **5**(*S*)] appear statistically disordered in the crystal; this induced an indetermination between C(6) and O(7) for these molecules.

metal or to an anomeric effect similar to that responsible for the axial orientation of a polar group located on a carbon α to the heteroatom in glucosides.[8] However, the similarity of the bond lengths C(6)–O(8) [1.41(2) Å] and C(6)–O(7) [1.43(2) Å] makes the reality of such an effect improbable as it should induce a lengthening of C(6)–O(8) and a shortening of C(6)–O(7).[9]

The formation of **5** results from a chain–ring isomerization of **2**. This transformation is quantitative, irreversible and does not require any catalyst. It is clear that this pathway which is not observed for **1** is made possible by the specific properties of the alkoxycarbonyl ligand.[10] In this ligand, the proximity of the metal increases the nucleophilic character and the mobility of the alkoxy group which can migrate on to the C(6) carbon and induce the cyclization. As the rate of the reaction is greatly enhanced when it is performed in methanol, it may be deduced that the process is intramolecular.

Footnotes

† All manipulations were performed under argon atmosphere using standard Schlenk techniques. *Synthesis of* **1** or **2**: to a suspension of 0.002 mol of $Li[Fe(COMe)(CO)_4]$[3a] or $Na[Fe(CO_2Me)(CO)_4]$[3b] in 20 ml of CH_2Cl_2 at −30 °C were added 1 equiv. of $ClCOCO_2Me$ or ClCOCOMe[4] respectively. After the solution was stirred for 1 h, the solvent was removed to give a brown solid residue which was washed with hexane at −50 °C. **1** or **2** were extracted from the residue by hexane–CH_2Cl_2 (95:5) at −30 °C and recrystallized at −30 °C after partial evaporation of this solution.

‡ *Selected spectral data*: **1**; IR (hexane), ν/cm^{-1} 2120, 2060, 2055, 2045, 1740, 1690, 1670; $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 201.0(2 CO) 200.3(1 CO) 198.0(1 CO) 242.1(COMe) 241.6($COCO_2Me$) 164.8($CO\text{-}CO_2Me$). **2**; IR(hexane), ν/cm^{-1} 2125, 2075, 2070, 2060, 1740, 1665, 1650; $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 201.3(2 CO) 199.2(1 CO) 198.2(1 CO) 245.7(COCOMe) 198.1(COCOMe) 193.9(CO_2Me). **3**; IR(hexane), ν/cm^{-1} 2080, 2050, 2045, 2035, 1680, 1660; $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) δ 201.4 (2 CO) 199.8(1 CO) 198.8(1 CO) 242.2(COMe) 195.3(CO_2Me). **5**; IR(hexane), ν/cm^{-1} 2125, 2085, 2060, 2050, 1685, 1720; $^{13}C\{^1H\}$ NMR (75.47 MHz), CD_2Cl_2) δ 199.4(1 CO) 198.9(1 CO) 198.6(1 CO) 196.7(1 CO) 245.8[C(O)C] 198.0[C(O)O] 109.7[C(OMe)(Me)].

§ *Crystal data for* **5**: single crystal obtained from hexane, $C_9H_6FeO_8$, M = 297.99, monoclinic, space group $P2_1/c$, a = 10.710(3), b = 11.880(3), c = 18.975 Å, β = 92.18(2)°, U = 2413(1) Å^3, Z = 8, D_c = 1.641 g cm^{-3}, T = 294 K, λ(Mo-Kα) = 0.70926 Å; 4725 reflections measured, 1731 independent [$I > 3\sigma(I)$]. Lorentz–polarization correction (μ = 12.746 cm^{-1}). The structure was solved by direct method with the program SHELX-86.[6] After isotropic refinement (R = 0.13), absorption correction (DIFABS: min. 0.87, max. 1.48)[7] and anisotropic refinement (R = 0.095), the hydrogen atoms of the methyl groups were fixed in theoretical positions. Full-matrix refinement with 344 variables led to R = 0.076 and R_w = 0.070, GOF = 2.608. Atomic coordinates, bonds lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/16.

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