Synthesis of the Ethyl Oxalyl Tetracarbonyl Iron Anion $[(CO)_4FeCOCO_2Et]^-$, its Methylation at the Metal into $(CO)_4Fe(Me)(COCO_2Et)$ and Further Carbon–Carbon Coupling into Ethyl Pyruvate

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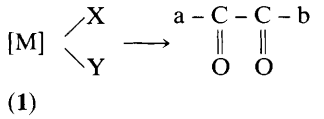
The stable anion $[(CO)_4FeCOCO_2Et]^-$ (**2**) [obtained after reaction of EtOCOCOCl on $Na_2Fe(CO)_4$] is methylated at the metal by reaction with $MeSO_3CF_3$ at −50 °C to give $(CO)_4Fe(Me)(COCO_2Et)$ (**3**) characterized *in situ* by ^1H and ^{13}C NMR; at −30 °C it decomposes according to two pathways: reductive elimination into $MeCOCO_2Et$ (**4**) and $Fe_3(CO)_{12}$ and rearrangement into $(CO)_4Fe(COMe)(CO_2Et)$ (**5**) which decarbonylates at +5 °C before giving $MeCO_2Et$ (**6**) and $Fe(CO)_5$.

The discovery of the double carbonylation reaction, essentially with cobalt[1] or palladium[2] as the catalysts, has spurred the synthesis of several organometallic models (**1**) to shed light on one of the key steps of the process: the XY coupling into an α,β-dicarbonylated organic product [equation (1)], (X = R, CO, COR; Y = COR, CO_2R', $CONR'_2$, COCOR', $COCO_2R'$; R,R′ = alkyl)



(1)

(**1**)

For M = Pd, X = COR and Y = $CONR'_2$, a coupling into an α-ketoamide is observed, but indirectly, since X and Y are in the unfavourable relative *trans* position.[3] The few available complexes bearing Y ligands such as COCOR′ or $COCO_2R'$ generally undergo a decarbonylation process which precludes the incorporation, as such, of this Y ligand in an organic substrate (M = Co,[4] M = Pd[5]), although the reverse reaction (*i.e.* Y = COR′ ⟶ COCOR′) has been described very recently under particular conditions for M = Mn.[6] No catalytic double carbonylation with iron has been observed so far.† Furthermore, studies on the rare available models (**1**) did not provide any significant information about the reaction step [equation (1)]; $(CO)_4Fe(CORf)_2$ (Rf: perfluoroalkyl), which has the favourable *cis* geometry, decarbonylates rapidly[8] and there is no evidence for any alkylation at the iron centre on the

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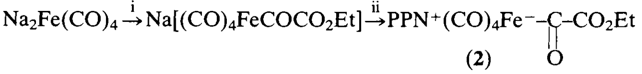
† However, a stoicheiometric formal insertion of an α-diketo group into a strained molecule *via* an acyl tetracarbonyl ferracycle has been reported.[7]

Table 1. NMR data for compounds (**2**), (**3**), and (**5**).[a]

		^1H(300 MHz)/δ			^{13}C(75.47 MHz)/δ					
Complexes	T/°C	CH_3	CH_2CH_3[b]	CH_2CH_3[b]	CO acyl	CO term.	CO_2	CH_2CH_3	CH_2CH_3	CH_3
(**2**)	−50		1.21	4.05	263.1	218.4	167.8	60.0	13.9	
(**3**)	−50	0.57	1.28	~4.2[c]	244.5	204.5(:2) 202.4(:1) 200.9(:1)	162.7	62.5	13.8	−6.7
(**5**) *trans*	−30	2.56	1.14	3.96	249.2[d]	201.9	194.8[d]	60.6[d]	14.3[d]	53.9[e]
(**5**) *cis*	−30	2.68	1.23	4.10	243.3[d]	201.2(:2) 199.5(:1) 198.7(:1)	194.3[d]	61.8[d]	14.4[d]	48.1

[a] In CD_2Cl_2 except otherwise stated. [b] $^3J_{H-H}$ 7.2 Hz. [c] Partially obscured by $MeSO_3CF_3$. [d] *cis–trans* Attribution not ascertained. [e] In $CDCl_3$ prior to decomposition.



$$Na_2Fe(CO)_4 \xrightarrow{i} Na[(CO)_4FeCOCO_2Et] \xrightarrow{ii} PPN^+(CO)_4Fe^-\!-\!\underset{\underset{O}{\|}}{C}\!-\!CO_2Et \quad (2)$$

Scheme 1. *Reagents and conditions:* i, $ClCOCO_2Et$, THF, −10 °C; ii, THF, room temperature, $(Ph_3P)_2N^+Cl^-$ followed by recrystallisation from CH_2Cl_2–hexane.

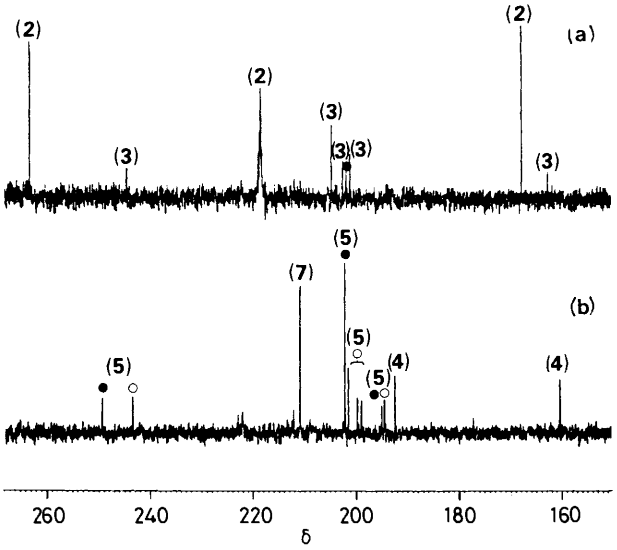
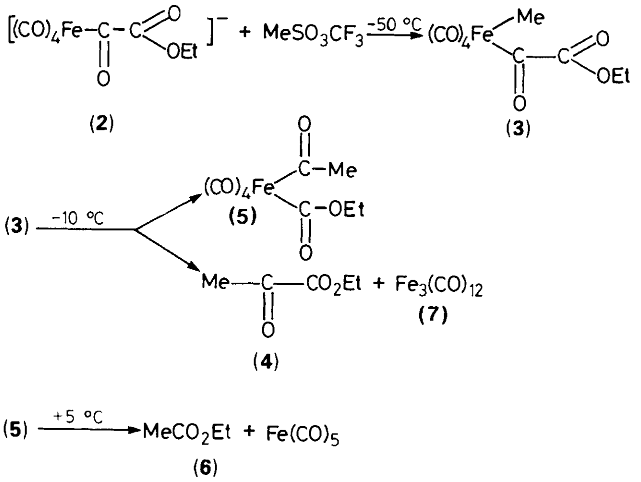


Figure 1. ^{13}C NMR spectra (75.47 MHz; CD_2Cl_2) in the carbonyl region (a) −50 °C, [● = traces of (**5**) *trans*]; (b) at −10 °C, complexes *cis*-(**5**) = ○ and *trans*-(**5**) = ●, $MeCOCO_2Et$ (**4**), and $Fe_3(CO)_{12}$ (**7**).

anion $[(CO)_4FeCOCOBu^t]^-$ gained after a tedious synthesis.[9]

Recently, we showed that the $[(CO)_4FeCO_2Me]^-$ anion could be alkylated at the metal to finally give an ester.[10] We report here a very simple and efficient synthesis of the $[(CO)_4FeCOCO_2Et]^-$ anion (**2**), the first evidence for its alkylation at the iron centre followed by decomposition into an α-ketoester.

Reaction of ethyl oxalyl chloride (1.5 mmol) with $Na_2Fe(CO)_4$, dioxan (1.5 mmol) in tetrahydrofuran (THF) (30 ml) at −10 °C for 30 min, followed by metathesis with bis(triphenylphosphoranilydene)ammonium chloride PPN^+Cl^-, led to isolation of the anion (**2**) (as a PPN^+ salt), in 64% yield (Scheme 1). This pink crystalline compound was found to be indefinitely stable at room temperature. IR and ^{13}C NMR spectroscopies highlighted the presence of both



Scheme 2

$Fe(CO)_4$ and $COCO_2Et$ groups.‡ Anion (**2**) proved to be less reactive than the $[(CO)_4Fe(CO_2Me)]^-$ anion[10] towards electrophiles since it did not react with MeI or $PhCH_2Br$. Its reaction with the powerful alkylating agent $MeSO_3CF_3$ was carefully monitored by high resolution ^1H and ^{13}C NMR under a N_2 atmosphere in CD_2Cl_2. At −50 °C, the reaction is very slow and after 3 h, only one product is formed and characterized as the alkyl complex (**3**) in 6% yield *vs.* (**2**) from NMR integration. After 6 h at −45 °C, (**3**) is formed in 15% yield *vs.* (**2**) with traces of (**4**) and (**5**) (see below). Methylation at the metal is clearly demonstrated by the very high field resonances (δ CH_3 0.57, CH_3 −6.7) recorded in the ^1H and ^{13}C NMR spectra. The ^{13}C resonances at δ 244.5 and 162.7 are unequivocally attributed to the ethyl oxalyl group (see Scheme 2, Table 1 and Figure 1). Furthermore, the signals observed for the terminal carbonyl ligands suggest a *cis*-disposition for the two organic ligands.

When the temperature is raised to −10 °C, the reaction

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‡ (**2**); Satisfactory elemental analysis (C,H,N). IR (CH_2Cl_2) ν(CO) 2023m, 1930sh, 1905vs (br.), 1716m, 1582m cm^{-1}; ^1H NMR (CD_2Cl_2; 300 MHz; 18 °C) δ 4.08 (q, CH_2) and 1.23 (t, CH_3, $^3J_{H-H}$ 7.2 Hz); ^{13}C NMR (CD_2Cl_2; 75.47 MHz; 18 °C) δ 262.2 ($FeCOCO_2Et$), 219.3 $[Fe(CO)_4]$, 168.1 ($FeCOCO_2Et$), 60.0 ($CO_2CH_2CH_3$), 14.4 ($CO_2CH_2CH_3$).

progresses faster and two different pathways are observed (Scheme 2). Firstly, reductive elimination yields ethyl pyruvate (**4**) and $Fe_3(CO)_{12}$.§ Secondly, rearrangement into an acyl alkoxycarbonyl complex (**5**). The latter is observed as a mixture of *cis* and *trans* isomers stable at this temperature. The most obvious evidence for this isomerism is given by the observation in ^{13}C NMR of the signals of the terminal CO ligands; a single signal for the *trans* isomer and three for the *cis* isomer (2:1:1 ratio). Other kinds of carbon atoms (acyl, ester, methyl, ethyl) also give two signals, one for each isomer. These observations are confirmed by ^1H NMR for the methyl and ethyl groups.¶ At the intermediate temperature of $-30\,°C$, (**2**), (**3**), (**4**), and (**5**), are observed altogether. Finally, above $+5\,°C$, (**5**) decomposes rapidly and quantitatively into ethyl acetate (**6**) and $Fe(CO)_5$ (Scheme 2)§ NMR data for (**2**), (**3**) and (**5**) are gathered in Table 1.

From these experiments it can be inferred that firstly, anion (**2**) is stable towards decarbonylation. Secondly, it can be alkylated at the metal to give the neutral *cis* methyl ethyloxalyl complex (**3**). Thirdly, there are two chemical paths for (**3**); one is its isomerization into (**5**), the other is the reductive elimination of the two ligands into ethyl pyruvate, providing the first evidence of the X–Y coupling without decarbonylation for X = Me and Y = $COCO_2Et$ [reaction (1)]. Fourthly, ethyl pyruvate does not come from X–Y coupling on (**5**) which decarbonylates prior to reductive elimination to give ethyl acetate.

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§ In the reaction, the organic compounds (**4**) and (**6**) were identified by ^1H, ^{13}C NMR, IR spectra and GC by comparison to authentic samples. In particular for (**4**); δ CH_3 (2.42), CO (192.3), CO_2 (160.3) and for (**6**); δ CH_3 (1.98), CO_2 (170.2). $Fe_3(CO)_{12}$ [δ CO (210.9)] and $Fe(CO)_5$ [δ CO (208.4)] were identified by ^{13}C NMR and IR spectra.

¶ The *cis*:*trans* ratio was found variable with temperature: 0.6 at $-30\,°C$ and 0.8 at $-10\,°C$.