Synthesis of Alkyl(alkoxycarbonyl)tetracarbonyliron Complexes $[(CO)_4Fe(CH_2CO_2Me)(CO_2R)]$: the First Evidence of their Relevance to the Catalytic Cycle in the Carbonylation of Organic Halides induced by Pentacarbonyliron

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Reaction of $[(CO)_4Fe(CO_2R)]^-$ (**1**) (R = Me or Bu^t) with $BrCH_2CO_2Me$ produces stable complexes $[(CO)_4Fe(CH_2CO_2Me)(CO_2R)]$ (**3**) which thermally decompose to yield $Fe(CO)_5$ and malonic esters under a CO atmosphere; these reactions provide the first demonstration of possible key steps in the catalytic cycle of the carbonylation of reactive halides into esters with $Fe(CO)_5$ and an alkoxide anion.

There is increasing evidence that alkoxycarbonyl complexes are intermediates in several important catalytic reactions, challenging the 'carbon monoxyde insertion' route.[1] The alkoxycarbonyltetracarbonyliron anions $[(CO)_4Fe(CO_2R)]^-$ (**1**), readily prepared by addition of an alkoxide anion to pentacarbonyliron,[2] are thought to be involved in stoicheiometric or catalytic processes of carbonylation of reactive organic halides to give esters.[3,4] The key step of these reactions, *i.e.* the addition of a halide (**2**) to the anion (**1**) to give the intermediate (**3**), has never before been demonstrated [equation (1)]. This is probably due to the putative high thermal instability of the complexes (**3**).†

We report here the synthesis of two stable complexes (**3**) (R = Me or Bu^t, R′ = CH_2CO_2Me), their spectroscopic characterization, and their thermal reaction which supports the catalytic cycle proposed for the carbonylation of reactive halides with the anion (**1**).

The addition at 0 °C of methyl bromoacetate (**2**) (R′X = $BrCH_2CO_2Me$) (10 mmol) to the anion (**1**) [obtained *in situ* in dry THF by reaction of $Fe(CO)_5$ (5 mmol) with NaOMe (5.2 mmol)][2] led to the complex (**3a**), which was isolated from hexane in 26% yield [based on $Fe(CO)_5$] as an off-white air-sensitive solid. Traces of $[(CO)_4Fe(CH_2CO_2Me)_2]$ (**4**) were detected by n.m.r. spectroscopy (see later). Mass spectral and spectroscopic data are fully consistent with the proposed structure (Scheme 1). I.r. data in particular highlight the *cis*-disposition of the two organic ligands: (**3a**) i.r. (hexane) ν(CO) 2120m, 2065vs, 2057s,sh, and 2038s, $\nu(CH_2CO_2Me)$ 1712m, $\nu(FeCO_2Me)$ 1680m,br cm^{-1}; ^1H n.m.r. (C_6D_6; 300 MHz) δ 3.38 (s, Me), 3.30 (s, Me), and 2.29 (s, CH_2); ^{13}C n.m.r. (C_6D_6; 75.47 MHz) δ 203.3, 200.7, and

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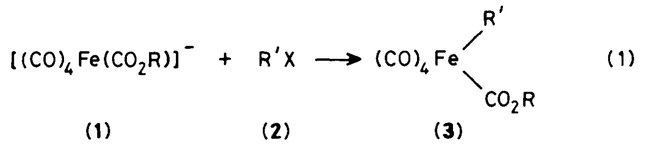
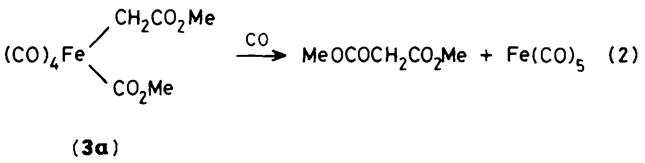
† The only known complex (**3**) (R = R′ = Me) was obtained from the reaction of $MeSO_3F$ with (**1**) at −78 °C. It rapidly decomposes at 0 °C to methyl acetate.[5]

We have previously reported[6] the role of the *in-situ*-generated acyltetracarbonyliron anion in the liquid–liquid phase-transfer carbonylation of reactive halides to give carboxylic acids or ketones.



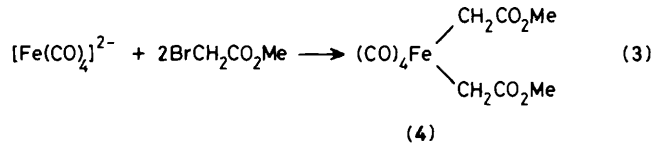
$[(CO)_4Fe(CO_2R)]^- + R'X \longrightarrow (CO)_4Fe(R')(CO_2R)$ (1)

(1) (2) (3)



$(CO)_4Fe(CH_2CO_2Me)(CO_2Me) \xrightarrow{CO} MeOCOCH_2CO_2Me + Fe(CO)_5$ (2)

(3a)



$[Fe(CO)_4]^{2-} + 2BrCH_2CO_2Me \longrightarrow (CO)_4Fe(CH_2CO_2Me)_2$ (3)

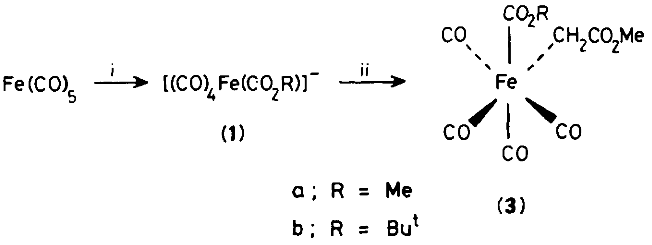
(4)

200.6 (ratio 2 : 1 : 1, CO), 191.8 ($FeCO_2Me$), 179.6 (CH_2CO_2Me), 53.3 (q, $FeCO_2CH_3$, $^1J_{CH}$ 147 Hz), 50.7 (q, $CH_2CO_2CH_3$, $^1J_{CH}$ 146 Hz), and 12.3 (t, CH_2, $^1J_{CH}$ 144 Hz). The yellow crystalline complex (**3b**) (R = Bu^t, R' = CH_2CO_2Me) was obtained (46% yield) in a similar way by using $KOBu^t$ instead of NaOMe.‡

The complex (**3a**) was stable for several hours at +15 °C. It decomposed cleanly and quantitatively at +30 °C within 3 h under a carbon monoxide atmosphere into $Fe(CO)_5$ and dimethylmalonate [equation (2)]. These results are relevant to the catalytic cycle of carbonylation of reactive halides. In particular for R'X = $BrCH_2CO_2Me$, we found a catalytic conversion into dimethyl malonate under the following experimental conditions: R'X : $Fe(CO)_5$ 10 : 1; MeO^- : $Fe(CO)_5$ 12 : 1 in THF at 5 atm CO and 55 °C, although the yield (45% based on $BrCH_2CO_2Me$) was severely limited by the competing Williamson synthesis of the ether $MeOCH_2CO_2Me$. This reaction and the aforementioned findings provide evidence for the first time of the reality of the catalytic cycle shown in Figure 1, at least for R'X = $BrCH_2CO_2Me$, and indicate directly the involvement of (**3a**). These results also indicate that the reductive elimination step is slow.

We then focused our attention on the by-product (**4**) detected as traces during the synthesis of (**3a**). Compound (**4**) was produced in significant yield by reaction of $Na_2Fe(CO)_4$ (1.22 mmol) with $BrCH_2CO_2Me$ (2.44 mmol) at 0 °C in THF [equation (3)] and was isolated as an air-sensitive green oil, stable only below +5 °C (58% yield). Compound (**4**) was shown to be a *cis*-dialkyl complex by mass spectral and spectroscopic data.‡ Thus the contamination of (**3a**) by (**4**) comes from the generation of the dianion $[Fe(CO)_4]^{2-}$ due to traces of sodium hydroxide in the sodium methoxide [equation (4)].[2b]

$Fe(CO)_5 + OH^- \rightleftharpoons [Fe(CO)_4(CO_2H)]^- \xrightarrow[-CO_2]{+OR^-} [Fe(CO)_4]^{2-}$ (4)



Scheme 1. *Reagents and conditions*: i, NaOMe or $KOBu^t$, THF; ii, $BrCH_2CO_2Me$, THF, 0 °C,

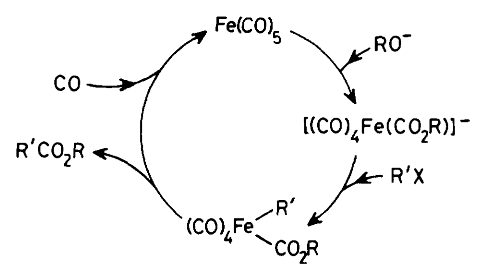


Figure 1

Dialkyl complexes such as (**4**) have been postulated as intermediates in the carbonylation reaction of alkyl halides by $Na_2Fe(CO)_4$,[7] but have never before been isolated.§

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‡ All compounds reported have mass spectral and spectroscopic data in accord with their assigned structures.

(**3b**): i.r. (hexane) ν(CO) 2123m, 2068vs, 2055s,sh, and 2043s, ν(CH_2CO_2Me) 1718m, ν(CO_2Bu^t) 1680m,br cm^{-1}; ^1H n.m.r. (C_6D_6; 300 MHz) δ 3.40 (s, Me), 2.32 (s, CH_2), and 1.27 (s, Bu^t); ^{13}C n.m.r. (C_6D_6; 75.47 MHz) δ 203.8, 201.4, and 200.6 (ratio 2 : 1 : 1, CO), 190.2 ($FeCO_2Bu^t$), 180.0 (CH_2CO_2Me), 83.8 [s, $C(CH_3)_3$], 50.7 (q, CO_2CH_3, $^1J_{CH}$ 146 Hz), 28.3 [q, $C(CH_3)_3$, $^1J_{CH}$ 127 Hz], and 12.8 (t, CH_2, $^1J_{CH}$ 143 Hz).

(**4**): i.r. (hexane) ν(CO) 2125m, 2070vs, 2060vs, and 2042s, ν(CH_2CO_2Me) 1720m cm^{-1}; ^1H n.m.r. (C_6D_6; 300 MHz) δ 3.36 (s, Me) and 1.57 (s, CH_2); ^{13}C n.m.r. (C_6D_6; 75.47 MHz) δ 205.6 and 201.7 (ratio 2 : 2, CO), 179.9 (CH_2CO_2Me), 50.7 (q, CH_3, $^1J_{CH}$ 146 Hz), and 11.5 (t, CH_2, $^1J_{CH}$ 142 Hz).

§ Fluoroalkyl complexes have been isolated from reactions of $Na_2Fe(CO)_4$ with acid chlorides R_FCOCl (R_F = C_2F_5 or n-C_3F_7).[8a] The analogous reaction with PhCOCl yields the dinuclear complex $[Fe_2(CO)_6(\mu\text{-}C_2Ph_2O)]$.[8b]