

## Synthesis of Alkyl(alkoxycarbonyl)tetracarbonyliron Complexes $[(\text{CO})_4\text{Fe}(\text{CH}_2\text{CO}_2\text{Me})(\text{CO}_2\text{R})]$ : 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  $[(\text{CO})_4\text{Fe}(\text{CO}_2\text{R})]^-$  (**1**) ( $\text{R} = \text{Me}$  or  $\text{Bu}^t$ ) with  $\text{BrCH}_2\text{CO}_2\text{Me}$  produces stable complexes  $[(\text{CO})_4\text{Fe}(\text{CH}_2\text{CO}_2\text{Me})(\text{CO}_2\text{R})]$  (**3**) which thermally decompose to yield  $\text{Fe}(\text{CO})_5$  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  $\text{Fe}(\text{CO})_5$  and an alkoxide anion.

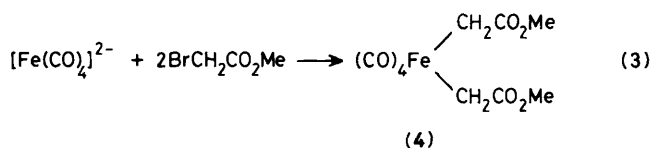
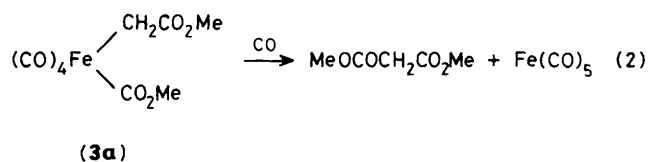
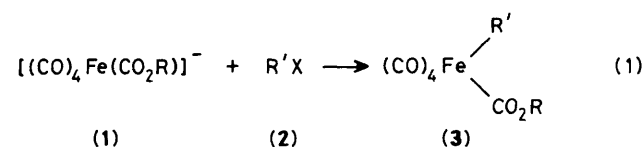
There is increasing evidence that alkoxycarbonyl complexes are intermediates in several important catalytic reactions, challenging the 'carbon monoxide insertion' route.<sup>1</sup> The alkoxycarbonyltetracarbonyliron anions  $[(\text{CO})_4\text{Fe}(\text{CO}_2\text{R})]^-$  (**1**), readily prepared by addition of an alkoxide anion to pentacarbonyliron,<sup>2</sup> are thought to be involved in stoichiometric or catalytic processes of carbonylation of reactive organic halides to give esters.<sup>3,4</sup> 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**).<sup>†</sup>

We report here the synthesis of two stable complexes (**3**) ( $\text{R} = \text{Me}$  or  $\text{Bu}^t$ ,  $\text{R}' = \text{CH}_2\text{CO}_2\text{Me}$ ), 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**) ( $\text{R}'\text{X} = \text{BrCH}_2\text{CO}_2\text{Me}$ ) (10 mmol) to the anion (**1**) [obtained *in situ* in dry THF by reaction of  $\text{Fe}(\text{CO})_5$  (5 mmol) with NaOMe (5.2 mmol)]<sup>2</sup> led to the complex (**3a**), which was isolated from hexane in 26% yield [based on  $\text{Fe}(\text{CO})_5$ ] as an off-white air-sensitive solid. Traces of  $[(\text{CO})_4\text{Fe}(\text{CH}_2\text{CO}_2\text{Me})_2]$  (**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)  $\nu(\text{CO})$  2120m, 2065vs, 2057s,sh, and 2038s,  $\nu(\text{CH}_2\text{CO}_2\text{Me})$  1712m,  $\nu(\text{FeCO}_2\text{Me})$  1680m,  $\text{br cm}^{-1}$ ;  $^1\text{H}$  n.m.r. ( $\text{C}_6\text{D}_6$ ; 300 MHz)  $\delta$  3.38 (s, Me), 3.30 (s, Me), and 2.29 (s,  $\text{CH}_2$ );  $^{13}\text{C}$  n.m.r. ( $\text{C}_6\text{D}_6$ ; 75.47 MHz)  $\delta$  203.3, 200.7, and

<sup>†</sup> The only known complex (**3**) ( $\text{R} = \text{R}' = \text{Me}$ ) was obtained from the reaction of  $\text{MeSO}_3\text{F}$  with (**1**) at  $-78^\circ\text{C}$ . It rapidly decomposes at 0 °C to methyl acetate.<sup>5</sup>

We have previously reported<sup>6</sup> 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.



200.6 (ratio 2:1:1, CO), 191.8 (FeCO<sub>2</sub>Me), 179.6 (CH<sub>2</sub>CO<sub>2</sub>Me), 53.3 (q, FeCO<sub>2</sub>CH<sub>3</sub>, <sup>1</sup>J<sub>CH</sub> 147 Hz), 50.7 (q, CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, <sup>1</sup>J<sub>CH</sub> 146 Hz), and 12.3 (t, CH<sub>2</sub>, <sup>1</sup>J<sub>CH</sub> 144 Hz). The yellow crystalline complex (3b) (R = Bu<sup>t</sup>, R' = CH<sub>2</sub>CO<sub>2</sub>Me) was obtained (46% yield) in a similar way by using KOBu<sup>t</sup> instead of NaOMe.‡

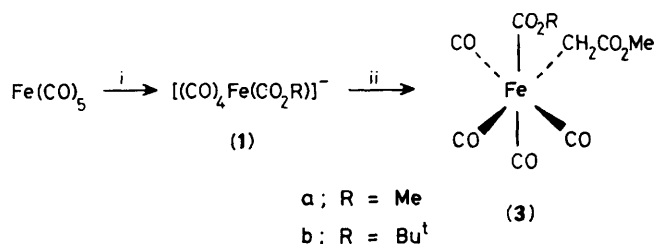
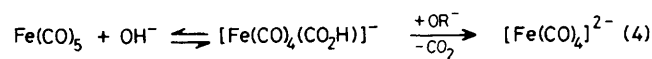
The complex (3a) was stable for several hours at +15 °C. It decomposed cleanly and quantitatively at +30 °C within 3 h under a carbon monoxide atmosphere into Fe(CO)<sub>5</sub> and dimethylmalonate [equation (2)]. These results are relevant to the catalytic cycle of carbonylation of reactive halides. In particular for R'X = BrCH<sub>2</sub>CO<sub>2</sub>Me, we found a catalytic conversion into dimethyl malonate under the following experimental conditions: R'X:Fe(CO)<sub>5</sub> 10:1; MeO<sup>-</sup>:Fe(CO)<sub>5</sub> 12:1 in THF at 5 atm CO and 55 °C, although the yield (45% based on BrCH<sub>2</sub>CO<sub>2</sub>Me) was severely limited by the competing Williamson synthesis of the ether MeOCH<sub>2</sub>CO<sub>2</sub>Me. 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<sub>2</sub>CO<sub>2</sub>Me, 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<sub>2</sub>Fe(CO)<sub>4</sub> (1.22 mmol) with BrCH<sub>2</sub>CO<sub>2</sub>Me (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

‡ 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<sub>2</sub>CO<sub>2</sub>Me) 1718m, ν(CO<sub>2</sub>Bu<sup>t</sup>) 1680m, br cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (C<sub>6</sub>D<sub>6</sub>; 300 MHz) δ 3.40 (s, Me), 2.32 (s, CH<sub>2</sub>), and 1.27 (s, Bu<sup>t</sup>); <sup>13</sup>C n.m.r. (C<sub>6</sub>D<sub>6</sub>; 75.47 MHz) δ 203.8, 201.4, and 200.6 (ratio 2:1:1, CO), 190.2 (FeCO<sub>2</sub>Bu<sup>t</sup>), 180.0 (CH<sub>2</sub>CO<sub>2</sub>Me), 83.8 [s, C(CH<sub>3</sub>)<sub>3</sub>], 50.7 (q, CO<sub>2</sub>CH<sub>3</sub>, <sup>1</sup>J<sub>CH</sub> 146 Hz), 28.3 [q, C(CH<sub>3</sub>)<sub>3</sub>, <sup>1</sup>J<sub>CH</sub> 127 Hz], and 12.8 (t, CH<sub>2</sub>, <sup>1</sup>J<sub>CH</sub> 143 Hz).

(4): i.r. (hexane) ν(CO) 2125m, 2070vs, 2060vs, and 2042s, ν(CH<sub>2</sub>CO<sub>2</sub>Me) 1720m cm<sup>-1</sup>; <sup>1</sup>H n.m.r. (C<sub>6</sub>D<sub>6</sub>; 300 MHz) δ 3.36 (s, Me) and 1.57 (s, CH<sub>2</sub>); <sup>13</sup>C n.m.r. (C<sub>6</sub>D<sub>6</sub>; 75.47 MHz) δ 205.6 and 201.7 (ratio 2:2, CO), 179.9 (CH<sub>2</sub>CO<sub>2</sub>Me), 50.7 (q, CH<sub>3</sub>, <sup>1</sup>J<sub>CH</sub> 146 Hz), and 11.5 (t, CH<sub>2</sub>, <sup>1</sup>J<sub>CH</sub> 142 Hz).



**Scheme 1.** Reagents and conditions: i, NaOMe or KOBu<sup>t</sup>, THF; ii, BrCH<sub>2</sub>CO<sub>2</sub>Me, THF, 0 °C,

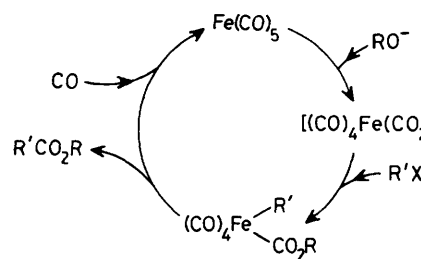


Figure 1

spectroscopic data.‡ Thus the contamination of (3a) by (4) comes from the generation of the dianion [Fe(CO)<sub>4</sub>]<sup>2-</sup> due to traces of sodium hydroxide in the sodium methoxide [equation (4)].<sup>2b</sup>

Dialkyl complexes such as (4) have been postulated as intermediates in the carbonylation reaction of alkyl halides by Na<sub>2</sub>Fe(CO)<sub>4</sub>,<sup>7</sup> but have never before been isolated.§

Received, 26th February 1988; Com. 8/00754C

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§ Fluoroalkyl complexes have been isolated from reactions of Na<sub>2</sub>Fe(CO)<sub>4</sub> with acid chlorides R<sub>F</sub>COCl (R<sub>F</sub> = C<sub>2</sub>F<sub>5</sub> or n-C<sub>3</sub>F<sub>7</sub>).<sup>8a</sup> The analogous reaction with PhCOCl yields the dinuclear complex [Fe<sub>2</sub>(CO)<sub>6</sub>(μ-C<sub>2</sub>Ph<sub>2</sub>O)].<sup>8b</sup>