

**The mild phase transfer syntheses of the ylide adduct  $(\text{CO})_4\bar{\text{Fe}}\text{CH}_2\overset{+}{\text{P}}\text{Ph}_3$ , the octacarbonyl( $\mu$ -methylene)diiron  $\mu\text{-CH}_2\text{Fe}_2(\text{CO})_8$ , and acyl tetracarbonyliron anions  $\text{RCOFe}(\text{CO})_4^-$  are consistent with the transient generation of the  $\text{Fe}(\text{CO})_4^{2-}$  dianion from  $\text{Fe}(\text{CO})_5$**

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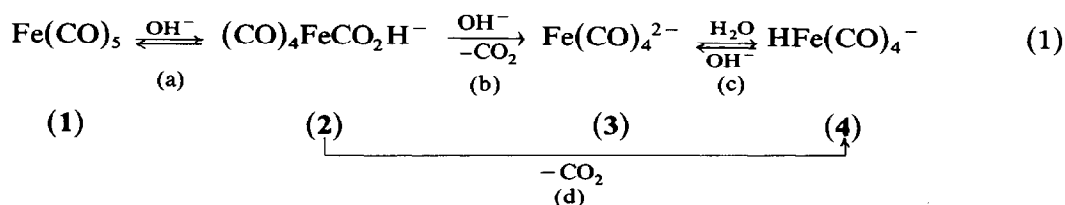
### Abstract

Addition of  $\text{Fe}(\text{CO})_5$  under a nitrogen or carbon monoxide atmosphere to the  $\text{CH}_2\text{XY}/\text{H}_2\text{O}$  phase transfer system ( $\text{X}, \text{Y} = \text{Cl}, \text{Br}$ ; 1 M NaOH and  $\text{Bu}_4\text{N}^+\text{HSO}_4^-$  added) after prior introduction of  $\text{PPh}_3$ , yields the ylide adduct  $(\text{CO})_4\bar{\text{Fe}}\text{CH}_2\overset{+}{\text{P}}\text{Ph}_3$  efficiently. In the absence of  $\text{PPh}_3$ , ( $\text{X} = \text{Br}, \text{Y} = \text{Cl}, \text{Br}$ ) the methylene bridged complex  $\mu\text{-CH}_2\text{Fe}_2(\text{CO})_8$  is obtained in high yields. In the presence reactive chlorides  $\text{RCl}$  ( $\text{R} = \text{CH}_2\text{C}_6\text{H}_5, \text{CH}_2\text{CO}_2\text{-t-Bu}, \text{CH}_2\text{CN}, \text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5$ ) under CO pressure (10 atm) ( $\text{X} = \text{Y} = \text{Cl}$ ), the acyltetracarbonyl iron anions  $\text{RCOFe}(\text{CO})_4^-$  were obtained as tetrabutylammonium salts (soluble in the organic solvent) in high yields. When  $\text{Fe}(\text{CO})_5$  was replaced by the  $\text{HFe}(\text{CO})_4^-$  anion there was no reaction, whereas the products mentioned were formed after introduction of the preformed dianion  $\text{Fe}(\text{CO})_4^{2-}$  into the PT system.

### Introduction

Phase transfer (PT) catalysis has found many application in organic chemistry, and increasingly the results can be accounted for in mechanistic terms [1]. The technique has recently been increasingly extended to organotransition metal chemistry [2]; in particular, some metal carbonyls widely used in organic synthesis [3] which readily give anionic species on reaction with hydroxide ion appear to be well fitted for use under PT conditions [4]. For example, pentacarbonyliron  $\text{Fe}(\text{CO})_5$  (1)

was successfully used under such conditions for the reduction of aromatic nitro compounds to aniline [5], and for stoichiometric or catalytic carbonylation of organic halides into ketones or carboxylic acids [6]. However, in these cases there have been no attempts to determine the nature of the reactive species generated. It is well known that, on reaction with pentacarbonyl iron **1** under homogeneous conditions, the hydroxide ion produces essentially the hydrido anion **4** [7], although when the hydrido ion is present in large excess, anion **3** can also be observed [8], in keeping with the estimated  $pK_a$ 's of the two involved acid-base couples (in water: 4 for  $H_2Fe(CO)_4/HFe(CO)_4^-$  and 12.7–14 for  $HFe(CO)_4^-/Fe(CO)_4^{2-}$ ) [9]. The results are accounted for in terms of sequence (a), (b) and (c), or sequence (a) and (d) in eq. 1 [10].



Anion **3**, very useful in organic synthesis [11], is generally prepared by reaction of ketyl sodium with **1** under anhydrous conditions [12]. In contrast, under PT conditions ( $H_2O/C_6H_6$ , 12.5 mol NaOH, and  $Bu_4N^+I$  as the PT catalyst), and in the absence of any reagent to trap the possibly-generated anion **3**, reaction of **1** only gives the less-basic anion **4** [13].

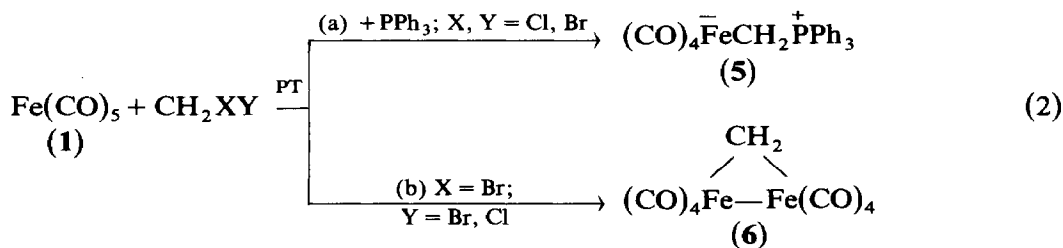
We give here a full account of some surprisingly mild and simple PT organometallic syntheses from **1** and an appropriate "in situ" reagent which are consistent with transient PT generation of anion **3** and not with that of anion **4** [14\*].

## Results

The following liquid-liquid PT system was used for this study: 10 ml  $H_2O$ , 10 ml  $CH_2XY$  ( $X, Y = Cl, Br$ ), 2 mmol  $Bu_4N^+HSO_4^-$ , 10 mmol NaOH under nitrogen or carbon monoxide. An additional reagent was sometimes added ( $PPh_3$  or a reactive halide, see below). The temperature was kept fixed at  $+10^\circ C$  unless otherwise specified, and the stirring speed at 1200 r.p.m. The  $Fe(CO)_5$  was added with stirring.

(a) Addition of  $Fe(CO)_5$  to the  $CH_2XY$  ( $X, Y = Cl, Br$ )/ $H_2O$  PT system with or without  $PPh_3$ . Syntheses of the ylide adduct **5** or the methylene bridged complex **6**

As shown in eq. 2 and entries 1–3 in Table 1, very different results are obtained in the presence and absence of triphenylphosphine.



\* Reference number with asterisk indicates a note in the list of references.

Table 1

PT syntheses of the ylide adduct  $(\text{CO})_4\text{FeCH}_2\text{PPh}_3$  (**5**), the methylene bridged complex  $\mu\text{-CH}_2\text{Fe}_2(\text{CO})_8$  (**6**), and tetracarbonyliron acyl anions  $\text{RCOFe}(\text{CO})_4^-$  (**7**)

Entry	PT system	Other reagents added	Products and % yields <sup>a</sup>			
			5	6	7	$\text{CO}_3^{2-}$
1a	$\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$ <sup>b</sup>					81
1b	$\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$ <sup>b</sup>	$\text{PPh}_3$	79	0		88
2a	$\text{CH}_2\text{Br}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$		0	76 <sup>c</sup>		100
2b	$\text{CH}_2\text{Br}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$	$\text{PPh}_3$	53	0		80
3a	$\text{CH}_2\text{BrCl}/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$		0	46		125
3b	$\text{CH}_2\text{BrCl}/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$	$\text{PPh}_3$	80	0		115
4	1a	$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ , $\text{CO}$			75	100
5	1a	<i>t</i> - $\text{BuOCOCH}_2\text{Cl}$ , $\text{CO}$				83
6	1a	$\text{NCCH}_2\text{Cl}$ , $\text{CO}$				65
7	1a	$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{Cl}$ , $\text{CO}$				64

<sup>a</sup> 100% yields for the following ratios vs. added  $\text{Fe}(\text{CO})_5$  (1): 5/1 1, 6/1 0.5, 7/1 1,  $\text{CO}_3^{2-}/1$  1.

<sup>b</sup>  $\text{Bu}_4\text{N}^+\text{OH}^-$  formed in situ by addition of an excess of  $\text{Bu}_4\text{N}^+\text{HSO}_4^-$  to aqueous sodium hydroxide.

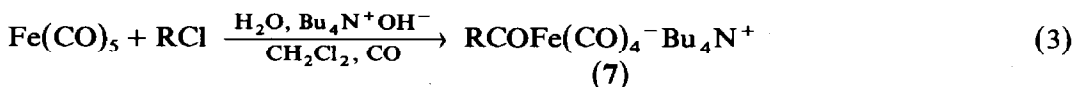
<sup>c</sup> 14% ethylene detected in the gases above the solution.

Ylide **5** cannot be made by the procedure that gives substituted ylides of the general formula  $(\text{CO})_4\text{FeCH}(\text{R})\text{PPh}_3$  [15]. Its dipolar structure is demonstrated by IR and NMR spectroscopy. The  $\text{Fe}(\text{CO})_4$  group bears the negative charge, and its geometry is near to  $\text{C}_{3v}$  symmetry:  $\nu(\text{C}\equiv\text{O})$  ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ) ( $\text{A}_1$ )<sub>1</sub> 2020m, ( $\text{A}_1$ )<sub>2</sub> 1920s, (E) 1905vs. The positive charge is largely on the phosphorus atom, as shown by  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\delta$  (ppm) vs. external  $\text{H}_3\text{PO}_4$  36.6(s)). The X-ray structural determination (fully described in ref. 16), clearly shows the  $sp^3$  character of the methylene group, and the slight distortion from  $\text{C}_{3v}$  symmetry for the  $\text{Fe}(\text{CO})_4$  group in the solid state.

The methylene bridged complex **6** was previously obtained by Pettit et al., by reaction of methylene iodide  $\text{CH}_2\text{I}_2$  with the  $\text{Fe}_2(\text{CO})_8^{2-}$  dianion [17]. Our structural data (see experimental section) are fully consistent with those given by Pettit.

(b) Addition of  $\text{Fe}(\text{CO})_5$  to the  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  PT system in the presence of a reactive chloride  $\text{RX}$  under carbon monoxide; synthesis of the tetracarbonyl iron acyl anions **7**

The  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  PT system described above was again used, but before the introduction of  $\text{Fe}(\text{CO})_5$  a reactive organic halide  $\text{RX}$  was introduced, and the pressure of carbon monoxide raised to 10 atm. Under these conditions the acyl anions **7** were obtained in high yields (entries 4–7 of Table 1 and eq. 3)) [18\*].



The first evidence for anion **7** came from an IR examination of the organic phase after reaction. For instance, for  $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$ , the following absorption frequencies were observed ( $\text{CH}_2\text{Cl}_2$ ,  $\nu(\text{cm}^{-1})$ )  $\nu(\text{C}\equiv\text{O})$  2015m, 1915sh, 1890vs, 1870sh,  $\nu(\text{C}=\text{O})$  1610m. Similar data were obtained (see experimental section) for the other anions **7** in Table 1, and found to be fully consistent with the values recorded previously [19]. As expected [19], addition of methyl iodide to dichloromethane

solutions of anions **7** (as tetrabutylammonium salts) obtained according to eq. 3 gave ketones  $\text{RCOCH}_3$  quantitatively.

As a further structural proof, anion **7** (for  $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ ) was prepared independently. Reaction of benzyllithium/DABCO (diazabicyclooctane) complex [20] on  $\text{Fe}(\text{CO})_5$  (**1**) under anhydrous conditions ( $\text{C}_6\text{H}_5\text{CH}_3$ ), and subsequent metathesis with the tetrabutylammonium cation (see Experimental section) gave the tetrabutylammonium salt of anion **7** ( $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$ ). Its  $^1\text{H}$  and  $^{13}\text{C}$  NMR data (not previously published) were found to be consistent with the proposed formula, and with the data recorded after the reaction shown in eq. 3:  $^1\text{H}$  NMR (60 MHz,  $(\text{CD}_3)_2\text{CO}$ , ppm vs. TMS) 4.35s 2H, 7.05m 5H,  $^{13}\text{C}$  NMR  $\{^1\text{H}\}$  (25 MHz,  $(\text{CD}_3)_2\text{CO}$ , ppm vs. TMS)  $\text{CH}_2$  72.2,  $\text{C}_6\text{H}_5$  126.3, 128.7, 130.9, 139.5;  $\text{C}=\text{O}$  261.4.

Other anions **7** ( $\text{R} = \text{CH}_2\text{CN}$ ,  $\text{CH}_2\text{CO}_2\text{-t-Bu}$ ) prepared by the reaction shown in eq. 3, underwent rapid decarbonylation during isolation to give the anions  $\text{RFe}(\text{CO})_4^-$  (**10**). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for these anions **10** were identical with those obtained after reaction of corresponding halides  $\text{RX}$  on  $\text{Na}_2\text{Fe}(\text{CO})_4$  under dry conditions and subsequent metathesis with the tetrabutylammonium cation.

*(c) Reaction of preformed anions  $\text{HFe}(\text{CO})_4^-$  (**4**),  $\text{Fe}(\text{CO})_4^{2-}$  (**3**),  $\text{Fe}_2(\text{CO})_8^{2-}$  (**8**) on  $\text{CH}_2\text{XY}$  ( $\text{X}, \text{Y} = \text{Cl}, \text{Br}$ ) under anhydrous or liquid-liquid PT conditions*

In order to shed light on the nature of the reactive species generated from  $\text{Fe}(\text{CO})_5$  in the PT systems described above, we designed experiments in which a preformed anion  $\text{HFe}(\text{CO})_4^-$  (**4**) [7], or  $\text{Fe}(\text{CO})_4^{2-}$  (**3**) [12], or  $\text{Fe}_2(\text{CO})_8^{2-}$  (**8**) [21] was introduced as a sodium (**4**, **3**) or tetraalkylammonium (**4**, **8**) salt into the PT system in the place of  $\text{Fe}(\text{CO})_5$ , or was treated with  $\text{CH}_2\text{XY}$  ( $\text{X} = \text{Cl}, \text{Br}$ ), under anhydrous conditions. The results, summarized in Table 2, clearly show that anion **4** was unreactive in each case (entries 1, 2, 3, 5). Furthermore, no isotopic exchange in anion **4** was observed when  $\text{D}_2\text{O}$  was used in the place of  $\text{H}_2\text{O}$  in the PT system of entry 4. No methylene bridged complex **6** was detected (IR) after introduction of dianion **8** into the  $\text{CH}_2\text{Br}_2/\text{H}_2\text{O}$  PT system (entry 10). In contrast, entries 6–9 show that anion **3** was reactive in each case. Furthermore protonation of this anion **3** under PT conditions of entry 8 was slower than its reaction to give the ylide adduct

Table 2

Reaction of preformed anions  $\text{HFe}(\text{CO})_4^-$  (**4**),  $\text{Fe}(\text{CO})_4^{2-}$  (**3**) and  $\text{Fe}_2(\text{CO})_8^{2-}$  (**8**) on  $\text{CH}_2\text{XY}$  ( $\text{X}, \text{Y} = \text{Cl}, \text{Br}$ ) under anhydrous or liquid-liquid PT conditions

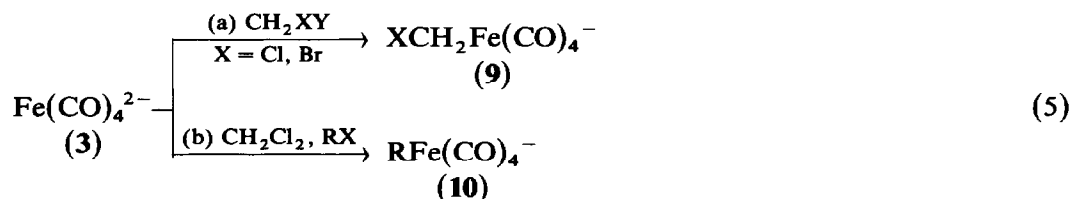
Entry	System <sup>a</sup>	Anion added <sup>b</sup>	Results
1	$\text{CH}_2\text{Cl}_2$	$\text{HFe}(\text{CO})_4^-$	No reaction
2	$\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$	$\text{HFe}(\text{CO})_4^-$	No reaction
3	$\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^- + \text{PPh}_3$	$\text{HFe}(\text{CO})_4^-$	No reaction
4	$\text{CH}_2\text{Cl}_2/\text{D}_2\text{O}/\text{Bu}_4\text{N}^+\text{OD}$	$\text{HFe}(\text{CO})_4^-$	No deuteration of $\text{HFe}(\text{CO})_4^-$
5	$\text{CH}_2\text{Br}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$	$\text{HFe}(\text{CO})_4^-$	No production of <b>6</b>
6	$\text{CH}_2\text{Cl}_2$	$\text{Fe}(\text{CO})_4^{2-}$	Reaction, no clean result
7	$\text{CH}_2\text{Cl}_2 + \text{PPh}_3$	$\text{Fe}(\text{CO})_4^{2-}$	Reaction, production of <b>5</b>
8	$\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^- + \text{PPh}_3$	$\text{Fe}(\text{CO})_4^{2-}$	Production of <b>5</b>
9	$\text{CH}_2\text{Br}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$	$\text{Fe}(\text{CO})_4^{2-}$	Transient production of <b>6</b>
10	$\text{CH}_2\text{Br}_2/\text{H}_2\text{O}/\text{Bu}_4\text{N}^+\text{OH}^-$	$\text{Fe}_2(\text{CO})_8^{2-}$	No production of <b>6</b>

<sup>a</sup> For PT systems, aqueous concentration of  $\text{OH}^-$ :  $1\text{ M l}^{-1}$ . <sup>b</sup> Counterion  $\text{Na}^+$  for all runs except for runs 1 ( $\text{Bu}_4\text{N}^+$ ) and 10 ( $\text{Et}_4\text{N}^+$ ).

**5** which was obtained in high yield: only traces of anion **4** were detected by IR spectroscopy. We also found that anion **4** (as a tetrabutylammonium salt) reacted only very slowly with benzyl chloride in dichloromethane solution, to give toluene. It is well known that benzyl halides readily react with anion **3** to give anion **10**, and hence anion **7** under a carbon monoxide atmosphere [11,19].

## Discussion

In each PT experiment described in Table 1, approximately one equivalent of the carbonate anion was produced for every equivalent of  $\text{Fe}(\text{CO})_5$  taken. This is consistent with the reaction of  $\text{Fe}(\text{CO})_5$  with the hydroxide anion to give either anion **3** or anion **4** (eq. 1). However, the results summarized in Table 2 are consistent with the generation of anion **3** and not anion **4**. It seems reasonable to propose that anion **3** is transiently generated under these PT conditions. This would take place by steps (a) and (b) and not steps (a), (d), and (c) of eq. 1: the former sequence gives anion **3** directly, whereas the latter gives **3** only after prior generation of anion **4**. The results summarized in Table 2 are completely inconsistent with the operation of the latter sequence. In particular, the deprotonation of anion **4** (step (c), eq. 1) is too slow under our PT conditions (entry 4). Additional supports for the sequence (a) + (b) of eq. 1 comes from other studies. Thus it has been shown that species **2** when generated under vacuum in a mass spectrometer is stable on the millisecond time scale of the experiment, and does not undergo spontaneous decarboxylation into **3** [10c, d]. In aqueous solution, the decarboxylation of species **2** is base-catalyzed, and initially gives anion **3** [10a, b]. Thus under PT conditions in an inert organic phase and with no reagent present that can trap anion **3**, anion **4** is observed [13]. In contrast, in our PT system, in which the organic phase  $\text{CH}_2\text{XY}$  (or a more reactive reagent  $\text{RX}$ ) can react with the transiently generated anion **3**, the reactions shown in eq. 5



can occur. In the presence of a reactive halide  $\text{RX}$  (eq. 5b), anion **10** is produced, and gives anion **7** after CO insertion. In the absence of  $\text{RX}$ , anion **9** would be produced (eq. 5a); its trapping by  $\text{PPh}_3$  would give the ylide adduct **5**. In the absence of  $\text{PPh}_3$ , and for  $\text{X} = \text{Br}$ , repetition of the process would give the methylene complex **6**. Because the hydroxide anion cannot be extracted into the organic phase as a tetrabutylammonium ion pair under such PT conditions [1f], steps (a) and (b) of eq. 1 would occur at the liquid-liquid interface of the PT system, and, reactions of eq. 5 would probably also occur near this interface.

## Conclusion

All the results described here are in full agreement with an initial phase transfer generation of the transient anion **3** from  $\text{Fe}(\text{CO})_5$ , probably at the liquid-liquid

interface. In these two respects (i) transient generation, and (ii) reaction at the liquid–liquid interface, these PT systems present close analogies with organic PT systems in which reactive carbanions or dihalocarbenes are generated. The generated species cannot be detected as such, but are characterized by their rapid in situ reactions with appropriate substrates [1b, c, d, e].

## Experimental

All experiments were conducted under N<sub>2</sub> or CO standard Schlenk tube and high vacuum line techniques unless otherwise specified. The PT reaction vessel was described previously [22]. Infrared spectra were recorded on a Philips Unicam SP 1100 spectrometer. <sup>1</sup>H NMR spectra were recorded on a Varian EM 360 spectrometer and were referenced, directly or indirectly, to tetramethylsilane (TMS) or, if necessary, to hexamethyldisiloxane; the usual solvent was CD<sub>2</sub>Cl<sub>2</sub>. <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a FT Bruker WP 80 spectrometer and were referenced for <sup>13</sup>C to TMS, and for <sup>31</sup>P, to external aqueous phosphoric acid for <sup>31</sup>P. Mass spectra were recorded on a Varian MAT 311 instrument (Electron impact 70 eV voltage, probe temperature range: 50–200 °C). Gas chromatography was conducted on a Intersmat IGC 1200 DFL FID model, interfaced with a 3390 Hewlett Packard integrator, a 1 m × 0.003 m column filled with Apiezon or DEGS on Chromosorb coated with hexamethyldisilazane was used. Elemental analyses were performed by CNRS Microanalytical Laboratory, Lyon Villeurbanne (France).

Solvents were freshly distilled under N<sub>2</sub> from an appropriate desiccant (sodium/benzophenone for THF, LiAlH<sub>4</sub> for hexane and calcium hydride for CH<sub>2</sub>Cl<sub>2</sub>) and degassed before use. Water was distilled twice under nitrogen and degassed. Sodium salts of the following anions were prepared by published methods: HFe(CO)<sub>4</sub><sup>-</sup> [7], Fe(CO)<sub>4</sub><sup>2-</sup> [12], Fe<sub>2</sub>(CO)<sub>8</sub><sup>2-</sup> [17,21]. The Fe(CO)<sub>5</sub>, NaOH, n-Bu<sub>4</sub>NHSO<sub>4</sub>, and the organic halides shown in Table 2, were purchased from the Aldrich Chemical Co. and used as received.

### *Synthesis of (CO)<sub>4</sub>FeCH<sub>2</sub>PPh<sub>3</sub><sup>+</sup> (5)*

Pentacarbonyliron **1** (2 mmol; 0.275 ml) was added (by means of a syringe) with stirring (1200 rpm) at +10 °C to the following PT system contained in the PT vessel under N<sub>2</sub> atmosphere: NaOH (10 mmol) Bu<sub>4</sub>NHSO<sub>4</sub> (2 mmol), PPh<sub>3</sub> (2 mmol), water (10 ml), dichloromethane (10 ml). After 0.5 h stirring, the IR spectrum of the organic layer showed complete disappearance of **1**, and revealed a new set of bands belonging to **5**. The in situ yield (80%) was estimated by comparison of this IR spectrum with spectra of solutions of pure **5** of known concentrations. The organic layer was then separated by means of a syringe introduced through a rubber septum, dried on MgSO<sub>4</sub>, and evaporated. The yellow pasty residue was extracted several times with portions of 30 ml Et<sub>2</sub>O and the extracts were filtered through cellulose gel. After evaporation of the pale yellow solution, the residual yellow powder was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 ml), and hexane (6 ml) was carefully added as an upper layer without mixing. After one night at -30 °C, the ylide **5** had separated as yellow crystals, which were filtered off and dried in vacuo. These crystals, of crystallographic quality, were extremely air sensitive. The overall yield of the isolated crystals was 25% with respect to the initial Fe(CO)<sub>5</sub>. The orange residue remaining after ethereal extraction was essentially (CO)<sub>4</sub>FePPh<sub>3</sub> (IR ν(C≡O) cm<sup>-1</sup>

2051(m), 1978(m), 1947(vs) ( $C_6H_6$ ) containing traces of  $(CO)_3Fe(PPh_3)_2$ . (IR  $\nu(C\equiv O)$   $cm^{-1}$ , 1886(vs) ( $C_6H_6$ ) [15]. These latter compounds came from decomposition of **5** during work up.

Similar results were obtained when anhydrous  $Na_2Fe(CO)_4$  was added to the same PT system instead of **1**. In this case, however, a small amount of  $n-Bu_4N^+HFe(CO)_4^-$  [7] was detected (IR  $\nu(C\equiv O)$   $cm^{-1}$ : 2000(w), 1915(m, sh), 1880(vs) ( $CH_2Cl_2$ )), in addition to the previously obtained mixture of  $(CO)_4FePPh_3$  and  $(CO)_3Fe(PPh_3)_2$ , in residue left after the ether extraction, and the salt was isolated for unambiguous IR characterisation.

The following reagents were stirred together under anhydrous conditions for 72 h at room temperature:  $Na_2Fe(CO)_4$  (4.67 mmol),  $PPh_3$  (4.67 mmol),  $n-Bu_4NBr$  (0.5 mmol),  $CH_2Cl_2$  (30 ml). After the work up described above **5** was isolated in 34% yield with respect to the  $Na_2Fe(CO)_4$  taken, and  $(CO)_4FePPh_3$  was isolated as a side-product (25%).

Data for **5**: dec. pt. 110–112°C. Anal. Found: C, 62.21; H, 3.74; Fe, 12.3; P, 7.14.  $C_{23}H_{17}FeO_4P$  calcd.: C, 62.19; H, 3.86; Fe, 12.57; P, 6.97%. MS calcd. 444.2; found 444; main fragments:  $(CO)_xFeCH_2PPh_3$  ( $x$  from 0 to 4).  $^1H$  NMR ( $\delta$  relative to external TMS,  $CD_2Cl_2$ ,  $-25^\circ C$ ) 1.56 (d, 2H)  $J(PH)$  12.5 Hz; 7.63 (m, 15 H).  $^{13}C\{^1H\}$  NMR ( $\delta$  relative to external TMS,  $CD_2Cl_2$ , 20.16 MHz,  $-20^\circ C$ ).  $Fe-CH_2$  at  $-16.18$  (d,  $J(C-P)$  29.29 Hz);  $PPh_3$  at 125, 129.1, 131, 131.7, 132, 135.4 and 135.88;  $C\equiv O$  at 220.1 and 220.4 ( $J(C-P)$  4.88 Hz).  $^{31}P$  NMR ( $\delta$  relative to external  $H_3PO_4$   $CD_2Cl_2$ ,  $-20^\circ C$ ) 36.6 (s). IR ( $\nu(C\equiv O)$   $cm^{-1}$ ) (KBr) 2020(m), 1930(ms), 1905(vs), 1880(s), 1840(sh); ( $CH_2Cl$ ) 2020(m), 1930(sh), 1905(vs), ( $C_6H_5CH_3$ ) 2035(ms), 1935(m), 1910(s) 1900(s). The results of an X-ray structural determination have been presented previously [16].

#### *Synthesis of $\mu CH_2Fe_2(CO)_8$ (**6**)*

$NaOH$  (10 mmol) and  $n-Bu_4NH_2SO_4$  (1 mmol) were dissolved in 10 ml  $H_2O$  in the PT vessel under  $CO$  (yields were slightly lower under  $N_2$ ) and  $CH_2Br_2$  (10 ml) was added. The temperature was kept at  $0^\circ C$  and stirring at 1200 rpm, and **1** (1 mmol) was added slowly (from a syringe) during 2 h. After stirring at  $0^\circ C$  for a further 10 h some **6**, insoluble in the aqueous phase and sparingly soluble in  $CH_2Br_2$  was separated from the liquid–liquid interface by filtration, and the remainder recovered was from the organic solution by evaporation and extraction of the residue with hexane. The overall yield of **6** was 76% with respect to the  $Fe(CO)_5$  taken. When anhydrous  $Na_2Fe(CO)_4$  was used in place of  $Fe(CO)_5$ , the transient production of **6** was detected by IR spectroscopy although its absorption bands has disappeared after half an hour. A separate experiment showed that  $Na_2Fe(CO)_4$  does react with complex **6**.

Data for **6** (fully consistent with those given in ref. 17;  $m/z$  calculated for  $C_9H_2Fe_2O_8$  349.8448; found 349.8452; main fragments  $CH_2Fe_2(CO)_n$ ,  $n$  from 8 to 0.  $^1H$  NMR (relative to internal TMS,  $CD_3COCD_3$ ) 5.65(s). IR ( $\nu(C\equiv O)$   $cm^{-1}$ ) (hexane) 2060, 2032, 2015(s); ( $CH_2Cl_2$ ) 2180(vs), 2060(s), 2020, 1998(sh).

#### *Synthesis of the tetrabutylammonium salts of $RCOFe(CO)_4^-$ anions **7** and $RFe(CO)_4^-$ anions **10***

(a) *PT synthesis of anions 7.* Reactions were carried out in a 50 ml stainless steel autoclave thermostated at  $+10^\circ C$  and equipped with a magnetic stirrer. The

following run is typical. Under one atmosphere of CO, NaOH (10 mmol) and  $n\text{-Bu}_4\text{NHSO}_4$  (2 mmol) were dissolved into 10 ml  $\text{H}_2\text{O}$ , and  $\text{CH}_2\text{Cl}_2$  (10 ml)  $\text{PhCH}_2\text{Cl}$  (1.5 mmol) and  $\text{Fe}(\text{CO})_5$  (1.5 mmol) were added. The CO pressure was raised to 10 atm and stirring kept at 1200 rpm overnight. GLC or TLC analysis showed that the benzyl chloride had disappeared, and the IR spectrum of the organic layer showed a set of bands identical with those from  $\text{PPN}^+$  salts of **7** [19]. IR data for anions **7** ( $n\text{-Bu}_4\text{N}^+$  salts in  $\text{CH}_2\text{Cl}_2$ ,  $\nu(\text{cm}^{-1})$ ): R =  $\text{C}_6\text{H}_5\text{CH}_2$ ,  $\nu(\text{C}\equiv\text{O})$  2015m, 1915sh, 1890vs, 1870sh;  $\nu(\text{C}=\text{O})$  1610. R =  $\text{NC-CH}_2$ ,  $\nu(\text{C}\equiv\text{O})$  2015m, 1910sh, 1890vs;  $\nu(\text{C}=\text{O})$  1620m;  $\nu(\text{C}\equiv\text{N})$  2195m. R =  $t\text{-BuO}(\text{O})\text{CCH}_2$ ,  $\nu(\text{C}\equiv\text{O})$  2005m, 1895vs,  $\nu(\text{C}=\text{O})$  1570w;  $\nu(\text{C}=\text{O})$  (ester) 1660m. R =  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2$ ,  $\nu(\text{C}\equiv\text{O})$  1995m, 1910sh, 1880vs;  $\nu(\text{C}=\text{O})$  1615w; ( $\nu(\text{C}=\text{C})$  1590w.

Further methylation (with  $\text{CH}_3\text{I}$ ) gave the expected methyl ketones  $\text{RCOCH}_3$ , which were identified from their IR and  $^1\text{H}$  NMR spectra (given in ref. 23 for R =  $\text{C}_6\text{H}_5\text{CH}_2$  and R =  $t\text{-BuO}(\text{O})\text{CCH}_2$ ) by comparison with those of authentic samples prepared as described previously [24,25] for R =  $\text{NCCH}_2$  and R =  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2$ .

(b) *Dry synthesis of anion 7 (R =  $\text{C}_6\text{H}_5\text{CH}_2$ ).*  $\text{Li}^+$  salt. A 2.5 M hexane solution (4 ml) of  $n\text{-BuLi}$  (10 mmol) was quickly added to a toluene (30 ml) solution of DABCO (diazabicyclooctane) (1.12 g, 10 mmol) [20]. The mixture was kept for 30 min at  $80^\circ\text{C}$ , then cooled to room temperature. The resulting yellow suspension was treated with 1.32 ml (10 mmol)  $\text{Fe}(\text{CO})_5$  at  $-10^\circ\text{C}$ . After 30 min the beige solid was filtered off and dried under reduced pressure.

$^1\text{H}$  NMR (60 MHz,  $(\text{CD}_3)_2\text{CO}$ ) 2.6, s, 12H (DABCO); 4.2, s, 2H; 7.0, m, 5H.  $^{13}\text{C}$  NMR  $\{^1\text{H}\}$  (25 MHz,  $(\text{CD}_3)_2\text{CO}$ ), 47.6 (DABCO);  $\text{CH}_2$  72.2;  $\text{C}_6\text{H}_5$  126.4, 128.7, 130.8, 138.7;  $\text{Fe}(\text{CO})_4^-$  221.4;  $\text{C}=\text{O}$  271.1. IR (THF,  $\nu(\text{cm}^{-1})$ ) 2013m, 1921m, 1891s, 1580br.  $n\text{-Bu}_4\text{N}^+$  salt of anion **7** (R =  $\text{C}_6\text{H}_5\text{CH}_2$ ) when a solution of the  $\text{Li}^+$  salt of **7** (R =  $\text{C}_6\text{H}_5\text{CH}_2$ ) in  $\text{CH}_2\text{Cl}_2$  was introduced into a PT system consisting of 20 ml, NaOH (1 M), 20 ml,  $\text{CH}_2\text{Cl}_2$ , 10 mmol  $n\text{-Bu}_4\text{NHSO}_4$ , work-up of the organic layer, yielded the  $n\text{-Bu}_4\text{N}^+$  salt of **7** (R =  $\text{C}_6\text{H}_5\text{CH}_2$ ), with NMR data identical with those obtained from PT reaction of eq. 3:  $^1\text{H}$  NMR (60 MHz,  $(\text{CD}_3)_2\text{CO}$ ) 4.35, s, 2H; 7.05, m, 5H.  $^{13}\text{C}$  NMR  $\{^1\text{H}\}$  (25 MHz,  $(\text{CD}_3)_2\text{CO}$ ),  $\text{CH}_2$  72.2;  $\text{C}_6\text{H}_5$  126.3, 128.7, 130.9, 139.5,  $\text{C}=\text{O}$  261.4.

(c) *Dry synthesis of anions 10 (R =  $\text{NCCH}_2$ ,  $t\text{-BuO}(\text{O})\text{CCH}_2$ ).*  $\text{ClCH}_2\text{CN}$  (126  $\mu\text{l}$ , 2 mmol) or  $\text{ClCH}_2\text{CO}_2\text{-}t\text{-Bu}$  (323  $\mu\text{l}$ , 2 mmol) was added at  $0^\circ\text{C}$  to a suspension of 692 mg (2 mmol) of  $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5$  dioxane in 20 ml THF. After 1 h stirring, the solvent was evaporated and crude  $\text{Na}^+$  salts of **10** were subjected to metathesis with  $n\text{-Bu}_4\text{N}^+$ , as above. The IR and NMR data were identical with those obtained after the work-up (during which decarbonylation occurred) of the organic phase from the reaction solution in eq. 3.  $^{13}\text{C}$  NMR  $\{^1\text{H}\}$  (75.49 MHz,  $(\text{CD}_3)_2\text{CO}$ ): R =  $\text{NCCH}_2$ :  $\text{CH}_2\text{CN}$  - 22.7;  $\text{CN}$  132.6. R =  $t\text{-BuO}(\text{O})\text{CCH}_2$ :  $\text{CH}_2\text{CO}_2$  5.18.

#### *Analysis of the carbonate anion in the aqueous phase of the PT systems of Table 1*

After the end of the PT reactions, the aqueous phase separated, then if necessary  $\text{NaB}(\text{C}_6\text{H}_5)_4$  was added to precipitate the tetrabutylammonium cation as the insoluble salt  $n\text{-Bu}_4\text{N}^+ \text{B}(\text{C}_6\text{H}_5)_4^-$ . After filtration, the aqueous solution was evaporated and the residue washed with ethanol and dried under high vacuum. The IR spectrum (KBr) showed, in addition to the bonds from the sulfate anion ( $\text{cm}^{-1}$ ) (1150(s, broad), 640(m, broad)) the bands from the carbonate anion (1470(s, very



broad, 890(m) 880(sh)). The previous powder or the aqueous phase was analysed by measuring the amount of carbon dioxide evolved upon acidification (HCl) [22].

*Analysis of the gaseous atmosphere of the PT experiment 2a (Table 1)*

Nitrogen or carbon monoxide were replaced by pure argon, and the gas above the reaction solution, after reaction examined by high resolution mass spectrography, which could clearly distinguish between  $C_2H_4$  (calc. 28.0313; found 28.0313) from CO (calc. 27.9949; found 27.9949) and  $N_2$  (calc. 28.0061; found 28.0061). Traces of  $CH_4$  (calc. 16.0313; found 16.0312) were also detected. A control experiment with analytically pure argon showed only traces of  $N_2$ , but no CO,  $CH_4$  or  $C_2H_4$ . Quantitative analysis of ethylene was by GLC.

*PT study of  $Bu_4NH^+Fe(CO)_4^-$  in the presence of  $D_2O$  (Table 2, entry 4)*

The tetrabutylammonium salt of anion 4 (1 mmol), prepared by a procedure similar to that used for preparation of the  $PPN^+$  salt [7], was added under  $N_2$  at  $+10^\circ C$ , to the following PT system:  $CH_2Cl_2$  (10 ml),  $D_2O$  (10 ml), NaOH (10 mmol). After 1 h stirring (1200 rpm), the organic layer was separated and evaporated in vacuo. The IR spectrum of the solid residue was that of the  $HFe(CO)_4^-$  anion ( $\nu(C\equiv O)$ ,  $cm^{-1}$ ) ( $CH_2Cl_2$ ): 2000(w), 1915(m, sh), 1880(s), and the  $^1H$  NMR spectrum ( $CD_2Cl_2$  int. ref. hexamethyldisiloxane) showed that there had been no change in the position of the hydride signal at  $-9.0$  ppm.

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