

# Versatile behaviour of iron–arylcarbene complexes towards alkoxides: C–Cl and C–C bond activation reactions

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## Abstract

The Cp-containing carbene complexes  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\{\kappa^2(\text{C},\text{O})\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-OMe}\}][\text{OTf}]$  (**2**) and  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})(\text{CH}_3\text{CN})\{\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}][\text{OTf}]$  (**3**) have been synthesised and characterised. Complex **2** has been characterised by a single-crystal X-ray diffraction analysis; the Fe–O distance of 2.045(5) Å suggests a rather strong bonding of the methoxy group. Substitution of one carbonyl ligand by PPh<sub>3</sub> allows the isolation of the chelate complex  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{PPh}_3)\{\kappa^2(\text{C},\text{Cl})\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}][\text{OTf}]$  (**4**). The reaction of  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\kappa^2(\text{C},\text{Cl})\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}][\text{OTf}]$  (**5**) with alkoxides R<sub>2</sub>Na (R = Me, Et) affords the chelate complexes  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\kappa^2(\text{C},\text{O})\text{-C}_6\text{H}_4\text{-}o\text{-C}(\text{OMe})(\text{OR})(\text{OR})\}][\text{OTf}]$  (**7** (R = Me) and **8** (R = Et), respectively. Similarly, the reaction of **3** with EtONa affords  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\{\kappa^2(\text{C},\text{O})\text{-C}_6\text{H}_4\text{-}o\text{-C}(\text{OEt})(\text{OEt})_2\}][\text{OTf}]$  (**9**), for which the Ar–Cl bond has been cleaved. No activation of the Ar–Cl bond is observed for the unchelated complex  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2\{\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}][\text{OTf}]$ . In contrast, treatment of the anisyl derivative  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\kappa^2(\text{C},\text{O})\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-OMe}\}][\text{OTf}]$  (**6**) with EtONa gives selectively the carbene complex  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{C}_6\text{H}_4\text{-}o\text{-OMe})\{\text{C}(\text{OEt})_2\}][\text{OTf}]$  (**12**). The Ar–OMe bond remains intact, but cleavage of the C $\alpha$ –CAr bond occurs. This rearrangement process, i.e.  $\alpha$ -elimination of the anisyl substituent, is favoured by the lability of the *ortho*-OMe group. Treatment of **2** with NaOEt gives as the only identified compound the ethyl ester  $[\text{MeOC}_6\text{H}_4\text{-}o\text{-}(\text{CO})\text{OEt}]$ . Clean formation of the methyl ester derivative  $[\text{MeOC}_6\text{H}_4\text{-}o\text{-}(\text{CO})\text{OMe}]$  is observed upon oxidation of **2** with C<sub>6</sub>H<sub>5</sub>I<sup>+</sup>O<sup>−</sup>. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Iron; C–Cl activation; C–C activation; Cleavage reactions; Carbene complexes

## 1. Introduction

The interest in Fischer-type carbene complexes has intensified as such derivatives play an important role in synthesis [1]. The reactivity of alkoxycarbene complexes towards nucleophiles is dominated by  $\alpha$ -addition at the carbene carbon atom [2,3]. However, such reactions frequently fail for iron complexes, principally due to the occurrence of secondary O-dealkylation reactions [4]. The latter process is inhibited in the case of chelated derivatives [5], and this allows us to study the reactivity of the complexes containing labile or hemilabile ligands, i.e.  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\kappa^2(\text{C},\text{X})\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-X}\}][\text{OTf}]$  (**5**, X = Cl; **6**, X = OMe) (OTf = CF<sub>3</sub>SO<sub>3</sub>) and their related Cp complexes  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\{\kappa^2(\text{C},\text{O})\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-OMe}\}][\text{OTf}]$  (**2**) and  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})(\text{CH}_3\text{CN})\{\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}][\text{OTf}]$  (**3**), towards alkoxides. We hypothesised that the combination of the Lewis acid character of the organometallic fragment of these highly electrophilic species and the presence of a potential vacant coordination site might promote new processes within the coordination sphere of the metal. In this paper, we report the bond activation reactions mediated by these carbene complexes leading to C–Cl and C–C bond cleavage, selectively. Preliminary results from this work have appeared [6].

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## 2. Results and discussion

### 2.1. Synthesis of the Cp-containing carbene complexes

The preparation of the C<sub>5</sub>Me<sub>5</sub>-containing complexes **5** and **6** has been previously described [5]. The C<sub>5</sub>H<sub>5</sub> complexes [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>{C(OMe)-C<sub>6</sub>H<sub>4</sub>-*o*-X}][OTf] (**1**, **a** X = Cl; **b** X = OMe) are synthesised by classical procedures from the dimer [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> [7]. The chelate complex [Fe(C<sub>5</sub>H<sub>5</sub>)(CO){κ<sup>2</sup>(C,*O*)-C(OMe)C<sub>6</sub>H<sub>4</sub>-*o*-OMe}][OTf]

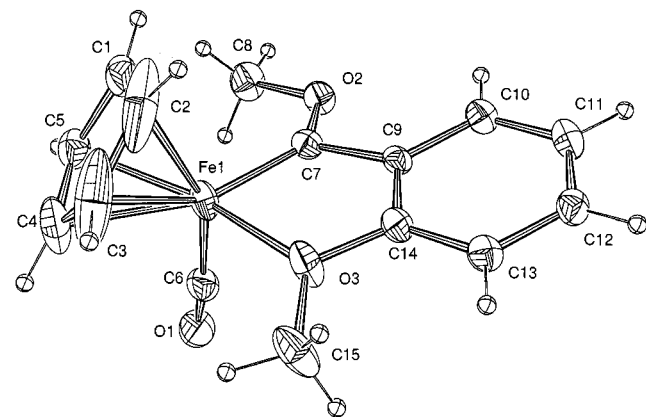
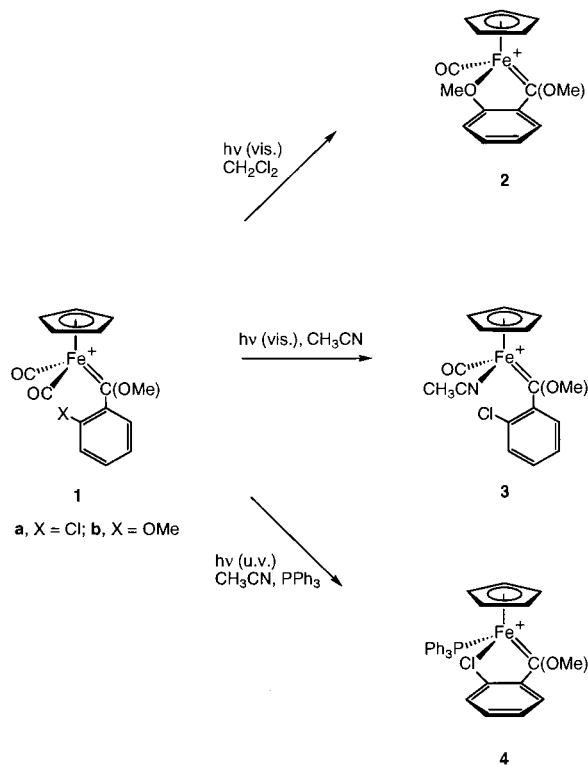


Fig. 1. ORTEP drawing of [Fe(C<sub>5</sub>H<sub>5</sub>)(CO){κ<sup>2</sup>(C,*O*)-C(OMe)C<sub>6</sub>H<sub>4</sub>-*o*-OMe}][OTf] (**2**).

Table 1

Selected bond lengths (Å) and angles (°)<sup>a</sup> for the complexes [Fe(C<sub>5</sub>H<sub>5</sub>)(CO){κ<sup>2</sup>(C,*O*)-C(OMe)C<sub>6</sub>H<sub>4</sub>-*o*-OMe}][OTf] (**2**)

Bond lengths			
Fe–C7	1.859(6)	C14–O3	1.367(7)
Fe–O3	2.045(5)	C7–C9	1.484(8)
C7–O2	1.299(7)	C9–C14	1.380(8)
Fe–C6	1.769(7)	C6–O1	1.145(8)
O3–C15	1.459(8)	O2–C8	1.457(8)
Bond angles			
Fe–C6–O1	172.9(6)	C14–O3–Fe	114.2(4)
O3–Fe–C7	81.8(2)	C14–C9–C7	115.4(5)
C6–Fe–C7	91(7)	C9–C14–O3	113.3(5)
C6–Fe–O3	99.5(3)	C7–O2–C8	120.0(5)
C9–C7–Fe	114.6(4)	O3–C14–C13	124.8(5)

<sup>a</sup> There are three independent molecules per unit cell; the selected data refer to one of them.

(**2**) is obtained upon photolysis (visible light) of **1b** in CH<sub>2</sub>Cl<sub>2</sub> (Scheme 1). In contrast to the C<sub>5</sub>Me<sub>5</sub> analogue, coordination of the chlorine atom does not take place; photolysis of **1a** under the same conditions leads to decomposition products. The chloroaryl fragment is a weak donor and the cationic [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)]<sup>+</sup> unit is not able to coordinate such a labile ligand. When irradiation is performed in a coordinating solvent such as CH<sub>3</sub>CN, the stable acetonitrile complex [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)(CH<sub>3</sub>CN){C(OMe)C<sub>6</sub>H<sub>4</sub>-*o*-Cl}][OTf] (**3**) is then isolated (Scheme 1).

Substitution of one carbonyl ligand by PPh<sub>3</sub> allows the isolation of the chelate complex [Fe(C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>){κ<sup>2</sup>(C,*Cl*)-C(OMe)C<sub>6</sub>H<sub>4</sub>-*o*-Cl}][OTf] (**4**). This latter compound is obtained in one step upon UV irradiation of **1a** in the presence of one equivalent of PPh<sub>3</sub> in CH<sub>3</sub>CN. The coordination of the Cl atom is indicated by the low-field chemical shift of the Ar<sub>Cl</sub> carbon atom in the <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (δ 143.3), whereas that of the non-chelated derivative **3** appears at δ 122.9. The downfield shift of the Ar<sub>Cl</sub> carbon resonance upon complexation of the Cl atom to the iron centre reflects a decrease in electronic density. This feature has been already observed for the related complex [Fe(C<sub>5</sub>Me<sub>5</sub>)(CO){κ<sup>2</sup>(C,*Cl*)-C(OMe)C<sub>6</sub>H<sub>4</sub>-*o*-Cl}][OTf] (**5**), for which the X-ray crystal structure has been established [5]. The phosphine ligand appears in this context to have the same electronic effect as the permethylation of the C<sub>5</sub> ring.

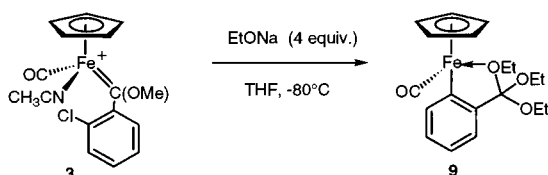
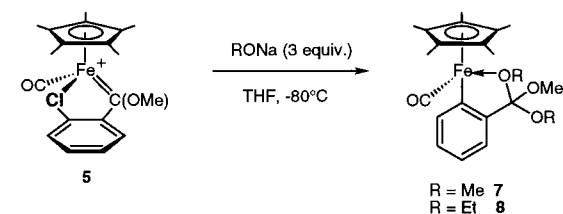
The structure of complex **2** has been unequivocally established by an X-ray crystal structure analysis (Fig. 1). Selected bond distances and angles are listed in Table 1. The data show the classical pseudo-octahedral geometry observed for three-legged piano-stool complexes. There are three independent molecules per unit cell. The Fe–C $\alpha$  distances [1.859(6), 1.879(5), 1.870(5) Å] compare well with those reported for other iron–carbene complexes (complex **5** — 1.857(6) Å) [5,8]. The

$C\alpha-O$  bond distances [1.299(7), 1.303(6), 1.299(7) Å] are typical for alkoxy-carbene complexes [5,8]. The Fe–O bonds [2.045(5), 2.043(4), 2.043(4) Å] are similar to those found for other oxygen-containing iron complexes [9]; for instance the Fe–O bond distances of  $[Fe(C_5Me_5)(dppe)(H_2O)]^+$  [9a] and  $[Fe(C_5Me_5)(dppe)-(OCMe_2)]^+$  [9b] are 2.063(6) and 2.031(4) Å, respectively.

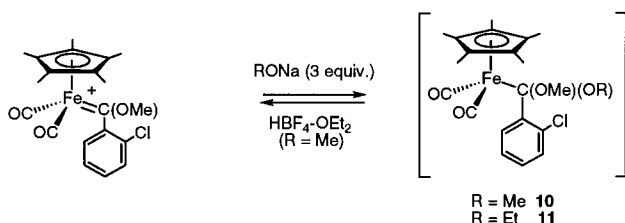
## 2.2. Reactivity towards alkoxides

The reactivity of these complexes towards alkoxides depends on the nature of the *ortho*-substituent X. Complex **5** reacts with an excess of RONa (R = Me, Et) to give in good yield (83–89%) the new chelate complexes  $[Fe(C_5Me_5)(CO)\{\kappa^2(C,O)-C_6H_4-o-C(OMe)(OR)(OR)\}]$  (**7**, R = Me; **8**, R = Et), which are isolated as dark brown crystals (Scheme 2).

The  $^1H$ -NMR spectrum ( $C_6D_6$ , 25°C) of **7** exhibits three broad signals for the methoxy groups at  $\delta$  3.02, 2.88 and 2.73. Three different signals ( $\delta$  56.3, 52.8 and 52.5), assigned to the magnetically non-equivalent OMe groups, are also observed in the  $^{13}C\{^1H\}$ -NMR ( $CDCl_3$ ) spectrum. One methoxy is coordinated to the iron centre, and the non-coordinated groups are diastereotopic. Variable-temperature NMR studies show that the signals coalesce at 42°C (300 MHz) and give one signal at  $\delta$  2.90 at 75°C; the exchange of the OMe groups is therefore rapid on the NMR timescale.



Scheme 2.



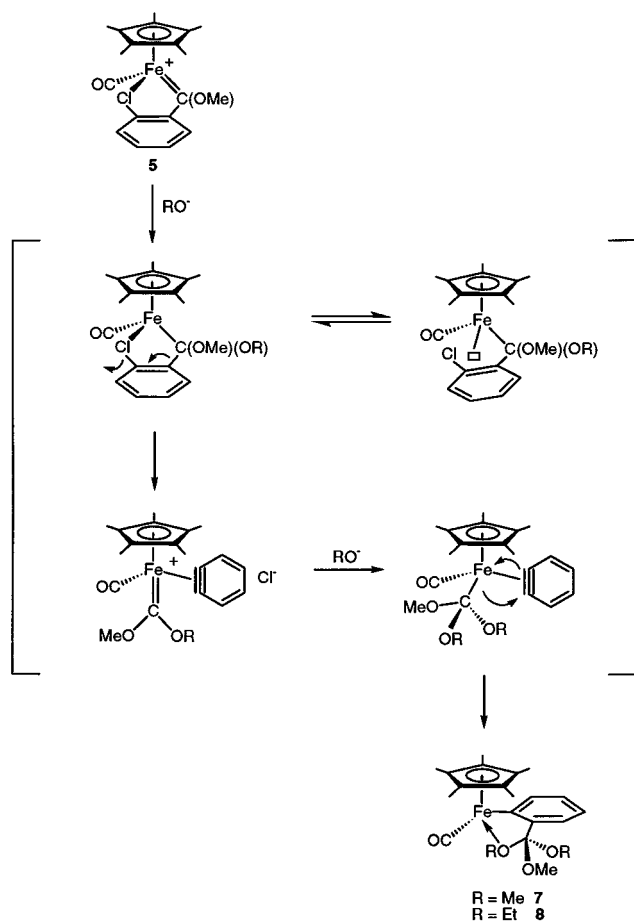
Scheme 3.

A similar phenomenon is observed in bimetallic systems bridged by  $Si(OSi(OMe)_3)_3$  [10]. Concerning derivative **8**, the two ethoxy groups are well-differentiated in the  $^1H$ - and  $^{13}C$ -NMR spectra. Moreover, the methylene protons of one EtO substituent are diastereotopic ( $\delta$  3.00, 2.78;  $^2J_{H-H} = 10$  Hz); this could be attributed to the coordination of this group to the stereogenic iron centre.

Similarly, complex **9** is formed upon treatment of **3** with EtONa–EtOH; the methoxy group has been exchanged by an ethoxy substituent, a feature also observed in the case of **6** (vide infra). The  $^1H$ -NMR (toluene- $d_8$ ,  $-20^\circ C$ ) spectrum shows two triplets at  $\delta$  1.01 (6H) and 0.82 (3H) attributed to the methyl protons of the ethoxy groups, whereas all the methylene protons are magnetically non-equivalent (see Section 3). The  $^{13}C$ -NMR ( $CDCl_3$ ) spectrum displays two signals for the methylene carbon at  $\delta$  63.0 and 59.9.

The formation of **7–9** involves the cleavage of the Ar–Cl bond, which could be promoted by the coordination of the chlorine atom or the presence of the potential vacant coordination site. In contrast, the Ar–Cl bond cleavage does not occur for the dicarbonyl carbene complex  $[Fe(C_5Me_5)(CO)_2\{C(OMe)C_6H_4-o-Cl\}][OTf]$ . Here, the reaction with  $EtO^-$  affords the ketal complex  $[Fe(C_5Me_5)(CO)_2\{C(OEt)(OMe)(C_6H_4-o-Cl)\}]$  (**11**), the formation of which results from addition at the electrophilic carbene centre (Scheme 3). Complex **11** is stable in the solid state as a yellow powder at  $-30^\circ C$ , but undergoes thermal decomposition in solution above  $0^\circ C$ , even in an aprotic medium [11]. The spectral properties of **11**, recorded at  $-30^\circ C$ , are in agreement with the proposed structure. The  $^1H$ - and  $^{13}C\{^1H\}$ -NMR spectra show two sets of signals, probably due to the presence of two geometric isomers. The rotation about the  $C\alpha-C_{Ar}$  bond would be hindered by the presence of the *ortho*-substituent on the  $C_6$  ring. For instance, in the  $^1H$ -NMR spectrum, the  $OCH_3$  resonances are observed at  $\delta$  3.31 and 2.98 as singlets, and the resonances of the  $OCH_2CH_3$  group appear at  $\delta$  3.55, 3.40 ( $CH_2$ ), and  $\delta$  3.25, 3.05 ( $CH_3$ ). In the  $^{13}C\{^1H\}$ -NMR spectrum, the  $C\alpha$  resonances are located at  $\delta$  116.5 and 114.9. These chemical shifts agree well with that observed for related ketal complexes [11]. However, we were unable to characterise the expected bis(methoxy) adduct  $[Fe(C_5Me_5)(CO)_2\{C(OMe)_2(C_6H_4-o-Cl)\}]$  (**10**), which is generated similarly by using sodium methoxide. Therefore, this intermediate has been chemically trapped as a carbene derivative. Addition of  $HBF_4 \cdot OEt_2$  ( $-80^\circ C$ ) to a solution of **10** quantitatively regenerates the starting carbene complex  $[Fe(C_5Me_5)(CO)_2\{C(OMe)C_6H_4-o-Cl\}]^+$  as a  $[BF_4]^-$  salt (Scheme 3). The spectral data of this latter species clearly show that the Ar–Cl bond is intact.

Although the formation of an *ortho*-ester group from carbene species has already been reported [12], such a

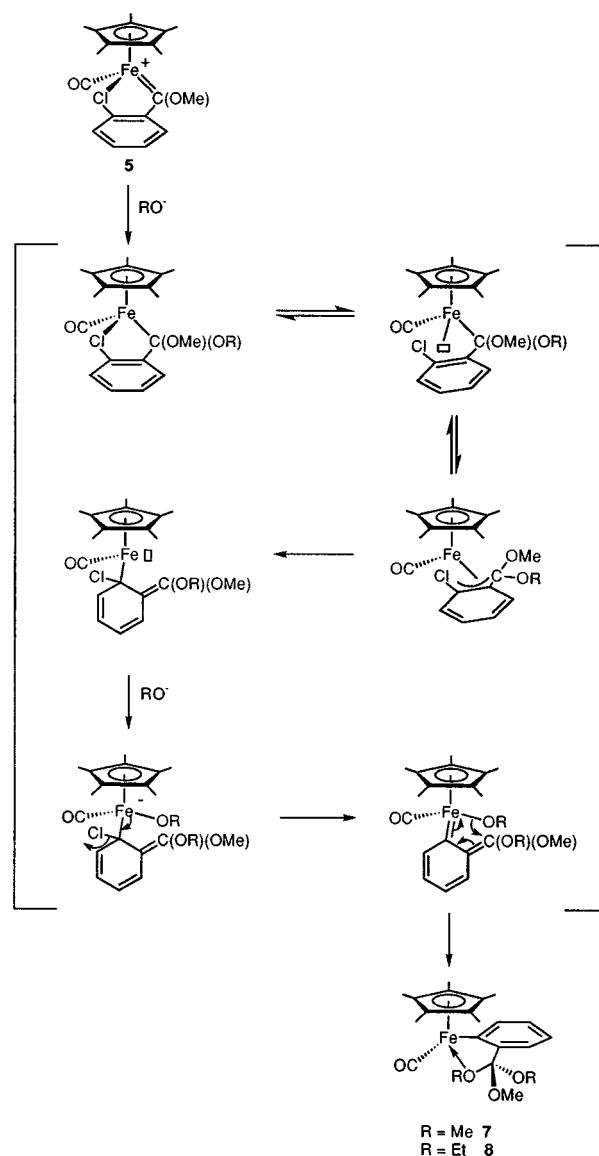


Scheme 4.

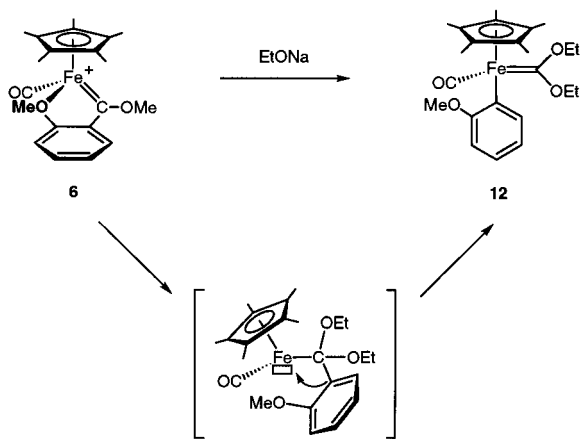
rearrangement process is without precedent. Nucleophilic attacks of Lewis bases at the halocarbon atom have been described previously [13]. However, such a process could not account for the formation of the observed products. Other examples of aryl-halide activation have been previously described by Green et al. [14]. For instance, the cleavage of the Ar-F bond of  $B(C_6F_5)_3$  by the iron complex  $[Fe(C_5H_5)(CO)_2Me]$  is proposed to involve a Fe-F interaction. We suggest that, in the first step, a  $\kappa^2(C,Cl)$  ketal derivative is formed by the addition of an alkoxide group at the  $C\alpha$ . This chelated species could be in equilibrium with the coordinatively unsaturated species, due to the facile decoordination of the chloro ligand (Schemes 4 and 5). If one considers this equilibrium, two scenarios are possible to explain the above results. The first would involve an initial cleavage of the C-Cl bond, as previously proposed by Green et al. [14]. The ketal derivative would rearrange into a benzyne complex. A nucleophilic addition of  $RO^-$  on the bis(alkoxy)carbene ligand affords the *ortho*-ester group (Scheme 4). Finally, the insertion of the benzyne ligand into the metal-carbon bond gives the observed compound. Alternatively, the presence of a potential vacant coordina-

tion site would allow the formation of a  $\pi$ -benzyl intermediate [15], since the benzyne intermediate is speculative (Scheme 5). The  $\pi$ -benzyl species would then rearrange into the  $\sigma$ -benzyl derivative. A nucleophilic attack of the alkoxide anion, followed by elimination of the chloride anion, and the migration of the alkoxy group to the exocyclic double bond affords the observed product. Both mechanisms could also be operative for **3**, since the  $CH_3CN$  ligand is labile. The exchange of the alkoxy group in the presence of an alkoxide has already been observed for carbene complexes [16]. However, our results do not allow a distinction between these two pathways.

In the present case, the initial substitution of the halide group by the alkoxide is ruled out, as indicated by the reactivity of the related anisyl derivative  $[Fe(C_5Me_5)(CO)\{\kappa^2(C,O)-C(OMe)C_6H_4-o-OMe\}][OTf]$



Scheme 5.



Scheme 6.

(6). Since methoxy groups are already present in the molecule, the ethoxide anion was used. Addition of EtONa (three equivalents) to a THF suspension of **6** ( $-80^{\circ}\text{C}$ ) gives, after work-up, a 93% yield of the bis(ethoxy)carbene complex  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})(\text{C}_6\text{H}_4\text{-}o\text{-OMe})\{\text{C}(\text{OEt})_2\}]$  (**12**) (Scheme 6). The structure of **12** has been established spectroscopically and the  $^{13}\text{C}$ -NMR ( $\text{CD}_2\text{Cl}_2$ ) spectrum exhibits the carbene carbon resonance characteristically downfield at  $\delta$  263.8.

Examples of selective activation of the Ar–OMe bond have been reported previously by Milstein and co-workers [17] by using Rh(I) complexes. However, the Lewis acid–base interaction in **6** appears not to weaken the Ar–OMe bond to the same extent as the Ar–Cl bond in the chloroaryl derivative **5**. Therefore, a different rearrangement process takes place. We assume that the mechanism involves the following steps: (i) formation of the ketal intermediate  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\kappa^2(\text{C},\text{O})\text{-C}(\text{OEt})_2(\text{C}_6\text{H}_4\text{-}o\text{-OMe})\}]$ ; and (ii) spontaneous de-insertion/migration of the anisyl substituent to the metal, promoted by the presence of a labile ligand. This final step corresponds to the reverse pathway of insertion/migration of an alkyl or aryl group to a carbene ligand (Scheme 6) [18]. When an alkyl or aryl migrates to a carbene fragment, the intramolecular C–C coupling reaction affords a coordinatively unsaturated complex, which usually rearranges via  $\beta$ -hydrogen elimination or is captured by an incoming ligand. The reverse process, i.e. migration of alkyl or aryl groups to give a carbene complex, is less common and requires the presence of a vacant coordination site [19]. The thermal instability of these ketal complexes might well provide the driving force for these clean rearrangement processes.

The parent Cp complex **2** was treated under the same reaction conditions with an excess of EtONa–EtOH; however, no carbene complex was formed. The only product that has been characterised is the ethyl ester derivative  $\text{MeOC}_6\text{H}_4\text{-}o\text{-(CO)OEt}$ , but we were unable

to spectroscopically identify or isolate any organometallic species. Moreover, it is noteworthy that the methoxy group has been exchanged by an ethoxy one during the course of the reaction, as in the former case. We assume that the bis(ethyl) ketal intermediate  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\{\kappa^2(\text{C},\text{O})\text{-C}(\text{OEt})_2\text{C}_6\text{H}_4\text{-}o\text{-OMe}\}]$  is formed, but again this species is too unstable to be spectroscopically detected. In contrast, the ketal intermediate does not evolve into a carbene species; the lability of the chelate OMe group appears to depend on the nature of the ancillary ligands ( $\text{C}_5\text{Me}_5$  vs.  $\text{C}_5\text{H}_5$ ). Clean and quantitative formation of the free methyl ester derivative  $\text{MeOC}_6\text{H}_4\text{-}o\text{-(CO)OMe}$  is observed upon oxidation of complex **2** by iodobenzene. The formation of a Re–formaldehyde complex from the corresponding methylene complex has already been reported [20,21].

In conclusion, this work demonstrates that the reaction pathways change dramatically, depending on the nature of the *ortho*-substituent and the electron-richness of the organometallic fragment. The approach that we have used — chelation assistance for a metal in order to facilitate bond activation — should be applicable more widely for selective organometallic processes.

### 3. Experimental

All manipulations were carried out under an Ar atmosphere with Schlenk techniques. Solvents were dried and distilled under nitrogen before use by standard methods. The compounds  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2\{\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-X}\}][\text{OTf}]$  and  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\kappa^2(\text{C},\text{X})\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-X}\}][\text{OTf}]$  (**5**, X = Cl; **6**, X = OMe) were prepared according to the literature procedure [5]. NMR spectra were recorded on Bruker DPX-200 and Bruker AC 300 (by S. Sinbandhit, CRMPO, Université de Rennes 1) spectrometers. Chemical shifts ( $\delta$ ) are given in ppm using  $\text{SiMe}_4$  as the external standard ( $^1\text{H}$ ,  $^{13}\text{C}$ ). Infrared spectra were obtained with a Bruker IFS28 FTIR spectrometer. Mass spectra were recorded on a Varian MAT 311 (70 eV) instrument and FABMS on a Micromass ZABSpec TOF spectrometer at the CRMPO. Microanalyses were performed by the ‘Centre de Microanalyse du CNRS’ at Vernaison, France.

#### 3.1. $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\{\text{C}(\text{O})\text{C}_6\text{H}_4\text{-}o\text{-X}\}]$ (X = Cl, OMe), general procedure

A suspension of 3 mmol (1 g) of  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$  and 7 mmol (210 mg) of potassium in 20 ml of THF was refluxed for 2 h. To the resulting orange mixture were added, at room temperature (r.t.), 7 mmol of the appropriate acid chloride X-*o*- $\text{C}_6\text{H}_4\text{C}(\text{O})\text{Cl}$ . The solu-

tion was stirred for 30 min, and the solvent removed in vacuo. The residue was extracted with ether (3 × 20 ml) and chromatography on alumina (eluent, pentane–CH<sub>2</sub>Cl<sub>2</sub> 4:1) afforded a yellow crystalline solid.

[Fe(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>{C(O)C<sub>6</sub>H<sub>4</sub>-*o*-Cl}] (80% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.38–7.16 (m, 3H, Ar), 6.92 (dd, <sup>3</sup>J(H–H) = 7.3 Hz, <sup>4</sup>J(H–H) = 1.9 Hz, 1H, Ar), 5.01 (s, 5H, C<sub>5</sub>H<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ = 256.8 (C=O), 213.8 (CO), 154.3 (Ar<sub>ipso</sub>), 130.2 (Ar), 128.6 (Ar), 127.3 (Ar), 124.4 (Ar<sub>Cl</sub>), 122.7 (Ar), 87.6 (C<sub>5</sub>H<sub>5</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1625 (s, νC=O), 1970 (s, νCO), 2025 (s, νCO). Anal. Found: C, 53.32; H, 3.07. Calc. for C<sub>14</sub>H<sub>9</sub>O<sub>3</sub>FeCl: C, 53.13; H, 2.87%.

[Fe(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>{C(O)C<sub>6</sub>H<sub>4</sub>-*o*-OMe}] (80% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.25 (td, <sup>3</sup>J(H–H) = 7.8 Hz, <sup>4</sup>J(H–H) = 1.6 Hz, 1H, Ar), 7.00–6.80 (m, 3H, Ar), 4.95 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 3.87 (s, 3H, OMe). <sup>13</sup>C{<sup>1</sup>H}-NMR: (CDCl<sub>3</sub>) δ = 258.1 (C=O), 214.4 (CO), 151.6 (Ar<sub>ipso</sub>), 146.4 (Ar<sub>OMe</sub>), 129.0 (Ar), 122.0 (Ar), 120.8 (Ar), 111.7 (Ar), 87.2 (C<sub>5</sub>H<sub>5</sub>), 55.7 (OMe). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1618 (s, νC=O), 1966 (s, νCO), 2022 (s, νCO). Anal. Found: C, 57.89; H, 3.85. Calc. for C<sub>15</sub>H<sub>12</sub>O<sub>4</sub>Fe: C, 57.73; H, 3.88%.

### 3.2. [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>{C(OMe)C<sub>6</sub>H<sub>4</sub>-*o*-X}][CF<sub>3</sub>SO<sub>3</sub>] (**1**, *a* X = Cl, *b* X = OMe), general procedure

A CH<sub>2</sub>Cl<sub>2</sub> solution (15 ml) of 1.1 mmol of [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>{C(O)C<sub>6</sub>H<sub>4</sub>-*o*-X}] (X = Cl, OMe) was treated with 1.43 mmol (0.16 ml) of CH<sub>3</sub>OSO<sub>2</sub>CF<sub>3</sub>. The mixture was stirred overnight and the solution was then concentrated under vacuum to ca. 3–5 ml. Compound **1** was washed with diethylether (3 × 10 ml). **1a** (yellow powder, 65%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.63–7.14 (m, 3H, Ar), 6.91 (dm, <sup>3</sup>J(H–H) = 7 Hz, 1H, Ar), 5.46 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.38 (s, 3H, OMe). <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ = 327.5 (=C), 208.1 (CO), 207.5 (CO), 147.4 (Ar), 132.6 (Ar), 130.5 (Ar), 128.9 (Ar), 123.9 (Ar) 122.9 (Ar<sub>Cl</sub>), 91.0 (C<sub>5</sub>H<sub>5</sub>), 70.7 (OMe). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2029 (s, νCO), 2074 (s, νCO). Anal. Found: C, 39.89; H, 2.49. Calc. for C<sub>16</sub>H<sub>12</sub>O<sub>6</sub>F<sub>3</sub>SFeCl: C, 39.99; H, 2.52%. **1b** (brown oil, 63%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.52 (t, <sup>3</sup>J(H–H) = 8.6 Hz, 1H, Ar), 7.28 (m, 2H, Ar), 7.05 (d, <sup>3</sup>J(H–H) = 8.6 Hz, 1H, Ar), 5.46 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.43 (s, 3H, OMe), 3.95 (s, 3H, OMe<sub>Ar</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2028 (s, νCO), 2071 (s, νCO). HRMS; *m/z*: Found 327.0318 [M<sup>+</sup>]. Calc. for C<sub>16</sub>H<sub>15</sub>O<sub>4</sub>Fe: 327.0320 [M<sup>+</sup>].

### 3.3. [Fe(C<sub>5</sub>H<sub>5</sub>)(CO){κ<sup>2</sup>(C,O)-C(OMe)C<sub>6</sub>H<sub>4</sub>-*o*-OMe}]-[CF<sub>3</sub>SO<sub>3</sub>] (**2**)

A CH<sub>2</sub>Cl<sub>2</sub> solution of 0.7 mmol (330 mg) of **1b** was irradiated (visible light) overnight. The yellow solution became red. After evaporation of the solvent, the residue was washed with ether (2 × 10 ml), affording a

red powder. Crystallisation in CH<sub>2</sub>Cl<sub>2</sub>–EtO<sub>2</sub> at –20°C gave red microcrystals (219 mg, 71%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.89 (d, <sup>3</sup>J(H–H) = 8 Hz, 1H, Ar), 7.69 (t, <sup>3</sup>J(H–H) = 7.7 Hz, 1H, Ar), 7.22 (m, 2H, Ar), 5.27 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.78 (s, 3H, OMe), 4.27 (s, 3H, OMe<sub>Ar</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ = 316.8 (=C), 212.2 (CO), 168.9 (Ar<sub>OMe</sub>), 137.9 (Ar), 133.8 (Ar), 124.3 (Ar<sub>ipso</sub>), 120.7 (Ar), 113.3 (Ar), 84.4 (C<sub>5</sub>H<sub>5</sub>), 70.9 (OMe), 70.7 (OMe). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2004 (s, νCO). Anal. Found: C, 42.81; H, 3.40. Calc. for C<sub>16</sub>H<sub>15</sub>O<sub>6</sub>FeSF<sub>3</sub>: C, 42.88; H, 3.37%.

### 3.4. Crystal structure analysis of **2**

C<sub>15</sub>H<sub>15</sub>O<sub>3</sub>Fe, CF<sub>3</sub>SO<sub>3</sub>, M 448.19 g mol<sup>-1</sup>, colour red, crystal size 0.42 × 0.23 × 0.20 mm, crystal system monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 13.4766(2), *b* = 23.4767(3), *c* = 16.8954(3) Å, β = 94.304(1)°, *V* = 5330.4(1) Å<sup>-3</sup>, *Z* = 12, ρ = 1.675 g cm<sup>-3</sup>, *T* = 110 K, μ = 10.28 cm<sup>-1</sup>, *F*(000) = 2736. The sample was studied on a Nonius Kappa CCD with graphite monochromatised Mo–Kα radiation, λ = 0.71073 Å. The data collection (2θ<sub>max</sub> = 60°) gave 63 738 integrated reflections (*hkl*: –0.17, 0.30, –22.22). The data reduction with Denzo and Scalepack [22] led to 12 672 independent reflections (10 157 with *I* > 2.0σ(*I*)). The structure was solved with SIR-97 [23], which reveals all the non-hydrogen atoms of the three complexes of the asymmetric unit. After anisotropic refinement, the three anions appeared disordered. The whole structure was refined with SHELXL97 [24] by the full-matrix least-squares techniques (use of *F*<sup>2</sup> magnitude; *x*, *y*, *z*, β<sub>*ij*</sub> for Fe, C and O atoms, and riding mode for H atoms; isotropic mode for the anions; 683 variables and 10 157 observations with *I* > 2.0σ(*I*). *w*<sub>calc</sub> = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.094*P*)<sup>2</sup> + 29.9*P*] where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3, with the resulting *R* = 0.088, *R*<sub>w</sub> = 0.232 and *S*<sub>w</sub> = 1.12 (residual Δρ < 1.6 e Å<sup>-3</sup>).

### 3.5. [Fe(C<sub>5</sub>H<sub>5</sub>)(CO)(CH<sub>3</sub>CN){C(OMe)C<sub>6</sub>H<sub>4</sub>-*o*-Cl}]-[CF<sub>3</sub>SO<sub>3</sub>] (**3**)

A CH<sub>3</sub>CN solution of 0.62 mmol (308 mg) of **1a** was irradiated (visible light) overnight. The yellow solution became orange. After evaporation of the solvent, the residue was washed with diethylether (2 × 10 ml) to afford a red oil (228 mg, 74%). <sup>1</sup>H-NMR (CD<sub>3</sub>CN): δ = 7.53 (m, 3H, Ar), 7.18 (m, 1H, Ar), 5.06 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.37 (s, 3H, OMe). <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ = (=C not observed due to coalescence), 214.9 (CO), 147.6 (Ar<sub>ipso</sub>), 134.6 (CN), 131.0 (Ar), 129.6 (Ar), 128.2 (Ar), 124.4 (Ar), 122.9 (Ar<sub>Cl</sub>), 88.8 (C<sub>5</sub>H<sub>5</sub>), 67.4 (OMe), 5.2 (CH<sub>3</sub>CN). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2019 (s, νCO). HRMS; *m/z*: Found: 344.0148 [M<sup>+</sup>]. Calc. for C<sub>16</sub>H<sub>15</sub>O<sub>2</sub>FeCl: 344.0141 [M<sup>+</sup>].

3.6.  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{PPh}_3)\{\kappa^2(\text{C},\text{Cl})\text{-C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}]\text{-}[\text{CF}_3\text{SO}_3]$  (**4**)

To a solution of 4 mmol (1.92 g) of **1a** in  $\text{CH}_3\text{CN}$  (200 ml) was added 5 mmol (1.3 g) of  $\text{PPh}_3$ . The solution was photolysed under UV for 16 h. The solvent was evaporated, and crystallisation of the residue in a  $\text{CH}_2\text{Cl}_2$ –ether mixture provided 2.7 g (90%) of a yellow-green powder.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 8.11\text{--}7.12$  (m, Ar/Ph) 4.92 (s, 5H,  $\text{C}_5\text{H}_5$ ), 4.45 (s, 3H, OMe).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 319.15$  (d,  $^2J(\text{P-C}) = 23$  Hz, =C), 146.0 ( $\text{Ar}_{\text{ipso}}$ ), 143.5 ( $\text{Ar}_{\text{Cl}}$ ), 135.3–121.7 (Ar/Ph), 80.9 ( $\text{C}_5\text{H}_5$ ), 67.8 (OMe).  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$  ext):  $\delta = 57.86$  ( $\text{PPh}_3$ ). HRMS;  $m/z$ : Found: 537.0835 [ $\text{M}^+$ ]. Calc. for  $\text{C}_{31}\text{H}_{27}\text{OFeP}$ : 537.0838 [ $\text{M}^+$ ].

3.7.  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})\{\kappa^2(\text{C},\text{O})\text{-C}_6\text{H}_4\text{-}o\text{-C}(\text{OMe})(\text{OR})\text{-}(\text{OR})\}]\text{-}(\text{OR})$  (**7**,  $R = \text{Me}$ ; **8**,  $R = \text{Et}$ )

A suspension of 1.5 mmol (785 mg) in 25 ml of THF of **5** was treated at  $-80^\circ\text{C}$  with a freshly prepared ROH ( $R = \text{Me}, \text{Et}$ ) solution of  $\text{RONa}$  (three equivalents). After stirring for 1 h, the solution was warmed up to r.t. and evaporated to dryness. The residue was extracted with pentane and crystallisation at  $-20^\circ\text{C}$  gave dark brown crystals. **7** (539 mg, 89%, dark brown crystals):  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta = 7.84$  (dd,  $^3J(\text{H-H}) = 7.5$  Hz,  $^4J(\text{H-H}) = 0.8$  Hz, 1H, Ar), 7.35 (td,  $^3J(\text{H-H}) = 7.4$  Hz,  $^4J(\text{H-H}) = 1.6$  Hz, 1H, Ar), 7.10 (td,  $^3J(\text{H-H}) = 7.4$  Hz,  $^4J(\text{H-H}) = 1$  Hz, 1H, Ar), 6.99 (dd,  $^3J(\text{H-H}) = 7.5$  Hz,  $^4J(\text{H-H}) = 1.5$  Hz, 1H, Ar), 3.02 (br s, 3H, OMe), 2.88 (br s, 3H, OMe), 2.73 (br s, 3H, OMe), 1.42 (s, 15H,  $\text{C}_5\text{Me}_5$ ).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 221.7$  (CO), 174.6 (Fe–Ar), 140.2 (Ar), 136.5 ( $\text{Ar}_{\text{C}}$ ), 127.9 (Ar), 126.8 ( $\text{C}(\text{OMe})_3$ ), 123.9 (Ar), 121.9 (Ar), 89.6 ( $\text{C}_5\text{Me}_5$ ), 56.3 (OMe), 52.7 (OMe), 52.5 (OMe), 10.8 ( $\text{C}_5\text{Me}_5$ ). IR (pentane): 1917 (s,  $\nu\text{CO}$ ). Anal. Found: C, 62.78; H, 7.12. Calc. for  $\text{C}_{21}\text{H}_{28}\text{O}_4\text{Fe}$ : C, 63.01; H, 7.05%. **8** (530 mg, 83%, dark brown crystals).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 7.57$  (d,  $^3J(\text{H-H}) = 7.5$  Hz, 1H, Ar), 7.17 (t,  $^3J(\text{H-H}) = 6.7$  Hz, 1H, Ar), 6.96 (t,  $^3J(\text{H-H}) = 7$  Hz, 1H, Ar), 6.84 (d,  $^3J(\text{H-H}) = 7$  Hz, 1H, Ar), 3.31 (q,  $^3J(\text{H-H}) = 7$  Hz, 2H,  $\text{OCH}_2\text{CH}_3$ ), 3.15 (s, 3H, OMe), 3.00 (m, 1H,  $\text{OCH}_2\text{CH}_3$ ), 2.79 (m, 1H,  $\text{OCH}_2\text{CH}_3$ ), 1.60 (s, 15H,  $\text{C}_5\text{Me}_5$ ), 1.14 (t,  $^3J(\text{H-H}) = 7$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ), 0.98 (t,  $^3J(\text{H-H}) = 7$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 221.4$  (CO), 173.5 (Fe–Ar), 139.7 (Ar), 137.4 ( $\text{Ar}_{\text{C}}$ ), 127.4 (Ar), 125.8 ( $\text{C}(\text{OMe})(\text{OEt})_2$ ), 123.4 (Ar), 121.5 (Ar), 89.2 ( $\text{C}_5\text{Me}_5$ ), 60.2 ( $\text{OCH}_2\text{CH}_3$ ), 59.8 ( $\text{OCH}_2\text{CH}_3$ ), 55.8 (OMe), 15.3 ( $\text{OCH}_2\text{CH}_3$ ), 14.8 ( $\text{OCH}_2\text{CH}_3$ ), 10.1 ( $\text{C}_5\text{Me}_5$ ). IR (pentane): 1914 (s,  $\nu\text{CO}$ ). HRMS;  $m/z$ : Found 428.1641 [ $\text{M}^+$ ]. Calc. for  $\text{C}_{23}\text{H}_{32}\text{O}_4\text{Fe}$ : 428.1649 [ $\text{M}^+$ ]. Anal. Found: C, 64.82; H, 7.47. Calc. for  $\text{C}_{23}\text{H}_{32}\text{O}_4\text{Fe}$ : C, 64.49; H, 7.53%.

3.8.  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\{\kappa^2(\text{C},\text{O})\text{-C}_6\text{H}_4\text{-}o\text{-C}(\text{OEt})(\text{OEt})_2\}]\text{-}(\text{OEt})$  (**9**)

A THF suspension of 1 mmol (490 mg) of **3** was treated at  $-80^\circ\text{C}$  with a freshly prepared EtOH solution of EtONa (4 mmol). After stirring for 1 h, the solution was warmed up to  $-30^\circ\text{C}$  and evaporated to dryness. The brown residue was extracted with pentane ( $2 \times 15$  ml), and evaporation to dryness gave a brown oil (310 mg, 83%).  $^1\text{H-NMR}$  (toluene- $d_8$ ,  $-20^\circ\text{C}$ ):  $\delta = 7.62$  (d,  $^3J(\text{H-H}) = 7$  Hz, 1H, Ar), 7.20 (t,  $^3J(\text{H-H}) = 7$  Hz, 1H, Ar), 7.04 (m, 2H, Ar), 4.09 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.75, 3.32, 3.12, 2.88, 2.82, 2.45 ( $6 \times \text{m}$ , 1H,  $\text{OCH}_2\text{CH}_3$ ), 1.01 (t,  $^3J(\text{H-H}) = 7$  Hz, 6H,  $\text{OCH}_2\text{CH}_3$ ), 0.82 (t,  $^3J(\text{H-H}) = 7$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 222.0$  (CO), 165.9 (Fe–Ar), 143.5 (Ar), 139.7 ( $\text{Ar}_{\text{C}}$ ), 127.4 (Ar), 124.3 (Ar), 122.6 (Ar), 114.3 ( $\text{C}(\text{OEt})_3$ ), 80.9 ( $\text{C}_5\text{H}_5$ ), 63.0 ( $\text{OCH}_2\text{CH}_3$ ), 59.9 ( $\text{OCH}_2\text{CH}_3$ ), 15.2 ( $\text{OCH}_2\text{CH}_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ ): 1925 (s,  $\nu\text{CO}$ ). HRMS;  $m/z$ : Found: 372.1014 [ $\text{M}^+$ ]. Calc. for  $\text{C}_{19}\text{H}_{24}\text{O}_4\text{Fe}$ : 372.1024 [ $\text{M}^+$ ].

3.9. Formation of  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2\{\text{C}(\text{OMe})\text{-}(\text{C}_6\text{H}_4\text{-}o\text{-Cl})\}][\text{BF}_4]$  via  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2\{\text{C}(\text{OMe})_2\text{-}(\text{C}_6\text{H}_4\text{-}o\text{-Cl})\}]\text{-}(\text{OEt})$  (**10**)

A THF suspension of 1 mmol (551 mg) of  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2\{\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}][\text{OTf}]$  was treated at  $-80^\circ\text{C}$  with a freshly prepared MeOH solution of MeONa (3 mmol). After stirring for 1 h at  $-80^\circ\text{C}$ , the solution was evaporated to dryness. The yellow residue was extracted with pentane ( $2 \times 15$  ml) at  $-80^\circ\text{C}$ . Addition of 1 mmol of  $\text{HBF}_4\text{-OEt}_2$  (150  $\mu\text{l}$ , 85% in  $\text{Et}_2\text{O}$ ) to the resulting solution caused precipitation of a yellow powder (400 mg, 81%).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 7.59\text{--}7.42$  (m, 3H, Ar), 7.28 (dd,  $^3J(\text{H-H}) = 7.6$  Hz, 1H, Ar), 4.49 (s, 3H, OMe), 2.00 (s, 15H,  $\text{C}_5\text{Me}_5$ ).  $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 210.8$  (CO), 147.6 ( $\text{Ar}_{\text{ipso}}$ ), 132.0 (Ar), 130.4 (Ar), 128.8 (Ar), 123.2 ( $\text{Ar}_{\text{Cl}}$ ), 122.5 (Ar), 103.9 ( $\text{C}_5\text{Me}_5$ ), 70.7 (OMe), 9.8 ( $\text{C}_5\text{Me}_5$ ). IR (Nujol): 2052 (s,  $\nu\text{CO}$ ), 2008 (s,  $\nu\text{CO}$ ), 1054 (s,  $\nu\text{BF}_4$ ). HRMS;  $m/z$ : Found: 401.0628 [ $\text{M}^+$ ]. Calc. for  $\text{C}_{20}\text{H}_{22}\text{O}_3\text{FeCl}$ : 401.0607 [ $\text{M}^+$ ].

3.10.  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2\{\text{C}(\text{OEt})(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}]\text{-}(\text{OEt})$  (**11**)

A suspension of 1 mmol (551 mg) of  $[\text{Fe}(\text{C}_5\text{Me}_5)(\text{CO})_2\{\text{C}(\text{OMe})\text{C}_6\text{H}_4\text{-}o\text{-Cl}\}][\text{OTf}]$  in 20 ml of THF was treated at  $-80^\circ\text{C}$  with a freshly prepared EtOH solution of EtONa (three equivalents). After stirring for 1 h, the solution was evaporated to dryness. The residue was extracted at  $-20^\circ\text{C}$  with pentane ( $3 \times 15$  ml), and evaporation of the solvent gave a yellow powder (390 mg, 93%). The solid decomposes at r.t.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $-30^\circ\text{C}$ ):  $\delta = 7.58, 7.47, 7.17, 6.98$  (m, Ar), 3.55, 3.40 (br m,  $\text{OCH}_2\text{CH}_3$ ), 3.31 (s, OMe), 3.25, 3.05

(br m, OCH<sub>2</sub>CH<sub>3</sub>), 2.98 (s, OMe), 1.73, 1.64 (s, C<sub>5</sub>Me<sub>5</sub>), 1.35, 1.17 (br m, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, –30°C): δ = 219.1, 218.8, 218.2 (CO), 149.6, 147.9 (Ar<sub>C</sub>), 131.3, 130.9 (Ar), 129.8, 129.2 (Ar<sub>Cl</sub>), 128.0, 126.9, 126.5, 125.9, 125.6 (Ar), 116.5, 114.9 (C<sub>z</sub>), 97.9, 96.6 (C<sub>5</sub>Me<sub>5</sub>), 58.9, 57.1 (OCH<sub>2</sub>CH<sub>3</sub>), 51.5, 50.8 (OMe), 15.5, 15.0 (OCH<sub>2</sub>CH<sub>3</sub>), 10.0, 9.8 (C<sub>5</sub>Me<sub>5</sub>). IR (pentane): 1997 (s, νCO), 1947 (s, νCO). Two isomers were observed at –30°C, resulting from a hindered C<sub>5</sub>\*-Ar rotation at the low temperature. However, decomposition at 0°C prevents the observation of any coalescence of the signals.

### 3.11. [Fe(C<sub>5</sub>Me<sub>5</sub>)(CO)(C<sub>6</sub>H<sub>4</sub>-*o*-OMe){C(OEt)<sub>2</sub>}] (12)

A suspension of 0.7 mmol (363 mg) of **6** in 15 ml of THF was treated at –80°C with a freshly prepared EtOH solution of EtONa (three equivalents). After stirring for 2 h, the solution was warmed up to r.t. and evaporated to dryness. The residue was extracted with pentane and crystallisation at –20°C gave yellow crystals (285 mg, 95%). <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>): δ = 7.75 (d, <sup>3</sup>J(H–H) = 6.6 Hz, 1H, Ar), 7.11 (t, <sup>3</sup>J(H–H) = 7.5 Hz, 1H, Ar), 6.96 (t, <sup>3</sup>J(H–H) = 7 Hz, 1H, Ar), 6.59 (d, <sup>3</sup>J(H–H) = 6.6 Hz, 1H, Ar), 4.05 (br m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.92 (br m, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 3.48 (s, 3H, OMe), 1.61 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 0.92 (br m, 6H, OCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 263.8 (=C), = 226.6 (CO), 166.7 (Fe–Ar), 154.3 (Ar<sub>OMe</sub>), 143.9 (Ar), 122.5 (Ar), 119.8 (Ar), 108.2 (Ar), 95.5 (C<sub>5</sub>Me<sub>5</sub>), 66.7 (br s, OCH<sub>2</sub>CH<sub>3</sub>), 55.1 (OMe), 14.6 (OCH<sub>2</sub>CH<sub>3</sub>), 9.7 (C<sub>5</sub>Me<sub>5</sub>). IR (pentane): 1936 (s, νCO). HRMS; *m/z*: Found: 383.1314 [M<sup>+</sup> – OEt], 355.1355 [M<sup>+</sup> – OEt – CO]. Calc. for C<sub>21</sub>H<sub>27</sub>O<sub>3</sub>Fe: 383.1310 [M<sup>+</sup> – OEt], 355.1361 [M<sup>+</sup> – OEt – CO]. Anal. Found: C, 64.82; H, 7.47. Calc. for C<sub>23</sub>H<sub>32</sub>O<sub>4</sub>Fe: C, 64.49; H, 7.53%.

### 3.12. Reaction of

[Fe(C<sub>5</sub>H<sub>5</sub>)(CO){κ<sup>2</sup>(C,O)-C(OMe)(C<sub>6</sub>H<sub>4</sub>-*o*-OMe)}][OTf] (**2**) with EtONa

A suspension of 0.7 mmol (330 mg) of **2** in 25 ml of THF was treated at –80°C with a freshly prepared EtOH solution of EtONa (three equivalents). After stirring overnight, extraction with pentane gave as the only identified product the ethyl ester derivative *o*-(OMe)-C<sub>6</sub>H<sub>4</sub>-C(O)OEt. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.79 (dd, 1H, <sup>3</sup>J(H–H) = 7.8 Hz, <sup>4</sup>J(H–H) = 1.3 Hz, Ar), 7.46 (td, 1H, <sup>3</sup>J(H–H) = 7 Hz, <sup>4</sup>J(H–H) = 1.2 Hz, Ar), 7.00 (m, 2H, Ar), 4.36 (d, 2H, <sup>3</sup>J(H–H) = 7 Hz, OCH<sub>2</sub>), 3.91 (s, 3H, OMe), 1.38 (t, 3H, <sup>3</sup>J(H–H) = 7 Hz, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ = 166.2 (C=O), 159.1 (Ar<sub>OMe</sub>), 133.3 (Ar), 131.5 (Ar), 120.5 (Ar<sub>ipso</sub>), 120.1 (Ar), 112.1 (Ar), 60.8 (CH<sub>2</sub>CH<sub>3</sub>), 56.0 (OMe), 14.3 (CH<sub>2</sub>CH<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1720 (s, νC=O).

### 3.13. Preparation of [o-(OMe)-C<sub>6</sub>H<sub>4</sub>-C(O)OMe] from [Fe(C<sub>5</sub>H<sub>5</sub>)(CO){κ<sup>2</sup>(C,O)-C(OMe)(C<sub>6</sub>H<sub>4</sub>-*o*-OMe)}]-[CF<sub>3</sub>SO<sub>3</sub>] (**2**) with C<sub>6</sub>H<sub>5</sub>I<sup>+</sup>-O<sup>–</sup>

To a solution of 1.4 mmol (630 mg) in 15 ml of CH<sub>2</sub>Cl<sub>2</sub> was added at r.t., 1.7 mmol (370 mg) of C<sub>6</sub>H<sub>5</sub>IO. The reaction mixture was stirred overnight. After evaporation to dryness, the residue was extracted with pentane. Evaporation gave a brown oil (100 mg, 43% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.85 (d, <sup>3</sup>J(H–H) = 7.2 Hz, 1H, Ar), 7.53 (t, <sup>3</sup>J(H–H) = 7.5 Hz, 1H, Ar), 7.04 (m, 2H, Ar), 3.96 (s, 3H, OMe), 3.95 (s, 3H, OMe); <sup>13</sup>C{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ = 167.2 (C=O), 159.6 (Ar<sub>OMe</sub>), 134.0 (Ar), 132.1 (Ar), 120.6 (Ar), 120.4 (Ar<sub>CO</sub>), 112.4 (Ar), 56.4 (OMe<sub>Ar</sub>), 52.5 (OMe). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1725 (s, νC=O).

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 155024 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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