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# One-electron reduction of the iron carbene complexes $[Fe(Cp^*)(CO)_2(=C(OMe)R)]^+$ (R = H or Me) and hydrogen-atom *vs*. alkyl-radical transfer in the 19-electron intermediates

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### Abstract

The one-electron reduction of the carbene complexes $[Fe(Cp^*)(CO)_2(=C(OMe)R)][X]$ (**2**, R = Me; **4**, R = H) affords the 19-electron intermediate $[Fe(Cp^*)(CO)_2(=C(OMe)R)]^{\cdot}$ which loses the methyl group from the methoxy fragment or abstracts a hydrogen atom from the medium. In the case of R = H, the iron formyl intermediate decomposes *in situ* into the metal hydride $[Fe(Cp^*)(CO)_2H]$ (**9**) which acts as a good hydrogen-atom source.

## Introduction

Since their discovery in 1964 by Fischer and Maasböl [1], the chemistry of transition metal-carbene complexes as in almost all organometallic chemistry has been dominated by the 16e/18e rule [2]. The weakly electrophilic character of the heterosubstituted carbene stabilized by Group 7 and 8 [3] transition metals has greatly restricted the scope of the reactions in which they are involved. Activation of the cationic heterocarbene complexes by one-electron reduction would open a new field of investigation. Such activation may be involved with heterogeneous catalysed processes such as Fischer–Tropsch synthesis, for which surface-bound carbene species are currently postulated [2a] and electron-transfer through the metal surface should be facile. As shown in Scheme 1, the possible pathways for the evolution of the 19e-metal complexes resulting from the one-electron reduction of the 18e-carbene compounds should be characteristic of a radical. It may dimerize by ligand–ligand coupling [4] (path A), abstract hydrogen atom from the

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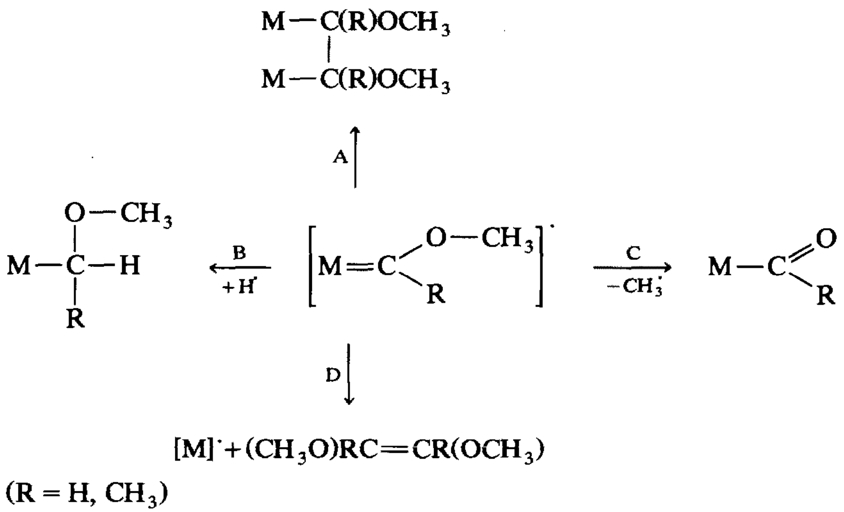


Scheme 1. Possible pathways for the formation of the 19 electron-metal alkoxy-carbene complexes.

solvent [5] (path B), liberate an alkyl radical (path C) [6], or be converted into a more stable 17e-metal species by releasing the two-electron carbene, which can couple (path D).

Previously, we reported that the thermally stable and unreactive iron-methylene complex [Fe(Cp*)(dppe)(=$CH_2$)][$BF_4$] (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) was activated by a single electron-transfer which promotes the loss of a methylene fragment (path D) [7]. We wish to report here the activation upon reduction by one electron of the two weakly electrophilic carbene complexes [Fe(Cp*)$(CO)_2$(=C(OMe)R)][X] (**2**, R = Me, X = $SO_3CF_3$; **4**, R = H, X = $PF_6$) and the behaviour of the resulting transient 19e radicals [Fe(Cp*)$(CO)_2$(=C(OMe)R)]$^{\cdot}$.

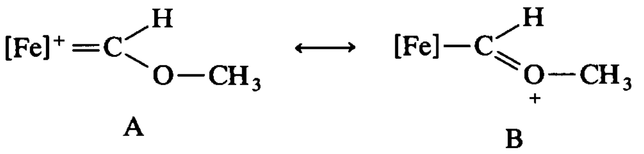
## Results and discussion

### *Synthesis and properties of the carbene complexes [Fe(Cp*)(CO)$_2$(=C(OMe)R)][X] (2, R = $CH_3$, X = $CF_3SO_3$; 4, R = H, X = $PF_6$)*

Whereas the secondary carbene complex **4** is obtained following the reported procedure [3], the new iron carbene [Fe(Cp*)$(CO)_2$(=C(OMe)Me)][$CF_3SO_3$] (**2**) is readily synthesized by treatment of [Fe(Cp*)$(CO)_2$(COMe)] (**1**) with methyl triflate. The reaction is complete overnight and the carbene complex **2** is obtained as a pure yellow powder in 90% yield (eq. 1).

$$\underset{(\mathbf{1})}{[\mathrm{Fe(Cp^*)(CO)_2(COMe)}]} + \mathrm{MeSO_3CF_3} \rightarrow \underset{(\mathbf{2})}{[\mathrm{Fe(Cp^*)(CO)_2({=}C(OMe)Me)}][\mathrm{CF_3SO_3}]} \qquad (1)$$

The initial cyclic voltammograms (CV) of complexes **2** and **4** from 0 to −1.5 V (20°C, 0.100 V $s^{-1}$, $CH_2Cl_2$, 0.1 *M* tetrabutylammonium hexafluorophosphate,



Scheme 2.

platinum electrode, V *vs.* SCE) are characterized by an irreversible wave (eq. 2). The cathodic peak potentials are −1.35 and −0.95 V for **2** and **4**, respectively. Bulk electrolysis of complex **2** performed at −1.5 V consumes one Faraday per mole of carbene, establishing the single electron nature of the reduction.

$$[Fe(Cp^*)(CO)_2(=C(OMe)R)]^+ + e^- \rightarrow [Fe(Cp^*)(CO)_2(=C(OMe)R)]^\cdot \qquad (2)$$

(**2**, R = Me; **4**, R = H)

The substitution of the hydrogen atom by a methyl group on the carbene ligand causes a shift of the $E_c$ value by −0.4 V, suggesting a significant increase of the contribution of the oxonium mesomeric form B (Scheme 2) to the the electronic structure. This is corroborated by the IR spectra, which display two bands 2017 and 2060 $cm^{-1}$ for **4** and 1999 and 2045 for **2**, in agreement with greater electron density at the metal in the compound **2**.

Compound **2** is thermally stable: it is quantitatively recovered after heating under reflux in acetonitrile for 2 hours. We have previously shown that the secondary carbene complex **4** is less stable and slowly decomposes in solution to give, *inter alia*, the tricarbonyl salt $[Fe(Cp^*)(CO)_3][PF_6]$ [3].

*Electron-transfer activation*

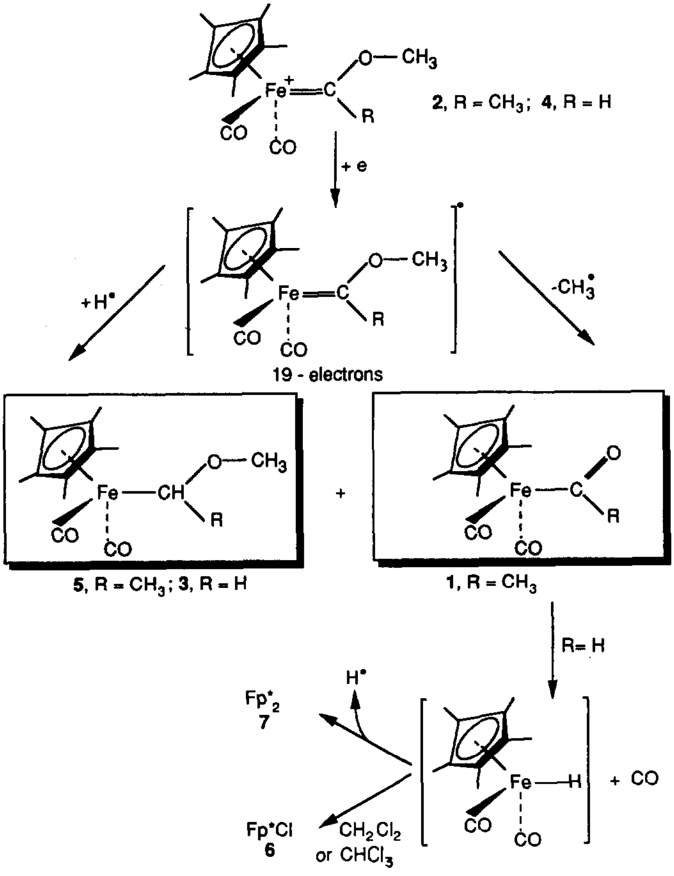
A stoichiometric amount of $[Cp_2Co]$ was added to a solution of **2** or **4** and stirred for 30 min at 20°C. The resulting mixture was evaporated to dryness, extracted with pentane, and analysed by IR and $^1H$ NMR spectroscopies. The pentane-insoluble residue contains a stoichiometric quantity of $[Cp_2Co][PF_6]$ as the only salt product, showing the completion of the reactions. The results obtained in various solvents are listed in Table 1.

The reaction of **2** in pentane or $CHCl_3$ affords the iron acyl complex **1** as a pure compound (Table 1). In THF, the new ether derivative $[Fe(Cp^*)(CO)_2(CH(OMe)Me)]$ (**5**) is isolated, together with the acyl complex **1** in a 1:1 ratio.

Table 1

NMR yield determined after reduction of **2** and **4** with one equiv. of $[Cp_2Co]$ at 20°C

| Solvent | carbene complex **2**, R = $CH_3$ | | carbene complex **4**, R = H | | |
|---|---|---|---|---|---|
| | **1** | **5** | **3** | **6** | **7** |
| Pentane | 100 | 0 | 50 | 0 | 50 |
| Benzene | – | – | 67 | 0 | 33 |
| Diethylether | – | – | 47 | 0 | 53 |
| THF | 50 | 50 | 60 | 0 | 40 |
| $CH_2Cl_2$ | – | – | 50 | 15 | 35 |
| $CH_3Cl$ | 100 | 0 | 40 | 50 | 10 |



Scheme 3.

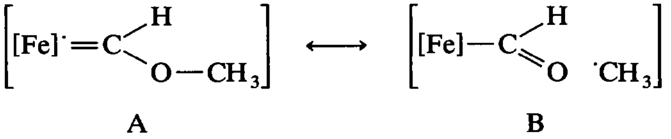
The chemical reduction of **4** in various solvents affords *ca.* 50% of the methoxymethyl derivative $[Fe(Cp^{\star})(CO)_2CH_2OMe]$ (**3**) and the dimer $[\{Fe(Cp^{\star})(CO)_2\}_2]$ (**7**). The chloro-complex $[Fe(Cp^{\star})(CO)_2Cl]$ (**6**) is also formed upon carrying out the reaction in chlorinated solvents. The organic compound (MeO)CH=CH(OMe) (**8**) which would result from coupling of the secondary carbene fragment [=CH(OMe)] is not detected by $^1H$ NMR spectroscopy even after performing the reaction directly in the NMR tube (Scheme 1, path D). However, high resolution mass spectral analysis of the reaction medium can detect a trace of **8**. Therefore, the formation of compounds **6** and **7** cannot be explained by the loss of the carbene moiety from the 19e intermediate.

A possible mechanism is outlined in Scheme 3. The transient 19e radical $[Fe(Cp^{\star})(CO)_2(=C(OMe)Me)]^{\cdot}$, resulting from the one-electron transfer, reacts by losing a methyl radical from the methoxy group; the formation of the 18e acyl derivative **1** as the single product (in pentane or $CH_3Cl$) constitutes the driving force. The transient can also react competitively with a good hydrogen atom donor (THF, $CHCl_3, \ldots$) to afford the ether derivative **5**. In the case of $R = H$, the supposed formyl complex formed by the former pathway, is known to decompose immediately into the hydride $[Fe(Cp^*)(CO)_2H]$ (**9**) [8] and it is now well recognized that several transition metal monohydrides act as hydrogen-atom donors [9]. Thus, the hydride **9** could react *in situ* with the 19e intermediate affording the iron methoxymethyl **3** and the 17e radical $[Fe(Cp^*)(CO)_2]^{\cdot}$. This last species dimerizes to give **7**, or abstract a chlorine atom from $CH_2Cl_2$ or $CHCl_3$ affording **6**, or a hydrogen atom from the solvent, regenerating **9**. The formation of the chloro-complex **6** can also be attributed to a fast reaction between **9** and the chlorinated solvents [2,10]. The reduction of the carbene complex **4** in $CDCl_3$ leads to the formation of monodeuterated **3**, consistent with the solvent being the hydrogen atom source. Although the iron hydride **9** is not observed among the reaction products, its formation as an intermediate is strongly supported by two independent experiments. Whereas no direct reaction occurs between **4** and **9**, reduction of a 1:1 mixture of **4** and **9** with $[Cp_2Co]$ in pentane affords the complex **3** in 97% yield. The reduction of **4** carried out in presence of 1 equiv. of monodeuterated **9** affords monodeuterated **3**.

Since only trace amounts of the alkene **8** resulting from the coupling of the carbene fragment are formed, the 19e metal carbene species does not lose the two-electron heterocarbene ligand, as was observed for the closely related complexes $[CpFe(CO)_2(L)]^{\cdot}$, $[CpFe(CO)L_2]^{\cdot}$ and $[Cp^*Fe(CO)L_2]^{\cdot}$ [11,12]. Dimerizations of many 19e metal-centred radicals by ligand-ligand coupling are often a kinetically favoured reactions [4,11] but they are sometimes inhibited by the bulky Cp* ligand [5]. However, hydrogen-atom abstraction from the solvent and competitive homolytic carbon-oxygen bond-cleavage appear here to be much faster that the carbon-carbon coupling. This could be a consequence of the electronic structure of the paramagnetic intermediate which can be described by the mesomeric forms A and B depicted in Scheme 4.

## Experimental section

*General data.* Reagent grade tetrahydrofuran (THF), diethylether, toluene, and pentane were predried and distilled over sodium benzophenone ketyl prior to use. All the manipulations were carried out under argon using Schlenk techniques or in a Jacomex 532 dry box filled with nitrogen. Routine NMR spectra were recorded using a Bruker AW 80 MHz. High field NMR (300 MHz) spectra experiments were performed on a multinuclear Bruker instrument. Chemical shifts are given in parts per million relative to tetramethylsilane for $^1H$ and $^{13}C$ NMR spectra, and to $H_3PO_4$ for $^{31}P$ NMR spectra. Low resolution mass spectra were obtained on a Varian MAT 311 instrument and IR spectra were recorded on a Nicolet 205 FT spectrometer. Cyclic voltammetry studies were carried out with a Princeton Applied Research 362 instrument and electrolysis performed with a Tacusel generator. Potentials were measured in V *vs.* sce and the ferrocene-ferri-



Scheme 4.

cinium couple was used as an internal calibrant. Elemental analyses were performed at the Centre for Microanalyses of the CNRS at Lyon–Villeurbanne. [Fe(Cp*)(CO)$_2$H] [8] and [Fe(Cp*)(CO)$_2$(=CHOMe)][PF$_6$] [3] were prepared by literature procedures.

*1. Preparation of [Fe(Cp*)(CO)$_2$(COMe)] (1).* A suspension of 2 mmol (1 g) of [Fe(Cp*)(CO)$_2$]$_2$ (7) and 4 mmol (0.16 g) of potassium in 15 mL of THF was heated under reflux for 2 h. To the resulting orange mixture was added at room temperature 4 mmol (284 μL) of MeCOCl. Compound **1** was then extracted with pentane (3 × 10 mL), and concentration of the solution afforded 930 mg (80%) of an orange crystalline solid.

$^1$H NMR (CDCl$_3$) δ 2.47 (s, 3H, Me), 1.75 (s, 15H, C$_5$Me$_5$). $^{13}$C{$^1$H} NMR (CDCl$_3$) δ 259.5 (C=O), 216.0 (CO), 97.0 (*C*$_5$Me$_5$), 51.1 (Me), 9.5 (C$_5$*Me*$_5$). IR (cm$^{-1}$, pentane) 1653 (s, ν(C=O)), 1945 (s, ν(CO)), 2003 (s, ν(CO)). Anal. Found: C, 57.70; H, 6.31. $C_{14}H_{18}FeO_3$ calcd. C, 57.96; H, 6.25%.

*2. Preparation of [Fe(Cp*)(CO)$_2$(=C(OMe)Me)][CF$_3$SO$_3$] (2).* A solution of 0.5 mmol (145 mg) of a Fe(Cp*)(CO)$_2$(COMe)] in CH$_2$Cl$_2$ was treated with 0.5 mmol (57 μL) of MeSO$_3$CF$_3$; the mixture was then stirred for 24 h. Compound **2** was precipitated as a yellow powder with diethyl ether and recrystallization from CH$_2$Cl$_2$/diethyl ether provided 170 mg (75%) of pure carbene complex **2**.

$^1$H NMR (CDCl$_3$) δ 4.62 (s, 3H, OMe), 3.05 (s, 3H, Me), 1.85 (s, 15H, C$_5$Me$_5$). $^{13}$C{$^1$H} NMR (CDCl$_3$) δ 334.9 (=C), 211.2 (CO), 100.9 (*C*$_5$Me$_5$), 68.5 (OMe), 45.8 (Me), 9.5 (C$_5$*Me*$_5$). IR (cm$^{-1}$, CH$_2$Cl$_2$) 1999 (s, νCO), 2045 (s, νCO). Anal. Found: C, 42.34; H, 4.75. $C_{16}H_{21}F_3FeO_6S$ calcd.: C, 42.29; H, 4.66%.

*3. Thermal reaction of [Fe(Cp*)(CO)$_2$(=C(OMe)Me)][CF$_3$SO$_3$] (2) in CH$_3$CN.* A CH$_3$CN solution (10 mL) of 0.5 mmol (227 mg) of [Fe(Cp*)(CO)$_2$(=C(OMe)Me)][CF$_3$SO$_3$] (2) was heated under reflux for 2 h. The CH$_3$CN was removed under reduced pressure, and the resulting yellow solid was identified as the starting compound **2** (yield 98%).

*4. Electrolysis of [Fe(Cp*)(CO)$_2$(=C(OMe)Me)][CF$_3$SO$_3$] (2).* Constant-current electrolysis of 1 mmol (454 mg) of **2** was carried out with platinum electrodes at −1.5 V in CH$_2$Cl$_2$ (150 mL)/0.015 *M* [$^n$Bu$_4$N][PF$_6$]. The solution of the carbene complex was electrolysed for the time required for the passage of 1 F/mol. The solution was evaporated to dryness and the resulting solid residue was extracted in pentane. The crude pentane-soluble species were analysed by $^1$H NMR and IR spectroscopies. Compounds **1** and **5** were detected in a 1/1 ratio as the pentane soluble products (overall yield 98%).

*5. Reaction of [Fe(Cp*)(CO)$_2$(=C(OMe)R)][X] (2, R = Me; 4, R = H) with [Cp$_2$Co], general procedure.* A stoichiometric amount of [Cp$_2$Co] (1 mmol, 189 mg) was added to a solution of 1 mmol of [Fe(Cp*)(CO)$_2$(=C(OMe)R)][X] **2**, [R = Me (454 mg); **4** R = H (436 mg)] and the mixture stirred at room temperature for 30 min. The solvent was evaporated to dryness and the resulting solid residue was extracted with pentane. The insoluble fraction was characterised by $^1$H NMR spectroscopy as [Cp$_2$Co][PF$_6$]. The crude pentane-soluble species were analysed by $^1$H NMR and IR spectroscopy. Yields of the reaction products and solvents are given in Table 1. Compounds **1** [3], **3** [3], **6** [10], and **7** were identified by comparison with authentic samples.

[Fe(Cp*)(CO)$_2$(CH(OMe)Me)] (5): $^1$H NMR (C$_6$D$_6$) δ 4.63 (q, $^3J$(H–H) 6Hz, 1H, CH), 3.29 (s, 3H, OMe), 1.89 (d, $^3J$(H–H) 6Hz, 3H, Me), 1.58 (s, 15H, C$_5$Me$_5$).

$^{13}C\{^1H\}$ NMR ($C_6D_6$) δ 219.9 (CO), 219.7 (CO), 95.9 ($C_5Me_5$), 82.3 (CH), 56.9 (OMe), 29.6 (Me), 9.3 ($C_5Me_5$). IR ($cm^{-1}$, pentane) 1926–1937 (s, ν(CO)); 1982–1994 (s, ν(CO)). Anal. Found: C, 58.67; H, 7.53. $C_{15}H_{22}FeO_3$ calcd.: C, 58.84; H, 7.24%.

*6. Mass spectral analysis of CH(OMe)=CH(OMe) (8).* Compound **4** (1 mmol, 436 mg) was dissolved in 3 mL of $CH_2Cl_2$, and treated at room temperature with 1 mmol (189 mg) of [$Cp_2Co$]. The reaction mixture was stirred for 30 min. and then analysed by high resolution mass spectroscopy. MS of **8**: Found 88.0521. $[C_4H_8O_2]^+$ calcd. 88.05243.

*7. Reaction of [Fe(Cp*)(CO)$_2$(=C(OMe)H)][PF$_6$] (4) with [Fe(C$_5$Me$_5$)(CO)$_2$(H)] (9).* To a suspension of 1 mmol (436 mg) of [Fe(Cp*)(CO)$_2$(=C(OMe)H)][PF$_6$] (**4**) in 10 mL of pentane was added 1 mmol (248 mg) of freshly prepared [Fe(Cp*)(CO)$_2$(H)] (**9**). The mixture was stirred for 30 min and the solvent evaporated to dryness. The starting compounds **4** and **9** were recovered unchanged as shown by $^1H$ NMR and IR analyses.

*8. Preparation of [Fe(Cp*)(CO)$_2$(D)] (monodeuterated 9).* The procedure (reaction conditions and work-up) was the same as for **9**, $LiAlD_4$ being used in place of $LiAlH_4$. The compound was obtained as a yellow oil in 95% yield (236 mg).

$^1H$ NMR ($C_6D_6$) δ 1.69 (s, $C_5Me_5$). $^2H$ NMR ($C_6H_6$, $C_6D_6$ as internal standard) δ − 11.41 (s, D). IR ($cm^{-1}$, pentane) 1931–1945 (s, ν(CO)), 1987–2002 (s, ν(CO)).

*9. Reaction of [Fe(Cp*)(CO)$_2$(=C(OMe)H)][PF$_6$] (4) with [Fe(Cp*)(CO)$_2$(H)] or [Fe(Cp*)(CO)$_2$D] in the presence of [Cp$_2$Co], general procedure.* A stoichiometric amount of [$Cp_2Co$] (1 mmol, 189 mg) was added to a stirred suspension of **4** (1 mmol, 436 mg) and **9** or monodeuterated **9** (1 mmol, 249 mg) in pentane. After stirring for 30 min., the solution was filtered and evaporated to dryness. The product **3** is isolated as a amber oil (97%, 283 mg). With the deuterated complex, mass spectral analysis of the reaction products indicated the presence of the following compounds: [Fe(Cp*)(CO)$_2$(CHDOMe)]: 65%, [Fe(Cp*)(CO)$_2$(CD$_2$ OMe)]: 25% [13*], [Fe(Cp*)(CO)$_2$-(CH$_2$OMe)]: 10%.

$^2H$ NMR ($C_6H_6$, $C_6D_6$ as internal standard) δ 4.40 (br.s, CHD, $CD_2$). $^1H$ NMR ($CDCl_3$) δ 4.31 (s, $CH_2$), 4.29 (s, CHD), 3.24 (s, OMe), 1.78, 1.76, 1.74 (3 × s, $C_5Me_5$). IR ($cm^{-1}$, pentane) 1934–1944 (s, ν(CO)), 1986–2001 (s, ν(CO)).

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13 The formation of didenterated **3** may be attributed to a hydrogen-atom abstraction from monodeuterated **3** by the transient radical $[FeCp^*(CO)_2]^\cdot$ followed by a deuterium-atom transfer from monodeuterated **9**.