

Preparation and characterization of substituted pentaaryl cyclopentadienyliron dicarbonyl bromide complexes containing methyl or fluorine substituents on the arene rings

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Abstract

The bromopentaaryl cyclopentadienes $C_5(C_6H_5)_4(Ar')(Br)$ ($Ar' = 3,5-C_6H_3Me_2$, **1a3**; $Ar' = 2,4,6-C_6H_2Me_3$, **1a5**; $Ar' = 3,5-C_6H_3F_2$, **1a7**; $Ar' = 2,6-C_6H_3F_2$, **1a8**), and $C_5(3,5-C_6H_3Me_2)_4(Ar')(Br)$ ($Ar' = 3-C_5H_4Me$, **1b2**; $3,5-C_5H_3Me_2$, **1b3**; $3,6-C_5H_3Me_2$, **1b4**; $2,4,6-C_5H_2Me_3$, **1b5**; $Ar' = 3-C_6H_4F$, **1b6**; $Ar' = 3,5-C_6H_3F_2$, **1b7**; $Ar' = 2,6-C_6H_3F_2$, **1b8**) containing either methyl groups or fluorine atoms on the Ar' rings were reacted with $Fe(CO)_5$. At 20 °C, the reaction quantitatively produces the corresponding radicals $[C_5(C_6H_5)_4(Ar')]^\bullet$ and $[C_5(3,5-C_6H_3Me_2)_4(Ar')]^\bullet$ which were isolated and characterized by ESR. A bromide-containing iron derivative, identified by far FTIR was also formed in this reaction. Above 50 °C, a second reaction took place yielding the corresponding bromo iron complexes $\{C_5(C_6H_5)_4(Ar')\}Fe(CO)_2Br$ ($Ar' = 3,5-C_6H_3Me_2$, **3a3**, $Ar' = 3,5-C_6H_3F_2$, **1a7**) and $\{C_5(3,5-C_6H_3Me_2)_4(Ar')\}Fe(CO)_2Br$ ($Ar' = 3-C_5H_4Me$, **3b2**; $3,5-C_5H_3Me_2$, **3b3**; $3,6-C_5H_3Me_2$, **3b4**; $Ar' = 3-C_6H_4F$, **3b6**; $Ar' = 3,5-C_6H_3F_2$, **3b7**). In the case of the bromopentaaryl cyclopentadienes **1a5**, **1a8**, **1b5**, and **1b8**, the presence of two methyl groups or two fluorine atoms on the *ortho* and *ortho'* position of Ar' prevents the complexation of the iron atom onto the substituted cyclopentadienyl radicals. A discussion of the mechanism of the reaction, supported by ESR, cyclic voltammetry, and far-FTIR spectroscopy, is also reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pentaaryl cyclopentadienyliron dicarbonyl bromide complexes; ESR; Cyclic voltammetry; Far-FTIR spectroscopy

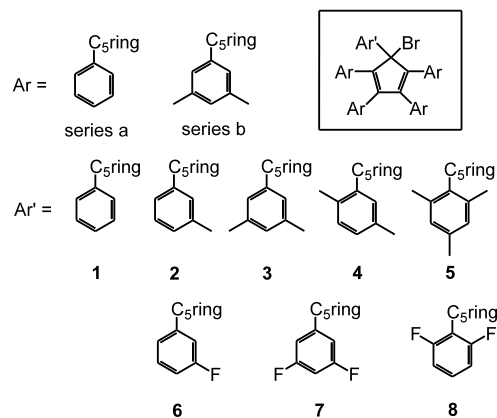
1. Introduction

The development of bulky and electron withdrawing pentasubstituted–cyclopentadienyl ligands is of interest in organometallic chemistry not only to stabilize anionic and radical complexes [1–10] but also in the design of new donor-acceptor organometallic molecular devices, which display preferential one-way electron transfer acting as a rectifier [11]. Moreover, the molecular dynamics of the propeller-type systems $(C_5Ar_5)ML_x$ is particularly rich, but the analysis of the rotational barriers requires incorporation of suitable labels on the molecule to monitor peripheral ring rotation

[10,12,13]. For these reasons, we have synthesized a series of iron complexes containing pentaaryl cyclopentadienyl ligands with methyl or fluorine groups in the *ortho* or *meta* positions of the C_6 rings. The ultimate goal of this project is the preparation of metal complexes with (i) better solubility, fine tuning of the (ii) steric and (iii) electronic environment of the metal center, (iv) labeling of the peripheral arene for NMR spectroscopy, and (v) stabilization of radicals. In a previous paper we reported a convenient route to bromopentaaryl cyclopentadienes containing methyl or fluorine substituents [14]. In this second paper, we now describe the synthesis of pentaaryl cyclopentadienyliron dicarbonyl bromide complexes containing methyl or fluorine substituents on the arene rings. We have prepared two families of bromo iron derivatives containing four equivalents arene rings $\{C_5Ar_4Ar'Br$ ($Ar =$

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Scheme 1.

C_6H_5 , series **a**; $\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$, series **b**)¹. The fifth arene bears either 0, 1, 2, or 3 methyl substituents or 0, 1, or 2 fluorine atoms (Scheme 1). To complement this work, we have also investigated the mechanism of the reaction of $\text{C}_5\text{Ar}_4\text{Ar}'\text{Br}$ with iron pentacarbonyl and show the formation of the radical $[\text{C}_5\text{Ar}_4\text{Ar}']^\bullet$ as an intermediate.

2. Results and discussion

2.1. Reaction of the substituted bromopentaaryl cyclopentadienes **1** with $\text{Fe}(\text{CO})_5$ at 20 °C

According to the pioneering study on pentaphenylcyclopentadienyliron compounds reported by Pauson in 1965 [1] the reaction of the $\text{C}_5\text{Ph}_5\text{Br}$ with iron pentacarbonyl still constitutes the best route to $(\eta^5\text{-C}_5\text{Ph}_5)\text{Fe}(\text{CO})_2\text{Br}$, the entry complex in this series [10,15–17]. Following the same way, we reacted the substituted bromopentaaryl cyclopentadienes **1a1**, **1a3**, **1a5**, **1a7**, **1a8**, and **1b2–1b8** with iron pentacarbonyl in toluene. At 20 °C, we observed that the solution progressively turned purple and after 2 h the corresponding pentaaryl cyclopentadienyl radicals **2** were isolated in 90% yield. The radicals were identified by ESR spectroscopy and comparison of the experimental spectra with the simulated ones. Additional characterizations were carried out for the radicals **2a5** and **2b5** ($\text{Ar}' = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$). The radicals **2a7**, **2a8**, **2b6**, **2b7**, and **2b8** which contain one or two fluorine atoms decompose around 110 °C. As pure compounds, all the other pentaaryl cyclopentadienyl radicals **2** are thermally very stable, since they can be recovered after refluxing for several hours in mesitylene [18–21]. The

considerable bulk of the five aryl rings prevents the coupling of two radicals. However, these radicals are very sensitive to small molecules like dioxygen and water as previously noted [18–20]. The EIMS of radical **2b5** ($\text{Ar}' = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$) does not display the molecular ion peak (m/z 599.3756). It appears that the radical reacts with water during the introduction process in the spectrometer and the molecular ion peaks of the resulting products $[\text{M}-\text{H}]$ (m/z 600.3764) and $[\text{M}-\text{OH}]$ (m/z 616.3713) were both observed [20]. Exposure to dioxygen of **2b5** gives a dioxygen adduct, the formula of which, $\text{C}_{46}\text{H}_{47}\text{O}_2$, was found by elemental analysis. Similar findings have previously been reported for the radical pentaisopropylcyclopentadienyl [21].

The $^1\text{H-NMR}$ spectra of **2a5** and **2b5** ($\text{Ar}' = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$) show two broad signals at $\delta = 2.17$ (CH_3 , $W_{1/2} = 100$ Hz) and $\delta = 6.81$ (Ph, $W_{1/2} = 150$ Hz) indicating the effect of the paramagnetic system on the proton resonances. The unique difference between these two spectra is the relative intensity of the signal of the methyl groups with respect to that of the phenyl which, are in a 9/22 and 33/14 ratio for **2a5** and **2b5**, respectively. The UV–vis spectrum of **2b5** shows strong and broad absorption bands without vibrational fine structure at 356 and 598 nm. Similar observations have previously been reported for other arylcyclopentadienyl radicals [18–20]. The out-of-plane aryl rings are subject to bond rotation affecting conjugation and the presence of a multitude of conformers in the solution could be responsible of the broadness of the absorption bands.

The ESR spectra of the radicals **2** obtained from either isolated samples or in situ generated species by reaction of **1** with $\text{Fe}(\text{CO})_5$ were run at 20 °C in toluene. As shown in Fig. 1 for **2b3** ($\text{Ar}' = 3,5\text{-C}_6\text{H}_3\text{Me}_2$), the spectra display a hyperfine structure due to the coupling

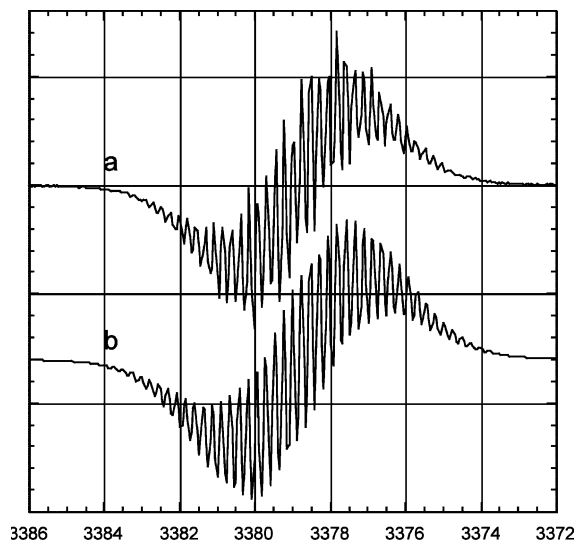


Fig. 1. EPR spectra of **2b3** (a) in toluene at 293 K, (b) a computer simulation using parameters given in Table 1.

¹ In the compounds numbers, the letter referring to series **a** or **b** together with the last digit, indicate the substitution of Ar' as shown on Scheme 1.

Table 1

ESR parameters for radicals **2** measured in toluene at 293 K. The hyperfine coupling constants were determined by simulation of the spectra

[C ₅ Ar ₄ Ar'] [•]	2a1	2a3	2a5	2a7	2a8	2b2	2b3	2b4	2b5	2b6	2b7	2b8
G	2.0014	2.0014	2.0014	2.0014	2.0014	2.0014	2.0014	2.0015	2.0013	2.0014	2.0014	2.0013
AH _{ortho} ^a	690	680		590	590	240	220	^c	340	230	170	356
	(10H)	(10H)		(10)	(10H)	(10H)	(10H)		(8H)	(10H)	(10H)	(8H)
AH _{meta} ^a or ACH _{3meta} ^a	340	370		590		470	480		680	460	370	712
	(10 H)	(8 H)		(8 H)		(27 H)	(30 H)		(24 H)	(24 H)	(24 H)	(24 H)
AX ^a		710	810		720	930		^d		720		178
		(2 CH ₃) _{meta}	(2 CH ₃) _{ortho}		(1 H)	(5 H _{para})				(1 H)		(2 H _{meta})
AF ^a				1140	1170					1380	1400	1424
				(2 F)	(2 F)					(1 F)	(2 F)	(2 F)
LW ^b	310	350	600	600	600	200	200		400	200	200	200

^a In 10^{−3} Gauss.^b Line width in 10^{−3} Gauss.^c The spectrum does not present an hyperfine structure.^d The hyperfine coupling with the methyl groups of the mesitylene ring cannot be detected.

with most of the hydrogen atoms of the aryl rings. The isotropic *g* values are not sensitive to the substitution of the phenyl groups (Table 1). Simulations of the spectra allow the determination of the $|a_H|$ and $|a_F|$ values. The assignments of the protons of the methyl groups and aryl rings in *para*, *ortho*, and *meta* positions were performed on the basis of their multiplicity (see Table 1). We were able to observe all the couplings in the unique case of the {C₅[(C₆H₃)(*m,m'*CH₃)₂]₅}[•] (**2b3**). Indeed, in most of the radicals studied the couplings with the protons located in the *para* position were not resolved even for the highly symmetric radical **2a1**. As expected, the $|a_F|$ values are significantly larger than the $|a_H|$ values [22,23]. Note that the spectrum of **2b4** (Ar' = 3,6-C₆H₃Me₂) did not display a hyperfine pattern. This unusual behavior in this series could be due to the lack of symmetry of this species.

2.2. Preparation of the substituted pentaarylcyclopentadienyliron dicarbonyl bromide complexes (**3**)

The polymethylated–pentaphenylcyclopentadienyl iron bromo complexes **3** were prepared by reaction of Fe(CO)₅ with the corresponding bromide derivatives C₅Ar₄Ar'Br, **1a3**, **1a5**, **1a7**, **1a8**, and **1b2–1b8** in toluene following Pauson's procedure (Scheme 3) [1]. Immediately after the addition of the iron pentacarbonyl at 20 °C, the yellow toluene solution turned dark purple as described above. We observed that this color remained for several days as long as the solution was kept below 50 °C. After warming for 2 h at 80 °C, the color of the solution turned from purple to red–brown indicating that the second step of the reaction had gone to completion in the case of the C₅Ar₄Ar'Br derivatives **1a3**, **1a7**, **1b2–1b4**, **1b6**, and **1b7**. In contrast, the bromopentaarylcyclopentadienes C₅Ar₄Ar'Br (**1a5**,

1a8, **1b5**, **1b8**), which contain either two methyl groups or two fluorine atoms on the *ortho* and *ortho'* positions of the Ar' ring, the solution remained purple even after refluxing overnight, suggesting the persistence of the radical [C₅Ar₄Ar'][•]. ESR monitoring of the reaction mixture confirmed this assumption. Replacement of toluene by mesitylene did not allow the radicals **2a5** and **2b5** to react. They remained stable even after refluxing for 48 h at 165 °C.

The iron complexes (C₅Ar₄Ar')Fe(CO)₂Br **3a3**, **3a7**, **3b2–3b4**, **3b6**, and **3b7** were isolated as orange powders in yields ranging from 60 to 80%. Note that the presence of one or two fluorine atoms on the *meta* and *meta'* position induces a significant decrease in the yield, whereas the presence of a single methyl group on one of the *ortho* position has no effect on the reactivity. These compounds are thermally stable as powders and in solution. However, the fluorine-containing complexes **3a7**, **3b6**, and **3b7** slowly decompose in solution, suggesting that the electron withdrawing effect of the fluorine facilitates the decoordination of the C₅Ar₄Ar' ligand. The bromo iron derivatives were characterized by multi NMR and FTIR spectroscopies, cyclic voltammetry and elemental analysis or FABMS.

The ¹H-NMR spectra clearly show that the presence of methyl groups on the *meta* and *meta'* positions of the Ar and Ar' substituents does not limit the free rotation of the peripheral rings. Indeed, in both series a and b, the two methyl groups on the *meta* and *meta'* positions are equivalent suggesting that the rotation of the aryl rings is not restricted on the ¹H-NMR time scale (300 MHz). As in the pentamethylcyclopentadienyl series, the 30 equivalent methyl protons in compound **3b3** (Ar' = 3,5-C₆H₃Me₂) constitute a valuable ¹H-NMR probe. Moreover, the chemical shift of the CH₃ protons is very sensitive to structural modifications on the pentaarylcyclopentadienyl ligand. For instance, in the case of the

complex **3b2** ($\text{Ar}' = 3\text{-C}_6\text{H}_4\text{Me}$), the absence of a methyl substituent on one of the *meta* positions of the aryl rings allows the observation of three distinct resonances at δ 2.05, 2.06 and 2.11 ppm in the 12:12:3 ratio for the 9 *meta* methyl groups. Similarly, in the case of the complex **3b4** ($\text{Ar}' = 3,6\text{-C}_6\text{H}_3\text{Me}_2$), which has a central C_5 ring bearing four $3,5\text{-C}_6\text{H}_3\text{Me}_2$ rings and one $2,5\text{-C}_6\text{H}_3\text{Me}_2$ ring, the ^1H -NMR spectrum displays four resonances at δ 1.53, 1.95, 2.10, and 2.31 in the 3:12:12:3 ratio. The signals at δ 1.95 and 2.10 correspond to the methyl groups in *meta* positions of the aryl rings occupying the α and β position with respect to Ar' . For the methyl groups of the Ar' ring significant upfield and downfield shifts are observed. This suggests that the *o*-substitution induces a significant change of the magnetic environment of the methyl groups. We assume that the *o*-methyl is mainly directed toward the opposite side of the C_5 ring with respect to the metal, whereas the *m*-methyl is directed toward the metal side. However, on the basis of the NMR data it cannot be attributed either to the hindrance towards free rotation of the C_6 ring or the orientation of the *ortho* methyl on the same or opposite sides of the C_5 ring with respect to the $\text{Fe}(\text{CO})_2\text{Br}$ moiety. More detailed investigations are necessary to shed light on this point. Nevertheless, it is noteworthy that it appears that **3b4** was formed as a unique isomer in contrast with the results reported for the related complex, $[(o\text{-tolyl})(\text{C}_6\text{H}_5)_4\text{C}_5]\text{Fe}(\text{CO})_2\text{Br}$, which was isolated as a mixture of two isomers with the *o*-methyl substituents oriented on the same and opposite sides of the C_5 ring in the 4:7 ratio, respectively [24].

The ^{13}C -NMR spectrum of the complex **3b3** ($\text{Ar}' = 3,5\text{-C}_6\text{H}_3\text{Me}_2$) shows a unique resonance for the C_5 ring at δ 101.2, whereas three distinct resonances are observed for the corresponding carbon atoms of the complex **3b2** ($\text{Ar}' = 3\text{-C}_6\text{H}_4\text{Me}$; δ 100.7, 101.0, 101.5). A similar pattern is observed for all other complexes as Ar and Ar' are different. In compound **3b4** ($\text{Ar}' = 3,6\text{-C}_6\text{H}_3\text{Me}_2$), the steric perturbation due to the presence of the *o*-methyl substituent has electronic consequences on the entire pentaarylcyclopentadienyl ligand, as shown by the ^{13}C resonances of the carbon atoms of the central ring (δ 97.5, 97.9, and 107.0). These chemical shifts appear out of the range usually observed for the carbon atoms of the C_5 ring in these series (99–101 ppm). These signals are consistent with a particular arrangement for the peripheral arenes around the central C_5 cycle resulting from the presence of the *o*-methyl.

IR characterization of the complexes were run in CH_2Cl_2 (Table 2). In all cases, the two strong absorption bands corresponding to the $\text{C}\equiv\text{O}$ symmetric and anti-symmetric stretching modes were observed. The absorption bands of the bromo iron complexes of the pentaarylcyclopentadienyl family are located between the bands observed for the complexes $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$

[25] and $(\text{C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Br}$ [26]. The absorption bands of the complex **3a3**, which contains ten methyl groups, is weakly shifted to lower wavenumbers (ca. 5 cm^{-1}) relative to the respective complex **3a1**. An opposite effect on the frequency of the CO stretch is observed when fluorine atoms are introduced on one of the arene rings.

Excluding the case of the meta-difluoro compound (**3b7**), the cyclic voltammograms (CV) of the iron complexes **3**, performed in the range +1.700 to -1.300 V versus the standard calomel electrode (SCE), display a reversible one-electron wave and a second irreversible process. The irreversible process observed between -0.896 for **3a1** and -1.191 V versus SCE for **3b4** ($\text{Ar}' = 3,6\text{-C}_6\text{H}_3\text{Me}_2$) also involves one electron and corresponds to the $\text{Fe}(\text{II})\text{--Fe}(\text{I})$ reduction of the iron bromo derivatives. This reduction process shows a weak reversible character in the case of the complexes **3a1** and **3b2**. The transient character of these iron(I) species is not surprising since it is well known that metal halide radical anions are not thermally stable [27].

The reversible process, located between 1.242 and 1.465 V versus SCE, corresponds to the metal-centered $\text{Fe}(\text{II})\text{--Fe}(\text{III})$ oxidation. It seems that the $\text{Fe}(\text{III})$ derivatives are stable at the Pt electrode. It is apparent that the electron-releasing methyl substituents make the oxidation of the iron(II) center easier. Moreover, the location of the methyl groups provides a fine-tuning of the redox potential. For instance, comparison of the E_0 values of **3b3** and **3b4** shows that the displacement of one methyl from the *meta* carbon to the *ortho* carbon of the same arene ring decreases the oxidation potential of 0.006 V . Surprisingly, the oxidation potential of **3b2** is 0.029 V smaller than that of **3b3** despite the presence of 9 and 10 *meta* methyl substituents, respectively, on the pentaarylcyclopentadienyl ligand. Such an effect could be due to a different averaged orientation of the out-of-plane aryl rings, affecting the conjugation between the C_6 and C_5 rings and therefore the electron density on the metal center. It can also be noted that the presence of fluorine atoms makes the oxidation of the iron(II) center more difficult and in the particular case of **3b7**, the oxidation wave is out of the observed potential range.

For purpose of comparison, we also ran the CV of the related bromo iron derivatives $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}$ [25] and $(\text{C}_5\text{Me}_5)\text{Fe}(\text{CO})_2\text{Br}$ [26] under the same conditions. It appears that the electronic effect of (C_5H_5) and (C_5Ph_5) are very close ($\Delta E_0 = 0.017\text{ V}$) and the introduction of two methyl groups on a single arene does not greatly modify the electron richness of the iron center. For instance, the oxidation potentials of the complexes **3a1** and **3a3** are very close ($\Delta E_0 = 0.010\text{ V}$). In the series of the complexes **3b** the oxidation potentials are ca. 100 mV lower than those of the derivatives of series **3a** and they appear intermediate between the values obtained for the related complexes with C_5H_5 and C_5Me_5 ligands.

Table 2
Electrochemical and IR data for complexes **3**

Compound	(C ₅ H ₅)Fe(CO) ₂ Br ^e	(C ₅ Me ₅)Fe(CO) ₂ Br ^f	3a1 ^c	3a3	3a7	3b2	3b3	3b4	3b6	3b7
<i>E</i> ₀ ^{a,b}	1.347	1.111	1.364	1.354	^g	1.242	1.271	1.265	1.333	^h
Δ <i>E</i> _p	0.160	0.190	0.131	0.100		0.120	0.068	0.105	0.113	
<i>I</i> _a / <i>i</i> _c	1	1	1	1		1	1	1	1	
<i>E</i> ₀ ^{a,c}	−1.083	^h	−0.896	−1.016	^g	−1.072	−1.170	−1.191	−1.133	−0.927
Δ <i>E</i> _p	—		0.190	—		0.120	—	—	—	0.250 ⁱ
<i>I</i> _c / <i>i</i> _a	0		0.5	0		0.3	0		0	0
ν _{CO} ^d	2003 2049	1975 2025	1996 2038	1995 2037	2001 2041	1994 2036	1991 2034	1992 2034	1994 2036	1996 2037

^a All *E* values in V vs. SCE. Conditions: CH₂Cl₂, 0.1 M [*n*-Bu₄N⁺][PF₆[−]] supporting electrolyte, 20 °C, Pt electrode, sweep rate 0.100 V s^{−1}. The ferrocene–ferrocenium [Fc–Fc⁺] was used as internal reference for potential measurements. *E*₀ values corrected for Fc–Fc⁺ at 0.460 vs. SCE in CH₂Cl₂.

^b Fe(II)–Fe(III) couple.

^c Fe(I)–Fe(II) couple.

^d Values in cm^{−1} obtained in CH₂Cl₂ solution.

^e From ref. [25].

^f From ref. [26].

^g Not determined.

^h Not observed in the range +1.700 to −1.300 V.

ⁱ This wave was attributed to a ECE process.

As the interest for pentaarylcyclopentadienyl organometallics might be lowered by poor solubility, we carried out the determination of the solubility for selected substituted pentaarylcyclopentadienyliron dicarbonyl bromide complexes (**3**) in pentane and diethyl ether. As expected, the solubility of these complexes increases with the number of methyl groups borne by the arene rings (Table 3). This effect is not considerable, but significant. In particular, the solubility of the complex **3b3**, which bears ten methyl substituents, was found to be four and ten times higher than that of the pentapentaarylcyclopentadienyliron derivative **3a1** in diethyl ether and pentane, respectively. In contrast, the presence of two fluorine atoms on **3b7** partly counter balance the positive effect of the methyl groups.

2.3. Mechanistic consideration

The formation of the radicals **2** upon treatment of the bromopentaarylcyclopentadienes **1** with Fe(CO)₅ are expected to proceed by an electron transfer process. To probe such a mechanism, we investigated the redox properties of the bromopentaarylcyclopentadiene **1b5**,

taken as a representative example of this series of compounds by CV (Fig. 2). The initial scan in the range +0.4 to −2.0 V versus SCE, only shows an irreversible reduction wave at −1.55 V (wave A), whereas the reverse oxidation presents an oxidation wave at −0.35 V which appeared to be reversible in the second reduction scan (wave B). These data are consistent with the one-electron reduction of **1b5** and subsequent cleavage of **1b5**^{•−} into [C₅Ar₄Ar'][•] (**2b5**) and Br[−]. The formation of the radical **2b5** was established by comparison of the CV of **1b5** and **2b5** (Fig. 2, waves B). Formally, the reaction between the bromopentaarylcyclopentadiene **1** and iron pentacarbonyl (Scheme 2) could involve an electron transfer (ET) process. However, the mechanism of this reaction cannot be as simple.

Table 3
Solubility (mg of complex per ml of solvent) for selected complexes **3**

Compound	Pentane	Diethyl ether
3a1	1	8
3a3	4	12
3b2	10	35
3b3	10	35
3b7	5	15
(C ₅ Me ₅)Fe(CO) ₂ Br	15	130

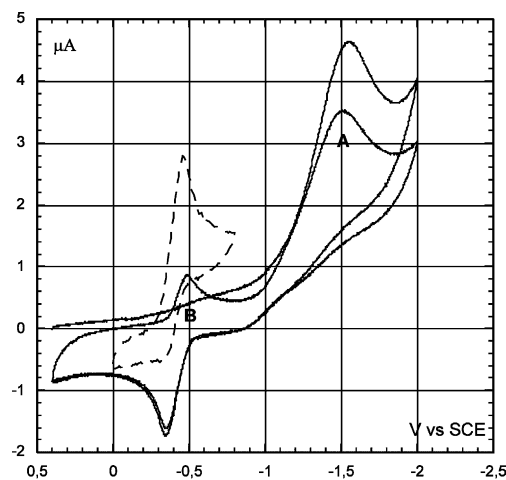
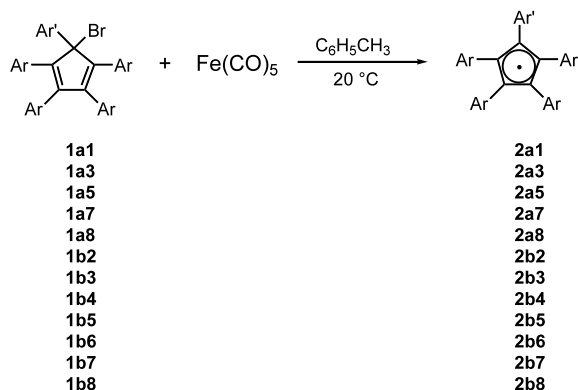


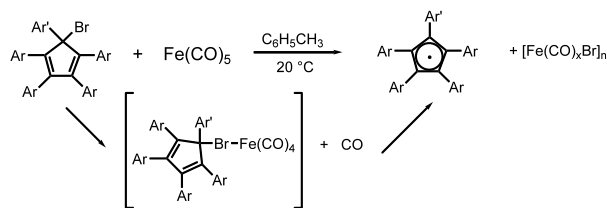
Fig. 2. Cyclic voltammograms of the **1b5** (plain line) and **2b5** (dashed line) in 0.1 M *n*-Bu₄N⁺ PF₆[−]–CH₂Cl₂ (Pt electrode, V vs. SCE, scan rate 0.100 V s^{−1}, 20 °C).



Scheme 2.

Indeed, comparison of the potentials for the redox couples $\text{Fe}(\text{CO})_5$ – $[\text{Fe}(\text{CO})_5]^\bullet$ ($E_0 > 1$ V) and $\text{C}_5\text{Ar}_4\text{Ar}'\text{Br}$ – $[\text{C}_5\text{Ar}_4\text{Ar}'\text{Br}^\bullet]$ ($E_0 > -1$ V) indicates that the reduction of the bromopentaarylcyclopentadiene **1** by $\text{Fe}(\text{CO})_5$ is strongly endergonic, and as an endergonic ET never proceeds, one can eliminate such an hypothesis.[27] As an alternative mechanism, the formation of a transient adduct between the bromo derivatives **1** and iron carbonyl as depicted on Scheme 4, constitutes a plausible assumption. In this mechanism, the directions of the ET and Br^- transfer are clearly opposite, so that the overall result is a Br^\bullet atom transfer and the reaction can be exergonic [28]. This is an inner sphere electron transfer process [27].

A far-IR investigation was performed to establish the formation of a Fe–Br bond-containing product. The bromopentaarylcyclopentadiene **1b5** was reacted with $\text{Fe}(\text{CO})_5$ in toluene at 20 °C. After 2 h, the solvent was removed and the Nujol-mull IR spectrum of the resulting crude product was recorded in the range 100–400 cm^{-1} (Fig. 3). The spectrum displays two bands at 295 and 136 cm^{-1} . On the basis of the literature data these bands of vibration may be assigned to the Fe–Br stretching and bending modes, respectively [29–32]. Similar frequencies have been reported for bromoiron complexes and the far-IR spectrum of the complex **3a1** also shows very close absorption band (Fig. 3, ν 302 and 135 cm^{-1}). Moreover, it has been



Scheme 4.

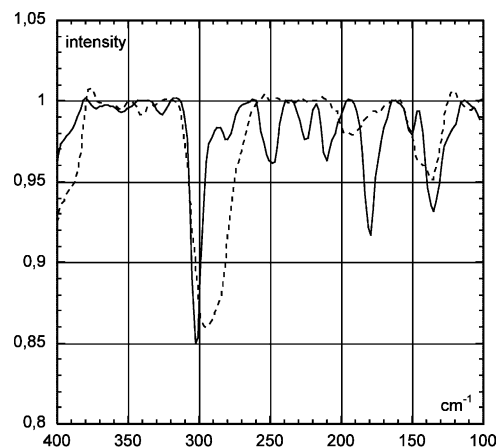
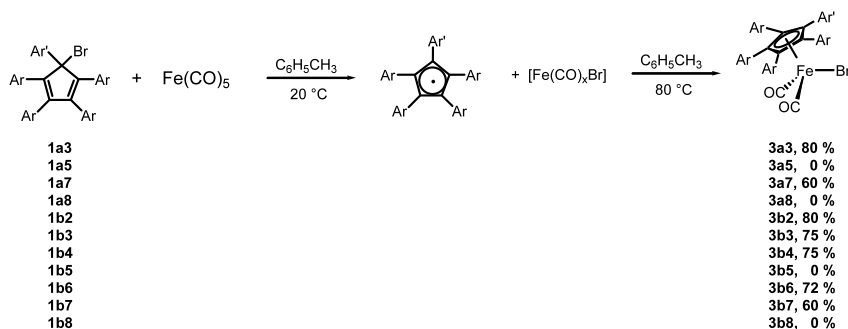


Fig. 3. Far IR spectra (polyethylene pellet, cm^{-1}) of the iron intermediate generated by reaction of **1b5** with $\text{Fe}(\text{CO})_5$ (dashed line) and **3a1** (plain line).

proven that metal carbonyl halides containing one to four CO groups per molecule are stable at moderate temperature [33].

The IR characterization of the iron intermediate from the reaction of complexation of the pentaarylcyclopentadienyl ligand was complemented by a crossed radical experiment. In a purple solution containing the bulky radical **2b5** and the bromine-containing iron intermediate, generated by adding $\text{Fe}(\text{CO})_5$ to **1b5** in toluene, was introduced the radical **2b3**, independently prepared (see Section 3). After warming the mixture to 80 °C for 30 min, the bromoiron complex **3b3** was isolated in a good yield. This experiment clearly confirms that the pentaarylcyclopentadienyl radical and a bromine-containing iron carbonyl derivative are key intermediates in the formation of the title complexes.



Scheme 3.

2.4. Conclusions

Adaptation of Pauson's procedure for the preparation of pentaarylcyclopentadienyliron dicarbonyl bromide complexes containing methyl or fluorine substituents on the arene rings allows facile access to these compounds in good yields. We found that the presence of two methyl groups or even two fluorine atoms on the two *ortho* positions of one of the five arene rings precludes the complexation of the C₅ ring on the metal center. We have clearly shown that the reaction does not proceed through an oxidative addition, but through a two-step process, which involves the formation of a pentaarylcyclopentadienyl radical and a bromoiron carbonyl intermediate. The presence of methyl or fluorine substituents on the *meta* positions does not apparently affect the free rotation of the C₆ rings around the central C₅ ring, but allows a fine tuning of the electron density at the metal center. Moreover, a positive effect of the methyl groups on the solubility of these complexes was noted.

3. Experimental

3.1. General data

All reactions were carried out either under an argon atmosphere using standard Schlenk techniques or in a Jacomex 532 dry box filled with nitrogen. Reagent grade tetrahydrofuran (THF), pentane, diethylether, toluene and mesitylene were predried and distilled over sodium benzophenoneketyl prior to use. Dichloromethane and acetonitrile were refluxed over P₂O₅ then distilled over Na₂CO₃. Bromopentaarylcyclopentadienes containing methyl or fluorine substituents were prepared as previously reported. [14] Deuterated solvents (Merck) were used as received, except CDCl₃ previously treated with P₂O₅, then Na₂CO₃ and stored on basic alumina under argon. High-field NMR spectra experiments were performed on a multinuclear Bruker 300 MHz instrument (AC300P). Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ¹H and ¹³C-NMR spectra, external H₃PO₄ for ³¹P-NMR spectra. ¹⁹F-NMR spectra were recorded at 288 MHz, and chemical shifts are reported in ppm relative to external CFC₃. Transmittance-FTIR spectra were recorded using a Bruker IFS28 spectrometer (400–4000 cm⁻¹) and a Bruker EQUINOX 55 spectrometer (100–500 cm⁻¹). UV–vis spectra were recorded on an UVIKON 942 spectrometer. Cyclic voltammograms were recorded using an EG&G-PAR model 263 potentiostat–galvanostat. The working electrode was a Pt wire (*d* = 1.0 mm) and the saturated calomel electrode (SCE) was used as a reference electrode. The Cp₂Fe^{0/+} couple was used as an internal calibrant for the potential measurements (0.460

V vs. SCE in CH₂Cl₂) [34]. X-band ESR spectra were recorded on a Bruker EMX-8/2.7 spectrometer and simulated spectra were obtained with the Bruker SIMFONIA program. MS analyses were recorded at the 'Centre Regional de Mesures Physiques de l'Ouest' (Rennes; C.R.M.P.O.); EIMS were obtained using a Varian MAT 311 spectrometer and FABMS with a high resolution MSMS ZabSpec TOF Micromass spectrometer (8 kV) using *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were performed at the Service Central d'Analyses, USR CNRS 59, at Lyon-Vernaison (France).

3.2. Reactions of the bromocyclopentadienes (η^5 -C₅Ar₄Ar')Br (**1**) with Fe(CO)₅ at 20 °C

In a Schlenk tube, iron pentacarbonyl (0.09 ml, 0.66 mmol) was added dropwise to a solution of **1** (0.5 mmol) in toluene (20 ml). After stirring 2 h, the solution became violet, and the solvent was removed under reduced pressure. Purification achieved by chromatography on a silica gel column with pentane-diethyl ether (9:1) provided a violet powder of the corresponding radical **2** in 85–90% yield. Radicals were characterized by ESR spectroscopy in toluene at 293 K. Additional characterizations were carried out for **2a5** and **2b5**.

3.2.1. [η^5 -C₅(C₆H₅)₄(2,4,6-C₆H₂Me₃)]• (**2a5**)

¹H-NMR (300 MHz, CDCl₃) 2.17 (s, 9 H, Me, *W*_{1/2} = 100 Hz); 6.81 (s, 22 H, Ph, *W*_{1/2} = 150 Hz).

3.2.2. [η^5 -C₅(3,5-C₆H₃Me₂)₄(2,4,6-C₆H₂Me₃)]• (**2b5**)

¹H-NMR (300 MHz, C₆D₆) 2.17 (s, 33 H, Me, *W*_{1/2} = 100 Hz); 6.81 (s, 14 H, Ph, *W*_{1/2} = 150 Hz). EIMS: Found 600.3764, 616.3713. Calc. for [M–H]⁺ 600.3756, and [M+OH]⁺ 616.3705. UV–vis; toluene; λ , nm (ϵ , l mol⁻¹ cm⁻¹): 356 (3.5 × 10⁶), 598 (0.72 × 10⁶). Anal. Found: C, 87.38; H, 7.57. Calc. for the dioxygen adduct C₄₆H₄₇O₂, C, 87.44; H, 7.50; O, 5.06%.

3.3. Syntheses of the (η^5 -C₅Ar₄Ar')Fe(CO)₂Br Complexes (**3**)

In a schlenk tube 2.0 mmol of the corresponding bromocyclopentadiene was dissolved in toluene (20 ml) and iron pentacarbonyl (2.5 mmol, 330 μ l) was added via syringe. The yellow solution was warmed to 80 °C for 2 h quickly became violet and then slowly turned to red–brown. After cooling to 20 °C, the solvent was removed under vacuum and the solid residue was dissolved in CH₂Cl₂ and filtered through a 15 cm Celite pad. Concentration of the solution (15 ml) and addition of pentane afforded the iron complexes **2** as an orange powder. Further recrystallization from CH₂Cl₂–diethyl ether yielded pure product.

3.3.1. **3a3** (1.065 g, 1.6 mmol, 80%)

IR (cm⁻¹, CH₂Cl₂) 1610 (Ph), 1995 (CO), 2037 (CO). ¹H-NMR (300 MHz, CDCl₃) 2.06 (s, 6H, Me), 6.67–7.23 (m, 23H, Ph). ¹³C-NMR (75 MHz, CDCl₃) 21.3 (q, ¹J_{C-H} = 126 Hz, Me), 100.3 (s, C-Ph), 101.7 (s, C-C₆H₃Me₂), 101.9 (s, C-Ph), 127.81 (d, ¹J_{C-H} = 161 Hz, *o*-Ph), 127.83 (d, ¹J_{C-H} = 161 Hz, *o*-Ph), 128.48 (d, ¹J_{C-H} = 162 Hz, *p*-Ph), 128.52 (d, ¹J_{C-H} = 162 Hz, *p*-Ph), 129.3, 130.0, 130.1 (3 s, *ipso*-Ph, C₆H₃Me₂), 130.2 (m, *o*-C₆H₃Me₂, *p*-C₆H₃Me₂), 130.3 (m, *o*-C₆H₃Me₂, *p*-C₆H₃Me₂), 132.4 (d, ¹J_{C-H} = 161 Hz, *m*-Ph), 132.5 (d, ¹J_{C-H} = 161 Hz, *m*-Ph), 137.1 (q, ²J_{C-H} = 5 Hz, *m*-C₆H₃Me₂), 213.8 (s, CO). Anal. Calc. for C₃₉H₂₉BrFeO₂: C, 70.40; H, 4.39. Found: C, 70.44; H, 4.49%.

3.3.2. **3a7** (0.810 g, 1.2 mmol, 60%)

IR (cm⁻¹, CH₂Cl₂) 2001 (CO), 2041 (CO). ¹⁹F-NMR (282 MHz, CDCl₃) 109.70 (t, ³J_{F-H} = 8 Hz). ¹³C-NMR (75 MHz, CDCl₃) 99.6 (s, C-C₆H₃F₂), 100.2 (s, C-C₆H₅), 102.0 (s, C-C₆H₅), 104.2 (dt, ¹J_{C-H} = 160 Hz, ²J_{C-F} = 23 Hz, *p*-C₆H₃F₂), 115.6 (dd, ¹J_{C-H} = 160 Hz, ²J_{C-F} = 26 Hz, *o*-C₆H₃F₂), 127.9 (d, ¹J_{C-H} = 160 Hz, *o*-C₆H₅), 128.7 (d, ¹J_{C-H} = 160 Hz, *p*-C₆H₅), 132.2 (d, ¹J_{C-H} = 160 Hz, *m*-C₆H₅), 133.9 (m, *ipso*-C₆H₃F₂), 162.1 (dm, ¹J_{C-F} = 248 Hz, *m*-C₆H₃F₂), 213.2 (s, CO); FABHRMS Calc. for [C₃₅H₂₃⁷⁹BrF₂⁵⁶Fe]⁺ ([M-2CO]⁺): 616.0303. Found: 616.0300.

3.3.3. **3b2** (1.260 g, 1.6 mmol, 80%)

IR (cm⁻¹, CH₂Cl₂) 1601 (Ph), 1994 (CO), 2036 (CO). ¹H-NMR (300 MHz, CDCl₃) 2.05 (s, 12H, CH₃), 2.06 (s, 12H, CH₃), 2.11 (s, 3H, CH₃), 6.68 (s, 8H, *o*-C₆H₃Me₂), 6.81 (s, 4H, *p*-C₆H₃Me₂), 6.93, 7.00 (2 d, 2H, C₆H₄Me). ¹³C-NMR (75 MHz, CDCl₃) 21.1 (q, ¹J_{C-H} = 126 Hz, C₆H₃Me₂), 21.3 (q, ¹J_{C-H} = 126 Hz, C₆H₄Me), 100.7 (s, C-C₆H₃Me₂), 101.0 (s, C-C₆H₃Me₂), 101.5 (s, C-C₆H₄Me), 127.3 (d, ¹J_{C-H} = 160 Hz, *m*-C₆H₄Me), 128.8 (dm, ¹J_{C-H} = 154 Hz, *p*-C₆H₄Me), 129.5 (dm, *o*-C₆H₄Me), 129.7 (dm, ¹J_{C-H} = 150 Hz, *p*-C₆H₃Me₂), 129.8 (dm, ¹J_{C-H} = 150 Hz, *p*-C₆H₃Me₂), 129.8 (s, *ipso*-C₆H₃Me₂), 129.9 (s, *ipso*-C₆H₃Me₂), 130.3 (d, ³J_{C-H} = 7 Hz, *ipso*-C₆H₄Me), 130.3 (dm, ¹J_{C-H} = 159 Hz, *o*-C₆H₃Me₂), 130.4 (dm, ¹J_{C-H} = 159 Hz, *o*-C₆H₃Me₂), 133.2 (dm, ¹J_{C-H} = 152 Hz, *o*-C₆H₄Me), 136.6 (m, *m*-C₆H₃Me₂), 136.7 (m, *m*-C₆H₃Me₂), 136.8 (m, *m*-C₆H₄Me), 214.2 (CO). FABHRMS Calc. for [C₄₄H₄₃⁷⁹Br⁵⁶Fe]⁺ ([M-2CO]⁺): 706.1898. Found: 706.1903.

3.3.4. **3b3** (1.17 g, 1.5 mmol, 75%)

IR (cm⁻¹, CH₂Cl₂) 1602 (Ph), 1991 (CO), 2034 (CO). ¹H-NMR (300 MHz, CDCl₃) 2.07 (s, 30 H, C₆H₃Me₂), 6.70 (s, 10 H, *o*-C₆H₃Me₂), 6.81 (s, 5 H, *p*-C₆H₃Me₂). ¹³C-NMR (75 MHz, CDCl₃) 21.2 (qt, ¹J_{C-H} = 126 Hz, ³J_{C-H} = 4.5 Hz, C₆H₃Me₂), 101.2 (t, ³J_{C-H} = 4 Hz,

C₅(C₆H₃Me₂)₅), 129.7 (dm, ¹J_{C-H} = 155 Hz, *p*-C₆H₃Me₂), 129.9 (s, *ipso*-C₆H₃Me₂), 130.4 (dq, ¹J_{C-H} = 159 Hz, ³J_{C-H} = 5 Hz, *o*-C₆H₃Me₂), 136.6 (q, ²J_{C-H} = 6 Hz, *m*-C₆H₃Me₂), 214.4 (s, CO). FABHRMS Calc. for [C₄₅H₄₅⁷⁹Br⁵⁶Fe]⁺ ([M-2CO]⁺): 720.2054. Found: 720.2061.

3.3.5. **3b4** (1.20 g, 1.5 mmol, 75%)

IR (cm⁻¹, CH₂Cl₂) 1601 (Ph), 1992 (CO), 2034 (CO). ¹H-NMR (300 MHz, CDCl₃) 1.53 (s, 3H, Me), 1.95 (s, 12H, Me), 2.10 (s, 12H, Me), 2.31 (s, 3H, Me), 6.49 (m, 4H, *o*-3,5-C₆H₃Me₂), 6.72 (m, 2H, *p*-3,5-C₆H₃Me₂), 6.78 (m, 4H, *o*-3,5-C₆H₃Me₂), 6.85 (m, 2H, *p*-3,5-C₆H₃Me₂), 6.93, 7.01, 7.76 (3 m, 3x1H, *o,m,p*-2,5-C₆H₃Me₂). ¹³C-NMR (75 MHz, CDCl₃) 19.9 (q, ¹J_{C-H} = 125 Hz, *o*-2,5-C₆H₃Me₂), 21.2 (q, ¹J_{C-H} = 125 Hz, other Me), 97.5 (s, C-2,5-C₆H₃Me₂), 97.9 (s, C-3,5-C₆H₃Me₂), 107.0 (s, C-3,5-C₆H₃Me₂), 129.4 (s+dm, *ipso,p*-3,5-C₆H₃Me₂), 129.8 (dm, ¹J_{C-H} = 160 Hz, *p*-3,5-C₆H₃Me₂), 129.9 (dm, ¹J_{C-H} = 160 Hz, *o*-3,5-C₆H₃Me₂), 130.2 (dm, ¹J_{C-H} = 160 Hz, *o*-3,5-C₆H₃Me₂), 130.4 (s, *ipso*-3,5-C₆H₃Me₂), 130.9 (s, *ipso*-2,5-C₆H₃Me₂), 134.5 (dm, ¹J_{C-H} = 160 Hz, 2,5-C₆H₃Me₂), 134.8 (m, 2,5-C₆H₃Me₂), 135.8 (m, 2,5-C₆H₃Me₂), 136.2 (q, ²J_{C-H} = 6 Hz, *m*-3,5-C₆H₃Me₂), 136.9 (q, ¹J_{C-H} = 160 Hz, ²J_{C-H} = 6 Hz, *m*-3,5-C₆H₃Me₂), 214.4 (s, CO). FABHRMS Calc. for [C₄₅H₄₅⁷⁹Br⁵⁶Fe]⁺ ([M-2CO]⁺): 720.2054. Found: 720.2055.

3.3.6. **3b6** (1.105 g, 1.45 mmol, 72%)

IR (cm⁻¹, CH₂Cl₂) 1603 (Ph), 1994 (CO), 2036 (CO). ¹H-NMR (300 MHz, CDCl₃) 2.05 (s, 12H, Me), 6.66 (s, 8H, *o*-C₆H₃Me₂), 6.81 (s, 4H, *p*-C₆H₃Me₂), 6.9–7.0 (m, C₆H₄F). ¹⁹F-NMR (282 MHz, CDCl₃) 113.9 (m, C₆H₄F). ¹³C-NMR (75 MHz, CDCl₃) 21.1 (q, ¹J_{C-H} = 127 Hz, Me), 99.7 (s, C-C₆H₄F), 100.0 (s, C-C₆H₃Me₂), 102.3 (s, C-C₆H₃Me₂), 115.07 (ddm, ¹J_{C-H} = 160 Hz, ²J_{C-F} = 21.3 Hz, *p*-C₆H₄F), 119.3 (ddm, ¹J_{C-H} = 161 Hz, ²J_{C-F} = 22.9 Hz, *o*-C₆H₄F), 128.5 (ddm, ¹J_{C-H} = 160 Hz, ⁴J_{C-F} = 2.44 Hz, *o*-C₆H₄F), 129.0 (ddm, ¹J_{C-H} = 160 Hz, ⁴J_{C-F} = 8.55 Hz, *m*-C₆H₄F), 129.36 (s, *ipso*-C₆H₃Me₂), 129.56 (s, *ipso*-C₆H₃Me₂), 129.87 (d, ¹J_{C-H} = 160 Hz, *p*-C₆H₃Me₂), 130.09 (d, ¹J_{C-H} = 160 Hz, *p*-C₆H₃Me₂), 130.17 (d, ¹J_{C-H} = 160 Hz, *o*-C₆H₃Me₂), 130.27 (d, ¹J_{C-H} = 160 Hz, *o*-C₆H₃Me₂), 133.22 (d, ²J_{C-H} = 7.33 Hz; *ipso*-C₆H₄F), 136.76 (q, ²J_{C-H} = 6 Hz, *m*-C₆H₄Me₂), 136.90 (q, ²J_{C-H} = 6 Hz, *m*-C₆H₄Me₂), 161.8 (dm, ¹J_{C-F} = 245 Hz, *m*-C₆H₄F), 213.9 (s, CO). FABHRMS Calc. for [C₄₃H₄₀⁷⁹Br⁵⁶Fe]⁺ ([M-2CO]⁺): 710.1649. Found: 710.1646.

3.3.7. **3b7** (1.18 g, 1.5 mmol, 75%)

IR (cm⁻¹, CH₂Cl₂) 1602 (Ph), 1996 (CO), 2037 (CO). ¹H-NMR (300 MHz, CDCl₃) 2.06 (s, 12H, Me), 2.09 (s,

12H, Me), 6.56 (s, 4H, *o*-C₆H₃Me₂), 6.62 (dt, 1H, ³J_{F-H} = 8.8 Hz, ⁴J_{H-H} = 2.3 Hz, *p*-C₆H₃F₂), 6.63 (s, 4H, *o*-C₆H₃Me₂), 6.71 (s, 2H, *p*-C₆H₃Me₂), 6.76 (s, 2H, *p*-C₆H₃Me₂), 7.11 (dd, 2H, ³J_{F-H} = 8.8 Hz, ⁴J_{H-H} = 2.3 Hz, *o*-C₆H₃F₂). ¹⁹F-NMR (282 MHz, CDCl₃) –110.55 (t, ³J_{F-H} = 8.8 Hz). ¹³C-NMR (75 MHz, CDCl₃) 21.1 (¹J_{C-H} = 126 Hz, Me), 21.2 (¹J_{C-H} = 126 Hz, Me), 99.1 (t, ⁴J_{C-F} = 2.5 Hz, C–C₆H₃F₂), 99.6 (s, C–C₆H₃Me₂), 102.4 (s, C–C₆H₃Me₂), 103.6 (tm, ²J_{C-F} = 18 Hz, *p*-C₆H₃F₂), 115.6 (dd, ²J_{C-F} = 27 Hz, ¹J_{C-H} = 165 Hz, *o*-C₆H₃F₂), 129.0 (s, *ipso*-C₆H₃Me₂), 129.3 (s, *ipso*-C₆H₃Me₂), 129.9 (d, ¹J_{C-H} = 165 Hz, *p*-C₆H₃Me₂), 130.0 (d, ¹J_{C-H} = 165 Hz, *o*-C₆H₃Me₂), 130.1 (d, ¹J_{C-H} = 165 Hz, *o*-C₆H₃Me₂), 130.3 (d, ¹J_{C-H} = 165 Hz, *p*-C₆H₃Me₂), 134.6 (t, ²J_{C-F} = 11 Hz, *ipso*-C₆H₃F₂), 136.6 (q, ²J_{C-H} = 6 Hz, *m*-C₆H₃Me₂), 136.8 (q, ²J_{C-H} = 6 Hz, *m*-C₆H₃Me₂), 161.9 (ddm, ¹J_{C-F} = 248 Hz, ³J_{C-F} = 13 Hz, *m*-C₆H₃F₂), 213.7 (s, CO). FABHRMS Calc. for [C₄₃H₃₉⁷⁹BrF₂⁵⁶Fe]⁺ ([M–2CO]⁺): 728.1555. Found: 728.1559.

3.4. Solubility measurements

In a test tube, an aliquot of the complexes was treated with 2 ml of the desired solvent. The mixture was shaken for 5 min, then allowed to stand for an additional 5 min. 1.0 ml of the supernatant solution was transferred via syringe into a test tube, then the solvent was removed in vacuo. The amount of soluble complex per ml of solvent was determined by weighing.

3.5. Crossed reaction with [η⁵-C₅(3,5-C₆H₃Me₂)₄(2,4,6-C₆H₂Me₃)]Br (**1b5**) and [η⁵-C₅(3,5-C₆H₃Me₂)₅][•] (**2b3**)

In a Schlenk tube, the bromopentaarylcyclopentadiene **1b5** (0.5 mmol, 340 mg) was dissolved in toluene (20 ml) with one equivalent of iron pentacarbonyl (0.5 mmol, 65 μl) to generate the radical **2b5**. In another Schlenk tube, the bromopentaarylcyclopentadiene **1b3** (0.5 mmol, 333 mg) was reacted with iron pentacarbonyl (0.5 mmol, 65 μl) in toluene (20 ml). Both solutions were stirred for 2 h at 20 °C. From the second solution, the solvent was removed and purification of the crude solid by chromatography on a silica gel column with pentane–diethyl ether (9:1) provided a violet powder of the corresponding radical **2b3**. Dissolved in toluene (20 ml), **2b3** was added to the first solution. The mixture was heated to 80 °C for 30 min, then the solvent was removed to dryness. The solid residue was washed with pentane, giving the radical **2b5**, identified by its ESR spectrum. Extraction with dichloromethane of the remaining solid allowed the isolation of the complex **3b3** (70%), which was characterized by comparison with an authentic sample.

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