

AN IMPROVED SYNTHESIS OF *P*-PHENYLENE-BRIDGED METHYLATED BINUCLEAR FERROCENEYUVARAJA DIBDALLI<sup>1</sup>, CRISTIAN VALDEBENITO<sup>2</sup>, MUNGALIMANE K. AMSHUMALI<sup>1</sup>, ELIES MOLINS<sup>3</sup>  
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## ABSTRACT

This contribution describes an updated synthetic route along with full characterization of  $[(\text{CpFe})_2\text{-}p\text{-Ph}']$  with  $p\text{-Ph}'$ :  $p\text{-Bis}\{2,3,4,5\text{-tetramethylcyclopentadienyl}\}$ benzene). The complex reported here was characterized by <sup>1</sup>H and <sup>13</sup>C NMR, elemental analysis, the X-ray crystal structure, and Mössbauer spectroscopy. From the crystallographic analysis, it was found that both {CpFe} fragments are coordinated to opposite sites of the  $p\text{-Ph}'$  ligand. In addition, the analysis through of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, confirm that the synthesis and yield of just one isomer of this compound.

**Keywords:** Homobimetallic compound, x-ray, ferrocene, Mössbauer spectroscopy.

## 1. INTRODUCTION

The bimetallic complexes are usually precursors of stability mixed-valence species due to strong electronic interaction bridging ligand.[1] In these systems, stability is possible, as the two metal centers exist in different oxidation states, generated chemically or electrochemically. The ionic mono-oxidized species produced, adopt a general strategy for the synthesis of the bridged bimetallic compound from the classical methods that involve the coupling of two metallic moieties. The group 8 metallocenes, their structures, synthesis, and organometallic chemistry are widespread have been investigated for their mixed-valence properties[2–8].

The syntheses of  $p\text{-Phenylene}$ - and  $p\text{-Biphenylene}$ -bridged methylated binuclear metallocenes derivatives, such as ferrocenes[9], germanocenes[10], and zirconocenes[11] have been published for different applications as a catalyst in propene polymerization and a burning rate (BR) catalysts on the thermal decomposition of ammonium perchlorate[12,13].

In this context, the ferrocene derivate from  $p\text{-Phenylene}$  despite being published thirty-two years ago[9], the characterization of this complex has not been well documented until now, since at that time the characterization of this type of compound was poor because NMR spectroscopy had not been developed as it is today and not was characterized accurately, the same way with the characterization through X-ray and Mössbauer spectroscopy was not achieved.

This information opens easy access to possible new studies of this homobimetallic compound and derivatives, thus following the research line of the strong electronic interactions between the metal centers, which might result in a range of interesting electronic, magnetic, and optical properties. We report here the synthesis of biferrocenes linked by an unsaturated organic group of  $p\text{-phenylene}$  for which the confirmed by X-Ray structure of  $[(\text{CpFe})_2\text{-}p\text{-Ph}']$ .

## 2. EXPERIMENTAL SECTION

## 2.1. General Information of the catalysts

All manipulations were carried out under a pure nitrogen atmosphere by using a vacuum atmosphere dry box equipped with a Model HE 493 Dri-Train purifier or with the use of a vacuum line by using standard Schlenk tube techniques.

Reagent grade solvents were distilled under an atmosphere of nitrogen from sodium benzophenone for toluene, hexane and thf (previously distilled from AlLiH<sub>4</sub>) and from P<sub>2</sub>O<sub>5</sub> for acetonitrile and dichloromethane.[14] The following compounds were prepared using literature procedures:

$p\text{-Phenylene}$  ( $p\text{-Ph}'$ :  $p\text{-Bis}\{2,3,4,5\text{-tetramethylcyclopentadienyl}\}$ benzene),[9] Fe(acac)<sub>2</sub>[15], Na(C<sub>5</sub>H<sub>5</sub>)[16].

## 2.1 Synthesis

2.1.1  $[(\text{Cp}^*\text{Fe})_2\text{-}p\text{-Ph}']$  (1)

An  $n\text{-butyl}$ -lithium solution (2.0 M in cyclohexane, 3.14 mmol) was added dropwise to a solution of  $p\text{-Phenylene}$  (0.5 g, 1.57 mmol) in THF (20 mL) at  $-80^\circ\text{C}$ . The resulting solution was vigorously stirred for 2 h at room temperature. Afterward, a solution of Fe(acac)<sub>2</sub> (0.80 g, 3.14 mmol) in THF (20 mL) was

slowly added to the suspension of the dilithiated compound  $[p\text{-Ph}']\text{[Li]}_2$  at  $-80^\circ\text{C}$ , and the mixture was vigorously stirred for 2 h at  $0^\circ\text{C}$ . The solution was recooled to  $-80^\circ\text{C}$ , and a solution of NaCp (0.28 g, 3.14 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight. After the complete removal of the solvent, the resulting solid product was dissolved with toluene and filtered off to remove the insoluble Li(acac) and Na(acac). An orange stable to air powder-like solid was obtained. Yield: 0.48 g (55.2%).

Anal. Calcd for C<sub>34</sub>H<sub>38</sub>Fe<sub>2</sub> (557.70): C, 73.14; H, 6.85. Found: C, 73.29; H, 6.87.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  1.87 (s, 12 H), 2.00 (s, 12 H), 3.77 (s, 10 H), 7.68 (s, 4 H).

<sup>13</sup>C NMR 100 MHz, ppm in C<sub>6</sub>D<sub>6</sub>:  $\delta$  10.78; 59.87; 125.31; 133.32; 134.06; 135.08; 136.40.

2.1.2  $[(\text{Cp}^*\text{Fe})_2\text{-}p\text{-Ph}']\text{[BF}_4\text{]} (1+)$ 

Complex **1** (0.20 g, 0.36 mmol) was dissolved in 20 mL of THF and was added to  $[\text{FeCp}_2]^+\text{[BF}_4\text{]}^-$  (0.09 g, 0.34 mmol). Then, the mixture was stirred at room temperature for 2 h resulting in the formation of a precipitate. The mixture was filtered and the insoluble material was washed with petroleum ether to remove all the ferrocene and dried under vacuum. Obtaining stables compound to air dark red dust. Yield 0.17 g (74%).

Anal. Calcd for C<sub>34</sub>H<sub>38</sub>Fe<sub>2</sub>BF<sub>4</sub> (644.51): C, 63.30; H, 5.89. Found: C, 63.92; H, 5.79.

## 2.2 X-Ray structure

The X-ray diffraction experiment was performed on a Bruker Smart Apex II diffractometer at 294 K using monochromatic MoK $\alpha$  radiation (wavelength = 0.71073 Å). Frames taken with a 0.3° separation afforded 6759 reflections up to a 2 $\theta$  max of ca. 61°. Data integration was performed using SAINT V6.45A and SORTAV20 in the diffractometer package. The crystal and collection data and structural refinement parameters are listed in Table 2. The structure was solved by direct methods using SHELXT-2014[17] and the Fourier difference method, and refined by least squares on F<sup>2</sup> using SHELXL-2014/7[17] inside the WinGX program environment.[18]

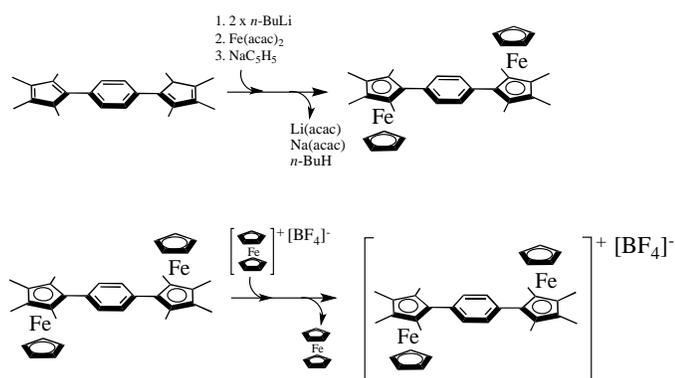
## 3. RESULTS AND DISCUSSION

## 3.1 Synthesis

The homobimetallic complex derived from  $p\text{-Phenylene}$  ligand was prepared using by previously reported route[9], with subtle changes which increased the reaction yield from 48% to 55% (scheme 1). These changes were (i) when adding Fe(acac)<sub>2</sub> to the dilithiated ligand, the temperature was not allowed to rise above 0°C during the 2h of reaction. (ii) The reaction was allowed to stir for 12h after the addition of the NaCp solution. (iii) Finally, unlike the original synthetic route, extraction of compound (**1**) was carried out toluene instead of being suspended in methanol, therefore, a better separation was obtained to remove the insoluble salts of Li(acac) and Na(acac).

In order to study the mixed-valence compound, the chemical mono-oxidation with ferrocenium tetrafluoroborate was carried out, obtaining a yield of 74%.

The characterization by means  $^1\text{H}$  and  $^{13}\text{C}$ -NMR and Mössbauer spectroscopies are detailed below.

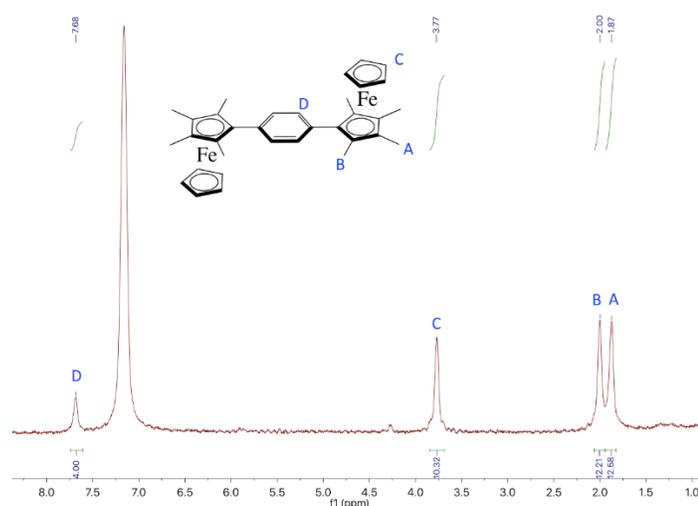


**Scheme 1.** Synthetic pathway of homobimetallic complex  $[\{\text{Cp}^*\text{Fe}\}_2\text{-}p\text{-Ph}\]^q$ ,  $q = 0, +1$ .

The spectroscopic analyses of each of the nuclei were carried out compared to previous works found in the literature[9,10].  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show that compound **(1)** is formed as a single isomer, namely the anti-configuration (*vide infra* see X-ray data). Previous studies have shown that the isomer ratio depends on a combination of several factors including steric hindrance, nature of the ancillary ligand, and symmetry of the indacene ligand[19]. Ceccon et al., studied this aspect in more detail for rhodium and iridium homobimetallic complexes, incorporating different ancillary ligands with different sizes.

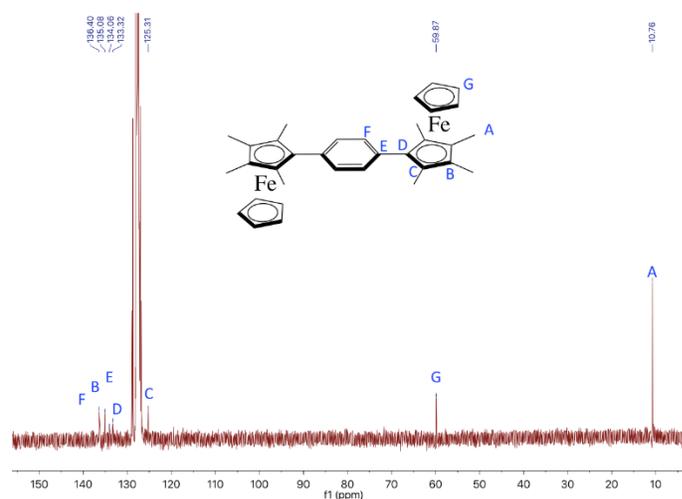
A large preference for the *syn* species is obtained with small ligands (COD or NBD), whereas the *anti* isomer is favored with cyclopentadienyl ligand. Here, we just obtained the *anti* isomer due to the  $\{\text{Cp}^*\text{Fe}\}$ - fragment imposing a steric hindrance to the entrance of the second organometallic fragment to the same side of the bridging *p*-Phenylene ligand, selectively yielding the *anti* isomer, explaining the formation of only one isomer as the final product.

The most notable feature in the  $^1\text{H}$  NMR spectrum is the simplicity of the assignment of the protons belonging to the coordinated five-membered ring of cyclopentadienyl (3.77 ppm) and *p*-Phenylene (1.87 and 2.00 ppm) ligands (Figure 1).



**Figure 1.**  $^1\text{H}$ -NMR (400 MHz) spectrum of  $[\{\text{Cp}^*\text{Fe}\}_2\text{-}p\text{-Ph}\]^q$  in  $\text{C}_6\text{D}_6$ .

The  $^{13}\text{C}$  NMR spectrum of the bimetallic complex was assigned using 2D NMR tools (Figure 2). This spectrum presents remarkable features, corresponding to the signals at 10.76 ppm consistent to  $-\text{CH}_3$  groups belonging to the bridging ligand and the signals at 59.87 ppm equivalent to Cp ancillary ligand.



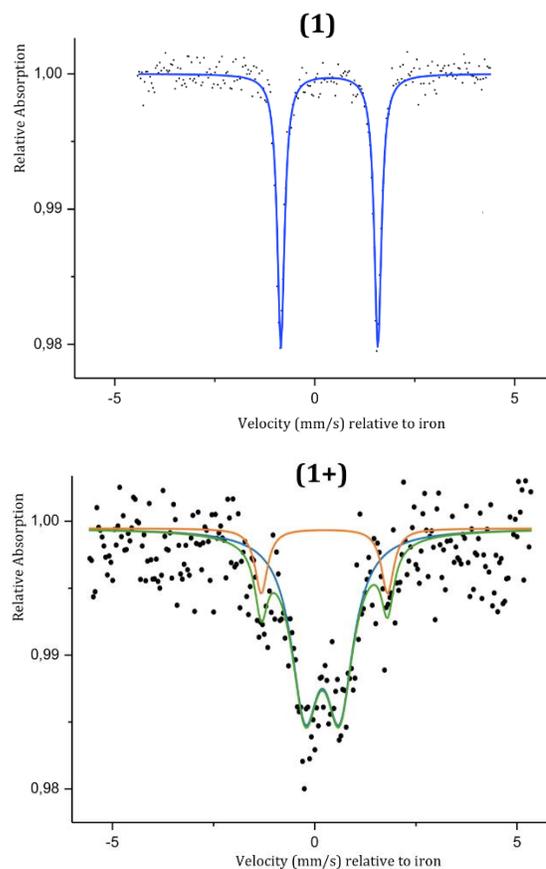
**Figure 2.**  $^{13}\text{C}$ -NMR (100 MHz) spectrum of  $[\{\text{Cp}^*\text{Fe}\}_2\text{-}p\text{-Ph}\]^q$  in  $\text{C}_6\text{D}_6$ .

### 3.2. $^{57}\text{Fe}$ Mössbauer Spectroscopy.

The Mössbauer spectra of the neutral (**1**) and mixed-valence (**1+**) species were obtained at temperatures 300 K. These spectra are shown in Figure 3, and the hyperfine parameters for these complexes are presented in Table 2

Complex (**1**) exhibits a large “ferrocene-like” quadrupolar splitting,  $\Delta E_q$ , characteristic of  $\text{Fe}^{2+}$ , and it was fitted to a single doublet associated with  $\text{Fe}^{2+}$ .

The spectrum of the mixed-valence compound (**1+**) was fitted using two symmetrical doublets corresponding to the two-oxidation states ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ). As was observed by Manriquez and coworkers[20], evidenced a trapping behavior at ambient temperature for the  $[\text{Cp}^*\text{Fe}^{\text{II-}as}\text{-indaceneFe}^{\text{III}}\text{Cp}]^{*+}$  compound, indicative of poor electronic communication through the bridging ligand, unlike iron complexes derived from *s*-indacene and pentalene[20].



**Figure 3.** Mössbauer spectra of  $[\{\text{Cp}^*\text{Fe}\}_2\text{-}p\text{-Ph}\]^q$ ;  $q = 0, +1$  at 300 K.

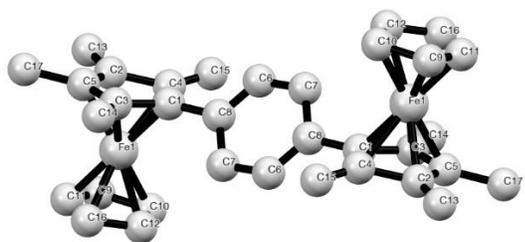
**Table 1.** Hyperfine parameters for the fitting of the Mössbauer spectra.

	T(K)	$\delta_{\text{Fe}}$ (mms <sup>-1</sup> )	$\Delta E_{\text{q}}$ (mms <sup>-1</sup> )
(1)	300	0.37	2.42
(1+)	300	0.35	0.87
		0.44	2.45

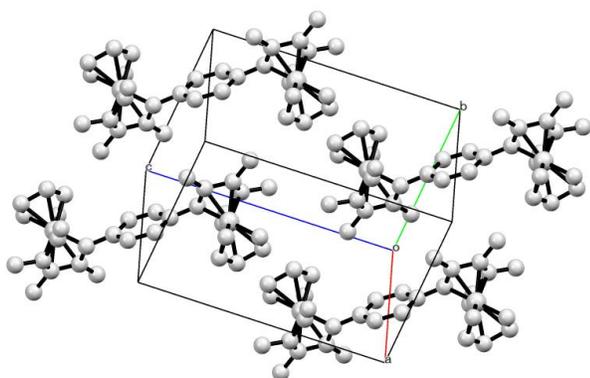
In this context and regarding the  $\Delta E_{\text{ox}}$  is related to the thermodynamic stability of the mixed-valence species where other energetic terms, apart from the one related to the electronic interactions, are also considered.[21] The homobimetallic compound (1), the difference of potential between the two oxidation peaks is  $\Delta E_{\text{ox}}=400$  mV,[12] giving a low comproportionation constant ( $K_c=5.8 \times 10^6$ )[22] compared to other homobimetallic iron complexes derived from *s*-indacene.[13,20,23] This small value of  $\Delta E_{\text{ox}}$  indicates the metals are noninteracting either because of the great distance between them or because the ligand does not provide an electronic coupling pathway, as in our case. Usually, these systems belong to class I or II, according to Robin and Day[25] classification. The low comproportionation constant, indicates a low communication between the two ferrocenyl moieties, as suggested by the Mössbauer spectrum for compound (1+).

### 3.3 X-ray structure.

Crystals of  $[\{\text{Cp}^*\text{Fe}\}_2\text{-}p\text{-Ph}']$  were grown by cooling a concentrated solution of toluene and pentane diffusion. A single-crystal X-ray diffraction experiment allowed solving the crystal structure. Because of the poor quality of the crystals, the presence of a twinned system, and disorder problems, a detailed discussion of the structure is not possible; however, the atom connectivity is clear. The structure determination revealed that, in the solid state, the molecule is centrosymmetric and the  $\{\text{CpFe}\}$ - organometallic fragments are located in an *anti* coordination mode to opposite sides of the *p*-phenylene ligand. This can be attributed to the steric hindrance provided by the two Cp moieties (Figure 4). Each unit cell consisted of four molecules of 1 (Figure 5), with the structure belonging to the triclinic space group *P*-1. Atom coordinates, bond distances and angles are given in Table 2. Figure 4 shows an ORTEP representation of  $[\{\text{Cp}^*\text{Fe}\}_2\text{-}p\text{-Ph}']$  with atom labelling. The molecule of  $[\{\text{Cp}^*\text{Fe}\}_2\text{-}p\text{-Ph}']$  evidences that both metallic centers present a nearly perfect  $\eta^5$  hapticity with Cp and *p*-Ph' ligands. The *p*-Ph' centroid distances to the iron atoms are 1.594 Å. Furthermore the distance between the Fe and Cp centroids are 1.644 Å, which provide evidence that iron has a stronger coordination to *p*-Ph' than the ligand Cp.



**Figure 4.** ORTEP representation of  $[\{\text{Cp}^*\text{Fe}\}_2\text{-}p\text{-Ph}']$ . Thermal ellipsoids are drawn at the 50% probability level.



**Figure 5.** Unit cell of the compound 1.

**Table 2.** Selected Bond Lengths [Å] and Angles [°] for Compound (1),  $[\{\text{CpFe}\}_2\text{-}p\text{-Ph}']$ .

Fe-C(1)	2.03(3)
Fe-C(2)	2.02(3)
Fe-C(3)	2.03(3)
Fe-C(4)	2.19(4)
Fe-C(5)	1.97(5)
Fe-C(9)	2.10(3)
Fe-C(10)	2.06(7)
Fe-C(11)	2.03(3)
Fe-C(12)	2.02(5)
Fe-C(16)	2.08(5)
Fe to centroid <i>p</i> -Ph'	1.594
Fe- <i>p</i> -Ph' average	2.045
Fe- <i>p</i> -Ph' range	1.972-2.189
Fe to centroid Cp	1.644
Fe-Cp average	2.059
Fe-Cp range	2.031-2.102
C-C average Cp ring	1.459
C-C range Cp ring	1.149-1.505
C-C average <i>p</i> -Ph' ring	1.516
C-C range <i>p</i> -Ph' ring	1.269-1.822
C(6)-C(8)	1.35(4)
C(7)-C(8)	1.49(5)
C(6)-C(7)	1.41(5)

## CONCLUSION

This work describes the update of the synthesis and full characterization including X-ray structural of a homobimetallic organometallic system entitled as  $[\{\text{CpFe}\}_2\text{-}p\text{-Ph}']$  (1) and the further oxidation affording a mixed-valent cation  $[\{\text{CpFe}\}_2\text{-}p\text{-Ph}']^+$  (1+), which presents a weak electronic communication between metal sites as suggested by cyclic voltammetry, previously reported, and Mössbauer spectroscopy studies. Experimental facts demonstrate that the mixed-valence system, is a localized one, and it can be classified as a Class I or II system according to Robin & Day classification.

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