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Synthesis of new star-like triply ferrocenylated compounds.

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Abstract: New ferrocenyl-substituted compounds containing two different central cores (isocyanurate and 1,3,5-phenylene) and extended by two kinds of branches bearing both vinyl ferrocenyl (**1** and **3**) and cross-conjugated ferrocenyl-chalcone (**2**, **4** and **5**) as endgroups have been synthesized and characterized both spectroscopically and electrochemically. These molecules have been synthesized in order to investigate the electronic properties imparted by both types of branches when they are connected to the central core. For all compounds, electrochemical studies have showed a simultaneous oxidation of all ferrocene units present in each compound. For all of them, except for compound **2**, a chemically reversible oxidation wave on the voltammograms has been observed. In contrast, for compound **2**, a chemically irreversible oxidation wave is obtained. Moreover, the vinyl ferrocenyl derivatives have presented a lower redox peak potential with respect to ferrocene standard compound, and the ferrocenyl-chalcone bearing derivatives, in accordance with a change in the electron releasing capability of these endgroups, have been oxidized at a higher potential.

Bathochromic shifts of the active transitions in Uv-Vis region have been observed, which are associated to the presence of carbonyl groups in those molecular structures containing it. These results are in agreement with theoretically calculated transition energies, which have been obtained for compounds **1** and **2** using Time Dependent Density Functional Theory (TD-DFT).

1. Introduction

The electron-donating characteristics of the ferrocenyl group, the electron-withdrawing properties of the oxidized ferrocenium species, the high thermal stability of both the

oxidized and the reduced states, and the electrochemical reversible nature of the Fc/Fc^+ couple are the main reasons for using ferrocene (Fc) derivatives as molecular sensors and/or energy transfer processes[1–6].

In view of this, in the last years an increasing interest has been devoted to the design and synthesis of complex systems capable of generating an electrochemical response, among them ferrocene moieties, in which the structural and electronic properties may be influenced by appropriate chemical or physical stimulus, has been the focus of many studies[7–10].

In this context, following the search for new ferrocene containing materials[11], we are describing here the synthesis and characterization of five new star-like compounds bearing ferrocenyl endgroups featuring isocyanurate and 1,3,5-phenylene cores. The main objective of this work is to evaluate the electron conjugation effect across the central cores bearing two kinds of branches: the vinyl ferrocenyl and the cross-conjugated ferrocenyl-chalcone, on the electrochemical potentials of the Fc/Fc^+ couple and on the changes produced on lowest energy transition of electronic absorption spectra.

2. Results and Discussion

2.1 Synthesis and Characterization

Two different C-C coupling reactions were used to obtain the described compounds (Scheme 1). Compounds **1** and **3** were synthesized using the Heck coupling reaction between the vinyl ferrocene, **1-Fc**[12], and one of the following center cores: **C1**[13] and **C2**[14]. Whereas for the compounds **2**, **4** and **5**, Sonogashira cross coupling reaction was used not only to link together the new ferrocenyl-chalcone, **2-Fc**[15] with **C1** center core but also, the bromide chalcones **3-Fc** and **4-Fc**[16] with **C3**[14] center core. All compounds were isolated as a dark-red powder with yields ranging from 40.6-56.5% and were spectroscopically characterized. In all of these compounds a ferrocenyl fragment was connected to a center core through a chalcone and/or a vinyl group as a linker moiety with the aim to study their electronic properties when they are connected to conjugated (*i.e.* vinyl) or cross-conjugated (*i.e.* chalcone) bridges and to understand their influence on the linear optical properties (Uv-Vis).

Scheme 1. Synthesis of compounds 1-5.

All the new compounds were characterized by IR, ^1H , ^{13}C NMR and Uv-visible spectroscopy. For compounds **1** and **3**, the presence of the vinyl group was evidenced by an absorption at 1590 cm^{-1} and 1578 cm^{-1} , respectively, in infrared spectroscopy, corresponding to the $-\text{C}=\text{C}-$ stretching mode. Whereas for the compounds **2**, **4** and **5** the conjugated double bond was observed at 1588 , 1589 and 1597 cm^{-1} , respectively. Ferrocene-chalcone backbone, showed a characteristic $\text{C}=\text{O}$ stretching peak at 1655 cm^{-1} , for **2** and **4**, and 1652 cm^{-1} for **5**, typical for conjugated carbonyls. Additionally, for compounds **1** and **2** a very strong absorption was also observed at 1713 and 1719 cm^{-1} , which can be attributed to one of the $\text{C}=\text{O}$ vibrating modes of the carbonyl group of the isocyanurate core (Table 1).

In the ^1H -NMR spectrum, three distinctive principal regions of signals could be identified for all compounds. The first one is the typical pattern of signals expected for the ferrocenyl fragment, with a singlet at *ca.* 4.17 ppm , corresponding to the unsubstituted cyclopentadienyl ring and two broad singlets at *ca.* 4.44 ppm and *ca.* 4.60 ppm , corresponding to the substituted cyclopentadienyl ring. A slight variation in the chemical shifts on the ferrocenyl protons was observed in those compounds containing the carbonyl moiety in their structure (*i.e.* compounds **2**, **4** and **5**), shifting the proton NMR signal to a lower field compared with those found in compounds **1** and **3**. Another set of signals corresponds to the vinylic protons. The coupling constants for these protons in all compounds are between $^3J = 15.0$ and 16.0 Hz , suggesting both a *trans* geometry of the double bond and a *s-cis* conformation with the carbonyl double bond, for **2**, **4** and **5**. The last sets of signals correspond to the aromatic protons with signals in the range of 7.59 - 7.97 ppm .

2.2 Uv-Vis Spectroscopy

The Uv-Vis spectra of all new compounds **1-5** were recorded in dichloromethane. These absorption spectra display two or four characteristic peaks (Table 1 and Supplementary Material, figures SI-7 to SI-9). The absorption coefficients vary from 7400 to 54700 $\text{M}^{-1}\cdot\text{cm}^{-1}$. The origin of the high-energy absorption band, in the range of 269-347 nm, is assumed to be an intraligand π - π charge-transfer (ILCT) transition. And the low-energy absorption band in the region of 463-511 nm is assumed to be a d-d transition of the iron in the ferrocene moiety and $d \rightarrow \pi^*$ metal-to-ligand charge transfer (MLCT) transition from the Fe(d) orbital to the organic moiety orbital (π^*)[17,18].

A bathochromic shift of this transition is observed in the compound **2**, with respect to compound **1**, possibly attributed to the presence of the two acceptor groups, central core and carbonyl group of the chalcone fragment in the structure **2**. Likewise, the MLCT takes place at even lower energy in the **4** and **5** when compared with **3**, which does not have a carbonyl group in its structure. Regarding the intense ILCT transition at higher energy in **1-5**, the latter experiences also a bathochromic shift depending on the size of the π -conjugated manifold of the central core. As expected based on such considerations, this intense ILCT transition is found at lowest energy for compound **2** (Figure 1). Time-dependent density functional theory (TD-DFT) calculations were used to obtain the theoretical absorption spectra and Kohn-Sham orbitals (Supplementary Material, pages SI-10 to SI-12). Among the result it can be mentioned that the bathochromic shift of the active transitions in Uv-Vis region was observed in the compounds **1** and **2**. The HOMO (H)-LUMO (L) gap in **1** (3.86 eV) is higher than **2** (3.14 eV) yielding transitions with lowest energies in the latter compound. Also, according to the TD-DFT calculations for compound **1**, the transitions located around 630 nm, are predicted mainly as transitions between the $d\pi$ -type orbitals (H-3, H-4 and H-5) of three Fe atoms to π^* -type orbitals (L+13, L+12, L+11) of the three cyclopentadienyl moieties.

When transitions around 508 nm were calculated, they showed that mainly involve the same transitions described before in addition with the transitions between the $d\pi$ -type orbitals (H-9, H-10 and H-11) centered over three Fe atoms to π^* -type orbitals (L+14, L+15, L+16) of the delocalized bridge were found. The transition with the highest oscillator strength, accounts for the band around 320 nm and constitute the π - π^* excitation from

ligand bridges. These transitions are mainly composed for contributions of H-6→L, H-7→L+2 and H-8→L+1 excitations.

Figure 1. UV-Vis spectra of compounds **1** and **2** in CH₂Cl₂.

Table 1. Characterization data of compound **1-5**: principal IR stretching absorptions and maximum wavelength of absorption.

Compound	Wavenumber (cm ⁻¹)			$\lambda_{\max}$ (nm)
	C=C	C=O *	C=O **	
1	1590	1713	---	269
				316
				379 (sh)
				463
2	1588	1719	1655	347
				366
				523
3	1578	---	---	343
				477
				274
4	1589	---	1655	327
				399 (sh)
				511
5	1597	---	1652	311
				391
				502

*Isocyanurate core carbonyl; ** Chalcone carbonyl

2.3 Electrochemistry

The electrochemical behaviors of compounds **1-5** were studied using cyclic voltammetry (CV) in $\text{CH}_2\text{Cl}_2/0.1\text{M } n\text{-Bu}_4\text{NPF}_6$ (Figure 2), peak potentials are summarized in Table 2. All compounds showed an oxidation signal corresponding to $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ couple of the ferrocenyl moiety. For compounds **1**, **3**, **4** and **5** this signal was found to be reversible. Moreover, compound **1** shows a second oxidation signal (See inset in Figure 2) of reversible behavior at 0.774 V ($\Delta E = 0.074$ V), that can be attributed to the differentiation of the ferrocenyl (Fc) moieties present in the molecule. These results are in agreement with those reported by Santi *et al.* for tris(ferrocenyl) systems, which depend on the kind of the electrolyte support used [19]. For compounds **1** and **3** where the arm's carbonyl group is absent, a lower current value was observed when compared with that found for compounds **2**, **4** and **5**, since the solution's working concentrations in all cases were the same (*i.e.* 10^{-3} M) the decrease in the current value can be attributed directly to a decrease in the diffusion coefficient of these molecules, in accordance with the Randles-Sevcik equation[20].

Figure 2. Cyclic Voltammograms of 10^{-3} M solution of all compounds versus Fc/Fc^+ (perpendicular central dot line) in CH_2Cl_2 . 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte with a glassy carbon working electrode, Pt wire auxiliary electrode, scan rate, 0.1 V s^{-1}

In addition, compounds **1** and **3** showed anodic peak potential values lower than ferrocene compound (-44 and -9 mV, respectively), this displacement can be explained if the center core behaves as electron donor. This phenomenon could be attributed to their enhanced electron delocalization facilitating the oxidation of the ferrocenyl moiety. For

compounds **2**, **4** and **5** bearing a carbonyl group at the 2-propen-1-one moiety, a displacement towards higher potentials values was observed with respect to the ferrocene compound (*i.e.* 129, 185 and 293 mV, respectively). This behavior can be explained by the electron-attracting character of the carbonyl group, thus hindering the oxidation of the ferrocenyl moiety.

When comparing the voltammetric profile of compounds **1** and **2**, both bearing the same isocyanurate core, it was found that they behave very different among them, it seems that the presence of the -ArC₂H₂CO- fragment, affects the redox mechanism of the Fc moieties, changing it from reversible to irreversible ($\Delta E = 375$ mV).

Table 2. Electrochemical data.

[a]	Compound	E_{pa} (V) ^[a]	E_{pc} (V) ^[b]	ΔE (mV)	i_{pa} (μA) ^[c]	i_{pc} (μA) ^[d]
	1	0.503	0.380	123	10.01	11.78
		0.774	0.700	74	0.99	
	2	0.676	0.301	375	39.00	39.16
	3	0.538	0.436	102	13.70	15.45
	4	0.732	0.557	175	38.41	39.97
	5	0.840	0.648	192	43.48	40.77
	Fc	0.547	0.405	142	62.16	60.41

Anodic peak potential. [b] Cathodic peak potential. [c] Anodic peak current. [d] Cathodic peak current.

3. Conclusion

In summary, we have reported here five new compounds, containing ferrocenyl fragments connected by different arm kinds to different central cores. For all of them, except for compound **2**, a chemically reversible oxidation wave was observed on the cyclic voltammograms. In contrast, for compound **2** a chemically irreversible oxidation wave was observed.

When a carbonyl group is present, as occurs in the chalcone bearing compounds, a displacement towards higher potentials values was observed with respect to the ferrocene standard compound, this being more evident for compound **5**. The conjugation with a nearby vinyl linker apparently facilitates the oxidation of ferrocene in compounds **1** and **3**. Finally, the study of the electronic absorption spectra reveals also a bathochromic

displacement effect produced by the arm linker's nature between the ferrocene and the central core on the lowest energy (MLCT) transition in these compounds.

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5. Experimental Section

5.1. Materials and physical measurements: Solvents were used as purchased. Reagents were purchased from commercial suppliers and used without further purification. Melting points were determined using a Stuart Scientific SMP3 melting point apparatus. IR spectra were obtained as KBr disks on a Perkin Elmer Spectrum Two FTIR Spectrometer, in the range of 4000-400 cm^{-1} . ^1H and ^{13}C spectra were acquired at 297 K on a Bruker Avance 400 NMR spectrometer. Electrochemical measurements were recorded on the Electrochemical Analyzer CH Instruments 620E attached to a desktop computer with the appropriate software for total control of the experiments, data acquisition and treatment; also, a conventional three-electrode cell was used. Glassy carbon electrode (GCE) of 3 mm diameter (model CHI104, CH Instruments) was used as working electrode. A 0.8 mm diameter Pt wire and Ag|AgCl|KCl (sat.) electrode (model CHI111, CH Instruments) were used as the counter and reference electrodes, respectively. Before each experiment the GCE was pretreated by polishing on 0.3 and 0.05 μm alumina. All the experiments were carried out at room temperature. All compounds under study were prepared in dichloromethane solutions (1.0×10^{-3} M) and 0.1 M in the supporting electrolyte $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$. All chemical shifts are reported in ppm (δ) relative to tetramethylsilane. Coupling constants (J) are reported in Hertz (Hz) and integrations are reported as number of protons. The following abbreviations are used to describe peak patterns: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; pst, pseudo triplet, dd, double doublet; brs, broad singlet. Elemental analyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer. The geometry optimizations of compound **1** and **2** were performed at the B3LYP[21,22]/SDD[23] level of calculation. The obtained structures were corroborated as minimum through vibrational analysis at B3LYP/6-31G*[24] and the SDD[25] basis set for iron. Excited state

calculations were performed within the time-dependent DFT methodology at the same calculation level. Solvent effect for simulating dichloromethane has been incorporated through the polarizable continuum model (PCM)[26]. All of these calculations were made using Gaussian09 package of programs (G09)[27]. Absorption spectra were obtained from using the GaussSum 3.0[28] suite of processing tools. A full width at half-maximum (fwhm) of the Gaussian curves corresponding to 3000 cm⁻¹ was employed to convolute the spectra. The representation of molecular orbitals was made using the G09 cubegen tool and has been visualized using GV09 package.

5.2. General procedure for compounds 1 and 3: In an Schlenk tube under argon one of the following central cores **C1**, or **C2** was mixed with 5% palladium (II) acetate, Pd(OAc)₂, 10% Tris(*o*-tolyl)phosphine, P(*o*-tol)₃, and vinyl ferrocene, **1-Fc**, in triethylamine/THF, 15 mL/15 mL. The resulting mixture was stirred and refluxed overnight. After removing the solvent under reduced pressure, the oil obtained was washed with distilled water and extracted in CH₂Cl₂ three times and dried over MgSO₄. The extract was concentrated to dryness and purified by column chromatography (silica gel 60) using hexane/CH₂Cl₂ 2:1 (V/V) mixtures as eluent. The corresponding compounds were isolated after removing the solvent in a rotary evaporator.

Compound 1. 1-Fc (187 mg, 8.84 mmol), **C1** (150 mg, 0.253 mmol), Pd(OAc)₂ (2.8 mg, 0.0126 mmol), P(*o*-tol)₃ (7.7 mg, 0.0253 mmol), triethylamine/THF, 15 mL/15 mL. Yield 49.5%. IR wavenumber (KBr): $\tilde{\nu}$ = 1713 cm⁻¹ (-C=O), 1590 cm⁻¹ (-C=C-). ¹H NMR (CDCl₃, 400 MHz): δ = 4.10 (15H, *pst*, C₅H₅), 4.27 (6H, *pst*-C₅H₄), 4.44 (6H, *s*, -C₅H₄), 6.68 (3H, *d*, *J* = 16.0 Hz, =CH), 6.89 (3H, *d*, *J* = 16.0 Hz, =CH), 7.31 (6H, *d*, *J* = 8.2 Hz, H_{arom}), 7.50 (6H, *d*, *J* = 8.4 Hz, H_{arom}). ¹³C NMR (100.6 MHz, CDCl₃): δ = 67.05, 69.25, 69.66, 82.76, 124.74, 126.48, 128.53, 128.60, 128.91, 131.70, 139.04. Analysis calculated for C₅₇H₄₅O₃Fe₃N₃: C, 69.3; H, 4.59; N, 4.26. Found: C, 68.61; H, 4.12; N, 4.32. MP: 199 °C - 200 °C.

Compound 3. 1-Fc (137 mg, 0.648 mmol), **C2** (100 mg, 0.162 mmol), Pd(OAc)₂ (1.8 mg, 0.0081 mmol), P(*o*-tol)₃ (5.0 mg, 0.0162 mmol), triethylamine/THF, 15 mL/15 mL. Yield 51.2%. IR wavenumber (KBr): $\tilde{\nu}$ = 2206 cm⁻¹ (-C≡C-), 1578 cm⁻¹ (-C=C-). ¹H NMR (CDCl₃, 400 MHz): δ = 4.16 (15H, *s*, C₅H₅), 4.32 (6H, *spt*-C₅H₄), 4.48 (6H, *spt*, -C₅H₄), 6.69 (3H, *d*, *J* = 16.1 Hz, =CH), 6.94 (3H, *d*, *J* = 16.1 Hz, =CH), 7.42 (6H, *d*, *J* = 8.7 Hz, H_{arom}), 7.49 (6H, *d*, *J* = 6.0 Hz, H_{arom}), 7.66 (3H, *t*, C₆H₃). ¹³C NMR (100.6 MHz, CDCl₃): δ = 67.05, 69.29, 69.32, 69.68, 82.92, 82.94, 88.33, 91.13, 100.00, 120.70, 122.91, 125.20,

125.71, 128.58, 131.73, 132.05, 133.11, 133.80, 138.30. Analysis calculated for $C_{66}H_{48}Fe_3$: C, 78.59; H, 4.80; Found: C, 78.30; H, 4.67. MP: 206 °C – 211 °C.

5.3. General procedure for compounds 2, 4 and 5: In an Schlenk tube under argon one of the following central cores **C1** or **C4** was mixed with 5% bis(triphenylphosphine)palladium(II) dichloride, $Pd(Cl)_2(PPh_3)_2$, 10% copper(I) iodide, CuI, and, **2-Fc**, **3-Fc** or **4-Fc**, in 15 mL of triethylamine. The resulting mixture was stirred at room temperature overnight. After removing the solvent under reduced pressure, the crude was redissolved in CH_2Cl_2 and filtrated through Celite®545. The extract was concentrated to dryness and purified by column chromatography (silica gel 60) in hexane/ CH_2Cl_2 2:1 (V/V). The corresponding compound was isolated after removing the solvent in a rotary evaporator.

Compound 2: 2-Fc (343 mg, 1.01 mmol), **C1** (200 mg, 0.337 mmol), $Pd(Cl)_2(PPh_3)_2$ (11.8 mg, 0.0169 mmol), CuI (6.4 mg, 0.0337 mmol), triethylamine 15 mL. Yield 53.0%. IR wavenumber (KBr): $\tilde{\nu}$ = 1719 cm^{-1} (-C=O, *core*), 1588 cm^{-1} (-C=C-) and 1655 cm^{-1} (-C=O, *chalcone*). 1H NMR ($CDCl_3$, 400 MHz): δ = 4.19 (15H, s, C_5H_5), 4.52 (6H, *pst*, $-C_5H_4$), 4.62 (6H, *pst*, $-C_5H_4$), 7.10 (3H, d, J = 15.3 Hz, =CH), 7.59-7.70 (17H, m, H_{arom}), 7.79 (3H, d, J = 15.3 Hz, =CH), 7.97 (7H, d, J = 8.4 Hz, H_{arom}). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 69.16, 69.89, 71.66, 76.37, 79.01, 82.17, 118.56, 123.70, 125.51, 128.36, 130.03, 131.85, 132.28, 132.68, 132.72, 138.88, 147.74, 148.01, 188.61. Analysis calculated for $C_{84}H_{57}O_6Fe_3N_3$: C, 73.54; H, 4.19; N, 3.06. Found: C, 74.35; H, 4.21; MP: 210 °C – 211 °C

Compound 4. 3-Fc (565mg, 1.43 mmol), **C4** (71.4 mg, 0.476 mmol), $Pd(Cl)_2(PPh_3)_2$ (16.7 mg, 0.0238 mmol), CuI (9.1 mg, 0.0476 mmol), triethylamine 15 mL. Yield 40.6%. IR wavenumber (KBr): $\tilde{\nu}$ = 1655 (-C=O-), 1589 (-C=C-). 1H NMR ($CDCl_3$, 400 MHz): δ = 4.18 (15H, s, C_5H_5), 4.50 (6H, *pst*, $-C_5H_4$), 4.59 (6H, *pst*, $-C_5H_4$), 7.06 (3H, d, J = 15.3 Hz, =CH), 7.62 (6H, d, J = 8.4 Hz, C_6H_3), 7.76 (3H, d, J = 15.3 Hz, =CH), 7.84 (6H, d, J = 8.4 Hz, C_6H_3). ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 69.11, 69.86, 71.60, 78.98, 118.46, 127.35, 129.89, 131.81, 137.38, 147.60, 188.62. Analysis calculated for $C_{69}H_{48}Fe_3O_3$: C, 75.85; H, 4.43; Found: C, 75.20; H, 4.67. MP: 203 °C – 200 °C

Compound 5. **4-Fc** (700 mg, 1.77 mmol), **C4** (88.5 mg, 0.590 mmol), Pd(Cl)₂(PPh₃)₂ (21 mg, 0.0295 mmol), CuI (11 mg, 0.0590 mmol), triethylamine 15 mL. Yield 56.5%. IR wavenumber (KBr): $\tilde{\nu}$ = 1652 (-C=O-), 1597 (-C=C-). ¹H NMR (CDCl₃, 400 MHz): δ = 4.22 (15H, s, C₅H₅), 4.61 (6H, *pst*, -C₅H₄), 4.91 (6H, *pst*, -C₅H₄), 7.10 (3H, d, *J* = 15.7 Hz, =CH), 7.53 (15H, dd, C₆H₃ and -C₆H₄-), 7.72 (3H, d, *J* = 15.7 Hz, =CH). ¹³C NMR (CDCl₃, 100.6 MHz, CDCl₃): δ = 69.76, 70.14, 72.92, 80.48, 123.51, 124.25, 129.63, 132.18, 133.68, 134.15, 139.47, 192.68. Analysis calculated for C₆₉H₄₈Fe₃O₃: C, 75.85; H, 4.43; Found: C, 75.15; H, 4.67. MP: 203 °C – 205 °C.

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Highlights:

- New star like ferrocenyl compounds containing two different central cores have been synthesized
- The oxidation of ferrocenyl is facilitated by conjugation of vinyl linker through central core
- Bathochromic shift in absorption spectra was observed based on the nature of linker