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Ferrocenyl-Terminated Redox Stars: Synthesis and Electrostatic Effects in Mixed-Valence Stabilization

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Abstract: A family of rigid ferrocenyl-terminated redox stars has been synthesized—by Negishi coupling, including hexa(ferrocenethynyl)benzene complexes, a dodecaferrocenyl star, and stars with extended rigid tethers—and fully characterized. Cyclic voltammetry (CV) studies of the parent complex hexa(ferrocenylethynyl)benzene, **1**, show a single wave for the six-electron oxidation of **1** using N*n*-Bu_4PF_6 as the supporting electrolyte on a Pt anode in CH_2Cl_2, whereas three distinct two-electron reversible CV waves are observed using N*n*-$Bu_4BAr^F_4$ ($Ar^F = 3,5\text{-}C_6H_3{-}(CF_3)_{2,}$). The CV of 1,3,5-tris(ferrocenylethynyl)benzene, **11**, also shows only one wave for the three-electron transfer with N*n*-Bu_4PF_6 and three one-electron waves using N*n*-$Bu_4BAr^F_4$. This confirms the lack of electronic communication between the ferrocenyl groups and a significant electrostatic effect among the oxidized ferrocenyl groups. This effect is not significant between *para*-ferrocenyl groups in 1,4-bis(ferrocenylethynyl)benzene for which only a single wave is observed even with N*n*-$Bu_4BAr^F_4$ as the supporting electrolyte. The *para*-ferrocenyl substituents are quite independent, which explains that two *para*-ferrocenyl groups are oxidized at about the same potential in a single CV wave of **1**. With the additional steric bulk introduced with a methyl substituent on the ferrocenyl group, however, even the *para*-methylferrocenyl groups are submitted to a small electrostatic effect splitting the six-electron transfer into six single-electron waves, probably because of the overall steroelectronic constraints. Contrary to **11**, 1,3-bis(ferrocenylethynyl)benzene and related complexes with a third, different substituent in the remaining *meta* position different from a ferrocenylethynyl only show a single two-electron wave using N*n*-$Bu_4BAr^F_4$, which is attributed to the transoïd conformation of the ferricinium groups minimizing the electrostatic effect. This shows that, in **11**, it is the steric frustration that is responsible for the electrostatic effect, and the same occurs in **1**. In several cases, ΔE_p is much larger than the expected 60 mV value, characterizing a quasi-reversible (i.e., relatively slow) redox process. It is suggested that this slower electron transfer be attributed to conformational rearrangement of the ferrocenyl groups toward the transoïd position in the course of electron transfer. Thus both the thermodynamic and kinetic aspects of the electrostatic factor (isolated from the electronic factor), including the frustration effect, are characterized. The distinction between the electronic communication and through-space electrostatic effect was made possible in all of these complexes in which the absence of wave splitting using a strongly ion-pairing electrolyte shows the absence of significant electronic communication, and was confirmed by the new frustration phenomenon.

Introduction

Electron transfer studies in multiredox systems such as polymers,[1] dendrimers,[2] and other nanoparticles[3] are of interest for their relevance to biological redox processes,[4] molecular conductors and semiconductors,[5] mixed-valence stabilization,[6] catalysis,[7] and redox recognition.[8] Most electron-transfer processes in nanosized systems have so far involved metalloproteins or their models[4] and metallodendrimers because of the well-defined structure and topology of the latter.[2,3] Among the redox systems involved in dendritic frameworks, ferrocenes occupy a privileged place because of the stability of both their Fe^{II} and Fe^{III} forms, at least on the electrochemical time scale.[9] Although

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rigid dendrimers are well-known,[10] there is no report of rigid ferrocene-containing dendrimers, presumably because of the synthesis problems related to their insolubility. In star-shaped systems, the number of branches is reduced, for instance to six in arene-cored stars. This reduced number of redox sytems and their localized positions at the rigid branch termini should allow us to better understand the parameters governing heterogeneous electron transfers with electrodes than those in dendritic redox systems in which the terminal redox centers are numerous and located on flexible tethers. Recently, we have reported the synthesis and electrochemistry of hexa(ferrocenylethynyl) benzenes.[11] Now we report our investigations of the synthesis of rigid ferrocenyl-terminated arene-cored stars and the comparison of their electron-transfer properties, especially the stabilization of mixed valences and the implication of the electrostatic factor.

Geiger's group has shown that, *inter alia*, when up to four ferrocene redox centers are equivalent around a small core, cyclic voltammograms using a supporting electrolyte that contains a perfluorinated anion can be split into several waves due to reduced ion pairing.[12] In the present work, we are using such a perfluorinated anion in order to provide the optimized separation beween the CV waves of the redox centers. In this way, it should be possible to investigate electrostatic effects among the redox centers of the various star systems and tentatively rationalize the comparison between flexible and rigid stars in terms of electron-transfer mechanisms and electrostatic effects. A few arene-centered star molecules containing terminal ferrocenyl groups are known in which the tethers are flexible, and the length of the tethers and lack of conjugation in these compounds result in the independency of the redox centers that give a single CV wave as in ferrocenyl-terminated dendrimers.[13] However, the extraordinary hexaferrocenylbenzene synthesized by the Vollhardt group shows an electrochemical behavior that seemingly results from the extreme bulk and distortion rather than from extended electronic communication among the six ferrocenyl groups.[14]

Results

Synthesis of Hexa(ferrocenylethynyl)arene Complexes. The chemistry of hexa(ethynyl)benzene derivatives has been pioneered by the Vollhardt group in the 1980s[15] and further developed by this group and by Rubin's group in the 1990s.[16] Then, the very useful Negishi reaction[17] was introduced by Tobe's group[18] for the syntheses of a series of these compounds and used with cyclopentadienylruthenium compounds by Carella et al.[19] The mono-, bis-, and tris(ferrocenylethynylation) of 1,3,5-tribromobenzene was reported by the groups of Long and Zanello[20] using Sonogashira coupling.[21] Various polyferrocenylarene complexes have also been reported.[22] Long and Zanello observed that their three compounds above gave only one cyclic voltammetry (CV) wave, which was taken into account by a lack of electronic communication between the redox centers.[20] We, however, met with failure while attempting to extend this Sonogashira coupling of ethynylferrocene to hexabromobenzene. Alternatively, we found that Negishi coupling of ferrocenylethynyl zinc chloride with hexabromobenzene provided a suitable route to hexa(ferrocenylethynyl)benzene (Scheme 1).

The reaction produced the dimer di(ferrocenyl)butadiyne[20] along with **1** (Figure 1), which requires the use of an excess of the zinc reagent. It also produced 7% of penta(ferrocenylethynyl)benzene, **2**, resulting from debromination. Such dehalogenation of hexahalogenobenzenes upon reactions of organometallic reagents is well-known;[13,22-24] it is probably due to side electron transfer from the organozinc reagent to the bulky penta(ferrocenylethynyl)bromobenzene intermediate.[24] The solubility of **1** is very low, although it could be characterized by MALDI-TOF mass and Mössbauer spectrocopy, CV, and elemental analysis. Other related star complexes in which the ethynylferrocenyl groups contains a differently substituted free cyclopentadienyl-type ring have been synthesized in the same way starting from ethynylpentamethylferrocene (Scheme 1),

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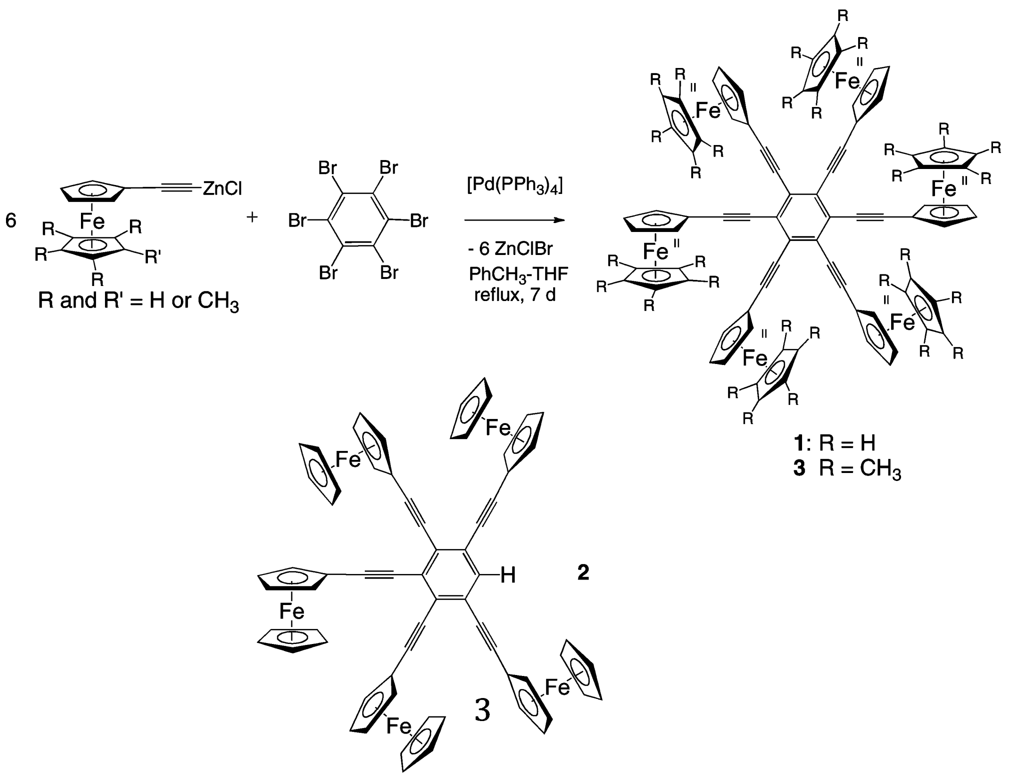
Scheme 1



1-ethynyl,1′-methylferrocene (Scheme 2) and a known ferrocenyl derivative **5**[25] in which a cyclopentadienyl ligand is linked to an octamethylferrocene via a vinyl bridge (Scheme 3).

The hexa(ferrocenylethynyl)benzene complexes **3** and **4** and the conjugated dodeca(ferrocenylethynyl) complex **6** that were synthesized by Negishi reactions with C_6Br_6 are soluble in common organic solvents and were characterized by ^{1}H and ^{13}C NMR, CV, and elemental analysis.

Large Ferrocenyl-Terminated Stars. The hexa(*p*.iodophenyl)benzene core was successfully submitted to the Sonogashira reaction with ethynylpentamethylferrocene, yielding the hexa(pentamethylethynylferrocenyl)-terminated star **7** with an hexa(phenyl)benzene core instead of benzene (Scheme 4). This compound was soluble in common organic solvents and could be characterized by the standard analytical and spectroscopic techniques.

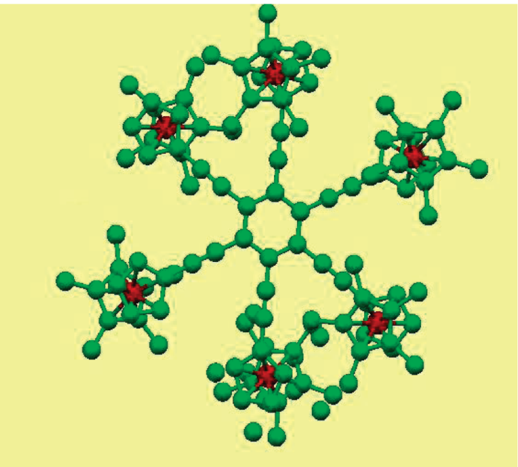
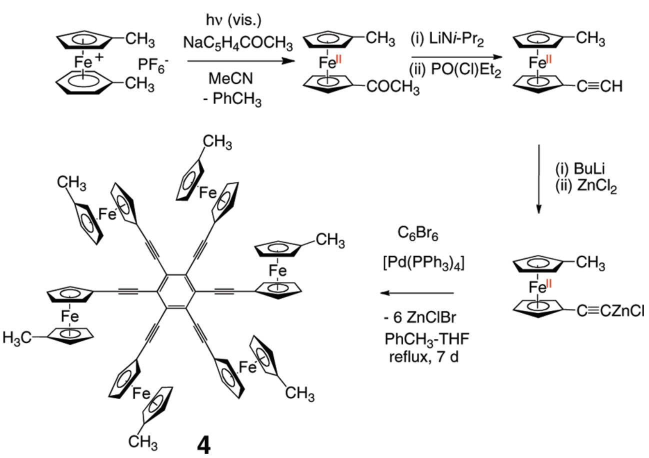


Figure 1. X-ray crystal structure of **1** (see ref 11).

Scheme 2



Finally, the rigid tether of the pentamethylferrocenylethynyl segment was lengthened by reaction with *p*-bromo(trimethylsilylethynyl)benzene yielding the alkyne **8** subsequently to deprotection before Negishi-type reaction with hexaiodobenzene. This series of reactions ended in the formation of the star complex **9** that was almost insoluble in all solvents. Very weak solubility was observed in hot toluene, and a weak reversible wave was obtained in cyclic voltammetry. The IR spectrum of **9** showed absorption at 2203 cm^{-1}, expected for triple carbon−carbon bonds. The structure of **9** is confirmed by the Mössbauer spectrum showing the typical ferrocenyl doublet, MALDI-TOF mass spectrum showing the molecular peak and elemental analysis (Scheme 5, Figure 2).

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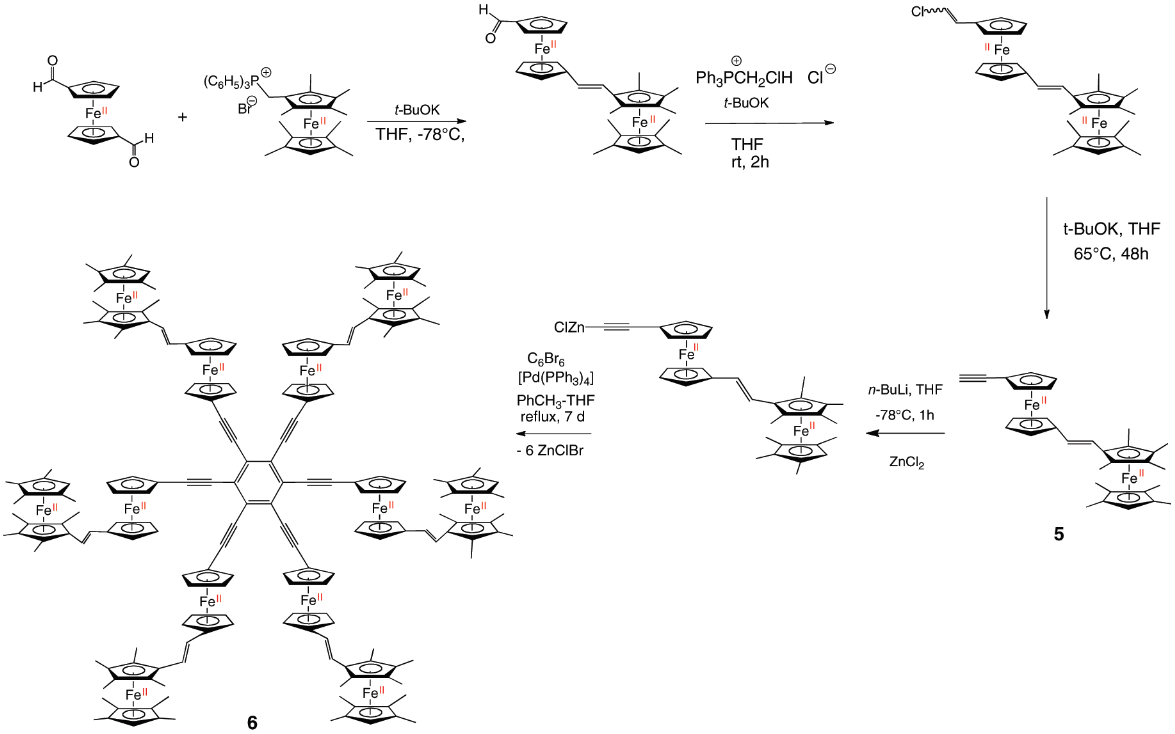
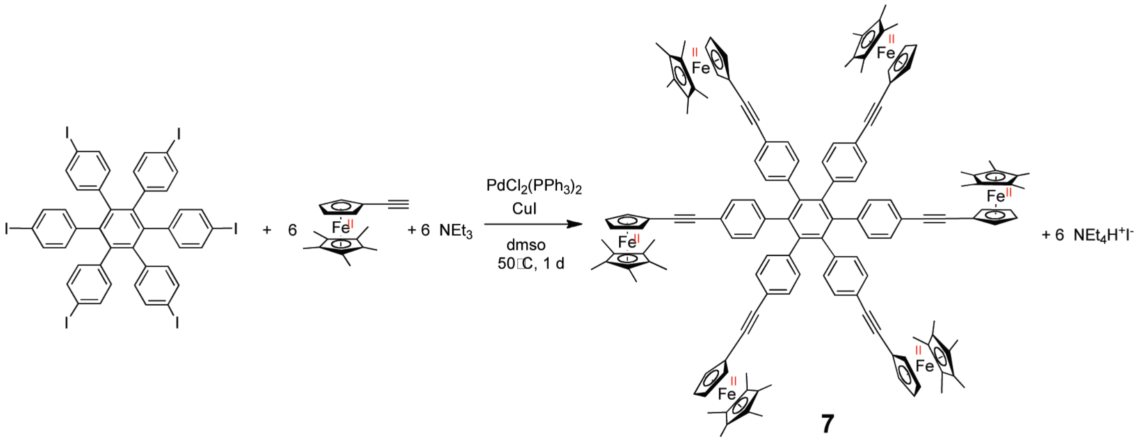
Scheme 3. Synthesis of the Dodeca(ferrocenyl) Complex **6**[a]



[a] The synthesis of the precursor binuclear complex **5** was adapted from ref 22a.

Scheme 4

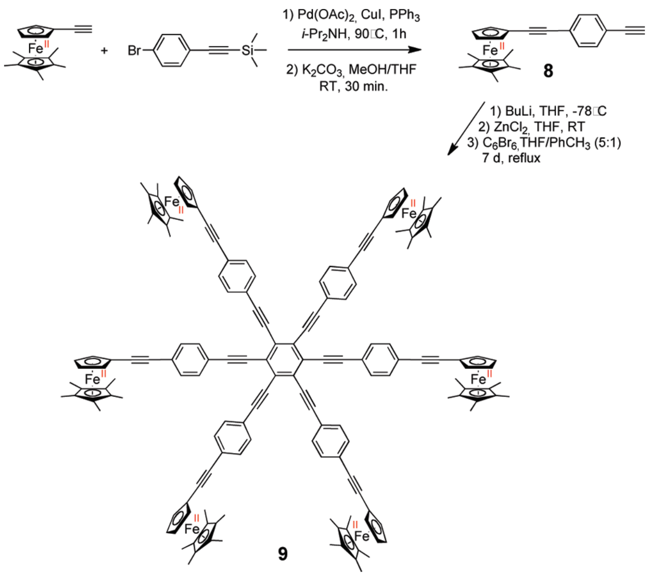


Six-Electron Redox Chemistry of the Hexa(ferrocenylethynyl)-benzene Complexes. The hexa(ferrocenylethynyl)benzene complexes **1** and **3** were oxidized using the tetrafluoroborate or hexafluorophosphate ferricinium salts [FeCp$_2$][PF$_6$] and [Fe(η^5-C$_5$H$_4$COCH$_3$][BF$_4$], depending on which reagent was appropriate for exergonic oxidation of a given star complex. Thus, the permethylated complex **3** was oxidized with 6 equiv [FeCp$_2$][PF$_6$] in DCM (dichloromethane) yielding ferrocene, and the dark-green hexacationic salt **3**[PF$_6$]$_6$ that was characterized by the typical broad signal with very small quadrupole splitting of ferricinium derivatives in the Mössbauer spectrum, UV−vis spectrum also characteristic of ferricinium (see the compared Mössbauer and UV−vis spectra of **3** and **3**[PF$_6$]$_6$ in Figure 3), IR, and elemental analysis.

The parent complex **1** and the star complex **4** were oxidized using 6 equiv [FeCp(η^5-C$_5$H$_4$COCH$_3$][BF$_4$] in dichloromethane (DCM) giving acetylferrocene and the dark-green complexes **1**[BF$_4$]$_6$ and **4**[BF$_4$]$_6$ that were also characterized by elemental analysis. The hexacationic salt **3**[PF$_6$]$_6$ was reduced back to **3** quantitatively using 6 equiv decamethylferrocene in DCM, which also produced 6 equiv [Fe(η^5-C$_5$Me$_5$)$_2$][PF$_6$] (Scheme 6). Attempts to selectively oxidize the terminal pentamethylferrocenyl groups in **6** led to decomposition, and clean oxidized products were not isolated.

Cyclic Voltammetry of the Poly(ferrocenylethynyl)arene Complexes. The cyclic voltammogramms (CVs) were recorded in DCM using a Pt anode and either N*n*-Bu$_4$PF$_6$ or N*n*-Bu$_4$BAr$^F{}_4$ (Ar^F = 3,5-C$_6$H$_3$(CF$_3$)$_2$) as the supporting electrolyte (Table 1). The CVs of the hexa(ferrocenylethynyl)arene complexes gave only one wave using N*n*-Bu$_4$PF$_6$, but they were split into a variable number of waves, depending on the nature and number of substituents on the free Cp ring. In the absence of substituent, three broad reversible waves were obtained for **1**. With C$_5$Me$_5$, a very broad envelope resulting from wave overlaps was observed for **3**. However, with only one methyl substituent, it is possible to distinguish six close waves for **4** (Figure 3).

Scheme 5



For the purpose of comparison, the CVs were also recorded using both supporting electrolytes for poly(ferrocenylethynyl)-arene and poly(ferrocenyl)benzene derivatives containing a reduced number of ferrocenylethynyl or ferrocenyl substituents (Chart 1). For 1,3-bis(ferrocenylethynyl)-5-bromobenzene, **10**, and 1,3,5-tris(ferrocenylethynyl)benzene, **11**, that had been reported to give a single reversible CV wave using N*n*-Bu$_4$PF$_6$ as electrolyte by Long and Zanello, we confirmed these results using N*n*-Bu$_4$PF$_6$, and we also found only one CV wave for **10** using N*n*-Bu$_4$BAr^F$_4$. For **11**, however, three very distinct reversible waves were obtained using N*n*-Bu$_4$BAr^F$_4$, strikingly resembling the CV obtained for **1**. In order to investigate the influence of the third ferrocenylethynyl substituent in *meta* position on the arene on the wave splitting, we also synthesized, by Sonogashira coupling, 1,3-bis(ferrocenylethynyl)benzene, **12**; 1,3-bis(ferrocenylethynyl)-5-(trimethylsilylethynyl) benzene, **13**; 1,3-bis(ferrocenylethynyl)-5-(ethynyl)benzene, **14**; and 1,3-bis(ferrocenyl-ethynyl)-5-(pentamethylferrocenylethynyl) benzene, **15** and recorded their CVs using N*n*-Bu$_4$BAr^F$_4$ as the supporting electrolyte. For all of these compounds, as for **10**, only one reversible CV wave was observed for the ferrocenyl group. For **15**, only one reversible wave was observed for the ferrocenyl group in addition to the expected reversible wave of the pentamethylferrocenyl group.

We also recorded the CV of tetra(ferrocenylethynyl)thiophene **16** that had been reported by Justin Thomas and Lin[26] to give two close reversible waves, and as expected, we found that the wave separation was much larger when N*n*-Bu$_4$BAr^F$_4$ was used. For 1,4-bis(ferrocenylethynyl)benzene, **17**, also synthesized by Sonogashira coupling, only one wave was observed using either N*n*-Bu$_4$PF$_6$ or N*n*-Bu$_4$BAr^F$_4$ as the supporting electrolyte, whereas for the *ortho* isomer **18** only one wave was observed using N*n*-Bu$_4$PF$_6$, and two well-separated waves were observed with N*n*-Bu$_4$BAr^F$_4$ (Table 1).

Discussion

Synthesis of the Family of Hexa(ferrocenylethynyl)benzene Complexes. The Negishi synthesis represents a clear improvement over the Sonogashira reaction for the synthesis of the

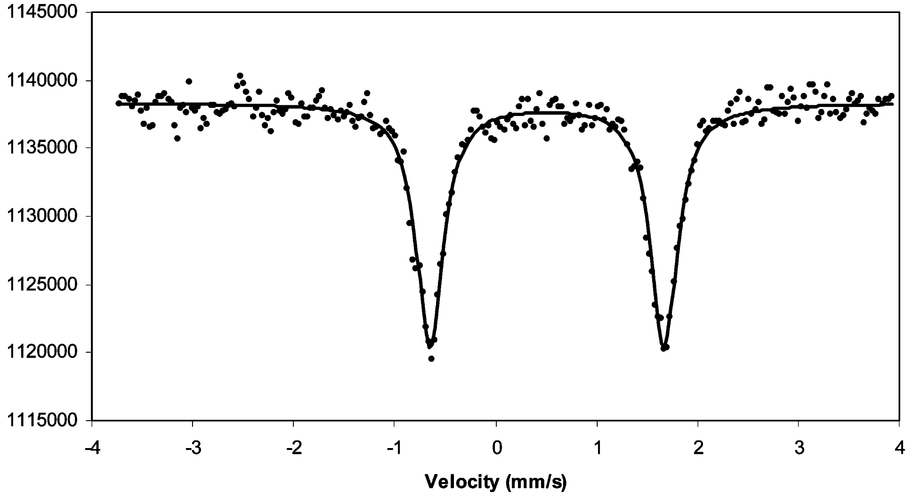


Figure 2. Mössbauer spectrum of the ferrocenyl-terminated star complex **9** at zero field. Isomer shift: 0.509 (6) mm s^{-1}; quadrupole splitting: 2.32 (1) mm s^{-1}.

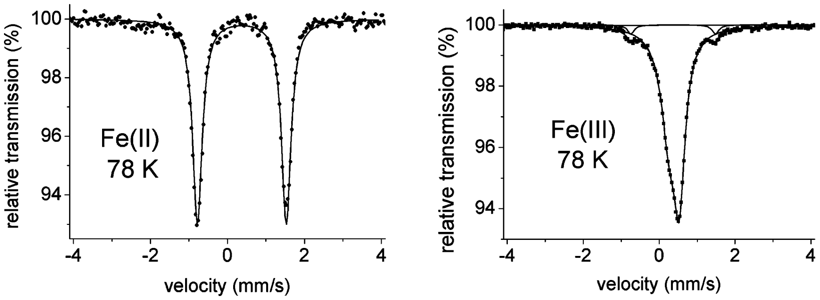
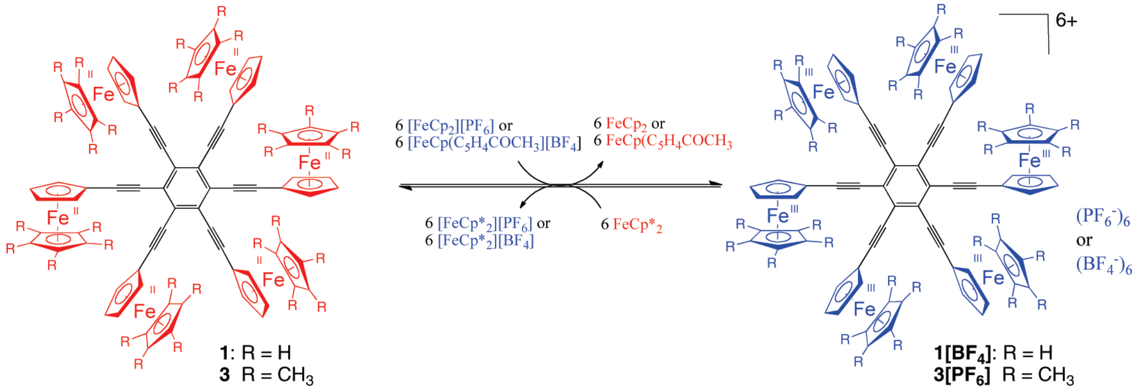


Figure 3. Zero-field Mössbauer spectra of **3** (left) and **3**(PF$_6$)$_6$ (right) at 78 K.

Scheme 6



1: R = H
3 R = CH_3

1[BF$_4$]: R = H
3[PF$_6$] R = CH_3

Table 1. Values of $E_{1/2}$ and ΔE_p (When They Are Large) for All the Ferrocene Derivatives[a]

complex	$E_{1/2} = (E_{pa} - E_{pc})/2$ [V], $n\mathrm{Bu_4NPF_6}$, (ΔE_p)	$E_{1/2} = (E_{pa} - E_{pc})/2$ [V], $n\mathrm{Bu_4NBAr^F_4}$, (ΔE_p)
1	0.690	0.57, 0.79, 0.98
3	0.410 (0.060)	0.480 (0.230)
4	0.650 (0.110)	0.64, 0.72, 0.82, 0.96, 1.05, 1.2
6	0.110, 0.785	
7	0.380	0.440 (0.220)
9	0.360	
10	0.690 (0.060)	780 (0.170)
11	0.680	0.640, 0.840, 1.060
12	0.670 (0.060)	0.750 (0.130)
13	0.690 (0.060)	0.740 (0.090)
14	0.680	0.760 (0.130)
15	0.410, 0.680	0.420 (0.070), 0.750 (0.100)
16	0.700, 0.810	0.750, 0.935
17	0.680	0.750
18	0.680	0.720, 0.870
19	0.680	0.620, 0.790, 0.980
20	0.540, 0.620	0.590, 0.800

[a] All of the CV measurements were made using a Pt anode, CH_2Cl_2 as the solvent, and either ferrocene or decamethyferrocene ($FeCp^*_{2)}$ as the internal reference.[27] The error is ±10 mV.[27]

hexa(ferrocenylethynyl)benzene derivatives. The latter was used by Long and Zanello[20] for the synthesis of **8**, but it is the decrease of the number of activating bromine atoms on the arene ring beyond the third substitution in 1,3,5 positions and the increasing bulk, in particular between two positions that are already substituted, that requires the more powerful Negishi method.[17] Given the low solubility of the parent complex **1**, access to methylated ethynylferrocenes was essential in order to develop this chemistry and bring about a family of hexa(ferrocenylethynyl)arene including the fully conjugated dodecaferrocenyl complex **6**. The visible-light photolysis of the large family of complexes $[Fe(\eta^5\text{-}CpR)(\eta^6\text{-toluene})][PF_6]$[28] in the presence of acetylcyclopentadienylsodium represents a very useful source of substituted acetylferrocene derivatives that are precursors of the substituted ethynylferrocene derivatives[29] usable in these Negishi coupling syntheses.[17] The two large hexaferrocenyl stars **7** and **9** only differ by the presence of a triple bond between the central and outer phenyl rings, yet the solubility difference between **7** and **9** is enormous, **7** being soluble in common organic solvents, whereas **9** is almost insoluble in all solvents.

Electrochemistry: through-Space Electrostatic Effect and Frustration. A number of electrochemical studies have been carried out on poly(ferrocenyl)arene and poly(ferrocenylethynyl)arene complexes, and all of these studies carried out using N*n*-Bu_4PF_6 as the supporting electrolyte have resulted in the observation of a single wave in CV. All of the authors have therefore accordingly concluded the absence of electronic communication between the ferrocenyl centers via the phenylene bridge.[18−22] Our measurements confirm these conclusions. When N*n*-Bu_4PF_6 is used as the supporting electrolyte in DCM, the strong ion pairing between the cation and anion of the electrolyte leave very little electrostatic effect, if any. This means that if a splitting between two CV waves of two equivalent redox centers is observed, the difference between the half-wave potential corresponds roughly to the electronic communication through a conjugated bridge in the absence of other significant factor. In the literature, there are myriads of such examples.[30] However, when a weakly nucleophilic perfluorinated anion such as in N*n*-$Bu_4BAr^F_4$ was used, Geiger has pointed out that large changes in $\Delta E_{1/2}$ values raise cautionary notes on the common usage of these values in estimating the degree of electronic interaction between different redox sites in a molecule.[31] This does not apply, however, to strongly ion-pairing salts such as N*n*-Bu_4PF_6. In the absence of such CV wave splitting with N*n*-Bu_4PF_6, it is concluded that the electronic communication, if any, is not significant. In such cases, recording the same system with N*n*-$Bu_4BAr^F_4$ as the supporting electrolyte in DCM allows to estimate the magnitude of the through-space electrostatic effect that may be visualized by the separation between two CV waves if it occurs, because it will not be mixed with the effect of a significant electronic communication.

***Para*-Substituted Arenes: Lack of Both Significant Electronic and Electrostatic Interactions.** The bis(ferrocenyl) complex **17** shows no wave separation with both supporting electrolytes

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(27) (a) Ruiz, J.; Astruc, D. *C. R. Acad. Sci., Sér. IIc* **1998**, 21–27. (b) Ruiz, J.; Daniel, M.-C.; Astruc, D. *Can. J. Chem.* **2006**, *84*, 288–299.
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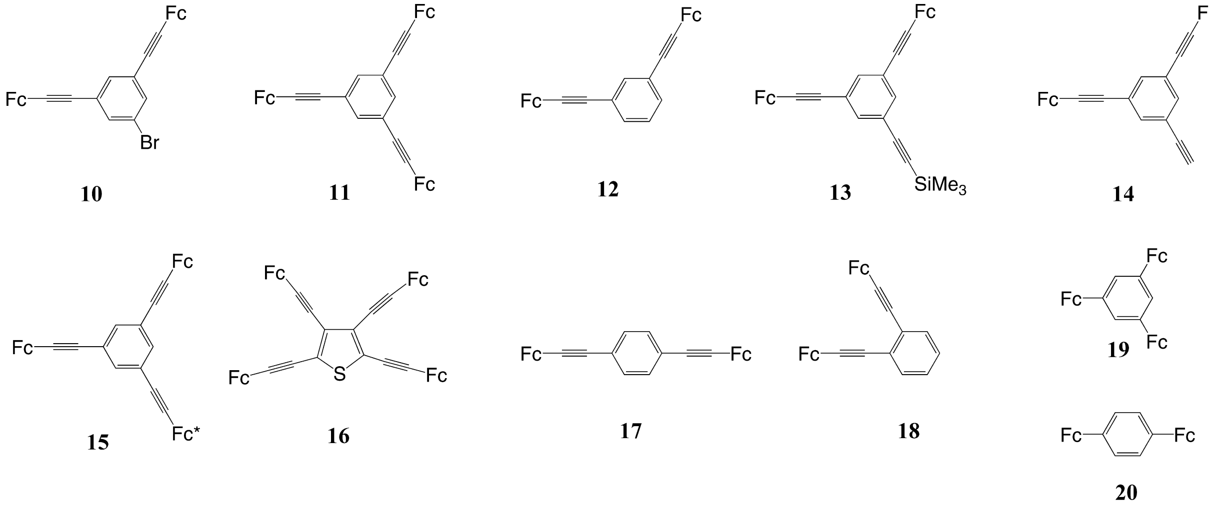
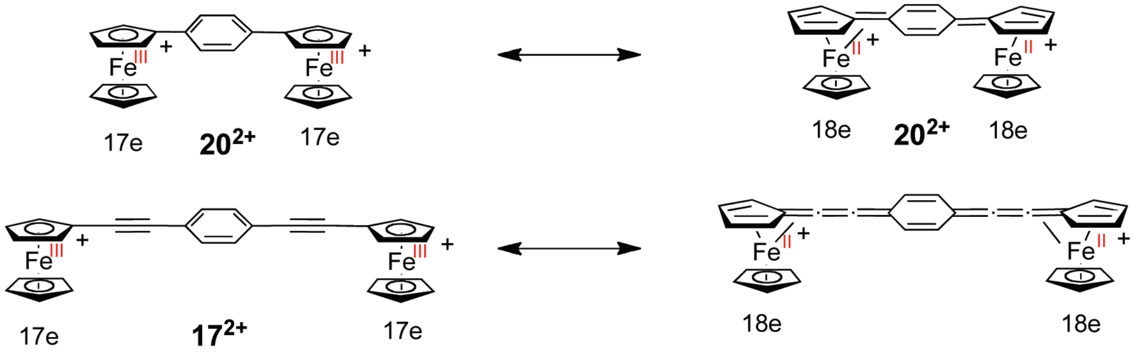
(30) (a) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910. (b) Geiger, W. E. *Organometallics* **2007**, *26*, 5738–5765, a historical review.
(31) (a) Barrière, F.; Camine, N.; Geiger, W. E.; Mueller-Westerhoff, U. T.; Sanders, R. *J. Am. Chem. Soc.* **2002**, *124*, 7262–7263. (b) Nafady, A.; Chin, T. T.; Geiger, W. E. *Organometallics* **2006**, *25*, 1654–1663. (c) Nafady, A.; Butterick, R., III; Carroll, P. J.; Chong, D.; Geiger, W. E. *Organometallics* **2007**, *26*, 4471–4482.

Chart 1. Poly(ferrocenylethynyl)benzenes and Poly(ferrocenyl)benzenes (Fc = Ferrocenyl; Fc*= 1,2,3,4,5-Pentamethylferrocenyl)



Scheme 7. Limit Mesomeric Forms Highlighting the Possible Electronic Communication between the Oxidized Iron-Sandwich Groups in Phenylene- and Bis(ethynyl)phenylene-Bridged Dinuclear Complexes $\mathbf{17}^{2+}$ and $\mathbf{20}^{2+}$



(contrary to **20**). This means that there is no significant electronic communication in the *para* position via the 1,4-bis(ethynyl) bridge in spite of the conjugation. Thus, the fulvalene/cumulenylidene limit forms of Scheme 7 has very little (if any) contribution to the stabilization of the ferricinium dication (possibly contrary to the case of $\mathbf{20}^{+/2+}$). In addition, the lack of splitting of the CV waves also indicate that there is no significant electrostatic interaction between the ferricinium groups of $\mathbf{17}^{2+}$, because the distance between these groups is large enough to also avoid this interaction (Figure 4, note that this distance is much shorter in $\mathbf{20}^{2+}$ which can be subjected to significant electrostatic effect with nonion-pairing anions).

***Ortho*-Substituted Arenes: No Significant Electronic Interaction, But Electrostatic Interaction.** The *ortho* disubstituted complex **18** shows a regular CV wave without splitting or even broadening using N*n*-Bu_4PF_6 as the supporting electrolyte, which

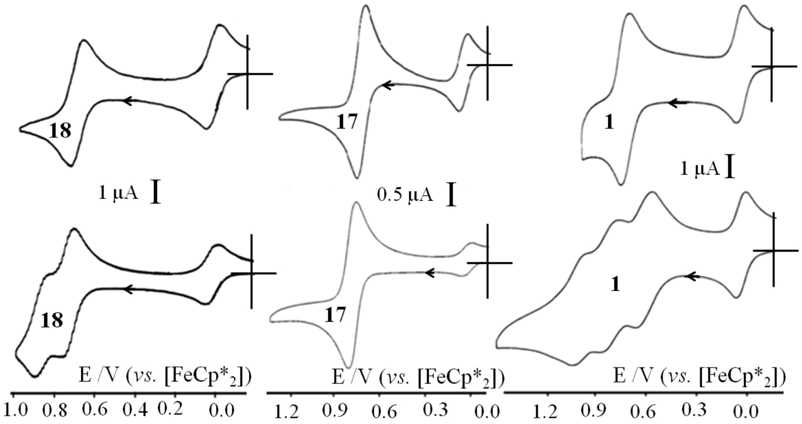


Figure 4. CVs of **17**, **18**, and **1** showing the absence of electronic (with N*n*-Bu_4PF_6, middle top) and electrostatic (with N*n*-$Bu_4BAr^F{}_4$, middle bottom) interaction in *para*-(**17**) and absence of electronic interaction (with N*n*-Bu_4PF_6, top left) and presence of electrostatic interaction (with N*n*-$Bu_4BAr^F{}_4$, left bottom) in *ortho*-(**18**). Similarly, the CV of **1** shows the absence of electronic interaction (with N*n*-Bu_4PF_6, top right) but the presence of electrostatic effects (with N*n*-$Bu_4BAr^F{}_4$, bottom right). Solvent: DCM; internal reference: $FeCp*_2$.

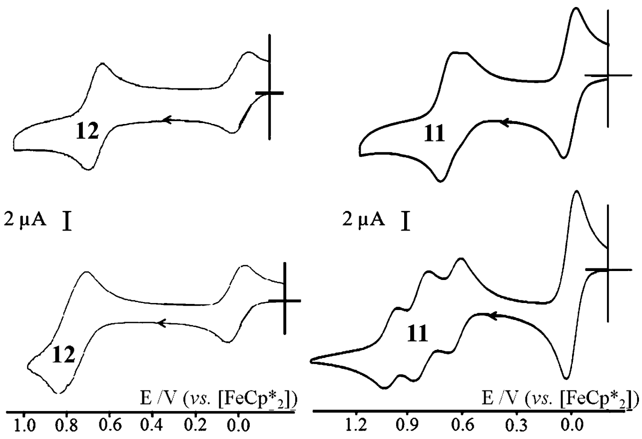


Figure 5. Comparison of the CVs of the *meta* disubstituted and trisubstituted complexes of **12**, respectively, **11** showing the lack of electronic (with N*n*-Bu_4PF_6, top left) and electrostatic (with N*n*-$Bu_4BAr^F_4$, bottom left) interaction in **12** and the lack of significant electronic (with N*n*-Bu_4PF_6, top right), but electrostatic interaction (with N*n*-$Bu_4BAr^F_4$, bottom right) in **11**. Solvent: DCM; internal reference: FeCp*$_2$.

signifies that there is no significant electronic communication between the two ferrocenyl redox centers. However, wave splitting is observed with N*n*-$Bu_4BAr^F_4$, which is the mark of a significant electrostatic repulsion between the two nonion-pairing cationic centers in the dication **18**$^{2+}$.

***Meta*-substituted Arenes: Electrostatic and Frustration Effects.** The 1,3,5-trisubstituted complexes **3** and **11** show a single CV wave with N*n*-Bu_4PF_6 as the supporting electrolyte, which indicates the absence of electronic communication, a phenomenon that has been well recognized for *meta* substituents in accord with the lack of conjugation of the multiple bonds.[32] Remarkably, however, three very well separated CV waves are recorded for both compounds with N*n*-$Bu_4BAr^F_4$ as the supporting electrolyte. However, for the 1,3-bis(ferrocenylethynyl)-benzene complex **12** (Figures 4 and 5) as well as for the 1,3-bis(ferrocenylethynyl)arene complexes **10**, **13**, **14**, and **15** containing a different substituent (bromo, ethynyl, trimethylsilyethynyl, and even pentamethylferrocenylethynyl) in the third *meta* position, only one wave is observed for the two ferrocenyl group with N*n*-$Bu_4BAr^F_4$ (Figure 6) In these compounds, the two ferrocenyl groups lie at opposite sides of the benzene ring, especially in the dicationic forms in order to minimize the electrostatic repulsion that then becomes negligible. When a third ferrocenyl group is present in *meta* position, there is frustration,[33] which means that two of the three groups have to lie on one side of the ring, enhancing the electrostatic repulsion. The situation is averaged among the three groups due to the free rotation around the exocyclic ferrocenyl single bond, but this frustration and enhancement of the electrostatic effect cause the splitting of the three ferrocenyl CV wave, i.e., the oxidation energy increases as the number of positive charges increases until the trication forms. When the third ferrocenyl group is pentamethylated, in **15**, the shielding of the charge on the iron center by the five methyl groups of this pentamethylferrocene forces this metallocene to undergo the frustration while the two nonmethylated ferrocenyl groups lie at opposite sides of the benzene ring, because they bear the maximum density of positive charge (Figures 5−7).

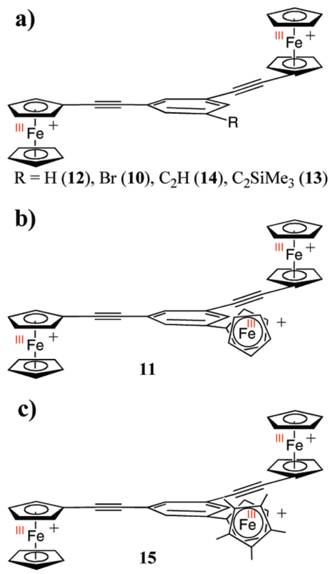


Figure 6. Frustration in the electrostatic effect observed upon oxidation of the ferrocenyl groups of the *meta*-substituted arene derivatives (counteranions: N*n*-$Bu_4BAr^F_4$): (a) Minimization of the charge repulsion in the dication, locating the metallocenes at opposite sides of the benzene ring in the preferred conformation. (b) The third ferricinium cation cannot minimize its electrostatic interaction with each of the two others by lying at an opposite benzene side, both sides being already occupied. It is frustrated, and must lie at an intermediate position enhancing the electrostatic effect among the three positively charged sites. (c) In pentamethylferricinium, the positive charge is partly shielded by the C_5Me_5 ligand shell. This decreases the electrostatic interaction with the two other ferricinium cations that accordingly locate at opposite sides of the benzene ring in order to minimize their repulsion.

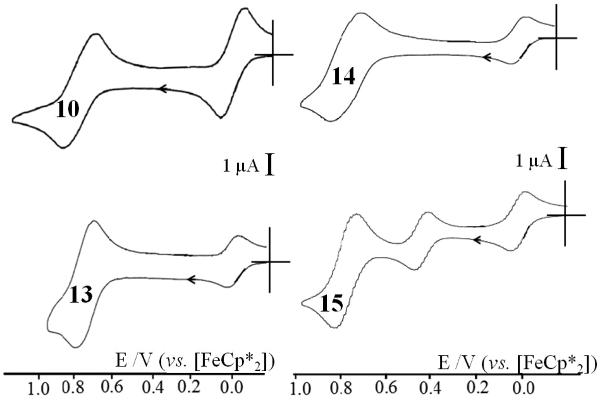


Figure 7. CVs of **10**, **13**, **14**, and **15** using N*n*-$Bu_4BAr^F_4$. All of these compounds contain an ancillary *meta* substituent that does not perturb the cisoïd conformation of the two ferrocenyl redox centers shown in Figure 6. Solvent: DCM; internal reference: FeCp*$_2$.

An additional effect should be noted concerning the electrochemical reversibility of the two-electron wave in **12** that reflects a quasi-reversible electron transfer with a difference of ΔE_p = 130 mV between the anodic and cathodic peak, whereas the internal decamethylferrocene reference has the standard value of ΔE_p = 60 mV. In the neutral form, there is no repulsion, and the two ferrocenyl groups have no preference to be on the same or opposite side of the benzene plane, but the two ferrocenium groups are forced to move to a transoïd conformation upon electron transfer. This rotation slows down electron transfer and causes the relatively large ΔE_p observed.[34]

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[32] March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1972, pp 507−514.

[33] The phenomenon of spin frustration is known for paramagnetic trimetallic complexes for which each metal center located at the summits of a triangle bears a spin. See for instance Kahn, O. *Molecular Magnetism*; VCH: New York, 1994; Chap. 10.5, pp 241−245.

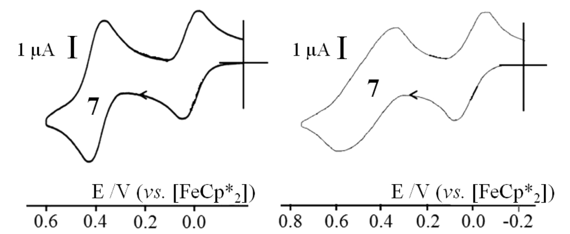

Figure 8. CVs of **7** with N*n*-Bu$_4$PF$_6$ (left) and N*n*-Bu$_4$BAr$^F{}_4$ (right) showing the quasi-reversibility of the oxidation in the later case. Solvent: DCM; internal reference: FeCp*$_2$.

An analogous effect is observed in other complexes, i.e., large ΔE_p (see the ΔE_p values in Table 1). For instance, for **7** this effect is very marked, the ΔE_p value being 210 mV. This means that a rather important conformational reorganization occurs from the neutral complex **7** to the hexacation **7**$^{6+}$ upon six-electron transfer, due to the requirement for the hexacation to locate all the redox centers in such a way that the overall electrostatic repulsion be minimized. The neighboring iron groups should be as far as possible from one another in the hexacation, whereas the conformations in the neutral state are not subjected to large intramolecular forces. This shows the kinetic aspect of the electrostatic effect. This effect is only observed with the supporting electrolyte N*n*-Bu$_4$BAr$^F{}_4$, whereas the electron transfer is characterized by a normal ΔE_p value of 60 mV when the electrolyte is N*n*-Bu$_4$PF$_6$. Finally, for **7**, the single wave is broad, signifying that a modest thermodynamic electrostatic effect is observable despite the large distance between the six ferrocenyl centers in this large star (Figure 8).

Hexa(ferrocenylethynyl)benzene: Mechanism of Sequential Electron Transfers. All the hexa(ferrocenylethynyl)benzene derivatives (**1**, **3**, and **4**) show a single wave in their CV when N*n*-Bu$_4$PF$_6$ is the supporting electrolyte, thus the six heterogeneous electron transfers occur at about the same potential, more exactly the redox potentials of these six electron transfers are statistically distributed around an average value represented by the $E_{1/2}$ value provided by the single CV wave, according to a binomial law as explained by Bard and Anson in their seminal article on ferrocene polymers.[35] This statistical factor is also included in Taube's expression providing the various factors of mixed-valence stabilization.[6,36] This situation is the classic one that has been encountered many times for ferrocenyl-terminated dendrimers.[9]

We now have to explain why the CV of **1** gives three distinct two-electron waves when N*n*-Bu$_4$BAr$^F{}_4$ is the supporting electrolyte. We start with the CVs of the *para*-substituted compound **17** that give a single wave even with N*n*-Bu$_4$BAr$^F{}_4$ is the supporting electrolyte. This means that there is no significant electronic or electrostatic interaction between the two redox centers of **17** located in *para* substituents, thus they are independent. However, there is splitting of the ferrocenyl waves of the *ortho*-disubstituted and *meta*-trisubstituted complexes **17** and **12**, signifying that it is more difficult to oxidize the second ferrocenyl group in these compounds. It has also been shown that there is no electronic communication between the two redox centers in *meta* positions of these compounds. Thus, the splitting observed in **18** and **12** with N*n*-Bu$_4$BAr$^F{}_4$ as the supporting electrolyte is purely electrostatic. By analogy in **1**, two ferrocenyl groups of *para* substituents are oxidized in the first two-electron wave at approximately the same potential. The first two-electron wave of **1** is broader than the two-electron wave of **17**, however, which indicates that the independency of the *para* ferrocenyl groups is not as clear-cut in **1** as in **17**. This results from the stereoelectronic influence of the four other ferrocenyl groups that probably perturb the transoid conformation of these two oxidized *para* ferrocenyl groups. Then, for the second two-electron wave, a ferrocenyl group in *ortho* position relative to one of the two first oxidized ferrocenyl groups is oxidized at a more positive potential, and the substituent located *para* to it is also oxidized quasi-independently, because it is submitted to the same *ortho* influence and is virtually almost independent of the other *para* substituent. Thus these two substituents are oxidized at almost the same potential, this wave being as broad as the first one. Finally, the two last ferrocenyls that are in *para* position versus each other should also be almost independent. They are submitted to the same influence of their two *ortho* substituents, and are thus oxidized at the almost same potential that is more positive than that of the previous CV wave, because they are submitted to the maximum electrostatic interactions (Scheme 8).

The fact that the three CV waves of **1** are broader than those of **18** shows the residual electrostatic interaction between the *para*-ferrocenyl groups in **1**. This phenomenon become even more marked for **4**, which can be taken into account by the enhanced steric bulk of the ferrocenyl groups due to the methyl substituent that may well inhibit the conformational rearrangement that would minimize the electrostatic repulsion. At this time, the six electron transfers become separated on the CV in a cascade of six one-electron waves. In **3**, the steric effects are even more pronounced, and there is a mixture of charge shielding, steric inhibition and quasi-reversibility of the electron transfers due to the difficult conformational rearrangement, upon oxidation, that slows down the electron transfer, so that the CV appears as a continuum of undefined waves spanning over a large potential value rather than well separated electron-transfer steps (Figure 9).

Conclusions

Ferrocenylethynyl benzene derivatives made accessible using the Negishi reaction show an electrochemistry that is strongly dependent on the nature of the supporting electrolyte and substituents on the ferrocenyl group. In these compounds, the electronic communication between the ferrocenyl groups appears to be nil or insignificant. Thus, literature data as well as the measurements carried out in the present study using N-*n*Bu$_4$PF$_6$ as the supporting electrolyte show a single wave for di-, poly- or hexa(ferrocenylethynyl)benzenes derivatives as well as for related poly(ferrocenyl)benzene derivatives (except in *ortho* position for the latter). In all other cases (*ortho*, *meta*, and *para* substituted arenes), the absence of wave splitting using N-*n*Bu$_4$PF$_6$ allows to indicate that the splitting, if any, resulting from the use of N*n*-Bu$_4$BAr$^F{}_4$, is purely electrostatic. This is the case for the 1,3,5-trisubstituted complexes whether or not they bear in addition three other ferrocenylethynyl substituents, whereas the simple *meta*- or *para*-disubstituted compounds do not provide CV wave splitting with N*n*-Bu$_4$BAr$^F{}_4$. This remarkable duality of behavior, i.e., the influence of the third ferrocenylethynyl substituent in *meta* position, is due to the

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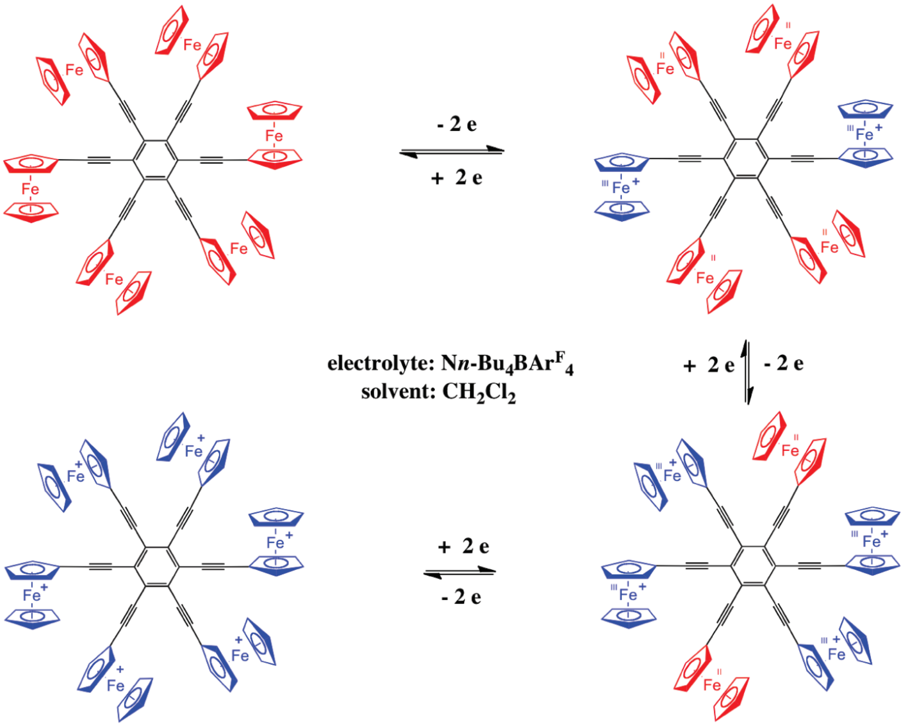
(34) (a) Bard, A. J.; Faulkner, R. L. *Electrochemical Methods*, 2nd ed.; Wiley: New York, 2001. (b) Geiger, W. E. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1985, *33*, p 275.

(35) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248–4253.

(36) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017–1024.

Scheme 8. Mechanism of the Oxidation of **1** in the Presence of N*n*-$Bu_4BAr^F{}_4$, with $Ar^F = 3,5\text{-}C_6H_3\text{-}(CF_3)_2$, in CH_2Cl_2, a Cascade of Three Two-Electron Oxidation Steps Shown in the CV of 1 (Figure 1)[a]



[a] The ferrocenylethynyl groups are represented in red whereas the ferroceniumethynyl groups are in blue.

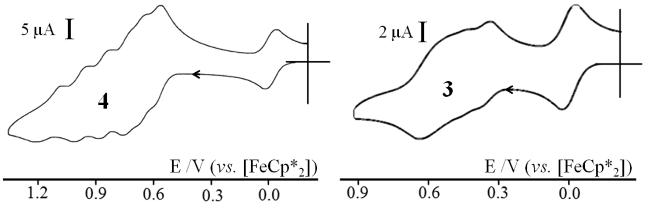


Figure 9. CVs of **4** and **3** using N*n*-$Bu_4BAr^F{}_4$ as supporting electrolyte in DCM. The CV of **4** splits in 6 single electron waves, whereas the broad overlapping area in the CV of **3** reflects both wave splitting and quasi-reversibility shapes. Solvent: DCM; internal reference: $FeCp^*_2$.

steric/electrostatic frustration among the three positively charged ferricinium groups.

It was also possible to characterize quasi-reversible heterogeneous electron transfer by CV, i.e., relatively slow electron transfers due to extensive conformational rearrangements of the ferrocenyl groups in several cases submitted to the electrostatic effects. In other words, both thermodynamic (potential values) and kinetic (quasi-reversibility of electron transfer) of the electrostatic effects could be characterized. The considerable variations of these electrostatic effects as a function of the nature of the subsituents show the sensitivity of these effects to the sterically controlled conformational rearrangements occurring upon electron transfer. In conclusion, it is the insignificant electronic communication among the ferrocenyl groups of these complexes[37] and the use of the weakly nucleophilic perfluorinated counteranion in the supporting electrolyte that made the characterization of the through-space electrostatic effect possible, an explanation confirmed *inter alia* by the stero-electrostatic frustration effect.

Experimental Section

General Data. Reagent-grade diethyl ether, THF, and toluene were predrilled over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride just before use. All manipulations were carried out using Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere drylab. ^1H NMR spectra were recorded at 25 °C with a Bruker AC 300 (300 MHz) spectrometer. ^{13}C NMR spectra were obtained in the pulsed FT mode at 75.0 MHz with a Bruker AC 300 spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si (TMS). Cyclic voltammogram (CV) measurements: All electrochemical measurements were recorded under nitrogen atmosphere. Solvent: methylene chloride; temperature: 20 °C; supporting electrolyte: [*n*-Bu_4N][PF_6] or [*n*-Bu_4N][$BAr^F{}_4$] 0.1 M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: $FeCp^*_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$); scan rate: 0.200 V s^{-1}. MALDI-TOF mass spectra were performed by CESAMO (Univ. Bordeaux I, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed N_2 laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflection and with an accelerating voltage of 20 kV. Samples were dissolved in CH_2Cl_2 at 10 mg/mL. The dithranol matrix solution was prepared by dissolving 10 mg in 1 mL of CH_2Cl_2. The solution was combined in 10: 1 volume ratio of matrix to sample. One to two microliters of the obtained solution was deposited onto the sample target and vacuum-dried. Elemental analyses were performed by the Center of Microanalyses of CNRS at Lyon SOLAIZE (France).

Negishi Reaction between Ethynylferrocene and Hexabromobenzene: Synthesis of Hexakis(ferrocenylethynyl)benzene 1 and Pentakis(ferrocenylethynyl)benzene 2. A 42-mg portion (0.076 mmol) of hexabromobenzene, 66 mg (0.057 mmol, 0.75 equiv) of [$Pd(PPh_3)_4$], and 10 mL of freshly distilled toluene under Na, were successively added into a Schlenk flask. A solution of ferrocenylethynyl zinc chloride[19] (2 mmol, 4 equiv per bromide) was then added. The mixture was heated at 80 °C for 24 h, an additional portion of catalyst [$Pd(PPh_3)_4$] (66 mg, 0.75 equiv) and ferrocenylethynyl zinc chloride (2 mmol, 4 equiv) were added with a syringe under N_2, the mixture was kept at 80 °C for six days, then was cooled down to rt. 47 mg (47% yield) of a crude dark-red solid identified by MALDI-TOF mass spectroscopy, Mössbauer spectroscopy, and CV as hexakis(ferrocenylethynyl)benzene **1**, that is almost insoluble in all solvents, was obtained, together with a soluble fraction that was adsorbed on silica. Purification by column chromatography (SiO_2; eluent: pentane) gave bis(ethynylferrocene) identified by comparison with reference[20] (75 mg), and using pentane-DCM (70:30) as eluent, dark-red penta(ferrocenylethynyl)benzene (**2**) (6 mg, 7% yield), identified as follow (see Supporting Information, SI).

Hexakis(ferrocenylethynyl)benzene 1. ^{13}C NMR solid: 65.6 (CH of Cp), 68.7, 69.4 (CH of *Cp*C≡C), 79.5 (Cq. of *Cp*C≡C), 82.2 and 96.9 (C≡C) 123.3 (Cq of aromatic). CV (CH_2Cl_2, 293 K): one reversible wave $E_{1/2} = 0.69$ V vs decamethylferrocene (supporting electrolyte [(*n*-Bu)$_4$N]PF$_6$); three reversible waves $E_{1/2}$ = 0.57 V, 0.79 and 0.98 V *vs*. decamethylferrocene (supporting electrolyte [*n*-Bu$_4$N][BAr$^F_4$]). MALDI-TOF MS: calcd. *m/z* for M$^+$ ($C_{78}H_{54}Fe_6$) 1326.369; found 1325.86 (M$^+$) and 1348.79 (MNa$^+$).

Pentakis(ferrocenylethynyl)benzene 2. ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 4.25−4.27 (d, 35H), 4.52 (s, 10H), 7.53 (s, 1H). ^{13}C NMR (75.0 MHz, $CDCl_3$, δ_{ppm}) 66.5 (CH of Cp), 68.6, 69.5 (CH of *Cp*C≡C), 85.1 (Cq. of *Cp*C≡C), 85.6 and 97.8 (C≡C) 128.1, 127.2, and 129.4 (Cq of aromatic); 131.3 (CH of aromatic). MALDI-TOF MS: calcd. *m/z* for M$^+$ ($C_{66}H_{46}Fe_5$) 1118.3; found 1117.90 (M$^+$), 1140.87 (MNa$^+$), 1173.96 (MFe$^+$), 1196.94 (MFeNa$^+$).

Synthesis of Hexakis(1,2,3,4,5-pentamethyl-1′-ferrocenylethynyl)benzene 3. A 328-mg portion (0.595 mmol) of hexabromobenzene, 515 mg (0.446 mmol, 0.75 equiv) of [Pd(Ph$_3$)$_4$], and 10 mL of freshly distilled toluene were successively added into a Schlenk tube under N_2. A solution of [(1,2,3,4,5-pentamethyl-1′-ferrocenyl)ethynyl] zinc chloride[19] (14 mmol, 4 equiv per bromide) was then added. The mixture was heated at 80 °C for 24 h, an additional portion of catalyst [Pd(PPh$_3$)$_4$] (515 mg, 0.75 equiv) and [(1,2,3,4,5-pentamethyl-1′-ferrocenyl)ethynyl] zinc chloride (14 mmol) were added with a syringe under N_2, and the mixture was kept at 80 °C for 6 d. The crude reaction mixture was evaporated under vacuum, and the dark-red product was then adsorbed on silica and purified by column chromatography (SiO_2) using the mixture pentane-DCM (90:10) as eluent. This yielded 700 mg of bis(1,2,2,3,4,5-pentamethyl-1′- ethynyl ferrocene), then, using pentane- DCM (80:20) as eluent, hexakis(1,2,3,4,5-pentamethyl-1′-ferrocenyl-ethynyl]benzene **3** and pentakis(1,2,3,4,5-pentamethyl-1′-ferrocenylethynyl)benzene were obtained. After crystallization using isooctane as the solvent at −20 °C, 280 mg (27% yield) of hexakis(1,2,3,4,5-pentamethyl-1′-ferrocenylethynyl) benzene were obtained. These crystals were used for the X-ray diffraction study.

Bis(1,2,3,4,5-pentamethyl-1′-ethynylferrocene): ^{1}H NMR(300 MHz, $CDCl_3$) δ_{ppm} 1.88 (s, 15H, *CH$_3$*Cp), 3.82 (s, 2H, CH of *Cp*C≡C), 3.96 (s, 2H, CH of *Cp*C≡C). ^{13}C NMR (75.0 MHz, $CDCl_3$), δ_{ppm} 10.6 (*CH$_3$*Cp), 65.1 (Cq. of *Cp*CH$_3$), 71.7, 73.2 (CH of *Cp*C≡C), 78.5 (C≡C), 85.1 (Cq. of *Cp*C≡C). Anal. Calcd. for $C_{34}H_{38}Fe_2$: C 73.14; H 6.86; found: C 73.29; H 6.91. CV (CH_2Cl_2; supporting electrolyte [(*n*-Bu)$_4$N]PF$_6$; 293 K): two reversible waves, $E_{1/2}$ = 0.4 and 0.52 V vs decamethylferrocene.

Hexakis(1,2,3,4,5-pentamethyl-1′-ferrocenylethynyl) benzene **3**: mp 131−133 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 1.92 (s, 15H), 3.94 (s, 2H), 4.16 (s, 2H). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ_{ppm} 9.8 (CH_3), 66.9 (Cq. of *Cp*CH$_3$), 72.3, 73.4 (CH of *Cp*C≡C), 75.6, 76, 76.4 (solvent peaks), 80.6 (C≡C), 85.1 (Cq. of *Cp*C≡C), 96.9 (C≡C), 124.8 (C aromatic). IR (KBr) cm^{-1}: 2199.42 (C≡C). Anal. Calcd. for $C_{108}H_{114}Fe_6$: C 74.14; H 6.58; found: C 74.22; H 6.47. MALDI-TOF MS: calcd. *m/z* for M$^+$ ($C_{108}H_{114}Fe_6$) 1747.175; found 1747.52.

Synthesis of MeCpFe(C_5H_4COMe).[38] (a) [MeCpFe(toluene)][PF$_6$][39] (14 g, 37.6 mmol) was photolyzed in acetonitrile at −45 °C. After 3 h, the yellow solution turned deep purple, and Na(C_5H_4COMe)[40] (9.783 g, 75.2 mmol) in acetonitrile were added at −45 °C. After the mixture was raised to room temperature, the solvent was removed, and the residue was dissolved in CH_2Cl_2. The solution was washed several times with water, and the organic phase was dried over Na_2SO_4. 2.6 g (29% yield) of red oil obtained after evaporation of the solvent was purified by column chromatography (SiO_2) using a 90:10 pentane-ether mixture.

(b) With [MeCpFe(CO)$_2$CNMe][PF$_6$],[39] the same procedure was used, and a 62% yield was obtained.

[MeCpFe(CO)$_2$CNMe][PF$_6$] was obtained by using the following procedure.[39] Di(methylcyclopentadienyl-dicarbonyl iron)[41] (1.39 g, 3.639 mmol) and $Cp_2Fe^+PF_6^-$ (2.409 g, 7.278 mmol) were stirred overnight in 100 mL of CH_2Cl_2/MeCN (2/1) mixtures. After evaporation of the solvents in vacuo and washing with ether, the residue was recrystallized from acetone/ether mixtures, and a yellow solid was obtained (0.823 g, 60% yield). ^{1}H NMR (300 MHz, CD_3COCD_3) δ_{ppm}: 2.04 (s, 3H, *CH$_3$*CN); 2.52 (s, 3H, *CH$_3$*Cp); 5.35 (s, 2H, *CH*$_\alpha$ of CpCH$_3$); 5.60 (s, 2H, *CH*$_\beta$ of CpCH$_3$). ^{13}C NMR (75.0 MHz, CD_3COCD_3) δ_{ppm}: 3.5 (*CH$_3$*CN), 12 (*CH$_3$*Cp), 83.9, 85 (*CH* of CpCH$_3$); 112.1 (Cq. of CpCH$_3$), 209.1 (CO). IR (KBr) cm^{-1}: 2065, 2010 (γ_{CO}); 2120(γ_{CN}).

MeCpFe(C_5H_4COMe). ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 1.99 (s, 3H, *CH$_3$*Cp); 2.37 (s, 3H, *CH$_3$*CO); 4.09 (s, 4H, *Cp*CH$_3$); 4.43 (m, 2H, *Cp*CO); 4.68 (m, 2H, *Cp*CO). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ_{ppm}: 13.8 (*CH$_3$*Cp), 27.5 (*CH$_3$*CO), 64.3 (Cq. of *Cp*CH$_3$), 69.1, 70.2, 70.8, 73.1 (CH of *Cp*CH$_3$ and *Cp*COCH$_3$), 85.6 (Cq. of *Cp*CO), 202.0 (CH$_3$*CO*).

IR (KBr) cm^{-1}: 1660 (γ_{CO}). Anal. Calcd. for $C_{13}H_{14}FeO$: C 64.50; H 5.83; found: C 64.56; H 5.74.

Synthesis of MeCpFe(C_5H_4C≡CH).[42] To a solution of 5.405 g (22.3 mmol) of CpMeFe(C_5H_4COMe) in THF at −78 °C, 1.1 equiv of lithium diisopropylamide (LDA) in THF, was added dropwise. After 1 h at −78 °C, 1.05 equiv of diethylchlorophosphate was added, and the temperature as maintained at −78 °C during an additional 1 h, after which the reaction mixture was raised to rt. An additional 2.3 equiv of LDA solution in THF was added at −78 °C. The solution was brought to room temperature and then hydrolyzed at 0 °C. The organic layer was extracted with CH_2Cl_2 and dried over Na_2SO_4. After evaporation of the solvent, MeCpFe(C_5H_4C≡CH) was purified by column chromatography (SiO_2) using a pentane, yielding 64% (3 g) of yellow oil obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 1.99 (s, 3H, *CH$_3$*Cp), 2.76 (s, 1H, *CH*≡C), 4.09 (s, 4H, *Cp*CH$_3$), 4.17 (m, 2H, *Cp*C≡CH), 4.38 (m, 2H, *Cp*C≡CH). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ_{ppm}: 13.5 (*CH$_3$*Cp), 64.3 (Cq. of *Cp*CH$_3$), 69, 69.2, 70.8, 72.3 (CH of *Cp*CH$_3$ and *Cp*C≡CH), 73.8 (*CH*≡C), 82.4 (*C*≡CH), 84.8 (Cq. of *Cp*C≡CH). IR (KBr) cm^{-1}: 2108.50 ($\gamma_{C\equiv C}$). Anal. Calcd. for $C_{13}H_{12}Fe$: C 69.68; H 5.40; found: C 70.26; H 5.41.

Synthesis of Hexakis(1-methyl-1′-ferrocenylethynyl)benzene 4. A 250-mg portion (0.453 mmol) of hexabromobenzene, 393 mg (0.340 mmol, 0.75 equiv) of [Pd(PPh$_3$)$_4$], and 10 mL of freshly distilled toluene were successively added into a Schlenk tube under N_2. A solution of [(1-methyl-1′-ferrocenyl)ethynyl] zinc chloride[19] (11 mmol, 4 equiv per bromide) was then added. The mixture was heated at 80 °C for 24 h, an additional portion of catalyst [Pd(PPPh$_3$)$_4$] (393 mg, 0.75 equiv) and [(1-methyl-1′-ferrocenyl)ethynyl] zinc chloride (11 mmol) were added with a syringe under N_2, and the mixture was kept at 80 °C for six days. The crude reaction mixture was evaporated under vacuum, and the dark-red

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(37) The situation is opposite in ferrocenyl oligomers and polymers in which the ferrocenyl groups are directly linked to another, which causes strong electronic-coupling interactions. (a) Aoki, K.; Chen, J.; Nishihara, H.; Hirao, T. *J. Electroanal. Chem.* **1996**, *416*, 151–155. (b) Nishihara, H. *Advan. Inorg. Chem.* **2002**, *53*, 41–86.

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product was then adsorbed on silica and purified by column chromatography (SiO_2) using the mixture pentane- DCM (90:10) as eluent. This yielded 300 mg of bis(1-methyl-1′-ethynylferrocene), then, using DCM as eluent, hexakis(1-methyl-1′-ferrocenylethynyl]benzene **4** and pentakis(1-methyl-1′-ferrocenylethynyl)benzene were obtained. After crystallization using DCM/diethyl ether as the solvent, 400 mg (62% yield) of hexakis(1-methyl-1′-ferrocenylethynyl) benzene were obtained.

Bis(1-methyl-1′-ethynylferrocene): ^1H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 1.92 (s, 3H, *CH_3Cp*), 4.05 (m, 4H, CH of *Cp*CH_3), 4.11 (s, 2H, CH of *Cp*C≡C), 4.34 (s, 2H, CH of *Cp*C≡C). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ_{ppm}: 13.6 (*CH_3Cp*), 64.1 (Cq. of *Cp*CH_3), 69.2, 69.8, 71.0, 72.6 (CH of *Cp*CH_3 and *Cp*C≡C), 78.8 (*C*≡C), 85.5 (Cq. of *Cp*C≡C). Elemental analysis: $C_{26}H_{22}Fe_2$ for calc: C 70.00; H 4.97; found: C 70.36; H 5.05. CV (CH_2Cl_2; supporting electrolyte [(*n*-Bu)$_4$N]PF_6; 293 K): two reversible waves, $E_{1/2} = 0.63$ V and 0.73 V vs decamethylferrocene.

Hexakis(1-methyl-1′-ferrocenylethynyl)benzene **4**: ^1H NMR(300 MHz, $CDCl_3$) δ_{ppm}: 1.96 (s, 3H, *CH_3Cp*), 4.12 (d, 4H, CH of *Cp*CH_3), 4.25 (s, 2H, CH of *Cp*C≡C), 4.55 (s, 2H, CH of *Cp*C≡C). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ_{ppm}: 13.5 (*CH_3Cp*), 66.2 (Cq. of *Cp*CH_3), 69.4, 69.9, 71.2, 72.3 (CH of *Cp*CH_3 and *Cp*C≡C), 76.2, 76.8, 77.4 (solvent peaks), 85.2 (Cq. of *Cp*C≡C), 85.6, 97.8 (C≡C), 126.4 (C aromatic). Anal. Calcd. for $C_{84}H_{66}Fe_6$: C 71.53; H 4.72; found: C 71.34; H 4.98. MALDI-TOF MS: calcd. *m*/*z* for M^+ ($C_{84}H_{66}Fe_6$) 1410.13; found 1409.96.

Synthesis of Hexakis[(pentamethylcyclopendienylferrocenium)-ethynyl]benzene Hexakis (Hexafluorophosphate) 3[PF_6]$_6$ 3. (40 mg, 2.29×10^{-2} mmol) and $Cp_2Fe^+PF_6^-$ (45 mg, 0.137 mmol, 6 equiv) were stirred in 20 mL of freshly distilled and degassed DCM. After evaporation of the solvent in vacuo and washing with ether (3 × 20 mL), 20 mg (80% yield) of dark-green salt were obtained. IR (KBr) cm^{-1}: 2204.52 ($\gamma_{C\equiv C}$), 834.94 (γ_{PF6-}). Anal. Calcd. for $C_{108}H_{114}F_{36}Fe_6P_6$: C 49.57; H 4.39; found: C 49.37; H 4.36.

Synthesis of 1[BF_4]$_6$ and 4[BF_4]$_6$. Products **1** and **4** were oxidized by acetylferrocenium tetrafluoroborate,[30a] using the same procedure as described above. **1[BF_4]$_6$**: Anal. Calcd. for $C_{78}H_{54}B_6F_{24}Fe_6$: C 50.72; H 2.95; found: C 50.18; H 2.58. **4[BF_4]$_6$**: Anal. Calcd. for $C_{84}H_{66}B_6F_{24}Fe_6$: C 52.24; H 3.44; found: C 51.72; H 2.99.

Synthesis of Hexakis[(*E*)-[2-(ethynylferrocenyl)ethynyl]-1′,2,2′,3,3′,4,4′,5-octamethyl-ferrocene]benzene 6. Twenty-three mg (0.042 mmol) of hexabromobenzene, 36 mg (0.031 mmol, 0.75 equiv) of [Pd(Ph_3)$_4$], and 10 mL of freshly distilled toluene were successively added into a Schlenk tube under N_2. A solution of [(E)-[2-(ethynylferrocenyl)ethynyl]-1′,2,2′,3,3′,4,4′,5-octamethylferrocene] zinc chloride[19,24] (0.672 mmol, 4 equiv per bromide) was then added. The mixture was heated at 80 °C for 24 h, an additional portion of catalyst [Pd(PPh_3)$_4$] (36 mg, 0.75 equiv) and [(*E*)-[2-(ethynylferrocenyl)ethynyl]-1′,2,2′,3,3′,4,4′,5-octamethyl-ferrocene] zinc chloride (0.672 mmol) were added with a syringe under N_2, and the mixture was kept at 80 °C for 6 d. The crude reaction mixture was evaporated under vacuum and the residue was washed several times with pentane. The product (96 mg, 70%) was isolated by a precipitation from DCM/methanol (10: 90). ^1H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 1.97−1.52 (m, 24H, CH_3), 3.38 (s, 1H, CH of Cp), 4.68−4.28 (m, 8H, CH of Cp), 6.40- 6.23 (m, 2H, CH═CH). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ_{ppm}: 9.3, 9.9, 11.1, 11.2 (CH_3), 66.4, 67.3, 70.9, 71.4, 72.3, 79.4, 86.0, 87.4, 97.4 (Cp and C≡C), 123.0, 125.6 (CH═CH), 127.0 (Car). Anal. Calcd. for $C_{198}H_{210}Fe_{12}$: C 72.95.48, H 6.49; found: C 72.05, H 6.50. MALDI-TOF MS: Calcd. for $C_{198}H_{210}Fe_{12}$: 3260.01, fond: 3259.52. CV (CH_2Cl_2; 293 K): two reversible waves $E_{1/2} = 0.11$ V, 0.785 V vs Decamethylferrocene; supporting electrolyte [(*n*-Bu)$_4$N][PF_6].

Synthesis of Hexakis(4-pentamethylferrocenylethynylphenyl)-benzene 7. A mixture of 0.250 g (0.19 mmol, 1 equiv), hexakis(4-iodophenyl) benzene, 0.350 g (1.25 mmol, 6.6 equiv) of ethynylpentamethylferrocene, 0.016 g (0.023 mmol, 0.12 equiv) of (PPh_3)$_2$$PdCl_2$ and 0.065 g (0.228 mmol, 1.8 equiv) of cuprous iodide, 10 mL of triethylamine, and 2 mL of DMSO was stirred magnetically in a Schlenk flask overnight at 50 °C. The solvent was removed under vacuum and the residue was dissolved in diethyl ether. The organic phase was washed with water and was dried on sodium sulfate, the solvent was removed under vacuum, and the crude reaction mixture was purified by silica gel column chromatography with pentane/DCM (90:10) as eluent, which provided 0.036 g (0.064 mmol, 5% yield) of bis(ethynylpentamethylferrocene), then, using pentane-DCM (80:20) as eluent, 0.240 g (0.109 mmol, yield 56%) of hexakis(4-pentamethylferrocenylethynylphenyl)benzene was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 1.91 (s, 15H, CH_3), 3.81, 3.91(2xs, 4H, Cp-H), 6.86 (d, 2H, CH of arom.), 7.15 (d, 2H, CH of arom.). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ_{ppm}: 10.8 (CH_3), 66.4 (Cq of Cp*), 72.8, 74.1 (CH of *Cp*C≡C), 81.2 (Cq of Cp), 86.4, 88.2 (C≡C), 121.5 (*Carom.*CC), 130.1, 131.4 (CH of *arom.*), 139.6, 140.1 (Cq of *arom.*). Anal. Calcd. for $C_{144}H_{138}Fe_6$: C 78.48, H 6.31; found: C 78.04, H. 6.04. MALDI-TOF MS: Calcd. for $C_{144}H_{138}Fe_6$: 2203.762; found: 2203.9.

CV (CH_2Cl_2; 293 K): $E_{1/2} = 0.38$ V vs decamethylferrocene (supporting electrolyte [(*n*-Bu)$_4$N]PF_6).

Synthesis of (1-Ethynyl-4-ferrocenylethynyl)benzene 8. Catalytic amounts of CuI (0.030 equiv, 6.96×10^{-2} mmol, 0.013 g), Pd(OAc)$_2$ (0.025 equiv, 5.800×10^{-2} mmol, 0.013 g), and PPh_3 (0.061 equiv, 1.415×10^{-2} mmol, 0.037 g) in diisopropylamine (100 mL) were stirred at 0 °C for 10 min. The mixture was then treated with 1,2,3,4,5-(pentamethyl)-1′-ethynyl-ferrocene (1 equiv, 2.320 mmol, 0.650 g) and (4-bromophenyl-ethynyl)trimethylsilane (1 equiv, 2.320 mmol, 0.588 g) and stirring continued at 0 °C for 1 h before warming to rt and then heating under reflux 1 h. After filtration and evaporation to dryness, the residue was washed with dilute HCl, Na_2CO_3 (10%), and water and then subjected to column chromatography on silica gel using a pentane-DCM (90:10) as eluent to obtain 0.828 g (1.932 mmol, 83% yield) of (4-pentamethylferrocenylethynylphenyl-ethynyl)trimethylsilane. This compound (0.828 g, 1.932 mmol) was dissolved in 25 mL THF and 25 mL MeOH. Then K_2CO_3 (0.534 g, 3.864 mmol) was added and the mixture was stirred at room temperature for 30 min. The reaction mixture was quenched with saturated ammonium chloride solution and then the product was extracted with DCM. The combined organic layers were dried over Na_2SO_4.After evaporation of the solvent; 0.470 g (1.236 mmol, 64% yield) of compound **8** was obtained. ^1H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 1.91 (s, 15H, CH_3), 3.19 (s, 1H, CH≡C), 3.84, 3.95 (2xs, 4H, Cp-H), 7.46−7.47 (m, 4H, CH of arom.). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ_{ppm}: 10.7 (CH_3), 65.9 (Cq of Cp*), 72.2, 74.3 (CH of *Cp*C≡C), 78.6 (CH≡C), 81.4 (Cq of Cp), 83.6, 85.7, 91.1 (C≡C), 125.0 (*Carom.*CC), 132.1 (CH of *arom.*). Anal. Calcd. for $C_{25}H_{24}Fe$: C 78.95, H 6.36; found: C 78.62, H. 6.54.

Synthesis of Hexakis(4-pentamethylferrocenylethynylphenyl-ethynyl)benzene 9. A 42-mg portion (0.076 mmol) of hexabromobenzene, 66 mg (0.057 mmol, 0.75 equiv) of [Pd(PPh_3)$_4$], and 10 mL of freshly distilled toluene under Na, were successively added into a Schlenk flask. A solution of (1-ethynyl-4-ferrocenylethynyl)benzene **8**[19] (2 mmol, 4 equiv per bromide) was then added. The mixture was heated at 80 °C for 24 h, an additional portion of catalyst [Pd(PPh_3)$_4$] (66 mg, 0.75 equiv) and ferrocenylethynyl zinc chloride (2 mmol, 4 equiv) were added with a syringe under N_2, the mixture was kept at 80 °C for six days, then was cooled down to rt. 84 mg (47% yield) of a crude dark-red solid identified by IR, Mössbauer spectroscopy and CV (see SI) as hexakis(4-pentamethylferrocenyl-ethynylphenylethynyl)benzene **9** that is almost insoluble in all solvents, was obtained, together with a soluble fraction that was adsorbed on silica. Purification by column chromatography (SiO_2; eluent: pentane/DCM; 80/20) gave 45% of bis(4-pentamethylferrocenylethynylphenylethynyl) (3.42×10^{-2} mmol, 26 mg).

Bis(4-pentamethylferrocenylethynylphenylethynyl): ^1H NMR (300 MHz, $CDCl_3$) δ_{ppm}: 1.91 (s, 15H, CH_3), 3.86, 3.96(2xs, 4H, Cp-H), 7.49 (s, 4H, CH of arom.). ^{13}C NMR (75.0 MHz, $CDCl_3$) δ_{ppm}: 10.6 (CH_3), 65.5 (Cq of Cp*), 73.1, 74.2 (CH of *Cp*C≡C), 75.3 ($C\equiv C$) 81.3 (Cq of Cp), 82.2, 85.8, 92.0 ($C\equiv C$), 125.4 (*Carom.*CC), 132.4 (Cq of *arom.*).

hexakis(4-pentamethylferrocenylethynylphenylethynyl)benzene **9**: IR (ATR) cm^{-1}: 2203.38 ($\gamma_{C\equiv C}$). MALDI-TOF MS: Calcd. for $C_{156}H_{138}Fe_6$: 2347.894; found: 2347.4.

CV (CH_2Cl_2; 293 K): one reversible waves $E_{1/2} = 0.360$ V vs decamethylferrocene (supporting electrolyte $[(n\text{-Bu})_4N]PF_6$).

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Supporting Information Available: ^{1}H and ^{13}C NMR, IR, and MALDI-TOF mass spectra for all the new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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