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The Metal-Catalyzed Cyclotrimerization of Ferrocenylethyne – Preparation and Characterization of 1,2,4-Triferrocenylbenzene

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1,2,4-Triferrocenylbenzene was isolated and fully characterized for the first time. It was obtained, together with 1,3,5-triferrocenylbenzene, by cyclotrimerization reaction, catalyzed either by metalloporphyrins or cobaltocene. The latter catalyst gave better results. The isomerically different triferrocenylbenzenes exhibit different properties.

Introduction

Ferrocenylic dendrimers are important species in that they are polymeric materials with diverse structure, properties and applications.[1] Moreover, macromolecular systems with multiple redox centres allow the possibility to control and modulate the extent of inter-center communication.[2] These dendrimers generally have peripheral ferrocenes.[3–20] Less common are dendrimers with the ferrocenyl moieties in the core.[21–27] It has not been yet exploited the possibility to have ferrocenes both as repetitive units and terminal groups, apart from occasional reports, dealing more with polymers than with dendrimers.[28] A strategy leading to such compounds might be a first generation dendrimer built from a benzene core substituted with functionalized ferrocenes. Compounds with these charcteristics were obtained from vinylferrocene and 1,3,5-tribromophenylbenzene or 1,3,5-tris(3,5-dibromophenyl)benzene[29] or from polybromobenzenes and ferrocenyllithium.[30] An alternative way to polyferrocenylbenzenes might be the cyclotrimerization of ferrocenylethyne. However, very few reports deal with homocyclotrimerization of ferrocenylethyne, the importance of ferrocenylarenes notwithstanding.[31] After the first report by Schlögl,[32] who obtained triferrocenylbenzenes heating ferrocenylalkynes at high temperatures, thirty years passed before the second report, where $TaCl_5$ was used as the catalyst.[33] A mixture of 1,3,5- and 1,2,4-triferrocenylbenzenes was obtained, with only the former compound isolated pure enough to be characterized by X-ray analysis and ^1H NMR spectroscopy. Later, 1,3,5-triferrocenylbenzene was obtained from acetylferrocene with $SiCl_4$-ethanol as the trimerization agent.[34] More recently, cocyclotrimerization of ferrocenylalkynes with α,ω-diynes was reported.[31]

Notice that both 1,3,5- and 1,2,4-triferrocenylbenzene can be the core of symmetrical and non symmetrical dendrimers, due to the easy functionalization of ferrocenyl moiety, for example via lithiation-iodination sequence and further coupling reactions.[35] Our finding that metalloporphyrins catalyze the cyclotrimerization of terminal alkynes[36] prompted us to extend the use of these versatile catalysts to ethynylferrocene and here we report the results obtained. Transition metal catalyzed [2+2+2] cycloaddition is an important reaction that was recently reviewed.[37]

Results and Discussion

The metalloporphyrin-catalyzed cyclotrimerization of ferrocenylethyne was performed with different porphyrins, in order to have an electron-rich not-crowded system [Ru(OEP)CO, where OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin] and, on the other hand, an electron-poor crowded system [Rh(TDCPP)Cl, where TDCPP is the dianion of 5,10,15,20-tetrakis-(2′,6′-dichlorophenyl)porphyrin]. These porphyrins had already given good results in phenylethyne cyclooligomerization.[36,38] Moreover, in order to evaluate the effect of the metal separated from that of the ligand, Ru(TPP)CO and Rh(TPP)Cl were used, TPP being the dianion of 5,10,15,20-tetraphenylporphyrin.

The reaction was carried out heating the substrate and the catalyst without solvent, under inert atmosphere, as described previously.[36] However, with ferrocenylethyne a number of problems were encountered, related to peculiar characteristics of the substrate.

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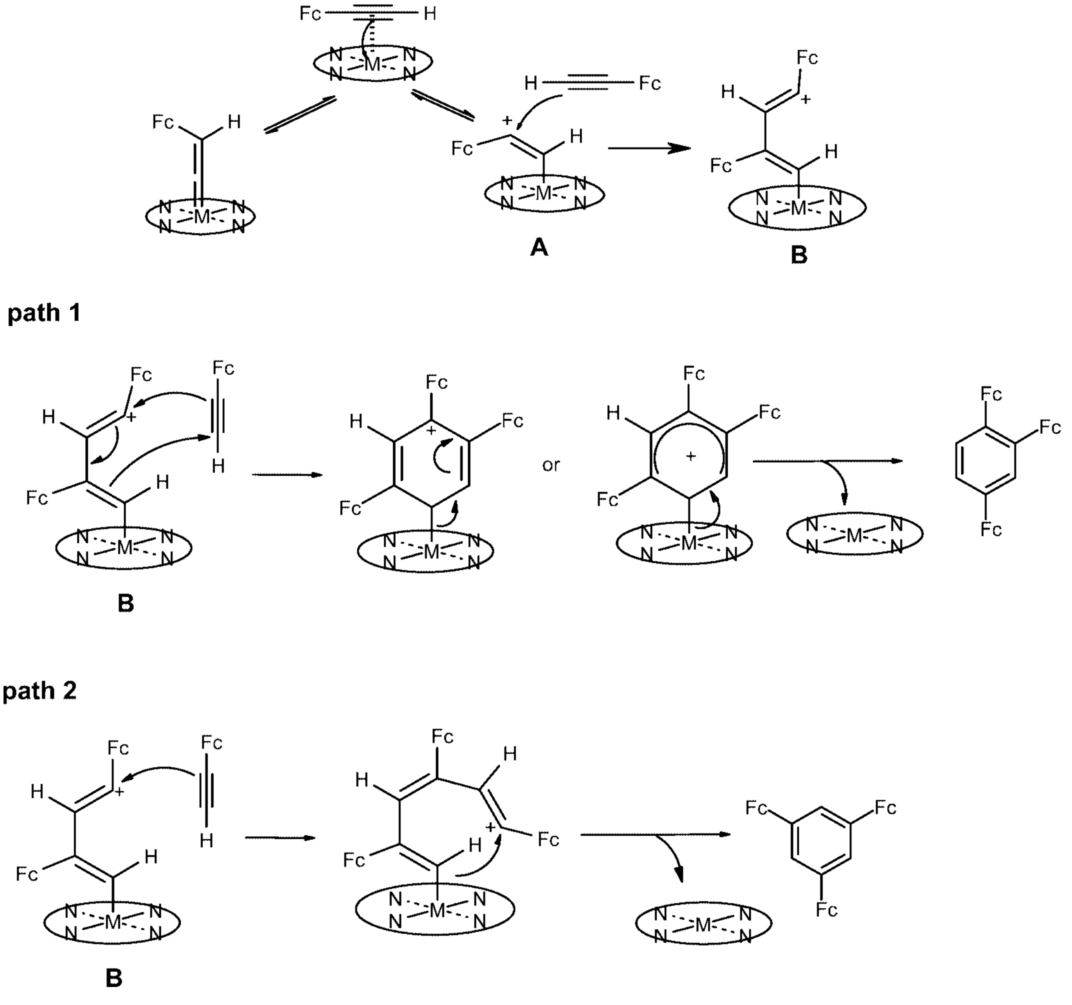
At temperatures lower than 140 °C, no product formed and ferrocenylethyne was recovered unchanged. At 140 °C, some reaction occurred, accompanied sometimes by decomposition of the alkyne. An additional problem was due to the density of liquid ferrocenylethyne that, once evaporated, did not reflux into the reaction vessel, but condensed on the cold walls of the Schlenk tube, thus remaining excluded from the reaction mixture. Attempts were made to push ferrocenylethyne back into the reaction, with the help of diethyl ether, that was added after cooling to room temperature and easily evaporated under a gentle nitrogen stream, before restarting heating. However, despite care in avoiding moisture, in these cases acetylferrocene only was recovered from the reaction workup. Apparently, metalloporphyrins catalyzed the alkyne hydration very efficiently: traces of water were effective, at variance with ethynylbenzene, where hydration was not observed.[36] By the way, this reaction was not welcomed, since ferrocenylethyne was pre-

Table 1. Cyclotrimerization of ferrocenylethyne with different catalysts.

Metal	Porphyrin	Alkyne % conversion	Absolute % yield[a]	Relative % yield[b]	Relative ratio 1,2,4	Relative ratio 1,3,5
Rh^{III}	TDCPP	70	5.0	7.0	70	30
	TPP	91	7.3	8.0	32	68
Ru^{II}	OEP	23	15.0	63.0	75	25
	TPP	95	14.0	15.0	64	36
		62[c]	15.3	24.7	64	36
Cp_2Co		96	88	93	63	37

[a] Relative to initial ferrocenylethyne. [b] Relative to converted ferrocenylethyne. [c] Reduced reaction time.



Scheme 1.

pared from acetylferrocene. The reaction was performed also in sealed vials, kept immersed completely in an oil bath at 140 °C, but the reaction output remained more or less the same. All these problems considered, low yields in cyclotrimers accompanied high conversions of ferrocenylethyne.

The results are reported in Table 1 and are average values of at least three runs each. Low yields notwithstanding, interesting reactivity patterns emerge, when we compare the relative percents of 1,2,4- and 1,3,5-triferrocenylbenzene.

In principle, Ru^{II} porphyrins are more electron-rich than Rh^{III} porphyrins, where a positive charge requires a Cl^- counterion. Also, Rh(TDCPP)Cl is more hindered than Rh(TPP)Cl. As a consequence of different electronic and steric properties of catalysts, the selectivity can be rationalized as in the following Scheme 1.

After initial coordination, the π complex between the metal and the carbon–carbon triple bond might give a vinylidene-metal complex, via hydride shift, as ethynylbenzene does.[38] Differently from ethynylbenzene, however, the vinylidene complex cannot undergo formal Diels–Alder reaction to dimers, due to structural reasons. Instead, the high electron-releasing ability of ferrocenyl group makes possible an intermediate with a somewhat positive charge on the α-carbon (**A**). **A** has to be a species reactive with nucleophiles and a second ethynylferrocene molecule adds, yielding another cationic intermediate (**B**), with an approach that minimizes steric hindrance between ferrocenyl groups. By the way, **A** may explain the high reactivity with water. The fate of **B** depends on the catalyst characteristics. With Ru(OEP)CO and Ru(TPP)CO, more electron rich, a formal Diels–Alder reaction with the third ethynylferrocene molecule may occur (Scheme 1, path 1). This time, the larger steric hindrance is experienced by the approaching molecule if Fc is close to the porphyrin, yielding 1,2,4-triferrocenylbenzene preferentially. On the other hand, with Rh(TPP)Cl as catalyst, **B** is more electrophilic and may easily undergo nucleophilic attack by ethynylferrocene (Scheme 1, path 2), with minimal steric hindrance. Ring closure leads to 1,3,5-triferrocenylbenzene.

Of course, both pathways may coexist, as indicated by results with Rh(TDCPP)Cl as catalyst. This porphyrin is electronically similar to Rh(TPP)Cl, but much more sterically crowded (Figure 1).

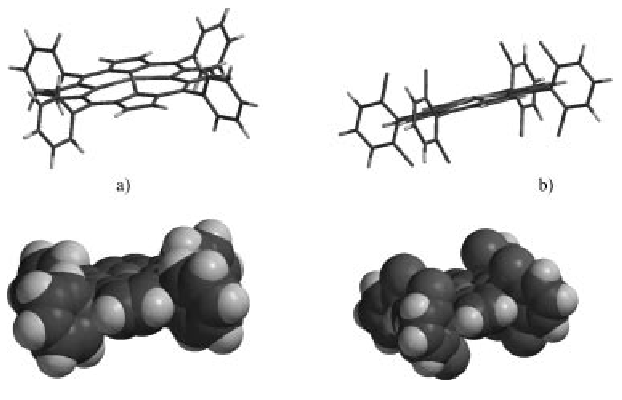


Figure 1. Optimized geometries of Rh(TPP)Cl (a) and Rh(TDCPP)-Cl (b), represented as sticks (above) and space filling (below) structures. For clarity, apical Cl was omitted: when inserted, the structures were not noticeably affected.

Finally, a completely different catalyst, i.e. cobaltocene, gave excellent results in terms of yields and reaction conditions. This catalyst was used first in co-cyclotrimerization of alkynes and nitriles,[39] leading to pyridines, but not for homo-cyclotrimerization, where $CpCoL_2$ complexes were used, L being a more labile ligand (CO or C_2H_4[40,41]). The mechanism at work with cobaltocene as the catalyst is likely to follow the classic formation of intermediate metallacycles[42] and 1,3,5-triferrocenylbenzene formation was slightly favoured with respect of the statistical ratio (Table 1).

The cobaltocene-catalyzed trimerization gave enough material to attempt separation of the two isomers. As already reported,[33] it was not possible to separate them

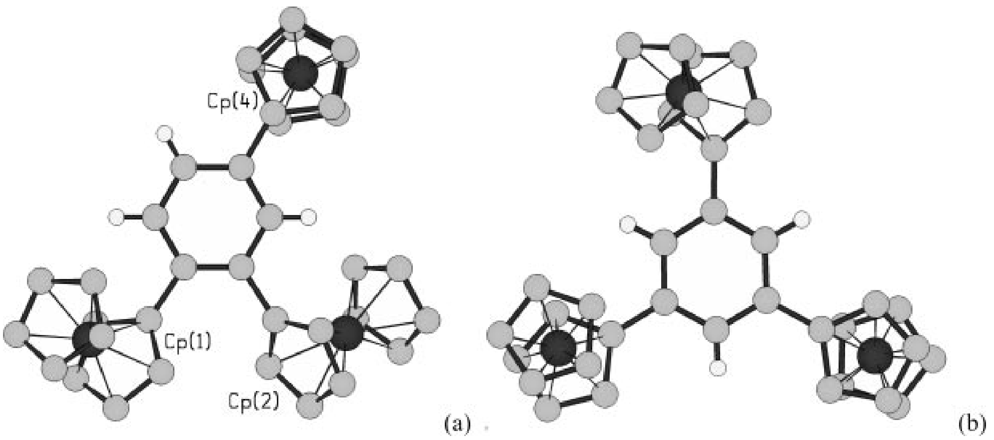


Figure 2. (a) The molecular structure of 1,2,4-triferrocenylbenzene, showing the different tilting of the three ferrocenyl units with respect to the central C_6H_3 ring. Dihedral angles between the six-membered ring and the five-membered rings Cp(1), Cp(2) and Cp(4) are 32.0(2), 48.6(1) and 3.7(2)°, respectively. (b) The molecular structure of the previously reported isomeric compound 1,3,5-triferrocenylbenzene.[33] [H atoms belonging to the Cp-rings not shown for clarity].

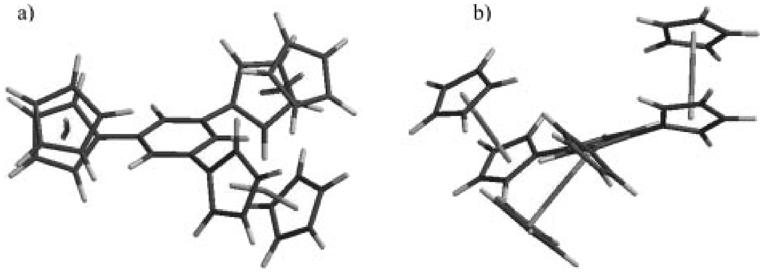


Figure 3. DFT optimized geometries of 1,2,4-triferrocenylbenzene (a) and 1,3,5-triferrocenylbenzene (b).

either by column chromatography or by fractional crystallization. Only preparative HPLC allowed to separate the trimers and, consequently to fully characterize for the first time 1,2,4-triferrocenylbenzene.

X-ray quality crystals were obtained from ethyl acetate containing 2.5% chloroform.

Figure 2 (a) shows the molecular structure of 1,2,4-triferrocenylbenzene. The three ferrocenyl groups, which are attached to the carbon atoms of the C_6H_3 ring in the 1, 2 and 4 positions [C–C distances 1.522(2), 1.510(2) and 1.513(2) Å, respectively], all present an eclipsed conformation of the cyclopentadienyl rings, and are arranged in a up-down-down fashion. The carbon atoms directly bound to the central ring are all coplanar with it, while the three ferrocenyl units are tilted by a different extent with respect to the C_6H_3 ring. Dihedral angles between the central C_6H_3 ring (C_6) and the five-membered rings in 1 [Cp(1)], 2 [Cp(2)] and 4 [Cp(4)] positions (see Figure 1, a) are 32.0(2), 48.6(1) and 3.7(2)°, respectively. Figure 2 (b) provides a comparison with the molecular structure of the previously reported compound[33] 1,3,5-triferrocenylbenzene.

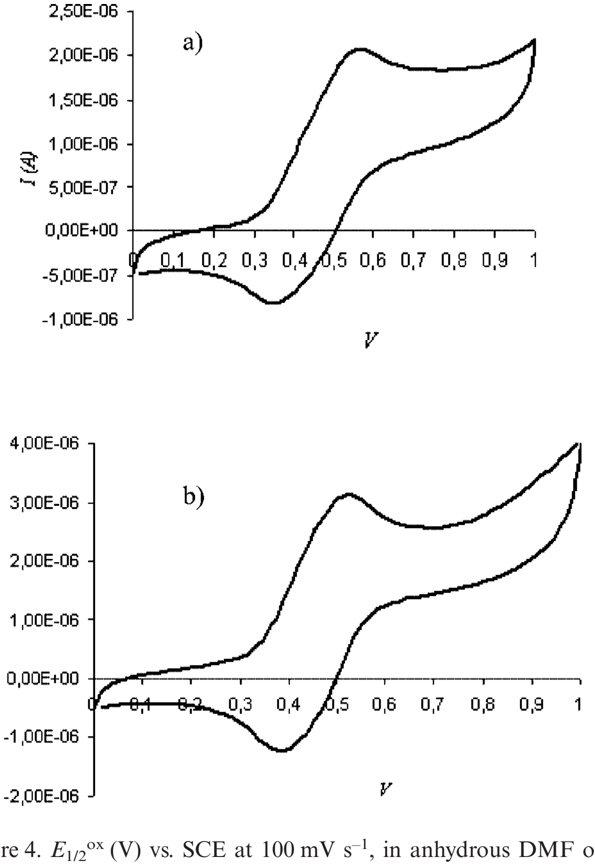


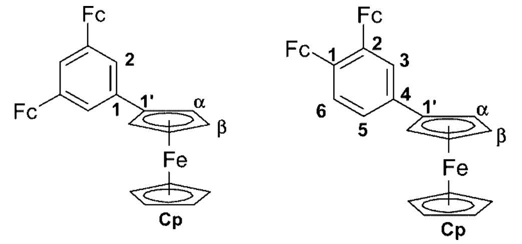
Figure 4. $E_{1/2}{}^{ox}$ (V) vs. SCE at 100 mV s^{-1}, in anhydrous DMF of 1,2,4-triferrocenylbenzene (a) and 1,3,5-triferrocenylbenzene (b).

The minimum energy conformation of 1,2,4-triferrocenylbenzene, as calculated by density functional theory (DFT) method, is in agreement with the structure from X-ray analysis, in that the two adjacent ferrocenyl moieties as far as possible (Figure 3, a) and there is a more significant steric hindrance than the symmetrical isomer (Figure 3, b).

In solution the situation may be different: there is no evidence of a difference among ferrocenyl groups in cyclic voltammetry, where a substantial equivalence of ferrocenes was found (Figure 4).

However, ^{13}C NMR spectrum shows two groups of signals in the region of ferrocenyl carbons (Table 2). It might be possible that rotation of ferrocenyl group is slow enough to maintain a magnetic difference in the NMR response time. However, a different picture emerges from DFT molecular orbital calculations (Titan[43] LACVP* basis set for iron atom and 6-31G* for light elements). In fact, HOMO of 1,2,4-triferrocenylbenzene is delocalized only along two ferrocenyl moieties (Figure 5, a).

Table 2. ^{13}C NMR chemical shifts for 1,3,5- and 1,2,4-triferrocenylbenzene in $CDCl_3$.



C1	138.99	136.25
C2	121.86	136.25
C3	138.99	128.64
C4	121.86	136.83
C5	138.99	123.64
C6	121.86	128.64
C1	85.57	79.59
C_α	68.88	79.79, 70.46
C_β	66.59	67.25, 66.23
C_{Cp}	69.63	69.43, 68.87

The different electron distribution makes ferrocenyl carbon atoms non identical. On the other hand, HOMO of

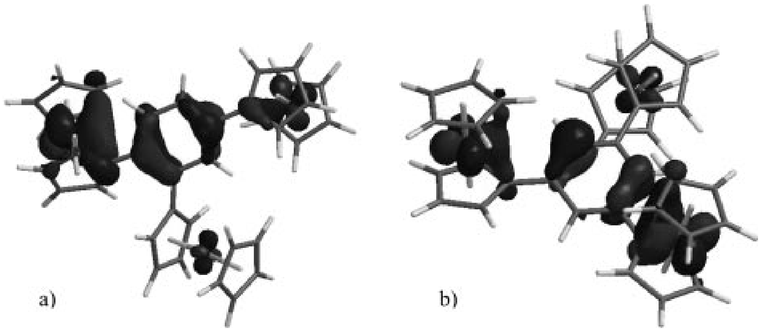


Figure 5. HOMO of 1,2,4-triferrocenylbenzene (a) and 1,3,5-triferrocenylbenzene (b) calculated with DFT method (LACVP* basis set for iron atom and 6-31G* for light elements).

1,3,5-triferrocenylbenzene, calculated in the same way, is completely delocalized through all the molecule (Figure 5, b).

Conclusions

Cyclotrimerization of ferrocenylethyne was obtained under relatively mild conditions, but metal porphyrins gave disappointingly low yields. Fortunately, cobaltocene worked well as catalyst, giving high yields enriched in 1,2,4-triferrocenylbenzene, that was isolated for the first time and fully characterized. As to 1,3,5-triferrocenylbenzene, we can conclude that ferrocenyl groups are equivalent, on the basis of calculations, NMR, and CV experiments. In 1,2,4-triferrocenylbenzene the situation is more complicated, because we had evidence of a non equivalence of ferrocenyl groups (calculations and ^{13}C NMR), whereas CV experiments gave one wave only. Further inversigation will be performed to fully understand the behaviour of this compound. The trimerization reaction, while opens a route to dendrimers with ferrocenes as repetitive units and terminal groups, gave interesting results relative to the properties of isomerically different triferrocenylbenzenes.

Experimental Section

General Procedures: All manipulations were carried out under inert atmosphere (nitrogen or argon) using standard Schlenk technique. Anhydrous commercial grade solvents were used. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer. Chemical shifs (δ, ppm) were reported with reference to Me_4Si. Infrared spectra were obtained with a Perkin–Elmer 983 spectrophotometer, in chloroform, with a NaCl cell. Mass spectra (EI or FAB) were obtained with a VG Quattro (triple quadrupole) spectrometer. GC analyses were performed with a Varian CP 3900, equipped with a SBP-35 capillary column 30 m × 0.25 mm, coated with a 0.25 µm film of methylsilicone. HPLC experiments were performed with a Shimadzu LC-10AD instrument equipped with a diode-array SPD-M10A spectrophotometer, using a 5 mµ 25 × 0.46 cm LC-Si column for analyses and a 5 µm 25 × 1 cm Kromasil semipreparative column for separation of milligrams.

Electronic spectra were collected with a Cary 50 SCAN Varian spectrophotometer in silica cells and $CHCl_3$ solution.

Cyclic voltammetry measurements were performed with an Autolab PGSTAT-12 potentiostat with a 10 mL cell equipped with nitrogen inlet, saturated calomel as the reference electrode, glassy-carbon as the working electrode, and platinum wire as the auxiliary electrode, in anhydrous DMF and 0.1 M Et_4NClO_4.

Ferrocenylethyne was prepared in a 72% yield according to the literature method, from acetylferrocene and the Vilsmeier reagent, followed by elimination.[44] The free bases H_2TDCPP, H_2TPP, and H_2OEP, where TDCPP is the dianion of 5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin, TPP is the dianion of 5,10,15,20-tetraphenylporphyrin, and OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin, were synthesized by literature methods.[45,46] Ru(OEP)CO was obtained by literature methods.[47] Rh(TDCPP)Cl was synthesised as described in another paper from our laboratory.[48] Ru(TPP) and Rh(TPP)Cl were prepared as described.[49]

Calculations were performed with the Titan[43] package software, using semiempirical PM3 method for geometry optimization of Rh porphyrins. Density functional theory (DFT) method, using LACVP* basis set for iron atom and 6-31G* for light elements, was used for geometry optimization and orbital calculations for triferrocenylbenzenes.

X-ray quality crystals were obtained by slow crystallization from ethyl acetate containing 2.5% v/v $CHCl_3$.

Crystal Structure Determination: Crystal data for 1,2,4-triferrocenylbenzene were collected at 293 K on a Bruker ApexII CCD diffractometer (Mo-$K\alpha$ radiation, λ = 0.71073 Å, monochromator: graphite). SHELX97[50a] was used for structure solution and refinement based on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in calculated positions, and refined riding on their respective carbon atoms. SCHAKAL99[50b] was used for the graphical representation of the results. $C_{36}H_{30}Fe_3$: monoclinic, space group $P2_1/c$, M_r = 1458.58, a = 18.1688(4), b = 12.4900(2), c = 11.9084(2) Å, β = 95.279(1) deg, V = 2690.89(9), μ(Mo-$_{K\alpha}$) = 1.621 mm^{-1}, $2\theta_{max}$ = 60 deg, measured reflections: 31262, unique reflections: 7865, refined parameters: 286, GOF on F^2 = 0.963, R_1 [on F, $I > 2\sigma(I)$] = 0.0462, wR_2 (on F^2, all data) = 0.1280.

CCDC-278164 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

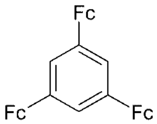
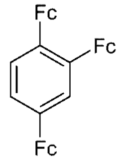
Cyclotrimerization Reactions: In a typical experiment, known amounts of ferrocenylethyne (150, 300 or 500 mg) and the catalyst, in a 100:1 (or 100:2) molar ratio were placed in a Schlenk tube, fluxed 15 min with argon and heated up to the melting point of ferrocenylethyne (53 °C). The mixture, stirred under inert atmosphere, was heated at 140 °C. Particular attention must be paid to avoid moisture, otherwise acetylferrocene is quantitatively formed. The reaction was interrupted when the mixture solidified (generally, two or three days). After cooling to room temperature, the solid was dissolved with diethyl ether and purified by column chromatography (silica gel; eluent, 40–70 °C petroleum ether, with increasing amounts of diethyl ether up to 10%, v/v), ferrocenylethyne being eluted first and cyclotrimers in the second fraction. With cobaltocene as the catalyst (0.01 mmol with 1 mmol ferrocenylethyne) the reaction was performed at 65 °C and lasted 3 hours. The results are reported in Table 1 as the average of at least three experiments, with percents reproducible within experimental error. Attempts to separate 1,2,4- and 1,3,5-triferrocenylbenzene by flash chromatography were unsuccessful. However, the product distribution was easily accomplished from integrated aromatic signals in ^{1}H NMR spectra.

The two isomers could be separated only by HPLC, with hexane containing 2% v/v ethyl acetate as eluent at a 1 mL/min flux. 40 runs were performed, 1 mL $1.1\cdot10^{-3}$ M solution each, allowing to separate 20 mg 1,2,4-triferrocenylethyne and 10 mg 1,3,5-triferrocenylethyne.

Characterization of Cyclotrimers

1,2,4-Triferrocenylbenzene: Elemental analysis: calcd. C 68.62, H 4.80; found C 68.65, H 5.13. MS (FAB, 3-nitrobenzyl alcohol), *m/z*: cluster around 630 (M$^+$, MF, 630.17); LC-MS (DMF/MeOH, 1:1, v/v), *m/z*: 630.4, with isotopic pattern identical to that calculated for $C_{36}H_{30}Fe_3$. IR, $\tilde{\nu}$ (cm^{-1}): 1106, 1002 (monosubstituted ferrocene[51]). UV-vis: λ_{max} (ε) = 275 (30500 ± 300), 350 (sh), 450 nm (1800 ± 50). ^{1}H NMR (ppm, CD_2Cl_2): δ = 7.88 (d, 1 H, J = 2.0 Hz, aromatic proton in 3), 7.65 (d, 1 H, J = 8.0 Hz, aromatic proton in 6), 7.35 (dd, 1 H, J = 8.0, 2.0 Hz, aromatic proton in 5), 4.10 (s, 5 H, unsubstituted cyclopentadienyl ring), partially superimposed with complex signals in the range 4.04–4.16 (complex, 4 H, α and β protons of the substituted Cp ring). ^{13}C NMR ($CDCl_3$) data are reported in Table 2. Oxidation potential is reported in Table 3.

Table 3. $E_{1/2}^{ox}$ (V) vs. SCE at 100 mV s^{-1}, in anhydrous DMF; concentration ca. 10^{-4}M.

Compound[a]	$E_{½}^{ox}$ (V)
Fc—C≡CH	0.553
	0.454
	0.450

[a] Fc = ferrocenyl.

1,3,5-Triferrocenylbenzene: Elemental analysis: calcd. C 68.62, H 4.80; found C 68.12, H 5.07. MS (FAB, 3-nitrobenzyl alcohol), *m/z*: cluster around 630 (M$^+$, MF, 630.17). IR: $\tilde{\nu}$ (cm^{-1}) = 1106, 1002 (monosubstituted ferrocene[51]). UV-vis: λ_{max} (ε) = 280 (25700 ± 300), 350 (sh), 450 nm (920 ± 20). ^{1}H NMR (ppm, CD_2Cl_2): δ = 7.45 (s, 3 H, aromatic protons), 4.10 (s, 5 H, unsubstituted cyclopentadienyl ring), 4.75 (complex, 2 H, α protons of the substituted Cp ring), 4.37 (complex, 2 H, β protons of the substituted Cp ring). ^{13}C NMR ($CDCl_3$) data are reported in Table 2. Oxidation potentials are reported in Table 3.

Acknowledgments

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