Facile synthesis of first generation ferrocene dendrimers by a convergent approach using ditopic conjugated dendrons†

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A facile synthesis of new conjugated ferrocenyl-based dendrimers is reported and the compounds obtained have been fully characterized. The synthetic method consists of a two-step procedure, which combines olefination by the Wittig procedure and Pd-mediated C–C coupling, leading to high yields of first generation dendrimers with 3, 6 and 12 peripheral ferrocene units. The crystal structure of the conjugated ditopic ferrocenyl dendron and its aldehyde precursor are also described.

Since Vögtle and coworkers obtained the first acyclic branched polyamines,[1] dendrimer chemistry has attracted the interest of a large number of chemists, who mainly pursued new synthetic routes to the production of high molecular weight compounds with as many generations as possible. More recently, the interest in dendrimer chemistry turned to the modification of the properties of dendritic compounds by either the introduction of internal or peripheral functionalities, as this can provide access to materials with potentially useful magnetic, electronic, photo-optical or catalytical properties. The introduction of metal atoms into the structure of the dendrimer has allowed the generation of a new type of molecules called *metallodendrimers*.[2–7] The inclusion of redox centers into the dendrimer widens the structural diversity and the properties of these materials. Many approaches have been used to introduce the metal centers into the dendrimer structure, but still we can see that the lack of systematic preparation procedures constitutes the bottleneck of the study of this new type of materials.

Among all the metallodendrimers obtained until now, those containing ferrocene seem to have attracted special attention,[4,8–31] undoubtedly because ferrocene combines chemical versatility with high thermal and redox stability. In our previous works, we have used ferrocenyl-based conjugated ligands in order to obtain bimetallic and heterometallic push-pull complexes,[32–35] and found interesting redox and spectroscopic properties that have been related to high non linear optical responses.[32,35] In all the cases that we studied, the connecting bridges between the redox centers were oligophenylenevinylene-based, which have recently demonstrated high efficiency electronic communication capabilities.[36] Our results prompted us to design facile methods for the preparation of phenylene-vinylene dendrimers, in order to study the effect of an extended, conjugated coplanar system in the structure of a metallodendrimer. In our first approach, we reported a high efficiency method for the preparation of bidimensional conjugated ferrocenyl minidendrimers.[29] Based on our experience, we now report the convergent synthesis of dendrimers with up to 12 peripheral ferrocenyl units. The electrochemical properties of these new materials, as well as the crystal structures of the conjugated ditopic ferrocenyl dendron and its aldehyde precursor, are also described.

Results and discussion

Small mononuclear and easily accessible metallocenes bearing reactive functional groups for condensation or cross-coupling reactions allow the application of well-established organic synthetic procedures. Palladium-mediated olefin formation *via* the Heck reaction has been widely used in organic chemistry for the synthesis of *E*-olefins. Some ferrocenyl olefin-containing complexes have been recently obtained by palladium-catalyzed procedures, showing high stereoselectivities to the *E* configuration and high yields.[37–40] The continuous search for more active and selective Pd catalysts has widely increased the number of olefins and halides that can be coupled by this procedure. Taking this into account, we decided to approach a new synthetic route to ferrocene-containing dendrimers, combining our experience in the Wittig olefination with the well-established Heck C–C coupling.

Our first objective was to obtain a dendron having two identical ferrocene units, connected by a conjugated bridge. We envisaged that **3** (Scheme 1) might allow electronic communication between the ferrocene units by virtue of the conjugated bridge. The preparation of **3** implies commercial and easily accessible compounds such as vinylferrocene (**1**) and 3,5-dibromobenzaldehyde. The palladium-mediated coupling of these two compounds yields the bisferrocene aldehyde **2** in high yield (72%) in just 12 h at 130 °C in DMA. Due to the high temperature used, we decided to utilize the thermally stable imidazolyl pincer Pd catalyst shown in Scheme 1, related to the one recently described by us with methyl instead of *n*-butyl terminal groups.[41] This catalyst showed a higher activity than its methyl analog. The preparation and catalytical properties of this new catalyst will be published in detail elsewhere. Olefination of **2** by the Wittig procedure using triphenylmethylphosphonium iodide afforded the bisferrocenyl dendron **3** in high yield (65%). Both compounds, **2** and **3**, were fully characterized by conventional spectroscopic methods and gave satisfactory elemental analysis. Both reactions yielded stereospecifically the *E* isomers, showing no significant amounts of side-products, so the purification procedures were rather simple.

Compounds **2** and **3** gave single crystals suitable for X-ray diffraction, so their crystal structures could be determined. Fig. 1 shows the ORTEP diagrams of **3** in two different perspectives. Both compounds crystallize in the centrosymmetric space group $P2_1/c$ and the molecular structures display a very

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† Electronic supplementary information (ESI) available: molecular structure of **2**. See http://www.rsc.org/suppdata/nj/b1/b108142j/

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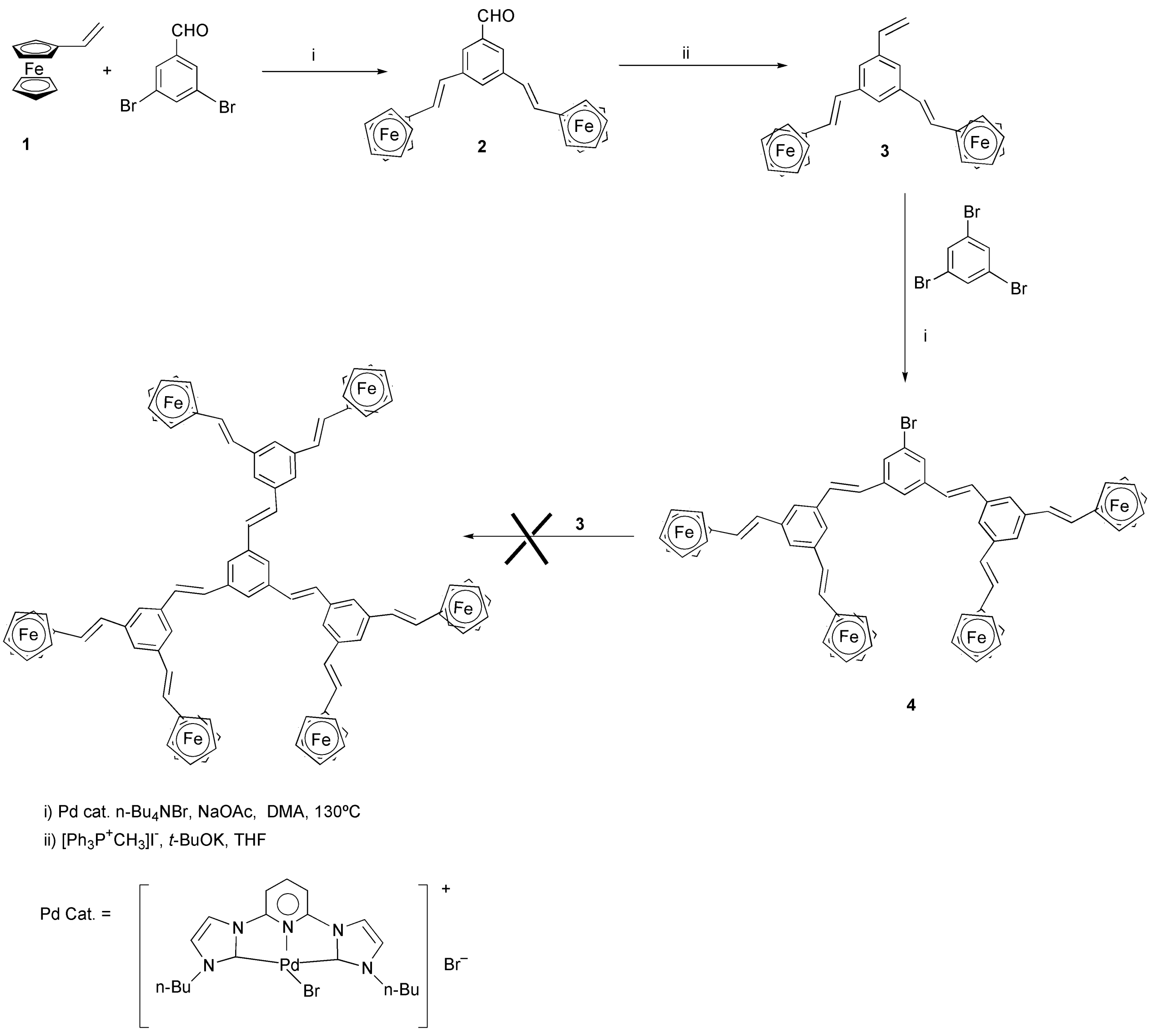


i) Pd cat. n-Bu_4NBr, NaOAc, DMA, 130ºC
ii) $[Ph_3P^+CH_3]I^-$, *t*-BuOK, THF

Scheme 1

similar atomic arrangement (the molecular structure of **2** can be found in the electronic suplementary information). The most remarkable feature of these two structures is that they show an almost coplanar structure between the Cp, vinylene and phenylene units, as can be seen in Fig. 1(b), confirming that the conjugation extends along the whole structure. As seen for most neutral ferrocenyl complexes, the Cp rings adopt a quasi-eclipsed conformation. Table 1 shows the most significant bond distances, angles and planes of **2** and **3**.

In an extension of our previously reported work on the preparation of ferrocenyl minidendrimers using 1,3,5-tribromobenzene,[29] we tried to use this compound as a core for our newly prepared dendron **3**. The reaction of a three-fold excess of **3** with 1,3,5-tribromobenzene, yielded unambiguously the tetraferrocenyl complex **4** (Scheme 1), whose structure was confirmed by means of FABMS. Higher excesses of **3** in the reaction procedure, higher amounts of catalyst or the use of higher temperatures did not afford the three-fold coupled dendrimer. We believe that the reason for this failure is the coplanarity imposed by the extended conjugated system; this clearly shows that the steric or 'starburst' limit of this two-dimensional dendrimer is already achieved in the first generation.

Since we believed that steric reasons were the only ones to blame for the failure in the synthesis of our hexaferrocenyl dendrimer, we decided to use compounds **5-Br$_3$** and **6-Br$_6$** as new cores. With these two compounds the steric strain is largely released because (*i*) the bromine atoms have a larger through-space separation than in 1,3,5-tribromobenzene and (*ii*) the less effective conjugation between the phenylene connections affords a lower C–C rotation barrier that can break the coplanarity of the whole molecule, while the coplanarity of each individual branch should be maintained. Compound **6-Br$_6$** was obtained by Miller *et al.*[42] and was satisfactorily used in the preparation of a series of monodisperse organic dendrimers. By a similar method to that leading to **6-Br$_6$**, we obtained **5-Br$_3$** in very high yield (*ca.* 80%) starting from commercially available 4-bromoacetophenone.

In order to test the C–C Heck coupling on these two new compounds, we started by coupling vinylferrocene, **1**, to **5-Br$_3$** and **6-Br$_6$**. These reactions afforded **7-Fc$_3$** and **8-Fc$_6$** in high yields (Scheme 2). The reactions could be followed *in situ* by extracting small amounts of the reaction mixture and making micro-extractions in CH_2Cl_2–H_2O. The solvent of the organic fraction was removed and the crude solid redissolved in $CDCl_3$ and introduced in an NMR tube. By this simple method we could monitor the reaction progress by ^1H NMR, by simply checking the disappearance of the signals due to the terminal olefin of complex **1**. After 14 h the reactions were completed according to the complete consumption of **1**. The compounds so obtained, **7-Fc$_3$** and **8-Fc$_6$**, were fully characterized by

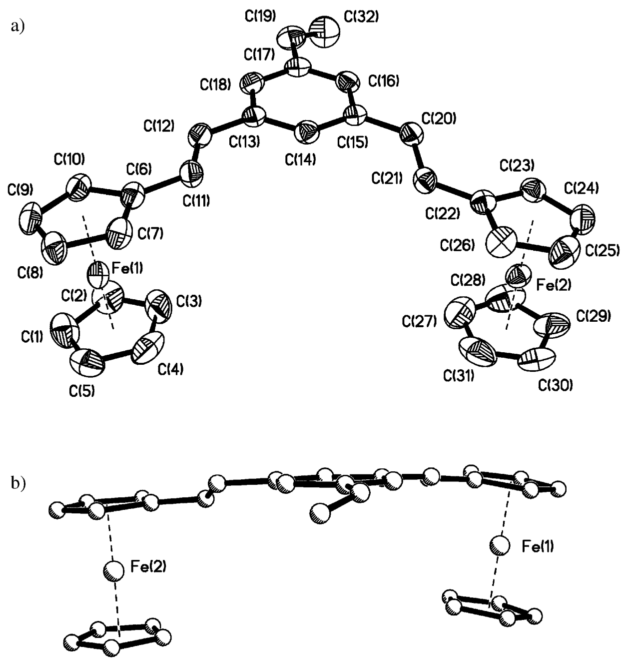


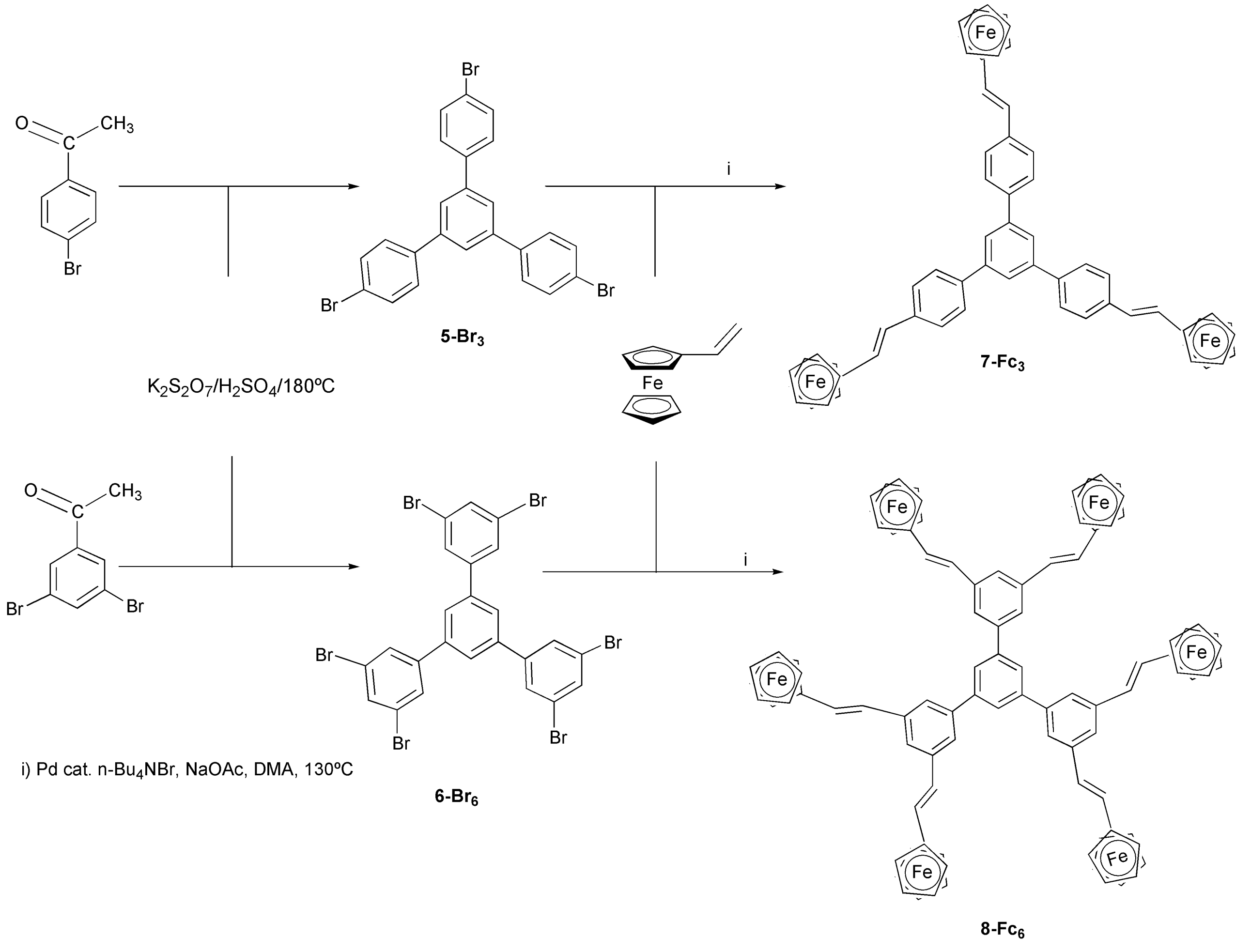
Fig. 1 (a) Ortep diagram of compound **3** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. (b) Molecular diagram showing the coplanarity of compound **3**.

Table 1 Selected bond distances (Å), angles and planes (deg.) for compounds **2** and **3**

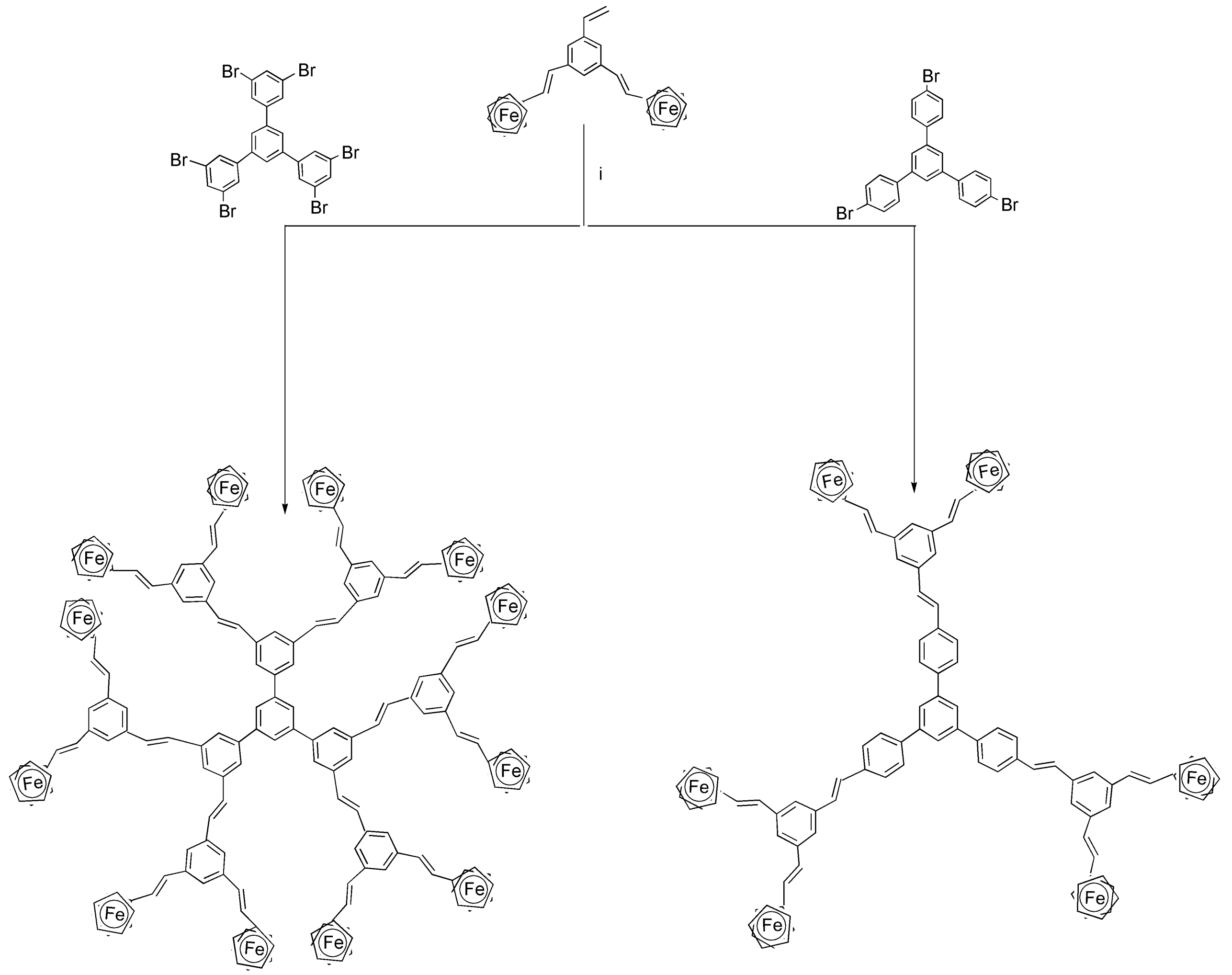
	2	**3**
Fe(1)–Cp (subst)	1.643	1.649
Fe(1)–Cp	1.652	1.644
Fe(2)–Cp (subst)	1.653	1.646
Fe(2)–Cp	1.649	1.651
C(19)–O(1)	1.188(5)	—
C(19)–C(32)	—	1.291(4)
Fe(1)···Fe(2)	9.82	9.72
C(6)–C(11)–C(12)–C(13)	−178.9(4)	−176.8(3)
C(15)–C(20)–C(21)–C(22)	178.5(4)	−178.8(3)
Planes		
Ph–[C(6),C(7),C(8),C(9),C(10)]	4.0	10.2
Ph–[C(22),C(23),C(24),C(25),C(26)]	7.4	4.2

conventional methods. The ^{1}H NMR spectra showed the typical pattern of monosubstituted ferrocenyl compounds, this confirming the equivalence of all the ferrocene units.

The reaction of **5-Br$_3$** and **6-Br$_6$** with **3** afforded the first generation dendrimers **9-Fc$_6$** and **10-Fc$_{12}$**, respectively (Scheme 3). As mentioned above, the reactions could be easily followed by ^{1}H NMR by the same method described, monitoring the disappearance of the signals due to the terminal olefin of **3**. The products were purified by column chromatography and no significant side-products were isolated. Although the ^{1}H and ^{13}C NMR spectra of **9-Fc$_6$** and **10-Fc$_{12}$** were very clean, the assignment of the signals could not be easily made due to the overlapping of the peaks corresponding



Scheme 2



10-Fc$_{12}$

9-Fc$_6$

i) Pd cat. n-Bu$_4$NBr, NaOAc, DMA, 130°C

Scheme 3

to the olefin and aromatic hydrogens. However, the $^3J_{\text{H-H}}$ couplings of the olefin hydrogen atoms were in all cases very close to 16 Hz, this unambiguously confirming the all-*E* configuration of the complexes. The ^{1}H NMR spectra also showed the pattern of monosubstituted ferrocenyl compounds, this confirming the equivalence of the peripheral ferrocene units.

The structures of the dendrimers **9-Fc$_6$** and **10-Fc$_{12}$** were corroborated by fast atom bombardment (FAB) mass spectrometry, which showed the molecular ions at *m*/*z* 1871 and 3440, respectively.

The electrochemical data obtained for the compounds studied are summarized in Table 2. All the complexes display the chemically reversible ferrocene/ferricinium couple in CH_2Cl_2.

The presence of the aldehyde in compound **2** leads to a higher redox potential (445 mV) compared to that of the vinyl-functionalized dendron **3** (415 mV), due to the electron-accepting capabilities of the aldehyde.

In general, all the dendrimer-type complexes show lower potentials than that shown for ferrocene (445 mV), probably due to their higher electron delocalization. In addition, a cooperative electron-donating behavior of each ferrocenyl unit may also be contributing to this redox potential lowering. Compounds **7-Fc$_3$**, **8-Fc$_6$**, **9-Fc$_6$** and **10-Fc$_{12}$** show a unique reversible electron wave, this corresponding to the simultaneous oxidation of 3, 6, 6 and 12 ferrocene units, respectively. This result indicates that the ferrocenyl centers in each compound are essentially non-interacting. However, this result may also be interpreted as a consequence of fast heterogeneous electron-transfer kinetics. It has been suggested that one of the reasons for this observation may be due to the fast rotation of

Table 2 Cyclic voltammetric data[a]

Compound	$E_{1/2}$/mV (ΔE_p/mV) Fe-based
Ferrocene	445 (105)
1	460 (100)
2	445 (150)
3	415 (90)
7-Fc$_3$	415 (100)
8-Fc$_6$	385 (125)
9-Fc$_6$	375 (65)
10-Fc$_{12}$	415 (57)

[a] All compounds were studied in CH_2Cl_2 between 0 and 1.25 V.

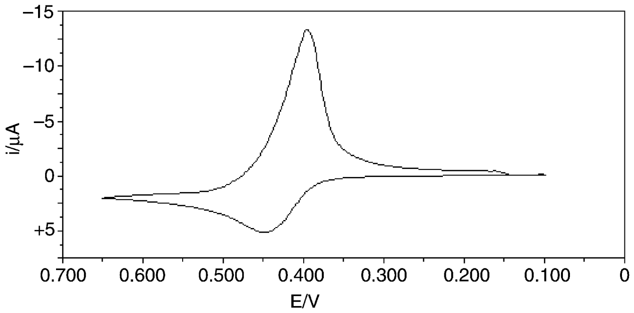


Fig. 2 Cyclic voltammogram of compound **10-Fc$_{12}$**.

the dendrimer compared to the electrochemical timescale, so that all redox centers come close to the electrode within this timescale.[13] A similar effect was observed for the compound 1,3,5-tris(ferrocenylethenyl)benzene.[29]

As it has been previously reported for other ferrocenyl dendrimers,[43] the redox behavior of the compounds **7-Fc$_3$**, **8-Fc$_6$**, **9-Fc$_6$** and **10-Fc$_{12}$** is marked by changes in solubility with the change in the oxidation state of the ferrocene units. Whereas the anodic wave has a typical diffusional shape, a sharp cathodic stripping peak is observed (Fig. 2), which indicates the precipitation of the dendrimers onto the electrode upon oxidation.

Conclusions

We have obtained a bisferrocenyl ethenyl-terminated compound, which has been satisfactorily used as a dendron in the preparation of a series of ferrocenyl-based dendrimers, which, according to the crystal structure of the conjugated dendron, must show three planar branches, the coplanarity only being disrupted at the central core. The new bromo-functionalized tetraphenyl cores have shown to be very convenient starting materials. We have established that Pd-mediated C–C double bond formation is an effective method for the synthesis of conjugated ferrocenyl dendrimers. The extension of this synthetic methodology to the construction of higher generation dendrimers is currently in progress in our laboratory.

Experimental

General details

NMR spectra were recorded on Varian Innova 300 MHz and 500 MHz spectrometers, using $CDCl_3$ as solvent unless otherwise stated. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR using NaCl pellets. Electronic absorption spectra were obtained on a Shimazdzu UV-1603 spectrophotometer. Cyclic voltammetry experiments were performed with an Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and an Ag/AgCl reference electrode containing aqueous 3 M KCl. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. All potential data reported are uncorrected for the junction potential. Mass spectra were run in the fast atom bombardment mode (FABMS, *m*-nitrobenzyl alcohol matrix) on a VG AutoSpec mass spectrometer. Vinylferrocene, **1**, was used as purchased (Aldrich) or synthesized by Wittig olefination of the ferrocenecarboxaldehyde, using $[Ph_3P^+CH_3]I^-$ and *t*-BuOK. Compound **6-Br$_6$** was obtained according to literature methods.[42] *N*,*N*-Dimethylacetamide (DMA) was anhydrous, 99.8% pure.

Synthesis of cores

Compound 2. A mixture (440 mg, 2.1 mmol) of CpFe(η^5-C_5H_4)–($CH{=}CH_2$), **1**, 3, 5-dibromobenzaldehyde (264 mg, 1.0 mmol), anhydrous sodium acetate (213 mg, 2.6 mmol), tetrabutylammonium bromide (20 mg, 0.06 mmol) and palladium pincer catalyst (20 mg, 0.03 mmol) in DMA (15 mL) was heated at 130 °C for 12 h. After removing the solvent under reduced pressure, the product was extracted with a CH_2Cl_2–H_2O–$NaHCO_3$ mixture and the organic phase was dried over $MgSO_4$. Purification was carried out by column chromatography on silica gel, washing with hexane to remove unreacted vinylferrocene **1** and using hexane–CH_2Cl_2 (1 : 1) as eluent to afford pure compound **2**. Yield: 72%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.07 (s, 1H, CHO); 7.82 (s, 2H, C_6H_3); 7.67 (s, 1H, C_6H_3); 7.05 (d, 2H, $^3J_{\text{H-H}} = 16.2$ Hz, CH=CH); 6.75 (d, 2H, $^3J_{\text{H-H}} = 16.2$, CH=CH); 4.52 (s, 4H, C_5H_4); 4.35 (s, 4H, C_5H_4); 4.18 (s, 10H, C_5H_5). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 67.8, 70.0 (18C, C_5H_4 and C_5H_5); 83.3 (2Cq, C_5H_4); 125.1, 125.4, 129.7, 129.9 (7C, CH=CH and C_6H_4); 137.9, 139.9 (3Cq, C_6H_4); 193.2 (1C, CHO). Anal. calcd for compound **2**, $C_{31}H_{26}Fe_2O$, $M_w = 526.24$: C, 70.8; H, 4.98; found: C, 70.9; H, 4.99. FABMS: *m*/*z* 526 (M^+).

Compound 3. To an ice-cold solution of $[Ph_3P^+CH_3]I^-$ (324 mg, 0.8 mmol) in THF (50 ml), potassium *tert*-butoxide (112 mg, 1.0 mmol) was added and the resulting solution stirred for 30 min. at 0 °C and 30 min. at room temperature. The aldehyde **2** (421 mg, 0.8 mmol) was added at 0 °C and the resulting solution stirred overnight at room temperature. After removing the solvent under reduced pressure, the product was extracted with CH_2Cl_2–H_2O–$NaHCO_3$ and dried over $MgSO_4$. The title compound was purified by column chromatography on silica gel using hexane–CH_2Cl_2 (7 : 3) as eluent. Recrystallization from CH_2Cl_2–hexane afforded pure compound **3**. Yield: 65%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.40 (s, 1H, C_6H_3); 7.36 (s, 2H, C_6H_3); 6.48 (d, 2H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.76–6.71 (m, 3H, CH=CH, CH=CH_2); 5.85 (d, 1H, $^3J_{\text{H-H}} = 17.5$ Hz, CH=CH_2); 5.32 (d, 1H, $^3J_{\text{H-H}} = 11.0$ Hz, CH=CH_2); 4.53 (s, 4H, C_5H_4); 4.36 (s, 4H, C_5H_4); 4.19 (s, 10H, C_5H_5). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 67.7, 69.8, 70.0 (18C, C_5H_4 and C_5H_5); 84.2 (2Cq, C_5H_4); 114.8, 122.9, 123.5, 126.6, 128.0, 139.0 (9C, CH=CH, CH=CH_2 and C_6H_4); 137.5, 138.9 (3Cq, C_6H_4). Anal. calcd for compound **3**, $C_{32}H_{28}Fe_2$, $M_w = 524.27$: C, 73.3; H, 5.38; found: C, 73.5; H, 5.39. FABMS: *m*/*z* 524 (M^+).

Compound 5-Br$_3$. 4-Bromoacetophenone (20 g, 100.5 mmol), 1 mL of H_2SO_4(c) and $K_2S_2O_7$ (30 g, 118 mmol) were heated at 180 °C for 14 h. The resulting crude solid was cooled to room temperature and refluxed in 100 mL of EtOH for 1 h. The solution was filtered and the resulting solid was refluxed in 100 mL of H_2O, yielding a pale-yellow solid that was filtered, dried under vacuum and recrystallized in $CHCl_3$. Yield 80%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.72 (s, 3H, C_6H_3); 7.63 (d, 6H, $^3J_{\text{H-H}} = 8.5$ Hz, C_6H_4); 7.55 (d, 6H, $^3J_{\text{H-H}} = 8.5$ Hz, C_6H_4). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 122.4 (3Cq, C_6H_4–Br); 125.2 (3C, C_6H_3); 129.1 (6C, C_6H_3), 132.3 (3Cq, C_6H_4); 139.9 (3Cq, C_6H_4); 141.8 (3Cq, C_6H_4).

General procedure for the synthesis of G1 dendrimers

A mixture of the olefin (**1** or **3**), the tri- or hexabromide core (**5-Br$_3$** or **6-Br$_6$**), anhydrous sodium acetate (NaOAc), tetrabutylammonium bromide (TBABr), and the pincer palladium catalyst in DMA (15 mL) was heated at 130 °C for 15 to 20 h. After removing the solvent under reduced pressure, the product was extracted with a CH_2Cl_2–H_2O–$NaHCO_3$ mixture and the organic phase was dried over $MgSO_4$. Purification was carried out by column chromatography on silica gel and the product recrystallized from CH_2Cl_2–hexane.

Compound 7-Fc$_3$. Olefin **1** (400 mg, 1.89 mmol), core **5-Br$_3$** (342 mg, 0.63 mmol), NaOAc (233 mg, 2.8 mmol), TBABr (20 mg, 0.06 mmol), DMA (15 mL), and palladium pincer catalyst (20 mg, 0.03 mmol) were used. Eluent used in the purification by column chromatography was hexane–CH_2Cl_2 (1 : 9). Yield 72%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.82 (s, 3H, C_6H_3); 7.70 (d, 6H, $^3J_{H\text{-}H} = 7.5$ Hz, C_6H_4); 7.57 (d, 6H, $^3J_{H\text{-}H} = 7.5$ Hz, C_6H_4); 6.97 (d, 3H, $^3J_{H\text{-}H} = 16.5$ Hz, CH=CH); 6.77 (d, 3H, $^3J_{H\text{-}H} = 16.5$, CH=CH); 4.53 (s, 6H, C_5H_4); 4.34 (s, 6H, C_5H_4); 4.19 (s, 15H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.7, 69.7, 70.1 (27C, C_5H_4 and C_5H_5); 84.3 (3Cq, C_5H_4); 125.2, 126.2, 127.0, 128.0, 128.2 (21C, CH=CH, C_6H_4 and C_6H_3); 137.9, 140.1, 142.7 (9Cq, C_6H_4, C_6H_3). Anal. calcd for compound **7-Fc$_3$**, $C_{60}H_{48}Fe_3$, $M_w = 936.58$: C, 76.9; H, 5.17; found: C, 76.8; H, 5.16. FABMS: m/z 935 (M^+).

Compound 8-Fc$_6$. Olefin **1** (500 mg, 2.36 mmol), core **6-Br$_6$** (306 mg, 0.40 mmol), NaOAc (295 mg, 3.6 mmol), TBABr (20 mg, 0.06 mmol), DMA (15 mL) and palladium pincer catalyst (20 mg, 0.03 mmol) were used. Eluent used in the purification by column chromatography was hexane–CH_2Cl_2 (7 : 3). Yield 68%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.45–7.30 (m, 12H, C_6H_3); 6.88 (d, 6H, $^3J_{H\text{-}H} = 16.2$ Hz, CH=CH); 6.70 (d, 6H, $^3J_{H\text{-}H} = 16.2$, CH=CH); 4.49 (s, 12H, C_5H_4); 4.31 (s, 12H, C_5H_4); 4.16 (s, 30H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.7, 70.0, 70.2 (54C, C_5H_4 and C_5H_5); 84.6 (6Cq, C_5H_4); 126.42, 126.8, 127.4, 129.2, 129.5 (24C, CH=CH and C_6H_4); 132.6, 133.5, 138.4 (12Cq, C_6H_4). Anal. calcd for compound **8-Fc$_6$**, $C_{96}H_{78}Fe_6$, $M_w = 1566.76$: C, 73.6; H, 5.02; found: C, 73.5; H, 5.03. FABMS: m/z 1567 (M^+).

Compound 9-Fc$_6$. Olefin **3** (400 mg, 0.76 mmol), core **5-Br$_3$** (138 mg, 0.25 mmol), NaOAc (98 mg, 1.2 mmol), TBABr (20 mg, 0.06 mmol), DMA (15 mL) and palladium pincer catalyst (20 mg, 0.03 mmol) were used. Eluent used in the purification by column chromatography was hexane–CH_2Cl_2 (5 : 6). Yield 62%. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 7.95 (s, 3H, C_6H_3); 7.84 (d, 6H, $^3J_{H\text{-}H} = 8.0$ Hz, C_6H_4); 7.75 (d, 6H, $^3J_{H\text{-}H} = 8.1$ Hz, C_6H_4); 7.37 (d, 3H, $^3J_{H\text{-}H} = 16.0$ Hz, CH=CH); 7.21 (d, 3H, $^3J_{H\text{-}H} = 16.0$, CH=CH); 7.05 (d, 6H, $^3J_{H\text{-}H} = 15.9$ Hz, CH=CH); 6.80 (d, 6H, $^3J_{H\text{-}H} = 16.2$, CH=CH); 4.55 (t, $^3J_{H\text{-}H} = 1.8$ Hz, 12H, C_5H_4); 4.34 (t, $^3J_{H\text{-}H} = 1.8$ Hz, 12H, C_5H_4); 4.20 (s, 30H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 67.0, 69.3, 69.5 (54C, C_5H_4 and C_5H_5); 83.5 (6Cq, C_5H_4); 122.5, 122.7, 124.7, 125.8, 127.0, 127.4, 127.5, 128.3, 128.8 (42C, CH=CH and C_6H_4); 136.6, 137.7, 138.4, 140.1, 141.8 (18Cq, C_6H_4). Anal. calcd for compound **9-Fc$_6$**, $C_{120}H_{96}Fe_6$, $M_w = 1873.16$: C, 76.9; H, 5.17; found: C, 77.0; H, 5.19. FABMS: m/z 1871 (M^+).

Compound 10-Fc$_{12}$. Olefin **3** (600 mg, 1.14 mmol), core **6-Br$_6$** (148 mg, 0.19 mmol), NaOAc (140 mg, 1.7 mmol), TBABr (20 mg, 0.06 mmol), DMA (15 mL) and palladium pincer catalyst (20 mg, 0.03 mmol) were used. Eluent used in the purification by column chromatography was hexane–CH_2Cl_2 (3 : 7). Yield 55%. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 8.23, 8.16, 8.03, 7.97, 7.89 (s, 30H, C_6H_3); 7.45 (m, 12H, CH=CH); 7.02 (d, 12H, $^3J_{H\text{-}H} = 16.2$ Hz, CH=CH); 6.77 (d, 12H, $^3J_{H\text{-}H} = 15.9$ Hz, CH=CH); 4.50 (s, 24H, C_5H_4); 4.30 (s, 24H, C_5H_4); 4.16 (s, 60H, C_5H_5). ^{13}C-NMR (300 MHz, CD_2Cl_2): δ 67.7, 69.9 (108C, C_5H_4 and C_5H_5); 83.9 (12Cq, C_5H_4); 143.0, 142.8, 139.6, 138.4, 130.2, 129.0, 128.3, 126.1, 125.3, 123.3, 123.0 (96C, CH=CH and C_6H_3). Anal. calcd for compound **10-Fc$_{12}$**, $C_{216}H_{174}Fe_{12}$, $M_w = 3439.92$: C, 75.4; H, 5.10; found: C, 75.5; H, 5.13. FABMS: m/z 3440 (M^+).

Table 3 Selected crystallographic data for **2** and **3**

	2	**3**
Empirical formula	$C_{31}H_{26}Fe_2O$	$C_{32}H_{28}Fe_2$
FW/g mol^{-1}	526.22	524.24
T/K	293(2)	293(2)
λ/Å	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	18.624(3)	19.198(2)
b/Å	11.2643(17)	11.1627(12)
c/Å	11.6667(16)	11.5538(12)
α/deg.	90	90
β/deg.	106.174(3)	102.890(2)
γ/deg.	90	90
U/Å^3	2350.6(6)	2413.6(4)
Z	4	4
μ/mm^{-1}	1.257	1.221
Collect. Reflect.	12 559	14 849
Indep. Reflect.	3994	4926
R_{int}	0.0512	0.0367
R_1 [$I > 2\sigma(I)$] R_1 [$I > 2\sigma(I)$]	0.0479	0.0333
wR_2 [$I > 2\sigma(I)$] wR_2 [$I > 2\sigma(I)$]	0.1135	0.0763
R_1 (all data)	0.0758	0.0565
wR_2 (all data)	0.1226	0.0939

X-Ray diffraction studies

Single crystals were grown by slow evaporation of hexane–CH_2Cl_2 mixtures and mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monocromated Mo-Kα radiation ($\lambda = 0.71073$ Å) with a nominal crystal-to-detector distance of 4.0 cm. A hemisphere of data was colleted based on three ω-scan runs (starting $\omega = -28°$) at values of $\phi = 0°$, 90° and 180° with the detector at $2\theta = 28°$. In each of these runs, frames (606, 435 and 230 respectively) were collected at 0.3° intervals and for 40 s per frame for compound **2** and 30 s per frame for compound **3**. Space group assignments are based on systematic absences, E statistics and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package.[44a] All non-hydrogen were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection and cell dimensions are given in Table 3. The diffraction frames were integrated using the SAINT package[44b] and corrected for absorption with SADABS.[44c]

CCDC reference numbers 178989 and 178990. See http://www.rsc.org/suppdata/nj/b1/b108142j/ for crystallographic data in CIF or other electronic format.

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