New phosphorus-containing dendrimers with ferrocenyl units in each layer

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Abstract – New phosphorus-containing dendrimers bearing ferrocenyl units within the branches were synthesised using a new 1,1'-disubstituted ferrocenyl building block. The structure of one of the synthetic intermediates was determined by X-ray analysis. In every case, one single oxidation was observed for each ferrocenic layer, corresponding to the independent oxidation of all ferrocenes within one layer to ferroceniums. The oxidation potential for a particular layer depends on substituents on ferrocenes, but not on their localisation within the dendrimers. *To cite this article: C.-O. Turrin et al., C. R. Chimie 5 (2002) 309–318* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

ferrocene / X-ray structure / dendrimers / phosphorus

Résumé – De nouveaux dendrimères phosphorés possédant des groupes ferrocényles dans chaque branche ont été synthétisés (jusqu'à deux couches de ferrocènes). Pour cela, une « brique de construction ferrocénique », possédant un groupe formyle sur un des cycles cyclopentadiényle et une fonction phénol liée à l'autre cycle cyclopentadiényle par un lien vinylique, a été synthétisée avec un excellent rendement (83 %), en quatre étapes, à partir du 2-(1'-formylferrocenyl)-1,3-dioxolane. La structure d'un des intermédiaires de cette synthèse a été déterminée par diffraction des rayons X. De plus, une étude électrochimique montre que, pour chaque dendrimère, tous les ferrocènes pour une couche donnée sont oxydés au même potentiel, indiquant l'absence de communication électronique entre les différents centres métalliques. Les potentiels d'oxydation dépendent des substituants directement liés au ferrocène et non de la localisation de la couche à l'intérieur du dendrimère. *Pour citer cet article : C.-O. Turrin et al., C. R. Chimie 5 (2002) 309–318* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

ferrocène / rayons X / dendrimères / phosphore

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1. Results and discussion

1.1. Introduction

In the last few years, dendrimers have generated an exponentially growing interest because of the unique and fascinating properties of these highly branched and well-defined macromolecules [1–4]. Amongst the numerous dendrimers that have already been synthesised, structures bearing organometallic centres attract particular attention owing to the specific physical properties of metals [5–10]. Ferrocenyl dendrimers appear to be especially interesting, because of the unique features of ferrocene, like its high thermal stability or its well-defined electrochemistry [11–12]. Furthermore, since the discovery of ferrocene, 50 years ago, progresses in synthetic procedures gave way to a very large variety of ferrocenyl derivatives. A very large range of substituents can be now selectively introduced on the desired position on ferrocene [13–16]. Consequently, ferrocenes found many applications in various fields, especially materials chemistry and asymmetric catalysis.

One ferrocenyl layer has been efficiently grafted on the surface of various kinds of dendrimers like

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silicon-based dendrimers [11, 12, 17, 18], polyamine dendrimers [11, 12, 19], polyarylether dendrimers [20, 21], polybenzyl dendrimers [22], small dendrimers with a polyester [23], an adamantane [24], a cyclophosphazene [25] or a tetraphenylmethane core [26]. Even organometallic species like an organoplatinum dendrimer [27] or ferrocene itself [28] have been covered by a ferrocenyl layer. These dendrimers are often rather small, but up to 243 ferrocenes could be attached [21]. Some of these dendrimers have been deposited onto electrode surfaces or used in carbon paste electrodes as mediators for amperometric biosensors [11, 12]. Some have been used as CO gas sensors [18]. Cholesteric first generation dendrimers have been found to be liquid crystals [23]. Some polybenzyl dendrimers are suitable to recognise small inorganic anions [22, 29, 30] and chiral dendrimers proved to be excellent catalysts for asymmetric hydrogenation [24, 25].

Recently, we also synthesised new phosphorus-containing dendrimers with various ferrocenyl units (eventually chiral) on the periphery [31, 32]. The 11th generation was reached meaning a theoretical number of ferrocenes up to 6144! The ferrocenyl units were easily grafted on the surface of the dendrimers by nucleophilic substitution of the phenol function borne by the ferrocenyl building block on P–Cl bonds of the dendrimers following a methodology developed by some of us [33–39].

In contrast to the grafting of ferrocenyl units on the periphery of dendrimers, which has been so often studied, very few publications deal with the presence of ferrocene only at the core of a dendrimer. A third generation dendron has been reported [40, 41]. Some carbosilane dendrimers of various sizes (up to the fourth generation) build up around a 1,1'-diphenylphosphinoferrocene (dppf) core were also described and successfully used for palladium-catalysed allylic substitution [42]. We also described a first generation phosphorus-containing dendrimer built from 1,1'-diphenylphosphinoferrocene [43] and a family of dendrimers built from 1,1'-ferrocenecarboxaldehyde up to the fourth generation [31].
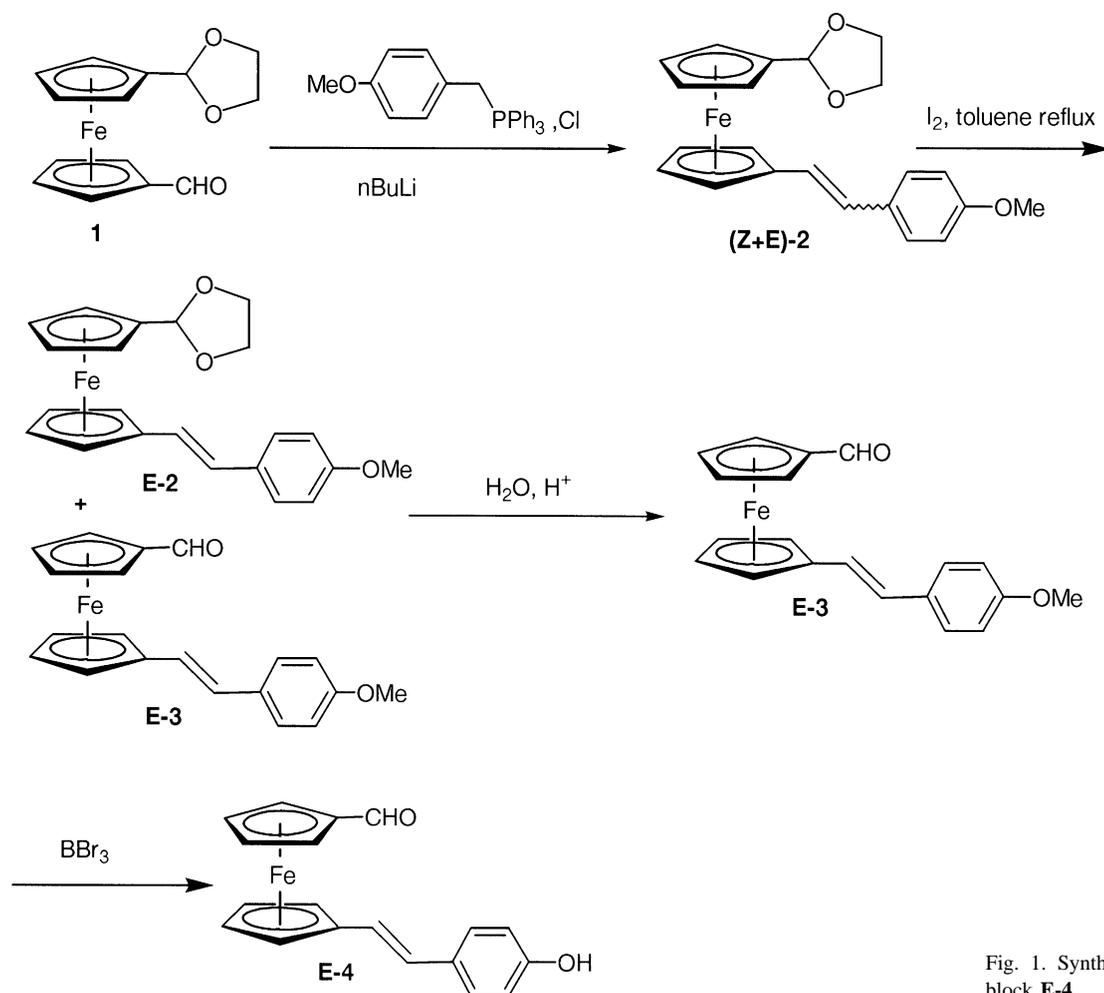

Fig. 1. Synthesis of the building block **E-4**.

Moreover, we described the only example of dendrimers having ferrocenes at each layer within the branches up to the second generation [31] as well as dendrimers having a single ferrocenyl layer located at a precise level within the dendritic structure [44]. The synthesis was based on the use of a ferrocenyl building block bearing a phenol function and a formyl group, namely 1'-(4-hydroxyphenyl)ferrocenecarboxaldehyde. We want now to disclose our results using a new building block **E-4** (Fig. 1) where the hydroxyphenyl part is tethered to the ferrocenecarboxaldehyde part by a vinyl link.

1.2. Synthesis of the ferrocenyl building block

Our synthetic target was compound **E-4** (Fig. 1). If the synthesis of symmetrically 1,1'-disubstituted ferrocenes is well documented and often easy by electrophilic trapping of the readily available 1,1'-dilithioferrocene [45], access to non-symmetrically 1,1'-disubstituted ferrocenes is trickier. Amongst the different methods described in the literature [15], we chose to use compound **1**, which allowed us to synthesise successfully similar 1'-styrylferrocenecarboxaldehyde [46]. The action of 4-methoxybenzyltriphenylphosphonium chloride in the presence

of *n*-BuLi yielded quantitatively compound **2** as a mixture of diastereoisomer (**E/Z** = 1) by a Wittig reaction. This mixture of **E-2** and **Z-2** was treated with I_2, following a procedure already successfully applied to the (**Z+E→E**) isomerisation of several styrylferrocenes [47, 48]. In these conditions, although the isomerisation was complete, the acetal ring has been partly hydrolysed into the corresponding aldehyde **E-3** (Fig. 1). The mixture of **E-2** and **E-3** was completely converted to **E-3** with an excellent yield (98% from the (**E+Z**)-**2** mixture) by acidic hydrolysis. The expected phenol **E-4** was finally synthesised by deprotection of the methoxy group of **E-3** with BBr_3 [49]. In conclusion, **E-4** could be obtained conveniently and efficiently in four steps with a really good overall yield (83% from **1**).

Crystals of **E-2** suitable for X-ray analysis were obtained by slow diffusion of hexane into a dichloromethane solution of **E-2**. The X-ray structure confirms the nature of this intermediate. In particular, the E configuration of the ethylenic fragment, which was deduced from the $^1H–^1H$ NMR coupling constants, was directly proved. A molecular view of compound **E-2** is shown in Fig. 2 with an atom-labelling scheme, whereas selected bond lengths and angles are given in
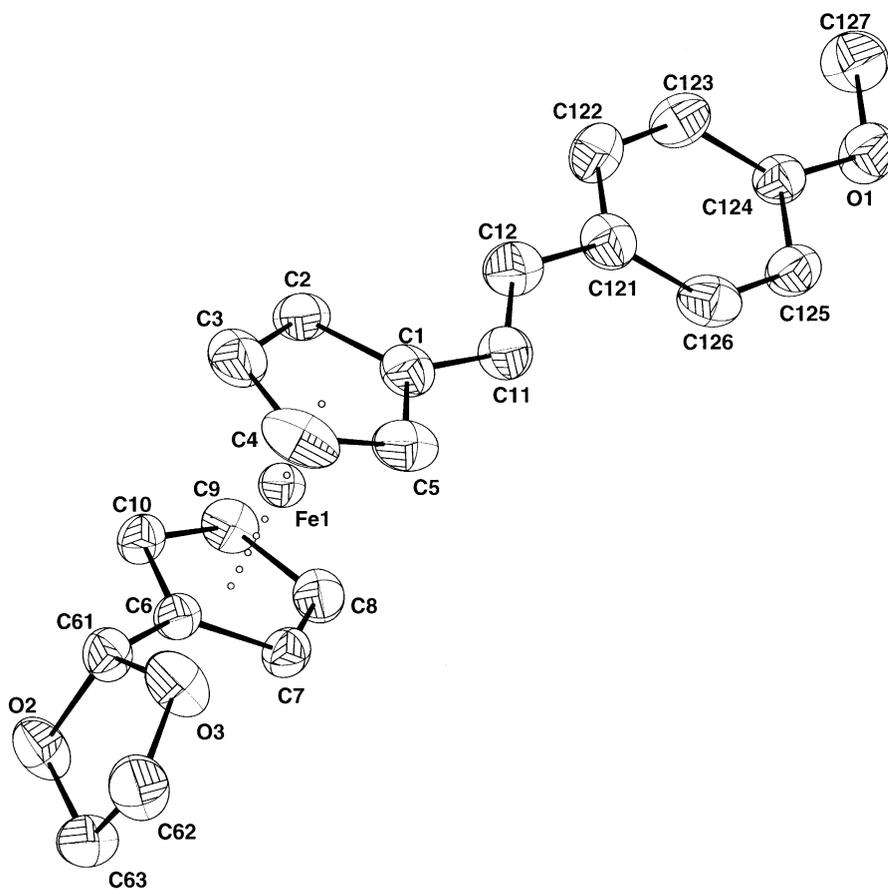

Fig. 2. Molecular view of compound **E-2** showing atoms labelling scheme. Ellipsoids are drawn at 50% probability. Hydrogens are omitted for clarity.

Table 1. Bond lengths (Å) and bond angles (°) for **E-2**. E.s.d.s in parentheses refers to the last significant digit.

O(1)–C(124)	1.366(4)	C(6)–C(61)	1.501(4)
O(1)–C(127)	1.420(4)	C(7)–C(8)	1.411(4)
O(2)–C(61)	1.412(4)	C(8)–C(9)	1.416(4)
O(2)–C(63)	1.414(5)	C(9)–C(10)	1.428(4)
O(3)–C(61)	1.419(4)	C(11)–C(12)	1.298(5)
O(3)–C(62)	1.419(4)	C(12)–C(121)	1.495(5)
C(1)–C(2)	1.414(5)	C(62)–C(63)	1.498(6)
C(1)–C(5)	1.425(5)	C(122)–C(121)	1.369(5)
C(1)–C(11)	1.469(4)	C(122)–C(123)	1.388(4)
C(2)–C(3)	1.399(5)	C(125)–C(124)	1.388(5)
C(3)–C(4)	1.398(6)	C(125)–C(126)	1.384(4)
C(4)–C(5)	1.413(5)	C(124)–C(123)	1.382(4)
C(6)–C(7)	1.419(4)	C(126)–C(121)	1.394(5)
C(6)–C(10)	1.417(4)		
C(124)–O(1)–C(127)	117.8(2)	C(1)–C(11)–C(12)	123.3(3)
C(61)–O(2)–C(63)	107.4(3)	C(11)–C(12)–C(121)	127.7(3)
C(61)–O(3)–C(62)	107.0(3)	O(2)–C(61)–O(3)	107.7(3)
C(2)–C(1)–C(5)	106.9(3)	O(2)–C(61)–C(6)	112.9(3)
C(2)–C(1)–C(11)	129.5(3)	O(3)–C(61)–C(6)	110.1(2)
C(5)–C(1)–C(11)	123.5(3)	O(3)–C(62)–C(63)	103.1(3)
C(1)–C(2)–C(3)	108.6(3)	O(2)–C(63)–C(62)	102.8(3)
C(2)–C(3)–C(4)	108.6(3)	C(121)–C(122)–C(123)	122.1(3)
C(3)–C(4)–C(5)	108.0(3)	C(124)–C(125)–C(126)	120.0(3)
C(1)–C(5)–C(4)	108.0(3)	O(1)–C(124)–C(125)	116.4(3)
C(7)–C(6)–C(10)	108.3(2)	O(1)–C(124)–C(123)	124.2(3)
C(7)–C(6)–C(61)	127.2(3)	C(125)–C(124)–C(123)	119.4(3)
C(10)–C(6)–C(61)	124.4(2)	C(125)–C(126)–C(121)	121.1(3)
C(6)–C(7)–C(8)	107.8(2)	C(12)–C(121)–C(122)	117.3(3)
C(7)–C(8)–C(9)	108.6(2)	C(12)–C(121)–C(126)	124.7(3)
C(8)–C(9)–C(10)	107.6(3)	C(122)–C(121)–C(126)	117.9(3)
C(6)–C(10)–C(9)	107.7(2)	C(122)–C(123)–C(124)	119.5(3)

Table 1. The (4-methoxyphenyl)ethenyl part is slightly out of plane to the ferrocenyl group resulting in a slightly twisted conformation with a dihedral angle of 7.9°. Such twisted conformation seems to be general for all previously reported complexes with values ranging from 4.8° to 48.1 [46–48]. The value observed for **E-2** indicates occurrence of a strong conjugation in the π system. It is worth pointing out that the methyl of the methoxy moiety deviates only from the phenyl plane by–0.024 Å, probably resulting in an optimised overlap between the oxygen lone pairs and the aromatic π system. The five-member dioxane ring is twisted with respect to the Cp ring to which it is attached resulting in a dihedral angle of 102.53°. There is no special feature within the ferrocene fragment.

1.3. Synthesis of the phosphorus-containing dendrimers

The action of a small excess of the sodium salt of **E-4** on trichlorophosphane sulphide yields quantitatively the trialdehyde **5-G'$_0$**. The formyl groups of **5-G'$_0$** allow the condensation with the –NH$_2$ group of dichlorothiophosphorhydrazide **6** to yield the first generation dendrimer **5-G$_1$** (Fig. 3). The reiteration of the

sequence of reactions was attempted on **5-G$_1$**. Dendrimer **5-G'$_1$** was obtained in good yield. However, reaction of **5-G'$_1$** with dichlorothiophosphorhydrazide always failed to yield the product of complete condensation, i.e. the second-generation dendrimer. The dendrimer **5-G'$_1$** is only slightly soluble in the solvent of the reaction (chloroform), therefore, the reaction is slow. Furthermore, **5-G'$_1$** is not stable enough in chloroform to sustain a prolonged time of reaction and it is not possible to use another solvent since the dichlorothiophosphorhydrazide **6** is stable only in solution in chloroform. The syntheses of dendrimers **5-G'$_0$**, **5-G$_1$** and **5-G'$_1$** are monitored by NMR. The substitution of chlorine by the phenolate induces a shielding of the signal in ^{31}P NMR (from $\delta = 62.0$ ppm for **5-G$_1$** to $\delta = 61.3$ ppm for **5-G'$_1$**). An intermediate signal at $\delta = 67.7$ ppm, corresponding to the monosubstitution on each P(S)Cl$_2$ end group, is observed during the course of the reaction and diminishes gradually to disappear totally at the end of the reaction. The condensation step is mainly monitored by ^{1}H NMR and IR, both techniques indicating the disappearance of the signal of the formyl group.

1.4. Electrochemistry

The cyclic voltammogram of dendrimer **5-G'$_0$** shows that the three ferrocenyl moieties are reversibly oxidised at the same potential ($E^{1/2} = 0.73$ V; $I_{pc}/I_{pa} = 1$ and $\Delta E_p = 0.08$ V, Table 2 and Fig. 4), indicating the absence of electronic communication. Bulk electrolysis at controlled potential ($E = E^{1/2} + 0.2$ V) confirmed the presence of three equivalent electroactive groups, 100% of the theoretical three electrons per molecule being actually transferred at this potential. Such experiment affords a stable and soluble tris ferrocenium dendrimer in the mixture of solvent (THF/acetone, 2:1).

Dendrimer **5-G'$_0$**, which possesses two layers of ferrocenyl moieties, exhibits a first wave at $E^{1/2} = 0.59$ V and a second one at $E^{1/2} = 0.75$ V, with a stripping band ($I_{pc}/I_{pa} \approx 2$) indicating drastic changes in the solubility properties of the ferroceniums (Fig. 5). The presence of two different waves unambiguously proves that both layers behave independently. The difference between both $E^{1/2}$ values can be well explained by the difference of electronic properties between formyl and hydrazido groups. Indeed, the replacement of the aldehyde groups by the hydrazido groups increases the electronic density of the first layer's metallic moieties. Consequently, their potential is shifted from 0.73 V (dendrimer **5-G'$_0$**) to 0.59 V (dendrimer **5-G'$_1$**), whereas the six electroactive complexes located in the second layer of **5-G'$_1$** are oxidised at 0.75 V. Similar results were already found for similar dendrimers [31]. Bulk electrolysis at controlled
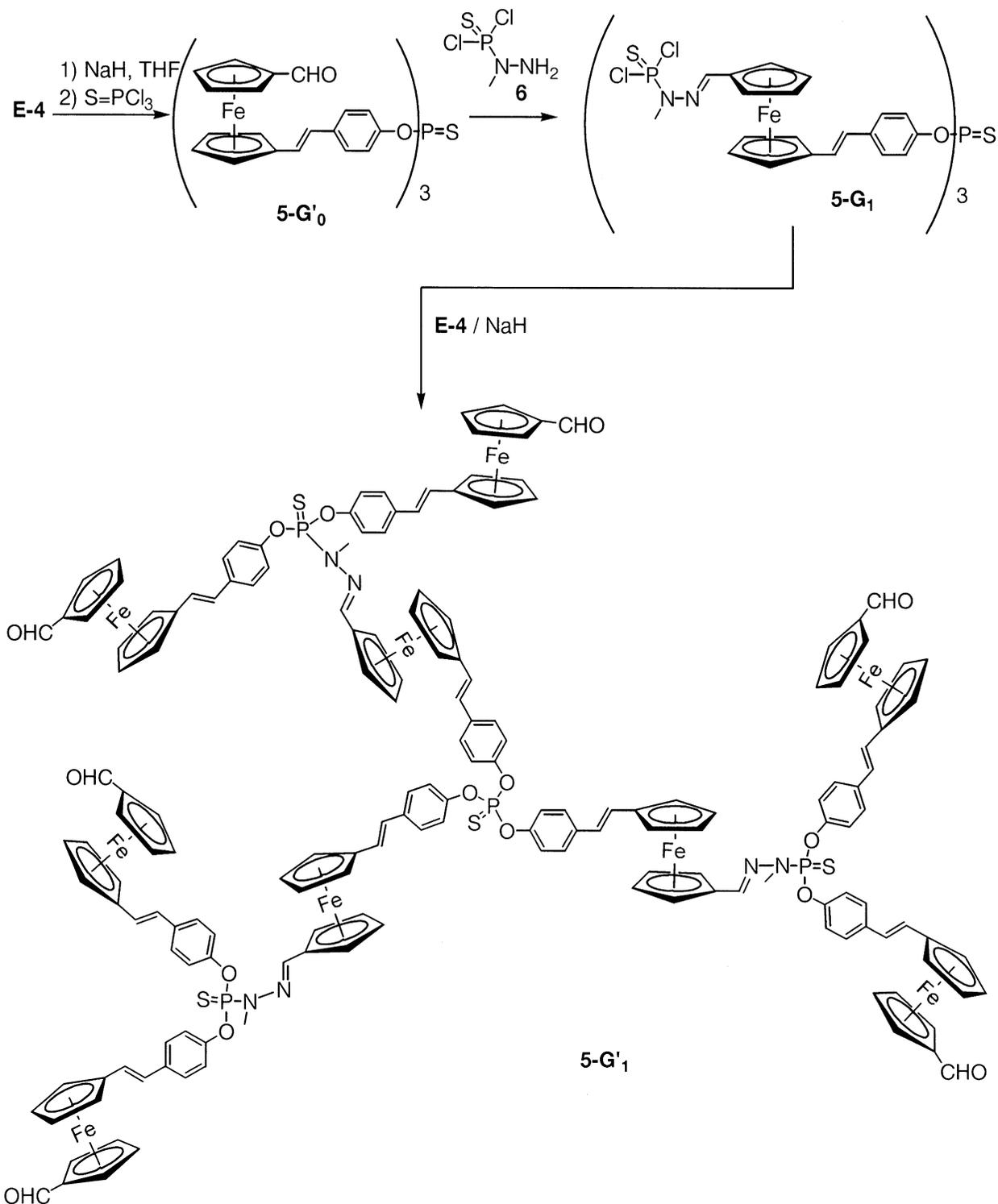
Fig. 3. Synthesis of the dendrimers **5-G'$_0$**, **5-G$_1$** and **5-G'$_1$**.
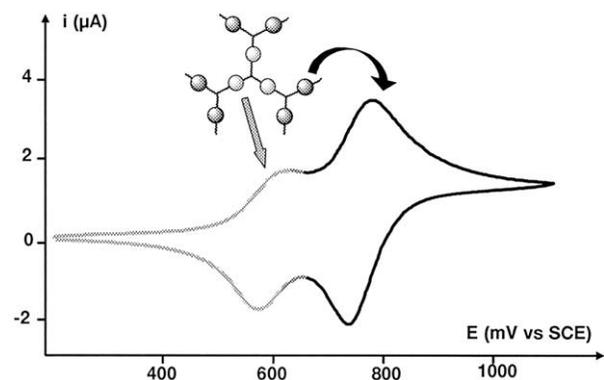
potential allowed to count three electrons (with a 95% oxidation ratio) involved in the first transfer: this fact confirms the assignment of this signal to the first layer. Further bulk electrolysis of this dendrimer containing three $Fe^{(III)}$ and six $Fe^{(II)}$ moieties was impossible to perform due to deposition upon the Pt working electrode. Nevertheless, using square wave voltammetry technique, we could assign the second wave to the ferrocenes of the second layer, comparing current peak intensities. As shown in Fig. 6, the sec-

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Table 2. Electrochemical measurements from voltammograms of dendrimers **5-G'$_0$** and **5-G'$_1$**.

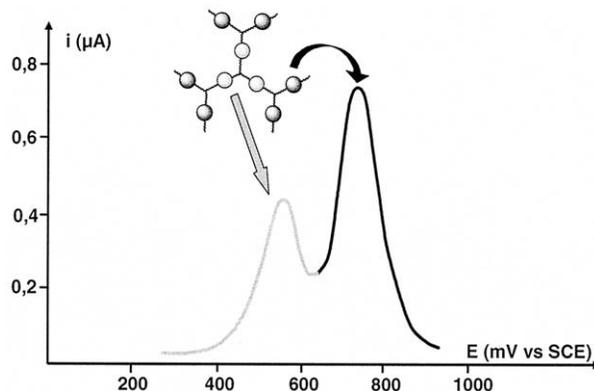| Compound	e [a]	E_{pc} [b]	E_{pa} [b]	$E^{1/2}$	ΔE_p [c]	I_{pc}/I_{pa}	Electrolysis[d] (%)
5-G'$_0$	3	0.69	0.77	0.73	0.08	1	100
5-G'$_1$ first layer	3	0.57	0.61	0.59	0.04	1.6	92
5-G'$_1$ second layer	6	0.72	0.78	0.75	0.06	1.9	—

[a] Number of electrons theoretically involved. [b] Peak potentials (V/SCE) at room temperature as determined by cyclic voltammetry at a Pt electrode: $E^{1/2}$ (approximated by $(E_{pc} + E_{pa})/2$) in V/SCE; supporting electrolyte nBu$_4$N$^+$BF$_4^-$ (0.1 M) in a mixture of THF/acetone (2:1), scan rate 0.1 V s^{-1}. [c] $(E_{pa} - E_{pc})$, in V. [d] Percentage of FeCp$_2$ sites oxidised in exhaustive coulometry.
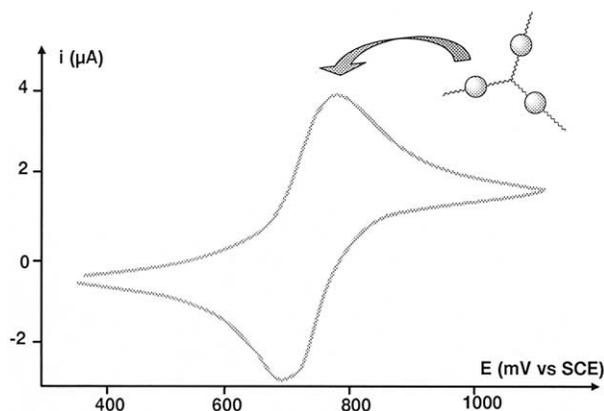
Fig. 4. Cyclic voltammograms (scan rate 100 mV s^{-1}) obtained for compound **5-G'$_0$**.

Fig. 6. Square wave voltammograms (frequency: 50 Hz, potential increment: 10 mV) obtained for compound **5-G'$_1$**.

Fig. 5. Cyclic voltammograms (scan rate 100 mV s^{-1}) obtained for compound **5-G'$_1$**.

ond peak is almost twice as high as the second one. The fact that we do not observe a perfect 1/2 ratio for these signals can be explained by a slight overlapping. However, these results appeared reliable enough to assign each wave of the cyclic voltammogram.

1.5. Conclusion

A new ferrocenyl building block for the synthesis of phosphorus-containing dendrimers bearing ferrocenyl units within the branches was successfully synthesised. The structure of the synthetic intermediate **E-2** was determined by X-ray analysis. Two layers of fer-

rocenes could be introduced on a phosphorus core but any attempts for further growing failed.

Electrochemical studies can differentiate the ferrocenes of the inner layer and of the outer layer which are oxidised at higher potential owing to the presence of electron-withdrawing formyl groups. Surprisingly, oxidation of the inner layers induces drastic changes in the solubility of dendrimers. This behaviour is in marked contrast with most previous observations, indicating that the solubility is mainly governed by the functions located on the surface.

2. Experimental section

2.1. General

All reactions were carried out in the absence of air, using standard Schlenk techniques and vacuum-line manipulations. Commercial samples were used as received. All solvents were dried before use. Thin layer chromatography was carried out on Merck Kieselgel 60F254 precoated silicagel plates. Preparative flash chromatography was performed on Merck Kieselgel. Instrumentation: Bruker AM250 (^{1}H–, ^{13}C– and ^{31}P NMR), Hewlett-Packard HP MSD 7590 (GC/MS), Hewlett-Packard HP 8452A (UV-vis). Elemental analyses were performed by the 'Service d'analyse' of the 'Laboratoire de chimie de coordina-

tion', Toulouse, France. Compounds **1** [46] and **6** [33–39] were synthesised according to published procedures.

2.2. Synthesis of the ferrocenyl building block

2.2.1. 2-(1'-(2-(4-methoxyphenyl)ethenyl)ferrocenyl)-1,3-dioxane 2

In a 250-ml two-necked flask under argon, 4.3 g of 4-methoxybenzyltriphenylphosphonium chloride (11 mmol, 1.5 equiv) were suspended in 90 ml of anhydrous THF. The white suspension was cooled down to –78 °C and 6.5 ml (10.4 mmol) of a 1.6 M solution of *n*-BuLi in pentane was added. After 15 min at –78 °C, the solution was allowed to come back to room temperature and stirred two additional hours at room temperature. The white solution steadily turned bright yellow. The solution was cooled down to 0 °C and then a solution of 1.86 g of **1** (6.52 mmol) in 60 ml of anhydrous THF was added. The reaction mixture was stirred for 18 h at RT. The solution was then diluted by 50 ml of dichloromethane, washed by three 50 ml portions of brine, dried on sodium sulphate and evaporated to yield an orange solid, which was purified by flash chromatography on silicagel. 2.54 g (yield = 99%) of **2** was obtained as a 1:1 mixture of the **Z** and **E** isomers.

The E diastereoisomer can be separated by fractional precipitation and characterised.

¹H NMR (CD$_3$COCD$_3$): δ (ppm) 7.44 (d, J = 8.8 Hz, 2H, Ar); 6.91 (d, J = 8.8 Hz, 2H, Ar); 6.85 (d (AB), J = 16.2 Hz, 1H, vinyl); 6.75 (d (AB), J = 16.2 Hz, 1H, vinyl), 5.68 (s, 1H, OCHO); 4.53 (t, J = 1.8 Hz, 2H, Cp); 4.30 (t, J = 1.8 Hz, 2H, Cp); 4.26 (t, J = 1.8 Hz, 2H, Cp); 4.14 (t, J = 1.8 Hz, 2H, Cp); 4.0–3.85 (m, 4H, CH$_2$); 3.81 (s, 3H, OCH$_3$). **¹³C {¹H} NMR** (CD$_3$COCD$_3$): δ (ppm) 159.3 (quat. Ar); 131.2 (quat. Ar); 127.3 (Ar); 126.2 (vinyl); 124.6 (vinyl); 114.4 (Ar); 102.6 (OCHO); 86.0 (quat. Cp); 85.1 (quat. Cp); 69.8 (Cp); 69.5 (Cp); 68.3 (Cp); 67.7 (Cp); 65.2 (CH$_2$); 55.3 (OCH$_3$). Anal. calcd for C$_{22}$H$_{22}$FeO$_3$: C, 67.70; H, 5.70. Found: C, 67.61; H, 5.53. **MS** (DCI, NH$_3$): m/z = 391 (M+1, 100%).

Isomerisation reaction. Into a one necked round bottom flask equipped with a condenser, were dissolved the mixture of **E** and **Z-2** (1.82 g, 4.66 mmol) in 50 ml of toluene and 10 mol% of I$_2$. The system was purged with argon and the mixture was warmed up to toluene reflux for 30 min. After cooling back to room temperature, the mixture was extracted with methylene chloride, washed with a sodium thiosulfate solution (c = 2 mol l^{-1}), then with brine, dried on sodium sulphate and evaporated. After flash chromatography on silicagel, 1.75 g of a dark red solid containing a mixture of **E-2** and **E-3** was isolated.

2.2.2. 1'-((E)-2-(4-methoxyphenyl)ethenyl)-ferrocenecarboxaldehyde 3

Under argon, the mixture of **E-2** and **E-3** (1.75 g) was dissolved in 30 ml of dichloromethane. To this solution was added a solution of *p*-toluenesulfonic acid (3.50 mmol) in 15 ml of water and the reaction mixture was heated up to 60 °C for 90 min. After cooling back to room temperature, the solution was diluted with 100 ml of ether, washed by three portions of brine, dried on sodium sulphate and evaporated to yield a red oil, which was dissolved in dichloromethane and filtered on celite. The celite was thoroughly washed with dichloromethane. After evaporation, 1.59 g of **E-4** (98% from the (**E+Z**)-**2** mixture, dark red solid) was obtained.

¹H NMR (CDCl$_3$): δ (ppm) 9.89 (s, 1H, CHO); 7.37 (d, J = 8.7 Hz, 2H, Ar); 6.87 (d, J = 8.7 Hz, 2H, Ar); 6.69 (d (AB), J = 16.2 Hz, 1H, vinyl); 6.59 (d (AB), J = 16.2 Hz, 1H, vinyl); 4.74 (t, J = 1.9 Hz, 2H, Cp); 4.52 (m, 4H, Cp); 4.34 (t, J = 1.9 Hz, 2H, Cp); 3.81 (s, 3H, OCH$_3$). **¹³C {¹H} NMR** (CDCl$_3$): δ (ppm) 193.8 (CHO); 159.1 (quat. Ar); 130.1 (quat. Ar); 127.7 (vinyl); 127.3 (Ar); 122.5 (vinyl); 114.2 (Ar); 86.0 (quat. Cp); 79.8 (quat. Cp); 74.4 (Cp); 70.6 (Cp); 70.2 (Cp); 67.9 (Cp); 55.3 (OCH$_3$). Anal. calcd for C$_{20}$H$_{18}$FeO$_2$: C, 69.40; H, 5.24. Found: C, 69.89; H, 5.52. **MS** (DCI, NH$_3$): m/z = 364 (M+NH$_4$, 100%), 347 (M+H, 89%).

2.2.3. 1'-((E)-2-(4-hydroxyphenyl)ethenyl)-ferrocenecarboxaldehyde 4

In a Schlenk tube under argon, 1.40 g of **E-3** (4.04 mmol) was dissolved in 40 ml of dry dichloromethane and the solution was cooled down to –78 °C. 15 ml of a molar solution of boron tribromide in pentane (15 mmol, 3.5 equiv) were then added. The brown solution was allowed to come back to room temperature and kept during 45 min at this temperature. The solution was then thrown in an ice/water bath, stirred during 15 min, washed three times with an aqueous 1 N solution of sodium thiosulfate, then by three portions of brine, dried on sodium sulphate and evaporated to yield a red solid which was purified by flash chromatography on silicagel (eluent = pentane/ether). 1.13 g (yield = 85%) of **4** was obtained as a dark red powder.

¹H NMR (CDCl$_3$): δ (ppm) 9.89 (s, 1H, CHO); 7.30 (d, J = 8.5 Hz, 2H, Ar); 6.80 (d, J = 8.5 Hz, 2H, Ar); 6.64 (d (AB), J = 16.2 Hz, 1H, vinyl); 6.57 (d (AB), J = 16.2 Hz, 1H, vinyl), 5.46 (s, 1H, OH); 4.75 (t, J = 1.8 Hz, 2H, Cp); 4.57 (t, J = 1.8 Hz, 2H, Cp); 4.53 (t, J = 1.8 Hz, 2H, Cp); 4.34 (t, J = 1.8 Hz, 2H, Cp). **¹³C {¹H} NMR** (CDCl$_3$): δ (ppm) 194.1 (CHO); 155.2 (quat. Ar); 130.1 (quat. Ar); 127.7 (vinyl); 127.4 (Ar); 122.4 (vinyl); 115.6 (Ar); 86.0 (quat. Cp);
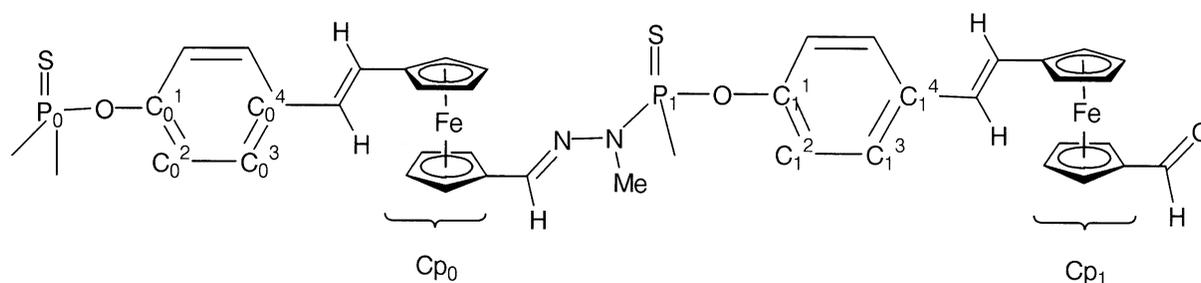
Fig. 7. Numbering scheme used for NMR.

79.6 (quat. Cp); 74.1 (Cp); 70.6 (Cp); 70.2 (Cp); 67.9 (Cp). Anal. calcd for $C_{19}H_{16}FeO_2$: C, 68.70; H, 4.85. Found: C, 68.49; H, 4.75. **MS** (DCI, NH_3): $m/z = 350$ ($M+NH_4$, 100%), 333 (M+H, 73%). **IR** (KBr pellet): 1646 cm^{-1}.

2.3. Synthesis of the phosphorus-containing dendrimers

The numbering scheme used for NMR is depicted in Fig. 7.

2.3.1. Compound 5-G'$_0$

To a solution of trichlorophosphane sulphide (32 μL, 0.315 mmol) in THF (10 ml) at 0 °C was added dropwise a slight excess of the sodium salt of **E-4** (358 mg, 1.006 mmol) in solution in THF (15 ml). The reaction mixture was stirred overnight at room temperature. After centrifugation and solvent removal under reduced pressure, the crude product was washed with a mixture of pentane and ether (1:1) and then with methanol to afford **5-G'$_0$** as a red powder (yield = 82%).

^{31}**P** {^{1}**H**} **NMR** (CDCl$_3$): δ (ppm) 53.1 (s, P$_0$). ^{1}**H NMR** (CDCl$_3$). δ (ppm) 9.89 (s, 3H, CHO); 7.45 (d, $^3J_{HH} = 8.5$ Hz, 6H, C$_0^3$–H); 7.21 (dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HP} = 1.6$ Hz, 6H, C$_0^2$–H); 6.70 (s, 6H, CH=CH); 4.75 (t, $^3J_{HH} = 1.9$ Hz, 6H, Cp$_0$–H); 4.54 (m, 12H, Cp$_0$–H); 4,36 (t, $^3J_{HH} = 1.9$ Hz, 6H, Cp$_0$–H). ^{13}**C** {^{1}**H**} **NMR** (CDCl$_3$): δ (ppm) 193.8 (s, CHO); 149.6 (d, $^2J_{CP} = 7.0$ Hz, C$_0^1$); 135.1 (s, C$_0^4$); 127.2 (s, C$_0^3$); 126.8 (s, CH=CH); 125.5 (s, CH=CH); 121.4 (d, $^3J_{CP} = 4.5$ Hz, C$_0^2$); 85.1 (s, quat C̲p$_0$–CH=N); 79.8 (s, quat C̲p$_0$–CH=CH); 74.4 (s, Cp$_0$); 70.6 (s, Cp$_0$); 70.5 (s, Cp$_0$); 68.2 (s, Cp$_0$). Anal. calcd for $C_{57}H_{45}Fe_3O_6PS$: C, 64.80; H, 4.29. Found: C, 64.90; H, 4.32. **IR** (KBr pellets): 1679 cm^{-1}. **MS** (FAB): $m/z = 1056$ ($[M+H]^+$, 100%).

2.3.2. Compound 5-G$_1$

To a solution of **5-G'$_0$** (270 mg, 0.256 mmol) in THF (20 ml) at 0 °C was added dropwise a slight excess of a freshly prepared solution of dichlorothiophosphorhydrazide **6** in chloroform. The mixture was stirred 4 h at room temperature and after solvent removal under reduced pressure the resulting powder was washed with a mixture of pentane and diethyl oxide (1:1) to afford **5-G$_1$** as a red powder (yield = 78%).

^{31}**P** {^{1}**H**} **NMR** (CDCl$_3$): δ (ppm) 62.0 (s, P$_1$); 52.8 (s, P$_0$). ^{1}**H NMR** (CDCl$_3$): δ (ppm) 7.1–7.6 (m, 15H, Ar and CH=N); 6.65 (m, 6H, CH=CH); 4.73 (s, 6H, Cp$_0$–H); 4.52 (s, 6H, Cp$_0$–H); 4.34 (s, 6H, Cp$_0$–H); 4.29 (s, 6H, Cp$_0$–H); 2.97 (d, $^3J_{HP} = 14$ Hz, 9H, N–CH$_3$). ^{13}**C** {^{1}**H**} **NMR** (CDCl$_3$): δ (ppm) 149.3 (d, $^2J_{CP} = 7,0$ Hz, C$_0^1$); 142.8 (d, $^3J_{CP} = 18.7$ Hz, CH=N); 134.9 (s, C$_0^4$); 126.8 (s, C$_0^3$); 126.3 (s, CH=CH); 125.4 (s, CH=CH); 121.5 (d, $^3J_{CP} = 4.5$ Hz, C$_0^2$); 84.5 (s, quat C̲p$_0$–CH=N); 79.8 (s, quat C̲p$_0$–CH=CH); 70.7 (s, Cp$_0$); 69.9 (s, Cp$_0$); 68.6 (s, Cp$_0$); 67.8 (s, Cp$_0$); 31.5 (d, $^3J_{CP} = 13.0$ Hz, P$_1$–N–CH$_3$). Anal. calcd for $C_{60}H_{54}Cl_6Fe_3N_6O_3P_4S_4$: C, 46.81; H, 3.53; N, 5.46. Found: C, 46.92; H, 3.59; N, 5.42.

2.3.3. Compound 5-G'$_1$

To a solution of **5-G$_1$** (200 mg, 0.129 mmol) in THF (10 ml) was added dropwise, at 0 °C, a slight excess of the sodium salt of **E-4** (302 mg, 0.853 mmol) in THF (15 ml). The reaction mixture was stirred overnight at room temperature. After centrifugation and solvent removal under reduced pressure, the crude product was washed with a mixture of pentane and diethyl oxide (1:1) and then with methanol, to afford **5-G'$_1$** as a red powder (yield = 80%).

^{31}**P** {^{1}**H**} **NMR** (CDCl$_3$): δ (ppm) 61.3 (s, P$_1$); 53.1 (s, P$_0$). ^{1}**H NMR** (CDCl$_3$): δ (ppm) 9.90 (s, 6H, CHO); 7.6–7.1 (m, 39H, Ar and CH=N); 6.62 (br s, 18H, CH=CH); 4.7–4.1 (m, 72H, Cp$_{0,1}$–H); 3.05 (d, $^3J_{HP} = 11$ Hz, 9H, N–CH$_3$). ^{13}**C** {^{1}**H**} **NMR** (CDCl$_3$): δ (ppm) 193.6 (s, CHO); 149.8 (d, $^2J_{CP} = 8.0$ Hz, C$_1^1$); 149.3 (d, $^2J_{CP} = 8.0$ Hz, C$_0^1$); 139.8 (d, $^3J_{CP} = 14$ Hz, CH=N); 135.1 (s, C$_0^4$); 134.5 (s, C$_1^4$); 126.9 (br s, Cp$_0$–CH=̲CH and C$_{0,1}^3$); 126.5 (s, Cp$_1$–CH=̲CH); 125.3 (s, Cp$_0$–CH=̲CH); 125.0 (s, Cp$_1$–CH=̲CH); 121.6 (d, $^3J_{CP} = 4.0$ Hz, C$_1^2$); 121.4 (d, $^3J_{CP} = 4.0$ Hz, C$_0^2$); 85.1 (s, quat C̲p$_1$–CH=N); 84.3 (s, quat C̲p$_0$–CH=N); 80.8 (s, quat C̲p$_1$–CH=CH);

79.6 (s, quat $\underline{Cp_0}$–CH=CH); 74.3 (s, Cp_1); 70.7 (s, Cp_0); 70.5 (s, Cp_1); 70.3 (s, Cp_1); 68.3 (s, Cp_0); 68.0 (s, Cp_1); 67.8 (s, Cp_0); 67.7 (s, Cp_0); 32.7 (d, $^3J_{CP} = 13.7$ Hz, P_1–N–CH_3). Anal. calcd for $C_{174}H_{144}Fe_9N_6O_{15}P_4S_4$: C, 63.07; H, 4.38; N, 2.54. Found: C, 63.12; H, 4.49; N, 2.47. **IR** (KBr pellets) = 1679 cm^{-1}.

2.4. Electrochemical measurements

Voltammetric and electrolytic measurements were carried out with a home-made potentiostat [50] using the interrupt method to minimise the uncompensated resistance (Ri) drop; square wave voltammetry measurements were carried out with a PAR model 273. Experiments were performed at room temperature in an airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solutions by a bridge compartment. The counter electrode was a spiral of ca 1 cm^2 apparent surface, made of a platinum wire 8 cm in length and 0.5 cm in diameter. The working electrode was a Pt electrode (1 mm diameter) for cycling voltammetry and a Pt gauze electrode for bulk electrolysis. $E^{1/2}$ values were determined as the average of the cathodic and the anodic peak potentials. The supporting electrolyte (nBu$_4$N)[BF$_4$] (Fluka, electrochemical grade) was used as received.

2.5. X-ray crystal structure analysis

Data for **E-2** were collected on an Enraf-Nonius CAD4 diffractometer equipped with a graphite oriented monochromator utilising Mo Kα radiation ($\lambda = 0.710\,73$). The final unit cell parameters were obtained by the least-squares refinement of 25 selected reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection.

The structure was solved by direct methods (SIR92 [51]) and refined by least-squares procedures on F_{obs}. All H atoms attached to carbon were introduced in calculation in idealised positions (d(C–H) = 0.96Å) and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Least-squares refinements were carried out by minimising the function $\Sigma w\,(|F_0| - |F_c|)^2$, where F_0 and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w'[1 - \{\Delta F/6\,\sigma(F_0)\}^2]^2$, where $w' = 1/\Sigma_1^n A_r\,T_r(x)$

Table 3. Crystal data for compound **E-2**.

Crystal parameters	
Formula	$C_{22}H_{22}O_3Fe$
FW (g)	390.26
Shape (colour)	plate (yellow)
Size (mm)	1.13, 0.38, 0.05
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	24.421(6)
b (Å)	5.824(2)
c (Å)	12.582(4)
β (°)	93.68(2)
V (Å^3)	1786(1)
Z	4
$F(000)$	817
ϱ (calcd) (g cm^{-3})	1.451
μ (MoKα) (cm^{-1})	8.63
Data collection	
Diffractometer	CAD4 Enraf-Nonius
Monochromator	graphite
Radiation	MoKα ($\lambda = 0.710\,73$)
Temperature (K)	293(2)
Scan type	$\omega/2\theta$
Scan range θ (°)	$0.8 + 0.345\,\tan\theta$
2θ range (°)	$3 < 2\theta < 50$
Absorption method	ϕ scan
Min. and Max. correction	1.00, 1.139
Number of reflections collected	3015
Number of independent reflections	2675
Merging factor R(int)	0.017
Reflections used, ($I > 2\,\sigma(I)$)	1934
Refinement	
R	0.0360
Rw	0.0422
Weighting scheme	Chebyshev
Coefficient Ar	2.98, 0.723, 2.44
$(\Delta/\sigma)_{max}$	0.001
$\Delta\varrho_{min}/\Delta\varrho_{max}$	–0.26/0.53
GOF	1.012
Variable parameters	235

with three coefficients A_r for the Chebyshev polynomial $A_r\,T_r(x)$, where x was $F_c/F_{c\,max}$ [52]. Models reached convergence with $R = \Sigma(\|F_0| - |F_c\|)/\Sigma(|F_0|)$ and $Rw = [\Sigma w\,(|F_0| - |F_c|)^2\,/\Sigma w(F_0)^2]^{1/2}$, having values listed in Table 3.

The calculations were carried out with the CRYSTALS package programs [53]. The drawing of the molecules was realised with the help of CAMERON [54]. Full details for data collection and refinement procedures, fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms and atomic coordinates for H atoms have been deposited with the Cambridge Crystallographic Data Centre (CCDC 179305).

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