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Facile synthesis of bidimensional ferrocenyl-based branched oligomers by palladium-catalyzed coupling reactions

Arantxa Peruga [a], José A. Mata [a], Daniel Sainz [b], Eduardo Peris [a,*]

[a] *Departamento de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellón, Spain*
[b] *Departamento de Química Inorgánica, Universitat de Barcelona, Barcelona, Spain*

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Abstract

New ferrocenyl-based star-shaped complexes have been obtained by palladium-catalyzed reactions. The synthetic method reported shows an advantage over the traditional Wittig reaction for the synthesis of olefinated compounds, both in yields and in selectivity towards the all-*E* isomers. The electrochemistry of the compounds has been studied. The crystal structure of *E*-ferrocenyl-4-(vinylphenyl)vinylene, one of the starting complexes to the star-shaped compounds, has been determined by means of single crystal X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal-containing long-chained conjugated systems have emerged as an important category of materials. The impetus for developing these materials is based on the premise that conjugated chains containing metals are expected to posses properties significantly different from those of conventional organic conjugated oligomers. Examples of these properties include: electrical conductivity, magnetic behavior, thermal stability, nonlinear optical (NLO) effects, and even superconductivity. Because of the special electronic and chemical properties of ferrocene, many efforts have been directed towards the incorporation of a ferrocene moiety into a polymer [1–19], in order to investigate novel properties such as those mentioned above. Besides, the preparation of ferrocenyl conjugated systems offers the possibility of electronic communication between terminal subunits, this being of particular interest in terms of modulating the electronic properties of the material.

Since the mid-1980s, interest in highly branched molecular architectures has emerged to become an intriguing area of research of scientists worldwide. The term *dendrimer* has been used to define a new type of highly branched regular three-dimensonal monodisperse macromolecules with a branch occurring at each monomer unit. The introduction of metal atoms into the structure of the dendrimer has allowed the generation of a new type of molecules called *metallodendrimers* [1,20–24]. Metallodendrimers are supramolecular species with interesting physical, optical, electrochemical, photochemical, biological and catalytic properties, promoted by the existence of redox centers into the molecule structure. 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 remains a bottleneck in the study of this new type of materials. The synthesis of low molecular weight organometallic dendrimers (or minidendrimers) [25–28], via single-step procedures, provides a series of precursors to higher molecular weight metallodendrimers with interesting and potentially exciting cross-linked metal-conjugated networks.

We have used ferrocenyl-based conjugated ligands in order to obtain bimetallic and heterometallic push–pull complexes [29–32], and have found interesting redox and spectroscopic properties that have been related to high nonlinear optical responses [29–32]. We now report, based on our previous findings, a facile synthetic

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* Corresponding author. Tel.: +34-964-728-243; fax: +34-964-728-214.

E-mail address: eperis@qio.uji.es (E. Peris).

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route to bidimensional ferrocenyl-based star-shaped complexes, with interesting physical properties. The compounds that we report in the present work can be considered as the germ for new types of conjugated metallodendrimers.

2. Results and discussion

2.1. Syntheses of the star-shaped compounds

In our previous works [29–32], we reported the synthetic procedures of several ferrocene-containing phenylene–vinylene oligomers by means of Wittig or Horner–Emmons–Wadsworth (HEW) methods. In fact, these two methods for olefin formation have been widely used in vinylene-containing organometallic species [3,33–38]. Although in most of the cases, these procedures afforded moderate to good yields in the desired products, the low stereoselectivity to the all-*E* isomers and the complicated work-ups, prompted us to look for better procedures in the synthesis of vinylene-containing ferrocenyl derivatives.

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 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 [39–42]. Besides, 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.

In the search of such mononuclear ferrocenyl fragments with reactive functional groups, we have considered complexes **1**–**3** as good candidates for Heck coupling reactions to 1,3,5-tribromobenzene, in order to obtain tri-branched conjugated complexes. Compounds **2** and **3** can be readily obtained by olefination of the corresponding aldehydes CpFe(η^5-C_5H_4)-*E*-(CH=CH)–4-(C_6H_4CHO) and CpFe(η^5-C_5H_4)-*E*-(CH=CH)–(η^5-C_5H_4)–Fe–(η^5-C_5H_4)–CHO by the Wittig procedure using $[Ph_3P^+CH_3]I^-$.

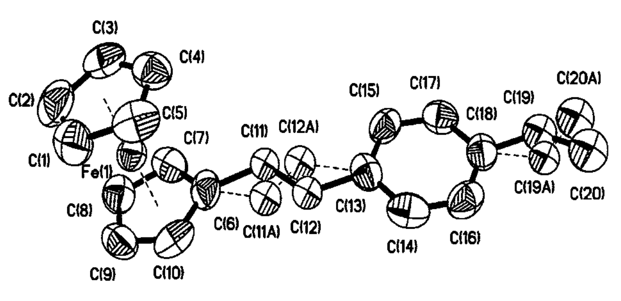
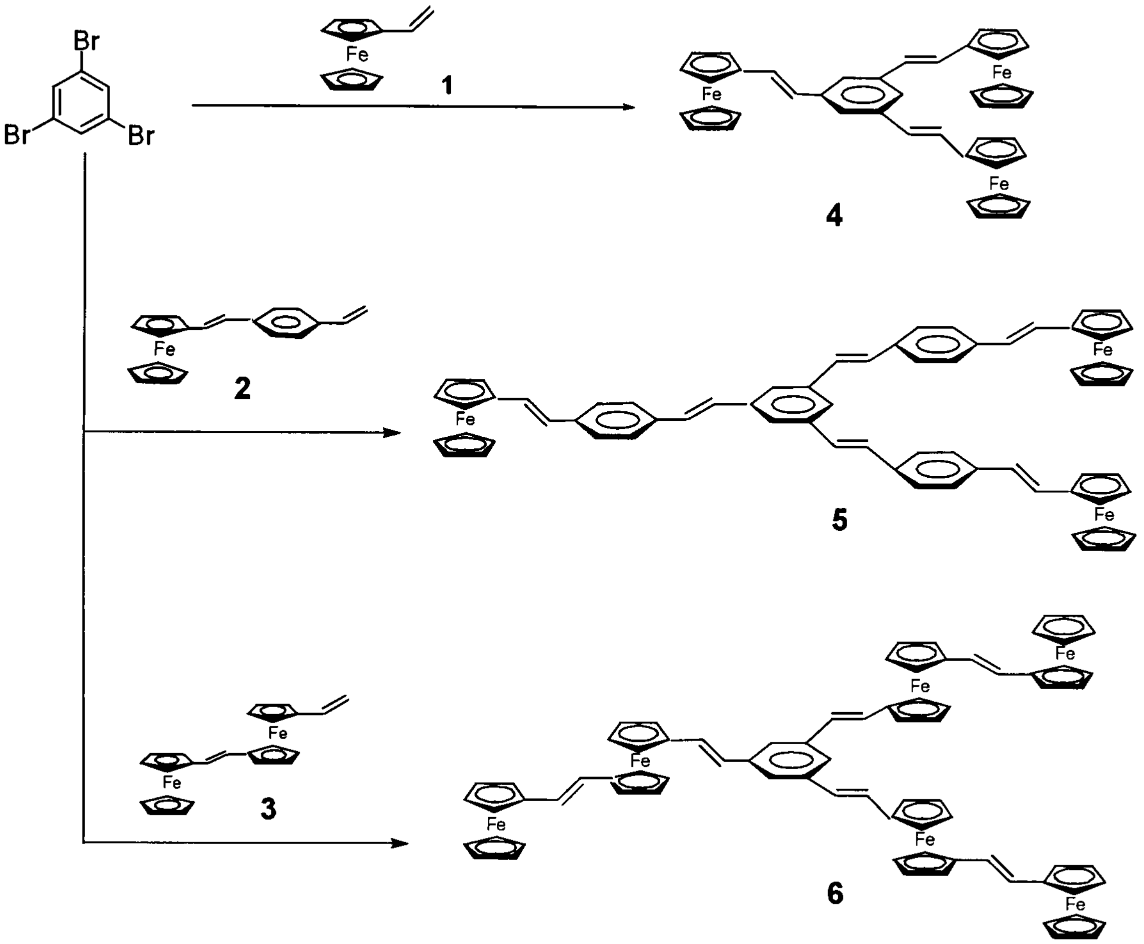


Fig. 1. Molecular structure and atomic labeling scheme for compound **2**, (*E*)-(η^5-C_5H_5)Fe(η^5-C_5H_4)–CH=CH–C_6H_4–CH=CH_2, with 50% anisotropic displacement ellipsoids. Hydrogen atoms are omitted for clarity. Distances: Fe(1)–C(20) (through space) = 10.65 Å, Fe(1)–C(20A) (through space) = 10.61 Å, and Fe(1)–C(20) (through bonds) = 13.34 Å, Fe(1)–C(20A) (through bonds) = 13.39 Å. Planes: Cp–Cp(Subs.) = 0.87(0.33)°, Cp(Subs.)–Ph = 14.86(0.24)°.

The structure of **2** (Fig. 1) was determined by using single crystal X-ray diffraction method. Bond distances and angles are in the usual range. The two Cp rings are almost perfectly parallel. Like other ferrocenyl-containing conjugated molecules, **2** exhibits a rigid-rod and almost perfect planar geometry, with a Fe–C(20) distance of 10.6 Å (through space) and 13.3 Å (through bonds). As shown in Fig. 1, compound **2** presents a disorder in a 7:3 ratio with regard to the orientation of the *trans* olefinic moieties. This kind of disorder has been previously observed in similar molecules [30,43,44].

For the synthesis of the star-shaped complexes by the Heck method, we decided to use the Pd compound *syn*-di(μ-chloro)-bis[*o*-(benzylphenylphosphyno)benzyl] dipalladium(II) as the catalyst, since it has shown to have an extremely good activity in C–Br activation [45]. Compounds **1**–**3** readily react with 1,3,5-tribromobenzene to give compounds **4**–**6**, respectively, in high yields, as shown in Scheme 1. The reaction conditions and the catalytic activity of the system are summarized in Table 1. Despite the fact that TON numbers may not seem to be very high, we have to consider that in all the cases the coupling is made between rather large fragments, and that the addition of each individual ferrocenyl fragment to the arene may cause its deactivation towards the subsequent Heck coupling, as a consequence of its electron-donating character. The three reactions are stereoselective to the all-*E* isomers. Although we were unsuccessful to get single crystals of any of these three compounds, we presume that compounds **4** and **5** must have a fully expanded and coplanar structure, as can be inferred from the structure shown by **2** and other related complexes [26]. In this regard, taking into account the head-to-tail distance of **2**, we estimate an approximate radius for **5** of 14 Å. Compound **4** has already been described in two previous papers [36,42]. In the most recent one [36], **4** was obtained by means of the Wittig reaction procedure, from 1,3,5-tris[(triphenylphosphonio)methyl]benzene tribromide and ferrocenecarboxaldehyde, but the product obtained was a mixture of *E* and *Z* isomers that could not be separated. In the other paper [42], König et al. obtained **4** in the all-*E* form, by means of a Pd-catalyzed reaction similar to ours, but the yields were significantly lower and the reaction time longer (two days), probably due to the fact that thermal stability of the catalyst that we used allowed us to raise the temperature to 130 °C and thus considerably reduce the reaction time to just a few hours.



Scheme 1.

2.2. Electrochemical studies

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 peak-to-peak separations are, however, significantly greater than the ideal value of 60 mV s^{-1} for a fully reversible one-electron process. This may be due to a combination of uncompensated solution resistance and slightly slow electron-transfer kinetics. The oxidation of the ferrocenyl centers is facilitated compared to that of free ferrocene, meaning that some degree of electron delocalization is occurring along the conjugated systems, this stabilizing the positive charge of the cationic oxidized species. Lower potentials are observed for those systems with higher electron delocalization abilities, **4**–**6.** Compounds **4** and **5** show a reversible three-electron wave, therefore, the three iron centers in each compound are essentially non-interacting. A similar effect is observed for the compound 1,3,5-tris(ferrocenylethynyl)benzene [26], for which the redox potential is considerably higher (490 mV) compared to the related ethenyl compound, **4** (410 mV). This difference may be explained by the more effective conjugation and stabilization of the oxidized species in the ethenyl complex.

Compounds **3** and **6** show two peaks corresponding to two reversible three-electron oxidations. In the cases where the two redox centers are equivalent, the peak difference is a direct measure of the communication between the two redox centers. In our case, the difference in the two potentials is a combination of their communication and their intrinsic inequivalence, so the measure of electronic communication in **3** and **6** must be less than that measured by the potential difference.

As it has been previously reported for similar compounds, the redox behavior of compounds **4**–**6** is marked by changes in solubility with the change in the oxidation state of the ferrocene units [46]. The intensity of the cathodic peak is slightly higher and sharper than the anodic one, which indicates the precipitation onto the electrode surface.

The rotation of the two Cp rings in 1,1′-bis-substituted ferrocenyl complexes makes them behave as 'hinge-like' complexes. 1,1′-Bis-substituted ferrocenyl compounds typically show structures far from the *anti*

Table 1
Reaction conditions and catalytic activity for the synthesis of compounds **4**–**6** (reactions carried out at 130 °C in DMF)

Compound	Catalyst (%)	Time (h)	TON	Yield (%)
4	3.4	9	81	90
5	12.5	8	20	82
6	16.7	8	15	78

Table 2
Cyclic voltammetric data for the ferrocenyl derivatives in CH_2Cl_2

Compound	$E_{1/2}$ (mV) (ΔE_p (mV))	
	[Fe(II)/Fe(III)]	[Fe′(II)/Fe′(III)]
Ferrocene	445 (105)	–
1	460 (200)	–
2	425 (100)	–
Fc–=–Fc–CHO	405 (90)	785 (85)
3	355 (150)	530 (120)
4	410 (170)	–
5	400 (160)	–
6	320 (100)	520 (90)

conformation with respect to the two ancillary ligands. This fact may be explained by the stabilization produced by an intramolecular π-stacking of the conjugated ancillary ligands (in the examples in which a *syn* conformation is observed), or to a better packing of the compressed geometry in the solid state. In compound **6**, we cannot discard that some of this effect also occurs or, in any case, that the compound is not showing a perfect *anti* configuration in its neutral form. Once it is fully oxidized, it must show a structural rearrangement to a fully expanded form in which the electrostatic repulsion between all the six iron centers is minimized (Scheme 2). This behavior makes **6** a good candidate to a size tunable complex, in which the radius of the star-shaped compound can be electrochemically switched.

3. Conclusions

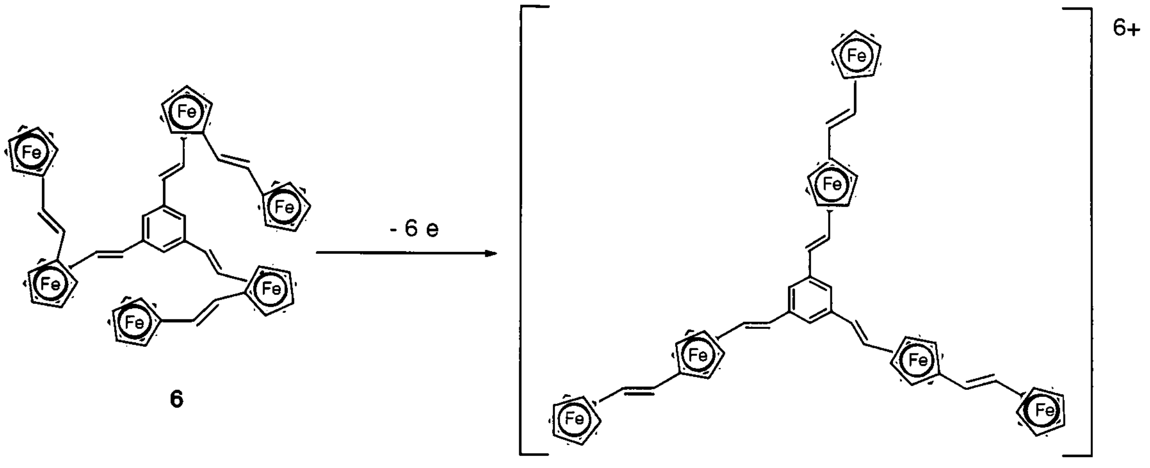
By means of palladium-catalyzed reactions we have designed an effective method for the synthesis of several star-shaped ferrocenyl containing compounds. The method shows clear advantages over the traditional Wittig method for the synthesis of olefinated complexes, both in yields and in selectivities on the all-*E* isomers. The electrochemical studies do not show any significant interactions between the iron centers of different branches of the complexes, although there is an important electronic coupling in those complexes in which the ferrocene units are separated by a vinylene unit.

4. Experimental

4.1. General details

All reactions were carried out under a N_2 atmosphere using standard Schlenk techniques. Solvents for synthesis and electrochemical measurements were dried and deoxygenated by standard methods before use. Chromatographic work was performed on silica gel 60 Å.

NMR spectra were recorded on Varian Innova 300 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 UV-1603 Shimadzu spectrophotometer. Elemental analyses were performed on an EA 1108 CHNS-O Carlo Erba instrument. Cyclic voltammetry experiments were performed with an Echochemie pgstat 20 electrochemical



Scheme 2.

analyzer. All measurements were carried out at room temperature (r.t.) with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag | AgCl reference electrode containing aqueous 3 M KCl. The solvent used in all experiments was CH_2Cl_2, which was obtained in HPLC grade and used as received. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium hexafluorophosphate, synthesized by reaction of tetra-*n*-butylammonium bromide and HPF_6, recrystallized from EtOH and dried under vacuum. $E_{1/2}$ values were determined as $(E_{pa} + E_{pc})/2$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. All reported potentials are not corrected for the junction potential.

*4.2. Synthesis of (E)-(η^5-C_5H_5)Fe(η^5-C_5H_4)–CH=CH–C_6H_4–CH=CH_2 (**2**)*

To a solution of methyltriphenylphosphonium iodide (1.4 g, 3.4 mmol) in THF (100 ml) was added potassium *tert*-butoxide (500 mg, 4.4 mmol) at 0 °C and the resulting suspension was allowed to warm to r.t. After 30 min, the yellow suspension indicated that the ylide was completely formed. CpFe(η^5-C_5H_4)-*E*-(CH=CH)–4-(C_6H_4CHO) (900 mg, 2.8 mmol), was then added at 0 °C and the solution was stirred for ca. 15 h at r.t. After removing the solvent under reduced pressure, the product was separated with a CH_2Cl_2–H_2O–$NaHCO_3$ mixture and the CH_2Cl_2 extract dried over $MgSO_4$. Purification by column chromatography on silica gel using hexane–CH_2Cl_2 (1:1) as eluent afforded pure **2** in 60% yield.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.40 (s, 4H, C_6H_4); 6.89 (d, 1H, $^3J_{H-H} = 16.5$ Hz, CH=CH); 6.77–6.66 (m, 2H, CH=CH, CH=CH_2); 5.76 (d, 1H, $^3J_{H-H} = 17.7$ Hz, CH=CH_2); 5.25 (d, 1H, $^3J_{H-H} = 10.5$ Hz, CH=CH_2); 4.48 (s, 2H, C_5H_4); 4.31 (s, 2H, C_5H_4); 4.15 (s, 5H, C_5H_5). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 138.2, 136.8 (2Cq, C_6H_4); 127.2, 126.6 (4C, C_6H_4); 137.3, 127.7, 126.6 (3C, CH=CH, CH=); 113.9 (1C, =CH_2); 84.1 (1Cq, C_5H_4); 69.9 (5C, C_5H_5), 69.8 (2C, C_5H_4), 67.6 (2C, C_5H_4). Anal. Found: C, 76.68; H, 5.75. Calc. for compound **2**-(*E*), $C_{20}H_{18}Fe$ (MW 314.21 g mol^{-1}): C, 76.50; H, 5.77%.

*4.3. Synthesis of (E)-(η^5-C_5H_5)Fe(η^5-C_5H_4)–CH=CH–(η^5-C_5H_4)Fe(η^5-C_5H_4)–CH=CH_2 (**3**)*

To a solution of methyltriphenylphosphonium iodide (769 mg, 1.9 mmol) in THF (100 ml) was added potassium *tert*-butoxide (320 mg, 2.8 mmol) at 0 °C and the resulting suspension was allowed to warm to r.t. After 30 min, the yellow suspension indicated that the ylide was completely formed. CpFe(η^5-C_5H_4)-*E*-(CH=CH)–(η^5-C_5H_4)–Fe–(η^5-C_5H_4)–CHO (600 mg, 1.4 mmol) was then added at 0 °C and the solution was stirred for ca. 15 h at r.t. After removing the solvent under reduced pressure, the product was separated with a CH_2Cl_2–H_2O–$NaHCO_3$ mixture, and the CH_2Cl_2 extract dried over $MgSO_4$. Purification by column chromatography on silica gel using hexane–CH_2Cl_2 (6:4) as eluent afforded pure **3** in 40% yield.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.47–6.35 (m, 3H, CH=CH, CH=CH_2); 5.35 (dd, 1H, $^3J_{H-H} = 17.5$ Hz, $^2J_{H-H} = 1.5$ Hz, CH=CH_2); 5.08 (dd, 1H, $^3J_{H-H} = 10.5$ Hz, $^2J = 1.5$ Hz, CH=CH_2); 4.38 (t, 2H, $^3J_{H-H} = 1.5$ Hz, C_5H_4); 4.28–4.29 (m, 4H, C_5H_4); 4.24 (t, 2H, $^3J_{H-H} = 1.5$ Hz, C_5H_4); 4.19–4.17 (m, 4H, C_5H_4); 4.14 (s, 5H, C_5H_5). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 135.0, 124.8, 124.1 (3C, CH=CH, CH=); 112.0 (1C, =CH_2); 85.7, 85.3, 84.9 (3Cq, C_5H_4); 70.7, 70.6, 69.9, 69.3, 68.6, 68.1, 66.9 (17C, C_5H_4, C_5H_5). Anal. Found: C, 68.41; H, 5.24. Calc. for compound **3**-*E*, $C_{24}H_{22}Fe_2$ (MW 422.13 g mol^{-1}): C, 68.30; H, 5.25%.

*4.4. Synthesis of (E)-{(η^5-C_5H_5)Fe(η^5-C_5H_4)–CH=CH}$_3$–C_6H_3 (**4**)*

A mixture of 2.3 mmol (500 mg) of CpFe(η^5-C_5H_4)–(CH=CH_2), 0.6 mmol of (184 mg) 1,3,5-tribromobenzene, 2.6 mmol (210 mg) of sodium acetate anhydrous, 0.2 mmol (50 mg) of tetrabutylammonium bromide, and 0.02 mmol (20 mg) of *syn*-di(μ-chloro)-bis[*o*-(benzylphenylphosphyno)benzyl]dipalladium(II) in DMF (15 ml) was heated at 130 °C for 16 h. After removing the solvent under reduced pressure, the product was separated with a CH_2Cl_2–H_2O–$NaHCO_3$ mixture, and the CH_2Cl_2 extract dried over $MgSO_4$. Purification by column chromatography on silica gel using CH_2Cl_2–acetone (10:1) as eluent afforded pure **4** in 90% yield.

*4.5. Syntheses of (E,E)-{(η^5-C_5H_5)Fe(η^5-C_5H_4)–CH=CH-(C_6H_4)–CH=CH}$_3$–C_6H_3 (**5**) and (E,E)-{(η^5-C_5H_5)Fe(η^5-C_5H_4)–CH=CH–(η^5-C_5H_4)Fe(η^5-C_5H_4)–CH=CH}$_3$–C_6H_3 (**6**)*

These compounds were obtained following the general procedure described for compound **4**, using compound **2** (0.6 mmol, 200 mg) or **3** (0.5 mmol, 200 mg) instead of **1**. Purification by column chromatography on silica gel using hexane–CH_2Cl_2 (1:1) as eluent afforded pure compounds **5** (yield 82%) and **6** (yield 78%).

^{1}H-NMR for compound **5** (500 MHz, $CDCl_3$): δ 7.59 (s, 3H, C_6H_3); 7.54 (d, 6H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.46 (d, 6H, $^3J_{H-H} = 8.0$ Hz, C_6H_4); 7.22 (d, 3H, $J_{H-H} = 16.5$ Hz, CH=CH); 7.17 (d, 3H, $J_{H-H} = 16.5$ Hz, CH=CH); 6.95 (d, 3H, $J_{H-H} = 16.0$ Hz, CH=CH); 6.73 (d, 3H, $J_{H-H} = 16.0$ Hz, CH=CH); 4.51 (s, 6H, C_5H_4); 4.33 (s, 6H, C_5H_4); 4.17 (s, 15H, C_5H_5). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 138.9, 138.2, 136.5 (9Cq, C_6H_4, C_6H_3); 129.7,

Table 3
Crystal data and structure refinement parameters for compound **2**

Empirical formula	$C_{20}H_{18}Fe$
Formula weight	314.19
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	6.2555(5)
b (Å)	7.8041(6)
c (Å)	15.5956(12)
α (°)	90
β (°)	90.590(2)
γ (°)	90
V (Å^3)	761.31(10)
Z	2
D_{calc} (g m^{-3})	1.371
Absorption coeffficient (mm^{-1})	0.980
F(000)	328
Crystal size (mm)	$0.35\times0.16\times0.12$
θ range for data collection (°)	1.31–30.52
Index ranges	$-8\leq h\leq 8$, $-8\leq k\leq 11$, $-22\leq l\leq 22$
Reflections collected	6431
Independent reflections	3679 [$R_{int}=0.0224$]
Data/restraints/parameters	3679/1/188
Final R indices [$I>2\sigma(I)$]	$R_1=0.0394$, $wR_2=0.1034$
R indices (all data)	$R_1=0.0712$, $wR_2=0.1149$
Goodness-of-fit-on F^2	0.655
Largest difference peak and hole (e Å^{-3})	0.421 and −0.194

128.5, 127.9, 127.6, 126.8, 126.4, 124.5 (27C, CH=CH, C_6H_4, C_6H_3); 84.3 (3Cq, C_5H_5); 70.0, 69.9, 67.7 (27C, C_5H_4, C_5H_5). Anal. Found: C, 78.18; H, 5.37. Calc. for compound **5**-(E,E), $C_{66}H_{54}Fe_3$ (MW 1014.70 g mol^{-1}): C, 78.10; H, 5.36%.

^{1}H-NMR for compound **6** (300 MHz, $CDCl_3$): δ 7.32 (s, 3H, C_6H_3); 6.90 (d, 3H, $^3J_{H-H}=16.5$ Hz, CH=CH); 6.70 (d, 3H, $^3J_{H-H}=16.2$ Hz, CH=CH); 6.41–6.39 (m, 6H, CH=CH); 4.43–4.09 (m, 51H, C_5H_5, C_5H_4). ^{13}C-NMR (300 MHz, $CDCl_3$): δ 138.9, 127.1, 126.9, 124.9, 123.7, 122.5 (18C, CH=CH, C_6H_3); 85.8, 84.8, 84.6 (9Cq, C_5H_4); 70.9, 70.5, 69.9, 69.4, 68.9, 68.3, 67.0 (51C, C_5H_4, C_5H_5). Anal. Found: C, 70.12; H, 4.98. Calc. for compound **6**-(E,E), $C_{78}H_{66}Fe_6$ (MW 1338.46 g mol^{-1}): C, 70.00; H, 4.97%.

4.6. X-ray diffraction studies

Single crystals of **2** were grown by slow diffusion of hexane into concentrated CH_2Cl_2 solutions and mounted on a glass fiber in a random orientation. Data collection was performed at r.t. on a Siemens Smart CCD diffractometer using graphite monochromated Mo–K$_\alpha$ 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 $\phi=0$, 90 and 180° with the detector at $2\theta=28°$. At each of these runs, frames (606, 435 and 230, respectively) were collected at 0.3° intervals and 40 s per frame. Space group assignment was based on systematic absences, E statistics and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and were refined using the SHELXTL 5.1 software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions and structure refinement are given in Table 3. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS [47].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 154164 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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