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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL STUDIES OF 1′,6′-BIS(ETHYNYL)BIFERROCENE AND SOME METAL COMPLEXES: NOVEL HETEROMETALLIC COMPOUNDS TOWARDS NON-LINEAR OPTICS*

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Abstract—The reaction of trimethylsilylacetylene and 1′,6′-diiodoferrocene (**1**) resulted in the formation of 1′,6′-bis(trimethylsilylethynyl)biferrocene (**2**) and, with subsequent desilylation, 1′,6′-bis(ethynyl)biferrocene (**3**), in excellent yields. The novel difunctional ligand **3** lends itself to metal coordination, and the multimetallic complexes 1′,6′-bis{manganese(I)tricarbonyl[1,2-bis(diphenylphosphino)methane]}biferrocene (**4**) and 1′,6′-bis{rutheniumbis[1,2-bis(diphenylphosphino)methane]chloride}biferrocene (**5**) were formed from {manganese(I)tricarbonyl[1,2-bis(diphenylphosphino)methane]bromide} and {rutheniumbis[1,2-bis(diphenylphosphino)methane]dichloride}, respectively. All the compounds have been fully characterized by analytical and spectroscopic methods. Cyclic voltammetry experiments indicate that there is a large electron delocalization between the iron atoms of the biferrocene moiety and the metal centres in the one-electron-oxidized complexes. Additionally, results show that the ruthenium and manganese centres donates electron density through the acetylene linkage to the $(FeCp_2)_2$ ligand.

At the present time, research into ferrocene-containing complexes is undergoing something of a 'renaissance'. Ferrocenes have been of use in molecular sensors,[1–3] electrochemical agents,[4,5] liquid crystals[6] and non-linear optics.[7,8]

Recent reports also indicate the importance of ferrocenyl derivatives in heterobimetallic mixed-valence species[9–11] and as donors in charge-transfer complexes.[12–14] Increasing demand for new materials has led us to design novel systems featuring 'donor–acceptor bimetallic characteristics,[15,16] which show potential for second-order non-linear optical behaviour.

With a view to extending this strategy to include materials for third-order non-linear optics and organometallic polymers, we have synthesized a series of ferrocenylacetylides[17] and, most recently, the novel difunctional ligand, 1′,6′-bis(ethynyl) biferrocene and some metal (manganese and ruthenium) complexes. The syntheses and charac-

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* Dedicated to Prof. E. W. Abel on the occasion of his retirement. Thank you Ed., for being a supervisor, colleague, mentor and, most importantly, a friend (NJL).

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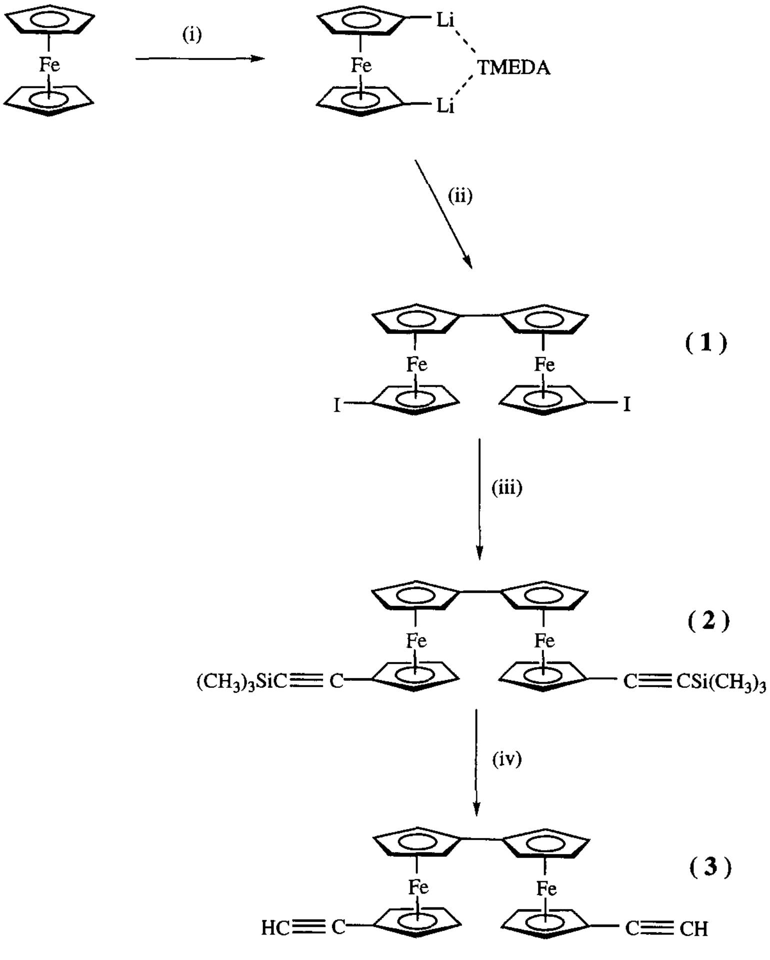
terization of these species are reported below, together with rigorous electrochemical studies of the ligand and the metal complexes. The complexes can be viewed as precursors for long-chain, π-delocalized, rigid-rod systems and could thus be of tremendous importance in material science.

RESULTS AND DISCUSSION

Interest in ferrocenylacetylides has spanned several decades, mainly because of their use in the synthesis of more complicated organometallic compounds. Several methods[18–20] involve acetyl- or diacetyl ferrocene as the starting material and conversion of the ketone group into an acetylenic one by various organic reactions. Coupling to iodo- and 1,1′-diiodo ferrocene with cuprous phenylacetylide[18] or trimethylsilylacetylene[21] has also proved successful. Our recent syntheses[15–17] have included the formation of ferrocenylacetylides followed by metal coordination to give novel bimetallic, mixed-valence species. However, the formation of difunctional ferrocenylacetylides, in this case 1′,6′-bis(trimethylsilylethynyl) biferrocene (**2**) and 1′,6′-bis(ethynyl)biferrocene (**3**) enables design of long chain transition metal σ-acetylide systems incorporating ferrocenyl moieties and types of organometallic polymers. This field is still rather underdeveloped but there is great potential in combining the attributes of flexibility, versatility and solubility of the organic groups with the magnetic, electrical and optical properties of the metals.

The syntheses of the ligands 1′,6′-diiodoferrocene (**1**), **2** and **3** are outlined in Scheme 1. Compound **1** was prepared in 1971 by Kovar *et al.*,[29] albeit in low yields, as interest was then focussed on forming 1,1′-dihalogenated ferrocenes. By careful handling of the well-known 1,1′dilithioferrocene·TMEDA intermediate[22] and addition of the appropriate



(i) = ^{n}BuLi, TMEDA (ii) = I_2 (iii) = $(CH_3)_3SiCCH$ (iv) = $K_2(CO_3)$ / CH_3OH

Scheme 1.

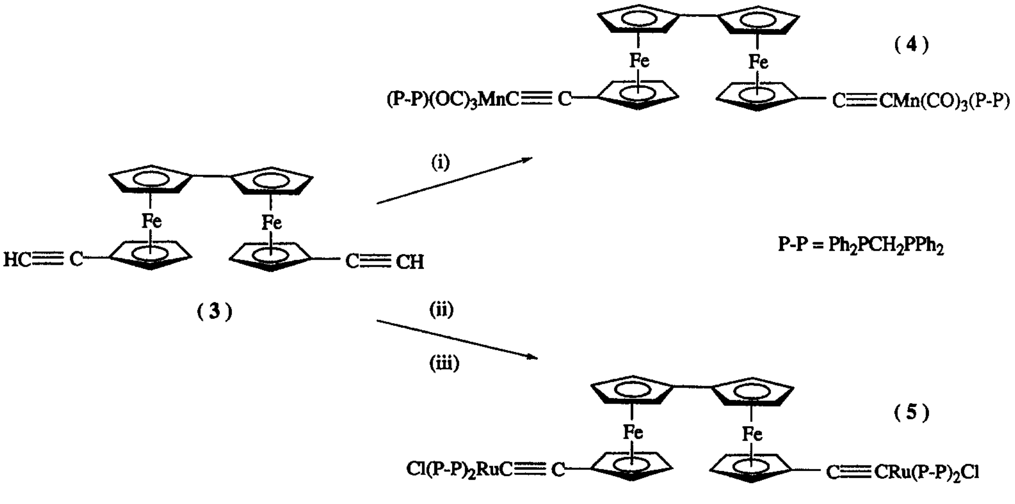
amount of iodine, a coupling of the reactive sites on the cyclopentadienyl rings can occur, and **1** was obtained in a reasonable yield of *ca* 40%.

Compound **2** was formed from another coupling reaction, this time between the iodine and trimethylsilylacetylene. The presence of catalytically small amounts of CuI, $Pd(O_2CCH_3)_2$ and PPh_3 are essential to ensure complete reaction. The product was formed in 70% yield and is stable to air and moisture, although as a precaution all the compounds **1–5** were stored under nitrogen and shielded from light. Compound **2** can be used as a reactive ligand in its own right, but for the metal complexing reactions detailed later, it was necessary to form the reactive, unsubstituted bis-acetylide species **3**. This was carried out in excellent yield (80%) by straightforward addition of K_2CO_3 to a solution of **2** in methanol and diethylether. Both **2** and **3** were able to withstand column chromatography on silica, using hexane and dichloromethane–hexane respectively, if further purification was necessary.

Scheme 2 illustrates the preparation of the metal complexes 1′,6′-bis{manganese(I)tricarbonyl[1,2-bis(diphenylphosphino)methane]}biferrocene (**4**) and 1′,6′-bis{rutheniumbis[1,2-bis(diphenylphosphino)methane]chloride}biferrocene (**5**) from **3**. Compound **4** was formed by treating the bromocarbonyl derivative of manganese with the silver(I) bisacetylide formed *in situ* from a mixture of $AgBF_4$ and **3** in CH_2Cl_2–H_2O. The reaction was monitored by IR spectroscopy, with **4** being isolated as a fine, orange powder in 25% yield. Compound **5** was also formed from **3**, using *cis*-$[Ru(dppm)_2Cl_2]$ and $NaPF_6$. The intermediate vinylidine complex was not isolated and reacted *in situ* to form the bis-acetylide **5** via the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu). An orange powder, **5** was recrystallized from a CH_2Cl_2–$(C_2H_5)_2O$ two-layered system to give dark orange crystals (that were unfortunately not suitable for X-ray analysis).

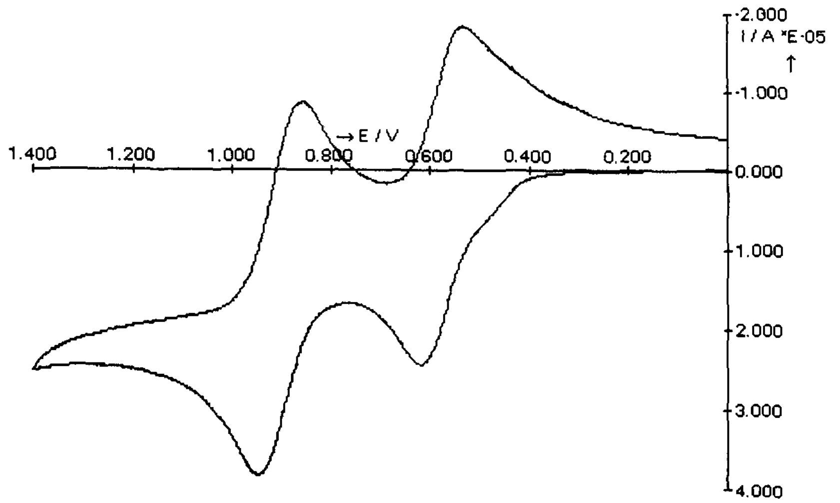
All the aforementioned compounds were characterized from their analytical data, mass, NMR and IR spectra. The singlet in the $^{31}P\{^1H\}$NMR and the strong, single $\nu(C{\equiv}C)$ absorption in the IR spectra of the complexes are consistent with a *trans* configuration of the acetylide units around the octahedral metal centres.

Rigorous electrochemical studies were carried out and these are detailed below. The important conclusion is that there is a large electron delocalization between the iron atoms of the biferrocenyl moiety and the metal (Mn^I and Ru^{II}) atoms in their one-electron-oxidized complexes. This is clearly important in our eventual aim of constructing large networks of conducting polymers. Current investigations are focussing on extending the length of the biferrocene–metal chains (by varying the metals and linking groups), studying the conjugation and electronic properties and the second-order (by incorporation of a chiral moiety) and third-order non-linear optical behaviour (as these species possess certain attributes that are known to be essential for non-linear optic activity[8]).

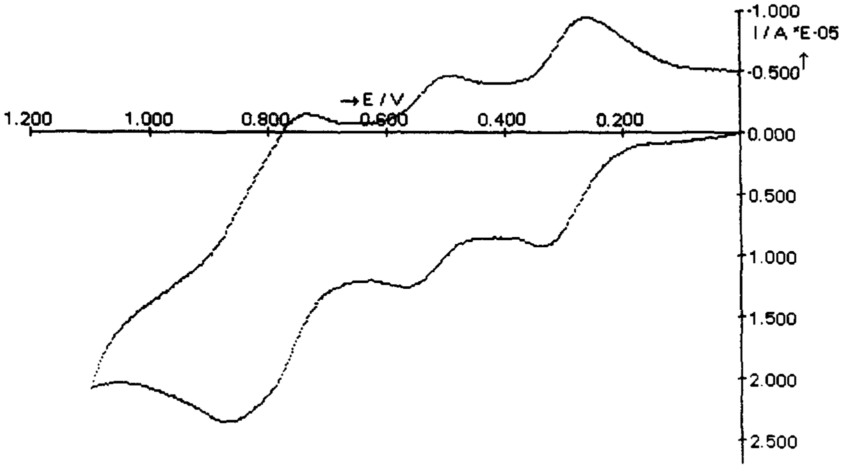


(i) = *fac*-$[Mn(CO)_3(P\text{-}P)Br]$, $AgBF_4$, CH_2Cl_2-H_2O (3:1), 24h
(ii) = *cis*-$[Ru(P\text{-}P)_2Cl_2]$, $NaPF_6$, CH_2Cl_2, 4h, r.t., N_2 (iii) = dbu, CH_2Cl_2, 2h, r.t., N_2

Scheme 2.



CV : **(a)** 0.1M $[NBu^t_4][BF_4]$ CH_2Cl_2 electrolyte, Scan rate 100mv/s



CV : **(b)** 0.5M $[NBu^t_4][BF_4]$ CH_2Cl_2 electrolyte, Scan rate 100mv/s

Fig. 1. Cyclic voltammograms of compounds 3 (a) and 4 (b). (a) 0.1 M $[NBu^t_4][BF_4]$ CH_2Cl_2 electrolyte, scan rate 100 mV s^{-1}. (b) 0.5 M $[NBu^t_4][BF_4]$ CH_2Cl_2 electrolyte, scan rate 100 mV s^{-1}.

Electrochemistry

The cyclic voltammogram of complex **3** in CH_2Cl_2/0.1 M $[NBu^t_4][BF_4]$ at 237 K showed two quasi-reversible oxidative processes at $E_{1\ 1/2} = 0.08$ V ($\Delta E_p = 70$ mV at 100 mV s^{-1}) and $E_{2\ 1/2} = 0.4$ V ($\Delta E_p = 75$ mV at 100 mV s^{-1}) versus Fc/Fc^+ (Fig. 1a). The cyclic voltammograms of **4** and **5** under the same conditions also showed two quasi-reversible waves assignable to these two processes, albeit at more cathodic potentials (Table 1), whilst also exhibiting additional processes arising from the pendant metal centres.

Complex **4** exhibits a quasi-reversible two-electron (by pulse voltammetry) process at $E_{3\ 1/2} = 0.30$ V ($\Delta E = 140$ mV at 100 mV s^{-1}) corresponding to the simultaneous oxidation of both $[Mn(CO)_3(dppm)]$ moieties in the complex, whilst **5** shows only two irreversible oxidations at high potentials (Table 1) arising from oxidation of the $[Ru(dppm)_2Cl]$ fragments in this compound (Fig. 1b).

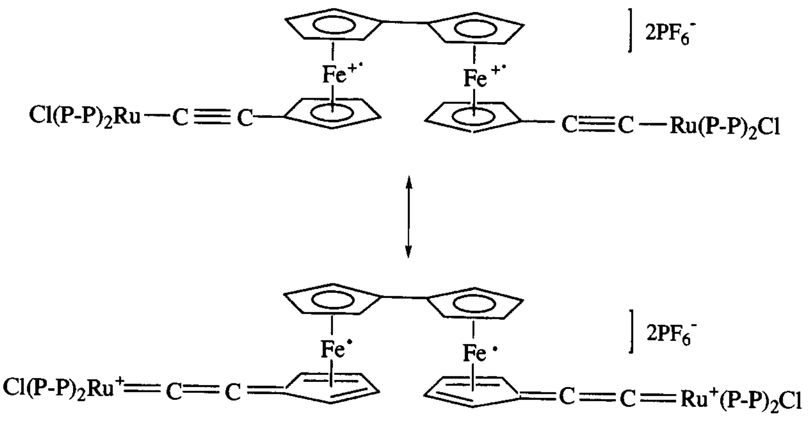
Pulse voltammetric experiments on **5** yields E^f_p/E^r_p ratio of 0.8 and 0.75 for the $Fe^{II/III}$ couples ($E_{1\ 1/2} = -0.37$ V and $E_{2\ 1/2} = -0.21$ V), whilst those of the irreversible $Ru^{II/III}$ couples ($E^{a_1}_p = 0.34$ V and $E^{a_2}_p = 0.51$ V) are 0.45 and 0.42, respectively. These peak potential ratios indicate partial decomposition of the oxidized species. Pulse voltammetry on **5** between -0.5 and 0.1 V gives E^f_p/E^r ratios for the $Fe^{II/III}$ couples ($E_{1\ 1/2}$ and $E_{2\ 1/2}$) as 0.98 and 0.97, respectively. This indicates that decomposition of **5** occurs after oxidation of the ruthenium centres. This proposal is strengthened

Table 1. Electrochemical data

Complex	$E_{1\,1/2}$	$E_{2\,1/2}$	$E_{3\,1/2}$	$E_{4\,1/2}$	$\Delta E_{1/2}\mathrm{Fe}_2$	$K_c\mathrm{Fe}_2$
3	0.08	0.40	—	—	0.32	2.5×10^5
4	−0.20	0.05	0.30	—	0.25	1.7×10^4
5	−0.37	−0.21	0.34[a]	0.51[a]	0.16	5.0×10^2

Working electrode platinum, reference electrode silver wire, supporting electrolyte 0.1 M $[\mathrm{NBu^t_4}][\mathrm{BF_4}]/\mathrm{CH_2Cl_2}$ solution, Scan rate 100 mV s^{-1}. At 237 K, all potentials referenced to $\mathrm{Fe^{II}\,Cp_2/Fe^{III}\,Cp_2}$ in the same system.

[a] Irreversible process anodic peak potential quoted.



P-P = $\mathrm{Ph_2PCH_2PPh_2}$

Fig. 2. The two limiting structures of the oxidized compound **5**.

by the stability of **5** when chemically oxidized. Chemical oxidation of **5** with two equivalents of $[\mathrm{FcCp_2}][\mathrm{PF_6}]$ yields a stable blue solid showing a ν(C=C) absorption at 1975 $\mathrm{cm^{-1}}$*. This is an intermediate absorption between that of the parent acetylene complex **5** (2084 $\mathrm{cm^{-1}}$) and that of a typical allenylidene complex (1926 $\mathrm{cm^{-1}}$)[23] and indicates that the structure lies somewhere between the two limiting structures indicated in Fig. 2. The ν(C=C) frequency suggests that the complex is stabilized by a large degree of conjugation between the $[\mathrm{Ru(dppm)_2Cl}]$ and ferrocenyl centres.

Controlled potential coulometry on complex **3** using platinum gauze working and counter electrodes in a three-compartment cell at 0.24 V reveals a two mole equivalent electron transfer, while subsequent generation at 0.5 V yields negligible further passage of electrons. This is attributable to the instability of the mixed-valence $[\mathrm{HCC{-}Cp_2Fe^{II}\,Fe^{III}\,Cp_2{-}CCH}]$ product of bulk electrolysis. We propose that the decomposition of the $\mathrm{Fe^{II}Fe^{III}}$ species [eq. (1)] gives rise to an $\mathrm{Fe^{III}}$ species that does not undergo further oxidation and to an $\mathrm{Fe^{II}}$-containing product which is itself oxidized at 0.24 V [eq. (2)] to yield one extra equivalent of electron flow. Reverse bulk electrolysis at 0.0 V showed no electron flow, demonstrating the irreversibility of the bulk oxidation. This rules out the disproportionation of $\mathrm{Fe^{II}Fe^{III}}$ [eq. (3)] as an explanation of the original bulk electrolysis at 0.24 V.

$$\mathrm{Fe^{II}Fe^{III}} \rightleftharpoons \mathrm{Fe^{II}} + \mathrm{Fe^{III}} \tag{1}$$

$$\mathrm{Fe^{II}} + e^- \rightarrow \mathrm{Fe^{III}} \tag{2}$$

$$2\mathrm{Fe^{II}Fe^{III}} \rightleftharpoons \mathrm{Fe^{II}Fe^{II}} + \mathrm{Fe^{III}Fe^{III}} \tag{3}$$

$$\mathrm{Fe^{III/III}} + \mathrm{Fe^{II/III}} \rightleftharpoons 2\mathrm{Fe^{II/III}} \tag{4}$$

$$\log K_c = 16.9(\Delta E_{1/2}\mathrm{Fe_2}) \tag{5}$$

The conproportionation constant K_{con} is the equi-

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* Full characterization and discussion of a series of oxidized ferrocenyl-metal acetylides will be detailed by the authors in a publication which is at present in preparation.

librium constant for the conproportionation reaction [eq. (4)]. K_{con} can be determined from cyclic voltammetry using eq. (5).[24,25] $\Delta E_{1/2}\text{Fe}_2$ is the difference in the electrode potentials of the Fe$^{\text{II/III}}$ redox couples in **3**, **4** and **5**. The stability of the mixed-valence state Fe$^{\text{II}}$Fe$^{\text{III}}$ relative to the isovalent species is reflected in the size of K_{con}, i.e. the larger the K_{con} value the greater the stability of Fe$^{\text{II}}$Fe$^{\text{III}}$.

The relative positions of the Fe$^{\text{II/III}}$ electrode potentials in **3**, **4** and **5** show significant stabilization of the Fe$^{\text{II}}$ centre towards oxidation on going from **3** to **5**. A comparison of the $E_{1/2}$ values of complex **3** and **5** highlights this by an overall 0.45 and 0.61 V decrease in the respective $E_{1\,1/2}$ and $E_{2\,1/2}$ values for the Fe$^{\text{II/III}}$ centres of the bridging ligand. This agrees with previous literature published on [(η-C_5H_5)L_2RuCCFeCp$_2$] systems.[26,27] These findings indicate that the ruthenium and manganese centres are donating electron density through the acetylene linkage to the (FeCp$_2$)$_2$ ligand.

It can also be seen that in going from complex **3** to **5**, the value of $\Delta E_{1/2}\text{Fe}_2$ decreases. This indicates that replacing the acetylene hydrogen by metal complexes reduces the relative stability of the Fe$^{\text{II}}$Fe$^{\text{III}}$ mixed-valence species. This is reflected in the decrease in the value of K_{con} on going from complex **3** to **5**.

EXPERIMENTAL

General

All preparations were carried out using standard Schlenk techniques.[28] All solvents were freshly distilled, dried and degassed before use and all reactions were performed under purified nitrogen. The following compounds were prepared by published methods: **1**,[29] *fac*-[Mn(CO)$_3$(dppm)Br][30] and *cis*-[Ru(dppm)$_2$Cl$_2$][31] [dppm = 1,2-bis(diphenylphosphino)-methane]. IR and mass spectra were recorded as CH$_2$Cl$_2$ solutions on a Perkin–Elmer 1710 Fourier Transform spectrometer and a Kratos MS890 spectrometer, respectively. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker WM-250 spectrometer as CDCl$_3$ solutions. The ^{31}P{^{1}H} spectra are referenced to the external standard trimethylphosphite, and ^{1}H spectra to solvent resonances. Elemental analyses were carried out at the Department of Chemistry, University of Cambridge.

Electrochemical studies were carried out using an Autolab PGSTAT20 potentiostat, platinum bead double (working/counter) electrode, Ag/Ag$^+$ reference electrode and 0.1 M [NBu$^t_4$][BF$_4$]/CH$_2$Cl$_2$ supporting electrolyte.

Synthesis of compounds

Preparation of 1′,6′-*bis*(*trimethylsilylethynyl*) *biferrocene* (**2**). To a stirred solution of **1** (2.00 g, 3.2 mmol) in diisopropylamine (50 cm^3) at 4°C was added (CH$_3$)$_3$SiC≡CH (0.7 g, 8.0 mmol), followed by catalytic amounts of CuI (1% molar), Pd(O$_2$CCH$_3$)$_2$ (1% molar) and PPh$_3$ (3% molar). The mixture was stirred at this temperature for a further 30 min and then refluxed for 24 h. To the cooled (to room temperature) solution, diethyl ether (100 cm^3) was added, with the solution then filtered and the solvent removed *in vacuo*. The solid was redissolved in diethyl ether and washed sequentially as follows: 0.1 M HCl (2 × 150 cm^3), H$_2$O (2 × 100 cm^3), aqueous NaHCO$_3$ (2 × 100 cm^3) and H$_2$O (2 × 100 cm^3). The organic layer was dried over magnesium sulphate, filtered and the solvent removed *in vacuo* to yield an orange solid. (If purification is necessary, the product can be subjected to column chromatography on silica using hexane as eluent.) Yield: 1.26 g, 70%, Found: 64.4; H, 6.0. Calc. for $C_{30}H_{34}Si_2Fe_2$: C, 64.2; H, 6.1%. IR (CH$_2$Cl$_2$): ν(C≡C) 2148 cm^{-1}. ^{1}H NMR (CDCl$_3$): 4.01 (4H, t, C$_5$H$_4$), 4.18 (4H, t, C$_5$H$_4$), 4.21 (4H, t, C$_5$H$_4$), 4.37 (4H, t, C$_5$H$_4$), 0.23 [18H, s, (CH$_3$)$_3$Si—] ppm. Mass spectrum (FAB + ve): M$^+$ 562 (calc. 562).

Preparation of 1′,6′-*bis*(*ethynyl*)*biferrocene* (**3**). Orange **2** (1.00 g, 1.8 mmol) was dissolved in a mixture of methanol–diethyl ether (60 cm^3 : 40 cm^3). To this was added anhydrous K$_2$CO$_3$ (0.40 g, 2.9 mmol) and the mixture stirred for 24 h. The solvents were removed *in vacuo*, before redissolving in diethyl ether (60 cm^3) and washing with water (2 × 50 cm^3). The organic layer was dried (MgSO$_4$), filtered and the solvent again removed *in vacuo*. The crude product was passed through a silica column using dichloromethane–hexane (1 : 1) as eluent, followed by drying *in vacuo* to leave a pale orange solid. Yield: 0.6 g, 80%. Found: 69.5; H, 4.4. Calc. for $C_{24}H_{18}Fe_2$: C, 69.2; H, 4.3%. IR (CH$_2$Cl$_2$): ν(C≡C) 2106 cm^{-1}, ν(C—H) 3298 cm^{-1}. ^{1}H NMR (CDCl$_3$): 4.02 (4H, t, C$_5$H$_4$), 4.22 (4H, t, C$_5$H$_4$), 4.25 (4H, t, C$_5$H$_4$), 4.40 (4H, t, C$_5$H$_4$), 2.64 (2H, s, C≡CH) ppm. Mass spectrum (EI): M$^+$ 418 (calc. 416).

The work-up procedures are modifications of a previous method.[32]

Preparation of 1′,6′-*bis*{*manganese*(I)*tricarbonyl* [1,2-*bis*(*diphenylphosphino*)*methane*]}*biferrocene* (**4**). A mixture of **3** (0.21 g, 0.5 mmol) and AgBF$_4$ (0.098 g, 0.5 mmol) in dichloromethane (45 cm^3) and water (15 cm^3) was stirred for 15 min with the exclusion of light. *Fac*-[Mn(CO)$_3$(PPh$_2$CH$_2$ PPh$_2$)Br] (0.30 g, 0.5 mmol) was added and the stirring continued until IR spectroscopy indicated the completion of the reaction. The mixture was filtered, evaporated to dryness, washed with sodium thiosulphate (2 × 20 cm^3) and water (2 × 20 cm^3), and then purified by silica thin layer chromatography using dichloromethane–hexane (1 : 1) as eluent. Compound **4** was isolated as an orange, microcrystalline powder. Yield: 0.18 g, 25%. Found: C, 65.2; H, 4.7. Calc. for $C_{80}H_{62}O_3P_4Mn_2Fe_2$: C, 65.7; H, 4.8%. IR ($CH_2Cl_2$): $\nu(C{\equiv}C)$ 2084 cm^{-1} (sh, wk), $\nu(C{\equiv}O)$ 2011, 1939, 1919 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): -120.19 (s) ppm. Mass spectrum (FAB + ve): M$^+$ 1461 (calc. 1462).

Preparation of 1′,6′-*bis*{*rutheniumbis*[1,2-*bis*(*diphenylphosphino*)*methane*]*chloride*}*biferrocene* (**5**). To a stirred solution of **3** (0.21 g, 0.5 mmol) in dichloromethane (75 cm^3) was added *cis*-[Ru($PPh_2CH_2PPh_2$)Cl_2] (0.47 g, 0.5 mmol) and $NaPF_6$ (0.17 g, 1.05 mmol). After 4 h, two drops of dbu were added to the yellow solution, which immediately turned orange. After further stirring at room temperature for 2 h, the solution was evaporated to dryness and washed with acetone (2 × 20 cm^3), to leave an orange, microcrystalline solid. Yield: 0.39 g, 35%. Found: C, 65.3; H, 4.7. Calc. for $C_{124}H_{104}Cl_2P_8Ru_2Fe_2$: C, 66.7; H, 4.7%. IR ($CH_2Cl_2$): $\nu(C{\equiv}C)$ 2083 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): -148.78 (s) ppm. Mass spectrum (FAB + ve): M$^+$ 2228 (calc. 2225).

The preparations of **4** and **5** are modifications of previously reported synthetic routes (refs 33 and 34 respectively).

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