Aryl (ferrocenyl)-capped ethenylazaferrocenes: synthesis, structure and electrochemistry

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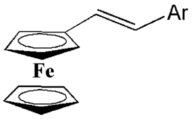
The Horner–Wadsworth–Emmons reaction of 2,5-dimethylazaferrocene-1′-carbaldehyde with diethyl benzylphosphonate, diethyl *p*-methoxybenzylphosphonate and diethyl (ferrocenylmethyl)phosphonate afforded (*E*)-1-(2,5-dimethylazaferrocen-1′-yl)-2-phenylethene (**2a**), (*E*)-1-(2,5-dimethylazaferrocen-1′-yl)-2-(*p*-methoxyphenyl)ethene (**2b**) and (*E*)-1-(2,5-dimethylazaferrocen-1′-yl)-2-ferrocenylethene (**2c**), respectively. Cyclic voltammetry showed significant difference in the electrochemical behaviour of these compounds in comparison to their ferrocenyl counterparts. The styryl group, which is an electron-withdrawing group in the ferrocenyl compound, displays a reverse effect in the azaferrocenyl complex **2a**. Introduction of the *p*-methoxystyryl group to 2,5-dimethylazaferrocene brings about a cathodic shift of the redox potential of 370 mV, whereas for the ferrocenyl analog the shift is only 60 mV. Compound **2c** shows two redox waves due to two non-equivalent metallocenyl moieties, but there is only weak electronic coupling between redox centres. The W(CO)$_5$-complex of **2c** (**4**) was synthesised and its structure determined by X-ray diffraction.

Introduction

Aryl-capped ethenylferrocenes (in most cases the more stable *E* isomers) **1** have attracted considerable interest due to their unusual nonlinear optical, electronic and magnetic properties.[1–14] Moreover, the backbone **1** is present in ferrocifene and related organometallic selective estrogen receptor modulators (SERMs), promising candidates for anticancer drugs.[15] When aryl is ferrocenyl, the binuclear compound, 1,2-diferrocenylethene, attracted attention because it showed electronic communication between metal centres and stabilisation of the mixed-valence oxidation product.[16–18]

Continuing our research program focused on the development of synthetic methods in chemistry of the nearest heteroanalog of ferrocene, azaferrocene,[19] we felt that it would of interest to elaborate a convenient route to conjugated π-systems containing this metallocene and to study their properties.

In this paper we disclose synthesis of 1′-(2-arylethenyl)-2,5-dimethylazaferrocenes **2** (including a compound in which aryl is ferrocenyl) and the study of their electronic and electrochemical properties. Moreover, the W(CO)$_5$-complex of the azaferrocenyl–ferrocenyl compound has been synthesised to study the influence of the coordination of the nitrogen atom to a metal on the electronic properties the bis-metallocene moiety. The structure of this complex has been determined by single-crystal X-ray diffraction.



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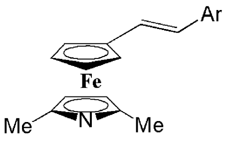

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Results and discussion

Synthesis

We have recently reported that lithiation of 2,5-dimethylazaferrocene with *sec*-BuLi–TMEDA, followed be quenching with dimethylformamide afforded 2,5-dimethylazaferrocene-1′-carbaldehyde **3** in 20% isolated yield.[19] Despite the low yield compound **3** can be conveniently isolated from the reaction mixture, allowing its use as a starting material in the further step of the synthesis of **2** (Scheme 1).

The Horner–Wadsworth–Emmons reaction of **3** with diethyl benzylphosphonate in the presence of potassium *tert*-butoxide in THF afforded compound **2a** in 70% isolated yield. Similarly, using diethyl *p*-methoxyphosphonate and diethyl (ferrocenylmethyl)phosphonate[20] compounds **2b** and **2c** were obtained in 27 and 60% yield, respectively. Their structures were confirmed by spectroscopic methods (^{1}H NMR, MS, IR), as well as by elemental analysis. The *E*-stereochemistry was deduced from large values (16–16.2 Hz) of coupling constants between vinylic protons. Compounds **2a,b** are air-stable orange oils, whereas **2c** is an air-stable orange solid. Compound **2c** treated with the photochemically generated W(CO)$_5$(THF) in THF at r.t. afforded the trinuclear complex

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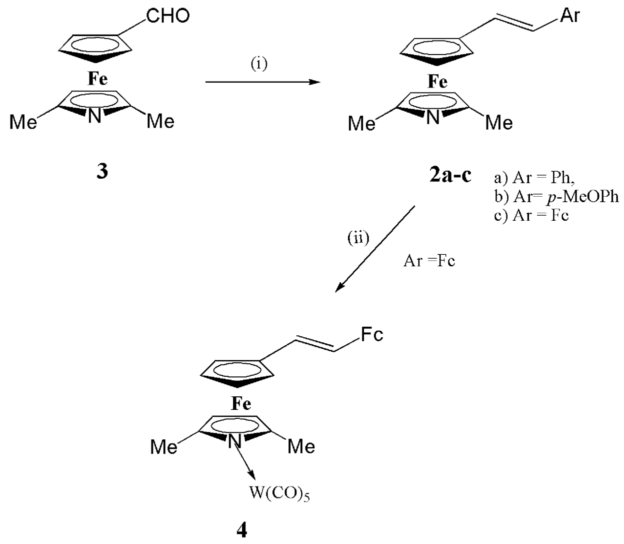


Scheme 1 *Reagents*: (i) $ArCH_2P(O)(OEt)_2$, *tert*-BuOK, THF; (ii) $W(CO)_5(THF)$.

4 in 80% yield. As expected, coordination of the $W(CO)_5$ group to the pyrrolyl nitrogen brought about a downfield shift of the signals of the methyl groups (0.3 ppm), β-pyrrolyl protons (0.2 ppm) and one of the vinylic protons (0.1 ppm), other signals being less influenced. The structure of **4** was determined by X-ray diffraction.

Electronic absorption spectra

Compounds **2a–c** show in the region 300–500 nm two absorption bands (Table 1, which also contains, for comparison, the data for styrylferrocene, (*E*)-1,2-diferrocenylethene and 2,5-dimethylazaferrocene). The high-energy (HE) band is observed at 314–332 nm and the low-energy (LE) band at 439–472 nm. These bands can be assigned to π–π* transitions in the conjugated π-ligand and to metal-centred d–d transitions of the azaferrocenyl (or ferrocenyl) group, respectively.[16,17] The electronic absorption spectrum of 2,5-dimethylazaferrocene is closely similar to the spectrum of ferrocene. The latter displays weak bands at 332 nm (ε = 160 M^{-1} cm^{-1}) and 439 nm (ε = 130 M^{-1} cm^{-1}) (Table 1), whereas the former at 325 nm (ε = 49 M^{-1} cm^{-1}) and 440 nm (ε = 91 M^{-1} cm^{-1}).[21]

The introduction of the styryl group to 2,5-dimethylazaferrocene brings about a bathochromic shift (+31 nm) of the LE band, which becomes more intense (ε = 210 M^{-1} cm^{-1}), whereas the HE band is shifted hypsochromically (−14 nm) (ε = 4300 M^{-1} cm^{-1}). A similar effect is observed on going from ferrocene to styrylferrocene (+24 and −11 nm). In the case of **2b** the HE and LE bands are at 315 nm (ε = 11 800 M^{-1} cm^{-1}) and 456 nm (ε = 730 M^{-1} cm^{-1}), respectively. Compound **2c** displays the HE band at 322 nm (ε = 4600 M^{-1} cm^{-1}) and the LE band at 472 nm (ε = 500 M^{-1} cm^{-1}), which are close to the values reported for 1,2-diferrocenylethene (314 and 458 nm).[17]

The presented data indicate that electronic structure of aryl (ferrocenyl)capped ethenylazaferrocenes is closely similar to that of their ferrocenyl counterparts. This means that azaferrocenyl group is able to form conjugated π-systems which may be of interest for various branches of materials science.

Table 2 Electrochemical data in CH_2Cl_2

Compound	$E_{1/2}$ (mV *vs.* Fc/Fc^+)	ΔE/mV
2a	179	62
2b	−143	133
2c	41	144
	249	72
4	42	84
	452	236
Styrylferrocene	25	111
2,5-Dimethylazaferrocene	237	157
(*E*)-1,2-Diferrocenylethene (**6**)	−79	119
	73	119

Electrochemistry

Electrochemical behaviour of the synthesised compounds (and, for comparison, of styrylferrocene, (*E*)-1,2-diferrocenylethene and 2,5-dimethylazaferrocene) was studied using cyclic voltammetry (CV). The measurements were carried out in dichloromethane solutions at room temperature. The data are gathered in Table 2.

Compounds **2a,b** and styrylferrocene displayed single, chemically reversible oxidation waves ($i_{pc}/i_{pa} \sim 1$) (Fig. 1). The observed peak separations were close to that measured for ferrocene under the same experimental conditions (140 mV) indicating that departure from the value of 59 mV expected for an electrochemically reversible one-electron transfer should be rather due to uncompensated solution resistances and/or slow electron transfer, than to significant structural reorganisation accompanying the charge transfer. Therefore, we assign these waves to one-electron oxidation of the metallocenyl groups.

It has been reported that azaferrocenium cation is rather unstable and reversible CV scans for azaferrocene were obtained only at relatively high potential sweep rates (> 20 V s^{-1}

Table 1 Electronic absorption spectra in CH_2Cl_2

Compound	λ_{max}/nm (ε_{max}/M^{-1} cm^{-1})	Compound	λ_{max}/nm (ε_{max} /M^{-1} cm^{-1})
2a	318 (4300)	Styrylferrocene	314 (19 000)
	470 (210)		464 (730)
2b	315 (11 800)	2,5-Dimethylazaferrocene	332 (160)
	456 (730)		439 (130)
2c	322 (4600)	Ferrocene[a]	325 (49)
	472 (500)		440 (91)

[a] Literature data.[21]

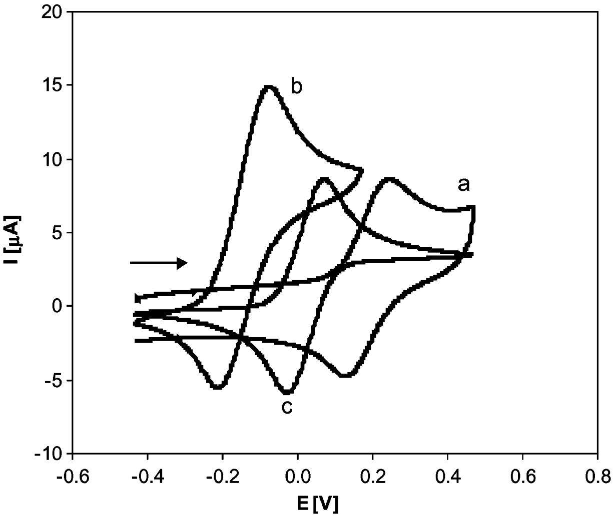


Fig. 1 Cyclic voltammogram of **2a** (a), **2b** (b) and styrylferrocene (c) in CH_2Cl_2 with 0.1 M Bu_4NClO_4 at a Pt-disk electrode, ϕ = 1.5 mm, scan rate: 0.1 V s^{-1}.

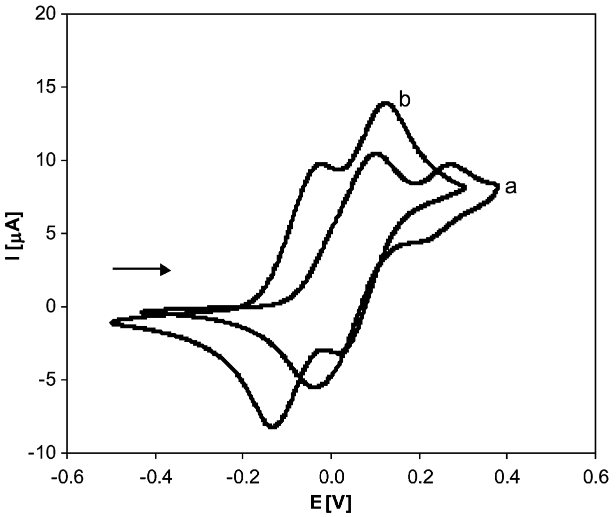


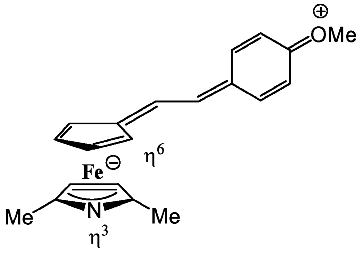
Fig. 2 Cyclic voltammogram of **2c** (a) and (*E*)-1,2-diferrocenylethene (b) in CH_2Cl_2 with 0.1 M Bu_4NClO_4 at a Pt-disk electrode, ϕ = 1.5 mm, scan rate: 0.1 V s^{-1}.

in acetonitrile).[22] More recently, it was reported that in dichloromethane solutions reversible CV scans can be obtained at lower rates (especially for 2,5-dimethylazaferrocene).[23] The results obtained in this work show that the oxidized **2a,b** are relatively stable and reversible redox processes were observed at rates as low as 100 mV s^{-1}.

It has been of interest to compare the oxidation potentials of **2a,b** and styrylferrocene with those of 2,5-dimethylazaferrocene and ferrocene, respectively.

The substitution of a hydrogen atom in ferrocene by the styryl group brings about an anodic shift of the oxidation potential equal to 25 mV. In contrast, the same substitution in the 1′-position of 2,5-dimethylazaferrocene causes *a cathodic* shift of 58 mV. This suggests that the electronic effect exerted by the styryl group in styrylferrocene and **2a** is completely different. In the former the styryl group behaves as an electron-withdrawing group, reducing the electron density at iron, whereas in the latter it behaves as an electron-donating group. A possible explanation of this difference is that azaferrocenyl group is more prone to accept an electron than the ferrocenyl group (the reduction potentials of ferrocene and azaferrocene are −2.93 and −2.56 V, respectively).[22]

A comparison of the effects of *p*-methoxystyryl group on the oxidation potential of ferrocenyl and azaferrocenyl group is also of interest. According to the literature (*p*-methoxystyryl) ferrocene has an oxidation potential 60 mV lower than the oxidation potential of ferrocene, indicating that this group behaves as an electron donor group towards the ferrocenyl moiety.[24] Surprisingly, we have found that the *p*-methoxystyryl group attached to the 2,5-dimethylazaferrocene exerts a much stronger effect lowering the oxidation potential of the metallocene moiety by 380 mV! This huge effect can be tentatively attributed to the greater electronegativity of nitrogen causing removal of electron density from iron (compare oxidation potential of 2,5-dimethylazaferrocene with that of ferrocene[22]) and to a tendency of pyrrolyl complexes for $\eta^5 \rightarrow \eta^3$ ring slippage.[25] Both effects may enable efficient transfer of electron density from the *p*-methoxyphenyl group to iron as is shown in the mesomeric structure **I**.



I

The above-mentioned data show that substituents effects in π-conjugated systems containing azaferrocenyl moiety can be different and much stronger than substituent effects in their ferrocenyl counterparts. This presents a considerable potential for synthesis of complexes with tailored redox properties for applications in materials science.

The electrochemical behaviour of **2c** was compared with those of (*E*)-1,2-diferrocenylethene, ferrocene and 2,5-dimethylazaferrocene. Cyclic voltammograms of **2c** and (*E*)-1,2-diferrocenylethene are shown in Fig. 2. Both compounds show two quasi-reversible oxidation waves due to the presence of two metallocenyl units. In the case of (*E*)-1,2-diferrocenylethene the ferrocenyl groups are equivalent and two oxidation waves result from the electronic coupling in the mixed-valence product of the one-electron oxidation.[16,17] The difference of potentials of the two waves, $(\Delta E) = E^{I}_{1/2} - E^{II}_{1/2}$, observed in our experiment (152 mV) is closely similar to the value reported in the literature (170 mV).[17]

In contrast, in **2c** there are two different metallocenyl groups and two oxidation waves are expected, regardless the presence or absence of the electronic coupling between metal centres. We assign the first wave to the oxidation of the ferrocenyl

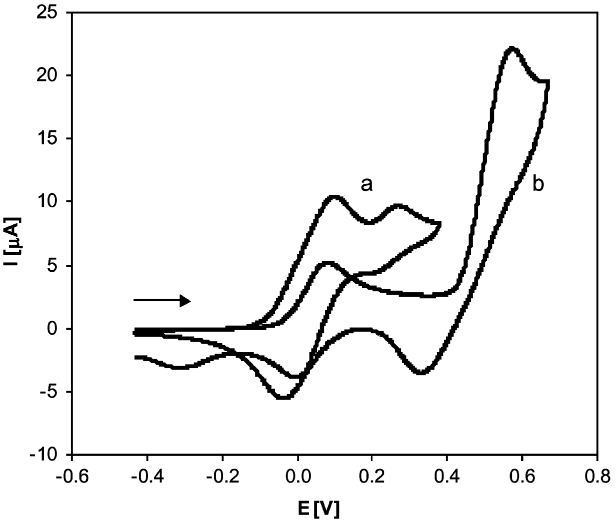


Fig. 3 Cyclic voltammogram of **2c** (a) and **4** in CH_2Cl_2 with 0.1 M Bu_4NClO_4 at Pt-disk electrode, ϕ = 1.5 mm, scan rate: 0.1 V s^{-1}.

group and the second wave to the oxidation of the azaferrocenyl moiety. This assignment is confirmed by the fact that coordination of **2c** to the $W(CO)_5$ moiety (compound **4**) practically does not influence the first wave but shifts anodically the second wave, which becomes chemically irreversible (Table 2 and Fig. 3). This shift (203 mV) is comparable to that observed on going from 2,5-dimethylazaferrocene to its $Cr(CO)_5$ complex (150 mV).[22] The potential of the first wave (41 mV) suggests that the azaferrocenylethenyl group is a stronger electron-withdrawing group than the styryl group. On the other hand, the oxidation of the azaferrocenyl moiety (second wave) occurs at the potential only slightly higher (difference 12 mV) than the oxidation of 2,5-dimethylazaferrocene, which means that the oxidised ferrocenylethenyl group has an electronic effect comparable with that of hydrogen. The redox behaviour of **2c** significantly differs from that of (*E*)-1,2-diferrocenylethene, where as a result of the electronic coupling and stabilisation of the mixed-valence mono-oxidised species, the first oxidation wave appears at a potential significantly lower, and the second wave at a potential higher by approximately the same value than the oxidation potential of ferrocene (−79 and +73 mV, respectively). In the case of **2c**, the first oxidation potential is higher than the oxidation potential of ferrocene, whilst the second oxidation potential is only slightly higher than that of 2,5-dimethylferrocene. This suggests only a weak electronic coupling between two iron centres in **2c**, corresponding to the $\Delta E \approx 2 \times 12$ mV = 24 mV. Interestingly, almost the same value (22 mV) is obtained by subtracting from the difference in the second oxidation potential of **2c** and that of 1,2-diferrocenylethene (176 mV) the difference in the oxidation potentials of **2a** and styrylferrocene (154 mV).

It has been well established that in heterobinuclear organometallic complexes with unsaturated carbon bridges the degree of interaction between metals decreases when the difference in their redox potentials increases.[26] Therefore, a significant difference in oxidation potentials of 2,5-dimethylazaferrocene and ferrocene (237 mV) may be one of the factors weakening the electronic coupling in **2c** in comparison to that in 1,2-diferrocenylethene. Another factor to be taken into account is that oxidation of azaferrocene may remove an electron which is not entirely localized at iron as it is in the case of ferrocene, but rather at the pyrrolyl ligand.[23] In fact, it has been observed that azaferrocenium cations exhibit reactivity typical for pyrrole radical cations and better stability of the 2,5-disubstituted species was explained by the lack of reactive, acidic α-hydrogen atoms in the pyrrolyl ligand.[23] If it is true, in **2c** there are not two metal-centred redox sites as in (*E*)-1,2-diferrocenylethene,[16,17] but one metal-centred and one rather delocalized site. The coupling between such sites is expected to be different (weaker) than the coupling between metal-centred sites.

Mass spectra

Some features of the mass spectra (EI) of compounds **2a–c** are worth noting. It is known that in the main fragmentation peak in the mass spectrum of the parent $(C_4H_4N)(C_5H_5)Fe$ is that corresponding to the $(C_5H_5)Fe^+$ ion, which reflects weaker bonding of the pyrrolyl ligand in the molecular ion in comparison to its carbocyclic counterpart.[27] The similar fragmentation pattern is observed in the case of **2a–b**, the main fragmentation peak corresponding to the loss by the molecular ion of the 2,5-dimethylpyrrolyl ligand, $(M - 94)^+$. However, in the case of **2c** the most intense fragmentation peak is that of $M - 65$ $(M - Cp)^+$ and the peak $(M - 94)^+$ is approximately 2.5 times weaker. This corroborates the electrochemical data indicating that the first oxidation step of **2c** occurs at the ferrocenyl group and lower ionization potential of ferrocene in comparison to azaferrocene.[27] However, the presence of the $(M - 94)^+$ ion suggests that ionization of the azaferrocenyl moiety in **2c** also occurs to some extent and may suggest intramolecular electron transfer $Fc(\text{III})^+AFc(\text{II}) \rightarrow Fc(\text{II})AFc(\text{III})^+$ in an energy-rich molecular ion.

Structural analysis of 4

Crystals suitable for analysis were grown from layered chloroform–heptane. The molecular structure of **4** is shown in Fig. 4 and selected bond distances and angles in Table 3.

Both metallocenyl groups have typical sandwich structures in nearly eclipsed conformations (torsional angles ~3–5°), with cyclic ligands nearly parallel to each other (angles between their best planes ~1–4°). The angle between the W–N bond and the best plane of the pyrrolyl ligand (tilt angle) is 5.8(6)°. The atoms C1C, C10, C11, C2B are practically

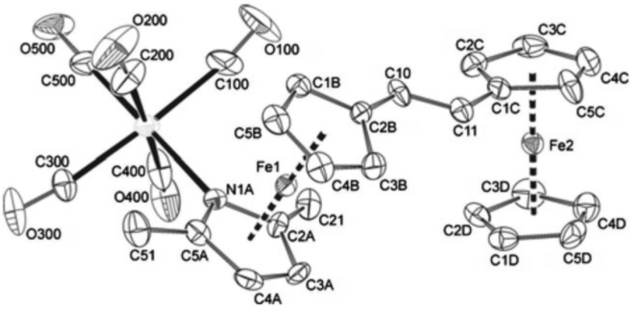


Fig. 4 Thermal ellipsoid plot (30% probability) of **4**. Hydrogen atoms omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) in **4**

W1–C400	1.992(11)	C10–C2B	1.480(16)
W1–C500	2.017(17)	C11–C1C	1.493(17)
W1–C200	2.019(15)	C100–O100	1.086(19)
W1–C300	2.057(15)	C200–O200	1.157(18)
W1–C100	2.058(19)	C300–O300	1.135(16)
W1–N1A	2.277(9)	C400–O400	1.130(18)
C10–C11	1.312(15)	C500–O500	1.123(17)
C400–W1–C500	84.7(8)	C500–W1–N1A	178.2(6)
C400–W1–C200	175.0(7)	C200–W1–N1A	91.4(6)
C500–W1–C200	90.4(7)	C300–W1–N1A	92.8(5)
C400–W1–C300	88.5(5)	C100–W1–N1A	92.1(4)
C500–W1–C300	87.1(7)	C11–C10–C2B	124.0(13)
C200–W1–C300	90.9(7)	C10–C11–C1C	122.5(12)
C400–W1–C100	90.0(8)	O100–C100–W1	171(2)
C500–W1–C100	88.1(6)	O200–C200–W1	176.8(15)
C200–W1–C100	90.2(9)	O300–C300–W1	171.9(16)
C300–W1–C100	175.0(6)	O400–C400–W1	175.8(18)
C400–W1–N1A	93.5(6)	O500–C500–W1	178.1(15)

coplanar as expected for an ethylene fragment, and their best plane makes with the planes of the adjacent CpB and CpC ligands angles ~22 and ~16°, respectively. The dihedral angle between the planes of these ligands is ~35°. The lengths of single- and double carbon–carbon bonds in the ethylene bridge are close to those reported for closely related derivatives of 1,2-diferrocenylethene[28] and the (*E*)-2-ferrocenylethenylcobaltocenium cation.[29] A peculiar feature of the structure is a *cis* arrangement of metallocenyl moieties with respect to the plane of the ethylenic spacer. A similar arrangement was reported for 1-ferrocenyl-2-(1,2,3,4,5-pentamethylferrocen-1′-yl)ethene.[30] However, the lengths of the W–N and W–C bonds are practically the same as those in the W(CO)$_5$(2,5-dimethylazaferrocene),[31] although it should be noticed that some of the atoms in the coordination sphere of tungsten are strongly vibrating, which limited the accuracy of the determination of the atomic coordinates and bond lengths (refinement of these atoms in disordered positions did not allow to improve the accuracy). The Fe···Fe distance in **4** is 6.529(3) Å. The structure of **4** shows a possibility of an extensive electronic coupling between the metallocenyl moieties across the ethylenic spacer, which contradicts the electrochemical data (the first oxidation potential is practically the same for **2c** and **4**). However, unfortunately, we cannot provide evidence that the solid-state structure persists in solution.

Conclusions

The results obtained in this work show that the aryl-capped ethenylazaferrocenes are, similarly as their ferrocenyl counterparts, conjugated π-systems. They exhibit quasi-reversible anodic electrochemistry at relatively low potential scan rates (~100 mV s^{-1}). However, since the azaferrocenyl group is stronger electron acceptor than the ferrocenyl group, the effect of electron-donating substituents on the redox potential of the metallocenyl moiety is much stronger for azaferrocene derivatives. In contrast to (*E*)-1,2-diferrocenylethene, (*E*)-2-ferrocenyl-1-(2,5-dimethylazaferrocen-1′-yl)ethene (**2c**), shows only weak electronic coupling between metal centres. However, this compound displays two redox waves in cyclic voltammetry, due to non-equivalence of the metallocenyl groups. The redox potential of the azaferrocenyl group can be changed by coordination to a metal centre, whereas the redox potential of the ferrocenyl group is less sensitive to such a structural modification. The above data indicate that aryl-capped ethenylazaferrocenes are of potential interest for construction of molecular devices with tailored electronic or opto-electronic properties.

Experimental

General

All reactions were carried out under argon. THF was distilled over sodium/benzophenone. Other solvents were reagent grade and were used without prior purification. Chromatographic separations were carried out using silica gel 60 (Merck, 230–400 mesh ASTM). ^{1}H NMR spectra were recorded on a Varian Gemini 200BB (200 MHz) spectrometer. IR spectra were recorded on a FT-IR Nexus Nicolet apparatus. Mass spectra were run on a Finnigan MAT 95 spectrometer. The combustion analyses were performed by Analytical Services of the Center of Molecular and Macromolecular Studies of the Polish Academy of the Sciences (Łódź).

2,5-Dimethylazaferrocene,[32] 2,5-dimethylazaferrocene-1′-carbaldehyde **3**,[19] styrylferrocene,[33] (*E*)-1,2-ferrocenylethene[34] and diethyl (ferrocenylmethyl)phosphonate[20] were prepared according to the literature procedures. Other compounds were commercial reagents (Aldrich) and were used as received.

Syntheses

General procedure for the synthesis of 2. The appropriate phosphonate (0.24 mmol) was dissolved in dry THF and cooled to 0 °C. Potassium *tert*-butoxide (31 mg, 0.28 mmol) was added and the mixture was stirred vigorously. A yellow coloration of the solution appears. After 30 min of stirring at 0 °C the solution was warmed to room temperature and 2,5-dimethylazaferrocene-1′-carbaldehyde (60 mg, 0.24 mmol) in 3 ml of THF was added. The reaction mixture was refluxed for 3 h, quenched by addition of water and extracted with diethyl ether. The ether layer was washed with brine and dried. After the evaporation of the solvent, the product was isolated by chromatography on silica using ethyl acetate as eluent.

2a (53 mg, 70%). Orange, air-stable oil (Found: C, 71.60; H, 6.17; N, 4.34. $C_{19}H_{19}FeN$ requires C, 71.94; H, 6.04; N, 4.42). δ_H (200 MHz; CDCl$_3$; Me$_4$Si): 7.48–7.24 (5H, m, 5H, Ph), 6.84 (1H, d, J = 16.2, vinyl), 6.75 (1H, d, J = 16.2, vinyl), 4.39 (2H, t, J = 1.7, Cp), 4.32 (2H, s, β-pyrrolyl), 4.28 (2H, t, J = 1.7, Cp), 2.19 (6H, s, CH$_3$). *m*/*z* (EI, 70 eV) 317.0862 (89, M$^+$ ≡ $C_{19}H_{19}NFe$ requires 317.0867), 223 (100, M − C_6H_8N), 94 (2, C_6H_8N).

2b (22.5 mg, 27%). Orange air-stable oil (Found: 69.31; H, 6.66. $C_{20}H_{21}FeNO$ requires C, 69.18; H, 6.16). δ_H (200 MHz; CDCl$_3$; Me$_4$Si): 7.40 (2H, d, J = 8.8, C$_6$H$_4$), 6.89 (2H, d, J = 8.8, C$_6$H$_4$), 6.75 (1H, d, J = 16.1, vinyl), 6.66 (1H, d, J = 16.1, vinyl), 4.37 (2H, t, J = 1.8, Cp), 4.32 (2H, s, β-pyrrolyl), 4.27 (2H, t, J = 1.8, Cp), 3.83 (3H, s, OCH$_3$), 2.20 (s, 6H, 2 × CH$_3$). *m*/*z* (EI, 70 eV) 347.0969 (100, M$^+$ ≡ $C_{20}H_{21}NOFe$ requires 347.0972), 253 (77, M − C_6H_8N), 94 (2, C_6H_8N).

2c (61 mg, 60%). Orange air-stable oily solid. δ_H (200 MHz; $CDCl_3$; Me_4Si): 6.50 (1H, d, J = 16.0, vinyl), 6.36 (1H, d, J = 16.0, vinyl), 4.39 (2H, t, J = 1.6, Cp-azaferrocenyl), 4.30 (4H, br, Cp-azaferrocenyl and β-pyrrolyl), 4.25 (2H, t, J = 1.9, Cp-ferrocenyl), 4.24 (2H, t, J = 1.9 Hz, Cp-ferrocenyl), 4.13 (5H s, Cp′-ferrocenyl), 2.23 (6H, s, 2 × CH_3). m/z (EI, 70 eV) 425.0534 (100, $M^+ \equiv C_{23}H_{23}Fe_2N$ requires 425.0529), 360 (66, M − Cp) 331 (25, M − C_6H_8N), 94 (7, C_6H_8N).

Synthesis of 4. Tungsten hexacarbonyl (53 mg, 0.15 mmol) dissolved in THF (20 ml) was photolysed with a 200 W high-pressure mercury lamp for 2 h. **2c** (30 mg, 0.08 mmol) was added to the photolyte and the resulting solution was stirred at room temperature for 4 h. Removal of solvent, column chromatography (SiO_2/hexane–chloroform 1 : 1) gave **4** (48 mg, 80%) as orange crystals (Found: C, 45.25; H, 3.33; N, 1.70. $C_{28}H_{23}O_5Fe_2NW$ requires C, 44.90; H, 3.09; N, 1.87). δ_H (200 MHz; $CDCl_3$; Me_4Si): 6.60 (1H, d, J = 16.0, vinyl), 6.34 (1H, d, J = 16.0, vinyl), 4.51 (2H, s, β-pyrrolyl), 4.41 (4H, s, Cp′-azaferrocenyl), 4.30 (4H, s, Cp-ferrocenyl), 4.13 (5H, s, 5H, Cp′-ferrocenyl), 2.53 (6H, s, 6H, 2 × CH_3). ν_{max} ($CHCl_3$)/cm^{-1}: 2067, 1921 ($C\equiv O$).

Cyclic voltammetry measurements

The cyclic voltammetry measurements were performed on a AUTOLAB (Eco Chimie BV) apparatus in a three-electrode system, where the working electrode was a Pt disk (ϕ = 1,5 mm), the reference electrode was a ferrocene electrode, and the counter electrode was a cylindrical platinum gauze. The experiments were carried out under an argon atmosphere with 0.1 M solutions of the complexes in CH_2Cl_2 containing 0.1 M Bu_4NClO_4 as supporting electrolyte.

Table 4 Crystal data and structure refinement for **4**

Empiric formula	$C_{28}H_{23}Fe_2NO_5W$
M_r	749.02
Crystal description	Prism
Crystal size/mm	0.5 × 0.4 × 0.2
Space group	*Pbca*
a/Å	17.771(4)
b/Å	24.755(3)
c/Å	12.338(4)
V/Å^3	5428(2)
D_c/g cm^{-3}	1.833
Data collection	
Diffractometer	Rigaku AFC5S
λ/Å (Mo-Kα)	0.71069
μ/mm^{-1}	5.321
T/K	293(2)
Data collected (*hkl*)	0 to 21, 0 to 29, 0 to 14
No. reflections measured	5025
No. reflections with $I > 2\sigma(I)$	2495
Solution and refinement	
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
No. parameters	337
$R(F)^a$ (all data)	
$wR(F^2)^b$ (all data)	
$R(F)^a$	0.067
$wR(F^2)^a$	0.174
$(\Delta/\sigma)_{max}$	0.0
Peak, hole/e Å^{-3}	2.949, −3.621

[a] $R(F) = \sum(|F_o - F_c|)/|F_o|$. [b] $wR(F^2) = [\sum w(|F_o - F_c|)^2/\sum|F_o|^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (0.1336P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

X-Ray diffraction analysis of 4

Crystals suitable for analysis were grown from layered chloroform–heptane.

X-Ray diffraction data were collected at 293 K on Rigaku AFC5S four-circle diffractometer using Mo-Kα radiation. The unit cells were determined from 45 reflections. The structure was solved by direct methods using SHELXS-97[35] and refined by full-matrix least squares method on F^2 using SHELXL-97.[36] After the refinement with isotropic displacement parameters, refinement was continued with anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were placed on geometrically idealized positions and constrained to ride on their parent atoms, with a C–H distance of 0.950 Å and $U_{iso}(H) = 1.2U_{eq}$ (C). The molecular geometry was calculated by PARST97[37] and PLATON.[38] Fig. 4 has been prepared using PLATON. Crystal data and structure refinement are collected in Table 4.

CCDC reference number 293101.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600022c

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References

1 E. Peris, *Coord. Chem. Rev.*, 2004, **248**, 279.
2 M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bardy, D. Bloor, P. V. Kolinsky and R. J. Jones, *Nature*, 1987, **330**, 360.
3 S. Di Bella, *Chem. Soc. Rev.*, 2001, **30**, 355.
4 I. R. Whittal, A. M. McDonagh, M. P. Humphrey and M. Samoc, *Adv. Organomet. Chem.*, 1998, **42**, 291.
5 N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.
6 D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.*, 1994, **94**, 195.
7 J. Heck, S. Dabek, T. Meyer-Friedrichsen and H. Wong, *Coord. Chem. Rev.*, 1999, **190–192**, 1217.
8 S. Barlow, H. C. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry and S. R. Marder, *J. Am. Chem. Soc.*, 1991, **121**, 3715.
9 I. Ledoux, J. Zyss, E. Barni, C. Barolo, N. Diulgeroff, P. Quagliotto and G. Viscardi, *Synth. Met.*, 2000, **115**, 213.
10 G. Balavoine, J.-C. Daran, G. Iftime, P. G. Lacroix, E. Manoury, J. A. Delaire, I. Maltey-Fanton, K. Nakatani and S. DiBella, *Organometallics*, 1999, **18**, 21.
11 G. Iftime, G. A. Gilbert, G. A. Balavoine, J. C. Daran, P. G. Lacroix and E. Manoury, *J. Organomet. Chem.*, 2001, **637–639**, 531.
12 M. Malaun, Z. R. Reeves, R. J. Paul, J. C. Jeffery, J. A. McCleverty, M. D. Ward, I. Asselberghs, K. Clays and A. Persoons, *Chem. Commun.*, 2001, 49.
13 Asselberghs, K. Clays, A. Persoons, A. M. McDonagh, M. D. Ward and J. A. McCleverty, *Chem. Phys. Lett.*, 2003, **368**, 408.
14 T. Kondo, S. Horiuchi, I. Yagi, S. Ye and K. Ukosaki, *J. Am. Chem. Soc.*, 1999, **121**, 391.
15 (*a*) G. Jaouen, S. Top, A. Vessières, G. Leclercq, J. Quivy, L. Jin and A. Croissy, *C. R. Acad. Sci. Paris Ser. IIc*, 2000, 89; (*b*) S. Top, A. Vessierès, C. Cabestaing, I. Laios, G. Leclercq, C. Provot and G. Jaouen, *J. Organomet. Chem.*, 2001, **637–639**, 500; (*c*) S. Top, A. Vessières, G. Leclercq, J. Quivy, J. Tang, J. Vaissermann,

M. Huché and G. Jaouen, *Chem. Eur. J.*, 2003, **9**, 5223; (*d*) A. Vessières, S. Top, P. Pigeon, E. Hillard, L. Boubeker, D. Spera and G. Jaouen, *J. Med. Chem.*, 2005, **48**, 3937.
16 S. Barlow and D. O'Hare, *Chem. Rev.*, 1997, **97**, 637.
17 A.-C. Ribou, J.-P. Launay, M. Sachtleben, H. Li and C. W. Spangler, *Inorg. Chem.*, 1996, **35**, 3735.
18 Y. J. Chen, D.-S. Pan, C.-F. Chiu, J.-X. Su, S. J. Lin and K. S. Kwan, *Inorg. Chem.*, 2000, **39**, 953.
19 (*a*) K. Kowalski, J. Zakrzewski and L. Jerzykiewicz, *J. Organomet. Chem.*, 2005, **690**, 764; (*b*) K. Kowalski and J. Zakrzewski, *J. Organomet. Chem.*, 2004, **689**, 1046.
20 S. Zheng, S. Barlow, C. T. Parker and S. R. Marder, *Tetrahedron Lett.*, 2003, **44**, 7989.
21 S.-F. Forgues and B. Delevaux-Nicot, *J. Photochem. Photobiol. A: Chem.*, 2000, **132**, 137.
22 M. G. Peterleitner, L. I. Denisovich, N. I. Pyshnograeva and D. N. Kravtsov, *Metaloorg. Khim.*, 1990, **3**, 581.
23 P. Audebert, F. Miomandre and J. Zakrzewski, *J. Electroanal. Chem.*, 2002, **530**, 63.
24 A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech and H. Keller, *Organometallics*, 1994, **13**, 1224.
25 D. L. Kershner and F. Basolo, *Coord. Chem. Rev.*, 1987, **79**, 279.
26 (*a*) A. Ceccon, S. Santi, L. Orian and A. Bisello, *Coord. Chem. Rev.*, 2004, **248**, 683; (*b*) M. J. Begley, P. Mountford, P. J. Stewart, D. Swallow and S. Wan, *J. Chem. Soc., Dalton Trans.*, 1996, 1323; (*c*) C. LeVanda, K. Bechgaard, D. O. Cowan and M. D. Rausch, *J. Am. Chem. Soc.*, 1977, **99**, 2964; (*d*) R. De la Rosa, P. J. Chang, F. Salaymeh and J. F. Curtis, *Inorg. Chem.*, 1985, **24**, 4229.
27 R. Catalotti, A. Foffani and S. Pignataro, *Inorg. Chem.*, 1970, **9**, 2594.
28 L. Cuffe, R. A. Hudson, J. F. Gallagher, S. Jennings, C. J. McAdam, R. B. T. Connelly, A. R. Manning, B. H. Robinson and J. Simpson, *Organometallics*, 2005, **24**, 2050.
29 G. Laus, C. E. Strasser, M. Holzer, K. Wurst, G. Purstinger, K.-H. Ongania, M. Rauch, G. Bonn and H. Schottenberg, *Organometallics*, 2005, **24**, 6085.
30 B. Bilstein, A. Hradsky, H. Kopacka, R. Malleier and K.-H. Ongania, *J. Organomet. Chem.*, 1997, **540**, 127.
31 J. Silver, J. Zakrzewski, A. Tosik and M. Bukowska-Strzyżewska, *J. Organomet. Chem.*, 1997, **540**, 169.
32 J. Zakrzewski, *Inorg. Chim. Acta*, 1998, **278**, 101.
33 D. Plażuk and J. Zakrzewski, *J. Organomet. Chem.*, 2006, **691**, 287.
34 P. Denifl, A. Hradsky, B. Bilstein and K. Wurst, *J. Organomet. Chem.*, 1996, **523**, 79.
35 G. M. Sheldrick, *SHELXS, Program for Crystal Structure Solution*, University of Göttingen, Germany, 1997.
36 G. M. Sheldrick, *SHELXL, Program for Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.
37 M. Nardelli, *J. Appl. Crystallogr.*, 1996, **29**, 296.
38 A. L. Spek, *PLATON - Molecular Geometry Program*, University of Utrecht, The Netherlands, 1998.