

Syntheses, crystal structures and electrochemical studies of bi- and trimetallic conjugated ferrocene-based complexes

José A. Mata and Eduardo Peris*

Dpto. de Química Inorgánica y Orgánica, Universitat Jaume I, E-12080 Castellón, Spain

Received 21st May 2001, Accepted 5th October 2001

First published as an Advance Article on the web 23rd November 2001

New bisferrocenyl pyridine, nitrile and nitro terminated compounds have been obtained by Wittig reactions. The coordination capabilities of the nitrile and pyridine compounds have been proved by coordination to $M(CO)_5$ fragments, M being Cr, Mo or W. The electrochemical properties of the compounds have been studied by means of cyclic voltammetry, showing an effective electronic coupling between the two ferrocenyl fragments. The crystal structures of several of the described complexes are reported, showing that, in all cases, the *syn* conformation on the 1,1' bis-substituted ferrocene is preferred over the *anti* one.

Introduction

Much attention has been lately devoted to the chemistry of ferrocenyl complexes because ferrocene combines chemical versatility with high thermal stability. These properties, together with the exceptional electrochemical properties of ferrocene, make ferrocene-based complexes good candidates for the preparation of new materials with applications in organic synthesis, catalysis and materials science.^{1,2} When two or more ferrocenyl fragments are connected to obtain compounds with linked ferrocenes, further interests are envisaged, since inter-metallic electronic communication affords a wide range of new applications, and many studies have been made regarding intramolecular electron-exchange reactions.^{3–9}

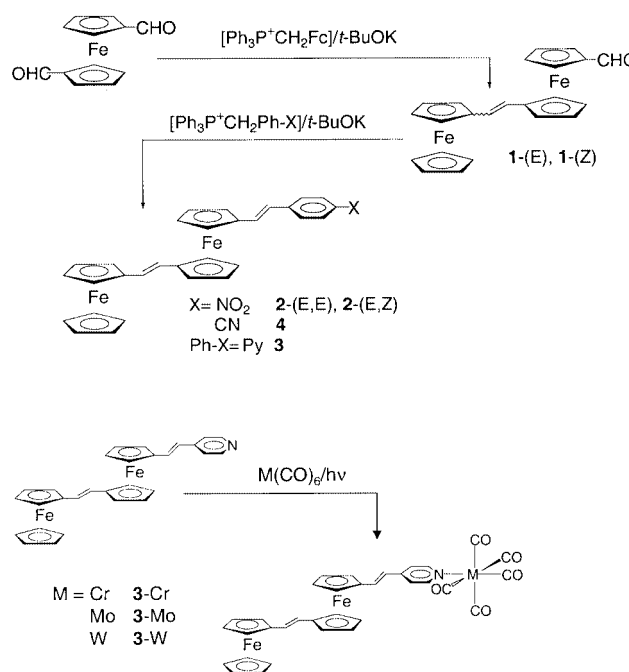
In the search of new materials with electronic communication between terminal subunits, we have focused our interest in the preparation of new conjugated ferrocenyl complexes with end capped nitro,¹⁰ pyridine¹¹ and nitrile¹² groups. End-capping ferrocene with pyridine and nitrile allows the ferrocenyl subunit to link to different metallic fragments, affording interesting bimetallic complexes, in which the terminal metallic fragments are connected by a conjugated bridge. Some of the compounds so obtained showed high non linear optical responses,^{10,13} which in most cases were envisaged from the molecular geometries and electronic properties of the compounds themselves.^{11,12} In this sense, electrochemical studies, electronic spectroscopy and molecular structure determinations constitute the best tools to predict interesting physical properties of the compounds under study.

We now report, based on our previous findings, several efficient routes to the preparation of conjugated linked-bisferrocenyl conjugated compounds with end-capped nitro, nitrile and pyridine groups. These compounds are obtained by Wittig reactions, for which the corresponding bisferrocenyl-aldehydes have also been obtained. Coordination of Group 6 carbonyl fragments to the nitrile and pyridine ligands affords the preparation of trimetallic complexes. The crystal structures of several of these compounds have been determined and their electrochemistry has also been investigated.

Results and discussion

Synthesis and characterization of the compounds

Scheme 1 shows the general procedure for the synthesis of the bisferrocenyl complexes 1–4. Since *E*-type isomers have shown

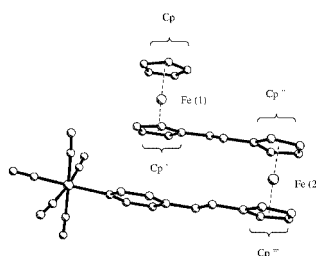


higher efficiency for electronic coupling than the *Z*-type, we tried to optimize the preparation of the *E*-type isomers. In this sense, only the preparation of compounds 1-(*E*) and 2-(*E,E*) afforded a mixture of the corresponding *E/Z* isomers which could be easily separated. Furthermore, the *Z* isomers were quantitatively converted to the *E* homologues by treatment with I_2 in refluxing toluene.^{12,14–16} The preparation of compounds 3 and 4 yielded the *E* isomers as the only isolable species.

The coordination capabilities of the end-capped pyridine (3) and nitrile (4) bisferrocenyl complexes allowed us to obtain the trimetallic species 3-M, and 4-M (3, M = Cr, Mo, W; 4, M = Cr, W), by reacting the ligands with $(thf)_5M(CO)_3$ which was photochemically generated *in situ*. The IR spectra of these heterometallic compounds are virtually identical, indicating the presence of a metal pentacarbonyl moiety, the bands being assigned to the two A_1 , B_2 and E modes for the pseudo C_{4v} metal center, by comparison with other monosubstituted metal carbonyl derivatives.^{12,17}

Table 1 Crystallographic data

Compound	1-(E)	3-Cr	3-Mo	3-W
Empirical formula	C ₂₃ H ₂₀ Fe ₂ O	C ₃₄ H ₂₅ Fe ₂ CrNO ₅	C ₃₄ H ₂₅ Fe ₂ MoNO ₅	C ₃₄ H ₂₅ Fe ₂ WNO ₅
Formula weight/g mol ⁻¹	424.09	691.25	735.19	823.10
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	22.861(3)	10.4406(8)	10.4088(11)	10.4332(6)
<i>b</i> /Å	7.5781(8)	15.0730(12)	15.1733(15)	15.1577(8)
<i>c</i> /Å	10.9377(12)	20.1531(16)	20.490(2)	20.3793(11)
<i>a</i> °	90	83.488(2)	83.278(2)	83.056(1)
<i>β</i> °	108.025(2)	77.095(2)	77.073(2)	76.951(1)
<i>γ</i> °	90	84.630(2)	85.000(2)	84.614(1)
<i>V</i> /Å ³	1801.9(3)	3063.8(4)	3126.1(6)	3109.2(3)
<i>Z</i>	4	4	4	4
<i>D_c</i> /Mg m ⁻³	1.563	1.499	1.562	1.758
<i>μ</i> /mm ⁻¹	1.618	1.325	1.352	4.653
<i>F</i> (000)	872	1408	1480	1608
Crystal size/mm ³	0.40 × 0.25 × 0.12	0.19 × 0.19 × 0.12	0.30 × 0.16 × 0.12	0.23 × 0.13 × 0.05
<i>θ</i> range/°	1.87 to 24.71	1.04 to 23.25	1.02 to 30.51	1.03 to 26.37
Index ranges	−25 ≤ <i>h</i> ≤ 26 −8 ≤ <i>k</i> ≤ 8 −12 ≤ <i>l</i> ≤ 12	−11 ≤ <i>h</i> ≤ 11 −16 ≤ <i>k</i> ≤ 16 −22 ≤ <i>l</i> ≤ 14	−10 ≤ <i>h</i> ≤ 14 −21 ≤ <i>k</i> ≤ 21 −27 ≤ <i>l</i> ≤ 29	−12 ≤ <i>h</i> ≤ 13 −17 ≤ <i>k</i> ≤ 18 −25 ≤ <i>l</i> ≤ 15
Reflections collected	4813	15180	26545	19707
Independent reflections	1538 [<i>R</i> _{int} = 0.0254]	8820 [<i>R</i> _{int} = 0.0466]	18642 [<i>R</i> _{int} = 0.0565]	12656 [<i>R</i> _{int} = 0.0441]
Data/restraints/parameters	1538/0/136	8820/0/775	18642/0/775	12656/0/775
Goodness-of-fit on <i>F</i> ²	1.078	0.906	0.794	0.902
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0570, <i>wR</i> 2 = 0.1575	<i>R</i> 1 = 0.0416, <i>wR</i> 2 = 0.0835	<i>R</i> 1 = 0.0467, <i>wR</i> 2 = 0.0819	<i>R</i> 1 = 0.0409, <i>wR</i> 2 = 0.0928
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0728, <i>wR</i> 2 = 0.1663	<i>R</i> 1 = 0.0929, <i>wR</i> 2 = 0.1062	<i>R</i> 1 = 0.2101, <i>wR</i> 2 = 0.1201	<i>R</i> 1 = 0.0761, <i>wR</i> 2 = 0.1002
<i>ρ</i> _{max} , <i>ρ</i> _{min} /e Å ⁻³	1.048, −0.489	0.339, −0.295	0.426, −0.603	1.406, −1.406

Table 2 Selected bond distances (Å) and angles (°)

	1-(E)	3-Cr	3-Mo	3-W
Environment Fe				
Fe(1)–Cp (cent.)	1.64	1.64	1.66	1.66
Fe(1)–Cp' (cent.)	1.65	1.65	1.65	1.65
Fe(2)–Cp'' (cent.)	—	1.64	1.66	1.64
Fe(2)–Cp''' (cent.)	—	1.64	1.66	1.64
Fe(1)–Fe(2) (bonds)	8.49	8.30	8.33	8.31
Fe(1)–Fe(2) (space)	7.15	7.18	7.21	7.18
Fe(1)–M(1)	—	6.47	6.58	6.50
Fe(2)–M(1)	—	10.10	10.19	10.19
Environment M				
M(1)–N(1)	—	2.159(4)	2.288(4)	2.271(5)
M–CO (min/max)	—	1.849–1.901	1.959–2.072	1.977–2.044
Tilt angles				
Cp–Cp'	0.70(0.18)	1.68(0.47)	3.93(0.27)	1.46(0.63)
Cp''–Cp'''	—	2.84(0.49)	1.77(0.30)	2.82(0.70)
π interaction				
Distance (Cp'–Py)	—	3.78	3.69	3.76
Angle (Cp'–Py)	—	8.03(0.41)	15.49(0.17)	8.25(0.55)
Coplanarity				
Cp'–Cp''	0	7.29(0.47)	2.84(0.28)	7.30(0.63)
Cp'''–Py	—	1.64(0.44)	18.12(0.18)	1.97(0.63)

Crystal structures

Crystals suitable for structure determination of compounds **1-(E)**, **3-Cr**, **3-Mo** and **3-W** were grown from dichloromethane/hexane mixtures, by slow evaporation. A summary of the crystal data, data collection and processing parameters is given in Table 1. Selected bond distances and angles are displayed in

Table 2. Figs. 1–4 display the ORTEP²⁹ diagrams of **1-(E)**, **3-Cr**, **3-Mo** and **3-W**. It is noteworthy that the compounds **3-Cr**, **3-Mo** and **3-W** are almost isostructural, so different orientations of the three molecules have been chosen in order to facilitate their visualization. All the complexes crystallize in centrosymmetric space groups, *C*2/*c* for compound **1-(E)** and *P* $\bar{1}$ for compounds **3-Cr**, **3-Mo** and **3-W**.

Compound **1**-(*E*) shows a center of inversion in the middle of the ethylene bridge. The asymmetric unit consists of a complete ferrocenyl fragment (100% occupancy), the ethenyl bridge (50% occupancy due to disorder) and the aldehyde group (50% occupancy). The other half of the molecule generated by the inversion center completes the molecule (Fig. 1).

For **3**-Cr, **3**-Mo and **3**-W, two independent molecules were found per asymmetric unit. As required by the presence of the center of symmetry the total number of molecules per unit cell is four. In all cases, there is a very similar geometrical arrangement in the two independent molecules. The iron distances to the Cp rings and the Cp(C–C) distances and angles lie in the expected range. In all the cases that we report in this paper, the complexes show a perfect eclipsed disposition of the Cp rings in all the ferrocene units, and a slightly tilting angle can be observed between the two Cp rings of every Fc unit (dihedral angles between 1.5 and 4.0°). As seen in some of the 1,1'-substituted bisferrocenyl complexes that we¹⁸ and other authors^{19,20} have reported so far, all these complexes adopt the sterically more hindered *syn* conformation, in a parallel disposition of the ancillary ligands in which intramolecular π -stacking may be having some effect. In the case of the complex **1**-(*E*), where π -stacking is not possible, the *syn* conformation is also observed, this indicating that packing effects may be having a more important effect in the steric disposition of the molecule in the crystal structure. In this sense, Lee *et al.* have reported a study in which the eclipsed/staggered conform-

ation of 1,1'-bis(ethenyl-4-pyridine)ferrocene is controlled by cocrystallization in various solvents.²⁰ This effect, together with the different conformations that 1,1'-bisferrocenyl complexes may adopt upon oxidation,²¹ make ferrocene behave as a 'hinge-like' compound, which can lead to interesting applications.

The orientation of the coordinated pyridyl rings with respect to the metal-carbonyl fragments is defined by the angles between the pyridyl plane and the plane defined by M (M = Cr, Mo, Cr) and three coplanar carbon atoms of the carbonyl ligands. In this regard, the pyridyl plane in **3**-Cr is at an angle of 44.6° to the Cr(1)–C(30)–C(33)–C(34) mean plane, this angle being 66.1 and 44.7° for **3**-Mo and **3**-W, respectively. M(d π)–pyridine(π^*) backbonding would be maximized when these angles are 0 or 90°. In our case, the carbonyl ligands adopt a quasi-staggered disposition with respect to the pyridine fragment (especially in the cases of **3**-Cr and **3**-W, where the angle is practically equal to the idealized staggered disposition, 45°), so minimizing the steric interactions. The expected *trans* influence

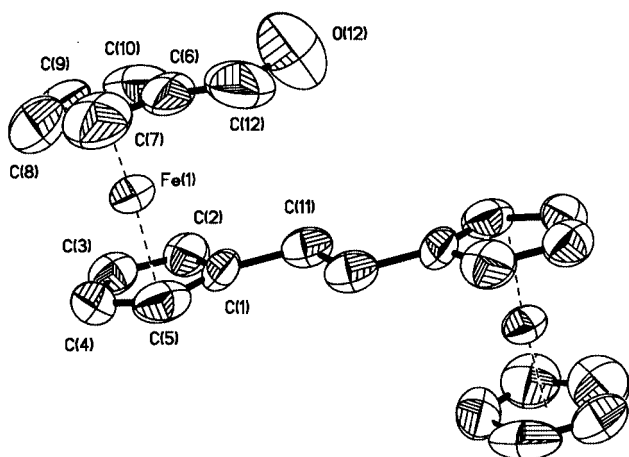


Fig. 1 Molecular structure and atomic labeling scheme for **1**-(*E*), $\{(E)-(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)(CH=CH)(\eta^5-C_5H_4)Fe(\eta^5-C_5H_4)CHO\}$, with 50% anisotropic displacement ellipsoids. Hydrogen atoms and disorder in the ethylene bridge and aldehyde have been omitted for clarity.

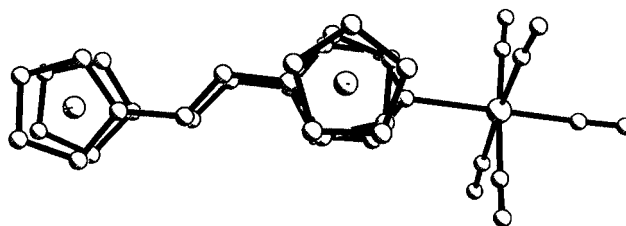


Fig. 3 Molecular structure for compound **3**-Mo, $\{(E,E)-(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)(CH=CH)(\eta^5-C_5H_4)Fe(\eta^5-C_5H_4)(CH=CH)PyMo(CO)_5\}$. Hydrogen atoms have been omitted for clarity.

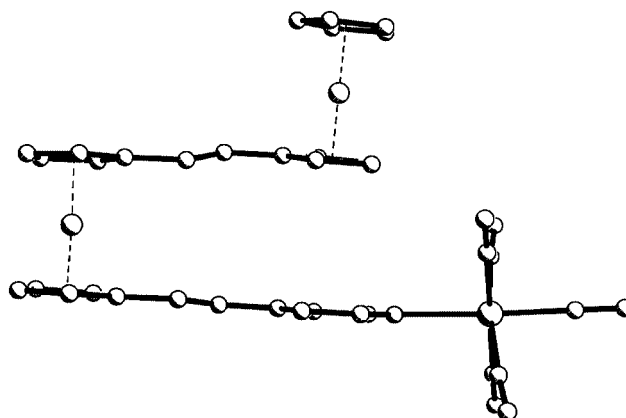


Fig. 4 Molecular structure for compound **3**-W, $\{(E,E)-(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)(CH=CH)(\eta^5-C_5H_4)Fe(\eta^5-C_5H_4)(CH=CH)PyW(CO)_5\}$. Hydrogen atoms have been omitted for clarity.

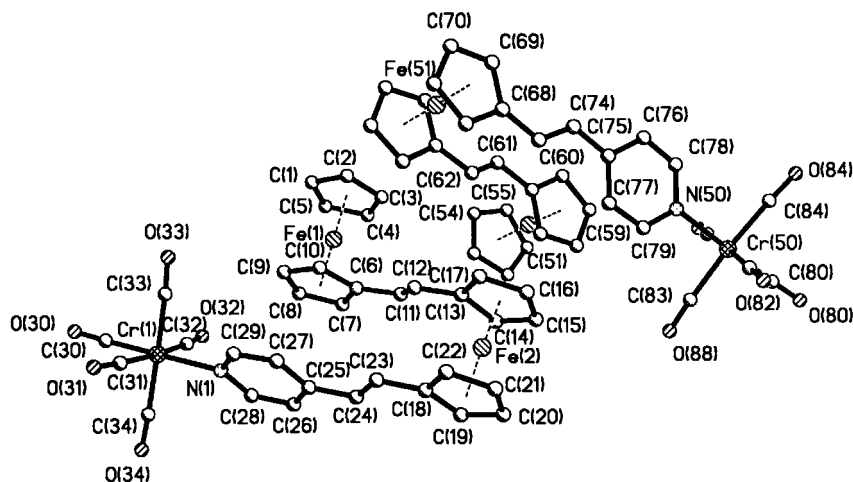


Fig. 2 Molecular structure and atomic labeling scheme for **3**-Cr, $\{(E,E)-(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)(CH=CH)(\eta^5-C_5H_4)Fe(\eta^5-C_5H_4)(CH=CH)PyCr(CO)_5\}$, with 50% displacement ellipsoids. The two molecules per asymmetric unit are shown. Hydrogen atoms have been omitted for clarity.

Table 3 Electrochemical data for the diferrocenyl derivatives^a

Compound	$E_{1/2}/\text{mV}$ ($\Delta E_p/\text{mV}$)		$E_{1/2}/\text{mV}$ ($\Delta E_p/\text{mV}$) M ^b -based	$\Delta E = (E_{1/2})_2 - (E_{1/2})_1(\text{mV})$	
	Ferrocene-based			Ferrocenes	K_c^d
Ferrocene	445(105)		—	—	
1-(<i>E</i>)	405(90)	785(85)	—	380	2.6×10^6
1-(<i>Z</i>)	400(110)	760(75)	—	355	1.0×10^6
2-(<i>E,E</i>)	350(80)	535(65)	—	185	1350
2-(<i>E,Z</i>)	370(110)	570(110)	—	195	1975
3	370(145)	570(140)	—	200	2400
3-Cr	375(130)	590(125)	950(130)	215	4300
3-Mo	360(95)	575(80)	1115 ^c	215	4300
3-W	380(160)	610(153)	1240 ^c	230	7725
4	360(145)	550(150)	—	190	1625
4-Cr	360(135)	555(110)	975(125)	195	1975
4-W	360(95)	540(85)	1140 ^c	185	1350

^a Measured in CH₂Cl₂. ^b M = Cr, Mo, W. ^c Irreversible peak, measured at 100 mV s⁻¹. ^d $\Delta E_{1/2}/\text{mV} = 59.15(\log K_c)$ at 298 K.

^a Measured in CH₂Cl₂. ^b M = Cr, Mo, W. ^c Irreversible peak, measured at 100 mV s⁻¹. ^d $\Delta E_{1/2}/\text{mV} = 59.15(\log K_c)$ at 298 K.

is present, with the M–C bonds *trans* to the pyridine ligand (Cr, 1.84; Mo, 1.95; W, 1.97 Å) being significantly shorter than the other M–C bonds (Cr, 1.90; Mo, 2.05; W, 2.02 Å). These results are in good agreement with the features on the molecular structures reported by Sakanishi *et al.* for other related ferrocenyl-pyridyl ligands coordinated to Cr(CO)₅.²²

Cyclic voltammetry

Electrochemical techniques have been the most widely used tools to investigate metal–metal interactions in metallocene systems and also to evaluate the donor–acceptor electronic influence. In this work we have used cyclic voltammetry in order to evaluate the redox properties of the metal centers, the degree of interaction, and the effect of the acceptor moiety. Electrochemical data obtained for the compounds studied are summarized in Table 3.

Fig. 5 shows three voltammograms corresponding to compounds 1-(*E*), 2-(*E,E*) and 3-Cr. As can be seen in Table 3, the redox bands corresponding to the two ferrocenyl fragments, are very little influenced by the nature of the ancillary ligands. Only in the case of the aldehyde complexes 1-(*E*) and 1-(*Z*), the half wave potential of the ferrocenyl moieties show a clear anodic shift compared to (*E*)-Fc–CH=CH–Fc, meaning some degree of electron transfer between the iron center and the electron-accepting aldehyde fragment. However, the halfwave potentials of the nitrile and pyridine derivatives with longer conjugated chains are similar to that shown for (*E*)-Fc–CH=CH–Fc indicating that the inclusion of the electron-accepting fragments (Py, CN), are somehow compensated by the delocalization of the charge along the longer conjugated system of the ligand, which makes oxidation easier.

Coordination of the neutral unit M(CO)₅ to the ferrocenyl nitrile and pyridine ligands does not have any significant effect on the redox potential of the ferrocene centers, compared to those of the uncoordinated ligands. The oxidation potential of the third step ascribed to the metal-carbonyl fragment depends on the metal present, this being higher for the W complexes compared to the Cr and Mo complexes. This band is only reversible in the case where Cr(CO)₆ was used. This result is consistent with those studies reported before where chromium and tungsten ferrocenyl derivatives show quasi-reversible and completely irreversible oxidation waves respectively.^{12,13,15,23,24}

The degree of separation or resolution of the two waves in the homobimetallic compounds is a quasi-direct measure of the degree of interaction of these metals, although we have to take into account the intrinsic inequivalency of the two metal centers. The presence of two one-electron oxidations instead of one two-electron oxidation indicates a stabilization of the mixed valence species. The separation between the two oxidation potentials was employed to calculate the comproportionation constant, K_c , from eqns. (1) and (3).

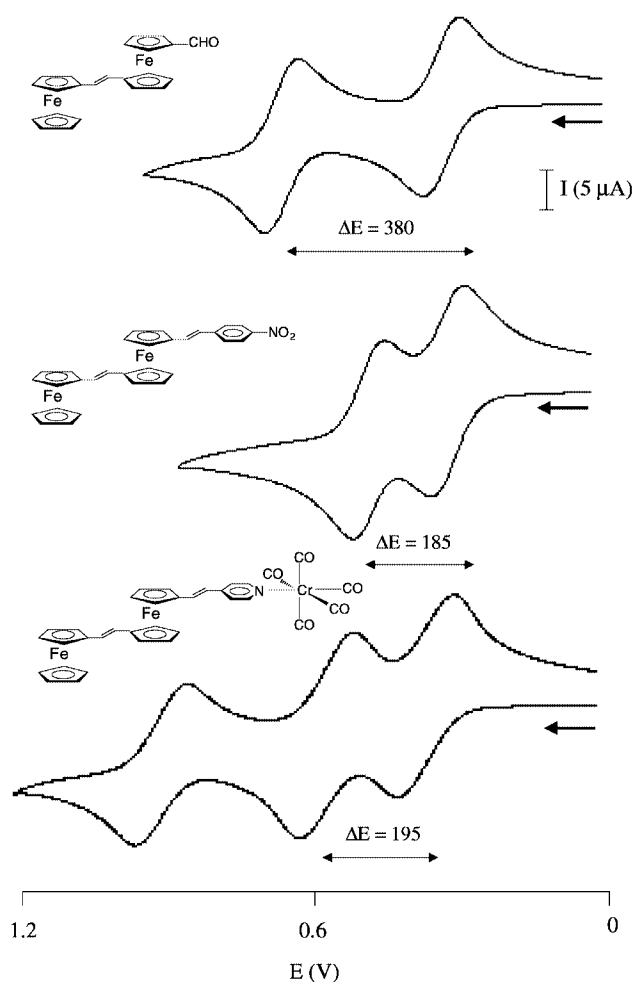
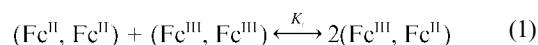


Fig. 5 Cyclic voltammograms (scan rate 100 mV s⁻¹) of 1-(*E*), 2-(*E,E*) and 3-Cr in 0.1M [NBu₄]⁺PF₆⁻·CH₂Cl₂.



$$\Delta E = \Delta E_{1/2}(\text{Fc}^{\text{III}}, \text{Fc}^{\text{III}}) - \Delta E_{1/2}(\text{Fc}^{\text{III}}, \text{Fc}^{\text{II}}) \quad (2)$$

$$\Delta E(\text{mV}) = 59.15(\log K_c) \text{ at } 298 \text{ K} \quad (3)$$

This is a crude estimation of the interaction between the iron centers due to their geometrical inequivalence, but it gives us an approximate estimation of the electronic communication between the two metal centers. This approximation has also been used in some other examples in which the two metal

centers were inequivalent, and even in cases in which the metals were different.²⁵ In any case, we are aware that the electronic communication between the redox centers must be less than that measured by the potential difference.

As can be seen in Table 3, K_c values lie in the range of the weakly connected class II mixed-valence complexes. For all the compounds (except **1-(E)** and **1-(Z)**) ΔE values are quite similar, *ca.* 190 mV.

The most interesting feature of this interaction between our diferrocenyl derivatives is the strong coupling observed for compounds **1-(E)** ($\Delta E = 380$ mV) and **1-(Z)** ($\Delta E = 355$ mV), especially when we compare these values to the ones published before. For example in the case of **(E)-Fc-CH=CH-Fc** the coupling constant is *ca.* 150 mV.²⁶ The coupling in **1-(E)** is larger than that of **(E)-Fc-CH=CH-Fc**, even if we consider an intrinsic inequivalence of 60 mV, which is approximately the difference in the redox potentials of ferrocene (445 mV) and ferrocenealdehyde (500 mV).

Experimental

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents for synthesis and electrochemical measurements were dried and degassed by standard methods before use. Chromatographic work was performed on Silica gel 60 Å or Neutral Alumina columns.

NMR spectra were recorded on a Varian Innova 300 MHz and 500 MHz, 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. Cyclic voltammetry experiments were performed with a Echochemie pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl. The solvents used in all experiments were CH_2Cl_2 or acetone, which were obtained in HPLC grade. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate, synthesized by counter ion exchange of tetrabutylammonium bromide and HPF_6 , recrystallized from ethanol and dried under vacuum. The $E_{1/2}$ values were determined as $1/2 (E_{p,a} + E_{p,c})$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively. All potentials reported are not corrected for the junction potential. Ferrocenealdehyde was used as purchased (Aldrich), and 1,1'-ferrocenebiscarboxaldehyde was obtained according to the literature method.²⁷

Syntheses

{(E)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-CHO}, **1-(E) and **{(Z)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-CHO}, **1-(Z)**. To an ice-cold solution of (ferrocenylmethyl)triphenylphosphonium iodide (1 g, 1.7 mmol) in THF (75 ml) potassium *tert*-butoxide (213.2 mg, 1.9 mmol) was added and the resulting solution stirred for 20 min and then 40 min at room temperature. 1,1'-Ferrocenebiscarboxaldehyde (411.5 mg, 1.7 mmol) was added at 0 °C and the resulting solution stirred overnight at room temperature. After removing the solvent under reduced pressure, the product was extracted with $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}/\text{NaHCO}_3$ and dried over MgSO_4 . The compounds were purified by column chromatography on silica gel using diethyl ether–hexane as eluent. Recrystallization of the first major fraction from CH_2Cl_2 –hexane mixtures afforded pure compound **1-(E)**. A second minor fraction containing **1-(Z)** was recrystallized by the same procedure. **1-(E)**. Yield: 65%. ¹H-NMR (300 MHz, CDCl_3): δ 9.94 (s, 1H, CHO); 6.48 (d, 1H, ³ $J_{\text{H-H}} = 16.2$ Hz, CH=CH); 6.31 (d, 1H, ³ $J_{\text{H-H}} = 16.2$ Hz, CH=CH); 4.74 (t, 2H, ³ $J_{\text{H-H}} = 1.9$ Hz, C₅H₄); 4.56 (t, 2H, ³ $J_{\text{H-H}} = 1.9$ Hz, C₅H₄); 4.48 (t, 2H, ³ $J_{\text{H-H}} = 1.9$ Hz, C₅H₄); 4.40 (t,****

2H, ³ $J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.35 (t, 2H, ³ $J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.27 (t, 2H, ³ $J_{\text{H-H}} = 1.7$ Hz, C₅H₄); 4.15 (s, 5H, C₅H₅). ¹³C-NMR (300 MHz, CDCl_3): δ 193.9 (1C, CHO); 126.5, 121.9 (2C, CH=CH); 86.8, 83.3, 80.7 (3C_q, C₅H₄); 74.8, 70.9, 70.3, 69.5, 69.2, 67.8, 66.8 (17C, C₅H₄ and C₅H₅). IR (cm⁻¹): 1680 (s), 1411 (w), 1664 (s). Elemental anal. Calc. for compound **1-(E)**, C₂₃H₂₀Fe₂O, $M = 424.11$: C, 65.1; H, 4.75. Found: C, 65.2; H, 4.74%.

1-(Z). Yield <15%. ¹H-NMR (300 MHz, CDCl_3): δ 9.86 (s, 1H, CHO); 6.24 (d, 1H, ³ $J_{\text{H-H}} = 12.0$ Hz, CH=CH); 6.00 (d, 1H, ³ $J_{\text{H-H}} = 11.7$ Hz, CH=CH); 4.70 (s, 2H, C₅H₄); 4.52 (s, 1H, C₅H₄); 4.42 (s, 2H, C₅H₄); 4.27 (s, 4H, C₅H₄); 4.18 (s, 2H, C₅H₄); 4.09 (s, 5H, C₅H₅). ¹³C-NMR (300 MHz, CDCl_3): δ 194.1 (1C, CHO); 127.7, 123.5 (2C, CH=CH); 85.4, 82.5, 80.4, (3C_q, C₅H₄); 75.1, 71.2, 70.3, 69.9, 69.8, 69.0, 67.2 (17C, C₅H₄ and C₅H₅). IR (cm⁻¹): 1679 (s), 1411 (w), 1663 (s). Elemental anal. Calc. for compound **1-(Z)**, C₂₃H₂₀Fe₂O, $M = 424.11$: C, 65.1; H, 4.75. Found: C, 65.2; H, 4.76%.

{(E,E)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-(CH=CH)Ph-NO₂}, **2-(E,E) and **{(E,Z)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)-(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)(CH=CH)Ph-NO₂}, **2-(E,Z)**. These compounds were obtained following the general procedure described for compound **1-(E)**, but the reaction was carried out overnight at 60 °C. [(*p*-nitrophenyl)methyl]triphenylphosphonium iodide (813.1 mg, 1.7 mmol), and sodium hydride (dispersion in mineral oil 60%; 72.0 mg, 1.8 mmol) were mixed in THF at 0 °C for 45 min. Then the aldehyde **1-(E)** (721.0 mg, 1.7 mmol) was added, and the suspension was heated at 60 °C overnight. The two isomers were separated by column chromatography on silica gel using CH_2Cl_2 –hexane (1 : 1) as eluent, the first major band containing **2-(E,E)** and the second (minor) **2-(E,Z)**. Recrystallization from CH_2Cl_2 –hexane mixtures afforded the pure compounds. Yield: 60%. **2-(E,E)**. Yield: 60%. ¹H-NMR (500 MHz, CDCl_3): δ 8.09 (2H, ³ $J_{\text{H-H}} = 8.0$ Hz, C₆H₄); 7.38 (2H, ³ $J_{\text{H-H}} = 8.5$ Hz, C₆H₄); 6.92 (d, 1H, ³ $J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.62 (d, 1H, ³ $J_{\text{H-H}} = 15.5$ Hz, CH=CH); 6.54 (d, 1H, ³ $J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.23 (d, 1H, ³ $J_{\text{H-H}} = 16.0$ Hz, CH=CH); 4.45 (s, 2H, C₅H₄); 4.37 (s, 2H, C₅H₄); 4.34 (s, 2H, C₅H₄); 4.24 (s, 2H, C₅H₄); 4.23 (s, 2H, C₅H₄); 4.18 (s, 2H, C₅H₄); 4.08 (s, 5H, C₅H₅). ¹³C-NMR (300 MHz, CDCl_3): δ 146.6, 144.9 (2C_q, C₆H₄); 133.1, 126.6, 125.9, 124.9, 124.6, 123.5 (8C, CH=CH and C₆H₄); 86.8, 85.3, 83.5 (3C_q, C₅H₄); 71.7, 70.5, 70.1, 69.6, 69.2, 68.2, 66.8 (17C, C₅H₄ and C₅H₅). Elemental anal. Calc. for compound **2-(E,E)**, C₃₀H₂₅Fe₂NO₂, $M = 543.23$: C, 66.3; H, 4.64; N, 2.58. Found: C, 66.4; H, 4.65; N, 2.57%.****

2-(E,Z). Yield: <10%. ¹H-NMR (500 MHz, CDCl_3): δ 8.10 (2H, ³ $J_{\text{H-H}} = 7.9$ Hz, C₆H₄); 7.46 (2H, ³ $J_{\text{H-H}} = 8.5$ Hz, C₆H₄); 6.46 (d, 1H, ³ $J_{\text{H-H}} = 12.0$ Hz, CH=CH); 6.42 (d, 1H, ³ $J_{\text{H-H}} = 12.0$ Hz, CH=CH); 6.36 (d, 1H, ³ $J_{\text{H-H}} = 12.0$ Hz, CH=CH); 6.22 (d, 1H, ³ $J_{\text{H-H}} = 15.5$ Hz, CH=CH); 4.43 (s, 2H, C₅H₄); 4.33 (s, 4H, C₅H₄); 4.21 (s, 4H, C₅H₄); 4.14 (s, 5H, C₅H₅); 4.12 (s, 2H, C₅H₄). ¹³C-NMR (300 MHz, CDCl_3): δ 146.6, 145.7 (2C_q, C₆H₄); 132.5, 129.9, 125.5, 125.4, 124.1, 123.1 (8C, CH=CH and C₆H₄); 86.2, 84.3, 81.5 (3C_q, C₅H₄); 71.5, 71.3, 70.8, 70.3, 69.8, 68.3, 66.9 (17C, C₅H₄ and C₅H₅). Elemental anal. Calc. for compound **2-(E,Z)**, C₃₀H₂₅Fe₂NO₂, $M = 543.23$: C, 66.3; H, 4.64; N, 2.58. Found: C, 66.3; H, 4.63; N, 2.59%.

{(E,E)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-(CH=CH)Py} **3. This compound was obtained following the general procedure described for compound **2-(E,E)**, using (4-pyridylmethyl)triphenylphosphonium chloride (389.5 mg, 1.0 mmol), potassium *tert*-butoxide (123.4 mg, 1.1 mmol) and the aldehyde **1-(E)** (424.1 mg, 1.0 mmol). The compound was purified by column chromatography on silica gel using CH_2Cl_2 –Acetone (4 : 1) as eluent. Recrystallization from CH_2Cl_2 –hexane mixtures afforded pure compound **3**. Yield: 57%. ¹H-NMR (300 MHz, CD_2Cl_2): δ 8.43 (2H, ³ $J_{\text{H-H}} = 4.9$ Hz, C₅H₄N); 7.20 (2H, ³ $J_{\text{H-H}} = 4.8$ Hz, C₅H₄N); 7.45 (d, 1H, ³ $J_{\text{H-H}} = 15.3$ Hz,**

CH=CH); 6.55 (d, 1H, $^3J_{\text{H-H}} = 15.6$ Hz, CH=CH); 6.38 (d, 1H, $^3J_{\text{H-H}} = 15.3$ Hz, CH=CH); 6.27 (d, 1H, $^3J_{\text{H-H}} = 15.3$ Hz, CH=CH); 4.45 (s, 2H, C₅H₄); 4.37 (s, 2H, C₅H₄); 4.32 (s, 2H, C₅H₄); 4.29 (s, 2H, C₅H₄); 4.23 (s, 2H, C₅H₄); 4.21 (s, 2H, C₅H₄); 4.09 (s, 5H, C₅H₅). ¹³C-NMR (500 MHz, CDCl₃): δ 150.8, 133.3, 125.6, 123.9, 123.2, 121.6 (8C, CH=CH and C₅H₄N); 146.0 (1C_q, C₅H₄N); 86.4, 84.7, 82.9 (3C_q, C₅H₄); 71.7, 70.5, 69.8, 69.5, 69.3 (17C, C₅H₄ and C₅H₅). Elemental anal. Calc. for compound **3**, C₂₉H₂₅Fe₂N, $M = 499.22$: C, 69.8; H, 5.05; N, 2.81. Found: C, 69.6; H, 5.09; N, 2.80%.

{(E,E)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-(CH=CH)PyCr(CO)₅} **3-Cr**. Chromium hexacarbonyl (330.1 mg, 1.5 mmol) was dissolved in THF (30 ml) and the resulting solution was irradiated using a Hg lamp for 1 h. Compound **3** (499.2 mg, 1 mmol) was added to the yellow solution formed upon irradiation in order to obtain compound **3-Cr**. The reaction mixture was stirred for another 30 min, filtered to remove the solid, and the solvent was removed under reduced pressure. Purification by column chromatography on neutral alumina with CH₂Cl₂-Hexane (3 : 1) afforded the pure compound **3-Cr**. Yield: 60%. ¹H-NMR (500 MHz, CDCl₃): δ 8.24 (2H, $^3J_{\text{H-H}} = 5.3$ Hz, C₅H₄N); 6.92 (2H, $^3J_{\text{H-H}} = 5.3$ Hz, C₅H₄N); 6.87 (d, 1H, $^3J_{\text{H-H}} = 15.9$ Hz, CH=CH); 6.35 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.25 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.05 (d, 1H, $^3J_{\text{H-H}} = 15.7$ Hz, CH=CH); 4.47 (s, 2H, C₅H₄); 4.39 (s, 2H, C₅H₄); 4.37 (s, 2H, C₅H₄); 4.27 (s, 2H, C₅H₄); 4.24 (s, 2H, C₅H₄); 4.19 (s, 2H, C₅H₄); 4.10 (s, 5H, C₅H₅). ¹³C-NMR (500 MHz, CDCl₃): δ 221.5, 215.3 (5C, CO); 146.8, 135.6, 126.0, 122.7, 122.1, 121.4 (8C, CH=CH and C₅H₄N); 155.8 (1C_q, C₅H₄N); 86.8, 84.5, 82.3 (3C_q, C₅H₄); 71.8, 70.3, 69.9, 69.5, 69.3, 68.1, 66.8 (17C, C₅H₄ and C₅H₅). IR (cm⁻¹): 2061 (s), 1980 (s), 1908 (vs). Elemental anal. Calc. for compound **3-Cr**, C₃₄H₂₅Fe₂NO₅Cr, $M = 691.27$: C, 59.1; H, 3.65; N, 2.03. Found: C, 59.0; H, 3.66; N, 2.03%.

{(E,E)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-(CH=CH)PyMo(CO)₅} **3-Mo**. This compound was obtained using the general procedure described for **3-Cr** but using molybdenum hexacarbonyl (396.0 mg, 1.5 mmol) instead of chromium hexacarbonyl. Yield 45%. ¹H-NMR (300 MHz, CDCl₃): δ 8.28 (2H, $^3J_{\text{H-H}} = 6.6$ Hz, C₅H₄N); 6.94 (2H, $^3J_{\text{H-H}} = 6.6$ Hz, C₅H₄N); 6.88 (d, 1H, $^3J_{\text{H-H}} = 16.2$ Hz, CH=CH); 6.37 (d, 1H, $^3J_{\text{H-H}} = 16.2$ Hz, CH=CH); 6.29 (d, 1H, $^3J_{\text{H-H}} = 16.2$ Hz, CH=CH); 6.10 (d, 1H, $^3J_{\text{H-H}} = 15.9$ Hz, CH=CH); 4.47 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.39 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.37 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.23 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.20 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.17 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.07 (s, 5H, C₅H₅). ¹³C-NMR (500 MHz, CDCl₃): δ 214.9, 205.4 (5C, CO); 155.5, 136.0, 126.4, 122.9, 122.5, 121.8 (8C, CH=CH and C₅H₄N); 147.1 (1C_q, C₅H₄N); 87.2, 84.9, 82.6 (3C_q, C₅H₄); 72.3, 70.7, 70.3, 69.9, 69.7, 68.5, 67.2 (17C, C₅H₄ and C₅H₅). IR (cm⁻¹): 2070 (s), 1970 (s), 1904 (vs). Elemental anal. Calc. for compound **3-Mo**, C₃₄H₂₅Fe₂NO₅Mo, $M = 735.21$: C, 55.5; H, 3.43; N, 1.91. Found: C, 55.6; H, 3.42; N, 1.91%.

{(E,E)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-(CH=CH)PyW(CO)₅} **3-W**. This compound was obtained using the general procedure described for **3-Cr** but using tungsten hexacarbonyl (527.9 mg, 1.5 mmol) instead of chromium hexacarbonyl. Yield 65%. ¹H-NMR (300 MHz, CDCl₃): δ 8.43 (2H, $^3J_{\text{H-H}} = 4.0$ Hz, C₅H₄N); 6.93 (2H, $^3J_{\text{H-H}} = 4.5$ Hz, C₅H₄N); 6.90 (d, 1H, $^3J_{\text{H-H}} = 16.2$ Hz, CH=CH); 6.36 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.29 (d, 1H, $^3J_{\text{H-H}} = 15.5$ Hz, CH=CH); 6.08 (d, 1H, $^3J_{\text{H-H}} = 15.5$ Hz, CH=CH); 4.47 (s, 2H, C₅H₄); 4.39 (s, 2H, C₅H₄); 4.37 (s, 2H, C₅H₄); 4.22 (s, 2H, C₅H₄); 4.20 (s, 2H, C₅H₄); 4.18 (s, 2H, C₅H₄); 4.07 (s, 5H, C₅H₅). ¹³C-NMR (500 MHz, CDCl₃): δ 203.0, 199.4 (5C, CO); 156.2, 136.0, 126.0, 122.6, 122.1, 121.9 (8C, CH=CH and C₅H₄N); 146.6 (1C_q, C₅H₄N); 86.8, 84.8, 82.2 (3C_q, C₅H₄); 71.9, 70.4, 69.9, 69.6, 69.3, 68.0,

66.7 (17C, C₅H₄ and C₅H₅). IR (cm⁻¹): 2069 (s), 1969 (s), 1898 (vs). Elemental anal. Calc. for compound **3-W**, C₃₄H₂₅Fe₂NO₅W, $M = 823.12$: C, 49.6; H, 3.06; N, 1.70. Found: C, 49.5; H, 3.02; N, 1.71%.

{(E,E)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-(CH=CH)PhCN} **4**. This compound was obtained following the general procedure described for compound **2-(E,E)**, using [(*p*-nitrophenyl)methyl]triphenylphosphonium iodide (500 mg, 1.1 mmol), potassium *tert*-butoxide (135 mg, 1.2 mmol) and the aldehyde **1-(E)** (460 mg, 1.1 mmol). The compound was purified by column chromatography on silica gel using CH₂Cl₂-hexane (4 : 6) as eluent. Recrystallization from CH₂Cl₂-hexane mixtures afforded pure compound **4**. Yield: 57%. ¹H-NMR (300 MHz, CD₂Cl₂): δ 7.52 (2H, $^3J_{\text{H-H}} = 8.4$ Hz, C₆H₄); 7.38 (2H, $^3J_{\text{H-H}} = 8.1$ Hz, C₆H₄); 6.91 (d, 1H, $^3J_{\text{H-H}} = 16.2$ Hz, CH=CH); 6.61 (d, 1H, $^3J_{\text{H-H}} = 16.2$ Hz, CH=CH); 6.37 (d, 1H, $^3J_{\text{H-H}} = 16.2$ Hz, CH=CH); 6.25 (d, 1H, $^3J_{\text{H-H}} = 16.2$ Hz, CH=CH); 4.45 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.37 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.31 (t, 2H, $^3J_{\text{H-H}} = 1.9$ Hz, C₅H₄); 4.24 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.23 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.19 (t, 2H, $^3J_{\text{H-H}} = 1.8$ Hz, C₅H₄); 4.08 (s, 5H, C₅H₅). ¹³C-NMR (500 MHz, CDCl₃): δ 142.9, 120.1 (2C_q, C₆H₄); 133.1, 131.8, 126.8, 125.9, 125.1, 123.7 (8C, CH=CH and C₆H₄); 110.0 (1C_q, CN); 86.7, 85.5, 83.8 (3C_q, C₅H₄); 71.6, 70.6, 70.1, 69.7, 69.1, 68.1, 66.8 (17C, C₅H₄ and C₅H₅). IR (cm⁻¹): 2222 (s), 1598 (s). Elemental anal. Calc. for compound **4**, C₃₁H₂₅Fe₂N, $M = 523.24$: C, 71.2; H, 4.82; N, 2.68. Found: C, 71.1; H, 4.82; N, 2.68%.

{(E,E)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-(CH=CH)PhCNCr(CO)₅} **4-Cr**. This compound was obtained using the general procedure described for **3-Cr** but using chromium hexacarbonyl (396 mg, 1.8 mmol) and compound **4** (523 mg, 1.0 mmol). Yield 65%. ¹H-NMR (300 MHz, CDCl₃): δ 7.51 (2H, $^3J_{\text{H-H}} = 8.0$ Hz, C₆H₄); 7.38 (2H, $^3J_{\text{H-H}} = 7.9$ Hz, C₆H₄); 6.90 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.53 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.30 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.15 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 4.40 (s, 2H, C₅H₄); 4.36 (s, 2H, C₅H₄); 4.35 (s, 2H, C₅H₄); 4.22 (s, 4H, C₅H₄); 4.20 (s, 2H, C₅H₄); 4.08 (s, 5H, C₅H₅). ¹³C-NMR (300 MHz, CDCl₃): δ 219.8, 214.5 (5C, CO); 143.7, 123.1 (2C_q, C₆H₄); 133.2, 133.0, 126.7, 126.5, 125.5, 124.4 (8C, CH=CH and C₆H₄); 108.2 (1C_q, CN); 86.4, 84.6, 83.0 (3C_q, C₅H₄); 71.7, 70.6, 69.9, 69.4, 69.2, 68.2, 66.9 (17C, C₅H₄ and C₅H₅). IR (cm⁻¹): 2072 (s), 1989 (s), 1929 (vs), 1901 (sh). Elemental anal. Calc. for compound **4-Cr**, C₃₆H₂₅Fe₂NCrO₅, $M = 715.29$: C, 60.5; H, 3.52; N, 1.96. Found: C, 60.4; H, 3.55; N, 1.97%.

{(E,E)-(η⁵-C₅H₅)Fe(η⁵-C₅H₄)(CH=CH)(η⁵-C₅H₄)Fe(η⁵-C₅H₄)-(CH=CH)PhCNW(CO)₅} **4-W**. This compound was obtained using the general procedure described for **3-Cr** but using tungsten hexacarbonyl (633 mg, 1.8 mmol) and compound **4** (523 mg, 1.0 mmol). Yield 70%. ¹H-NMR (500 MHz, CDCl₃): δ 7.51 (2H, $^3J_{\text{H-H}} = 8.0$ Hz, C₆H₄); 7.39 (2H, $^3J_{\text{H-H}} = 7.9$ Hz, C₆H₄); 6.93 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.58 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.47 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz, CH=CH); 6.24 (d, 1H, $^3J_{\text{H-H}} = 15.5$ Hz, CH=CH); 4.44 (s, 2H, C₅H₄); 4.38 (s, 2H, C₅H₄); 4.35 (s, 2H, C₅H₄); 4.24 (s, 4H, C₅H₄); 4.22 (s, 2H, C₅H₄); 4.10 (s, 5H, C₅H₅). ¹³C-NMR (300 MHz, CDCl₃): δ 196.8, 191.2 (5C, CO); 144.1, 123.0 (2C_q, C₆H₄); 133.6, 133.3, 126.8, 125.6, 124.3, 123.0 (8C, CH=CH and C₆H₄); 107.2 (1C_q, CN); 86.5, 84.6, 82.9 (3C_q, C₅H₄); 71.8, 70.5, 69.9, 69.4, 69.2, 68.2, 66.9 (17C, C₅H₄ and C₅H₅). IR (cm⁻¹): 2068 (s), 1925 (vs), 1891 (sh). Elemental anal. Calc. for compound **4-W**, C₃₆H₂₅Fe₂NWO₅, $M = 847.14$: C, 51.0; H, 2.97; N, 1.65. Found: C, 51.1; H, 2.98; N, 1.65.

X-Ray diffraction studies

Single crystals were grown by slow diffusion of hexane into

CH₂Cl₂ solutions and mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) with a nominal crystal to detector distance of 4.0 cm. An hemisphere of data was collected based on three ω -scans runs (starting $\omega = -28^\circ$) at values $\phi = 0, 90$ and 180° with the detector at $2\theta = 28^\circ$. At each of these runs, frames (606, 435 and 230 respectively) were collected at 0.3° intervals and 40 s per frame for compound **1**-(E), 60 s for compound **3**-Cr, 30 s for compound **3**-Mo and 20 s for compound **3**-W. Space group assignments are based on systematic absences, E statistics and successful refinement of the structures. Structures were solved by direct methods with the aid of successful difference Fourier maps and were refined using the SHELXTL 5.1 software package.²⁸ All non-hydrogen were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection and cell dimensions are given in Table 1 and structure refinement. The diffraction frames were integrated using the SAINT³⁰ package and corrected for absorption with SADABS.³¹

CCDC reference numbers 164936–164939.

See <http://www.rsc.org/suppdata/dt/b1/b104433h/> for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the DGESIC (PB98–1044) and BANCAIXA (P1B98–07) for financial support. We would also like to thank the Generalitat Valenciana for a fellowship (J. A. M.). We are very thankful to Dr Rosa Llusar for her useful advice on the determination of the crystal structure of **1**-(E).

References

- 1 A. Togni and T. Hayashi, *Ferrocenes*; VCH, Weinheim, Germany, 1995.
- 2 N. J. Long, *Metalloenes*; 1st edn., Blackwell Science Ltd., London, 1997.
- 3 S. Barlow and D. O'Hare, *Chem. Rev.*, 1997, **97**, 637.
- 4 M. Kurosawa, T. Nankawa, T. Matsuda, K. Kubo, M. Kurihara and H. Nishihara, *Inorg. Chem.*, 1999, **38**, 5113.
- 5 T. Horikoshi, K. Kubo and H. Nishihara, *J. Chem. Soc., Dalton Trans.*, 1999, 3355.
- 6 T.-Y. Dong, P.-H. Ho, X.-Q. Lai, Z.-W. Lin and K.-J. Lin, *Organometallics*, 2000, **19**, 1096.
- 7 Y. J. Chen, D.-S. Pan, C.-F. Chiu, J.-X. Su, S. J. Ling and K. S. Kwan, *Inorg. Chem.*, 2000, **39**, 953.
- 8 T. Y. Dong, C. K. Chang, C. H. Cheng and K. J. Lin, *Organometallics*, 1999, **18**, 1911.
- 9 N. J. Long, A. J. Martin, R. Vilar, A. J. P. White, D. J. Williams and M. Younus, *Organometallics*, 1999, **18**, 4261.
- 10 J. A. Mata, E. Peris, I. Asselberghs, R. van Boxel and A. Persoons, *New J. Chem.*, 2001, **25**, 299.
- 11 J. A. Mata, S. Uriel, R. Llusar and E. Peris, *Organometallics*, 2000, **19**, 3797.
- 12 J. A. Mata, E. Falomir, R. Llusar and E. Peris, *J. Organomet. Chem.*, 2000, **616**, 80.
- 13 J. A. Mata, S. Uriel, E. Peris, R. Llusar, S. Houbrechts and A. Persoons, *J. Organomet. Chem.*, 1998, **562**, 197.
- 14 G. G. A. Balavoine, J. C. Daran, G. Iftime, P. G. Lacroix, E. Manoury, J. A. Delaire, I. Maltey-Fanton, K. Nakatani and S. Di Bella, *Organometallics*, 1999, **18**, 21.
- 15 M. Bhadbhade, A. Das, J. C. Jeffery, J. A. McCleverty, J. A. N. Badiola and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1995, 2769.
- 16 H. E. Bunting, M. L. H. Green, S. R. Marder, M. E. Thompson, D. Bloor, P. V. Kolinsky and R. J. Jones, *Polyhedron*, 1992, **11**, 1489.
- 17 E. Peris, J. A. Mata and V. Moliner, *J. Chem. Soc., Dalton Trans.*, 1999, 3893.
- 18 J. A. Mata, E. V. Peris, R. Llusar, S. Uriel, M. P. Cifuentes, M. G. Humphrey, M. Samoc and B. Luther-Davies, *Eur. J. Inorg. Chem.*, 2001, **8**, 2113.
- 19 A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech and H. Keller, *Organometallics*, 1994, **13**, 1224.
- 20 I. S. Lee, Y. K. Chung, J. Mun and C. S. Yoon, *Organometallics*, 1999, **18**, 5080.
- 21 A. Peruga, J. A. Mata, D. Sainz and E. Peris, *J. Organomet. Chem.*, 2001.
- 22 S. Sakanishi, D. A. Bardwell, S. Couchman, J. C. Jeffery, J. A. McCleverty and M. D. Ward, *J. Organomet. Chem.*, 1997, **528**, 35.
- 23 L. K. Yeung, J. E. Kim, Y. K. Chung, P. H. Rieger and D. A. Sweigart, *Organometallics*, 1996, **15**, 3891.
- 24 I. P. Gubin and V. S. Khabdkarova, *J. Organomet. Chem.*, 1970, **22**, 449.
- 25 J. Y. Chen, C.-H. Kao, S. J. Lin, C.-C. Tai and K. S. Kwan, *Inorg. Chem.*, 2000, **39**, 189.
- 26 A.-C. Ribou, J. P. Launay, M. L. Sachtleben, H. Li and C. W. Spangler, *Inorg. Chem.*, 1996, **35**, 3735.
- 27 G. G. A. Balavoine, G. Doisneau and T. Fillebeenkhan, *J. Organomet. Chem.*, 1991, **412**, 381.
- 28 SHELXTL 5.1, Bruker AXS, Madison, WI, 1999.
- 29 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 30 SAINT, v. 5.0, Bruker Analytical X-Ray Systems, Madison, WI, 1998.
- 31 G. M. Sheldrick, SADABS, Empirical Absorption Program, University of Göttingen, Germany, 1996.