Electrochemistry of acetylide complexes of iron

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Abstract

The synthesis of a symmetrical acetylide-bridged, diiron(II) complex, $ClFe(DMPE)_2(C\equiv CC_6H_4C\equiv C)$-$(DMPE)_2FeCl$ (**1**) (DMPE = bis(dimethylphosphine)ethane) is reported. Electrochemistry and EPR spectroscopy are used to examine the redox properties of **1** as well as the mononuclear iron(II) complexes $Fe(DMPE)_2Cl_2$ (**2**), $ClFe(DMPE)_2(C\equiv CPh)$ (**3**), and $Fe(DMPE)_2(C\equiv CPh)_2$ (**4**). Evidence for the corresponding iron(III) and iron(IV) species is provided. The structural rearrangements accompanying redox changes are discussed on the basis of the electrochemical characteristics. The electrochemical behaviour of the bridged diiron species **1** provides evidence that the two metal centres interact electronically.

Introduction

Recent reports of the synthesis and properties of transition metal acetylide polymers have highlighted their importance as new materials·particularly in the area of non-linear optics [1]. We previously reported the synthesis and spectroscopic characterization of a number of bis(acetylide) complexes of iron and suggested their potential use in the assembly of oligomeric organometallic species containing metal centres separated by conjugated hydrocarbon fragments [2]. Here we report the formation of a binuclear acetylide-bridged complex $ClFe(DMPE)_2(C\equiv CC_6H_4C\equiv C)(DMPE)_2FeCl$ (**1**) (DMPE = bis(dimethylphosphino)ethane) and an examination of its electrochemical behaviour, together with that of the related mononuclear species **2**, **3** and **4**.

Electrochemistry of mononuclear complexes

The cyclic voltammetric behaviour exhibited by **2** in dichloromethane solution (Fig. 1) shows that the iron(II) complex undergoes two distinct anodic processes (at

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(1)   P   P = DMPE

(2)

(3)   (4)
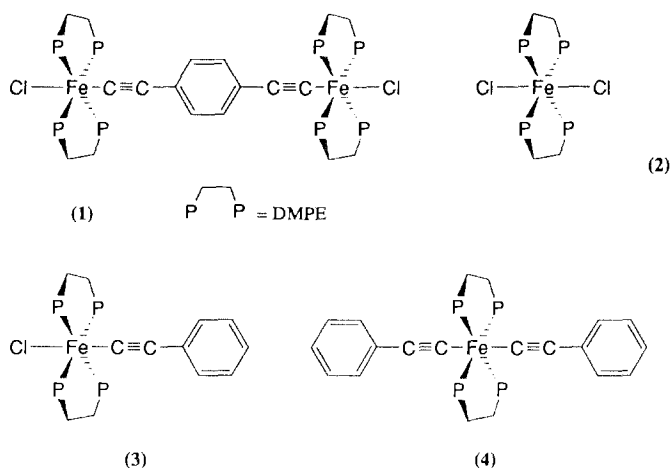
peaks A and B, respectively), each one exhibiting a directly associated reduction response in the reverse scan (at peaks C and D, respectively). Controlled potential coulometry ($E_w = +0.3$ V) indicated that the first anodic step consumes one electron/molecule. Concomitantly, the solution turns from a pale green to a magenta colour ($Fe^{2+} \rightarrow Fe^{3+}$) and gives a cyclic voltammetric response complementary to the peak system A/D in Fig. 1. The data confirm the full chemical reversibility of the iron(II)/iron(III) redox change in complex 2.

Analysis [3] of the cyclic voltammetric response A/D with scan rate, ν, varying from 0.02 V s^{-1} to 20.48 V s^{-1} indicates that: (i) the peak–current ratio i_{p_D}/i_{p_A} remains equal to 1; (ii) the peak-to-peak separation ΔE_p ($= E_{p_A} - E_{p_D}$) progressively increases from 69 mV to 272 mV; and (iii) the current function $i_{p_A} \times \nu^{-1/2}$ remains essentially constant.

A previous brief investigation of the electrochemistry of $Fe(DMPE)_2Cl_2/[Fe(DMPE)_2Cl_2]^+$ reported the electron transfer as irreversible in acetonitrile solu-
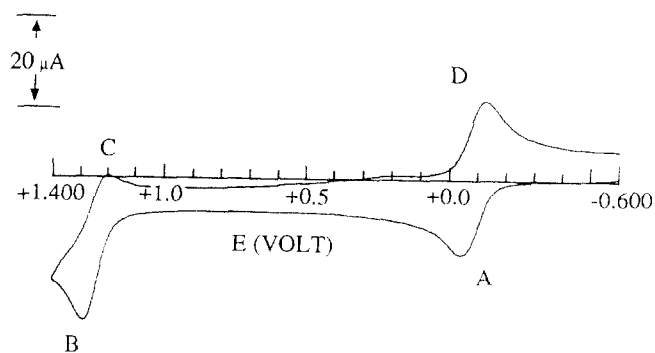
Fig. 1. Cyclic voltammogram of $Fe(DMPE)_2Cl_2$ (2) (1.3×10^{-3} mol dm^{-3} in CH_2Cl_2) recorded at a platinum electrode (electrolyte: $[NBu_4][ClO_4]$, 0.2 mol dm^{-3}; scan rate 0.2 V s^{-1}).

tion [4], in sharp contrast not only with the present results, but also with the observed stability of both the members of this Fe^{II}/Fe^{III} redox couple [5,6].

On the short time scale of cyclic voltammetry, the second anodic step (B/C) is confidently attributed to an Fe^{III}/Fe^{IV}, one-electron transfer. Access to the iron(IV) oxidation state is not unusual for this type of complex [4,18]. On the longer time-scale of macroelectrolysis, the oxidation is a multielectron process ($n_e > 3$), indicating that the instantaneously electrogenerated iron(IV) complex $[Fe(DMPE)_2Cl_2]^{2+}$ $[2]^{2+}$ may react to form products, which are further oxidized. Additionally, the ratio i_{p_C}/i_{p_B} is significantly less than 1 (about 0.5 at 0.2 V s^{-1}) and this further indicates the non-reversibility of the Fe^{III}/Fe^{IV} couple.

The electrochemical behaviour of 2 is particularly useful in correlating the electrochemical responses with the structural changes accompanying electron transfer processes according to criteria used for mononuclear [7–10], as well as polynuclear complexes [11–14]. The crystal structure of both the iron(II) [5] and iron(III) [6] dichloride complexes, 2 and $[2]^+$, respectively, have been elucidated by X-ray diffraction. On one-electron removal, the P_4Cl_2 donor set around the iron centre maintains a distorted octahedral geometry, even with shortening of the Fe–Cl distances (from 2.35 to 2.24 Å) together with an elongation of the Fe–P distances (from 2.23 to 2.30 Å).

The trend in ΔE_p with scan rate can be assumed to be an index of the stereodynamic strain occurring upon the redox change, provided that solvation processes of the redox couple can be neglected. An electrochemically reversible one-electron step is expected to display a constant ΔE_p value of 59 mV. Nevertheless, since uncompensated solution resistance causes departure from this value, it is preferable to compare ΔE_p with that exhibited by the one electron oxidation of ferrocene, under the same experimental conditions, since its structural reorganizations are known [15–17]. The trends in ΔE_p for the one-electron oxidation of $Fe(DMPE)_2Cl_2$ and ferrocene are shown Table 1. At relatively low scan rates, where presumably uncompensated solution resistance does not interfere appreciably, the structural reorganization experienced by 2 gives rise to a barrier to the electron transfer which is of the same order as (or less than) that experienced by ferrocene. In the latter case, reorientation of the cyclopentadienyl rings from a staggered conformation (or at least, from a random distribution of staggered and

Table 1

Variation of the peak-to-peak separations (ΔE_p) with scan rate (ν) for the one-electron oxidation of 2 and ferrocene [a]

Scan rate ν (V s^{-1})	2/[2]$^+$ [b]		Ferrocene/[ferrocene]$^+$ [c]	
	ΔE_p (mV)	i_p (μA)	ΔE_p (mV)	i_p (μA)
0.02	69	5.4	69	6.0
0.05	74	8.3	75	9.2
0.10	75	11.5	78	12.6
0.20	78	15.8	85	17.7
0.50	90	24.3	100	26.9
1.00	104	33.0	125	37.2

[a] 2 (1.3×10^{-3} mol dm^{-3}), ferrocene (1.0×10^{-3} mol dm^{-3}). Platinum working electrode, CH_2Cl_2 solution containing [NBu$_4$][ClO$_4$] (0.2 mol dm^{-3}) as supporting electrolyte. [b] $E^{o\prime} = -0.09$ V. [c] $E^{o\prime} = +0.45$ V.
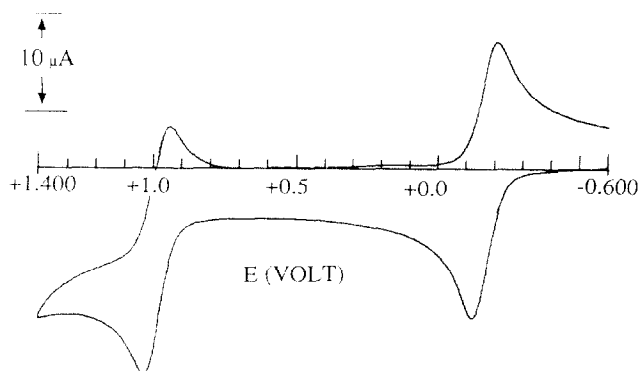
Fig. 2. Cyclic voltammogram of Fe(DMPE)$_2$(C≡CPh)$_2$ (4) (9.8 × 10^{-4} mol dm^{-3} in CH$_2$Cl$_2$) recorded at a platinum electrode (electrolyte: [NBu$_4$][ClO$_4$], 0.2 mol dm^{-3}; scan rate 0.2 V s^{-1}).

eclipsed conformations) to an eclipsed conformation occurs, together with an elongation of about 0.04 Å of the Fe-ring centre distance (from a mean of 1.66–1.70 Å) [15–17].

Responses qualitatively similar to those illustrated in Fig. 1 are exhibited by the related acetylide complexes 3 and 4. The cyclic voltammogram obtained for a dichloromethane solution of 4 is shown in Fig. 2.

The redox potentials for the mononuclear iron(II) species are summarized in Table 2, together with those of the related complexes [Fe(o-C$_6$H$_4$(PMe$_2$)$_2$)$_2$Cl$_2$]$^+$ (5) and [Fe(o-C$_6$F$_4$(PMe$_2$)$_2$)$_2$Cl$_2$]$^+$ (6). The peak-to-peak separation of the iron(II)/(III) electron transfer at a constant scan rate value (0.2 V s^{-1}) provides some insight into the extent of geometrical reorganizations accompanying the 3/[3]$^+$ and 4/[4]$^+$ redox changes. Based on the previous considerations of the 2/[2]$^+$ electron removal, both the cations [3]$^+$ and [4]$^+$ appear to maintain the

Table 2

Electrochemical parameters for the oxidation of mononuclear iron(II) complexes 2–6

Complex	$E^{o\prime}$ (V) Fe^{II}/Fe^{III}	ΔE_p (mV) [a]	$E^{o\prime}$ (V) Fe^{III}/Fe^{IV} [b]	Solvent	Ref.
Fe(DMPE)$_2$Cl$_2$ (2)	−0.09	78	+1.33	CH$_2$Cl$_2$	[c]
	−0.18 [d]	–	+1.22	MeCN	4
Fe(DMPE)$_2$(C≡CPh)Cl (3)	−0.14	77	+1.07	CH$_2$Cl$_2$	[c]
Fe(DMPE)$_2$(C≡CPh)$_2$ (4)	−0.16	86	+0.99	CH$_2$Cl$_2$	[c]
	+0.01	134	+0.98	THF	[c]
	−0.21	76	+0.88	MeCN [c]	[c]
[Fe(o − C$_6$H$_4$(PMe$_2$)$_2$)$_2$Cl$_2$]$^+$ (5)	+0.06	–	+1.39	MeCN	18
	+0.05	70	+1.43	MeCN	4
[Fe(o − C$_6$F$_4$(PMe$_2$)$_2$)$_2$Cl$_2$]$^+$ (6)	+0.34	90	+1.69	MeCN	4
(C$_5$H$_5$)$_2$Fe	+0.45	115	–	CH$_2$Cl$_2$	[c]
	+0.54	197	–	THF	[c]
	+0.38	124	–	MeCN	[c]

[a] Measured at a scan rate of 0.02 V^{-1}. [b] Redox change complicated by following chemical reactions. [c] Present work. [d] Peak potential value for an irreversible process. [e] Compound only slightly soluble in this solvent.

Table 3

X-band EPR parameters for the electrogenerated mononuclear iron(III) cations $[2]^+$, $[3]^+$ and $[4]^+$ [a]

Complex	$T = 100$ K		$T = 300$ K	
	g [b]	ΔH (G) [c]	g [b]	ΔH (G) [c]
$[Fe(DMPE)_2Cl_2]^+$ $[2]^+$	1.980	290	–	–
$[Fe(DMPE)_2(C{\equiv}CPh)Cl]^+$ $[3]^+$	1.988	255	2.009	185
$[Fe(DMPE)_2(C{\equiv}CPh)_2]^+$ $[4]^+$	1.980	245	1.995	170

[a] CH_2Cl_2 solution (electrolyte: $[NBu_4]^+[ClO_4]^-$, 0.2 mol dm^{-3}). [b] ± 0.008. [c] ± 8 G.

octahedral structure of their neutral congeners **3** [19] and **4** [22] probably accompanied by elongation of the Fe–P distances and shortening of the axial Fe–ligand distances.

The sequential substitution of the axial chlorides for the acetylide fragment (C≡CPh) makes it progressively easier to access the iron(III) species, indicating that the acetylide ligand is more electron-donating than the halide ligand.

EPR characterization of the mononuclear cations

The X-band EPR parameters for the electrogenerated iron(III) cations $[2]^+$, $[3]^+$ and $[4]^+$ are summarized in Table 3. EPR spectra were recorded in CH_2Cl_2 solution, both at 100 K and 300 K. Under the same experimental conditions, the corresponding iron(II) precursors, **2**, **3** and **4**, are EPR silent. The diamagnetic behaviour of the iron(II) species indicates a low-spin $3d^6$ electronic structure [20].

A lineshape analysis of the spectrum exhibited by $[3]^+$ (Fig. 3), reveals the presence of a $S > \frac{1}{2}$ unpaired electron system, with a typically large and unresolved absorption pattern, and large temperature dependence.
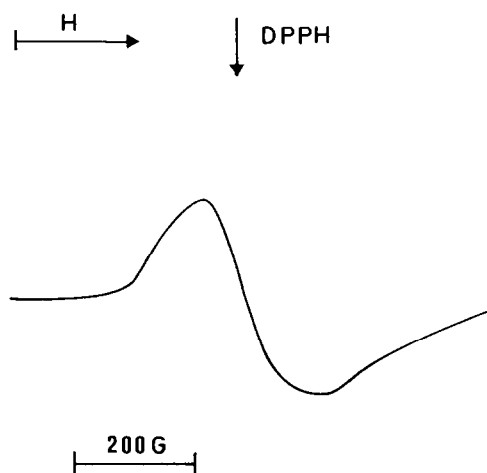

Fig. 3. X-band EPR spectrum of $[ClFe(DMPE)_2(C{\equiv}CPh)]^+$ $[3]^+$ electrogenerated in CH_2Cl_2 solution (electrolyte: $[NBu_4][ClO_4]$, 0.2 mol dm^{-3}; $T = 100$ K).

It is known that the iron(III), $S = \frac{5}{2}$ system gives rise to very broad EPR signals with no spectral resolution of the fine structure and which are more intense at low temperature [21,22]. The overall lineshape is suitably interpreted in terms of the so-called zero field splitting (ZFS) Hamiltonian, arising from the ligand field interaction with the five unpaired $3d$ electrons. In the general iron(III) electron spin Hamiltonian [21,22], the modulation of the ZFS term constitutes the main electron spin relaxation process, with a characteristic temperature dependence. The temperature induced motional dynamics of the iron(III) monocations in solution produces significant variations of the EPR parameters (particularly line-narrowing effects at higher temperatures) as would be expected if the ZFS terms dominated relaxation processes.

From analysis of the EPR data of complexes [2]$^+$, [3]$^+$ and [4]$^+$, it is apparent that the nature of the axial substituents does not significantly affect the X-band EPR lineshape, indicating that the unpaired spin density is predominantly metal-centred. Additionally, the analysis of the paramagnetism of these iron(III) systems, together with their temperature dependence in terms of the ZFS modulation, suggests that the starting "low-spin" t_{2g}^6 configuration is probably converted to a "high-spin" $t_{2g}^3 e_g^2$ configuration upon one-electron oxidation.

The binuclear acetylide complex, ClFe(DMPE)$_2$(C≡CC$_6$H$_4$C≡C)(DMPE)$_2$FeCl (1)

The bridged diiron complex *trans*, *trans*-ClFe(DMPE)$_2$(C≡CC$_6$H$_4$C≡C) (DMPE)$_2$FeCl (1) was synthesised by the reaction of 1 equiv. of 1,4-diethynylbenzene with 2 equiv. of *trans*-FeCl$_2$(DMPE)$_2$ (2) in the presence of sodium methoxide in methanol. The complex precipitates from solution as a yellow/brown solid. The cyclic voltammogram of 1 in dichloromethane solution displays two closely spaced, chemically reversible oxidation processes separated by 0.2 V (Fig. 4). Step-by-step controlled potential coulometric tests ($E_w = -0.25$ V and $+0.20$ V, respectively) revealed that each step involves a one-electron transfer. The gradual removal of the two electrons does not lead to any breakage of the starting framework (Fig. 5).
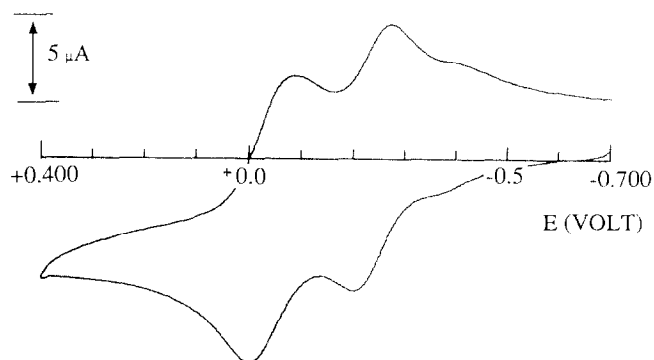

Fig. 4. Cyclic voltammogram of ClFe(DMPE)$_2$(C≡CC$_6$H$_4$C≡C)(DMPE)$_2$FeCl (1) (5.8 × 10^{-4} mol dm^{-3} in CH$_2$Cl$_2$) recorded at a platinum electrode (electrolyte: [NBu$_4$][ClO$_4$], 0.2 mol dm^{-3}; scan rate 0.2 V s^{-1}).

Fig. 5. Cyclic voltammogram of $ClFe(DMPE)_2(C\equiv CC_6H_4C\equiv C)(DMPE)_2FeCl$ (1) (5.8×10^{-4} mol dm^{-3} in CH_2Cl_2) recorded at a platinum electrode (electrolyte: $[NBu_4][ClO_4]$, 0.2 mol dm^{-3}; scan rate 0.2 V s^{-1}). (a) Initial; 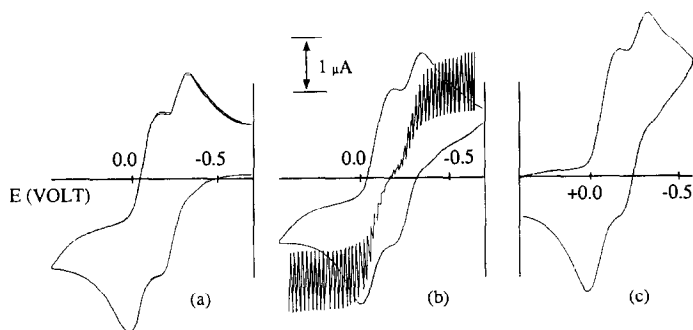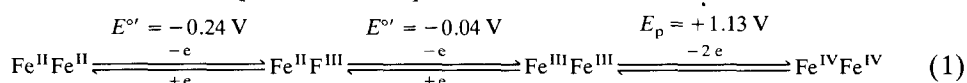(b) after exhaustive one-electron oxidation at -0.15 V; (c) after further exhaustive one-electron oxidation at $+0.3$ V. The superimposed d.c. voltammogram in (b) has been recorded at 0.01 V s^{-1}.

In the course of the electrolysis of **1**, the colour changes from yellow-brown to red amaranth (monocation), to green (dication). An irreversible, single-step two-electron process is present at higher potential values. The overall electrochemical behaviour of **1** is represented in eq. 1.

$$Fe^{II}Fe^{II} \underset{+e}{\overset{-e}{\rightleftarrows}} Fe^{II}F^{III} \underset{+e}{\overset{-e}{\rightleftarrows}} Fe^{III}Fe^{III} \overset{-2e}{\rightleftarrows} Fe^{IV}Fe^{IV} \quad (1)$$

with $E^{\circ\prime} = -0.24$ V, $E^{\circ\prime} = -0.04$ V, $E_p = +1.13$ V

The peak-to-peak separations (ΔE_p) for the first two anodic processes (ΔE_p for the **1**/[**1**]$^+$ couple is 70 mV and ΔE_p for the [**1**]$^+$/[**1**]$^{2+}$ couple is 81 mV, at 0.2 V s^{-1}) indicates that there is no significant structural reorganization as a consequence of the two successive one-electron removals.

The ability of binuclear complexes to add/remove two electrons in a single step or in two separate one-electron steps is one method which can be used to assess the electronic connectivity between the two metal centres [23]. The separation ($\Delta E = 0.2$ V) between the two one-electron steps gives rise to a comproportionation constant, $K_{COM} = 2.4 \times 10^3$ for the equilibrium

$$Fe^{II}Fe^{II} + Fe^{IV}Fe^{IV} \rightleftharpoons 2Fe^{II}Fe^{III}$$
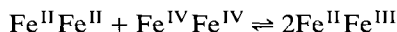
This value suggests that the electrogenerable $Fe^{II}Fe^{III}$ monocation [**1**]$^+$ should belong to the Robin–Day "Class II" (slightly delocalized) mixed valent species. The two iron centres in **1** are separated by a distance of about 13 Å and the presence of electronic communication between the metal atoms over this distance may be attributed to the effective conjugation exerted by the $-(C\equiv CC_6H_4C\equiv C)-$ bridge.

The powder X-band EPR spectrum of **1** recorded at 100 K exhibits two different absorption signals. The low-field signal, centred at $g = 4.276 \pm 0.008$, is weak in intensity, while the high-field signal shows axial symmetry, with $g_\perp = 2.348$ and $g_\parallel = 2.042 \pm 0.008$. On increasing the temperature, the overall signal intensity drops rapidly and at $T > 150$ K, the diiron(II) complex becomes EPR silent. The signal intensity recovers on lowering the temperature.

In CH_2Cl_2 solution at 100 K, **1** exhibits a similar line shape with a very weak low-field signal at $g = 4.413$ and a more intense signal, axially structured, at

$g_\perp = 2.390$ and $g_{||} = 2.042$. The EPR signal intensity drops with increasing temperature, disappearing before the glassy-liquid phase transition. The 100 K EPR spectrum of cation $[1]^+$, electrogenerated in CH_2Cl_2 solution, is more complex and exhibits an absorption pattern interpretable in terms of the superimposition of two different signals: the signal for **1**, already discussed, but less intense and a broad, unstructured absorption with $\Delta H = 220 \pm 5$ G and $g_{av} = 1.951$. The EPR spectrum of $[1]^{2+}$ electrogenerated in CH_2Cl_2 solution at 100 K, exhibits a broad signal with an unresolved lineshape ($g_{av} = 1.996$ and $\Delta H = 185$ G), very similar to that of $[3]^-$. In this signal, there is no evidence of the starting diiron(II) axial structure. On raising the temperature, the signal intensity remains almost constant, while the overall signal narrows slightly ($\Delta H = 140$ G, $g = 2.014$).

The paramagnetic nature of the dimeric complex **1** strongly affects the relaxation of ^{31}P and ^{13}C nuclei in solution. In the ^{13}C NMR spectrum of **1**, the resonances of the quaternary carbon atoms which lie along the axis of the molecule, could not be detected and this would be consistent with rapid relaxation of these nuclei due to unpaired spin density along the axis of the molecule. The EPR and electrochemical data support a high-spin configuration for all the $Fe^{II}Fe^{II}$, $Fe^{II}Fe^{III}$ and $Fe^{III}Fe^{III}$ congeners of **1**.

Conclusion

Electrochemistry of the series of the mononuclear complexes $Fe(DMPE)_2Cl_2$ (**2**), $ClFe(DMPE)_2(C{\equiv}CPh)$ (**3**), and $Fe(DMPE)_2(C{\equiv}CPh)_2$ (**4**) indicates that they are oxidized readily to Fe^{III} and Fe^{IV} species. The symmetrical complex $ClFe(DMPE)_2(C{\equiv}CC_6H_4C{\equiv}C)(DMPE)_2FeCl$ (**1**) undergoes two distinct reversible one-electron oxidations indicating that the oxidation of one iron centre substantially influences the oxidation of the other. The fact that there is electronic communication between the iron centres in the acetylide-bridged bimetallic system suggests that electronic interaction in trimeric, oligomeric and more highly condensed organometallic species will also be possible.

Experimental

Materials and apparatus for electrochemistry and EPR spectroscopy have been described elsewhere [24]. Potential values are referred to an aqueous saturated calomel electrode (SCE). $Fe(DMPE)_2Cl_2$ (**2**) was synthesised by reported procedures [25] and 1,4-diethynylbenzene was synthesised by Hay's method [26]. ^{31}P NMR spectra (162.0 MHz) were referenced to external, neat, trimethyl phosphite taken as 140.85 ppm. ^1H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) spectra were referenced to solvent resonances.

Synthesis of trans, trans-$ClFe(DMPE)_2(C{\equiv}CC_6H_4C{\equiv}C)(DMPE)_2FeCl$ *(1)*

Sodium metal (5 mg) was dissolved in a methanol solution (2 mL) of 1,4-diethynylbenzene (70 mg, 555 μmol) and the resulting solution was added to $FeCl_2(DMPE)_2$ (**2**), (476 mg, 1.11 mmol) in methanol (2 mL) with stirring. After 30 min the precipitate was filtered off, washed with methanol, and recrystallised from benzene to give *trans, trans*-$ClFe(DMPE)_2(C{\equiv}CC_6H_4C{\equiv}C)(DMPE)_2FeCl$ (**1**) as a brown-yellow solid (270 mg, 27%). $^{31}P\{^1H\}$ NMR (tetrahydrofuran-d_8): δ 65.9. ^1H

NMR (tetrahydrofuran-d_8): δ 1.49 (br.s, 24H, CH_3); 1.56 (br.s, 24H, CH_3); 2.11, (br.s, 16H, CH_2); 6.50 (s, 4H, CH). $^{13}C\{^{31}P, {}^1H\}$ NMR (dichloromethane-d_2): δ 13.6 (CH_3); 16.2 (CH_3); 31.0 (CH_2); 129.7 (CH); no quarternary carbons could be detected. λ_{max} (tetrahydrofuran, log ϵ) 213 (3.23); 264 (3.04); 395 (3.28) nm. ν(Nujol) 2042, 1571 cm^{-1}. Anal. Found: C, 44.69; H, 7.10. $Fe_2C_{34}H_{68}P_8Cl_2$ calc.: 44.99; H, 7.50%.

Acknowledgement

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