

# Mixed metal cluster complexes containing the bis-ferrocenylbutadiyne ligand: their structures and electrochemical responses

Richard D. Adams\*, Bo Qu

Department of Chemistry and Biochemistry, University of South Carolina, Columbia SC 29208, USA

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## Abstract

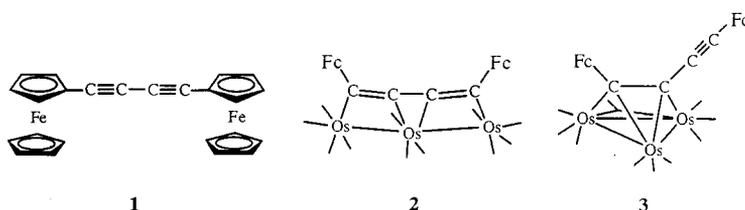
Two new platinum-triosmium cluster complexes  $\text{PtOs}_3(\text{CO})_9(\text{COD})(\mu_4\text{-FcC}_4\text{Fc})$  (**4**) and  $\text{Pt}_2\text{Os}_3(\text{CO})_{10}(\text{COD})(\mu_5\text{-FcC}_4\text{Fc})$  (**5**) containing the electroactive 1,4-bis-ferrocenylbutadiyne ligand  $\text{FcC}_4\text{Fc}$  were obtained from the reaction of  $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-FcC}_4\text{Fc})$  (**3**) with  $\text{Pt}(\text{COD})_2$ . Compounds **4** and **5** were characterized by IR and  $^1\text{H-NMR}$  spectroscopy, by single crystal X-ray diffraction analysis and by differential pulse voltammetry. Compound **4** consists of a butterfly cluster of one platinum and three osmium atoms with the platinum atom in one of the wing-tip positions. The cluster is co-ordinated to one of the C–C triple bonds of the  $\text{FcC}_4\text{Fc}$  ligand in the  $\mu_4$ -bonding mode. Cluster **5** exhibits the bow tie structure for five metal atoms: two of platinum and three of osmium. Both triple bonds of the butadiyne ligand are co-ordinated in this complex. Both products show two one electron oxidations for the ferrocenyl groups: for **4** at  $E^\circ = +0.356$  and  $+0.503$  V versus  $\text{Ag}|\text{AgCl}$ , and for **5** at  $E^\circ = +0.478$  and  $+0.576$  V. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Bis-ferrocenylbutadiyne ligand; Platinum-triosmium clusters; Mixed-metal clusters

## 1. Introduction

Due to interest in the use of polyunsaturated hydrocarbons as ‘molecular’ wires in futuristic nanoscale electronic devices, there has recently been a great deal of study of their ability to transmit electrons [1]. A typical way to test the ‘electronic communication’ between the two ends of a such a molecule is to place electroactive groups at the termini and measure the effect of the oxidation of one group upon the other [2]. 1,4-bis-(ferrocenyl)butadiyne =  $\text{FcC}_4\text{Fc}$  (**1**),  $\text{Fc} = \text{C}_5\text{H}_4\text{FeC}_5\text{H}_5$  is an example of one such molecule that has been studied for this purpose [3]. We have recently

shown that **1** can co-ordinate to the metal atoms of osmium cluster complexes in two significantly different ways, as illustrated by the two triosmium cluster complexes  $\text{Os}_3(\text{CO})_{11}(\mu_3\text{-FcC}_4\text{Fc})$  (**2**) and  $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-FcC}_4\text{Fc})$  (**3**) [4]. We have also found that the nature of the bonding of the osmium atoms to the butadiyne fragment can significantly affect the electronic communication between the two ferrocenyl groups [4]. For example, in compound **2** the communication is increased relative to that in **1**, while in compound **3** it is decreased. This has been attributed to the influence of the metal atoms on the  $\pi$ -orbital network of the butadiyne grouping.



\* Corresponding author. Tel.: +1-803-7777187; fax: +1-803-7776781.

E-mail address: adams@mail.chem.sc.edu (R.D. Adams).

We have now prepared two new expanded mixed-metal cluster complexes of **3** by the addition of platinum containing groupings. The synthesis, characterization and electrochemical response of these new complexes is reported here.

## 2. Experimental

### 2.1. General data

All reactions were performed under an atmosphere of nitrogen, unless otherwise indicated. Reagent grade solvents were freshly distilled prior to use.  $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-FcC}_4\text{Fc})$  [4] and  $\text{Pt}(\text{COD})_2$  [5], COD = 1,5-cyclooctadiene, were prepared according to the reported procedures. Separation of the products was performed by TLC in air on Analtech 0.25 mm silica gel (E. Merck) 60 Å  $F_{254}$  glass plates. Infrared spectra were recorded on a Nicolet 5 DXBO FT-IR spectrophotometer.  $^1\text{H-NMR}$  spectra were recorded on a Varian Mercury spectrometer operating at 300.13 MHz. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. Differential pulse voltammetric measurements were performed at room temperature on a

CV-50W electro-analyzer (Bioanalytical Systems, West Lafayette, IN) on solutions of the compounds at 1.0 mM concentration in a  $\text{CH}_3\text{CN-CH}_2\text{Cl}_2$  (1:1) solvent mixture containing 0.1 M tetrabutylammonium hexafluorophosphate. A three-electrode system was employed, consisting of a glassy carbon working electrode, a platinum counter and a  $\text{Ag}|\text{AgCl}$  reference electrode.

### 2.2. Reaction of $\text{Os}_3(\text{CO})_{10}(\mu_3\text{-FcC}_4\text{Fc})$ with $\text{Pt}(\text{COD})_2$

A 50 mg amount of **3** (0.0394 mmol) was dissolved in 55 ml of heptane in a 100 ml three-necked flask. A 71 mg amount of  $\text{Pt}(\text{COD})_2$  (0.173 mmol) was added to the flask, and the solution was then heated to gentle reflux for 1 h. The solvent was then removed in vacuo and the residue was dissolved in a minimal amount of  $\text{CH}_2\text{Cl}_2$  and was separated by TLC on silica gel (E. Merck) with a hexane- $\text{CH}_2\text{Cl}_2$  (4:1) solvent mixture. The two principal products (in order of elution) were: dark grey  $\text{Pt}_2\text{Os}_3(\text{CO})_{10}(\text{COD})(\mu_3\text{-FcC}_4\text{Fc})$  (**5**), 11.0 mg (16%); brown  $\text{PtOs}_3(\text{CO})_9(\text{COD})(\mu_4\text{-FcC}_4\text{Fc})$  (**4**), 11.8 mg (19%). For **4**: IR  $\nu_{\text{CO}}$  ( $\text{cm}^{-1}$  in hexane): 2075 (s), 2037 (s), 2025 (vs), 2004 (m), 1984 (m), 1980 (m), 1970 (m), 1952 (m), 1946 (w).  $^1\text{H-NMR}$  ( $\delta$  in  $\text{CDCl}_3$ ): 5.41–4.77 (m, 4H, COD); 4.57–4.56 (m, 1H,  $\text{C}_5\text{H}_4$ ); 4.43–4.42 (m, 1H,  $\text{C}_5\text{H}_4$ ); 4.39–4.37 (m, 1H,  $\text{C}_5\text{H}_4$ ); 4.30–4.23 (m, 1H,  $\text{C}_5\text{H}_4$ ); 4.26 (s, 5H, Cp); 4.20–4.15 (m, 4H,  $\text{C}_5\text{H}_4$ ); 4.13 (s, 5H, Cp). Anal. Calc. (found): C = 31.89, (31.73); H = 1.94, (2.00%). For **5**: IR  $\nu_{\text{CO}}$  ( $\text{cm}^{-1}$  in hexane): 2075 (s), 2044 (vs), 2022 (w), 2001 (w), 1987 (m), 1974 (m), 1960 (s), 1952 (m).  $^1\text{H-NMR}$  ( $\delta$  in  $\text{CDCl}_3$ ): 5.95–5.07 (m, 4H, COD); 5.55–5.56 (m, 1H,  $\text{C}_5\text{H}_4$ ); 5.04–5.05 (m, 1H,  $\text{C}_5\text{H}_4$ ); 4.91–4.88 (m, 2H,  $\text{C}_5\text{H}_4$ ); 4.86–4.84 (m, 1H,  $\text{C}_5\text{H}_4$ ); 4.57–4.55 (m, 2H,  $\text{C}_5\text{H}_4$ ); 4.23–4.25 (m, 1H,  $\text{C}_5\text{H}_4$ ); 4.24 (s, 5H, Cp); 4.17 (s, 5H, Cp); 2.52–0.84 (m, 8H, COD). Anal. Calc. (found): C = 28.55, (28.71); H = 1.71, (1.63%).

### 2.3. Crystallographic analyses

Brown crystals of **4** were grown by slow evaporation of the solvent from a hexane- $\text{CH}_2\text{Cl}_2$ (3:1) solution of the complex at  $-5^\circ\text{C}$ . Dark crystals of **5** were grown by slow evaporation of the solvent from a solution in benzene-octane(3:1) at  $25^\circ\text{C}$ . The data crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo- $\text{K}_\alpha$  radiation at  $20^\circ\text{C}$ . Unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. The data were processed on a Silicon-Graphics INDIGO [2] Workstation by using the TEXSAN structure solving program library

Table 1  
Crystallographic data for compounds **4** and **5**

Compound	<b>4</b>	<b>5</b>
Empirical formula	$\text{PtOs}_3\text{Fe}_2\text{C}_{41}\text{O}_9\text{H}_{30}$	$\text{Pt}_2\text{Os}_3\text{Fe}_2\text{C}_{42}\text{O}_{10}\text{H}_{30}$
Formula weight	1544.09	1767.17
Crystal system	Triclinic	Monoclinic
Lattice parameters		
$a$ (Å)	11.359(2)	11.632(3)
$b$ (Å)	18.684(5)	18.024(3)
$c$ (Å)	10.827(2)	20.859(4)
$\alpha$ (°)	96.41(2)	90.0
$\beta$ (°)	107.87(2)	102.06(2)
$\gamma$ (°)	81.71(3)	90.0
$V$ (Å <sup>3</sup> )	2158.4(9)	4277(1)
Space group	$P\bar{1}(2)$	$P2_1/n(14)$
$Z$ value	2.0	4.0
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	2.51	2.74
$\mu$ (Mo- $\text{K}_\alpha$ ), ( $\text{cm}^{-1}$ )	128.36	160.74
Number observed [ $I > 3\sigma(I)$ ]	4001	3808
Number of variables	527	508
Residuals <sup>a</sup> $R$ ; $R_w$	0.039; 0.055	0.047; 0.060
Goodness-of-fit (GOF) <sup>b</sup>	1.10	1.31
Maximum shift/error on final cycle	0.01	0.01
Absorbance correction, max/min	DIFABS, 0.52–1.00	DIFABS, 0.59–1.00
Largest residual peak ( $\text{e} \text{ \AA}^{-3}$ )	1.58	2.24

<sup>a</sup>  $R = \sum_{hkl} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{hkl} |F_{\text{obs}}|$ ;  $R_w = [\sum_{hkl} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{hkl} w F_{\text{obs}}^2]^{1/2}$ ,  $w = 1/\sigma^2(F_{\text{obs}})$ .

<sup>b</sup>  $\text{GOF} = [\sum_{hkl} (w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}}))]^{1/2}$ .

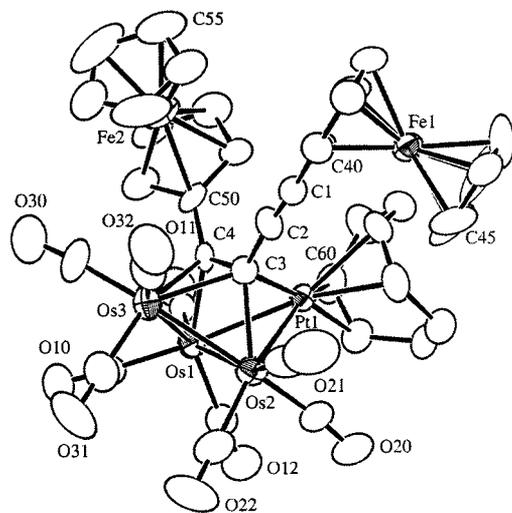


Fig. 1. An ORTEP diagram of  $\text{PtOs}_3(\text{CO})_9(\text{COD})(\mu_4\text{-FcC}_4\text{Fc})$  (**4**) showing 40% probability thermal ellipsoids. Selected bond distances (Å) and angles (°) are: Pt(1)–Os(1) = 2.6974(9), Pt(1)–Os(2) = 2.7817(9), Os(1)–Os(2) = 2.8383(8), Os(1)–Os(3) = 2.8351(8), Os(2)–Os(3) = 2.7245(9), Pt(1)–C(3) = 2.18(1), Pt(1)–C(4) = 2.40(1), Os(1)–C(4) = 2.16(1), Os(2)–C(3) = 2.22(1), Os(3)–C(3) = 2.25(1), Os(3)–C(4) = 2.20(1), C(1)–C(2) = 1.19(2), C(2)–C(3) = 1.43(2), C(3)–C(4) = 1.45(2); C(1)–C(2)–C(3) = 171(2), C(2)–C(3)–C(4) = 123(1).

obtained from the Molecular Structure Corp., The Woodlands, TX. Neutral-atom scattering factors were calculated by the standard procedures [6a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [6b]. Lorentz polarization (Lp) corrections were applied to the data. Full matrix least-squares refinements minimized the function:  $\sum_{hkl} w(|F_o| - |F_c|)^2$ , where  $w = 1/[\sigma(F)^2]$ ,  $\sigma(F) = \sigma(F_o^2)/2F_o$  and  $\sigma(F_o^2) = [\sigma(I_{\text{raw}})^2 + (0.06 I_{\text{net}})^2]^{1/2}/Lp$ .

Compound **4** crystallized in the triclinic crystal system. The space group  $P\bar{1}$  was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (SIR92) and difference Fourier syntheses. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were calculated by assuming idealized geometries with C–H distances of 0.95 Å and were included in the structure factor calculations without refinement.

Compound **5** crystallized in the monoclinic crystal system. The space group  $P2_1/n$  was established on the basis of the systematic absences observed during the collection of the data. The structure of **5** was solved by a combination of direct methods (SIR92) and difference Fourier syntheses. Attempted refinement by using all non-hydrogen atoms with anisotropic thermal parameters was unsuccessful because five carbon atoms yielded negative thermal parameters. This was probably due to error introduced by X-ray absorption effects. These

atoms C(2), C(4), C(53), C(60) and C(70) were subsequently refined successfully with isotropic thermal parameters to complete the analysis. The positions of the hydrogen atoms were calculated by assuming idealized geometries with C–H distances of 0.95 Å and were included in the structure factor calculations without refinement.

### 3. Results

The two new platinum-triosmium cluster complexes  $\text{PtOs}_3(\text{CO})_9(\text{COD})(\mu_4\text{-FcC}_4\text{Fc})$  (**4**) and  $\text{Pt}_2\text{Os}_3(\text{CO})_{10}(\text{COD})(\mu_5\text{-FcC}_4\text{Fc})$  (**5**) were obtained in 19% and 16% yields, respectively, from the reaction of **3** with  $\text{Pt}(\text{COD})_2$  in a heptane solution at reflux. Compounds **4** and **5** were characterized by IR and  $^1\text{H-NMR}$  spectroscopy, by single-crystal X-ray diffraction analyses and by differential pulse voltammetry. An ORTEP diagram of the molecular structure of **4** is shown in Fig. 1. Compound **4** consists of a butterfly cluster of metal atoms consisting of one platinum and three osmium atoms. The platinum atom occupies one of the wing-tip positions. Each osmium atom contains three linear terminal carbonyl ligands. The platinum atom contains one chelated COD ligand. The cluster is co-ordinated to one of the C–C triple bonds of the  $\text{FcC}_4\text{Fc}$  ligand in the well established  $\mu_4$ -bonding mode. Examples of butterfly  $M_4$  complexes co-ordinated to a single triple bond of a conjugated polyene molecule have been reported previously [7–9]. As expected, the co-ordinated C–C triple bond is elongated C(3)–C(4) = 1.45(2) Å while the uncoordinated C–C triple bond is characteristically short C(1)–C(2) = 1.19(2) Å. The  $^1\text{H-NMR}$  spectrum of **4** shows two singlets, 4.26 and 4.13 ppm, for the  $\text{C}_5\text{H}_5$  ring on each of the two inequivalent ferrocenyl groups.

An ORTEP diagram of the molecular structure of **5** is shown in Fig. 2. This cluster contains five metal atoms, two of platinum and three of osmium. The metal atoms have adopted the ‘bow tie’ structural arrangement with the platinum atom Pt(2) at the vertex-sharing site. The platinum–platinum bond is long, Pt(1)–Pt(2) = 3.084(1) Å but this length is not unusual. The other metal–metal bond distances are normal, Pt(1)–Os(1) = 2.678(1), Pt(2)–Os(1) = 2.752(2), Pt(2)–Os(2) = 2.799(1), Pt(2)–Os(3) = 2.833(1) and Os(2)–Os(3) = 2.684(1) Å. Both triple bonds of the butadiyne ligand are co-ordinated in this complex. Atoms C(1) and C(2) are co-ordinated to the triangular group Os(1), Pt(1) and Pt(2), while atoms C(3) and C(4) are co-ordinated to Os(2), Os(3) and Pt(1). The C–C distances of both triple bonds are elongated as a result of this coordination, C(1)–C(2) = 1.46(3) and C(3)–C(4) = 1.37(3) Å. There are two established types of coordination for triply bridging alkyne ligands on triangular metal groupings:

the  $\mu\text{-}\parallel$  and the  $\mu\text{-}\perp$  modes [10]. The C–C triple bond co-ordinated to the Os(2), Os(3) and Pt(1) triangle exhibits the  $\mu\text{-}\parallel$  mode, while the one co-ordinated to the Os(1), Pt(1) and Pt(2) triangle has the  $\mu\text{-}\perp$  mode. The  $\mu\text{-}\parallel$  mode is typical of electron precise clusters, while the  $\mu\text{-}\perp$  mode is commonly found in electron deficient ones. Interestingly, the metal atoms in cluster **5** have a total of 76 valence electrons which is two less than the 78 required for the bow tie structure of five metal atoms when all of the metal atoms obey the 18 electron rule. This can be attributed to the presence of platinum in the cluster. Platinum is often found with fewer than 18 electrons (e.g. 16 electron configurations are stable for many mononuclear platinum complexes). Very few compounds similar to **5** have been reported. One is the compound  $\text{Ru}_3\text{Co}_2(\text{CO})_{14}(\mu_5\text{-PhC}_4\text{Ph})$ ; (**6**) that was reported by Bruce et al. in which both C–C triple bonds are co-ordinated in the  $\mu\text{-}\parallel$  mode [11].

The differential pulse voltammograms of **4** and **5** show two one electron oxidations for the ferrocenyl groups: for **4** at  $E^\circ = +0.356$  and  $+0.503$  V versus  $\text{Ag}|\text{AgCl}$ ,  $\Delta E^\circ = 0.147$  V and for **5** at  $E^\circ = +0.478$  and  $+0.576$ ,  $\Delta E^\circ = 0.098$  V. For comparison, compound **2** shows two one electron oxidations at  $E_1^\circ = +0.300$  and  $E_2^\circ = +0.484$ ,  $\Delta E^\circ = 0.184$  V, while compound **3** shows two very poorly resolved one electron oxidations centered at  $E^\circ = +0.512$  with  $\Delta E^\circ \approx 0.057$  V [4]. The free molecule 1,4-bis-ferrocenylbutadiyne also shows two one electron oxidations for the ferrocenyl groups,  $E_1^\circ = +0.476$  and  $E_2^\circ = +0.0576$ ,  $\Delta E^\circ = 0.100$  V [3b].

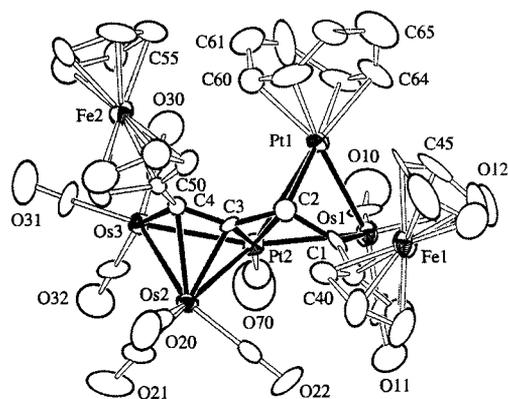


Fig. 2. An ORTEP diagram of  $\text{Pt}_2\text{Os}_3(\text{CO})_{10}(\text{COD})(\mu_5\text{-FcC}_4\text{Fc})$  (**5**) showing 40% probability thermal ellipsoids. Selected bond distances (Å) and angles ( $^\circ$ ) are: Pt(1)–Pt(2) = 3.084(1), Pt(1)–Os(1) = 2.678(1), Pt(2)–Os(1) = 2.752(2), Pt(2)–Os(2) = 2.799(1), Pt(2)–Os(3) = 2.833(1), Os(2)–Os(3) = 2.684(1), Os(1)–C(1) = 2.07(2), Pt(1)–C(2) = 2.05(2), Pt(2)–C(2) = 2.21(2), Pt(2)–C(3) = 2.19(2), Os(3)–C(4) = 2.09(2), Os(2)–C(3) = 2.13(2), Os(2)–C(4) = 2.33(2), C(1)–C(2) = 1.46(3), C(2)–C(3) = 1.40(3), C(3)–C(4) = 1.37(3); C(1)–C(2)–C(3) = 133(2), C(2)–C(3)–C(4) = 146(2).

## 4. Discussion

Compounds **4** and **5** were obtained by the addition of one and two equivalents of platinum to the triosmium cluster **3** from the reagent  $\text{Pt}(\text{COD})_2$ .  $\text{Pt}(\text{COD})_2$  readily sheds one or both of its COD ligands [12], and has been widely used by us and others as a reagent to prepare mixed metal cluster complexes containing platinum [13]. Surprisingly, efforts to obtain **5** from **4** by reaction with additional quantities of  $\text{Pt}(\text{COD})_2$  at heptane reflux were unsuccessful, suggesting that **4** is not an intermediate en route to **5**.

We have recently observed that the electronic communication between the ferrocenyl groups in **2** is considerably greater than that of **3**, and is even greater than that in **1** [4]. This was attributed to the unusual coordination of the bis-(ferrocenyl)butadiyne ligand in **2**. In compound **2** the coordination of the metal atoms produced a shortening of the C–C single bond between the two C–C triple bonds. However, in **3** both of the  $\pi$ -bonds of one of the C–C triple bonds are co-ordinated to the triosmium cluster. In this case the interaction between the  $\pi$ -orbitals of the two triple bonds is decreased. Since the electronic communication in compounds with extended  $\pi$ -systems is believed to be transmitted principally along the  $\pi$ -orbital network [2a], it is reasonable to expect that the communication between the ferrocenyl groups in **3** would be less than that in **2**, as observed. The same argument could be used to explain the fact that electronic communication between the ferrocenyl groups in **4** is less than that in **2**. Interestingly, however the value of  $\Delta E^\circ$  for **4** is larger than that for **3**. This, however, does not mean that the electronic communication between the ferrocenyl groups in **4** is larger than that in **3**, because in both **3** and **4** the ferrocenyl groups are inequivalent, and this also contributes to the difference in the electrode potentials of these two groupings. It is not possible to separate the combined effects of chemical inequivalence and electronic communication through the carbon chain to determine the relative contribution of each factor to the total, and so the  $\Delta E^\circ$  value in **3** and **4** is not a direct measure of the electronic communication. This reasoning also applies to the interpretation of the difference in oxidation potentials of the two ferrocenyl groups in **5**. In the case of **5**, however, the value of  $\Delta E^\circ$  is even smaller. This may be due to the extensive coordination of both C–C triple bonds to the cluster through their  $\pi$ -orbitals.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC) CCDC no. 150289 for compound

4 and 150290 for 5. Copies of these data may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk

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