

Synthesis and crystal structure of the double cluster $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4)]_2(p\text{-C}_6\text{H}_4)$ [☆]

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Abstract

$[\text{Cp}_4\text{Fe}_4(\text{CO})_4]$ (**1**) reacts with $p\text{-BrC}_6\text{H}_4\text{Li}$ and MeOH in sequence to afford the functionalized cluster $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Br})]$ (**2**), while the reaction of **2** with $n\text{-BuLi}$ and MeOH produces $[\text{Cp}_2\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4\text{Bu})(\text{C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Br})]$ (**3**). The double cluster $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4)]_2(p\text{-C}_6\text{H}_4)$ (**4**) has been prepared by treatment of $[\text{Cp}_4\text{Fe}_4(\text{CO})_4]$ with $p\text{-C}_6\text{H}_4\text{Li}_2$ and MeOH in sequence. The electrochemistry of **2** and **4**, as well as the crystal structure of **4** have been investigated.

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1. Introduction

$[\text{Cp}_4\text{Fe}_4(\text{CO})_4]$ (**1**), originally reported by King [1], is one of the first substance containing a tetrahedral cluster of metal atoms. A unique feature of this stable cluster is that it is electroactive, reversibly undergoing both reduction and oxidation [2,3], which property is essential to perform important functions such as solar energy conversion and multielectron catalysis [4,5]. Recently, assembling higher nuclearity clusters with well-defined dimensions provides a new field of chemistry with prospective application in areas including molecular recognition and nanotechnology [6–10]. It is therefore of interest to construct oligomers of **1** and study their electroactivity [11]. We have previously prepared the double clusters $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4)]_2$ and $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4)]_2[(\text{C}_5\text{H}_4)_2\text{Fe}]$ by treating the anion $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4)]^-$ with **1** and dibromoferrocene, respectively [12]. Now we report an arene-bridged dou-

ble cluster $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4)]_2(p\text{-C}_6\text{H}_4)$ (**4**) but with a different synthetic approach.

2. Results and discussion

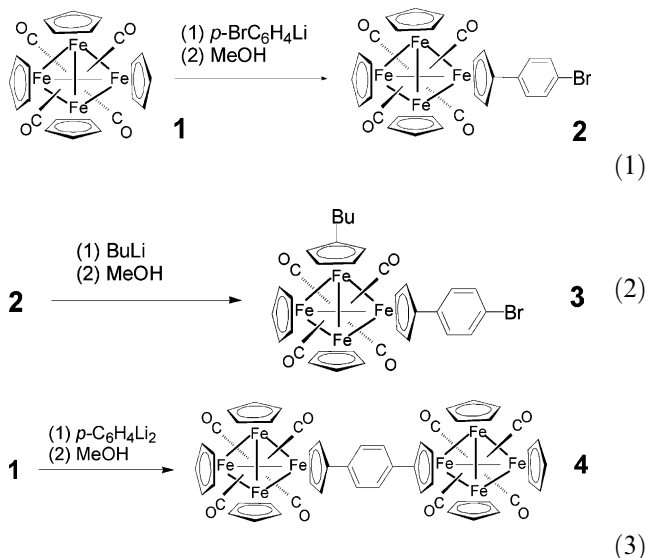
Compound **1** reacted with $p\text{-BrC}_6\text{H}_4\text{Li}$ and MeOH in sequence to afford the functionalized cluster $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Br})]$ (**2**) in 30% yield (Eq. (1)), where the nucleophile $p\text{-BrC}_6\text{H}_4^-$ added to a cyclopentadienyl ring of **1**. It was thought that subsequent treatment of **2** with $n\text{-BuLi}$ might abstract the bromine atom to generate $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4)]^-$, which can then react with **1** to produce **4**. In fact, the $n\text{-Bu}^-$ anion attacked a separate Cp group to produce $[\text{Cp}_2\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4\text{Bu})(\text{C}_5\text{H}_4\text{-}p\text{-C}_6\text{H}_4\text{Br})]$ (**3**) in 40% yield (Eq. (2)). A reverse way by treating **2** with the anion $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4)]^-$ did not afford **4**, too. We then prepared the dianion $p\text{-C}_6\text{H}_4\text{Li}_2$ by treating $p\text{-C}_6\text{H}_4\text{Br}_2$ with two equivalent of $n\text{-BuLi}$ [13], which reacted with **1** and MeOH in sequence to give **4** in 24% yield after purification by column chromatography and crystallization (Eq. (3)). In these reactions, however, the starting clusters were recovered in 48–57% yield even though the reactions monitored by IR showed no presence of them

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after introduction of the nucleophiles. Since these carbonyl clusters are easily reduced, as the electrochemical studies have shown, reduction of them probably competes with nucleophilic addition here and limits the yields of products [11]



The new clusters **2–4** form air-stable, dark green crystalline solids which have been characterized by elemental analyses, mass, IR and NMR. Their IR spectra in the carbonyl region present one broad absorption around 1635 cm^{-1} for the triply bridging carbonyl ligands, suggesting that their tetrahedral iron cores remain intact. Their ^1H NMR spectra are closely related, where the unsubstituted Cp groups display a singlet resonance at ca. 4.5 ppm and each substituted C_5H_4 group shows two sets of multiplet resonances in the range 4.9–4.3 ppm. The $\text{C}_6\text{H}_4\text{Br}$ group in **2** and **3** presents two doublet resonances at 7.6 and 7.5 ppm, while the bridging C_6H_4 group of **4** shows a singlet resonance at 7.78 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** displays the triply bridging carbonyl signals at 290.8 and 290.5 ppm in an approximate ratio of 1:3, four signals for the $\text{C}_6\text{H}_4\text{Br}$ group in the range 131.5–122.3 ppm, three signals for the C_5H_4 group at 104.4, 100.6 and 95.2 ppm,

and the Cp group resonance at 99.1 ppm, consistent with a molecule of idealized C_s symmetry in solution.

The molecular structure of **4** is illustrated in Fig. 1. Selected bond distances and bond angles are collected in Table 1. There is a crystallographic center of symmetry imposed on the molecule. The coordination about each Fe_4 cluster shows great resemblance to that of **1** [14,15]. The two Fe_4 clusters are located in opposite sides of the $\text{C}_5\text{H}_4\text{--C}_6\text{H}_4\text{--C}_5\text{H}_4$ link. The two C_5H_4 groups are about coplanar, while the bridging C_6H_4 group is tilted from the plane by 11.5° . The average Fe–Fe lengths and Fe–C(Cp) lengths are 2.52 and 2.12 Å, respectively. The individual Fe–CO distances range from 1.964(3) to 1.999(3) Å and the C–O distances from 1.197(4) to 1.202(4) Å, while Fe–C–O angles are in the range $131.7(2)^\circ\text{--}134.6(2)^\circ$. The C–C bond lengths within the cyclopentadienyl and benzene rings are averaged 1.42 and 1.39 Å, respectively, and the C(9)–C(10) length is 1.470(4) Å.

Cyclic voltammogram studies of **2** and **4** were taken in dry, oxygen-free CH_2Cl_2 at 27°C . The $E_{1/2}$ values (versus $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple) relating each oxidation state are depicted in Scheme 1. Analogous to **1**, compound **2** also exists in four electrochemically reversible oxidation states, $[\text{Cp}_3\text{Fe}_4(\text{CO})_4(\text{C}_5\text{H}_4\text{--}p\text{-C}_6\text{H}_4\text{Br})]^{2+/+^0/-}$, while the redox potentials are shifted anodically by 56–130 mV due to the electron-withdrawing substituent. On the other hand, compound **4** displays three redox waves in correspondence to a $4^{3+} \leftrightarrow 4^{2+} \leftrightarrow 4^0 \leftrightarrow 4^{2-}$ transformation. The two-electron reduction (and oxidation) wave is likely the overlap of two closely spaced one-electron redox couples for each Fe_4 cluster with slight electronic interactions between them, presumably because the $\text{C}_5\text{H}_4\text{--C}_6\text{H}_4\text{--C}_5\text{H}_4$ link is not planar and therefore is not in full conjugation [16,17].

In summary, the double cluster **4** has been prepared by the reaction of $p\text{-C}_6\text{H}_4\text{Li}_2$ with two molecules of **1**. Since compound **1** is susceptible to two nucleophilic additions to form **3**, it is promising that further treatment of **4** and **1** with $p\text{-C}_6\text{H}_4\text{Li}_2$ or other dianionic

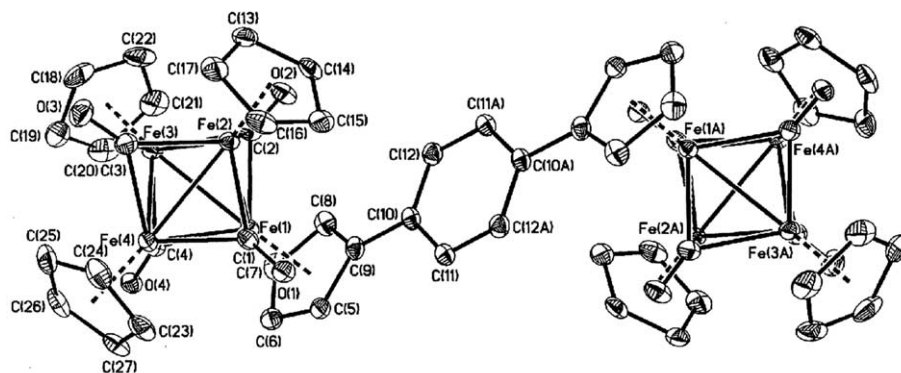
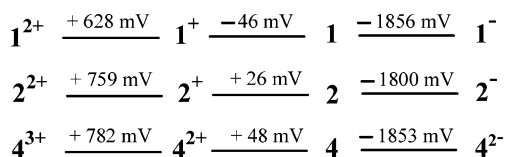


Fig. 1. Molecular structure of **4**. The hydrogen atoms have been omitted for clarity.

Table 1
Selected bond distances (Å) and bond angles (°) for **4**

<i>Bond distances</i>			
Fe(1)–C(2)	1.979(3)	Fe(1)–C(4)	1.983(3)
Fe(1)–C(1)	1.991(3)	Fe(1)–C(7)	2.102(3)
Fe(1)–C(6)	2.108(3)	Fe(1)–C(8)	2.114(3)
Fe(1)–C(5)	2.117(3)	Fe(1)–C(9)	2.137(3)
Fe(1)–Fe(4)	2.5071(6)	Fe(1)–Fe(3)	2.5130(6)
Fe(1)–Fe(2)	2.5168(6)	Fe(2)–C(1)	1.964(3)
Fe(2)–C(2)	1.986(3)	Fe(2)–C(3)	1.991(3)
Fe(2)–C(13)	2.109(3)	Fe(2)–C(14)	2.119(3)
Fe(2)–C(16)	2.123(3)	Fe(2)–C(15)	2.123(3)
Fe(2)–C(17)	2.123(3)	Fe(2)–Fe(3)	2.5120(6)
Fe(2)–Fe(4)	2.5406(6)	Fe(3)–C(4)	1.968(3)
Fe(3)–C(2)	1.980(3)	Fe(3)–C(3)	1.993(3)
Fe(3)–C(22)	2.100(3)	Fe(3)–C(21)	2.105(4)
Fe(3)–C(19)	2.111(3)	Fe(3)–C(20)	2.112(3)
Fe(3)–C(18)	2.116(4)	Fe(3)–Fe(4)	2.5026(6)
Fe(4)–C(3)	1.972(3)	Fe(4)–C(4)	1.987(3)
Fe(4)–C(1)	1.999(3)	Fe(4)–C(27)	2.107(3)
Fe(4)–C(23)	2.108(3)	Fe(4)–C(24)	2.113(3)
Fe(4)–C(26)	2.116(3)	Fe(4)–C(25)	2.120(3)
O(1)–C(1)	1.198(4)	O(2)–C(2)	1.197(4)
O(3)–C(3)	1.201(4)	O(4)–C(4)	1.202(4)
<i>Bond angles</i>			
Fe(4)–Fe(1)–Fe(2)	60.755(17)	Fe(3)–Fe(1)–Fe(2)	59.924(17)
Fe(4)–Fe(1)–Fe(3)	59.802(18)	Fe(3)–Fe(2)–Fe(4)	59.377(17)
Fe(1)–Fe(2)–Fe(4)	59.436(17)	Fe(1)–Fe(2)–Fe(3)	59.965(17)
Fe(4)–Fe(3)–Fe(2)	60.879(17)	Fe(4)–Fe(3)–Fe(1)	59.982(17)
Fe(2)–Fe(3)–Fe(1)	60.111(17)	Fe(3)–Fe(4)–Fe(2)	59.744(17)
Fe(1)–Fe(4)–Fe(2)	59.810(17)	Fe(1)–Fe(4)–Fe(3)	60.216(18)
O(1)–C(1)–Fe(2)	131.8(2)	O(1)–C(1)–Fe(1)	133.4(3)
Fe(2)–C(1)–Fe(1)	79.03(12)	O(1)–C(1)–Fe(4)	133.2(2)
Fe(2)–C(1)–Fe(4)	79.74(12)	Fe(1)–C(1)–Fe(4)	77.86(11)
O(2)–C(2)–Fe(1)	133.8(3)	O(2)–C(2)–Fe(3)	131.8(2)
Fe(1)–C(2)–Fe(3)	78.82(11)	O(2)–C(2)–Fe(2)	133.0(2)
Fe(1)–C(2)–Fe(2)	78.80(12)	Fe(3)–C(2)–Fe(2)	78.60(12)
O(3)–C(3)–Fe(4)	132.8(3)	O(3)–C(3)–Fe(2)	132.4(3)
Fe(4)–C(3)–Fe(2)	79.76(12)	O(3)–C(3)–Fe(3)	133.6(3)
Fe(4)–C(3)–Fe(3)	78.28(12)	Fe(2)–C(3)–Fe(3)	78.19(12)
O(4)–C(4)–Fe(3)	134.6(2)	O(4)–C(4)–Fe(1)	131.7(3)
O(4)–C(4)–Fe(4)	132.6(2)	Fe(3)–C(4)–Fe(4)	78.53(12)
Fe(1)–C(4)–Fe(4)	78.32(11)		



Scheme 1.

nucleophiles could lead to higher cluster oligomers. The investigation is in progress in our laboratory.

3. Experimental

3.1. General methods

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk

techniques. $[\text{Cp}_4\text{Fe}_4(\text{CO})_4]$ (**1**) was prepared as described in the literature [12]. 1,4-dibromobenzene (from Aldrich) and *n*-butyl lithium (2.5 M in *n*-hexane, from Merck) were used as received. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Infrared spectra were recorded with a 0.1 mm-path CaF_2 solution cell on a Hitachi I-2001 IR spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer at 500 and 125.7 MHz, respectively. Fast-atom-bombardment (FAB) mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the National Chen-Kung University, Tainan, Taiwan.

3.2. Preparation of **2**

Under a nitrogen atmosphere, *n*-butyl lithium (0.68 mmol) was slowly added into a solution of

1,4-dibromobenzene (160 mg, 0.68 mmol) in 5 ml of toluene at 0 °C. The resulting *p*-BrC₆H₄Li reagent was then added into a solution of **1** (200 mg, 0.336 mmol) in 20 ml of THF. The mixture was stirred at 50 °C for 5 h, followed by addition of MeOH (2 ml). The solvent was removed under vacuum and the residue subjected to column chromatography (silica gel), with *n*-hexane/dichloromethane/ethyl acetate (3:1:1) as eluant. Compound **2** (75 mg, 30%) was obtained from the second green band. Anal. Calc. for C₃₀H₂₃BrFe₄O₄: C, 47.99; H, 3.09. Found: C, 47.62; H, 3.04%. IR (CH₂Cl₂, ν_{CO}): 1636 cm⁻¹. ¹H NMR (CDCl₃, 25 °C): 7.62 (d, 2H, *J*_{H-H} = 10 Hz), 7.55 (d, 2H, *J*_{H-H} = 10 Hz, C₆H₄), 4.96 (br, 2H), 4.86 (br, 2H, C₅H₄), 4.59 (s, 15H, Cp) ppm. ¹³C{¹H} NMR (CDCl₃, 25 °C): 290.8, 290.5 (μ₃-CO), 131.5, 131.3, 127.9, 122.3 (C₆H₄), 104.4, 100.6, 95.2 (C₅H₄), 99.1 (Cp) ppm. MS (FAB) *m/z* 750 [M⁺, ⁷⁹Br].

3.3. Preparation of **3**

Under a nitrogen atmosphere, *n*-butyl lithium (0.35 mmol) was slowly added into a solution of **2** (126 mg, 0.16 mmol) in 5 ml of toluene at 0 °C. The mixture was stirred at room temperature for 1 h, followed by addition of MeOH (1 ml). The reaction was worked up in a fashion identical with that above. Compound **3** (56 mg, 40%) was obtained from the first green band. Anal. Calc. for C₃₄H₃₁BrFe₄O₄: C, 50.61; H, 3.87. Found: C, 51.03; H, 3.95%. IR (CH₂Cl₂, ν_{CO}): 1634 cm⁻¹. ¹H NMR (CDCl₃, 25 °C): 7.61 (d, 2H), 7.56 (d, 2H, *J*_{H-H} = 10 Hz, C₆H₄), 4.93 (m, 2H), 4.82 (m, 2H, C₅H₄), 4.52 (s, 10H, Cp), 4.46 (m, 2H), 4.30 (m, 2H, C₅H₄), 2.43 (t, 2H, *J*_{H-H} = 12 Hz), 1.26 (m, 4H), 0.93 (t, 3H, *J*_{H-H} = 12 Hz, Bu) ppm. MS (FAB) *m/z* 806 [M⁺, ⁷⁹Br].

3.4. Preparation of **4**

Under a nitrogen atmosphere, *n*-butyl lithium (1.74 mmol) was slowly added into a solution of 1,4-dibromobenzene (200 mg, 0.85 mmol) in 5 ml of toluene at 0 °C. The mixture was heated at 50 °C for 4 h to result in a pale yellow precipitate of *p*-C₆H₄Li₂. The supernatant was removed by a syringe, and the solid washed with freshly distilled toluene (3 × 5 ml). A solution of **1** (150 mg, 0.251 mmol) in 40 ml of THF was added. The resulting mixture was vigorously stirred at 50 °C for 5 h, followed by addition of MeOH (2 ml). The reaction was worked up in a fashion identical with that above. Compound **4** (38 mg, 24%) was obtained from the fourth green band. Anal. Calc. C₅₄H₄₂Fe₈O₈: C, 51.24; H, 3.34. Found: C, 50.93; H, 3.58%. IR (CH₂Cl₂, ν_{CO}): 1632 cm⁻¹. ¹H NMR (CDCl₃, 25 °C): 7.78 (s, 4H, C₆H₄), 5.01 (br, 4H), 4.86 (br, 4H, C₅H₄), 4.55 (s, 30H, Cp) ppm. MS (FAB) *m/z* 1266 [M⁺].

Table 2
Crystal data and refinement details for **4**

Formula	C ₅₄ H ₄₂ Fe ₈ O ₈
<i>T</i> (K)	150(1)
Crystal system	Rhombohedral
Crystal solvent	4(C ₆ H ₆) + 0.67(CHCl ₃)
Space group	<i>R</i> $\bar{3}$
Unit cell dimensions	
<i>a</i> (Å)	33.696(1)
<i>b</i> (Å)	33.696(1)
<i>c</i> (Å)	15.0885(5)
γ (°)	120
<i>V</i> (Å ³)	14836.6(8)
<i>Z</i>	9
<i>D</i> _{calc} (g cm ⁻³)	1.670
<i>F</i> (000)	7602
Radiation λ (Å)	0.71073
μ (mm ⁻¹)	1.849
θ range (°)	1.21–27.50
<i>R</i> ₁	0.0470
<i>wR</i> ₂	0.1133
Goodness-of-fit on <i>F</i> ²	1.118

3.5. Cyclic voltammetric measurements for **2** and **4**

Electrochemical measurements were taken with a CV 50 W system. Cyclic voltammetry was performed with a Pt button working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl reference electrode. The experiments were carried out with 1 mM of **2** and **4**, respectively, in dry CH₂Cl₂ solvent containing 0.1 M (*n*-C₄H₉)₄NPF₆ as the supporting electrolyte. Potential was scanned at 100 mV s⁻¹ at 27 °C.

3.6. Structure determination for **4**

A crystal of **4** with approximate dimensions of 0.5 × 0.08 × 0.08 mm³ was mounted in a thin-walled glass capillary and aligned on the Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). The data were collected at 150 K. All data were corrected for the effects of absorption. The structures were solved by the direct method and refined by full-matrix least-square on *F*². The program used was the SHELXTL package [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included but not refined. A summary of relevant crystallographic data is provided in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis of **4** has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 217582. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ,

UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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