

Synthesis and structures of dinuclear iron, molybdenum and tungsten complexes derived from (PhCHCHPh)-coupled bis(cyclopentadiene)

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Abstract

Reductive coupling of phenylfulvene with amalgamated calcium metal followed by hydrolysis yields CpPhCHCHPhCp (**1**) in high yield. Refluxing ligand **1** and Fe(CO)₅ in xylene produces (PhCHCHPh)-coupled bis(cyclopentadienyl) tetracarbonyl diiron (PhCHCHPh)[(η⁵-C₅H₄)Fe(CO)₂]₂ (**2**) as a mixture of *meso* (**2-meso**) and *racemic* isomers (**2-rac**). The pure *racemic* isomers of the Mo and W analogues (**3-rac** and **4-rac**) have been synthesized by lithiation of ligand **1** and addition of (MeCN)₃M(CO)₃ (M = Mo, W) followed by oxidation with 2 equiv. of ferrocenium tetrafluoroborate. All the new complexes have been fully characterized. The molecular structures of **1-meso**, **2-meso**, **2-rac**, **3-rac**, and **4-rac** have been determined by X-ray diffraction analysis. © 2005 Elsevier B.V. All rights reserved.

Keywords: Metal–metal bond; Cyclopentadienyl; Metal carbonyl

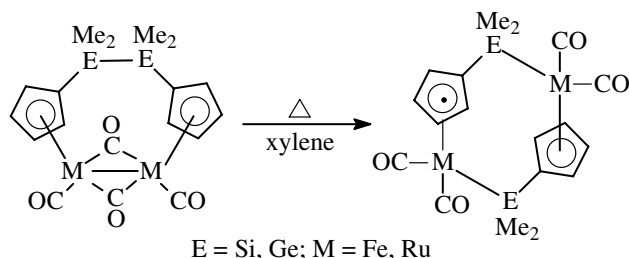
1. Introduction

The chemistry of the group 6 and 8 metal carbonyl dimers with cyclopentadienyl-type ligands have been intensively investigated as a class of organometallic compounds [1–3]. Dinuclear metal complexes are often postulated as simple models with which to study the interactions of molecules with metal surfaces [4,5]. In contrast to the unbridged bis(cyclopentadienyl) metal carbonyl dimers, which exist both as *trans* and *cis* isomers and form single metal sites after the metal–metal bond cleavage, introduction of a bridge between the two cyclopentadienyl ligands makes the complex as

only a *cis* isomer, and maintains two metal centers in close proximity, even after the metal–metal bond cleavage. The nature of a bridge has important effect on the metal–metal bond and its reactivity. The single carbon bridged bis(cyclopentadienyl) dinuclear iron, molybdenum and tungsten carbonyl complexes in general have the shortest metal–metal bonds [6–10], while the carbon and silicon doubly bridged bis(cyclopentadienyl) dinuclear iron, molybdenum and tungsten carbonyl complexes have the longest metal–metal bonds [9,11]. The tetramethyldisilylene or digermylene bridged bis(cyclopentadienyl) tetracarbonyl diiron or diruthenium complexes (Me₂EEMe₂)[(η⁵-C₅H₄)M(CO)]₂(μ-CO)₂ can occur a thermal rearrangement involving the metathesis between the E–E (E = Si, Ge) and M–M (M = Fe, Ru) bonds (Scheme 1) [12,13]. The Me₂C bridged bis(cyclopentadienyl) and Me₂Si bridged

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Scheme 1.

bis(tetramethylcyclopentadienyl) tetracarbonyl diruthenium complexes can undergo photo rearrangement reactions involving the cleavage of Ru–Ru bonds [14].

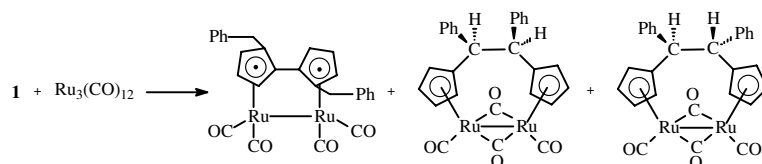
As a part of systematic study the structure–reactivity relationship of the bridged bis(cyclopentadienyl or indenyl) metal carbonyl dimers, especially the effect of the bridge on the metal–metal bond length and its reactivity [9,11–13], we synthesized the (PhCHCHPh)-bridged bis(cyclopentadienyl) metal carbonyl dimers. One of our primary goals is to test whether the thermal or photo rearrangement undergoes in two carbon atoms bridged analogues.

When ligand CpPhCHCHPhCp (**1**) reacted with $\text{Ru}_3(\text{CO})_{12}$, a new C–C cleavage product was produced indeed except for the normal bridged bis(cyclopentadienyl) metal carbonyl dimers (Scheme 2). However, it is difficult to explain the result and the mechanism is still under investigation, so the result will be described separately later. But ligand **1** reacting with $\text{Fe}(\text{CO})_5$ and $\text{M}(\text{CO})_6$ (M = Mo, W) did not give the analogous C–C cleavage products. Here, we describe the synthesis of (PhCHCHPh)[$(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2$]₂ (**2**) (*meso* and *rac* isomers) (Scheme 3) and (PhCHCHPh)[$(\eta^5\text{-C}_5\text{H}_4)\text{-M}(\text{CO})_3$]₂ [M = Mo (**3-rac**), W (**4-rac**)] (Scheme 4). The molecular structures of **1-meso**, **2-meso**, **2-rac**, **3-rac**, and **4-rac** determined by X-ray diffraction analysis are also presented.

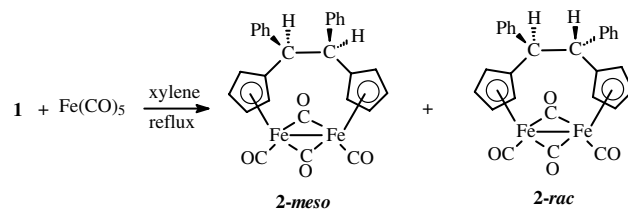
2. Results and discussion

2.1. Synthesis and characterization of ligand **1**

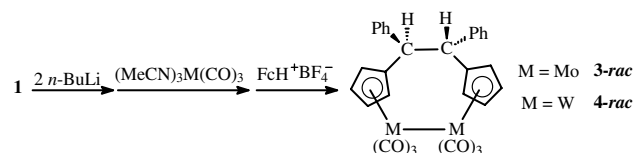
Ligand CpPhCHCHPhCp (**1**) was synthesized followed the method of Shapiro's group (reductive coupling of phenylfulvene) [15] and Erker's group [16] as a



Scheme 2.



Scheme 3.



Scheme 4.

mixture of *racemic* and *meso* isomers (70:30). Fortunately, the pure *meso* isomer **1-meso** suitable for X-ray crystallography was obtained while the crude **1** was recrystallized with pentane/ CH_2Cl_2 at -30°C . Its ^1H NMR spectrum shows Cp proton resonances at 6.30, 6.19, 6.05, and 5.82 ppm (ratio 1:1:1:1) and benzylic protons at 4.43 and 4.40 ppm, indicating the existence of a pure isomer.

2.2. Crystal and molecular structures of **1-meso**

The structure of **1-meso** is similar to 2,3-dicyclopentadiene-2,3-dimethylbutane $\text{C}_5\text{H}_5\text{CMe}_2\text{CMe}_2\text{C}_5\text{H}_5$ (**6**) [17]. Two views of the molecular structure of **1-meso** are presented in Fig. 1. It followed the rules for substituted ethane and formed a staggered conformation with the largest substituents in *trans*-position to minimize the intramolecular steric interaction (see Fig. 1(b)). The deviation from the tetrahedral angle around C(1) ranges from 4.5° to 6° , which is larger than that of **6** [17]. The C(1)–C(1A) bond distance of 1.456(8) Å is much shorter than that of **6** [1.600(3) Å] [17] and those in related highly substituted and strained ethane, e.g., 2,3-dimethyl-2,3-di-*p*-tolylbutane [1.590 Å] [18], 2,3-dimethyl-2,3-diphenylbutane [1.598 Å] [19] and 2,3-di-1-adamantyl-2,3-dimethylbutane [1.634 Å] [20]. The shortness of the central C(1)–C(1A) bond is due to the less steric repulsion around C(1) and C(1A), compared to **6** and other substituted ethane mentioned above.

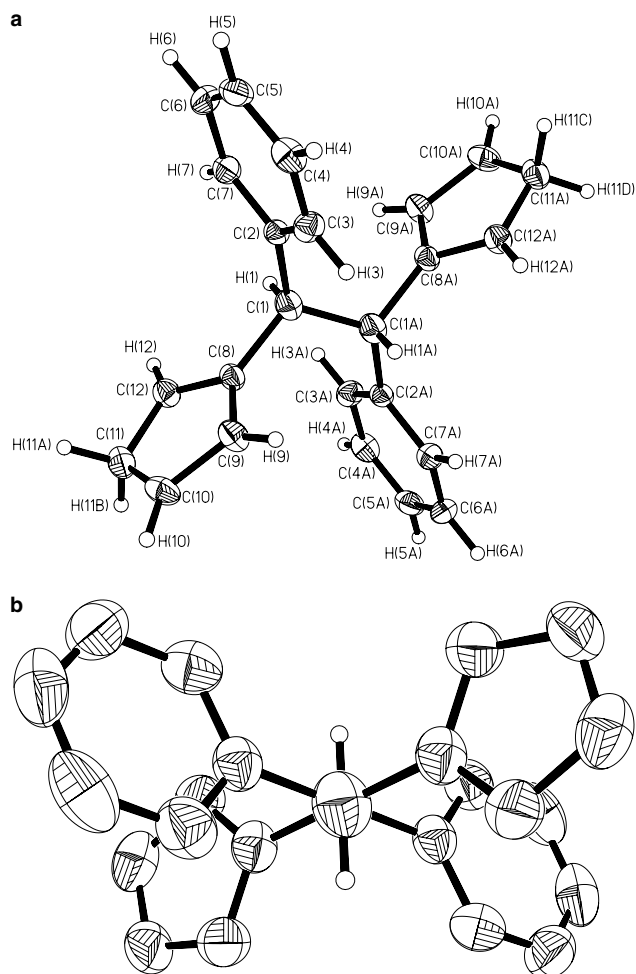


Fig. 1. Molecular structure of **1-meso**. Thermal ellipsoids are shown at the 30% level. (a) Side view. (b) View down the C(1)–C(1A) axis. Selected bond lengths (Å) and angles (°): C(1)–C(1A) = 1.456(8), C(1)–C(8) = 1.510(5), C(1)–C(2) = 1.535(6), C(8)–C(12) = 1.353(5), C(8)–C(9) = 1.392(5), C(9)–C(10) = 1.411(6), C(10)–C(11) = 1.379(6), C(11)–C(12) = 1.435(6); and C(1A)–C(1)–C(8) = 113.7(5), C(1A)–C(1)–C(2) = 115.5(5), C(8)–C(1)–C(2) = 112.2(3), C(12)–C(8)–C(9) = 108.4(3), C(12)–C(8)–C(1) = 124.0(4), C(9)–C(8)–C(1) = 127.4(4), C(8)–C(9)–C(10) = 108.0(4), C(11)–C(10)–C(9) = 108.2(4), C(10)–C(11)–C(12) = 106.5(4), C(8)–C(12)–C(11) = 109.0(4).

2.3. Synthesis and molecular structures of **2-meso** and **2-rac**

Ligand **1** (as a mixture of *racemic* and *meso* isomers) reacted with $\text{Fe}(\text{CO})_5$ in refluxing xylene for 24 h to give $(\text{PhHCCHPh})[(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\mu\text{-CO})_2)$ (**2-meso** and **2-rac**) in low yield as dark red crystals (Scheme 3). No C–C cleavage product was observed, even when **2-meso** and **2-rac** were heated in refluxing xylene for 24 h. The two isomers can be easily separated by column chromatography. The observed differences of the ^1H NMR spectrum of **2-meso** and **2-rac** may simply due to anisotropic differences. The IR spectra of **2-meso** and **2-rac** shows a pattern of major bands at 1989(s), 1752(s)

cm^{-1} , and 1997(s), 1736(s) cm^{-1} , respectively, indicating the existence of both terminal and bridging carbonyl groups. This is similar to many analogues such as $\text{Me}_2\text{C}[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2(\mu\text{-CO})_2]$ [6] and $(\text{Me}_2\text{SiSiMe}_2)[\text{C}_5\text{H}_4\text{Fe}(\text{CO})_2(\mu\text{-CO})_2]$ [12a].

The molecular structures of **2-meso** and **2-rac** are presented in Figs. 2 and 3, respectively. There are two independent molecules with the ratio of 1/1 (A/B) in the unit cell of **2-meso**. One fourth of water molecule was also found to incorporate in it. The two independent molecules of **2-meso** has slight different in Fe–Fe distance [2.5134(13), 2.5106(12) Å] and the dihedral angle between two cyclopentadienyl ring planes (90.1° , 89.4°), while the torsion angle CEN–M1–M2–CEN (CEN is the centroid of the five-membered ring) differs greatly (2.4° , 0.3°). From the orientation of the two hydrogen atoms at the bridge we can easily differentiate the two isomers. The two phenyl groups arranging greatly differently are also due to their configurations. For **2-meso** the torsion angle C(21)–C(14)–C(15)–C(27) of $55.5(6)^\circ$ in A and C(45)–C(38)–C(39)–C(51) of $57.7(6)^\circ$ in B are much larger than that of **2-rac** [torsion angle C(17)–C(15)–C(16)–C(23) of $44.8(5)^\circ$]. The Fe–Fe distance in **2-meso** (average 2.5120 Å) is a little longer than that in **2-rac** [2.5016(11) Å]. In both **2-meso** and **2-rac**, the bridged carbon atoms are bent out of the linked cyclopentadienyl planes by the range 0.1217–0.1852 Å, so there is enough space for the PhCHCHPh-bridge.

From the structural parameters of a series of bridged bis(cyclopentadienyl) diiron complexes listed in Table 2, it can found the following relation between the Fe–Fe distance and the bridging group: $\text{R}_2\text{C} < \text{PhCHCHPh} \approx \text{Me}_2\text{Si} < \text{Me}_2\text{SiSiMe}_2 < \text{unbridged} < \text{doubly bridged}$. Complex **2** has a shorter Fe–Fe distance than $(\text{Me}_2\text{SiSiMe}_2)$ -bridged analogue (in spite of complex **2** has a larger $\angle\text{Cp}–\text{Cp}$ fold angle) may due to the shorter C–C distance than Si–Si distance and the less steric repulsion between the four groups around the two bridging atoms. More interestingly, the $\angle\text{Cp}–\text{Cp}$ fold angle has a reversed order: $\text{R}_2\text{C} > \text{PhCHCHPh} \approx \text{Me}_2\text{Si} > \text{Me}_2\text{SiSiMe}_2$.

2.4. Synthesis and molecular structures of **3-rac** and **4-rac**

Refluxing ligand **1** with $\text{M}(\text{CO})_6$ or $(\text{MeCN})_3\text{M}(\text{CO})_3$ (M = Mo, W) in DME, toluene or xylene only produced very small amount of **3-rac** (Mo) and **4-rac** (W). Moderate yields were got by lithiation of ligand **1** in THF and addition of $(\text{MeCN})_3\text{M}(\text{CO})_3$ (M = Mo, W) with heating followed by oxidation with 2 equiv. of ferrocenium tetrafluoroborate [24] (Scheme 4). To our surprise, only **3-rac** and **4-rac** were separated by this method. The ^1H NMR spectra of **3-rac** and **4-rac** are similar to that of **2-rac**. The IR spectra of **3-rac** and **4-rac** show only terminal carbonyl groups that are close to uncoupled and coupled analogues. In order to confirm the structure,

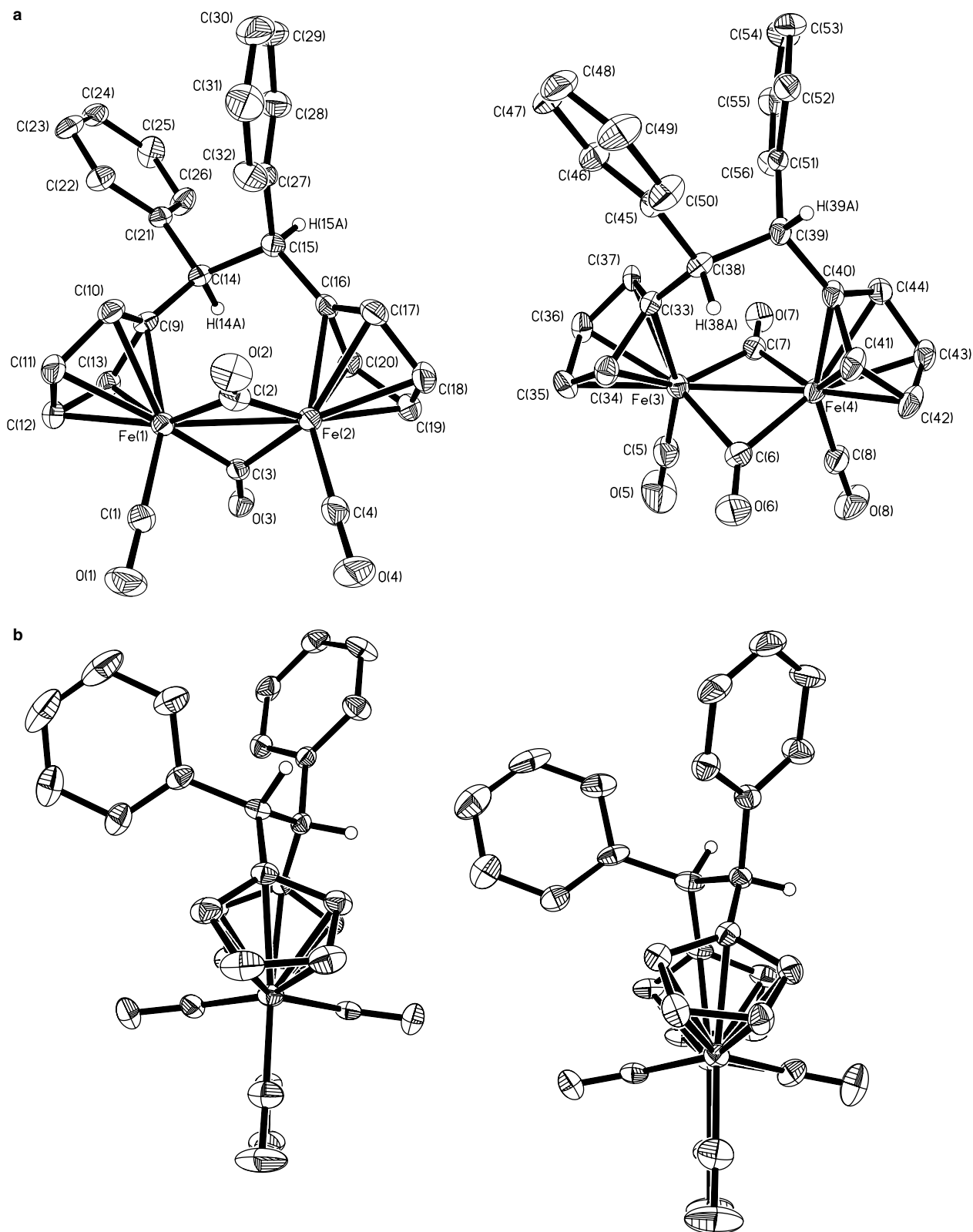


Fig. 2. Molecular structure of **2-meso** (two independent molecules in a cell). Thermal ellipsoids are shown at the 30% level. (a) side view. (b) view down the Fe–Fe axis. Selected bond lengths (Å) and angles (°): (a) Fe(1)–Fe(2) = 2.5134(13), Fe(1)–C(9) = 2.130(5), Fe(2)–C(16) = 2.162(5), C(9)–C(14) = 1.509(7), C(14)–C(15) = 1.567(7), C(15)–C(16) = 1.517(7), Fe(1)–C(9)–C(14) = 130.8(3), Fe(2)–C(16)–C(15) = 133.0(4), C(9)–C(14)–C(15) = 119.6(4), C(14)–C(15)–C(16) = 113.4(4); and (b) Fe(3)–Fe(4) = 2.5106(12), Fe(3)–C(33) = 2.148(5), Fe(4)–C(40) = 2.162(5), C(33)–C(38) = 1.513(7), C(38)–C(39) = 1.567(7), C(39)–C(40) = 1.523(7), Fe(3)–C(33)–C(38) = 130.8(3), Fe(4)–C(40)–C(39) = 133.7(3), C(33)–C(38)–C(39) = 117.6(4), C(38)–C(39)–C(40) = 112.0(4).

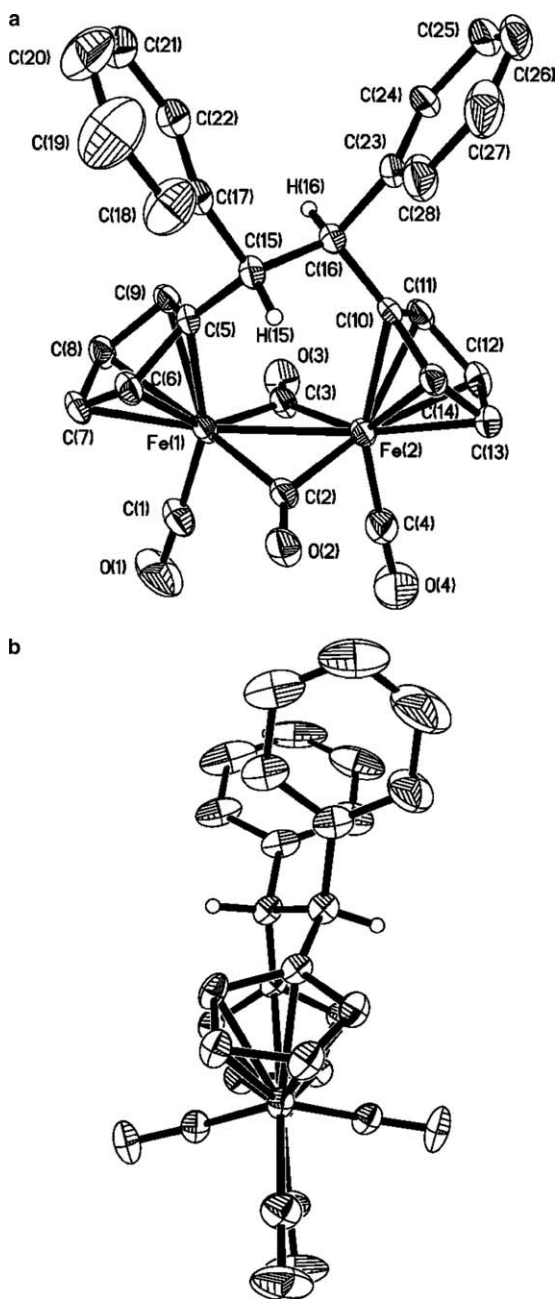


Fig. 3. Molecular structure of **2-rac**. Thermal ellipsoids are shown at the 30% level. (a) Side view. (b) View down the Fe–Fe axis. Selected bond lengths (Å) and angles (°): Fe(1)–Fe(2) = 2.5016(11), Fe(1)–C(5) = 2.141(4), Fe(2)–C(10) = 2.154(4), C(5)–C(15) = 1.502(6), C(15)–C(16) = 1.527(6), C(10)–C(16) = 1.504(6); and Fe(1)–C(5)–C(15) = 131.3(3), Fe(2)–C(10)–C(16) = 133.2(3), C(5)–C(15)–C(16) = 112.0(4), C(15)–C(16)–C(10) = 113.4(3).

X-ray structure determinations of **3-rac** and **4-rac** were undertaken.

The molecular structures of **3-rac** and **4-rac** are shown in Figs. 4 and 5, respectively. The two hydrogen atoms at the bridge clearly represent the configuration of the two complexes. The molecular structures of com-

Table 2
Structural parameter comparison for bis(cyclopentadienyl) diiron complexes

Complexes	M–M (Å)	PL–PL (°) ^a	Reference ^b
<i>cis</i> -[CpFe(CO)] ₂ (μ-CO) ₂	2.531(2)	92.8	[21]
<i>trans</i> -[CpFe(CO)] ₂ (μ-CO) ₂	2.534(2)		[22]
Me ₂ C[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂	2.4836(6)	109.6	[6]
		109.3	
(CH ₂) ₅ C[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂	2.466(1)	108.4	[7]
Me ₂ Si[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂	2.512(3)	97.2	[23]
(Me ₂ C)(Me ₂ Si)[C ₅ H ₃ Fe(CO) ₂] ₂	2.7747(6)	126.9	[11]
(<i>cis</i> -PhCHPhCH)-[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂ (2-meso)	2.5134(13)	90.1	tw
	2.5106(12)	89.4	
(<i>trans</i> -PhCHPhCH)-[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂ (2-rac)	2.5016(11)	93.1	tw
(Me ₂ SiSiMe ₂)[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂	2.526(2)	85.3	[12a]

^a PL, plane of the cyclopentadienyl ring.

^b tw, this work.

plexes **3-rac** and **4-rac** are very similar. The two complexes both possess crystallographically imposed C₂ symmetry. The torsion angles C(10)–C(9)–C(9A)–C(10A) of 43.4° for **3-rac** and 44.6° for **4-rac** are very close to that of **2-rac**. From the structural parameters listed in Table 3 it also can be found the effects of the bridges on the metal–metal bond lengths. For the unbridged and singly bridged bis(cyclopentadienyl) dinuclear molybdenum and tungsten complexes, the M–M bond length follows the order – R₂C < PhCHCHPh ≈ Me₂Si < Me₂SiSiMe₂ < unbridged – similar to the diiron analogues. The doubly bridged complexes (Me₂C)(Me₂Si)[C₅H₃M(CO)₃]₂ showed the longest M–M bond lengths due to the inflexibility of the doubly bridged ligand [9]. Significantly, complexes **3-rac** and **4-rac** show the smallest dihedral angle between two Cp ring planes (108.1° and 109.3°, respectively), compared with the uncoupled and coupled analogues. But the torsion angle CEN–M1–M2–CEN of **3-rac** (54.9°) and **4-rac** (56.5°) are the largest, which can also be attributed to the intramolecular non-bonded interaction of the (PhCHCHPh)-bridge.

3. Experimental details

Schlenk and vacuum line techniques were employed for all manipulations. Solvents were purified and degassed by standard procedures prior to use. Phenylfulvene [28], (MeCN)₃M(CO)₃ (M = Mo, W) [29], and ferrocenium tetrafluoroborate [30] were prepared by the literature procedures. ¹H NMR spectra were recorded on a BRUKER AC-P200 or a Bruker AV300 spectrometer at room temperature. Chemical shifts for

^1H NMR spectra were recorded in ppm relative to the residual proton of CDCl_3 (δ 7.24). Infrared spectra were obtained as KBr disks and recorded on a Nicolet 5DX FT-IR spectrometer. Elemental analyses were performed using a Perkin–Elmer 240C Elemental analyzer. ESI Mass spectra were obtained using a Thermo Finnigan LCQ Advantage.

3.1. Synthesis of $\text{C}_5\text{H}_4\text{CHC}_6\text{H}_5\text{CHC}_6\text{H}_5\text{C}_5\text{H}_4$ (**1**)

Ligand CpPhCHCHPhCp (**1**) was synthesized followed the method of Shapiro's group [15] and Erker's group [16] as white solids in 60% yield. Mp: 105–106 °C. Anal. Calc. for $\text{C}_{24}\text{H}_{22}$: C, 92.86; H, 7.14. Found: C, 92.63; H, 7.20. MS (ESI): m/z 311 (M + H).

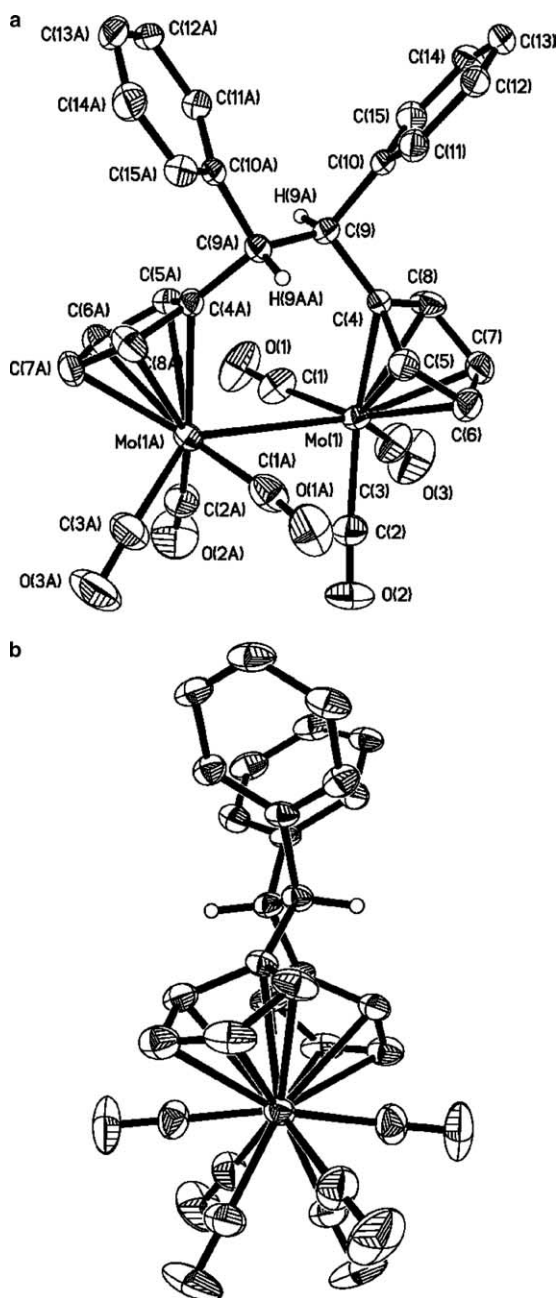


Fig. 4. Molecular structure of **3-rac**. Thermal ellipsoids are shown at the 30% level. (a) Side view. (b) View down the Mo–Mo axis. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(1A) = 3.1598(10), Mo(1)–C(4) = 2.376(4), Mo(1)–C(5) = 2.415(5), Mo(1)–C(6) = 2.387(6), Mo(1)–C(7) = 2.317(5), Mo(1)–C(8) = 2.335(5), C(4)–C(9) = 1.532(6), C(9)–C(9A) = 1.521(9); and Mo(1)–C(4)–C(9) = 133.3(3), C(4)–C(9)–C(9A) = 114.6(4).

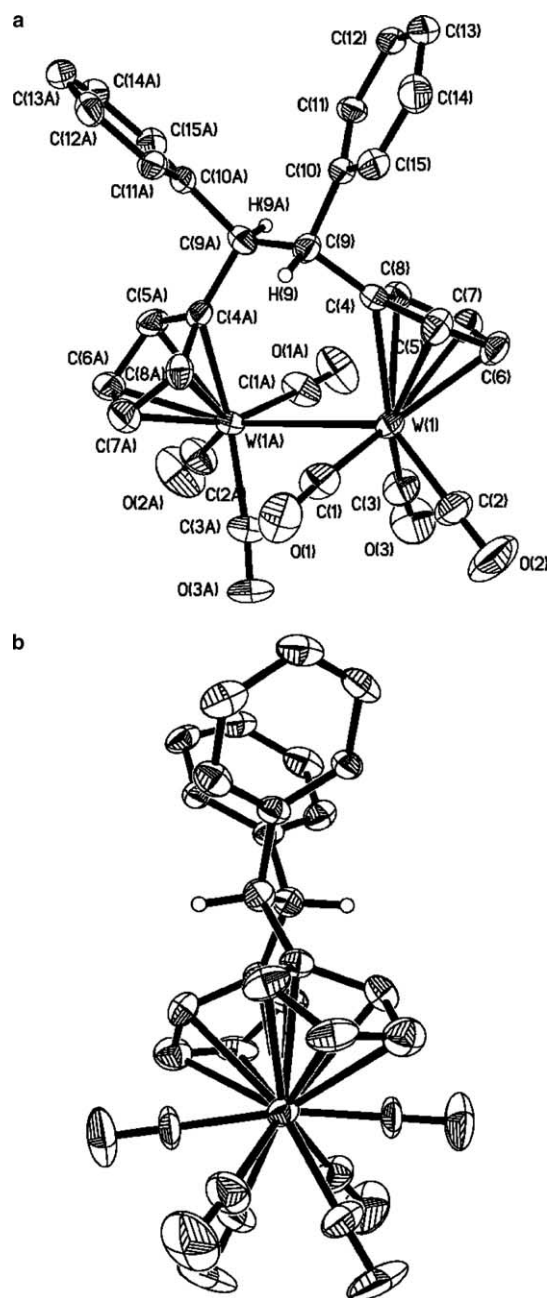


Fig. 5. Molecular structure of **4-rac**. Thermal ellipsoids are shown at the 30% level. (a) Side view. (b) View down the W–W axis. Selected bond lengths (Å) and angles (°): W(1)–W(1A) = 3.1488(10), W(1)–C(4) = 2.343(9), W(1)–C(5) = 2.325(10), W(1)–C(6) = 2.316(11), W(1)–C(7) = 2.394(12), W(1)–C(8) = 2.427(10), C(4)–C(9) = 1.554(14), C(9)–C(9A) = 1.50(2); and W(1)–C(4)–C(9) = 134.8(6), C(4)–C(9)–C(9A) = 113.8(7).

Table 3
Structural parameter comparison for bis(cyclopentadienyl) dimolybdenum or ditungsten complexes

Complexes	M–M (Å)	PL–PL (°)	CEN–M–M–CEN torsion angles ^a	Reference ^b
<i>trans</i> -[CpMo(CO) ₃] ₂	3.235(1)			[25]
CH ₂ [C ₅ H ₄ Mo(CO) ₃] ₂	3.1406			[8]
(CH ₂) ₅ C[C ₅ H ₄ Mo(CO) ₃] ₂	3.1708(18)	120.5	46.4	[9]
Me ₂ Si[C ₅ H ₄ Mo(CO) ₃] ₂	3.2018(13)	140.7	51.6	[26]
(Me ₂ C)(Me ₂ Si)[C ₅ H ₃ Mo(CO) ₃] ₂	3.4328(12)	149.3	0	[9]
(<i>trans</i> -PhCHPhCH)[C ₅ H ₄ Mo(CO) ₃] ₂ (3-rac)	3.1598(10)	108.1	54.9	tw
(<i>trans</i> -PhCHPhCH)[C ₅ H ₄ W(CO) ₃] ₂ (4-rac)	3.1488(10)	109.3	56.5	tw
<i>trans</i> -[CpW(CO) ₃] ₂	3.222(1)			[25]
CH ₂ [C ₅ H ₄ W(CO) ₃] ₂	3.166(1)		47.8(6)	[10]
(CH ₂) ₅ C[C ₅ H ₄ W(CO) ₃] ₂	3.1582(16)	120.4	45.3	[9]
Me ₂ Si[C ₅ H ₄ W(CO) ₃] ₂	3.196(1)		~47.8	[27]
(Me ₂ C)(Me ₂ Si)[C ₅ H ₃ W(CO) ₃] ₂	3.403(2)	149.2	0	[9]
<i>trans</i> -(CH ₂ CH ₂)[C ₅ H ₆ W(CO) ₃] ₂	3.1581(8)		50.5	[24]

^a CEN, centroid of the cyclopentadienyl ring.

^b tw, this work.

¹H NMR (CDCl₃, 300 MHz): **1** (mixture): 7.28–6.95 (m, total 20H, C₆H₅), 6.47–6.43, 6.36–6.28, 6.21–6.16, 6.11, 6.08–6.01, 5.82 (m, m, m, s, m, s, total 12H, –CH=), 4.44, 4.42, 4.41, 4.37 (s, s, s, s, total 4H, PhCHCp), 2.89, 2.84, 2.73–2.65 (s, t, m, total 8H, –CH₂–). **1-meso**: δ 7.28–7.09 (m, 10H, C₆H₅), 6.32–6.28, 6.21–6.16, 6.08–6.01, 5.82 (m, m, m, s, total 6H, –CH=), 4.44 (s, 1H, PhCH Cp), 4.42 (s, 1H, PhCH Cp), 2.73–2.65 (m, 4H, –CH₂–).

3.2. Preparation of meso- and rac-(CHC₆H₅CHC₆H₅)-(η⁵-C₅H₄)Fe(CO)₂(μ-CO)₂ (**2-meso** and **2-rac**)

To a solution of ligand **1** (0.93 g, 3.0 mmol) in 50 mL of xylene was added Fe(CO)₅ (1.0 mL, 7.6 mmol), and the resulting mixture was refluxed for 24 h. After removal of solvent under reduced pressure, the residue, which was dissolved in a minimum of CH₂Cl₂ and chromatographed on an alumina column using petroleum ether/CH₂Cl₂ as an eluent. The first brown band affords oil, which could not be characterized. The second brown-red band afforded 68 mg (4.2%) of **2-meso** as red crystals and the third brown band afforded 36 mg (2.2%) of **2-rac** as brown-red crystals. For **2-meso**, m.p.: 201 °C (dec.). Anal. Calc. for C₂₈H₂₀Fe₂O₄: C, 63.20; H, 3.79. Found: C, 62.97; H, 3.66. ¹H NMR (CDCl₃, 200 MHz): 7.23–7.07 (m, 6H, C₆H₅), 6.90–6.82 (m, 4H, C₆H₅), 5.29 (s, 2H, C₅H₄), 5.24 (s, 2H, C₅H₄), 5.21 (s, 2H, C₅H₄), 5.09 (s, 2H, C₅H₄), 3.95 (s, 2H, PhCHCp). IR (ν_{CO}, cm⁻¹): 2002 (s), 1989 (s), 1799 (m), 1752 (s). For **2-rac**, mp: 223 °C (dec.). Anal. Calc. for C₂₈H₂₀Fe₂O₄: C, 63.20; H, 3.79. Found: C, 63.06; H, 4.09. ¹H NMR (CDCl₃, 200 MHz): 6.98–6.82 (m, 10H, C₆H₅), 5.21 (s, 4H, C₅H₄), 5.15 (s, 2H, C₅H₄), 4.97 (s, 2H, C₅H₄), 3.59 (s, 2H, PhCHCp). IR (ν_{CO}, cm⁻¹): 1997 (s), 1958 (s), 1755 (s), 1736 (s).

3.3. Preparation of rac-(CHC₆H₅CHC₆H₅)-(η⁵-C₅H₄)-M(CO)₃ (M = Mo (**3-rac**), W (**4-rac**))

To a solution of ligand **1** (0.58 g, 1.87 mmol) in THF (30 mL) under argon was added dropwise *n*-butyl lithium hexane solution (1.98 mL, 1.89 M, 3.74 mmol), and the resulting mixture was stirred for 4 h. The lithium salt solution was added to a THF solution of (MeCN)₃Mo(CO)₃, prepared from Mo(CO)₆ (1.00 g, 3.75 mmol) in refluxing acetonitrile (10 mL) over about 6 h. The resulting mixture was heated under reflux for 18 h. The intense red solution was then cooled to –78 °C and [FeCp₂][BF₄] (1.02 g, 3.74 mmol) was quickly added. The solution was stirred for 1 h at low temperature, and then it was evaporated in vacuo. The residue was dissolved in minimum of CH₂Cl₂ and chromatographed on an alumina column. Elution with petroleum ether/CH₂Cl₂ (1:1) gave a red band, which afforded 0.51 g (41%) of **3-rac** as brown-red crystals. Mp: 165 °C (dec.). Anal. Calc. for C₃₀H₂₀Mo₂O₆: C, 53.91; H, 3.02. Found: C, 53.90; H, 3.06. ¹H NMR (CDCl₃, 300 MHz): 7.10–6.96 (m, 10H, C₆H₅), 5.35 (s, 2H, C₅H₄), 5.19 (s, 4H, C₅H₄), 4.98 (s, 2H, C₅H₄), 4.21 (s, 2H, PhCHCp). IR (ν_{CO}, cm⁻¹): 2010 (s), 1954 (s), 1942 (s), 1914 (s), 1851 (s), 1839 (s).

Complex **4-rac** was prepared similarly as described above for **3** from 1.0 g (2.85 mmol) of W(CO)₆ and 0.44 g (1.42 mmol) of ligand **1** in 18% yield as red crystals. Mp: 205 °C (dec.). Anal. Calc. for C₃₀H₂₀W₂O₆: C, 42.68; H, 2.39. Found: C, 42.67; H, 2.48. ¹H NMR (CDCl₃, 300 MHz): 7.12–6.92 (m, 10H, C₆H₅), 5.45 (s, 2H, C₅H₄), 5.27 (t, 2H, C₅H₄), 5.15 (t, 2H, C₅H₄), 5.18 (s, 2H, C₅H₄), 4.21 (s, 2H, PhCHCp). IR (ν_{CO}, cm⁻¹): 2007 (s), 1953 (s), 1937 (s), 1902 (m), 1848 (m), 1832 (m).

Table 1
Summary of crystallographic data for complexes **1-meso**, **2-meso**, **2-rac**, **3-rac** and **4-rac**

	1-meso	2-meso · 1/4H ₂ O	2-rac	3-rac	4-rac
Formula	C ₂₄ H ₂₂	C ₂₈ H _{20.25} Fe ₂ O _{4.13}	C ₂₈ H ₂₀ Fe ₂ O ₄	C ₃₀ H ₂₀ Mo ₂ O ₆	C ₃₀ H ₂₀ O ₆ W ₂
Fw	310.42	534.39	532.14	668.34	844.16
Crystal system	Monoclinic	Monoclinic	Monoclinic	Tetragonal	Tetragonal
Space group	C2/c	P2(1)/c	C2/c	I-42d	I-42d
<i>Unit cell dimensions</i>					
<i>a</i> (Å)	15.889(6)	21.350(7)	28.210(9)	19.636(3)	19.583(3)
<i>b</i> (Å)	7.991(3)	14.529(5)	12.670(5)	19.636(3)	19.583(3)
<i>c</i> (Å)	14.745(6)	15.659(5)	16.159(7)	13.670(5)	13.653(5)
α (°)	90	90	90	90	90
β (°)	105.978(7)	105.154(7)	117.603(13)	90	90
γ (°)	90	90	90	90	90
<i>V</i> (Å ³)	1799.9(12)	4688(3)	5118(3)	5271(2)	5236(2)
<i>Z</i>	4	8	8	8	8
<i>D</i> _{calcd} (g cm ⁻³)	1.146	1.514	1.381	1.684	2.142
μ (mm ⁻¹)	0.064	1.271	1.164	0.995	8.824
<i>F</i> (00 0)	664	2186	2176	2656	3168
Cryst size (mm)	0.22 × 0.20 × 0.10	0.18 × 0.12 × 0.06	0.24 × 0.20 × 0.18	0.24 × 0.18 × 0.16	0.18 × 0.16 × 0.12
Max. 2θ (°)	52.90	52.86	52.98	52.78	52.78
No. of reflns. collected	4098	26439	14289	11095	14481
No. of indep. reflns./ <i>R</i> _{int}	1784/0.0363	9606/0.0838	5261/0.0543	2701/0.0644	2687/0.0594
No. of params.	109	622	307	172	172
Goodness-of-fit on <i>F</i> ²	1.016	1.056	1.089	1.017	1.022
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0794, 0.1996	0.0637, 0.1072	0.0486, 0.1274	0.0391, 0.0599	0.0347, 0.0702
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1931, 0.2621	0.1368, 0.1365	0.0945, 0.1422	0.0769, 0.0675	0.0602, 0.0786
Largest diff. peak and hole (e Å ⁻³)	0.341 and -0.172	0.905 and -0.463	0.740 and -0.252	0.460 and -0.352	1.375 and -0.515

3.4. Crystallographic studies

Crystals of **1-meso**, **2-meso**, **2-rac**, **3-rac**, and **4-rac** suitable for X-ray diffraction were obtained from CH₂Cl₂-pentane or CH₂Cl₂-hexane solution. Data collection was performed on a BRUKER SMART 1000, using graphite-monochromated Mo K α radiation ($\omega - 2\theta$ scans, $\lambda = 0.71073$ Å). Semi-empirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-square. All calculations were using the SHELXL-97 program system. The crystal data and summary of X-ray data collection are presented in Table 1.

4. Supplementary materials

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 260978–260982 for compounds **1-meso**, **2-meso**, **2-rac**, **3-rac** and **4-rac**, respectively. Copies of this information may be obtained free of charge The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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