

Ferrocene bridged and substituted tetramethylcyclopentadienyl (or indenyl) carbonyl complexes of iron, ruthenium, and molybdenum

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Abstract

Reactions of ferrocene bridged and substituted tetramethylcyclopentadiene ligands 1,1'-Fc(C₅Me₄H)₂ (**1**) (Fc = 1,1'-ferrocenediyl) and (C₅H₅FeC₅H₄)C₅Me₄H (**5**) with Ru₃(CO)₁₂, Fe(CO)₅, and Mo(CO)₃(CH₃CN)₃ in refluxing xylene gave the corresponding trinuclear and tetranuclear complexes Fc[(C₅Me₄)M(CO)]₂(μ-CO)₂ [M = Ru (**2**), Fe (**3**)], Fc[(C₅Me₄)Mo(CO)]₃ (**4**) and [(C₅H₅ FeC₅H₄)C₅Me₄M(CO)]₂(μ-CO)₂ [M = Ru (**6**), Fe (**7**)], [(C₅H₅FeC₅H₄)C₅Me₄Mo(CO)]₃ (**8**). Reactions of (3-indenyl)ferrocene (**9**) with Ru₃(CO)₁₂ or Fe(CO)₅ in refluxing xylene or heptane, also gave the corresponding tetranuclear metal complexes [(C₅H₅FeC₅H₄)C₉H₆M(CO)]₂(μ-CO)₂ [M = Ru (**10**), Fe (**11**)]. The molecular structures of **2** and **3** were determined by X-ray diffraction analysis.

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Keywords: Metal–metal bond; Metal carbonyl; Ferrocene; Tetramethylcyclopentadienyl

1. Introduction

The chemistry of the group 6 and 8 metal carbonyl dimers with cyclopentadienyl-type ligands has 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]. For the bridged bis(cyclopentadienyl) metal carbonyl dimers, the nature of a bridge has important effect on the metal–metal bond and its reactivity [6–16]. 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]. As a part of systematic study the structure-reactivity relationship of the bridged bis(cyclopentadienyl) metal carbonyl dimers, especially the effect of the bridge on the metal–metal

bond length and its reactivity [9,11–13], in this work a series of ferrocene bridged bis(tetramethylcyclopentadienyl) trinuclear metal carbonyl complexes were synthesized and characterized by X-ray diffraction analysis. The ferrocene substituted tetramethylcyclopentadienyl and indenyl tetranuclear metal carbonyl complexes were also synthesized.

2. Experimental details

2.1. General procedures and starting materials

Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon prior to use. ¹H NMR spectra were recorded on a Bruker AV 300 instrument, while IR spectra were recorded as KBr disks on a Nicolet 560 ESP FTIR spectrometer. Elemental analyses were performed on a Perkin–Elmer 240 C analyzer. 1,1'-Bis(2,3,4,5-tetramethylcyclopentadienyl)ferrocene (**1**) [17], 2-ferrocenyl-1,3,4,5-tetramethylcyclopentadiene (**5**) [18], (3-indenyl)ferrocene (**9**) [19], and Mo(CO)₃(CH₃CN)₃ [20] were prepared according to the literature methods.

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2.2. Complexes synthesis

2.2.1. Synthesis of complexes 2

A solution of ligand **1** (0.30 g, 0.70 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (0.30 g, 0.47 mmol) in 30 mL of xylene was refluxed for 10 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/ CH_2Cl_2 as eluent. The orange band afforded 0.09 g (17%) of **2** as red crystals. m.p. 231 °C (dec.). Anal. Calc. for $\text{C}_{32}\text{H}_{32}\text{O}_4\text{FeRu}_2$: C, 52.04; H, 4.37. Found: C, 52.17, H, 4.30%. ^1H NMR (ppm in CDCl_3): 4.19(m, 4H, C_5H_4), 3.94(m, 4H, C_5H_4), 2.12(s, 12H, C_5Me_4), 2.11(s, 12H, C_5Me_4). IR (ν_{CO} , cm^{-1}): 1979(s), 1926(s), 1742(s).

2.2.2. Synthesis of 3 and 4

Using similar procedures as described above, reactions of ligand **1** with $\text{Fe}(\text{CO})_5$ and $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ gave **3** and **4** as deep red crystals in 16% and 10% yields, respectively. **3**: m.p. >300 °C (dec.). Anal. Calc. for $\text{C}_{32}\text{H}_{32}\text{O}_4\text{Fe}_3$: C, 59.30; H, 4.98. Found: C, 59.29, H, 4.77%. ^1H NMR (ppm in CDCl_3): 4.13(br s, 4H, C_5H_4), 4.07(br s, 4H, C_5H_4), 2.16(s, 12H, C_5Me_4), 1.94(s, 12H, C_5Me_4). IR (ν_{CO} , cm^{-1}): 1969(s), 1917(s), 1741(s). **4**: m.p. 138 °C (dec.). Anal. Calc. for $\text{C}_{34}\text{H}_{32}\text{O}_6\text{FeMo}_2$: C, 52.07; H, 4.11. Found: C, 52.47, H, 4.43%. ^1H NMR (ppm in CDCl_3): 4.17(br s, 4H, C_5H_4), 3.99(br s, 4H, C_5H_4), 2.43(s, 12H, C_5Me_4), 2.31(s, 12H, C_5Me_4). IR (ν_{CO} , cm^{-1}): 1983(s), 1912(m), 1898(s), 1874(m), 1865(m), 1851(s).

2.2.3. Synthesis of 6–8

Using similar procedures as described above, reactions of ligand **5** with $\text{Ru}_3(\text{CO})_{12}$, $\text{Fe}(\text{CO})_5$, and $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ gave **6–8** as orange red or deep red crystals in 26%, 28%, and 38% yields, respectively. **6**: m.p. 206 °C (dec.). Anal. Calc. for $\text{C}_{42}\text{H}_{42}\text{O}_4\text{Fe}_2\text{Ru}_2$: C, 54.56; H, 4.58. Found: C, 54.38, H, 4.58%. ^1H NMR (ppm in CDCl_3): 4.49(br s, 4H, C_5H_4), 4.27(br s, 4H, C_5H_4), 4.16(s, 10H, C_5H_5), 2.15(s, 12H, C_5Me_4), 1.76(s, 12H, C_5Me_4). IR (ν_{CO} , cm^{-1}): 1926(s), 1758(s). **7**: m.p. 216 °C (dec.). Anal. Calc. for $\text{C}_{42}\text{H}_{42}\text{O}_4\text{Fe}_4$: C, 60.47; H, 5.07. Found: C, 60.33, H, 5.48%. ^1H NMR (ppm in CDCl_3): 4.50(br s, 4H, C_5H_4), 4.25(m, 4H, C_5H_4), 4.12(s, 10H, C_5H_5), 2.02(s, 12H, C_5Me_4), 1.73(d, 12H, C_5Me_4). IR (ν_{CO} , cm^{-1}): 1921(s), 1758(s). **8**: m.p. 138 °C (dec.). Anal. Calc. for $\text{C}_{44}\text{H}_{42}\text{O}_6\text{Fe}_2\text{Mo}_2$: C, 54.46; H, 4.36. Found: C, 54.26, H, 4.53%. ^1H NMR (ppm in CDCl_3): 4.41(m, 2H, C_5H_4), 4.32(m, 2H, C_5H_4), 4.26(m, 2H, C_5H_4), 4.23(m, 2H, C_5H_4), 4.18(s, 5H, C_5H_5), 4.11(s, 5H, C_5H_5), 2.37(s), 2.28(s), 2.24(s), 2.17(s), 2.14(s), 2.04(s), 1.99(s), 1.92(s) (total 24H, C_5Me_4). IR (ν_{CO} , cm^{-1}): 1937(s), 1932(s), 1891(s), 1863(s), 1836(s).

2.2.4. Synthesis of 10 and 11

Using similar procedures as described above, reactions of ligand **9** with $\text{Ru}_3(\text{CO})_{12}$ in refluxing xylene for 10 h or with $\text{Fe}(\text{CO})_5$ in refluxing heptane for 72 h gave **10** and

11 as orange red or deep red crystals in 12% and 7% yields, respectively. **10**: m.p. 229 °C (dec.). Anal. Calc. for $\text{C}_{42}\text{H}_{30}\text{O}_4\text{Fe}_2\text{Ru}_2$: C, 55.28; H, 3.31. Found: C, 55.30, H, 3.18%. ^1H NMR (ppm in CDCl_3): 7.60 (d, $J = 6.8$ Hz, 2H, C_9H_6), 7.32(t, $J = 6.8$ Hz, 4H, C_9H_6), 7.02(d, $J = 6.8$ Hz, 2H, C_9H_6), 5.75(d, $J = 2.6$ Hz, 2H, C_9H_6), 5.14(d, $J = 2.6$ Hz, 2H, C_9H_6), 4.66(d, $J = 15.9$ Hz, 4H, C_5H_4), 4.32(d, $J = 15.9$ Hz, 4H, C_5H_4), 4.08(s, 10H, C_5H_5). IR (ν_{CO} , cm^{-1}): 1958(s), 1775(s). **11**: m.p. 203 °C (dec.). Anal. Calc. for $\text{C}_{42}\text{H}_{30}\text{O}_4\text{Fe}_4$: C, 61.36; H, 3.68. Found: C, 61.52, H, 3.28%. ^1H NMR (ppm in $\text{DMSO}-d_6$): 7.87(d, $J = 6.0$ Hz, 2H, C_9H_6), 7.46(t, $J = 6.0$ Hz, 4H, C_9H_6), 7.30(d, $J = 6.0$ Hz, 2H, C_9H_6), 5.59(br s, 2H, C_9H_6), 4.92(d, $J = 10.5$ Hz, 4H, C_5H_4), 4.75(br s, 2H, C_9H_6), 4.42(d, $J = 10.5$ Hz, 4H, C_5H_4), 4.02(s, 10H, C_5H_5). IR (ν_{CO} , cm^{-1}): 1933(s), 1780(s).

2.3. Crystallographic studies

Crystals of complexes **2** and **3** suitable for X-ray diffraction were obtained from hexane/ CH_2Cl_2 solution. Data collection was performed on a Bruker SMART 1000 detector, using graphite-monochromated Mo $\text{K}\alpha$ radiation (ω - 2θ scans, $\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied for all data. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were performed using the SHELXTL-97 program system. The crystal data and summary of X-ray data collection are presented in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3.

Table 1
Summary of crystallographic data for complexes **2** and **3**

	2	3
Empirical formula	$\text{C}_{32}\text{H}_{32}\text{FeO}_4\text{Ru}_2$	$\text{C}_{32}\text{H}_{32}\text{Fe}_3\text{O}_4$
Formula weight	738.57	648.13
T (K)	293(2)	294(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Tetragonal
Space group	$P2(1)/c$	$P4(2)/ncm$
a (Å)	10.342(3)	10.8939(9)
b (Å)	11.757(3)	10.894
c (Å)	23.391(6)	22.6308(19)
α (°)	90	90
β (°)	92.129(4)	90
γ (°)	90	90
V (Å ³)	2842.2(12)	2685.8(3)
Z	4	4
D_{calcd} (g/cm ³)	1.726	1.603
μ (mm ⁻¹)	1.589	1.636
$F(000)$	1480	1336
Crystal size (mm)	10.00 × 0.26 × 0.18	0.42 × 0.38 × 0.22
θ range (°)	1.74–25.01	2.60–26.38
Reflections collected	14,272	14,212
Independent reflections (R_{int})	5000(0.0452)	1490(0.0399)
Number of parameters	359	144
Goodness-of-fit on F^2	1.152	1.053
R_1 , wR_2 ($I > 2\sigma(I)$)	0.0663, 0.1601	0.0278, 0.0595
R_1 , wR_2 (all data)	0.0802, 0.1682	0.0439, 0.0695

Table 2
Selected bond lengths (Å) and bond angles (°) for **2**

Ru(1)–Ru(2)	2.7785(11)
Ru(1)–C(5)	2.298(10)
Ru(1)–C(6)	2.310(10)
Ru(1)–C(7)	2.217(10)
Ru(1)–C(8)	2.218(11)
Ru(1)–C(9)	2.284(10)
Ru(2)–C(24)	2.303(9)
Ru(2)–C(25)	2.284(10)
Ru(2)–C(26)	2.215(10)
Ru(2)–C(27)	2.233(10)
Ru(2)–C(28)	2.332(10)
C(2)–Ru(1)–C(3)	94.2(4)
C(2)–Ru(1)–Ru(2)	48.0(3)
C(3)–Ru(1)–Ru(2)	46.3(3)
C(3)–Ru(2)–C(2)	94.4(4)
C(3)–Ru(2)–Ru(1)	47.3(3)
C(2)–Ru(2)–Ru(1)	47.1(3)
Ru(1)–C(2)–Ru(2)	84.9(4)
Ru(2)–C(3)–Ru(1)	86.4(4)

Table 3
Selected bond lengths (Å) and bond angles (°) for **3**

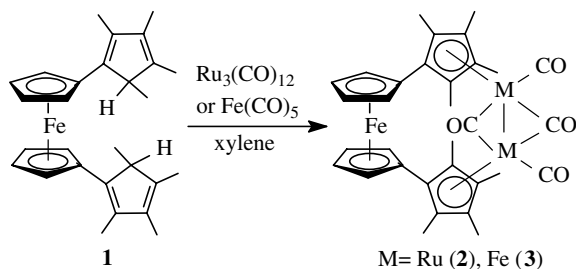
Fe(2)–Fe(2A)	2.568
Fe(2)–C(5)	2.085(5)
Fe(2)–C(6)	2.109(6)
Fe(2)–C(4)	2.133(7)
Fe(2)–C(7)	2.170(7)
Fe(2)–C(3)	2.185(3)
C(3)–C(12)	1.476(4)
Fe(2A)–C(1)–Fe(2)	83.93(14)
C(1)–Fe(2)–C(1A)	96.06(14)

3. Results and discussion

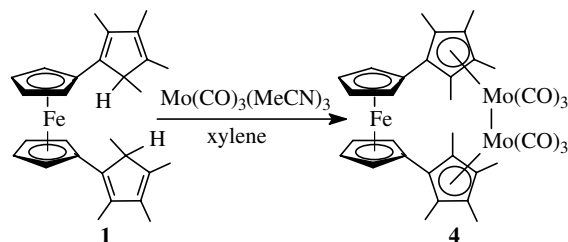
3.1. Complexes synthesis

When ligand **1** reacted with $\text{Ru}_3(\text{CO})_{12}$, $\text{Fe}(\text{CO})_5$, and $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ in refluxing xylene for 10 h, the corresponding trinuclear complexes **2** (17%), **3** (16%), and **4** (10%) were obtained (Schemes 1 and 2). All their ^1H NMR spectra showed two groups of broad singlets or multiplets for the cyclopentadienyl protons and two singlets for the methyl protons. The IR spectra exhibited two strong terminal and a strong bridging carbonyl absorptions for **2** and **3**, but six terminal carbonyl absorptions for **4**.

Similarly, reactions of ligand **5** with $\text{Ru}_3(\text{CO})_{12}$, $\text{Fe}(\text{CO})_5$, and $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$ in refluxing xylene gave



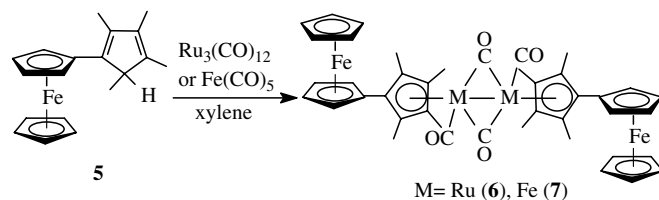
Scheme 1.



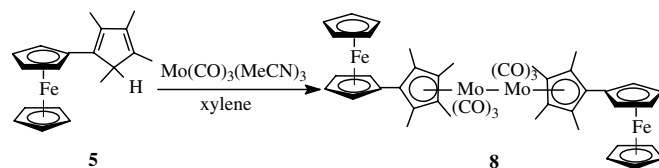
Scheme 2.

the corresponding tetranuclear complexes **6** (26%), **7** (28%), and **8** (38%). (Schemes 3 and 4). The yields of **6–8** are higher than that of complexes **2–4**, because ferrocene only acted as a common substituent instead of a rigid bridge in **6–8**. The ^1H NMR spectra of **6** and **7** showed two groups of broad singlets or multiplets for the substituted cyclopentadienyl protons, one singlet for C_5H_5 protons, and two singlets for the methyl protons. But the ^1H NMR spectrum of **8** revealed four groups of multiplets for the substituted cyclopentadienyl protons, two singlets for C_5H_5 protons, and eight singlets for the methyl protons, indicating that it exists as a mixture of *cis* and *trans* isomers. The IR spectra of **6** and **7** showed a strong terminal and a strong bridging carbonyl absorptions, while the IR spectrum of **8** exhibited strong five terminal carbonyl absorptions, consistent with their ^1H NMR spectra.

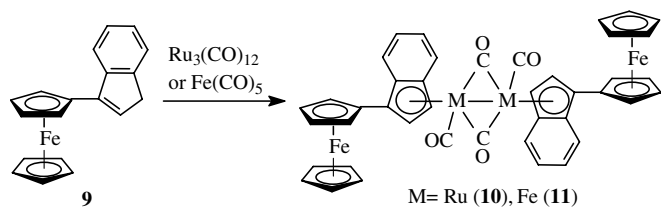
When the indenyl ligand **9** reacted with $\text{Ru}_3(\text{CO})_{12}$ in refluxing xylene for 10 h, or with $\text{Fe}(\text{CO})_5$ in refluxing heptane for 72 h, the corresponding tetranuclear ruthenium and iron complexes **10** (12%) and **11** (7%) were obtained in low yields (Scheme 5), due to the poor reactivity of indene. All their ^1H NMR spectra showed two doublets and a triplet for the six-membered ring protons of indenyl, two doublets or broad singlets for the five-membered ring protons of indenyl, four broad singlets for the substituted cyclopentadienyl protons (C_5H_4), and a singlet for the cyclopentadienyl protons (C_5H_5). The IR spectra both of **10** and **11** showed a strong terminal and a strong bridging carbonyl absorptions.



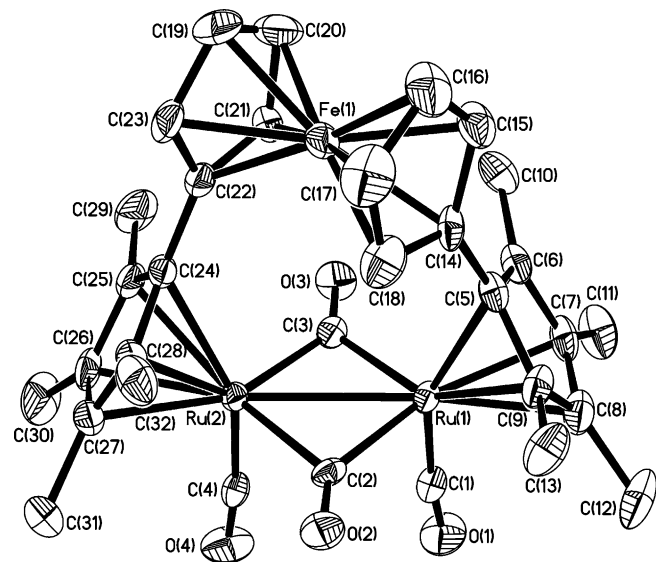
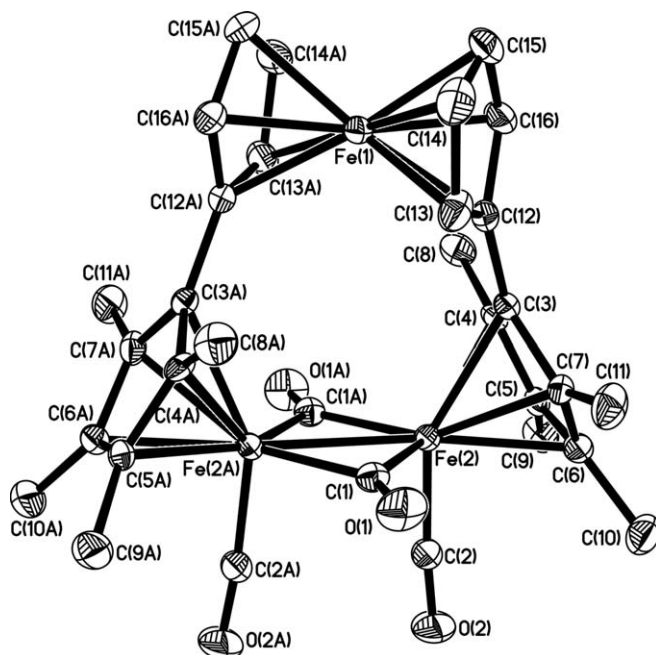
Scheme 3.



Scheme 4.



Scheme 5.

Fig. 1. Molecular structure of **2**. Thermal ellipsoids are shown at the 30% level.Fig. 2. Molecular structure of **3**. Thermal ellipsoids are shown at the 30% level.

3.2. Crystal and molecular structures of **2** and **3**

The crystal structures of **2** and **3** were determined by X-ray diffraction analysis. The molecular structures of **2** and **3** were presented in Figs. 1 and 2, respectively.

Similar to the ligand $\text{Fc}(\text{C}_5\text{Me}_4\text{H})_2$ [17], the ferrocene units both in **2** and **3** are only slightly distorted [Cen–Fe–Cen (Cen means the centroid of the cyclopentadienyl ring): 175.0° for **2**, 175.4° for **3**] with the dihedral angles between the two cyclopentadienyl rings of 6.0° and 5.3° for **2** and **3**, respectively. The dihedral angles between the mean planes of the ferrocene Cp rings and attached tetramethyl Cp rings are 44.9° , 47.3° , and 41.7° for **2** and **3**, respectively, much larger than that of the ligand $\text{Fc}(\text{C}_5\text{Me}_4\text{H})_2$ (24.0°) [17] to accommodate $\text{M}_2(\text{CO})_4$ groups. The fold angle between the two tetramethylcyclopentadienyl planes (115.3° for **2**, 121.3° for **3**) are generally larger than those in many single bridged analogues (Table 4), but smaller than those in the more rigid fulvalene[$\text{Ru}(\text{CO})_2$] $_2$ (151.5°) [16] and the doubly dimethylsilylene bridged analogue $(\text{Me}_2\text{Si})_2[(\eta^5\text{-C}_5\text{H}_3)\text{Ru}(\text{CO})_2]_2$ (122.86°) [21]. This makes the Ru–Ru and Fe–Fe bond distance [$2.7785(11)$, 2.568 \AA] in **2** and **3** longer than those in the unbridged and many bridged analogues (Table 4). It is reported that the bridging carbonyl groups tend to shorten metal–metal distances [22], and the dicyclopentadienyl dinuclear metal complexes without the bridging carbonyls usually show longer M–M distances than those with the bridging carbonyls. So the Ru–Ru bond distance in **2** is the longest one among the dicyclopentadienyl tetracarbonyl diruthenium complexes with the bridging carbonyls, and even longer than those in $(\text{CH}_2)[(\eta^5\text{-C}_5\text{H}_4)\text{Ru}(\text{CO})_2]_2$ [$2.766(1) \text{ \AA}$] [23], which has no the bridging carbonyls. In general, the large fold angles correspond with the longer M–M bonds in the dicyclopentadienyl dinuclear metal complexes. But the Fe–Fe bond distance in **3** are smaller than that in $(\text{Me}_2\text{GeGeMe}_2)[(\eta^5\text{-C}_5\text{Me}_4)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ [$2.581(5) \text{ \AA}$] [12b] and $(\text{Me}_2\text{SiGeMe}_2)[(\eta^5\text{-C}_5\text{Me}_4)\text{Fe}(\text{CO})]_2(\mu\text{-CO})_2$ [$2.572(2) \text{ \AA}$] [12h], although the later two with a small fold angles between the two cyclopentadienyl planes (107.12° , 111.7°). The twisted rigid ferrocenyl bridge should be responsible for the large fold angles between the two cyclopentadienyl planes and the long M–M bond distances in **2** and **3**. The torsion angle Cen(1)–Fe(2)–Fe(2a)–Cen(1a) in **3** (16.3°) is much larger than that in the ruthenium analogue **2** [Cen(1)–Ru(1)–Ru(2)–Cen(2): 1.7°], possibly due to the smaller atom radius of iron than that of ruthenium. But complex **3** (with C_2 symmetry) is more symmetrical than **2** from the space group.

4. Supplementary materials

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 286721 and 286722 for compounds **2** and **3**, respectively. Copies of this information may be obtained free of charge The Director, CCDC, 12 Union Road, Cam-

Table 4
Structural parameter comparison for bis(cyclopentadienyl) diiron or diruthenium complexes

Complexes	M–M (Å)	PL–PL (°) ^a	Cen–M–M–Cen torsion angles ^b	Reference ^c
<i>trans</i> -[CpRu(CO)] ₂ (μ-CO) ₂	2.735(2)			[24]
<i>trans</i> -[C ₅ Me ₄ EtRu(CO)] ₂ (μ-CO) ₂	2.7584(5)			[25]
CH ₂ [C ₅ H ₄ Ru(CO)] ₂	2.766(1)	112.9		[23]
Me ₂ C[C ₅ H ₄ Ru(CO)] ₂	2.7879(4)			[14b]
(Me ₂ Si)[C ₅ H ₄ Ru(CO)] ₂ (μ-CO) ₂	2.706(1)	103.53		[26]
(Me ₂ Si)[C ₅ Me ₄ Ru(CO)] ₂ (μ-CO) ₂	2.7121(4)		5.0	[14c]
(Me ₂ Ge)[C ₅ H ₄ Ru(CO)] ₂ (μ-CO) ₂	2.7036(6)	101.98		[27]
(CH ₂ CH ₂)[C ₅ H ₄ Ru(CO)] ₂ (μ-CO) ₂	2.7037(10)		0.9	[15]
(Me ₂ SiSiMe ₂)[C ₅ H ₄ Ru(CO)] ₂ (μ-CO) ₂	2.700(1)	91.9		[13a]
(Fe)[C ₅ Me ₄ Ru(CO)] ₂ (μ-CO) ₂ (2)	2.7785(11)	115.3	1.7	tw
Fulvalene[Ru(CO)] ₂	2.821(1)	151.5		[16]
(Me ₂ Si) ₂ [C ₅ H ₃ Ru(CO)] ₂	2.8180(3)	122.86	24.2	[22]
<i>cis</i> -[CpFe(CO)] ₂ (μ-CO) ₂	2.531(2)	92.8		[28]
<i>trans</i> -[CpFe(CO)] ₂ (μ-CO) ₂	2.534(2)			[29]
<i>trans</i> -[C ₅ M ₄ HFe(CO)] ₂ (μ-CO) ₂	2.5480(9)			[30]
<i>trans</i> -[C ₅ Me ₅ Fe(CO)] ₂ (μ-CO) ₂	2.560(1)			[31]
Me ₂ C[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂	2.4836(6)	109.6		[6]
(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		[32]
(Me ₂ SiSiMe ₂)[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂	2.526(2)	94.7		[12a]
(Me ₂ GeGeMe ₂)[(η ⁵ -C ₅ Me ₄)Fe(CO)] ₂ (μ-CO) ₂	2.581(5)	107.12		[12b]
(Me ₂ SiGeMe ₂)[(η ⁵ -C ₅ Me ₄)Fe(CO)] ₂ (μ-CO) ₂	2.572(2)	111.7		[12h]
(Fe)[C ₅ Me ₄ Fe(CO)] ₂ (μ-CO) ₂ (3)	2.568	121.3	16.3	tw
(CH ₂)(Me ₂ Si)[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂	2.4833(13)	117.5		[11b]
(Me ₂ C)(Me ₂ Si)[C ₅ H ₃ Fe(CO)] ₂	2.7747(6)	126.9		[11b]
(CH ₂)(Me ₂ Ge)[C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂	2.4877(11)	117.03		[11b]
(Me ₂ C)(Me ₂ Ge)[C ₅ H ₃ Fe(CO)] ₂ (μ-CO) ₂	2.4816(18)	117.0		[11b]
(Me ₂ Ge) ₂ [C ₅ H ₄ Fe(CO)] ₂ (μ-CO) ₂	2.494(2)	110.3		[11a]
(Me ₂ SiSiMe ₂) ₂ [C ₅ H ₃ Fe(CO)] ₂ (μ-CO) ₂	2.5440(8)	100.26		[11a]

^a PL, plane of the cyclopentadienyl ring.

^b Cen, centroid of the cyclopentadienyl ring.

^c tw, this work.

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