

基于两个取代四甲基环戊二烯基配体的金属羰基化合物的合成及晶体结构

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摘要: 配体[C₅Me₄HR] [R=4-BrPh (**1**), (MeC₅H₃N)CH₂ (**2**)]分别与 Mo(CO)₆, Ru₃(CO)₁₂ 和 Fe(CO)₅ 在二甲苯中加热回流, 得到了 6 个双核配合物 *trans*-[η⁵-C₅Me₄R]₂Mo₂(CO)₆ (**3, 4**), *trans*-[(η⁵-C₅Me₄R)Ru(CO)(μ-CO)]₂ (**5, 6**) 和 *trans*-[η⁵-(C₅Me₄R)Fe(CO)(μ-CO)]₂ (**7, 8**)。通过元素分析、红外光谱、核磁共振氢谱对配合物的结构进行了表征, 并用 X-射线单晶衍射法测定了配合物 **3, 5, 6** 和 **8** 的结构。

关键词: 环戊二烯; 金属羰基化合物; X-射线衍射; 结构

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Syntheses and Structures of Metal Carbonyl Complexes Based on Two Substituted Tetramethylcyclopentadienyl Ligands

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Abstract: Via thermal reactions of the substituted tetramethylcyclopentadienes [C₅Me₄HR] [R = 4-BrPh (**1**), (MeC₅H₃N)CH₂ (**2**)] with Mo(CO)₆, Ru₃(CO)₁₂ and Fe(CO)₅, respectively in refluxing xylene, the responding dinuclear metal carbonyl complexes *trans*-[η⁵-C₅Me₄R]₂Mo₂(CO)₆ (**3, 4**), *trans*-[(η⁵-C₅Me₄R)Ru(CO)(μ-CO)]₂ (**5, 6**), and *trans*-[η⁵-(C₅Me₄R)Fe(CO)(μ-CO)]₂ (**7, 8**) have been obtained. These complexes have been characterized by elemental analysis, IR, and ¹H NMR spectra. The crystal structures of **3, 5, 6** and **8** have been determined by X-ray crystallography. CCDC: 934733, **3**; 944267, **5**; 926404, **6**; 926405, **8**.

Key words: cyclopentadiene; metal carbonyl complex; X-ray diffraction; structure

0 Introduction

The cyclopentadienyl groups have been among the most important ligands in organometallic chemistry, and group 6 and 8 metal carbonyl dimers with

cyclopentadienyl-type ligands have been intensively investigated as a class of organometallic compounds. Cyclopentadienyl metal carbonyl complexes have been received much attention because of their potential utility as catalysts in many organic catalytic reactions^[1-4].

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The steric and electronic factors of cyclopentadienyl ring substituents have great influence on catalytic activity, thus subtle changes in cyclopentadienyl ligand substitution can have profound consequences on chemistry reactivity. The changes can be easily tailored by replacement of both the cyclopentadienyl fragment and anionic ancillary ligands. Ligand modification not only opens access to construct new compounds, but also has the most profound effect on catalyst performance^[5-6]. Investigations in our laboratory focusing on the chemistry of group 6 and 8 metallocenes have demonstrated the importance of cyclopentadienyl substituent effects^[7-12]. On going our works to gain a deeper understanding of the steric and electric influences of substituents on the molecular structures and reactions of the corresponding cyclopentadienyl binuclear metal carbonyl complexes, herein, we reported the syntheses and characterization of a series of dinuclear metal carbonyl complexes bearing the substituted tetramethylcyclopentadienyl ligands.

1 Experimental

1.1 General considerations

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. All solvents were distilled from appropriate drying agents under an atmosphere of nitrogen prior to use. ¹H NMR spectra were recorded on a Bruker AV 500 instrument, while IR spectra were recorded as KBr disks on a FT IR 8900 spectrometer. X-ray measurements were made on a Bruker Smart APEX diffractometer with graphite monochromated Mo K α ($\lambda=0.071\ 073$ nm) radiation. Elemental analyses were performed on a Vario EL III analyzer. The ligand precursors C₅Me₄HR (R = 4-BrPh (**1**), (MeC₅H₃N)CH₂ (**2**)) were synthesized according to the literature^[13-14]. Mo(CO)₆, Fe(CO)₅ and Ru₃(CO)₁₂ were purchased from J&K Scientific Ltd and used without further purification, other reagents were purchased from commercial suppliers.

1.2 Synthesis of *trans*-[η^5 -C₅Me₄(4-BrC₆H₄)]₂Mo₂(CO)₆ (**3**)

A solution of ligand precursor **1** (0.832 g, 3 mmol)

and Mo(CO)₆ (0.794 g, 3 mmol) in 30 mL of xylene was refluxed for 10 h. After removal of solvent under reduced pressure, the residue was chromatographed on an alumina column using petroleum ether/CH₂Cl₂ (6:1, V/V) as eluent. The only red band was eluted and collected. After vacuum removal of the solvents from the above eluate, the residue was recrystallized from n-hexane/CH₂Cl₂ (1:2, V/V) at room temperature to give complex **3** as dark-red crystals (Yield: 0.733 g, 53.5%). m.p. 169~171 °C (dec.). Anal. Calcd.(%) for C₃₆H₃₂Br₂Mo₂O₆: C, 47.39; H, 3.54. Found(%): C, 47.28; H, 3.53. ¹H NMR (500 MHz, CDCl₃): δ 7.53 (d, 4H, $J=8.0$ Hz C₆H₄), 7.22 (d, 4H, $J=8.0$ Hz C₆H₄), 1.98 (s, 12H, C₅Me₄), 1.93 (s, 12H, C₅Me₄), IR (KBr, ν_{CO} / cm⁻¹): 1 944(s), 1 926(s), 1 898(s).

1.3 Synthesis of *trans*-[η^5 -C₅Me₄CH₂(MeC₅H₃N)]₂Mo₂(CO)₆ (**4**)

Complex **4** was prepared in the same way as **3**. The reaction of ligand precursor **2** with Mo(CO)₆ in xylene refluxing 10 h afforded complex **4** as dark red crystals in 43.6% yield. m.p. 127~129 °C (dec.). Anal. Calcd.(%) for C₃₈H₄₀Mo₂N₂O₆: C, 56.17; H, 4.96; N, 3.45. Found(%): C, 56.21; H, 4.99; N, 3.41. ¹H NMR (500 MHz, CDCl₃): δ 7.54 (t, 2H, $J=7.5$ Hz, Py-H), 7.04 (d, 2H, $J=7.5$ Hz, Py-H), 6.87 (d, 2H, $J=7.5$ Hz, Py-H), 3.77 (s, 4H, -CH₂-), 2.53 (s, 6H, Py-CH₃), 2.00 (s, 12H, C₅Me₄), 1.99 (s, 12H, C₅Me₄). IR (KBr, ν_{CO} / cm⁻¹): 1 932(s), 1 892(s), 1 871(s).

1.4 Synthesis of *trans*-[(η^5 -C₅Me₄(4-BrC₆H₄))Ru(CO)(μ -CO)]₂ (**5**)

Complex **5** was prepared in the same way as **3**. The reaction of ligand precursor **1** with Ru₃(CO)₁₂ in xylene refluxing 10 h afforded complex **5** as yellow crystals in 60.7% yield. m.p. 216 °C. Anal. Calcd.(%) for C₃₄H₃₂Br₂Ru₂O₄: C, 47.12; H, 3.72. Found(%): C, 47.15; H, 3.73. ¹H NMR (500 MHz, CDCl₃): δ 7.55 (d, 4H, $J=8.0$ Hz, C₆H₄), 7.38 (d, 4H, $J=8.0$ Hz, C₆H₄), 1.85(s, 12H, C₅Me₄), 1.77 (s, 12H, C₅Me₄), IR (KBr, ν_{CO} / cm⁻¹): 1 930(s), 1 747(s).

1.5 Synthesis of *trans*-[(η^5 -C₅Me₄CH₂(MeC₅H₃N))Ru(CO)(μ -CO)]₂ (**6**)

Complex **6** was prepared in the same way as **3**. The reaction of ligand precursor **2** with Ru₃(CO)₁₂ in

xylene refluxing 10 h afforded complex **6** as yellow crystals in 62.7% yield. m.p. 178 °C. Anal. Calcd.(%) for $C_{36}H_{40}N_2Ru_2O_4$: C, 56.38; H, 5.26; N, 3.65. Found (%): C, 56.35; H, 5.27; N, 3.69. 1H NMR (500 MHz, $CDCl_3$): δ 7.48 (t, 2H, $J=7.5$ Hz, Py-H), 6.98 (d, 2H, $J=7.5$ Hz, Py-H), 6.79 (d, 2H, $J=8.0$ Hz, Py-H), 3.88 (s, 4H, $-CH_2-$), 2.53 (s, 6H, Py- CH_3), 1.93 (s, 12H, C_5Me_4), 1.84 (s, 12H, C_5Me_4). IR (KBr, ν_{CO} / cm^{-1}): 1 921(s), 1 756(s).

1.6 Synthesis of *trans*- $[(\eta^5-C_5Me_4(4-BrC_6H_4))Fe(CO)(\mu-CO)]_2$ (**7**)

Complex **7** was prepared in the same way as **3**. The reaction of ligand precursor **1** with $Fe(CO)_5$ in xylene refluxing 10 h afforded complex **7** as dark red crystals in 45.6% yield. m.p. 173 °C. Anal. Calcd(%). for $C_{34}H_{32}Br_2Fe_2O_4$: C, 52.62; H, 4.16. Found (%): C, 52.61; H, 4.18. 1H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, 4H, $J=8.0$ Hz, C_6H_4), 7.35 (d, 4H, $J=8.0$ Hz, C_6H_4), 1.88 (s, 12H, C_5Me_4), 1.71 (s, 12H, C_5Me_4), IR (KBr, ν_{CO} / cm^{-1}): 1 928(s), 1 768(s).

1.7 Synthesis of *trans*- $[(\eta^5-C_5Me_4CH_2(MeC_5H_3N))Fe(CO)(\mu-CO)]_2$ (**8**)

Complex **8** was prepared in the same way as **3**. The reaction of ligand precursor **2** with $Fe(CO)_5$ in xylene refluxing 10 h afforded complex **8** as dark red

crystals in 45.2% yield. m.p. 147 °C. Anal. Calcd.(%) for $C_{36}H_{40}Fe_2N_2O_4$: C, 63.92; H, 5.96; N, 4.14. Found (%): C, 63.90; H, 5.97; N, 4.09. 1H NMR (500 MHz, $CDCl_3$): δ 7.44 (t, 2H, $J=7.5$ Hz, Py-H), 6.98 (d, 2H, $J=7.5$ Hz, Py-H), 6.73 (d, 2H, $J=7.5$ Hz, Py-H), 3.76 (s, 4H, $-CH_2-$), 2.51 (s, 6H, Py- CH_3), 1.73 (s, 12H, C_5Me_4), 1.68 (s, 12H, C_5Me_4). IR (KBr, ν_{CO} / cm^{-1}): 1 922(s), 1 758(s).

1.8 Crystal structure determination

Crystals of the complexes **3**, **5**, **6** and **8** suitable for X-ray diffraction were isolated from the slow evaporation of hexane-dichloromethane solution. Data collection were performed on a Bruker SMART APEX (II)-CCD detector with graphite monochromated Mo $K\alpha$ ($\lambda=0.071\ 073$ nm) radiation using the φ - ω scan technique. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 using the SHELX-97 program system. Hydrogen atoms were included in calculated positions riding on the parent atoms and refined with fixed thermal parameters. Crystallographic data and experimental details of the structure determinations are given in Table 1.

CCDC: 934733, **3**; 944267, **5**; 926404, **6**; 926405, **8**.

Table 1 Crystal data and structure refinement parameters for the complexes **3**, **5**, **6** and **8**

	3	5	6	8
Empirical formula	$C_{36}H_{32}Br_2Mo_2O_6$	$C_{34}H_{32}Br_2O_4Ru_2$	$C_{38}H_{44}Cl_4N_2O_4Ru_2$	$C_{38}H_{44}Cl_4Fe_2N_2O_4$
Formula weight	912.32	866.56	936.69	846.25
Temperature / K	298(2)	298(2)	298(2)	298(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / nm	1.174 9(5)	0.988 2(6)	0.836 1(3)	0.836 5(7)
b / nm	1.186 1(5)	1.303 8(7)	0.956 4(3)	0.959 0(8)
c / nm	1.424 2(6)	1.356 4(7)	1.335 2(4)	1.336 7(11)
α / (°)	71.124(4)	104.577(7)	74.332(4)	106.587(11)
β / (°)	86.412(5)	97.493(7)	89.242(4)	90.406(11)
γ / (°)	66.930(5)	103.991(7)	76.501(4)	103.955(11)
V / nm ³	1.723 1(12)	1.606 8(15)	0.998 2(6)	0.994 0(14)
Z	2	2	1	1
$F(000)$	900	852	474	438
D_c / (g·cm ⁻³)	1.758	1.791	1.558	1.414
Crystal dimension / mm	0.41×0.32×0.22	0.31×0.17×0.10	0.43×0.35×0.31	0.48×0.32×0.02
θ range / (°)	1.89~25.50	1.58~25.50	1.59~25.10	2.37~25.10

Continued Table 1

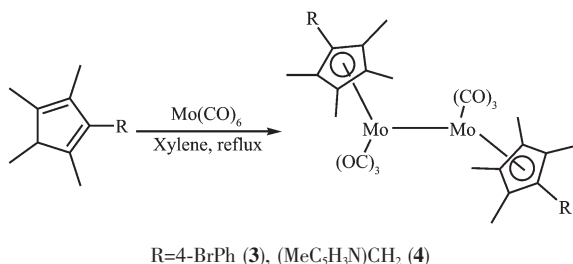
Reflections collected	8 939	8 262	5 034	4 756
Independent reflections	6 521	5 798	3 473	3 351
R_{int}	0.038 7	0.047 6	0.031 7	0.038 4
Parameters	423	405	232	231
Goodness of fit on F^2	1.047	1.104	1.133	1.125
$R_1, wR_2^a [I > 2\sigma(I)]$	$R_1=0.061\ 5, wR_2=0.157\ 1$	$R_1=0.076\ 5, wR_2=0.217\ 7$	$R_1=0.043\ 2, wR_2=0.109\ 9$	$R_1=0.124\ 9, wR_2=0.373\ 2$
R_1, wR_2^a (all data)	$R_1=0.082\ 4, wR_2=0.178\ 2$	$R_1=0.092\ 2, wR_2=0.225\ 0$	$R_1=0.045\ 0, wR_2=0.115\ 0$	$R_1=0.136\ 3, wR_2=0.380\ 0$

^a Complex **3**: $w=1/[\sigma^2(F_o^2)+(0.093\ 5P)^2+7.940\ 7P]$, where $P=(F_o^2+2F_c^2)/3$; Complex **5**: $w=1/[\sigma^2(F_o^2)+(0.084\ 3P)^2+25.548\ 0P]$, where $P=(F_o^2+2F_c^2)/3$; Complex **6**: $w=1/[\sigma^2(F_o^2)+(0.075\ 8P)^2+0.946\ 8P]$, where $P=(F_o^2+2F_c^2)/3$; Complex **8**: $w=1/[\sigma^2(F_o^2)+(0.153\ 7P)^2+19.260\ 3P]$, where $P=(F_o^2+2F_c^2)/3$.

2 Results and discussion

2.1 Reactions of ligand precursors $\text{C}_5\text{Me}_4\text{HR}$ ($\text{R}=4\text{-BrPh}$ (**1**), $(\text{MeC}_5\text{H}_3\text{N})\text{CH}_2$ (**2**)) with $\text{Mo}(\text{CO})_6$

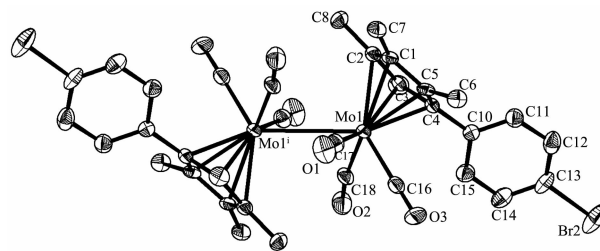
Reactions of ligand precursors $\text{C}_5\text{Me}_4\text{HR}$ ($\text{R}=4\text{-BrPh}$ (**1**), $(\text{MeC}_5\text{H}_3\text{N})\text{CH}_2$ (**2**)) with $\text{Mo}(\text{CO})_6$ in refluxing xylene afforded the corresponding products **3** (53.5%) and **4** (43.6%) respectively (Scheme 1).

Scheme 1 Synthesis of the complexes **3** and **4**

Based on their ^1H NMR and IR spectra, **3** and **4** were assigned as the normal Mo-Mo single bonded dinuclear complexes. The IR spectra of **3** and **4** all exhibited only terminal carbonyl bands (**3**: 1 944, 1 926, 1 898 cm^{-1} ; **4**: 1 932, 1 892, 1 871 cm^{-1}). The ^1H NMR spectra of **3** and **4** all displayed two groups of singlets for the four methyl protons, in addition, **3** displayed two doublets for the phenyl protons and **4** displayed one singlet for the methylene protons and three groups of peaks for pyridyl protons, indicating the symmetrical structures in solution.

Single crystals of **3** suitable for X-ray diffraction was obtained from the slow evaporation of exane- CH_2Cl_2 solution. Single crystals of **4** can be isolated in the same way but it is easily weathered. The single-crystal X-ray determination of **3** is presented in Fig.1. It consists of two $(\text{C}_5\text{Me}_4\text{PhBr-4})\text{Mo}(\text{CO})_3$ units, and

each of the molybdenum atoms is coordinated with a Cp (where Cp=cyclopentadienyl ligand) in an η^5 mode and three terminal carbonyl ligands. It has trans conformation and linked by a Mo-Mo bond, lying on a crystallographic inversion. Two independent but chemically equivalent molecules appear in the unit cell. The fifth coordination position is occupied by a cyclopentadienyl ring that is essentially planar. The structural parameters of **3** are similar to those in $[\eta^5\text{-C}_5\text{Me}_4\text{RMo}(\text{CO})_3]_2$, and Mo-Mo bond distances for **3** are 0.328 9 nm (Mo1-Mo1ⁱ) and 0.329 4 nm (Mo2-Mo2ⁱⁱ), which are comparable to other metal-metal bond distances found for analogous derivatives of the type $[\eta^5\text{-C}_5\text{Me}_4\text{RMo}(\text{CO})_3]_2$ ($\text{R}=\text{Ph-Me}$, (0.328 3 nm); $\text{R}=\text{Ph-OMe}$ (0.330 7 nm)^[15]; $\text{R}=n\text{-butyl}$ (0.328 6 nm)^[16]). However, Mo-Mo bond distances of **3** are longer than that of *trans*- $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ (0.323 5(1) nm)^[17] and $[(\eta^5\text{-C}_5\text{H}_4\text{Pr})\text{Mo}(\text{CO})_3]_2$ (0.322 2(5) nm)^[18], due to the bulky steric effect of the phenyl and four methyl groups.



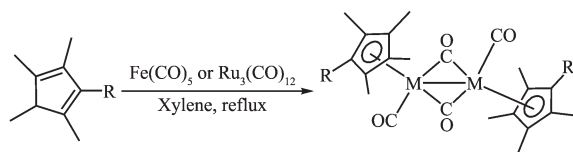
Hydrogen atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: ⁱ 1-x, -y, -z

Fig.1 Molecular structure of complex **3**

2.2 Reactions of ligands $[\text{C}_5\text{Me}_4\text{HR}]$ [$\text{R}=4\text{-BrPh}$ (**1**), $(\text{MeC}_5\text{H}_3\text{N})\text{CH}_2$ (**2**)] with $\text{Ru}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$

To develop a wider generality of the reactions of

type, we further introduced $\text{Ru}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$, carried out by similar reaction conditions in the refluxing xylene and products **5**~**8** were obtained (Scheme 2).



M=Ru; R=4-BrPh (**5**), $(\text{MeC}_5\text{H}_3\text{N})\text{CH}_2$ (**6**)

M=Fe; R=4-BrPh (**7**), $(\text{MeC}_5\text{H}_3\text{N})\text{CH}_2$ (**8**)

Scheme 2 Synthesis of the complexes **5**~**8**

Based on their ^1H NMR and IR spectra, **5**~**8** were assigned as the normal M-M single bonded dinuclear complexes. The IR spectra of complexes **5**~**8** all exhibited a strong terminal carbonyl absorption at $1\,921\sim 1\,930\text{ cm}^{-1}$ and a strong bridging carbonyl absorption at $1\,747\sim 1\,768\text{ cm}^{-1}$, which is comparable to other metal-metal bond spectra found in other substituted cyclopentadienyl ruthenium or iron carbonyl dimers. In their ^1H NMR spectra, **5**~**8** all displayed two groups of singlets for the four methyl protons, in addition, both complexes **5** and **7** displayed two doublets for the phenyl protons and complexes **6** and **8** displayed one singlet for the methylene protons and three groups of peaks for pyridyl protons,

indicating the symmetrical structures in solution.

Our initial idea is to introduce the pyridyl group to Cp ring as a functionalized side and then study the reactions of the side-chain-functionalized cyclopentadiene with metal carbonyls. For the pyridyl side-chain-functionalized cyclopentadienyl ligand, the nitrogen atom can act as a good two-electron donor site and can coordinate to a variety of metals, for example, thermal treatment of the pyridyl side-chain-functionalized cyclopentadiene with $\text{Ru}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$ could give different intramolecular C-H activated products besides the normal dinuclear metal complexes^[22]. Although we used different solvents, the pyridyl group only acted as substituent and did not coordinate with the Ru and Fe atoms, and the preconceived C-H activated products were not obtained yet.

Selected bond lengths and angles for complexes **3**, **5**, **6** and **8** are given in Table 2. The single-crystal X-ray determination of complexes **5**, **6** and **8** are illustrated in Fig.2~4.

The crystal structure of **5** is shown in Fig.2, in a unit cell there are two different environmental molecules Ru(1) and Ru(2), which have the same

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for complexes **3**, **5**, **6** and **8**

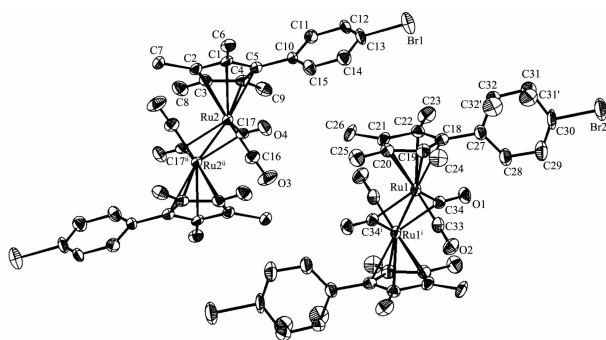
3					
Mo(1)-Mo(1 ¹)	0.328 9	Mo1-C2	0.242 6(8)	Mo1-C4	0.230 5(7)
Mo1-C1	0.239 0(7)	Mo1-C3	0.237 1(8)	Mo1-C5	0.229 4(7)
C(5)-C(1)-Mo(1)	68.7(4)	C(7)-C(1)-Mo(1)	127.9(5)	O(1)-C(17)-Mo(1)	171.5(8)
C(1)-C(5)-C(6)	124.2(7)	C(17)-Mo(1)-C(3)	152.6(3)	C(17)-Mo(1)-C(5)	102.6(3)
5					
Ru(1)-Ru(1 ¹)	0.275 3(2)	C(2)-Ru(2)	0.229 2(11)	C(4)-Ru(2)	0.222 9(11)
Ru(2)-Ru(2 ²)	0.276 9(2)	C(3)-Ru(2)	0.228 2(11)	C(5)-Ru(2)	0.229 6(11)
C(1)-Ru(2)	0.231 3(11)				
C(8)-C(3)-Ru(2)	126.0(8)	C(6)-C(1)-Ru(2)	127.8(8)	C(9)-C(4)-Ru(2)	124.3(8)
C(7)-C(2)-Ru(2)	127.6(8)	C(10)-C(5)-Ru(2)	129.5(8)	C(18)-C(22)-C(23)	126.6(12)
6					
Ru(1)-Ru(1 ¹)	0.275 79(8)	C(2)-Ru(1)	0.230 8(4)	C(4)-Ru(1)	0.228 3(4)
C(1)-Ru(1)	0.225 7(4)	C(3)-Ru(1)	0.230 2(4)	C(5)-Ru(1)	0.222 2(4)
C(6)-C(1)-Ru(1)	124.3(3)	C(8)-C(3)-Ru(1)	128.3(3)	C(10)-C(5)-Ru(1)	124.8(3)
C(7)-C(2)-Ru(1)	127.8(3)	C(9)-C(4)-Ru(1)	126.3(3)	C(2)-Ru(1)-Ru(1 ¹)	112.29(10)

Continued Table 1

8					
Fe(1)-Fe(1 ⁱ)	0.258 1(3)	C(3)-Fe(1)	0.218 1(12)	C(7)-Fe(1)	0.215 0(12)
C(2)-Fe(1)	0.216 0(10)	C(6)-Fe(1)	0.218 5(11)	C(9)-Fe(1)	0.210 1(11)
C(10)-C(9)-Fe(1)	127.0(8)	C(8)-C(7)-Fe(1)	126.3(9)	C(4)-C(3)-Fe(1)	130.9(9)
C(1)-C(2)-Fe(1)	130.4(9)	C(5)-C(6)-Fe(1)	130.5(9)	O(1)-C(18)-Fe(1)	174.5(12)

Symmetry codes: for **3**: ⁱ 1-x, -y, -z; for **5**: ⁱ 1-x, 1-y, 1-z; ⁱ 1-x, 2-y, 2-z; for **6**: ⁱ -x, 2-y, -z; for **8**: ⁱ 2-x, 2-y, 2-z.

structure basically, just small differences in some bond lengths and angles. Similar to the cyclopentadienyl analogue *trans*-[η^5 -CpRu(CO)(μ -CO)]₂, both the structures are trans form and have C_i symmetry. Two carbonyls are bridged and two carbonyls are terminal. The two cyclopentadienyl ring planes are parallel. The Ru-Ru distances are 0.275 3(2) nm (Ru1-Ru1ⁱ) and 0.276 9(2) nm (Ru2-Ru2ⁱⁱ), respectively. Although there are two kinds of different environmental molecules in the unit cell, the ¹H NMR spectrum of **5** shows the existence of only one. This indicates that they may exist as one form in solution; however, the fact that a rapid fluxional process exist cannot be excluded^[19-20]. Disorder on the location of C31 and C32 has been shown in Fig.2. The disorder share of C31 is 0.50 and the disorder share of C32 is 0.50.



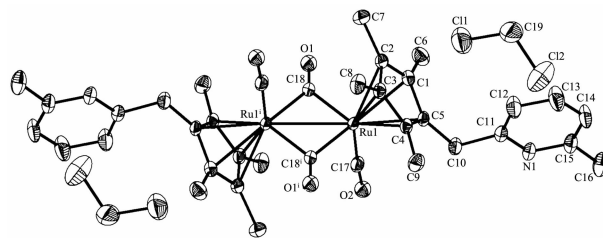
Hydrogen atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: ⁱ 1-x, 1-y, 1-z; ⁱⁱ 1-x, 2-y, 2-z

Fig.2 Molecular structure of complex **5**

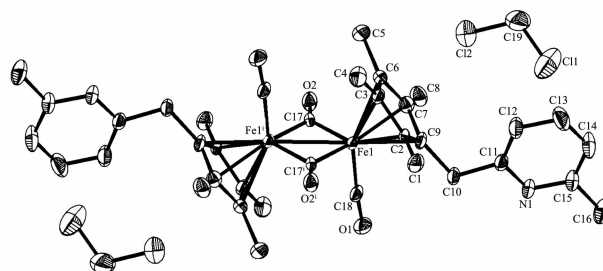
Ru-Ru bond distance of **5** is slightly longer than that in *trans*-[η^5 -CpRu(CO)(μ -CO)]₂ (0.273 5(2) nm)^[21], this may be attributed to the bulky steric effect of the phenyl and four methyl groups; but slightly shorter than *trans*-[[η^5 -C₅Me₄Ph]Ru(CO)(μ -CO)]₂ (0.277 69(4) nm) and *trans*-[[η^5 -C₅Me₄(4-OCH₃)C₆H₄]Ru(CO)(μ -CO)]₂

(0.277 01(6) nm), which may be attributed to their different electrical effects of -Br, -OCH₃ and -H at the 4-position of the phenyl.

The crystal structures of **6** and **8** are shown in Fig.3~4. The structures of **6** and **8** are similar, and both have two types of carbonyl ligands, namely, terminal and bridging, in their molecular structures. Both structures are the symmetrical (trans) isomers. The two cyclopentadienyl ring planes and pyridyl ring planes are parallel, respectively. There are two solvent molecules in their unit cells. For complex **6**, the Ru-Ru bond distance (0.275 79(8) nm) is slightly longer than those of analogous complexes *trans*-[C₅H₄Ru(CO)(μ -CO)]₂ (0.273 5(2) nm)^[21] and [(C₅H₃NCH₃)CH₂Me₂C(C₅H₄)Ru(CO)]₂(μ -CO)₂ (0.273 69(8) nm)^[22], and very



Hydrogen atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: ⁱ -x, 2-y, -z

Fig.3 Molecular structure of complex **6**

Hydrogen atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: ⁱ 2-x, 2-y, 2-z

Fig.4 Molecular structure of complex **8**

close to *trans*- $[(\eta^5\text{-C}_5\text{Me}_4\text{Bz})\text{Ru}(\text{CO})(\mu\text{-CO})_2]$ (0.275 37(4) nm)^[23], but slightly shorter than that in $[(\eta^5\text{-C}_5\text{Me}_4\text{Ph})\text{Ru}(\text{CO})(\mu\text{-CO})_2]$ (0.277 69(4) nm), $[(\eta^5\text{-C}_5\text{Me}_4\text{PhOMe})\text{Ru}(\text{CO})(\mu\text{-CO})_2]$ (0.277 01(6) nm)^[15] and $[(\eta^5\text{-C}_5\text{H}_3\text{Ph}_2)\text{Ru}(\text{CO})(\mu\text{-CO})_2]$ (0.276 36(3) nm)^[24]. Ru-CEN (CEN means centroid of the cyclopentadienyl ring) distance (0.191 87 nm) is slightly longer than *trans*- $\{[(\eta^5\text{-C}_5\text{Me}_4\text{Bz})\text{Ru}(\text{CO})(\mu\text{-CO})_2]\}$ (0.191 61 nm)^[23], and very close to *trans*- $\{[(\eta^5\text{-C}_5\text{Me}_4(4\text{-OCH}_3)\text{C}_6\text{H}_4)\text{Ru}(\text{CO})(\mu\text{-CO})_2]\}$ (0.191 8 nm), but slightly shorter than *trans*- $\{[(\eta^5\text{-C}_5\text{Me}_4\text{Ph})\text{Ru}(\text{CO})(\mu\text{-CO})_2]\}$ (0.192 9 nm)^[15]. These distances are comparable to those found in other substituted cyclopentadienyl ruthenium carbonyl dimers. For complex **8**, the Fe-Fe bond distance is 0.258 1(3) nm, which is slightly longer than those in the unbridged analogs, *trans*- $[(\eta^5\text{-C}_5\text{Me}_4\text{Ph})\text{Fe}(\text{CO})(\mu\text{-CO})_2]$ (0.256 35(6) nm), *trans*- $[(\eta^5\text{-C}_5\text{Me}_4\text{PhOMe})\text{Fe}(\text{CO})(\mu\text{-CO})_2]$ (0.256 30(8) nm)^[15] and *trans*- $[(\eta^5\text{-C}_5\text{Me}_4\text{Bz})\text{Fe}(\text{CO})(\mu\text{-CO})_2]$ (0.255 70(5) nm)^[9], and even longer than those in the singly bridged analogs, $(\text{Me}_2\text{C})[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2]_2$ (0.248 36(6) nm) and $(\text{Et}_2\text{C})[(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\text{CO})_2]_2$ (0.246 71(6) nm)^[18]. To the best of our knowledge, the Fe-Fe bond distance is the longest distance in the unbridged analogs so far.

3 Conclusions

Reactions of substituted tetramethylcyclopentadienes $\text{C}_5\text{Me}_4\text{HR}$ ($\text{R}=4\text{-BrPh}$ (**1**), $(\text{MeC}_5\text{H}_3\text{N})\text{CH}_2$ (**2**)) with $\text{Mo}(\text{CO})_6$, $\text{Ru}_3(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$ in the refluxing xylene were studied, respectively. Six new metal carbonyl complexes were obtained and four of them were determined by single-crystal X-ray diffraction. The results clearly revealed the coordination mode of these cyclopentadienyl metal complexes is η^5 and the N atom of pyridine did not coordinate to the metal atoms. These substituted cyclopentadienyl ligands are *trans* in the dimeric structures in the solid state. Substituent group variations display some influence on the M-M bond length of dinuclear tetramethylcyclopentadienyl metal carbonyl complexes.

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