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# Synthesis and structures of aryl-substituted tetramethylcyclopentadienyl dinuclear metal carbonyl complexes

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# Abstract

A series of 14 aryl-substituted tetramethylcyclopentadienyl dinuclear metal carbonyl complexes have been synthesized by treating the corresponding ligands ( $C_5Me_4C_6H_4X$ -4) (X = H, Me, Cl, OMe) with  $Ru_3(CO)_{12}$ , Fe(CO)<sub>5</sub>, or Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub>, respectively in refluxing xylene. It showed that the electronic effects of the substituents had influence on the molecular structures and reactions of the complexes, especially for the ruthenium and molybdenum complexes. In the reactions of aryl-substituted tetramethylcyclopentadiene with Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub>, the electron-withdrawing effect of the substituent in the *para* position of benzene ring is favorable to produce the Mo–Mo triple bonded complexes. In a given condition, the Mo–Mo single bonded complex could be transformed into the corresponding Mo–Mo triple bonded complex. The structures of nine complexes were determined by single crystal X-ray diffraction. © 2006 Elsevier B.V. All rights reserved.

Keywords: Tetramethylcyclopentadienyl; Metal-metal bond; Ruthenium carbonyl; Iron carbonyl; Molybdenum carbonyl

### 1. Introduction

Cyclopentadienyl metal complexes have been extensively investigated since ferrocene has been discovered. Replacement of the hydrogen atoms by other substituents alters both the steric and electronic influences of the  $\eta^5$ -cyclopentadienyl ring, resulting in differing reactivity and stability of the substituted cyclopentadienyl metal complexes [1]. Especially for metallocene polymerization catalysts, the steric and electronic effects of cyclopentadienyl ring substituents greatly influence catalytic activity [2]. Because of the special electronic and steric effect of the phenyl group [3], in this study, the reactions of a series of aryl-substituted tetramethylcyclopentadiene with Ru<sub>3</sub>(CO)<sub>12</sub>, Fe(CO)<sub>5</sub>, or Mo(CO)<sub>3</sub>(MeCN)<sub>3</sub> were reported. The aim is

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to obtain a deeper insight into the steric and electronic influences of substituents on the molecular structures and reactions of the corresponding biscyclopentadienyl dinuclear metal carbonyl complexes, especially the electronic influences of different substituents at the 4-position of phenyl.

# 2. Experimental

# 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. <sup>1</sup>H NMR spectra were recorded on a Bruker AV 300 or 400 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. The ligands ( $C_5Me_4C_6H_4$ -4-X) [X = H (1), Me (2), Cl (3), or OMe (4)] were prepared according to the literature [3]].

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#### 2.2. Complexes synthesis

# 2.2.1. Synthesis of complex $[(\eta^5 - C_5 Me_4 Ph)Ru(CO)]$ $(\mu - CO)]_2$ (5)

A solution of ligand 1 (0.28 g, 1.41 mmol) and Ru<sub>3</sub>(CO)<sub>12</sub> (0.3 g, 0.47 mmol) in 30 mL of xylene was refluxed for 12 h. After removal of solvent, the residue was chromatographed on an alumina column using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> as eluent. The orange band afforded complex **5** as orange-red crystals (0.26 g, 52%). M.p. 230–231 °C. *Anal.* Calc. for C<sub>34</sub>H<sub>34</sub>O<sub>4</sub>Ru<sub>2</sub>: C, 57.62; H, 4.81. Found: C, 57.48; H, 4.56%. <sup>1</sup>H NMR (300 M, in CDCl<sub>3</sub>): 7.46–7.32 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 1.99 (s, 12H, CH<sub>3</sub>), 1.87 (s, 3H, CH<sub>3</sub>), 1.86 (s, 9H, CH<sub>3</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1933(s), 1746(s).

# 2.2.2. Synthesis of $[(\eta^5 - C_5 M e_4 C_6 H_4 - 4 - X) Ru(CO)]_2$ [X = Me (6), Cl (7), OMe (8)]

Using a procedure similar to that described above, the reactions of ligands 2, 3, and 4 with Ru<sub>3</sub>(CO)<sub>12</sub> afforded complexes 6, 7, and 8 as orange-red crystals in 31%, 53%, and 96% yields, respectively. 6: M.p. 158-159 °C. Anal. Calc. for C<sub>36</sub>H<sub>38</sub>O<sub>4</sub>Ru<sub>2</sub>: C, 56.68; H, 5.20. Found: C, 56.37; H, 5.68%. <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.38 (d, 4H, J = 7.57 Hz, C<sub>6</sub>H<sub>4</sub>), 7.22 (d, 4H, J = 7.57 Hz, C<sub>6</sub>H<sub>4</sub>), 2.39 (s, 6H, C<sub>6</sub>H<sub>4</sub>Me), 1.98 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 1.87 (s, 9H, C<sub>5</sub>Me<sub>4</sub>), 1.86 (s, 3H, C<sub>5</sub>Me<sub>4</sub>), 1.76 (s, 9H, C<sub>5</sub>Me<sub>4</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1929(s), 1767(s). 7: M.p. 241 °C(dec.). Anal. Calc. for C<sub>34</sub>H<sub>32</sub>O<sub>4</sub>Cl<sub>2</sub>Ru<sub>2</sub>: C, 52.51; H, 4.15. Found: C, 52.05; H, 4.36%. <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.45–7.28 (m, 8H, C<sub>6</sub>H<sub>4</sub>), 2.00 (s, 9H, CH<sub>3</sub>), 1.85 (s, 12H, CH<sub>3</sub>), 1.77 (s, 3H, CH<sub>3</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1937(s), 1753 (s). 8: M.p. 230 °C (dec.). Anal. Calc. for C<sub>36</sub>H<sub>38</sub>O<sub>6</sub>Ru<sub>2</sub>: C, 56.24; H, 4.98. Found: C, 56.51; H, 4.65%. <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.43 (d, 4H, J = 8.57 Hz, C<sub>6</sub>H<sub>4</sub>), 6.95 (d, 4H, J = 8.57 Hz, C<sub>6</sub>H<sub>4</sub>), 3.85 (s, 6H, OMe), 1.87 (s, 12H, CH<sub>3</sub>), 1.76 (s, 12H, CH<sub>3</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1940(s), 1746(s).

# 2.2.3. Synthesis of $[(\eta^5 - C_5 Me_4 Ph)Fe(CO)(\mu - CO)]_2$ (9)

Using a procedure similar to that described above, the reaction of ligand 1 with Fe(CO)<sub>5</sub> in refluxing xylene afforded complex **9** as red crystals (85%). M.p. 195 °C (dec.). *Anal.* Calc. for  $C_{34}H_{34}O_4Fe_2$ : C, 66.04; H, 5.54. Found: C, 65.90; H, 5.60%. <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.41 (br s, 10H, C<sub>6</sub>H<sub>5</sub>), 1.63 (br s, 24H, CH<sub>3</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1915(s), 1765(s).

# 2.2.4. Synthesis of $[(\eta^5 - C_5 Me_4 C_6 H_4 - 4 - X)Fe(CO)]_2$ [X = Me (10), Cl (11), OMe (12)]

Using a procedure similar to that described above, the reactions of ligands **2**, **3**, and **4** with Fe(CO)<sub>5</sub> afforded complexes **10**, **11**, and **12** as red crystals in 23%, 42%, and 86% yields, respectively. **10**: M.p. 206 °C (dec.). *Anal.* Calc. for  $C_{36}H_{38}O_4Fe_2$ : C, 66.89; H, 5.93. Found: C, 66.46; H, 5.87%. <sup>1</sup>H NMR (300 M, in CDCl<sub>3</sub>): 7.34–7.18 (m, 8H,  $C_6H_4$ ), 2.39 (br s, 6H,  $C_6H_4$ Me), 1.88 (br s, 12H,  $C_5Me_4$ ),

1.73 (br s, 12H, C<sub>5</sub>Me<sub>4</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1923(s), 1769(s). **11**: M.p. 205 °C (dec.). *Anal.* Calc. for C<sub>34</sub>H<sub>32</sub>O<sub>4</sub>Cl<sub>2</sub>Fe<sub>2</sub>: C, 59.42; H, 4.69. Found: C, 59.39; H, 4.44%. <sup>1</sup>H NMR (300 M, in CDCl<sub>3</sub>): 7.39 (m, 8H, C<sub>6</sub>H<sub>4</sub>), 1.88 (s, 12H, CH<sub>3</sub>), 1.70 (s, 12H, CH<sub>3</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1927(s), 1771(s). **12**: M.p. 165 °C (dec.). *Anal.* Calc. for C<sub>36</sub>H<sub>38</sub>O<sub>6</sub>Fe<sub>2</sub>: C, 63.74; H, 5.65. Found: C, 63.51; H, 5.38%. <sup>1</sup>H NMR (400 M, in CDCl<sub>3</sub>): 7.37 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 6.98 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 3.85 (s, 6H, OMe), 1.67 (s, 12H, CH<sub>3</sub>), 1.63 (s, 12H, CH<sub>3</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1921(s), 1773(s).

# 2.2.5. Synthesis of $[(\eta^5 - C_5 M e_4 C_6 H_4 - 4 - X) Mo(CO)_2]_2$ [X = H (13), Cl (14)]

Using a procedure similar to that described above, the reactions of ligands **1** and **3** with  $Mo(CO)_3(MeCN)_3$  in refluxing xylene for 12 h afforded complexes **13** and **14** as dark red crystals in 52% and 49% yields, respectively. **13**: M.p. 169 °C (dec.). *Anal.* Calc. for  $C_{34}H_{34}O_4Mo_2$ : C, 58.46; H, 4.91. Found: C, 58.73; H, 4.85%. <sup>1</sup>H NMR (300 M, in CDCl<sub>3</sub>): 7.41–7.27 (m, 10H, C<sub>6</sub>H<sub>5</sub>), 2.01 (s, 12H, CH<sub>3</sub>), 1.93 (s, 12H, CH<sub>3</sub>). IR (KBr,  $\nu_{CO}$ , cm<sup>-1</sup>): 1871(s), 1825(s). **14**: M.p. 184 °C (dec.). *Anal.* Calc. for  $C_{34}H_{32}O_4Cl_2Mo_2$ : C, 53.21; H, 4.20. Found: C, 53.20; H, 4.20%. <sup>1</sup>H NMR (300 M, in CDCl<sub>3</sub>): 7.40–7.34 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 7.32–7.26 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 2.02 (s, 12H, CH<sub>3</sub>), 1.93 (s, 12H, CH<sub>3</sub>). IR (KBr,  $\nu_{CO}$ , cm<sup>-1</sup>): 1873(s), 1838(s).

# 2.2.6. Synthesis of $[(\eta^5 - C_5 M e_4 C_6 H_4 - 4 - X) Mo(CO)_3]_2$ [X = Me (15), OMe (16)]

Using a procedure similar to that described above, the reactions of ligands **2** and **4** with  $Mo(CO)_3(MeCN)_3$  in refluxing xylene for 12 h only afforded complexes **15** and **16** as dark red crystals in 32% and 51% yields, respectively. **15**: M.p. 188 °C (dec.). *Anal.* Calc. for  $C_{38}H_{38}O_6Mo_2$ : C, 58.32; H, 4.89. Found: C, 58.59; H, 4.60%. <sup>1</sup>H NMR (300 M, in CDCl<sub>3</sub>): 7.24–7.14 (m, 8H, C<sub>6</sub>H<sub>4</sub>), 2.39, 2.37, 2.36 (s, s, s, total 6H, C<sub>6</sub>H<sub>4</sub>Me), 2.17–1.90 (m, 24H, C<sub>5</sub>Me<sub>4</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1950(m), 1927(m), 1896(s), 1883(s), 1875(s) 1834(s). **16**: M.p. 157 °C (dec.). *Anal.* Calc. for C<sub>38</sub>H<sub>38</sub>O<sub>8</sub>Mo<sub>2</sub>: C, 56.03; H, 4.70. Found: C, 56.09; H, 4.81%. <sup>1</sup>H NMR (300 M, in CDCl<sub>3</sub>): 7.24–7.14 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 6.90–6.80 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 3.77–3.74 (m, 6H, OMe), 2.15–1.77 (m, 24H, CH<sub>3</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 2035(w), 1952(m), 1927(s), 1900(s), 1892(s), 1869(s).

# 2.2.7. Synthesis of $[(\eta^5 - C_5 M e_4 C_6 H_4 - 4 - X) Mo(CO)_2]_2$ [X = Me (17), OMe (18)]

Using a procedure similar to that described above, the reactions of ligands **2** and **4** with  $Mo(CO)_3(MeCN)_3$  in refluxing xylene for 48 h afforded complexes **17** (48%) and **18** (11%), in addition to the Mo–Mo single bonded complexes **15** (13%) and **16** (57%). **17**: M.p. 170 °C (dec.). *Anal.* Calc. for  $C_{36}H_{38}O_4Mo_2$ : C, 59.51; H, 5.27. Found: C, 59.41; H, 5.32%. <sup>1</sup>H NMR (300 M, in CDCl<sub>3</sub>): 7.29–7.17 (m, 8H, C<sub>6</sub>H<sub>4</sub>), 2.38 (s, 6H, C<sub>6</sub>H<sub>4</sub>Me), 2.02 (s, 12H, C<sub>5</sub>Me<sub>4</sub>), 1.94 (s, 12H, C<sub>5</sub>Me<sub>4</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>):

1867(s), 1832(s).**18**: M.p. 146 °C (dec.). *Anal.* Calc. for  $C_{36}H_{38}O_6Mo_2$ : C, 57.00; H, 5.05. Found: C, 57.48; H, 5.39%. <sup>1</sup>H NMR (300 M, in CDCl<sub>3</sub>): 7.22–7.14 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 6.91–6.80 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 3.76 (t, 6H, OMe), 2.16–1.83 (m, 24H, CH<sub>3</sub>). IR (KBr,  $v_{CO}$ , cm<sup>-1</sup>): 1929(s), 1881(s).

#### 2.2.8. The transformation of 15 to 17

Thermal treatment of complex **15** (0.37 g, 0.47 mmol) in refluxing xylene for 48 h afforded 0.21 g of complex **17** (62%), and 0.08 g (22%) of unreacted **15** was recovered.

# 2.3. Crystallographic studies

Crystals of complexes 5, 8, 9, and 12-17 suitable for X-ray diffraction were investigated with a BRUKER SMART 1000 CCD detector, using graphite monochromated Mo K $\alpha$  radiation ( $\omega$ -2 $\theta$  scans,  $\lambda = 0.71073$  Å) at room temperature. Semiempirical absorption corrections were applied for all complexes using the SADABS program [4]. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on  $F^2$  using the SHELxTL-97 program. All hydrogen atoms were generated geometrically (C-H bond lengths fixed at 0.93-0.98 Å), assigned appropriate isotropic thermal parameters and included in structure factor calculations. The crystal data and summary of the X-ray data collection for complexes 5, 8, 9, and 12-17 are presented in Tables 1 and 2. Selected bond lengths and angles are listed in Tables 3 and 4.

Table 1

# Crystal data and summary of the X-ray data collection for complexes 5, 8, 9, 12, and 13

#### 3. Results and discussion

#### 3.1. Complexes synthesis

When the ligands ( $C_5Me_4HC_6H_4X-4$ ) [X = H (1), Me (2), Cl (3), or OMe (4)] reacted with  $Ru_3(CO)_{12}$  or Fe(CO)<sub>5</sub> under refluxing xylene for 12 h, the corresponding Ru–Ru or Fe–Fe bonded dinuclear complexes 5 (52%), 6 (31%), 7 (53%), 8 (96%), 9 (85%), 10 (23%), 11 (42%), and 12 (86%) were obtained, respectively (Scheme 1).

When ligands 1 and 3 reacted with  $Mo(CO)_3(MeCN)_3$ under refluxing xylene for 12 h, the corresponding Mo– Mo triple bonded dinuclear complexes 13 (52%) and 14 (49%) were obtained, respectively (Scheme 2). But the reactions of ligands 2 and 4 with  $Mo(CO)_3(MeCN)_3$  under refluxing xylene for 12 h gave the corresponding Mo–Mo single bonded complexes 15 (32%) and 16 (51%) (Scheme 3). This indicated that the electron-donor groups Me and MeO at the 4-position of the phenyl are favorable to produce the Mo–Mo single bonded complexes, while H and the electron-withdrawing group Cl at the 4-position of the phenyl are favorable to produce the Mo–Mo triple bonded complexes.

If ligands 2 or 4 reacted with  $Mo(CO)_3(MeCN)_3$  under refluxing xylene for 48 h, the corresponding Mo–Mo triple bonded dinuclear complexes 17 (48%) or 18 (11%) were also obtained, in addition to the corresponding Mo–Mo single bonded complexes 15 (13%) or 16 (57%) (Scheme 4). The higher yield of 17 than those of 18 suggested that with a more stronger electron donor, it is more difficult

	5	8	9	12	13
Empirical formula	$C_{34}H_{34}O_4Ru_2$	C36H38O6Ru2	C34H34Fe2O4	C36H38Fe2O6	$C_{34}H_{34}Mo_2O_4$
Formula weight	708.75	768.80	618.31	678.36	698.50
<i>T</i> (K)	294(2)	294(2)	294(2)	294(2)	294(2)
Wavelength, $\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	rhombohedral	monoclinic	monoclinic	monoclinic
Space group	P2(1)/n	R3	P2(1)/c	P2(1)/c	P2(1)/n
a (Å)	8.3485(10)	28.316(3)	11.6220(15)	12.476(2)	8.660(4)
b (Å)	16.879(2)	28.316(3)	16.286(2)	8.1187(15)	16.632(8)
<i>c</i> (Å)	11.2425(14)	11.194(2)	15.294(2)	15.723(3)	10.786(5)
α (°)	90	90	90	90	90
β (°)	111.213(2)	90	90.670(2)	97.985(3)	108.824(7)
γ (°)	90	120	90	90	90
$V(\text{\AA}^3)$	1476.9(3)	7773.0(19)	2894.6(7)	1577.2(5)	1470.5(12)
Z	2	9	4	2	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.594	1.478	1.419	1.428	1.578
$\mu (\mathrm{mm}^{-1})$	1.059	0.916	1.039	0.965	0.890
<i>F</i> (000)	716	3510	1288	708	708
Crystal size (mm)	$0.28 \times 0.20 \times 0.20$	$0.38 \times 0.30 \times 0.20$	$0.32 \times 0.26 \times 0.20$	$0.34 \times 0.30 \times 0.24$	$0.30 \times 0.26 \times 0.24$
$\theta$ Range (°)	2.29-26.32	2.00-25.02	1.75-26.35	1.65-26.23	2.34-26.93
Reflections collected	8192	13284	16047	8424	8287
Independent reflections	3007	3057	5900	3167	3128
R <sub>int</sub>	0.0209	0.0286	0.0491	0.0334	0.0262
Parameters	185	208	370	204	186
Goodness-of-fit on $F^2$	1.066	1.158	1.003	1.035	1.077
$R_1, wR_2 [I > 2\sigma(I)]$	0.0206, 0.0481	0.0299, 0.0910	0.0379, 0.0805	0.0369, 0.0918	0.0233, 0.0556
$R_1$ , $wR_2$ (all data)	0.0275, 0.0511	0.0408, 0.0994	0.0814, 0.0969	0.0567, 0.1020	0.0324, 0.0601

Table 3

Table 2				
Crystal data and summar	y of the X-ray data	collection for 14	, 15, 16	, and 17

	14	15	16	17
Empirical formula	C <sub>34</sub> H <sub>32</sub> Cl <sub>2</sub> Mo <sub>2</sub> O <sub>4</sub>	C <sub>38</sub> H <sub>38</sub> Mo <sub>2</sub> O <sub>6</sub>	C <sub>38</sub> H <sub>38</sub> Mo <sub>2</sub> O <sub>8</sub>	C <sub>36</sub> H <sub>38</sub> Mo <sub>2</sub> O <sub>4</sub>
Formula weight	767.38	782.56	814.56	726.54
<i>T</i> (K)	294(2)	294(2)	294(2)	294(2)
Wavelength, $\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\overline{1}$	$P\overline{1}$	C2/c	$P\bar{1}$
a (Å)	9.2233(15)	11.7541(16)	14.728(3)	9.2051(16)
b (Å)	9.7323(15)	11.7617(15)	8.8049(16)	9.7436(17)
c (Å)	10.5699(17)	14.2953(19)	27.474(5)	10.6881(19)
α (°)	115.644(2)	71.163(2)	90	116.283(2)
$\beta$ (°)	106.228(2)	86.495(2)	92.999(3)	106.452(3)
γ (°)	96.772(2)	65.903(2)	90	96.391(3)
$V(Å^3)$	789.4(2)	1701.7(4)	3557.9(12)	792.5(2)
Z	1	2	8	1
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.614	1.527	1.521	1.522
$\mu ({\rm mm}^{-1})$	1.000	0.782	0.756	0.829
<i>F</i> (000)	386	796	1656	370
Crystal size (mm)	$0.30 \times 0.26 \times 0.18$	$0.22 \times 0.20 \times 0.20$	$0.28 \times 0.20 \times 0.08$	$0.22 \times 0.12 \times 0.10$
$\theta$ Range (°)	2.30-25.01	1.51-26.32	1.48-26.24	0.22-25.01
Reflections collected	4021	9641	9688	4019
Independent reflections	2759	6813	3573	2780
R <sub>int</sub>	0.0124	0.0203	0.0500	0.0138
Parameters	194	425	222	195
Goodness-of-fit on $F^2$	1.066	1.066	1.018	1.111
$R_1, wR_2 [I > 2\sigma(I)]$	0.0240, 0.0596	0.0515, 0.1228	0.0368, 0.0691	0.0218, 0.0562
$R_1$ , $wR_2$ (all data)	0.0283, 0.0625	0.0734, 0.1348	0.0788, 0.0794	0.0244, 0.0588

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Selected bond lengths	(Å) and bond angles (	<sup>o</sup> ) for 5, 8, 9, and 12

	<b>5</b> (M = Ru)	$8 \\ (\mathbf{M} = \mathbf{R}\mathbf{u})$	<b>9</b> (M = Fe)	12 (M = Fe)
M–M	2.7769(4)	2.7701(6)	2.5632(6)	2.5630(8
M–C(11) or C(21)	2.267(2)	2.251(4)	2.133(3)	2.115(2)
			2.128(3)	
M-C(12) or C(22)	2.308(2)	2.295(4)	2.104(3)	2.103(3)
			2.103(3)	
M-C(13) or C(23)	2.305(2)	2.283(4)	2.129(3)	2.148(3)
			2.138(3)	
M-C(14) or C(24)	2.286(2)	2.284(4)	2.161(3)	2.171(2)
			2.163(3)	
M-C(15) or C(25)	2.238(2)	2.238(4)	2.162(3)	2.165(3)
			2.166(3)	
M-CEN(1) <sup>a</sup>	1.929	1.918	1.759	1.763
			1.763	
PL(Cp)–PL(Ph) <sup>b</sup>	53.2	64.8	51.1	53.3
			49.9	

<sup>a</sup> PL, plane of the cyclopentadienyl (Cp) or phenyl ring (Ph).

<sup>b</sup> CEN: centroid of the cyclopentadienyl ring.

to produce the Mo–Mo triple bonded complex. Under refluxing xylene for 48 h, the Mo–Mo single bonded complex 15 could be transformed into the corresponding Mo–Mo triple bonded complex 17 in 62% yield (Scheme 5).

The <sup>1</sup>H NMR spectra of **5** and **7** are similar and show one group of multiplets for the phenyl protons and three groups of singlets for the four methyls protons, indicating the unsymmetrical structures in solution although **5** is  $C_i$ symmetrical in crystal state. The <sup>1</sup>H NMR spectra of **6**  and **8** are similar and show two doublets for the phenyl protons, four or two groups of singlets for the four methyls protons, and a singlet for the methyl or methoxyl protons, indicating the symmetrical structures in solution, consistent with the crystal structures. The electron-donor effect of Me and MeO groups seems to make the coupling split of the phenyl protons more clear, and the chemical shift difference between the two groups of doublets with a stronger electron-donor group MeO (0.48 ppm) is more larger than that with a methyl group (0.16 ppm).

The <sup>1</sup>H NMR spectra of the diruthenium and diiron complexes **5–12** are similar and show one or two groups of peaks for the phenyl protons, and one or two groups of singlets for the four methyl protons. Only the signal of phenyl protons in **12** with a stronger electron-donor group MeO was split into two groups ( $\Delta \delta = 0.39$  ppm). The IR spectra of diruthenium and diiron complexes **5–12** are very similar and all show a strong terminal carbonyl absorption at 1915–1940 cm<sup>-1</sup> and a strong bridging carbonyl absorption at 1746–1773 cm<sup>-1</sup>. This indicates that the electronic effect of the substituents has very less influence on the diruthenium and the diiron complexes, which agrees with the single crystal X-ray diffraction analysis results.

The <sup>1</sup>H NMR spectra of the Mo–Mo triple bonded complexes **13**, **14**, **17**, and **18** are similar and show one or two groups of peaks for the phenyl protons, one or two groups of peaks for the four methyl protons, and one group of peaks for the methyl or methoxyl protons. But the <sup>1</sup>H NMR spectra of the Mo–Mo single bonded complexes **15** and **16** are more complex. The signals of the methyl or

Table 4 Selected bond lengths (Å) and bond angles (°) for **13–17** 

	13	14	15 <sup>a</sup>	16	17
Мо–Мо	2.5376(11)	2.5285(5)	3.283	3.307	2.5254(5)
		· · · · · · · · · · · · · · · · · · ·	3.289		
Mo-C(11) or C(21)	2.335(2)	2.321(2)	2.311(5)	2.307(4)	2.324(2)
			2.316(5)		
Mo-C(12) or C(22)	2.337(2)	2.338(2)	2.373(5)	2.313(4)	2.329(2)
			2.381(5)		
Mo-C(13) or C(23)	2.377(2)	2.375(3)	2.421(5)	2.374(3)	2.367(2)
			2.434(5)		
Mo-C(14) or C(24)	2.377(2)	2.375(3)	2.379(5)	2.409(3)	2.370(2)
			2.394(5)		
Mo-C(15) or C(25)	2.340(3)	2.338(2)	2.316(5)	2.368(3)	2.337(2)
			2.318(5)		
Mo-CEN(1)	2.014	2.011	2.024	2.019	2.007
			2.034		
PL(Cp)-PL(Ph)	45.3	55.7	60.2	64.7	55.6
			51.4		

<sup>a</sup> Two independent molecules in an unit with a ratio of 1/1.



Scheme 1.



Scheme 2.

methoxyl protons were split into three singlets or a group of multiplets, indicating the presence of a restricted rotation along the Mo–Mo single bond in solution.



Scheme 3.

The Mo–Mo triple bonded complexes 13, 14, 17, and 18 show two strong terminal carbonyl absorptions, while the Mo–Mo single bonded complexes 15, and 16 show six strong terminal absorptions in their IR spectra. Complexes 16 and 18 with a stronger electron-donor group MeO show carbonyl absorptions at much higher wavenumber in their IR spectra than the corresponding analogues 15, and 13, 14, 17, respectively, indicating the larger influence of the electronic effect of substituents on the dimolybdenum complexes.

# 3.2. Crystal and molecular structures

The crystal structures of 5, 8, 9, and 12-17 were determined by X-ray diffraction analysis. The molecular structures of 5, 9, 13, and 16 are presented in Figs. 1-4, respectively.

Complexes **5** and **8** are diruthenium complexes and have similar structures. Similar to the cyclopentadienyl analogue *trans*- $[\eta^5$ -CpRu(CO)( $\mu$ -CO)]<sub>2</sub> [5], both the structures are



Scheme 4.

15 
$$\xrightarrow{\text{xylene}}$$
 17  
reflux, 48h  $\searrow$  17  
Scheme 5.

*trans* form and have  $C_i$  symmetry. The two cyclopentadienyl ring planes are parallel. Two carbonyls are bridged and two carbonyls are terminal. The Ru–Ru bond distances [2.7769(4) Å for **5**, 2.7701(6) Å for **8**] are slightly longer than that in *trans*-[ $\eta^5$ -CpRu(CO)( $\mu$ -CO)]<sub>2</sub> [2.735(2) Å] [5], [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(CO)( $\mu$ -CO)]<sub>2</sub> [2.752(1) Å] [6], and [( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>Et)Ru(CO)( $\mu$ -CO)]<sub>2</sub> [2.7584(5) Å] [7], respectively. This may be attributed to the bulky steric effect of the phenyl and four methyl groups. The Ru–C(Cp), Ru–CEN (CEN means centroid of the cyclopentadienyl ring), even the Ru–Ru distances (Table 3) in **8**, are slightly shorter than that in **5**, indicating that introduction of a strong electron-donor group MeO at the 4-position of the phenyl enhanced the interaction between Ru atom and the cyclopentadienyl ligand.

Complexes 9 and 12 have similar molecular structures although 12 is  $C_i$  symmetrical but 9 is not. The dihedral angle between the two cyclopentadienyl planes in 9 is only 0.3°, very close to parallel. They also have two bridge and two terminal carbonyls. The Fe–Fe bond distances [2.5635(6) Å for 9, 2.5630(8) Å for 12] are also slightly longer than that in analogous complexes *trans*-[CpFe-(CO)( $\mu$ -CO)]<sub>2</sub> [2.490 Å] [8], [( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>H)Fe(CO)( $\mu$ -CO)]<sub>2</sub>



Fig. 1. ORTEP diagram of 5. Thermal ellipsoids are shown at the 30% level.

[2.5480(9) Å] [9], and  $[(\eta^5-C_5Me_5)Fe(CO)(\mu-CO)]_2$ [2.560(1) Å] [10], due to the bulky steric effect of the phenyl and four methyl groups. The Fe–C(Cp), Fe–CEN, and Fe–Fe distances (Table 3) in 9 and 12 are very similar, indicating that the influence of electronic effect on the molecular structures of diiron complexes is very less, in

comparison with that of the diruthenium complexes.

level

Complexes **15** and **16** are Mo–Mo single bonded complexes with  $C_i$  symmetry. The Mo–Mo bond distances [3.283 Å for **15**, 3.307 Å for **16**] are also slightly longer than that in [ $\eta^5$ -CpMo(CO)<sub>3</sub>]<sub>2</sub> [3.235(1) Å] [11], [( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)-Mo(CO)<sub>3</sub>]<sub>2</sub> [3.251(1) Å] [12], and [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Mo(CO)<sub>3</sub>]<sub>2</sub> [3.278(10) Å] [13], due to the bulky steric effect of the phenyl and four methyl groups. The Mo–C(Cp) and Mo–CEN distances (Table 4) in **16** are slightly shorter than that in **15**, indicating the enhanced interaction between Mo atom and

Fig. 3. ORTEP diagram of **13**. Thermal ellipsoids are shown at the 30% level.

the cyclopentadienyl ligand due to the more stronger electron-donor effect of MeO than those of methyl group at the 4-position of the phenyl. This will also increase the intramolecular nonbonding interaction. And as a result, the Mo–Mo bond distance [3.307 Å] of **16** is longer than that of **15** [3.283 Å]. This may explain why the ligand with an electron donor group is difficult to produce the Mo–Mo triple bonded complex.

Complexes 13, 14, and 17 are Mo–Mo triple bonded complexes and all have  $C_i$  symmetry. The Mo–Mo bond distances [2.5374(10) Å for 13, 2.5286(5) Å for 13, 2.5253(5) Å for 17] are significantly longer than those of  $[\eta^{5}-CpMo(CO)_{2}]_{2}$  [2.448(1) Å] [14],  $[(\eta^{5}-C_{5}Me_{5})Mo(CO)_{2}]_{2}$ 

C(10)

0(4)

СŪ

C(8)



0(2)

C(17A)







[2.488(3) Å] [15], and  $[(\eta^5-C_9H_7)Mo(CO)_2]_2$  [2.500(1) Å] [16], also due to the bulky steric effect of the phenyl and four methyl groups. The Mo–C(Cp) and Mo–CEN distances (Table 4) in **13**, **14**, and **17** are similar. The Mo–Mo bond distance of **17** is slightly shorter than that of **13**. So for the ligand with an electron donor group to form the Mo–Mo triple bonded complex, it needs to shorten the long Mo–Mo single bond but to form the short Mo–Mo triple bond, more energy is needed. The dihedral angles between the cyclopentadienyl and phenyl ring planes in these complexes are between 45.3° and 64.8°, to further decrease the intramolecular non-bonding interaction.

In conclusion, the bulky steric effect of the phenyl and four methyl groups makes the M–M bond distances of the aryl-substituted tetramethylcyclopentadienyl dinuclear metal carbonyl complexes increase. Introduction of a strong electron-donor group at the 4-position of the phenyl enhanced the interaction between the metal atom and the cyclopentadienyl ligand, especially for the dimolybdenum complexes, in which the intramolecular nonbonding interaction was also increased, and the Mo–Mo triple bonded complexes were difficult to form.

# 4. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 292403–292411 for compounds **5**, **13**, **15**, **14**, **9**, **16**, **8**, **17**, and **12**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk of www: http://www.ccdc.cam.ac.uk.

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