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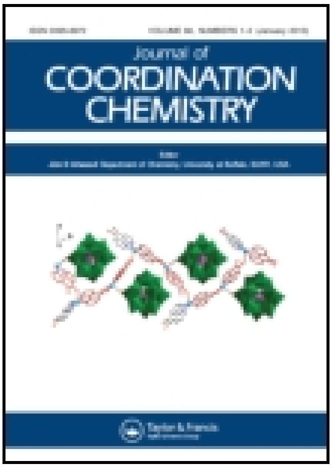

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Five dinuclear iron carbonyl complexes based on substituted tetramethylcyclopentadienyl ligands: synthesis and crystal structures

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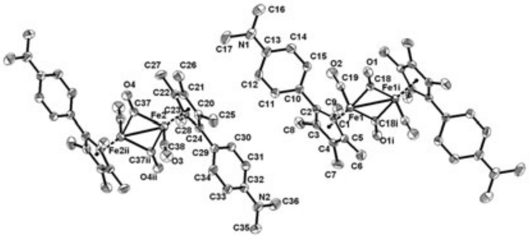

Thermal treatment of the substituted tetramethylcyclopentadienes [C_5Me_4HR] [R = *n*-propyl (**1**), *i*-propyl (**2**), cyclopentyl (**3**), cyclohexyl (**4**), and 4-NMe_2Ph (**5**)] with $Fe(CO)_5$ gave five new substituted tetramethylcyclopentadienyl dinuclear iron carbonyl complexes, [η^5-$C_5Me_4CH_2CH_2CH_3$]$_2Fe_2(CO)_4$ (**6**), [η^5-$C_5Me_4CH(CH_3)_2$]$_2Fe_2(CO)_4$ (**7**), [η^5-$C_5Me_4CH(CH_2)_4$]$_2Fe_2(CO)_4$ (**8**), [η^5-$C_5Me_4CH(CH_2)_5$]$_2$ Fe_2 $(CO)_4$ (**9**), and [(η^5-C_5Me_4)(4-NMe_2Ph)]$_2Fe_2(CO)_4$ (**10**). The new complexes were characterized by elemental analysis, IR, and ^{1}H NMR spectra. The molecular structures of **6**, **8**, **9,** and **10** were determined by X-ray single crystal diffraction.

Keywords: Substituted tetramethylcyclopentadienyl; Structure; X-ray single crystal diffraction; Iron carbonyl

1. Introduction

Complexes containing cyclopentadienyl (Cp) ligands have received attention, currently focused on the synthesis and study of metal–metal bonded transition metal complexes, due to their important role in catalytic processes [1–4]. The steric and electronic factors of Cp ring substituents influence catalytic activity. Cp groups have been among the most important ligands in organo-transition metal chemistry, forming a range of derivatives

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*Corresponding author. Email: linjin@mail.hebtu.edu.cn whose steric and electronic factors can be easily tailored by replacement of both the Cp fragment and ancillary ligands. Ligand modification opens access to new compounds and has a most profound effect on catalyst performance [5–8]. To obtain deeper insight into the steric and electronic factors of substituents on molecular structures and reactions of the corresponding Cp binuclear metal carbonyl complexes, in this article, we have prepared a series of Cp diiron complexes and determined their structures.

2. Experimental

2.1. *General considerations*

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Solvents were distilled from appropriate drying agents under an atmosphere of nitrogen before use. ^{1}H 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-$K\alpha$ ($\lambda = 0.071073$ nm) radiation. Elemental analyses were performed on a Vario EL III analyzer. The ligand precursors [C_5Me_4HR] [R = *n*-propyl (**1**), *i*-propyl (**2**), cyclopentyl (**3**), cyclohexyl (**4**), and 4-NMe$_2$Ph (**5**)] were prepared according to literature methods [9, 10].

2.2. *Preparation of [η^5-$C_5Me_4(CH_2)_2CH_3Fe(CO)(\mu$-$CO)]_2$ (6)*

A solution of $C_5Me_4H(CH_2)_2CH_3$ (0.820 g, 5 mM) (**1**) and $Fe(CO)_5$ (0.7 mL, 5 mM) in 25 mL of xylene was refluxed for 12 h. The solvent was removed under reduced pressure, and the residue was placed in an Al_2O_3 column (2.1 cm × 25 cm). Elution with petroleum ether/CH_2Cl_2 developed a dark-red band, which was collected and after concentration afforded **6** (0.320 g, 57.1% yield) as dark-red crystals. M.p. 181 °C. Anal. Calcd for $C_{28}H_{38}Fe_2O_4$: C, 61.11; H, 6.96. Found: C, 61.14; H, 6.92. ^{1}H NMR ($CDCl_3$): δ 2.20 (t, $J = 5.0$ Hz, 4H, CH_2), 1.77–1.87 (m, 24H, C_5Me_4), 1.27–1.30 (m, 4H, CH_2), 0.99 (t, $J = 11$ Hz, 6H, CH_3). IR (υ_{CO}, cm^{-1}): 1931(s), 1740(s).

2.3. *Preparation of [η^5-$C_5Me_4CH(CH_3)_2Fe(CO)(\mu$-$CO)]_2$ (7)*

Using similar procedure as described above, $C_5Me_4HCH(CH_3)_2$ (**2**) reacted with $Fe(CO)_5$ in refluxing xylene for 12 h; after chromatography and elution with petroleum ether/CH_2Cl_2, **7** was obtained (0.230 g, 77% yield) as dark-red solid. M.p. 125 °C. Anal. Calcd for $C_{28}H_{38}Fe_2O_4$: C, 61.11; H, 6.96. Found: C, 61.08; H, 6.93. ^{1}H NMR ($CDCl_3$): δ 2.62 (m, 2H, CH), 1.80–1.85 (m, 24H, C_5Me_4), 1.31 (d, $J = 5.5$ Hz, 12H, CH_3). IR (υ_{CO}, cm^{-1}): 1919(s), 1755(s).

2.4. *Preparation of [η^5-$C_5Me_4CH(CH_2)_4Fe(CO)(\mu$-$CO)]_2$ (8)*

Using similar procedure as described above, [$C_5Me_4HCH(CH_2)_4$] (**3**) reacted with $Fe(CO)_5$ in refluxing xylene for 12 h and after chromatography and elution with petroleum ether/

CH_2Cl_2, **8** was obtained (0.357 g, 74.5% yield) as black–red crystals. M.p. 216 °C. Anal. Calcd for $C_{32}H_{42}Fe_2O_4$: C, 63.81; H, 7.03. Found: C, 63.85; H, 7.07. ^1H NMR ($CDCl_3$): δ 2.72 (t, $J = 6.0$ Hz, 2H, CH), 1.81–2.03 (m, 24H, C_5Me_4), 1.24–1.55 (m, 16H, CH_2). IR (υ_{CO}, cm^{-1}): 1927(s), 1755(s).

2.5. *Preparation of [η^5-$C_5Me_4CH(CH_2)_5Fe(CO)(\mu$-$CO)]_2$ (9)*

Using similar procedure as described above, [$C_5Me_4HCH(CH_2)_5$] (**4**) reacted with $Fe(CO)_5$ in refluxing xylene for 12 h. After chromatography and eluting with petroleum ether/CH_2Cl_2, **9** was obtained (0.56 g, 89% yield) as red crystals. M.p. 204 °C. Anal. Calcd for $C_{34}H_{46}Fe_2O_4$: C, 64.78; H, 7.35. Found: C, 64.71; H, 7.32. ^1H NMR ($CDCl_3$): δ 2.42 (t, $J = 12$ Hz, 2H, CH), 1.84–1.94 (m, 18H, C_5Me_3), 1.22–1.37 (m, 6H, CH_3), 1.54–1.75 (m, 20H, CH_2). IR (υ_{CO}, cm^{-1}): 1925(s), 1747(s).

2.6. *Synthesis of [(η^5-C_5Me_4)(4-NMe_2Ph)$Fe(CO)(\mu$-$CO)]_2$ (10)*

Using similar procedure as described above, [C_5Me_4H(4-NMe_2Ph)] (**5**) reacted with Fe$(CO)_5$ in refluxing xylene for 12 h; after chromatography and elution with petroleum ether/CH_2Cl_2, **10** was obtained (0.347 g, 49.2% yield) as red crystals. M.p. 178 °C

Table 1. Crystal data and structure refinement parameters for **6**, **8**, **9** and **10**.

Complex	**6**	**8**	**9**	**10**
Empirical formula	$C_{28}H_{38}Fe_2O_4$	$C_{32}H_{42}Fe_2O_4$	$C_{34}H_{46}Fe_2O_4$	$C_{38}H_{44}Fe_2N_2O_4$
Formula weight	550.28	602.36	630.41	704.45
Temperature (*K*)	298(2)	298(2)	298(2)	298(2)
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	*P-1*	*Pbca*	*C2/c*	*P-1*
a (nm)	0.86576(13)	0.99851(19)	1.715(3)	1.11656(19)
b (nm)	0.86944(13)	1.6551(3)	0.8863(13)	1.2185(2)
c (nm)	0.95736(15)	1.7437(3)	2.269(3)	1.2455(2)
α (°)	82.207(2)	90	90	87.814(2)
β (°)	64.529(2)	90	101.51(2)	82.025(2)
γ (°)	83.051(2)	90	90	84.929(2)
V (nm^3)	0.64299(17)	2.8818(9)	3.380(9)	1.6710(5)
Z	1	4	4	2
F (000)	290	1272	1336	740
D_{Calcd} (g/cm^3)	1.160	1.388	1.239	1.400
Crystal dimensions (mm)	0.34 × 0.26 × 0.11	0.26 × 0.22 × 0.10	0.26 × 0.13 × 0.03	0.45 × 0.37 × 0.16
θ Range (°)	2.37–25.50	2.34–25.50	2.42–25.50	1.65–25.50
Reflections collected	3378	14,027	8551	8824
Independent reflections	2347	2683	3131	6103
R_{int}	0.0137	0.0398	0.0694	0.0203
Parameters	159	185	185	427
Goodness of fit on F^2	1.114	1.053	1.025	1.033
R_1, wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0338$, $\omega R_2 = 0.0941$	$R_1 = 0.0346$, $\omega wR_2 = 0.0892$	$R_1 = 0\ .0591$, $\omega R_2 = 0.1300$	$R_1 = 0.0446$, $\omega R_2 = 0.1090$
R_1, wR_2 (all data)	$R_1 = 0.0361$, $\omega R_2 = 0.0958$	$R_1 = 0.0429$, $\omega R_2 = 0.0948$	$R_1 = 0.0917$, $\omega R_2 = 0.1410$	$R_1 = 0.0588$, $\omega R_2 = 0.1179$
CCDC deposition no.	883,604	891,373	837,726	834,000

Complex **6**: $w = 1/[\sigma^2(F_o^2) + (0.0513\,p)^2 + 0.3306\,p]$, where $p = (F_o^2 + 2F_c^2)/3$.
Complex **8**: $w = 1/[\sigma^2(F_o^2) + (0.0456\,p)^2 + 1.3285\,p]$, where $p = (F_o^2 + 2F_c^2)/3$.
Complex **9**: $w = 1/[\sigma^2(F_o^2) + (0.0478\,p)^2 + 0.0000\,p]$, where $p = (F_o^2 + 2F_c^2)/3$.
Complex **10**: $w = 1/[\sigma^2(F_o^2) + (0.0649\,p)^2 + 0.0189\,p]$, where $p = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond distances (nm) and angles (°) for **6**, **8**, **9**, and **10**.

6		**8**		**9**		**10**	
Fe(1)–Fe(1i)	0.25543(7)	Fe(1)–Fe(1i)	0.25577(7)	Fe(1)–Fe(1i)	0.2555(3)	Fe(1)–Fe(1i)	0.25786(8)
C(1)–Fe(1)	0.2132(2)	C(1)–Fe(1)	0.2109(2)	C(1)–Fe(1)	0.2140(4)	Fe(2)–Fe(2ii)	0.25626(8)
C(2)–Fe(1)	0.2149(2)	C(2)–Fe(1)	0.2138(2)	C(2)–Fe(1)	0.2104(4)	C(1)–Fe(1)	0.2174(3)
C(3)–Fe(1)	0.2158(2)	C(3)–Fe(1)	0.2154(2)	C(3)–Fe(1)	0.2133(4)	C(3)–Fe(1)	0.2112(3)
C(14)–O(1)	0.1146(3)	C(16)–O(1)	0.1176(3)	C(16)–O(1)	0.1197(5)	C(18)–O(1)	0.1168(3)
C(13)–O(2)	0.1171(3)	C(15)–O(2)	0.1140(3)	C(17)–O(2)	0.1148(5)	C(19)–O(2)	0.1136(4)
C(2)–C(1)–Fe(1)	71.19(13)	C(2)–C(1)–Fe(1)	71.43(13)	C(2)–C(1)–Fe(1)	68.8(2)	C(2)–C(1)–Fe(1)	68.85(16)
C(3)–C(2)–Fe(1)	71.00(13)	C(3)–C(2)–Fe(1)	71.43(14)	C(3)–C(2)–Fe(1)	71.9(2)	C(21)–C(20)–Fe(2)	71.60(17)
O(2)–C(13)–Fe(1)	138.4(2)	O(1)–C(16)–Fe(1)	138.71(19)	O(1)–C(16)–Fe(1)	137.3(3)	O(1)–C(18)–Fe(1)	137.4(2)
Fe(1i)–C(13)–Fe(1)	82.94(10)	Fe(1i)–C(16)–Fe(1)	83.26(9)	Fe(1i)–C(16)–Fe(1)	83.75(18)	Fe(1i)–C(18)–Fe(1)	83.91(11)
C(14)–Fe(1)–Fe(1i)	96.74(8)	C(15)–Fe(1)–Fe(1i)	96.21(8)	C(17)–Fe(1)–Fe(1i)	96.32(17)	C(19)–Fe(1)–Fe(1i)	97.53(9)

(dec.). Anal. Calcd for $C_{38}H_{44}Fe_2N_2O_4$: C, 64.79; H, 6.30. Found: C, 64.75; H, 6.28. ^{1}H NMR ($CDCl_3$): 1.61 (s, 12H, C_5Me_4), 1.72 (s, 12H, C_5Me_4), 3.00 (s, 12H, N-CH_3), 6.78 (d, 4H, $J = 8.5$ Hz, C_6H_4), 7.32 (d, 4H, $J = 8.5$ Hz, C_6H_4). IR (υ_{CO}, cm^{-1}): 1929(s), 1911(s), 1767(s), 1751(s).

2.7. *Crystallographic studies*

Single crystals of **6**, **8**, **9,** and **10** suitable for X-ray diffraction were obtained from slow evaporation of hexane–dichloromethane solution. Data collections were performed on a Bruker Smart APEX diffractometer with graphite monochromated Mo-$K\alpha$ ($\lambda = 0.071073$ 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. The crystal data and summary of X-ray data collection are presented in table 1.

3. Results and discussion

3.1. *Synthesis of the complexes*

Upon thermal treatment of [C_5Me_4HR] [R = *n*-propyl (**1**), *i*-propyl (**2**), cyclopentyl (**3**), cyclohexyl (**4**), and 4-NMe_2Ph (**5**)] with $Fe(CO)_5$ in refluxing xylene, the corresponding Fe–Fe-bonded binuclear complexes **6–10** were obtained (scheme 1).

The ^{1}H NMR spectra of **6**–**10** show one or two groups of peaks for the four methyl protons. The ^{1}H NMR spectrum of **10** shows two group peaks for the phenyl protons. The IR spectra of **6**–**9** show similar patterns and display characteristic absorptions for terminal *v* (CO) and bridged *v*(CO), indicating that there are two terminal CO ligands which have the same chemical environment and two bridging CO ligands which have the same chemical environment. The solid state FT-IR spectrum of **10** unlike **6**–**9** shows two strong terminal carbonyl group absorptions at 1929 and 1911 cm^{-1} and two strong bridging carbonyl group absorptions at 1767 and 1751 cm^{-1}. This is consistent with the presence of two iron environments in the crystal structure as described below.

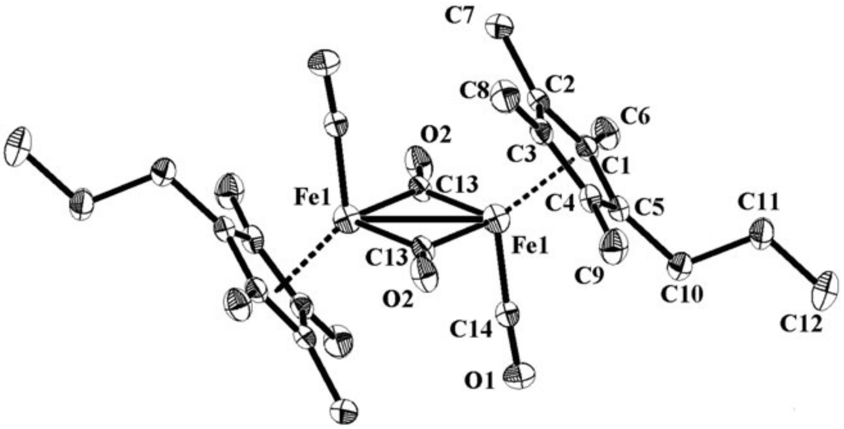


Figure 1. The molecular structure of **6**. Ellipsoids correspond to 30% probability. Hydrogens are omitted for clarity.

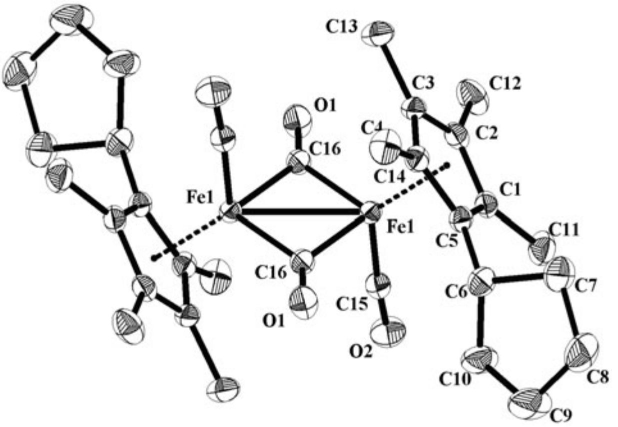


Figure 2. The molecular structure of **8**. Ellipsoids correspond to 30% probability. Hydrogens are omitted for clarity.

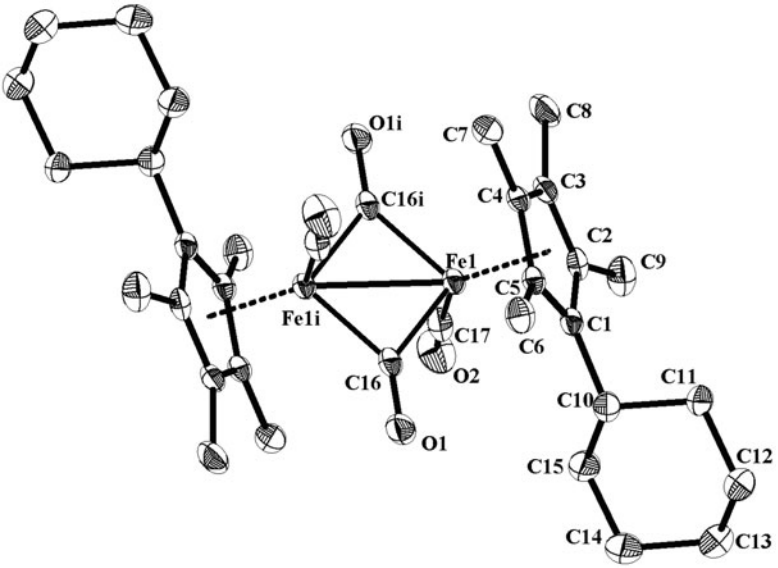


Figure 3. The molecular structure of **9**. Ellipsoids correspond to 30% probability. Hydrogens are omitted for clarity.

3.2. *Crystal structures*

Selected bond parameters for **6**, **8**, **9,** and **10** are listed in table 2 and their molecular structures are depicted in figures 1–4, respectively.

The structures of **6**, **8**, **9,** and **10** are similar. X-ray diffraction analyses confirm that all the complexes are symmetrical (*trans*) isomers. All the complexes are ditetramethylcyclopentadienyl-coordinated diiron complexes, in which two irons are coordinated by two tetramethylcyclopentadienyl ligands in η^5-bonding mode, each carrying a terminal

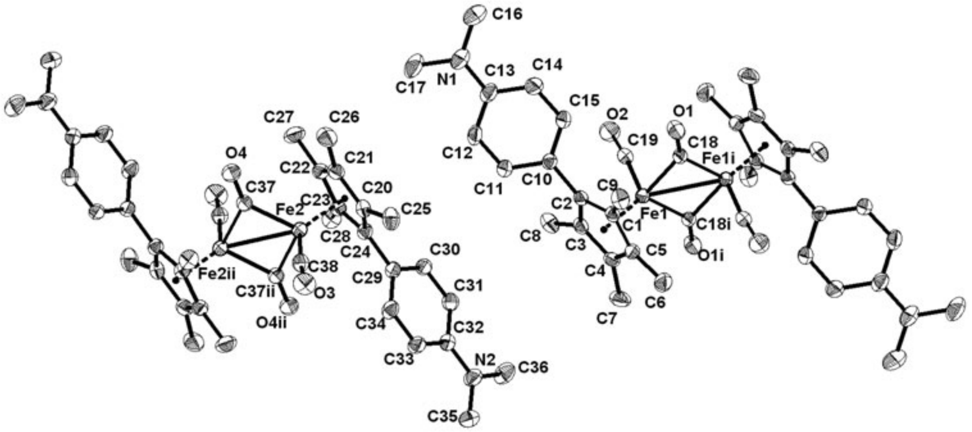
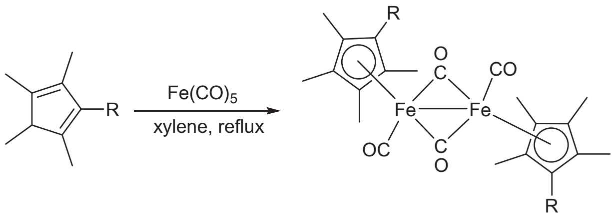


Figure 4. The molecular structure of **10**. Ellipsoids correspond to 30% probability. Hydrogens are omitted for clarity.



Scheme 1. Synthesis of **6–10**.

carbonyl, and bridged by two bridging carbonyl ligands. For **9**, the configuration of the cyclohexyl ring shows a very steady chair form. The Fe–Fe bond distances (0.25543(7) nm for **6**, 0.25577(7) nm for **8,** and 0.2555(3) nm **9,** respectively) are slightly longer than those in analogous complexes *trans*-[CpFe(CO)(μ-CO)]$_2$ (0.2490 nm) [11] and [(η^5-C_5Me_4H)Fe(CO)(μ-CO)]$_2$ (0.25480(9) nm) [12], due to the steric effect of the substituents on the Cp ring. Fe–Fe bond distances for **6**, **8,** and **9** are slightly shorter than that reported for *trans*-[(η^5-C_5Me_4Ph)Fe(CO)(μ-CO)]$_2$ (0.25632(6) nm) and *trans*-[(η^5-C_5Me_4PhOMe)Fe(CO)(μ-CO)]$_2$ (0.25630(8) nm) [13], which indicates that the steric effect of the ring substituents are smaller than that of the phenyl. The asymmetric unit of **10** contains two crystallographically independent half molecules. However, the differences between Fe(1) and Fe(2) environments are small. In Fe(1), the dihedral angle of five-membered ring and six-membered ring is 55.08°; in Fe(2), the dihedral angle of five-membered ring and six-membered ring is 58.07°. The Fe–Fe distances are 0.25786(8) nm (**1**) and 0.25626(8) (**2**) nm, respectively. Although there are two iron environments in the solid state, the ^{1}H NMR spectrum of **10** suggests that there is just one type of iron in solution. This indicates that they may exist as one form in solution; however, a rapid fluxional process cannot be excluded [14, 15].

4. Conclusion

Reactions of substituted tetramethylcyclopentadienes with $Fe(CO)_5$ in refluxing xylene gave five new diiron carbonyl complexes with four of their crystal structures obtained. The ligands coordinate to iron center by η^5-mode. Comparing the range of structures that have been determined for complexes of the type $Cp^*_2Fe_2(CO)_4$ (where Cp* = substituted cyclopentadienyl ligand), we find that the overall structure with two bridging and two terminal CO groups is present in all compounds. The Cp* ligands are *trans* in the dimeric structures in the solid state. Changing the substituents of Cp has some influence on the Fe–Fe bond length.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 883604, 891373, 837726, and 834000 for **6**, **8**, **9,** and **10**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44-1223-336033, E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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