Polyhedron 38 (2012) 7–14

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis of ortho-diferrocenylbenzene with cobalt clusters as reaction precursors: Crystal structure and electrochemical properties

Rui-Jun Xie, Li-Min Han *, Ning Zhu, Hai-Long Hong, Quan-Ling Suo, Peng Fu

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot 010051, PR China

ARTICLE INFO

Article history:
Received 29 November 2011
Accepted 2 February 2012
Available online 3 March 2012

Keywords:
Ortho-diferrocenylbenzene derivatives
Carbonyl cobalt
Electronic interaction

ABSTRACT

Five new ortho-diferrocenylbenzene derivatives, 1,2-diferrocenyl-4,5-dimethylbenzene (**2**), 1,2-diferrocenyl-4,5-diphenylbenzene (**3**), 1,2-diferrocenyl-4,5-ditrimethylsilylbenzene (**4**), 1,2-diferrocenyl-3,4,5,6-tetramethylbenzene(**5**), and 1,2-diferrocenyl-3,4,5,6-tetraphenyl -benzene (**6**), were synthesized through the cycloaddition reactions of alkynes with the cobalt cluster $Co_2(CO)_6(\mu^2$-alkyne) as reaction precursors, and characterized by elemental analysis, FT-IR, NMR, and MS. The molecular structures of compounds (**2**–**6**) were identified using single-crystal X-ray diffraction, and the electron interactions between two ferrocenyl units of each of the five compounds were investigated using cyclic voltammetric techniques. The results of electrochemical experiment indicated that the charge density of the aryl bridge is the key factor that influences electron communications between two ferrocenyl units.

1. Introduction

The intramolecular electron transfer processes of multi-ferrocenyl derivatives are highly interesting in the field of organometallic electrochemistry [1–6]. In the frame of a general study of such processes, we had examined the factors that affect the charge transfer processes of aliphatic carbon-bridged biferrocenyl derivatives, and found that the charge density of the carbon bridge was a key factor for intramolecular electron transfers [7]. Determining the phenomena that should be present in aromatic-bridged diferrocenyl derivatives is the backbone of this research on the synthesis and electrochemistry of aromatic-bridged ortho-diferrocenylbenzene derivatives.

Diferrocenylbenzene derivatives are prepared via the Nigishi or Suzuki reactions. A typical synthesis, for instance, involves the Nigishi reaction of dihalobenzenes and ferrocenylzinc chloride with the catalyst of $Pd(PPh_3)_4$ form para-diferrocenylbenzene [8]; para-diferrocenylbenzene and meta-diferrocenylbenzene are synthesized through the Suzuki reaction of ferrocenylboronic acid and dihalobenzenes in a dimethoxyethane/aqueous NaOH mixture solution, using $PdCl_2$(dppf) as a catalyst [9,10]. Unfortunately, these cross-coupling reactions are not suitable for the synthesis of ortho-diferrocenylbenzene, and the highest yield of ortho-diferrocenylbenzene reported for these methods is only 8% [11]. Thus, it is necessary to devise a simple and efficient method of preparing ortho-diferrocenylbenzene derivatives.

Krüerke and Hübel utilized the cobalt carbonyl cluster $[Co_2(CO)_8]$-catalyzed cycloaddition reactions of alkynes to prepare substituted benzene derivatives, and described a logical and rational catalytic reaction mechanism (see Scheme 1) [12]. Based on this mechanism, as well our previous work on the synthesis of cobalt clusters [13–15], we modified Krüerke's one-step synthesis method and turned it into a two-step method: The cobalt cluster $[Co_2(CO)_6(\mu^2$-alkyne)] was synthesized in the first step, and then used as a reaction precursor in the cycloaddition reaction with other alkynes in the second step. This synthetic method could conveniently control the position, type and number of substituted ferrocenyl groups in the benzene ring in the resulting products.

In this paper, the position-controlled synthesis of several ortho-diferrocenylbenzenes was realized for the first time using $Co_2(CO)_6(\mu^2$-diferrocenyl acetylene) and $Co_2(CO)_6(\mu^2$-2-butyne) as precursors. Five new ortho-diferrocenylbenzene derivatives were prepared via our two-step synthesis method, and the effect of the aromatic bridge on the electron communication processes between two ferrocenyl units is investigated using cyclic voltammetry.

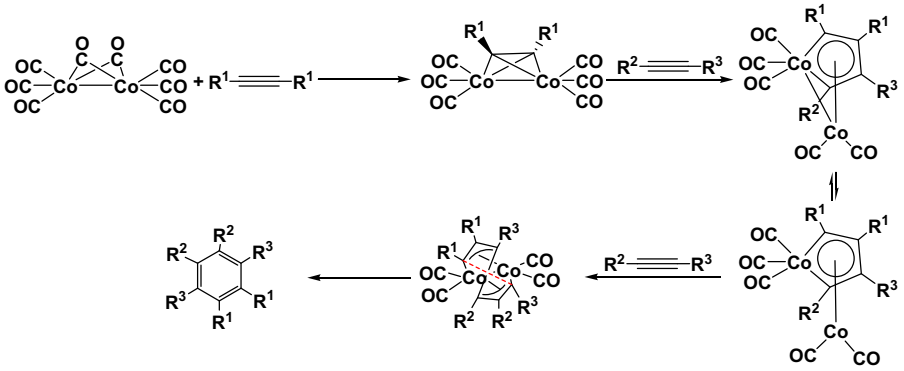
2. Experimental

2.1. General procedures

All operations were carried out under an atmosphere of purified argon using standard Schlenck techniques. Solvents were dried and distilled according to standard procedures. Reactions were monitored by thin layer chromatography (TLC). $Co_2(CO)_8$, $HC{\equiv}CC_6H_5$, $HC{\equiv}CSi(CH_3)_3$, $H_3CC{\equiv}CCH_3$ and $H_5C_6C{\equiv}CC_6H_5$ were obtained

* Corresponding author. Tel.: +86 471 6576137; fax: +86 471 6575722.
E-mail address: hanlimin_442@hotmail.com (L.-M. Han).

0277-5387/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2012.02.018



Scheme 1. The mechanism of $Co_2(CO)_8$-catalyzed cycloaddition of alkynes.

from Alfa-Asia Chem. Ferrocenylacetylene and 1,2-diferrocenylacetylene were prepared using methods found in the literature [16,17]. Infrared (IR) spectra were measured on a Nicolet FT-IR spectrometer using KBr pellets. Elemental analyses were carried out on an Elementar var III-type analyzer. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ were recorded on a Jeol-Jnm-Al 500 FT-MHz spectrometer. The mass spectra were determined using a Micromass LCT instrument. The crystal structures of $Co_2(CO)_6(\mu^2$-diferrocenylacetylene) (**1**), 1,2-diferrocenyl-4,5-dimethylbenzene (**2**), 1,2-diferr ocenyl-4,5-diphenylbenzene (**3**), 1,2-diferrocenyl-4,5-ditrimethylsilylbenzene (**4**), 1,2-diferrocenyl-3,4,5,6-tetramethylbenzene (**5**), and 1,2-diferrocenyl-3,4,5,6-tetraphenyl-benzene (**6**) were determined on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Data were collected using the φ and ω scan techniques. The structures were solved using direct methods and expanded using Fourier techniques. An absorption correction based on the SADABS was applied. Structure solution and refinement were performed using SHELXSL-97 software.

Cyclic voltammetry was performed on a CHI 760C electrochemical analyzer, using a platinum disk as the working electrode; the electrode surface was polished with 0.05 μm alumina prior to each run. The reference electrode was an Ag/AgCl electrode, and the auxiliary electrode was a coiled platinum wire. The solvent was composed of dichloromethane and acetonitrile (1:1, v/v) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte. The scan rate was 0.1 V/s. The different concentration (3.8 mmol/L for **2**, 6.0 mmol/L for **3**, 3.2 mmol/L for **4**, 6.1 mmol/L for **5** and 2.3 mmol/L for **6**) were used for the cyclic voltammetries. Oxygen was purged from the one-compartment cell before each electrochemical run.

2.2. Synthesis of $Co_2(CO)_6(\mu^2$-diferrocenylacetylene) (**1**)

A dioxane solution of $Co_2(CO)_8$ (123 mg, 0.36 mmol) and diferrocenylacetylene (142 mg, 0.36 mmol) was stirred for 2 h at room temperature, after which the solvent was removed under reduced pressure. The residue was dissolved in a minimal amount of hexane and subjected to chromatographic separation on a silica gel column (2.0 cm × 30 cm). Elution with hexane afforded a dark green band **1**. Crystals of **1** were obtained by recrystallizing solid **1** from hexane at −20 °C. Yield: 229 mg (94%). M.p. 141 °C. *Anal.* Calc. for $C_{28}H_{18}Fe_2Co_2O_6$: C, 49.46; H, 2.67. Found: C, 49.32; H, 2.86%. IR (KBr, cm^{-1}): 3089 ν(CH, Cp), 2058, 1986 ν(CO), 1103, 1002 δ(CH, Cp), 816 λ(CH, Cp). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.063–4.616 (m, 18H, Cp–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 69.3, 69.9, 70.2, 86.2, 92.9 (Cp), 199.9 (CO) ppm. MS (ESI) *m/z*: 680.0 [M]$^+$.

2.3. Synthesis of 1,2-diferrocenyl-4,5-dimethylbenzene (**2**)

$Co_2(CO)_6(\mu^2$-2-butyne) (109 mg, 0.32 mmol) and ferrocenylacetylene (134 mg, 0.64 mmol) were dissolved in 10 mL dioxane at room temperature. The solution was stirred for 3 h at 70 °C and then cooled to room temperature. The solvent was removed under vacuum. The residues were dissolved in a minimal amount of CH_2Cl_2 and subjected to chromatographic separation on a neutral alumina column (2.0 cm × 30 cm). Elution with a mixture of hexane and CH_2Cl_2 (3:1, v/v) afforded an orange band **2**. Crystals of **2** were obtained by recrystallizing solid **2** from a mixture of hexane and CH_2Cl_2 at −20 °C. Yield: 94 mg (63%). M.p. 155 °C. *Anal.* Calc. for $C_{28}H_{26}Fe_2$: C, 70.92; H, 5.53. Found: C, 70.68; H, 5.16%. IR (KBr cm^{-1}): 3089 ν(CH, Cp), 3058 ν(CH, Ph), 2958, 2861 ν(CH, CH_3), 1599, 1501 ν(CC, Ph). 1108, 1002 δ(CH, Cp, monosubstituted ferrocene) [18,19], 816 λ(CH, Cp). ^{1}H NMR (500 MHz $CDCl_3$): δ 2.33 (s, 6H, CH_3), 3.99–4.19 (m, 18H, Cp–H), 7.53 (s, 2H, Ph–H) ppm. ^{13}C NMR (125 MHz $CDCl_3$): δ 19.7 (CH_3), 66.8, 67.2, 69.3, 69.5, 69.6, 70.7, 71.2, 72.9, 88.0 (Cp), 132.7, 134.1, 134.7 (benzene) ppm. MS (ESI) *m/z*: 474.2 [M$^+$].

2.4. Synthesis of compounds **3**–**6**

The synthetic method for the preparation of **3**–**6** is very similar. $Co_2(CO)_6(\mu^2$-diferrocenylacetylene) and corresponding alkynes were dissolved in 10 mL dioxane at room temperature. The mixture solution was stirred for 3 h at 70 °C and then cooled to room temperature (the mixture solution was stirred for 1 h at 0 °C and for 3 h at 70 °C and then cooled to room temperature for the synthesis of compound **5**), after which the solvent was removed under vacuum. The residues were dissolved in a minimal amount of CH_2Cl_2 and subjected to chromatographic separation on a neutral alumina column (2.0 cm × 30 cm). Elution with a mixture of hexane and CH_2Cl_2 afforded an orange band. Crystals were obtained by recrystallizing solid from a mixture of hexane and CH_2Cl_2 at −20 °C.

2.4.1. Compound **3**

$Co_2(CO)_6(\mu^2$-diferrocenylacetylene) (96 mg, 0.14 mmol) and HC≡CC_6H_5 (0.03 mL, 0.28 mmol) were used as starting material. After finished the reaction, a mixture of hexane and CH_2Cl_2 (3:1, v/v) was used for eluent in the purification process. Yield: 54 mg (64%). M.p. 290 °C. *Anal.* Calc. for $C_{38}H_{30}Fe_2$: C, 76.28; H, 5.05. Found: C, 76.06; H, 4.89%. IR (KBr cm^{-1}): 3081 ν(CH, Cp), 3023 ν(CH, Ph); 1602, 1484 ν(CC, Ph), 1104, 1069 δ(CH, Cp), 812 λ(CH, Cp), 762, 699 λ(CH, Ph). ^{1}H NMR (500 MHz $CDCl_3$): δ 3.57–4.32 (m, 18H, Cp–H), 7.09–7.62 (br, 10H, substituted benzene), 7.85 (s, 2H, central phenyl ring) ppm. ^{13}C NMR (500 MHz $CDCl_3$): δ 67.4,

69.5, 70.7, 87.2 (Cp), 126.5, 126.8, 128.1, 129.7, 133.6, 136.6, 137.8, 141.4 (benzene) ppm. MS (ESI) *m/z*: 598.3 [M^+].

*2.4.2. Compound **4***

$Co_2(CO)_6(\mu^2$-diferrocenylacetylene) (95 mg, 0.14 mmol) and $HC{\equiv}CSi(CH_3)_3$ (0.04 mL, 0.30 mmol) were used as starting material. After finished the reaction, a mixture of hexane and CH_2Cl_2 (3:1, v/v) was used for eluent in the purification process. Yield: 53 mg (65%). M.p. 220 °C. *Anal.* Calc. for $C_{32}H_{38}Fe_2Si_2$: C, 65.09; H, 6.49. Found: C, 65.14; H, 6.38%. IR (KBr cm^{-1}): 3089 *v*(CH, Cp), 3054 *v*(CH, Ph), 2953, 2898, 2848 *v*(CH, CH_3), 1633, 1528 *v*(CC, Ph), 1248 *δ*(CH, TMS), 1108, 1003 *δ*(CH, Cp), 839 *v*(SiC, TMS), 812 *λ*(CH, Cp), 754 *λ*(CH, Ph). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 0.47 (s, 18H, TMS–H), 4.04–4.14 (m, 18H, Cp–H), 8.08 (s, 2H, Ph–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 2.3 (CH_3), 67.5, 69.6, 70.9, 87.9 (Cp), 136.6, 138.8, 142.4 (benzene) ppm. MS (ESI) *m/z*: 590.1 [M^+].

*2.4.3. Compound **5***

$Co_2(CO)_6(\mu^2$-diferrocenylacetylene) (106 mg, 0.16 mmol) and $H_3CC{\equiv}CCH_3$ (0.03 mL, 0.35 mmol) were used as starting material. After finished the reaction, a mixture of hexane and CH_2Cl_2 (2:1, v/v) was used for eluent in the purification process. Yield: 55 mg (68%). M.p. 275 °C. *Anal.* Calc. for $C_{30}H_{30}Fe_2$: C, 71.74; H, 6.02. Found: C, 71.61; H, 6.28%. IR (KBr cm^{-1}): 3089 *v*(CH, Cp), 2958, 2878 *v*(CH, CH_3), 1602, 1498 *v*(CC, Ph), 1104, 1053 *δ*(CH, Cp), 816 *λ*(CH, Cp). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 2.317 (s, 6H, CH_3), 2.934 (s, 6H, CH_3), 3.766–4.049 (m, 18H, Cp–H) ppm. ^{13}C NMR (125 MHz $CDCl_3$): *δ* 17.04, 18.87 (CH_3), 66.4, 69.1, 73.3, 89.9 (Cp), 133.0, 134.2, 134.7 (benzene) ppm. MS(ESI) *m/z*: 502.2 [M^+].

*2.4.4. Compound **6***

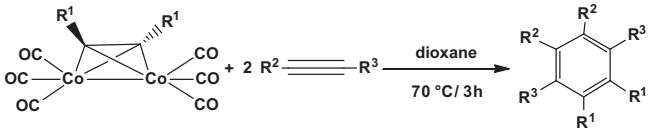
$Co_2(CO)_6(\mu^2$-diferrocenylacetylene) (103 mg, 0.15 mmol) and $H_5C_6C{\equiv}CC_6H_5$ (54 mg, 0.30 mmol) were used as starting material. After finished the reaction, a mixture of hexane and CH_2Cl_2 (2:1, v/v) was used for eluent in the purification process. Yield: 65 mg (58%). M.p. 302 °C. *Anal.* Calc. for $C_{50}H_{38}Fe_2$: C, 80.02; H, 5.10. Found: C, 79.87; H, 5.35%. IR (KBr cm^{-1}): 3089 *v*(CH, Cp), 3046, 3015 *v*(CH, Ph), 1633, 1524 *v*(CC, Ph), 1108, 1003 *δ*(CH, Cp), 812 *λ*(CH, Cp), 762, 699 *λ*(CH, Ph). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 3.681–3.922 (m, 18H, Cp–H), 6.645–7.256 (m, 20H, Ph–H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 67.3, 69.5, 73.4 (Cp), 124.9, 126.5, 126.6, 126.7, 131.6, 133.2, 138.0, 138.7, 140.7, 141.0, 141.1 (benzene) ppm. MS (ESI) *m/z*: 750.0 [M^+].

3. Results and discussion

*3.1. Synthetic methods of compounds (**2**–**6**)*

Transitional-metal-catalyzed cycloaddition reactions are widely used to synthesize various substituted benzene derivatives. For example, Fe, Co, Ni, Pd, Ru, Rh, and Zr have been used to catalyze the cycloaddition reactions of alkynes. In this work, we prepared ortho-diferrocenylbenzenes using the following procedure. First, we performed a $Co_2(CO)_8$-catalyzed cycloaddition reaction using diferrocenylacetylene and diphenylacetylene as reactants to prepare substituted benzene. Unfortunately, hexaphenylbenzene was produced at a yield of 76%, and no ferrocenylbenzene was obtained (see Supplementary Materials). This result could be attributed to the steric hindrance effect of ferrocenyl units [20]. After changing our synthetic strategy, we produced $Co_2(CO)_6(\mu^2$-diferrocenylacetylene), which then be used as a precursor to react with $HC{\equiv}CC_6H_5$ or $HC{\equiv}CSi(CH_3)_3$. Ortho-diferrocenyl compounds **3** and **4** were obtained with high yields (64% and 65%, respectively), and the trimethylsilyl and phenyl groups were located at the 4 and 5 positions of the central phenyl ring due to the steric hindrance effect of ferrocenyl. These results indicate that the synthesis method we selected was suitable for constructing ortho-diferrocenylbenzene derivatives, and the stereoselectivity of the 4 and 5 positions appeared to be a common law for this synthetic strategy. Guided by the experiments above, we synthesized $Co_2(CO)_6(\mu^2$-2-butyne) and used it as a precursor to react with ferrocenylacetylene. The ortho-diferrocenyl **2** was obtained (see Table 1). The experimental results showed that this synthetic strategy we selected was highly efficient for the synthesis of ortho-diferrocenylbenzene derivatives. Moreover, compounds **5** and **6**, which have large steric hindrance, could be prepared successfully by our synthetic method. This further proved the effectiveness of our synthetic strategy for the ortho-diferrocenylbenzene derivatives.

Table 1
Synthesis of ortho-diferrocenylbenzene with cobalt clusters as reaction precursors.



Compounds	R^1	R^2	R^3
2	CH_3	Fc	H
3	Fc	Ph	H
4	Fc	$Si(CH_3)_3$	H
5	Fc	CH_3	CH_3
6	Fc	Ph	Ph

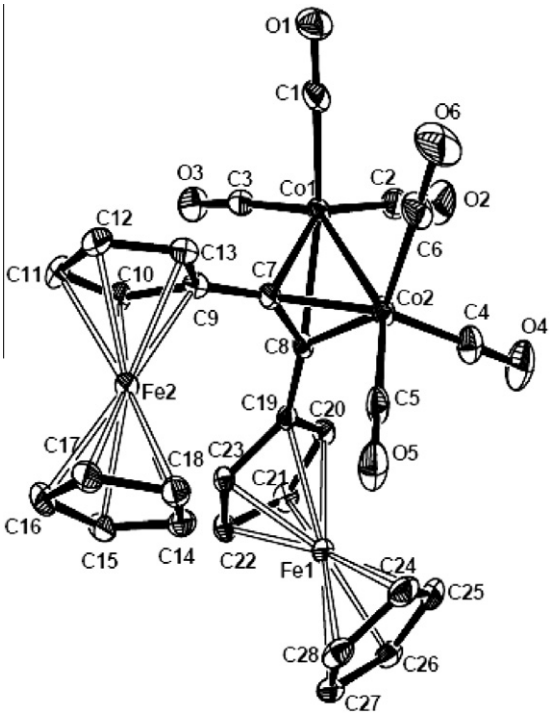


Fig. 1. The molecular structure of compound **1**. The H atoms have been omitted for clarity.

*3.2. Characterization and molecular structure of complex (**1**)*

The molecular structure and IR spectra of $Co_2(CO)_6(\mu^2$-diferrocenylacetylene) were similar to those of our previously reported structures [$Co_2(CO)_6(\mu^2$-R′–C≡C–R)] [14]. An approximately tetrahedral (μ^2-alkyne) dicobalt moiety was bound to the cyclopentadiene rings of two ferrocenyls (see Fig. 1). The CO ligands

Table 2
Crystal data and relevant structural parameters for compounds (**1–6**).

Compounds	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{28}H_{18}Co_2Fe_2O_6$	$C_{28}H_{26}Fe_2$	$C_{38}H_{30}Fe_2$	$C_{32}H_{38}Fe_2Si_2$	$C_{30}H_{30}Fe_2$	$C_{50}H_{38}Fe_2$
Formula weight	679.98	474.19	598.32	590.50	502.24	750.17
Temperature (K)	173(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	$P2(1)/n$	$C2/c$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a (Å)	15.598(3)	12.606(11)	10.0480(16)	6.1995(2)	10.672(5)	18.3617(19)
b (Å)	9.9595(17)	19.884(17)	22.584(4)	12.7645(5)	11.382(5)	15.8469(16)
c (Å)	17.267(3)	9.859(15)	12.425(2)	18.8821(7)	11.809(6)	14.0760(15)
α (°)	90.00	90.00	90.00	89.231(2)	63.639(8)	90.00
β (°)	108.868(3)	115.031(10)	94.016(3)	85.928(2)	82.366(9)	98.250(7)
γ (°)	90.00	90.00	90.00	78.566(2)	63.099(8)	90.00
Volume (Å^3), Z	2538.2(8), 4	2239(4), 4	2812.6(8), 4	1460.86(9), 2	1142.0(9), 2	4053.4(7), 4
Density (Mg/m^3)	1.779	1.407	1.413	1.342	1.461	1.369
μ(mm^{-1})	2.447	1.307	1.058	1.094	1.286	0.883
F(000)	1360	984	1240	620	524	1728
Crystal size (mm)	0.50 × 0.48 × 0.42	0.20 × 0.05 × 0.05	0.20 × 0.05 × 0.05	0.30 × 0.20 × 0.10	0.20 × 0.05 × 0.05	0.15 × 0.10 × 0.10
θ range (°)	1.53–30.01	2.06–27.94	1.80–28.40	1.63–27.68	1.93–25.00	1.71–27.94
Limiting indices	$-21 \leqslant h \leqslant 20$ $-14 \leqslant k \leqslant 14$ $-18 \leqslant l \leqslant 24$	$-15 \leqslant h \leqslant 15$ $-26 \leqslant k \leqslant 25$ $-7 \leqslant l \leqslant 12$	$-13 \leqslant h \leqslant 13$ $-25 \leqslant k \leqslant 30$ $-15 \leqslant l \leqslant 14$	$-8 \leqslant h \leqslant 8$ $-16 \leqslant k \leqslant 15$ $-24 \leqslant l \leqslant 24$	$-12 \leqslant h \leqslant 12$ $-11 \leqslant k \leqslant 13$ $0 \leqslant l \leqslant 14$	$-21 \leqslant h \leqslant 24$ $-20 \leqslant k \leqslant 16$ $-18 \leqslant l \leqslant 18$
Reflections collected	25 723	6784	18 100	24 702	3930	18 095
Independent reflections	7206	2592	6874	6665	3930	4754
Completeness to θ	97.4%	96.0%	97.2%	97.6%	97.6%	97.7%
Maximum and minimum	0.358/0.306	0.937/0.925	0.948/0.938	0.8985/0.7349	0.938/0.926	0.915/0.899
Data/restraints/parameters	7206/0/344	2592/0/137	6874/0/361	6665/15/331	3930/0/294	4754/0/249
Goodness-of-fit on F^2	1.209	1.069	0.948	0.995	1.018	1.036
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0567 wR_2 = 0.1142	R_1 = 0.0312 wR_2 = 0.0819	R_1 = 0.0540 wR_2 = 0.1017	R_1 = 0.0558 wR_2 = 0.1263	$R1$ = 0.0928 $wR2$ = 0.2429	R_1 = 0.0539 wR_2 = 0.1590
R indices (all data)	R_1 = 0.0622 wR_2 = 0.1171	R_1 = 0.0392 wR_2 = 0.0859	R_1 = 0.1332 wR_2 = 0.1268	R_1 = 0.1267 wR_2 = 0.1529	$R1$ = 0.1424 $wR2$ = 0.2685	R_1 = 0.0990 wR_2 = 0.1863
Largest differences in peak and hole (e Å^{-3})	0.452/−0.613	0.397/−0.208	0.471/−0.378	0.448/−0.653	1.014/−1.045	0.873/−0.667

Table 3
Selected bond lengths (Å) of compounds (**1–6**).

1		**2**		**3**		**4**		**5**		**6**	
C7–C8	1.351(5)	C1–C1^2	1.426(4)	C1–C2	1.389(5)	C1–C2	1.392(5)	C1–C2	1.447(15)	C1–C1^2	1.401(7)
C7–C9	1.448(5)	C1^2–C2^2	1.409(3)	C2–C3	1.400(4)	C2–C3	1.392(5)	C2–C3	1.380(16)	C1^2–C2^2	1.423(4)
C8–C19	1.447(4)	C2^2–C3^2	1.396(3)	C3–C4	1.391(5)	C3–C4	1.402(5)	C3–C4	1.379(18)	C2^2–C3^2	1.400(5)
C7–Co1	1.992(3)	C3^2–C3	1.412(4)	C4–C5	1.407(5)	C4–C5	1.444(5)	C4–C5	1.457(19)	C3^2–C3	1.400(7)
C7–Co2	1.959(3)	C3–C2	1.396(3)	C5–C6	1.386(4)	C5–C6	1.388(5)	C5–C6	1.365(18)	C3–C2	1.400(5)
C8–Co1	1.974(3)	C1–C2	1.409(3)	C1–C6	1.389(4)	C6–C1	1.397(5)	C6–C1	1.414(16)	C2–C1	1.423(4)
C8–Co2	1.978(3)	C1–C4	1.495(3)	C1–C7	1.485(4)	C1–C13	1.482(5)	C1–C7	1.497(16)	C1–C4	1.496(4)
Co1–Co2	2.4567(7)	C1^2–C4^2	1.495(3)	C2–C17	1.482(5)	C2–C23	1.479(5)	C2–C17	1.501(16)	C1^2–C4^2	1.496(4)
		C3–C14	1.517(3)	C4–C27	1.486(4)	C4–Si1	1.882(4)	C3–C27	1.523(17)	C2–C14	1.472(5)
		C3^2–C14^2	1.517(3)	C5–C33	1.491(5)	C5–Si2	1.891(4)	C4–C28	1.526(19)	C2^2–C14^2	1.472(5)
								C5–C29	1.459(19)	C3–C20	1.496(5)
								C6–C30	1.518(18)	C3^2–C20^2	1.496(5)

coordinated with Co atoms are terminal (vide infra). Each of the cobalt atoms carries an 'axial' CO and two 'pseudoequatorial' CO ligands, as indicated by the corresponding bond angles. The Co–Co bond distance is 2.4567(7) Å and the C–C bond length of the C_2Co_2 fragment is 1.351(5) Å, which are typical for alkyne dicobalt complexes [21]. The well-defined molecular structure of **1** is a good precondition for the synthesis of compounds (**3–6**).

3.3. Characterization and molecular structure of compounds (*2–6*)

The successful synthesis of compounds (**2–6**) was determined by elemental analysis, FT-IR, NMR, and MS (corresponding data are listed in the Section 2). As expected, the chemical shifts of the protons and carbons of the central benzene ring are sensitive to the electron-withdrawing or electron-donating effects of substituents. For instance, the proton NMR peaks of the central benzene ring of **4** locate at 8.084 ppm, which shows a downfield shift compared to **2** (7.526 ppm). The carbon NMR peaks of the central benzene ring of **4** locate at the region of 136.61–142.44 ppm, which also show a downfield shift compared to **2** (132.70–134.69 ppm).

The molecular structures of compounds (**2–6**) were determined using single crystal X-ray diffraction. Crystal data and relevant structural parameters are listed in Table 2. Selected bond lengths are listed in Table 3, and selected angles are listed in Table 4. The selected torsion angles see Supplementary Materials.

The molecular structure of **2** is shown in Fig. 2. The bond lengths and bond angles of central phenyl ring are ranging from 1.396(3) to 1.426(4) Å and from 117.90(11) to 123.50(19)°, respectively. And its maximum torsion angle is 4.4(2)° (C_2–C_1–$C_1{}^2$–$C_2{}^2$), which shows that the six carbon atoms of the central phenyl ring are

Table 4
Selected bond angles (°) of compounds (**2–6**).

2		**3**		**4**		**5**		**6**	
C1–C1^2–C2^2	117.90(11)	C1–C2–C3	117.7(3)	C1–C2–C3	118.0(3)	C1–C2–C3	119.2(12)	C1–C1^2–C2^2	118.33(19)
C1^2–C2^2–C3^2	123.50(19)	C2–C3–C4	123.8(3)	C2–C3–C4	124.8(4)	C2–C3–C4	121.9(12)	C1^2–C2^2–C3^2	119.2(3)
C2^2–C3^2–C3	118.50(12)	C3–C4–C5	118.0(3)	C3–C4–C5	117.2(3)	C3–C4–C5	119.5(11)	C2^2–C3^2–C3	119.9(2)
C3^2–C3–C2	118.50(12)	C4–C5–C6	117.8(3)	C4–C5–C6	116.4(3)	C4–C5–C6	118.4(12)	C3^2–C3–C2	119.9(2)
C3–C2–C1	123.50(19)	C5–C6–C1	124.1(3)	C5–C6–C1	125.5(4)	C5–C6–C1	122.4(13)	C3–C2–C1	119.2(3)
C2–C1–C1^2	117.90(11)	C6–C1–C2	118.6(3)	C6–C1–C2	118.1(3)	C6–C1–C2	118.0(11)	C2–C1–C1^2	118.33(19)

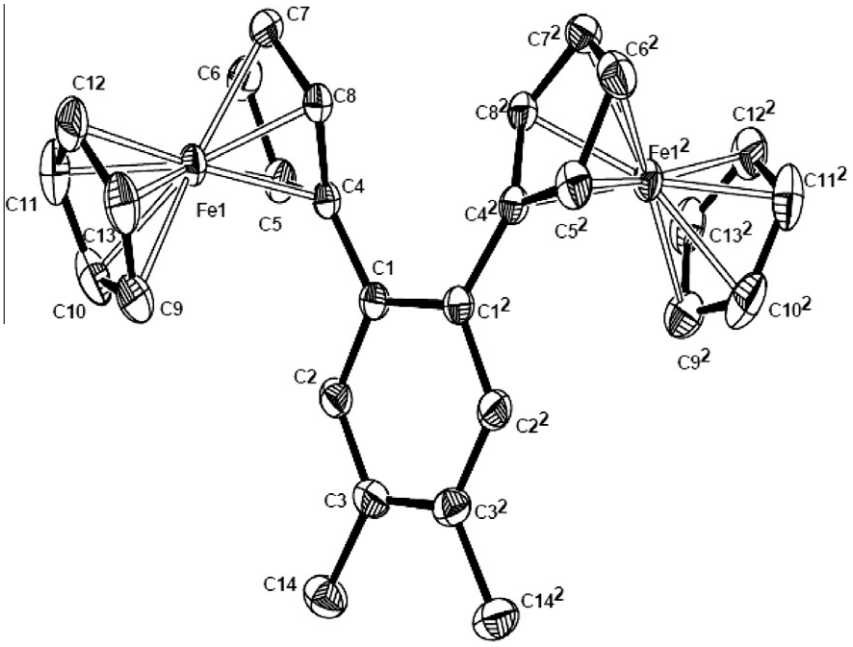


Fig. 2. The molecular structure of compound **2**. The H atoms have been omitted for clarity.

approximately co-planar. Two ferrocenyl groups are attached to the central phenyl ring at the 1 and 2 positions with bond lengths of 1.495(3) Å (C_1–C_4 and C_1^2–C_4^2). Two cyclopentadienyls (Cps) present an eclipse configuration and adopt an approximate up-down fashion. Both of dihedral angles of the central phenyl ring and Cp planes are 37.7°, which are smaller than the reported value (42.3°) for ortho-diferrocenyl benzene derivatives [22].

Fig. 3 shows the molecular structure of **3**. The bond lengths and bond angles of central phenyl ring are 1.386(4)–1.407(5) Å and 117.7(3)–124.1(3)°, respectively. The maximum torsion angle of central phenyl ring is 2.9(9)° (C_6–C_1–C_2–C_3). So the central phenyl ring maintains a planar character. Two ferrocenyl groups are attached to the central phenyl ring at the 1 and 2 positions with bond lengths of 1.485(4) Å (C_1–C_7) and 1.482(5) Å (C_2–C_{17}). Two phenyl groups are attached to the central phenyl ring at the 4 and 5 positions, and the bonds lengths of C_4–C_{27} and C_5–C_{33} are 1.486(4) and 1.491(5) Å, respectively. In contrast to **2**, the two Cp planes attached to the central phenyl ring of **3** are arranged in an approximately face-to-face fashion, the dihedral angles of which are 40.7° and 44.7°, respectively.

Fig. 4 shows the molecular structure of **4**. The bond lengths and bond angles of central phenyl ring are ranging from 1.388(5) to 1.444(5) Å and 116.4(3) to 124.8(4)°, respectively. And its maximum torsion angle is 2.9(9)° (C_3–C_4–C_5–C_6). This shows the six carbon atoms of the central phenyl ring are also approximately co-planar. The two ferrocenyl groups are attached to the central phenyl ring at the 1 and 2 positions with bond lengths of 1.482(5) Å (C_1–C_{13}) and 1.479(5) Å (C_2–C_{23}). Two trimethylsilyl

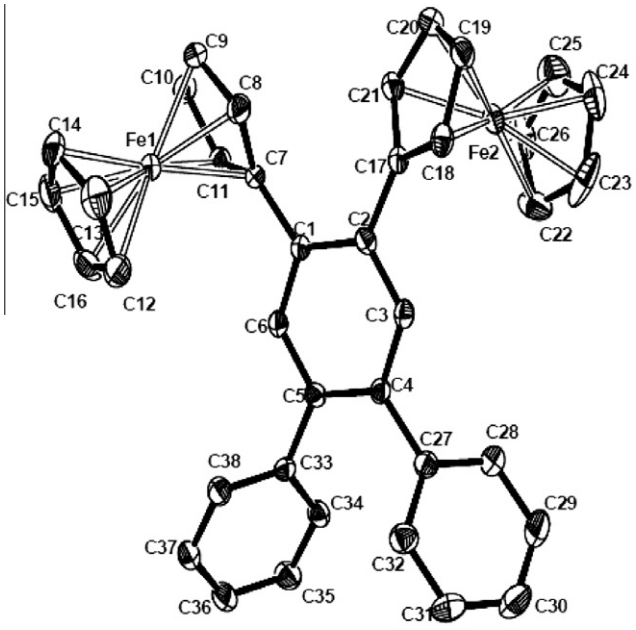


Fig. 3. The molecular structure of compound **3**. The H atoms have been omitted for clarity.

groups are attached to the central phenyl ring at the 4 and 5 positions, and the bond lengths of Si_1–C_4 and Si_2–C_5 are 1.882(4) and

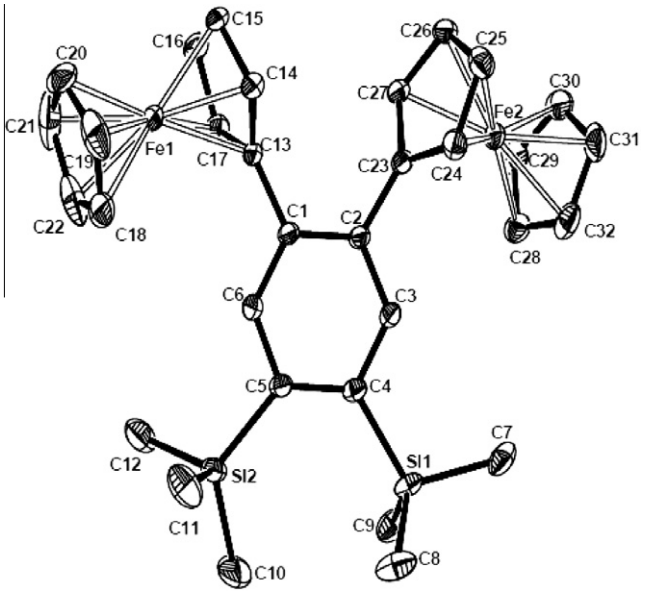


Fig. 4. The molecular structure of compound **4**. The H atoms have been omitted for clarity.

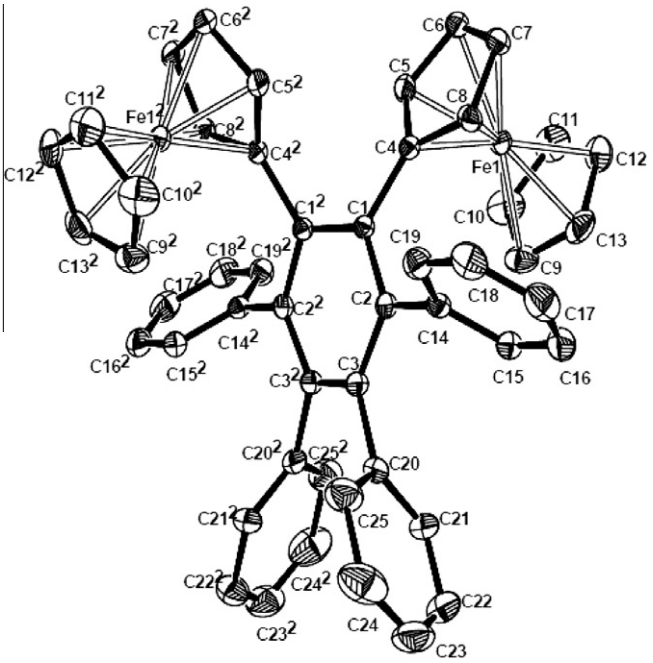


Fig. 6. The molecular structure of compound **6**. The H atoms have been omitted for clarity.

1.891(4) Å, respectively, which close to the average bond length of the Si–C bond (1.922 Å) reported for hexamethylsilyl-substituted benzene [20]. Two Cp planes attached to the central phenyl ring are arranged in an approximate face-face fashion, and the dihedral angles of which are 48.9° and 59.8°, respectively.

The molecular structure of **5** is described in Fig. 5. The bond lengths and bond angles of central phenyl ring are 1.365(18)–1.457(19) Å and 118.0(11)–121.9(12)°, respectively. The maximum torsion angle of central phenyl ring is 7.7(5)° (C_3–C_4–C_5–C_6). Although there are six substituents on the central phenyl ring, the six carbon atoms are approximately co-planar. Two ferrocenyl groups are attached to the central phenyl ring at the 1 and 2 positions with bond lengths of 1.497(16) Å (C_1–C_7) and 1.501(16) Å (C_2–C_{17}). The Cps of the two ferrocenyl groups present an eclipse configuration and adopt an approximate up-down form relative to the central phenyl ring. The dihedral angles of the Cps and the central phenyl ring are 37.6° and 44.4°.

A comparison of the four molecular structures discussed above shows that the central phenyl rings of compounds (**2**–**5**) easily maintain their planar character. Hence, the central phenyl ring can serve as a conjugated aromatic bridge between two ferrocenyl groups to realize their charge transfer functions.

Although the bond lengths (1.400(5)–1.423(4) Å) and bond angles (118.33(19)–119.9(2)°) have no significant deviation contrast to normal phenyl ring, the configuration of the central phenyl ring of compound **6** (Fig. 6) is obviously different from that of **2**–**5**. The six carbon atoms of **6** are not co-planar due to the large steric

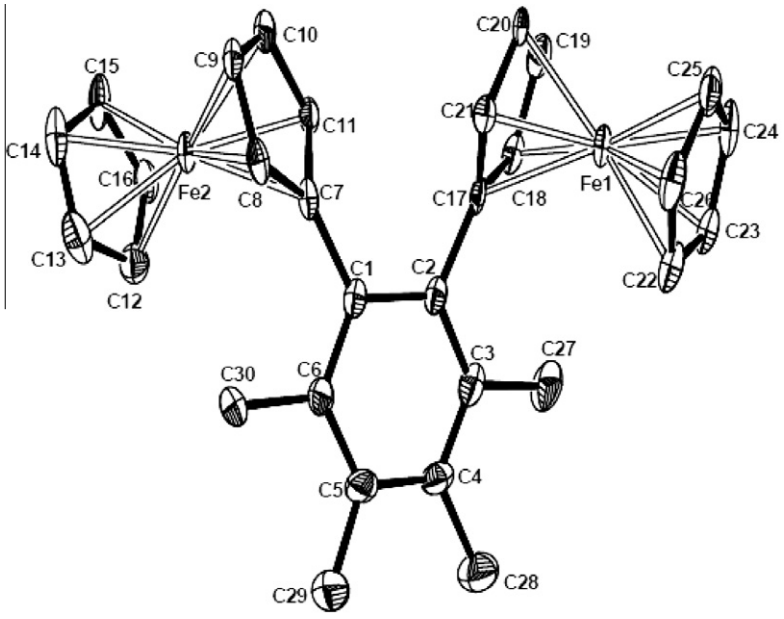


Fig. 5. The molecular structure of compound **5**. The H atoms have been omitted for clarity.

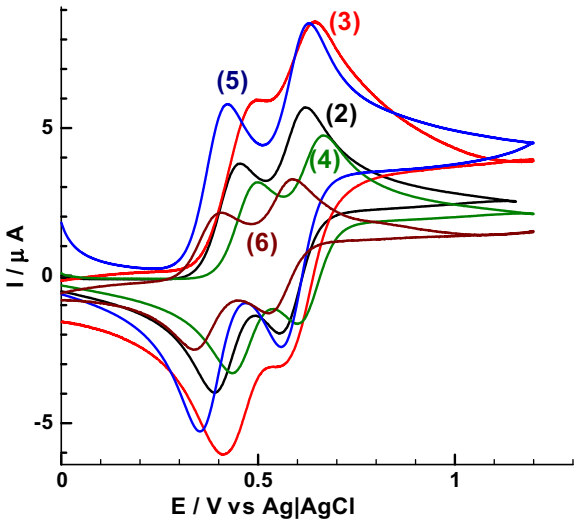


Fig. 7. The cyclic voltammograms of compounds (**2**, black line), (**3**, red line), (**4**, green line), (**5**, blue line), (**6**, brown line). (Color online.)

hindrance among them. The compound adopts a twist-boat configuration with torsion angles of 26.0(1)° ($C_2-C_1-C_1^2-C_2^2$) and 13.1(3)° ($C_2-C_3-C_3^2-C_2^2$). The central phenyl ring is partially deformed and the aromatic characters of the normal phenyl ring are lost.

3.4. Electrochemistry of compounds (2–6)

The redox potential and reversibility of compounds (**2**–**6**) were determined using cyclic voltammetry. All of compounds display two redox waves in the range of 0–1.2 V (Fig. 7), which are assigned to the two Fe^{II}/Fe^{III} redox couples. The electrochemical data was reported in Table 5. From the Ipa/Ipc (≈1) values of each couple, it can be seen that the redox processes were chemically reversible processes [23].

The difference in first oxidation potentials can be ascribed to the electron-donating or electron-withdrawing effects of substituents and the characteristics of central phenyl rings. The electron-donating effect of methyl was identified by the upfield ^{1}H NMR chemical shift of the central phenyl in compound **2**. The electron-withdrawing effects of phenyl and trimethylsilyl in **3** and **4** could also be identified by the downfield shift in their ^{1}H NMR. From the molecular structures of compounds (**2**–**5**), we can see that the configurations and the original planar characteristics of the central phenyl rings have no change. The electron-donating and electron-withdrawing effects of substituents can be partially transferred to ferrocenyls through the central phenyl rings. Thus, the first oxidation potentials of **2** and **5** are more negative, and the first oxidation potentials of **3** and **4** are more positive.

Compound **6** has four electron-withdrawing phenyl groups on the central phenyl ring, and the first oxidation potential should be more positive. However, the first oxidation potential of **6** is the most negative, which indicates that the electron-withdrawing effects have no influence on the ferrocenyls. This phenomenon can be ascribed to the central phenyl ring is not planar and the conjugated bridge effect disappears.

The order of oxidation potential difference ($\Delta E_{1/2}$) of compounds (**2**–**5**) (Table 5) is **5** > **2** > **4** > **3**. This order is also a representation of the electron transfer abilities of the four compounds [24]. The electron transfer between two ferrocenyls of an ortho-diferrocenylbenzen derivative is controlled by the style and number of substituents and the characteristic of central phenyl ring. The electron transfers between two ferrocenyls can be increased with increasing electron-donating groups.

The special $\Delta E_{1/2}$ of compound **6** is attributed to the deformed structure of the central phenyl ring. The two ferrocenyls of **6** appear like diferrocenylethylene. Therefore, the oxidation potential difference of **6** is also similar to that of diferrocenylethylene [25].

Table 5
CV data of compounds (**2**–**6**).

Compounds	E_{pa1} (mV)	E_{pc1} (mV)	$E_{1/2}^1$ (mV)	E_{pa2} (mV)	E_{pc2} (mV)	$E_{1/2}^2$ (mV)	$\Delta E_{1/2}$ (mV)	I_{pa1}/I_{pc1}	I_{pa2}/I_{pc2}
2	449	381	415	618	550	584	169	1.05	0.97
3	486	422	454	646	578	612	158	1.08	1.04
4	496	416	456	662	580	621	165	0.99	1.06
5	419	351	385	630	558	594	209	1.02	0.99
6	399	343	371	579	522	552	181	1.06	1.05

4. Conclusion

Five new ortho-diferrocenylbenzene derivatives: 1,2-diferrocenyl-4,5-dimethylbenzene (**2**), 1,2-diferrocenyl-4,5-diphenylbenzene (**3**), 1,2-diferrocenyl-4,5-ditrimethylsilylbenzene (**4**), 1,2-diferrocenyl-3,4,5,6-tetramethylbenzene (**5**), and 1,2-diferrocenyl-3,4,5,6-tetraphenyl-benzene (**6**) were obtained through the cycloaddition reaction. This work is the first time to report the position-controlled synthesis of ortho-diferrocenylbenzenes using $Co_2(CO)_6(\mu^2$-diferrocenylacetylene) and $Co_2(CO)_6(\mu^2$-2-butyne) as precursors. The electron transfer abilities of five ortho-diferrocenylbenzene derivatives were investigated using cyclic voltammetry. The electron-donating or electron-withdrawing effect of substituents on the central phenyl ring and the planar characteristics of the central phenyl ring were the key factors for the electron communication between two ferrocenyls.

Acknowledgements

We are grateful to the Program for New Century Excellent Talents in University (NCET-08-858), the Natural Science Foundation of China (NSFC 21062011) and the Natural Science Foundation of the Inner Mongolia (20080404MS020).

Appendix A. Supplementary data

CCDC 817283, 816928, 816927, 816935, 816926 and 816936 contains the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5** and **6**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2012.02.018.

References

[1] R.J. Crutchley, Adv. Inorg. Chem. 41 (1994) 273.
[2] A.C. Ribou, J.P. Launay, M.L. Sachtleben, H. Li, C.W. Spangler, Inorg. Chem. 35 (1996) 3735.
[3] C. Creutz, Prog. Inorg. Chem. 30 (1983) 1.
[4] A.C. Benniston, V. Goulle, A. Harriman, J.M. Lehn, B. Marczinke, J. Phys. Chem. 98 (1994) 7798.
[5] M. Haga, M.M. Ali, S. Koseki, K. Fujimoto, A. Yoshimura, K. Nozaki, T. Ohno, K. Nakajima, D. Stufkens, Inorg. Chem. 35 (1996) 3335.
[6] M.E. Elliot, D.L. Derr, S. Ferrere, M.D. Newton, Y.P. Liu, J. Am. Chem. Soc. 118 (1996) 5221.
[7] R.J. Xie, L.M. Han, Q.L. Suo, H.L. Hong, M.H. Luo, J. Coord. Chem. 63 (2010) 1700.
[8] M.T. Lee, B.M. Foxman, M. Rosenblum, Organometallics 4 (1985) 539.
[9] R. Knapp, M. Rehahn, J. Organomet. Chem. 452 (1993) 235.
[10] Y. Yu, A.D. Bond, P.W. Leonard, U.J. Lorenz, Chem. Commun. 24 (2006) 2572.

[11] C. Patoux, C. Coudret, J.P. Launay, C. Joachim, A. Gourdon, Inorg. Chem. 36 (1997) 5037.
[12] U. Krüerke, W. Hübel, Chem. Ber. 94 (1961) 2829.
[13] L.M. Han, Q.L. Suo, Y.B. Wang, J.H. Ye, N. Zhu, X.B. Leng, Polyhedron 24 (2005) 759.
[14] L.M. Han, G.B. Zhang, N. Zhu, R.J. Xie, Q.L. Suo, J. Clust. Sci. 21 (2010) 789.
[15] Q.L. Suo, L.M. Han, Y.B. Wang, J.H. Ye, N. Zhu, X.B. Leng, J. Coord. Chem. 57 (2004) 1591.
[16] S.H. Sun, L.K. Yeung, D.A. Sweigart, Organometallics 14 (1995) 2613.
[17] C. LeVanda, D.O. Cowan, C. Leitch, K. Bechgaard, J. Am. Chem. Soc. 96 (1974) 6788.
[18] C.R. Simionescu, T. Lixandru, I. Mazilu, L. Tataru, J. Organomet. Chem. 113 (1976) 23.
[19] C.M. Liu, W.Y. Liu, Y.M. Liang, Y.X. Ma, Synth. Commun. 30 (2000) 1755.
[20] H. Sakurai, K. Ebata, C. Kabuto, A. Sekiguchi, J. Am. Chem. Soc. 112 (1990) 1799.
[21] J.G. Rodriguez, A. Onate, R.M. Martin-Villamil, I. Fonseca, J. Organomet. Chem. 513 (1996) 71.
[22] R.M.G. Roberts, J. Silver, B.M. Yamin, M.G.B. Drew, U. Eberhardt, J. Chem. Soc., Dalton Trans. 6 (1988) 1549.
[23] W.H. Feng, W. Du, C.L. Ran, H.J. Lu, Y. Xu, Y.T. Fan, Synth. React. Inorg. M. 40 (2011) 386.
[24] C.B. Hollandsworth, W.G. Hollis, C. Slebodnick, P.A. Deck, Organometallics 18 (1999) 3610.
[25] K.I. Son, S.Y. Kang, Y.E. Oh, D.Y. Noh, J. Kor, Chem. Soc. 53 (2009) 79.