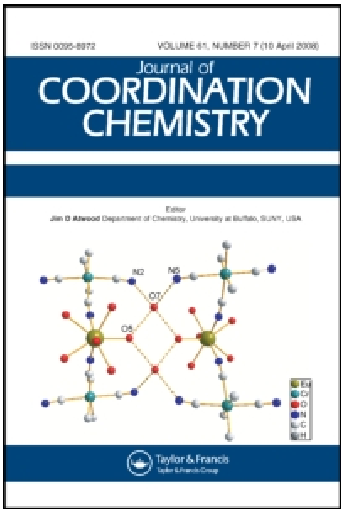

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Synthesis, molecular structure and reactivity of new biferrocenylpropane derivatives

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New biferrocenylpropane derivatives FcC$(CH_3)_2$Fc′-C≡C–R [Fc = $C_5H_5FeC_5H_4$; Fc′ = $C_5H_5FeC_5H_3$, R = C_6H_5 (**L₁**), Fc (**L₂**)] and their complexes [FcC$(CH_3)_2$Fc′-C≡C–R][$Co_2(CO)_6$] [R = C_6H_5 (**1**); R = Fc (**2**)] have been synthesized by the Castro-Stephens coupling reaction and the reactions of ligands **L₁**, **L₂** with $Co_2(CO)_8$. Compounds **L₁**, **L₂**, **1** and **2** were characterized by elemental analysis, IR, ^{1}H (^{13}C) NMR and MS, and the molecular structures of ligands L₁, L₂ were determined by X-ray single crystal analysis. The electrochemical properties of **L₁**, **L₂**, **1** and **2** demonstrate two or three resolved one-electron redox processes.

Keywords: Biferrocenylpropane derivative; Castro-Stephens coupling reaction; Cobalt carbonyl cluster; Molecular structure

1. Introduction

Although ferrocene has been known for more than 50 years, its derivatives are still a fountain of youth for the synthesis of new compounds with electrochemical properties [1–5]. Ferrocene derivatives with alkynyl bridges are important because of their applications as electronic materials [6–9]. Research on redox properties of *bis*-ferrocenyl alkanes shows electronic communication between the two ferrocenyl redox centers, and the extent of interaction is relative to the molecular conformation of the spacer unit [10, 11]. Although the synthesis and characterization of alkynyl *bis*-ferrocenyl propane derivatives have been reported in our previous work [12, 13], research on their electrochemical properties is scarce.

We now report the synthesis and structural characterization of new biferrocenylpropane derivatives FcC$(CH_3)_2$Fc′-C≡C-R [Fc = $C_5H_5FeC_5H_4$; Fc′ = $C_5H_5FeC_5H_3$, R = C_6H_5 (**L₁**), Fc (**L₂**)] and their Pauson-Khand complexes [FcC$(CH_3)_2$Fc′-C≡C–R][$Co_2(CO)_6$] [R = C_6H_5 (**1**); R = Fc (**2**)]. We have also studied the redox properties of these compounds.

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2. Experimental

Unless it is stated otherwise, all reactions and manipulations were carried out using standard Schlenk techniques under an atmosphere of pure nitrogen. Solvents were purified, dried and distilled under a nitrogen atmosphere prior to use. Reactions were monitored by TLC. Chromatographic separations and purification were performed on a 200–300 mesh silica gel column. The $Co_2(CO)_8$ and C_6H_5I were purchased from Alfa Aesar. Published procedures or extensions thereof, were used to synthesize FcI [14], $FcC(CH_3)_2Fc'$-C≡CH and $FcC(CH_3)_2$ Fc′-C≡CCu [15, 16].

IR spectra were recorded on a Nicolet FT-IR spectrometer with KBr discs. Elemental analyses were carried out on a Elementar var-type analyzer. ^1H (^{13}C) NMR spectra in $CDCl_3$ were recorded on a Inova 500 FT-MHz spectrometer. Mass spectra were determined by using a Polaris Q MS and a Micromass Autospec Ultima-TOF instrument. Electrochemical properties were determined by a BAS 100A-type analyzer. Melting points were determined using XT-4 melting point apparatus.

2.1. *X-ray crystallography of L_1 and L_2*

The crystals of $\mathbf{L_1}$ and $\mathbf{L_2}$ were mounted on a glass fiber. All measurements were made on Bruker SMART APEX CCD diffractometers with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. All data were collected at 20°C using the φ and ω scan techniques. All structures were solved by direct methods and expanded using Fourier techniques [17]. An absorption correction based on SADABS was applied [18]. All non-hydrogen atoms were refined by the full matrix least-squares on F^2. Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection and reduction were done by Bruker SMART and SAINT [19]. The structure solution and refinement were performed by SHELXSL 97 [20].

2.2. *Synthesis of biferrocenylpropane derivative $FcC(CH_3)_2Fc'$-C≡C–C_6H_5 (L_1)*

CuI (150 mg, 0.79 mmol) was dissolved in 75 mL ammonia (30%), which was dropped into a 100 mL absolute alcohol solution of $FcC(CH_3)_2Fc'$-C≡CH (200 mg, 0.46 mmol) at room temperature. The solution was stirred for 20 min, then filtered. The solid was washed by water, ethanol and absolute ethyl ether. The product $FcC(CH_3)_2Fc'$-C≡CCu was dried at 80°C and 121 mg (Yield, 52%) $FcC(CH_3)_2Fc'$-C≡CCu.

$FcC(CH_3)_2Fc'$-C≡CCu (100 mg, 0.2 mmol) and C_6H_5I (0.03 mL, 0.3 mmol) were dissolved in 10 mL pyridine. The mixture was stirred and refluxed for 6 h, then poured into 30 mL water at 0°C. The resulting mixture was extracted with ethyl ether. The organic phase was combined, then washed by 2 M HCl and H_2O, respectively, and dried by using dehydrated $MgSO_4$, and filtered. The filtrate was concentrated and the residue was subjected to chromatographic separation on a neutral alumina column (2.0 × 30 cm). Elution with a mixture of hexane-ether (4 : 1, v/v) afforded a yellow band. The yellow crystal of ligand $\mathbf{L_1}$ was obtained by recrystallizing from hexane-ether. Yield, 61%; m.p., 144–145°C. Anal. Calcd for $C_{31}H_{28}Fe_2$: C, 72.64; H, 5.51%. Found: C, 72.19; H, 5.58%. IR (KBr disk, cm^{-1}): ν(C≡C) 2207.7 (m), $\nu(CH_3)$ 2863.2 (w), 2929.7 (m), 2975.8 (s). ^{1}HNMR ($DCCl_3$, δ): 7.26–7.49 (m, 5H, C_6H_5), 4.01–4.46 (17H, m, Fc or Fc′), 1.54–1.68 [6H, m, $C(CH_3)_2$]. ^{13}CNMR ($DCCl_3$, δ): 123.98, 124.56, 128.24, 128.8, 131.31, 131.35 (C_6H_5), 85.55, 88.64, 100.74, 102.34 (C≡C), 63.77, 65.95, 66.69, 67.88, 68.43, 69.29, 70.52, 71.85 (Fc or Fc′), 30.35, 33.26 [$C(CH_3)_2$]. MS (EI, *m/z*, Relative Abundance): 512 (M^+, 82%).

2.3. *Synthesis of biferrocenylpropane derivative FcC(CH$_3$)$_2$Fc′-C≡C–Fc (L$_2$)*

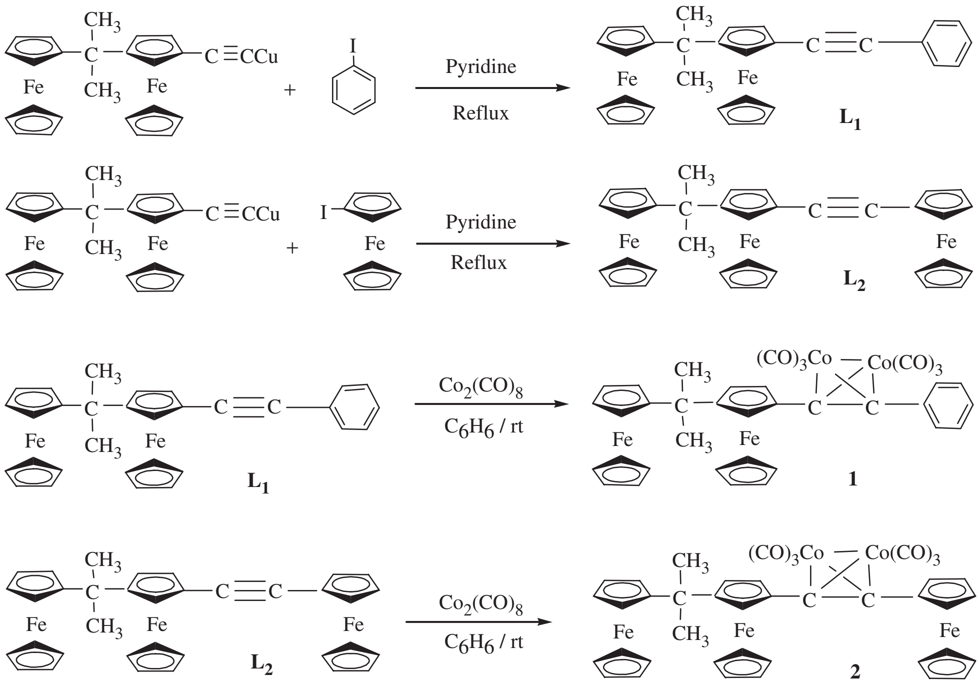
$FcC(CH_3)_2Fc'$-C≡CCu (100 mg, 0.2 mmol) and FcI (94 mg, 0.3 mmol) were dissolved in 15 mL pyridine. The solution was stirred and refluxed for 8 h, then poured into 50 mL water at 0°C. The resulting mixture was extracted by CH_2Cl_2. The organic phase was combined, then washed by 2 M HCl and H_2O and dried by using dehydrated $MgSO_4$, and filtered. The filtrate was concentrated and the residue was subjected to chromatographic separation on a neutral alumina column (2.0 × 30 cm). Elution with a mixture of hexane–ether (2 : 1, v/v) afforded a yellow band. Yellow crystals of **L$_2$** were obtained by recrystallizing from hexane–CH_2Cl_2. Yield, 86%; m.p. 245–246°C. Anal. Calcd for $C_{35}H_{32}Fe_3$: C, 67.78; H, 5.20%. Found: C, 67.97; H, 5.34%. IR (KBr disk, cm^{-1}): ν(C≡C) 2217.9 (w), $\nu(CH_3)$ 2858.0 (w), 2919.5 (m), 2965.6 (s). ^{1}HNMR ($DCCl_3$, δ): 4.03–4.45 (26H, m, Fc or Fc′), 1.61–1.68 [6H, m, $C(CH_3)_2$]. ^{13}CNMR ($DCCl_3$, δ): 83.66, 84.26, 100.83, 102.03 (C≡C), 64.79, 66.11, 67.89, 68.45, 69.37, 70.56, 71.67 (Fc or Fc′), 30.32, 33.24 [$C(CH_3)_2$]. MS (EI, *m/z*, Relative Abundance): 620 (M^+, 44%).

2.4. *Synthesis of [FcC(CH$_3$)$_2$Fc′-C≡C–C$_6$H$_5$][Co$_2$(CO)$_6$] (1)*

A benzene solution of $Co_2(CO)_8$ (79 mg, 0.23 mmol) and **L$_1$** (118 mg, 0.23 mmol) was stirred for 3 h at room temperature and the solvent removed *in vacuum*. The residue was dissolved in a minimal amount of benzene and subjected to chromatographic separation on a silica gel column (2.0 × 40 cm). Elution with hexane-benzene (6 : 1, v/v) afforded a green band (**1**). A dark-green oil of **1** was obtained. Yield, 90%. Anal. Calcd for $C_{37}H_{28}O_6Co_2Fe_2$: C, 55.64; H, 3.51%. Found: C, 55.09; H, 3.37%. IR (KBr disk, cm^{-1}): ν(CO) 2013.1 (vs), 2048.9 (vs), 2084.8 (s), $\nu(CH_3)$ 2852.9 (w), 2919.5 (m), 2960.5 (s). ^{1}HNMR ($DCCl_3$, δ): 7.26–7.82 (m, 5H, C_6H_5), 4.00–4.46 (17H, m, Fc or Fc′), 1.63–1.67 [6H, m, $C(CH_3)_2$]. ^{13}CNMR ($DCCl_3$, δ):199.47(CO), 127.78, 127.83, 128.31, 128.81, 129.64, 129.71, 130.57(C_6H_5), 83.84, 84.85, 101.02, 102.56 (C≡C), 65.75, 66.79, 67.23, 68.54, 69.49, 70.52 (Fc or Fc′), 30.37, 33.54 [$C(CH_3)_2$]. MS (FAB, *m/z*, Relative Abundance): 686 ($M^+ - 4CO$, 50%), 630 ($M^+ - 6CO$, 100%).

2.5. *Synthesis of [FcC(CH$_3$)$_2$Fc′-C≡C–Fc][Co$_2$(CO)$_6$] (2)*

A benzene solution of $Co_2(CO)_8$ (79 mg, 0.23 mmol) and **L$_2$** (143 mg, 0.23 mmol) was stirred for 5 h at room temperature and the solvent removed in vacuum. The residue was dissolved in a minimal amount of benzene and subjected to chromatographic separation on a silica gel column (2.0 × 40 cm). Elution with hexane–benzene (4 : 1, v/v) afforded a green band (**2**). The dark-green oil of **2** was obtained. Yield, 79%. Anal. Calcd for $C_{41}H_{32}O_6Co_2Fe_3$: C, 54.30; H, 3.53%. Found: C, 54.11; H, 3.23%. IR (KBr disk, cm^{-1}): ν(CO) 2002.8 (vs), 2043.8 (vs), 2074.5 (s), $\nu(CH_3)$ 2858.0 (w), 2919.5 (s), 2965.6 (s). ^{1}HNMR ($DCCl_3$, δ): 4.04–4.59 (26H, m, Fc or Fc′), 1.67–1.70 [6H, m, $C(CH_3)_2$]. ^{13}CNMR ($DCCl_3$, δ):199.78(CO), 84.50, 85.85, 100.96, 102.45 (C≡C), 65.94,



Scheme 1. The reactions of the ligands and complexes.

66.89, 67.96, 68.38, 69.76, 70.24 (Fc or Fc′), 30.47, 33.56 [$C(CH_3)_2$]. MS (FAB, *m*/*z*, Relative Abundance): 822 ($M^+ - 3CO$, 5%), 794 ($M^+ - 4CO$, 20%), 738 ($M^+ - 6CO$, 100%).

3. Results and discussion

3.1. *Synthesis and characterization of L_1, L_2, 1 and 2*

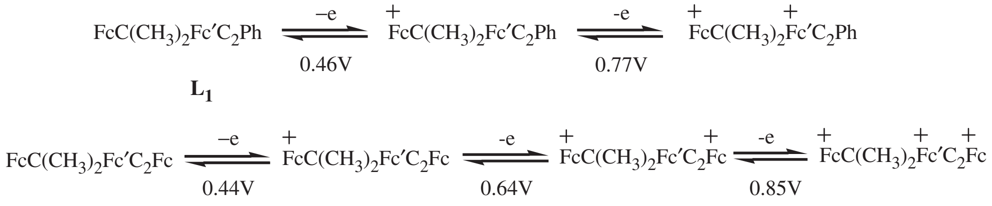
The reactions carried out in this work are summarized in scheme 1. Ligand $\mathbf{L_1}$ or $\mathbf{L_2}$ was synthesized by Castro-Stephens cross coupling reaction of C_6H_5I (for $\mathbf{L_1}$) or FcI (for $\mathbf{L_2}$) and $FcC(CH_3)_2Fc'$-C≡CCu and the self-coupling by–product $FcC(CH_3)_2Fc'$-C≡C–C≡C-$Fc'C(CH_3)_2Fc$ was found in the separation process. Pauson-Khand complexes **1** and **2** were easily prepared by reaction of $\mathbf{L_1}$ and $\mathbf{L_2}$, respectively, with $Co_2(CO)_8$ but crystals of complexes **1**, **2** could not be obtained. $\mathbf{L_1}$ and $\mathbf{L_2}$ are yellow, air-stable compounds soluble in both non-polar solvents such as benzene and polar solvents such as acetonitrile and chloroform, and sparingly soluble in hexane and petroleum ether. Although all kinds of purification treatments were adopted, only dark-green oily complexes **1** and **2** were obtained. The solubility of **1** and **2** is similar to their ligands.

FTIR spectra of $\mathbf{L_1}$ and $\mathbf{L_2}$ show that there are CH_3 (2975.8, 2929.7, 2863.2 cm^{-1} for $\mathbf{L_1}$; 2965.6, 2919.5, 2858.0 cm^{-1} for $\mathbf{L_2}$) and C≡C (2207.7 $cm^{-1}$for $\mathbf{L_1}$; 2217.9 cm^{-1} for $\mathbf{L_2}$) groups. The coordinated $Co_2(CO)_6$ units in **1** and **2** were identified by their FTIR spectra (ν_{CO}, 2003–2085 cm^{-1}). The Fc or Fc′, $C(CH_3)_2$, C≡C and C_6H_5 groups in the ligands and complexes were confirmed by ^1H and ^{13}C NMR. ^{13}CNMR data of

Table 1. Voltammetric data.[a]

Compounds	E_1^0(0/1+)	E_2^0(0,0/1+,1+)	E_3^0(0,0,0/1+,1+,1+)	ΔE_1^0	ΔE_2^0
L_1	0.46	0.77	–	0.31	–
L_2	0.44	0.64	0.85	0.20	0.21
1	0.46	0.80	–	0.34	–
2	0.43	0.60	0.77	0.17	0.17
$FcC(CH_3)_2Fc'CCH$	0.50	0.85	–	0.35	–
$FcC(CH_3)_2Fc$	0.41	0.65	–	0.24	–

[a] Platinum electrode (Ag/Ag$^+$ standard) with 0.001 M TEAP at 20°C in 100 mV scan rate. E_{pc} = cathodic peak potential (V); E_{pa} = anodic peak potential (V); $E^0 = 1/2(E_{pc} + E_{pa})(V)$; $\Delta E^0 = E_2^0 - E_1^0$ (V).



$$FcC(CH_3)_2Fc'C_2Ph \underset{0.46V}{\xrightleftharpoons{-e}} \overset{+}{Fc}C(CH_3)_2Fc'C_2Ph \underset{0.77V}{\xrightleftharpoons{-e}} \overset{+}{Fc}C(CH_3)_2\overset{+}{Fc'}C_2Ph$$

L_1

$$FcC(CH_3)_2Fc'C_2Fc \underset{0.44V}{\xrightleftharpoons{-e}} \overset{+}{Fc}C(CH_3)_2Fc'C_2Fc \underset{0.64V}{\xrightleftharpoons{-e}} \overset{+}{Fc}C(CH_3)_2Fc'C_2\overset{+}{Fc} \underset{0.85V}{\xrightleftharpoons{-e}} \overset{+}{Fc}C(CH_3)_2\overset{+}{Fc'}C_2\overset{+}{Fc}$$

L_2

Scheme 2. The redox process of ligands **L_1, L_2**.

complexes **1** and **2** show the signals of CO groups. The composition and structures of **L_1**, **L_2**, **1** and **2** were further identified by the MS, elemental analysis and X-ray crystallography.

3.2. *Electrochemical properties of L_1, L_2, 1 and 2*

The electrochemical properties of **L_1**, **L_2**, **1** and **2** have been studied by cyclic voltammetry at 293 K in a standard three-electrode system with Et_4NClO_4 in CH_3CN as the supporting electrolyte. The results are given in table 1.

Two successive, resolved, one-electron redox waves have been observed at $E_1^0 = 0.46$ and $E_2^0 = 0.77$ V, respectively from the electrochemical data of table 1, ascribed to two ferrocenyl units (Fc^0/Fc^+, Fc'^0/Fc'^+) as redox active centres in **L_1**. Three successive one-electron redox waves in **L_2** appear at $E_1^0 = 0.44$ V, $E_2^0 = 0.64$ V, $E_3{}^0 = 0.85$ V, from three ferrocenyl groups yielding mono-, di- and trications ($\mathbf{L_2^+}, \mathbf{L_2^{++}}, \mathbf{L_2^{+++}}$), respectively. In $FcC(CH_3)_2Fc$, two redox waves (not one redox wave) show that the two Fc groups locate in different positions. ΔE^0 value (0.35 V) for $FcC(CH_3)_2Fc'$-C≡CH is bigger than ΔE^0 value (0.24 V) of $FcC(CH_3)_2Fc$, which indicate the alkynyl-C≡CH unit is an electron-withdrawing group. Therefore, in compound $FcC(CH_3)_2Fc'$-C≡CH, the first redox will happen on the Fc group and the second on the Fc′ group. The ΔE_1^0 value (0.31 V) of $FcC(CH_3)_2Fc'$-C≡C–C_6H_5 (**L_1**) is less than the ΔE_1^0 (0.35 V) of compound $FcC(CH_3)_2Fc'$-C≡CH due to more conjugation from the phenyl. According to the inducement effect of electron-withdrawing groups, the orders of redox in **L_1** and **L_2** were deduced (scheme 2). The ΔE^0 data (see table 1) of **1** and **2** demonstrate that coordination of $Co_2(CO)_6$ does not change the order for **L_1** and **L_2**.

Table 2. Crystal data and relevant structural parameters of $\mathbf{L_1}$ and $\mathbf{L_2}$.

Ligands	$\mathbf{L_1}$	$\mathbf{L_2}$
Empirical formula	$C_{31}H_{28}Fe_2$	$C_{35}H_{32}Fe_3$
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2(1)2(1)2(1)$
a (Å)	6.217(2)	7.461(10)
b (Å)	12.353(5)	10.819(14)
c (Å)	16.137(6)	33.54(4)
α (°)	102.282(6)	90.00
β (°)	94.061(6)	90.00
γ (°)	101.044(6)	90.00
Volume, Z	1180.4(8), 2	2708(6), 4
D_c (g/cm^{-3})	1.441	1.521
μ (mm^{-1})	1.246	1.609
$F(000)$	532	1280
θ range (°)	1.30–25.01	1.98–25.01
Reflections collected	5006	9512
Independent reflections	4112	4756
Completeness to θ (%)	98.5	99.6
Max. and min. transmission	0.9755 and 0.7887	0.8821 and 0.6891
Data/restraints/parameters	4112/0/300	4756/0/343
Goodness-of-fit	0.909	1.092
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0674$; $wR_2 = 0.1639$	$R_1 = 0.0548$, $wR_2 = 0.1310$
R indices (all data)	$R_1 = 0.1029$; $wR_2 = 0.1749$	$R_1 = 0.0603$, $wR_2 = 0.1341$
Largest diff. peak and hole (e Å^{-3})	1.504 and −0.268	0.521 and −1.011

3.3. *Molecular structures of L_1 and L_2*

The molecular structures of $\mathbf{L_1}$ and $\mathbf{L_2}$ were determined by X-ray single crystal analysis. Crystal data and relevant structural parameters are enumerated in table 2. The structures with the atom numbering scheme are shown in figures 1 and 2, respectively, and the selected bond lengths and angles for $\mathbf{L_1}$ and $\mathbf{L_2}$ are listed in table 3.

$\mathbf{L_1}$ contains a bisferrocenylpropane group, with one cyclopentadiene ring of the Fc′ joined to propyl and phenyl acetylene (see figure 1). The bond distance C(12)–C(13) (1.19 Å) shows there is a carbon–carbon triple bond in $\mathbf{L_1}$. As a result of conjugation of the alkynyl, phenyl and cyclopentadiene ring, the C(9)–C(12) (1.43 Å) and C(13)–C(14) (1.44 Å) bond distances are nearly the same as an aromatic bond C(8)–C(9) (1.43 Å). The bond distances C(5)–C(6) (1.52 Å) and C(6)–C(7) (1.52 Å) are normal carbon–carbon single bond. The data of the bond angles [C(9)–C(12)–C(13), 176.7°; C(12)–C(13)–C(14), 177.4°] reveal the carbon chain C(9) C(12) C(13) C(14) is nearly linear. The bond angles C(5)–C(6)–C(7) (105.6°), C(5)–C(6)–C(20) (110.2°) and C(8)–C(9)–C(12) (126.0°), C(13)–C(14)–C(15) (119.2°) slightly deviate from 109° around the sp^3-hybridized C(6) and 120° of the sp^2-hybridized C(9) or C(14) in $\mathbf{L_1}$, respectively.

$\mathbf{L_2}$ contains an alkyne bond, with bisferrocenylpropane and ferrocenyl groups (see figure 2). The relevant bond distances in $\mathbf{L_2}$ are similar to $\mathbf{L_1}$, also demonstrating the conjugated interaction among alkynyl and cyclopentadiene rings. The bond angle data (see table 3) reveal the carbon chain C(17) C(24) C(25) C(26) of $\mathbf{L_2}$ is nearly linear.

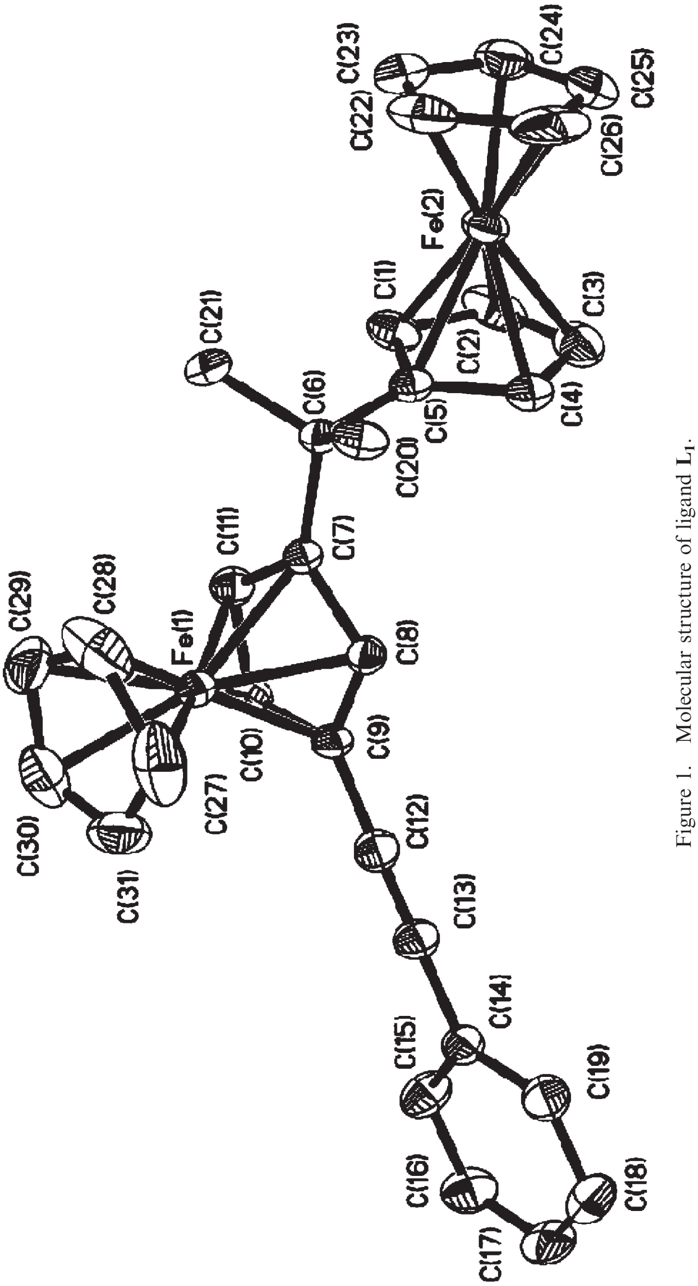


Figure 1. Molecular structure of ligand $\mathbf{L_I}$.

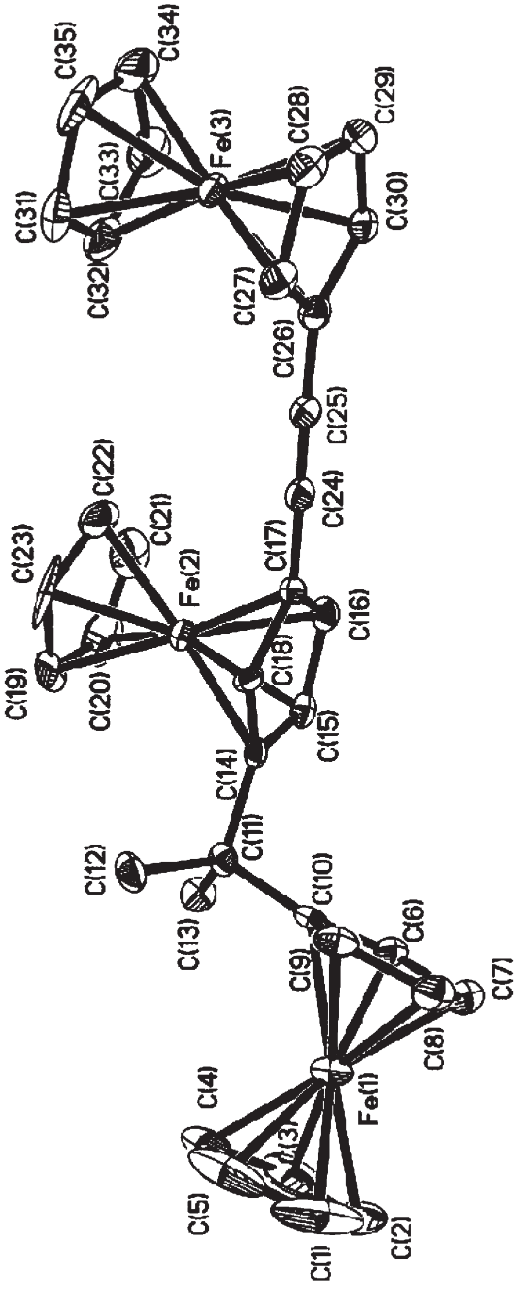


Figure 2. Molecular structure of ligand $\mathbf{L}_2$.

Table 3. Selected bond lengths [Å] and angles [°] for ligands L_1 and L_2.

L_1			
C(5)–C(6)	1.52(8)	C(6)–C(7)	1.53(7)
C(8)–C(9)	1.43(8)	C(9)–C(12)	1.43(8)
C(12)–C(13)	1.19(8)	C(13)–C(14)	1.44(8)
C(5)–C(6)–C(7)	105.6(4)	C(5)–C(6)–C(20)	110.2(5)
C(8)–C(9)–C(12)	126.0(6)	C(9)–C(12)–C(13)	176.7(7)
C(12)–C(13)–C(14)	177.4(7)	C(13)–C(14)–C(15)	119.2(6)
L_2			
C(10)–C(11)	1.50(8)	C(11)–C(14)	1.53(7)
C(16)–C(17)	1.42(8)	C(17)–C(24)	1.44(8)
C(24)–C(25)	1.20(8)	C(25)–C(26)	1.42(8)
C(10)–C(11)–C(12)	110.6(5)	C(10)–C(11)–C(14)	106.5(4)
C(16)–C(17)–C(24)	126.6(5)	C(17)–C(24)–C(25)	179.7(7)
C(24)–C(25)–C(26)	177.2(6)	C(25)–C(26)–C(27)	126.7(5)

4. Conclusion

The ligands $FcC(CH_3)_2Fc'$-C≡C–Ph (**L_1**) and $FcC(CH_3)_2Fc'$-C≡C–Fc (**L_2**) have been synthesized by the Castro-Stephens coupling the reaction of the ligands and their reactivity has been studied by reaction with $Co_2(CO)_8$. The syntheses and structural characterization of **L_1**, **L_2**, **1** and **2** are reported. The electrochemical data show that two or three resolved one-electron redox processes have been observed in compounds **L_1** and **1** or **L_2** and **2**, respectively.

Supplementary material

Crystallographic data for structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 638453 for **L_1**, 638454 for **L_2**. 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; Email: deposit@ccdc.cam.ac.uk).

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