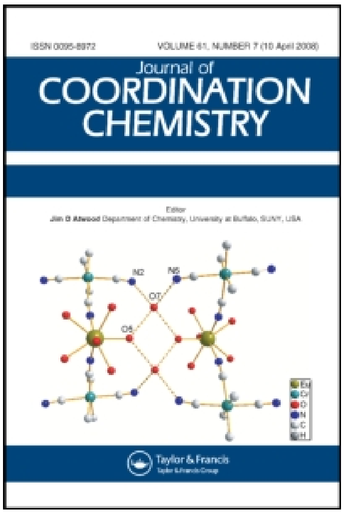

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Synthesis and structural characterization of new multiferrocenyl diyne ligands and their cobalt carbonyl complexes

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Synthesis and structural characterization of new multiferrocenyl diyne ligands and their cobalt carbonyl complexes

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New multiferrocenyl diyne ligands $FcC(CH_3)_2Fc'–C{\equiv}C–C{\equiv}C–Fc$ [$\mathbf{L_1}$; $Fc = C_5H_5FeC_5H_4$; $Fc' = C_5H_5Fe$(1,3-disubstituted)C_5H_3], $FcC(CH_3)_2Fc'–C{\equiv}C–C{\equiv}C–Fc'C(CH_3)_2Fc$ ($\mathbf{L_2}$) and their complexes $[FcC(CH_3)_2Fc'–C{\equiv}C–C{\equiv}C–Fc][Co_2(CO)_6]_n$ [$n = 1$, (**1**); $n = 2$, (**2**)], $[FcC(CH_3)_2Fc'–C{\equiv}C–C{\equiv}C–Fc'C(CH_3)_2Fc][Co_2(CO)_6]_n$ [$n = 1$, (**3**); $n = 2$, (**4**)] have been synthesized by the coupling reaction of terminal ferrocenylacetylene and the reaction of ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ with $Co_2(CO)_8$. The composition and molecular structure of the ligands $\mathbf{L_1}$, $\mathbf{L_2}$ and their cobalt complexes were characterized by element analysis, IR, $^1H(^{13}C)$NMR and MS. The electrochemical properties of compounds $\mathbf{L_1}$, $\mathbf{L_2}$, **1**, **2**, **3**, **4** were studied by cyclic voltammetry(CV). The results of the electrochemical research reveal that all three ferrocenyl groups in $\mathbf{L_1}$ become redox active centers, but there are only two (not four) ferrocenyl redox active centers in $\mathbf{L_2}$.

Keywords: Diyne ligand; Multiferrocenyl group; Cobalt complex; Electrochemical property

1. Introduction

Ferrocenyl compounds with π-conjugated carbon bridges have attracted attention because of their efficiency in transmitting electronic interactions between the ferrocenyl units [1–5]. Metal carbonyl clusters bearing ferrocenylacetylene possess interesting redox properties [6] and electronic communication [7]. The reactivity of diyne compounds with $Co_2(CO)_8$ has been studied in some detail and electronic communication of the ferrocenyl terminal with the redox-active center has been revealed [8–12], but there are few reports on synthesis, characterization and electrochemistry of the multiferrocenyl compounds with π conjugated carbon bridges [13,14].

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Here we describe the synthesis, structural characterization and electrochemical properties of new ligands FcC$(CH_3)_2$Fc′–C≡C–C≡C–Fc(**L_1**; Fc = $C_5H_5FeC_5H_4$; Fc′ = C_5H_5Fe(1,3-disubstituted)C_5H_3), FcC$(CH_3)_2$Fc′–C≡C–C≡C–Fc′C$(CH_3)_2$Fc(**L_2**) and their complexes [FcC$(CH_3)_2$Fc′–C≡C–C≡C–Fc][$Co_2(CO)_6$]$_n$ [$n = 1$, (**1**); $n = 2$, (**2**)], [FcC$(CH_3)_2$Fc′–C≡C–C≡C–Fc′C$(CH_3)_2$Fc][$Co_2(CO)_6$]$_n$ [n = 1, (**3**); $n = 2$, (**4**)]. The CV data of **L_1** show that there are three ferrocenyl redox active centers in **L_1**.

2. Experimental

Unless otherwise stated, 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 200–300 mesh silica gel column. The $Co_2(CO)_8$ was purchased from Aldrich. Published procedures or extensions thereof were used to synthesize the initial complexes FcC$(CH_3)_2$ Fc′–C≡CH and FcC≡CH [15–16].

IR spectra were recorded on a Nicolet FT-IR spectrometer, KBr disc. Elemental analyses were carried out on a Elementar Var III-type analyzer. $^1H(^{13}C)$NMR spectra in $CDCl_3$ were recorded on a Inova 500FT-MHz spectrometer. The mass spectra were determined by using Polaris Q MS, Autospec Ultima-TOF and JMS-T100LC instruments. The electrochemical properties were determined by a BAS 100A-type analyzer. Melting points were determined using XT-4 melting point apparatus.

2.1. *Synthesis of FcC(CH_3)$_2$Fc′–C≡C–C≡C–Fc(L_1)*

FcC$(CH_3)_2$Fc′–C≡CH (70 mg, 0.16 mmol), Fc–C≡CH (66 mg, 0.32 mmol) and CuCl(7 mg, 0.07 mmol) were dissolved in 8mL pyridine. The solution was stirred for 3 h in air at 60°C and the solvent removed under reduced pressure. The resulting mixture was washed with saturated NH_4Cl solution and extracted with CH_2Cl_2. The organic phase was combined and then dried using dehydrated $MgSO_4$. 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-benzene (3 : 2, v/v) afforded a yellow band. Yellow crystals of **L_1** were obtained by recrystallizing from hexane-benzene. Yield, 48%; m.p., 158–160°C. Anal. Calcd for $C_{37}H_{32}Fe_3$: C, 68.99; H, 5.01%. Found: C, 69.04; H, 4.90%. MS(EI): 644(M^+).

2.2. *Synthesis of FcC(CH_3)$_2$Fc′–C≡C–C≡C–Fc′C(CH_3)$_2$Fc(L_2)*

FcC$(CH_3)_2$Fc′–C≡CH (100 mg, 0.23 mmol) and CuCl (5 mg, 0.05 mmol) were dissolved in 8 mL pyridine. The mixture solution was stirred for 3 h in air at 60°C and the solvent removed under reduced pressure. The resulting mixture was washed with saturated NH_4Cl solution and extracted with CH_2Cl_2. The organic phase was combined and then dried using the dehydrated $MgSO_4$ and filtered. The filtrate was concentrated and the residue subjected to chromatographic separation on neutral alumina column (2.0 × 30 cm). Elution with a mixture of hexane-CH_2Cl_2 (3 : 1, v/v) afforded a yellow band. Yellow crystals of $\mathbf{L_2}$ were obtained by recrystallizing from hexane-CH_2Cl_2. Yield, 90%; m.p., 197–200°C. Anal. Calcd for $C_{50}H_{46}Fe_4$: C, 69.00; H, 5.33%. Found: C, 68.74; H, 5.44%. MS(EI): 870(M^+).

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

A benzene solution of $Co_2(CO)_8$ (27 mg, 0.08 mmol) and $\mathbf{L_1}$ (50 mg, 0.08 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 (3 : 1, v/v) afforded a green band **1**. The dark-green oil of **1** was obtained. Yield, 83%. Anal. Calcd for $C_{43}H_{32}O_6Co_2Fe_3$ C, 55.53; H,3.47%. Found: C, 56.38; H, 3.16%. MS(FAB): 930(M^+), 846(M^+–3CO), 818(M^+–4CO), 762(M^+–6CO), 185(Fc^+).

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

A benzene solution of $Co_2(CO)_8$ (75 mg, 0.22 mmol) and $\mathbf{L_1}$ (70 mg, 0.11 mmol) were stirred for 6h at room temperature. The solvent of the resulting mixture was removed in vacuum. The residue was dissolved in a minimum of benzene and subjected to chromatographic separation on a silica gel column (2.0 × 40 cm). Elution with hexane-benzene (5 : 1, v/v) afforded a green band **2**. The dark-green solid of **2** was obtained by crystallizing from hexane-benzene. Yield, 70%; m.p., 140°C (dec.). Anal. Calcd for $C_{49}H_{32}O_{12}Co_4Fe_3$ C, 48.40; H, 2.65%. Found: C, 47.94; H, 2.57%. MS(FAB): 1132(M^+–3CO), 1076(M^+–5CO), 1020(M^+–7CO), 964(M^+–9CO), 908(M^+–11CO), 880(M^+–12CO), 185(Fc^+).

2.5. *Synthesis of [FcC(CH$_3$)$_2$Fc′–C≡C–C≡C–Fc′C(CH$_3$)$_2$Fc][Co$_2$(CO)$_6$] (3)*

A benzene solution of $Co_2(CO)_8$ (32 mg, 0.09 mmol) and $\mathbf{L_2}$ (80 mg, 0.09 mmol) were stirred for 5 h at room temperature and the solvent removed in vacuum. The residue was dissolved in a minimum of benzene and subjected to chromatographic separation on a silica gel column (2.0 × 40 cm). Elution with hexane-benzene (3 : 1, v/v) afforded a dark-green band **3**. The dark-green oil of **3** was obtained. Yield, 71%. Anal. Calcd for $C_{56}H_{46}O_6Co_2Fe_4$ C, 58.17; H, 4.01%. Found: C, 59.12; H, 4.39%. MS(CSI): 1156(M^+).

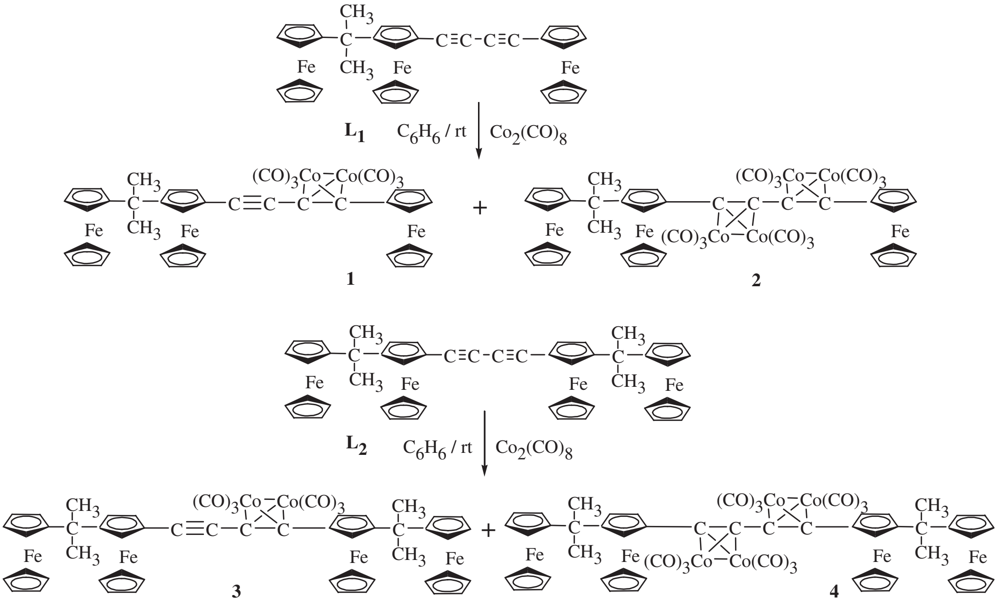
2.6. *Synthesis of [FcC(CH$_3$)$_2$Fc′–C≡C–C≡C–Fc′C(CH$_3$)$_2$Fc][Co$_2$(CO)$_6$]$_2$ (4)*

A benzene solution of $Co_2(CO)_8$ (89 mg, 0.26 mmol) and $\mathbf{L_2}$ (110 mg, 0.13 mmol) were stirred for 11 h at room temperature. The solvent of the resulting mixture was 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 (5 : 1, v/v) afforded a brown-green band **4**. The brown-green solid **4** was obtained by crystallizing from hexane-benzene. Yield, 93%; m.p., 120°C (dec.). Anal. Calcd for $C_{62}H_{46}O_{12}Co_4Fe_4$ C, 51.64; H, 3.21%. Found: C, 50.96; H, 3.20%. MS(CSI): 1442(M^+).

3. Results and discussion

3.1. *Characterization of compounds L_1, L_2, 1, 2, 3, 4*

The reactions carried out in this work are summarized in scheme 1. Spectral data of **L_1**, **L_2**, **1**, **2**, **3**, and **4** are in table 1.



Scheme 1. The synthesis reaction of complexes **1**, **2**, **3**, **4**.

Table 1. Spectral data of **L_1**, **L_2**, **1**, **2**, **3** and **4**.

Compound	FTIR (cm^{-1})	^1H NMR (ppm)	^{13}C NMR (ppm)	MS (m/z, FAB)
L_1	3087.3, 2971.2, 2924.6, 2864. 5, 2214.8, 2148.4, 1102.2, 999.0, 818.4	4.0–4.5, 1.6	102.6, 71.1, 71.0, 70.9, 70.7, 70.1, 69.9, 69.5, 69.2, 68.1, 67.8, 67.1, 63.9, 63.4, 79.2, 78.9, 72.5, 72.1, 33.1, 30.3	644(M^+)
L_2	3091.7, 2969.2, 2928.3, 2862.2, 2147.6, 1107.5, 999.6, 818.7	4.0–4.5, 1.6	102.7, 101.1, 70. 9, 70.8, 70.7, 70.2, 69.8, 69.4, 68.9, 67.9, 67.7, 67.3, 67.1, 66.3, 63.5, 62.2, 79.3, 79.1, 72.5, 71.1, 33.2, 33.1, 30.3	870(M^+)
1	2171.6, 2088.4, 2051.0, 2021.8	4.0–4.6, 1.6, 1.7	198.9, 65.9–72.2, 30.6, 29.7	930(M^+)
2	2095.6, 2074.4, 2052.7, 2035.6, 2016.8, 2009.2, 2000.3	4.0–4.6, 1.6	199.4, 102.5, 101.3, 97.9, 88.6, 66.2–71.5, 33.4, 30.7	1132(M^+-3CO), 1076, 1020, 964, 908, 880, 185
3	2171.8, 2084.8, 2052.0, 2022.7	4.0–4.4, 1.6	198.9, 103.8, 65.9–70.6, 30.6	870, 581, 553, 522, 430, 338, 185
4	2093.3, 2073.3, 2051.3, 2015.3	4.1, 1.6	199.2; 102.5, 100.1, 65.9–71.6; 30.4, 29. 5	MS (CSI) 1442(M^+)

Ligands $\mathbf{L_1}$ or $\mathbf{L_2}$ was synthesized by the cross coupling reaction (for $\mathbf{L_1}$) of $FcC(CH_3)_2Fc'–C{\equiv}CH$ and $Fc–C{\equiv}CH$ or the self-coupling reaction (for $\mathbf{L_2}$) of $FcC(CH_3)_2Fc'–C{\equiv}CH$. It is very difficult to separate L_1 from the self-coupling by-products $Fc–C{\equiv}C–C{\equiv}C–Fc$ and $FcC(CH_3)_2Fc'–C{\equiv}C–C{\equiv}C–Fc'C(CH_3)_2Fc$ ($\mathbf{L_2}$). Complexes **1**, **2**, **3** and **4** were easily prepared by the reaction of $\mathbf{L_1}$, $\mathbf{L_2}$ with $Co_2(CO)_8$ typical for $C{\equiv}C$ triple bond and the Co–Co bond. $\mathbf{L_1}$ and $\mathbf{L_2}$ are yellow, air-stable crystalline compounds, soluble in both non-polar solvents such as hexane, petroleum ether, benzene and polar solvents such as acetonitrile and chloroform. The dark-green oils (for **1**, **3**) were obtained while the mole ratio of $Co_2(CO)_8$ to ligand was fixed to 1 : 1 and the dark-green solid for **2** and the brown-green solid for **4** were obtained for a mole ratio of 1 : 2. The solubility of all four complexes is similar to their relevant ligands.

FTIR spectra of $\mathbf{L_1}$ and $\mathbf{L_2}$ show Cp(3087.3, 1102.2, 999.0, 818.4 for $\mathbf{L_1}$; 3091.7, 1107.5, 999.6, 818.7 for $\mathbf{L_2}$), CH_3(2971.2, 2924.6, 2864.5 for $\mathbf{L_1}$; 2969.2, 2928.3, 2862.2 for $\mathbf{L_2}$) and $C{\equiv}C$ (2214.8, 2148.4 for $\mathbf{L_1}$; 2147.6 for $\mathbf{L_2}$). The $C_5H_5FeC_5H_4$ or $C_5H_5FeC_5H_3$ (4.0–4.6 ppm) and $C(CH_3)_2$(1.6–1.7 ppm) groups in the ligands and the complexes were confirmed by ^1H NMR. The ^{13}C NMR data of the $\mathbf{L_1}$ and $\mathbf{L_2}$ show the signals of $C_5H_5FeC_5H_4$ or $C_5H_5FeC_5H_3$ (63.4–71.1, 102.6 for $\mathbf{L_1}$; 62.2–70.9, 101.1, 102.7 for $\mathbf{L_2}$), $C{\equiv}C$ (79.2, 78.9, 72.5, 72.1 for $\mathbf{L_1}$; 79.3, 79.1, 72.5, 71.1 for $\mathbf{L_2}$) and $C(CH_3)_2$ (33.1, 30.3 for $\mathbf{L_1}$; 33.2, 33.1, 30.3 for $\mathbf{L_2}$) groups. ^{13}C NMR data of complexes **1**, **2**, **3**, **4** show CO (198.9–199.4 ppm), $C_5H_5FeC_5H_4$ or $C_5H_5FeC_5H_3$ (65.9–72.2 ppm), $C(CH_3)_2$ (29.5–33.4 ppm) groups and the coordinated triple bonds (88.6–103.8 ppm). The molecular ion peaks (644, for $\mathbf{L_1}$; 870, for $\mathbf{L_2}$; 930, for **1**; 1442, for **4**) were found in ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ and complexes **1** and **4.** The composition and structure of complexes **2** and **3** were further identified by fragment ion peaks 1132 (M^+–3CO), 1076 (M^+–9CO), 1020 (M^+–7CO), 964 (M^+–11CO), 908 (M^+–5CO), 880 (M^+–12CO), 185 (Fc) for **2** and 870 ($[FcC(CH_3)_2Fc'C{\equiv}C–C{\equiv}CFc'C(CH_3)_2Fc]^+$), 581 ($[(CO)Co_2CCFc'C(CH_3)_2Fc]^+$), 553 ($[Co_2CCFc'C(CH_3)_2Fc]^+$), 522 ($[(CO)CoCCFc'C(CH_3)_2Fc]^+$), 430 ($[FeC_5H_4CCCo_2(CO)_6]^+$), 338 ($[C_5H_4C(CH_3)_2Fc'C{\equiv}C–C{\equiv}C]^+$), 185 (Fc) for **3**. According to the spectral data (see table 1) and element analysis of ligands $\mathbf{L_1}$, $\mathbf{L_2}$ and complexes **1**, **2**, **3**, **4** and our previous determined similar molecular structure [17], composition and structures are shown in scheme 1.

3.2. *Electrochemical properties of compounds L_1, L_2, 1, 2, 3 and 4*

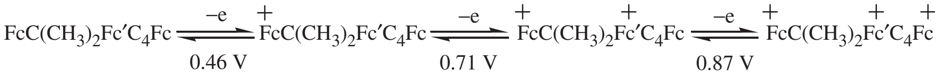
The electrochemical properties of $\mathbf{L_1}$, $\mathbf{L_2}$, **1**, **2**, **3** and **4** have been studied by cyclic voltammetry at 293 K in a standard three-electrode system with NEt_4ClO_4 in CH_3CN as the supporting electrolyte. The results are given in table 2.

One of the most popular methods for testing electronic communication through a potential molecular wire is to examine the interaction between redox active groups located at its terminal [18]. The difference in the two potentials ΔE^0 represents the magnitude of electronic communication between individual ferrocenyl redox active centers [19] although the wave separation ΔE^0 is affected by conditions such as solvent, supporting electrolyte, solution concentration [20], the distance between the redox-active centres [21] and the extent of electronic delocalization along the molecular chain, etc. [22]. The results in table 2, show three resolved one-electron redox waves at E_1^0

Table 2. Voltammetric data.

Complex	$E_{\mathrm{red}}^{\mathrm{pc}}$	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
1	−1.25	0.45	0.79	0.92	0.34	0.13
2	−1.29	0.48	0.68	0.86	0.20	0.18
3	−1.33	0.56	1.06	–	0.50	–
4	−1.28	0.46	0.75	–	0.29	–
L_1	–	0.46	0.71	0.87	0.25	0.16
L_2	–	0.48	0.87	–	0.39	–
Fc-C_2–C_2–Fc	–	0.67	0.80	–	0.13	–
FcC$(CH_3)_2$Fc	–	0.41	0.65	–	0.24	–
Ferrocene	–	0.51	–	–	–	–

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); $E^0 = 1/2(E_{\mathrm{pc}} + E_{\mathrm{pa}})$(V); $\Delta E^0 = E_2^0 - E_1^0$ (V).



$$\mathrm{FcC(CH_3)_2Fc'C_4Fc} \xrightleftharpoons[0.46\ \mathrm{V}]{-e} \overset{+}{\mathrm{Fc}}\mathrm{C(CH_3)_2Fc'C_4Fc} \xrightleftharpoons[0.71\ \mathrm{V}]{-e} \overset{+}{\mathrm{Fc}}\mathrm{C(CH_3)_2}\overset{+}{\mathrm{Fc'}}\mathrm{C_4Fc} \xrightleftharpoons[0.87\ \mathrm{V}]{-e} \overset{+}{\mathrm{Fc}}\mathrm{C(CH_3)_2}\overset{+}{\mathrm{Fc'}}\mathrm{C_4}\overset{+}{\mathrm{Fc}}$$

L_1

Scheme 2. The redox process of ligand **L_1**.

(0.45 V), E_2^0 (0.79 V), E_3^0 (0.92 V) respectively, ascribed to three ferrocenyl units (Fc^0/Fc^+, Fc'^0/Fc'^+, Fc^0/Fc^+) as redox active centres in **L_1**. However, in **L_2** there are two (not four) resolved ferrocenyl redox waves at E_1^0 (0.48 V), E_2^0 (0.87 V). ΔE^0 (0.39 V) for **L_2** is bigger than the values of contrasting compounds (0.24 V for FcC$(CH_3)_2$Fc, 0.13 V for Fc–C_2–C_2–Fc). The ΔE^0 value ($\Delta E_1^0 = 0.25$ V) for **L_1** is nearly equal to the value ($\Delta E_1^0 = 0.24$) of FcC$(CH_3)_2$Fc while the concentration of CH_3CN solution with Et_4NClO_4 was fixed to 0.001 M. The ΔE_1^0 value is bigger than the ΔE_2^0 value whether it is for ligand **L_1** or complex **1** or **2**. The ΔE_1^0 values of complexes **2**, **4** are less than that of **L_1** and **L_2** because of the weakening of conjugation induced by coordination of the metal cluster core with the C_4 diyne chain of ligands. It is an abnormality that the ΔE_1^0 values (0.34 for **1**, 0.50 for **3**) of complexes **1** and **3** are bigger than the values (0.25 for **L_1**, 0.39 for **L_2**) of the relevant ligands **L_1** and **L_2**, perhaps, from the Co_2 cluster core asymmetry coordination with one acetylene group of the ligands. The irreversible reduction waves at $E_{\mathrm{pc}} = -1.25$, -1.29, -1.33, -1.28 V, respectively are regarded as the result of reduction of $Co_2(CO)_6$ in **1**, **2**, **3** and **4** [8]. At the present time, the relationship between ΔE_0 value and the electronic communication is not completely known and further study is still needed. The redox process of **L_1** is been shown in scheme 2.

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