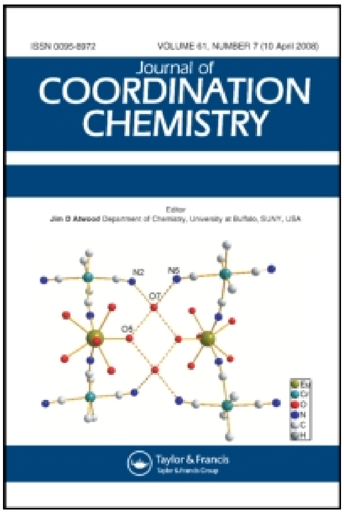

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Quan-Ling Suo[a]; Li-Min Han[a]; Yi-Bing Wang[a]; Jie-Hui Ye[a]; Ning Zhu[a]; Xue-Bing Leng[b]; Jie Sun[c]
[a] Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, P.R. China [b] Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, P.R. China [c] Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences, Shanghai, P.R. China

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SYNTHESES AND MOLECULAR STRUCTURES OF NEW FERROCENYLACETYLIDE-BRIDGED BINUCLEAR COBALT CARBONYL CLUSTER COMPOUNDS

QUAN-LING SUO[a,*], LI-MIN HAN[a], YI-BING WANG[a], JIE-HUI YE[a],
NING ZHU[a], XUE-BING LENG[b] and JIE SUN[c]

[a]*Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, 010062, P.R. China;* [b]*Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, P.R. China;* [c]*Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences, Shanghai, 200032, P.R. China*

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The reaction of ferrocenylacetylide compounds with $Co_2(CO)_8$ at room temperature affords four complexes bearing ferrocenyl units with approximately tetrahedral (μ-alkyne)dicobalt moieties $[R\text{–}(C{\equiv}C)_n\text{–}R'][Co_2(CO)_6]_{n'}$ [$R = C_5H_5FeC_5H_4\text{-}C(CH_3)_2\text{-}C_5H_4FeC_5H_4$, $R' = H$, $n = 1$, $n' = 1$ (**1**); $R = C_5H_5FeC_5H_4$ [ferrocenyl (Fc)], $R' = \text{–}CH{=}CHCl$, $n = 1$, $n' = 1$ (**2**); $R = Fc$, $R' = Fc$, $n = 2$, $n' = 1$ (**3**), $n' = 2$ (**4**)]. The compounds were characterized by elemental analysis, IR, $^1H(^{13}C)$ NMR, MS and single-crystal X-ray diffraction analysis. The X-ray analyses show that coordination of the carbon–carbon triple bond and the dicobalt unit result in the formation of a Co_2C_2 tetrahedral core, and the substituents on the acetylenic units show a distortion from linearity that reflects this coordination mode.

Keywords: Ferrocenylacetylide ligand; Cobalt carbonyl cluster; Synthesis; Molecular structure

INTRODUCTION

Interaction of the C≡C functional group with a metal cluster core continues to command the attention of researchers [1–6]. The main types of complexes include $Fc^{II}\text{-}C{\equiv}C\text{-}Cu_3L_6\text{-}C{\equiv}C\text{-}Fc^{III}$ [7], $[Me_3Si\text{-}C{\equiv}C\text{-}(Fc)_3\text{-}C{\equiv}C\text{-}SiMe_3]Co_4(CO)_{12}$ [8], $L_3Pt\text{-}(C{\equiv}C)_n\text{-}PtL_3$ ($n = 4$, 6) [9] and L_5Ru(or Fc)-$C{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}C\text{-}RuL_5$(or Fc) [10]. Previous studies indicate the compounds are electron delocalized and useful materials for constructing molecular switches [11] and wires [12]. Compounds containing two or four alkyne groups of ligand $Fc\text{-}(C{\equiv}C)_2\text{-}Fc$ (**L$_3$**) or $Fc\text{-}(C{\equiv}C)_4\text{-}Fc$ (**L**) coordinated parallel to a linear chain of three osmium atoms have been obtained by the reactions of compound **L$_3$** or **L** with triosmium carbonyl clusters [13]. The osmium atoms coordinate on the π-bonds of the unsaturated polyyne chain and there may

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*Corresponding author. Tel.: +86-471-6575796. Fax: +86-471-6575796. E-mail: szj@imut.edu.cn

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be electrocommunication between the two ferrocenyl groups [14]. Reaction of metal hydride with ligand **L** gives cyclization and *trans*-hydrogenation of alkyne groups, but no significant electrocommunication between the two ferrocenyl groups [15]. The structure of the compounds affects the electron transfer between metal centers [16].

Reaction of π-conjugated dienes with $Co_2(CO)_8$ were reported in 1996 [17], and several substitution reactions involving diyne metal cluster compounds have been studied [18]. The complexes may be regarded as starting compounds for synthesizing polynuclear mixed-metal clusters by metal exchange or enlarging nuclearity [19]. The reactivity and potential uses of the complexes have not been fully rationalized up to now; the chemistry of acetylene- or ferrocenylacetylide-substituted transition metal clusters is still an active research field.

In this article, reactions of ligands [Fc-$C(CH_3)_2$-$(C_5H_4Fe)C_5H_4$-C≡CH (**L_1**), Fc-C≡C-CH=CHCl (**L_2**) and Fc-C≡C-C≡C-Fc (**L_3**)] with $Co_2(CO)_8$, respectively, have been studied and four new crystal and molecular structures of complexes with ferrocenylacetylide coordinated to cobalt carbonyl clusters have been determined by single-crystal X-ray diffraction analysis. To our knowledge, the crystal and molecular structures of **1**, **2**, **3** and **4** have not been reported.

EXPERIMENTAL

General Procedures

All manipulations were carried out using standard Schlenk techniques under an atmosphere of pure nitrogen. Solvents were purified, dried and distilled under nitrogen prior to use. Reactions were monitored by TLC. Chromatographic separations and purification were performed on 200–300 mesh silica gel. The $Co_2(CO)_8$ was purchased from Aldrich. The ligands Fc-$C(CH_3)_2$-$(C_5H_4Fe)C_5H_4$-$COCH_3$ [20], Fc-C≡C-CH=CHCl (**L_2**) and Fc-C≡C-C≡C-Fc (**L_3**) [21] were prepared according to the literature method.

IR spectra were recorded on a Nicolet FT-IR spectrometer in KBr discs. Elemental analyses were carried out on a Elementar var III-type analyzer. $^1H(^{13}C)$ NMR spectra in $CDCl_3$ were recorded on a Jeo-Jnm-Al 300FT-MHz spectrometer. The mass spectra were determined by using a Micromass LCT instrument. Melting points were determined using an XT-4 melting point apparatus.

Synthesis of Ligand Fc-$C(CH_3)_2$-$(C_5H_4Fe)C_5H_4$-C≡CH (L_1)

$POCl_3$ (1.6 cm^3, 17.6 mmol) was dissolved in 5 cm^3 solution of *N*,*N*-dimethylformamide (DMF), which was dropped into a 10 cm^3 DMF solution of Fc-$C(CH_3)_2$-(C_5H_4Fe) C_5H_4-$COCH_3$ (1.0 g, 2.2 mmol) at 0°C. The solution was stirred for 1.5 h at 0°C and 2 h at room temperature. The reaction mixture was transferred to 30 cm^3 solution of NaAc (20%) and stirred for 1.5 h. The resulting red mixture was extracted with CH_2Cl_2, the organic phase was combined, dried using anhydrous $MgSO_4$ 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 red band. A red solid was obtained by concentrating and precipitating the red solution. The red solid was dissolved in 11 cm^3 1,4-dioxane, which was heated to reflux temperature, and then NaOH (2.6 cm^3, 0.5 M) was added.

After refluxing for 5 min the reaction mixture was cooled to room temperature, poured into 50 g water at 0°C, and then the solution was neutralized with HCl (0.5 M). The mixture was extracted with diethyl ether and the ether layer was washed with water, dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by neutral alumina column chromatography using hexane as eluant. The ligand $\mathbf{L_1}$ was obtained as an orange-yellow solid. Yield 18%. m.p. 95–97°C. Anal. Calc. for $C_{25}H_{24}Fe_2$: C, 68.86; H, 5.73. Found: C, 68.37; H, 5.19%. IR (KBr disk) ν 819s, 1035m, 1103m, 2105m, 2853m, 2930m, 2978m, 3094w, 3273w cm^{-1}. ^1H-NMR ($DCCl_3$, δ): 4.2–4.5 (m, 17H, Fc_2-H), 2.5 (s, 1H, ≡C-H), 1.2 [s, 6H, $C(CH_3)_2$]. MS(ESI) 437 ($M^+ + 1$).

Synthesis of $Co_2(CO)_6$ [Fc-$C(CH_3)_2$-(C_5H_4Fe)C_5H_4-C≡CH] (1)

A benzene solution of $Co_2(CO)_8$ (178 mg, 0.52 mmol) and ligand $\mathbf{L_1}$ (226 mg, 0.52 mmol) was stirred for 24 h at room temperature. The solvent of the resulting dark green mixture was removed in vacuo. The residue was dissolved in a minimal amount of benzene and subjected to chromatographic separation on a silica gel column. Elution with hexane afforded a dark green band (**1**). Crystals of **1** were obtained by recrystallizing the solid **1** from hexane at −20°C. Yield 62%. m.p., 92°C. Anal. Calc. for $C_{31}H_{24}O_6Co_2Fe_2$: C, 51.52; H, 3.32. Found: C, 51.78; H, 3.08%. IR (KBr disk) ν(CO) 2092s, 2055s, 2013vs, 1998vs cm^{-1}. ^1H-NMR ($DCCl_3$, δ): 6.6 (s, 1H, –C≡C-H), 4.0–4.3 (m, 17H, Fc_2-H), 1.6 [s, 6H, $C(CH_3)_2$]. ^{13}C-NMR ($DCCl_3$, δ): 203.7 (CO), 100.9, 102.4 (–C≡CH), 65.8–73.7 (Cp), 30.6 (CH_3). MS(ESI): 722 (M^+).

Synthesis of $Co_2(CO)_6$ [Fc-C≡C-CH=CHCl] (2)

A benzene solution of $Co_2(CO)_8$ (178 mg, 0.52 mmol) and ligand $\mathbf{L_2}$ (140 mg, 0.52 mmol) was stirred for 24 h at room temperature. The solvent of the resulting dark green mixture was removed in vacuo. The residue was dissolved in a minimal amount of benzene and subjected to chromatographic separation on a silica gel column. Elution with hexane afforded a dark green band (**2**). Crystals of **2** were obtained by recrystallizing the solid **2** from hexane at −20°C. Yield 61%. m.p., 140°C. Anal. Calc. for $C_{20}H_{11}O_6ClCo_2Fe$: C, 43.13; H, 1.98. Found: C, 42.97; H, 2.04%. IR (KBr disk) ν(CO) 2084s, 2051w, 2026vs, 1988vs cm^{-1}. ^1H-NMR ($DCCl_3$, δ): 7.1 (d, 1H, C≡C-CH=), 6.7 (d, 1H, =CClH), 4.2–4.4 (m, 9H, Fc-H). MS (ESI): 556 (M^+).

Synthesis of $Co_2(CO)_6$[Fc-C≡C-C≡C-Fc] (3)

A benzene solution of $Co_2(CO)_8$ (110 mg, 0.32 mmol) and ligand $\mathbf{L_3}$ (134 mg, 0.32 mmol) was stirred for 24 h at room temperature. The solvent of the resulting dark green mixture was removed in vacuo, the residue was dissolved in a minimal amount of benzene and subjected to chromatographic separation on a silica gel column. Elution with hexane afforded a green-black band (**3**). Crystals of **3** were obtained by recrystallizing solid **3** from hexane at −20°C. Yield 21%. m.p., 158°C. Anal. Calc. for $C_{30}H_{18}O_6Co_2Fe_2$: C, 51.18; H, 2.58. Found: C, 51.03; H, 2.64%. IR (KBr disk) ν(–C≡C–) 2177w; ν(CO) 2088vs, 2047vs, 2014s, 2000s cm^{-1}.

Synthesis of $Co_4(CO)_{12}$[Fc-C≡C-C≡C-Fc] (4)

A benzene solution of $Co_2(CO)_8$ (220 mg, 0.64 mmol) and ligand $\mathbf{L_4}$ (134 mg, 0.32 mmol) was stirred for 24 h at room temperature. The solvent of the resulting red-brown mixture was removed in vacuo. The residue was dissolved in a minimal amount of benzene and subjected to chromatographic separation on a silica gel column. Elution with hexane afforded a red-brown band (**4**); crystals of **4** were obtained by recrystallizing solid **4** from hexane at −20°C. Yield 61%. m.p., 165°C. Anal. Calc. for $C_{36}H_{18}O_{12}Co_4Fe_2$: C, 43.68; H, 1.83. Found: C, 43.97; H, 1.74%. IR (KBr disk) ν(CO) 2076m, 2052s, 2027vs, 2000vs cm^{-1}. ^{1}H-NMR($DCCl_3$, δ): 3.9–4.5 (m, 18H, Fc-H). ^{13}C-NMR ($DCCl_3$, δ): 203.4 (CO), 126.0, 126.7 (–C≡C–C≡C–), 69.3, 69.5 (C_5H_5,C_5H_4). MS(ESI): 992 ($M^+ + 2$).

X-Ray Crystallography of the Complexes 1–4

Crystals of **1**–**4** were mounted on a glass fiber. All measurements were made on the Bruker SMART 1000 CCD (for **1** and **3**) and Bruker SMART APEX CCD (for **2** and **4**) 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 [22]. An absorption correction based on SADABS was applied [23]. All non-hydrogen atoms were refined by 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 [24]. The structure solution and refinement were performed by SHELXSL97 [25]. Further crystal data and details of measurements are shown in Table I.

RESULTS AND DISCUSSION

Characterization of the Ferrocenylacetylide Complexes

The FTIR spectra of these compounds have characteristic absorption bands of the terminal carbonyl ligands coordinated on Co in the region 2092–1988 cm^{-1}. In complex **3**, an absorption of the C≡C triple bond-stretching vibration is at 2177 cm^{-1}, indicating that there is one uncoordinated C≡C triple bond. ^{1}H and ^{13}C NMR spectra indicate Fc, C≡C, CH=CHCl, CH_3 and CO groups in complexes **1**–**4**. The complexes are soluble in non-polar solvents such as hexane, petroleum ether, benzene and polar solvents such as acetonitrile and chloroform.

Molecular Structures of the Complexes 1–4

The molecular structures of the complexes **1**, **2**, **3** and **4** were determined by X-ray single crystal analysis. Crystal data and relevant structural parameters are given in Table I. The structures with the atom numbering scheme are shown in Figs. 1–4, and selected bond lengths and angles are listed in Tables II–V.

Molecules of **1**–**4** contain one (for **2**) or two (for **1**, **3**, **4**) ferrocenyl units with approximately tetrahedral (μ-alkyne)dicobalt moieties bound to a cyclopentadiene ring. In the four complexes the CO ligands coordinated to Co atoms are terminal (vide infra).

TABLE I Crystal data and structure refinement for **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{31}H_{24}O_6Co_2Fe_2$	$C_{20}H_{11}O_6ClCo_2Fe$	$C_{30}H_{18}O_6Co_2Fe_2$	$C_{36}H_{18}O_{12}Co_4Fe_2$
Formula weight	722.06	556.45	704.00	989.92
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P\bar{1}$	$P2_1\ 2_12_1$	$P2_1\ 2_12_1$	$P\bar{1}$
Unit cell dimensions				
a (Å)	7.989(7)	8.2898(7)	10.644(3)	9.0501(7)
b (Å)	10.370(8)	11.0985(10)	11.528(3)	9.3096(8)
c (Å)	17.723(14)	23.133(2)	22.328(6)	11.8334(10)
α (°)	97.065(15)	90	90	81.821(2)
β (°)	91.937(15)	90	90	88.098(2)
γ (°)	101.831(14)	90	90	65.1440(10)
Volume (Å^3), Z	1424(2), 2	2128.3(3), 4	2739.7(14), 4	895.05(13), 1
Density (calc.) (Mg/m^3)	1.684	1.737	1.707	1.837
Absorption coeff. (mm^{-1})	2.187	2.372	2.270	2.663
F(000)	728	1104	1408	490
Crystal size (mm)	$0.35 \times 0.25 \times 0.20$	$0.62 \times 0.35 \times 032$	$0.38 \times 0.32 \times 0.10$	$0.71 \times 0.28 \times 0.22$
θ range for data collection (°)	2.20 to 25.02	1.76 to 28.29	1.99 to 26.40	2.44 to 28.27
Limiting indices	$-9 \leq h \leq 9$, $-12 \leq k \leq 11$, $-21 \leq l \leq 16$	$-11 \leq h \leq 7$, $-14 \leq k \leq 13$, $-30 \leq l \leq 30$	$-13 \leq h \leq 8$, $-13 \leq k \leq 14$, $-27 \leq l \leq 27$	$-10 \leq h \leq 11$, $-11 \leq k \leq 12$, $-9 \leq l \leq 15$
Reflections collected	5636	13038	15234	5497
Independent reflections	4812 (Rint = 0.0539)	4912 (Rint = 0.0358)	5620 (Rint = 0.0220)	3972 (Rint = 0.0220)
Completeness to θ (°, %)	25.02, 95.6	28.29, 96.1	26.40, 99.7	28.27, 89.4
Max., min. transmission	1.000000, 0.713562	1.00000, 0.51968	1.000000, 0.577859	1.00000, 0.68512
Data/restraints/parameters	4812/0/372	4912/0/315	5620/0/361	3972/3/281
Goodness-of-fit on F^2	1.016	0.896	1.037	1.004
R_1, wR_2 [$I = 2\sigma(I)$]	0.0698, 0.1412	0.0358, 0.0629	0.0399, 0.0797	0.0491, 0.1279
R_1, wR_2 (all data)	0.1442, 0.1699	0.0446, 0.0648	0.0581, 0.0857	0.0528, 0.1308
Largest diff. peak, hole eÅ^{-3}	0 .936, −0.686	0.550, −0.411	0.333, −0.458	1.024, −0.909
Weighing scheme, w (calc.) [where $P = (F_o^2 + 2F_c^2)/3$]	$1/[\sigma^2(F_o^2) + (0.0600P)^2 + 0.0000P]$	$1/[\sigma^2(F_o^2) + (0.0231P)^2 + 0.0000P]$	$1/[\sigma^2(F_o^2) + (0.0408P)^2 + 0.0000P]$	$1/[\sigma^2(F_o^2) + (0.0908P)^2 + 0.0000P]$

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 distances in the range 2.454–2.474 Å are typical for alkyne dicobalt complexes. In the four complexes the alkyne bonds adopt typical μ_2-η^2 coordination with the alkyne bond lying essentially perpendicular to the Co–Co bond in the C_2Co_2 unit. The C–C bond lengths of the C_2Co_2 fragment are 1.342(13), 1.328(4), 1.355(6), 1.350(4) Å for complexes **1**, **2**, **3**, **4**, respectively, showing the bond distance of the coordinated C≡C bond is similar to a C=C double bond. The Fe–C distances of ferrocenyl moieties in the four complexes vary from 2.006(6) to 2.059(8) Å, comparable with those found in compounds with ferrocenylalkynyl units [8].

In **1** the C_2Co_2 unit is coordinated to the alkyne in a *trans* configuration and linked to the unsubstituted cyclopentadiene ring of Fc by a short single bond (1.459 Å) between C(8) and C(9). This bond distance suggests some degree of electron delocalization between the alkyne and the unsubstituted cyclopentadiene ring. The distortion of the quasi tetrahedral C_2Co_2 core is evidenced by the nonequivalence of the Co–C bond lengths [Co(1)–C(7) 1.949(9), Co(1)–C(8) 1.990(8), Co(2)–C(7) 1.960(10), Co(2)–C(8) 1.955(9) Å] and bond angles [C(7)–Co(1)–Co(2) 51.0(3), C(7)–Co(2)–Co(1) 50.6(3), C(8)–Co(1)–Co(2) 50.6(2), C(8)–Co(2)–Co(1) 51.9(2), C(7)–C(8)–Co(1) 68.5(5), C(8)–C(7)–Co(1) 71.7(6), C(7)–C(8)–Co(2) 70.2(6), C(8)–C(7)–Co(2) 69.7(6)°]. The bond angle C(7)–C(8)–C(9) 144.3(9)° is much smaller than 180° of sp-hybridized C(8) and the angles C(8)–C(9)–C(10) 126.2(8) and C(7)–C(9)–C(13) 127.4(9)° are larger than 120°, attributed to steric interactions between the (μ-alkyne)dicobalt and ferrocenyl moieties. The angles around C(19) deviate from 109° as a result of steric influences. The bond distances of C(18)–C(19) [1.509(11)] and C(19)–C(22) [1.538(11) Å] indicate the two ferrocenyl units in **1** are linked by two single bonds of the $C(CH_3)_2$ group.

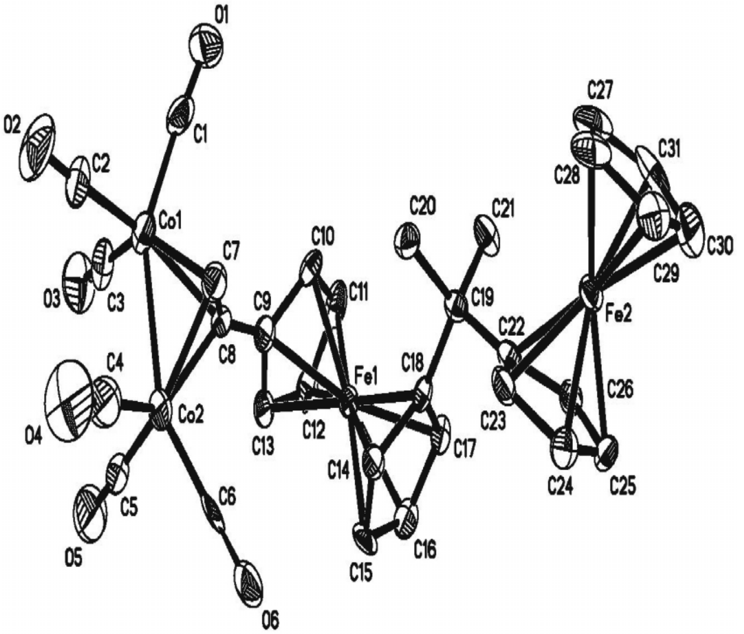

FIGURE 1 Molecular structure of **1**.

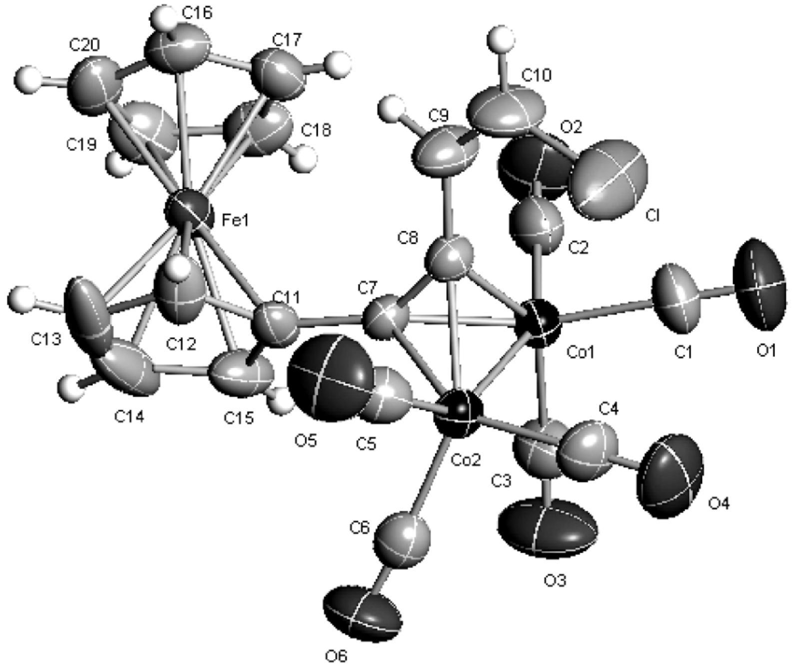

FIGURE 2 Molecular structure of **2**.

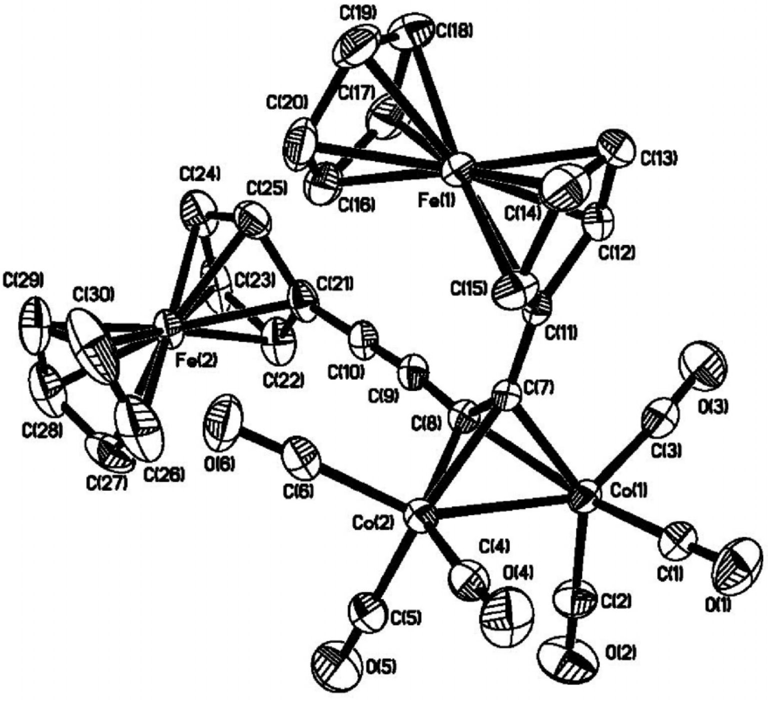

FIGURE 3 Molecular structure of **3**.

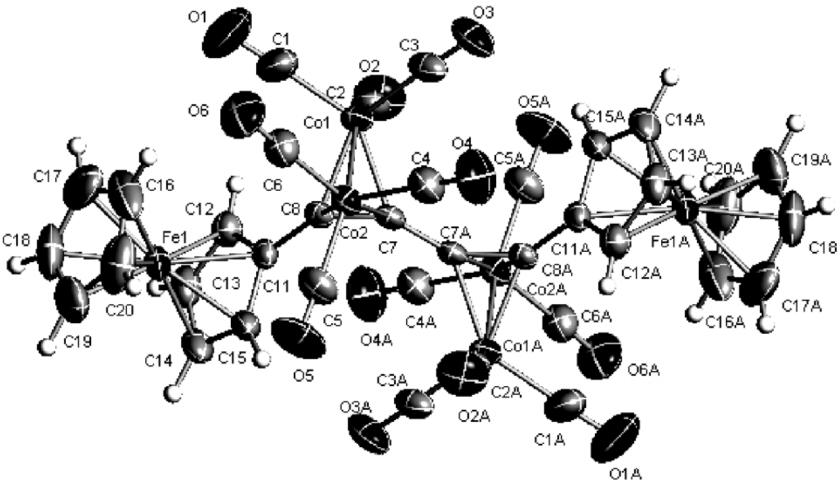

FIGURE 4 Molecular structure of **4**.

TABLE II Selected bond lengths (Å) and angles (°) for **1**

Co(1)–Co(2)	2.470(2)	C(19)–C(22)	1.538(11)
Co(1)–C(1)	1.801(13)	C(22)–C(23)	1.395(12)
Co(1)–C(7)	1.949(9)	Fe(1)–C(9)	2.049(8)
Co(1)–C(8)	1.990(8)	Fe(1)–C(10)	2.029(8) (min)
Co(2)–C(7)	1.960(10)	Fe(1)–C(13)	2.059(8) (max)
Co(2)–C(8)	1.955(9)	Fe(1)–C(18)	2.054(8)
C(7)–C8)	1.342(13)	Fe(2)–C(22)	2.045(8)
C(8)–C(9)	1.459(12)	Fe(2)–C(27)	2.054(10) (max)
C(18)–C(19)	1.509(11)	Fe(2)–C(30)	2.010(11) (min)
C(1)–Co(1)–Co(2)	146.5(3)	C(8)–C(7)–Co(2)	69.7(6)
C(2)–Co(1)–Co(2)	99.6(4)	C(7)–C(8)–C(9)	144.3(9)
C(3)–Co(1)–Co(2)	100.2(4)	C(8)–C(9)–C(10)	126.2(8)
C(7)–Co(1)–Co(2)	51.0(3)	C(8)–C(9)–C(13)	127.4(9)
C(8)–Co(1)–Co(2)	50.6(2)	C(18)–C(19)–C(20)	111.2(7)
C(7)–Co(2)–Co(1)	50.6(3)	C(18)–C(19)–C(22)	105.7(6)
C(8)–Co(2)–Co(1)	51.9(2)	C(19)–C(18)–C(14)	127.7(7)
C(7)–C(8)–Co(1)	68.5(5)	C(19)–C(18)–C(17)	125.7(7)
C(8)–C(7)–Co(1)	71.7(6)	C(19)–C(22)–C(23)	126.6(7)
C(7)–C(8)–Co(2)	70.2(6)	C(19)–C(22)–C(26)	125.1(8)

In **2** the alkyne rather than the alkene bond coordinates with Co–Co bond and the alkyne unit adopts the normal *cis*-bent configuration, as expected for perpendicular acetylenes. The significant variation between the alkyne bend-back angles to the CH=CHCl, C(7)–C(8)–C(9) 137.3(3)°, and to the ferrocene, C(8)–C(7)–C(11) 142.6(3)°, undoubtedly reflects minimization of steric interactions between the (μ-alkyne) dicobalt and ferrocenyl unit. The coordinated alkyne bond length [C(7)–C(8) 1.328(4) Å] is nearly the same as the alkene bond length [C(9)–C(10) 1.310(6) Å]. The C(8)–C(9) bond distance [1.453(5) Å] is shorter than a normal C–C single bond as a result of electron delocalization. The bond angles [C(7)–C(8)–C(9) 137.3(3), C(8)–C(7)–C(11) 142.6(3), C(8)–C(9)–C(10) 130.1(4)°] show the carbon chain [C(11)C(7)C(8)C(9)C(10)] is nonlinear. The bond lengths C(8)–Co(1) [1.962(3) Å], C(8)–Co(2) [1.964(3) Å] and angles C(8)–Co(1)–Co(2) 51.34(9)°, C(8)–Co(2)–Co(1)

TABLE III Selected bond lengths (Å) and angles (°) for **2**

Co(1)–Co(2)	2.454(6)	C(7)–C(11)	1.446(4)
Co(1)–C(1)	1.833(4)	C(8)–C(9)	1.453(5)
Co(1)–C(7)	1.952(3)	C(9)–C(10)	1.310(6)
Co(1)–C(8)	1.962(3)	C(10)–Cl	1.678(5)
Co(2)–C(7)	1.986(3)	C–Fe(1)	2.031 (avg)
Co(2)–C(8)	1.964(3)	C(11)–Fe(1)	2.048(3) (max)
C(7)–C8)	1.328(4)	C(20)–Fe(1)	2.018(4) (min)
C(1)–Co(1)–Co(2)	98.91(11)	C(8)–C(7)–Co(1)	70.56(19)
C(2)–Co(1)–Co(2)	153.67(12)	C(7)–C(8)–Co(2)	71.25(19)
C(3)–Co(1)–Co(2)	94.24(11)	C(8)–C(7)–Co(2)	69.45(19)
C(7)–Co(1)–Co(2)	52.07(9)	C(7)–C(8)–C(9)	137.3(3)
C(8)–Co(1)–Co(2)	51.34(9)	C(7)–C(11)–C(12)	124.7(3)
C(7)–Co(2)–Co(1)	50.85(9)	C(7)–C(11)–C(15)	127.8(3)
C(8)–Co(2)–Co(1)	51.29(9)	C(8)–C(7)–C(11)	142.6(3)
C(7)–C(8)–Co(1)	69.76(19)	C(8)–C(9)–C(10)	130.1(4)

TABLE IV Selected bond lengths (Å) and angles (°) for **3**

Co(1)–Co(2)	2.474(10)	C(8)–C(9)	1.406(6)
Co(1)–C(1)	1.829(5)	C(9)–C(10)	1.193(6)
Co(1)–C(2)	1.829(5)	C(10)–C(21)	1.429(6)
Co(1)–C(3)	1.788(5)	C(21)–C(22)	1.440(7)
Co(1)–C(7)	1.981(4)	C(11)–Fe(1)	2.037(4)
Co(1)–C(8)	1.964(4)	C(15)–Fe(1)	2.051(4) (max)
Co(2)–C(7)	1.944(4)	C(12)–Fe(1)	2.010(4) (min)
Co(2)–C(8)	1.967(4)	C(21)–Fe(2)	2.025(4)
C(7)–C(8)	1.355(6)	C(23)–Fe(2)	2.041(5) (max)
C(7)–C(11)	1.435(6)	C(26)–Fe(2)	2.006(6) (min)
C(1)–Co(1)–Co(2)	100.70(15)	C(8)–C(7)–Co(2)	70.6(2)
C(2)–Co(1)–Co(2)	99.70(16)	C(7)–C(8)–C(9)	140.7(4)
C(7)–Co(1)–Co(2)	50.26(12)	C(7)–C(11)–C(12)	127.0(4)
C(8)–Co(1)–Co(2)	51.04(12)	C(7)–C(11)–C(15)	126.5(4)
C(7)–Co(2)–Co(1)	51.59(12)	C(8)–C(9)–C(10)	172.7(4)
C(8)–Co(2)–Co(1)	50.95(11)	C(8)–C(7)–C(11)	141.6(4)
C(7)–C(8)–Co(1)	70.6(2)	C(9)–C(10)–C(21)	176.2(5)
C(8)–C(7)–Co(1)	69.3(2)	C(10)–C(21)–C(22)	126.0(5)
C(7)–C(8)–Co(2)	68.8(2)	C(10)–C(21)–C(25)	126.1(5)

TABLE V Selected bond lengths (Å) and angles (°) for **4**

Co(1)–Co(2)	2.468(5)	Co(2)–C(8)	1.995(3)
Co(1)–C(1)	1.823(4)	C(7)–C(7A)	1.428(6)
Co(1)–C(2)	1.779(4)	C(7)–C(8)	1.350(4)
Co(1)–C(3)	1.814(3)	C(8)–C(11)	1.454(4)
Co(1)–C(7)	1.977(3)	C(11)–Fe(1)	2.047(3)
Co(1)–C(8)	1.950(3)	C(14)–Fe(1)	2.049(4) (max)
Co(2)–C(7)	1.958(3)	C(16)–Fe(1)	2.028(4) (min)
C(7)–Co(1)–Co(2)	50.80(8)	C(7)–C(8)–Co(2)	68.56(16)
C(7)–Co(2)–Co(1)	51.51(8)	C(8)–C(7)–Co(2)	71.52(17)
C(8)–Co(1)–Co(2)	52.09(8)	C(7)–C(8)–C(11)	137.7(3)
C(8)–Co(2)–Co(1)	50.45(7)	C(8)–C(7)–C(7A)	142.5(3)
C(7)–C(8)–Co(1)	71.00(16)	C(8)–C(11)–C(12)	125.3(3)
C(8)–C(7)–Co(1)	68.80(16)	C(8)–C(11)–C(15)	126.6(3)

51.29(9)° reveal C(8)Co(1)Co(2) is almost an isoceles triangle indicating equivalent interaction between C(8) and Co(1), Co(2). Distortion of the quasi tetrahedral C_2Co_2 core also takes place in **2** (see Table III). Coordination of C_2Co_2 with the alkyne and the linkage of C(7)–C(11) [1.446(4) Å] between the cyclopentadiene ring and the alkyne unit are similar to those in complex **1**.

Molecules of complexes **3** and **4** consist of a 1,4-diferrocenyl-1,3-butadiyne ligand with one (for **3**) or two (for **4**) approximately tetrahedral (μ-alkyne)dicobalt cores, typical of perpendicular alkyne complexes [18]. The CO coordination geometry around the Co atoms deviates more from the idealized "sawhorse" configuration in **4** than in **3**, evidenced by the corresponding torsion angles, C(1)–Co(1)–Co(2)–C(4) −5.3(2), C(2)–Co(1)–Co(2)–C(5) −8.5(2), C(3)–Co(1)–Co(2)–C(6) −6.2(4)° for **3** and C(1)–Co(1)–Co(2)–C(6) −16.69(19), C(2)–Co(1)–Co(2)–C(5) −35.2(3), C(3)–Co(1)–Co(2)–C(4) −13.38(17)° for **4**. The torsion angles show the CO coordinated to Co atoms in **3** are close to the anticipated eclipsed conformation, whereas the conformation of CO in **4** deviates from this. In **3** the two Cp rings of the –C≡C-C≡C– acetylenic linkage on the ends adopt the *cis*-bent configuration relative to C(7)–C(8) and the C_2Co_2 core is coordinated to the alkyne [C(7)–C(8)] in a *trans* configuration. Complex **4** has a crystallographic center of inversion located at the midpoint of the C(7)–C(7A) bond, but **3** adopts an asymmetric structure. In **4** the two C_2Co_2 units are coordinated to the diyne in a *trans* configuration and linked by a short bond [1.428(6) Å] between C(7) and C(7A). The outer C atoms of the diyne chain, C(8) and C(8A), carry ferrocenyl substituents also oriented *trans* to each other. The bond angle data [C(7)–C(8)–C(9) 140.7(4), C(8)–C(9)–C(10) 172.7(4), C(8)–C(7)–C(11) 141.6(4), C(9)–C(10)–C(21) 176.2(5)°] of **3** show the carbon chain [C(8)–C(9)–C(10)–C(21)] is nearly linear and the linkage [C(9)–C(8)–C(7)–C(11)] is nonlinear, due to steric influences between the C_2Co_2 core and ferrocenyl units. The –C≡C-C≡C– acetylenic linkage in **4** is nonlinear, proved by the bond angles [C(7)–C(8)–C(11) 137.7(3), C(8)–C(7)–C(7A) 142.5(3)°], contrasting sharply with the linear –C≡C-C≡C–carbon chain of ligand $\mathbf{L_3}$ [21]. In **3** one of the acetylide ligands is coordinated to the Co–Co bond in an μ_2-η^2 coordination mode and the C≡C triple bond of other acetylide is the same as the –C≡C–bond length of the ligand $\mathbf{L_3}$ [C(9)–C(10), 1.193(6) Å for **3**; –C≡C–, 1.198(4) Å for $\mathbf{L_3}$] [21]. In **4** the shorter C(7)–C(7A) [1.428(6) Å] and C(8)–C(11) [1.454(4) Å] bond distances result from electron delocalization between the acetylide and ferrocenyl units.

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Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 221868, 221866, 230234 and 221865 for complexes **1**, **2**, **3** and **4**, 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).

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