Preparation and characterization of μ-alkyne-hexacarbonyldicobalt complexes derived from 1,1′-dialkynylferrocene. Molecular structures of $\{(\eta^5\text{-}C_5H_4C\equiv CPh)_2Fe\}\{Co_2(CO)_6\}_2$ and $\{(\eta^5\text{-}C_5H_4C\equiv CPh)_2Fe\}Co_2(CO)_6$

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Abstract

The reaction of 1,1′-dialkynylferrocene $(\eta^5\text{-}C_5H_4C\equiv CR)_2Fe$ (**1**) R = Ph, $SiMe_3$, Me, Fc; Fc = ferrocenyl) with excess octacarbonyldicobalt (**2**) results in the formation of dark green complexes $\{(\eta^5\text{-}C_5H_4C\equiv CR)_2Fe\}\{Co_2(CO)_6\}_2$ (**3**) (R = Ph, $SiMe_3$, Me, Fc), in which a $Co_2(CO)_6$ group coordinates to each of the two C≡C bonds of **1**. When 1,1′-di(phenylethynyl)ferrocene (**1a**) was treated with an equimolar amount of **2**, $\{(\eta^5\text{-}C_5H_4C\equiv CPh)_2Fe\}Co_2(CO)_6$ (**4**), as well as **3a**, was obtained. In the thermal reaction of **4** intermolecular $Co_2(CO)_6$ group migration to give **3a** was observed. Molecular structures of $\{(\eta^5\text{-}C_5H_4C\equiv CPh)_2Fe\}\{Co_2(CO)_6\}_2$ (**3a**) and $\{(\eta^5\text{-}C_5H_4C\equiv CPh)_2Fe\}Co_2(CO)_6$ (**4**) have been determined by single-crystal X-ray analyses.

Key words: Ferrocene; Cobalt; Alkyne; Carbonyl; X-ray diffraction

1. Introduction

We have been interested in the chemistry of ferrocenyl transition metal complexes. A number of transition metal complexes containing ferrocene has been synthesized, but in most of them transition metal atoms were linked to ferrocene by heteroatoms such as phosphorus and sulfur [1]. Previously we have reported the syntheses of some σ-ferrocenylsilyl transition metal complexes [2]. Some σ-ferrocenyl complexes, in which transition metal atoms were directly bonded to the cyclopentadienyl group of ferrocene by a σ-bond, have also been found [3].

It is known that alkyne is able to coordinate to transition metals in a variety of bonding modes [4] and molecules having two or three alkynyl groups can act as a chelate ligand [5]. Octacarbonyldicobalt reacts readily with alkyne to give the μ-alkyne complexes $(RC\equiv CR')Co_2(CO)_6$ [6,7], and it was reported that the reactions of dicobaltoctacarbonyl with ethynylferrocene and diferrocenylacetylene gave $(HC\equiv CFc)Co_2(CO)_6$ (Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$) [8] and $(FcC\equiv CFc)Co_2(CO)_6$ [9], respectively. In addition, 1,1′-dialkynylferrocene is able to control the distance and the arrangement between two alkynyl groups by the rotation of the cyclopentadienyl ring. These make it a strong possibility that the complex prepared from 1,1′-dialkynylferrocene should have a unique structure. Furthermore, transition metals which coordinate to the C≡C triple bonds of 1,1′-dialkynylferrocene may interact with the iron atom of ferrocene either directly or through alkynyl and cyclopentadienyl groups.

In this paper we describe the reaction of 1,1′-dialkynylferrocene with dicobaltoctacarbonyl in detail, and an X-ray crystallographic study of the resulting complexes [10].

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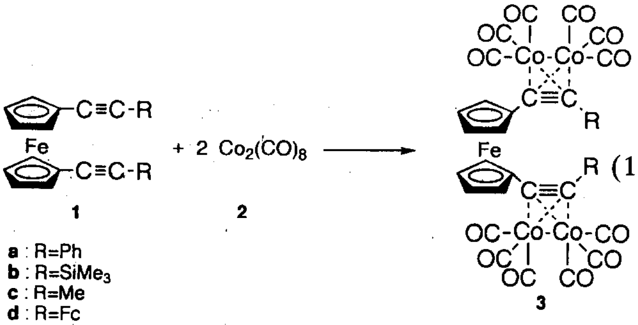
2. Results and discussion

2.1. Preparation and characterization of μ-alkyne-hexacarbonyldicobalt complexes derived from 1,1′-dialkynylferrocene

1,1′-Bis(phenylethynyl)ferrocene (**1a**) was treated with a slight excess of **2** in benzene for 2 h at room temperature under a nitrogen atmosphere. The colour of the reaction mixture changed from brown to purple and finally to green with the progress of the reaction. After purification by column chromatography on alumina using hexane as an eluent under a nitrogen atmosphere followed by recrystallization from hexane, dark green crystals of **3a** were obtained in 62% yield. Complex **3a** is stable in air in the solid state and soluble in common organic solvents. The IR spectrum of **3a** showed very strong absorptions in the CO stretching region indicating that cobaltcarbonyl groups coordinate to the alkynyl groups of **1a**. The ^{1}H NMR spectrum of **3a** exhibited two triplets at δ 4.54 and 4.32 assigned to the protons of cyclopentadienyl rings and two multiplets at δ 7.89–7.87 and 7.16–7.06 assigned to the protons of phenyl groups. In the ^{13}C NMR spectrum acetylenic carbon resonances were observed at δ 92.62 and 91.77, which are in lower magnetic field than those of **1a** at δ 87.94 and 87.59, and a resonance owing to the carbonyl appeared at δ 199.74. These data are consistent with the structure of **3a**, which is produced by the coordination of a $Co_2(CO)_6$ group to each of the two C≡C bonds of **1a**, and the molecular structure of **3a** was determined by X-ray diffraction (see below).



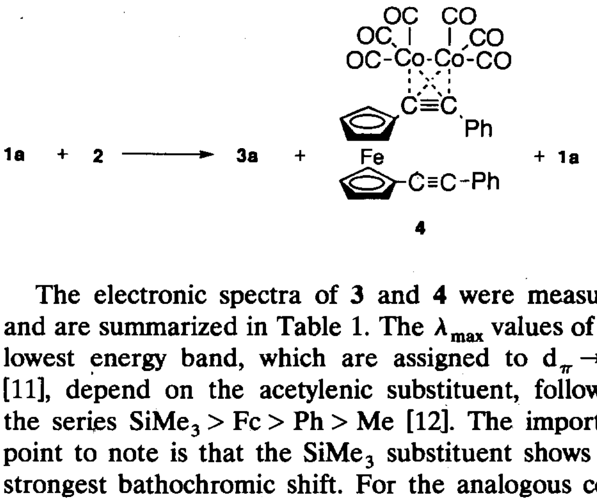
(1)

1 2 3

a : R=Ph
b : R=SiMe$_3$
c : R=Me
d : R=Fc

Similar treatments of 1,1′-bis(trimethylsilylethynyl)-ferrocene (**1b**) and 1,1′-dipropynylferrocene (**1c**) with **2** gave **3b** in 27% yield and **3c** in 89% yield, respectively. In the reaction of **1b** no complexes except **3b** were obtained, and the solubility of **3b** is so poor that its isolation is difficult. Therefore pure **3b** was obtained only in low yield. 1,1′-Bis(ferrocenylethynyl)-ferrocene (**1d**) also reacted with **2** to give dark green crystals of **3d** in 74% yield. These complexes were also characterized by spectroscopic analysis.

The reaction of **1a** with an equimolar amount of **2** afforded not only **3** (17% yield) but also a new complex **4** (22% yield), and 20% of **1a** was recovered. The appearance of four ν_{CO} absorptions in the IR spectrum of **4** suggests the coordination of cobaltcarbonyl group to the C≡C triple bond. The ^{1}H NMR of **4** showed four resonances of the Cp ring protons at δ 4.48, 4.40, 4.23 and 4.00. In the ^{13}C NMR spectrum four signals of acetylenic carbons were observed at δ 92.36, 91.89, 88.25 and 87.41, the chemical shifts of the two former signals are close to those of **3a**, and those of the two latter signals are similar to those of **1a** (δ 87.22 and 86.59). These NMR data suggest that the two CpC≡CPh groups of **4** are magnetically inequivalent. Microanalytical data in conjunction with these spectroscopic data enabled characterization of complex **4**, in which a $Co_2(CO)_6$ group coordinates to one of the two C≡C bonds of **1a**. From this result we conclude that the coordination of a $Co_2(CO)_6$ group to one of the two C≡C bonds does not affect coordination to the other C≡C bond. In the ^{13}C NMR spectrum of **4** the chemical shifts of acetylenic carbons to which a $Co_2(CO)_6$ group does not coordinate may indicate that the interaction between uncoordinated acetylenic bond and Co_2C_2 group through ferrocene is not so large.



(2)

4

The electronic spectra of **3** and **4** were measured and are summarized in Table 1. The λ_{max} values of the lowest energy band, which are assigned to $d_\pi \rightarrow \sigma^*$ [11], depend on the acetylenic substituent, following the series $SiMe_3$ > Fc > Ph > Me [12]. The important point to note is that the $SiMe_3$ substituent shows the strongest bathochromic shift. For the analogous com-

TABLE 1. Electronic spectra for 3 and 4 (in cyclohexane)

Complex	λ_{max} /nm (ϵ)
3a	216 (7.2×10^4), 430 (3.3×10^3), 597 (2.2×10^3)
3b	215 (4.4×10^4), 621 (1.5×10^3)
3c	215 (6.7×10^4), 595 (2.7×10^3)
3d	221 (7.2×10^4), 607 (3.7×10^3)
4	214 (4.8×10^4), 300 (2.6×10^4), 436 (1.9×10^3), 565 (1.0×10^3)

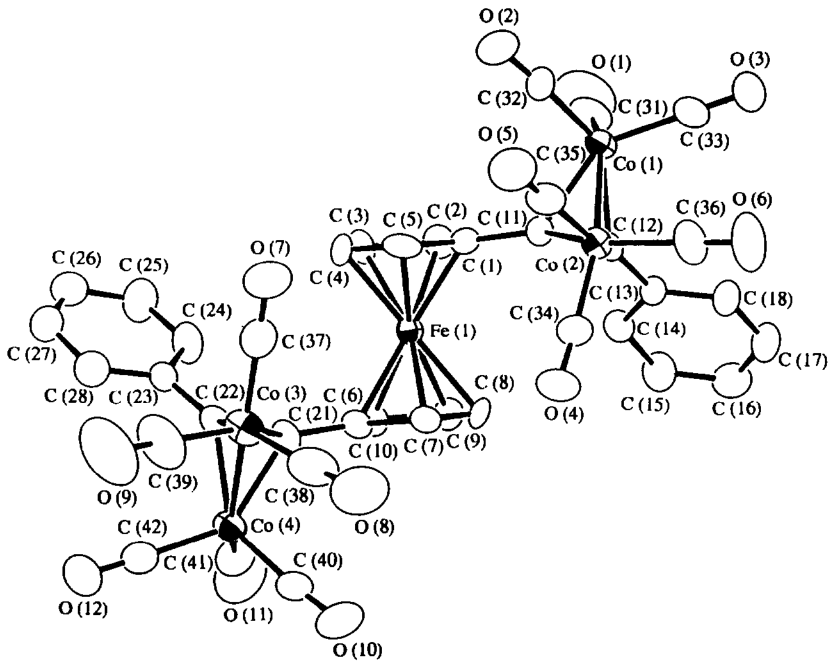


Fig. 1. ORTEP drawing of $\{(\eta^5\text{-}C_5H_4C{\equiv}CPh)_2Fe\}\{Co_2(CO)_6\}_2$ (**3a**). The non-hydrogen atoms are represented by 30% probability thermal ellipsoids, and the hydrogen atoms are omitted for clarity.

TABLE 2. Crystallographic data for **3a** and **4**

	3a	**4**
Empirical formula	$C_{38}H_{18}O_{12}Co_4Fe$	$C_{32}H_{18}O_6Co_2Fe$
Formula weight	958.13	672.20
Crystal color, Habit	green, prismatic	green, prismatic
Crystal dimensions	0.25 × 0.25 × 0.20 mm	0.70 × 0.30 × 0.20 mm
Crystal system	monoclinic	orthorhombic
Lattice parameters	a = 14.023(6) Å	a = 10.731(2) Å
	b = 17.817(10) Å	b = 12.374(3) Å
	c = 15.441(3) Å	c = 21.321(2) Å
	β = 94.06(2)°	
	V = 3848(5) Å^3	V = 2381(1) Å^3
Space group	$P2_1/a$ (No. 14)	$P2_12_12_1$ (No. 19)
Z value	4	4
D_{calcd}	1.654 g cm^{-3}	1.577 g cm^{-3}
F_{000}	1904	1352
μ(Mo Kα)	21.14 cm^{-1}	17.04 cm^{-1}
2θ range	6° < 2θ < 50.1°	6° < 2θ < 55.1°
No. of reflections measured	7382	3696
No. observations	3279 ($I > 9.0\sigma(I)$)	2801 ($I > 6.0\sigma(I)$)
No. variables	496	370
Residuals: R; R_w	0.048; 0.035	0.029; 0.029
Goodness of Fit indicator	1.89	2.64
Max. peak in final diff. map	0.64 e$^-$ Å^{-3}	0.92 e$^-$ Å^{-3}
Min. peak in final diff. map	−0.34 e$^-$ Å^{-3}	−0.28 e$^-$ Å^{-3}

$R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o)^2$. Goodness of Fit indicator: standard deviation of an observation of unit weight $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$; N_o = Number of observations, N_v = Number of variables.

TABLE 3. Positional parameters and B_{eq} for complex **3a**

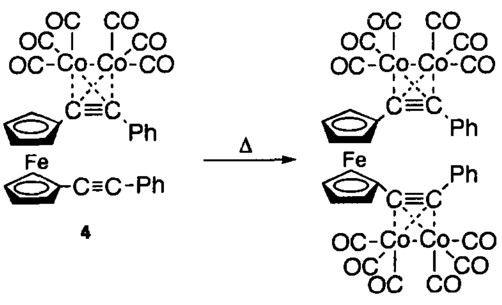
Atom	x	y	z	B_{eq}
Co(1)	0.78899(7)	0.09389(7)	0.74845(7)	4.23(6)
Co(2)	0.91893(8)	0.12888(7)	0.85567(7)	4.12(6)
Co(3)	1.34389(9)	−0.11721(8)	0.86716(8)	5.49(7)
Co(4)	1.46172(8)	−0.08184(7)	0.76431(8)	4.90(7)
Fe(1)	1.12038(8)	0.00229(7)	0.69017(7)	3.44(5)
O(1)	0.7287(6)	0.0669(6)	0.5690(5)	12.1(6)
O(2)	0.7374(5)	−0.0488(4)	0.8273(5)	8.2(5)
O(3)	0.6468(5)	0.2071(4)	0.7894(5)	8.8(5)
O(4)	1.1194(4)	0.1554(4)	0.9084(4)	7.0(4)
O(5)	0.8861(5)	0.0115(4)	0.9832(4)	8.7(5)
O(6)	0.8378(6)	0.2678(4)	0.9217(5)	10.2(5)
O(7)	1.1530(5)	−0.1641(4)	0.9014(4)	8.0(5)
O(8)	1.3618(6)	0.0126(5)	0.9852(5)	11.1(6)
O(9)	1.4541(7)	−0.2366(6)	0.9525(6)	16.3(8)
O(10)	1.5218(5)	0.0598(4)	0.8478(5)	8.9(5)
O(11)	1.5018(7)	−0.0418(5)	0.5887(5)	12.0(6)
O(12)	1.6073(6)	−0.1981(5)	0.7973(7)	12.4(7)
C(1)	0.9799(5)	0.0118(5)	0.7149(5)	3.3(4)
C(2)	0.9885(5)	−0.0080(5)	0.6257(5)	4.3(4)
C(3)	1.0383(5)	−0.0776(5)	0.6244(5)	4.4(5)
C(4)	1.0600(5)	−0.0996(4)	0.7108(6)	3.9(4)
C(5)	1.0250(5)	−0.0472(5)	0.7651(5)	4.6(5)
C(6)	1.2657(5)	−0.0065(5)	0.7199(5)	3.7(4)
C(7)	1.2248(5)	0.0535(5)	0.7666(5)	3.8(4)
C(8)	1.1828(6)	0.1038(4)	0.7108(6)	4.4(5)
C(9)	1.1950(6)	0.0791(5)	0.6252(6)	4.8(5)
C(10)	1.2448(5)	0.0106(5)	0.6299(5)	4.0(4)
C(11)	0.9281(5)	0.0758(5)	0.7454(4)	3.5(4)
C(12)	0.9068(5)	0.1485(5)	0.7302(5)	3.7(4)
C(13)	0.9334(6)	0.2121(5)	0.6762(5)	3.6(4)
C(14)	0.9915(6)	0.1996(5)	0.6086(6)	4.6(5)
C(15)	1.0213(7)	0.2602(6)	0.5607(6)	6.4(6)
C(16)	0.9925(7)	0.3310(6)	0.5785(7)	6.6(7)
C(17)	0.9317(8)	0.3427(6)	0.6431(8)	6.8(7)
C(18)	0.9026(6)	0.2834(5)	0.6904(6)	5.3(5)
C(21)	1.3218(5)	−0.0694(5)	0.7564(5)	4.0(5)
C(22)	1.3432(5)	−0.1414(5)	0.7437(5)	4.1(5)
C(23)	1.3150(6)	−0.2068(5)	0.6898(6)	4.1(5)
C(24)	1.2547(7)	−0.1961(5)	0.6159(6)	5.9(6)
C(25)	1.2252(8)	−0.2571(7)	0.5670(6)	7.1(7)
C(26)	1.2527(8)	−0.3290(7)	0.5904(8)	7.5(8)
C(27)	1.3138(8)	−0.3378(6)	0.6607(9)	7.4(8)
C(28)	1.3473(7)	−0.2778(7)	0.7095(7)	6.3(6)
C(31)	0.7511(6)	0.0765(6)	0.6394(6)	6.6(6)
C(32)	0.7546(6)	0.0086(5)	0.7988(6)	5.5(6)
C(33)	0.7022(6)	0.1630(6)	0.7736(6)	5.8(6)
C(34)	1.0421(7)	0.1471(5)	0.8872(5)	4.9(5)
C(35)	0.8996(6)	0.0581(6)	0.9340(6)	5.8(6)
C(36)	0.8689(7)	0.2144(6)	0.8985(6)	6.5(6)
C(37)	1.2296(8)	−0.1452(6)	0.8890(6)	5.9(6)
C(38)	1.3564(8)	−0.0394(7)	0.9413(6)	7.6(7)
C(39)	1.4109(9)	−0.1904(8)	0.9207(8)	10.4(9)
C(40)	1.5023(6)	0.0031(6)	0.8166(6)	5.6(6)
C(41)	1.4876(8)	−0.0579(6)	0.6555(7)	7.2(7)
C(42)	1.5522(7)	−0.1524(6)	0.7858(7)	6.8(7)
H(2)	0.9634	0.0209	0.5737	4.7
H(3)	1.0596	−0.1037	0.5738	5.1
H(4)	1.0903	−0.1467	0.7308	4.3
H(5)	1.0321	−0.0489	0.8293	5.0
H(7)	1.2255	0.0599	0.8303	4.6
H(8)	1.1504	0.1504	0.7254	4.8

TABLE 3 (continued)

Atom	x	y	z	B_{eq}
H(9)	1.1710	0.1047	0.5720	5.9
H(10)	1.2634	−0.0192	0.5795	4.2
H(14)	1.0140	0.1506	0.5971	5.5
H(15)	1.0631	0.2518	0.5141	7.3
H(16)	1.0110	0.3737	0.5433	7.5
H(17)	0.9098	0.3943	0.6555	7.6
H(18)	0.8606	0.2930	0.7385	6.3
H(24)	1.2332	−0.1458	0.6001	7.0
H(25)	1.1803	−0.2491	0.5157	8.4
H(26)	1.2320	−0.3704	0.5550	8.5
H(27)	1.3366	−0.3883	0.6786	7.9
H(28)	1.3895	−0.2850	0.7629	7.1

plexes, $(RC{\equiv}CSiMe_2H)Co_2(CO)_6$, where R = HMe_2Si or Ph, the order is Ph > HMe_2Si. Furthermore the λ_{max} value of the lowest energy band in **3a** is larger than that in **4**. These data may indicate that two dicobalt tetrahedrane chromophores of **3** conjugate through ferrocene and vacant d-orbitals of silicon atoms.

In an attempt to prepare a novel ferrocenediyl cobaltcarbonyl cluster, in which a cluster bridges two cyclopentadienyl groups of ferrocene intramolecularly, we have examined the reactions of **3a** by the irradiation of ultraviolet light or thermal reaction under reflux in benzene [13], but no reaction occurred and **3a** was recovered. The reaction of **3a** under reflux in dioxane gave an unstable product which could not be characterized. On the other hand, in the thermal reaction of **4** intermolecular $Co_2(CO)_6$ group migration was observed. Complex **4** was treated in benzene under reflex for 2 h to give **3a** in 18% yield. Although it is well known that μ-alkyne-hexacarbonyldicobalt complexes undergo facile exchange reactions with alkynes at ambient temperature [7,14], in this reaction an exchange product **1a** was not obtained. We therefore believe that **4** is less stable than **3a** and $Co_2(CO)_6$ species generated by decomposition of **4** coordinate to another molecule of **4** to give **3a**. With UV irradiation of **4**, we could not find complexes other than unchanged **4**.



4 → **3a**

2.2. Molecular structure of $\{(\eta^5\text{-}C_5H_4C{\equiv}CPh)_2Fe\}\{Co_2(CO)_6\}_2$ (3a)

The molecular structure of **3a** is shown in Fig. 1. The crystallographic data and positional parameters with equivalent B values are summarized in Tables 2 and 3, and selected bond distances and angles are listed in Table 4. As suggested by the spectroscopic analyses, a $Co_2(CO)_6$ unit coordinates to each of the two alkynyl groups of **1**. The Co_2C_2 core adopts a pseudo-tetrahedral geometry. The overall conformations of the two $(C_5H_4C{\equiv}CPh)Co_2(CO)_6$ moieties in **3a** resemble each other. Two Co–Co bond lengths are both 2.454(2) Å, slightly shorter than those of other μ-alkyne-hexacarbonyldicobalt complexes [7]. The Co–C bond distances in the Co_2C_2 core are in the range 1.917(8)–1.981(8) Å, comparable with those of related dicobalt complexes [7]. Separations between Co and Fe lie in the range 4.540(2)–5.069(2) Å, too long for any significant interaction to exist between Co and Fe. The ferrocenediyl group has an eclipsed conformation and the tilt angle between the two cyclopentadienyl rings is 1.1°.

TABLE 4. Selected bond distances (Å) and angles (°) for **3a**

Co(1)–Co(2)	2.454(2)	Co(3)–Co(4)	2.454(2)
Co(1)–C(11)	1.981(8)	Co(3)–C(21)	1.917(8)
Co(1)–C(12)	1.954(8)	Co(3)–C(22)	1.954(8)
Co(2)–C(11)	1.960(7)	Co(4)–C(21)	1.970(8)
Co(2)–C(12)	1.963(8)	Co(4)–C(22)	1.979(9)
C(11)–C(12)	1.35(1)	C(21)–C(22)	1.34(1)
Co(2)–Co(1)–C(11)	51.1(2)	Co(4)–Co(3)–C(21)	51.8(2)
Co(2)–Co(1)–C(12)	51.4(2)	Co(4)–Co(3)–C(22)	51.8(2)
C(11)–Co(1)–C(12)	40.0(3)	C(21)–Co(3)–C(22)	40.3(3)
Co(1)–Co(2)–C(11)	51.9(2)	Co(3)–Co(4)–C(21)	49.9(2)
Co(1)–Co(2)–C(12)	51.0(2)	Co(3)–Co(4)–C(22)	50.9(2)
C(11)–Co(2)–C(12)	40.1(3)	C(21)–Co(4)–C(22)	39.5(3)
C(1)–C(11)–C(12)	144.2(8)	C(6)–C(21)–C(22)	143.3(8)
C(11)–C(12)–C(13)	141.0(8)	C(21)–C(22)–C(23)	142.2(8)

The C(11)–C(12) and C(21)–C(22) distances are 1.35(1) and 1.34(1) Å, respectively, in the normal region of μ-alkyne-hexacarbonyldicobalt complexes [7]. The bond angles C(1)–C(11)–C(12), C(11)–C(12)–C(13), C(6)–C(21)–C(22) and C(21)–C(22)–C(23) are 144.2(8)°, 141.0(8)°, 143.3(8)° and 142.2(8)°, respectively. These also lie in the normal range [7]. The deviations of C(11) and C(21) from the cyclopentadienyl ring are very small (both 0.09 Å). The torsion angles of coordinated alkyne, C(1)–C(11)–C(12)–C(13) and C(6)–C(21)–C(22)–C(23), are both −10(2)°. The dihedral angles between cyclopentadienyl rings and phenyl groups, C(1)–C(5) and C(13)–C(18), and C(6)–C(10) and C(23)–C(28), are 43.5° and 40.1°, respectively. The molecules are separated by normal van der Waals distances.

2.3. Molecular structure of $\{(\eta^5\text{-}C_5H_4C{\equiv}CPh)_2Fe\}Co_2(CO)_6$ (4)

The molecular structure of **4** is shown in Fig. 2. The positional parameters and selected bond distances and angles are listed in Tables 5 and 6. The overall geometry of the $(C_5H_4C{\equiv}CPh)Co_2(CO)_6$ moiety is similar to that of **3a**. The Co(1)–Co(2) bond length of 2.4634(9) Å is slightly longer than those of **3a** and is in the normal range of related alkyne-dicobalt complexes [7]. The Co–C distances in the Co_2C_2 core are in the range 1.950(4)–1.986(4) Å, and the Co–Fe distances are 5.069(1) and 4.663(1) Å, respectively.

An interesting conformation of the ferrocenediyl group is observed in **4**; the two cyclopentadienyl groups have an eclipsed conformation with rotational angle 72.8°, in contrast with that of 138.3° in **3**. The rotational barrier of ferrocene has been reported to be 3.8(1.3) kJ mol^{-1} (in the gas phase) [15] and 7.5–9.6 kJ mol^{-1} (in the low temperature crystal) [16]. The difference of the rotational angle is likely to depend on the substituent effect of a $Co_2(CO)_6$ group as well as on crystal packing, because the rotational barrier is not large and no interaction between cobalt atoms and uncoordinated acetylenic carbons was observed. The two cyclopentadienyl rings are parallel and the tilt angle is 1.76°.

The C(21)–C(22) distance of 1.334(5) Å is comparable with that in **3a**, but longer than the C(31)–C(32) distance of 1.186(6) Å. The bond angles C(1)–C(21)–

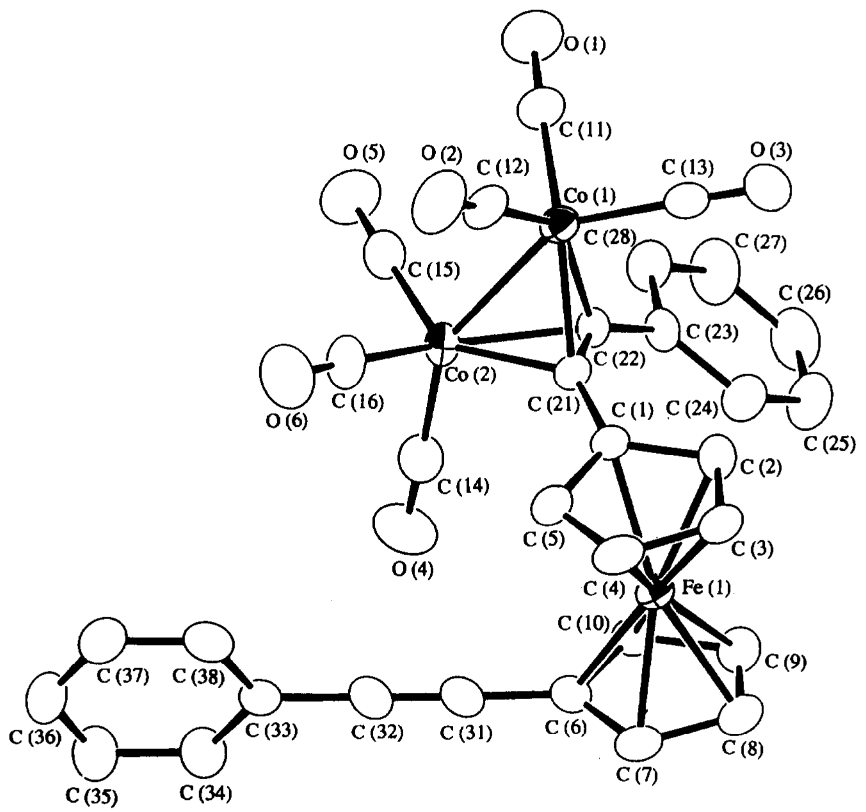


Fig. 2. ORTEP drawing of $\{(\eta^5\text{-}C_5H_4{\equiv}CPh)_2Fe\}Co_2(CO)_6$ (4). The non-hydrogen atoms are represented by 30% probability thermal ellipsoids, and the hydrogen atoms are omitted for clarity.

TABLE 5. Positional parameters and B_{eq} for complex **4**

Atom	x	y	z	B_{eq}
Co(1)	0.84581(6)	0.15179(5)	0.60853(3)	3.45(3)
Co(2)	0.61731(6)	0.13261(5)	0.60859(3)	3.61(3)
Fe(1)	0.69319(6)	−0.23392(5)	0.58608(3)	3.56(3)
O(1)	0.8830(5)	0.3755(3)	0.5664(2)	7.6(3)
O(2)	0.8773(4)	0.1474(3)	0.7457(2)	7.1(2)
O(3)	1.0830(4)	0.0607(4)	0.5683(2)	6.6(2)
O(4)	0.3881(4)	0.0355(4)	0.5606(2)	7.0(2)
O(5)	0.5637(4)	0.3602(3)	0.5793(2)	7.8(3)
O(6)	0.5652(4)	0.1074(4)	0.7430(2)	8.5(3)
C(1)	0.7684(4)	−0.0877(3)	0.6126(2)	3.0(2)
C(2)	0.8604(4)	−0.1596(4)	0.5857(2)	3.9(2)
C(3)	0.8657(4)	−0.2528(4)	0.6221(2)	4.6(2)
C(4)	0.7763(5)	−0.2441(4)	0.6710(2)	4.4(2)
C(5)	0.7184(4)	−0.1438(4)	0.6654(2)	3.8(2)
C(6)	0.5064(4)	−0.2558(4)	0.5766(2)	4.3(2)
C(7)	0.5682(5)	−0.3577(4)	0.5839(3)	4.9(3)
C(8)	0.6546(5)	−0.3679(5)	0.5343(3)	5.7(3)
C(9)	0.6493(5)	−0.2754(5)	0.4964(2)	5.5(3)
C(10)	0.5574(5)	−0.2048(4)	0.5221(2)	4.3(2)
C(11)	0.8683(5)	0.2907(4)	0.5837(2)	4.7(3)
C(12)	0.8676(5)	0.1521(4)	0.6928(2)	4.6(3)
C(13)	0.9921(5)	0.0969(4)	0.5843(2)	4.3(2)
C(14)	0.4770(5)	0.0714(5)	0.5786(3)	4.6(3)
C(15)	0.5826(5)	0.2725(5)	0.5911(3)	5.2(3)
C(16)	0.5858(5)	0.1193(5)	0.6917(2)	5.3(3)
C(21)	0.7443(4)	0.0211(3)	0.5931(2)	3.0(2)
C(22)	0.7402(4)	0.0878(4)	0.5440(2)	3.3(2)
C(23)	0.7407(4)	0.0913(4)	0.4751(2)	3.5(2)
C(24)	0.7573(6)	−0.0049(4)	0.4420(2)	4.8(2)
C(25)	0.7583(6)	−0.0033(5)	0.3776(2)	5.9(3)
C(26)	0.7427(6)	0.0913(6)	0.3456(2)	6.5(3)
C(27)	0.7263(6)	0.1865(5)	0.3778(2)	6.5(3)
C(28)	0.7267(5)	0.1869(4)	0.4426(2)	4.9(3)
C(31)	0.4190(4)	−0.2109(4)	0.6186(2)	4.2(2)
C(32)	0.3471(5)	−0.1726(4)	0.6545(2)	4.3(2)
C(33)	0.2611(4)	−0.1254(4)	0.6983(2)	3.6(2)
C(34)	0.1371(5)	−0.1206(5)	0.6853(2)	5.1(3)
C(35)	0.0540(5)	−0.0765(5)	0.7287(3)	5.7(3)
C(36)	0.0962(6)	−0.0360(5)	0.7830(3)	5.5(3)
C(37)	0.2228(6)	−0.0383(4)	0.7971(2)	5.3(3)
C(38)	0.3032(5)	−0.0836(4)	0.7548(3)	5.1(3)
H(2)	0.9106	−0.1457	0.5484	4.9
H(3)	0.9211	−0.3139	0.6158	5.6
H(4)	0.7590	−0.2993	0.7030	5.4
H(5)	0.6523	−0.1174	0.6924	4.5
H(7)	0.5525	−0.4103	0.6176	5.8
H(8)	0.7088	−0.4301	0.5269	7.0
H(9)	0.6982	−0.2638	0.4589	6.7
H(10)	0.5350	−0.1316	0.5065	5.1
H(24)	0.7668	−0.0716	0.4652	5.9
H(25)	0.7687	−0.0708	0.3552	7.1
H(26)	0.7435	0.0921	0.3005	7.4
H(27)	0.7164	0.2542	0.3558	7.7
H(28)	0.7145	0.2535	0.4658	5.9
H(34)	0.1058	−0.1512	0.6483	5.9
H(35)	−0.0344	−0.0749	0.7181	6.7
H(36)	0.0389	−0.0036	0.8131	6.5
H(37)	0.2525	−0.0087	0.8363	6.1
H(38)	0.3927	−0.0850	0.7654	6.4

TABLE 6. Selected bond distances (Å) and angles (°) for **4**

Co(1)–Co(2)	2.4634(9)	Co(1)–C(21)	1.977(4)
Co(1)–C(22)	1.950(4)	Co(2)–C(21)	1.967(4)
Co(2)–C(22)	1.986(4)	C(21)–C(22)	1.334(5)
C(31)–C(32)	1.186(6)		
Co(2)–Co(1)–C(21)	51.2(1)	Co(2)–Co(1)–C(22)	51.9(1)
C(21)–Co(1)–C(22)	39.7(2)	Co(1)–Co(2)–C(21)	51.5(1)
Co(1)–Co(2)–C(21)	50.6(1)	C(21)–Co(2)–C(22)	39.4(2)
C(1)–C(21)–C(22)	144.7(4)	C(21)–C(22)–C(23)	143.3(4)
C(6)–C(31)–C(32)	178.9(5)	C(11)–C(12)–C(13)	179.3(5)

C(22) and C(21)–C(22)–C(23) are 144.4(4)° and 143.3(4)°, in contrast with the C(6)–C(31)–C(32) angle of 178.9(5)° and the C(31)–C(32)–C(33) angle of 179.3(5)°. These differences of bond distances and angles between two alkynyl groups are due to the coordination of a $Co_2(CO)_6$ group [7]. The torsion angles of coordinated alkyne, C(1)–C(21)–C(22)–C(23), is 13(1)°. The dihedral angle between the cyclopentadienyl ring C(1)–C(5) and the phenyl group C(23)–C(28) that are linked by coordinated C≡C triple bond is 46.6°, which is comparable with those of **3a** but smaller than that of the uncoordinated side, C(6)–C(10) and C(33)–C(38), in **4** (76.6°). The molecules are separated by normal van der Waals distances and no unusual interaction was observed.

3. Experimental details

All reactions were carried out under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were measured on a JEOL GX 400 spectrometer using $SiMe_4$ as an internal standard. IR spectra were recorded on a JASCO A-202 Infrared Spectrophotometer, and electronic spectra on a Shimadzu UV-160A Spectrophotometer.

Benzene was distilled on CaH_2 and stored over Na wire. $Co_2(CO)_8$ was purchased from Strem Chemicals and used as received. 1,1′-Bis(phenylethynyl)ferrocene and 1,1′-bis(ferrocenylethynyl)ferrocene were prepared from the reaction of 1,1′-diiodoferrocene [17] with phenylacetylene and ferrocenylacetylene in the presence of $Pd(PPh_3)_2Cl_2$ and $Cu(OAc)_2$ catalyst in diisopropylamine under reflux [18], respectively. 1,1′-Bis(trimethylsilylethynyl)ferrocene and 1,1′-dipropynylferrocene were prepared according to the literature method [19].

3.1. Preparation of $\{(\eta^5\text{-}C_5H_4C{\equiv}CPh)_2Fe\}\{Co_2(CO)_6\}_2$ (3a)

1,1′-Bis(phenylethynyl)ferrocene (220 mg, 0.57 mmol) was treated with dicobaltoctacarbonyl (500 mg, 1.4 mmol) in benzene (40 ml) at room temperature. After being stirred for 2 h, the solvent was removed under reduced pressure and the residue purified by chromatography on alumina using hexane as an eluent. Recrystallization from hexane gave dark green crystals (332 mg, 62%). Mp 124–125°C; IR (KBr): 3150w, 2090vs, 2050vs, 2030vs, 2000vs, 1625w, 1585w, 1565w, 1480m, 1440m, 1385w, 1260w, 1080w, 1040m, 1025w, 840m, 825m, 805w, 760m, 695s, 660m, 630m, 605m, 595m, 585m, 570m, 540m, 520s, 495s, 465s cm^{-1}; ^1H NMR (C_6D_6): 7.89–7.87 (4H, m, Ph), 7.16–7.06 (6H, m, Ph), 4.54 (4H, t, $J = 2$ Hz, Cp), 4.32 (4H, t, $J = 2$ Hz, Cp); ^{13}C NMR (C_6D_6): 199.74 (CO), 138.74 (Ph), 129.83 (Ph), 129.27 (Ph), 128.45 (Ph), 92.64 (C≡), 91.77 (C≡), 86.61 (Cp), 72.73 (Cp), 71.11 (Cp); UV (c-C_6H_{12}) $\lambda_{max} = 216$ ($\epsilon = 7.2 \times 10^4$), 430 ($\epsilon = 3.3 \times 10^3$), 597 nm ($\epsilon = 2.2 \times 10^3$); Anal. Found: C, 47.44; H, 1.87. Calcd. for $C_{38}H_{18}O_{12}Co_4Fe$: C, 47.64; H, 1.89%.

3.2. Preparation of $\{(\eta^5\text{-}C_5H_4C{\equiv}CSiMe_3)_2Fe\}\{Co_2(CO)_6\}_2$ (3b)

1,1′-Bis(trimethylsilylethynyl)ferrocene (189 mg, 0.50 mmol) was treated with dicobaltoctacarbonyl (360 mg, 1.05 mmol) as described in the preparation of **3a** to give a dark green powder (130 mg, 27%). Mp 184–187°C (dec. in N_2); IR (KBr): 3080w, 2965m, 2900w, 2095vs, 2065vs, 2055vs, 2010vs, 1990vs, 1965s, 1955s, 1605m, 1420m, 1410m, 1260m, 1250m, 1220m, 1205w, 1045w, 1035m, 940w, 865m, 850s, 840s, 820m, 790m, 760w, 700w, 660w, 640w, 615m, 525s, 505s, 475s, 460s cm^{-1}; ^1H NMR ($CDCl_3$): 4.41 (4H, s, Cp), 4.34 (4H, s, Cp), 0.45 (18H, s, Me); ^{13}C NMR ($CDCl_3$): 200.11 (CO), 86.23 (Cp), 72.49 (Cp), 70.61 (Cp), 1.25 (Me). The resonances of acetylenic carbon were not detected due to low solubility of **3b**. UV (c-C_6H_{12}) $\lambda_{max} = 215$ ($\epsilon = 4.4 \times 10^4$), 621 nm ($\epsilon = 1.5 \times 10^3$); Anal. Found: C, 40.19; H, 2.60. Calcd. for $C_{32}H_{26}O_{12}Si_2Co_4Fe$: C, 40.25; H, 2.76%.

3.3. Preparation of $\{(\eta^5\text{-}C_5H_4C{\equiv}CMe)_2Fe\}\{Co_2(CO)_6\}_2$ (3c)

Similar treatment of 1,1′-dipropynylferrocene (169 mg, 0.65 mmol) with dicobaltoctacarbonyl (908 mg, 2.66 mmol) as described in the preparation of **3a** gave dark green crystals (480 mg, 89%). Mp 210–237°C (dec. in N_2); IR (KBr): 3080w, 2960w, 2900w, 2095vs, 2055vs, 2045vs, 2000vs, 1980vs, 1420w, 1385w, 1365w, 1245w, 1205w, 1065w, 1050w, 1030w, 1015w, 825m, 700m, 640w, 565w, 520s, 505s, 470s cm^{-1}; ^1H NMR ($CDCl_3$): 4.39 (8H, s, Cp), 2.86 (6H, s, Me); ^{13}C NMR ($CDCl_3$): 199.78 (CO), 94.72 (C≡), 91.23 (C≡), 86.06 (Cp), 71.31 (Cp), 70.16 (Cp), 21.00 (Me); UV (c-C_6H_{12}) $\lambda_{max} = 215$ ($\epsilon = 6.7 \times 10^4$), 595 nm ($\epsilon = 2.7 \times 10^3$); Anal. Found: C, 40.07; H, 1.61. Calcd. for $C_{28}H_{14}O_{12}Co_4Fe$: C, 40.33; H, 1.69%.

3.4. Preparation of $\{(\eta^5\text{-}C_5H_4C{\equiv}CFc)_2Fe\}\{Co_2(CO)_6\}_2$ (3d)

The reaction of 1,1′-bis(ferrocenylethynyl)ferrocene (44 mg, 0.073 mmol) with dicobaltoctacarbonyl (200 mg, 0.58 mmol) by a method similar to that of **3a** gave dark green crystals (48 mg, 74%). Mp 180–184°C; IR (KBr): 3070w, 2090vs, 2050vs, 2030vs, 2005vs, 1995vs, 1980vs, 1545w, 1410w, 1380w, 1260w, 1200w, 1110m, 1040m, 1020w, 1000w, 850w, 820m, 760m, 640w, 515s, 500s, 470s cm^{-1}; ^1H NMR ($CDCl_3$): 4.70 (4H, br, Cp), 4.62 (4H, br, Cp), 4.46 (8H, br, Cp), 4,24 (10H, s, Cp); ^{13}C NMR ($CDCl_3$): 199.69 (CO), 93.30 (C≡), 91.74 (C≡), 86.96 (Cp), 85.93 (Cp), 72.49 (Cp), 70.54 (Cp), 70.13 (Cp), 69.84 (Cp), 69.26 (Cp); UV (c-C_6H_{12}) λ_{max} = 221 ($\epsilon = 7.2 \times 10^4$), 607 nm ($\epsilon = 3.7 \times 10^3$); Anal. Found: C, 46.93; H, 1.86. Calcd. for $C_{46}H_{26}O_{12}Co_4Fe_3$: C, 47.06; H, 2.23%.

3.5. Preparation of $\{(\eta^5\text{-}C_5H_4C{\equiv}CPh)_2Fe\}Co_2(CO)_6$ (4)

1,1′-Bis(phenylethynyl)ferrocene (193 mg, 0.50 mmol) was treated with dicobaltoctacarbonyl (171 mg, 0.50 mmol) in benzene (20 ml) at room temperature for 4 h. The solvent was evaporated under reduced pressure and the residue was redissolved in a small portion of hexane. Separation by column chromatography on alumina with hexane gave three bands. The first red band is 1,1′-bis(phenylethylyl)ferrocene recovered (20%), the second green band is **3a** (17%) and the third green band is **4**. Dark green crystals of **4** (73 mg, 22%) were obtained by recrystallization from hexane. Mp 78–80°C; IR (KBr): 3055w, 3045w, 2090vs, 2050vs, 2005vs, 1990vs, 1625w, 1590w, 1490m, 1480m, 1435m, 1385w, 1260w, 1200w, 1070w, 1040w, 1030m, 920w, 825s, 760s, 690s, 660m, 625w, 605w, 590w, 580w, 570m, 540m, 515s, 495s cm^{-1}; ^1H NMR (C_6D_6): 7.97–7.95 (2H, m, Ph), 7.57–7.56 (2H, m, Ph), 7.19–7.16 (3H, m, Ph), 7.08–7.01 (3H, m, Ph), 4.48 (2H, s, Cp), 4,40 (2H, s, Cp), 4.23 (2H, s, Cp), 4,00 (2H, s, Cp); ^{13}C NMR (C_6D_6): 199.77 (CO), 138.74 (Ph), 131.74 (Ph), 129.97 (Ph), 129.29 (Ph), 128.73 (Ph), 128.56 (Ph), 128.17 (Ph), 124.35 (Ph), 92.36 (C≡), 91.89 (C≡), 88.25 (C≡), 87.41 (C≡), 86.58 (Cp), 73.14 (Cp), 72.73 (Cp), 71.81 (Cp), 71.25 (Cp), 67.15 (Cp); UV (c-C_6H_{12}) λ_{max} = 214 ($\epsilon = 4.8 \times 10^4$), 300 ($\epsilon = 2.6 \times 10^4$), 436 ($\epsilon = 1.9 \times 10^3$), 565 nm ($\epsilon = 1.0 \times 10^3$); Anal. Found: C, 57.33; H, 2.55. Calcd. for $C_{32}H_{18}O_6Co_2Fe$: C, 57.18; H, 2.70%.

3.6. Reaction of $\{(\eta^5\text{-}C_5H_4C{\equiv}CPh)_2Fe\}Co_2(CO)_6$ (4)

Complex **4** (40 mg, 0.06 mmol) was dissolved in 20 ml of benzene and the solution was stirred for 2 h under reflux. The solvent was removed *in vacuo*, and the residue was purified by alumina column chromatography using hexane as an eluent. Recrystallization from hexane gave green crystals of **3a** (10 mg, 18%).

3.7. X-ray crystallography of 3a and 4

Single crystals suitable for an X-ray diffraction analysis were obtained by recrystallization from hexane, and mounted on glass fibres with epoxy resin. Diffraction measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å) using a ω–2θ scan technique with a scan rate 8 deg cm^{-1}. Unit cells were determined and refined by a least-squares method using 24 reflections in the range $18° < 2\theta < 25°$ for **3a** and 25 reflections in the range $34° < 2\theta < 35°$ for **4**. The data of weak reflections ($I < 10\sigma(I)$) were measured twice and averaged. Three standard reflections were monitored at every 150 measurements and no damage was observed. Intensities were collected for Lorentz and polarization effects and an empirical absorption collection was made using program DIFABS.

Complexes **3a** and **4** crystallized in monoclinic and orthorhombic systems, respectively. The positions of metal atoms were located by direct method. Subsequent difference Fourier maps revealed the positions of all non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included at the calculated positions using isotropic thermal parameters. The final cycles of full matrix least-squares refinement were converged, and the largest parameter shifts against errors were 0.48 for **3a** and 0.73 for **4**, respectively. The unweighted and weighted agreement factors are $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.048$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2} = 0.035$ for **3a**, and $R = 0.029$ and $R_w = 0.029$ for **4**, respectively. All calculations were performed with a VAX station 3100 using the TEXSAN crystallographic software package.

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