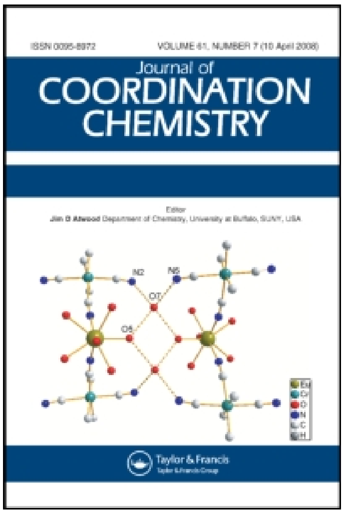

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PREPARATION AND CHARACTERIZATION OF CLUSTER COMPLEXES DERIVED FROM FERROCENYLACETYLENE

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Note

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Reaction of ferrocenylacetylene with octacarbonyldicobalt resulted in the formation of μ-$FcCCHCo_2(CO)_6$ (**1**). When (**1**) was treated with an equimolar amount of the sodium salt of cyclopentadienyl carbonyl molybdenum(tungsten) anion, $RC_5H_4M(CO)_3^-$ ($R = H$, CH_3), the chiral heterobimetallic cluster complexes μ-$FcCCHCo(CO)_3M(CO)_2C_5H_4R$ [(**2**): $M = Mo$, $R = H$; (**3**): $M = W$, $R = H$; (**4**): $M = Mo$, $R = CH_3$; (**5**): $M = W$, $R = CH_3$] were obtained. These complexes were characterized by analyses, IR and ^1H NMR spectra. The molecular structure of complex (1) was determined by single-crystal X-ray diffraction methods.

Keywords: Ferrocentylacetylene; cluster complexes; crystal structure

INTRODUCTION

It has been known for some time that the ferrocenylacetylene reacts with transition metal complexes to give cyclic oligomers.[1] From the viewpoint of developing a new functionalized material, the chemistry of ferrocenylacetylene has been revived. Ferrocenylacetylene reacts with rutheniumdodecacarbonyl to give a new type of trinuclear complex.[2] Ru(II),[3] Fe(II),[4] Ni(II),[5]

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* Corresponding author.

Pd(II)[5] and Pt(II) ferrocenylacetylide complexes[6] have been reported. The reaction of Re(I) phenylacetylide and ferrocentylacetylene was also reported.[7] The reaction product of silver ferrocenylacetylene with BrMn(dppe)$(CO)_3$ was reported to have potential for non-linear optics.[8] In contrast, ferrocenylacetylene bimetallic complexes are rarely reported.[9] We report here the syntheses and characterization of μ-FcCCHCo$(CO)_3$-M$(CO)_2C_5H_4$R (R = H, CH_3; M = Mo, W) and the molecular structure of μ-FcCCH$Co_2(CO)_6$.

EXPERIMENTAL

All reactions were carried out under highly pure nitrogen using standard Schlenk vacuum techniques. All solvents were dried according to standard procedure[10] before use. Chromatographic separations and purifications were performed on 160–200 mesh silica gel. Mo$(CO)_6$ and W$(CO)_6$ were purchased from Fluka and the Aldrich Co. $Co_2(CO)_8$[11] and FcC≡CH[12] were prepared according to published methods. IR spectra were recorded on a Nicolet FT-IR 10DX spectrophotometer, and ^{1}H NMR on a Bruker-AM 400 MHz spectrometer; C/H determination was performed using a Carlo-Erba 1160 microanalyser.

Preparation of Cluster (1)[9]

A solution of $Co_2(CO)_8$ (4.20 g, 12.3 mmol) and ferrocenylacetylene (2.60 g, 12.4 mmol) in benzene was stirred at room temperature for 16 h. After the solvent was removed, the residue was chromatographed on a 2.5 × 60 cm column of silica. Elution of a dark green band with petroleum ether (60–90°) gave dark green, air-stable crystals, 4.50 g, 80.4% yield. Calcd. for $C_{18}H_{10}Co_2FeO_6$%: C, 43.44; H, 2.03. Found: C, 43.38; H, 2.07. IR (KBr disk): 3103m, 2087vs, 2048vs 2020–1850vs (br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.28 (s, 1H, CH), 4.35 (m, 4H, C_5H_4), 4.16 (s, 5H, C_5H_5).

Syntheses of Cluster (2) and (4)

To a solution of 25 cm^3 of THF containing 1.0 mmol of C_5H_5Na, Mo$(CO)_6$ (0.264 g, 1.0 mmol) was added. The mixture was heated under reflux for 12 h and cooled to room temperature; then FcC≡CH$Co_2(CO)_6$ (0.496 g, 1.0 mmol) was added with stirring at 60°C for 1.5 h. The solvent was removed under vacuum. The residue was chromatographed on a 2.5 × 20 cm silica column with petroleum ether (60–90°)–CH_2Cl_2 (4 : 1) as eluent to gave a red band. From this band, compound (**2**) was obtained as a dark red solid, 0.440 g, 76.9% yield. Calcd. for $C_{22}H_{15}CoFeMoO_5$%: C, 46.36; H, 2.63. Found: C, 46.38; H, 2.51. IR (KBr disk): 3096m, 2050vs, 1983vs, 1959vs, 1927vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.96 (s, 1H, CH), 5.36 (s, 5H, C_5H_5Mo), 4.18 (t, 4H, C_5H_4Fe), 4.13 (s, 5H, C_5H_5Fe).

Compound (**4**) was prepared using the same procedure as that for (**2**). $CH_3C_5H_4Na$ was used instead of C_5H_5Na; some 0.393 g of (**4**) was obtained, 67.2% yield. Calcd. for $C_{23}H_{17}CoFeMoO_5$%: C, 47.11; H, 2.92. Found: C, 47.32; H, 2.88. IR (KBr disk): 3096m, 2039vs, 1990vs, 1961vs, 1934vs, 1890vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.93 (s, 1H, CH); 5.24 (s, 4H, C_5H_4Mo), 4.20 (t, 4H, C_5H_4Fe), 4.14 (s, 5H, C_5H_5Fe), 2.01 (s, 3H, CH_3).

Syntheses of Cluster (3) and (5)

Some 0.352 g (1.0 mmol) of $W(CO)_6$ was added to a solution of 25 cm^3 of DME (dimethoxylethane) containing 1.0 mmol of C_5H_5Na. The mixture was heated to reflux for 30 h. Upon cooling to room temperature, 0.496 g (1.0 mmol) of μ-FcC≡CHCo$_2$(CO)$_6$ was added and the reaction mixture was stirred at 60°C for 1.5 h. The solvent was removed at reduced pressure. The residure was chromatographed on a 2.5 × 20 cm silica column with petroleum ether (60–90°)–CH_2Cl_2 (4 : 1) as eluent to give a dark red solid (**3**) 0.400 g, 60.7% yield. Calcd. for $C_{22}H_{15}CoFeWO_5$(%): C, 41.08; H, 2.55. Found: C, 41.13; H, 2.50. IR (KBr disk): 3094m, 2047vs, 1987vs, 1956vs, 1921vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.83 (s, 1H, CH), 5.27 (s, 5H, C_5H_5W), 4.11 (t, 4H, C_5H_4Fe), 4.06 (s, 5H, C_5H_5Fe).

Compound (**5**) was prepared using the same procedure as that for (**3**). $CH_3C_5H_4Na$ was used instead of C_5H_5Na. Some 0.368 g of (**5**) was obtained as a dark-red solid, 54.8% yield. Calcd. for $C_{23}H_{17}CoFeWO_5$(%): C, 40.13; H, 2.30. Found: C, 40.16; H, 2.99. IR (KBr disk): 3102m, 2037vs, 1987vs, 1967vs, 1928vs, 1883vs cm^{-1}. ^{1}H NMR: δ 5.85 (s, 1H, CH), 5.27 (s, 4H, C_5H_4W), 4.10 (t, 4H, C_5H_4Fe), 4.06 (s, 5H, C_5H_5Fe), 2.15 (s, 3H, CH_3).

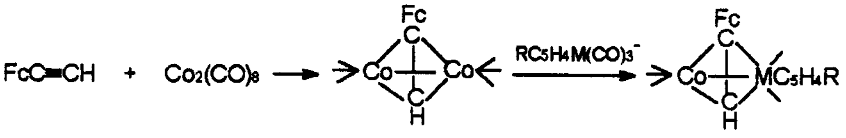
Crystallography of Cluster (1)

The black crystals used for X-ray determination were obtained from hexane at −20°C. A crystal of approximate dimensions 0.20 × 0.20 × 0.30 mm was chosen and mounted on a glass fibre. The single-crystal X-ray diffraction data were collected on a Rigaku AFC7R diffractometer with graphite monochromatized Mo-Kα (0.710069 Å) radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 17 carefully centred reflections in the range $18.43° < 2\theta < 21.45°$. The data were collected at a temperature of 20.0°C using the ω–2θ scan technique.

The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed using the TEXSAN Crystallographic software package of the Molecular Structure Corporation. Full lists of crystallographic data are available from the authors upon request.

RESULTS AND DISCUSSION

The reactions described in this work are summarized in Scheme 1. $FcC{\equiv}CH$ reacted with $Co_2(CO)_8$ in benzene at room temperature to give μ-$FcCCHCo_2(CO)_6$. The sodium salts of cyclopentadienyl tricarbonylmolybdenum(tungsten), $C_5H_5M(CO)_3^-$ (M = Mo, W) prepared from $M(CO)_6$ and C_5H_5Na *in situ* reacted with the homobimetallic alkyne cluster (**1**) to give the expected compounds (**2**)–(**5**) in 54–76% yield. This could be regarded as a result of displacement of $Co(CO)_3$ (d^9ML_3) in μ-$FcCCHCo_2$(-$CO)_6$ by its isoloble metal fragments η^5-$RC_5H_4M(CO)_2$ (d^5ML_5).[13] Further consideration of the structures of (**2**)–(**5**) reveals that this general class of compounds becomes chiral around the C_2CoM core.



R = H, CH₃; M = Mo, W

SCHEME 1

The IR and ^{1}H NMR of cluster (**1**) are consistent with results previously reported.[9] For clusters (**2**)–(**5**), four strong peaks appeared in the region 2050–1883 cm^{-1}, characteristic of terminal carbonyls and a single peak at *c.* 3100 cm^{-1} is characteristic of the C–H absorption of the ferrocenyl group. For the ^{1}H NMR assignment of clusters (**2**)–(**5**), a singlet at δ 6.28 was assigned to the alkyne proton. The singlet in the region δ 5.36–5.24 was assigned to cyclopentadienyl (Mo,W) protons and the signals between δ 4.18–4.06 to the cyclopentadienyl protons of the ferrocenyl group.

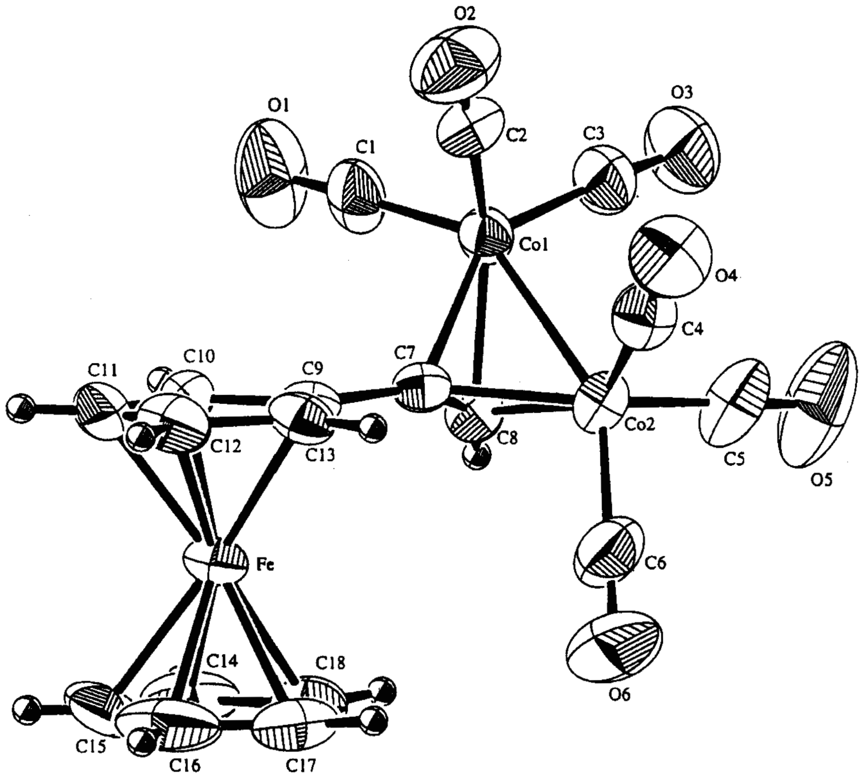


FIGURE 1 Molecular structure of cluster (**1**).

The molecular structure of cluster (**1**) is shown in Figure 1. Crystal data are collected in Tables I and II gives selected bond lengths and angles. As suggested by spectroscopic analyses, a Co_2C_2 unit coordinates to alkynyl and the Co_2C_2 core adopts a *pseudo*-tetrahedral geometry. The Co–Co and C–C bond lengths in the Co_2C_2 core are 2.465(1) and 1.305(8) Å respectively, and Co–C bond lengths are in the range of 1.945(7)–1.993(6) Å. They are all in the normal range for related alkyne-dicobalt complexes.[14]

Finally, it is worth pointing out that the bond length C(9)–C(7) [1.454(8) Å] is much shorter than that of a normal C–C single bond (1.54 Å), but longer than that of C=C double bond (1.34 Å). This reveals that the ferrocenyl group conjugates quite well with the Co_2C_2 framework and suggests that there is electron delocalization between the two structure units. Thus the clusters may be suitable precursors for conducting materials.

TABLE I Summary of crystal and intensity data for cluster (**1**)

Formula	$C_{18}H_{10}Co_2FeO_6$
F.W.	495.99
Crystal system	Monoclinic
Lattice parameters	$a = 14.538(2)$, $b = 7.452(2)$, $c = 17.408(3)$ Å; $\beta = 90.80°$; $V = 1885.7(6)$ Å^3
Z	4
Space group	$P2_1/a$
D_c (g cm^{-3})	1.747
F(000)	984.00
μ(Mo-Kα) (cm^{-1})	25.28
Radiation (Mo-Kα) (Å)	0.71069
Temp. (°C)	20.0
Scan type	ω–2θ
$2\theta_{max}$ (°)	50.0
No. of reflections measured	Total: 3614 Unique: 3466 ($R_{int} = 0.027$)
No. of observations [$I > 3.00\sigma(I)$]	1644
No. of variables	285
Residual: R^a, $R_w{}^a$	0.034; 0.034

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w F_o^2]^{1/2}$.

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

Co(1)–Co(2)	2.465(1)	Co(2)–C(8)	1.950(7)
Co(1)–C(7)	1.993(6)	C(7)–C(8)	1.305(8)
Co(1)–C(8)	1.945(7)	C(7)–C(9)	1.454(8)
Co(2)–C(7)	1.966(6)		
Co(2)–Co(1)–C(7)	51.0(2)	Co(1)–C(7)–Co(2)	77.0(2)
Co(2)–Co(1)–C(8)	50.8(2)	Co(1)–C(7)–C(8)	68.7(4)
C(7)–Co(1)–C(8)	38.7(2)	Co(2)–C(7)–C(8)	69.9(4)
Co(1)–Co(2)–C(7)	52.0(2)	Co(1)–C(8)–Co(2)	78.5(2)
Co(1)–Co(2)–C(8)	50.6(2)	Co(1)–C(8)–C(7)	72.7(4)
C(7)–Co(2)–C(8)	38.9(2)	Co(2)–C(8)–C(7)	71.2(4)

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