

# Synthesis and expansion reaction of ferrocenylacetylene dimetal carbonyl compounds. The molecular structures of $\mu$ -FcCCHCoMo(CO)<sub>5</sub>Cp and $\mu_3$ -FcCHCFeCo<sub>2</sub>(CO)<sub>9</sub>

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## Abstract

Two ferrocenylacetylene dimetal carbonyl clusters  $\mu$ -FcCCHCo(CO)<sub>3</sub>M(CO)<sub>2</sub>Cp (**2**, M = Mo; **3**, M = W) were obtained from the reactions of the precursor  $\mu$ -FcCCHCo<sub>2</sub>(CO)<sub>6</sub> **1** with metal exchange reagents NaM(CO)<sub>3</sub>Cp in THF under reflux. The dimetal compounds **1**, **2**, and **3** can further react with Fe<sub>2</sub>(CO)<sub>9</sub> in the presence of benzylideneacetone (BDA) to give the corresponding  $\mu_3$ -ferrocenylvinylidene bridged trimetal clusters  $\mu_3$ -FcCHCFeCo<sub>2</sub>(CO)<sub>9</sub> **4** and  $\mu_3$ -FcCHCFeCoM(CO)<sub>8</sub>Cp (**5**, M = Mo; **6**, M = W), respectively, probably through the formation of the intermediate (BDA)Fe(CO)<sub>3</sub> which acts as an Fe(CO)<sub>3</sub> transfer-reagent. The new compounds **2–6** were characterized by C/H analysis, IR and <sup>1</sup>H-NMR spectroscopies. The molecular structures of **2** and **4** were determined by X-ray structural analysis. **2** is triclinic with space group  $P\bar{1}$  (# 2),  $a = 8.733(2)$  Å,  $b = 14.870(3)$  Å,  $c = 8.200(2)$  Å,  $\alpha = 92.77(2)^\circ$ ,  $\beta = 101.78(2)^\circ$ ,  $\gamma = 78.41(2)^\circ$ ,  $V = 1021.2(4)$  Å<sup>3</sup>, and  $Z = 2$ ; final  $R = 0.025$ ,  $R_w = 0.034$  for 2988 reflections. Cluster **4** is orthorhombic with space group  $P2_12_12_1$  (# 19),  $a = 12.186(5)$  Å,  $b = 14.870(5)$  Å,  $c = 7.800(6)$  Å,  $V = 2340(2)$  Å<sup>3</sup> and  $Z = 4$ ; final  $R = 0.062$ ,  $R_w = 0.065$  for 2401 reflections. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Ferrocenylacetylene; Dimetal clusters; Trimetal clusters; Expansion

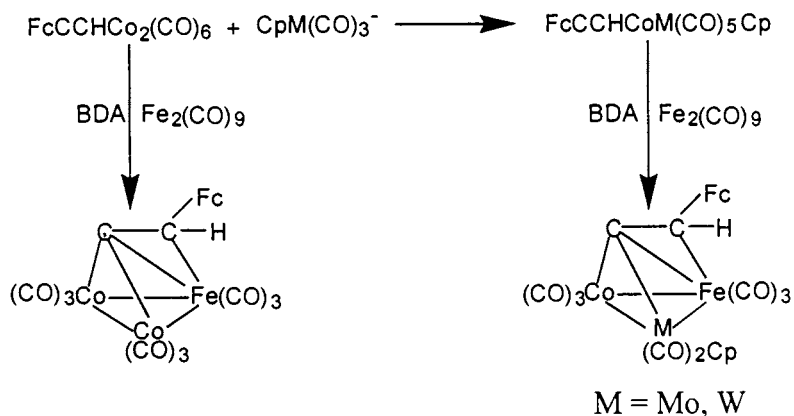
## 1. Introduction

Transition metal carbonyl clusters are regarded as model system whose study can provide insight into the complicated reaction processes at catalytically active metal surfaces. This fact, together with the hope of employing the cluster themselves in catalytic processes, has led to a considerable research potential in this area [1]. Alkyne and alkynyl species bearing a C≡C functional group belong to a class of surface species which may play pivotal role in various catalytic reactions such as CO hydrogenation (F-T processes) [2], therefore, alkyne-bridged di- or polynuclear metal carbonyls

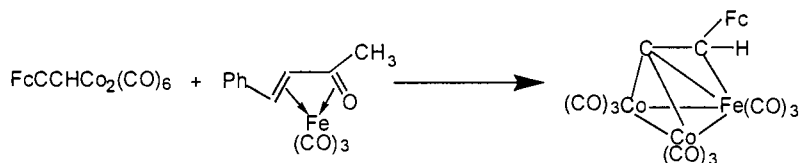
could serve as model compounds in heterogeneous catalysis. A ligand bonded to metal cluster can simulate the absorption of same species on metal surface and, are of interesting alkyne-bridged ligand rearrangement [3] and diastereoselective transformation [4] on tri- or quart-metal clusters.

An astonishing variety of alkyne-bridged clusters have been synthesized and structurally characterized. However, reports on the ferrocenylacetylene cluster compounds are relatively rare in the literature [5] and no example of ferrocenylacetylene heterometal clusters has been investigated. Others [6] and we believed that incorporation of the ferrocenyl group into clusters through an organic conjugated bridge would lead to some interesting properties based on the well-known

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Scheme 1.



Scheme 2.

fact: both ferrocene [7] and low-valency transition-metal clusters [8] can function as redox centers electron-transfer entities. In this article we report the synthesis of ferrocenylacetylene heterodimetal clusters, and their expansion reaction with  $\text{Fe}_2(\text{CO})_9$  in the presence of benzyldeneacetonetricarbonyliron. The molecular structures of **2** and **4** were determined by X-ray diffraction.

## 2. Experimental

### 2.1. General details

All reactions were carried out under prepurified nitrogen atmosphere using standard Schlenk or vacuum line techniques. All solvents were dried and deoxygenated according to standard procedures [9] before use. Chromatographic separations and purifications were performed on 160–200 mesh silica gel.  $\text{Mo}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$ , and  $\text{Fe}_2(\text{CO})_9$  were purchased from Fluka and Aldrich Chem.  $\mu\text{-FcCCHCo}_2(\text{CO})_6$  ([5]a) and benzyldeneacetonetricarbonyliron (BDA) $\text{Fe}(\text{CO})_3$  [10] were prepared according to the literature methods.

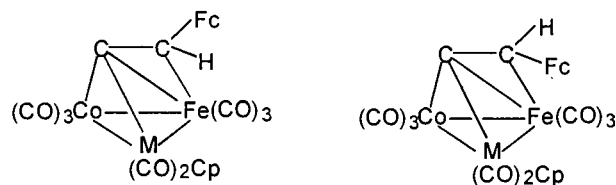
IR spectra were recorded on a Nicolet FT-IR spectrophotometer,  $^1\text{H-NMR}$  were recorded on a Bruker AM 400 MHz spectrometer. C/H determination was performed using a Carlo-Erba 1160 type microanalyzer.

### 2.2. Synthesis of clusters **1**, **2** and **3**

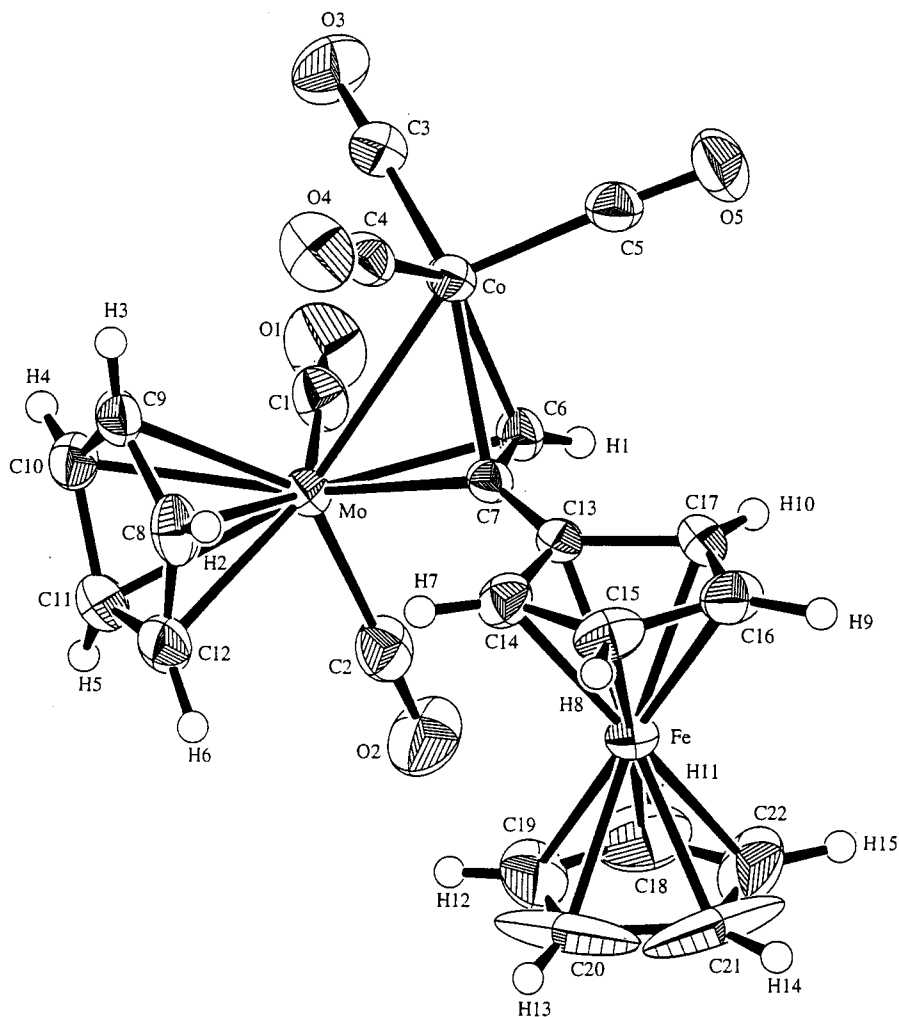
A solution of  $\text{Co}_2(\text{CO})_8$  (4.20 g, 12.3 mmol) and ferrocenylacetylene (2.60 g, 12.4 mmol) in 100 ml

benzene was stirred for 16 h at room temperature. The solvent was removed under reduced pressure to yield a dark-green crystalline residue. Chromatography on a  $2.5 \times 60$  cm column of silica gel eluting with petroleum ether. First removed a small yellow band ( $\text{FcC}\equiv\text{CH}$ ), Further elution with petroleum ether gave a large green band which was collected and evaporated to dryness to afford 4.50 g (80.4%) of dark-green crystals of **1**. Anal. Calc. for  $\text{C}_{18}\text{H}_{10}\text{O}_6\text{FeCo}_2$ : C, 43.44; H, 2.03%. Found: C, 43.38; H, 2.07%. IR (KBr disk): 3103m, 2087s, 2048vs, 2019–1850vs(br.)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{DCCl}_3$ ,  $\delta$ ): 6.28(s, 1H, C–H), 4.35(s, 4H,  $\text{C}_5\text{H}_4$ ), 4.16(s, 5H,  $\text{C}_5\text{H}_5$ ).

$\text{Mo}(\text{CO})_6$  (0.264 g, 1.0 mmol) was added to a solution of ca. 1.0 mmol sodium pentadienide in 25 ml THF. The mixture was heated under reflux for 12 h and cooled to room temperature. Then **1** (0.500 g, 1.0 mmol) was added and stirred for 1.5 h at  $60^\circ\text{C}$ . The solvent was removed under vacuum. The red-brown residue was chromatographed on a  $2.5 \times 20$  cm silica gel column using petroleum ether/ $\text{CH}_2\text{Cl}_2$  as eluent and gave 0.440 g (76.9%) of dark-red solid **2**. Anal. Calc. for  $\text{C}_{22}\text{H}_{15}\text{O}_5\text{FeCoMo}$ : C, 46.36; H, 2.63%. Found: C, 46.38; H, 2.51%. IR (KBr disk): 3096m, 2050s, 1983vs, 1959vs, 1927s  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$ ( $\text{CDCl}_3$ ,  $\delta$ ): 5.96(s, 1H,



Scheme 3.

Fig. 1. Molecular structure of **2**

C–H), 5.36(s, 5H, C<sub>5</sub>H<sub>5</sub>Mo), 4.18(s, 4H, C<sub>5</sub>H<sub>4</sub>Fe), 4.13(s, 5H, C<sub>5</sub>H<sub>5</sub>Fe).

Complex **3** was prepared by the same procedure as that of for **2**, W(CO)<sub>6</sub> was used instead of Mo(CO)<sub>6</sub>. A total of 0.400 g (60.7%) of **3** was obtained as a dark-red solid. Anal. Calc. for C<sub>22</sub>H<sub>15</sub>O<sub>5</sub>FeCoW: C, 39.67; H, 1.59%. Found: C, 39.52; H, 1.61%. IR (KBr disk): 3094m, 2047s, 1987vs, 1956vs, 1921s cm<sup>-1</sup>. <sup>1</sup>H-NMR(CDCl<sub>3</sub>, δ): 5.83(s, 1H, C–H), 5.27(s, 5H, C<sub>5</sub>H<sub>5</sub>W), 4.11 (s, 4H, C<sub>5</sub>H<sub>4</sub>Fe), 4.06(s, 5H, C<sub>5</sub>H<sub>5</sub>Fe).

### 2.3. Expansion reaction of **1**, **2** and **3**

These reactions were carried out at 55–60°C in toluene with ca. 1:2:3 ratios of the dimetal clusters, BDA and Fe<sub>2</sub>(CO)<sub>9</sub>. A detailed description of the reaction among **1**, BDA and Fe<sub>2</sub>(CO)<sub>9</sub> is provided to illustrate the procedure. Other reactions and workup were conducted similarly.

A solution of **1** (0.250 g, 0.5 mmol), BDA (0.146 g, 1.0 mmol) and Fe<sub>2</sub>(CO)<sub>9</sub> (0.546 g, 1.5 mmol) in 30 ml

toluene was stirred at 55–60°C for 48 h. The solvent was removed and the residue was loaded onto a chromatographic column. Elution with petroleum ether removed trace of **1** and Fe<sub>3</sub>(CO)<sub>12</sub>. Then elution with petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (7:1) produced a dark red-brown band of μ<sub>3</sub>-FeCHCFeCo<sub>2</sub>(CO)<sub>9</sub>, **4** (0.215 g, 66.0%), and followed by an orange band of (BDA)Fe(CO)<sub>3</sub> (0.018 g).

Complex **4**: Anal. Calc. for C<sub>21</sub>H<sub>10</sub>O<sub>9</sub>Fe<sub>2</sub>CO<sub>2</sub>: C, 39.67; H, 1.59%. Found: C, 39.52; H, 1.61%. IR (KBr disk): 3095m, 2095s, 2056s, 2027vs, 2008vs, 1971s cm<sup>-1</sup>. <sup>1</sup>H-NMR(CDCl<sub>3</sub>, δ): 6.84(s, 1H, C–H), 4.33–4.40 (m, 4H, C<sub>5</sub>H<sub>4</sub>Fe), 4.24 (s, 5H, C<sub>5</sub>H<sub>5</sub>Fe).

Complex **4** can also be obtained by the reaction of **1** with (BDA)Fe(CO)<sub>3</sub> (1:3) in the similar reaction condition in 58% yield.

μ<sub>3</sub>-FeCHCFeCoMo(CO)<sub>8</sub>Cp **5** was obtained from **2** in 66.9% as a dark-red solid. Anal. Calc. for C<sub>25</sub>H<sub>15</sub>O<sub>8</sub>CoFe<sub>2</sub>Mo: C, 42.29; H, 2.13. Found: C, 42.45; H, 2.08%. IR (KBr disk): 3100m, 2064s, 2004vs, 1939vs, 1888s cm<sup>-1</sup>. <sup>1</sup>H-NMR(CDCl<sub>3</sub>, δ), 6.81, 6.62(s, s, ca. 1:1, 1H, C–H), 5.74 (s, 5H, C<sub>5</sub>H<sub>5</sub>Mo), 4.24(m, 9H, Fe).

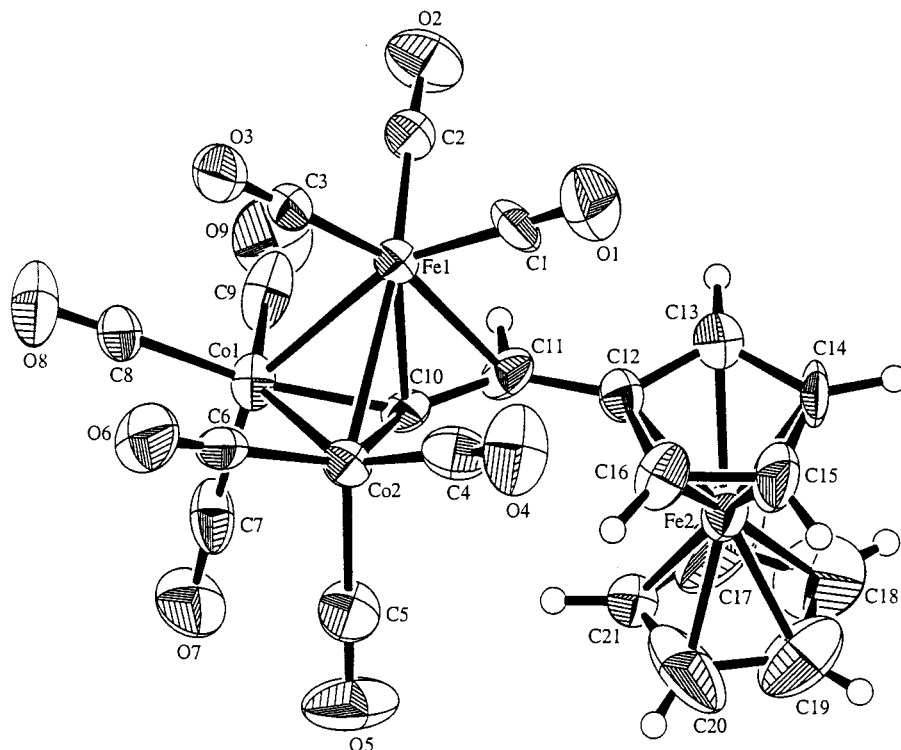


Fig. 2. Molecular structure of **4**

$\mu_3$ -FcCHCFeCoW(CO)<sub>8</sub>Cp **6** was obtained from **3** in 62.7% as a dark red solid **6**. Anal. Calc. for C<sub>25</sub>H<sub>15</sub>O<sub>8</sub>CoFe<sub>2</sub>W: C, 37.63; H, 1.89%. Found: C, 37.54; H, 1.92%. IR (KBr disk): 3094m, 2062s, 2002vs, 1935vs, 1883s cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ ), 7.07, 6.46(s, s, ca. 3:1, 1H, C–H), 5.59, 5.49(s, s ca. 3:1, 5H, C<sub>5</sub>H<sub>5</sub>Mo), 4.23(m, 9H, Fc).

#### 2.4. X-ray crystallography of **2** and **4**

Single crystals suitable for an X-ray diffraction analysis were obtained from hexane at –20°C. Both crystals approximate dimensions 0.20 × 0.20 × 0.30 mm<sup>3</sup> were chosen and mounted on glass fibres. All measurements were made on a Rigaku AFC 7R diffractometer with graphite monochromated Mo–K $\alpha$  ( $\lambda$  = 0.71069 Å) radiation. Cell constants and orientation matrix for data collection, were obtained from a least-squares refinement using the setting angles of 20 carefully centered reflections in the range 18.87 < 2 $\theta$  < 24.46° for **2** and 13 reflections in the range 13.34 < 2 $\theta$  < 21.50° for **4**. The data were collected at a temperature of 20.0°C using a  $\omega$ -2 $\theta$  scan technique with a scan rate of 16° min<sup>-1</sup>.

The structures were solved by direct methods and expanded Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atoms scattering factors were taken from Cromer and Waber [11]. All calcula-

tions were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of **2** and **3**

The reactions described in this work are summarized in Scheme 1. Dicobalt Octacarbonyl reacts readily with alkyne to give the ( $\mu$ -RC $\equiv$ CR')Co<sub>2</sub>(CO)<sub>6</sub> [12]. Similarly, Yanez [13] and Coville [14] found CpM(CO)<sub>3</sub>Co(CO)<sub>3</sub> (M = Mo, W) reacted with alkyne to afford ( $\mu$ -RC $\equiv$ CR')Co(CO)<sub>3</sub>M(CO)<sub>2</sub>Cp, but the yields were poor and sometimes (RC $\equiv$ CR')<sub>2</sub>Co(CO)<sub>2</sub>M(CO)Cp were the major products. Isolobal substitution of a different organometallic vertex on an appropriate alkyne-homodimetal clusters which represents a logical routes to synthesize heterometal clusters has attracted considerable attention [15]. Therefore, in the present work, ferrocenylacetylene reacted with Co<sub>2</sub>(CO)<sub>8</sub> in benzene for 16 h at room temperature, cluster **1** was obtained in 80.4% yield. Complex **1** was treated with CpM(CO)<sub>3</sub><sup>-</sup> (M = Mo, W), which were prepared from M(CO)<sub>6</sub> and C<sub>5</sub>H<sub>5</sub>Na in situ, in THF under reflux during 1.5 h to give cluster **2** and **3** in 76.8 and 60.7%, respectively. The dimer M<sub>2</sub>(CO)<sub>4</sub>Cp<sub>2</sub> were always present as byproducts. When the reactions in the case of Mo were carried out at an elevated temperature, for example, in DME under

reflux, the twice exchange product  $\mu\text{-FcC}\equiv\text{CHMo}_2\text{-(CO)}_4\text{Cp}_2$  could also be isolated.

The new clusters **2** and **3** are stable in air in solid state and soluble in common organic solvents. They were characterized by elemental analysis, IR and  $^1\text{H-NMR}$ . Both show same pattern of five peaks in their IR spectra consisting of one absorption (ca.  $3100\text{ cm}^{-1}$ ), which we ascribed to ferrocenyl group, and four strong peaks in the range of  $2050\text{--}1921\text{ cm}^{-1}$ , we assigned to the terminal carbonyls. Their  $^1\text{H-NMR}$  exhibited the resonances of alkynyl H ( $65.96\text{--}5.83$ ), Cp(Mo, W)( $65.36\text{--}5.27$ ) and ferrocenyl group ( $64.18\text{--}4.06$ ). It is curious that the chemical shifts of  $\text{H}_{2,5}$  and  $\text{H}_{3,4}$  in ferrocenyl group are not differentiated just same as in the case of  $\text{FcCCO}_3(\text{CO})_9$  ([6]a) and other related com-

pounds ([6]c). It appears that the magnetic effects of diamagnetic clusters are dominating the complex shielding/deshielding interaction in these ferrocene derivatives.

The  $^1\text{H-NMR}$  data suggested that the cluster cores  $\text{C}_2\text{CoM}$  have deshielding effects on the protons of both ferrocenyl and alkynyl groups, the degree depends on the *M* fragments, following the series  $\text{Co}(\text{CO})_3 > \text{Mo}(\text{CO})_2\text{Cp} > \text{W}(\text{CO})_2\text{Cp}$ .

### 3.2. Expansion reaction, and characterization of products **4**, **5** and **6**

One of the established routes to higher nuclearity alkyne clusters is the reaction of preformed alkyne complexes with suitable metal fragments H. Vahrenkamp ([4]a) reported that  $\text{Co}_2(\text{CO})_6(\mu\text{-C}_2\text{R}_2)$  reacted with  $\text{Fe}_3(\text{CO})_{12}$  in refluxing toluene resulting in the formation of the corresponding trimetal clusters  $(\mu_3\text{-C}_2\text{R}_2)\text{FeCo}_2(\text{CO})_9$ . Moreover, the terminal alkyne often undergoes rearrangement to form cluster-bonded vinylidene. However, we found such an expansion reaction applied to clusters **1**, **2** and **3** can lead to complete decomposition of the starting materials. When **1** was treated with an excess of  $\text{Fe}_2(\text{CO})_9$  instead of  $\text{Fe}_3(\text{CO})_{12}$  in THF under reflux, the black air-stable vinylidene-bridged cluster **4** was obtained in ca. 19% yield, but for **2** or **3**, only a trace of **5** or **6** was isolated. On the other hand, when this reaction was carried out in the presence of benzylideneacetone (BDA) in toluene at  $55\text{--}60^\circ\text{C}$  for 48 h, the yields of **4**, **5** and **6** increased to 66.0, 66.9 and 62.7%, respectively. Benzylideneacetone-tricarbonyliron [(BDA)Fe(CO)<sub>3</sub>] [10] was also isolated. Therefore, we believe that benzylideneacetone can be used catalytically for the reaction between the dimetal compounds and  $\text{Fe}_2(\text{CO})_9$ , probably through the formation of an intermediate (BDA)Fe(CO)<sub>3</sub>. This has been confirmed by the reaction of **1** with (BDA)Fe(CO)<sub>3</sub> (Scheme 2). Although (BDA)Fe(CO)<sub>3</sub> has already been known, using it as an expansion reagent is unprecedented in literatures.

The new clusters **4**, **5** and **6** were characterized by elemental analysis, IR and  $^1\text{H-NMR}$  spectra. Cluster **4** shows five strong terminal carbonyl absorptions between  $2095\text{--}1971\text{ cm}^{-1}$  in its IR spectrum, but only four peaks appear in the range of  $2064\text{--}1883\text{ cm}^{-1}$  for **5** and **6**. The  $^1\text{H-NMR}$  spectra consist of the resonances of the vinylidene proton, Cp (for **5** and **6**), and ferrocenyl group, all of which show unexceptional chemical shifts. It is noticeable that the  $^1\text{H-NMR}$  of **5** and **6**, each contains two singlet signals of vinylidene proton in the ratio of ca. 1:1 for **5** and ca. 1:3 for **6**, indicating the existence of two isomeric forms of each these clusters, which should differ in the positions of H and Fc as suggested by Vahrenkamp ([4]a) (Scheme 3). Unfortunately, the two isomers of both **5** and **6** can not be

Table 1  
Crystallographic data **2** and **4**

	<b>2</b>	<b>4</b>
Empirical formula	$\text{C}_{22}\text{H}_{15}\text{O}_5\text{FeCoMo}$	$\text{C}_{21}\text{H}_{10}\text{O}_9\text{Fe}_2\text{Co}_2$
<i>M</i>	570.08	635.86
Crystal dimension (mm)	$0.20 \times 0.20 \times 0.30$	$0.20 \times 0.20 \times 0.30$
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (# 2)	$P2_12_1$ (# 19)
Lattice parameters		
<i>a</i> (Å)	8.733(2)	12.186(5)
<i>b</i> (Å)	14.870(3)	24.624(5)
<i>c</i> (Å)	8.200(2)	7.800(6)
$\alpha$ (°)	92.77(2)	
$\beta$ (°)	101.78(2)	
$\gamma$ (°)	78.41(2)	
<i>V</i> (Å <sup>3</sup> )	1021.2(4)	2340(2)
<i>Z</i>	2	4
<i>D</i> <sub>calc.</sub> (g cm <sup>-3</sup> )	1.854	1.804
<i>F</i> (000)	564.00	1256.00
$\mu$ (Mo-K $\alpha$ ) (cm <sup>-1</sup> )	21.38	26.55
Radiation (Mo-K $\alpha$ ) (Å)	0.71069	0.71069
Temperature (°C)	20.0	20.0
Scan type	$\omega-2\theta$	$\omega-2\theta$
$2\theta$ max (°)	49.7	50.0
No. of reflections measured	Total: 2988; Unique: 2717 ( $R_{\text{int}} = 0.060$ )	Total: 2401
No. of Observations	2416 [ $I > 3.00\sigma(I)$ ]	1507 [ $I > 2.00\sigma(I)$ ]
No. of variables	272	307
Residuals: <i>R</i> ; <i>R</i> <sub>w</sub>	0.025; 0.034	0.062; 0.065
Goodness-of-fit indicator	1.59	1.85
Maximum peak in final difference map (e Å <sup>-1</sup> )	0.52	0.91
Minimum peak in final difference map (e Å <sup>-1</sup> )	-0.43	-0.62

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}}{w = 4F_o / \sigma^2(F_o)^2}$$

Goodness-for-fit indicator, standard deviation of observations of unit weight  $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ ,  $N_o$ , number of observations;  $N_v$ , number of variables.

Table 2  
Non-hydrogen atom coordinates and  $B_{\text{iso}}/B_{\text{eq}}$  for **2**

Atom	x	y	z	$B_{\text{eq}}$
Mo	0.96731(4)	0.23293(2)	0.24359(4)	2.315(8)
Co	0.75430(6)	0.38609(3)	0.28550(6)	2.52(1)
Fe	0.55255(7)	0.19638(4)	−0.21619(7)	2.65(1)
O(1)	1.0086(4)	0.2042(3)	0.6264(4)	6.0(1)
O(2)	0.9080(4)	0.0321(2)	0.2339(5)	6.1(1)
O(3)	0.9171(4)	0.4341(3)	0.6187(4)	5.81(10)
O(4)	0.8322(4)	0.5042(2)	0.0506(4)	5.12(9)
O(5)	0.4210(4)	0.4636(2)	0.2948(4)	5.16(9)
C(1)	0.9909(5)	0.2158(3)	0.4861(6)	3.7(1)
C(2)	0.9264(5)	0.1061(3)	0.2324(5)	3.8(1)
C(3)	0.8532(5)	0.4156(3)	0.4907(5)	3.6(1)
C(4)	0.8038(5)	0.4599(3)	0.1443(5)	3.29(10)
C(5)	0.5504(5)	0.4361(3)	0.2897(5)	3.12(10)
C(6)	0.7200(5)	0.2601(3)	0.2729(5)	2.70(9)
C(7)	0.7262(4)	0.2926(2)	0.1186(4)	2.27(8)
C(8)	1.0723(5)	0.2886(3)	0.0350(5)	3.5(1)
C(9)	1.1423(5)	0.3248(3)	0.1863(5)	3.16(9)
C(10)	1.2325(5)	0.2518(3)	0.2872(5)	3.37(10)
C(11)	1.2198(5)	0.1691(3)	0.1991(5)	3.41(10)
C(12)	1.1198(5)	0.1937(3)	0.0402(5)	3.7(1)
C(13)	0.6209(4)	0.2936(2)	−0.0444(4)	2.33(8)
C(14)	0.6581(5)	0.3074(3)	−0.2010(5)	3.07(9)
C(15)	0.5177(6)	0.3223(3)	−0.3243(5)	3.53(10)
C(16)	0.3907(5)	0.3173(3)	−0.2453(5)	4.0(1)
C(17)	0.4532(5)	0.2989(3)	−0.0740(5)	3.5(1)
C(18)	0.601(1)	0.0721(4)	−0.1089(7)	6.4(2)
C(19)	0.7110(7)	0.0779(4)	−0.092(1)	8.0(2)
C(20)	0.646(2)	0.0921(5)	−0.335(1)	11.2(3)
C(21)	0.477(1)	0.0957(4)	−0.368(1)	10.5(2)
C(22)	0.4601(8)	0.0831(4)	−0.211(1)	

$$B_{\text{eq}} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha).$$

separated chromatographically in the present work, therefore, we can not determined which isomer of **6** formed preferentially.

### 3.3. Molecular structures of **2** and **4**

The molecular structures of **2** and **4** were established by X-ray single crystal analysis. The structures with the atom numbering scheme are shown in Figs. 1 and 2. The crystallographic data and non-hydrogen atom coordinates with equivalent  $B$  values are summarized in Tables 1–3, and selected bond lengths and angles are listed in Tables 4 and 5, respectively.

Generally, the structure of **2** is similar to its analogue ( $\mu$ -CF<sub>3</sub>CCCF<sub>3</sub>)CoMo(CO)<sub>5</sub>Cp [16] previously described. It has a quasi-tetrahedral core that approaches a dimetaltetrahedron structure. The C≡C bond (1.339(5) Å) is shorter than that found in ( $\mu$ -CF<sub>3</sub>CCCF<sub>3</sub>)CoMo(CO)<sub>5</sub>Cp (1.371 Å), probably due to the electron-donating character of ferrocenyl group compared with CF<sub>3</sub>. Because of the highly unsymmetrical cluster framework and the greater steric requirement of ferrocenyl group, the C≡C bond is inclined at an angle  $\theta$  of 84.0° to the Co–Mo bond, somewhat deviat-

ing from perpendicular relationship just as in the case of ( $\mu$ -CF<sub>3</sub>CCCF<sub>3</sub>)CoMo(CO)<sub>5</sub>Cp ( $\theta = 88.5^\circ$ ), and the dihedral angles between C(6)–C(7)–C(13) and C(6)–C(7)–Mo planes (156.9°) and between C(6)–C(7)–C(13) and C(6)–C(7)–Co planes (116.7°) are not equivalent. The dihedral angles between C(6)–C(7)–C(13) and the adjacent Cp planes and between C(6)–C(7)–Mo and the Cp(ferrocene) planes are 12.1 and 167.1°, respectively.

The Co–Mo bond length is 2.6924(6) Å; the C(6)–Co and average C–Mo( $\mu$ -C) bond lengths are 1.951(4) and 2.160(4) Å, respectively, and the distance of Mo to the centroid of Cp ring is 2.011 Å. These data are comparable to the corresponding values in ( $\mu$ -CF<sub>3</sub>CCCF<sub>3</sub>)CoMo(CO)<sub>5</sub>Cp [16], but the C(7)–Co bond (2.084(4) Å) is longer than C(6)–Co and the corresponding values of ( $\mu$ -CF<sub>3</sub>CCCF<sub>3</sub>)CoMo(CO)<sub>5</sub>Cp.

Both cobalt and molybdenum atoms achieve distorted octahedral environments if the  $\mu$ -FcCCH and Cp(Mo) ligand are considered to occupy two and one coordination sites, respectively. The two pseudooctahedron share the  $\mu$ -C<sub>2</sub> edge and the Co–Mo axis. The atoms C(2) and C(5) occupy pseudoaxial position.

Table 3  
Non-hydrogen atom coordinates and  $B_{\text{iso}}/B_{\text{eq}}$  for **4**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
Co(1)	0.0224(2)	0.78932(8)	0.4397(3)	3.62(5)
Fe(1)	0.1311(2)	0.83533(10)	0.2046(4)	3.46(6)
Co(2)	-0.0751(2)	0.82418(9)	0.1844(4)	3.60(6)
Fe(2)	-0.0228(3)	1.02740(10)	0.38783(3)	4.43(6)
O(1)	0.184(1)	0.9078(6)	-0.077(2)	7.8(5)
O(2)	0.351(1)	0.8446(7)	0.354(2)	7.7(5)
O(3)	0.158(1)	0.3718(5)	0.029(2)	6.1(4)
O(4)	-0.077(2)	0.8832(6)	-0.140(2)	7.4(4)
O(5)	-0.285(1)	0.8514(8)	0.328(2)	9.1(6)
O(6)	-0.108(1)	0.7152(6)	0.042(2)	6.7(4)
O(7)	-0.169(1)	0.7782(7)	0.667(2)	7.0(5)
O(8)	0.046(1)	0.6730(5)	0.363(2)	6.8(4)
O(9)	0.199(1)	0.8043(8)	0.683(2)	8.6(6)
C(1)	0.163(2)	0.8800(8)	0.0031(3)	5.6(6)
C(2)	0.269(2)	0.8395(7)	0.300(3)	4.9(5)
C(3)	0.148(1)	0.7730(7)	0.096(3)	4.0(5)
C(4)	-0.072(2)	0.8640(9)	-0.006(3)	5.0(5)
C(5)	-0.204(2)	0.8408(9)	0.271(3)	5.5(6)
C(6)	-0.096(1)	0.7565(8)	0.100(3)	4.3(5)
C(7)	-0.094(2)	0.7874(8)	0.582(3)	5.0(3)
C(8)	0.038(2)	0.7175(7)	0.395(2)	4.2(4)
C(9)	0.312(2)	0.7989(8)	0.579(3)	5.1(6)
C(10)	0.010(1)	0.8601(6)	0.355(2)	3.2(4)
C(11)	0.066(1)	0.9074(6)	0.365(2)	3.9(4)
C(12)	0.055(1)	0.9595(6)	0.284(2)	3.6(4)
C(13)	0.126(2)	1.0036(7)	0.291(3)	5.1(5)
C(14)	0.081(2)	1.0480(6)	0.200(4)	7.3(7)
C(15)	-0.017(2)	1.0305(7)	0.131(3)	6.1(6)
C(16)	0.031(2)	0.9778(7)	0.171(2)	4.7(5)
C(17)	-0.022(4)	1.040(2)	0.625(4)	11(1)
C(18)	-0.044(3)	1.086(1)	0.557(5)	10(1)
C(19)	-0.136(3)	1.077(1)	0.469(4)	9(1)
C(20)	-0.165(3)	1.024(2)	0.497(5)	10(1)
C(21)	-0.092(5)	1.001(1)	0.621(5)	16(1)

$$B_{\text{eq}} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha).$$

Ferrocene unit is *cis* to the Cp(Mo) ring. The Cp rings in the ferrocenyl group are staggered with an angle of ca. 31° and, as expected both are planar and parallel each other with a dihedral of 1.49°. Further-

Table 4  
Selected bond lengths (Å) and angles(°) for **2**

Co–Mo	2.6924(6)	Co–C(6)	1.951(4)
Mo–C(6)	2.177(4)	Co–C(7)	2.028(4)
Mo–C(7)	2.144(4)	C(6)–C(7)	1.339(5)
C(7)–C(13)	1.456(5)	Co–C (CO)	1.800 <sup>a</sup>
Mo–C(CO)	1.982 <sup>a</sup>	Mo–Cp <sup>b</sup>	2.011
Co–Mo–C(6)	45.7(1)	Co–Mo–C(7)	47.94(9)
C(6)–Mo–C(7)	36.1(1)	Mo–Co–C(6)	53.0(1)
Mo–Co–C(7)	51.7(1)	C(6)–Co–C(7)	39.3(1)
Mo–C(6)–C(7)	70.6(2)	Co–C(6)–C(7)	73.5(2)
Mo–C(6)–Co	81.2(1)	Mo–C(7)–Co	80.3(1)
Mo–C(7)–C(6)	73.3(2)	Co–C(7)–C(6)	67.3(2)
C(6)–C(7)–C(13)	137.8(3)		

<sup>a</sup> Averaged value.

<sup>b</sup> Center of the Cp ring.

Table 5  
Selected bond lengths (Å) and angles(°) for **4**

Fe(1)–Co(1)	2.531(3)	Fe(1)–Co(2)	2.534(3)
Co(1)–Co(2)	2.473(4)	Fe(1)–C(10)	1.98(2)
Co(1)–C(10)	1.86(2)	Co(2)–C(10)	1.91(2)
Fe(1)–C(11)	2.31(2)	C(10)–C(11)	1.35(2)
C(11)–C(12)	1.44(2)	Fe–C (CO)	1.80 <sup>a</sup>
Co–C (CO)	1.79 <sup>a</sup>	C–O	1.13 <sup>a</sup>
Co(1)–Fe(1)–Co(2)	58.5(1)	Co(1)–Fe(1)–C(10)	47.0(4)
Co(2)–Fe(1)–C(10)	48.0(5)	Fe(1)–Co(1)–Co(2)	60.83(9)
Fe(1)–Co(1)–C(10)	50.8(5)	Co(2)–Co(1)–C(10)	49.8(5)
Fe(1)–Co(2)–Co(1)	60.7(1)	Fe(1)–Co(2)–C(10)	50.5(5)
Co(1)–Co(2)–C(10)	48.4(5)	Fe(1)–C(10)–Co(1)	82.2(6)
Fe(1)–C(10)–Co(2)	81.3(6)	Co(1)–C(10)–Co(2)	81.8(6)
Fe(1)–C(10)–C(11)	85(1)	Fe–C(11)–C(10)	56.8(8)

<sup>a</sup> Averaged value.

more, shorter C(7)–C(13) bond (1.456(5) Å) than typical C–C single bond may suggest conjugation between the C≡C bond and the adjacent Cp ring.

The molecular structure of **4** is based on a ferrocene unit and a triangle of two cobalt and one iron atoms. The two Co–Fe bonds which equal in length (2.531(3) and 2.534(3) Å), together with Co–Co bond (2.473(4) Å) comprise an isosceles triangle.

Nine carbonyls, three on each metal are terminally bound to the metal atoms (the angles of Co–C–O and Fe–C–O are in the range 170–179°). The metal triangle is spanned by triply bridging ferrocenyl vinylidene fragment which is formally  $\sigma$ -bound to the two cobalt atoms and  $\pi$ -bound to iron as a 4e donor. The  $\mu_3$ -C atom C(10) caps the metal triangle plane unsymmetrically, which constructs a distorted tetrahedron with the Fe(1)–C(10) bond length of 1.98(2) Å and the two Co–C(10) bond lengths of 1.91(2) and 1.86(2) Å, respectively. The distance of Fe–C(11) (2.31(2) Å) is longer than that of Fe–C(10).

The dihedral angles between the C(10)–C(11)–C(12) plane and the adjacent Cp ring and between C(10)–C(11)–C(12) and C(10)–Co(1)–Co(2) planes are 7.3 and 170.0°, so, the three planes slightly deviate from co-planarity. Plane C(10)–C(11)–Fe(1) is perpendicular to the Fe(1)–Co(1)–Co(2) and C(10)–Co(1)–Co(2) planes, with the dihedral angles of 89.8 and 90.9°, respectively.

The C(10)–C(11) bond length of 1.35(2) Å is typical for  $\mu_3$ -vinylidene ligand ([3]a,d). The Cp rings in the ferrocenyl group are eclipsed and as expected parallel each other with a dihedral angle of 2.74°. It is noticeable that C(11)–C(12) bond length of 1.44(2) Å is much shorter than a normal C–C single bond, indicating that there is a delocalization between ferrocene unit and the cluster framework.

Two preceding X-ray structures of heteronuclear trimetal clusters with a  $\mu_3$ -vinylidene of  $\mu_3$ - $\sigma$ : $\sigma'$ : $\eta^2$ -C=CRR' type have been known:  $\mu_3$ -CH<sub>2</sub>=CFeW<sub>2</sub>-(CO)<sub>7</sub>Cp [17] and  $\mu_3$ -MeCH=CRuMo<sub>2</sub>(CO)<sub>7</sub>Cp [18].

Then, **4** appears to be the first FeCo<sub>2</sub> core cluster which X-ray structure was determined.

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