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## Note

Synthesis and characterization of new rhodium–cobalt mixed-metal octahedral linked clusters containing  $\eta^2$ -diyne ligandsBao-Hua Zhu<sup>a,b</sup>, Bin Hu<sup>a</sup>, Wei-Qiang Zhang<sup>a</sup>, Yu-Hua Zhang<sup>a</sup>, Yuan-Qi Yin<sup>a,b,\*</sup>,  
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## Abstract

Six new Rh–Co mixed-metal linked cluster complexes  $[\text{Rh}_2\text{Co}_2(\text{CO})_8(\mu\text{-CO})_2(\mu_4, \eta^2\text{-HC}\equiv\text{CCH}_2\text{O-})_2]\text{R}$  ( $\text{R} = \text{C}_6\text{H}_4\text{-1,4}$  (**1**);  $\text{C}_6\text{H}_4\text{-1,4}(\text{C}(\text{O}))_2$  (**2**);  $(\text{C}(\text{O})\text{CH}_2)_2$  (**3**);  $(\text{C}(\text{O})\text{CH})_2$  (**4**);  $(\text{C}(\text{O}))_2\text{CH}_2$  (**5**);  $(\text{C}(\text{O}))_2$  (**6**)) have been synthesized from reactions of  $[\text{Rh}_2\text{Co}_2(\text{CO})_{12}]$  (**7**) with the appropriate diyne compounds  $[(\text{HC}\equiv\text{CCH}_2\text{CO})_2]\text{R}$  ( $\text{R} = \text{C}_6\text{H}_4\text{-1,4}$  (**8**);  $\text{C}_6\text{H}_4\text{-1,4}(\text{C}(\text{O}))_2$  (**9**);  $(\text{C}(\text{O})\text{CH}_2)_2$  (**10**);  $(\text{C}(\text{O})\text{CH})_2$  (**11**);  $(\text{C}(\text{O}))_2\text{CH}_2$  (**12**);  $(\text{C}(\text{O}))_2$  (**13**)) in *n*-hexane at room temperature, respectively. The acetylene moieties of diyne ligands insert into the Co–Co bonds of two tetranuclear clusters to give linked octahedral clusters containing two  $[\text{Rh}_2\text{Co}_2\text{C}_2]$  units. The structure of cluster **1** was determined by single-crystal X-ray diffraction analysis and all clusters were characterized by elemental analysis (C/H), IR and <sup>1</sup>H-NMR spectroscopy.

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**Keywords:** Mixed-metal; Rhodium and cobalt; Linked cluster; Diyne ligand; Crystal structures

## 1. Introduction

Constructing higher nuclearity clusters with well-defined dimensions and structures provides a rather active field of chemistry with potential applications in areas including nanotechnology, molecular recognition, and catalysis [1–7]. The linked clusters have been receiving considerable attention in recent years because of their potential application as polymeric materials and their unusual structures and reactions [8–10]. It is well known that alkynes are able to coordinate to transition metals in a variety of bonding modes [11] and molecules containing two acetylene groups can act as chelating ligands [12]. Some bis-cluster complexes containing two  $[\text{Co}_2(\text{CO})_6\text{C}_2]$  units have been reported previously [13–22]. Additionally, it has been shown that the tetranuclear cluster  $[\text{Rh}_2\text{Co}_2(\text{CO})_{12}]$  can react with several

alkynes to yield clusters of the type  $[\text{Rh}_2\text{Co}_2(\text{CO})_{10}(\mu_4, \eta^2\text{-R}_1\text{C}\equiv\text{CR}_2)]$  which feature a transversely bridging alkyne ligand [23–26]. Examples of related clusters involving the other elements of Groups 6 and 9 have also been reported [27–29].

However, no reactions of  $[\text{Rh}_2\text{Co}_2(\text{CO})_{12}]$  with diyne ligands were reported, to our knowledge. In order to investigate the reactivity of the Rh–Co mixed-metal cluster with functionally substituted diyne compounds and construct higher nuclearity linked clusters, herein, we report the synthesis and characterization of the novel Rh–Co mixed-metal linked octahedral clusters  $[\text{Rh}_2\text{Co}_2(\text{CO})_8(\mu\text{-CO})_2(\mu_4, \eta^2\text{-HC}\equiv\text{CCH}_2\text{O-})_2]\text{R}$  ( $\text{R} = \text{C}_6\text{H}_4\text{-1,4}$  (**1**);  $\text{C}_6\text{H}_4\text{-1,4}(\text{C}(\text{O}))_2$  (**2**);  $(\text{C}(\text{O})\text{CH}_2)_2$  (**3**);  $(\text{C}(\text{O})\text{CH})_2$  (**4**);  $(\text{C}(\text{O}))_2\text{CH}_2$  (**5**);  $(\text{C}(\text{O}))_2$  (**6**)) obtained by the reactions of  $[\text{Rh}_2\text{Co}_2(\text{CO})_{12}]$  (**7**) with six diyne compounds in hexane at room temperature. To confirm the structures of the linked cluster products, the structure of cluster **1** was also determined by the single-crystal X-ray diffraction analysis.

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## 2. Experimental

### 2.1. General details

All preparative work was carried out under an atmosphere of pure nitrogen by using standard Schlenk or vacuum-line techniques. Solvents were carefully dried: *n*-hexane and petroleum ether (60–90 °C) were dried and deoxygenated by distillation from sodium benzo-phenone ketyl, and CH<sub>2</sub>Cl<sub>2</sub> was distilled from calcium hydride. Chromatographic separations were carried out using silica gel columns (160–200 mesh) of varying length. Thin-layer chromatography (TLC) was performed on commercial Merck plates coated with a 0.20 mm layer of silica gel.

Infrared (IR) spectra were recorded in NaCl cells on a Bruker 120 HR FTIR spectrophotometer. Absorptions are designated in cm<sup>-1</sup> relative to an internal laser standard. Spectra of compounds in the solid state were recorded as pressed KBr discs. <sup>1</sup>H-NMR spectra were measured on a Bruker AM-400 MHz spectrometer in chloroform-*d*<sub>1</sub> solvent and chemical shifts are given on the δ scale relative to tetramethylsilane (0.0 ppm). Elemental analyzes (C, H) were performed on a Carlo-Erba 1106 type analyzer.

[Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>12</sub>] [30], [(HC≡CCH<sub>2</sub>CO)-]<sub>2</sub>R [R = C<sub>6</sub>H<sub>4</sub>-1,4; C<sub>6</sub>H<sub>4</sub>-1,4(C(O))<sub>2</sub>; (C(O)CH<sub>2</sub>)<sub>2</sub>; (C(O)CH)<sub>2</sub>; (C(O))<sub>2</sub>CH<sub>2</sub>; (C(O))<sub>2</sub>] [31] were prepared according to literature methods.

### 2.2. Synthesis of cluster 1

To a solution of [Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>12</sub>] (7) (198 mg, 0.3 mmol) in 20 ml of hexane at room temperature (r.t.) was added dropwise a solution of [(HC≡CCH<sub>2</sub>CO)-]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-1,4 (8) (28 mg, 0.15 mmol) in 10 ml of *n*-hexane under nitrogen. The mixture was stirred at r.t. for 3 h. During the stirring the color of the solution gradually changed from reddish brown to purple and monitoring by TLC showed the disappearance of the starting material. After hexane was removed, the residue was extracted by a small amount of CH<sub>2</sub>Cl<sub>2</sub> and transferred to the top of a 2.5 cm × 40 cm silica gel chromatography column. Elution with CH<sub>2</sub>Cl<sub>2</sub>-petroleum ether (1:1) afforded the major purple band. Condensing the solvent and crystallization at -20 °C gave dark purple crystals [[Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>10</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>CH<sub>2</sub>O-)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-1,4 (1) (176 mg, 84%, based on 7). Anal. Found: C, 27.51; H, 0.70. Calc. for [C<sub>16</sub>H<sub>5</sub>O<sub>11</sub>Co<sub>2</sub>Rh<sub>2</sub>]<sub>2</sub>: C, 27.58; H, 0.72%. IR (cm<sup>-1</sup>): ν (CO) 2097m, 2047vs, 2026s, 2018vs, 1981s, 1869s, 1856m. <sup>1</sup>H-NMR: δ 8.86 (s, 1H, ≡CH), 8.32 (s, 1H, ≡CH), 6.82 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 4.31 (s, 4H, 2OCH<sub>2</sub>).

The preparation procedures for cluster complexes 2–6 were similar to 1.

[[Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>10</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>CH<sub>2</sub>O-)]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-1,4(C(O))<sub>2</sub> (2) (178 mg, 82%, based on 7). Anal. Found:

C, 28.11; H, 0.88. Calc. for [C<sub>34</sub>H<sub>10</sub>O<sub>24</sub>Co<sub>4</sub>Rh<sub>4</sub>]: C, 28.17; H, 0.70%. IR (cm<sup>-1</sup>): ν (CO) 2099m, 2034vs, 2013vs, 1990s, 1877s; ν (C=O) 1715m. <sup>1</sup>H-NMR: δ 8.94 (s, 1H, ≡CH), 8.31 (s, 1H, ≡CH), 8.18 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 4.94 (s, 4H, 2OCH<sub>2</sub>).

[[Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>10</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>CH<sub>2</sub>O-)]<sub>2</sub>(C(O)CH<sub>2</sub>)<sub>2</sub> (3) (174 mg, 83%, based on 7). Anal. Found: C, 25.62; H, 0.77. Calc. for [C<sub>30</sub>H<sub>10</sub>O<sub>24</sub>Co<sub>4</sub>Rh<sub>4</sub>]: C, 25.71; H, 0.72%. IR (cm<sup>-1</sup>): ν (CO) 2099m, 2067s, 2030vs, 1999vs, 1872s; ν (C=O) 1728m. <sup>1</sup>H-NMR: δ 8.85 (s, 2H, 2≡CH), 4.63 (s, 4H, 2OCH<sub>2</sub>), 2.69 (s, 4H, 2CH<sub>2</sub>).

[[Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>10</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>CH<sub>2</sub>O-)]<sub>2</sub>(C(O)CH)<sub>2</sub> (4) (166 mg, 79%, based on 7). Anal. Found: C, 25.59; H, 0.64. Calc. for [C<sub>30</sub>H<sub>8</sub>O<sub>24</sub>Co<sub>4</sub>Rh<sub>4</sub>]: C, 25.74; H, 0.58%. IR (cm<sup>-1</sup>): ν (CO) 2101m, 2075s, 2061s, 2024vs, 1877s; ν (C=O) 1726m. <sup>1</sup>H-NMR: δ 8.88 (s, 1H, ≡CH), 8.31 (s, 1H, ≡CH), 6.36 (s, 2H, 2 = CH), 4.72 (s, 4H, 2OCH<sub>2</sub>).

[[Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>10</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>CH<sub>2</sub>O-)]<sub>2</sub>(C(O))<sub>2</sub>CH<sub>2</sub> (5) (158 mg, 76%, based on 7). Anal. Found: C, 25.35; H, 0.71. Calc. for [C<sub>29</sub>H<sub>8</sub>O<sub>24</sub>Co<sub>4</sub>Rh<sub>4</sub>]: C, 25.10; H, 0.58%. IR (cm<sup>-1</sup>): ν (CO) 2098m, 2057s, 2044s, 2032s, 1873m; ν (C=O) 1736m. <sup>1</sup>H-NMR: δ 8.84 (s, 1H, ≡CH), 8.28 (s, 1H, ≡CH), 4.75 (s, 4H, 2OCH<sub>2</sub>), 3.49 (s, 2H, CH<sub>2</sub>).

[[Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>10</sub>(μ<sub>4</sub>,η<sup>2</sup>-HC<sub>2</sub>CH<sub>2</sub>O-)]<sub>2</sub>(C(O))<sub>2</sub> (6) (162 mg, 79%, based on 7). Anal. Found: C, 24.41; H, 0.52. Calc. for [C<sub>28</sub>H<sub>6</sub>O<sub>24</sub>Co<sub>4</sub>Rh<sub>4</sub>]: C, 24.48; H, 0.44%. IR (cm<sup>-1</sup>): ν (CO) 2101m, 2058vs, 2042vs, 2021vs, 1996s, 1876m, 1863m; ν (C=O) 1764m. <sup>1</sup>H-NMR: δ 8.86 (s, 1H, ≡CH), 8.29 (s, 1H, ≡CH), 4.84 (s, 4H, 2OCH<sub>2</sub>).

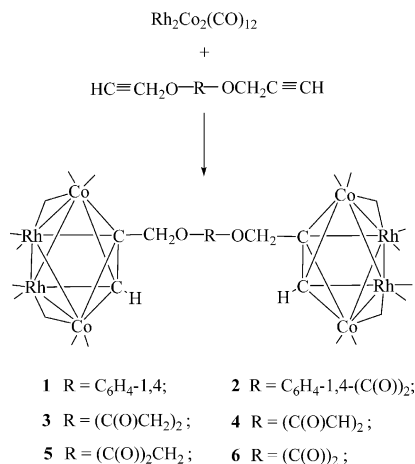
### 2.3. Crystal data of cluster 1

Suitable crystals of cluster 1 were obtained from *n*-hexane-CH<sub>2</sub>Cl<sub>2</sub> at -20 °C. The crystals were mounted on a glass fiber. Preliminary examination and data collection were performed with Mo-K<sub>α</sub> radiation (λ = 0.71073 Å) on a Bruker CCD APEX diffractometer equipped with graphite monochromator for 1. The empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and expanded using Fourier techniques and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F<sup>2</sup> using the SHELXL-97 crystallographic program package. Hydrogen atoms were added according to geometrical method.

## 3. Results and discussion

### 3.1. Synthesis of 1–6

The reactions described in this work are summarized in Scheme 1. Our previous work has shown that [Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>12</sub>] is prone to open its cluster framework to give a butterfly structure in the presence of 1-alkynes [26]. In order to further investigate the reactivity of the



Scheme 1.

Rh–Co mixed-metal cluster with diynes and construct higher nuclearity linked clusters, we treated the cluster  $[\text{Rh}_2\text{Co}_2(\text{CO})_{12}]$  in *n*-hexane with functionally substituted diyne compounds  $[(\text{HC}\equiv\text{CCH}_2\text{CO})\text{-}]_2\text{R}$  (R = C<sub>6</sub>H<sub>4</sub>-1,4; C<sub>6</sub>H<sub>4</sub>-1,4(C(O))<sub>2</sub>; (C(O)CH<sub>2</sub>)<sub>2</sub>; (C(O)CH)<sub>2</sub>; (C(O))<sub>2</sub>CH<sub>2</sub>; (C(O))<sub>2</sub>) in 2:1 molar ratio at room temperature and obtained six new alkyne-bridged linked octahedral cluster derivatives  $[\text{Rh}_2\text{Co}_2(\text{CO})_8(\mu\text{-CO})_2(\mu_4, \eta^2\text{-HC}\equiv\text{CCH}_2\text{O})\text{-}]_2\text{R}$  (R = C<sub>6</sub>H<sub>4</sub>-1,4 (**1**); C<sub>6</sub>H<sub>4</sub>-1,4(C(O))<sub>2</sub> (**2**); (C(O)CH<sub>2</sub>)<sub>2</sub> (**3**); (C(O)CH)<sub>2</sub> (**4**); (C(O))<sub>2</sub>CH<sub>2</sub> (**5**); (C(O))<sub>2</sub> (**6**)) as the major products, respectively. The tetranuclear Rh–Co cluster reacts readily with these diyne ligands under the conditions. During the capping reactions, the color of solution changed from reddish brown to purple and higher yields are obtained.

These new linked cluster complexes **1–6** are sensitive to tetrahydrofuran and light sensitive in air in solid state, and soluble in other common organic solvents. This behavior is similar to their precursor cluster  $[\text{Rh}_2\text{Co}_2(\text{CO})_{12}]$  [30].

### 3.2. Characterization of **1–6**

The IR spectra of all clusters resemble each other and show a large number of strong terminal carbonyl absorption bands located in the range 2101–1981 cm<sup>-1</sup>. It is similar to that described previously [26], i.e. the absorption of carbonyl ligands coordinated to Co atoms occurs at higher wave numbers than those coordinated to Rh atoms in the IR spectra of **1–6**. Absorption bands of the bridging carbonyls of **1–6** were found between 1877 and 1856 cm<sup>-1</sup>. In the IR spectra of **2–6**, besides the terminal and bridged carbonyl absorption bands, there are absorption bands at 1764–1715 cm<sup>-1</sup>, which are characteristic of ester carbonyl.

The <sup>1</sup>H-NMR spectra of all of clusters **1–6** are consistent with the functionally substituted diyne-bridged butterfly structure and show the presence of

hydrogen atoms in their corresponding organic groups. The singlets at about  $\delta$  8.94–8.28 are caused by the protons of acetylenic hydrogens in the <sup>1</sup>H-NMR spectra of **1–6**. This noteworthy down-field shift of the acetylenic hydrogen is characteristic of the hydrogen atoms bound to carbons interacting either  $\sigma$  or  $\pi$  with metals and similar to that of monobutterfly Rh–Co 1-alkyne-bridged clusters reported by us [26]. For the protons of methylene (CH<sub>2</sub>) bonded to ether or ester group, the <sup>1</sup>H-NMR spectra of **1–6** exhibit a singlet in the range  $\delta$  4.94–4.31, respectively. In the <sup>1</sup>H-NMR spectrum of cluster **1**, the broad singlet at  $\delta$  6.82 is assigned to the protons of the phenyl ring. However, comparing the <sup>1</sup>H-NMR spectrum of **2** with that of **1**, it can be seen that the signal of the protons of the phenyl rings shifts from  $\delta$  6.82 to the lower-field  $\delta$  8.18, which may be caused by the higher deshielding effect of the ester alkyl group (–COOR) than that of the ether group (–COR). For the clusters **3** and **5**, besides the characteristic shifts of acetylenic hydrogen atoms and the singlets of methylene (CH<sub>2</sub>) bonded to ether group, the singlets at  $\delta$  3.49 and 2.69 reveal the presence of the protons of the methylene (CH<sub>2</sub>) connected to the ester alkyl group (–COOR). In addition, the singlet at  $\delta$  6.36 also reveals the presence of the protons of the alkene moiety in the <sup>1</sup>H-NMR spectrum of cluster **4**.

Table 1  
Crystal and refinement data for the cluster **1**

Empirical formula	C <sub>32</sub> H <sub>10</sub> O <sub>22</sub> Co <sub>4</sub> Rh <sub>4</sub>
Formula weight	1393.76
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>F</i> (000)	666
Unit cell dimensions	
<i>a</i> (Å)	8.8533(13)
<i>b</i> (Å)	8.8641(13)
<i>c</i> (Å)	13.858(2)
$\alpha$ (°)	92.976(3)
$\beta$ (°)	108.512(3)
$\gamma$ (°)	92.473(2)
<i>V</i> (Å <sup>3</sup> )	1027.8(3)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.252
Absorption coefficient (mm <sup>-1</sup> )	3.219
Radiation (Mo–K $\alpha$ ) (Å)	0.71073
Temperature (°C)	20
Scan type	$\phi$ – $\omega$
$\theta$ <sub>max</sub> (°)	28.34
Number of observations [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	3492
Number of variables	288
<i>R</i> <sup>a</sup>	0.0519
<i>R</i> <sub>w</sub> <sup>b</sup>	0.1485
Largest difference peak and hole (e Å <sup>-3</sup> )	1.642 and –1.602

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ .

<sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ .

Table 2  
Selected bond lengths (Å) and angles (°) for cluster **1**

Bond lengths					
Rh(1)–C(12)	2.096(7)	Rh(1)–Co(2)	2.5610(11)	Co(1)–C(11)	2.105(7)
Rh(1)–Co(1)	2.5696(11)	Rh(1)–Rh(2)	2.6570(9)	Co(2)–C(12)	2.132(7)
Rh(2)–C(11)	2.083(7)	Rh(2)–Co(2)	2.5413(12)	Co(2)–C(11)	2.049(7)
Rh(2)–Co(1)	2.5526(11)	Co(1)–C(12)	2.075(6)	Co(2)–C(10)	1.846(8)
Rh(2)–C(10)	2.109(8)	Co(1)–C(9)	1.867(8)	Rh(1)–C(9)	2.128(7)
C(14)–C(16)#1	1.389(10)	C(16)–C(14)#1	1.389(10)	C(11)–C(12)	1.410(10)
Bond angles					
C(12)–Rh(1)–Co(2)	53.36(19)	C(12)–Rh(1)–Co(1)	51.60(18)	C(11)–Co(1)–Rh(2)	52.1(2)
Co(2)–Rh(1)–Co(1)	89.75(4)	C(12)–Rh(1)–Rh(2)	72.97(18)	Rh(2)–Co(1)–Rh(1)	62.49(3)
Co(2)–Rh(1)–Rh(2)	58.25(3)	Co(1)–Rh(1)–Rh(2)	58.44(3)	C(11)–Co(2)–Rh(2)	52.7(2)
C(11)–Rh(2)–Co(2)	51.46(19)	C(11)–Rh(2)–Co(1)	52.85(19)	Rh(2)–Co(2)–Rh(1)	62.76(3)
C(11)–Rh(2)–Rh(1)	72.3(2)	Co(2)–Rh(2)–Rh(1)	58.98(3)	C(11)–C(12)–Rh(1)	106.2(4)
Co(1)–Rh(2)–Rh(1)	59.07(3)	C(11)–Co(1)–C(12)	39.4(3)	C(12)–Co(2)–Rh(1)	52.09(19)
C(11)–Co(2)–C(12)	39.4(3)	C(12)–Co(1)–Rh(1)	52.34(19)	C(12)–C(11)–Rh(2)	108.5(5)
C(14)#1–C(16)–H(16)	120.0	C(14)#1–C(16)–C(15)	120.0(7)	O(11)–C(14)–C(16)#1	124.2(7)
C(15)–C(14)–C(16)#1	120.1(7)	C(12)–Rh(1)–Rh(2)–C(11)	–1.8(3)		

Symmetry transformations used to generate equivalent atoms: #1  $-x, -y+1, -z+2$ .

### 3.3. Crystal structure of **1**

The crystal structure of **1** was determined by X-ray structural analyzes. Crystal data and experimental details for **1** are collected in Table 1. Table 2 gives the selected bond lengths and angles. An ORTEP drawing of **1** with numbering is shown in Fig. 1.

As seen in Fig. 1, the acetylene bridges insert into the Co–Co bonds of two tetrahedral Rh<sub>2</sub>Co<sub>2</sub> cores and coordinate to all metal atoms as a  $\mu_4 \eta^2$ -ligand forming two distorted *closo*-Rh<sub>2</sub>Co<sub>2</sub>C<sub>2</sub> octahedral frameworks which are connected via [C<sub>6</sub>H<sub>4</sub>(OCH<sub>2</sub>)<sub>2</sub>-1,4] as a bridging unit. In the octahedral Rh(1)Rh(2)Co(1)–Co(2)C(11)C(12) core, the cobalt atoms occupy the wing-tip positions of the butterfly metal skeleton and the nonbonding distance between the two cobalt atoms Co(1) and Co(2) is 3.611 Å. The acetylene moiety is coordinated to the concave side such that the C(11)–C(12) bond is nearly parallel to the hinge of the butterfly

resulting from the sum (180.8°) of the bond angles Rh(1)–Rh(2)–C(11) and Rh(2)–C(11)–C(12). The Rh(1) atom is bonded to C(12) and Rh(2) is bonded to C(11) of the acetylenic moiety. The Rh(1)–C(12) and Rh(2)–C(11) belong to two  $\sigma$ -bonds and there is a delocalized four-center  $\pi$ -bonding system between Co(1), Co(2), C(11) and C(12). Each metal atom is linked to two linear terminal carbonyl and one bridged carbonyl ligands. The two bridged carbonyl ligands ( $\mu$ -C(9)O(9),  $\mu$ -C(10)O(10)) are about the same, due to the asymmetric parameter  $\alpha = (d_2 - d_1)/d_1 = 0.140, 0.142$ , respectively [32].

It is noticeable that the C(11)–C(12) bond length (1.410(10) Å) has double-bond character and is longer than the reported C–C distance for [Rh<sub>2</sub>Co<sub>2</sub>(CO)<sub>10</sub>-( $\mu_4 \eta^2$ -F<sub>5</sub>C<sub>6</sub>C $\equiv$ CCF<sub>5</sub>)] (1.369(2) Å) [24a]. This reveals that the diyne ligand [(HC $\equiv$ CCH<sub>2</sub>CO)-]<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-1,4] has a stronger interaction with the butterfly cluster than that of the alkyne ligand with electron-drawing groups [F<sub>5</sub>C<sub>6</sub>C $\equiv$ CCF<sub>5</sub>].

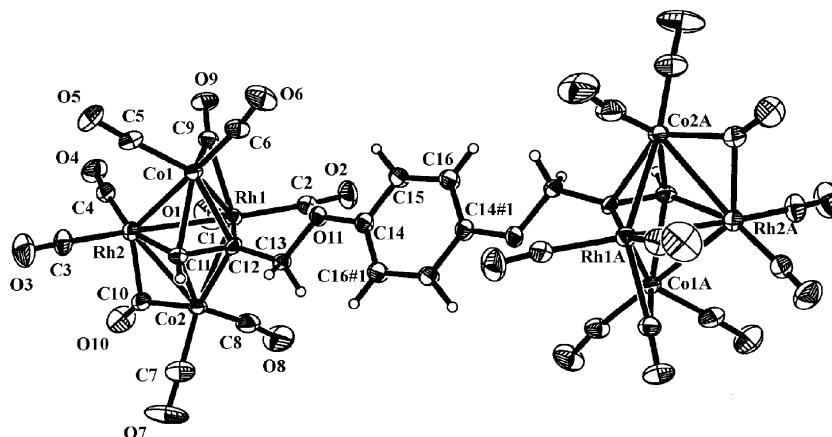


Fig. 1. Crystal structure of the cluster **1**. Thermal ellipsoids are drawn at the 30% probability level.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 193609 for cluster **1**. 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 or www: <http://www.ccdc.cam.ac.uk>).

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