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Journal of Organometallic Chemistry 650 (2002) 181–187

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis, characterization of new Rh–Co mixed-metal clusters and reactions of clusters containing [$Rh_2Co_2C_2$] core with 1-alkynes and/or carbon monoxide

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Received 9 November 2001; received in revised form 28 January 2002; accepted 29 January 2002

Abstract

Six new cluster derivatives [$Rh_2Co_2(CO)_6(\mu\text{-}CO)_4(\mu_4,\eta^2\text{-}HC{\equiv}CR)$] ($R = FeCp_2$ **1**, CH_2OH **2**, $(CH_3O)C_{10}H_6CH(CH_3)COOCH_2C{\equiv}CH$ **3**) and [$RhCo_3(CO)_6(\mu\text{-}CO)_4(\mu_4,\eta^2\text{-}HC{\equiv}CR)$] ($R = FeCp_2$ **4**, CH_2OH **5**, $(CH_3O)C_{10}H_6CH(CH_3)COOCH_2C{\equiv}CH$ **6**) were obtained by the reactions of [$Rh_2Co_2(CO)_{12}$] and [$RhCo_3(CO)_{12}$] with substituted 1-alkyne ligands $HC{\equiv}CR$ [$R = FeCp_2$ **7**, CH_2OH **8**, $(CH_3O)C_{10}H_6CH(CH_3)$ $COOCH_2C{\equiv}CH$ **9**] in *n*-hexane at room temperature, respectively. Alkynes insert into the Co–Co bond of the tetranuclear clusters to give butterfly clusters. [$Rh_2Co_2(CO)_6(\mu\text{-}CO)_4(\mu_4,\eta^2\text{-}HC{\equiv}CFeCp_2)$] (**1**) was characterized by a single-crystal X-ray diffraction analysis. Reactions of **1**, **2** with **7**, **8** and ambient pressure of carbon monoxide at 25 °C gave two known cluster complexes [$Co_2(CO)_6(\mu_2, \eta^2\text{-}HC{\equiv}CR)$] ($R = FeCp_2$ **10**, CH_2OH **11**), respectively. All clusters were characterized by element analysis, IR and ^1H-NMR spectroscopy. © 2002 Published by Elsevier Science B.V.

Keywords: Functionally substituted 1-alkynes; Mixed-metal; Cluster complexes; Crystal structure

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1. Introduction

Mixed-transition-metal clusters have recently attracted a great deal of attention since the mid-70s, due to their high potential to serve as efficient catalysts for a variety of homogeneous catalytic reactions [1]. The reactions of mixed-metal clusters with alkynes can result in either substitution or degradation of the cluster to lower nuclearity complexes [2]. Further it is well known that the coordination of an organic molecule to metal center increases the stability of the whole system and makes the coordinated substrate active towards specific reactions that may not be possible through classical organic procedures [3]. It has been reported that the reactions of [$Rh_2Co_2(CO)_{12}$] with several alkynes gives Rh–Co mixed-metal butterfly complexes [1b,4–6], and the reaction of silylformylation of 1-hexyne is catalyzed by [$Rh_2Co_2(CO)_{12}$] [7]. In addition, it has also been shown that [$Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}RC{\equiv}CR)$] ($R = C_6F_6$, Ph) react with carbon monoxide to give clusters of [$RhCo(CO)_6(\mu, \eta^2\text{-}RC{\equiv}CR)$] ($R = C_6F_6$, Ph) and [$CoRh(CO)_7$] [4], and identified that [$CoRh(CO)_7$] acts as an active catalytic species in the hydroformylation–amidocarbonylation of pentafluorostyrene catalyzed by mixed-metal systems of cobalt and rhodium [8].

However, the reactions of [$Rh_nCo_{4-n}(CO)_{12}$] ($n = 1$, 2) with functionally substituted alkynes containing ferrocenyl, hydroxyl and ester alkyl group were still not investigated in the literature [1b,4–6]. To gain more understanding about the cobalt and rhodium mixed-metal clusters, explore the reactions of [Rh_n-$Co_{4-n}(CO)_{12}$] ($n = 1$, 2) with functionally substituted alkynes and their derivatives with alkynes and/or carbon monoxide, in this paper we report the synthesis and characterization of six new Rh–Co mixed-meal butterfly clusters [$Rh_nCo_{4-n}(CO)_6(\mu\text{-}CO)_4(\mu_4,\eta^2\text{-}HC{\equiv}CR)$] ($n = 2$, $R = FeCp_2$ **1**, CH_2OH **2**, $(CH_3O)C_{10}H_6CH(CH_3)COOCH_2C{\equiv}CH$ **3**; $n = 1$, $R = FeCp_2$ **4**,

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0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(02)01219-6

CH_2OH **5**, $(CH_3O)C_{10}H_6CH(CH_3)COOCH_2C{\equiv}CH$ **6**) and two known bimetallic alkyne-bridged cobalt clusters $[Co_2(CO)_6(\mu_2, \eta^2\text{-}HC{\equiv}CR)]$ ($R = FeCp_2$ **10**, CH_2OH **11**) [12,13] by the reactions of **1** and **2** with 1-alkynes $HC{\equiv}CR$ ($R = FeCp_2$ **7**, CH_2OH **8**) and/or CO, respectively. The crystal structure of cluster **1** was determined by X-ray diffraction.

2. Experimental

2.1. General details

All preparative work was carried out under an atmosphere of pure nitrogen by using standard techniques. Solvents were carefully dried; *n*-hexane and petroleum ether (60–90 °C) were dried and deoxygenated by distillation from sodium benzophenone ketyl, and dichloromethane 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 spectra were recorded in NaCl cells on a Nicolet FTIR 10DX spectrophotometer. Absorptions are designated in cm^{-1} relative to an internal laser standard. Spectra of compounds in the solid state were recorded as pressed KBr discs. ^1H-NMR spectra were measured on a Brucker AM-400 MHz spectrometer in chloroform-d_1 solvent and chemical shifts are given on the δ scale relative to tetramethylsilane (0.0 ppm). Elemental analyses were performed on a Carlo–Erba 1106 type analyzer.

$Rh_2Co_2(CO)_{12}$ [9], $RhCo_3(CO)_{12}$ [9a], ferrocenylacetylene [$HC{\equiv}CFeCp_2$ ($Cp = C_5H_5$)] [10], (S)-(2-Propinyl)-2-(6-methoxy-2-naphthyl)-propionate [$(CH_3O)C_{10}H_6CH(CH_3)COOCH_2C{\equiv}CH$] [11] were prepared according to literature methods and $HC{\equiv}CCH_2OH$ was commercial sample.

2.2. Synthesis of compound 1

To a solution of $Rh_2Co_2(CO)_{12}$ (99 mg, 0.15 mmol) in 20 ml of *n*-hexane at room temperature (r.t.) was added dropwise a solution of **7** (42 mg, 0.2 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 brown to violet. After *n*-hexane was removed, the residue was extracted by a small amount of CH_2Cl_2 and transferred to the top of a 2.5 × 40 cm silica gel chromatography column. Elution with CH_2Cl_2–petroleum ether (1:8) afforded the major purple band. Condensing the solvent and crystallization at −20 °C gave dark purple crystals **1** (96 mg, 78.6%). Crystals suitable for single crystal X-ray analysis were grown from *n*-hexane at −20 °C. Anal. Found: C, 32.41; H, 1.29. Calc. for $[C_{22}H_{10}Co_2FeO_{10}Rh_2]$: C, 32.47; H, 1.24%. IR (cm^{-1}): ν (CO) 2095m, 2056s, 2030vs, 1993s, 1976m, 1888w, 1872s, 1852m. ^1H-NMR: δ 8.56 (s, 1H, ≡CH), 7.94 (s, 1H, ≡CH), 4.29–4.18 (d, 4H, C_5H_4), 3.99 (s, 5H, C_5H_5).

2.3. Synthesis of compound 2

$Rh_2Co_2(CO)_{12}$ (99 mg, 0.15mmol) reacted with **8** (11.2 mg, 0.2 mmol) in 30 ml *n*-hexane at r.t. for 2.5 h with stirring. Removal of the solvent under reduced pressure and the residue was purified by chromatography on silica gel using CH_2Cl_2–petroleum ether (3:1) as an eluent and gave the orange needle shaped crystals **2** (81 mg, 81.8%) which crystallized from a 1:1 mixture of CH_2Cl_2–*n*-hexane at −20 °C. Anal. Found: C, 23.61; H, 0.58. Calc. for $[C_{13}H_4Co_2O_{11}Rh_2]$: C, 23.66; H, 0.61%. IR (cm^{-1}): ν (CO) 2099m, 2059s, 2037vs, 1995s, 1976ms, 1895m, 1868m. ^1H-NMR: δ 8.86 (s, 1H, ≡CH), 8.31 (s, 1H, ≡CH), 4.09 (s, 2H, CH_2).

2.4. Synthesis of compound 3

In the same manner, $Rh_2Co_2(CO)_{12}$ (99 mg, 0.15 mmol) reacted with **9** (53.6 mg, 0.2 mmol) in 30 ml *n*-hexane at r.t. for 3.5 h with stirring. Removal of the solvent under vacuum and the residue was purified by chromatography on silica gel using CH_2Cl_2–petroleum ether (2:1) as an eluent and gave the purple product **3** (87 mg, 66.5%) which crystallized from a 1:1 mixture of CH_2Cl_2–*n*-hexane at −20 °C. Anal. Found: C, 37.24; H, 1.79. Calc. for $[C_{27}H_{16}Co_2O_{13}Rh_2]$: C, 37.18; H, 1.85%. IR (cm^{-1}): ν (CO) 2099m, 2068s, 2027vs, 1976m, 1877m; ν (C=O) 1736m. ^1H-NMR: δ 8.36 (s, 1H, ≡CH), 7.66 (s, 6H, $C_{10}H_6$), 4.61 (s, 2H, CH_2), 3.89 (s, br, 4H, OCH_3, CH), 1.54 (s, br, 3H, CH_3).

2.5. Synthesis of compound 4

To a solution of $RhCo_3(CO)_{12}$ (92 mg, 0.15 mmol) in 30 ml of *n*-hexane at r.t. was added **7** (42 mg, 0.2 mmol) under nitrogen. The mixture was stirred at r.t. for 3 h. During the stirring, the color of the solution gradually changed from brown to purple. Removal of the solvent and the residue was extracted by CH_2Cl_2 and transferred to the silica gel chromatography column. Elution with CH_2Cl_2–petroleum ether (1:8) gave the major purple band. Condensing the solvent and crystallization at −20 °C gave dark purple crystals **4** (93 mg, 80.5%). Anal. Found: C, 34.27; H, 1.24. Calc. for $[C_{22}H_{10}Co_3FeO_{10}Rh]$: C, 34.32; H, 1.31%. IR (cm^{-1}): ν (CO) 2096m, 2058s, 2028vs, 1993s, 1872m. ^1H-NMR: δ 8.58 (s, w, 1H, ≡CH), 4.18 (s, br, 9H, C_5H_5, C_5H_4).

2.6. Synthesis of compound **5**

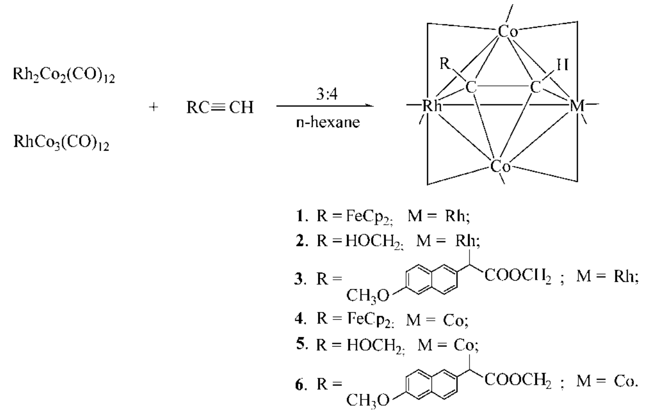
The preparation procedure for **5** was similar to **4**. $RhCo_3(CO)_{12}$ (92 mg, 0.15 mmol) reacted with **8** (11.2 mg, 0.2 mmol) in 30 ml *n*-hexane at r.t. for 2.5 h with stirring. Removal of the solvent under reduced pressure and the residue was purified by chromatography on silica gel using CH_2Cl_2–petroleum ether (3:1) as an eluent and gave the purple **5** (71 mg, 76.8%) which recrystallized from *n*-hexane at −20 °C. Anal. Found: C, 25.26; H, 0.71. Calc. for $[C_{13}H_4Co_3O_{11}Rh]$: C, 25.35; H, 0.65%. IR (cm^{-1}): ν (CO) 2097m, 2055s, 2030vs, 1876m. ^1H-NMR: δ 8.77 (s, 1H, ≡CH), 8.23 (s, 1H, ≡CH), 4.01 (s, 2H, CH_2).

2.7. Synthesis of compound **6**

$RhCo_3(CO)_{12}$ (92 mg, 0.15mmol) reacted with **9** (53.6 mg, 0.2 mmol) in 30 ml *n*-hexane at r.t. for 3 h with stirring. Removal of the solvent under vacuum and the residue was purified by chromatography on silica gel using CH_2Cl_2–petroleum ether (5:3) as an eluent and gave the purple product **6** (78 mg, 62.8%) which crystallized from a 1:1 mixture of CH_2Cl_2–*n*-hexane at −20 °C. Anal. Found: C, 39.04; H, 1.82. Calc. For $[C_{27}H_{16}Co_3O_{13}Rh]$: C, 39.16; H, 1.95%. IR (cm^{-1}): ν (CO) 2098m, 2060s, 2034vs, 1992s, 1872s; ν (C=O) 1735m. ^1H-NMR: δ 8.34 (s, 1H, ≡CH), 8.04 (s, 1H, ≡CH), 7.66–7.04 (m, 6H, $C_{10}H_6$), 4.56 (s, 2H, CH_2), 3.83 (s, br, 4H, OCH_3, CH), 1.52 (s, br, 3H, CH_3).

2.8. Reaction of **1** with **7** and carbon monoxide

Compound **7** (21 mg, 0.1 mmol) was added to a solution of **1** (81 mg, 0.1 mmol) in 25 ml of *n*-hexane at 25 °C and 5 bar of carbon monoxide for 4 h with stirring. The color of the solution changed from purple to dark green. Removal of the solvent under reduced pressure, and then the residue was separated on a silica gel column. Petroleum ether as an eluent and the major dark green product **10** [12] was obtained (21 mg, 84.7%) which crystallized from *n*-hexane at −20 °C. Anal. Found: C, 43.41; H, 2.08. Calc. for $[C_{18}H_{10}Co_2FeO_6]$: C, 43.59; H, 2.03%. IR (cm^{-1}): ν (CO) 2087s, 2049s, 2020vs, 1999s. ^1H-NMR: δ 6.29 (s, 1H, ≡CH), 4.35 (d, 4H, C_5H_4), 4.16 (s, 5H, C_5H_5).



Scheme 1.

2.9. Reaction of **2** with **8** and carbon monoxide

Compound **8** (11.2 mg, 0.2 mmol) was added to a solution of **2** (132 mg, 0.2 mmol) in 25 ml of *n*-hexane at 25 °C and 5 bar of carbon monoxide for 6 h with stirring. The color of the solution changed from purple to orange. The solvent was condensed under vacuum and the residue was separated on a silica gel column. Using CH_2Cl_2–petroleum ether (6:1) as an eluent to give the main orange product **11** [13] (27 mg, 78.9%), which recrystallized from *n*-hexane at −20 °C. Anal. Found: C, 31.49; H, 1.23. Calc. for $[C_9H_4Co_2O_6]$: C, 31.61; H, 1.18%. IR (cm^{-1}): ν (OH) 3275w and ν (CO) 2097m, 2062s, 2050s, 2026vs. ^1H-NMR: δ 6.04 (s, 1H, ≡CH), 4.74–4.68 (d, 2H, CH_2).

2.10. Reaction of **1** and **2** with carbon monoxide

Procedures for the reaction were similar to that described above. Compounds **1** (122 mg, 0.15 mmol) and **2** (132 mg, 0.2 mmol) were dissolved in 25 ml of *n*-hexane at 25 °C and 5 bar of carbon monoxide for 4 and 6 h with stirring, and then the major products **10** and **11** were obtained, respectively.

2.11. X-ray structure characterization of cluster **1**

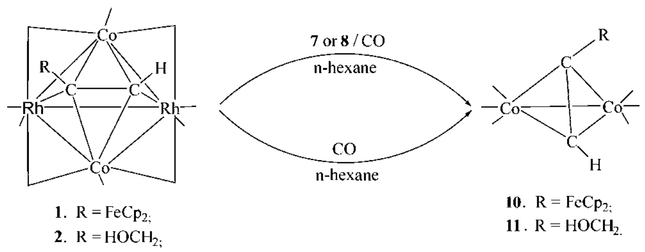
Suitable crystals of cluster **1** were obtained from *n*-hexane at −20 °C. The crystals were mounted on a glass fiber. Preliminary examination and data collection were performed with Mo–K_α radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD-4 diffractometer equipped with graphite monochromator for **1**.

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined by the full-matrix least-squares method anisotropically and hydrogen atoms were refined isotropically. The calculations were performed using the SHELXTL-97 crystallographic software package.

3. Results and discussion

3.1. Synthesis of **1**–**6**

The reactions described in this work are summarized in Scheme 1. It has been shown that tetranuclear clusters are prone to open their cluster framework to give a



Scheme 2.

butterfly structure in the presence of alkynes [1b,4–6,14]. In order to further investigate the selective cleavage of the metal–metal bonds in this system of Rh–Co mixed-metal cluster, we treated the clusters $[Rh_nCo_{4-n}(CO)_{12}]$ ($n = 1, 2$) in n-hexane with functionally substituted 1-alkynes $HC{\equiv}CR$ ($R = FeCp_2$ **7**, CH_2OH **8**, $(CH_3O)\ C_{10}H_6CH(CH_3)COOCH_2C{\equiv}CH$ **9**) in 3:4 molar ratio at r.t. and obtained five new alkyne-bridged butterfly cluster derivatives $[Rh_nCo_{4-n}(CO)_6(\mu\text{-}CO)_4(\mu_4,\eta^2\text{-}HC{\equiv}CR)]$ ($n = 2$, $R = FeCp_2$ **1**, CH_2OH **2**, $(CH_3O)C_{10}H_6CH(CH_3)COO\ CH_2C{\equiv}CH$ **3**; $n = 1$, $R = FeCp_2$ **4**, CH_2OH **5**, $(CH_3O)C_{10}H_6CH(CH_3)$-$COOCH_2C{\equiv}CH$ **6**) as the major products, respectively. The tetranuclear Rh–Co clusters $[Rh_nCo_{4-n}(CO)_{12}]$ ($n = 1, 2$) react readily with these 1-alkynes at r.t. During the inserting reactions, the color of solution changed from reddish–brown to purple and higher yields are obtained.

The new cluster complexes **1**–**6** are light sensitive in air in solid state and soluble in most organic solvents. The solubility of the six clusters in the same solvent follows as the series of **1** > **3** > **2** and **4** > **6** > **5**.

3.2. Characterization of **1**–**6**

The IR spectra of all clusters resemble each other in spite of the fact that they are coordinated by quite different 1-alkynes and show a large number of strong terminal carbonyl absorption bands located at 2099–1976 cm^{-1}. The strong absorption around 2099 cm^{-1} is characteristic of the $Co(CO)_3$ unit [15a], it is similar to that described by H.P. Wu [15b] that the absorptions of carbonyl ligands coordinated to Co atoms occur at higher wavenumbers than those coordinated to Rh atoms in the IR spectra of **1**–**6**. The absorption bands of the bridged carbonyl of **1**–**6** were shown at round 1895–1852 cm^{-1}. In the IR spectra of **3** and **6**, besides the terminal and bridged carbonyl absorption bands, there is an absorption band at 1736 and 1735 cm^{-1} characteristic of the ester carbonyl, respectively.

The ^1H-NMR spectra of all of clusters **1**–**6** are consistent with the 1-alkyne-bridged butterfly structure and show the presence of hydrogen atoms in their corresponding organic groups. The singlets at round δ 8.86–7.94 are caused by the protons of acetylenic hydrogens in the ^1H-NMR spectra of **1**–**6** and there are two singlets in this range, respectively, except for the clusters **3** and **4**. This noteworthy downfield shift of the acetylenic hydrogen is characteristic of the hydrogen atoms bound to carbons interacting either σ or π with metals [1b,16]. For the cyclopentadienyl rings of the ferrocenyl, the ^1H-NMR spectra of **1** exhibits a triplet in the range δ 4.29–3.99, comprising an upfield singlet δ 3.99 assignable to the protons of the unsubstituted cyclopentadienyl ring and the downfield doublet at round δ 4.29–4.18 assignable to the protons of the substituted cyclopentadienyl ring, whereas **4** only shows a broad singlet at δ 4.18 ppm corresponding to the protons of two cyclopentadienyl rings. In the ^1H-NMR spectra of clusters **2** and **5** besides the characteristic bands of acetylenic hydrogen atoms, the singlets at δ 4.09–4.01 reveal the presence of the protons of the methylene (CH_2) connected to the hydroxyl. For the clusters **3** and **6**, the signals at 7.66–7.04 are assigned the protons of the naphthalene ring; the singlets at δ 4.62–4.56 and 3.89–3.83 are caused by the protons of the CH_2 connected to the ester alkyl group and the protons of the OCH_3 group connected to the naphthalene ring, respectively; and the signals at δ 1.54 and 1.52 give the evidence of the protons of the methyl group. It is worthy to note that we did not observe the signal of the CH group bonded to the naphthalene ring, which perhaps was concealed by the broad protons' signal of the OCH_3 group. Comparing the ^1H-NMR spectra of **2** and **5** with that of **3** and **6**, it can be seen that the signal of the protons of the CH_2 shift from δ 4.09 to 4.01 to lower field δ 4.62 to 4.56, resulting from the higher deshielding effect of the ester alkyl group –OCOR than that of the hydroxyl group.

3.3. Reactions of **1**, **2** with **7**, **8** and/or carbon monoxide, respectively

The reactions of $[Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}RC{\equiv}CR)]$ ($R = C_6F_6$, Ph) with carbon monoxide to give clusters $[RhCo(CO)_6(\mu,\ \eta^2\text{-}RC{\equiv}CR)]$ ($R = C_6F_6$, Ph) and $[CoRh(CO)_7]$ were investigated [4]. According to this method, we hoped to obtain two chiral bimetallic tetrahedral clusters $[CoRh(CO)_6(\mu_2,\ \eta^2\text{-}HC{\equiv}CR)]$ ($R = FeCp_2$, CH_2OH) by reactions of **1** and **2** with 1-alkyne ligands $HC{\equiv}CR$ ($R = FeCp_2$ **7**, CH_2OH **8**) and/or CO in n-hexane at 25 °C, respectively. Then, we could attempt to separate their enantiomers and further explore their activities in the reaction of asymmetric catalysis that is induced by their chiral tetrahedral cluster frameworks.

Unfortunately, we did not get the expected products and only obtained two known bimetallic cobalt clusters **10** and **11** (see Scheme 2) in spite of the effort that we changed the amount of 1-alkyne ligands and the pressure of carbon monoxide from 2 to 10 bar at 25 °C.

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

Empirical formula	$C_{22}H_{10}Co_2FeO_{10}Rh_2$
Formula weight	813.83
Crystal system	Orthorhombic
Space group	$P2(1)2(1)2(1)$
$F(000)$	1568
a (Å)	11.5318(7)
b (Å)	12.6572(7)
c (Å)	17.0179(10)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	2483.9(3)
Z	4
D_{calc} (g cm^{-3})	2.176
Absorption coefficient (mm^{-1})	3.233
Radiation (Mo–K$_\alpha$) (Å)	0.71073
Temperature (°C)	20
Scan type	Φ–ω
θ_{max} (°)	28.26
Number of observations [$I > 2\sigma(I)$]	5367
Number of variables	339
Goodness-of-fit on F^2	1.030
R [a], R_w [b]	0.0366, 0.0899
Largest difference peak and hole (e Å^{-3})	0.952, −1.190

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

During the reactions, the color of the solutions changed from purple to green and orange, respectively. The evidences of element analysis, IR spectra and ^{1}H-NMR spectra have shown that the results are not consistent with I.T. Horváth's [4] and the clusters **10** and **11** are the same as that of reported by C.V. Pittman [12a] and H.W. Sternberg [13], respectively. And the characteristic downfield shifts (δ 6.29, 6.04) of the acetylenic hydrogen atoms in the ^{1}H-NMR spectra of the clusters **10** and **11** have also identified that the alkyne ligands are coordinated to metal cobalt atoms [11]. So we can assume that the heteronuclear metal–metal bond might be weaker than the homonuclear bonds in the systems of **1** and **2** under the pressure of carbon monoxide.

It should be noted that we could not get the clusters $[Rh_2(CO)_6(\mu_2, \eta^2\text{-HC}\equiv\text{CR})]$ ($R = FeCp_2$, CH_2OH) or others containing rhodium atoms. It is not clear if this is due to the unstability of this kind of binuclear rhodium carbonyl clusters, which would make them decompose readily at room temperature. Further studies concerning the mechanism of the reactions of **1** and **2** with corresponding substituted 1-alkynes and/or carbon monoxide are currently underway.

3.4. Crystal structure of **1**

The crystal structure of **1** was determined by X-ray structural analyses. Crystal data and experimental details for **1** are collected in Table 1. Selected bond lengths and angles are listed in Table 2. Fig. 1 shows the molecular structures of **1**.

As seen in Fig. 1, the metal skeleton of **1** is similar to its analogue $[Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-RC}\equiv\text{CR})]$ ($R = C_6F_6$, Ph) [4] preciously described. It has a butterfly structure, in which the cobalt atoms occupy the wingtip positions. The nonbonding distance between the two cobalt atoms Co1 and Co2 is 3.1497 Å and the dihedral angle between the wings Rh1–Rh2–Co1 and Rh1–Rh2–Co2 is 94.57°. The acetylene moiety inserts into the Co–Co bond and is coordinated to the concave side such that the C11–C12 bond is nearly parallel to the hinge of the butterfly (the sum of the bond angles Rh1–Rh2–C11 and Rh2–C11–C12 is 181.34°). It coordinates to all metal atoms as a μ_4,η^2-ligand forming a distorted *closo*-$Rh_2Co_2C_2$ octahedron framework. The Rh1 atom is bonded to C12 and Rh2 is bonded to C11 of the acetylenic moiety. According to the well-known De-

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

Bond lengths					
Rh(1)–C(12)	2.093(4)	Rh(2)–C(11)	2.090(4)	Co(1)–C(12)	2.140(4)
Rh(1)–Co(2)	2.5586(7)	Rh(2)–Co(2)	2.5301(8)	Co(2)–C(11)	2.098(5)
Rh(1)–Co(1)	2.5630(7)	Rh(2)–Co(1)	2.5372(8)	Co(2)–C(12)	2.160(5)
Rh(1)–Rh(2)	2.7524(5)	Co(1)–C(11)	2.085(5)	C(11)–C(12)	1.419(6)
Bond angles					
C(12)–Rh(1)–Co(2)	54.23(13)	C(11)–Rh(2)–Rh(1)	70.14(12)	C(11)–Co(2)–C(12)	38.90(16)
C(12)–Rh(1)–Co(1)	53.58(12)	Co(2)–Rh(2)–Rh(1)	57.757(18)	C(11)–Co(2)–Rh(2)	52.68(12)
Co(2)–Rh(1)–Co(1)	90.15(2)	Co(1)–Rh(2)–Rh(1)	57.792(18)	C(12)–Co(2)–Rh(2)	76.54(12)
C(12)–Rh(1)–Rh(2)	72.67(12)	C(11)–Co(1)–C(12)	39.23(16)	C(11)–Co(2)–Rh(1)	74.26(12)
Co(2)–Rh(1)–Rh(2)	56.758(19)	C(11)–Co(1)–Rh(2)	52.66(12)	C(12)–Co(2)–Rh(1)	51.83(10)
Co(1)–Rh(1)–Rh(2)	56.888(19)	C(12)–Co(1)–Rh(2)	76.73(12)	Rh(2)–Co(2)–Rh(1)	65.485(19)
C(11)–Rh(2)–Co(2)	52.99(14)	C(11)–Co(1)–Rh(1)	74.36(12)	C(11)–C(12)–C(13)	123.3(4)
C(11)–C(12)–Rh(1)	106.0(3)	C(12)–C(11)–Rh(2)	111.2(3)	C(13)–C(12)–Rh(1)	130.6(3)
C(11)–Rh(2)–Co(1)	52.49(14)	C(12)–Co(1)–Rh(1)	51.91(11)	Rh(1)–Rh(2)–C(11)–C(12)	0.1(3)
Co(2)–Rh(2)–Co(1)	91.39(2)	Rh(2)–Co(1)–Rh(1)	65.319(19)	C(12)–Rh(1)–Rh(2)–C(11)	−0.1(3)

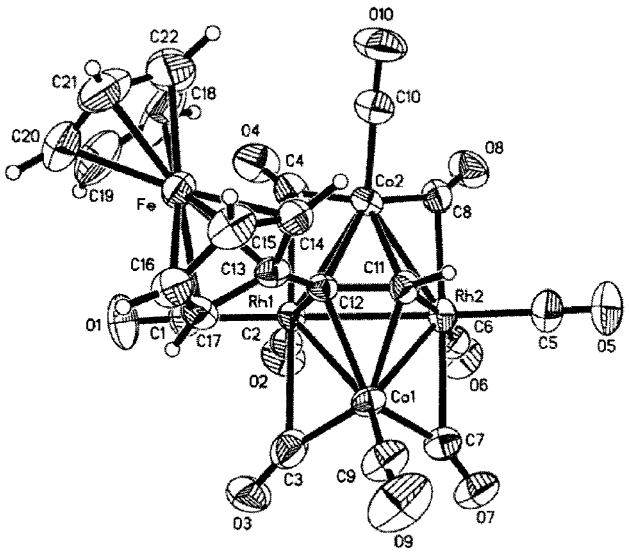


Fig. 1. The molecular structure of cluster **1**.

war–Chatt–Duncanson model, the Rh1–C12 and Rh2–C11 belong to two σ-bonds and there is a delocalized four-center π-bonding system between Co1, Co2, C11 and C12. Each cobalt atom is linked to one linear terminal carbonyl and two bridged carbonyl ligands along cobalt–rhodium bonds, whereas each rhodium atom is linked to two linear terminal carbonyl and two bridged carbonyl ligands.

The Rh1C12Rh2C11 ring can be looked as an isosceles trapezoid configuration due to the sum of the four internal angles (360.01°) and the bond lengths of Rh1–C12 (2.093(4) Å) and Rh2–C11 (2.090(4) Å) and the torsion angles (Rh1–Rh2–C11–C12, 0.1(3)°; C12–Rh1–Rh2–C11, − 0.1(3)°). The steric hindrance effect results in the ferrocenyl far away from the metal cluster (C15–C12–C11, 123.3(4)°; Rh1–C12–C13, 130.6(3)°) and four long (Rh1–Co1, 2.5630(7); Rh1–Co2, 2.5586(7); Co1–C12, 2.140(4); Co2–C12, 2.160(5) Å) and four short (Rh2–Co1, 2.5372(8); Rh2–Co2, 2.5301(8); Co1–C11, 2.085(5); Co2–C11, 2.098(5) Å) bond distances. The Cp rings in the ferrocenyl group are staggered and both are planar and parallel to each other. It is noticeable that the C11–C12 bond length (1.419(6) Å) has double-bond character and is longer than the reported C–C distance for $[Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}F_6C_6C{\equiv}CC_6F_6)]$ (1.369(2) Å) [4]. It is consistent with our knowledge that alkyne ligands with electron-donating groups have stronger interactions with the butterfly clusters and the stronger the interaction of alkynes with the cluster, the greater the possibility of finding long C–C distances.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 170066 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).

Acknowledgements

We are grateful to the National Science Foundation of China for the financial support of this work.

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