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Reactions of linked tetrahedron clusters [Co$_2$(CO)$_6$(μ-HC$_2$CH$_2$O)–]$_2$R with Rh$_2$(CO)$_4$Cl$_2$ to give mixed-metal linked alkyne-bridged butterfly clusters containing C$_2$Co$_2$Rh$_2$ unit

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Abstract

The reactions of compound Rh$_2$(CO)$_4$Cl$_2$, **1** with [Co$_2$(CO)$_6$(μ-HC$_2$CH$_2$O)–]$_2$R (R = C$_6$H$_4$, **2**; (COCH$_2$)$_2$, **3**; C$_6$H$_4$-1,4-(CO)$_2$, **4**; (COCH)$_2$, **5**; (CO)$_2$, **6**) in benzene at 60 °C produce five new mixed-metal linked clusters Rh$_2$Co$_2$(CO)$_{10}$(μ$_4$,η^2-HC$_2$CH$_2$O–R–OCH$_2$C$_2$H-μ)Co$_2$(CO)$_6$ (R = C$_6$H$_4$, **7a**; (COCH$_2$)$_2$, **7b**; C$_6$H$_4$-1,4-(CO)$_2$, **7c**; (COCH)$_2$, **7d**; (CO)$_2$, **7e**) and five known linked octahedral clusters [Rh$_2$Co$_2$(CO)$_{10}$(μ$_4$,η^2-HC$_2$CH$_2$O–)]$_2$R (R = C$_6$H$_4$, **8a**; (COCH$_2$)$_2$, **8b**; C$_6$H$_4$-1,4-(CO)$_2$, **8c**; (COCH)$_2$, **8d**; (CO)$_2$, **8e**), respectively. Treatment of clusters **7a**–**8e** in benzene at room temperature under air for 24 h with stirring afford the precursor clusters **2**–**6**, respectively. The structure of cluster **7a** has been determined by single-crystal X-ray diffraction. The linked cluster **7a** possesses two isomers A and B in its structures, the Rh$_2$(CO)$_4$ unit inserts into one of two Co–Co bonds and coordinates to the Co$_2$C$_2$ core forming one distorted *closo*-Rh$_2$Co$_2$C$_2$ octahedron framework which is connected to the Co$_2$C$_2$ tetrahedron unit via C$_6$H$_4$(OCH$_2$)$_2$-1,4 as a bridging ligand. All clusters were characterized by C, H elemental analysis, IR and ^{1}H NMR spectroscopy.
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Keywords: Mixed-metal linked cluster; Rh and Co; Crystal structure

1. Introduction

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 [1–6]. The chemistry of transition metal complexes bridged by unsaturated hydrocarbons developed rapidly and extensively in recent years resulting from the relevance to the chemistry of metal-catalyst surfaces [7,8]. It has been shown that an astonishing variety of alkyne-bridged clusters, including the synthesis and the reactivity of some linked alkyne-bridged clusters containing Co$_2$-(CO)$_6$C$_2$ unit have been reported [9–23]. Additionally, rho-

dium is especially active and implicated in a number of catalytic organic reactions [24,25]. Several examples of the heterometal alkyne-bridged cluster compounds containing Rh atom were investigated in the literature [26–30]. However, no reactions of the linked alkyne-bridged clusters with the metal expansion reagent containing Rh atom have been reported up to now. Furthermore, it has also been shown that Rh$_2$(CO)$_4$Cl$_2$ can provide a mononuclear or binuclear carbonyl rhodium fragment as metal exchange reagent [27] or metal expansion reagent [31,32] in some cases.

Because of the current interest in metal–alkyne cluster complexes, and in order to investigate the reactivity of the linked metal–alkyne carbonyl clusters with Rh$_2$(CO)$_4$Cl$_2$ and obtain the heterometal alkyne-bridged carbonyl linked clusters containing Rh atom, we have examined the reactions

of $Rh_2(CO)_4Cl_2$ with several alkyne-bridged linked tetrahedron clusters containing $Co_2(CO)_6C_2$ unit. Interestingly, we did not observe the metal exchange reaction, but it has been found that $Rh_2(CO)_4Cl_2$ reacts with these alkyne-bridged tetrahedron clusters as a binuclear carbonyl rhodium expansion reagent and the $Rh_2(CO)_4$ unit inserts into the Co–Co bonds leading to a Rh–Co butterfly system coordinated to the alkyne unit forming one distorted *closo*-$Rh_2Co_2C_2$ octahedron framework. Particularly, the expansion reaction in the linked tetrahedron clusters appears to be regiospecific. In this paper, we report these results of our study, including the crystal structure of the cluster **7a** and the new preparation method of the alkyne-bridged octahedron cluster containing the $Rh_2Co_2C_2$ core.

2. Experimental

2.1. General details

All operations were carried out under pure nitrogen with the use of standard Schlenk techniques. Reaction solvents were carefully dried and distilled under dinitrogen atmosphere prior to use. Chromatographic separations were performed on 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.

$Rh_2CO_4Cl_2$ [33], $[Co_2(CO)_6(\mu\text{-}HC_2CH_2O)\text{–}]_2R$ (R = $C_6H_4\text{-}1,4$ [34], $(COCH_2)_2$ [35], $C_6H_4\text{-}1,4\text{-}(CO)_2$ [35], $(COCH)_2$ [35], $(CO)_2$ [35]) were prepared by the literature methods.

Infrared spectra were recorded on a Bruker 120 HR FTIR 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 Bruker AM-400 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.

2.2. Reaction of $Rh_2CO_4Cl_2$ (1) with $[Co_2(CO)_6\text{-}(\mu\text{-}HC_2CH_2O)\text{–}]_2R$ (2–6). To give $Rh_2Co_2(CO)_{10}\text{-}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{–}R\text{–}OCH_2C_2H\text{-}\mu)Co_2(CO)_6$ (7a–e)

To a solution of $Co_2(CO)_6(\mu\text{-}HC_2CH_2O)\text{–}]_2C_6H_4$, **2** (152 mg, 0.2 mmol) in 20 ml of benzene at 60 °C, was added $Rh_2CO_4Cl_2$, **1** (78 mg, 0.2 mmol) under nitrogen. The mixture was stirred for 1.5 h and the color of the solution gradually changed from orange-red to violet. A TLC analysis of the reaction mixture showed the disappearance of **1**. Removal of the solvent and the residue was extracted by a minimum amount of CH_2Cl_2 and transferred to the silica gel chromatography column. Elution with CH_2Cl_2/petroleum ether (2:5) gave the major purple band **7a** (155 mg, 72.0% based on **1**). Black single crystals of **7a** suit-

able for single crystal X-ray analysis were obtained by cooling of a CH_2Cl_2/*n*-hexane solution at −20 °C.

$Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{–}C_6H_4\text{-}1,4\text{-}OCH_2C_2H\text{-}\mu)\text{-}Co_2(CO)_6$ (**7a**): Anal. Found: C, 31.38; H, 1.03. Calc. for $C_{28}H_{10}O_{18}Co_4Rh_2$: C, 31.26; H, 0.94%. IR: $v(CO)$ 2098(m), 2056(s), 2026(vs), 1876(s) cm^{-1}; ^1H NMR: δ 8.90 (s, 1H, ≡CH), 6.90 (s, 4H, C_6H_4), 6.07 (s, 1H, ≡CH), 5.16 (s, 2H, OCH_2), 4.34 (s, 2H, OCH_2).

The preparation procedures for **7b**–**7e** were similar to that described above. $Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{–}(COCH_2)_2\text{–}OCH_2C_2H\text{-}\mu)Co_2(CO)_6$ (**7b**): black crystal (151 mg, 69.7% based on **1**). Anal. Found: C, 29.06; H, 1.11. Calc. for $C_{26}H_{10}O_{20}Co_4Rh_2$: C, 28.81; H, 0.93%. IR: $v(CO)$ 2097(m), 2056(s), 2032(vs), 1870(m); $v(C=O)$ 1735(m) cm^{-1}; ^1H NMR: δ 8.87 (s, 1H, ≡CH), 6.08 (s, 1H, ≡CH), 5.32 (s, 2H, OCH_2), 4.68 (s, 2H, OCH_2), 2.76 (s, 4H, $2CH_2$).

$Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{–}C_6H_4\text{-}1,4\text{-}(CO)_2\text{–}OCH_2\text{-}C_2H\text{-}\mu)Co_2(CO)_6$ (**7c**): black crystal (154 mg, 68.0% based on **1**). Anal. Found: C, 31.58; H, 0.77. Calc. for $C_{30}H_{10}O_{20}\text{-}Co_4Rh_2$: C, 31.83; H, 0.89%. IR: $v(CO)$ 2099(m), 2060(s), 2033(vs), 1868(m) cm^{-1}; $v(C=O)$ 1719(m) cm^{-1}; ^1H NMR: δ 8.92 (s, 1H, ≡CH), 8.22–8.12 (m, 4H, C_6H_4), 6.14 (s, 1H, ≡CH), 5.30 (s, 2H, OCH_2), 4.92 (s, 2H, OCH_2).

$Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{–}(COCH)_2\text{–}OCH_2C_2H\text{-}\mu)Co_2(CO)_6$ (**7d**): (141 mg, 65.3% based on **1**). Anal. Found: C, 28.62; H, 1.01. Calc. for $C_{26}H_8O_{20}Co_4Rh_2$: C, 28.87; H, 0.75%. IR: $v(CO)$ 2100(s), 2059(vs), 2028(vs), 1886(m); $v(C=O)$ 1732(m) cm^{-1}. ^1H NMR: δ 8.89 (s, 1H, ≡CH), 6.36 (s, 2H, 2=CH), 6.09 (s, 1H, ≡CH), 5.40 (s, 2H, OCH_2), 4.81 (s, 2H, OCH_2).

$Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{–}(CO)_2\text{–}OCH_2C_2H\text{-}\mu)\text{-}Co_2(CO)_6$ (**7e**): (133 mg, 62.8% based on **1**). Anal. Found: C, 27.24; H, 0.55. Calc. for $C_{24}H_6O_{20}Co_4Rh_2$: C, 27.30; H, 0.57%. IR: $v(CO)$ 2097(m), 2056(s), 2032(vs), 1884(m), 1870(m); $v(C=O)$ 1735(w) cm^{-1}. ^1H NMR: δ 8.91 (s, 1H, ≡CH), 6.04 (s, 1H, ≡CH), 5.36 (s, 2H, OCH_2), 4.91 (s, 2H, OCH_2).

2.3. Reaction of $Rh_2CO_4Cl_2$ with $[Co_2(CO)_6\text{-}(\mu\text{-}HC_2CH_2O)\text{–}]_2R$. To give $[Rh_2Co_2(CO)_{10}\text{-}(\mu_4,\eta^2\text{–}HC_2CH_2O\text{–})]_2R$ (8a–e)

To a solution of $Co_2(CO)_6(\mu\text{-}HC_2CH_2O)\text{–}]_2C_6H_4$, **2** (76 mg, 0.1 mmol) in 20 ml of benzene at 60 °C, was added an excess of $Rh_2CO_4Cl_2$, **1** (117 mg, 0.3 mmol) under nitrogen. The mixture was stirred for 2 h and the color of the solution gradually changed from orange-red to violet. After benzene was removed, the residue was extracted by a small amount of CH_2Cl_2 and transferred to the silica gel chromatography column. Elution with CH_2Cl_2/petroleum ether (2:5) gave the predominant purple band **8a** (97 mg, 69.6% based on **2**).

$[Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{–})]_2C_6H_4$ (**8a**): Anal. Found: C, 27.69; H, 0.90. Calc. for $C_{32}H_{10}O_{22}Co_4Rh_4$: C, 27.58; H, 0.72%. IR: $v(CO)$ 2097(m), 2048(vs), 2018(vs),

1978(s), 1871(m), 1854(m) cm^{-1}. ^{1}H NMR: δ 8.86 (s, 1H, ≡CH), 6.82 (s, 4H, C$_6$H$_4$), 4.31 (s, 4H, 2OCH$_2$).

The following cluster complexes were similarly prepared.

[Rh$_2$Co$_2$(CO)$_{10}$(μ_4,η^2-HC$_2$CH$_2$O–)]$_2$(COCH$_2$)$_2$ (**8b**): black crystal (94 mg, 67.1% based on **3**). Anal. Found: C, 25.88; H, 0.96. Calc. for C$_{30}$H$_{10}$O$_{24}$Co$_4$Rh$_4$: C, 25.71; H, 0.72%. IR: v(CO) 2097(m), 2060(s), 2038(vs), 1995(vs), 1875(m); v(C=O) 1723(m) cm^{-1}. ^{1}H NMR: δ 8.85 (s, 2H, 2≡CH), 4.63 (s, 4H, 2OCH$_2$), 2.69 (s, 4H, 2CH$_2$).

[Rh$_2$Co$_2$(CO)$_{10}$(μ_4,η^2-HC$_2$CH$_2$O–)]$_2$C$_6$H$_4$-1,4-(CO)$_2$ (**8c**): black crystal (96 mg, 66.2% based on **4**). Anal. Found: C, 27.89; H, 0.83. Calc. for C$_{34}$H$_{10}$O$_{24}$Co$_4$Rh$_4$: C, 28.17; H, 0.70%. IR: v(CO) 2099(m), 2030(vs), 2018(vs), 1987(s), 1877(m); v(C=O) 1716(m) cm^{-1}. ^{1}H NMR: δ 8.94 (s, 2H, 2≡CH), 8.18 (s, 4H, C$_6$H$_4$), 4.94 (s, 4H, 2OCH$_2$).

[Rh$_2$Co$_2$(CO)$_{10}$(μ_4,η^2-HC$_2$CH$_2$O–)]$_2$(COCH)$_2$ (**8d**): (94 mg, 67.2% based on **5**). Anal. Found: C, 25.61; H, 0.77. Calc. for C$_{30}$H$_8$O$_{24}$Co$_4$Rh$_4$: C, 25.74; H, 0.58%. IR: v(CO) 2100(m), 2058(s), 2020(vs), 1882(m); v(C=O) 1721(m) cm^{-1}. ^{1}H NMR: δ 8.89 (s, 2H, 2≡CH), 6.32 (s, 2H, 2=CH), 4.74 (s, 4H, 2OCH$_2$).

[Rh$_2$Co$_2$(CO)$_{10}$(μ_4,η^2-HC$_2$CH$_2$O–)]$_2$(CO)$_2$ (**8e**): (86 mg, 62.6% based on **6**). Anal. Found: C, 24.67; H, 0.58. Calc. for C$_{28}$H$_6$O$_{24}$Co$_4$Rh$_4$: C, 24.48; H, 0.44%. IR: v(CO) 2099(m), 2056(s), 2035(vs), 1993(m), 1881(m); v(C=O) 1739(m) cm^{-1}. ^{1}H NMR: δ 8.86 (s, 2H, 2≡CH), 4.87 (s, 4H, 2OCH$_2$).

2.4. Oxidative decomposition of clusters 7a–8e. To give clusters 2–6

The cluster **7a** (108 mg, 0.1 mmol) was dissolved in 20 ml of benzene at r.t. under air. The solution was stirred for 24 h and the violet solution gradually changed to orange-red and some deposits were formed. After benzene was removed, the residue was extracted by a small amount of CH$_2$Cl$_2$ and transferred to the silica gel chromatography column. Elution with CH$_2$Cl$_2$/petroleum ether (1:5) gave the predominant orange-red band **2** (32 mg, 42.2% based on **7a**).

[Co$_2$(CO)$_6$(μ-HC$_2$CH$_2$O)–]$_2$C$_6$H$_4$ (**2**): Anal. Found: C, 37.98; H, 1.42. Calc. for C$_{24}$H$_{10}$O$_{14}$Co$_4$: C, 38.03; H, 1.33%. IR: v(CO) 2097(m), 2058(vs), 2023(vs), 1975(s) cm^{-1}. ^{1}H NMR: δ 6.92 (s, 4H, C$_6$H$_4$), 6.04 (s, 2H, 2≡CH), 5.12 (s, 4H, 2OCH$_2$).

The following cluster complexes **3–6** were obtained according to the similar procedure.

[Co$_2$(CO)$_6$(μ_4,η^2-HC$_2$CH$_2$O–)]$_2$(COCH$_2$)$_2$ (**3**): (28 mg, 36.6% based on **7b**). Anal. Found: C, 34.62; H, 1.37. Calc. for C$_{22}$H$_{10}$O$_{16}$Co$_4$: C, 34.49; H, 1.32%. IR: v(CO) 2100(m), 2064(s), 2032(vs); v(C=O) 1725(m) cm^{-1}. ^{1}H NMR: δ 6.05 (s, 2H, 2≡CH), 5.32 (s, 4H, 2OCH$_2$), 2.75 (s, 4H, 2CH$_2$).

[Co$_2$(CO)$_6$(μ_4,η^2-HC$_2$CH$_2$O–)]$_2$C$_6$H$_4$-1,4-(CO)$_2$ (**4**): (33 mg, 40.6% based on **7c**). Anal. Found: C, 38.29; H, 1.22. Calc. for C$_{26}$H$_{10}$O$_{16}$Co$_4$: C, 38.36; H, 1.24%. IR: v(CO) 2099(m), 2060(vs), 2028(vs), 1977(s); v(C=O) 1716 m cm^{-1}. ^{1}H NMR: δ 8.18 (s, 4H, C$_6$H$_4$), 6.15 (s, 2H, 2≡CH), 5.54 (s, 4H, 2OCH$_2$).

[Co$_2$(CO)$_6$(μ_4,η^2-HC$_2$CH$_2$O–)]$_2$(COCH$_2$)$_2$ (**5**): (25 mg, 32.7% based on **7d**). Anal. Found: C, 34.48; H, 1.17. Calc. for C$_{22}$H$_8$O$_{16}$Co$_4$: C, 34.59; H, 1.06%. IR: v(CO) 2100(m), 2058(s), 2022(vs); v(C=O) 1736(m) cm^{-1}. ^{1}H NMR: δ 6.30 (s, 2H, 2=CH), 6.09 (s, 2H, 2≡CH), 5.34 (s, 4H, 2OCH$_2$).

[Co$_2$(CO)$_6$(μ_4,η^2-HC$_2$CH$_2$O–)]$_2$(CO)$_2$ (**6**): (22 mg, 29.8% based on **7e**). Anal. Found: C, 32.57; H, 0.85. Calc. for C$_{20}$H$_6$O$_{16}$Co$_4$: C, 32.55; H, 0.82%. IR: v(CO) 2101(m), 2076(s), 2055(vs), 2023(vs); v(C=O) 1759(m) cm^{-1}. ^{1}H NMR: δ 6.08 (s, 2H, 2≡CH), 5.49 (s, 4H, 2OCH$_2$).

Procedures for the oxidative decomposition of clusters **8a–e** were similar to that described above. **8a–e** (0.1 mmol) were dissolved in 20 ml of benzene at r.t. under air for 24 h with stirring, and then the products **2–6** and a little **7a–e** were obtained, respectively.

2.5. Single-crystal X-ray diffraction analysis of 7a

Suitable crystals were mounted on a glass fiber and place on a Bruker CCD APEX diffractometer equipped with graphite-monochromator. The empirical absorption corrections were applied using the SADABS program [36]. The structures were solved by direct methods (SHELXS-97) [37] and expanded using Fourier techniques and all non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using the SHELXL-97 [38] crystallographic program package. Hydrogen atoms were added according to geometrical method.

3. Results and discussion

3.1. Synthesis of clusters 7a–8e

The reactions described in this work are summarized in Scheme 1. To explore the behaviour of Rh$_2$(CO)$_4$Cl$_2$ towards the linked alkyne-bridged tetrahedron clusters, complex Rh$_2$(CO)$_4$Cl$_2$, **1** was treated with an equiv of [Co$_2$(CO)$_6$(μ-HC$_2$CH$_2$CO)-]$_2$R (R = C$_6$H$_4$, **2**; (COCH$_2$)$_2$, **3**; C$_6$H$_4$-1,4-(CO)$_2$, **4**; (COCH)$_2$, **5**; (CO)$_2$, **6**) under the similar condition of that described above to afford monoexpanded dimeric clusters Rh$_2$Co$_2$(CO)$_{10}$(μ_4,η^2-HC$_2$CH$_2$O–R–OCH$_2$C$_2$H-μ)Co$_2$(CO)$_6$(R = C$_6$H$_4$, **7a**; (COCH$_2$)$_2$, **7b**; C$_6$H$_4$-1,4-(CO)$_2$, **7c**; (COCH)$_2$, **7d**; (CO)$_2$, **7e**) as the predominant product and diexpanded clusters [Rh$_2$Co$_2$-(CO)$_{10}$(μ_4,η^2-HC$_2$CH$_2$O–)]$_2$R (R = C$_6$H$_4$, **8a**; (COCH$_2$)$_2$, **8b**; C$_6$H$_4$-1,4-(CO)$_2$, **8c**; (COCH)$_2$, **8d**; (CO)$_2$, **8e**) as the minor product. But clusters **8a–e** were got in good yield by the reaction of excess Rh$_2$(CO)$_4$Cl$_2$ with the linked alkyne-bridged tetrahedron clusters. It indicates that the reaction appears to be regiospecific.

All products of **7a–8e** are stable in the solid or solution under an inert atmosphere and sensitive to tetrahydrofuran.

3.2. Oxidative decomposition of clusters 7a–8e

To gain more understanding of the expanded cluster products, the oxidative decomposition reaction of clusters
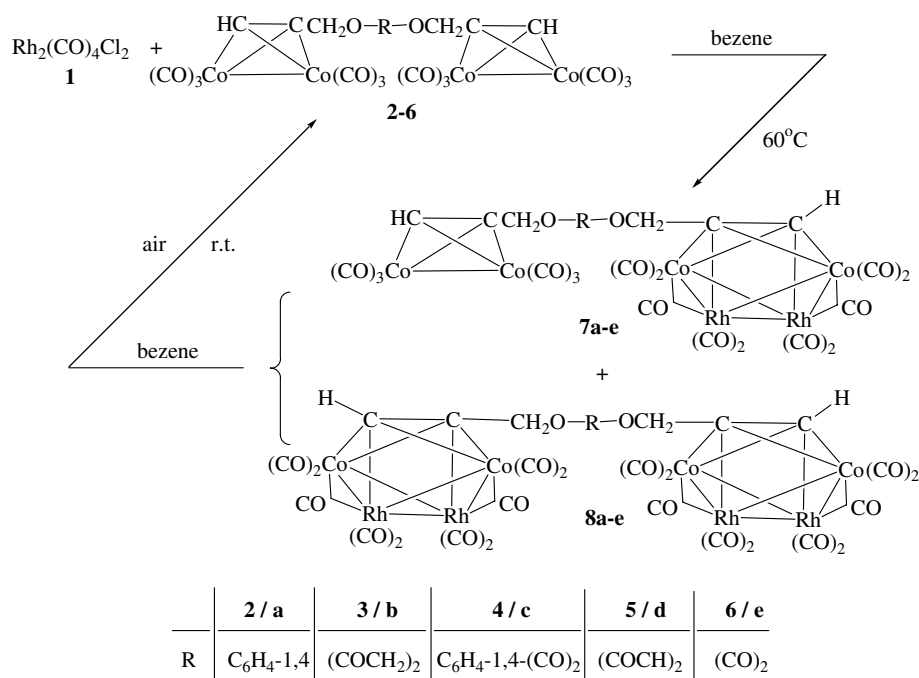
Scheme 1.

7a–8e were checked in the benzene under air at room temperature (see Scheme 1). The results show that the clusters **7a–8e** are unstable in solution and decompose gradually to give the corresponding orange-red solution and some deposits, which are unsolved in organic solvent under air at r.t.

The evidences of element analysis, IR and ^{1}H NMR spectra have shown that the data of these orange-red compounds are the same as that of clusters **2–6**, respectively. So we can conclude that the homonuclear Co–Co bonds might be stabler than the Rh–Co heteronuclear metal–metal bond during the oxidative reaction.

It should be noted that we could not get the cluster products containing rhodium atom. This may be due to the instability of binuclear rhodium carbonyl cluster complexes, which would make them decompose readily at r.t. Further studies on the oxidative decomposition mechanism of clusters **7a–8e** are currently underway.

3.3. Characterization of clusters 7a–8e

The IR and ^{1}H NMR spectra of **7a–e** and **8a–e** show the presence of their respective alkyne-bridged ligands. In the IR spectra, all linked clusters show intense terminal carbonyl and bridged carbonyl absorption bands in the range 2100–1854 cm^{-1} and a characteristic absorption band of the ester carbonyl at 1739–1716 cm^{-1} for clusters **7a–8e**, respectively. From the ^{1}H NMR spectra, configurations of clusters **7a–e** and **8a–e** could be distinguished. For instance, for **7a–e** the two protons of the two C$_2$H groups appear as two singlets at δ 8.87–8.92 and 6.04–6.14, respectively. Compared with the ^{1}H NMR spectra of the literature values, the singlet at δ 8.87–8.92 can be assigned to the proton of the terminal alkyne (C$_2$H) coordinated

to Rh$_2$Co$_2$ core [28b,29] and at δ 6.04–6.14 to the proton of the C$_2$H group coordinated to Co–Co [18,19,34]. In addition, the singlets at δ 5.16–5.40 and 4.34–4.92 also identify that the chemical environment of two OCH$_2$ groups is different in **7a–e**, which has been confirmed by single-crystal X-ray diffraction for cluster **7a**. However, in the ^{1}H NMR spectrum of **8a–e**, these protons of two

Table 1
Crystal and refinement data for the cluster **7a**

Empirical formula	C$_{28}$H$_{10}$O$_{18}$Co$_4$Rh$_2$
Formula weight	1075.90
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.0417(11)
b (Å)	13.7307(17)
c (Å)	28.952(4)
α (°)	93.313(3)
β (°)	90.425(3)
γ (°)	94.989(3)
V (Å^3)	3574.5(8)
Z	4
D_{calc} (g/cm^3)	1.999
$F(000)$	2080
μ (mm^{-1})	2.790
Radiation (Mo Kα) (Å)	0.71073
Scan type	Φ–ω
θ_{max} (°)	25.50
Total reflections	18 979
Unique reflections	13 119
Number of variables	952
Goodness-of-fit on F^2	0.734
R^{a}	0.0723
$R_w{}^{b}$	0.1463
Largest difference in peak and hole (e Å^{-3})	0.766, −1.383

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

Table 2
Selected bond lengths (Å) and angles (°) for **7a**

Rh(1)–Co(2)	2.539(3)	Rh(3)–Co(5)	2.580(2)	Co(7)–Co(8)	2.447(4)
Rh(1)–Co(1)	2.560(2)	Rh(3)–Rh(4)	2.624(2)	C(17)–C(18)	1.390(19)
Rh(1)–Rh(2)	2.644(2)	Rh(4)–Co(5)	2.501(3)	C(27)–C(28)	1.198(17)
Rh(2)–Co(2)	2.506(3)	Rh(4)–Co(6)	2.524(3)	C(45)–C(46)	1.296(19)
Rh(2)–Co(1)	2.513(3)	Co(3)–Co(4)	2.446(3)	C(55)–C(56)	1.258(19)
Rh(3)–Co(6)	2.553(3)				
Co(2)–Rh(1)–Co(1)	90.03(8)	Rh(4)–Co(6)–Rh(3)	62.24(7)	Rh(2)–Co(1)–Rh(1)	62.83(7)
Co(2)–Rh(1)–Rh(2)	57.78(7)	Co(5)–Rh(4)–Rh(3)	60.39(7)	Rh(4)–Co(5)–Rh(3)	62.16(7)
Co(1)–Rh(1)–Rh(2)	57.71(7)	Co(6)–Rh(4)–Rh(3)	59.42(7)	C(45)–Co(6)–Rh(4)	51.4(4)
Co(2)–Rh(2)–Co(1)	91.88(9)	Co(5)–Rh(4)–Co(6)	91.05(8)	Co(5)–Rh(3)–Rh(4)	57.44(7)
Co(2)–Rh(2)–Rh(1)	59.00(7)	Co(6)–Rh(3)–Co(5)	88.62(8)	Co(6)–Rh(3)–Rh(4)	58.33(7)

C_2H and two OCH_2 groups have the same chemical shift at the range of δ 8.86–8.94 and 4.31–4.94, respectively, which reveals that these corresponding protons occur in the same chemical environment. It should be noted that the evidences of element analysis (C, H), IR and ^1H NMR spectra have shown that the clusters $[Rh_2Co_2(CO)_{10}(\mu_4,\eta^2-HC_2CH_2O–)]_2R$ **8a–e**, are the same as that of our previous report [30], respectively, but the preparation procedures never be reported previously.

3.4. Crystal structure of cluster **7a**

The molecular structure of **7a** was determined by single crystal X-ray analysis. Crystal data and experimental details for **7a** are collected in Table 1. Table 2 gives the selected bond lengths and angles. The ORTEP drawing with numbering is shown in Fig. 1.

As can be seen in Fig. 1, the linked cluster **7a** possesses two isomers **A** and **B** in its structures. To demonstrate **A** as an example, in the structure of **A**, the $Rh_2(CO)_4$ unit inserts into one of two Co–Co bonds and coordinates to the Co_2C_2 core forming one distorted *closo*-$Rh_2Co_2C_2$ octahedron framework which is connected to the Co_2C_2 tetrahedron unit via $C_6H_4(OCH_2)_2$-1,4 as a bridging ligand. In the octahedral $Rh_2Co_2C_2$ core the cobalt atoms occupy the wing positions of the butterfly metal skeleton and the nonbonding distance between the two cobalt atoms Co(1) and Co(2) is 3.779 Å. The bonding distance of
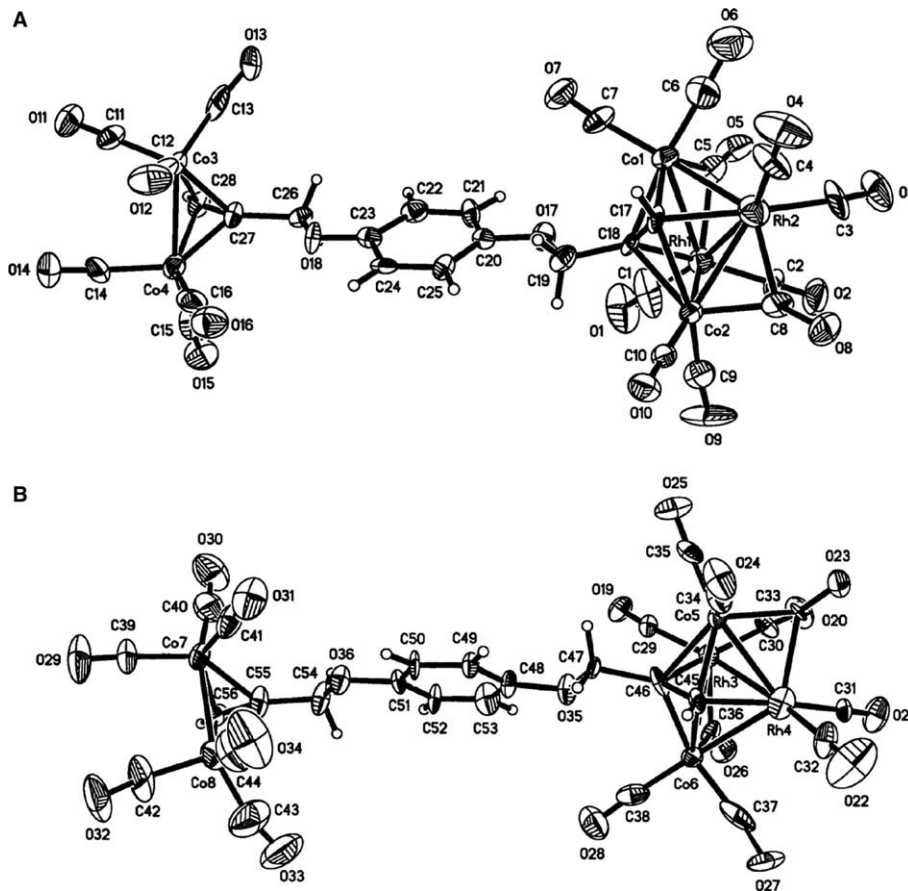

Fig. 1. ORTEP drawing of **7a**, showing the atom-labelling scheme with 30% thermal ellipsoids.

Rh(1)–Rh(2) and the Rh–Co average bond length is 2.644(2) and 2.530 Å, respectively. The Rh(1) atom is bonded to C(18) and Rh(2) is bonded to C(17) of the acetylenic moiety. According to the well-known Dewar-Chatt-Duncanson model, the Rh(1)–C(18) and Rh(2)–C(17) belong to two -bonds and there is a delocalized four-center π-bonding system between Co(1), Co(2), C(17) and C(18). So, the μ_4,η^2-HC≡CR ligand may be viewed as a 6-electron donor, with the result that the $Rh_2Co_2C_2$ core contains a total of 62 electrons and is consistent with the butterfly structure. Each metal atom is linked to two linear terminal carbonyl and one bridged carbonyl ligands.

It is noticeable that the C–C bond lengths of the acetylenic moiety in **A** has double-bond character and the C(27)–C(28) bond length (1.198(17) Å) of Co_2C_2 tetrahedron core is shorter than the C(17)–C(18) distance (1.390(19) Å) of the octahedral $Rh_2Co_2C_2$ unit. This indicates that the acetylenic moiety has stronger interaction with the Rh_2Co_2 butterfly cluster core than that of the Co_2 bimetallic unit.

4. Supplementary material

Full tables of crystal data, atomic coordinates, thermal parameters, and bond lengths and angles for cluster **7a** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 273371. 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).

References

[1] M.G. Karpov, S.P. Tunik, V.R. Denisov, G.L. Starova, A.B. Nikolskii, F.M. Dolgnskin, A.I. Yanovsky, Yu.T. Sryuchkov, J. Organomet. Chem. 485 (1995) 219.

[2] W.-Y. Wong, H.-Y. Lam, S.-M. Lee, J. Organomet. Chem. 595 (2000) 70.

[3] H. Adams, L.V.Y. Guio, M.J. Morris, F.A. Wildgoose, J. Organomet. Chem. 659 (2002) 142.

[4] R.D. Adams, B. Qu, M.D. Smith, Organometallics 21 (2002) 3867.

[5] N.T. Lucas, E.G.A. Notaras, M.P. Cifuentes, M.G. Humphrey, Organometallics 22 (2003) 284;
N.T. Lucas, E.G.A. Notaras, S. Petrie, R. Stranger, M.G. Humphrey, Organometallics 22 (2003) 708.

[6] L.-C. Song, J. Cheng, Q.-M. Hu, F.-H. Gong, H.-Z. Bian, L.-X. Wang, Organometallics 24 (4) (2005) 472.

[7] H.E. Amouri, M. Gruselle, Chem. Rev. 96 (1996) 1077.

[8] H. Lang, D.S.A. George, G. Rheinwald, Coord. Chem. Rev. 206–207 (2000) 101.

[9] D. Seyferth, H.P. Withers, Inorg. Chem. 22 (1983) 2931.

[10] P. Magnus, D.P. Becker, J. Chem. Soc., Chem. Commun. (1985) 640.

[11] T.M. Wido, G.H. Young, A. Wojcicki, M. Calligaris, G. Nardin, Organometallics 7 (1988) 452.

[12] Y. Rubin, C.B. Knobler, F. Diederich, J. Am. Chem. Soc. 112 (1990) 4966.

[13] K.I. Hardcastle, A.J. Deeming, D. Neul, N.I. Pauwell, J. Organomet. Chem. 384 (1990) 181.

[14] A.A. Koridze, A.I. Yanovsky, Yu.T. Struchkov, J. Organomet. Chem. 441 (1992) 277.

[15] C.E. Housecroft, B.F.G. Johson, M.S. Khan, J. Lewis, P.R. Raithby, M.E. Robson, D.A. Wilkinson, J. Chem. Soc., Dalton Trans. (1992) 3171.

[16] K. Onitsuku, X.-Q. Tao, W.-Q. Wang, Y. Otsuka, K. Sonogashira, T. Adachi, T. Yoskida, J. Organomet. Chem. 473 (1994) 195.

[17] F.-Y. Jiao, Y.-Q. Yin, P. Braunstein, J. Rose, Acta Chim. Sin. 49 (1991) 711;
S.-L. Wu, E.-R. Ding, Y.-Q. Yin, J. Organomet. Chem. 570 (1998) 71.

[18] X.N. Chen, J. Zhang, Y.Q. Yin, X.Y. Huang, Organometallics 18 (1999) 3164;
J. Zhang, Y.H. Zhang, X.N. Chen, E.R. Ding, Y.Q. Yin, Organometallics 19 (2000) 5032.

[19] K. Schmidt, M. Jung, R. Keilitz, B. Schnurr, R. Gust, Inorg. Chim. Acta 306 (2000) 6.

[20] J.A. Dunn, J.F. Britten, J.-C. Daran, M.J. McGlinchey, Organometallics 20 (22) (2001) 4690;
J.H. Kaldis, P. Morawietz, M.J. McGlinchey, Organometallics 22 (6) (2003) 1293.

[21] A. Choualeb, J. Rosé, P. Braunstein, R. Welter, Organometallics 22 (13) (2003) 2688.

[22] H. Yan, A.M. Beatty, T.P. Fehlner, J. Am. Chem. Soc. 125 (52) (2003) 16367.

[23] J.A. Cabeza, P. García-Alvarez, E. Pérez-Carreño, Organometallics 24 (8) (2005) 2000.

[24] J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978.

[25] D.A. Roberts, W.C. Mercer, S.M. Zahurak, G.L. Geoffroy, C.W. DeBrosse, M.E. Cass, C.G. Pierpont, J. Am. Chem. Soc. 104 (1982) 910.

[26] I.T. Horváth, L. Zsolnai, G. Huttner, Organometallics 5 (1986) 180;
I.T. Horváth, Polyhedron 7 (1988) 2345.

[27] T. Albiez, H. Bantel, H. Vahrenkamp, Chem. Ber. 123 (9) (1990) 1805.

[28] (a) I. Ojima, P. Ingallina, R.J. Donovan, N. Clos, Organometallics 10 (1991) 38;
(b) I. Ojima, N. Clos, R.J. Donovan, P. Ingallina, Organometallics 10 (1991) 3211.

[29] B.-H. Zhu, W.-Q. Zhang, B. Hu, Z.-G. Bian, Q.-Y. Zhao, Y.-H. Zhang, Y.-Q. Yin, J. Sun, J. Organomet. Chem. 650 (2002) 180.

[30] B.-H. Zhu, B. Hu, W.-Q. Zhang, Y.-H. Zhang, Y.-Q. Yin, J. Sun, J. Organomet. Chem. 681 (2003) 275.

[31] S. Attali, R. Mathieu, J. Organomet. Chem. 291 (1985) 205;
S. Attali, F. Dahan, R. Mathieu, Organometallics 5 (1986) 1316.

[32] T.J. Henly, J.R. Shapley, A.L. Rheingold, S.J. Gelb, Organometallics 7 (1988) 441.

[33] C.V. Pittman, L.R. Smith, J. Organomet. Chem. 80 (1975) 203.

[34] X.-N. Chen, J. Zhang, S.-L. Wu, Y.-Q. Yin, W.-L. Wang, J. Sun, J. Chem. Soc., Dalton Trans. (1999) 1987.

[35] Y.-H. Zhang, W.-J. Lao, Y.-Q. Liu, Y.-Q. Yin, J.-J. Wu, Z.-X. Huang, Polyhedron 20 (2001) 1107;
Y.-H. Zhang, Ph.D. Dissertation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, 2001, p. 91..

[36] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Germany, 1996.

[37] G.M. Sheldrick, SHELXS-97. Program for Crystal Structure Solution, University of Gottingen, Germany, 1997.

[38] G.M. Sheldrick, SHELXL-97. Program for Crystal Structure Refinement, University of Gottingen, Germany, 1997.