SHORT PAPER

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Synthesis and crystal structure of a new butterfly cluster $[Rh_2Co_2\ (CO)_6(\mu\text{-}CO)_4(\mu_4,\eta^2\text{-}HC{\equiv}CFeCp_2)]$

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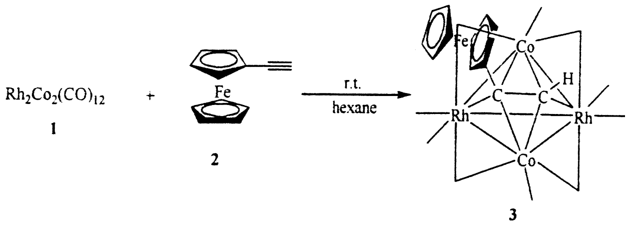
The new butterfly cluster $[Rh_2Co_2(CO)_6(\mu\text{-}CO)_4(\mu_4,\ \eta^2\text{-}HC{\equiv}CFeCp_2)]$ **3** was obtained by the reaction of $[Rh_2Co_2(CO)_{12}]$ **1** with the 1-alkyne ligand $HC{\equiv}CFeCp_2$ **2**, and the structure of cluster **3** has been established by single-crystal X-ray diffraction methods.

Keywords: butterfly cluster $[RH_2CO_2(CO)_6(\mu\text{-}CO)_4(\mu_4\eta^2\text{-}HC{\equiv}CFeCp_2)]$

Mixed-metal clusters have attracted a great deal of attention since the mid 1970s, due to their high potential to serve as efficient catalysts for a variety of homogeneous catalytic reactions as well as unique reagents for organic syntheses.[1,2] The reactions of $[Rh_2Co_2(CO)_{12}]$ with several alkynes to give Rh-Co mixed-metal butterfly complexes,[2-5] and the reaction of silylformylation of 1-hexyne catalysed by $[Rh_2Co_2(CO)_{12}]$[6] have been reported. In order to gain more understanding about the cobalt and rhodium mixed-metal cluster and further investigate the selective cleavage of the metal–metal bonds, we have synthesised the new Rh–Co mixed-meal butterfly cluster$[Rh_2Co_2(CO)_6\ (\mu\text{-}CO)_4(\mu_4,\eta^2\text{-}HC{\equiv}CFeCp^2)]$ **3** by reaction of $[Rh_2Co_2(CO)_{12}]$ **1** with functionally substituted 1-alkyen $HC{\equiv}CFeCp_2$ **2** in hexane at room temperature (Scheme 1). The cluster **3** gives light air-sensitive dark purple crystals and is soluble in common organic solvents.



Scheme 1 Synthesis of compound **3**.

The IR spectrum shows a large number of strong terminal carbonyl and bridged carbonyl absorption bands located at 2095–1852 cm^{-1}. The strong absorption at 2095 cm^{-1} is typical of terminal carbonyl coordinated to a cobalt atom,[7] and the weak absorption frequency around 1888–1852 cm^{-1} also indicate that a bridged or semi-bridged carbonyl exits in the cluster. The ^1H-NMR spectrum of cluster **3** is consistent with the 1-alkyne-bridged butterfly structure. The remarkable downfield shift (δ 8.86) of the acetylenic hydrogen is characteristic of the hydrogen atom bound to carbons interacting either σ or π with metals.[2,8,9] For the cyclopentadienyl rings of the ferrocenyl, the ^1H-NMR spectra of **3** 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.

The structure features of compound **3** have been established by X-ray diffraction analysis of a suitable crystal. As seen in Fig. 1, the cluster **3** has a butterfly metal skeleton, 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 bridge 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 resulting from the sum (181.34°) of the bond angles Rh1–Rh2–C11 and Rh2–C11–C12. It coordinates to all metal atoms as a μ_4, η^2-ligand forming a distorted *closo*-$Rh_2Co_2C_2$ octahedral framework. The Rh1 atom is bonded to C12 and Rh2 is bonded to C11 of the acetylenic moiety. According to

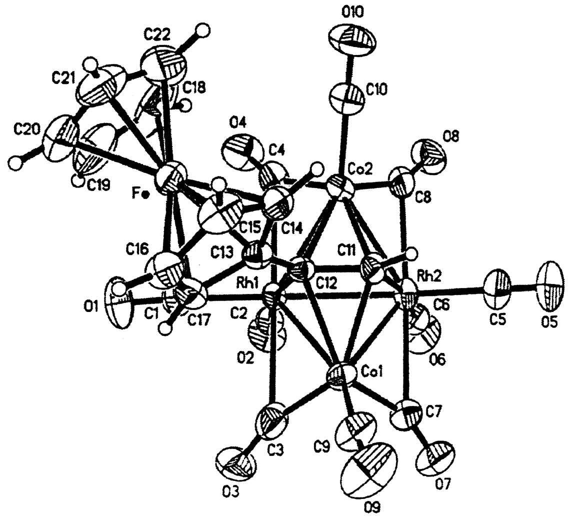


Fig.1 Crystal structure of the cluster **3**. Selected bond distances (Å) and angles (°):
Rh(1)–C(12) 2.093(4); Rh(1)–Co(2) 2.5586(7); Rh(1)–Co(1) 2.5630(7); Rh(1)–Rh(2) 2.7524(5); Rh(2)–C(11) 2.090(4); Rh(2)–Co(2) 2.5301(8); Rh(2)–Co(1) 2.5372(8); Co(1)–C(11) 2.085(5); Co(1)–C(12) 2.140(4); Co(2)–C(11) 2.098(5); Co(2)–C(12) 2.160(5); C(11)–C(12) 1.419(6); C(12)–Rh(1)–Co(2) 54.23(13); C(12)–Rh(1)–Co(1) 53.58(12); Co(2)–Rh(1)–Co(1) 90.15(2); C(12)–Rh(1)–Rh(2) 72.67(12); Co(2)–Rh(1)–Rh(2) 56.758(19); Co(1)–Rh(1)–Rh(2) 56.888(19); C(11)–Rh(2)–Co(2) 52.99(14); C(11)–Rh(2)–Co(1) 52.49(14); C(11)–Rh(2)–Rh(1) 70.14(12); Co(2)–Rh(2)–Rh(1) 57.757(18); Co(1)–Rh(2)–Rh(1) 57.792(18); C(11)–Co(1)–C(12) 39.23(16); C(11)–Co(1)–Rh(2) 52.66(12); C(12)–Co(1)–Rh(2) 76.73(12); C(11)–Co(1)–Rh(1) 74.36(12); C(12)–Co(1)–Rh(1) 51.91(11); Rh(2)–Co(1)–Rh(1) 65.319(19); C(11)–Co(2)–C(12) 38.90(16); C(11)–Co(2)–Rh(2) 52.68(12); C(12)–Co(2)–Rh(2) 76.54(12); C(11)–Co(2)–Rh(1) 74.26(12); C(12)–Co(2)–Rh(1) 51.83(10); Rh(2)–Co(2)–Rh(1) 65.485(19); C(13)–C(12)–C(11) 123.3(4)°; Rh(1)–C(12)–C(13) 130.6(3).

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

the well-known Dewar–Chatt–Duncanson model, the Rh1–C12 and Rh2–C11 belong to two σ-bonds and there is a delocalised four-centre π-bonding system between Co1, Co2, C11 and C12. Each rhodium atom is linked to two linear terminal carbonyl and two bridged carbonyl ligands along cobalt–rhodium bonds, whereas each cobalt atom is only linked to one linear terminal carbonyl and two bridged carbonyl ligands. The steric hindrance effect results in the ferrocenyl being far away from the metal cluster (C13–C12–C11, 123.3(4)°; Rh1–C12–C13, 130.6(3)°). The Cp rings in the ferrocenyl group are staggered and both are planar and parallel to each other.

Experimental

All preparative work was carried out under an atmosphere of pure nitrogen by using standard Schlenk or vacuum-line techniques. Column chromatography was carried out by using silica gel columns of 160–200 mesh. $Rh_2Co_2(CO)_{12}$, and [10] $HC{\equiv}CFeCp_2$ (Cp = C_5H_5)[11] were prepared according to literature methods. Infrared spectra were recorded on a Nicolet FTIR 10DX spectrophotometer. ^{1}HNMR spectra were measured on a Brucker AM-400 MHz spectrometer; Elemental analysis (C, H) was performed on a Carlo-Erba 1106 type analyzer.

Synthesis of compound $[Rh_2Co_2(CO)_6(\mu\text{-}CO)_4(\mu_4, \eta^2\text{-}HC{\equiv}CFeCp_2)]$ **3**: To a solution of $Rh_2Co_2(CO)_{12}$ **1** (99 mg, 0.15 mmol) in 20 ml of hexane at room temperature was added dropwise a solution of $HC{\equiv}CFeCp_2$ **2** (42 mg, 0.2 mmol) in 10 ml of *n*-hexane under nitrogen. The mixture was stirred at room temperature for 3 h. During the stirring the color of the solution gradually changed from 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_2Cl_2 and transferred to the top of a 2.5 cm × 40 cm silica gel chromatography column. Elution with CH_2Cl_2/petroleum ether (1:8) afforded a major purple band. Condensing the solvent and crystallisation at –20°C gave dark purple crystals **3** (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 (KBr disc): ν (CO) 2095m, 2056s, 2030vs, 1993s, 1976m, 1888w, 1872s, 1852m cm^{-1}; ^{1}H-NMR($CDCl_3$, 400MHz): δ 8.56 (s, H, ≡CH), 4.29–4.18 (d, 4H, C_5H_4), 3.99 (s, 5H, C_5H_5).

Crystal data of cluster **3**: Suitable crystals of cluster **3** $[C_{22}H_{10}Co_2FeO_{10}Rh_2]$ (Mr = 813.83) were obtained from hexane at –20°C. The space group was *P*2(1)2(1)2(1). The cell parameters were determined on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation: a = 11.5318(7) , b = 12.6572(7), c = 17.0179(10) Å, α = 90°, β = 90°, γ = 90°. V = 2483.9(3) Å^3, Z = 4, D_c = 2.176 g/cm^3, μ = 32.33 cm^{-1}, θ_{max} = 28.26° and F(000) = 1568.00. 5785 unique reflections were collected at 293K. The final cycle of full-matrix least-squares refinement was based on 5367 observed reflections $[I{>}2\sigma(I)]$ and 339 variable parameters and converged at final R = 0.0366, R_w = 0.0899. Minimum and maximum final electron densities were –1.190 and 0.952 e/Å^3. All the calculations were performed using the SHELXTL-97 crystallographic software package of Molecular Structure Corporation. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined istropically.

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