SHORT PAPER

J. Chem. Research (S),
2002, 622–623

Syntheses and characterisation of new Rh–Co mixed-metal octahedral linked clusters[†]

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The new Rh–Co mixed-metal dimer $[Rh_2Co_2(CO)_8(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}HC{\equiv}CCH_2O\text{-})]_2C_6H_4$ **4** and trimer $[Rh_2Co_2(CO)_8(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}HC{\equiv}CCH_2O\text{-})]_3B$ **5** have been synthesised from reactions between $Rh_2Co_2(CO)_{12}$ **1** and the appropriate diyne and triyne ligands. The crystal structure of cluster **4** has been determined.

Keywords: Rh-Co mixed-metal octahedral linked clusters

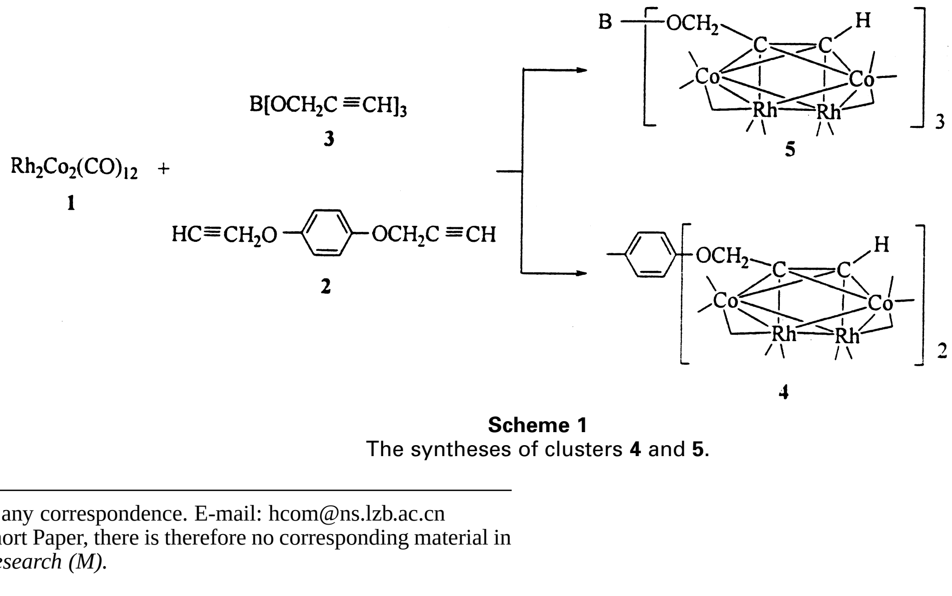
It is well known that alkynes are able to coordinate to transition metals in a variety of bonding modes[1] and molecules containing two or three alkynyl groups can act as chelating ligands.[2] It has been shown that the reactions of $Rh_2Co_2(CO)_{12}$ with several alkynes yield clusters of the type $Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}R_1C{\equiv}CR_2)$ which feature a transversely bridging alkyne ligand,[3–6] but no reactions of $Rh_2Co_2(CO)_{12}$ with diynes or triyne have been reported to our knowledge. Here, the new Rh–Co mixed-metal double octahedral cluster $[Rh_2Co_2(CO)_8(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}HC{\equiv}CCH_2O\text{-})]_2C_6H_4$ **4** and triple octahedral cluster $[Rh_2Co_2(CO)_8(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}HC{\equiv}CCH_2O\text{-})]_3B$ **5** have been obtained by reactions of $Rh_2Co_2(CO)_{12}$ **1** with the diyne $(HC{\equiv}CCH_2O\text{-})_2C_6H_4$ **2** and the triyne $(HC{\equiv}CCH_2O\text{-})_3B$ **3** in hexane at room temperature (Scheme 1). The clusters **4** and **5** are sensitive to tetrahydrofuran and light sensitive in air in solid state, and soluble in other common organic solvents. Satisfactory C, H analyses were obtained for the two clusters.

The IR spectra of **4** and **5** show intense terminal carbonyl and bridged carbonyl absorption bands in the range 2100–1856 cm^{-1}. The ^1H NMR spectra of clusters **4** and **5** are consistent with the alkyne-bridged structure. The signals at about δ 8.86–8.30 can be assigned to the protons of the terminal alkynes (C_2H) and a single peak at δ 4.31–4.10 can be assigned to methylene protons (CH_2) adjacent to the $C{\equiv}CH$ group. For the cluster **4**, the singlet at 6.82 reveals the protons of the benzene ring.

The structure features of this kind of clusters have been established by X-ray diffraction analysis of a suitable crystal of **4**. In the molecule the acetylene bridge inserts into the Co–Co bond and coordinates to all metal atoms as a μ_4,η^2-ligand forming two distorted closo-$Rh_2Co_2C_2$ octahedron framework which are connected via $C_6H_4(OCH_2)_2$-1,4 as a bridging unit (Fig. 1). In the octahedral core ($Rh_2Co_2C_2$) the cobalt atoms occupy the wing positions of the butterfly metal skeleton and the nonbonding distance between the two cobalt atoms Co1 and Co2 is 3.611 Å. The Rh1 atom is bonded to C12 and Rh2 is bonded to C11 of the acetylenic moiety. According to 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 metal atom is linked to two linear terminal carbonyl and one bridged carbonyl ligands.

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. $Rh_2Co_2(CO)_{12}$,[7] $(HC{\equiv}CCH_2O\text{-})_2C_6H_4$,[8] $(HC{\equiv}CCH_2O\text{-})_3B$ [9] were prepared according to literature methods. Infrared spectra were recorded on a Bruker 120 HR FT-IR spec-



Scheme 1
The syntheses of clusters **4** and **5**.

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

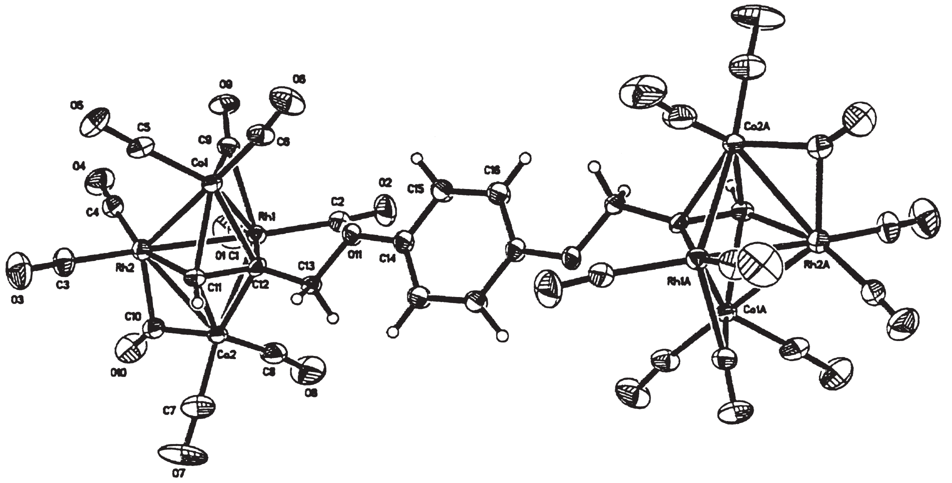

Fig.1 Crystal structure of the cluster **4**. Selected bond distances (Å) and angles (°): Rh(1)–C(12) 2.096(7); Rh(1)–Co(2) 2.5610(11); Rh(1)–Co(1) 2.5696(11); Rh(1)–Rh(2) 2.6570(9); Rh(2)–C(11) 2.083(7); Rh(2)–Co(2) 2.5413(12); Rh(2)–Co(1) 2.5526(11); Co(1)–C(11) 2.105(7); Co(1)–C(12) 2.075(6); Co(2)–C(11) 2.049(7); Co(2)–C(12) 2.132(7); C(11)–C(12) 1.410(10); C(14)–C(16)#1 1.389(10); C(16)–C(14)#1 1.389(10); C(12)–Rh(1)–Co(2) 53.36(19); C(12)–Rh(1)–Co(1) 51.60(18); Co(2)–Rh(1)–Co(1) 89.75(4); C(12)–Rh(1)–Rh(2) 72.97(18); Co(2)–Rh(1)–Rh(2) 58.25(3); Co(1)–Rh(1)–Rh(2) 58.44(3); C(11)–Rh(2)–Co(2) 51.46(19); C(11)–Rh(2)–Co(1) 52.85(19); C(11)–Rh(2)–Rh(1) 72.3(2); Co(2)–Rh(2)–Rh(1) 58.98(3); Co(1)–Rh(2)–Rh(1) 59.07(3); C(11)–Co(1)–C(12) 39.4(3); C(11)–Co(1)–Rh(2) 52.1(2); C(12)–Co(1)–Rh(1) 52.34(19); Rh(2)–Co(1)–Rh(1) 62.49(3); C(11)–Co(2)–C(12) 39.4(3); C(11)–Co(2)–Rh(2) 52.7(2); C(12)–Co(2)–Rh(1) 52.09(19); Rh(2)–Co(2)–Rh(1) 62.76(3); Symmetry transformations used to generate equivalent atoms: #1 *-x*,*-y*+1,*-z*+2.

trophotometer. ^{1}H NMR spectra were measured on a Bruker AM-400 MHz spectrometer; Elemental analyses (C, H) were performed on a Carlo-Erba 1106 type analyzer.

Synthesis of cluster **4**: To a solution of **1** (99 mg, 0.15 mmol) in 15 ml of hexane at room temperature was added dropwise a solution of **2** (28 mg, 0.15 mmol) in 10 ml of *n*-hexane under nitrogen. The mixture was stirred at room temperature for 2 h. During stirring the colour of the solution gradually changed from brown to purple, and monitoring by TLC showed the disappearance of the starting material. After the 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 (1:1) afforded the major purple band. Condensing the solvent and crystallisation at –20^{o}C gave dark purple crystals **4** (63 mg, 60.3%). IR (KBr disc): ν (CO) 2097m, 2047vs, 2026s, 2018vs, 1981s, 1869s, 1856m cm^{-1}; ^{1}H-NMR($CDCl_3$, 400MHz): δ 8.86 (s, 1H, ≡CH), 8.32 (s, 1H, ≡CH), 6.82 (s, 4H, C_6H_4), 4.31 (s, 2H, CH_2).

Synthesis of cluster **5**: The preparation procedure for **5** was similar to **4**. To a solution of **1** (99 mg, 0.15 mmol) in 15 ml of *n*-hexane at room temperature was added dropwise a solution of **3** (18 mg, 0.10 mmol) in 5 ml of CH_2Cl_2 under nitrogen. The mixture was stirred at room temperature for 3 h. The product was purified by chromatography on silica gel using CH_2Cl_2/petroleum ether (2:1) as an eluent and gave the dark purple **5** (57 mg, 57.4%). IR(KBr disc): ν (CO) 2100m, 2038vs, 1996s, 1895m, 1868m cm^{-1}; ^{1}H-NMR($CDCl_3$, 400 MHz): δ 8.86 (s, 1H, ≡CH), 8.30 (s, 1H, ≡CH), 4.10 (s, 2H, CH_2).

Crystal data of cluster **4**: Suitable crystals of cluster **4** ($C_{32}H_{10}O_{22}Co_4Rh_4$) (Mr = 1393.76) were obtained from CH_2Cl_2-hexane at –20^{o}C. The crystal system and pace group was triclinic and *P–1*, respectively. The cell parameters were determined on a Bruker CCD APEX diffractometer with graphite-monochromated Mo–K_α radiation: $a = 8.8533(13)$, $b = 8.8641(13)$, $c = 13.858(2)$ Å, $\alpha = 92.976(3)^\circ$, $\beta = 108.512(3)^\circ$, $\lambda = 92.473(2)^\circ$. $V = 1027.8(3)$ Å^3, $Z = 2$, $D_c = 2.252$ g/cm^3, $\mu = 32.19$ cm^{-1}, $\theta_{max} = 28.34^\circ$ and $F(000) = 666$. A total of 6227 reflections were collected with 4542 unique reflections ($R_{int} = 0.0657$). The structure was solved by direct method and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3492 observed reflections [$I>2\sigma(I)$] and 288 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.0519$, $R_w = 0.1485$. The minimum and maximum final electron densities were –1.602 and 1.642 eÅ^{-3}. All the calculations were performed using the SHELXL-97 crystallographic program package.

Received 17 June 2002; accepted 17 August 2002
Paper 02/1427

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