Synthesis and crystal structure of the chiral-linked tetrahedral cluster $[(\mu_3\text{-Se})RuCo_2(CO)_8]_2$ (DIOP)

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The new chiral Ru–Co mixed-metal linked tetrahedral cluster $[(\mu_3\text{-Se})RuCo_2(CO)_8]_2$(DIOP) **3** has been synthesised from reaction between $(\mu_3\text{-Se})RuCo_2(CO)_9$ **1** and the (–)-DIOP [**2** (2,2-dimethyl-1,3-dioxolane-4,5-diylbis-methylene) bisdiphenylphosphine] diphosphine compound. The structure of cluster **3** has been established by single-crystal X-ray diffraction method.

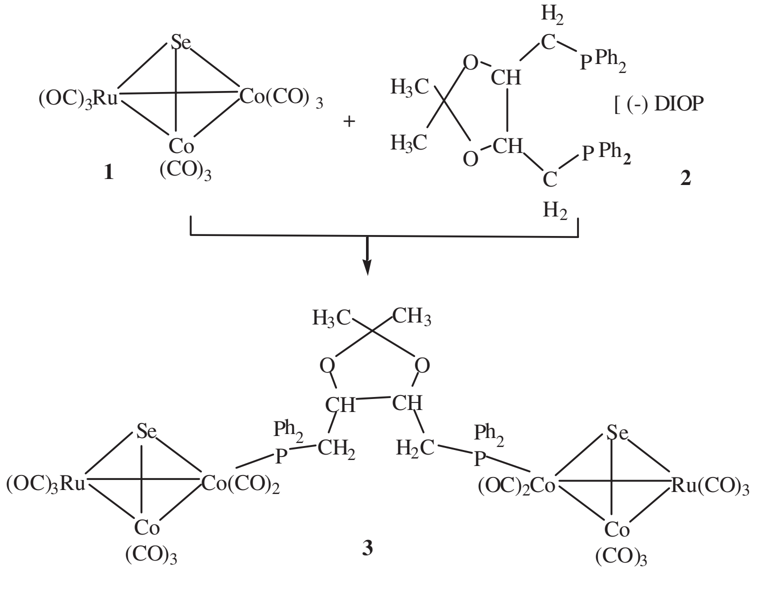
Keywords: chiral, Ru–Co cluster, tetrahedral, DIOP, X-ray

Transition metal carbonyl cluster compounds have attracted significant interest for a variety of reasons including, inter alia, the transition from molecular to bulk metallic properties which should ensue upon increasing cluster size,[1-4] as models for metal surfaces in chemisorption and catalysis,[5-8] and as precursors for metal particles active in heterogeneous catalysis.[5,6,8] It is well known that phosphine ligands containing aromatic substituents are versatile and widely used reagents in organometallic chemistry,[9-11] for example, some organometallic compounds containing the DIOP ligand have been reported previously.[12-16] However, no reactions of mixed-metal tetrahedral carbonyl clusters with DIOP were reported, to our knowledge. Herein, the new Ru–Co mixed-metal linked tetrahedral cluster $[(\mu_3\text{-Se})RuCo_2(CO)_8]_2$(DIOP) **3** has been obtained by reaction of $(\mu_3\text{-Se})RuCo_2(CO)_9$ **1** with diphosphine compound (–)-DIOP **2** in hexane at room temperature (Scheme 1). The cluster **3** is stable in air in solid state and soluble in common organic solvents. Satisfactory C, H analysis was obtained for **3.**

The IR spectrum of **3** shows a weak absorption band around 3054 cm^{-1} and intense absorption bands in the range 2084–1872 cm^{-1}, characteristic of the benzene rings of DIOP attached to the cobalt atom and the terminal carbonyl and semi-bridged carbonyl ligand, respectively. The ^1H NMR spectrum of cluster **3** is consistent with the DIOP-bridged structure. The signals at about δ 7.64–7.12 reveal the protons of the benzene ring. The doublet at 3.93–3.83 can be assigned to the protons of the CH group of the DIOP and the signals at δ 2.62–2.37 which can be assigned to methylene protons (CH_2). The singlet at δ 1.27 reveals the protons of the methyl. The ^{31}P NMR spectrum of 3 shows a doublet at δ 53.21–52.04, assigned to the phosphorus atoms bonded to cobalt atom.

The structure features of cluster **3** have been established by X-ray diffraction analysis of a suitable crystal. As seen in Fig. 1, the structure of **3** contains two slightly distorted tetrahedral cores $SeRuCo_2$, which are connected *via* DIOP as a bridging unit. The phosphorus atoms of DIOP ligand substituted one carbonyl of one of two cobalt atom of each $SeRuCo_2$ core, respectively, and the average bond distance between the cobalt atom and phosphorus atom is 2.187 Å. So, both $SeRuCo_2$ cores can be viewed as chiral units resulting from the different coordination environments of the two cobalt atoms in each tetrahedral framework. It should be noted that each $SeRuCo_2$ core contains a total of 48 electrons and is electronically saturated.

Co(1)–Se(1) 2.299(3); Co(2)–Se(1) 2.290(3); Ru(1)–Se(1) 2.438(3); Co(1)–Co(2) 2.533(3); Ru(1)– Co(2) 2.636(3); Ru(1)–Co(1) 2.649(3); Co(3)–Se(2) 2.317(3); Co(4)–Se(2)



Scheme 1 The synthesis of cluster 3.

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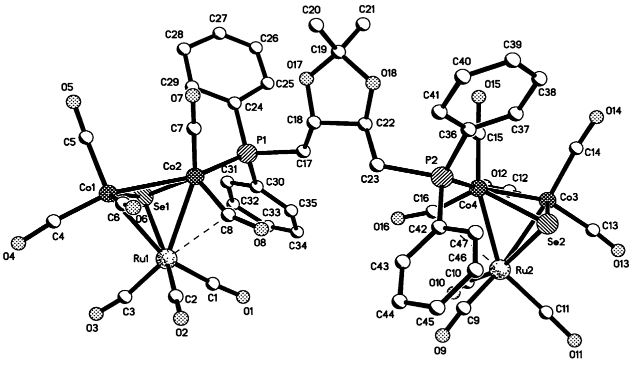

Fig.1 Crystal structure of the cluster **3** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (°):

2.298(3); Ru(2)–Se(2) 2.431(3); Co(3)–Co(4) 2.536(3); Ru(2)–Co(3) 2.641(3); Ru(2)–Co(4) 2.660(3); Co(2)–P(1) 2.192(5); Co(4)–P(2) 2.185(5); Co(2)–C(8) 1.72(2); Ru(1)–C(8) 2.45(2); Co(4)–C(16) 1.72(2); Ru(2)–C(16) 2.61(2); Se(1)–Ru(1)–Co(2) 53.50(8); Co(2)–Ru(1)–Co(1) 57.27(9); Se(1)–Co(1)–Co(2) 56.34(9); Se(1)–Co(2)– Ru(1) 58.82(9); Se(1)–Co(1)–Ru(1) 58.51(9); Co(2)–Co(1)–Ru(1) 61.10(9); Co(1)–Co(2)–Ru(1) 61.63(9); Co(2)–Se(1)–Ru(1) 67.68(10); Co(1)–Se(1)–Ru(1) 67.94(10); Se(1)–Co(2)–Co(1) 56.68(9); Se (2)–Co(4)–Ru(2) 58.18(9);Co(4)–Se(2)–Co(3) 66.65(10); Se(2)–Ru(2) –Co(4) 53.45(8); Co(3)– Se (2)–Ru(2) 67.54(9); Se(2)–Co(3)–Co(4) 56.32(9).

Experimental

All preparative work was carried out under an atmosphere of pure dinitrogen by using standard Schlenk or vacuum-line techniques. Column chromatography was carried out using silica gel columns of 160–200 mesh. (μ_3-Se)RuCo$_2$(CO)$_9$ [17] was prepared according to the literature method with little modification and (–)-DIOP was a commercial sample. Infrared spectra were recorded on a Bruker 120 HR FT–IR spectrophotometer. ^{1}H(^{31}P)NMR spectra were measured on a BrukerAM-400 MHz spectrometer. Elemental analyses (C, H) were performed on a Carlo-Erba 1106 type analyzer.

Synthesis of cluster [(μ_3-Se)RuCo$_2$(CO)$_8$]$_2$(DIOP) **3**: To a solution of 1 (166 mg, 0.30 mmol) in 20 ml of *n*-hexane at room temperature was added dropwise a solution of **2** (75 mg, 0.15 mmol) in 5 ml of CH$_2$Cl$_2$ under nitrogen. The mixture was stirred at room temperature for 2 h. During the stirring the colour of the solution gradually changed from brown-red to black-red and monitoring by TLC showed the disappearance of the starting material. After hexane removed, the residue was extracted by a small amount of CH$_2$Cl$_2$ and transferred to the top of a 2.5 cm × 40 cm silica gel chromatography column. Elution with CH$_2$Cl$_2$/petroleum ether (1:3) afforded the major brown-red band. Condensing the solvent and crystallisation at –20°C gave black crystals **3** (210 mg, 90.8%, based on **2**). IR (KBr disc): ν (Ar–H) 3054w; ν (CO) 2084s, 2051vs, 2011vs, 1964s, 1872m cm^{-1}; ^{1}H NMR(CDCl$_3$, 400MHz): δ 7.64–7.12 (m, 20H, 4C$_6$H$_5$), 3.93-3.83 (d, 2H, 2CH), 2.62–2.37 (m, 4H, 2CH$_2$), 1.27 (s, 6H, 2CH$_3$) ppm. ^{31}P-NMR(CDCl$_3$, 400MHz): δ 53.21–52.04 (d, 2P) ppm.

Crystal data of cluster **3**: Suitable crystals of cluster **3** (C$_{47}$H$_{32}$O$_{18}$Se$_2$P$_2$Co$_4$Ru$_2$) (Mr = 1542.45) were obtained from CH$_2$Cl$_2$–hexane at –20°C. The crystal system and pace group was orthorhombic and *P2(1)2(1)2(1)*, respectively. The cell parameters were determined on a Bruker APEX CCD diffractometer with graphite-monochromated Mo-K$_\alpha$ radiation: a = 9.625(3), b = 20.134(7), c = 28.140(10) Å, β = 90°, V = 5453(3) Å^3, Z = 4, D_c = 1.879 g/cm^3, μ = 31.91 cm^{-1}, θ_{max} = 25.00° and $F(000)$ = 3008. A total of 26948 reflections were collected with 9576 unique reflections (R_{int} = 0.1855). The structure was solved by direct methods and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added according to the geometrical method. The final cycle of full-matrix least-squares refinement was based on 9576 observed reflections [$I > 2\sigma(I)$] and 680 variable parameters and converged with unweighted and weighted agreement factors of R = 0.0850, R_w = 0.1692. The minimum and maximum final electron densities were -0.906 and 1.694 eÅ^{-3}. All the calculations were performed using the SHELXL-97 crystallographic program package.

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