Synthesis and *X*-Ray Crystal Structure of the Mixed-metal Cluster $H_2Ru_2Rh_2(CO)_{12}$

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The *X*-ray analysis of $H_2Ru_2Rh_2(CO)_{12}$, the first example of a unsubstituted Ru–Rh cluster, reveals a $Rh_4(CO)_{12}$-like cluster core in which the hydrogen atoms bridge a Ru–Ru and a Ru–Rh bond.

Although there have been a number of studies of mixed-metal clusters recently,[1] clusters containing ruthenium and rhodium atoms are virtually unknown, the only examples being two clusters having large organic ligands.[2] Mixed-metal clusters of this type might prove useful, *e.g.* in catalysis of the reactions relevant to C_1-chemistry, and the need for their synthesis has been mentioned.[3] We report here the synthesis and *X*-ray crystal structure of a carbonyl hydride cluster containing ruthenium and rhodium, apparently a promising parent compound for ruthenium–rhodium derivative chemistry.

Reaction of $NaRh(CO)_4$[4] and $Ru_3(CO)_{12}$ in tetrahydrofuran (THF) at room temperature gave a reddish-brown solution in one hour. After evaporation *in vacuo*, the residue was treated with 85% H_3PO_4 and the neutral hydride was then extracted into hexane. The impure product was chromatographed on silica gel; a broad yellow band (ruthenium species) followed by a reddish-brown band $[H_2Ru_2Rh_2(CO)_{12}]$ were eluted, with a total yield of *ca.* 25% based on the starting $Ru_3(CO)_{12}$. Air-stable red crystals suitable for *X*-ray analysis† were grown by slow evaporation of a saturated solution (CH_2Cl_2–hexane, 1:1). The complex $H_2Ru_2Rh_2(CO)_{12}$ exhibits ν_{CO} stretching frequencies at 2108vw, 2084vs, 2064vs, 2056vs, 2044w, 2034s, 2021m, 2012m, 1913m, and 1860m cm^{-1}. Its structure is shown in Figure 1. A qualitative elemental analysis confirmed the presence of ruthenium and rhodium.

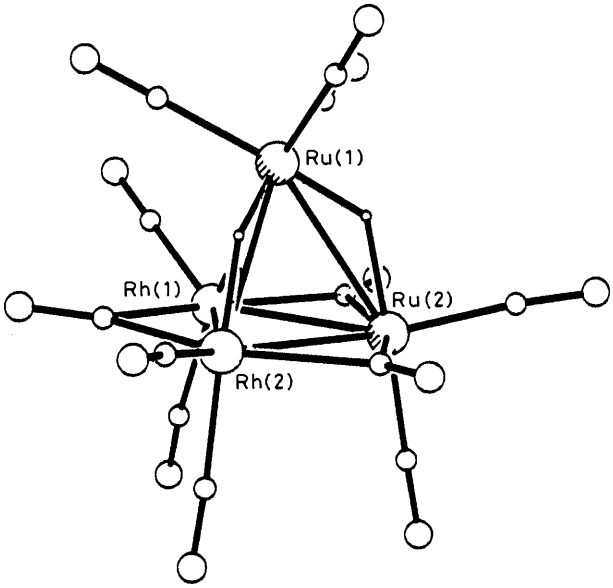

Figure 1. The molecular structure of $H_2Ru_2Rh_2(CO)_{12}$. Selected bond lengths (mean values of the two clusters in a unit cell): Rh(1)–Ru(1) 2.729, Ru(1)–Rh(2) 2.900, Ru(1)–Ru(2) 2.909, Rh(1)–Ru(2) 2.756, Ru(2)–Rh(2) 2.783, Rh(1)–Rh(2) 2.748 Å.

Two hydride clusters of this type, $H_2Co_2Os_2(CO)_{12}$[6] and $H_2Co_2Ru_2(CO)_{12}$,[7] are known. The $Rh_4(CO)_{12}$-like cluster core is distorted by the greater lengths of the hydrogen-bridged metal bonds,[9] and by the repulsive effect of the hydrogen atoms on the carbonyl groups. The hydrogen atoms are in asymmetric positions with respect to the metal core, which indicates that hydrogen prefers to bridge the Ru–Ru bond.

The four different Ru–Rh bond distances are between the Rh–Rh bond length in $Rh_4(CO)_{12}$ (mean value 2.73 Å)[8] and Ru–Ru bond lengths in $H_4Ru_4(CO)_{12}$ (mean values:

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†*Crystal data:* $C_{12}H_2O_{12}Ru_2Rh_2$, $M = 746.1$, triclinic, space group $P1$, $a = 9.841(4)$, $b = 9.883(4)$, $c = 10.033(3)$ Å, $\alpha = 94.70(3)$, $\beta = 90.84(3)$, $\gamma = 98.19(3)°$, $U = 962.2(6)$ Å^3, $Z = 2$, $D_c = 2.59$ g cm^{-3}, $F(000) = 722$. 3681 intensities in the range $5° < 2\theta < 50°$ were recorded on a Nicolet R3m diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). 3389 absorption-corrected data with $I \geqslant 2.5\sigma(I)$ were used to find the positions of the metal atoms and the carbonyls by direct methods and Fourier synthesis in the space group $P\bar{1}$. The two hydrogen atoms were assigned by the method of La Placa and Ibers.[5] A series of difference Fourier maps based on low angle reflection data were calculated with sin θ/λ limits of 0.35, 0.30, and 0.25 Å^{-1}. The peaks due to the hydrogen atoms were enhanced strongly relative to the others. Difference Fourier maps were then calculated with all the metal atoms treated as ruthenium or rhodium. From the positive and negative electron density differences the metal atoms were assigned as one ruthenium atom, one rhodium atom, and two disordered Ru–Rh atoms. The structure was subsequently refined in the space group $P1$. The disorder in the two metal atoms was resolved with a non-centrosymmetric arrangement, which produced featureless difference maps and lowered R from 0.0258 to 0.0248 for the metal atoms, when the rest of the clusters were fixed to the centrosymmetric structure. Full refinement of both the clusters led to final values $R = 0.0232$ and $R_w = 0.0239$. The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

hydrogen–bridged 2.95 Å, non-bridged 2.79 Å).[10] The Rh(1)–Ru(1) bond is shorter than the non-bridged Rh-Ru bonds in $[Ru_3Rh_2(CO)_{13}(PEt_3)(\mu_4\text{-}PPh)]$ (2.783 and 2.758 Å). The present cluster provides the first example of hydrogen-bridged and carbonyl-bridged Ru–Rh bonds.

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