Novel Co-ordination Modes for Bimetallic HgCo and HgMo Fragments when Bonded to Clusters; *X*-Ray Crystal Structure of $RuCo_3(\mu\text{-}CO)_3(CO)_9[\mu_3\text{-}HgCo(CO)_4]$

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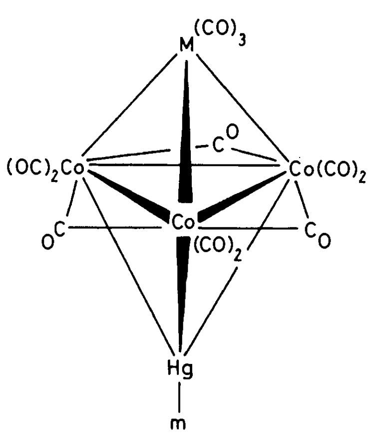
Hexametallic clusters have been prepared and characterized in which the $Hg\text{–}Co(CO)_4$ or $Hg\text{–}Mo(CO)_3(\eta\text{-}C_5H_5)$ fragment is μ_3-bonded below the Co_3 face of the MCo_3 (M = Fe, Ru) tetrahedral precursor species; the structure of $RuCo_3(\mu\text{-}CO)_3(CO)_9[\mu_3\text{-}HgCo(CO)_4]$ has been determined by *X*-ray diffraction.

The bimetallic $Hg\text{–}Co(CO)_4$ group has previously been found bonded to other metals in only two ways: a linear co-ordination to Fe and Co in $(\eta\text{-}C_5H_5)(OC)_2Fe\text{–}Hg\text{–}Co(CO)_4$[1] and $Hg[Co(CO)_4]_2$,[2] respectively; and an edge-bridging position in $\{Ge[Co_2(CO)_7][Co_2(CO)_6(\mu\text{-}Hg(CO)_4)]\}^-$.[3]

We report here our preliminary results on a new cluster where for the first time the $Hg\text{–}Co(CO)_4$ group is in a face-bridging position, and also our results on related molecules.

The reaction of the cluster $Na[RuCo_3(CO)_{12}]$[4] with one equivalent of $HgBr_2$ (toluene, 25 °C, 1 h), followed by evaporation to dryness, extraction, and crystallisation from hexane, yielded (**1**)† as black crystals (10%). Further extraction of the solid residue with CH_2Cl_2 gave (**2**)† (40%).



(**1**); M = Ru, m = $Co(CO)_4$
(**4**); M = Fe, m = $Mo(CO)_3(\eta\text{-}C_5H_5)$
(**5**); M = Ru, m = $Mo(CO)_3(\eta\text{-}C_5H_5)$

$MCo_3(CO)_{12}HgBr$
(**2**); M = Ru
(**3**); M = Fe

Complexes (**1**) and (**2**) have analogous spectroscopic properties† and are chemically related since (**1**) can also be prepared by reaction of (**2**) with one equivalent of $Na[Co(CO)_4]$ (CH_2Cl_2, 25 °C, 0.5 h) (56%).

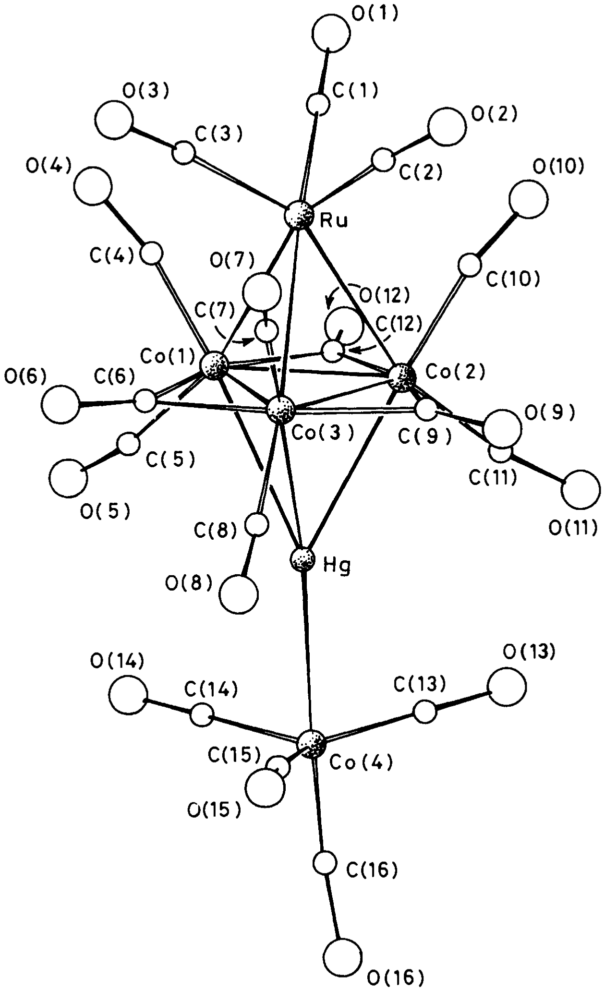


Figure 1. Molecular structure of the complex $RuCo_3(CO)_{12}[\mu_3\text{-}HgCo(CO)_4]$ (**1**). Important bond distances (Å) and angles (°): Hg–Co(1) 2.765(5), Hg–Co(2) 2.706(5), Hg–Co(3) 2.799(5), Hg–Co(4) 2.526(5), Ru–Co(1) 2.686(5), Ru–Co(2) 2.686(5), Ru–Co(3) 2.677(6), Co(1)–Co(2) 2.509(6), Co(1)–Co(3) 2.519(7), Co(2)–Co(3) 2.499(7); Co(1)–Hg–Co(4) 148.2(2), Co(2)–Hg–Co(4) 145.7(2), Co(3)–Hg–Co(4) 150.9(2), Co(1)–Hg–Co(2) 54.6(1), Co(1)–Hg–Co(3) 53.8(1), Co(2)–Hg–Co(3) 54.0(1), Co(1)–Ru–Co(2) 55.7(1), Co(1)–Ru–Co(3) 56.0(1), Co(2)–Ru–Co(3) 55.6(2), Co(2)–Co(1)–Co(3) 59.6(2), Co(1)–Co(2)–Co(3) 60.4(2), Co(1)–Co(3)–Co(2) 60.0(2).

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† Satisfactory analytical data were obtained for all new compounds. Selected data: compound (**1**) i.r. (CH_2Cl_2) ν(CO) at 2102w, 2082s, 2041s, 1998m, and 1877m cm^{-1}; u.v. (CH_2Cl_2) λ_{max} at 326, 400 (sh), and 506 nm; *m/z*: 988; (**2**) i.r. (CH_2Cl_2) ν(CO) at 2101m, 2058sh, 2045s, and 1884m cm^{-1}; u.v. (CH_2Cl_2) λ_{max} at 316, 350 (sh), 394 (sh), and 495 nm; (**3**) i.r. (CH_2Cl_2) ν(CO) at 2090w, 2048s, 2020m, and 1883m cm^{-1}; u.v. (CH_2Cl_2) λ_{max} 335, 395, (sh), and 565 nm; (**4**) i.r. (hexane) ν(CO) at 2079w, 2038s, 2028s, 2005s, 1940w, 1919s, 1879w, and 1872m cm^{-1}; u.v. (CH_2Cl_2), λ_{max} at 336, 400 (sh), and 572 nm; *m/z*: 1015; (**5**) i.r. (hexane) ν(CO) at 2092m, 2045s, 2032s, 2017w, 2004m, 1939m, 1919m, 1878m, and 1871m cm^{-1}; u.v. (CH_2Cl_2), λ_{max} at 333, 390 (sh), and 505 nm; ^1H n.m.r. ($CDCl_3$) δ at 5.27 (C_5H_5); *m/z*: 1060.

The structure of (**1**) has been determined by *X*-ray diffraction,‡ and is shown in Figure 1. It consists of a $RuCo_3$ tetrahedron, of which the Co_3 face is capped by a $[HgCo(CO)_4]$ fragment. Each Co–Co edge is asymmetrically bridged by a carbonyl group. The mercury atom is in a strongly distorted tetrahedral arrangement involving the three Co atoms of the tetrahedron and Co(4) atom from the $Co(CO)_4$ group. The $RuCo_3Hg$ core forms a trigonal bipyramid with the Ru and Hg atoms at the apices, 2.26 Å above and 2.34 Å below the plane of the Co atoms, respectively. This arrangement is quite similar to the MCo_3M' cores (M = Fe or Ru; M' = Cu, Ag, Au) where the $M' \leftarrow PR_3$ fragments triply bridge the Co_3 face through the M' metal.[4—6] The bridging unit in (**1**) can be considered as the formally d^{10} $[HgCo(CO)_4]^+$ cation and behaves as the $CuPR_3^+$ or $AuPR_3^+$ units. Moreover it provides an analogy with the recently reported d^{10} Ag^+ cation acting as a Lewis acid,[7,8] all these fragments possessing electronic and symmetry properties similar to the hydride ligand. Although the bonding mode reported here for the $[HgCo(CO)_4]$ fragment is unprecendented, it can now be anticipated that it will be found in other polymetallic systems.

This could be extended to other Hg–m fragments which are formally equivalent to H or $M' \leftarrow PR_3$ (M' = Cu, Ag, Au). Thus we have found that (**3**),† prepared from $K[FeCo_3(CO)_{12}]$,[9] and (**2**) react with one equivalent of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ (CH_2Cl_2, 25 °C, 0.5 h) to give the new pentametallic clusters (**4**)† and (**5**)†, respectively, containing four different metals.

The $Hg\text{–}Mo(CO)_3(\eta\text{-}C_5H_5)$ moiety has previously been found in the clusters $(C_2Bu^t)Ru_3(CO)_9HgMo(CO)_3(\eta\text{-}C_5H_5)$[10] and $[MoHgMo(CO)_3(\eta\text{-}C_5H_5)]_4$,[11] but never, to our knowledge, μ_3-capping a *closo* triangular face.

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‡ *Crystal data* for: (**1**) (single crystals from hexane), $C_{16}Co_4HgRuO_{16}$, $M = 985.56$, orthorhombic, space group *Pbca*, $a = 37.028(18)$, $b = 10.247(4)$, $c = 12.802(10)$ Å, $U = 4857(5)$ Å^3, $Z = 8$, $D_c = 2.695$ g cm^{-3}, $F(000) = 3648$, $\mu(\text{Mo-}K_\alpha) = 96.36$ cm^{-1}. The intensities of 3373 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3—23°), using Nb-filtered Mo-K_α radiation and the $\theta/2\theta$ scan technique. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares on the basis of 1532 observed reflections having $I \geqslant 2\sigma(I)$ to an R value of 7.3%. 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, W. Germany. Any request should be accompanied by the full literature citation for this communication.