Synthesis and *X*-Ray Crystal Structure of the $[Rh_5(CO)_8(\mu\text{-}CO)_6I]^{2-}$ Anion Containing a Trigonal Bipyramidal Rhodium Cluster

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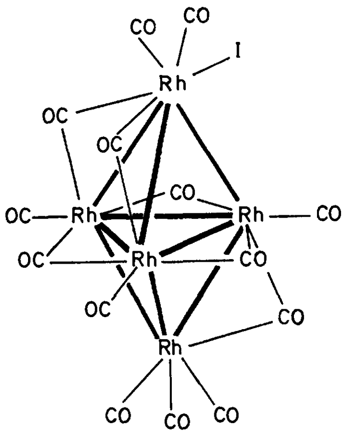
Summary The anion $[Rh_5(CO)_{14}I]^{2-}$ (**1**) has been obtained by reaction of I^- with $Rh_4(CO)_{12}$; the cluster, containing five metal atoms, consists of an elongated trigonal bipyramid with the iodide ligand terminally bound to an apical rhodium atom.

Five-atom compact clusters are uncommon. There are two known examples of homonuclear trigonal bipyramidal species, $Os_5(CO)_{16}$[1] and $[Ni_5(CO)_{12}]^{2-}$[2] and a few examples of heteronuclear species, such as $[Ni_3M_2(CO)_{16}]^{2-}$ (M=Cr, Mo, or W),[3] $Pt_3Co_2(CO)_9(PEt_3)_3$,[4] and $[PtRh_4(CO)_{14}]^{2-}$.[5] We report here the synthesis and *X*-ray characterization of the new pentanuclear dianion $[Rh_5(CO)_{14}I]^{2-}$ (**1**).[6]

We have already shown that the reaction of $Rh_6(CO)_{16}$ with NR_4I in a 1:1 molar ratio as well as the reaction of $Rh_4(CO)_{12}$ with NR_4I in a 3:2 molar ratio gives rise to the $[Rh_6(CO)_{15}I]^-$ anion,[7] and that the reaction of $Rh_6(CO)_{16}$ with an excess of NR_4I under certain conditions gives rise to the $[Rh_7(CO)_{16}I]^{2-}$ dianion.[8] We have now found that the reaction of $Rh_4(CO)_{12}$ with NBu_4I or $AsPh_4I$ in a 1:2 molar ratio gives rise to the new $[Rh_5(CO)_{14}I]^{2-}$ dianion (**1**).



(1)

The reaction is carried out by stirring the reactants for 24 h in $\mathrm{Pr^iOH}$ under a CO atmosphere, according to the overall equation (1). The product separates out as a red powder and is purified by crystallization from tetrahydrofuran (THF)–$\mathrm{Pr^iOH}$ under CO using the slow diffusion

$$3\,Rh_4(CO)_{12} + 6\,NBu_4I \xrightarrow[\mathrm{Pr^iOH}]{25\,^{\circ}C} \underset{(\mathbf{1})}{2[NBu_4]_2\,[Rh_5(CO)_{14}I]} \downarrow + 2[NBu_4]\,[Rh(CO)_2I_2] + 4CO \qquad (1)$$

technique. The tetra-n-butylammonium salt of the $[Rh_5(CO)_{14}I]^{2-}$ anion has been investigated by *X*-ray diffraction.

Crystal data: $C_{46}H_{72}IN_2O_{14}Rh_5$, $M = 1518\cdot5$, orthorhombic, space group $Pn2_1a$ [non-standard setting of $Pna2_1$ (No. 33)], with $a = 27\cdot767(16)$, $b = 18\cdot652(11)$, $c = 11\cdot678(6)$ Å, $D_m = 1\cdot65(2)$, $D_c = 1\cdot67$ g cm^{-3} for $Z = 4$. The intensity data were collected on an automatic diffractometer with graphite monochromatized Mo-K_α radiation ($\lambda = 0\cdot7107$ Å) within the limits $3 < \theta < 25$ °. The structure was solved by conventional Patterson and Fourier methods and refined by block-matrix least-squares on the basis of 3151 independent observed reflections [$\sigma(I)/I \leqslant 0\cdot25$], up to a current R value of 5·0%.†

The anion is shown in the Figure. It contains a trigonal bipyramid of rhodium atoms elongated in the direction of the three-fold axis. The cluster can be described as an equatorial triangle of metal atoms, with normal Rh–Rh bond distances (mean 2·706 Å), plus two apical Rh atoms capping the triangle, which exhibit long bond distances from the equatorial ones (mean 2·979 Å). The iodide ligand is terminally bound to the apical metal atom Rh(5), with a long bond length of 2·861(3) Å.

The carbonyl ligands are bonded eight terminally and six edge-bridging. The latter are of two kinds: three are bridging on the equatorial triangular edges and are symmetric (mean Rh–C and C–O distances 2·09 and 1·16 Å, respectively) and three are bridging on the apical–equatorial edges and are significantly asymmetric (mean Rh_{eq}–C, Rh_{ap}–C, and C–O distances 1·95, 2·11, and 1·19 Å, respectively). For the terminal CO groups the Rh–C and C–O bond distances have mean values of 1·86 and 1·18 Å, respectively. As a result, each metal atom is connected to four carbonyl groups.

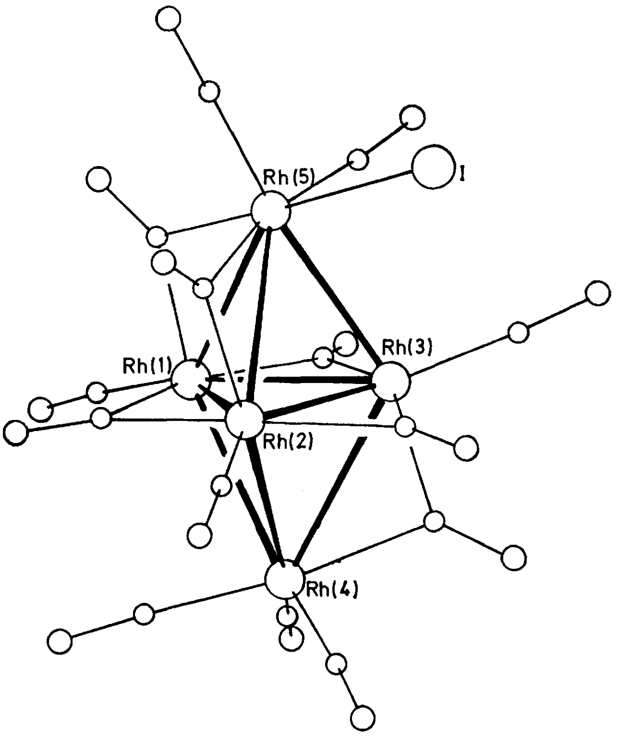


FIGURE. A view of the anion $[Rh_5(CO)_{14}I]^{2-}$. The Rh–Rh bond lengths are: Rh(1)–Rh(2) 2·672, Rh(1)–Rh(3) 2·719, Rh(2)–Rh(3) 2·726, Rh(4)–Rh(1) 2·955, Rh(4)–Rh(2) 3·038, Rh(4)–Rh(3) 2·928, Rh(5)–Rh(1) 3·014, Rh(5)–Rh(2) 2·948, Rh(5)–Rh(3) 2·989 Å (mean e.s.d.'s 0·002 Å).

The elongation of the cluster, which is in accord with the predictions of recent semi-empirical M.O. calculations[9] for trigonal bipyramidal species with 76 valence electrons, can be associated with the presence of four extra valence electrons and resembles that observed in $[Ni_5(CO)_{12}]^{2-}$,[2] although in our case the difference between the apical–equatorial distances and the other ones is less pronounced (mean values 2·979 *vs.* 2·706 Å).

The i.r. spectrum of the $AsPh_4^+$ salt in THF solution shows absorptions at 2050 (w), 2020(s), 2010(sh), and 1972(vs) cm^{-1} in the terminal CO region, and at 1870(vw), 1822(s), and 1762(m) cm^{-1} in the bridging CO region, in agreement with the *X*-ray structure.

The anion is stable only under a CO atmosphere, whose absence causes decomposition to uncharacterized products. It reacts with 0·5 mol. equiv. of $Rh_4(CO)_{12}$ or with 1 mol. equiv. of $[Rh(CO)_2(MeCN)_2]^+$ to give complex reactions which afford mainly $[Rh_7(CO)_{16}I]^{2-}$ or $[Rh_6(CO)_{15}I]^-$, respectively. The anion has now also been recognized as

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† The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universitat, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, West Germany; any request should be accompanied by the full literature citation for this communication.

one of the products of the reaction of $[Rh_7(CO)_{16}I]^{2-}$ with CO.[8] These reactions suggest that the new anion could play an important role in the comprehension of the chemistry of the halide-substituted rhodium carbonyl cluster anions.[9]

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