

Preliminary communication

HIGH NUCLEARITY Pt–Rh CARBONYL CLUSTERS. SYNTHESIS AND X-RAY CHARACTERIZATION OF THE $[\text{Pt}_2\text{Rh}_9(\text{CO})_{22}]^{3-}$ TRIANION

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Summary

The new mixed Pt–Rh cluster trianion $[\text{Pt}_2\text{Rh}_9(\text{CO})_{22}]^{3-}$ has been isolated as a minor product of the pyrolysis of $[\text{PtRh}_5(\text{CO})_{15}]^-$, and has been characterized by X-ray diffraction. The metal skeleton, which has ideal D_{3h} symmetry, consists of three face-to-face condensed octahedra, as previously found in the isoelectronic species $[\text{Rh}_{11}(\text{CO})_{23}]^{3-}$, with the Pt atoms on the three-fold axis, in the positions of maximum M–M connectivity.

We previously reported that prolonged pyrolysis of $[\text{PtRh}_5(\text{CO})_{15}]^-$ [2,3] in refluxing methanol yields the anions $[\text{Pt}_2\text{Rh}_{11}(\text{CO})_{24}]^{3-}$ and $[\text{PtRh}_{12}(\text{CO})_{24}]^{4-}$ together with some by-products [1]. When the crude $\text{K}_3[\text{Pt}_2\text{Rh}_{11}(\text{CO})_{24}]$ was submitted to purification by fractional precipitation of the Cs^+ salts from water, the first fraction obtained at a concentration of about 1.3% CsCl, after further metathesis performed by the slow diffusion of a 2-propanol solution of $[\text{NEt}_4]\text{Br}$ into a MeOH solution of the Cs^+ salts, gave, besides $[\text{NEt}_4]_3[\text{Pt}_2\text{Rh}_{11}(\text{CO})_{24}]$ as the main component, a few crystals of a new species which, after X-ray analysis, was characterized as $[\text{NEt}_4]_3[\text{Pt}_2\text{Rh}_9(\text{CO})_{22}]$.

The IR spectrum of $[\text{NEt}_4]_3[\text{Pt}_2\text{Rh}_9(\text{CO})_{22}]$, in MeCN solution shows two broad bands in the CO stretching region at 1993s and 1812 ms cm^{-1} .

Crystal data. $\text{C}_{46}\text{H}_{60}\text{N}_3\text{O}_{22}\text{Pt}_2\text{Rh}_9$, $M = 2323.3$, monoclinic, space group $P2_1/c$ (No.14), a 13.587(3), b 20.175(4), c 24.351(5) Å, β 103.48(2)°, $Z = 4$. The structure was solved by direct methods and refined by least-squares, on

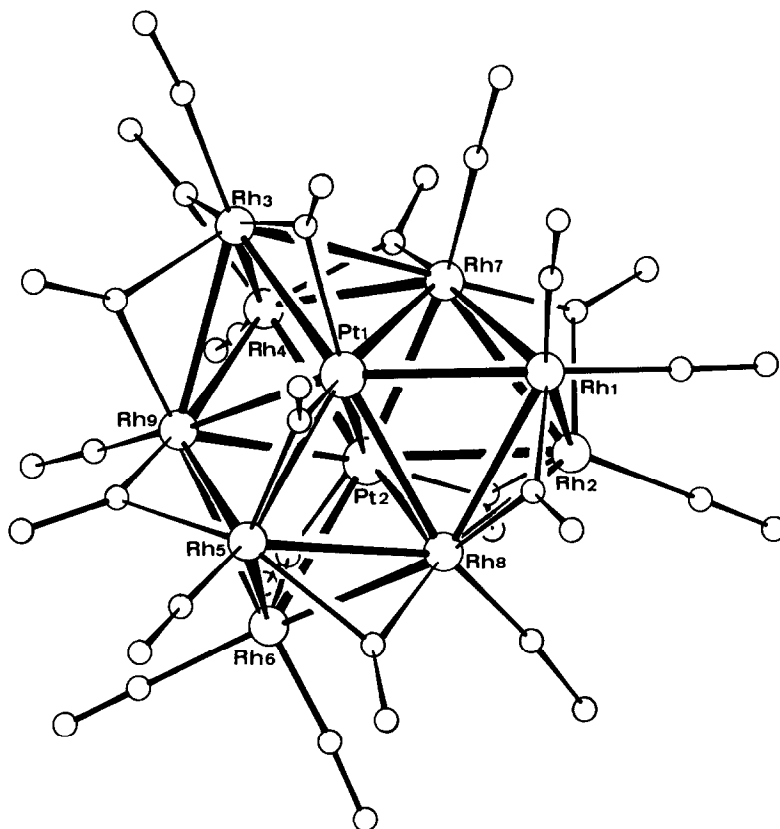


Fig. 1. A view of the anion $[\text{Pt}_2\text{Rh}_9(\text{CO})_{22}]^{3-}$. The individual metal—metal bond lengths (Å) are: Pt(1)—Pt(2) 2.812(2), Pt(1)—Rh(1) 2.666(3), Pt(1)—Rh(3) 2.735(3), Pt(1)—Rh(5) 2.720(3), Pt(1)—Rh(7) 2.743(3), Pt(1)—Rh(8) 2.666(3), Pt(1)—Rh(9) 2.698(3), Pt(2)—Rh(2) 2.687(3), Pt(2)—Rh(4) 2.679(3), Pt(2)—Rh(6) 2.654(3), Pt(2)—Rh(7) 2.669(3), Pt(2)—Rh(8) 2.761(3), Pt(2)—Rh(9) 2.765(3), Rh(1)—Rh(2) 2.721(4), Rh(1)—Rh(7) 2.911(4), Rh(1)—Rh(8) 2.792(4), Rh(2)—Rh(7) 2.834(4), Rh(2)—Rh(8) 2.944(4), Rh(3)—Rh(4) 2.734(4), Rh(3)—Rh(7) 2.997(4), Rh(3)—Rh(9) 2.854(4), Rh(4)—Rh(7) 2.826(4), Rh(4)—Rh(9) 2.954(4), Rh(5)—Rh(6) 2.781(4), Rh(5)—Rh(8) 2.820(4), Rh(5)—Rh(9) 2.893(3), Rh(6)—Rh(8) 2.893(4), Rh(6)—Rh(9) 2.824(3).

the basis of 2322 significant [$I > 3\sigma(I)$] counter data, up to a current conventional R value of 0.047*.

The structure of the anion $[\text{Pt}_2\text{Rh}_9(\text{CO})_{22}]^{3-}$ is shown in Fig. 1. The metal cluster, of idealized D_{3h} symmetry, is of the type found in the isoelectronic $[\text{Rh}_{11}(\text{CO})_{23}]^{3-}$ [4], consisting of three octahedral units condensed face-to-face, with a common edge, Pt(1)—Pt(2), coincident with the ideal three-fold axis. The two platinum atoms thus occupy the two positions with the highest metal—metal connectivity (7 M—M interactions). The anion bears 11 terminal and 11 edge-bridging carbonyls; the stereochemistry of the ligands is such that the overall anion does not show any symmetry. The 28 metal—metal

*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. Any request should be accompanied by a full literature citation for this communication.

bond lengths show considerable variation over the range 2.654(3)–2.997(4) Å, a feature observed also in the isoelectronic Rh₁₁ species, and essentially ascribed to the distortions required by the condensation of the three octahedral units. A comparison of the two undecametal arrays shows that the cluster possesses a certain flexibility. The central Pt(1)–Pt(2) bond, 2.812(2) Å, is markedly shorter than the corresponding Rh–Rh interaction in the Rh₁₁ anion, 2.965(1) Å. The 12 Pt–Rh bonds are similar, with a mean value of 2.707 Å, which is rather short when compared with the Pt–Rh interactions in [PtRh₅(CO)₁₅][–] (2.790 Å) [2] and in [PtRh₁₂(CO)₂₄]^{4–} (2.776 Å) [1]. The 15 Rh–Rh bond lengths exhibit the largest spread, the 7 bridged edges being on average shorter (mean 2.822 Å) than the unbridged ones (mean 2.878 Å). The location of the carbonyl is not related to that in [Rh₁₁(CO)₂₃]^{3–} except in the fact that the two platinum atoms do not possess terminal CO groups and are connected to two edge bridging ligands as is the case for the two corresponding Rh atoms of the other anion. Seven of the Rh atoms bear one terminal CO, while the other two, Rh(1) and Rh(6), bear two such ligands. The mean value of the Rh–C and C–O bond distances for the terminal groups are 1.82 and 1.15 Å, respectively. The bridging CO on the Rh(3)–Rh(4) edge is quite asymmetric (Rh(3)–C 2.36(4) Å, Rh(4)–C 1.87(4) Å), while the other ten show, only in some cases, a moderate asymmetry, with mean values of the Rh–C and C–O bond lengths of 1.95 and 1.27 Å, respectively.

The very small amount isolated indicates that this anion is an intermediate, unstable under the pyrolytic conditions used for the growth of the clusters, as previously observed for the isoelectronic [Rh₁₁(CO)₂₃]^{3–} [4], and it is probably the stage prior to the closure to the compact [Pt₂Rh₁₁(CO)₂₄]^{3–}. This can help in understanding of the pyrolytic cluster growing process which, from simple polyhedra, gives species of higher nuclearity with increasing compactness, and eventually fragments of metallic lattices with closest packing (hcp or ccp), containing a twelve coordinate interstitial metal as in [Pt₂Rh₁₁(CO)₂₄]^{3–} and [PtRh₁₂(CO)₂₄]^{4–}.

We are trying to develop new syntheses of [Pt₂Rh₉(CO)₂₂]^{3–} under mild conditions involving condensation of smaller clusters at room temperature.

References

- 1 A. Fumagalli, S. Martinengo and G. Ciani, *J. Chem. Soc., Chem. Commun.*, (1983) 1381.
- 2 A. Fumagalli, S. Martinengo, P. Chini, A. Albinati, S. Brückner, and B.T. Heaton, *J. Chem. Soc., Chem. Commun.*, (1978) 195.
- 3 A. Fumagalli, S. Martinengo, P. Chini, D. Galli, B.T. Heaton and R. DellaPergola, *Inorg. Chem.*, 1984 in press.
- 4 A. Fumagalli, S. Martinengo, G. Ciani and A. Sironi, *J. Chem. Soc., Chem. Commun.*, (1983) 453.