

Synthesis and Molecular Structure of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\mu\text{-Cl})_2(\mu\text{-CO})(\text{CO})_3]$, A Unique Triangular Rhodium Cluster Derivative

By RAYMOND J. HAINES* and N. D. C. T. STEEN

(Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, Republic of South Africa)

and ROBIN B. ENGLISH*

(Department of Chemistry, University of South Africa, P.O. Box 392, Pretoria, Republic of South Africa)

Summary Reaction of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ with PPh_2H in benzene produces a unique '56 electron' closed trinuclear rhodium cluster derivative $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\mu\text{-Cl})_2(\mu\text{-CO})(\text{CO})_3]$, in which each rhodium-rhodium edge is bridged by a diphenylphosphino-ligand as well as by either a chloro- or carbonyl group.

It has been patented¹ that treatment of $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]$ with PPh_2H in benzene leads to the formation of a product which, on the basis of analytical data, was proposed to be a non-closed tetranuclear species of stoichiometry $[\text{Rh}_4(\mu\text{-PPh}_2)_2(\mu\text{-Cl})_4(\text{CO})_4(\text{PPh}_2\text{H})_2]$. As part of a project aimed at the synthesis and chemistry of metal cluster compounds capped and/or bridged by various donor ligands we have reinvestigated this particular reaction and found that it affords at least three products, the structure of one of which is described in this communication.

Fractional crystallisation of the product mixture from the reaction employing a $[\{\text{Rh}(\text{CO})_2\text{Cl}\}_2]:\text{PPh}_2\text{H}$ molar ratio of 1:2 led to the isolation of an orange diamagnetic compound of stoichiometry $[\text{Rh}_3(\text{PPh}_2)_3(\text{Cl})_2(\text{CO})_4]$ (**1**), with a very simple band pattern in the C-O stretching region of both its solid state and solution i.r. spectra comprising one bridging and two terminal carbonyl peaks $[\nu(\text{C-O}): 2027(\text{sh}), 2008(\text{s}), \text{and } 1821(\text{m}) (\text{C}_6\text{H}_{12}) \text{ cm}^{-1}]$. It was apparent that the compound had an unusual structure and thus the structure was determined by an X-ray crystallographic study.

Crystal data: $[\text{Rh}_3(\text{PPh}_2)_3\text{Cl}_2(\text{CO})_4]\cdot\text{CH}_2\text{Cl}_2$, $M = 1132.14$, monoclinic, space group $P2_1/n$, $a = 12.461(5)$, $b = 32.867(5)$, $c = 11.149(5)$ Å, $\beta = 99.29(1)^\circ$, $U = 4506.2$ Å³, $D_m = 1.71(5)$, $D_c = 1.67$ g cm⁻³ {for $Z = 4$; $\mu(\text{Mo-K}\alpha) = 1.37$ mm⁻¹. Data were collected on a Philips PW1100 diffractometer (N.P.R.L., C.S.I.R., Pretoria) with graphite-monochromatized Mo-K α radiation in the 2θ range 7.5–46°. The structure was solved by direct methods on the basis of 6250 independent Lorenz- and polarisation-corrected reflections having $I > \sigma(I)$ and refined by blocked-matrix least squares to $R = 0.085$. R_w was 0.095 with a weighting scheme $w = 5.583/\sigma^2 F$.†

The molecular geometry of the compound is illustrated in the Figure. The complex adopts a triangular configuration with each rhodium-rhodium distance corresponding to a formal bond. Each of these bonds is bridged by a diphenylphosphino-ligand with two of the phosphorus atoms being cisoid with respect to the trirhodium plane and the third transoid. Two of the rhodium-rhodium bonds are also bridged by chloro-groups while the third is additionally bridged by a carbonyl ligand. Each rhodium atom has a

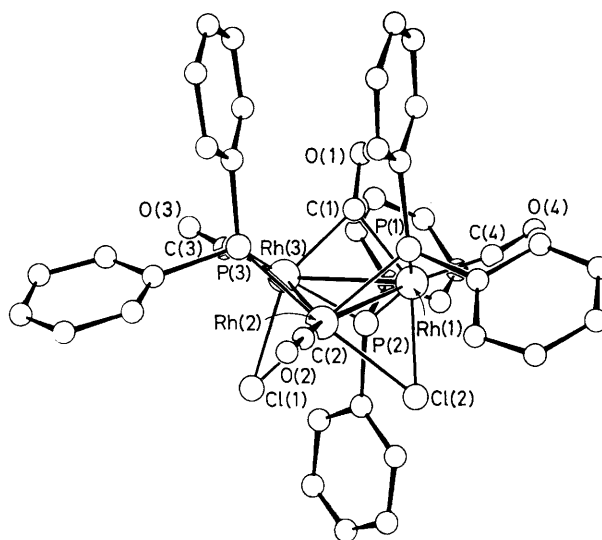


FIGURE. The molecular stereochemistry of $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\mu\text{-Cl})_2(\mu\text{-CO})(\text{CO})_3]$ (**1**). Bond lengths: Rh(1)-Rh(2), 2.783(1); Rh(1)-Rh(3), 2.698(1); Rh(2)-Rh(3), 2.814(1); Rh(1)-P(1), 2.321(3); Rh(2)-P(1), 2.286(3); Rh(1)-P(2), 2.335(3); Rh(3)-P(2), 2.331(3); Rh(2)-P(3), 2.290(3); Rh(3)-P(3), 2.320(3); Rh(2)-Cl(1), 2.487(3); Rh(3)-Cl(1), 2.559(3); Rh(1)-Cl(2), 2.576(3); Rh(2)-Cl(2), 2.471(4); Rh(1)-C(1), 2.016(12); Rh(3)-C(1), 2.002(12) Å.

terminal carbonyl co-ordinated to it. The overall disposition of all the bridging groups is such that the molecule contains an approximate plane of symmetry through Rh(2), P(2), the bridging carbonyl, and the terminal carbonyl co-ordinated to Rh(2).

A formal electron count on the basis that each carbonyl contributes two electrons to the metal framework, each diphenylphosphino-ligand three, each chloro-group three, and each rhodium-rhodium bond two electrons, gives 56, two in excess of that required by the 18-electron rule. This is quite unprecedented for closed trinuclear clusters; one other example of a trinuclear derivative containing more than 54 electrons is known, *viz.*, $[\text{Co}_3(\mu\text{-PPh})(\text{CO})_9]^2$ but this contains only one in excess. It is now apparent that, contrary to widely accepted views, the formalised 18-electron rule need not hold for metal clusters of any nuclearity.³ The rhodium-rhodium distances in (**1**) are very similar to those for $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ ⁴ which is not inconsistent with the two 'excess' electrons occupying an

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

orbital which is non-bonding with respect to the rhodium atoms.

Not surprisingly, the chloro-groups in (1) can be readily abstracted to produce, in the presence of carbon monoxide, $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]^4$ but, most unexpectedly, treatment of the latter with carbon tetrachloride leads to the regeneration of (1).

We thank the South African Council for Scientific and

Industrial Research and the Universities of Natal and South Africa for financial support, the National Institute for Metallurgy for a studentship (N.D.C.T.S.), Dr. J. Coetzer, N.P.R.L., C.S.I.R., Pretoria, for the data collection, and Johnson Matthey Ltd for the loan of rhodium salts.

(Received, 19th January 1981; Com. 057.)

¹ D. T. Thompson, Brit. Pat., 1969, 1 156 336.

² H. Beurich, T. Madach, F. Richter, and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 690.

³ It is well established that metal clusters of nuclearity of five and greater show a marked tendency to deviate from the 18-electron rule, E. L. Muetterties, T. N. Rhodin, E. Bond, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, 1979, **79**, 91.

⁴ R. J. Haines, N. D. C. T. Steen, and R. B. English, *J. Organomet. Chem.*, in the press.