

Mixed Rh–Pt Carbonyl Clusters: Synthesis and X-Ray Crystallographic Characterisation of $[\text{Rh}_5\text{Pt}(\text{CO})_{15}]^- [(\text{Ph}_3\text{P})_2\text{N}]^+$

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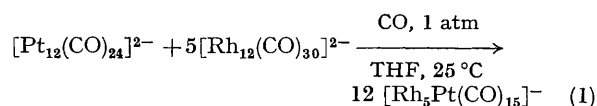
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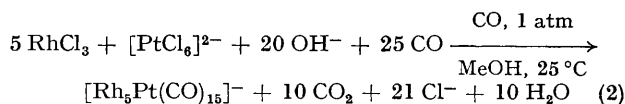
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Summary The $[\text{Rh}_5\text{Pt}(\text{CO})_{11}(\mu_3\text{-CO})_4]^-$ anion, which has been prepared by two independent routes, is shown to be structurally related to $[\text{Rh}_6(\text{CO})_{12}(\mu_3\text{-CO})_4]$ [one $\text{Rh}(\text{CO})_2$ group is replaced by a $\text{Pt}(\text{CO})$ group] both in the solid state (X-ray) and in solution (n.m.r.); evidence is also presented for a further reduced mixed anion $[\text{Rh}_2\text{Pt}(\text{CO})_x]_n^-$.



obtained on a larger preparative scale by reducing a mixture of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in methanol with carbon monoxide and Na_2CO_3 according to the stoichiometry in reaction (2). The pure $[\text{NMe}_4]^+$, $[\text{NEt}_4]^+$, and



MIXED metal clusters are of potential interest as catalysts,¹ especially for obtaining small metallic particles of both controlled size and composition, but unfortunately little is known about mixed clusters containing transition metals of the second and third rows.² Since both platinum and rhodium are particularly susceptible to form large metal carbonyl clusters,³ we have investigated the mixed platinum rhodium carbonyl system.

The dodecametal carbonyl dianions of platinum and rhodium react cleanly according to reaction (1) (THF = tetrahydrofuran). The same mixed species has been

$[(\text{Ph}_3\text{P})_2]^+$ salts were prepared by metathesis from the sodium salt and were recrystallised from THF–pentane. In THF they all have $\nu(\text{CO})$ at 2082vw, 2038s, 2011m, and 1791ms cm^{-1} ; the last absorption is clearly due to face-bridging carbonyls and indicates a structure related to that of $[\text{Rh}_6(\text{CO})_{16}]$.⁴

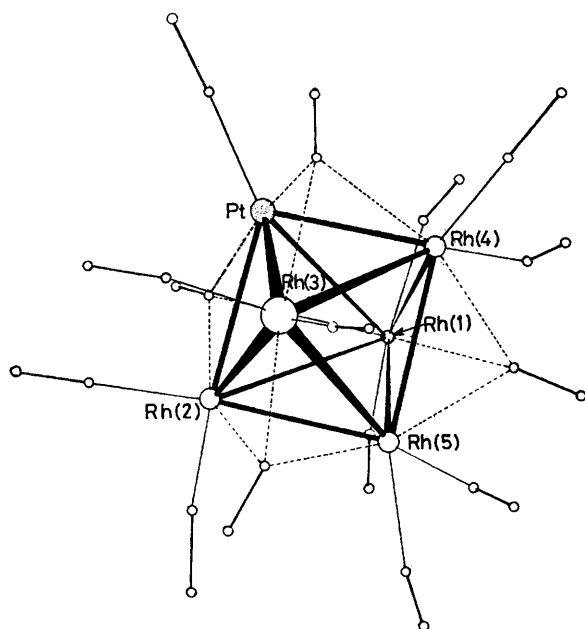


FIGURE 1. A perspective view of the $[\text{Rh}_5\text{Pt}(\text{CO})_{11}(\mu_3\text{-CO})_4]^-$ anion. Average distances are: Pt-Rh 2.790; Rh-Rh 2.760; Rh-CO_{term.} 1.76. Individual distances are Pt-Rh(1) 2.776; Pt-Rh(2) 2.780; Pt-Rh(3) 2.811; Pt-Rh(4) 2.794; Rh(1)-Rh(2) 2.827; Rh(1)-Rh(4) 2.698; Rh(2)-Rh(3) 2.725; Rh(3)-Rh(4) 2.805; Rh(1)-Rh(5) 2.746; Rh(2)-Rh(5) 2.755; Rh(3)-Rh(5) 2.758; Rh(4)-Rh(5) 2.768; Pt-CO 1.80. All distances are in Å; e.s.d.'s 0.002 Å for M-M and 0.02 Å for M-CO.

This hypothesis has been substantiated by an X-ray analysis of the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt.[†] In the cluster anion (Figure 1) the octahedron is slightly elongated along the Pt-Rh(5) diagonal [3.935(2); Rh(1)-Rh(3) 3.906(2), and Rh(2)-Rh(4) 3.910(2) Å] in agreement with the different values of the metallic radii. The platinum atom has only one terminal carbonyl group, and bonds to two face-bridging carbonyl groups. Both these Pt- μ_3 -CO bonds are shorter [av. 2.13(2) Å] than those to the rhodium atoms [av. 2.22(2) Å], an asymmetry which suggests localisation of some negative charge on platinum.

Further reduction of the brown monoanion $[\text{Rh}_5\text{Pt}(\text{CO})_{15}]^-$ occurs readily to give, under CO, a yellow-brown anion isolated in crystalline form as its $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt. A crystallographic study is presently under way; analytical data indicate a composition $[\text{Rh}_2\text{Pt}(\text{CO})_x]_n^-$ [$\nu(\text{CO})$ in THF: 2000s, 1956s, 1810m, 1790m,[‡] and 1735w cm^{-1}].

[†] Crystal data: $\text{C}_{51}\text{H}_{30}\text{NO}_{15}\text{P}_3\text{PtRh}_5$, M 1668.36, triclinic, space group $P\bar{1}$, $a = 16.596(7)$, $b = 15.655(7)$, $c = 10.692(6)$ Å, $\alpha = 95.02(9)$, $\beta = 85.35(8)$, $\gamma = 81.37(8)^\circ$ (least-squares refined values), $U = 2719.9$ Å³, $D_c = 2.036$ g cm^{-3} , $Z = 2$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[‡] Depending on the cation, this band may not be observed.

§ The apparently larger value of 2J compared with 1J could be accounted for by invoking either or both of the following: (a) a change of sign on going from a one- to two-bond coupling; (b) strong interaction through the centre of the octahedron and/or enhanced interaction through the exterior of the octahedron, but it is presently not possible to comment further.

¹ J. H. Sinfelt, *Accounts Chem. Res.*, 1977, **10**, 15.

² For a list of the more relevant examples see: P. Chini and B. T. Heaton, *Topics in Current Chem.*, 1977, **71**, 1; and references therein.

³ P. Chini, V. G. Albano, and G. Longoni, *Adv. Organometallic Chem.*, 1976, **14**, 285.

⁴ E. R. Corey, L. F. Dahl, and W. Beck, *J. Amer. Chem. Soc.*, 1963, **85**, 1202.

⁵ C. Brown, B. T. Heaton, P. Chini, A. Fumagalli, and G. Longoni, *J.C.S. Chem. Comm.*, 1977, 309.

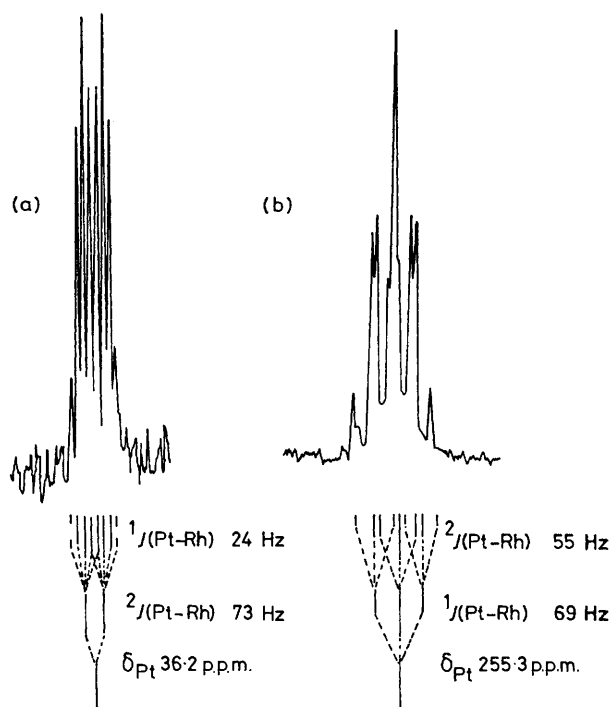


FIGURE 2. ^{195}Pt n.m.r. spectrum of (a) $[\text{NEt}_4][\text{Rh}_5\text{Pt}(\text{CO})_{15}]$ in THF containing 20% $(\text{CD}_3)_2\text{CO}$; (b) $[\text{NBu}_4]_n[\text{Rh}_2\text{Pt}(\text{CO})_x]_n^-$ in $(\text{CD}_3)_2\text{CO}$ at 23°C. (For explanation of δ_{Pt} see ref. 5).

Because of coupling to ^{103}Rh ($I = 1/2$), ^{195}Pt n.m.r. spectroscopy is especially useful for obtaining information about the stereochemistry of the metal polyhedron of these clusters in solution. The spectrum of $[\text{Rh}_5\text{Pt}(\text{CO})_{15}]^-$ at room temperature (Figure 2a) consists of a doublet [2J -(Pt-Rh(5)) 73.2 Hz] of quintets [1J (Pt-Rh(1)-(4)) 24.4 Hz]§ showing that the octahedral structure is maintained in solution. The ^{195}Pt resonance of the anion $[\text{Rh}_2\text{Pt}(\text{CO})_x]_n^-$, at both -80°C and room temperature, is a triplet of triplets (Figure 2b); this is consistent with a fluxional metal polyhedron structure ($n = 2$) in which the two Rh_2Pt -triangles rotate with respect to each other, similar to the known behaviour of $[\text{Pt}_3(\text{CO})_6]_n^{2-5}$.

Other mixed Pt-Rh carbonyl species have been observed, but they have not, as yet, been isolated in pure form.

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