

Rhodium–Platinum Cluster Compounds. Relationships with Olefin–Platinum Complexes and X-Ray Crystal Structures of $[\text{PtRh}_4(\mu\text{-CO})_4(\eta\text{-C}_5\text{Me}_5)_4]$ and $[\text{PtRh}_2(\mu\text{-H})(\mu\text{-CO})_2(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{Me}_5)_2][\text{BF}_4]$

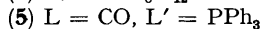
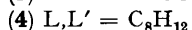
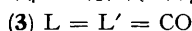
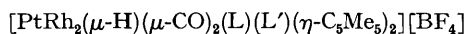
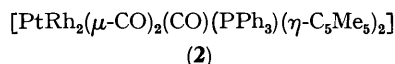
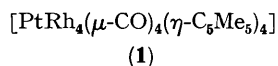
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Summary The cluster compounds $[\text{PtRh}_4(\mu\text{-CO})_4(\eta\text{-C}_5\text{Me}_5)_4]$ and $[\text{PtRh}_2(\mu\text{-H})(\mu\text{-CO})_2(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{Me}_5)_2][\text{BF}_4]$ have been prepared and their structures established by X-ray diffraction; the dirhodium–platinum species undergoes novel dynamic behaviour in solution, revealed by n.m.r. studies, as do other salts of this type.

ISOLOBAL relationships,¹ *e.g.* those that exist between CH_2 , PtL_2 , or $\text{Rh}(\text{CO})_2^-$, or between CH , $\text{Co}(\text{CO})_3$, or $\text{W}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$, are useful in rationalising the products of reactions between low-valent transition metal compounds and mononuclear metal–carbene or –carbyne complexes.^{2,3} There is a particularly interesting isobal analogy between the ethylene molecule and $[\text{Rh}_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]$, a concept¹ we have employed⁴ to prepare rhodium–platinum clusters by adding the species Pt_2L [$\text{L}_2 = (\text{CO})_2$, $(\text{CO})(\text{PPh}_3)$, and cycloocta-1,5-diene] to $[\text{Rh}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$; the products are formally similar to the well known $[\text{Pt}(\text{C}_2\text{H}_4)\text{L}_2]$ complexes. Since the ethylene ligands in $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ are very labile we have studied their replacement by $\text{Rh}=\text{Rh}$ groups.

Treatment of $[\text{Pt}(\text{C}_2\text{H}_4)_3]$ ⁵ with $[\text{Rh}_2(\mu\text{-CO})_2(\eta\text{-C}_5\text{Me}_5)_2]$ ⁶ in toluene at 0 °C afforded (*ca.* 90% yield) dark red-black crystals of $[\text{PtRh}_4(\mu\text{-CO})_4(\eta\text{-C}_5\text{Me}_5)_4]$ (**1**) (ν_{CO} (Nujol), 1776w, 1756w, 1716s, and 1702s cm^{-1} ; δ (¹⁹⁵Pt) $(\text{CD}_3\text{C}_6\text{D}_5)$ [to high frequency of \mathcal{E} (¹⁹⁵Pt) 21.4 MHz] 288 p.p.m. [quintet, J (RhPt) 68 Hz]; δ (¹³C) $(\text{CD}_3\text{C}_6\text{D}_5)$ 241.5 [t, $\mu\text{-CO}$, J (RhC) 44, J (PtC) 150 Hz], 101.7 [d, C_5Me_5 , J (RhC) 3 Hz], and 9.9 p.p.m. (s, C_5Me_5). A single-crystal X-ray diffraction study was carried out to establish whether the PtRh_4 core atoms of compound (**1**) adopt D_{2h} or D_{2d} symmetry. For



the hypothetical molecule $[\text{Ni}(\text{C}_2\text{H}_4)_2]$ it is not possible to differentiate, on the basis of theoretical calculations,⁷ between D_{2h} and D_{2d} structures; however, the quasitetrahedral geometry (D_{2d}) should be favoured for compound (**1**), since the $\text{Pt}(5d)\text{-Rh}_2(2b_2)$ energy separation should be small.

Crystals chosen for the X-ray diffraction study were originally monoclinic at 293 K (i), and underwent a non-reversible phase change when cooled to 200 K and rewarmed

to room temperature to give an orthorhombic cell (ii). Diffracted intensities were collected for both the monoclinic and orthorhombic room-temperature forms of the same crystal, but not for the low-temperature triclinic phase.

Crystal data: $\text{C}_{44}\text{H}_{60}\text{O}_4\text{PtRh}_4$, $M = 1259.1$; (i) monoclinic, space group $A2/a$, $a = 17.826(4)$, $b = 13.944(3)$, $c = 18.112(5)$ Å, $\beta = 97.19(2)^\circ$, $U = 4466(2)$ Å³, $Z = 4$, $D_c = 1.88$ g cm^{-3} , $F(000) 2456$, $\mu(\text{Mo-K}\alpha) 46$ cm^{-1} , current $R 0.066$ ($R' 0.070$) for 1718 independent reflections [$2\theta \leq 40^\circ$, $I \geq 1.5\sigma(I)$]; (ii) orthorhombic, space group $Pnma$, $a = 17.945(5)$, $b = 17.978(6)$, $c = 13.764(4)$ Å, $U = 4440(2)$ Å³, $Z = 4$, current $R 0.046$ ($R' 0.047$) for 1606 independent reflections [$2\theta \leq 45^\circ$, $I \geq 3\sigma(I)$] (Nicolet P3m diffractometer, ω scan mode, $\text{Mo-K}\alpha$ X-radiation, graphite monochromator, $\lambda = 0.71069$ Å).[†] Both forms exhibit essentially the same molecular geometry (Figure 1) with the metal

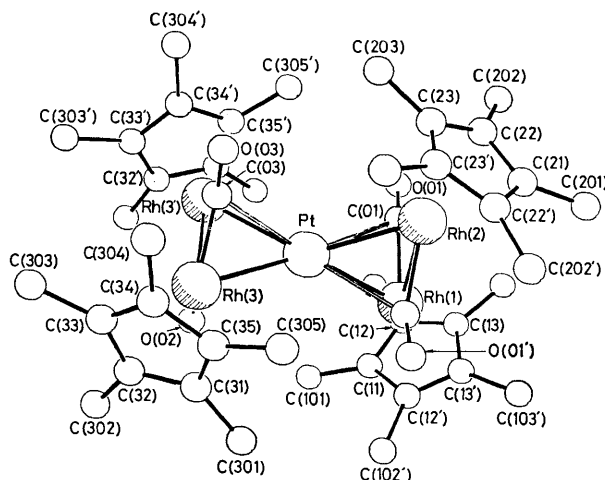


FIGURE 1. Molecular structure of $[\text{PtRh}_4(\mu\text{-CO})_4(\eta\text{-C}_5\text{Me}_5)_4]$ (**1**): the molecule shown has m symmetry and the primes indicate mirror relationships. Important (mean) internuclear separations include Pt–Rh 2.618(2), Rh–Rh 2.620(2), Rh–C(O) 1.99(3), and Pt–C(O) 2.55(2) Å.

atoms in a pseudotetrahedral arrangement, but there are interesting differences. In (i) the Pt atom lies on a crystallographic two-fold axis, thus relating the Rh atoms in pairs, whereas in (ii) the symmetry axis is replaced by a mirror plane which imposes a higher molecular symmetry. Thus, with (ii) the PtRh_4 core has an angle of 90° between the two PtRh_2 planes, while the corresponding angle for (i) is 100° . The conformations of the $\eta\text{-C}_5\text{Me}_5$ rings differ in the two modifications; in (i) these are staggered, with respect

[†] 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.

to their associated Rh–Rh vectors, whereas in (ii) the pair related by the mirror plane are necessarily eclipsed, while those lying astride the mirror are staggered. Deviation of the metal core from D_{2d} symmetry by 10° necessitates staggering of the C_5Me_5 groups to avoid impossibly close Me group contacts. For both forms there is weak inter-

action between Pt and the Rh(μ -CO)Rh bridges [Pt–CO, mean distance 2.54(2) Å] similar to that found⁴ in [PtRh₂(μ -CO)₂(CO)(PPh₃)(η -C₅Me₅)₂] (2).

The salts [PtRh₂(μ -H)(μ -CO)₂(L)(L')(η -C₅Me₅)₂][BF₄] (3)–(5)[†] form quantitatively by addition of HBF₄ in diethyl ether to the appropriate neutral complexes,⁴ such as compound (2). Variable temperature n.m.r. data[‡] for the cations revealed dynamic behaviour in solution, and consequently to ascertain the ground-state structure an X-ray diffraction study was made on compound (5).

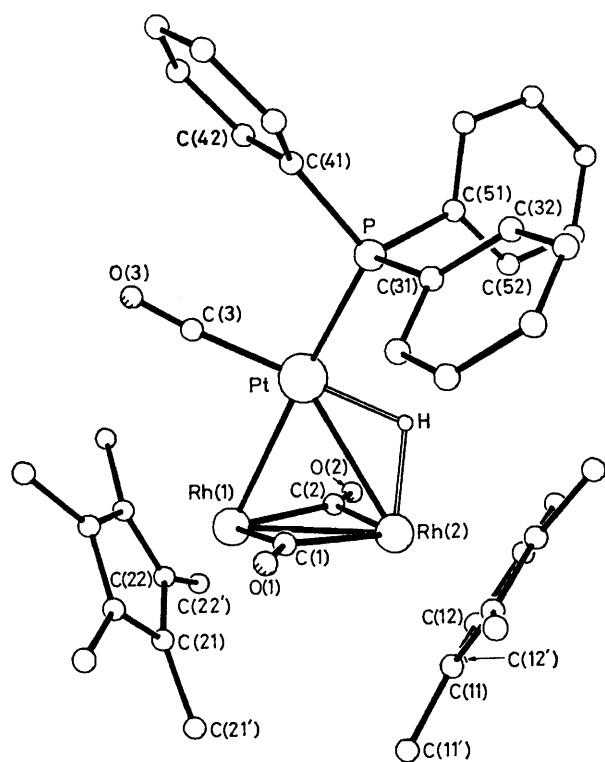


FIGURE 2. Molecular structure of the cation [PtRh₂(μ -H)(μ -CO)₂(CO)(PPh₃)(η -C₅Me₅)₂]⁺. Important internuclear separations include Pt–Rh(1) 2.705(1), Pt–Rh(2) 2.805(1), Rh(1)–Rh(2) 2.667(2), Pt–C(1) 2.733(11), Pt–C(2) 2.760(11), Rh(1)–C(1) 1.989(11), Rh(1)–C(2) 1.977(11), Rh(2)–C(1) 2.026(11), Rh(2)–C(2) 2.044(11), P–Pt 2.297(3), and Pt–C(3) 1.960(17) Å.

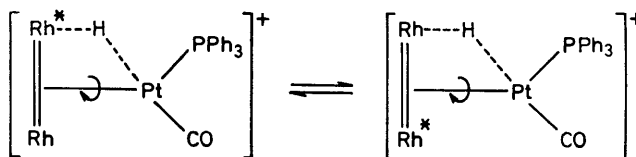
[†] ν (Nujol) (3), 2 048vs, 2 010vs, 1 806m, and 1 740s; (4), 1 805m and 1 755vs; and (5), 2 065s, 1 773vs, and 1 769vs cm⁻¹.

[‡] Compound (3), δ (¹H) (CDCl₃, 25 °C) 1.89 (s, 30 H, C₅Me₅) and –13.17 [t, 1 H, μ -H, J (RhH) 14.7, J (PtH) 367 Hz]; δ (¹H) (CD₂Cl₂, –50 °C) 1.83 (s, 15 H, C₅Me₅), 1.77 (s, 15 H, C₅Me₅), and –13.33 [d, 1 H, μ -H, J (RhH) 29.4, J (PtH) 365 Hz]; compound (4), δ (¹H) (CDCl₃, 25 °C) 5.44 [s, 2 H, CH, J (PtH) 58 Hz], 5.39 [s, 2 H, CH, J (PtH) 78 Hz], 2.1 (br m, 8 H, CH₂), 1.86 (s, 30 H, C₅Me₅), and –14.40 [t, 1 H, μ -H, J (RhH) 12.5, J (PtH) 582 Hz]; δ (¹H) (–50 °C) 5.47 (s, 2 H, CH), 5.38 (s, 2 H, CH), 2.1 (br m, 8 H, CH₂), 1.95 (s, 15 H, C₅Me₅), 1.80 (s, 15 H, C₅Me₅), and –14.26 [d, 1 H, μ -H, J (RhH) 25, J (PtH) 576 Hz]; δ (¹³C{¹H}) (25 °C) 234 [t, CO, J (RhC) 39 Hz], 105 (C₅Me₅), 98 [CH, J (PtC) 84 Hz], 95.5 [CH, J (PtC) 120 Hz], 31 (CH₂), and 30.5 p.p.m. (CH₂); compound (5), δ (¹H) (CDCl₃, 25 °C) 7.6–7.1 (m, 15 H, Ph), 1.76 (s, 30 H, C₅Me₅), and –11.83 [d of t, 1 H, μ -H, J (PH) 13, J (RhH) 11.5, J (PtH) 426 Hz]; δ (¹H) (–50 °C) 7.6–7.1 (m, 15 H, Ph), 1.94 (s, 15 H, C₅Me₅), 1.61 (s, 15 H, C₅Me₅), and –11.81 [d of d, 1 H, μ -H, J (PH) 13, J (RhH) 23, J (PtH) 426 Hz]; δ (³¹P{¹H}) (25 °C) (to high frequency of H₃PO₄) 11.1 p.p.m. [t, J (RhP) 3, J (PtP) 3 266 Hz]; δ (³¹P{¹H}) (–50 °C) 11.1 p.p.m. [d, J (RhP) 6, J (PtP) 3 260 Hz]; δ (¹³C{¹H}) (25 °C) 235.5 [t, μ -CO, J (RhC) 39, J (PtC) 49 Hz], 187.5 (br, PtCO), 135–129 (Ph), 105.5 [d, C₅Me₅, J (RhC) 5 Hz], and 9.0 p.p.m. (s, C₅Me₅).

Crystal data: C₄₁H₄₆BF₄O₃PPtRh₂, $M = 1 105$, orthorhombic, space group $Pbca$, $a = 21.503(12)$, $b = 23.728(8)$, $c = 15.896(5)$ Å, $U = 8 111(6)$ Å³, $Z = 8$, $D_c = 1.81$ g cm⁻³, $F(000) 4 320$, μ (Mo- K_α) 43.6 cm⁻¹; current $R 0.048$ (R' 0.050) for 4 901 independent reflections [293 K, $2\theta \leq 55^\circ$, $I \geq 3\sigma(I)$].

The structure of the cation (Figure 2) is in many respects similar to that of its precursor (2), with essentially planar co-ordination about the Pt atom and with the μ -CO ligands leaning towards the Pt atom [Pt–CO, mean distance 2.75(1) Å], but less so than in compound (2) [Pt–CO, mean distance 2.51(1) Å]. Although the hydrido-ligand could not be located unequivocally from electron density difference maps, nevertheless it must bridge the Pt–Rh(2) vector on the basis that this edge [2.805(1) Å] is longer than Pt–Rh(1) [2.705(1) Å], that the Rh(2)–Pt–P angle is wider [117.4(1)° compared with 105.7(2)° in compound (2)], and from the calculation of a minimum potential energy site in this position.⁸

At –50 °C, the ¹H and ³¹P n.m.r. spectra of compound (5)[‡] are in accord with the solid-state structure. Thus, the hydrido-ligand resonance shows coupling to phosphorus, to platinum, and to one rhodium atom, while the signal for the phosphorus nucleus shows coupling to the *trans*-rhodium atom and strong coupling to platinum. At room temperature, the hydrido-resonance becomes a doublet of triplets with ¹⁹⁵Pt satellite peaks, as expected for time-averaged coupling to two rhodium nuclei. The ³¹P n.m.r. resonance changes from a doublet to a triplet. Since the J (PtH) and J (PH) couplings do not change between the limiting spectra observed at –50 °C and the spectra measured at 25 °C, while the J (RhH) and J (RhP) couplings are halved over this range, the dynamic process must involve rotation of the Rh₂(μ -CO)₂(η -C₅Me₅)₂ fragment about an axis through Pt and the mid-point of the Rh=Rh unit, while the Pt(H)–(CO)(PPh₃) moiety retains its integrity at all times (Scheme).



SCHEME. Ligands on Rh omitted for clarity.

From the ¹H n.m.r. spectra and the coalescence temperatures of the η -C₅Me₅ signals, the activation energy (ΔG^\ddagger) for the dynamic process is estimated as 49.3, 56.0, and 58.1 kJ mol⁻¹ for complexes (3), (4), and (5), respectively. Similar values are found for the rotation of alkenes in alkene–platinum compounds.^{9,10}

In contrast with the dynamic behaviour of compounds (3)—(5), the cation $[\text{Rh}_3(\mu\text{-H})(\mu_2\text{-CO})_2(\mu_3\text{-CO})(\eta\text{-C}_5\text{Me}_5)_3]^+$ does not exhibit dynamic behaviour up to 55 °C.¹¹

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