Synthesis and Crystal Structure of the Pentanuclear Metal Cluster Complex $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ †

By **Michael Green, Judith A. K. Howard, Geoffrey N. Pain,** and **F. Gordon A. Stone,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

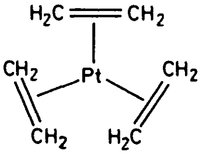
The compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ reacts with $[Pt(C_2H_4)_3]$ to give the pentanuclear cluster complex $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$, the structure of which has been established by *X*-ray diffraction. Crystals grown from light petroleum–dichloromethane belong to the monoclinic system but on cooling to 200 K and rewarming to room temperature undergo an irreversible phase change to the orthorhombic system. Data were collected for both phases: (I) orthorhombic, space group *Pnma*, with $Z = 4$ in a unit cell of dimensions $a = 17.945(5)$, $b = 17.978(6)$, and $c = 13.764(4)$ Å; (II) monoclinic, space group *A2a*, with $Z = 4$, $a = 17.826(4)$, $b = 13.944(3)$, $c = 18.112(5)$ Å, and $\beta = 97.19(2)°$. Intensities were measured to $2\theta \leqslant 45°$ for (I) and to $2\theta \leqslant 40°$ for (II), and were refined for (I) to *R* 0.048 (*R'* 0.050) and for (II) to *R* 0.066 (*R'* 0.070) for 1 606 and 1 718 independent reflections respectively. The two molecules have very similar structures, based on the platinum atom being 'co-ordinated' to two $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ fragments. The four rhodium atoms are disposed around the platinum in an essentially tetrahedral arrangement, with the dihedral angles between the $PtRh_2$ planes being 90° for (I) and 100° for (II). In both molecules the $PtRh_2$ groups form essentially equilateral triangles [Rh–Rh(mean) and Pt–Rh(mean) 2.618(2) Å]. The four CO ligands, in addition to bridging the Rh–Rh vectors, weakly interact with the platinum atom, a feature which persists in solution, as deduced from ^{195}Pt–^{13}C coupling observed in the ^{13}C n.m.r. spectrum of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$.

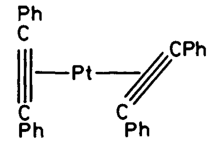
We have previously shown [1] that the compound $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ combines with zero-valent platinum complexes which are sources of the fragments PtL_2 [L_2 = cyclo-octa-1,5-diene, $(CO)_2$, or $(CO)(PPh_3)$] giving the platinumdirhodium species $[PtRh_2(\mu\text{-}CO)_2L_2(\eta\text{-}C_5Me_5)_2]$. Because $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ has frontier orbitals similar to those of ethylene,[2] there is an analogy between the adducts formed by the dirhodium compound with PtL_2 fragments and the well known species $[Pt(alkene)L_2]$. Moreover, we have previously reported that $[Pt(C_2H_4)_3]$ (1) reacts with PhC≡CPh and with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ to give compounds (2) and (3), respectively.[3,4] These results prompted a study [5] of the reaction between $[Pt(C_2H_4)_3]$ and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ in the expectation that a platinum–rhodium cluster compound would be formed by displacement of ethylene groups from platinum by molecules of the dirhodium species which formally contains a Rh=Rh bond.[6]

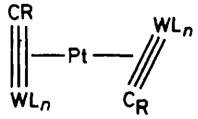
RESULTS AND DISCUSSION

Addition of a toluene solution of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ to $[Pt(C_2H_4)_3]$ afforded a black crystalline compound formulated as $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ on the basis of analysis and spectroscopic properties. The i.r. spectrum (Experimental section) showed the presence of bridging carbonyl groups, and the ^1H and ^{13}C n.m.r. spectra indicated that the $\eta\text{-}C_5Me_5$ ligands were in equivalent environments. In addition, the ^{13}C spectrum revealed a triplet signal [*J*(RhC) 44 Hz] for the CO ligands with platinum satellite peaks [*J*(PtC) 150 Hz]. The ^{195}Pt n.m.r. spectrum consists of a symmetrical 1 : 4 : 6 : 4 : 1 quintet [*J*(RhPt) 68 Hz]. The n.m.r. data are thus consistent with $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ groups retaining their integrity in a $PtRh_4$ cluster.

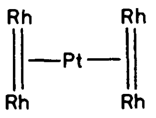
It was clearly important to establish the molecular structure of the platinum–rhodium cluster complex in the solid state, and accordingly a single-crystal *X*-ray diffraction study was carried out. Crystals of the compound grow at room temperature (r.t.) from light petroleum–dichloromethane mixtures as dark red prisms belonging to the monoclinic system. On cooling, however, the crystals undergo a phase change to form apparently a triclinic unit cell at 200 K, which was poorly defined and weakly diffracting. Hence data were not recorded at the low temperature. On warming to r.t.

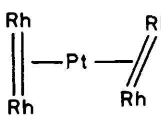

(1); D_{3h}


(2); D_{2d}


$L_n = (CO)_2\,(\eta\text{-}C_5H_5)$

(3); C_2


(4a); D_{2h}


(4b); D_{2d}

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† Tetra-μ_3-carbonyl-bis[bis(η-pentamethylcyclopentadienylrhodio)(*Rh–Rh*)]platinum(4 *Pt–Rh*).

specimens which had been cooled to 200 K, a further phase change occurred to give crystals of an orthorhombic form of a slightly smaller volume. There was no evidence of reversion to the original monoclinic cell after a time lapse, and hence the changes on cycling from r.t. to 200 K to r.t. were irreversible. Diffracted intensities were, therefore, recorded on one crystal in both its orthorhombic and its monoclinic phases, and the data so obtained are given in Tables 1—4. Figures 1 and 2 show the molecular structures of the orthorhombic and monoclinic forms respectively, together with the atom numbering schemes. The primed and unprimed atoms in the orthorhombic form (I) (Figure 1) are related by mirror symmetry, and in the monoclinic form (II) (Figure 2) by a two-fold rotation axis.

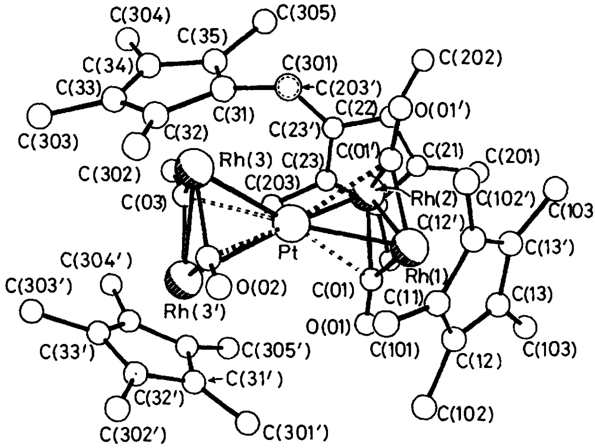

Figure 1 Molecular structure of orthorhombic $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ (I) showing the crystallographic numbering

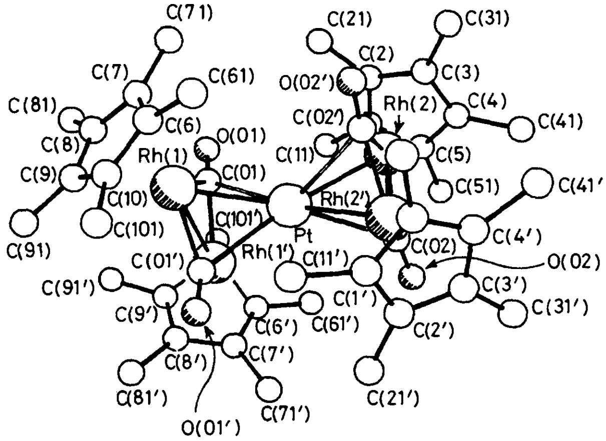

Figure 2 Molecular structure of monoclinic $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ (II) showing the crystallographic numbering

In both structures the rhodium atoms are arranged around the platinum atom in a *pseudo*-tetrahedral manner. In (I) the angle between the two planes PtRh(1)-Rh(2) and PtRh(3)Rh(3') is 90°, and in (II) the corresponding interplanar angle is 100°. In both molecules the $PtRh_2$ groups form essentially equilateral triangles: Rh–Rh (I) 2.618_5, (II) 2.619_5; Pt–Rh (I) 2.618_5, (II) 2.616_5 Å. In (I) the platinum atom lies on a crystallographic mirror plane, whereas in (II) this is replaced by a symmetry axis. The orientation of the C_5Me_5 rings relative to the Rh–Rh vectors in (I) and (II) differs as a consequence of the change in internal molecular symmetry. In (I) where the crystallographic mirror plane exists, the two rings related by it are necessarily eclipsed, whereas those lying across it are staggered. In (II), the two-fold axis related the η-C_5Me_5 rings in staggered pairs only. The reason for this difference stems from the increase (10°) in the interplanar $PtRh_2$ angles in going from (I) to (II), which bring the CH_3 hydrogen atoms into impossibly close contact if attempting to retain the eclipsed conformation. The closest intramolecular contacts involve CH_3 and CO groups. In (I) these occur between some of the methyl hydrogens on Rh(3)(η-C_5Me_5) and some of the hydrogens on Rh(2)-(η-C_5Me_5), and also between O(3) and these hydrogens. In (II) the closest intramolecular contacts are of approximately the same magnitude (H · · · H 2.7, and H · · · O 2.6 Å), and occur between hydrogens of Rh(2)(η-C_5Me_5) and those of Rh(1)(η-C_5Me_5), and between the former and O(1). The similarity of the intramolecular contacts presumably compensates for the rotational changes which occur for the C_5 rings between the two phases.

Table 1

Atomic positional (fractional co-ordinates) parameters for the orthorhombic form of the complex $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0.198 68(6)	0.25 *	0.077 12(7)
Rh(1)	0.276 65(10)	0.25 *	−0.083 82(16)
Rh(2)	0.130 94(11)	0.25 *	−0.091 23(15)
Rh(3)	0.187 62(9)	0.322 88(8)	0.241 10(10)
C(11)	0.401(1)	0.25 *	−0.055(2)
C(12)	0.382(1)	0.186(1)	−0.112(2)
C(13)	0.356(1)	0.209(1)	−0.197(1)
C(101)	0.425(2)	0.25 *	0.045(3)
C(102)	0.397(2)	0.109(1)	−0.071(2)
C(103)	0.331(1)	0.161(1)	−0.276(2)
C(21)	0.062(1)	0.25 *	−0.225(2)
C(22)	0.042(1)	0.188(1)	−0.173(1)
C(23)	0.013(1)	0.212(1)	−0.086(1)
C(201)	0.087(3)	0.25 *	−0.329(3)
C(202)	0.050(2)	0.109(2)	−0.207(2)
C(203)	−0.016(2)	0.164(2)	0.000(2)
C(31)	0.232(1)	0.439(1)	0.229(2)
C(32)	0.240(2)	0.413(1)	0.330(2)
C(33)	0.161(2)	0.398(1)	0.366(1)
C(34)	0.118(2)	0.419(1)	0.298(2)
C(35)	0.154(1)	0.439(1)	0.211(2)
C(301)	0.290(1)	0.464(2)	0.162(2)
C(302)	0.307(2)	0.410(2)	0.377(2)
C(303)	0.149(2)	0.373(2)	0.459(2)
C(304)	0.028(1)	0.414(2)	0.297(2)
C(305)	0.117(2)	0.471(2)	0.120(2)
C(01)	0.207(1)	0.168(1)	−0.074(1)
O(01)	0.206(1)	0.102(1)	−0.76(1)
C(02)	0.268(2)	0.25 *	0.240(3)
O(02)	0.334(1)	0.25 *	0.251(3)
C(03)	0.111(2)	0.25 *	0.220(3)
O(03)	0.041(1)	0.25 *	0.214(2)

* Atom resides on mirror plane.

The closest intermolecular contacts occur between methyl hydrogens (minimum found 2.2 Å), while for all non-hydrogen atoms intermolecular contacts are >3 Å.

All carbon atoms of the methyl groups lie out of their C_5-ring plane by up to 0.15 Å for (I) and 0.09 Å for (II), these deviations being away from the rhodium atoms to which the rings are bonded.[7] The η-C_5Me_5 ligands are inclined away from the platinum atom so that the angles Rh–Rh–C_5(centroid) are approximately 160°. The geometry of the η-C_5Me_5 rings is otherwise unremarkable.

TABLE 2

Internuclear distances (Å) and angles (°) for the orthorhombic form of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$, with estimated standard deviations in parentheses

(a) Distances [a]		(b) Angles [b]	
Pt–Rh(1)	2.620(2)	Rh(1)–Pt–Rh(2)	60.0(1)
Pt–Rh(2)	2.617(2)	Rh(1)–Pt–Rh(3)	140.3(1)
Pt–Rh(3)	2.617(2)	Rh(3)–Pt–Rh(3′)	60.1(1)
Pt–Rh(3′)	2.617(2)	Rh(2)–Pt–Rh(3)	136.8(1)
Rh(1)–Rh(2)	2.617(3)	Rh(2)–Pt–Rh(3′)	136.8(1)
Rh(3)–Rh(3′)	2.620(3)	Rh(1)–Pt–Rh(3′)	140.3(1)
Rh(1)–C(01)	1.94(2)	Rh(1)–C(01)–Rh(2)	82(1)
Rh(2)–C(01)	2.03(2)	Rh(1)–C(01)–O(01)	140(1)
Rh(1)–C(01′)	1.94(2)	Rh(2)–C(01)–O(01)	136(1)
Rh(2)–C(01′)	2.03(2)	Rh(2)–C(01) · · · Pt	69(1)
C(01)–O(01)	1.19(2)	Pt · · · C(01)–O(01)	127(1)
Pt · · · C(01)	2.55(2)	Rh(3)–C(03)–Rh(3′)	86(1)
Pt · · · C(03)	2.56(2)	Rh(3)–C(02)–Rh(3′)	85(1)
Pt · · · C(02)	2.52(2)	Rh(3)–C(03)–O(03)	136(1)
Rh(3)–C(03)	1.92(2)	Rh(3)–C(02)–O(02)	137(1)
Rh(3)–C(02)	1.94(2)	Rh(3)–C(02) · · · Pt	70(1)
Rh(3′)–C(02)	1.94(2)	Rh(3)–C(03) · · · Pt	71(1)
Rh(3′)–C(03)	1.92(2)	Pt · · · C(02)–O(02)	126(1)
C(03)–O(03)	1.25(2)	Pt · · · C(03)–O(03)	125(1)
C(02)–O(02)	1.19(2)		
Rh(1)–C(11)	2.27(3)	cp(1)–Rh(1)–Rh(2)	157
Rh(1)–C(12)	2.25(2)	cp(1)–Rh(1)–Pt	143
Rh(1)–C(13)	2.24(2)		
Rh(2)–C(21)	2.21(2)	cp(2)–Rh(2)–Rh(1)	158
Rh(2)–C(22)	2.25(2)	cp(2)–Rh(2)–Pt	142
Rh(2)–C(23)	2.22(2)		
Rh(3)–C(31)	2.24(2)	cp(3)–Rh(3)–Rh(3′)	161
Rh(3)–C(32)	2.24(3)	cp(3)–Rh(3)–Pt	139
Rh(3)–C(33)	2.24(2)		
Rh(3)–C(34)	2.28(3)		
Rh(3)–C(35)	2.21(2)		

(c) Distances within the C_5Me_5 rings

C(11)–C(12)	1.44(3)	C(11)–C(101)	1.43(5)
C(12)–C(13)	1.32(3)	C(12)–C(102)	1.51(3)
C(13)–C(13′)	1.47(4)	C(13)–C(103)	1.46(3)
C(21)–C(22)	1.37(2)	C(21)–C(201)	1.51(3)
C(22)–C(23)	1.37(3)	C(22)–C(202)	1.49(4)
C(23)–C(23′)	1.36(5)	C(23)–C(203)	1.57(4)
C(31)–C(32)	1.47(4)	C(31)–C(301)	1.46(4)
C(32)–C(33)	1.52(5)	C(32)–C(302)	1.37(5)
C(33)–C(34)	1.27(4)	C(33)–C(303)	1.38(4)
C(34)–C(35)	1.41(4)	C(34)–C(304)	1.61(4)
C(35)–C(31)	1.42(3)	C(35)–C(305)	1.53(4)

[a] Atoms designated with primes are related to corresponding atoms which are not primed, by the symmetry operator (x, $\frac{1}{2} - y$, z). [b] cp(1), *etc.* define the centroids of the η-C_5Me_5 rings.

The CO ligands, in addition to bridging the Rh–Rh vectors, are weakly interacting with the platinum atoms [Pt · · · CO, 2.54 Å in (I) and 2.57 Å in (II)]. The (O)-

TABLE 3

Atomic positional (fractional co-ordinates) parameters for the monoclinic form of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0.75 *	0.181 11(7)	0 *
Rh(1)	0.823 34(8)	0.343 67(11)	−0.000 53(9)
Rh(2)	0.727 43(9)	0.018 72(11)	−0.071 73(9)
C(01)	0.737(1)	0.326(1)	−0.084(1)
O(01)	0.731(1)	0.331(1)	−0.147(1)
C(02)	0.665(2)	0.032(2)	0.014(1)
O(02)	0.604(1)	0.026(2)	0.029(1)
C(1)	0.669 3(8)	0.051 0(9)	−0.186 5(10)
C(11)	0.627(2)	0.144(2)	−0.209(2)
C(2)	0.745 8(8)	0.026 7(9)	−0.191 8(10)
C(21)	0.801(2)	0.093(2)	−0.221(2)
C(3)	0.757 7(8)	−0.069 3(1)	−0.166 9(10)
C(31)	0.828(1)	−0.128(3)	−0.162(2)
C(4)	0.688 5(8)	−0.104 4(9)	−0.146 2)10)
C(41)	0.670(2)	−0.203(3)	−0.116(3)
C(5)	0.633 9(8)	0.030 0(9)	−0.158 3(10)
C(51)	0.553(2)	−0.040(3)	−0.147(2)
C(6)	0.950(1)	0.320(1)	0.013(1)
C(61)	0.991(2)	0.232(3)	0.034(3)
C(7)	0.926(1)	0.353(1)	−0.060(1)
C(71)	0.936(2)	0.298(3)	−0.129(2)
C(8)	0.894(1)	0.446(1)	−0.055(1)
C(81)	0.861(3)	0.509(3)	−0.118(2)
C(9)	0.898(1)	0.470(1)	0.022(1)
C(91)	0.874(3)	0.565(3)	0.051(2)
C(10)	0.933(1)	0.393(1)	0.064(1)
C(101)	0.949(3)	0.394(3)	0.147(2)

* Parameter not refined, atom resides on two-fold axis.

TABLE 4

Internuclear distances (Å) and angles (°) for the monoclinic form of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$, with estimated standard deviations in parentheses

(a) Distances [a,b]

Pt–Rh(1)	2.617(2)	Rh(1)–C(01)	2.03(3)
Pt–Rh(2)	2.616(2)	C(01)–O(01)	1.14(4)
Pt–Rh(1′)	2.617(2)	Pt · · · C(01)	2.53(3)
Pt–Rh(2′)	2.616(2)	Rh(2)–C(02)	2.04(3)
Rh(1)–Rh(1′)	2.617(2)	C(02)–O(02)	1.15(4)
Rh(2)–Rh(2′)	2.622(3)	Pt · · · C(02)	2.61(3)
Rh(2)–C(1)	2.25(2)	Rh(1)–C(6)	2.27(2)
Rh(2)–C(2)	2.24(2)	Rh(1)–C(7)	2.25(2)
Rh(2)–C(3)	2.24(2)	Rh(1)–C(8)	2.21(2)
Rh(2)–C(4)	2.24(1)	Rh(1)–C(9)	2.21(1)
Rh(2)–C(5)	2.25(2)	Rh(1)–C(10)	2.25(2)
C(1)–C(11)	1.54(3)	C(6)–C(61)	1.46(4)
C(2)–C(21)	1.49(4)	C(7)–C(71)	1.50(4)
C(3)–C(31)	1.49(3)	C(8)–C(81)	1.50(4)
C(4)–C(41)	1.53(4)	C(9)–C(91)	1.50(4)
C(5)–C(51)	1.50(4)	C(10)–C(101)	1.49(4)

(b) Angles

Rh(1)–Pt–Rh(1′)	60.0(1)
Rh(1)–Pt–Rh(2)	142.5(1)
Rh(1)–Pt–Rh(2′)	134.9(1)
Rh(2)–Pt–Rh(2′)	60.1(1)
Rh(2)–Pt–Rh(1′)	142.5(1)
Rh(1)–C(01)–Rh(1′)	81.1(9)
Rh(1)–C(01)–O(01)	136(2)
Pt · · · C(01)–Rh(1)	69.1(7)
Rh(2)–C(02)–Rh(2′)	79.3(11)
Rh(2)–C(02)–O(02)	143(2)
Rh(2)–C(02) · · · Pt	67.2(8)

[a] Atoms designated with primes are related to the corresponding atoms which are not by the symmetry operator ($\frac{1}{2} - x$, y, $-z$). [b] The η-C_5Me_5 rings were refined as regular pentagons, and hence their internal geometry is not given.

CRh_2 planes are not perpendicular to the $PtRh_2$ plane but lean towards the platinum by 7°. Additional evidence for the CO ligands being semi-triply bridging is the relatively low CO stretching bands in the i.r. spectrum, and the $^{195}Pt-^{13}C$ coupling observed in the ^{13}C n.m.r. spectrum.

The oxygen atoms of the CO ligands are not in the $(O)CRh_2$ planes but lie *ca.* 0.2 Å away from the platinum atom. It is interesting to compare the stereochemistry of the bridging CO ligands in $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ with that in the compounds $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ [1] and $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2][BF_4]$.[8] In $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$, Pt–(μ-CO)(mean) is 2.52 Å and the tilt of the $(O)CRh_2$ planes towards the platinum is 11°. The corresponding parameters for the cation $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]^+$ are 2.75 Å and 5°.

In $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ the metal–metal distances are somewhat contracted compared with the corresponding distances in the two $PtRh_2$ complexes mentioned above. Thus the Rh–Rh separation in the $PtRh_4$ cluster is 2.618(2)(mean) Å compared with 2.647(2) Å in $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ and 2.667(2) Å in $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]^+$. A similar trend is found in the Pt–Rh distances, but with these the situation is complicated by the presence of the bridging hydrido-ligand in the cation, and the differing steric and *trans* influences of the CO and PPh_3 groups on the metal–metal bonds.

Perhaps the most interesting feature of the structure of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ is the D_{2d} symmetry (4b) adopted by the core metal atoms (Figure 3). For the hypothetical molecule $[Ni(C_2H_4)_2]$, calculations [9] indicate only a small energy difference (*ca.* 6 kJ mol^{-1}) between D_{2h} and D_{2d} structures since the ligand π* and metal *d* orbitals are far apart in energy and non-degenerate perturbation theory predicts similar stabilization. Rösch and Hoffmann [9] also studied the case where the energy separation of the π* and *d* orbitals is small, as might be expected for the $2b_2$ orbitals [2] of the two $Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2$ moieties and the 5*d* orbitals of platinum. In this situation degenerate perturbation theory [9] leads to a clear preference for the D_{2d} structure, as confirmed by the *X*-ray crystallographic study on the orthorhombic form, and deviating by only 10° from it in the monoclinic. However, it may be noted that a metal atom core with D_{2h} symmetry would seemingly result in impossibly crowded C_5Me_5 groups. Although no *X*-ray diffraction studies have been made on molecules $[M(C_2H_4)_2]$, since they have only a fleeting existence,[10] a stable family of compounds $[Pt(alkyne)_2]$ [3,11] is known, and have structures (2) in which the ligated carbon atoms adopt a *pseudo*-D_{2d} arrangement around the platinum atom. In the compound $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (3) the dihedral angle between the two PtCW planes is 97°, close to that found (98°) for the PtC_2 planes in $[Pt(PhC_2Ph)_2]$. It is interesting that in each of the three compounds $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$, $[PtW_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$, and $[Pt(PhC_2Ph)_2]$ the four atoms bonded to platinum adopt a similar 'tetrahedral' geometry. In contrast, in the cluster complexes $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd or Pt) [12] the five metal atoms are virtually coplanar, and in $[AuOs_6(CO)_{20}H_2]^-$ the gold atom is in a square-planar co-ordination with respect to the four osmium atoms to which it is bound.[13] Also relevant to the structure of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ is that of the pentanuclear osmium compound $[Os_5(CO)_{19}]$.[14] The latter has a structure in which the metal atoms form two isosceles triangles with a common vertex with the dihedral angle between the two Os_3 planes being 21°. Just as $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ from the standpoint of isolobal relationships [2] can be regarded as related to the species $[Pt(C_2H_4)_2]$, so $[Os_5(CO)_{19}]$ can be formally viewed as related to $[Os(CO)_3(C_2H_4)_2]$; two C_2H_4 molecules in the latter having replaced two $(OC)_4Os{=}Os(CO)_4$ groups in $[Os_5(CO)_{19}]$.

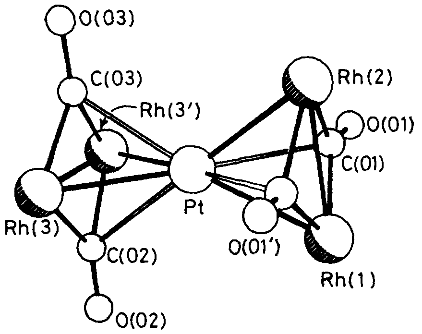

FIGURE 3 The core atoms in the orthorhombic form (I) of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$

EXPERIMENTAL

The techniques used and the instrumentation employed were as described previously.[1] The compounds $[Pt(C_2H_4)_3]$ [15] and $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ [6,16] were prepared using methods reported earlier.

Synthesis of the Compound $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$.—A toluene solution (15 cm^3) of $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ (0.355 g, 0.66 mmol) was added to $[Pt(C_2H_4)_3]$ (0.093 g, 0.33 mmol) at 0 °C. The resulting black mixture was filtered, the solvent removed *in vacuo*, and the residue chromatographed on alumina using light petroleum (b.p. 30—40 °C)–dichloromethane (4 : 1). A black eluate afforded black *crystals* of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ (0.378 g, 90%) (Found: C, 42.8; H, 5.2. $C_{44}H_{60}O_4PtRh_4$ requires C, 42.0; H, 4.8%); $\nu_{max.}$(CO) (Nujol) 1 776w, 1 756w, 1 716s, and 1 702s cm^{-1}. N.m.r.: ^1H ([$^2H_1$]chloroform), δ 1.68 p.p.m. (s, η-C_5Me_5); $^{13}C\text{-}\{^1H\}$ ([$^2H_8$]toluene), δ 241.5 [t, μ-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_5*Me*$_5$); ^{195}Pt ([$^2H_8$]toluene) [to high frequency of Ξ(^{195}Pt) 21.4 MHz] δ 288 p.p.m. [quintet, *J*(RhPt) 68 Hz].

Crystal Structure Determination.—Crystals of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ grow as very dark red prisms belonging to the monoclinic system. Diffracted intensities were collected at 298 K employing the ω scan mode on a crystal of approximate dimensions 0.12 × 0.10 × 0.19 mm, using a Nicolet P3M diffractometer. Of the 2 252 intensities ($2.9 \leqslant 2\theta \leqslant 40°$), 1 718 were deemed independent and observable using the criterion $I \geqslant 1.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation based on counting statistics. On cooling the crystal to 200 K it changed phase and became weakly diffracting (see Discussion section). On warming to r.t. an orthorhombic unit cell was observed, and using the ω scan mode 3 606 reflections were measured ($2\theta \leqslant 45°$), with 1 606 of these being independent and observable when applying the criterion $I \geqslant 3\sigma(I)$. Corrections were made for *X*-ray absorption, Lorentz, and polarisation effects.

Crystal data. $C_{44}H_{60}O_4PtRh_4$, $M = 1\ 259.1$; (I) orthorhombic, $a = 17.945(5)$, $b = 17.978(6)$, $c = 13.764(4)$ Å, D_m not measured, $Z = 4$, $D_c = 1.88$ g cm^{-3}, $U = 4\ 440(2)$ Å^3, $F(000) = 2\ 456$, space group *Pnma*, μ(Mo-K_α) = 46.3 cm^{-1}, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\ 69$ Å; (II) monoclinic, $a = 17.826(4)$, $b = 13.944(3)$, $c = 18.112(5)$ Å, $\beta = 97.19(2)°$, $Z = 4$, $U = 4\ 446(2)$ Å^3, space group *A*2/*a*.

Structure solutions and refinements. The structures were solved by heavy-atom methods for all the non-hydrogen atoms. The hydrogen atoms were included in the calculations with C–H = 0.96 Å, and refined as members of rigid methyl groups with a common isotropic temperature factor. All other atoms, except the methyl carbon atoms of these rigid groups, were refined using anisotropic thermal parameters. The possible ambiguity in (I) between the space groups *Pnma* and $Pn2_1a$ was tested and the former was shown to give the most stable refinement. Refinements converged for (I) at *R* 0.048 (*R'* 0.050), and for (II) at *R* 0.066 (*R'* 0.070), using the weighting scheme $w = [\sigma^2(F) + \alpha|F_o|^2]^{-1}$, where $\sigma(F)$ is the estimated error in the observed structure factor based on counting statistics only. This gave a satisfactory analysis for (I) with $\alpha = 0.000\ 95$ and for (II) with $\alpha = 0.0036$. Final electron-density difference peaks showed no significant features; the maxima (*ca.* 1 e Å^{-3}) being in the vicinity of the metal atoms. Scattering factors were taken from ref. 17 for hydrogen, ref. 18 for carbon and oxygen, and ref. 19 for Pt and Rh, all being corrected for the effects of anomalous dispersion. All calculations and plots for Figures were carried out using the SHELXTL system of programs on a Data General 'Eclipse' S230 computer and Tektronix 4006 plotter. The observed and calculated structure factors, thermal parameters, and all hydrogen atom parameters for both forms of $[PtRh_4(\mu\text{-}CO)_4(\eta\text{-}C_5Me_5)_4]$ and the interbond angles of the η-C_5Me_5 rings for the orthorhombic form are listed in Supplementary Publication No. SUP 23284 (30 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.