

## Synthesis and Structural Characterisation of $[\text{Au}_8\text{Cl}_2(\text{PPh}_3)_6\text{Rh}(\text{CNC}_8\text{H}_9)_2](\text{PF}_6)$ : a Novel Hetero-metallic Cluster Compound of Gold with a Hemi-spherical Topology

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$[\text{Au}_8\text{Cl}_2(\text{PPh}_3)_6\text{Rh}(\text{CNC}_8\text{H}_9)_2](\text{PF}_6)$  has been synthesised by the  $\text{NaBH}_4$  reduction of a mixture of  $\text{Au}(\text{PPh}_3)\text{Cl}$  and  $\text{Rh}(\text{CNC}_8\text{H}_9)_3\text{Cl}$ , and a single crystal X-ray study has shown that it has a hemispherical geometry of gold atoms based on an icosahedron, with the rhodium atom occupying the centre of the open face and bonded to all eight gold atoms.

Although a large number of high nuclearity gold cluster compounds with interstitial atoms have been characterised,<sup>1</sup> there are few examples where the interstitial atom has been replaced by another transition metal atom. J. J. Bour *et al.*<sup>2</sup> have described the structure of  $[\text{PtAu}_8(\text{PPh}_3)_8]^{2+}$ , which has a centred crown geometry identical to that reported for the isoelectronic cluster  $[\text{Au}_9\{\text{P}(p\text{-OMeC}_6\text{H}_4)_3\}_8]^{3+}$  (ref. 3) and Smith *et al.*<sup>4</sup> have reported that  $[\text{Au}_6\text{Pt}(\text{CCBu}^t)(\text{PPh}_3)_7]^+$  has a structure consisting of two  $\text{PtAu}_4$  square-pyramids sharing a common  $\text{PtAu}_2$  triangular face. In this paper we describe the structural characterisation of the first example of a high nuclearity gold-rhodium cluster with the rhodium atom occupying the interstitial site.

Addition of an ethanolic solution of  $\text{NaBH}_4$  to a 1:1 suspension of  $[\text{Au}(\text{PPh}_3)\text{Cl}]$  and  $[\text{Rh}(\text{CNC}_8\text{H}_9)_3\text{Cl}]$  ( $\text{CNC}_8\text{H}_9 = \text{xylyl isocyanide}$ ) in EtOH yielded a dark red solution after 20 min. Subsequent addition of  $\text{NH}_4\text{PF}_6$  yielded a red solid, which on recrystallisation gave yellow crystals of  $[\text{Au}_5(\text{PPh}_3)_5\text{Rh}(\text{CNC}_8\text{H}_9)_3](\text{PF}_6)_2$  (**1**) (30% yield). Red crystals of  $[\text{Au}_8\text{Cl}_2(\text{PPh}_3)_6\text{Rh}(\text{CNC}_8\text{H}_9)_2](\text{PF}_6)$  (**2**) (10% yield) were obtained from the red EtOH solution after layering with acetone and hexane. Complex (**1**) was also obtained from  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$  and  $[\text{Rh}(\text{CNC}_8\text{H}_9)_3\text{Cl}]$  in 80% yield.  $^1\text{H}$  and variable temperature  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. data for (**1**)<sup>†</sup> indicated that it is isostructural with

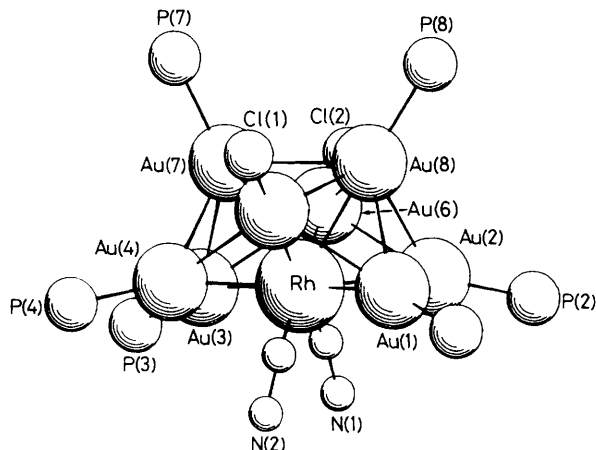
$[\text{Au}_5\text{Re}(\text{H})_4(\text{PPh}_3)_7]^{2+}$ .<sup>5</sup> This is not surprising since both cluster compounds have a total of 78 valence electrons. Compound (**2**) was not so amenable to characterisation on the basis of spectroscopic data and a single crystal X-ray analysis was completed.<sup>‡</sup>

The skeletal geometry of the  $[\text{Au}_8\text{Cl}_2(\text{PPh}_3)_6\text{Rh}(\text{CNC}_8\text{H}_9)_2]^+$  (**2**) cation is illustrated in Figure 1. Although no symmetry is crystallographically imposed, the metal cage has approximately  $C_{2v}$  symmetry. The gold atoms define a hemispherical bowl and the rhodium atom occupies a central position in the top face. The eight gold atoms occupy the vertices of an icosahedron which remain after a butterfly of four atoms has been removed. This geometry has been noted previously for  $\text{B}_8\text{H}_{12}$ <sup>6</sup> but has not been observed in metal cluster chemistry.  $[\text{Au}_9\{\text{P}(p\text{-MeC}_6\text{H}_4)_3\}_8]^{3+}$  (**3**)<sup>7</sup> also has a geometry based on a centred icosahedron, but in this case two pairs of gold atoms have been removed to generate a  $D_{2h}$  toroidal  $\text{Au}_8$  geometry (see Scheme 1). The peripheral Au–Au bond lengths in (**2**) fall in the range 2.781(2)—3.009(2)

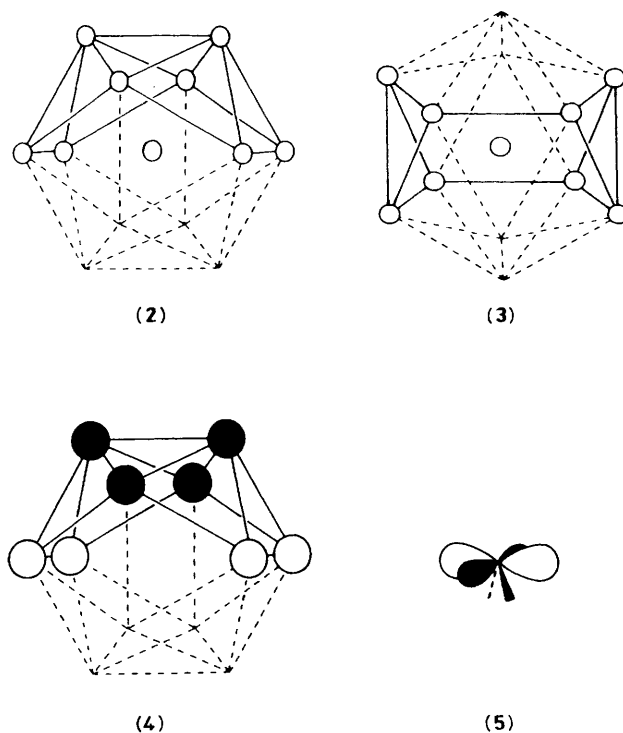
<sup>‡</sup> Crystal data for  $\text{C}_{126}\text{H}_{108}\text{Au}_8\text{Cl}_2\text{F}_6\text{N}_2\text{P}_7\text{Rh}$ :  $M = 3730.63$ , monoclinic,  $P2_1/n$ ,  $a = 27.748(8)$ ,  $b = 14.546(4)$ ,  $c = 34.04(1)$  Å,  $\beta = 100.12(3)^\circ$ ,  $U = 13\,524$  Å<sup>3</sup>,  $D_c = 1.83$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 6992$ ,  $\mu(\text{Mo-K}\alpha) = 89.17$  cm<sup>-1</sup>. 13736 reflections were measured on an Enraf-Nonius CAD-4F diffractometer in the range  $2.0 \leq 2\theta \leq 40^\circ$ . The structure was solved by a combination of direct methods, Patterson and Fourier methods and refined by block matrix least-squares [Au, Rh, Cl, P(1)—(8) anisotropic; P(9), C, F, N isotropic] to  $R = 0.066$  for 6508 unique observed reflections [ $I \geq 3\sigma(I)$ ].

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

<sup>†</sup> Spectroscopic data for (**1**); i.r. (Nujol):  $\nu(\text{CN})$  at 2118 s and 2085 s cm<sup>-1</sup> and  $\nu(\text{PF}_6^-)$  at 843 s cm<sup>-1</sup>;  $^1\text{H}$  n.m.r. ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.92 (s, 18H,  $\text{CH}_3$ ) and 6.77–7.25 (m, 84H, ArH);  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  36.7 [d,  $^2J(\text{Rh-P})$  9 Hz],  $-150.2$  [septet,  $^2J(\text{P-F})$  704 Hz]; on cooling to 180 K the doublet collapses to two broad signals in a ratio of 4:1.



**Figure 1.** Molecular structure of the  $[\text{Au}_8\text{Cl}_2(\text{PPh}_3)_6\text{Rh}(\text{CNC}_6\text{H}_5)_2]^+$  cation (2). For clarity, the phenyl and isocyanide rings have been omitted. Important bond lengths include: Rh(1)–Au(1) 2.708(3), Rh(1)–Au(2) 2.779(3), Rh(1)–Au(3) 2.724(3), Rh(1)–Au(4) 2.771(3), Rh(1)–Au(5) 2.700(3), Rh(1)–Au(6) 2.654(3), Rh(1)–Au(7) 2.819(3), Rh(1)–Au(8) 2.815(3), Au(1)–Au(2) 2.799(2), Au(1)–Au(5) 2.869(2), Au(1)–Au(8) 2.901(2), Au(2)–Au(6) 2.909(2), Au(2)–Au(8) 2.793(2), Au(3)–Au(4) 2.800(2), Au(3)–Au(6) 2.978(2), Au(3)–Au(7) 2.891(2), Au(4)–Au(5) 2.822(2), Au(4)–Au(7) 2.848(2), Au(5)–Au(7) 2.864(2), Au(5)–Au(8) 2.785(2), Au(6)–Au(7) 2.781(2), Au(6)–Au(8) 2.854(2), and Au(7)–Au(8) 3.009(2) Å.



**Scheme 1**

Å and are comparable to those found in other high nuclearity gold cluster compounds.<sup>8</sup> The rhodium atom has a particularly interesting and unusual co-ordination environment since it is bonded to eight gold atoms and two terminal isocyanide ligands [C–N–C 165.0(33) and 165.5(32)°], which lie *trans* to Au(5) and Au(6). The Rh–Au bond lengths to the less sterically crowded Au–Cl fragments [2.700(3) and 2.654(3) Å] are shorter than those to the remaining Au–PPh<sub>3</sub> fragments [2.708(3)–2.819(3) Å]. The occurrence of shorter radial than tangential metal–metal bonds is a common feature of high nuclearity centred clusters and reflects the greater strength of the radial metal–metal bonding.<sup>9</sup>

The structures of high nuclearity centred gold cluster compounds generally fall into two distinct topological groups.<sup>10</sup> Clusters with a spherical topology are characterised by  $12n_s + 18$  valence electrons ( $n_s$  = number of surface gold atoms) and result from the occupation of a d shell on the central gold and skeletal MO's with the pseudo-spherical symmetry labels  $S^\sigma$ ,  $P_x^\sigma$ ,  $P_y^\sigma$ , and  $P_z^\sigma$ . In contrast, clusters with toroidal geometries are characterised by  $12n_s + 16$  valence electrons, corresponding to occupation of  $S^\sigma$ ,  $P_x^\sigma$ , and  $P_y^\sigma$ , with  $P_z^\sigma$  being too high-lying to be available for skeletal bonding. MO calculations have indicated that the relatively high lying  $P_z^\sigma$  MO for  $[\text{Au}_8\text{Cl}_2(\text{PH}_3)_6]$ , shown in (4), is stabilised by overlap with the filled 'δ-like' orbital of the Rh(CNH)<sub>2</sub> fragment shown in (5). Consequently, hemispherical clusters of this type are associated with  $12n_s + 18$  valence electrons. In addition to the current example (2) ( $n_s$  = 8; 114 valence electrons) other clusters which conform to this generalisation include  $[\text{Au}_6\text{Pt}(\text{CCBu}^t)(\text{PPh}_3)(\text{PPh}_3)_6]$  ( $n_s$  = 6; 90 valence electrons) and  $[\text{Au}_8(\text{PPh}_3)_8]^{2+}$  ( $n_s$  = 7; 102 valence electrons).<sup>11</sup>

The chemical and catalytic implications of having a rhodium atom bonded to eight metal atoms, and yet in an exposed site with relatively labile ligands, are interesting and are currently being investigated.

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