Synthesis and Structural Characterisation of Hexakis(triphenyl phosphine)-hexagold(2+) Nitrate, $[Au_6(PPh_3)_6][NO_3]_2$, and Related Clusters with Edge-sharing Bitetrahedral Geometries†

Clive E. Briant, Kevin P. Hall, D. Michael P. Mingos,* and Allison C. Wheeler
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR

$[Au_6(PPh_3)_6][NO_3]_2$ has been synthesised in low yield from $[Au_8(PPh_3)_8][NO_3]_2$ and $K[Ag(CN)_2]$ and characterised by a single-crystal *X*-ray diffraction study. The compound crystallises as $[Au_6(PPh_3)_6][NO_3]_2 \cdot 3CH_2Cl_2$ in the monoclinic space group $P2_1/a$ with four formula units in a cell of dimensions a = 25.674(5), b = 15.843(10), c = 26.368(4) Å, and β = 91.76(2)°. Least-squares refinement of the structure has led to a final R value of 0.049 using 4 430 unique absorption corrected reflections with $I \geqslant 3\sigma(I)$. The gold atoms in the structure define a pair of tetrahedra which share a common edge and therefore the structure is significantly different from the octahedral geometry reported for the related cluster $[Au_6\{P(C_6H_4Me\text{-}p)_3\}_6][BPh_4]_2$. Nevertheless, the observed structure supports an earlier theoretical prediction which suggested that the edge-bridged bitetrahedral structure was electronically preferred for $[Au_6(PR_3)_6]^{2+}$ clusters. The Au–Au bond lengths fall in the range 2.651(2)—2.839(2) Å. The related cluster compounds $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6]Y_2$ (Y = NO_3, ClO_4, or BF_4) and $[Au_6\{P(C_6H_{11})Ph_2\}_6][NO_3]_2$ (C_6H_{11} = cyclohexyl) have been subsequently synthesised in good yield from the corresponding mononuclear compounds and either $NaBH_4$ or $[Ti(\eta\text{-}C_6H_5Me)_2]$. These compounds have been characterised on the basis of their $^{31}P\text{-}\{^1H\}$ n.m.r. and electronic spectral characteristics. Only at low temperatures are the $^{31}P\text{-}\{^1H\}$ n.m.r. data consistent with the solid-state structure and at room temperature only an average single resonance is observed. Some reactions of the hexanuclear clusters are also described.

Bellon *et al.*[1] reported that a few yellow crystals of $[Au_6\{P(C_6H_4Me\text{-}p)_3\}_6][BPh_4]_2$ could be isolated from the reduction of $[Au(NO_3)\{P(C_6H_4Me\text{-}p)_3\}]$ with $NaBH_4$ if $NaBPh_4$ were added to the reaction mixture.[1] A single-crystal *X*-ray crystallographic analysis demonstrated the presence of a distorted octahedron of weakly bonded gold atoms, average Au–Au 3.02 Å. Attempts in several laboratories to repeat the synthesis and to obtain sufficient quantities of this compound for a detailed examination of its spectroscopic and chemical properties have failed.[2] Such studies are of interest in view of a theoretical analysis which suggested that an undistorted octahedral cluster of this type should be paramagnetic with two unpaired electrons.[3]

A recent molecular orbital analysis of the bonding in low-nuclearity gold cluster compounds[4] suggested that in an octahedral $[Au_6L_6]^{2+}$ cation (L = phosphine) the gold–gold bonding is weak because the Au–L fragments form only a single six-centre, two-electron bond.[4] This is consistent with the long Au–Au bonds reported for $[Au_6\{P(C_6H_4Me\text{-}p)_3\}_6][BPh_4]_2$. It was also established that more effective gold–gold bonding could be achieved for a structure based on two gold tetrahedra sharing a common edge. This structure was favoured because it allows the formation of a pair of four-centre, two-electron bonds, one for each tetrahedron.

This paper describes the synthesis and characterisation of some gold cluster compounds of the type $[Au_6(PR_3)_6]^{2+}$ and confirmation of this theoretical prediction. A preliminary description of this work has already appeared.[5]

Results and Discussion

The first example of an $[Au_6L_6]^{2+}$ cluster with an edge-sharing bitetrahedral geometry was synthesised fortuitously and in low yield when $K[Ag(CN)_2]$ was added to a methanolic solution of $[Au_8(PPh_3)_8][NO_3]_2$[6] in a 1:1 molar ratio. The solution was stirred for 1 h, the product precipitated using Et_2O and recrystallised from CH_2Cl_2–toluene. A single-crystal *X*-ray crystallographic analysis which is described in more detail below confirmed the composition $[Au_6(PPh_3)_6][NO_3]_2 \cdot 3CH_2Cl_2$ (1) and the edge-sharing bitetrahedral geometry illustrated in Figure 1. Starting from $[Au(NO_3)(PPh_3)]$, this three-step synthesis resulted in a low overall yield (5%) and therefore alternative routes of stabilising this skeletal geometry were sought. The cone angle of the phosphine ligand[7] plays an important role in influencing the nuclearity of gold cluster compounds resulting from the reduction of mononuclear Au^I complexes.[8] Since the reduction of $[Au(NO_3)(PPh_3)]$ with

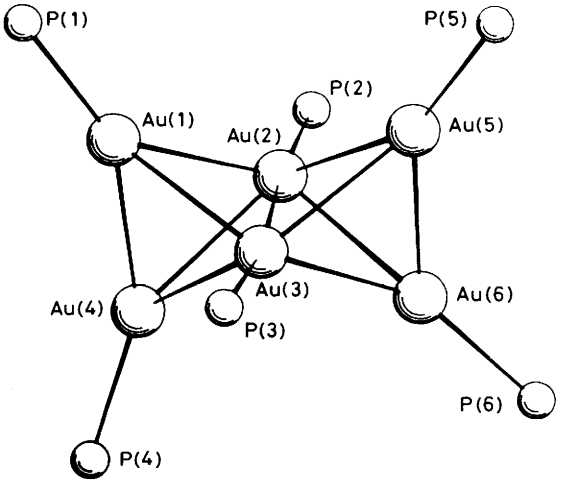

Figure 1. Molecular structure of the cation in $[Au_6(PPh_3)_6][NO_3]_2$. For clarity, the phenyl ligands have been omitted

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† *Supplementary data available* (No. SUP 56428, 7 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Summary of electronic spectral data (in CH_2Cl_2) for $[Au_6(PRPh_2)_6]Y_2$ (R = Ph, C_6H_4Me-*o*, or C_6H_{11}; Y = NO_3, BF_4, or ClO_4)

	Compound	$\lambda_{max.}$/nm
(**1**)	$[Au_6(PPh_3)_6][NO_3]_2$	476, 452 (sh), 331 (sh), 319
(**2b**)	$[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][NO_3]_2$	466, 439, 330, 308 (sh)
(**2c**)	$[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][ClO_4]_2$	464, 439, 333
(**2a**)	$[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][BF_4]_2$	462, 439, 331
(**3**)	$[Au_6\{P(C_6H_{11})Ph_2\}_6][NO_3]_2$	474, 445 (sh), 320, 307

Table 2. Some important intramolecular bond lengths (Å) for $[Au_6(PPh_3)_6][NO_3]_2\cdot 3CH_2Cl_2$, with estimated standard deviations in parentheses

Au–Au		Au(3)–Au(6)	2.762(2)
Au(1)–Au(2)	2.820(2)	Au(5)–Au(6)	2.663(2)
Au(1)–Au(3)	2.776(2)		
Au(1)–Au(4)	2.669(2)	Au–P	
Au(2)–Au(3)	2.651(2)	Au(1)–P(1)	2.307(3)
Au(2)–Au(4)	2.797(2)	Au(2)–P(2)	2.299(3)
Au(2)–Au(5)	2.775(2)	Au(3)–P(3)	2.317(3)
Au(2)–Au(6)	2.808(2)	Au(4)–P(4)	2.291(3)
Au(3)–Au(4)	2.790(2)	Au(5)–P(5)	2.273(3)
Au(3)–Au(5)	2.839(2)	Au(6)–P(6)	2.286(3)

$NaBH_4$ results in the formation of $[Au_9(PPh_3)_8][NO_3]_3$[9] we argued that the replacement of PPh_3 by phosphines with larger cone angles might result in the isolation of $[Au_6(PR_3)_6][NO_3]_2$ clusters. In agreement with this proposal the cluster compounds $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][BF_4]_2$ (**2a**) and $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][NO_3]_2$ (**2b**) were obtained in 50—76% yields from the corresponding mononuclear gold(I) compounds and either $NaBH_4$ or $[Ti(\eta\text{-}C_6H_5Me)_2]$ as the reducing agents. The corresponding ClO_4^- salt (**2c**) was formed from (**2b**) and $NaClO_4$ in EtOH. In addition $[Au_6\{P(C_6H_{11})Ph_2\}_6][NO_3]_2$ (**3**) (C_6H_{11} = cyclohexyl) was obtained in *ca.* 90% yield from $[Au(NO_3)\{P(C_6H_{11})Ph_2\}]$ and $NaBH_4$.

The compounds (**1**)—(**3**) have similar electronic spectral properties in solution (see Table 1) and crystallise as either red or red-green crystalline solids. Single-crystal *X*-ray crystallographic analyses of (**2a**) and (**2c**) have confirmed that they also have edge-sharing bitetrahedral geometries.[10]

Structure of $[Au_6(PPh_3)_6][NO_3]_2$.—The skeletal geometry of (**1**) as determined by a single-crystal *X*-ray crystallographic study is illustrated in Figure 1 and the relevant intramolecular bond length and bond angle data are summarised in Tables 2 and 3. The structural data confirm the edge-sharing bitetrahedral structure theoretically predicted for $[Au_6(PH_3)_6]^{2+}$.[4]

A similar geometry has been reported for the electronically related mixed-metal cluster $[Au_6(PPh_3)_4\{Co(CO)_4\}_2]$ (**4**).[9] The structure of (**1**) differs very significantly from that reported for the closely related gold cluster cation $[Au_6\{P(C_6H_4Me\text{-}p)_3\}_6][BPh_4]_2$. The latter has a distorted octahedral cluster geometry with an average Au–Au bond length of 3.02 Å.[1] The occurrence of two cluster compounds of gold having almost identical stoicheiometries and different skeletal geometries in the solid state is not unique. Indeed, we have recently reported an example[11] of skeletal isomerism whereby $[Au_9\{P(C_6H_4OMe\text{-}p)_3\}_8][NO_3]_3$ co-crystallises in two modifications: one tetragonal having a skeletal geometry derived from a centred icosahedron and the second orthorhombic, which has a skeletal geometry with idealised D_{4d} symmetry based on a centred crown.

Electronic factors suggest a preference for the edge-sharing bitetrahedral geometry over the octahedral geometry for $[Au_6(PH_3)_6]^{2+}$,[4] but clearly steric factors could favour the location of six triarylphosphine ligands around an octahedron, rather than a pair of edge-sharing tetrahedra. These two factors must be finely balanced for $[Au_6\{P(C_6H_4X\text{-}p)_3\}_6]^{2+}$ (X = Me or H) clusters and lead to the observation of the alternative structures. The significant contraction in the Au–Au bond lengths in going from the octahedron (average 3.02 Å) to the edge-sharing bitetrahedron [average 2.76 Å in (**1**)] confirms the theoretical conclusion that the metal–metal bonding is significantly stronger in the latter.

Although no crystallographic symmetry is imposed on the $[Au_6(PPh_3)_6]^{2+}$ cation, the bond lengths can be grouped in terms of the idealised D_{2h} skeletal geometry for an edge-sharing bitetrahedron. Table 4 summarises the relevant crystallographic data for $[Au_6(PPh_3)_6][NO_3]_2$ (**1**), $[Au_6(PPh_3)_4\{Co(CO)_4\}_2]$ (**4**), and $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][ClO_4]_2$ (**2c**).[10] The computed overlap populations for the Au–Au bonds in the hypothetical $[Au_6(PH_3)_6]^{2+}$ ion with D_{2h} symmetry are also given.[4] For each of the compounds the Au–Au bonds radiating from the shared edge are the longest

Table 3. Some important intramolecular bond angles (°) for $[Au_6(PPh_3)_6][NO_3]_2\cdot 3CH_2Cl_2$, with estimated standard deviations in parentheses

Au–Au–Au		Au(3)–Au(5)–Au(6)	60.2(1)
Au(2)–Au(1)–Au(3)	56.5(1)	Au(2)–Au(6)–Au(3)	56.8(1)
Au(2)–Au(1)–Au(4)	61.2(1)	Au(2)–Au(6)–Au(5)	60.9(1)
Au(3)–Au(1)–Au(4)	61.6(1)	Au(3)–Au(6)–Au(5)	63.1(1)
Au(1)–Au(2)–Au(3)	60.9(1)		
Au(1)–Au(2)–Au(4)	56.7(1)	Au–Au–P	
Au(1)–Au(2)–Au(5)	99.6(1)	Au(2)–Au(1)–P(1)	132.7(2)
Au(1)–Au(2)–Au(6)	121.4(1)	Au(3)–Au(1)–P(1)	143.8(2)
Au(3)–Au(2)–Au(4)	61.6(1)	Au(4)–Au(1)–P(1)	153.4(2)
Au(3)–Au(2)–Au(5)	63.0(1)	Au(1)–Au(2)–P(2)	111.0(2)
Au(3)–Au(2)–Au(6)	60.7(1)	Au(3)–Au(2)–P(2)	171.9(2)
Au(4)–Au(2)–Au(5)	124.4(1)	Au(4)–Au(2)–P(2)	114.8(2)
Au(4)–Au(2)–Au(6)	91.0(1)	Au(5)–Au(2)–P(2)	120.8(2)
Au(5)–Au(2)–Au(6)	56.9(1)	Au(6)–Au(2)–P(2)	127.3(2)
Au(1)–Au(3)–Au(2)	62.5(1)	Au(1)–Au(3)–P(3)	121.9(2)
Au(1)–Au(3)–Au(4)	57.3(1)	Au(2)–Au(3)–P(3)	174.7(2)
Au(1)–Au(3)–Au(5)	99.1(1)	Au(4)–Au(3)–P(3)	122.5(2)
Au(1)–Au(3)–Au(6)	124.8(1)	Au(5)–Au(3)–P(3)	114.8(2)
Au(2)–Au(3)–Au(4)	61.8(1)	Au(6)–Au(3)–P(3)	113.2(2)
Au(2)–Au(3)–Au(5)	60.6(1)	Au(1)–Au(4)–P(4)	154.9(2)
Au(2)–Au(3)–Au(6)	62.5(1)	Au(2)–Au(4)–P(4)	130.0(2)
Au(4)–Au(3)–Au(5)	122.1(1)	Au(3)–Au(4)–P(4)	143.4(2)
Au(4)–Au(3)–Au(6)	92.1(1)	Au(2)–Au(6)–P(6)	151.3(2)
Au(5)–Au(3)–Au(6)	56.7(1)	Au(2)–Au(5)–P(5)	136.9(2)
Au(1)–Au(4)–Au(2)	62.1(1)	Au(3)–Au(6)–P(6)	145.1(2)
Au(1)–Au(4)–Au(3)	61.1(1)	Au(3)–Au(5)–P(5)	151.2(2)
Au(2)–Au(4)–Au(3)	56.6(1)	Au(5)–Au(6)–P(6)	137.1(2)
Au(2)–Au(5)–Au(5)	56.4(1)	Au(6)–Au(5)–P(5)	143.3(2)
Au(2)–Au(5)–Au(5)	62.2(1)		

Table 4. Comparison of averaged bond lengths (Å) and computer overlap populations for $[Au_6(PR_3)_6]^{2+}$ clusters

	Compound			
Bond	(**1**)	(**2c**)	(**4**)	Overlap population
Au(2)–Au(3)	2.651(2)	2.615(2)	2.65	0.211
Au(1)–Au(4) (av. of 2 bonds)	2.666(3)	2.641(3)	2.62	0.299
Au(1)–Au(2) (av. of 8 bonds)	2.796(9)	2.808(9)	2.79	0.177

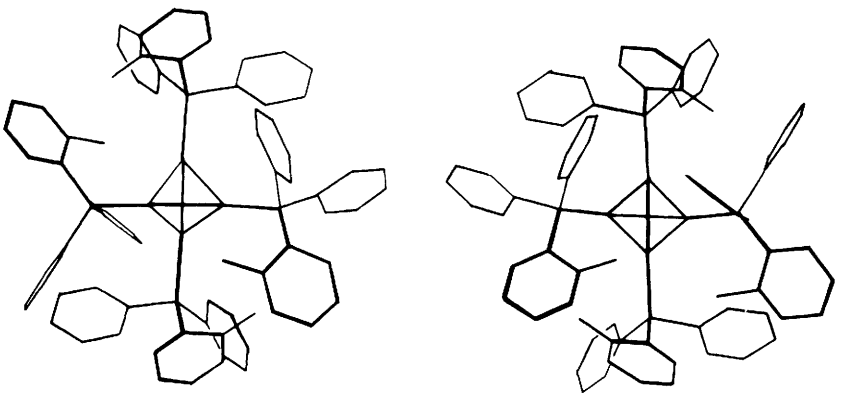

(*a*) (*b*)

Figure 2. Illustration of the phenyl ring conformations in $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6]Y_2$: (*a*) Y = ClO_4, (*b*) Y = BF_4. For clarity, only one of the gold tetrahedra of each cluster is shown

Table 5. Summary of $^{31}P\text{-}\{^1H\}$ n.m.r. data (CH_2Cl_2) for $[Au_6(PRPh_2)_6]^{2+}$ clusters

Compound	Chemical shift (p.p.m.)[a]	T/K
(1)	49.6 (s, 4 P) 60.7 (s, 2 P)	203
	53.3 (s, 6 P)	303
(**2b**)	46.5 (m, 4 P) 56.1 (s, 2 P)	173
	J(A–B), rotational isomer 1, 95 Hz[b]	
	J(A–B), rotational isomer 2, 87 Hz[b]	
	46.3 (s, 4 P) 56.9 (s, 2 P)	220
	50.2 (s, 6 P)	303
(3)	62.2 (m, 2 P) 65.4 (s, 2 P) 71.8 (m, 2 P)	183
	J(A–B), 80 Hz *J*(A–B), 124 Hz	
	63.5 (s, 4 P) 72.3 (s, 2 P)	263
	62.3 (s, 6 P)	303

[a] To high field with respect to trimethyl phosphate. [b] Interpreted in terms of two rotational isomers in the ratio 2:3.

and are approximately 2.80 Å. This is consistent with the low computed overlap population for this bond (0.177). The overlap populations suggest that the shared Au–Au bond should be longer than the parallel pair of outer bonds. Whilst this trend appears to be reproduced for $[Au_6(PPh_3)_4\{Co(CO)_4\}_2]$ (**4**) (although the absence of reported standard deviations for this compound leave unanswered the question of whether the difference is statistically significant), it is not reproduced for $[Au_6(PPh_3)_6][NO_3]_2$ (**1**) and $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][ClO_4]_2$ (**2c**). This divergence from the theoretically computed trend could arise from the simplification of representing the PPh_3 and $P(C_6H_4Me\text{-}o)Ph_2$ ligands by PH_3. Clearly, the cluster cations derived from the arylphosphine ligands are more sterically crowded than $[Au_6(PPh_3)_4\{Co(CO)_4\}_2]$ (**4**) and the cluster geometry distorts to limit the extent of steric compression. Two observations support this proposal. First, the divergence between theory and observation is larger for the $P(C_6H_4Me\text{-}o)Ph_2$ complex than the PPh_3 complex and secondly, for the outer gold atoms the Au–P vectors do not point towards the centres of the tetrahedra.

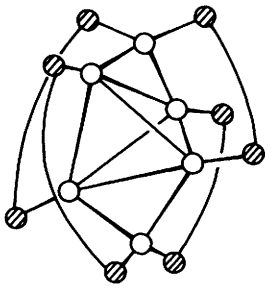
$^{31}P\text{-}\{^1H\}$ *N.M.R. Studies.*—The room temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the $[Au_6(PRPh_2)_6]^{2+}$ cations (**1**)—(**3**) do not correspond to their observed solid-state structures and only a single resonance is observed: at +53.3 for (**1**), +50.2 for (**2b**), and +62.3 p.p.m. for (**3**) (see Table 5). As the temperature is lowered, however, the signals broaden and separate into two sharp resonances with the anticipated ratio of 4:2. The less intense resonance is always observed at lower fields and the chemical shift difference is *ca.* 10 p.p.m. For (**3**) this type of spectrum is observed at 243 K, but for (**1**) and (**2b**) temperatures lower than 230 K were required. The complexes do not exchange with free phosphine at 200 K, but since they react with phosphines at room temperature (see below) it is difficult to prove unambiguously that the clusters are undergoing an intra- rather than an inter-molecular exchange process. It did not prove possible to resolve the spectra sufficiently under these conditions to observe P–P couplings.

Below 200 K the spectra of the complexes (**2b**) and (**3**) show additional splittings which we have attributed to the freezing out of rotational conformers for the lower symmetry phosphines, $P(C_6H_4Me\text{-}o)Ph_2$ and $P(C_6H_{11})Ph_2$. The resonance at 63.5 p.p.m. for $[Au_6\{P(C_6H_{11})Ph_2\}_6]^{2+}$ (**3**) separates into an AB quartet and a singlet, and the resonance at 72.3 p.p.m. resolves into an AB quartet if the temperature is lowered below 203 K.

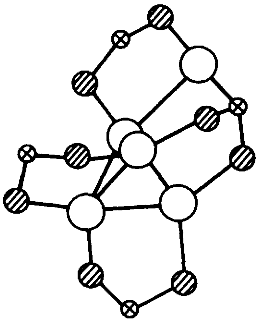
In contrast, for (**2b**), the lower field resonance does not show any additional fine structure, but the higher field line splits into a multiplet of eight lines. Attempts at computer simulation of the spectrum in terms of two AB quartets arising from a single conformation of (**2b**) were not successful. The spectrum could, however, be successfully analysed in terms of two AB quartets arising from two conformers in the ratio of 3:2.

The clusters $[Au_6(PRPh_2)_6]^{2+}$ (R = $C_6H_4Me\text{-}o$ or C_6H_{11}) could adopt a wide range of conformations in solution which could account for the above observations. Figure 2 illustrates two possible conformations which have been revealed by single-crystal *X*-ray crystallographic analyses of $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6]Y_2$ [Y = BF_4 (**2a**) or ClO_4 (**2c**)].

Reactions of $[Au_6\{P(C_6H_{11})Ph_2\}_6]^{2+}$.—Compound (**3**) reacts rapidly with dppp [dppp = 1,3-bis(diphenylphosphino)propane] to give an intense blue solution. The electronic spectral characteristics of this solution correspond precisely with those for $[Au_6(dppp)_4]^{2+}$ (**5a**), which has been characterised as a nitrate salt by a single-crystal *X*-ray crystallographic determination.[12] A similar compound (**5b**) was obtained from $[Au_6\{P(C_6H_{11})Ph_2\}_6]^{2+}$ and dppb [dppb = 1,4-bis(diphenylphosphino)butane]. Therefore, with these ligands cluster degradation has not occurred, but the replacement of the $P(C_6H_{11})Ph_2$ ligands by the chelating diphosphines has resulted in a skeletal rearrangement. Presumably, the Au_4L_4 tetrahedron with edge-bridging AuL_2



(5a), (5b)



(6)

○ Au
▨ P
⊗ C

fragments is better able to accommodate the co-ordination requirements of the chelating diphosphines.

When dppm [bis(dimethylphosphino)methane] was added to a solution of $[Au_6\{P(C_6H_{11})Ph_2\}_6]^{2+}$ in methanol a reddish orange solution resulted. Large red crystals of the compound were obtained on recrystallisation from CH_2Cl_2–toluene. Unit-cell parameters of these crystals demonstrated that they were the previously characterised pentanuclear cluster $[Au_5(dppm)_3(dppm - H)][NO_3]_2$ **(6)**.[12] The cluster consists of a tetrahedron of gold atoms with the fifth gold atom acting as a terminal ligand to the apical gold atom. A proton has been lost from a methylene group of one of the dppm ligands and the resulting $Ph_2P–CH–PPh_2$ anion functions as a bridging tridentate ligand.

Experimental

Reactions were routinely carried out using standard Schlenk line procedures under an atmosphere of pure dry N_2 or, in the experiments involving the use of $[Ti(\eta\text{-}C_6H_5Me)_2]$, pure dry argon and using dry O_2-free solvents. Microanalyses (C,H) were carried out by Mr. M. Gascoyne and his staff of this Laboratory. Infrared spectra were recorded as Nujol mulls using a Pye-Unicam SP2000 spectrometer. Solution electronic spectra were recorded on a Perkin-Elmer 552 u.v.–visible spectrophotometer using 10 mm quartz cells. $^{31}P\text{-}\{^1H\}$ N.m.r. spectra were recorded using a Bruker AM 250 spectrometer and were referenced to trimethyl phosphate in D_2O. All samples were run in deuteriated solvents.

Synthesis of Hexakis(triphenylphosphine)hexagold(2+) Nitrate.—$[Au_8(PPh_3)_8][NO_3]_2$[6] (0.033 g, 0.0087 mmol) was dissolved in methanol (20 cm^3) giving a red solution, solid $K[Ag(CN)_2]$ (0.0017 g, 0.0087 mmol) was then added with stirring. At 10-min intervals small aliquots of the gradually darkening solution were taken and electronic spectra recorded. Changes in these spectra indicated that a reaction was occurring. After *ca.* 1 h no further changes were recorded and the reaction was assumed to have reached completion. Addition of an excess of diethyl ether caused the precipitation of a brown solid, the mixture was then left to stand for 12 h at −18 °C after which the precipitate was filtered off and dried *in vacuo*. The brown precipitate was recrystallised by the slow evaporation of solvent (at 0 °C) from a mixture made up by dissolving the cluster compound in dichloromethane and adding small amounts of toluene until precipitation almost occurred. Small red-brown needles of the *product* separated and were filtered off, washed with a little diethyl ether and dried *in vacuo*. Crystals suitable for a single-crystal *X*-ray diffraction study were grown by the slow diffusion of toluene into a dichloromethane solution of the cluster compound. Yield 0.02 g, 30% (based on gold) (Found: C, 44.0; H, 3.1; N, 0.9. $C_{108}H_{90}Au_6N_2O_6P_6\cdot 3CH_2Cl_2$ requires C, 44.1; H, 3.0; N, 0.9%). The i.r. spectrum (Nujol mull) showed peaks characteristic of the nitrate ion at 828 and 692 cm^{-1}.

Synthesis of Hexakis[diphenyl(o-tolyl)phosphine]hexagold(2+) Nitrate–Dichloromethane (1/2).—$[Au(NO_3)\{P(C_6H_4Me\text{-}o)Ph_2\}]$ (0.18 g, 0.34 mmol) was suspended in ethanol (20 cm^3) and an ethanolic $NaBH_4$ solution (0.004 g, 0.11 mmol in 2 cm^3 EtOH) was added dropwise with stirring. A green-brown solution formed immediately which was allowed to stir for 1 h until all the $[Au(NO_3)\{P(C_6H_4Me\text{-}o)Ph_2\}]$ had dissolved and reacted. The solution was then filtered on a Buchner funnel and the solvent volume was reduced to 10 cm^3 under reduced pressure. The *product* was precipitated by the slow addition of hexane. The green powder was collected by filtration and dried *in vacuo*. The compound was recrystallised by the slow diffusion of diethyl ether into a dichloromethane solution of the cluster compound, this afforded dark red-green crystals which immediately disintegrated to a leaf-green powder when the solvent was removed. Yield 0.08 g, 54% (based on Au) (Found: C, 44.6; H, 3.3; N, 1.0. $C_{114}H_{102}Au_6N_2O_6P_6\cdot C_2H_4Cl_4$ requires C, 44.4; H, 3.4; N, 1.0%).

Synthesis of Hexakis[diphenyl(o-tolyl)phosphine]hexagold(2+) Tetrafluoroborate, using $[Ti(\eta\text{-}C_6H_5Me)_2]$ *as a Reducing Agent.*—This is an alternative preparation of the hexanuclear gold cluster compound described above. $[AuCl\{P(C_6H_4Me\text{-}o)Ph_2\}]$ (0.4 g, 0.79 mmol) was reacted with $[Ti(\eta\text{-}C_6H_5Me)_2]$ (0.1 g, 0.43 mmol) in toluene. The unknown gold–titanium intermediate was worked-up with EtOH (15 cm^3) and the product was precipitated out using aqueous 40% HBF_4 (3 cm^3). The green powder was filtered off, dried *in vacuo* and characterised as $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][BF_4]_2$. The gold cluster compound was recrystallised by the slow diffusion of hexane through a dichloromethane solution of the product. The deep red-green crystals formed on recrystallisation tended to disintegrate to a leaf-green powder once the mother-liquor was removed. Yield 0.32 g, 76% (based on Au) (Found: C, 44.0; H, 3.4. $C_{114}H_{102}Au_6B_2F_8P_6\cdot C_2H_4Cl_4$ requires C, 43.7; H, 3.3%).

Synthesis of Hexakis[diphenyl(o-tolyl)phosphine]hexagold(2+) Perchlorate.—The perchlorate salt was made by a simple metathetical reaction from the nitrate salt. $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][NO_3]_2$ (0.1 g, 0.037 mmol) was dissolved in ethanol to give a red-brown solution, excess $NaClO_4$ in warm ethanol was slowly added. The volume of the solution was reduced until a persistent cloudiness appeared and the solution left for 18 h at −18 °C. The green microcrystalline *solid*, $[Au_6\{P(C_6H_4Me\text{-}o)Ph_2\}_6][ClO_4]_2$ was collected by filtration and dried *in vacuo*. Yield 0.08 g, 78% (Found: C, 44.5; H, 3.4. $C_{114}H_{102}Au_6Cl_2O_8P_6$ requires C, 45.0; H, 3.4%).

Synthesis of Hexakis(cyclohexyldiphenylphosphine)hexagold(2+) Nitrate.—$[Au(NO_3)\{P(C_6H_{11})Ph_2\}]$ (0.2 g, 0.38 mmol) was suspended in ethanol, $NaBH_4$ (0.005 g, 0.13 mmol) was added and the solution stirred for *ca.* 1 h until all the $[Au(NO_3)\{P(C_6H_{11})Ph_2\}]$ had dissolved. The volume of the solution was reduced and the addition of hexane led to precipitation of a yellow-brown solid. Recrystallisation from CH_2Cl_2–hexane gave dark brown crystals of the *product*. Yield 0.17 g (90%) (Found: C, 44.1; H, 3.9. $C_{108}H_{126}Au_6N_2O_6P_6$ requires C, 44.5; H, 4.4%).

Reaction of $[Au_6(PRPh_2)_6][NO_3]_2$ *with dppp and dppb.*—The phosphine dppp (0.09 g, 0.2 mmol) was added to a solution

Table 6. Fractional atomic co-ordinates for (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Au(1)	0.685 84(5)	0.210 70(8)	0.198 87(5)
Au(2)	0.778 69(5)	0.305 72(8)	0.198 15(4)
Au(3)	0.725 60(5)	0.298 12(8)	0.282 71(5)
Au(4)	0.679 57(5)	0.378 84(8)	0.198 58(5)
Au(5)	0.829 78(5)	0.238 07(8)	0.283 03(5)
Au(6)	0.811 32(5)	0.403 43(8)	0.282 14(5)
P(1)	0.664 1(3)	0.077 9(5)	0.168 8(3)
P(2)	0.815 7(3)	0.300 4(6)	0.119 7(3)
P(3)	0.686 5(3)	0.292 7(6)	0.360 5(3)
P(4)	0.651 5(3)	0.507 4(6)	0.168 4(3)
P(5)	0.890 6(3)	0.135 3(6)	0.299 3(4)
P(6)	0.848 8(3)	0.522 1(5)	0.316 5(3)
C(111)	0.609 4(11)	0.087 7(21)	0.124 7(11)
C(112)	0.608 2(14)	0.156 3(24)	0.096 3(14)
C(113)	0.570 4(17)	0.168 2(28)	0.052 7(16)
C(114)	0.531 1(14)	0.111 1(25)	0.050 9(15)
C(115)	0.530 9(20)	0.045 5(35)	0.083 2(21)
C(116)	0.571 8(18)	0.032 9(30)	0.118 1(17)
C(121)	0.644 6(12)	0.001 2(22)	0.216 7(13)
C(122)	0.642 0(13)	0.027 0(24)	0.264 7(15)
C(123)	0.632 1(14)	−0.033 7(26)	0.300 5(14)
C(124)	0.623 0(14)	−0.115 3(26)	0.289 0(16)
C(125)	0.625 6(14)	−0.142 2(25)	0.241 2(15)
C(126)	0.638 5(14)	−0.082 8(26)	0.202 8(15)
C(131)	0.711 6(11)	0.028 5(20)	0.131 3(12)
C(132)	0.752 8(14)	−0.016 0(23)	0.154 8(13)
C(133)	0.792 0(14)	−0.055 5(23)	0.129 9(15)
C(134)	0.791 9(15)	−0.053 6(26)	0.079 7(16)
C(135)	0.755 6(18)	−0.007 7(30)	0.054 5(17)
C(136)	0.714 9(18)	0.033 4(30)	0.081 6(19)
C(211)	0.846 0(10)	0.399 3(18)	0.103 5(11)
C(212)	0.880 5(12)	0.440 7(21)	0.138 0(12)
C(213)	0.903 3(13)	0.511 4(24)	0.126 0(14)
C(214)	0.896 8(13)	0.544 6(23)	0.080 5(15)
C(215)	0.868 7(16)	0.509 0(27)	0.042 1(16)
C(216)	0.841 8(13)	0.433 5(22)	0.053 6(13)
C(221)	0.866 6(11)	0.220 8(19)	0.114 7(11)
C(222)	0.913 1(11)	0.239 0(19)	0.094 8(11)
C(223)	0.949 8(14)	0.175 8(23)	0.092 9(13)
C(224)	0.942 8(13)	0.096 8(23)	0.110 3(13)
C(225)	0.899 4(13)	0.080 7(22)	0.134 9(13)
C(226)	0.860 1(12)	0.141 3(22)	0.136 3(12)
C(231)	0.770 8(12)	0.273 0(20)	0.067 2(12)
C(232)	0.725 4(13)	0.312 6(22)	0.062 7(13)
C(233)	0.689 9(14)	0.299 3(24)	0.025 9(14)
C(234)	0.704 6(14)	0.245 6(24)	−0.014 2(14)
C(235)	0.747 7(17)	0.205 8(27)	−0.011 7(16)
C(236)	0.786 6(15)	0.220 7(26)	0.028 8(16)
C(311)	0.659 3(13)	0.395 9(21)	0.378 1(12)
C(312)	0.609 7(15)	0.403 9(26)	0.395 8(15)
C(313)	0.590 6(18)	0.480 4(33)	0.411 5(17)
C(314)	0.620 7(15)	0.546 1(25)	0.409 4(14)
C(315)	0.669 9(16)	0.540 1(26)	0.392 6(15)
C(316)	0.692 3(15)	0.463 9(26)	0.377 7(14)
C(321)	0.633 3(12)	0.220 8(20)	0.363 8(13)
C(322)	0.597 7(13)	0.211 9(21)	0.327 0(13)
C(323)	0.553 7(15)	0.166 0(25)	0.329 7(15)
C(324)	0.545 7(17)	0.120 4(29)	0.370 3(19)
C(325)	0.577 0(17)	0.129 7(28)	0.413 2(17)
C(326)	0.624 4(15)	0.177 6(25)	0.411 1(15)
C(331)	0.730 6(14)	0.264 6(24)	0.413 9(15)
C(332)	0.734 6(17)	0.308 7(28)	0.457 4(17)
C(333)	0.771 0(17)	0.282 5(30)	0.496 1(17)
C(334)	0.800 5(17)	0.220 5(31)	0.484 3(19)
C(335)	0.802 5(15)	0.178 9(26)	0.442 7(16)
C(336)	0.765 6(17)	0.201 6(28)	0.404 5(16)
C(411)	0.700 6(11)	0.586 7(20)	0.164 4(11)
C(412)	0.750 3(14)	0.565 4(23)	0.160 1(14)
C(413)	0.792 6(14)	0.621 1(24)	0.156 4(14)
C(414)	0.779 5(14)	0.706 0(25)	0.155 9(14)
C(415)	0.731 3(14)	0.731 9(23)	0.161 6(14)
C(416)	0.691 8(13)	0.673 4(22)	0.165 2(13)
C(421)	0.625 0(10)	0.494 9(18)	0.105 0(10)
C(422)	0.637 7(15)	0.551 4(26)	0.066 5(16)
C(423)	0.613 5(19)	0.544 8(32)	0.019 0(19)
C(424)	0.582 3(15)	0.482 9(26)	0.008 1(15)
C(425)	0.570 3(12)	0.423 5(22)	0.042 3(13)
C(426)	0.592 3(12)	0.432 2(20)	0.093 1(12)
C(431)	0.601 7(12)	0.560 1(19)	0.203 3(12)
C(432)	0.610 7(12)	0.570 9(21)	0.254 8(13)
C(433)	0.577 0(15)	0.617 1(24)	0.282 8(15)
C(434)	0.530 7(15)	0.642 6(25)	0.261 1(16)
C(435)	0.517 9(15)	0.627 1(26)	0.211 4(16)
C(436)	0.554 7(13)	0.584 5(21)	0.183 5(12)
C(511)	0.913 1(12)	0.126 7(22)	0.366 0(12)
C(512)	0.931 7(14)	0.202 6(26)	0.387 0(15)
C(513)	0.949 4(19)	0.195 8(34)	0.438 3(20)
C(514)	0.948 6(17)	0.121 4(33)	0.462 6(18)
C(515)	0.933 1(18)	0.051 5(32)	0.444 0(18)
C(516)	0.914 1(15)	0.051 7(26)	0.391 0(15)
C(521)	0.868 8(11)	0.031 1(19)	0.281 3(11)
C(522)	0.894 3(13)	−0.027 2(23)	0.257 6(13)
C(523)	0.873 9(14)	−0.107 8(24)	0.247 6(14)
C(524)	0.827 2(13)	−0.125 8(21)	0.261 8(13)
C(525)	0.795 7(16)	−0.068 5(27)	0.289 9(15)
C(526)	0.817 7(13)	0.014 9(23)	0.297 3(13)
C(531)	0.947 8(12)	0.156 0(22)	0.266 0(12)
C(532)	0.997 0(14)	0.115 3(22)	0.273 6(14)
C(533)	1.039 2(13)	0.132 8(23)	0.245 4(13)
C(534)	1.037 2(16)	0.199 0(29)	0.217 3(16)
C(535)	0.992 4(17)	0.249 9(29)	0.205 8(16)
C(536)	0.948 9(13)	0.224 2(23)	0.233 4(14)
C(611)	0.902 3(11)	0.564 4(19)	0.278 5(11)
C(612)	0.898 8(14)	0.638 8(24)	0.255 1(14)
C(613)	0.943 8(16)	0.670 5(27)	0.229 6(15)
C(614)	0.984 0(16)	0.617 6(29)	0.226 8(16)
C(615)	0.984 9(16)	0.540 9(28)	0.246 4(16)
C(616)	0.944 6(14)	0.511 0(23)	0.272 0(13)
C(621)	0.881 9(11)	0.496 1(19)	0.377 5(11)
C(622)	0.923 1(12)	0.542 4(21)	0.394 4(13)
C(623)	0.946 8(14)	0.520 8(25)	0.442 4(15)
C(624)	0.928 8(15)	0.458 2(27)	0.467 9(15)
C(625)	0.889 0(14)	0.409 5(25)	0.451 7(14)
C(626)	0.864 7(13)	0.427 4(23)	0.402 8(14)
C(631)	0.805 4(11)	0.610 4(18)	0.326 7(11)
C(632)	0.811 5(13)	0.662 3(23)	0.369 7(13)
C(633)	0.776 6(17)	0.731 0(28)	0.377 1(17)
C(634)	0.737 7(16)	0.741 5(27)	0.346 1(16)
C(635)	0.731 2(13)	0.689 7(23)	0.305 7(13)
C(636)	0.762 1(14)	0.625 5(23)	0.297 0(13)
N(1)	0.411 0(13)	0.191 5(20)	0.584 9(6)
O(11)	0.367 0(14)	0.158 9(27)	0.582 3(8)
O(12)	0.449 6(16)	0.151 2(32)	0.570 7(8)
O(13)	0.416 4(22)	0.264 0(21)	0.602 6(7)
N(2)	0.075 5(8)	0.181 7(13)	0.904 4(9)
O(21)	0.041 6(9)	0.125 5(13)	0.899 7(12)
O(22)	0.105 9(10)	0.196 3(19)	0.869 5(12)
O(23)	0.078 1(10)	0.222 6(14)	0.944 7(10)
C(1)	0.451 1(18)	0.249 2(40)	0.938 0(19)
Cl(11)	0.391 0(11)	0.206 6(19)	0.953 8(11)
Cl(12)	0.467 5(11)	0.197 5(20)	0.882 2(11)
C(2)	0.039 7(12)	0.210 6(58)	0.580 0(9)
Cl(21)	0.074 3(8)	0.187 8(14)	0.636 3(8)
Cl(22)	0.085 4(9)	0.206 9(16)	0.532 2(8)
C(3)	0.696 0(11)	−0.002 8(46)	0.445 4(16)
Cl(31)	0.709 0(8)	0.045 5(14)	0.504 0(8)
Cl(32)	0.754 4(10)	−0.036 7(18)	0.420 1(10)

of $[Au_6\{P(C_6H_{11})Ph_2\}_6][NO_3]_2$ (0.1 g, 0.03 mmol) in CH_2Cl_2 (10 cm^3). After stirring for a few minutes the solution turned an intense blue colour. Addition of cyclohexane yielded crystals of tetrakis{1,3-bis(diphenylphosphino)propane}hexagold(2+) nitrate which were identified by their characteristic absorption spectrum and $^{31}P-\{^1H\}$ n.m.r.[12] Tetrakis{1,4-bis(diphenylphosphino)butane}hexagold(2+) nitrate was prepared in a similar fashion.

Reaction of $[Au_6\{P(C_6H_{11})Ph_2\}_6][NO_3]_2$ *with dppm*.—The phosphine dppm (0.08 g, 0.2 mmol) was added to a solution of $[Au_6\{P(C_6H_{11})Ph_2\}_6][NO_3]_2$ (0.1 g, 0.03 mmol) in methanol (20 cm^3) and the solution stirred until all the dppm had dissolved (*ca.* 15 min). The volume of the solution was reduced, Et_2O was added and a flesh coloured precipitate formed. This was filtered off, washed with Et_2O and dried. Yield 0.07 g, 92.5%. Recrystallisation from CH_2Cl_2–toluene yielded single crystals suitable for *X*-ray diffraction. The compound was shown to be $[Au_5(dppm)_3(dppm - H)][NO_3]_2$ by its unit-cell characteristics (a = 15.796, b = 23.190, c = 15.280 Å).[12]

Crystal Data for (**1**).—$C_{108}H_{90}Au_6N_2O_6P_6 \cdot C_3H_6Cl_6$, M = 3 134.4, monoclinic, a = 25.674(5), b = 15.843(10), c = 26.368(4) Å, β = 91.76(2)°, U = 10 636 Å^3 (by least-squares refinement of 25 high-angle reflections which were automatically centred), λ = 0.710 69 Å, space group $P2_1/a$, Z = 4, D_c = 1.96 g cm^{-3}, $F(000)$ = 5 960. Red-brown crystals were grown from CH_2Cl_2–toluene and mounted in a 0.5-mm Lindemann capillary tube. Crystal dimensions 0.1 × 0.1 × 0.1 mm, μ(Mo-K_α) = 87.94 cm^{-1}.

Geometric diffraction data were collected on a CAD4F diffractometer, $\omega/2\theta$ with ω scan width 0.8°, graphite-monochromated Mo-K_α, 6 144 reflections measured ($1.5 < \theta < 17.5°$), 4 430 unique absorption corrected reflections with $I \geqslant 3\sigma(I)$.

The structure was solved by Patterson methods followed by successive blocked least-squares refinement and difference Fourier syntheses to a conventional R = 0.049, R' = 0.066. Au and P atoms were given anisotropic thermal parameters, the remainder isotropic. A Chebyschev weighting system with coefficients of 112.46, 140.00, and 43.54 gave satisfactory agreement analyses. The hydrogen atom contributions were added on the basis of calculated positions. Programs and computers used and sources of scattering factor data are given in refs. 13 and 14. Atomic co-ordinates are given in Table 6.

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