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Some theoretical and structural aspects of gold cluster chemistry

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The bonding in tertiary phosphine cluster compounds of gold is sufficiently straightforward to permit an effective interaction between theoretical concepts developed from semi-empirical molecular orbital calculations and synthetic and structural chemistry. At the simplest conceptual level the isolobal nature of the $Au(PR_3)$ fragment and either the CH_3 or H radicals provides a basis for understanding the structures of a wide range of homonuclear and heteronuclear clusters, e.g. $Os_3(CO)_{10}$-$H(AuPPh_3)$ and $(OC)_5VAu_3(PPh_3)_3$. However, this simplified approach neglects some secondary gold–gold interactions between adjacent gold atoms, which arise from the availability of the higher-lying gold 6p orbitals.

In low-nuclearity clusters tetrahedral fragments, which permit the effective formation of four-centre two electron bonds between the $Au(PR_3)$ fragments, are preferred to larger deltahedra. In higher-nuclearity clusters the stabilities of the clusters depend on the presence of a central gold atom that provides strong radial gold–gold bonding. The relative importance of the radial and tangential components to the total bonding has been effectively demonstrated by a structural comparison of alternative $Au_9(PR_3)_8^{3+}$ clusters. The predictive capability of the theoretical approach has been demonstrated by the synthesis and structural characterization of the icosahedral cluster $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$.

Although credible technological and biochemical reasons may be given for studying cluster compounds of the transition metals (Muetterties 1975, 1977), our interest in these compounds derives from a more innocent desire to understand in detail the electronic and steric factors that govern the structures and stoichiometries of these complex yet aesthetically pleasing chemical species. The first examples of gold tertiary phosphine cluster compounds, namely $Au_{11}I_3(PR_3)_7$ and $[Au_9(PPh_3)_8](BF_4)_3$, were reported approximately 10 years ago by Malatesta and Naldini (McPartlin *et al.* 1969; Bellon *et al.* 1971) and resulted from an investigation of the reactions of mononuclear gold phosphine compounds with $NaBH_4$. These compounds provided a particularly suitable vehicle for our attempt to merge synthetic and theoretical chemistry because these clusters are derived from the simple $AuPR_3$ fragment, which does not pose difficult theoretical problems because it does not have alternative stereochemical possibilities and the phosphine ligand does not, unlike the related carbonyl ligand, adopt alternative terminal and bridging coordination modes.

The $M(PH_3)$ fragment (M = Cu, Ni, Pd, Pt, Ag or Au) is a common constituent of cluster compounds of the platinum and Group Ia metals and has the frontier molecular orbitals represented schematically in figure 1. For these metals the five orbitals with a predominance of d orbital character are filled, and the bonding characteristics of the fragment are determined primarily by the hy(s–z) and higher-lying metal p_x and p_y orbitals. For the lighter metals, e.g. Ni or Cu, all three orbitals are used for skeletal bonding and consequently $Ni(PR_3)$ and $Cu(PR_3)$ fragments may be accurately described as being isolobal with CH or the conical

$M(CO)_3$ fragment. For the heavier elements the p_x and p_y orbitals are higher-lying and less available for bonding, and therefore the $AuPPh_3$ and $PtPPh_3$ fragments are more correctly described as being isolobal with either CH_3 or $Mn(CO)_5$ (Elian *et al.* 1976). The structural and chemical ramifications of these isolobal analogies have been discussed at some length in a recent publication (Evans & Mingos 1982).

A noteworthy limitation associated with describing $Au(PH_3)$ as isolobal with CH_3 or H can be illustrated by the recent structural determination of $Au_2(dppm\text{-}H)_2$ (Briant *et al.* 1982)

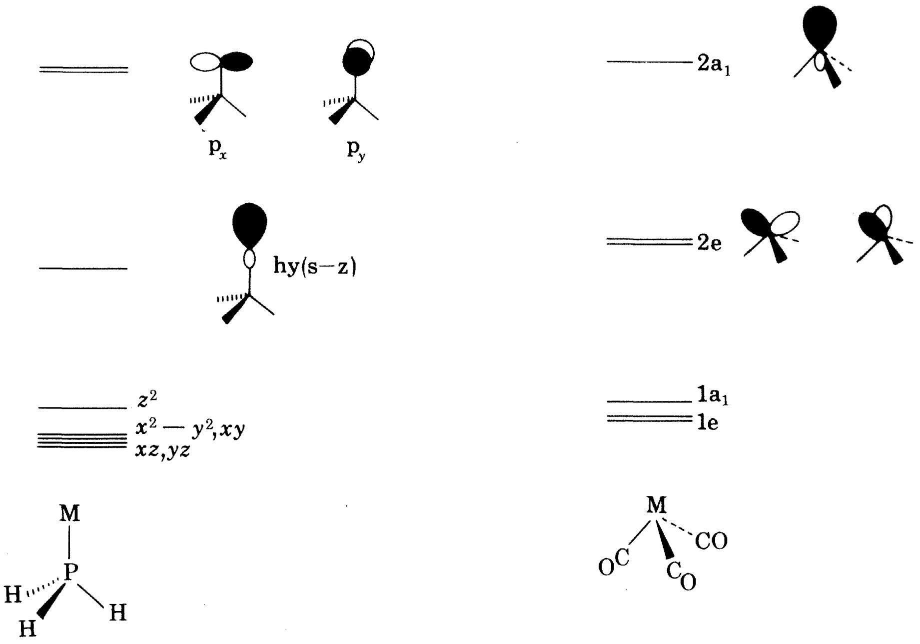


Figure 1. A comparison of the frontier molecule orbitals of $M(CO)_3$ and $M(PH_3)$ fragments.

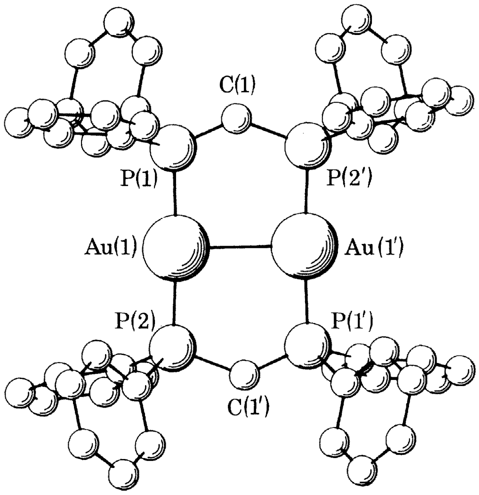


Figure 2. The molecular structure of $Au_2\{(Ph_2P)_2CH\}_2$. For reasons of clarity the hydrogen atoms have been omitted, and only one of the molecules that represent the total crystallographically disordered situation has been illustrated. The gold–gold distance is 2.883(3) Å.

(dppm = $Ph_2PCH_2PPh_2$). This compound resulted from the reaction of $[Au_{13}Cl_2(PMe_2Ph)_{10}](PF_6)_3$ with bis(diphenylphosphino)methane (dppm), and its molecular structure is illustrated in figure 2. In this compound the two parallel linear gold (I) (d^{10}) P–Au–P units are separated by an Au–Au distance of only 2.88 Å.† This distance, which is comparable with the gold–gold distance in the metal, can only be rationalized if the gold–gold repulsive interactions arising from the filled d orbitals on each gold atom are mitigated by the intervention of the higher-lying gold 6p orbitals, an interaction that is not available to isolobal fragments such as CH_3, $Mn(CO)_5$ or H.

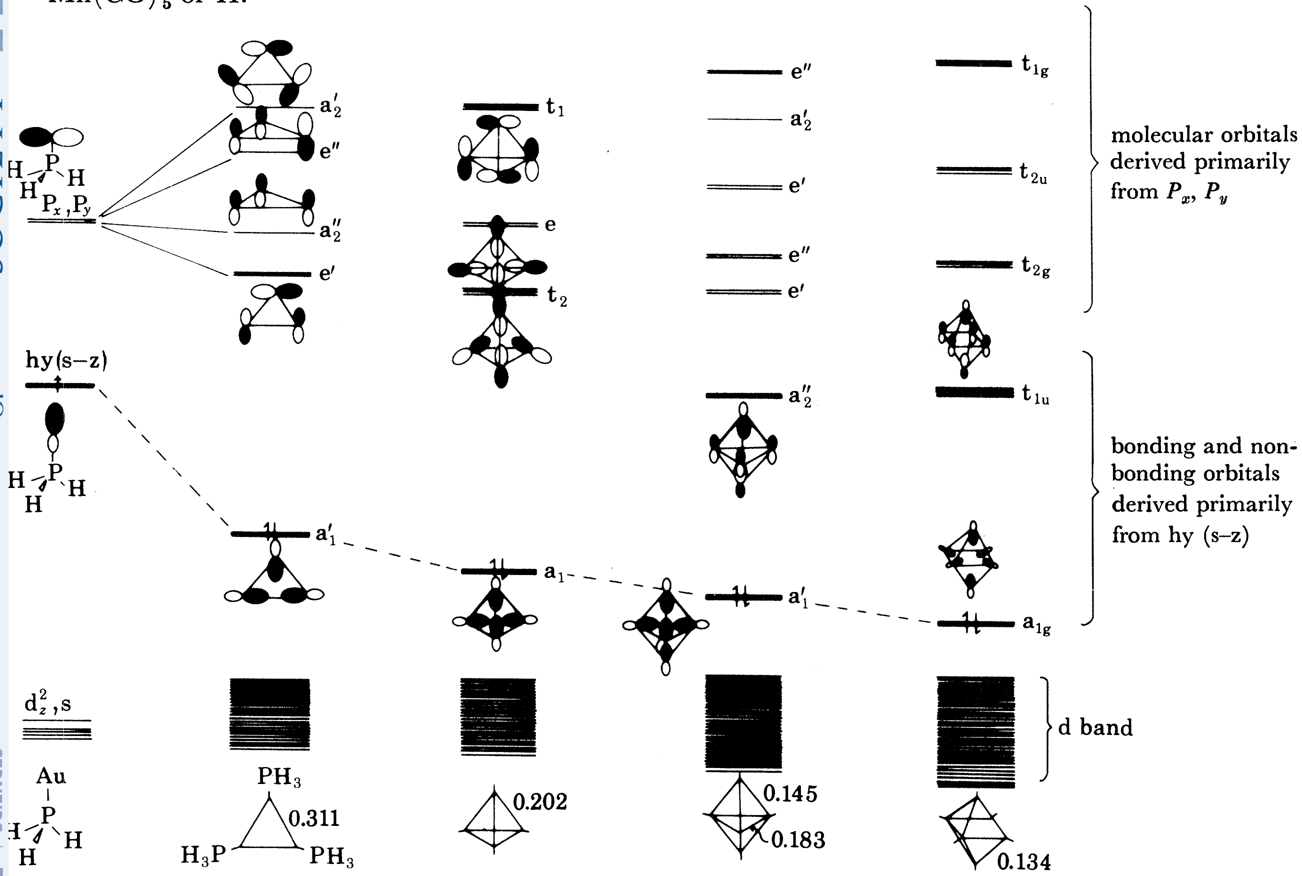


FIGURE 3. A summary of the computed bonding and non-bonding molecular orbitals of $Au_n(PH_3)_n^{x+}$ ($x = n-2$) with triangular, tetrahedral, trigonal bipyramidal and octahedral geometries. The computed Au–Au overlap populations for these ions are also given at the bottom of the figure.

The isolobal relations discussed above have been extended to homonuclear cations derived from $Au(PH_3)$ fragments (Evans & Mingos 1982) and have been used to account qualitatively for the molecular orbital diagrams illustrated in figure 3. The symmetries, nodal characteristics and relative energies of the molecular orbitals derived from hy(s–z) of the $Au(PH_3)$ fragments are entirely analogous to those of H_n^{x+} aggregates, and the coefficients of the molecular orbitals may be derived from spherical harmonics in the elegant manner described by Stone (1981 *a*, *b*). From figure 3 it is apparent that this analogy is valid because the higher-lying gold 6p orbitals do not make a large direct contribution to cluster bonding.

It follows from the simple molecular orbital analysis that the cluster metal–metal bonding

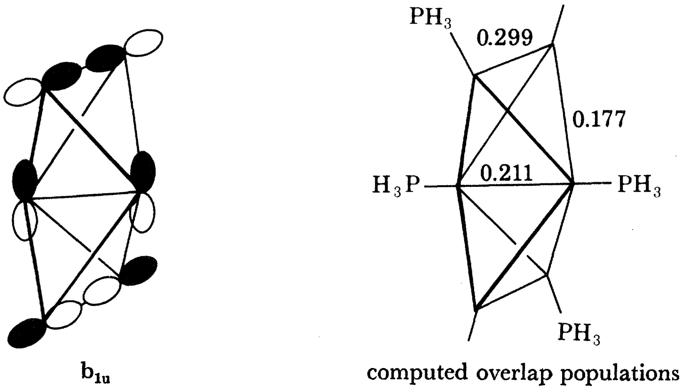
† 1 Å = 10^{-10} m = 10^{-1} nm.

interactions are maximized for polyhedra with triangular faces because these generate the largest number of next-neighbour interactions between the hy(s–z) orbitals of the individual Au(PH_3) fragments. The bonding may therefore be approximately described as a multicentre two-electron bond, represented in the molecular orbital terms of figure 3 as the totally symmetric (a_{1g} or a_1) filled orbital. As the nuclearity of the cluster increases, the stability of this particular molecular orbital increases (see figure 3), but the computed bond orders between individual gold atoms decreases, falling from 0.311 for the triangular cluster to 0.134 for the octahedral cluster. A suitable compromise between these opposing effects appears to be achieved for the tetrahedron and consequently this tetranuclear fragment is a common component in gold cluster and indeed mixed-metal cluster compounds containing gold. Examples of clusters containing the tetrahedral unit include $Au_4I_2(PPh_3)_4$ (Demartin *et al.* 1981), $Au_6(PPh_3)_4\{Co(CO)_4\}_2$ (Bour *et al.* 1981), $(OC)_5VAu_3(PPh_3)_3$ (Ellis 1981) and $Os_4(CO)_{13}$-$H_2Au_2(PPh_3)_2$ (Johnson *et al.* 1982).

FIGURE 4. Comparison of the observed bond lengths (ångströms) in $[Au_6\{(p\text{-}C_6H_4Me)_3P\}_6](BPh_4)_2$ (octahedral) and $[Au_6(PPh_3)_6](NO_3)_2$ (edge-shared tetrahedral) clusters.

In 1973 Bellon *et al.* isolated (in minute quantities) a few yellow crystals of $[Au_6\{(p\text{-tol})_3P\}_6]$-$(BPh_4)_2$ and by a single X-ray structural analysis established that it had an octahedral cluster geometry. In recent months an analogous compound $[Au_6(PPh_3)_6](NO_3)_2$ was synthesized in good yield from $[Au_8(PPh_3)_8](NO_3)_2$ and $Ag(CN)_2^-$ (Hall *et al.* 1982*b*) as a red–brown crystalline solid. Although the $^{31}P\{^1H\}$ n.m.r. spectrum of the latter showed only a single resonance at room temperature, consistent with an octahedral cluster geometry, at −70 °C the spectrum showed two resonance in the approximate ratio 2:1. A single crystal X-ray structural analysis of this compound established that its solid-state structure, namely edge-shared tetrahedral, was consistent with the low-temperature n.m.r. data. Figure 4 contrasts the observed bond lengths for these two hexanuclear gold cluster compounds. The much shorter bond lengths in the edge-shared tetrahedral cluster can be attributed to the occurrence of a pair of four-centre two-electron bonds (each associated with a single tetrahedron), rather than a single six-centre two-electron bond in the octahedron. Molecular orbital calculations (Mingos 1976) on octahedral gold clusters have shown that the second electron pair resides in a non-bonding orbital of t_{1u} symmetry. The dispersion of gold–gold bond lengths in the edge-shared tetrahedral structure can be attributed to the nodal characteristics of the highest occupied skeletal molecular orbital of b_{1u} symmetry illustrated in scheme 1. Since this orbital is strongly bonding along those metal–metal edges that are parallel and less bonding along the remaining edges an asymmetry in the computed Mulliken overlap populations (also shown in scheme 1) results.

The isolation of two clusters such as $[Au_6\{(p\text{-tol})_3P\}_6](BPh_4)_2$ and $[Au_6(PPh_3)_6](NO_3)_2$ with almost identical stoichiometries yet markedly different physical and structural properties raises many interesting questions about the relative thermodynamic stabilities of the alternative structural forms, the size of the kinetic barrier connecting them and the origin of their different physical properties. However, in the absence of a high-yield synthetic route to the octahedral cluster compound it is difficult to establish the answers to these interesting questions. For higher-nuclearity clusters we have established that apparently small changes in the phosphine ligands can result in gross changes in the polyhedral cluster geometries, and this aspect will be discussed in more detail below.



b_{1u}

computed overlap populations

SCHEME 1

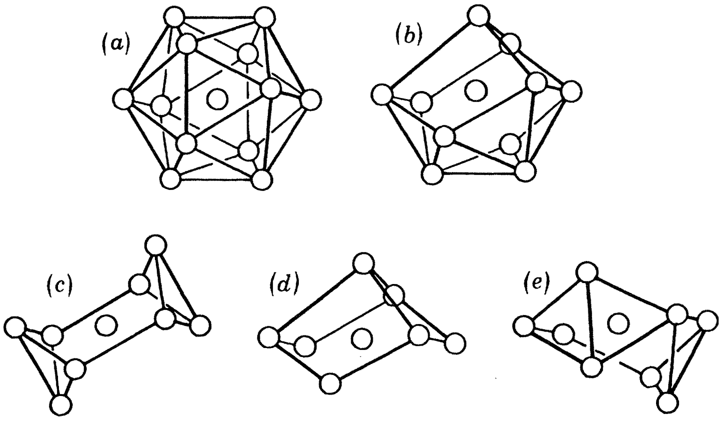


FIGURE 5. Some examples of high-nuclearity gold cluster compounds. For reasons of clarity only the cluster gold atoms have been illustrated. The compounds are: (a) $[Au_{13}Cl_2(PMe_2Ph)_{10}](PF_6)_3$; (b) $Au_{11}I_3(P(p\text{-}C_6H_4F)_3)_7$; (c) $[Au_9\{(p\text{-}C_6H_4CH_3)_3\}_8](PF_6)_3$; (d) $[Au_8(PPh_3)_8]X_2$ and (e) $Au_9(SCN)_3(PCy_3)_5$.

Higher-nuclearity cluster compounds of gold cannot be stabliized solely by the formation of multicentre bonds between the gold atoms on the periphery of the cluster, and consequently their stabilities are enhanced substantially by the presence of a central gold atom at the origin of the cluster, which can form effective radial metal–metal bonds with all the peripheral gold atoms. Some examples of such gold cluster compounds are illustrated in figure 5.

Extended Hückel molecular orbital calculations, which we have completed on a wide range of high-nuclearity gold cluster cations of the type $[Au_xL_{x-1}]^{m+}$ (Gilmour & Mingos 1982), where L is a neutral two-electron ligand, have demonstrated that the stoichiometries of these cations are decided primarily by the topology of the polyhedron defined by the peripheral gold atoms, a situation that arises from the high proportion of s character in the hy(s–z) orbitals of the Au(PH$_3$) fragments and the spherical harmonic nature of the resultant bonding problem.

If the peripheral gold atoms define a closed spherical polyhedron, then the cluster molecular orbitals can be represented, in order of decreasing stabilities, as S, P, D functions etc. (Stone 1981). When x = 7–13 only the S and P functions are bonding and therefore in such complexes there are only four bonding skeletal molecular orbitals corresponding to S, P_x, P_y and P_z $(x-1)$ Au–L bonding molecular orbitals and a d-band with $5x$ molecular orbitals, resulting in a filled closed shell and stable electronic configuration when $12x+6$ valence electrons are present. Interactions between the S and P molecular orbital functions derived from the hy(s–z) orbitals of the Au(PR$_3$) fragments and the 6s and 6p atomic wavefunctions of the central gold atom reinforce this bonding pattern to an important extent (Mingos 1976). $Au_{13}Cl_2(PMe_2Ph)_{10}^{3+}$ (162 valence electrons), $Au_{11}I_3(PPh_3)_7$ (138 valence electrons) confirm the reliability of this generalization (Briant *et al.* 1981; McPartlin *et al.* 1969).

square antiprism

puckered crown

Scheme 2

If the peripheral gold atoms have a topology related to a ring or torus, then only the spherical harmonic solutions corresponding to S, P_x and P_y functions are bonding and the P_z function is either non-bonding or anti-bonding. The consequence of this topological distinction on the molecular orbitals of the peripheral gold atoms may be appreciated by a comparison of the P_z functions for a square antiprism (spherical topology) and a puckered crown of eight gold atoms (torus topology) shown in scheme 2. The wavefunction is bonding in the former case and anti-bonding in the latter. It follows that for gold cluster cations with torus topology for the peripheral atoms the total electron count is $12x+4$ valence electrons. $Au_9(PPh_3)_8^{3+}$ (112 valence electrons) and $Au_8(PR_3)_7^{2+}$ (100 valence electrons) provide examples of such open cluster species (Bellon *et al.* 1971; Cooper *et al.* 1980; Hall *et al.* 1982*a*; Manassero *et al.* 1979; Vollenbroek *et al.* 1979; van der Velden *et al.* 1981).

The potential energy surface for the interconversion of the alternative polyhedral forms that conform to the topological requirements outlined above is calculated to be soft, because the radial Au–Au interactions are energetically more significant than the peripheral Au–Au interactions. For the cluster compounds with torus topology the computed energy differences separating the alternative cluster geometries are sufficiently small for ligand packing and crystal packing effects to exert a dominant influence on the observed structures. The reliability of these conclusions has been demonstrated by the structural determinations which have been completed on the related cations $[Au_9\{P(p\text{-}C_6H_4Me)_3\}_8](PF_6)_3$ and $[Au_9\{P(p\text{-}C_6H_4OMe)_3\}_8](BF_4)_3$ (Bellon *et al.* 1971; Hall *et al.* 1982*a*, *b*). The cluster geometries for these two very closely related cations, which are illustrated in figure 6, show that the replacement of a methyl substituent in the *para* position of the phenyl rings by a methoxy group has led to a dramatic difference in the cluster geometries. The cluster geometry in the former may be described in terms of a centred icosahedron from which four peripheral gold atoms have been removed, but the latter compound provides a unique example of a cluster compound derived by placing a metal atom at the centre of a puckered ring (or crown) of like gold atoms. The X-ray structural analysis of $Au_9(SCN)_3(PCy_3)_5$ (Cooper *et al.* 1980) has demonstrated an alternative cluster geometry for this neutral cluster, which may also be derived from the icosahedron by atom removal and bond breaking processes. The structure of this compound is also illustrated in figure 6.

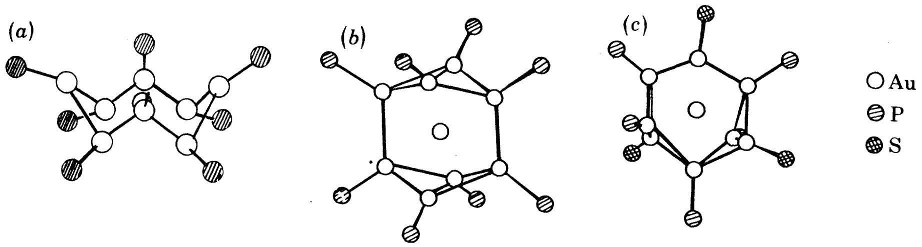


FIGURE 6. Comparison of the structures of (*a*) $Au_9\{P(p\text{-}C_6H_4OMe)_3\}_8^{3+}$, (*b*) $Au_9\{P(p\text{-}C_6H_4Me)_3\}_8^{3+}$ and (*c*) $Au_9(SCN)_3(PCy_3)_5$.

A comparison of the alternative structures for the Au_9 polyhedra illustrated in figure 6 also supports a previous conclusion derived from the molecular orbital calculations about the relative stabilities of the radial and tangential gold–gold interactions. Although all the compounds illustrated in figure 6 have the same number of radial gold–gold bonds, $[Au_9\{P(p\text{-}C_6H_4OMe)_3\}_8](BF_4)_3$ has four fewer tangential gold–gold bonds, which clearly suggests that the radial bonding is more significant energetically than the tangential bonding (Hall *et al.* 1982*a*, *b*). Mössbauer and X-ray photoelectron spectral studies have also been applied to this problem, although the conclusions have been less clearcut (Battistoni *et al.* 1977; Vollenbroek *et al.* 1978).

Solution $^{31}P\{^1H\}$ n.m.r. studies have also indicated that the gold cluster compounds with torus topologies are highly fluxional and undergo very rapid cluster rearrangement processes (Vollenbroek *et al.* 1978). However, the absence of limiting n.m.r. spectral data and the absence of a suitable nuclear spin on gold have limited such studies. Furthermore, although $[Au_9\{P(p\text{-}C_6H_4Me)_3\}_8](PF_6)_3$ and $[Au_9\{P(p\text{-}C_6H_4OMe)_3\}_8](BF_4)_3$ have very different electronic spectral characteristics in the solid state (see figure 7 for example), in solution the spectra are similar. This indicates that the cluster compounds share a common polyhedral structure in the solution phase (Hall *et al.* 1982*a*).

For gold cluster compounds with spherical topologies the computed energy differences between alternative polyhedral geometries are somewhat larger, and the most stable polyhedron is that which maximizes the number of next-nearest neighbours, e.g. the icosahedron for the $Au_{13}L_{12}^{5+}$ cluster cation. It is perhaps pertinent to indicate that the prediction of such a cluster cation (Mingos 1976) and its subsequent synthesis and structural characterization (Briant *et al.* 1981) represents by far the most important vindication of our theoretical approach. However, this prediction was made naïvely without the full realization of how small the energy differences were between the predicted icosahedron and the alternative possible polyhedral geometries. This only became apparent when n.m.r. studies on $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$

(Briant *et al.* 1981) indicated that the structure observed in the solid state with the chloro ligands occupying *para* positions on the icosahedral cluster was not maintained in solution. The $^{31}P\{^1H\}$ n.m.r. studies have indicated the presence of the alternative *meta* and *ortho* isomers in addition to the *para* isomer in solution at room temperatures. It is important to appreciate how small the energy barriers separating these alternative isomers are compared with those reported for the corresponding isomers of the icosahedral carboranes $C_2B_{10}H_{12}$ (Wade 1971).

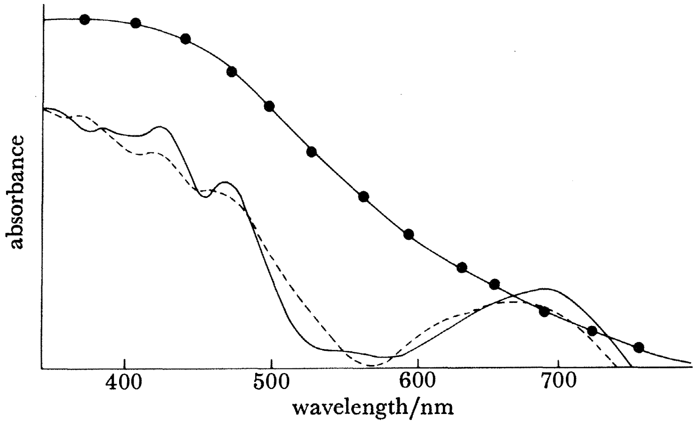


FIGURE 7. Comparison of the solid-state reflectance spectra of some $[Au_9(PR_3)_8](BF_4)_3$ cluster compounds: —, $[Au_9(PPh_3)_8](BF_4)_3$; ●—●, $[Au_9\{P(p\text{-}C_6H_4OMe)_3\}_8](BF_4)_3$; – – –, $[Au_9\{P(p\text{-}C_6H_4Me)_3\}_8](BF_4)_3$.

Although this paper has emphasized the electronic factors that govern the stoichiometries and stereochemistries of gold cluster compounds, the successful synthesis of high-nuclearity gold cluster compounds required an adequate appreciation of the steric requirements of the ligands coordinated to the peripheral gold atoms. For example, although it is possible to place eight triphenylphosphine ligands around the Au_9 torus clusters illustrated in figure 6, simple steric considerations suggested that it is not possible to arrange twelve triphenylphosphine ligands around an icosahedral gold cluster. Consequently our development of suitable synthetic routes into icosahedral gold cluster compounds utilized the tertiary phosphine ligands PMe_2Ph and $PMePh_2$, whose steric requirements are less demanding. Recently an attempt has been made to put these steric arguments onto a more quantitative basis by defining a *cluster cone angle*, which is closely related to the Tolman cone angle (Mingos 1982). This approach appears to have some utility not only for the gold cluster compounds described in this paper, but also accounting for the limiting stoichiometries in metal carbonyl cluster compounds. It will come as no surprise to chemists that cluster chemistry, like other branches of chemistry, requires the consideration simultaneously of subtle electronic and steric effects.

None of the work described above would have been possible without the dedication and experimental skills of those coworkers of mine who participated in this difficult project: Brian Theobald, James White and Kevin Hall did the synthetic studies, Clive Briant and Alan Welch the crystallographic structural determinations and David Evans and David Gilmour assisted me with the molecular orbital calculations. The S.E.R.C. is thanked for financial support, and Johnson-Matthey for a loan of gold metal.

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