Gold – a flexible friend in cluster chemistry*

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The role of metal–metal bonding interactions is reviewed in the context not only of cluster chemistry, but also in linear gold(I) compounds. The latter, although much weaker than the former, can lead to interesting infinite and catenane structures which arise from supramolecular interactions.

Gold has proved to be remarkably attractive to mankind from earliest times and even though our greater understanding of its properties has removed much of its mystical and occult connotations it retains a special place in our cultures. Indeed the history of the world has been significantly influenced at key moments by man's attempt to acquire and control the sources of gold. Even C(l)uster's Last Stand had its origins in the encroachment by gold prospectors into the Indian reservations in the Black Hills. The origins of modern chemistry are also closely allied with early attempts to convert base metals into gold, an early example of research targeted at wealth creation. With this long history it is interesting to review the special role of gold in cluster chemistry, where its flexible metal–metal bonding modes enable it not only to form a wide range of polyhedral molecules, but also make it an important component in supramolecular chemistry.

I should like to draw particular attention to the following important aspects of gold–gold bonding.

1. In the gas phase gold is able to form stable dimeric molecules, Au_2, which have a dissociation energy of 228 kJ mol^{-1} and a bond length of 2.472 Å and the element itself has a heat of atomisation equal to 368 kJ mol^{-1} and a metal–metal distance in the cubic closed-packed lattice of 2.884 Å. Therefore, although these energies are smaller than those of the earlier transition metals they are sufficient for gold to form strong metal–metal bonds in a wide range of compounds. These strong bonds are particularly obvious in the cluster compounds of gold stabilised by phosphine ligands and found when gold has an intermediate oxidation state between (+1) and (0). It is also able to form cluster compounds with a wide range of other metals. In the (+2) oxidation state gold forms a more limited range of compounds with gold–gold bonds. In general these are dimeric and the metal–metal bond is supported by additional bridging ligands.

2. Gold and in particular the $Au(PR_3)$ fragment has a unique ability to form hypervalent compounds of the main group elements. Thus compounds such as $[C\{Au(PPh_3)\}_6]^{2+}$ and $[N\{Au(PPh_3)\}_5]^{2+}$ which contain carbon and nitrogen in unusual six- and five-co-ordinate situations have been discovered by Schmidbaur.[1] He has argued that gold's unique ability to bring out such high co-ordination numbers is related to the ability of the $Au(PR_3)$ fragments to form weak gold–gold bonds. In these hypervalent compounds the gold–gold distances are approximately 3.00 Å which is significantly longer than the bond length in the metal and therefore they are individually weak, but cumulatively could contribute to the overall stability of the molecule because of the large number of such interactions. For example in octahedral $[C\{Au(PPh_3)\}_6]^{2+}$ there are twelve interactions of this type.

3. In many gold(I) compounds the geometry about the metal is linear and the hybridisation about the metal may be described[2] as sd. However, in many of these compounds there are additional contacts to other gold atoms which are significantly longer than the metal–metal distance found in the metal (2.884 Å), but shorter than that expected from the sum of the estimated van der Waals radii of gold (3.60 Å). Therefore, the situation is analogous to that described above for hypervalent compounds. It has been suggested on the basis of NMR measurements that these interactions may contribute as much as 30 kJ mol^{-1} and therefore may be considered to be analogous to hydrogen bonds.[3] The directionality of these interactions has encouraged this view, although Pathenini and Desiraju[4] proposed that a better analogy is $S \cdots S$ or halogen–halogen intermolecular interactions.

These weak interactions between d^{10} gold atoms were initially interpreted using semiempirical molecular orbital calculations in terms of electron donation from filled d orbitals on one metal centre to empty p orbitals on the second and *vice versa*.[5] However, more sophisticated *ab initio* calculations have suggested these conventional bonding effects do not make a significant contribution to the binding energies calculated at the Hartree–Fock level and the origin of the stabilisation is electron correlation effects similar to those found in van der Waals molecules such as Ar_2, Mg_2 and $Cl_2 \cdots Cl_2$,[6] which are enhanced in the case of gold by relativistic effects.[7]

In summary, gold has a remarkable ability to form metal–metal bonds with a wide range of strengths. If the metal–metal bond length approaches the distance found in Au_2, *i.e.* 2.47 Å, then its strength must be approximately 200 kJ mol^{-1}, but in cluster compounds where the metal–metal bond lengths approximate to those found in the bulk metal (2.884 Å) then each metal–metal bond will be associated with approximately 60–100 kJ mol^{-1} and in those compounds where the metal–metal contacts are 3.0–3.2 Å then each of these interactions probably contributes 10–30 kJ mol^{-1}. The interaction will be energetically insignificant only when the metal–metal distances exceed 3.50–3.60 Å. In the discussion below all three types of interaction will be discussed and illustrated by recent examples from our research.

Gold(I) Compounds

The development of gold(I) chemistry has been dominated by the perception that gold is a prototypical Class B (or soft) Lewis acid which forms its most stable complexes with soft Lewis bases. There is an abundance of gold(I) phosphine complexes which are very commonly used as reagents in organometallic and cluster chemistry,[8,9] and their biological role as drugs for the treatment of rheumatoid arthritis has been developed and investigated in some depth.[10] In contrast the chemistry of gold(I) with nitrogen ligands has been neglected.[11] There have

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been reports that gold(I) halides react with liquid ammonia to give adducts [AuX(NH₃)ₓ] (X = Cl, Br or I, x = 1–3) and [AuCl(NH₃)] has been isolated when AuCl is dissolved in aqueous ammonia and acidified with HCl, but not structurally characterised.[12] The ion [Au(NH₃)₂]⁺ has been identified in solution and its equilibrium constants measured,[13] but surprisingly its salts have not been isolated and structurally characterised. This is particularly noteworthy given the stability of [Ag(NH₃)₂]⁺,[14] which is quoted in elementary textbooks as the paradigm for linear co-ordination and whose structure was first investigated in 1934.[15] We have recently described the synthesis, isolation and spectroscopic characterisation of [Au(NH₃)₂]⁺ and [Au(NH₂R)₂]⁺ salts and the structure of [Au(NH₃)₂]Br.[16] The [Au(NH₃)₂]⁺ salts are formed when ammonia gas is bubbled through a solution of [Au(NCPh)₂]⁺[17] in MeCN for 45 min at room temperature. The resulting colourless solution yields colourless crystals when the volume is decreased under reduced pressure. The BF₄⁻ and SbF₆⁻ salts may be recrystallised from MeCN–Et₂O. The salts may be obtained in approximately 90% yields based on gold. The compounds are photosensitive, but may be stored indefinitely under nitrogen in a darkened tube at −25 °C. The structure of the [Au(NH₃)₂]Br salt is illustrated in Fig. 1 and it has two features which are frequently observed in the solid state for linear gold(I) compounds. The individual gold(I) co-ordination compounds adopt a mutually staggered arrangement and are
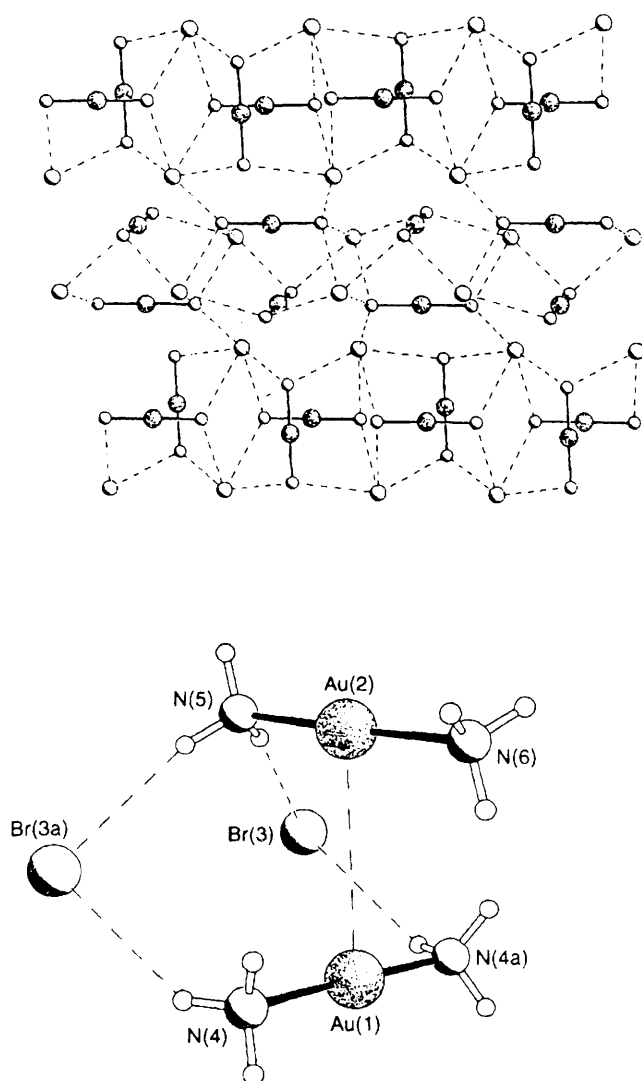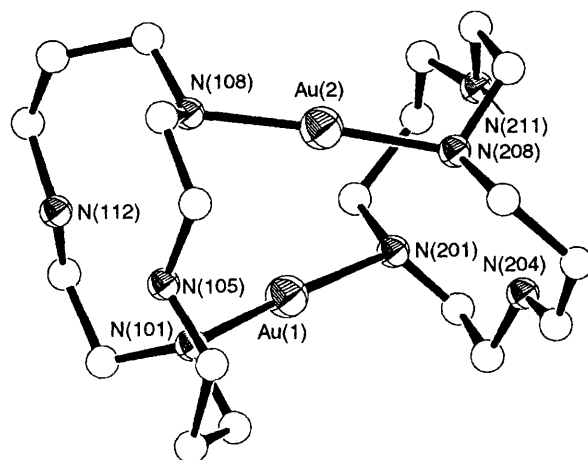
linked through the lattice by weak gold–gold interactions of 3.414(1) Å.

The related amine complexes [Au(NH₂R)₂]BF₄ (R = Me, Et or Buᵗ) were synthesised in a similar fashion and their relative stabilities are Buᵗ > Et > Me. The salt [Au₂(cyclam)₂]-[BF₄]₂[18] is formed when cyclam (1,4,8,11-tetraazacyclotetradecane) in CH₂Cl₂ is added to a solution of [Au(NCPh)₂]⁺[16] in MeCN at −40 °C. The resulting colourless solution was allowed to stand for 1 h and then the colourless solid precipitated with a large volume of diethyl ether. Colourless crystals in 65% yield were obtained after recrystallising from MeCN–Et₂O. The structure of [Au₂(cyclam)₂][BF₄]₂ is illustrated in Fig. 2.

The ion [Au₂(dien)₂]²⁺ (dien = diethylenetriamine)[19] may be formed in a similar fashion and has also been obtained as colourless single crystals. Its structure, which is illustrated in Fig. 3, is very different from that described above for the cyclam complex. Indeed although [Au(NH₃)₂]⁺, [Au₂(cyclam)₂]²⁺ and [Au₂(dien)₂]²⁺ have similar linear N–Au–N geometries they have very different arrangements of gold–gold interactions. In [Au₂(cyclam)₂]²⁺ the gold atoms are sandwiched between two cyclam ligands whilst maintaining linear geometries about the gold atoms. The gold atoms are separated by 3.370(1) Å and there are significant interactions between adjacent cyclam dimers with the closest contacts being approximately 8.00 Å. In contrast [Au₂(dien)₂]²⁺ has sixteen-membered rings with the dien ligands acting only as bidentate ligands between the linear gold(I) centres. The rings are linked by weak gold–gold interactions [3.312(1) Å] to form chains which extend right through the crystal lattice in the (111) direction. The intermolecular gold–gold interactions in these complexes with nitrogen ligands are generally 0.2–0.3 Å longer than those in related phosphine complexes presumably because the residual

Fig. 2 Structure of [Au₂(cyclam)₂][BF₄]₂. Atoms Au(1) and Au(2) are separated by 3.370(1) Å

Fig. 1 Structure of [Au(NH₃)₂]Br. The basic interaction between pairs of gold(I) centres is shown at the bottom and the network of hydrogen bonds linking the ions at the top
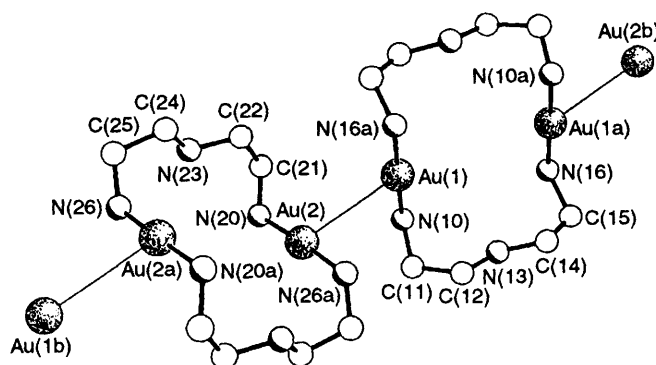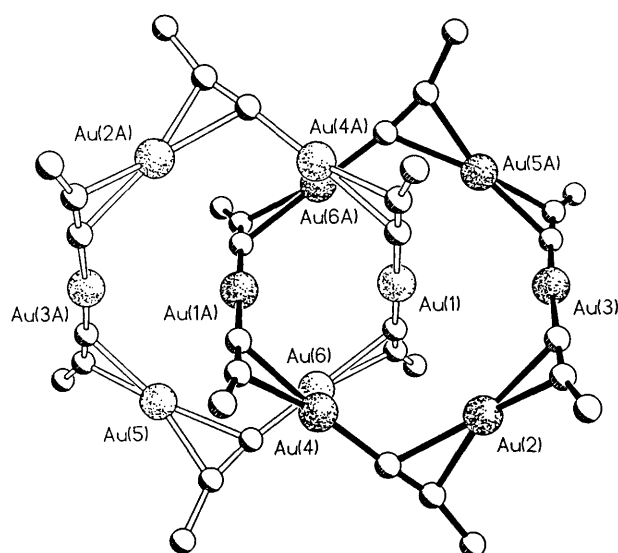

Fig. 3 Structure of [Au₂(dien)₂][BF₄]₂. The intermolecular gold–gold interactions are clearly visible and lead to infinite chains, which are packed in an approximately hexagonal fashion

Fig. 4 Molecular structure of [{Au$_6$(CCBu^t)$_6$}$_2$], illustrating the catenane structure resulting from the interlinking of the two hexagonal gold rings

⌒ represents a bridging ligand

.... represents Au· · ·Au interaction

—— represents a linear L–Au–L or L–Au–X co-ordination entity

Fig. 5 Schematic illustration of some of the intermolecular gold–gold interactions which have been observed in the solid state
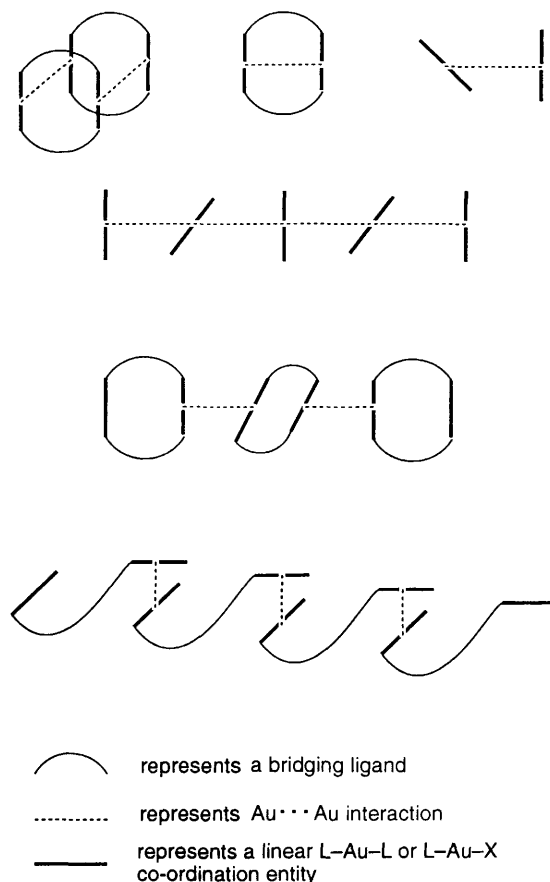
positive charge on the gold is slightly larger and contributes a greater electrostatic repulsion between the metals.

When [Au(NH$_3$)$_2$]$^+$ is treated with HCCBu^t then a pale yellow compound with the empirical formula [Au(CCBu^t)]$_n$ separates. An identical compound had been reported by Coates and Parkin[20] more than thirty years ago and formulated as a simple tetramer on the basis of spectroscopic data. A single-crystal structural analysis has revealed that the gold ethynide has spontaneously self assembled to form a very interesting catenane structure based on the formula {[Au(CCBu^t)]$_6$}$_2$ and having two interlocking hexagonal gold rings. Each ring has the ethynyl ligands co-ordinated in η^1:η^1, η^2:η^1 and η^2:η^2 co-ordination modes leading to a ring with C_2 symmetry. The two interlocking hexagonal rings (see Fig. 4) have a composite point group of D_2. The gold–gold intra- and inter-ring contacts lie in the range 3.215(2)–3.351(2) Å and the symmetrical arrangement of gold atoms suggests that weak gold–gold bonding interactions contribute significantly to the self assembly of the structure.[20]

Considerable attention is being shown currently in the possibility of using hydrogen-bonding interactions and in particular complementary ones for designing the structures of molecular solids. This crystal engineering is particularly important for the design of materials which might display superior non-linear optical or magnetic interactions. The work described above on gold(I) compounds suggests that it may be possible to use the analogy with hydrogen bonding to construct infinite solids where the predominant gold–gold intermolecular interactions may lead to predictable supramolecular structures. The basic types of interactions which would serve as a basis for such studies are summarised in Fig. 5.

Cluster Compounds

The cluster compounds of gold are generally stabilised by tertiary phosphine ligands and the first examples were reported by Malatesta in Milan in the late 1960s.[21] Since then many examples of gold cluster compounds have been characterised and a sufficient number are known for reliable bonding principles to have emerged. In addition during the last ten years many examples of high-nuclearity heterometallic gold cluster compounds have been discovered. The geometries of these clusters can also be rationalised within the theoretical framework originally proposed for homometallic gold clusters, although interesting problems have arisen regarding the site

preferences of the non-gold atoms within the cluster and require theoretical interpretation.

Cluster compounds of gold with 4 to 13 metal atoms are well established and those with more than seven have an interstitial gold atom located in the centre of the cluster. The simplest clusters have a tetrahedron of metal atoms, either with no bridging ligands, e.g. [Au$_4$(PBu$^t_3$)$_4$]$^{2+}$,[21] or with bridging ligands on two of the edges, e.g. [Au$_4$(μ-I$_2$)(PPh$_3$)$_4$] and [Au$_4$(μ-SnCl$_3$)$_2$(PPh$_3$)$_4$]. The latter which was recently characterised in our laboratories provides an unusual example of an SnCl$_3$ ligand acting as a bridge between two metal atoms.[22] In contrast, in the higher-nuclearity cluster [Au$_8$(SnCl$_3$)(PPh$_3$)$_7$]$^+$ the SnCl$_3$ ligand bonds only to the interstitial gold atom.[23]

In the tetrahedral clusters the two valence electrons occupy a molecular orbital which results from the in-phase overlap of 6s orbitals from the four gold atoms [S^σ]^2 and they are therefore formally derivatives of [Au$_4$(PPh$_3$)$_4$]$^{2+}$. For clusters with six and seven metal atoms, the presence of a single multicentred two-electron bond is insufficient to stabilise the cluster geometry and additional electrons are required to occupy delocalised molecular orbitals which have a single node and therefore resemble p atomic wavefunctions. These molecular orbitals are therefore designated by the symbol P^σ.[24,25] A spherical cluster geometry therefore will only result when the P^σ set of three molecular orbitals is either completely empty or completely filled and partial occupation of the P^σ set results in non-spherical geometries. For example [Au$_6$(PPh$_3$)$_6$]$^{2+}$ has a prolate skeletal geometry based on two tetrahedra sharing an edge because the delocalised molecular orbitals which are occupied correspond to [S^σ]^2[P^σ]^2 and [Au$_7$(PPh$_3$)$_7$]$^+$ has an oblate geometry based on a pentagonal bipyramid corresponding to the electron configuration [S^σ]^2[P^σ]^4. For higher-nuclearity clusters the relatively weak metal–metal bonding

resulting from the overlap of 6s valence orbitals is enhanced by the introduction of an interstitial gold atom which strengthens the radial metal–metal bonds.[26,27] Naturally, this type of stabilisation is only available to those higher-nuclearity clusters where the size of the interstitial hole is sufficiently large to accommodate a gold atom.

Higher-nuclearity gold cluster compounds with the interstitial atom have geometries which may be classified as spherical or toroidal[28] and which also reflect the number of valence electrons occupying the molecular orbitals derived primarily from the 6s valence orbitals. The spherical clusters have a complete shell resulting from the electron configuration $[S^\sigma]^2[P^\sigma]^6$ and the toroidal clusters have the incomplete shell configuration $[S^\sigma]^2[P^\sigma]^4$ which leads to an oblate electron distribution which is compatible with a toroidal geometry. These clusters also have a filled d^{10} shell associated with the interstitial atom, therefore they are characterised by $12n_s + 18$ (spherical) or $12n_s + 16$ (toroidal) valence electrons, where n_s = the number of surface $Au(PR_3)$ fragments, each of which has a single Au–P σ bond and a filled d shell associated with the gold atom.

The dominance of the radial bonding in these clusters results in a soft potential-energy surface for the interconversion of alternative polytopal geometries. The broad topological classifications of spherical or toroidal are therefore more appropriate than polyhedral classifications based on specific geometries when the energy differences separating different structures are very small. The structures of gold clusters based on the spherical–toroidal paradigm are summarised in Fig. 6. It is significant that all of the structures may be related either to a centred chair or a centred crown of atoms. The spherical clusters have additional atoms located along the principal symmetry axes of these fragments and the toroidal clusters have the additional atoms located away from these axes in order to maintain the oblate nature of the structure. The structural flexibility associated with gold clusters has many consequences for the observed structures of these clusters in solution and the solid state.

The stereochemical non-rigidity of gold clusters has several important manifestations. First, alternative structures are observed for the clusters in the solid state depending on the precise nature of the ligands, the counter anions and the mode of crystallisation. For example, although the cluster $[Au_{11}I_3\{P(C_6H_4F-p)_3\}_7]$ has a C_{3v} geometry in the solid state[29] which may be described in terms of an icosahedron with one triangular face replaced by a single gold atom, the related gold cluster $[Au_{11}(PMePh_2)_{10}]^{3+}$[30] has a more conventional deltahedral D_{4d} geometry based on a square antiprism. Although the D_{4d} symmetry of the latter predicts two distinct phosphorus chemical environments in the ratio 2:8, the ^{31}P-$\{^1H\}$ NMR spectra in the solid state and in solution show only a single resonance suggesting either that these environments have very similar chemical shifts or the compound is stereochemically non-rigid in solution and the solid state.[31] An examination of the detailed cluster geometries in these C_{3v} and D_{4d} variants shows that only small atomic motions are required to interconvert them. Furthermore, the process is symmetry allowed because both geometries are associated with $[S^\sigma]^2[P^\sigma]^6$ closed-shell configurations.[32] Both of these factors contribute to the low activation energy for the polytopal rearrangement.

The structures of the toroidal gold clusters $[Au_9(PR_3)_8]^{3+}$ (R = aryl) depend on the counter ion and either a D_{2h} geometry derived from the removal of four vertices from an icosahedron or an alternative crown geometry derived from removal of the two low-connectivity vertices of the square antiprism observed for $[Au_{11}(PMe_2Ph)_{10}]^{3+}$ are found. Indeed with the correct combination of counter ion and phosphine it is possible to isolate both skeletal isomers for the same compound. The compound $[Au_9\{P(C_6H_4OMe-p)_3\}_8][NO_3]_3$ thereby provided
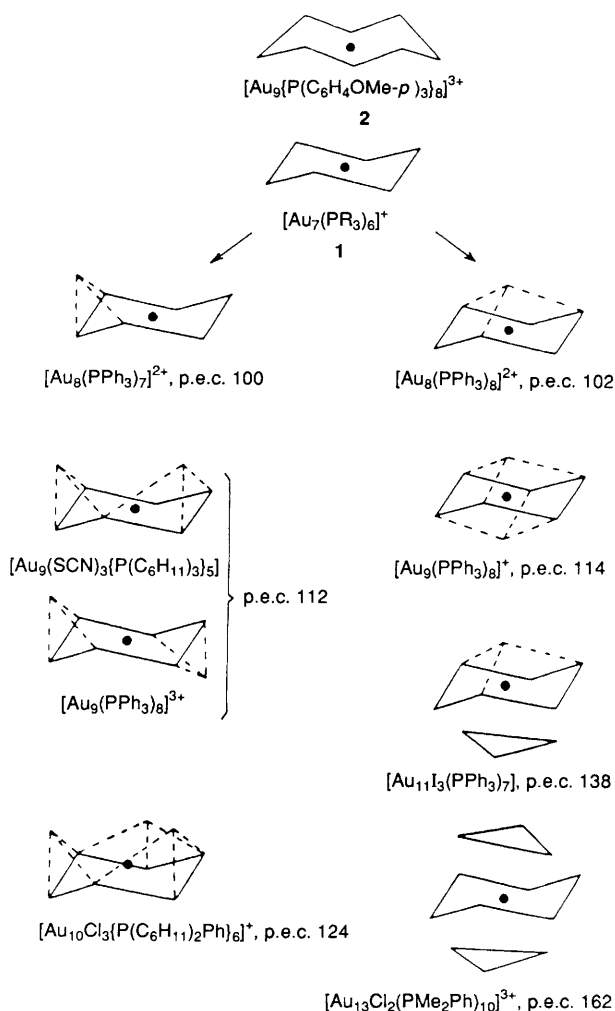

Fig. 6 Summary of the structures of spherical and toroidal gold cluster compounds. The polyhedral electron count (p.e.c.) is the total number of valence electrons associated with the cluster

the first example of skeletal isomerism in cluster chemistry.[33] The two isomers do not have identical crystallographic cell volumes and therefore it has proved possible to interconvert them in the solid state using large hydrostatic pressures.[34] The transformation may be conveniently monitored using differences in the electronic spectra of the two isomers. More recently we have reported the interconversion of a similar pair of isomeric rhodium–gold cluster compounds by exerting high pressures on solid-state samples.[35]

The only gold clusters which are stereochemically rigid at room temperature and on the NMR time-scale are those based on the icosahedron. The first icosahedral gold cluster was predicted on the basis of theoretical calculations in 1976[26] and experimentally realised for $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$ in 1981.[36] This compound was synthesised from $[Au_{11}(PMe_2Ph)_{10}]^{3+}$ and either $[AuCl(PMe_2Ph)]$ or NEt_4Cl. If the ^{31}P-$\{^1H\}$ NMR spectrum of $[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+}$ is recorded at low temperatures it is consistent with the observed solid-state structure based on an icosahedron with the *para* gold vertices co-ordinated to chloride ligands. However, it is apparent that at room temperature the icosahedron disproportionates according to equation (1). Subsequently the corresponding icosahedral

$$3[Au_{13}Cl_2(PMe_2Ph)_{10}]^{3+} \rightleftharpoons$$
$$[Au_{11}(PMe_2Ph)_{10}]^{3+} + 2[Au(PMe_2Ph)]^+ +$$
$$2[Au_{13}Cl_3(PMe_2Ph)_9]^{2+} \quad (1)$$
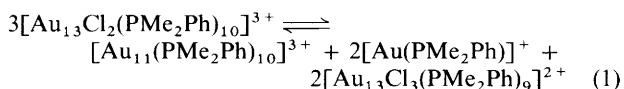
clusters $[Au_{13}Br_3(PMePh_2)_9]^{2+}$ and $[Au_{13}X_4(PMePh_2)_8]^+$ (X = Cl, Br or I) have been isolated and characterised by NMR

and FAB mass spectrometry.[37] In each case the NMR evidence is consistent with a stereochemically rigid icosahedral structure. Interestingly the magnitude of the $^4J(P-P)$ coupling constants is most helpful in distinguishing alternative isomeric structures because they depend on the angle subtended at the central gold atoms by the Au–P bonds which are involved in the spin–spin coupling. Furthermore, these compounds show no tendency to revert to the lower-nuclearity $[Au_{11}(PMePh_2)_{10}]^{3+}$ cluster. The nuclearity of the gold clusters is very sensitive to the steric requirements of the ligands as defined by the 'cluster cone angle' and presumably the replacement of phosphines by the less sterically demanding halides stabilises the icosahedral clusters.[38]

Recently Teo et al.[39] have reported the synthesis and characterisation of $[Au_{39}Cl_6(PPh_3)_{14}]Cl_2$ which has a three-layer hexagonal close-packed structure. The layers contain respectively $1:9:9:1:9:9:1$ gold atoms. In addition a gold-55 cluster compound has been widely studied with a very large number of physical techniques, but unfortunately it has not proved possible to generate single crystals of it and thereby unambiguously characterise it.[40]

Hypervalent Gold Compounds

The higher-nuclearity spherical gold cluster compounds described above have an interstitial gold atom and are characterised by a total of $12n_s + 18$ valence electrons, where the contribution of 18 originates from the occupation of the $[S^\sigma]^2[P^\sigma]^6$ skeletal molecular orbitals and the filled d shell of the interstitial atom. Similar cluster compounds with interstitial main-group atoms are in principle possible and are associated with $12n_s + 8$ valence electrons,[27] since the main-group atom does not have a filled d shell associated with it and only the S^σ and P^σ skeletal molecular orbitals are used in bonding. The existence of such centred cluster compounds was first predicted in 1976 as a result of molecular orbital calculations,[26] but only realised many years later as a result of the elegant synthetic work by Schmidbaur and his co-workers.[1,41] The interstitial main-group atoms include C, N, O, P and S and some examples are illustrated in Fig. 7.

Although these compounds may be formulated as cluster compounds they may also be viewed as molecular co-ordination compounds of main-group atoms with the Au(PR₃) radical bonded to the central atom in a manner analogous to that for H and CH₃. This view is encouraged by the observation that the majority of these compounds have Au ··· Au distances which are approximately 3.00 Å. These are longer than those found either in the bulk metal or in the majority of gold cluster compounds and more similar to those found in those linear gold(I) compounds which show intermolecular interactions. Therefore, these compounds may either be considered as cluster compounds where the radial bonding is much stronger than the tangential bonding, or as molecular co-ordination compounds with linear gold(I) ligands which show supplementary weak intramolecular gold–gold interactions. If they are viewed as molecular compounds then the isolobal relationship between Au(PR₃) and H suggests the analogies illustrated in Fig. 8. The colourless nature of the compounds also supports their formulation as molecular co-ordination compounds of gold(I) and may be contrasted with the intense colours associated with the gold(0)/gold(I) cluster compounds.

All of these compounds obey the octet rule, but clearly the Au(PR₃) fragment is much more effective than H at bringing out the hypervalency of the central atom. Specifically the ions CH_6^{2+}, NH_5^{2+} and OH_4^{2+} cannot be isolated as simple salts although they are important as intermediates and transition states in super acid media[42] whereas the isolobal gold-containing compounds may be obtained as air-stable solids. Schmidbaur[1] has proposed that this ability of the Au(PR₃) fragment is related to its ability to form weak gold–gold

$n_s = 4$; 56 valence electrons
Tetrahedron

$n_s = 5$; 68 valence electrons
Trigonal bipyramid

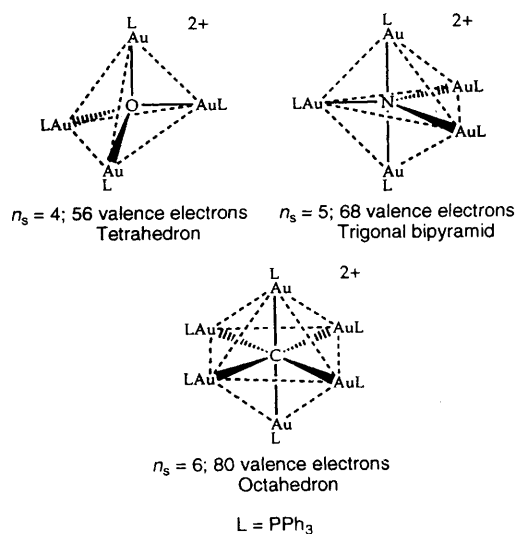$n_s = 6$; 80 valence electrons
Octahedron

L = PPh₃

Fig. 7 Examples of gold cluster compounds with interstitial main-group atoms. These compounds may also be viewed as molecular co-ordination compounds of the main-group element with Au(PR₃) radicals

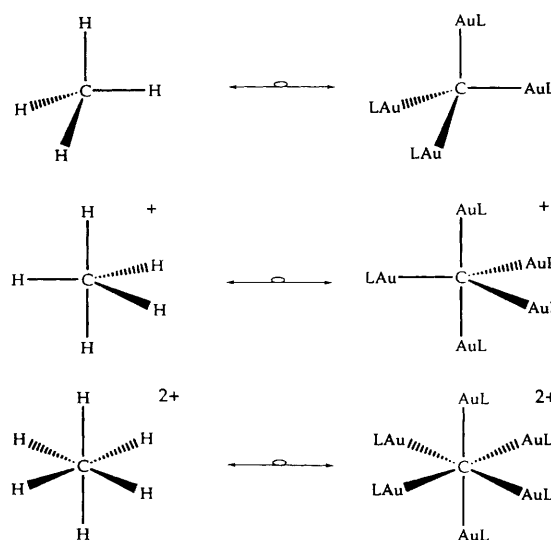**Fig. 8** Examples of isolobal main-group co-ordination compounds with H and Au(PR₃) ligands

interactions which cumulatively stabilise the higher co-ordination numbers in these hypervalent compounds. He has coined the term 'aurophilicity' to describe this phenomenon. An interesting consequence of this 'aurophilicity' is the observation that some of the compounds which formally have an octet adopt non-spherical geometries. For example, $[As\{Au(PPh_3)\}_4]^+$ has a square-planar arrangement of gold atoms with the arsenic atom completing a square pyramid rather than the classical tetrahedral structure. Schmidbaur and co-workers[43,44] argued that the pyramidal geometry leads to much stronger gold–gold interactions (see also ref. 6).

Other factors may also play a part. For example, the lack of hypervalent compounds of hydrogen is in part related to the sizes of ligating atoms. Specifically the 'hard sphere' radius sum for hydrogen precludes trigonal-bipyramidal CH_5^+ and octahedral CH_6^{2+}. In the latter the H ··· H distance in an octahedron based on C–H 1.10 Å is equal to 1.554 Å which is significantly smaller than the hard-sphere sum of 1.84 Å suggesting significant H ··· H repulsions.[45] In contrast, for the corresponding hypervalent octahedral gold compound the Au ··· Au interactions at 3.00 Å are attractive rather than repulsive. In addition, the higher electronegativity of H

compared to that of the Au(PR$_3$) fragment leads to a less polar C–H bond and less residual electron density on the central atom. Consequently, the carbon atom in tetrahedral [C{Au-(PR$_3$)}$_4$] is more negatively charged than that in CH$_4$ and is able to expand its co-ordination number more readily and incorporate additional Au(PR$_3$)$^+$ fragments into the co-ordination sphere.

In conclusion, the flexible nature of the metal–metal bonding interactions in compounds of gold has led to the isolation and characterisation not only of molecular cluster compounds, but also ring and chain compounds, some of which result in infinite lattices. In the cluster compounds the gold–gold bonds are comparable in strength to those found in the metal and the resulting compounds maintain their identity in solution. Even in these compounds the predominance of the radial bonding interactions between the gold atoms makes the polyhedra stereochemically non-rigid on the NMR time-scale for all but the icosahedral clusters. In contrast those compounds where the intermolecular gold–gold distances are longer than 3.00 Å the interactions are more similar to those associated with hydrogen bonds and they probably exist as monomers in solution. The gold–gold interactions are, however, sufficiently strong to influence the packing of the molecules in the solid state. I think that we shall see during the next few years a major expansion in the use of gold(I) centres as supramolecular components for designing infinite structures with interesting properties.

Acknowledgements

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