# LUDWIG MOND LECTURE. High-carat Gold Compounds

**Hubert Schmidbaur**
*Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany*

## 1 Introduction

The title of this lecture was chosen in an attempt to catch the eye of the large majority of potential readers, who probably have a genuine interest in gold, but perhaps less so in the *chemistry* of gold. 'Carat' is the traditional measure of the gold content of alloys which are used for coins, jewellery and objects of art and cult, in dentistry and in engineering. 'High-carat gold' thus has been an emblem of wealth and culture throughout the history of mankind.

The most common secondary components of gold alloys are the congeners copper and silver, but also, *e.g.* palladium or – more recently – titanium. The composition of the alloy determines the colour and malleability of the metal, its corrosion- and wear-resistance, and other physical properties. The cubic close-packed structure of pure gold changes gradually at first as gold atoms are substituted by other metal atoms in the lattice, but eventually the structure changes more fundamentally.

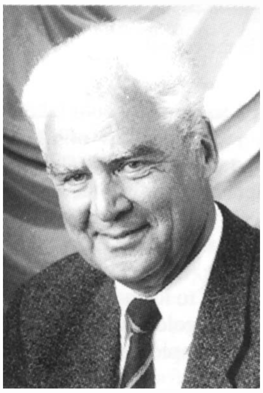
Initially as serendipitous discoveries, and later as a result of concentrated research, the last forty years have seen the appearance of small fragments of such gold and gold alloy lattices as *clusters in chemical compounds* on the molecular level, representing what may be described as the world of nano-gold.[1] Owing to its relevance *inter alia* for materials science, for homo- and hetero-geneous catalysis, and for medicine, the cluster chemistry of gold and other elements has grown rapidly into one of the most active and competitive research areas in chemistry. Even old recipes for producing gold colloids in glass and ceramics (gold purple) have been reconsidered in this context as classical examples of cluster chemistry in alchemy.[1]

Nano-nuggets of *pure gold* now have their molecular counterparts in homonuclear gold clusters, *e.g.* with 13 atoms in the form of a centred icosahedron, first discovered by Malatesta,[1] and systematized later in the extremely useful theoretical treatments proposed by Mingos,[2,3] Wade[4] and others. The group of Schmid was able to find synthetic pathways to even larger clusters, the size of which reaches out beyond the first few layers of close-packing with their 'magic numbers' of gold atoms.[1]

Miniature domains of *gold alloys* are present in the heteronuclear (mixed-metal) clusters prepared mainly in the laboratories of Steggerda, Pignolet,[5] Teo, Braunstein, Strähle and Hussain *et al.*, who found that gold and silver or platinum may often mix freely in coordination compounds as they do in binary alloys.

The early period of gold cluster research did not include *gold clusters with interstitial atoms*, which is not surprising considering that gold metal – unlike most other heavy transition elements – forms only very few interstitial phases. In particular there are *e.g.* no stable binary hydrides, oxides, nitrides, carbides or borides of gold, while these small first-row elements are found quite frequently in the interstices of the early transition elements, like tungsten, rhenium *etc.* Nevertheless, based on theoretical calculations a few positive predictions were made regarding gold clusters with interstitial elements,[6] but experimental data were contradictory.[7] It was only in the last decade that a rapid expansion of this new field took place, and the present review is an account of the present state of the art.

*Hubert Schmidbaur is Professor of Inorganic and Analytical Chemistry at the Technical University of Munich, Garching Campus. He completed his Dr. rer. nat. with Professor Max Schmidt at the University of Munich (1960), obtained his Habilitation at the University of Marburg (1964), and became Professor of Inorganic Chemistry at the University of Würzburg in 1966, from where he moved to his present position in 1973. He was a visiting professor at Edinburgh, Kyoto, Melbourne, London/Ontario, Hiroshima, and Auckland. Among many other awards he held the RSC 1985 Centenary Lectureship and the 1995 Ludwig Mond Lectureship. He is a member of several scientific societies and academies. His general research interest is in the inorganic, organometallic, and coordination chemistry of the main group elements (mainly silicon, aluminium and their homologues), but also in gold chemistry.*



## 2 Auriophilicity[8]

Most of the research leading to new gold cluster compounds with interstitial metalloid elements was initiated following the *auriophilicity principle* proposed as a working hypothesis on the basis of a large number of structural data for virtually all classes of gold compounds. It is now recognized and accepted that small (not stereochemically inhibited) mononuclear gold complexes undergo *inter*molecular aggregation *via* short sub-van der Waals gold–gold contacts of *ca.* 3.05 Å associated with a bond energy of the order of 5—10 kcal mol$^{-1}$ (Fig. 1; 1 cal = 4.184 J). This energy is comparable to that of standard hydrogen bonds, and thus has similar consequences for the supramolecular chemistry of gold compounds. *Intra*molecular Au···Au contacts lend significant stabilization to multinuclear gold complexes, including in particular clusters with interstitial atoms. Such intramolecular bonding is not associated with a loss of entropy characteristic for intermolecular aggregation, and therefore what may be called an 'entropy-kick' is provided for extra auriophilic bonding.

Auriophilicity has been the subject of a number of theoretical treatments, using advanced *ab initio* and density functional methods, and including relativistic and correlation effects.[9—13] For quite a number of selected simplified cases the experimental data could be reproduced, and useful predictions could be made, which have led to several successful new preparative studies. Most examples are taken from complexes of gold(I), but there is also growing information on similar results with gold(III) and gold in less common oxidation states.

## 3 The Building of Supramolecular Aggregates

Gold(I) is two-coordinate in most of its complexes and has a linear coordination geometry. Neutral complex molecules L–Au–X are formed through the combination of one anionic (X) and one neutral ligand (L), with a preference for large, soft (easily polarizable) donor atoms. Homoleptic species (2L or 2X) give rise to cationic and anionic units, respectively, *i.e.* $[AuL_2]^+$ and $[AuX_2]^-$.

If X and L are sufficiently small, the individual complexes can become associated into pairs or strings depending on the nature and geometry of the ligands. More recent examples are the complexes

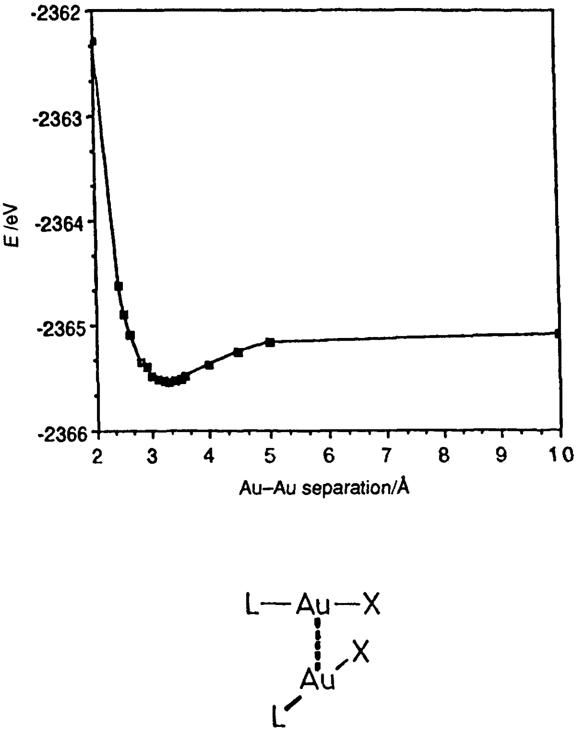


**Figure 1** Intermolecular interaction (Au···Au) of linear, two-coordinate gold(I) complexes (auriophilicity). There is a calculated energy minimum at a distance slightly above 3.0 Å, which is confirmed widely by experiment.

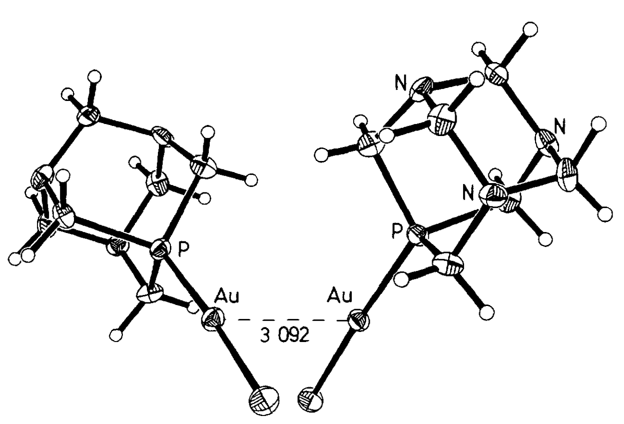


**Figure 2** Dimer of the strongly luminescent phosphatriazaadamantane (PTA) gold(I) chloride complex.

with the phosphatriazaadamantane ligand (PTA) attached to AuCl, AuBr or AuI, where in all cases a dimerization is observed through Au···Au contacts[14] (Fig. 2). This aggregation in the form of 'crossed-lollipops' is associated with a strong photoluminescence, which is often diagnostic for auriophilicity phenomena.

(Trimethylphosphine)gold(I) halides are associated even more extensively in the solid state, one-dimensional helices being formed through extended Au···Au···Au interactions[15] (Fig. 3). The dinuclear complexes of difunctional ligands also give rise to the formation of one-dimensional coordination polymers, although metal pairing occurs only at each end of the individual unit[8] (Fig. 4). Accordingly, tripod ligands give cages or networks with trinuclear units engaged in intermolecular Au···Au interactions.[8]

As the steric requirements of L are reduced further, as in cases where L represents 'slim' isocyanides, the packing occurs in chains and sheets, as shown for RNC–Au–X compounds in Figure 5.

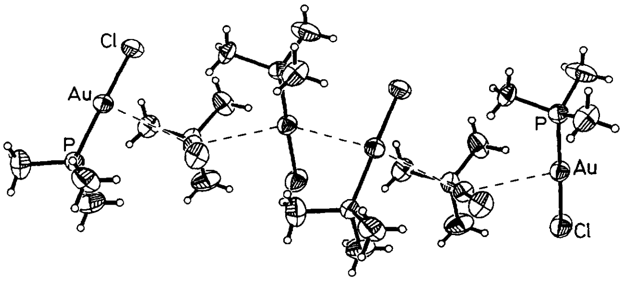


**Figure 3** Chain structure of chloro(trimethylphosphine)gold in the crystal.

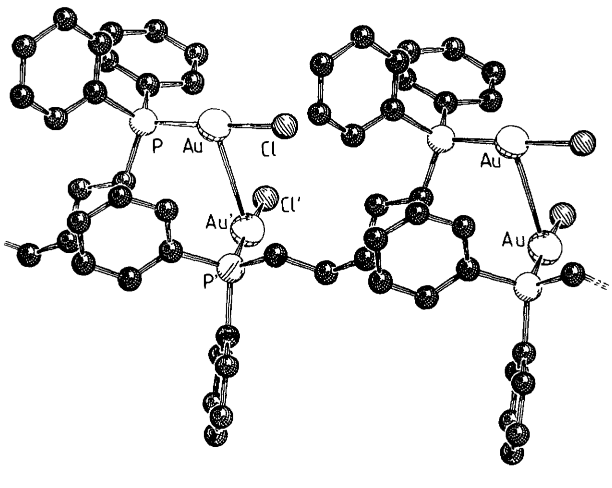


**Figure 4** Chain structure of ClAu(Ph$_2$P[CH$_2$]$_5$PPh$_2$)AuCl in the crystal.

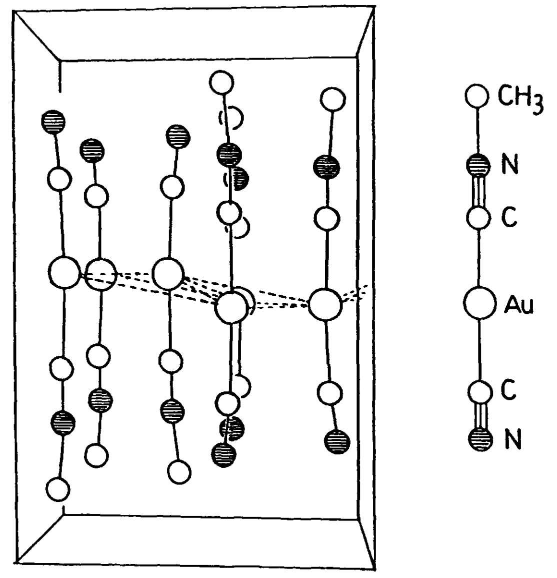
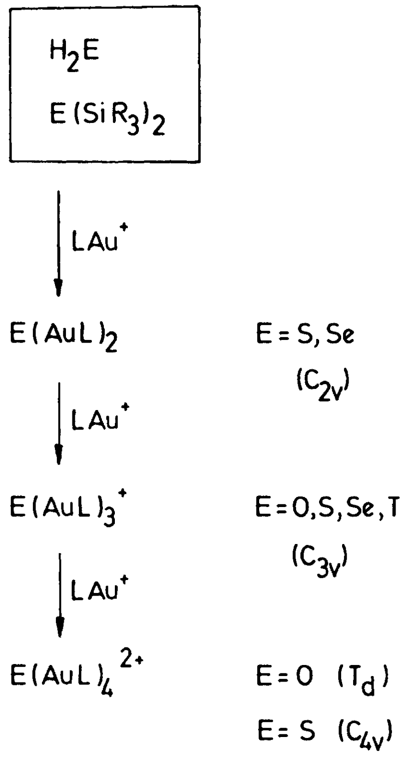


**Figure 5** Sheet structure of MeNCAuCN in the crystal.

In early observations in the laboratory of Nesmeyanov, it was recognized that any potential donor atom attached to a gold(I) centre would readily accept another gold(I) unit and become a centre of gold clustering. Thus even a Ph$_3$PAuCl molecule would take on a $Ph_3PAu^+$ cation to form stable *chloronium* cations of the type $(Ph_3PAu)_2Cl^+$ with a small Au–Cl–Au angle to allow for a short direct Au···Au contact.[8] In independent experiments in the 1970s by Abel and by Schmidbaur it was observed that the isoelectronic complexes of digold sulfide, $S(AuL)_2$, are also readily available and feature similar small angles at sulfur, but – more interestingly – would even accept readily a third $LAu^+$ unit to form a small triangle of gold atoms as part of a pyramidal trigold sulfonium cation (Scheme 1). Any attempts to prepare complexes of gold selenides or tellurides met directly with the formation of related chalcogenonium salts $[E(AuL)_3]^+$ with E = S, Se, Te, because the cluster-forming secondary reactions are often faster than the initial chalcogenide formation step. [The Nesmeyanov school has also discovered the trigold oxonium salts, which are extremely useful synthons in gold cluster chemistry, as also demonstrated in the author's laboratory and by Sharp and others (below)].

Crystal structure work has revealed an interesting supramolecular chemistry of the oxonium, sulfonium and selenonium salts: the cations are aggregated to form either dimers or – ligand bulk permitting – strings of pyramids or double-pyramids. The intercationic contacts finally lead to the formation of pairs, triangles and squares of gold atoms, or combinations of these (Scheme 1).[16]



**Scheme 1** Auriation of chalkogen centres (L = PR$_3$).

While most of the oxonium salts show virtually the same principles of structure as the compounds of the heavier chalcogens, that with the small trimethylphosphine ligand shows a unique motif of dimerization characterized by the formation of a tetrahedron of gold atoms through more intimate intercationic contacts[17] (Fig. 6). It should be noted that all intra- and inter-cationic Au···Au contacts have the same distances (*ca.* 3.1 Å) indicating that the same type of interaction is operative.

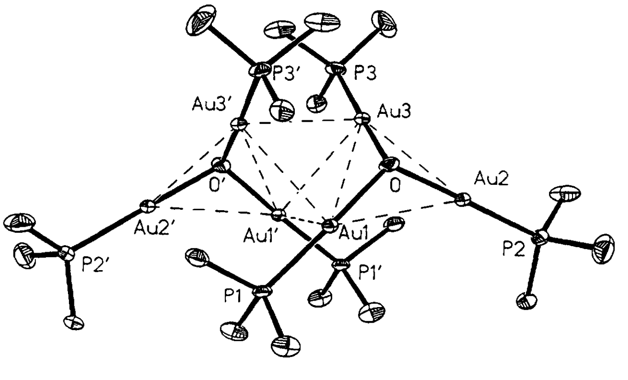


**Figure 6** Structure of the dimeric cation in the crystal of [(Me$_3$P)Au]$_3$O$^+$ BF$_4^-$.

## 4 Interlude. The Isolobal Principle in Gold Chemistry

It was pointed out by Lewis, Stone, Hoffmann[18] and others in the 1960s that LAu$^+$ cations can be classified as isolobal with the proton H$^+$ and the carbenium ions R$^+$ following the symmetry rules as applied to their frontier orbitals. This heuristic concept has been very fruitful in systemizing many seemingly unrelated species, and – more importantly – in predicting new types of compounds with otherwise unexpected stoichiometries and structures.

**Table 1** Isolobality of H$^+$, R$^+$, and LAu$^+$ units at oxygen, nitrogen and carbon centres

| H$^+$ | R$^+$ | LAu$^+$ |
|---|---|---|
| H$_2$O | R$_2$O | (LAu)$_2$O |
| H$_3$O$^+$ | R$_3$O$^+$ | (LAu)$_3$O$^+$ |
| H$_4$O$^{2+}$ | R$_4$O$^{2+}$ | (LAu)$_4$O$^{2+}$ |
| H$_3$N | R$_3$N | (LAu)$_3$N |
| H$_4$N$^+$ | R$_4$N$^+$ | (LAu)$_4$N$^+$ |
| H$_5$N$^{2+}$ | R$_5$N$^{2+}$ | (LAu)$_5$N$^{2+}$ |
| H$_4$C | R$_4$C | (LAu)$_4$C |
| H$_5$C$^+$ | R$_5$C$^+$ | (LAu)$_5$C$^+$ |
| H$_6$C$^{2+}$ | R$_6$C$^{2+}$ | (LAu)$_6$C$^{2+}$ |

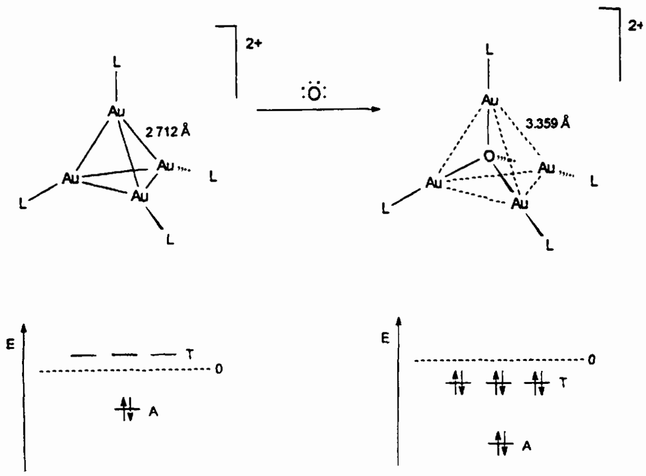
In Table 1 are listed several groups of isolobal molecules and cations with oxygen, nitrogen and carbon as the acceptor centres for increasing numbers of protons H$^+$, simple carbenium ions R$^+$, and LAu$^+$ cations. On the H$^+$/R$^+$ side this list thus contains familiar molecules like water (dialkylethers), ammonia (tertiary amines) and methane (branched alkanes), as well as common cations like OH$_3^+$ (OR$_3^+$, the cations of Meerwein's salts) and NH$_4^+$ (NR$_4^+$), but also more elusive species like the carbenium ions CH$_3^+$ and Olah's CH$_5^+$. Finally the system requires the consideration of less familiar *di*cations such as OH$_4^{2+}$, NH$_5^{2+}$ and CH$_6^{2+}$, which are unknown and predicted to be either intrinsically unstable or to represent shallow minima in the energy profiles.

Some of the earlier cationic examples have their LAu$^+$ counterparts in the trigold oxonium cations O(AuL)$_3^+$ (above) and in the tetragold ammonium cations N(AuL)$_4^+$ (below), while simple digold oxides O(AuL)$_2$ or trigold amines N(AuL)$_3$ are missing. Attempts to prepare such neutral compounds failed, because secondary reactions lead directly to the more highly auriated cations (auriophilicity!).

This observation suggests that in contrast to the more highly protonated or alkylated congeners, on the LAu$^+$ side the more highly auriated formulae should quite generally correspond to 'existing' species. The existence of CH$_5^+$ could be taken as encouraging regarding experiments to prepare C(AuL)$_5^+$ or even C(AuL)$_6^{2+}$, while the synthesis of C(AuL)$_4$ should perhaps be difficult because of the 'danger' of higher auriation. It was with this background in mind that studies were initiated a few years ago to probe the isolobal principle even for the more extreme cases in Table 1, including *e.g.* tetragold oxonium(2$^+$) salts, O(AuL)$_4^{2+}$ 2X$^-$, and other unprecedented compounds.

## 4 Hyper-auriation at Chalcogen Centres

Treatment of Nesmeyanov's trigold oxonium salts with the potent auriating agents R$_3$PAu$^+$BF$_4^-$ in a polar inert solvent leads to novel products of the stoichiometry O(AuPR$_3$)$_4^{2+}$ (BF$_4^-$)$_2$ in high yields[19] (Scheme 2). The salts are stable at room temperature in an inert atmosphere and are readily characterized by analytical and spectroscopic data. Single crystals were obtained for R = *o*-tolyl, and the structure of this compound could be determined (Fig. 7). The cations are tetrahedral by crystallographic symmetry constraints with the *o*-tolyl groups disordered as components of four right- or left-handed propellers. These compounds are the first examples of tetrahedral oxo complexes outside a metal oxide lattice and in the



**Scheme 2** Structural relations between tetranuclear gold clusters with and without interstitial oxygen atoms [L = $PPh_3$ or $P(o\text{-Tol})_3$], and the qualitative core molecular orbital diagram.

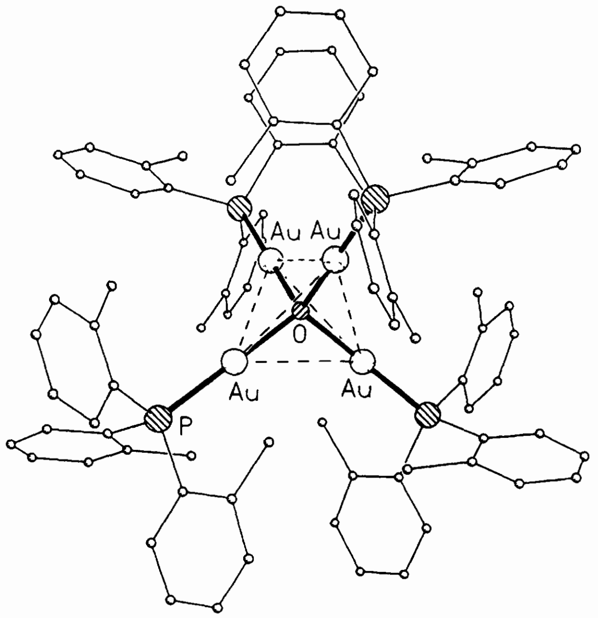


**Figure 7** Structure of the dication $[(o\text{-Tol})_3PAu]_4O^{2+}$ in the tetrafluoroborate salt.

absence of ligand clamps between the metals [like acetate in the well known $Be_4O(OAc)_6$ molecules]. It is striking that a fourth gold cation is readily accommodated at the trigold oxonium cation against Coulomb repulsion and against the formal pile-up of positive charge at the electronegative oxygen atom. Again the concept of Au···Au interaction as a support of cluster formation can be employed to account for this unusual finding. It should be noted that there is still no direct experimental evidence for $OH_4^{2+}$ or $OR_4^{2+}$, although at least for the former a local stability trough has been calculated.[20] A theoretical treatment of the gold analogues is in progress.

It is worthwhile mentioning that the 'empty' tetranuclear, tetrahedral cluster dication $(LAu)_4^{2+}$ has recently been discovered and its structure determined[21] (Fig. 8). It has six short edges of equal length (by symmetry), and its bonding can be described by a simple molecular orbital diagram. Only one strongly bonding cluster orbital is occupied by one pair of electrons, while three degenerate states are empty.

It is easy to conceive now that insertion of an oxygen atom (with six valence electrons) will lead to a completion of the cluster octet which is again a stable (diamagnetic) situation, in agreement with all experimental data. This approach is closely related to the case of an interstitial carbon atom in the $(AuL)_6^{2+}$ cluster considered in the pioneering work by Mingos[2,3,6] (below).

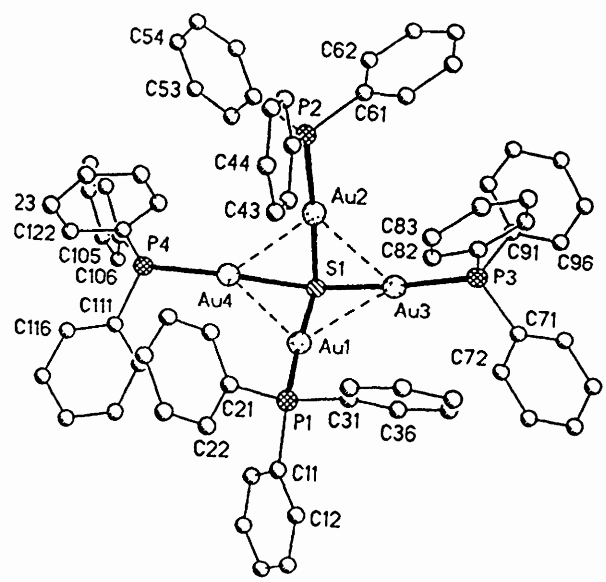
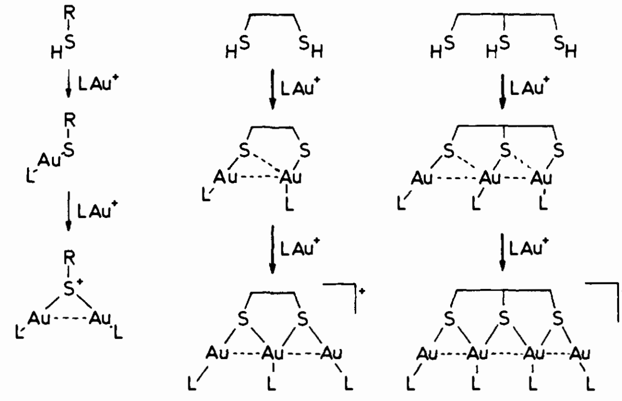


**Figure 8** Structure of the hyper-coordinated dications $[(Ph_3P)Au]_4S^{2+}$ in the tetrafluoroborate salt.

The development in gold–chalcogen chemistry as summarized in Scheme 1 has also seen recently the discovery by Laguna and his collaborators[22] that trigold sulfonium cations can accept a fourth $LAu^+$ unit to form the unprecedented tetragold sulfonium(2+) salts $[S(AuL)_4]^{2+}$. These cations have a square-pyramidal structure, however, clearly at variance with any of the classical rules of structure and bonding, which demand a sulfur-centered tetrahedral cluster similar to the oxonium(2+) case (above). There is precedent for such a non-classical pyramidal structure only in the analogous (isoelectronic) tetragold arsonium cation[23] $As(AuL)_4^+$ (below), which was also found to be square pyramidal instead of tetrahedral as required for standard arsonium salts $R_4As^+$.

Both structures can be rationalized, however, using *ab initio* or density functional methods including relativistic effects.[24] Following the auriophilicity concept, the system is lower in energy with close contacts of the gold atoms, which are impossible in a tetrahedron centred by a large sulfur (or arsenic) atom, but readily secured in a small square capped by the heteroatom (Scheme 1). For the oxygen-centred case, the tetrahedron is probably just large enough to produce acceptable Au···Au contacts at its six edges.

Alcohols (phenols, silanols), ROH, and thiols (benzenethiols, silanethiols), RSH, are known to form gold(I) compounds of the general formula LAuOR and LAuSR, respectively. Only very few of such alkoxy/aryloxy species have been well characterized. By contrast, the thiolates are very common and are in fact used extensively in gilding technology, in photography and in medicine. It is only recently, however, that more highly auriated compounds have become available. These include cations of the type $RO(AuL)_2^+$ and $RS(AuL)_2^+$ and analogous derivatives of polyols and polythiols (Scheme 3). Illustrative examples are the structures determined for



**Scheme 3** Auriation of polythiols ( L = $PR_3$).

the trinuclear complexes of dithioglycol or dithiocatechol, as well as of di- and tri-thioglycerol. Extensive gold clustering occurs in all of these complexes.

There is a vast literature on gold compounds of thiocarboxylic acids, thiocarbamates, thiophosphates and related compounds, but for most systems polyauriation has not yet been probed. Donor-free AuSR compounds form oligomers $(AuSR)_n$ with short Au···Au contacts, but no oxo-analogues are known.

## 5 Nitrogen-centred Gold Clusters

Ammonia, primary and secondary amines, amides and other more complicated substrates with amino/imino groups are readily auriated to give polynuclear gold compounds. Cations of the type of Nesmeyanov's tetragold ammonium cations $[N(AuL)_4]^+$, complemented by tri- and di-gold organoammonium cations $[RN(AuL)_3]^+$ or $[R_2N(AuL)_2]^+$, are well established, including species with R = alkyl, aryl, silyl *etc.* If neighbouring group assistance is provided, however, as exemplified by auriated 8-aminoquinolines, the nitrogen centres can even become five-coordinated (Fig. 9).

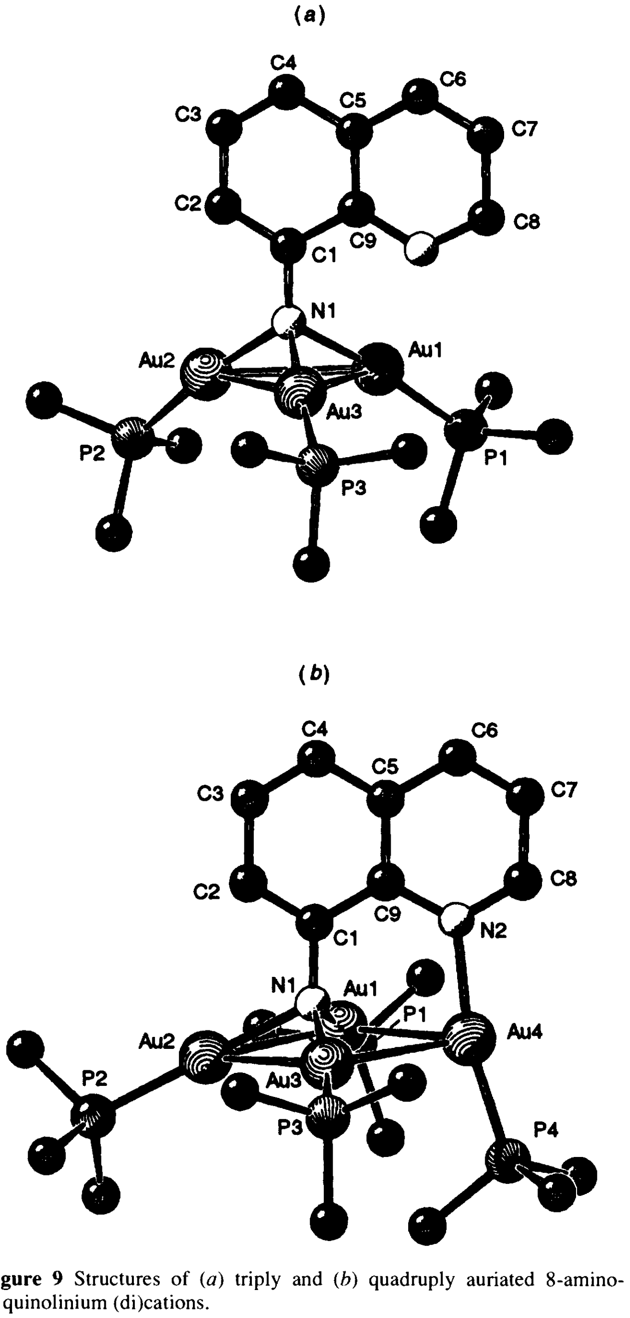


**Figure 9** Structures of (*a*) triply and (*b*) quadruply auriated 8-aminoquinolinium (di)cations.

The most striking case of hyper-coordination at nitrogen is certainly the pentakis[(phosphine)gold] ammonium(2+) species[25] (Fig. 10), which is readily prepared from the tetragold ammonium cation with one equivalent of a gold(I) fluoroborate. The molecular structure of such species was initially confirmed by single-crystal X-ray diffraction work for the $Ph_3P$ complex, and more recently also for the analogue with $Me_3P$ ligands. The latter was found to form a 1:2 addition compound with $Me_3PAuCl$, in which the central trigonal bipyramid $NAu_5$ has its equatorial base enlarged by two more gold atoms to form a trapezoidal pattern composed of three almost equilateral triangles (Fig. 11). This adduct is a very impressive example of 'auriophilicity at work.'[26]

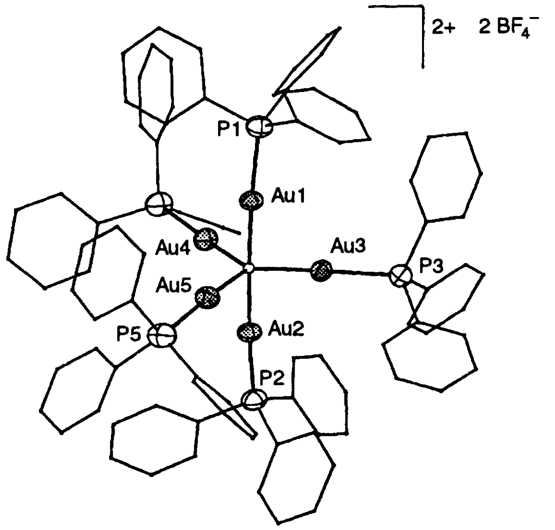


**Figure 10** Hyper-coordinated nitrogen in the dication of the salt $[(Ph_3P)Au]_5N^{2+}$ 2 $BF_4^-$.

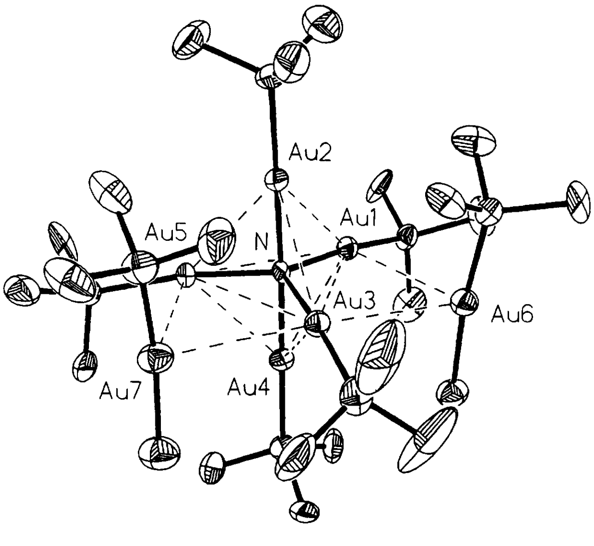


**Figure 11** Crystal structure of the adduct $[(Ph_3P)Au]_5N^{2+}$ $2Me_3PAuCl$.

With regard to isolobality (above), the $(LAu)_5N^{2+}$ dications are recognized as being related to $H_5N^{2+}$, which has not been observed experimentally, and has been calculated to be inherently unstable. The same holds for hyperalkylated ammonia species. In *ab initio* and density functional calculations it was possible, however, to rationalize the existence and stability of nitrogen-centred gold clusters, including also a six-coordinate trication $(LAu)_6N^{3+}$, but preliminary experimental accounts of such a species have not yet been confirmed.

## 6 Auriation of Phosphorus and Arsenic Centres

While mononuclear complexes of gold(I) with phosphine ligands of the type R$_3$PAuX are among the most common coordination compounds of gold, more highly auriated phosphorus-centred clusters were discovered relatively recently. Secondary phosphines were shown to form poly- or oligo-meric gold diorganophosphides (R$_2$PAu)$_n$, but only a few of these have been characterized. For primary phosphines, RPH$_2$, and phosphine, PH$_3$, it was demonstrated, however, that their phosphorus atoms can again be centres of hyperauriation with a large variety of surprising stoichiometries and structures.

Thus phenylphosphine gives rise not only to a standard tetrahedral trigold phenylphosphonium cation PhP(AuL)$_3^+$, but also to dications with five-coordinate phosphorus of the type PhP(AuL)$_4^{2+}$. Structural data are available for an *o*-tolyl analogue, which features a characteristic square pyramid with the tolyl group in the apical position and the four gold atoms at the base with small Au—P—Au angles and short Au···Au contacts[27] (Fig. 12).

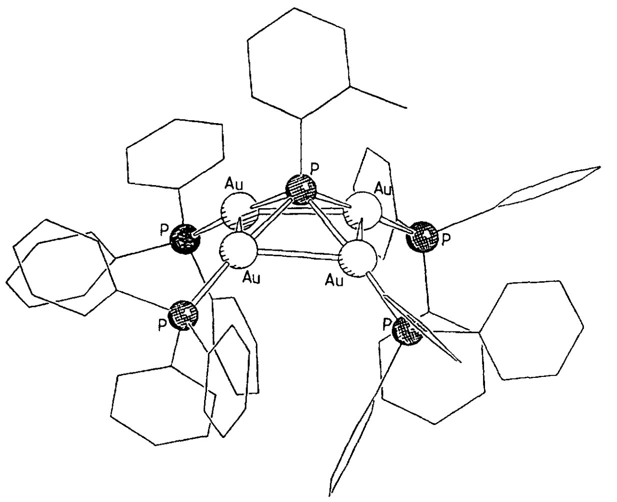


**Figure 12** Hyper-coordinate phosphorus in the dication of the salt $o$-TolP[Au(PPh$_3$)]$_4^{2+}$ 2 BF$_4^-$.

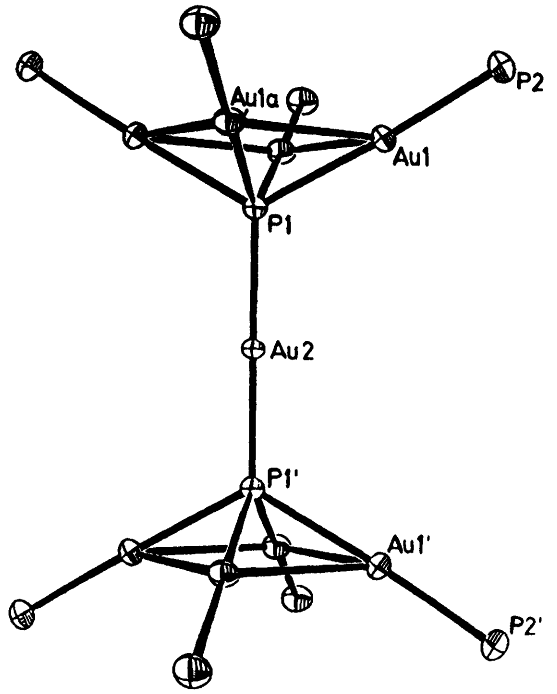
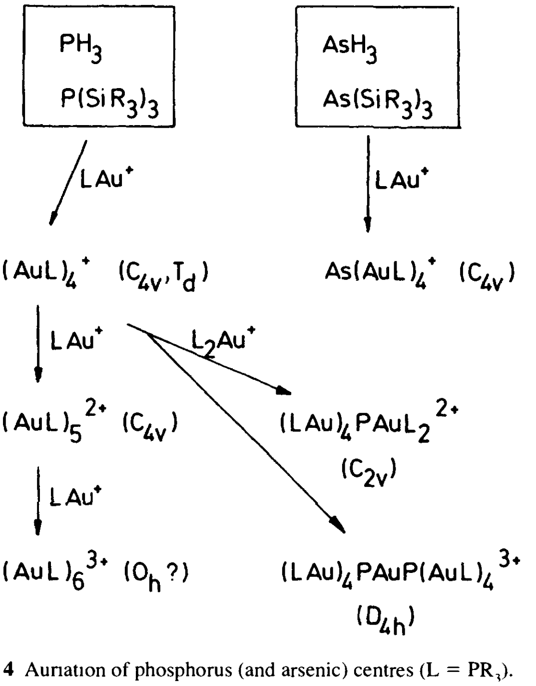


**Figure 13** Structure of the nonanuclear trication [(Ph$_3$P)Au]$_4$P—Au—P[Au(PPh$_3$)]$_4^{3+}$ in the tetrafluoroborate salt.

Phosphine or tris(trimethylsilyl)phosphine can be auriated using oxonium or LAu$^+$ BF$_4^-$ reagents to give four-, five-, and six-coordinate phosphonium centres. Surprisingly, the isolation of the classical tetragold phosphonium state turned out to be the most difficult, and it was only with tri(*tert*-butyl)phosphine ligands that salts with a standard tetrahedral structure could be obtained. Systems with less bulky ligands appear to have a different ground-state structure, most likely square-pyramidal, which leads to fast secondary reactions at the strongly basic phosphorus apex (Scheme 4). This idea is supported by the isolation of several derivatives of such square-pyramidal units, including a nonanuclear trication,[28] in which a central gold cation accepts two of these pyramids as ligands (Fig. 13).

Reactions with an excess of auriating agents afford the phosphorus-analogues of the (LAu)$_5$N$^{2+}$ cations (above), but these have a different structure. The crystal structure analysis of the complex with five Ph$_3$PAu ligands revealed a square-pyramidal unit, P(AuL)$_4^+$, attached to an apical LAu$^+$ unit (Fig. 14). The same



**Scheme 4** Auriation of phosphorus (and arsenic) centres (L = PR$_3$).

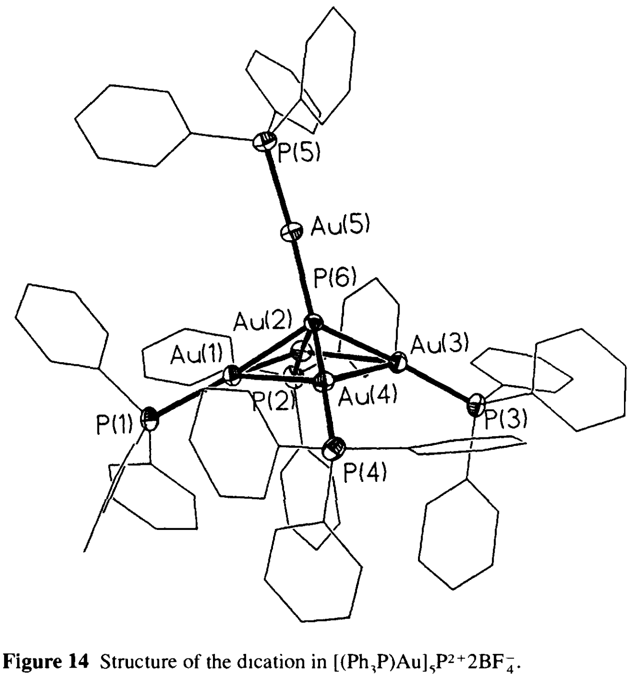


**Figure 14** Structure of the dication in [(Ph$_3$P)Au]$_5$P$^{2+}$2BF$_4^-$.

square-pyramidal $(LAu)_4P^+$ moiety appears in a dication of the formula $PAu_5L_6^{2+}$, with L = $PPh_3$ An evaluation of this structure suggests an adduct of $(LAu)_4P^+$ with $L_2Au^+$ (Fig 15) The dimensions of the square-pyramidal unit are similar in all cases, but none of the preparative studies provided an example where this moiety appeared as an independent structural unit

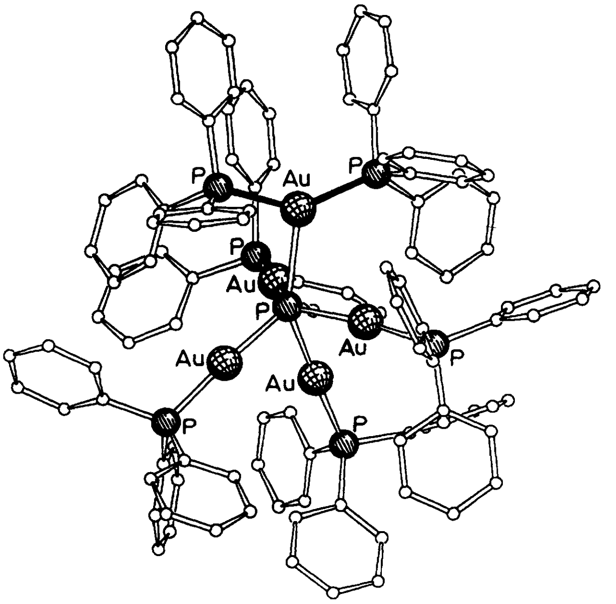


**Figure 15** Structure of the pentanuclear dication in the salt $[(Ph_3P)Au]_4P[Au(PPh_3)_2]^{2+}$ 2 $BF_4$

Fortunately, however, with arsenic as a central atom – introduced *via* tris(trimethylsilyl)arsine – this square-pyramidal $(LAu)_4As^+$ unit could be detected and structurally characterized easily in no less than three different forms (with different kinds of solvent) [23] The geometry – although at variance with classical rules of structure and bonding in 'arsonium cations' – is as predicted from the auriophilicity concept small Au—As—Au angles and short Au Au contacts in the As-capped square clearly lead to a dramatic stabilisation of this configuration over the tetrahedral form (Fig 16) In contrast with phosphorus, to date no adducts of this unit and no penta-auriated dications could be observed with arsenic

With phosphorus even the synthesis of octahedral hexa-auriation products is possible, however Starting from $PH_3$ or $P(SiMe_3)_3$ as the phosphorus source, and using various $LAu^+BF_4$ reagents, solutions containing $(LAu)_6P^{3+}$ trications can be obtained, which are readily identified by NMR data The septet–doublet multiplicity of the two $^{31}P$ NMR signals is direct proof for the stoichiometry of the P-centred clusters (Scheme 4) No single crystals of any of the salts could be obtained for detailed structural studies Based on simple geometrical calculations using standard bond distances, the $PAu_6$ octahedra are likely to be distorted in order to allow the most intimate Au Au contacts in the solid Such low-symmetry species may give rise to complicated, slowly growing lattices [29]

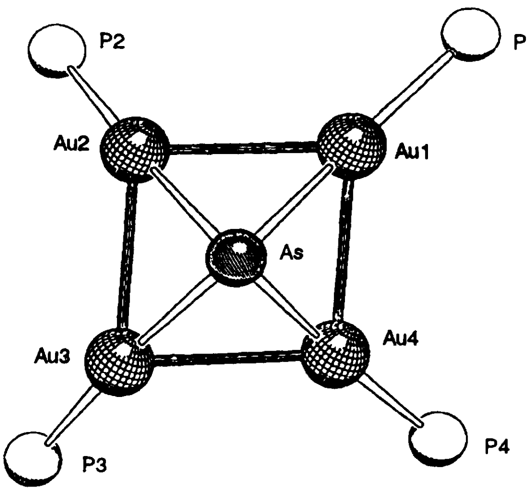


**Figure 16** Square-pyramidal structure of the cation $[(Ph_3P)Au]_4As^+$ in its tetrafluoroborate salt

Neither antimony nor bismuth could be incorporated into gold clusters All experiments met with failure and produced gold metal or homonuclear gold clusters

## 7 Carbon in Gold Clusters

Organogold compounds with at least one gold-to-carbon bond were among the first organometallic compounds to be discovered Because of their high stability towards hydrolysis and oxidation, their chemistry was developed during the first few decades of this century Any summary of this early work has shown, however, that polygold compounds remained a rare variation of this chemistry It was only during the late 1970s that multiple auriation of carbon was first accomplished In these initial studies the auriation of arylgold and ferrocenylgold complexes to give products with $CAu_2$ units was reported, which indicated that aggregation of gold atoms at carbon centres is a surprisingly facile process [8]

Tri-gold-substituted carbon was first obtained with phosphorus ylides starting with silylated precursors, trigold methyltriarylphosphonium salts could be generated, in which the $R_3P$—C unit caps a triangle of gold atoms[30] (Fig 17) Similar structural units were obtained in auriated methyloxazolines, and the completely unexpected structures of these and some of their adducts with AuX salts showed that complete auriation and even hyperauriation at carbon is also possible Only with very bulky phosphine ligands is the auriation reaction halted at the tetragold methane level, as shown for $[(Cy_3P)Au]_4C$, Cy = cyclohexyl (Fig 18) [31] With smaller ligands, including triphenylphosphine, no tetragold methanes can be obtained, and penta- or hexa auriation takes place

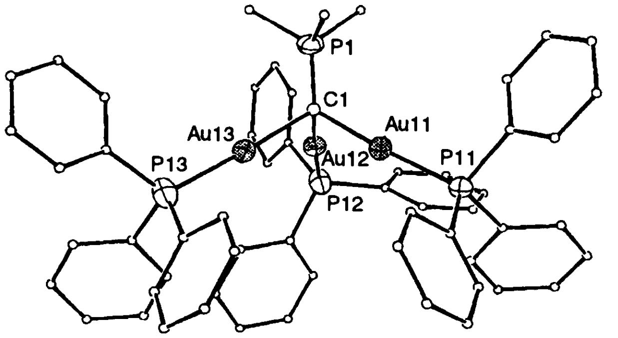


**Figure 17** Triauriated carbon in the phosphonium cation $Me_3P$—C $[Au(PPh_3)]_3^+$

The synthetic strategy employed to obtain such species was developed with polyborylmethanes as the key intermediates In a

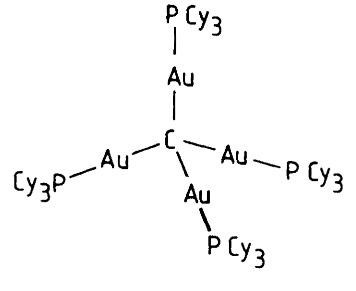


**Figure 18** Tetrakis[(tricyclohexylphosphine)gold] methane the first tetragold methane molecule

matter of a few months, di-, tri- and tetra-borylmethanes could be converted into tetra-, penta- and even hexa-gold–methane compounds or cations Spectacular prototypes are the (di)cations $[(Ph_3P)Au]_5C^+$ and $[(Ph_3P)Au]_6C^{2+}$ with their electron-deficient trigonal-bipyramidal and octahedral cluster structures, respectively[8] (Figs 19, 20) The triphenylphosphines can be exchanged for other tertiary phosphines including chelating ligands which span the edges of the polyhedra The structures were confirmed by analytical, spectroscopic and diffraction data, and these results also served to correct erroneous reports in the literature, which had suggested 'empty' octahedral clusters[7]

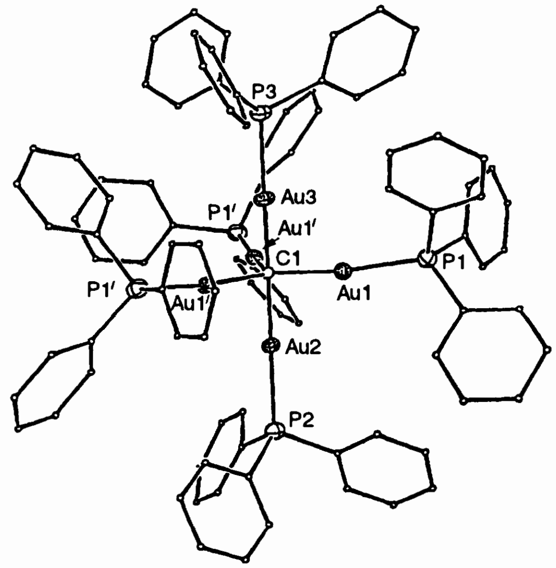


**Figure 19** Hyperauriated carbon in the trigonal-bipyramidal $[(Ph_3P)Au]_5C^+$ cation

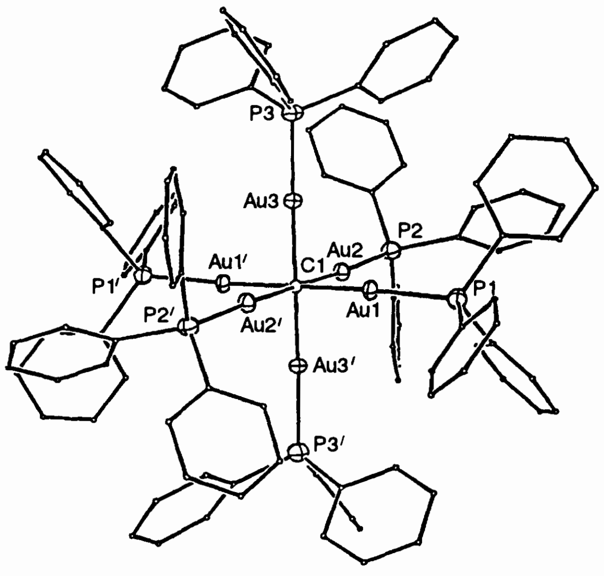


**Figure 20** Hyperauriated carbon in the octahedral $[(Ph_3P)Au]_6C^{2+}$ dication

On the other hand the new findings also confirmed pertinent predictions based on molecular orbital arguments,[6] which had indicated that carbon-centred octahedral gold clusters should be stable dicationic species A detailed analysis of the structure and bonding in the $Au_6C^{2+}$ units with state-of-the-art calculations including relativistic effects have given a very convincing account of the bonding situation in these species[11,12]

The isolobal relation with the known $CH_5{}^+$ cation and the unknown $CH_6^{2+}$ dication has been introduced above, but should be addressed here briefly again, because of its heuristic value Since the protonation of an alkane hydrocarbon is established not only for $CH_4$, but also for $C_2H_6$, multiple auriation of ethane appeared to be a feasible process And in fact 1,1,1-tris(dimethoxyboryl)ethane was found to give not only a 1,1,1-trigold–ethane, but even a tetra-auriated ethanium cation $\{CH_3{-}C[Au(PPh_3)]_4\}^+$ with a square-pyramidal structure[32] (Fig 21)

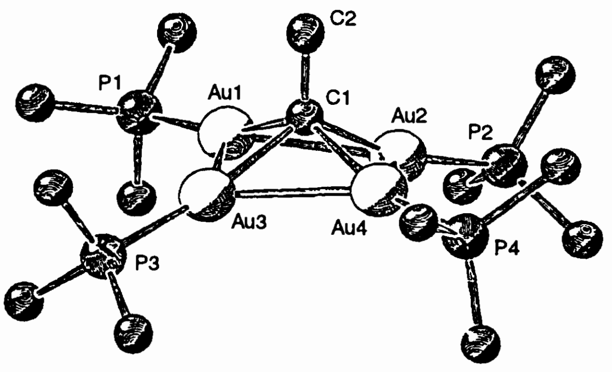


**Figure 21** Hyperauriated carbon in the square-pyramidal cation $Me{-}C[Au(PPh_3)]_4^+$

Hyper-coordinate carbon has also been produced in the auriation of a disilyl–digold–methane compound, which gave the disilyl–trigold–methanium cation[33] (Fig 22) Like the previous examples, this result clearly indicates that a large variety of carbon-centred or carbon-based gold clusters are available, the properties of which need to be explored in order to delineate the scope of this new organogold chemistry

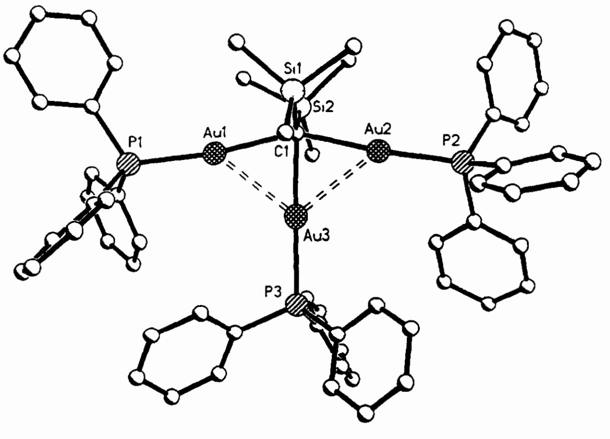


**Figure 22** The distorted trigonal pyramidal structure of the digold trisilyl methanium cation, $(Me_3Si)_2C[Au(PPh_3)]_3^+$

The last two decades have seen the discovery of quite a number of compounds with gold–silicon bonds, but no examples with silicon as a clustering centre for gold have been encountered The situation is similar for the chemistry of gold–germanium compounds, the first representatives of which have been found only very recently[34] (Fig 23), and for gold–tin chemistry A molecular chemistry of the gold–lead system does not yet exist It is probably the lack of suitable starting materials which hampers progress in these areas

## 8 The First Gold–Boron and Gold–Indium Clusters

Compounds with gold–boron bonds have been detected in quite a number of areas of boron chemistry As a general rule, however, this has always been a chemistry of *gold in boron clusters*, rather than a chemistry of *boron in gold clusters*

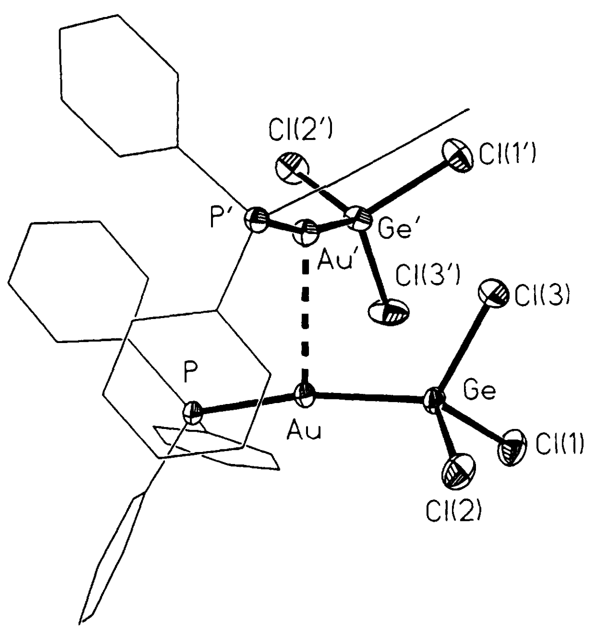


**Figure 23** The dimeric structure of $Cl_3GeAuPPh_3$.

Following the discovery of carbon-based gold clusters, the synthesis of the corresponding boron systems was also undertaken using the same strategy. More general theoretical studies of clusters centred by main-group elements clearly suggested that species of the type $(LAu)_6B^+$ or $LB(AuL)_4^+$ should in fact be stable and have structure and bonding characteristics similar to those of their carbon analogues.[11,12]

While the absence of any preparative methods for polysilylboranes precluded the synthesis of a homoleptic gold–boron cluster, it was a lucky coincidence that the first synthesis of a monosilylboron complex $R_3P-BH_2-SiMe_3$ was published when there was a need for it. Its reaction with auriating agents was straightforward and gave high yields of an exceedingly stable compound of the type expected from the above considerations (Fig. 24). Two salts of the cation $Cy_3P-B[Au(PPh_3)]_4^+$ could be crystallized and their structure determined.[35] The cation features a square pyramid centred by a boron atom, with the tricyclohexylphosphine ligand at the apex and four gold atoms at the base. It is thus isostructural (and isoelectronic) with cations of the type $R-C[AuL]_4^+$ (above). The preparation of other stable boron–centred gold clusters may be imminent, but presently no preparative pathway has been opened up to reach this goal.

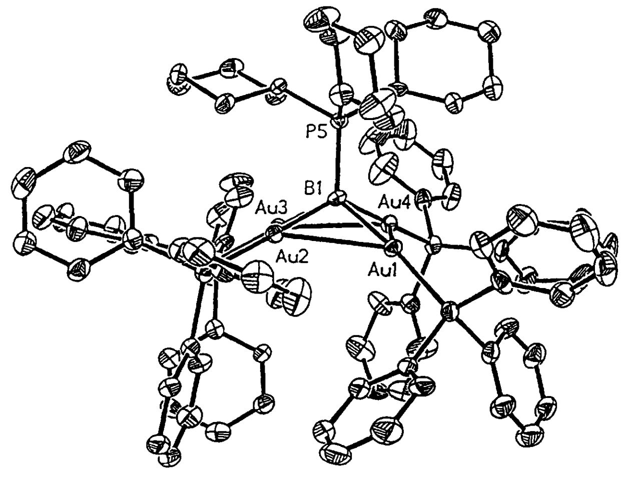


**Figure 24** The cation $(Cy_3P)B[Au(PPh_3)]_4^+$ in its tetrafluoroborate salt.

The inventory of mixed-metal clusters of gold does not include stable gold–aluminium, gold–gallium or gold–thallium species. The first gold–indium cluster was isolated in recent investigations, however, and this appears to be encouraging evidence for a new family of clusters composed of coinage and Group 13 metals.

This cluster was obtained from the insertion of InCl into $Ph_3PAuCl$ molecules in tetrahydrofuran solution containing bis(diphenylphosphino)ethane.[36] The stoichiometry $Au_3In_3(dppe)_2Cl_6(thf)_3$ of this mixed-metal cluster was confirmed by analytical, mass spectrometric and NMR spectroscopic data. $^{197}Au$ Mössbauer spectra indicate a mixed-valence cluster with gold in the oxidation states 0 (×2) and +I (×1), which suggests the assignment of oxidation states of +I (×2) and +III (×1) to the indium atoms. The crystal structure is in good agreement with this proposal. It shows a pair of gold atoms (as part of an isosceles triangle) with an extremely short Au–Au distance of 2.735(3) Å, and the gold atoms colinear with their ligand phosphorus atoms (Fig. 25). It should be noted that phosphine complexes of the diatomic molecule $Au_2$ of the form LAuAuL have been considered in many experimental and theoretical studies in the past. It appears that such a unit can now be distinguished in the new Au–In cluster, where it is side-on coordinated to two indium atoms and one gold atom. The indium atoms also form an isosceles triangle, which is perpendicular to the triangle of gold atoms, and each In atom carries two chlorine atoms and one thf ligand. A more detailed theoretical treatment of this peculiar cluster arrangement is under way.

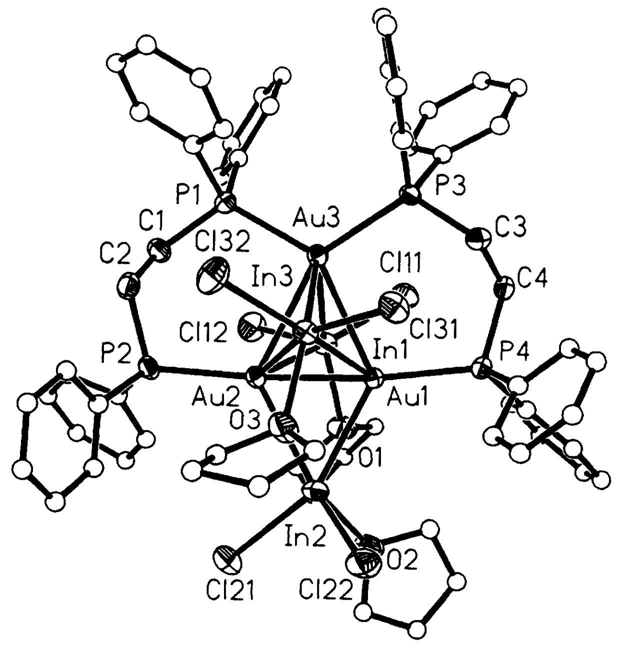


**Figure 25** The mixed-valent, mixed-metal gold–indium cluster $(dppe)_2Au_3In_3Cl_6(thf)_3$, with dppe = 1,2-bis(diphenylphosphino)ethane and thf = tetrahydrofuran.

## 9 Outlook

From sporadic observations of a few isolated, seemingly unrelated cases, the chemistry of gold clusters with interstitial elements has grown into a rich field of research, for which a consistent picture of the governing principles is gradually emerging. During the compilation of cross-fertilizing experimental data and theoretical results, some simple rules, like the isolobal and isoelectronic relations, or the auriophilicity concept, have been extremely helpful more than once to decide the next move. The unavoidable simplifications could gradually be eliminated as the data became complete for the individual cases, and the rules could be replaced by more sophisticated principles at least for the simple benchmark examples. Even if many of the new 'high-carat gold compounds' will not be important in their own right, they will continue to play a role as useful model systems for a better understanding of nanostructures of metals, alloys and interstitial phases

Auriophilicity-based supramolecular aggregates of gold complexes are presently attracting growing interest not only because of the intriguing luminescence properties associated with the oligomerization, but also because of their potential use for various imaging techniques, for the design of framework structures, for the stabilization of mesogenic, dendrimeric and highly porous phases, for surface matrices, for influencing the rheological behaviour of 'liquid gold' pastes (preferably in non-organic, aqueous solvents), and for the formulation of water-soluble, high-gold-content chrysotherapy drugs It appears that the majority of these projects are likely to succeed in the long term, because three decades of fundamental research in many laboratories have provided an excellent basis for applied studies

## 10 Acknowledgement

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