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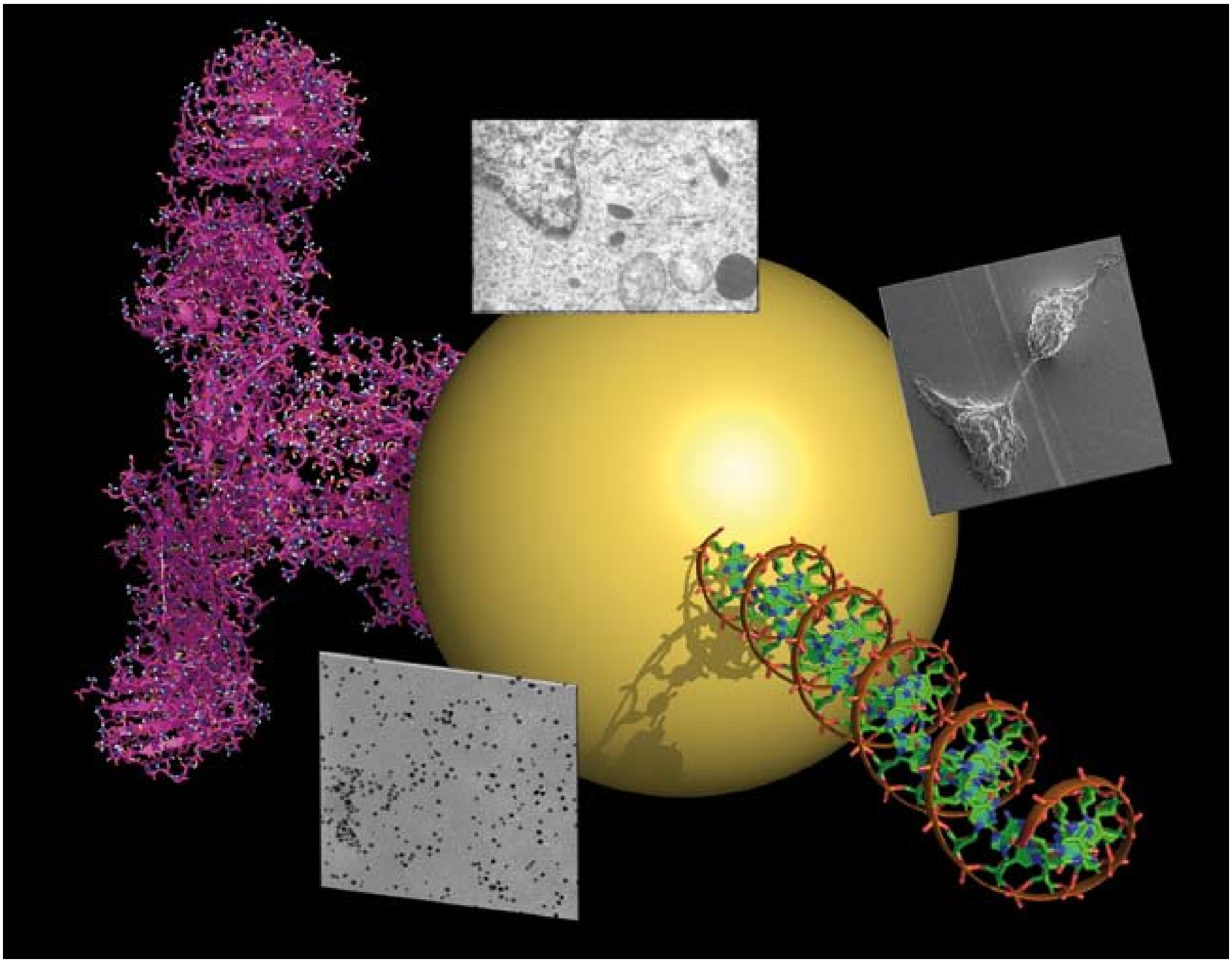

A briefing on aurophilicity†

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There is now compelling experimental evidence for the existence of specific intra- and intermolecular bonding between seemingly closed-shell gold(I) centers ($5d^{10}$) which manifests itself in all areas of gold chemistry. This "aurophilic interaction", which had not been predicted by conventional valence theory, was found to be associated with binding energies in some cases exceeding even those of strong hydrogen bonds and therefore to be highly significant in co-determining molecular structure and dynamics. In high-level theoretical treatments the attraction is rationalized as a "super van der Waals bonding" based on particularly strong relativistic, dispersion and correlation effects (*critical review*, 265 references).

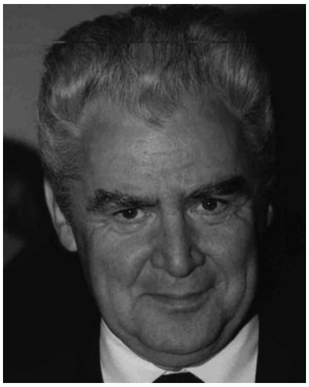
1. Introduction

Gold chemistry is currently one of the most rapidly growing fields of chemistry because of its relevance to a large number of topics of materials science.[1,2] This is easily illustrated by naming just a few of the prominent areas: owing to their superior performance, gold metal and gold alloys are required in all forms, and in particular in minute dimensions, for the electrical and electronics industry.[1,2] The surface of pure gold metal is the number one playground for surface engineering. Gold clusters are the active centers on supports for important catalytic reactions.[3] Gold nanoparticles are produced in a broad range of sizes and forms for their optical effects and for imaging, but also for anchoring a variety of functional groups on their large specific surface.[4] Gold salts and gold complexes were not only discovered to be highly active homogeneous catalysts for organic reactions,[5] but also shown to have intriguing physical properties, including luminescence,[6] liquid crystalline[7] or non-linear optical behaviour.[8,9]

Modern chemistry tries to relate all properties of matter to the specific structure of matter, and gold chemistry of course is no exception. With the advent of potent methods to determine crystal and molecular structures routinely and with almost foolproof instrumentation, in the last few decades a wealth of structural information has been compiled for gold and its compounds. This plethora of data can now form the basis for a better understanding of the unusual characteristics of bulk gold, its surface, its nano-sized particles and clusters, and its molecular and ionic compounds.

Even in early history, gold has held a special position among all metals owing to its lustre and "noble character" which in modern terminology is related to its extreme electrochemical potential. Over the years, theoretical physicists and chemists were able to "explain" most of these very special properties of gold by the fact that the valence electrons in a gold atom are subject to the strongest relativistic contraction of their orbitals, making gold also the most electronegative metal.[10]

However, even the most advanced theoretical treatments did not lead to the prediction that in the chemistry of gold in its most common cationic oxidation state Au^+—with a closed-shell electronic configuration ($5d^{10}$)—there should emerge specific metal–metal interactions which are significant not only for the conformation, configuration and even stoichiometry of



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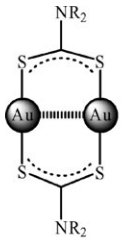
molecules, but also cause unusual modes of aggregation of molecules in the condensed phase thus co-determining the structure of molecules and molecular and ionic crystals, and finally the properties of the systems. These phenomena were observed empirically from the unexpected course of chemical reactions and by carefully considering the growing structural information on gold and its compounds. The studies led to the proposal of the "aurophilicity" concept, which was later generalized into "metallophilicity" as effects already documented for neighbouring elements were recognized to follow the same pattern and to have the same origin.

In this article the most important experimental observations and their interpretation are summarized in a rather concise form quoting some early, some fundamental and some very recent publications. A comprehensive account of the field, which would require coverage of another two hundred and fifty publications, is not possible within the framework of the present multi-authored special issue on gold chemistry. In several of the other contributions to this issue various aspects of the topic are also addressed and provide further key references for specific in-depth studies. Short reviews on aurophilicity were published in 1990 and 2000.[11]

2. Early observations

In the first comprehensive book on "*The Chemistry of Gold*" by Puddephatt, published in 1978, the author was pointing out that there were several reactions and structures of gold compounds published in the literature which could not be explained by the standard rules of valence.[12] Among these were examples from very different classes of compounds, such as dimeric gold(I) dithiocarbamates (**1**),[13] dialkylphosphonium-bismethylides (**2**)[14] and dialkyldithiophosphates (**3**),[15] with eight-membered ring structures showing an unusual twist which brings the two gold atoms in each molecule close together. Even more intriguing, the molecules of the latter were found to be aggregated forming a chain of almost equidistant gold atoms along one axis of the crystals. The dinuclear complex of bis(phenylphosphino)methane with AuCl, (dppm)$(AuCl)_2$ (**4**), had been shown to adopt a Z-conformation in which the two gold atoms are held in close proximity.[16] The mononuclear complex (piperidine)AuCl was found to exist as a tetramer in the crystal featuring a square of gold atoms (**5**, Pip = piperidine),[17] and the rod-like isocyanide complex molecules of the formula (MeNC)AuCN were shown to be aggregated into sheets (**6**) with the gold atoms of a given layer gathering in only slightly puckered planes.[18]

Most surprising, by the school of Nesmeyanov in Moscow it had been observed[19] that the reaction of complexes of the type $(R_3P)AuCl$ with silver oxide gave directly and in high yields exceedingly stable tri(gold)oxonium salts $\{[(R_3P)Au]_3O\}^+X^-$ (**7**). According to the results of a later crystallographic investigation, in the cations of the products the three gold atoms are clustering together at the oxygen atom to form a pyramidal unit.[20] At about the same time and independently, the corresponding tri(gold)sulfonium and -selenonium salts had also been obtained.[21,22] Further it was also found that electrophilic diauration of aromatic hydrocarbons (benzene,[23] toluene (**9**), ferrocene (**8**),[24] cymantrene *etc.*) gave products of a *geminal*-substitution showing again that the first gold substituent was drawing the second one to the same carbon atom. In a structure determination of the diaurated ferrocene very short Au–Au distances and very small Au–E–Au angles (E = O, S, C) were noted.



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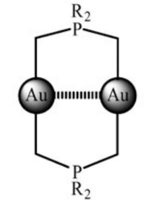

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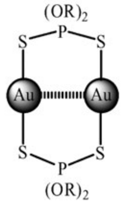

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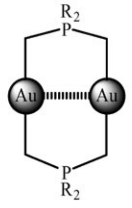

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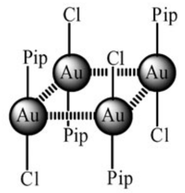

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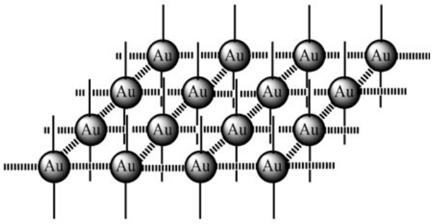

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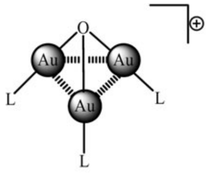

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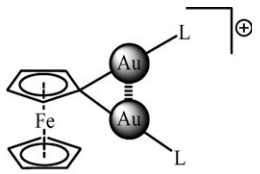

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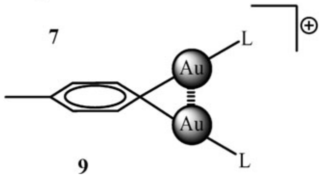

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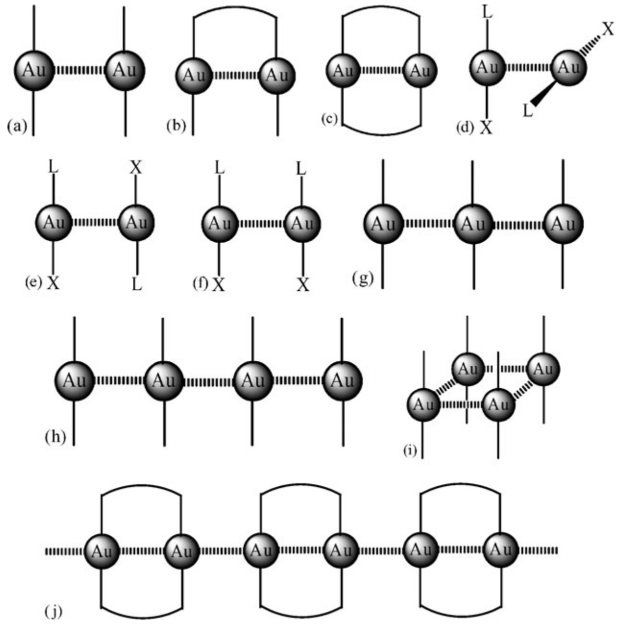
In retrospect, this collection of early examples was already showing all the phenomena of conformation, configuration and multidimensional aggregation which have later been observed throughout the chemistry of low-valent gold. Summarizing his observations, Puddephatt noted the following: "In these complexes the nature of the gold–gold interactions is not clearly understood. Indeed some authors have suggested that there is no bonding interaction and that short Au–Au contacts in the solid state are caused by simple packing forces. The frequency of occurrence of short Au–Au distances in different complexes, however, is not consistent with this view. Further theoretical studies are required, however, before a profitable discussion of the nature and strength of the gold–gold bonding in gold(I) complexes is possible."[25]

In 1981, Jones started to publish a series of surveys of recent structural work in gold chemistry which for a growing number of examples suggested an unusual mutual affinity of gold centres in virtually any molecule.[26] This phenomenon became particularly obvious in preparative and structural work of *multi*nuclear complexes of gold with unexpected stoichiometry, stability and structure. Owing to this affinity, gold atoms in molecules, cations and anions again seemed to be literally drawn to any existing mono- or polynuclear gold seed nucleus and make it grow. These observations prompted one of the present authors to propose the special term "aurophilicity" for this type of at first sight unprecedented interactions which gave rise to a variety of novel and fascinating types of compounds.[27] Particularly striking discoveries were the spontaneous, unforced formation of an extremely stable square pyramidal tetra(gold)methanium cation $[(LAu)_4CH]^+$ and of a tetra(gold)arsonium cation $[(LAu)_4As]^+$.[28–30] The former is the protonated form of a tetra(gold)methane molecule $[(LAu)_4C]$, which was found to be one of the strongest Brønsted bases.[28] The arsonium cation is the first example of a spontaneous, non-forced rearrangement of a quaternary onium salt from a tetrahedral to a square pyramidal structure violating the classical van't Hoff rule.

3. Definition

The terms "aurophilicity" and "aurophilic bonding" are now widely used to describe various kinds of Au–Au interactions within and between gold compounds and their consequences for the properties of the systems. It is therefore important to have a sufficiently clear definition of the effect.

In the standard case, aurophilicity appears to be operative between closed-shell gold centres in the formal oxidation state Au^{+1} (with the valence electronic configuration $5d^{10}$) and in the linearly two-coordinate state. The low coordination number is an important prerequisite since it minimizes steric repulsions between ligands in the aggregates. The attraction is therefore rarely observed for coordination numbers >2, although there are exceptions (below). For independent mononuclear molecules or ions, or parts of multinuclear complexes with a flexible skeleton, the approach of the metal centres takes place vertically to the molecular axis to reach an equilibrium Au–Au distance of *ca.* 3 Å (**10a–c**). The conformation of the aggregates may be staggered (crossed) or eclipsed (parallel) with—where applicable—like or opposite directions of the individual units (**10d–f**), regardless of the charge (+, 0, −) of the units considered. Examples in the literature cover the whole range of dihedral angles X–Au–Au–X from 0 to 180°. A gold(I) center can entertain only one or several aurophilic contacts. The most common arrangements are dimers and chainlike polymers (linear, zigzag or helical), but oligomers with a linear or compact arrangement are also known (**10a**, **10g–j**). If ligands impose restraints, then the approach may also follow a different geometry. This is particularly common if several gold atoms are gathering at a common central atom (*e.g.* **11a,b**). For these units, small angles Au–E–Au (often <90°) are indicative of the aurophilicity effects. Structural alternatives to the cyclic form **10c** with the same stoichiometry are polymers (**12a**) or folded macrocyclic arrangements (**12b**).



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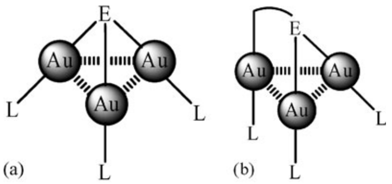

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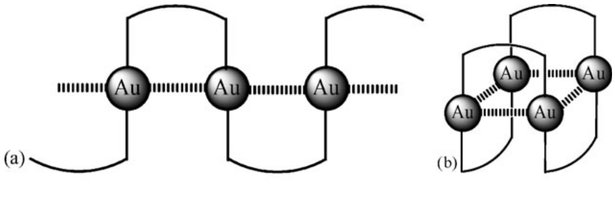

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The energy associated with aurophilic binding has been estimated using data from several different methods, and consistent results were obtained. The data place aurophilicity into the category of *weak forces*, comparable to hydrogen bonding, and definitely stronger than standard van der Waals forces. The energy profile of the mutual approach of two gold centres appears to be relatively flat, allowing for a wide range of distances (2.8–3.5 Å) for which bonding can still be considered. Also, the binding energy of only one gold atom (**10a**) is not very different from that of a gold atom in multinuclear aggregates (**10g–j**). The geometry of the individual units (L–Au–X) is showing only minor deviations from linearity in the aggregates, but the slight bendings observed are all in the direction which brings the Au atoms closer together, indicating attraction, not repulsion.

The above definition excludes bonding between gold atoms with partially open valence electron configurations, in particular the bonding between Au^{2+} centres with a $5d^9$ configuration which can be described as a regular two-centre two-electron metal–metal single bond. One of the strongest regular Au–Au bonds is present in the Au_2 molecule in the gas phase arising from interactions of the $5d^{10}6s^1$ states of Au^0. It should also be noted that the majority of presently known gold clusters contain gold atoms in mixed oxidation states, with components Au^0 and Au^+, of which the former provide electrons for conventional metal–metal bonding, which can be described in the same way as the bonding in bulk metallic gold. In all these cases aurophilic bonding may make some very minor contributions to the overall cluster bonding which is generally much stronger.

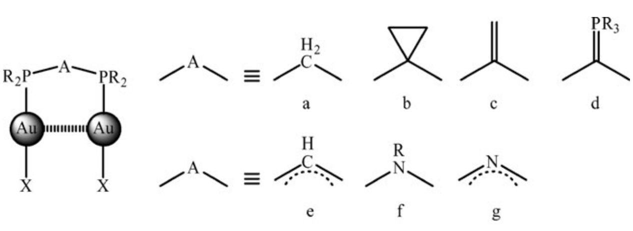
Theoretical treatments on various levels of sophistication have been published for simple model systems which provide data in good agreement with the experimental results, although for the special problem of aurophilicity the procedures and results of computational chemistry are not always lucid. This means that in valence terms there is as yet no simple picture of the interaction, and therefore descriptions such as "super-van der Waals" and others have been used instead. Regardless of these deficits, the evidence for the significance of the effect is meanwhile overwhelming, and the concept therefore has quickly been employed successfully in many areas of gold chemistry.

4. Experimental evidence for aurophilicity effects

4.1 Intramolecular effects

Aurophilic interactions are most readily identified if they occur within a given molecule (**10b**). These *intra*molecular contacts are not associated with a major loss of entropy, and in most cases they are impaired less by peripheral steric congestions. The most common cases are gold(I) complexes with the number of gold atoms equal to the number of donor atoms of ligands with short to medium-long flexible chains between the donor centres. For very short bridges, in particular with one atom acting as the common donor centre (**11a,b**), intimate clustering may be virtually compulsory, making the aurophilicity effect less obvious. For long ligand bridges, entropy and molecular packing contributions can favour *inter*- over *intra*molecular contacts. Most 1 : 1 complexes of gold(I) with difunctional ligands give dimers with cyclic structures showing transannular aurophilic interactions (**10c**).

4.1.1 Non-cyclic polynuclear complexes of flexible polyfunctional ligands. The 2 : 1 complexes of bis(diorganophosphino)-methanes (**13a**),[16,31] -cyclopropanes (**13b**),[32] -ethylenes-(1,1) (**13c**),[33] phosphonium-methylides (**13d**),[34] -methylides (**13e**),[35] carbonyl-bis(phosphoniummethylides)[36] or amines and amides (**13f,g**)[37,38] are protypes of this family of compounds (**10b**). Most of the examples have halide anions (X = Cl, Br, I) attached to the gold centres, but phenyl derivatives such as $(dppm)(AuPh)_2$ show the same phenomena.[39] Without any exception, in crystals of these complexes the molecules are in a *Z*-conformation with short Au–Au contacts of *ca.* 3.0 Å. Many authors have noted that regarding the internal conformation of the diphosphines and the orientation of the anions attached to the gold atoms the structures represent an unfavourable eclipsed conformation, and yet they are the ground states of the molecules. Moreover, both P–Au–X angles are found to deviate from linearity thus facilitating the mutual approach of the metal atoms.[16,34]



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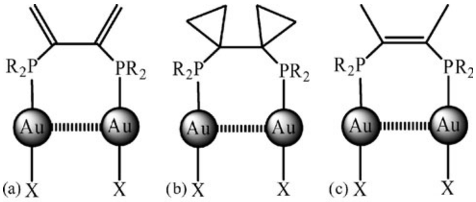
With a two-atom bridge between the P-atoms, as in the butadiene-2,3-diyl (**14a**) or bi(cyclopropane)-1,1′-diyl compounds (**14b**), the *intra*molecular Au–Au attractions are still obvious.[40,41] This is also true for the complexes of the more rigid *cis*-bis(diphenylphosphino)ethene (**14c**), while with the *trans* isomer of this ligand only *inter*molecular aurophilic contacts are possible.[42,43] *cis–trans* Isomerization is a photochemically induced process, for which the aurophilic bonding appears to be significant.[44,45]



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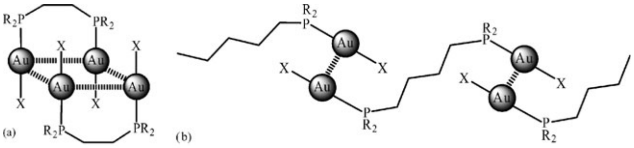
For longer $-(CH_2)_n-$ linkages between two phosphorus donor centres, the aggregation also changes to *inter*molecular (n = 2–6) (*e.g.* **15a,b**).[46–49] The extended chains of the dinuclear complexes $XAuPh_2P(CH_2)_nPPh_2AuX$, with X = Cl, $AuSC_6H_4$-4-Me *etc.*, become either attached to each other in a head-to-tail fashion, crosslinked by aurophilic bonding or even woven into braids.[46–49] Examples taken from the series of complexes of dithioethers $RS(CH_2)_nSR$ show an analogous behaviour.[50,51]



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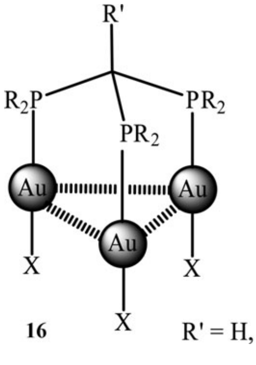
Accordingly, in 3 : 1 complexes of trifunctional tertiary phosphines with linear or branched structures triatomic chains or triangular triples of gold atoms are formed (**16**).[52] With very small substituents at the P atoms, a layer structure is preferred.[53] The same tendency becomes obvious for branched systems with very flexible arms as in $N(CH_2CH_2PPh_2)_3$. The trinuclear complexes with AuCl, AuBr and AuI have either chain or layer structures.[54] With other ligand geometries, aggregated molecules with intra- and/or intermolecular interactions are observed (**17a**, **17b**).[55–58] Gold triangles are also formed in the cations of a compound of the net composition $[(dppm)(AuCCPh)_2]_2$ [59] and two pairs of gold atoms in $[(dppe)(AuCCPh)_2]_2$.[60] Probably for steric reasons, for 4 : 1 complexes of tetra-tertiary phosphines such as $PhP(CH_2CH_2PPh_2)_3$ the intermolecular mode of aggregation is fully dominant.[61] A summary of related work is available.[62]



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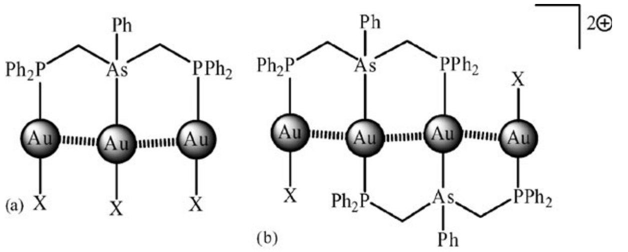

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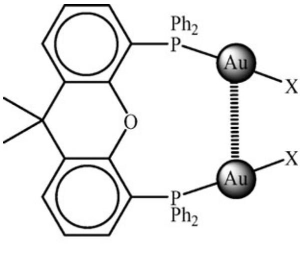
Even a true wide-span ligand based on 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos) has been shown to form 1 : 2 complexes with AuCl and $AuNO_3$ which adopt a screwed configuration bringing the two gold atoms together (**18**).[63]



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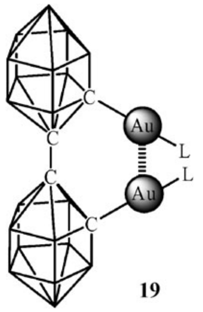
Dinuclear gold(I) complexes of bis(*ortho*-carboranes) of the type $[B_{10}C_2H_{10}AuPPh_3]_2$ adopt a conformation in the solid state which is clearly determined by aurophilic interactions (**19**). The investigation of the molecular dynamics in solution allowed one of the early determinations of the corresponding binding energy.[64]



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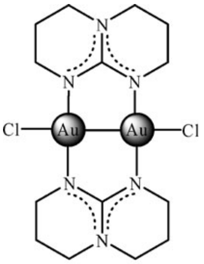
Complexes of type **10b** are rare for ligands with donor functions other than P or S atoms. With N much smaller than P, the distance between two gold atoms at ligands such as 1,8-naphthyridine or guanidinate anions is too short and the systems rearrange to other stoichiometries and geometries. A prominent example is the polycyclic dinuclear guanidinate complex **20** obtained from (tht)AuCl and the sodium guanidinate in dichloromethane.[65] In the course of this reaction, the gold atom becomes oxidized and a regular Au–Au bond between Au(II) centres is formed, which has an extremely short Au–Au distance.



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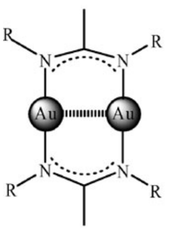
4.1.2. Transannular aurophilic interaction in cyclic polynuclear complexes. A large variety of neutral or anionic 1,3- and 1,4-difunctional ligands form cyclic 2 : 2 gold(I) complexes adopting extended conformations which allow transannular aurophilic interactions (*e.g.* **10c**). Classical examples are the dithiocarbamates (**1**)[13] and dialkyldithiophosph(on)ates (**3**)[15] with sulfur donor atoms, di(phosphino)-methanes (**13a**),[66,67] -methanides (**13e**)[34] and -amines (**13f**)[38] with phosphorus donor atoms, amidinates with nitrogen donor atoms (**21**),[68] and phosphonium bis(methylides) with carbon donor atoms (**2**).[69,70] Similar arrangements are observed with mixed donor atoms, as in methylene(thio)phosphinates (**22**)[70,71] or with 2-diorganophosphinopyridines (**23**),[72] and with dimethylaminomethylphenyl (**24a**),[73] 2-diorganophosphinomethylphenyl (**24b**)[74] and thiouracylate ligands (**24c**).[75] This family of compounds is presently the largest collection of species which show all characteristics of aurophilic bonding (ease of formation, high thermal stability, reluctance to undergo polymerization, short transannular contacts, facile formation of transannular Au–Au bonds upon oxidation, short Au–Au contacts, inward-bent X–Au–X axes *etc.*). And yet, the argument has always been brought up that the short contacts may be induced mainly by the ligand bite. To clarify this point, for one of the earliest examples a Raman study was carried out which produced data suggesting a bond order of at least 0.15 for the transannular interaction.[76] There is no other direct experimental evidence for this binding, but all the structural details of the compounds with a large variety of ligands are fully consistent with the bonding concept. Many of these eight-membered ring compounds undergo association into larger aggregates through aurophilic bonding. Apart from oligomers and linear or zig-zag chains, helical structures are also formed.[75,77]



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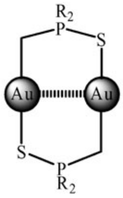

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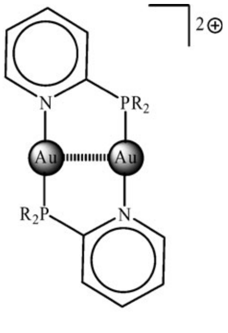

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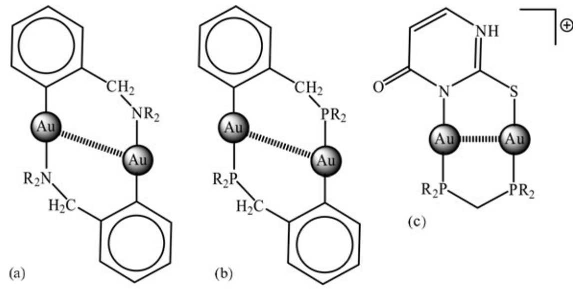

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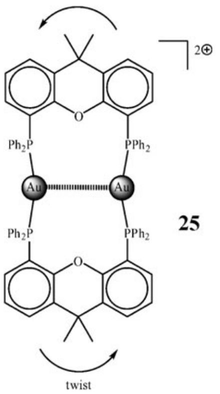
The xantphos ligand already mentioned above forms a dicationic 2 : 2 complex with Au^+ which adopts an 8-type configuration in which the crossing of the loops is held together by a transannular Au–Au contact (**25**).[63]



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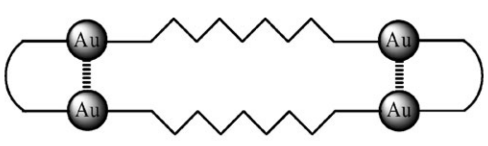
Even more convincing is the peculiar folding of macrocycles containing several gold atoms. Gold(I) dithiocarboxylates,[76] triazenides,[78] amidinates,[79,80] and guanidinates[81] are all forming tetramers with 16-membered rings in a conformation which has the four gold atoms arranged in a small square and with ligand loops connecting each neighbouring pair of metal atoms (**12b**). It should be noted that these flexible tetranuclear macrocycles in principle could adopt many other different conformations, and that other degrees of oligomerisation (*e.g.* trimers) could be envisaged, but structures of the type **12b** appear to be strongly preferred throughout this type of complexes. Tetranuclear metallacycles with the gold atoms appearing as closely separated pairs form extended loops with two transannular interactions (**26**).[38]



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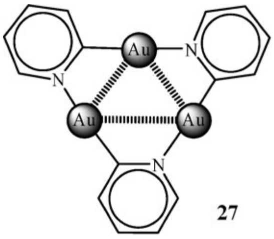
For macrocycles with ligands imposing configurational restraints, in particular ligands which require planarity of all substituents including the metal atoms, the influence of intramolecular aurophilic bonding is less obvious. This is true *e.g.* for the trinuclear gold(I) 2-pyridyls (**27**),[82] pyrazolates (**28**),[83–85] imidazolyls (**29**),[86] and carbeniates (**30**)[87,88] which form planar ring systems with a triangular core unit of gold atoms. These molecular structures are clearly enforced by the ligand geometries, but at the same time they also favour metal–metal interactions. The same reasoning applies to the small pentagon of gold atoms which is present in pentameric mesitylgold (**31**).[89]



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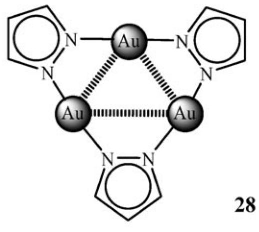

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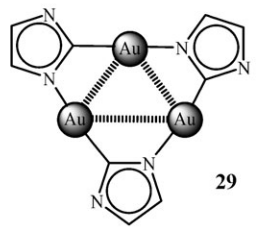

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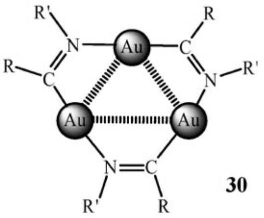

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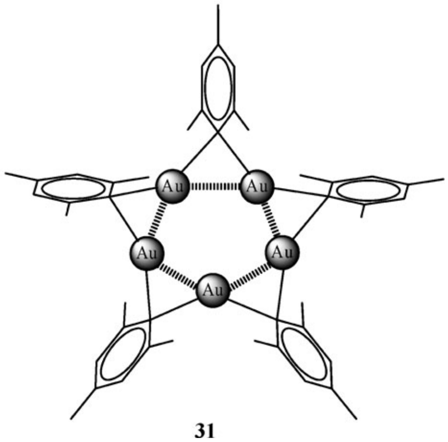

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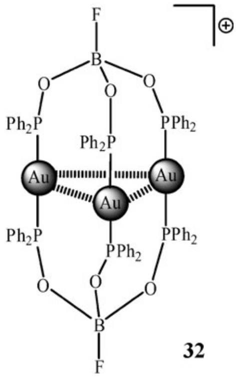
In polycyclic systems, transannular aurophilic interactions can form triangular units of bonded gold atoms as in a tris(diphenylphosphito)fluoroborate complex (**32**)[90] which has two tripodal ligands in a trinuclear monocation: $\{[FB(OPPh_2)_3]_2Au_3\}^+$.[91]



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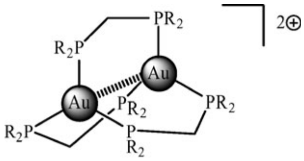
All the above mentioned systems with trans-annular Au–Au contacts have two-coordinate gold atoms (not counting the Au–Au contact). Examples with analogous interactions between gold(I) centres with higher coordination numbers are rare. An early observation was made for the bicyclic dicationic 3 : 2 complex $[(dmpm)_3Au_2]^+$ with dmpm = $Me_2PCH_2PMe_2$, which shows an Au–Au distance of 3.04 Å between trigonally three-coordinated metal atoms (**33**).[92] In the 1 : 1 complex with the same ligand, $[(dmpm)_2Au_2]^{2+}$, a regular eight-membered ring structure (**10c**) with linearly two-coordinate gold atoms is present.[93]



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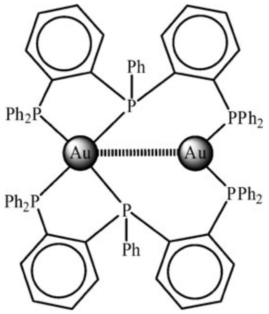
Short Au–Au contacts between gold atoms of higher coordination numbers occur only if severe constraints are imposed by ligands, as with bis(2-diphenylphosphino-phenyl)-phenylphosphine (bdpp). In dications $[(bdpp)_2Au_2]^{2+}$ one of the two gold atoms is in a strongly bent two-coordinate state (P–Au–P 147.4°) while the other is tetra-coordinated with one P–Au–P angle as wide as 150.7°. And yet, the intra-cationic Au–Au distance is one of the shortest observed, *viz*. 2.878 Å (**34**).[94]



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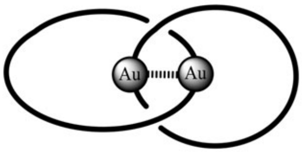
4.1.3. Catenanes, Borromean rings and rotaxanes. Macrocycles containing several gold atoms may not only reach a maximum of intramolecular aurophilic bonding by appropriate folding, but also by threading one ring through the other to form catenanes (**35**). This phenomenon was first observed by the groups of Mingos[95] and Puddephatt[96] using different substrates. Non-catenated rings of various sizes were shown to be in an equilibrium with the catenanes, in which efficient inter-ring Au–Au contacts appear to stabilize the threaded rings. The mechanism of the surprisingly facile catenane formation can be assumed to include various intermediates with different forms of aurophilic interactions which lower the activation barriers of significant steps of the ractions. A more complex weaving which leads to a Borromean sheet (three interwoven rings) was observed in a hexanuclear complex of 1,4-bis(2-methylimidazol-1-yl)benzene with $AgBF_4$. The folding and threading in this case appears to be supported by argentophilic interactions (**36**).[97] Aurophilic interactions are again held responsible for the assembly of a novel rotaxane, in which a cationic dumbbell $[R_3PAuPR_3]^+$ forms the axle for a trinuclear macrocyclic molecule generated by deprotonation of a 1-propargyl-3-vinyl-imidazolium cation in the presence of Me_3PAuCl (**37a,b**).[98] The Mercedes-star type arrangement with approximate C_{3h} point group symmetry has also been discovered in a tetramer of ^{t}BuNCAuC≡CSiMe$_3$ (**38**, X = alkynyl, L = isocyanide).[99]



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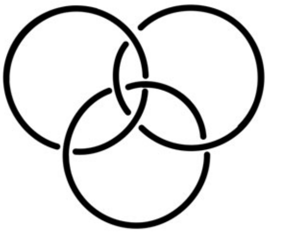

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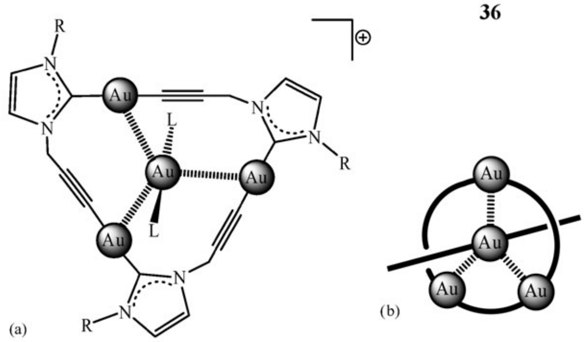

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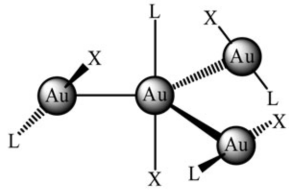

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4.1.4. Polynuclear complexes with the gold atoms clustering at a common central atom. It has escaped the attention of many scientists that there are no complexes of a simple gold amide,

Table 1 Aurophilicity-supported clustering of gold atoms at non-metallic elements. (L represents an electron-pair donor ligand, most frequently a tertiary phosphine.) For structures see formulae **39–46**, for literature see text

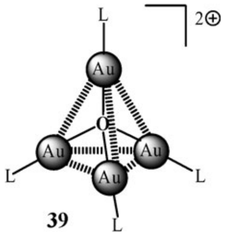
(a) *Homoleptic substitution*			
$C(AuL)_4$	—	—	—
$[C(AuL)_5]^+$	$[N(AuL)_4]^+$	$[O(AuL)_3]^+$	—
$[C(AuL)_6]^{2+}$	$[N(AuL)_5]^{2+}$	$[O(AuL)_4]^{2+}$	—
—	—	—	—
—	—	$S(AuL)_2$	—
—	$[P(AuL)_4]^+$	$[S(AuL)_3]^+$	$[Cl(AuL)_2]^+$
—	$[P(AuL)_5]^{2+}$	$[S(AuL)_4]^{2+}$	—
—	$[P(AuL)_6]^{3+}$	$[S(AuL)_5]^{3+}$	—
—	—	$[S(AuL)_6]^{4+}$	—
—	—	—	—
—	$[As(AuL)_4]^+$	$[Se(AuL)_3]^+$	$[Br(AuL)_2]^+$
—	—	$[Te(AuL)_3]^+$	—
(b) *Heteroleptic substitution*			
$RC(AuL)_3$	—	—	—
—	$[R_2N(AuL)_2]^+$	—	—
—	$[RN(AuL)_3]^+$	—	—
$[R_2C(AuL)_3]^+$	$[RN(AuL)_4]^{2+}$	—	—
—	$[RP(AuL)_3]^+$	$[RS(AuL)_2]^+$	—
—	$[RP(AuL)_4]^{2+}$	$[RS(AuL)_3]^{2+}$	—
—	$[R_2P(AuL)_3]^{2+}$	—	—
$[(L)B(AuL)_4]^+$	—	$[RSe(AuL)_2]^+$	—

primary phosphide, hydroxide, or hydrogen sulfide with formulae LAuX and X = NH_2, PH_2, OH, or SH, respectively, and L representing an auxiliary ligand such as a tertiary phosphine or arsine, a thioether or an isocyanide. In attempts to prepare such complexes with L = R_3P, in all cases complete or almost complete auration of the N, P, O, or S atom occurs. As already mentioned, this phenomenon was first observed by the school of Nesmeyanov,[19] who isolated salts with tri(gold)oxonium cations of the type $[(Ph_3PAu)_3O]^+$ when treating *e.g.* Ph_3PAuCl with KOH (**7**). It thus appears that the second and third auration steps are particularly facile such that no clean mono-auration can be accomplished. In extensive work it has later not only been shown that this clustering behaviour—where "gold is drawn to gold"—is quite general, but that even higher auration steps can be reached.

Table 1 presents a list of the hitherto isolated and structurally characterized neutral or cationic species of the type $[E(AuL)_m]^{n+}$ with m in the range 2–6 and n in the range 0–4.

The examples with E = O can serve to illustrate the unusual behaviour: In attempts to aurate, stepwise, the water molecule or the hydroxide and oxide anion, the first stable gold(I) complexes to be isolated are salts with tri(gold)oxonium cations $[(LAu)_3O]^+$, which even can be further converted[100] into salts with the tetra(gold)oxonium dication $[(LAu)_4O]^{2+}$ (**39**). To date no simple di(gold)oxide complexes $(LAu)_2O$ could be prepared (and the same is true for a tri(gold)amine, $(LAu)_3N$). It is only in the system with E = S, that simple gold sulfide complexes $(LAu)_2S$ can be obtained, which are intermediates on the way to salts with the sulfonium cations $[(LAu)_3S]^+$.[101] However, further auration of the latter can exceed the tetrasubstitution and lead to higher coordination numbers at the sulfur atom.[102,103] For E = Te, only the triauration has been structurally confirmed.[104]

The facile formation and in particular the structures of these E-centred aggregates of gold atoms (all in the oxidation state +1) have suggested specific attractions between the metal atoms. The Au–E–Au angles of the low-coordinate species (E = O, S, Se, Te; m = 2, 3) are not only much smaller than the reference angle of a tetrahedron, but in many cases even smaller than 90°. For m = 4 stable compounds with a tetrahedral structure can only be obtained with a very small atom E (N and O) (**39**, **40**), while for larger atoms E (C, P, S) the corresponding molecules or cations can only be prepared with extremely bulky auxiliary ligands L (C,[105] N[106]) or not at all (S). For E = As (**41**) and S, square-pyramidal cations have been discovered instead.[29,102,103] For m = 5, 6, a standard trigonal bipyramid is only found for E = C[107] and N,[108–110] (**42**) while for E = P this polyhedron is transformed into a square pyramid in which the EAu_4 base has exceedingly small Au–E–Au angles (**43**).[111,112] Octahedral structures have been confirmed[27] for E = C and proposed for E = P,[113] S (**44**).[102,103]



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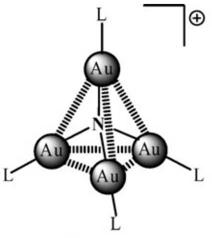

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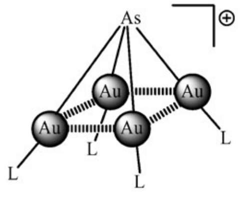

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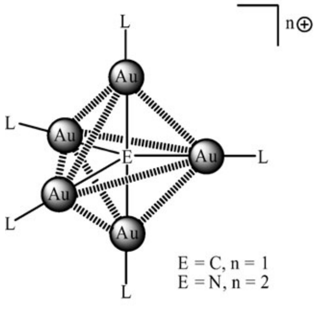

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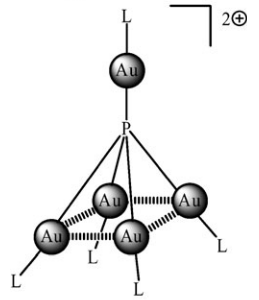

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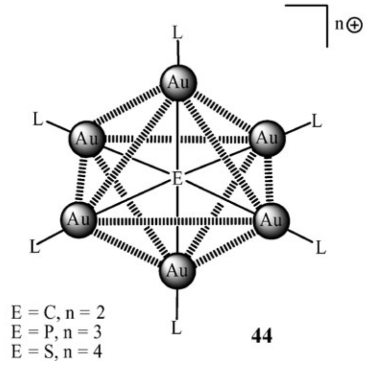

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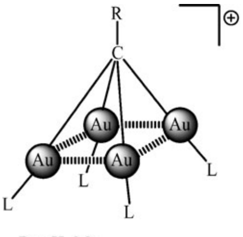
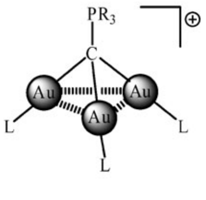
In this context, the compounds with hypercoordinated carbon atoms deserve special attention. This is not only true for the homoleptically substituted species $[C(AuL)_5]^+$ and $[C(AuL)_6]^{2+}$, but also cations with mixed substituents.[30] Apart from the cations formally generated by protonation of tetra(gold)methane, $[HC(AuL)_4]^+$,[28] alkylated (**45**)[114] and silylated species[115] have also been isolated as stable salts: $[MeC(AuL)_4]^+$ and $[(Me_3Si)_2C(AuL)_3]^+$. In all these cases L represents a tertiary phosphine. Triauration was observed for phosphonium methylides[116] which yield cations of the formula $[R_3PC(AuL)_3]^+$ (**46**). Related observations have been made in the auration of unsaturated hydrocarbons[19,117] including the heterocycles furan and thiophene (**47**).[118] Two gold atoms can also be readily attached to the central carbon atom of carbodiphosphoranes (**48**).[119,120]



R = H, Me **45**



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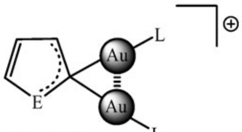

E = O, S

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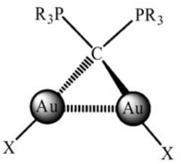

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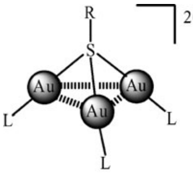
Clustering of gold(I) cations has further been documented for the O- and S-atoms in gold alkoxides[121] and mercaptides (**49**),[122–126] as for the N- and P-atoms in primary amides,[127–131] diamides,[132] silylamides,[133] carbodiimides,[134] hydroxylamides (**50**),[135] phosphides,[136–138] phosphinimides (**51**),[139] and sulfoximides,[140] which give products of di-, tri- or even tetra-auration with one organic group at a vertex of the respective polyhedron. The oligomers of $[AuSMe]_n$ were the subject of DFT calculations and the structures of compounds with various ring sizes have been optimized. Particularly favourable conformations were established for $n = 12$.[141]



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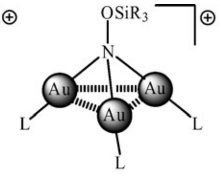

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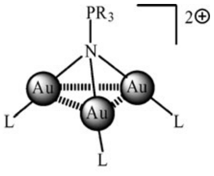

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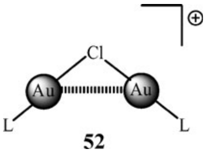
Uson and co-workers published in an early report that gold(I) halides can be converted into cationic dinuclear complexes $[E(AuPR_3)_2]^+$ in which the halogen atom E is bridging two metal atoms (**52**).[142,143] In this and in more comprehensive later work it was shown that in these cations the Au–X–Au angles are very small for E = Cl, Br (<90°) suggesting very significant intracationic Au–Au interactions.[144–146] This structural detail is reminiscent of the crystal structure of AuCl in which the zigzag chains $(AuCl)_n$ have similar dimensions.[147] It should also be noted that the $[R_3PAu–Cl–AuPR_3]^+$ unit is isoelectronic with the Au–S–Au unit, which shows distinct structural analogies.[148]



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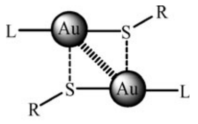
In all these homo- or heteroleptically substituted polyhedra, or parts of polyhedra, the edges Au–Au are found to be short (correlated with the small Au–E–Au angles) and in the range which is considered relevant for aurophilic binding. The details have been reviewed,[2,10,11] and more recent results can be extracted from the publications that have appeared since the deadlines for these reviews. In theoretical calculations these parameters have been reproduced confirming considerable contributions from aurophilic interactions to the surprising stability of the clusters.

Many of the polynuclear molecules or cations of the type $[E(AuL)_n]^{m+}$ show also single or multiple intermolecular/intercationic aurophilic interactions as described below.

4.2 Self-assembly of molecules in crystals

The most common stoichiometry and structure of gold(I) complexes can be expressed by the formula L–Au–X which indicates (a) the presence of a neutral donor ligand L and an anionic ligand X and (b) a linear molecular axis connecting the donor atoms with the metal atom. As a rule, in the crystalline state of the compounds the large majority of these molecules are found aggregated into oligomers or polymers. The most common oligomers are dimers (**10d–f**), trimers (**10g**) and tetramers (**10h,i**), while 1D chains are the most common polymers (**10h**, extended chains). The complexes remain in the monomeric form only in cases where the steric bulk of L and/or X prevents any close intermolecular Au–Au contacts. With an increase in the steric bulk of the ligands the degree of poly- and oligomerization decreases, meaning that with the more voluminous ligands monomers or staggered ("crossed") dimers (**10d**) are the prevailing form, while for medium-sized ligands trimers and tetramers (**10g,h**) are the preferred patterns of aggregation. This more or less obvious dependence of degree of association on steric bulk may be altered if there are specific interactions between the ligands, in particular hydrogen bonding or π–π stacking. Hydrogen bonding may support the formation of oligomers *via* Au–Au contacts, but it may also overrule aurophilic bonding if the geometrical orientation of the donor/acceptor sites is unfavourable or if several hydrogen bonds can be formed. An early summary has appeared in 1993.[149]

It should be noted that the Au–Au contacts are clearly preferred over any Au–X or Au–L contacts, with the exception of some Au–S interactions in gold(I) thiolates (**53**) which clearly reflect the high affinity of gold for sulfur.[150,151]



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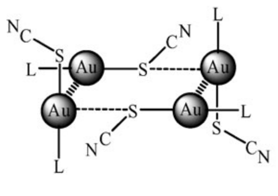
The heteroleptic molecules L–Au–X are often found in a ligand exchange equilibrium in solution, and the crystalline precipitate may therefore also be an ionic crystal of the same stoichiometry but with homoleptically substituted cations and anions (eqn (1)). These cases are summarized in the following chapter (4.3).

$$2\text{L–Au–X} \rightarrow [\text{L–Au–L}]^{+}[\text{X–Au–X}]^{-} \qquad (1)$$

The aggregates of molecular complexes L–Au–X were first summarized by Jones in 1981 and the following years[26] and then again by Ahrland in 1993.[152] It appears that the first observation of the phenomenon was made by Arai for Cl_3PAuCl in 1962,[153] followed by work on pyridine and dialkyl sulfide complexes by Strähle *et al.*,[154–156] and on thiophene and selenophene complexes by Ahrland *et al.*[152] All of these compounds form chain structures since their ligands are small.

Complexes with a small tertiary phosphine such as Me_3P as in Me_3PAuCl and Me_3PAuCN form also chains,[157] while for Me_3PAuI only a dimer is formed.[158] $Me_3PAuSCN$ appears as an aurophilicity-bound dimer, but is further associated into tetramers *via* Au–S bonding (**54**).[151] With a larger tertiary phosphine, as in Et_3PAuCl, $^{i}Pr_3PAuCl$ or $^{t}Bu_2HPAuCl$, only monomers are present in the crystal.[158–161] For the same reason, the triphenylphosphine complexes Ph_3PAuX with X = Cl, Br, I, CN, Ph are all monomers.[39,162–164] By contrast, the complex with a cage-type phosphine having a small cone angle such as triazaphosphaadamantane (TPA) the molecules form dimers (**55**).[165,166] Association to dimers is also observed for tertiary phosphine complexes of gold(I) thiolates,[167,168] dithiolates,[169] and sulfinates,[170] while the trifluoroacetate forms a chain polymer.[171] The trichlorothioacetate complex is associated into a dimer with a slipped contact leading to mixed Au–Au/Au–S contacts (**53**).[171]



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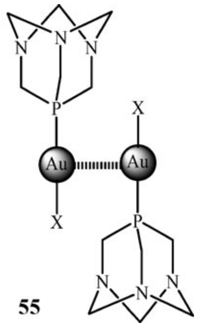

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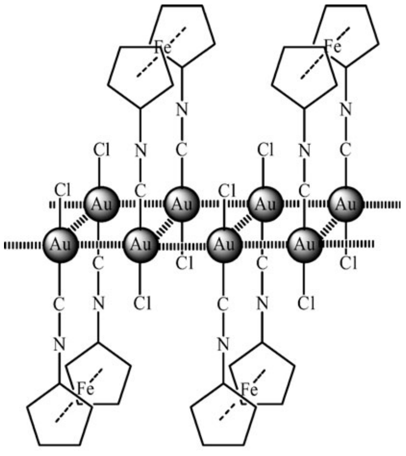
Association *via* aurophilic bonding is particularly common for isocyanide complexes (RNC)AuX owing to the linear structure of the functional group of these RNC ligands.[172,173] The chemistry has recently been reviewed.[174] The mode of interaction is thus governed by the substituent R more distant from the gold centre,[175] and examples include dimers, tetramers and 1D polymers (**10d–h**, L = RNC),[176–180] most of which have interesting photophysical properties.[181]

(Isocyanide)gold thiolates have structures with intermolecular contacts intermediate between Au–Au and Au–S bonding (**53**, L = RNC) and have low stability.[182,183]

Dinuclear complexes of difunctional isocyanides have also been probed and showed similar aggregation patterns like the monofunctional counterparts.[184] A large variety of organic isocyanides with flexible and rigid skeletons have been used in combination with gold(I) salts for the construction of multidimensional frameworks, in which aurophilic hapticities play a significant role. Particularly large oligomers were found for bis[(isocyanide)gold]-1,3,4-thiadiazole-2,5-disulfides.[185] Another unusual principle of structure was discovered for a dinuclear complex of 1,1′-di(isocyano)ferrocene.[186] In the crystal, the complexes are aggregated into corrugated ribbons of gold atoms (**56**). Owing to the limited space in the present account, for more information on isocyanide complexes the reader is directed to the most recent review.[174]



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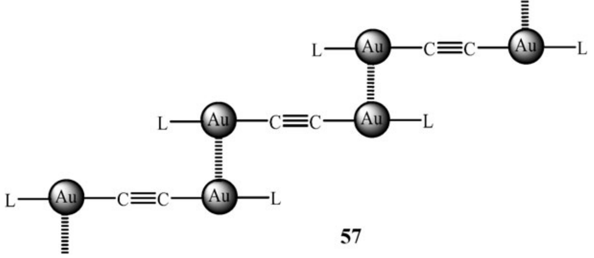
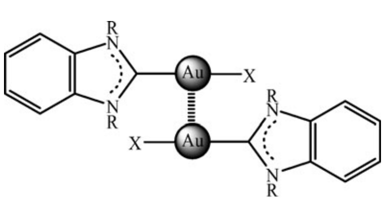
Complexes with a combination of tertiary phosphines or isocyanides as the neutral ligands L and an alkynyl group as the anionic component X in L–Au–X are particularly numerous, and many of these compounds show the expected aggregation. The complex $Me_3PAuC{\equiv}CPh$ which forms long zigzag chains may serve as a simple example.[187] The chains of molecules $(TPA)AuC{\equiv}CCMe(Et)OH$ are further stabilized by hydrogen bonds.[188] α,ω-Dialkynyldigold complexes become associated in a head-to-tail fashion producing also 1D aggregates (**57**).[189]



57

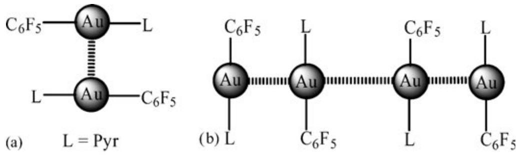
A selection of tailor-made gold(I) alkynyl complexes has been prepared with auxiliary ligands L which impose some restraints to the structures in several dimensions, expecting special photoemissive, mesophase or NLO properties. Most of these structures are co-determined by aurophilic interactions. Reviews are available.[174,181]

The coordination chemistry of carbene complexes with gold(I) has also recently been reviewed.[190] Owing to the complexity of this chemistry, no details can be considered here. Suffice it to mention that common N-heterocyclic carbene complexes of the imidazol- and benzimidazol-2-ylidene type are aggregated *via* aurophilic bonding into dimers (**58**) or chains if small substituents are present at the nitrogen atoms, but with larger groups only monomers are present in crystals.[191–193] The same applies for oxazolinyl and -thienyl complexes.[194]



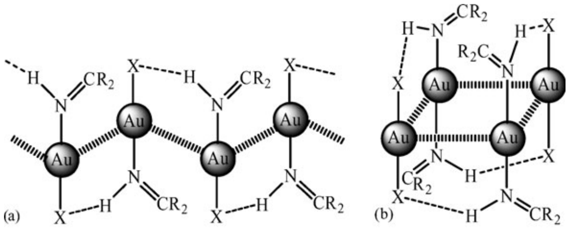
58

A large number of pentahalophenylgold(I) complexes with flat ligands such as pyridines $C_6X_5Au(pyr)$, where X = F, Cl, are all associated into chains. In general, along the chains there are alternating long and short Au–Au contacts suggesting the oligomerization of dimers (**59a,b**). This chemistry has recently been reviewed.[195,196] With thioethers instead of pyridines, $C_6X_5Au(SR_2)$, *e.g.* for X = F and R_2 = $-(CH_2)_4-$, similar arrangements were found.[197]



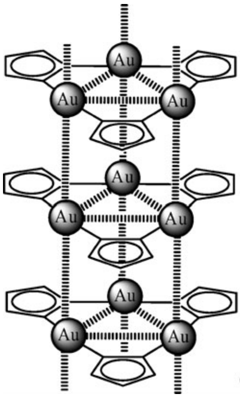
59

Ketimines, as another type of N-donor ligands, form complexes of the type $(R_2C{=}NH)AuX$ which are again associated into chains (**60a**), *e.g.* with X = Cl and R = Ph. However, the same compound can be precipitated as the ionic isomer $[(Ph_2C{=}NH)_2Au]^+[AuCl_2]^-$ which crystallizes as a tetranuclear assembly of ions with a square of gold atoms based on aurophilic bonding (**60b**). This ionic form is also obtained for X = Br.[198] In both forms the aggregation *via* aurophilic bonding is supported by weak hydrogen bonding (X - - - H–N) as indicated.



60

It has been recognized in early structural studies that in crystals of the flat, triangular, trinuclear gold(I) pyrazolates, imidazolates, triazolates, carbeniates and 2-pyridyls (**27–30**)[82–88] the molecules are stacked into columns in such a way that the highest possible number of intermolecular Au–Au contacts are formed. These crystals have been investigated extensively owing to their interesting photophysical properties, which can be employed in sensors and phosphors. Formula **61** gives a schematic example. This stacking with threefold symmetry can be modified or distorted by steric influences exerted by substituents at the ligands or by packing forces.[199]



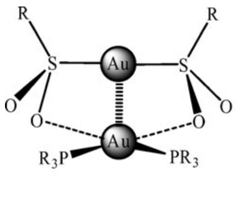
61

A search in the crystallographic data base for structures of gold compounds exhibiting aurophilic interactions has established a correlation between the number of independent molecules in an asymmetric unit of a crystal structure, the dihedral angle M–Au–Au–M in dimers or larger aggregates, and the polarity and steric bulk of the ligands. The "size differential" or disparity of the substituents appears to be a major factor for the crystal packing.[200] This new study is an extension of an earlier summary of aurophilic binding in supramolecular chemistry.[149]

4.3 Self-assembly of ionic compounds in crystals

Various families of gold(I) complexes feature ionic homoleptic species of types $[X{-}Au{-}X]^-$ and $[L{-}Au{-}L]^+$ or a combination of both. As pointed out above, these components may be in an equilibrium with neutral molecules L–Au–X (eqn (1)). Moreover, the ions may also be heteroleptic, $[X{-}Au{-}Y]^-$ and $[L{-}Au{-}L']^+$.

It is of course as expected that these ionic components —having opposite charges—in principle form ionic crystals, but for the gold(I) complexes the mode of aggregations in these crystals is exceptional. Steric requirements of the ligands permitting, they are all organized in chains with the shortest inter-ionic contacts between the gold atoms. The self-assembly in chains is particularly common for combinations of which at least one ion is a slim rod or a dumbbell with a long bar, for which a close approach of the metal atoms is without steric hindrance. Examples are anions taken from the series with X = CN, Cl, C≡CR and of cations with L = RNC, pyr, SR_2 *etc.* With more bulky ligands X and L only dinuclear ion-pairs are formed, as in $[(Ph_3P)_2Au]^+[(RSO_2)_2Au]^-$ with R = 4-MeC_6H_4 (**62**),[170] or tetranuclear ion quadruples as in $[(Ph_2C{=}NH)_2Au]^+[AuCl_2]^-$ (**60b**).[198] The former are stabilized by O–Au contacts while in the latter N–H–Cl hydrogen bonding lends extra stability to the tetranuclear package. Other more recently discovered examples are the chain structures of $[(Me_3P)_2Au]^+[Au(C\equiv CPh)_2]^-$(**63**),[201,202] $[(4\text{-}Me_2NC_5H_4N)_2Au]^+[AuCl_2]^-$ (**64a**),[203] $[(4\text{-}MeC_5H_4N)_2Au]^+[AuCl_2]^-$ (**64b**) and $[(MesNC)_2Au]^+[Au(GeCl_3)_2]^-$ (**65**).[204] In the latter, like in several other examples, the Au–Au contacts along the chain are all equidistant by crystal symmetry, but alternating distances are also common.



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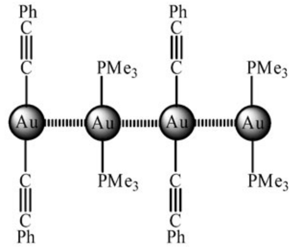

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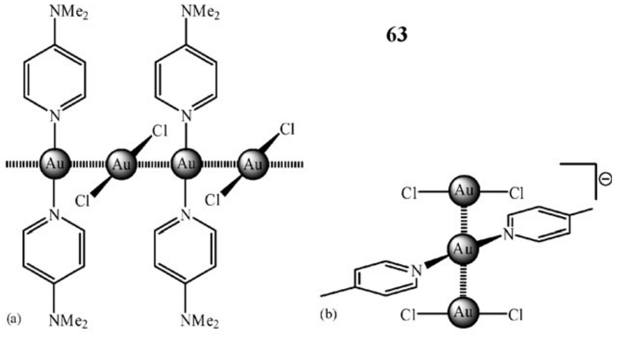

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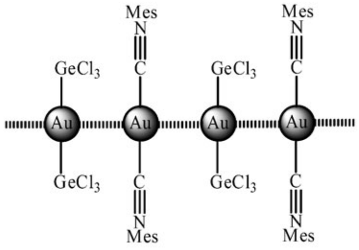

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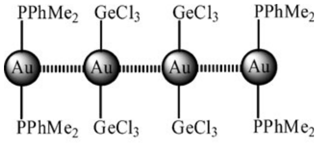
Interionic Au–Au contacts are more striking as they occur between ions of like charge, *i.e.* between cations or between anions, where Coulomb repulsion is expected to counteract any aurophilic attractions. And yet this phenomenon is quite common in structural gold(I) chemistry. Most surprising is the aggregation of the rod-like $[Au(CN)_2]^-$ in various types of its salts with large and small cations, which may even play a role in the adsorption of alkali cyanoaurates(I) on the surface of active carbon which is the basis of the carbon-in-pulp process of gold recovery from ores.[205] The subject is reviewed in another chapter of this issue.[206] Together with $[(TPA)_2Au]^+$ cations, the $[Au(CN)_2]^-$ anions form chains of alternating ions with equidistant gold atoms.[166]

With certain combinations of ligands, ion packages with an unusual sequence of charges are observed, such as in $\{[(Me_2PhP)_2Au]^+[Au(GeCl_3)_2]^-\}_2$ with its charge sequence $+--+$ (**66**).[207] A theoretical study has demonstrated that this unusual sequence can still lead to an overall stable molecular structure,[208] as also shown experimentally for compounds of the type $\{[(pyr)_2Au]^+[AuX_2]^-\}_2$ with X = Br, I.[154,155] With substituted pyridines, a regular sequence $[+-+-+-]$ is present (**64a**). Very surprisingly, the salts of $[(pyr)_2Au]^+$ cations with innocent counterions like PF_6^- have crystal structures in which solely the cations are aggregated either into chains $[+++++++]$ or into trinuclear units which are further associated with an isolated cation $[+++][+]$ to give extended patterns, all based on aurophilic bonding (**67**).[203] Chain-like cation aggregates were also found for $[(Me_2C{=}NH)_2Au]^+[CF_3SO_3]^-$, where N–H–O hydrogen bonds at the periphery of the chains assist in the assembly,[99] and similarly in bis(pyridinethione)gold(I) perchlorate.[209] With two bulky ligands, only dimeric cations can be formed as in $[(^tBuH_2N)AuPMe_3]^+BF_4^-$ assisted by N–H–F hydrogen bonds.[210]



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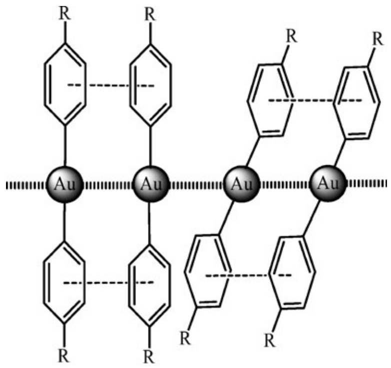

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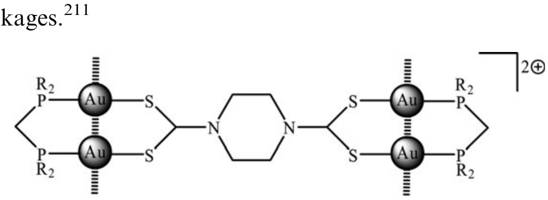
Dications (**68**) generated from the 2 : 1 reaction of $(dppm)(AuCl)_2$ with potassium piperazine-1,4-dicarbodithiolate in methanol have been found to be aggregated into compact tetramers forming an Au_{16} macrocycle. This octacation is chiral owing the peculiar array of transannular linkages.[211]



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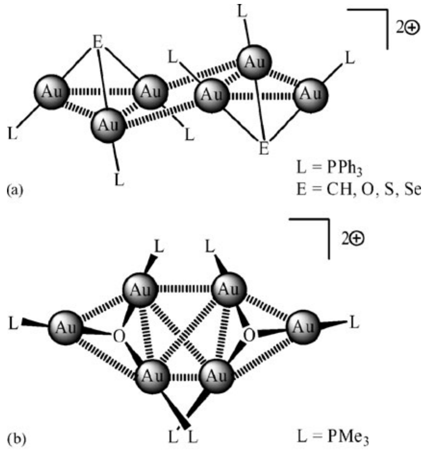
Aggregation of multinuclear ions *via* multiple aurophilic bonding is particularly strong and therefore a wide-spread phenomenon.[2,11] In the absence of severe steric hindrance, most trinuclear cations of the type $[E(AuL)_3]^+$ with E = CH, O, S, Se, Te (**11**) form dimers with two Au–Au contacts. Two modes of aggregation have been observed, depending on the nature of L. In the more common mode (with larger ligands L) the gold atoms forming the interionic contacts form a square (**69a**),[212,213] while in the dimers with smaller ligands L they form a tetrahedron (**69b**).[214] The two situations have been analyzed by DFT calculations.[215] Similar contacts are found between the dinuclear cations of the type $[RS(AuL)_2]^+$ (**70**)[216] and related species (Table 1). It should again be noted that these intercationic binding overrules a very significant Coulomb barrier which arises as the two cations approach each other. Recent experimental and theoretical work has shown that this barrier indeed is overcome by aurophilic interactions (below).



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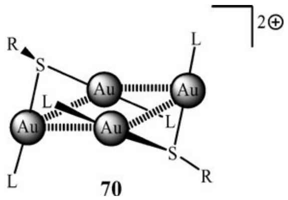

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4.4 Aggregation of molecules and ions *via* aurophilic bonding in solution

It has long been argued that *unsupported* aurophilic bonding between molecules or ions would not be retained in solution in most cases since the energy of solvation of the individual molecules would more than compensate the rather small gain in energy obtained from the Au–Au interactions (below). However, evidence for aggregation of the components obtained from the colligative properties and spectral data of the compounds in solution is growing to a level, where the effect can no longer be ruled out.

Even for the very simple case of aqueous solution of salts with $[Au(CN)_2]^-$ anions, the concentration dependence of the absorption spectra shows deviations from Beer's law, which indicate aggregation of the anions as the photoactive species.[217]

As a recent example, the molar electrical conductivity of compounds of the type $[(pyr)_2Au]^+[AuCl_2]^-$, where pyr is a (substituted) pyridine, in acetonitrile at room temperature is much smaller than estimated for 1 : 1 electrolytes. The corresponding salts $[(pyr)_2Au]^+[PF_6]^-$ show higher conductivities, but still do not reach that of a standard 1 : 1 electrolyte. Since the crystal structures of the hexafluorophosphates and dichloroaurates(I) have been shown to feature aggregated trinuclear cations or 1D chains of alternating cations and anions, respectively, both associated *via* aurophilic bonding, it appears that smaller aggregates of ions, *e.g.* di-, tri- or in particular tetranuclear units, for which there is ample precedent, are the solvated species in solution.[203] Moreover, for solutions of the same family of compounds, the UV/Vis absorption spectra are temperature *and* concentration dependent. For the temperature-dependent spectra of the PF_6^- salt, an isosbestic point is observed, which indicates that two species are in equilibrium. An increase in concentration of a compound results in a drastic growth of one of the two prominent bands, while the other (at lower energy) strongly decreases with concentration and disappears at lowest concentrations, again suggesting an equilibrium. From the *K vs.* $1/T$ plot, a binding energies of *ca.* 14 kcal/unit was calculated for the (probably anion-assisted) aggregation of two cations.[203] Since for the $AuCl_2^-$ salt no isosbestic point was detected, more than two species must be involved, most probably ion pairs and quadruples, for which there is ample precedent.[154,155,198]

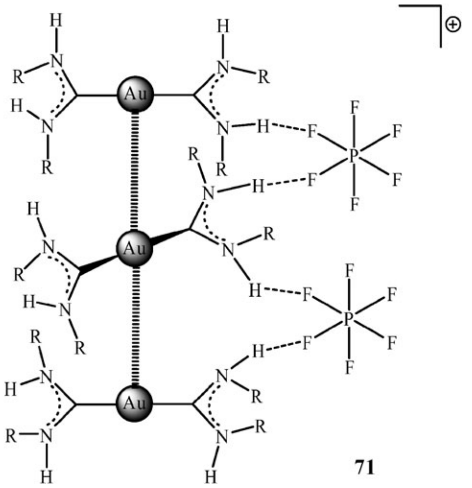
The UV/Vis spectra of solutions of $4\text{-}MeC_6H_4SO_3CH_2N\text{-}CAuCl$ in acetonitrile show a concentration dependence with major negative deviations from Beer's law, which must be ascribed to significant aggregation of the molecules with increasing concentration.[218] (Similar results had previously been obtained for solution of (CO)AuCl.[219]) From the association constants obtained for the *p*-tolylsulfonylmethylisocyanide complex, which is a dimer in the crystalline state,[220] a ΔG value for the association of *ca.* 5 kcal mol^{-1} was calculated.[218]

Association of gold(I) thiolate complexes of ditertiary phosphines was also studied by concentration-dependent absorption spectroscopy. Rather small ΔG values (2.5–4.0 kcal mol^{-1}) were found, which probably underestimate the quality of intermolecular binding.[221] More recent studies with complementary methodologies arrived at significantly higher values (below).[203]

EXAFS studies have also been carried on solutions of fully-supported, semi-supported and unsupported dinuclear complexes (**10a–c**, in chloroform or acetonitrile). Not surprisingly, the solution results have fully confirmed the Au–Au distances known from previous X-ray diffraction investigations of the fully-supported cases with their rather rigid structures (**10c**, $(dppm)_2Au_2X_2$, X = Cl, BF_4). However, for solutions of the semi-supported cases (**10b**, *e.g.* **18**), the fit of the data has so far been satisfactory only for one case (**10b**, $[O(2\text{-}C_6H_4PPh_2AuSC_6H_4\text{-}3Me)_2]$), while for unsupported cases (**10a**, $Ph_3PAuSPh$) no evidence for association in solution was obtained.[221a]

For very large macrocyclic systems, which show transannular aurophilic contacts in the crystal it is questionable in principle if this bond is retained in solution where solvation may change the energy characteristics. To clarify this point for the 16-membered ring dinuclear complex of xantphos (**18**, **25**), an X-ray scattering experiments was carried out in nitromethane solution. The difference radial distribution function showed a peak at 2.91 Å which can be assigned to the Au–Au contact, in excellent agreement with the distance of 2.858 Å found in the crystal.[63]

Qualitative evidence for the association of mono- or polynuclear gold(I) carbene or carbeniate complexes has also accumulated. The solvent and concentration dependence of the absorption and luminescence properties suggest extensive association of the molecular or ionic components in solution. This is particularly true in frozen glasses of the solutions. Examples are the planar $[(ROC{=}NR')Au]_3$ molecules (**30**) which are known to be stacked in the crystal into columns with short Au–Au contacts between neighbouring units.[222] An analogous aggregation is assumed to cause the significant structural changes in concentrated and frozen solutions. Similar observation were made for highly substituted, trimeric gold(I) imidazolates, pyrazolates[84,86,199,223] and triazolates[224] (**27–30**). In crystals of ionic bis(carbene)gold(I) hexafluorophosphates the cations are assembled into Au–Au bonded strings with supportive cation–anion–cation hydrogen bonding assisting in the aggregation (**71**). This type of cation association appears to persist in solution.[222]



71

The cations $[RS(AuL)_2]^+$ (Table 1)[122–126] have been found to be associated to dimers **70** not only in the solid state, but also in methanol solution. Both electron spray ionization mass spectrometry (ESI MS) and diffusion ordered NMR spectroscopy (DOSY) were used to demonstrate that at least for small ligands L there is extensive aggregation to tetranuclear dications.[225]

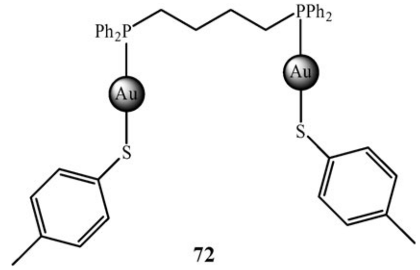
5. Estimation of thermodynamic data of aurophilic bonding

Several attempts have been made to measure or at least estimate the binding energy associated with aurophilic contacts. Almost all of these experiments were carried out on solutions of molecules with *intra*molecular Au–Au bonding, since very few examples are known were *inter*molecular contacts are preserved in solution. One of these rare examples are the salts $[(pyr)_2Au]^+X^-$ for which there is experimental evidence for aggregation in solution (above).[203]

Solution NMR spectroscopy was used in all earlier estimations of *intra*molecular Au–Au bond energies. The first model system was a dinuclear AuCl complex of the ylide $Me_3P{=}C(PPh_2)_2$ (**13d**). The free ylide is known to have its Ph_2P groups in an *anti* or *E* conformation, whereas the complex has the (electrostatically and sterically unfavourable) *syn* or *Z* conformation tied up by aurophilic bonding. At low temperature the ligand thus has inequivalent P atoms, while the latter has equivalent P atoms (on the NMR time scale). The energy barriers can be measured by following the ^{31}P NMR spectrum to the coalescence temperatures, and a value of *ca.* 8.5 kcal mol^{-1} is obtained.[34] A similar experiment was carried out with 1,1′-bis(diphenylphosphino)dicyclopropyl (**14b**), which has the same *syn*/*anti* or *E*/*Z* preference. The results were similar (6–8 kcal mol^{-1}) and thus confirmed that aurophilic binding was of the same strength as hydrogen bonding.[40]

In another approach, the molecular dynamics of a 2,2′-disubstituted bis(1,2-dicarbaclosododecaborane) (**19**) were followed by temperature-dependent ^{31}P NMR spectroscopy. This molecule has a preferred conformation (regarding the rotation about the C–C bond connecting the two icosahedra) which has the two gold atoms in close, aurophilic contact as demonstrated in a crystal structure analysis. In solution at low temperature only a very small contingent of molecules is freely rotating about the C–C axis which gives rise to a small and broad extra signal. With increasing temperature (in $CDCl_3$), Au–Au decoupling increases leading to a growth of the second signal and finally to coalescence. The thermodynamic parameters obtained led to an activation energy for Au–Au decoupling of no less than 11 kcal mol^{-1}. The higher value was ascribed to the strongly electrophilic nature of the carborane cages.[64] Aurophilic binding has recently also been observed in $1,2\text{-}C_2B_9H_{10}\text{-}1,2\text{-}(PPh_2AuBr)_2$.[226]

Solutions of the dinuclear complexes $(dppb)(AuSC_6H_4\text{-}4\text{-}Me)_2$ (**72**) in CD_2Cl_2 were found to show only a singlet ^{31}P NMR signal at ambient temperature, which splits into two resonances at lower temperature indicating that two species are in equilibrium. From a line-shape analysis the activation energy for the interconversion of these species was calculated as 10 ± 1 kcal mol^{-1}. The two peaks were assigned to an open, flexible molecule and to a cyclic form with Au–Au bonding, respectively. This idea is also supported by the UV/Vis spectrum of this complex which is significantly different from the spectra of the long-chain analogues $RSAuPh_2P(CH_2)_n\text{-}PPh_2AuSR$.[47]



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Temperature- and concentration-dependent solution ^1H and ^{31}P NMR studies were carried out (in CD_2Cl_2) for the cyclic dinuclear complex of $AuNO_3$ with 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (**25**). The line shape analysis of the changes in the spectra, which showed a non-equivalence of the ^{31}P nuclei at low temperature, gave a value of 11.7 (^{1}H) and 11.6 kcal mol^{-1} (^{31}P) for the activation barrier which appears to be correlated with the rapture of the transannular aurophilic bonding in the dication.[63]

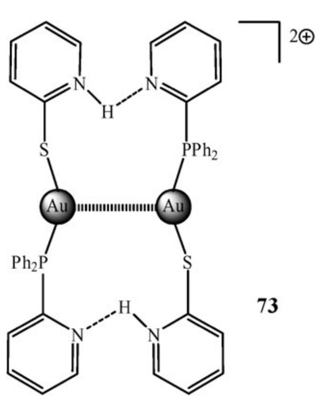
For trigoldselenonium complexes of the type **11a** with 2,5-bis(diphenylphosphino)thiophene as a ligand, a multinuclear aggregate was observed stabilized by pairwise contacts of the type shown in **69a**. Surprisingly, this binding is so strong that aggregates can be detected in the mass spectrum of the compound. DFT and *ab initio* (SCS-MP) calculations have shown that there is indeed very efficient multiple aurophilic bonding which is so strong that the Coulomb barrier of the mutual approach of the cations is readily overcome. These experiments have been the first to demonstrate that aurophilic bonding not supported by ligands can be observed in the gas phase.[227] The theoretical calculations followed earlier DFT studies on the model system $\{[O(AuPH_3)_3]_2\}^{2+}$ (**69b**) employing also point charge models for a Madelung field which markedly stabilizes the dimerization of the cations in the crystal.[215]

The results of this series of experiments are consistent in that they all confirm that aurophilic binding is a weak force the action of which is associated with bond energies in the range of 5–15 kcal mol^{-1}. Both the lower and upper limits are probably under- and overestimations, respectively, arising from specific steric or electrostatic interactions in the periphery of the Au–Au contacts. It should also be remembered that for intra- and in particular for intermolecular aurophilic associations there is a loss of entropy which modifies the thermodynamic characteristics in all cases. Even at the lower end of the above range the binding energy of aurophilic interactions is definitely and significantly higher than the energy associated with standard van der Waals bonding giving this effect a very special place in the collection of chemical interactions.

6. The comparison with hydrogen bonding

Extensive structural studies of gold(I) complexes with ligands bearing functions which can form hydrogen bonds have shown that hydrogen bonding may overrule aurophilic bonding such that in a given crystal the association of the molecules or ions into packages, chains or networks is based solely on hydrogen bonding. This observation confirmed the result of the thermodynamical studies that hydrogen bonding may be comparable or stronger than aurophilic bonding. Since the energy of hydrogen bonding also covers a relatively broad range, there are cases where one or the other of the two binding modes is dominant in a given system.

In this context it is particularly worthwhile to view a few of the earlier structures of compounds where both hydrogen bonding and aurophilic bonding are mutually supportive in building stable aggregates.[18,228–238] The hydrogen bonds employed in these examples cover the whole range from very weak to quite strong, including *e.g.* C–H–Cl,[236] N–H–F, Cl, Br (**60a**, **60b**, **71**),[229] N–H–N (**73**),[237] N–H–O,[216,238] O–H–N,[188] and O–H–O as in **74a,b**,[231–234,238] and in **75**.[230] Solvate molecules may also be involved in hydrogen bonding.[239] This area has grown rapidly in recent years, and no comprehensive coverage is possible in this short briefing.



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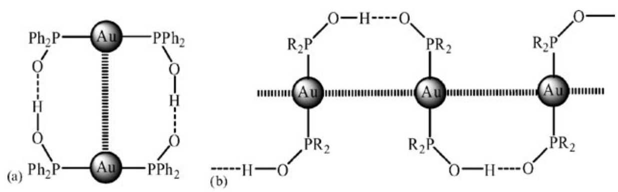

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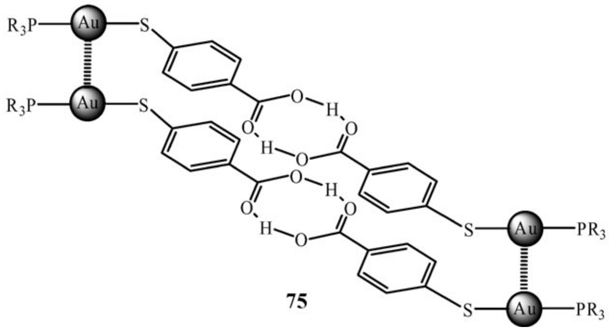

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There are a few parallels between hydrogen bonding and aurophilic bonding other than the comparable binding energies. The Au–Au distances can vary in a broad range (2.7–3.5 Å) similar to the large spread of hydrogen bond lengths (X–H–Y). In the most common cases, a two-coordinate gold(I) centre can form aurophilic contacts with one or two other gold atoms, analogous to the single and "bifurcated" hydrogen bonds. However, there are also systems where three or more nearest neighbours are accommodated around a gold(I) centre, just as positively polarized hydrogen atoms may entertain hydrogen bonding contacts to at least three contact sites. Both types of weak bonding therefore are very flexible and can be operative in a large variety of bonding modes.[240,241]

7. Theoretical approaches

Early theoretical approaches to the aurophilicity phenomenon (not yet named that then) were carried out using the Extended Hückel method and focused on a model compound $[(H_2PS_2)_2Au_2]$ for molecules of the type **3** (**10c**) in various conformations and for its oligomers (**10j**). In this qualitative analysis Au–Au bonding was observed which originated from 6s, 6p and 5d orbital mixing.[242,243]

Over the following 20 years, aurophilic binding has been the subject of numerous theoretical studies at various levels of sophistication. The results have recently been reviewed periodically in the general context of the theoretical chemistry of gold.[244–246] Regarding the structures and energies associated with aurophilic bonds, the results presented in these comprehensive accounts are generally in good agreement with the experimental data. In short, aurophilic attraction is just another van der Waals interaction, but a particularly strong one occurring unexpectedly in systems which long have been taken as "closed-shell" (nd^{10}) implying no capability for extra valence activity.

In another short formula, aurophilicity presently is described as to arise "from a combination of relativistic and correlation effects," which—as mentioned above—is not a very lucid and visual description for those not in command of a clear rationalization of dispersion forces and correlation effects. For a closer approach to a deeper understanding there is no other choice but to become involved in the details of contemporary versions of *ab initio* and MP2 (or MP4, CCSD or CCSD(T)) treatments of suitable models. Density functional theory methods (DFT) may generally give doubtful values for the description of van der Waals type systems, and aurophilic bonding is no exception.

Nevertheless, early DFT calculations of highly symmetrical clusters gave a rather comprehensive picture of the bonding situation as drawn for complex cations of the types **39**, **42** and **44**,[247] complementing earlier extended Hückel calculations,[248] a relativistic pseudopotential analysis,[249] MP2 and DS-DV X_α calculations.[250,251] For theoretical treatments of other examples of the large family of compounds featuring aurophilic interactions published during the last two decades, the reader is directed to the periodical summaries.[244–246]

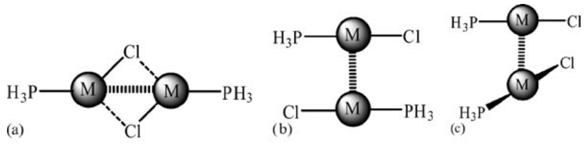
In a very recent DFT treatment of the $[E(AuPH_3)_4]^+$ clusters with E = N, P, As, Sb, the T_d structure of E = N and the C_{4v} structure of E = As were again confirmed.[252] Surprisingly, a T_d structure was predicted also for E = P, which is at variance with indirect experimental findings,[111,112] while for E = Sb the C_{4v} structure appears to be valid.[252]

These results could not be confirmed in an even more recent study, and the latest data again support a pyramidal C_{4v} structure for $[P(AuPH_3)_4]^+$. In this investigation, the basis-set limits of *ab initio* calculations on the MP2 level were explored. Approaches with Karlsruhe split-level valence and Dunning correlation-consistent basis sets were found to converge to the same limit. Obviously, f-type functions play a significant role, and the way in which these are included.[253*a*] This result is in agreement with experimental findings. Although no structures containing the isolated cations in question have been determined, there are several derivatives in which these units are present in a pyramidal form (*e.g.* **43** *etc*., above).[253*b*]

There are as yet no experimental data on simple antimony-centred gold clusters, even though a complex multicentred aggregate which features extensive aurophilic bonding has been obtained.[254]

A few recent theoretical studies were concerned with the place of aurophilic bonding in the general context of metallophilic bonding, and of binding between the elements of the coinage metal group in particular. In a second order MP study it has been shown that in pairs $(H_3PMCl)_2$ (**76b,c**) metallophilic bonding is indeed decreasing from M = Au *via* Ag to Cu, with the reductions in the attraction estimated to be 10–20 and 25–35%, respectively. Closed-shell (nd^{10}–nd^{10}) interactions (with dispersive and non-dispersive components) account for approximately one half of the total energy of intermolecular bonding for M = Au, but are much less for M = Ag, Cu. Pure van der Waals type interactions are complemented by ionic excitations and charge transfer contributions.[255]

Based on considerations regarding the influence of relativistic effects on the chemistry of gold, it has for a long time been openly or tacitly assumed that the known maximum relativistic effect for gold is also reflected by or even responsible for strong aurophilic bonding. This conclusion has been questioned in *ab initio* and density functional studies of dimeric molecules $(H_3P–M–Cl)_2$ (M = Cu, Ag, Au, E111). Strong relativistic effects were found not only for the M–P and—to a lesser extent—for the M–Cl bonds in the monomers, but also for the dimers and their M–M interactions. For M = Cu, Ag, the structure of minimum energy is that of dimers (**76a**) without significant metallophilic bonding, while for M = Au the antiparallel structure (**76b**) is found as the minimum. This structure (**76b**) is mainly dictated by dipolar contributions and not a result of an optimum in aurophilic binding as compared to the crossed configuration (**76c**), for which in fact this binding is particularly obvious, least masked by the dipolar effects. However, depending on the theoretical approach (choice of pseudopotentials, correlation consistent basis sets, polarization functions, relativistic and non-relativistic), the strength of metallophilic binding within the dimer may increase steadily towards gold, Cu < Ag < Au, or reach an unexpected maximum for silver: Cu < Ag > Au. More and more sophisticated methods are obviously required to account for the trends observed experimentally in systems with metallophilicity effects.[256] It is a useful guideline to remember that the atomic and ionic radii of the three coinage metals (Cu, Ag, Au) have a clear maximum for silver reflecting in a most obvious way the pronounced relativistic contraction of the orbitals of the gold atom.[10,257] This fact alone is greatly improving the metallophilic interaction for the heaviest, but not the largest atoms of the three elements. This contribution appears to improve also the metallophilic binding between gold and other metals.



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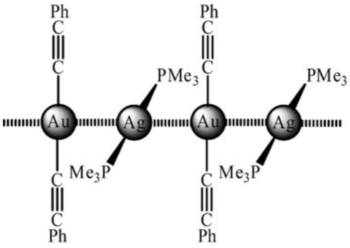
Some of the recent theoretical studies of aurophilic bonding also included models for interactions between gold atoms in higher oxidation states (Au^{I}–Au^{III}, Au^{III}–Au^{III}). The results indicate that this type of metallophilic bonding may be weaker than for AuI–Au^{I}, but not negligible.[258]

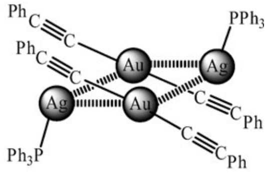
8. Metallophilic bonding in mixed-metal systems

Both experimental and theoretical studies have shown that metallophilic interactions which can be observed in gold chemistry can also be discovered in related mixed-metal systems.

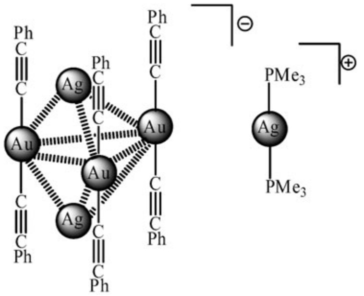
This is particularly obvious for combinations of the three coinage metals (Cu, Ag, Au). By the above definition, this applies to the closed-shell situation [nd^{10}(n + 1)s^0 with n = 3, 4, 5] of the univalent state of these metals. Complexes of copper(I), silver(I) and gold(I) with various combinations of neutral and anionic ligands (L, X) have been shown to form aggregates through direct M–M interactions discernible from short ligand-supported or -unsupported M–M contacts. In most of the fundamental patterns of structure illustrated by formulae **10a–j**, part of the gold atoms can be substituted by silver atoms to represent the structural motifs found for compounds with metallophilic Au–Ag contacts. This type of bonding is most common for ionic compounds where gold and silver are the coordination centres of the anions and cations, respectively. A representative example is given in formula **77**.[202,259] Au–Ag contacts are also the basis for the formation of cluster aggregates as discovered for (phosphine)silver/gold phenylalkynyls of different stoichiometry (**78**, **79**).[202] Similar clusters are known for the "pure" gold and silver systems, but also for the Au/Cu combination.[260,261]



77



78



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There are as yet no reliable estimates from experimental data for the strength of metallophilic Au–Ag or Au–Cu bonding, and only few quantum chemical studies were carried out. As an example, the electronic structure in the penta-nuclear cation of **79** was been analyzed by DFT calculations.[251] It has been shown that the aggregation is largely governed by electrostatic interactions, complemented by weak metallophilic bonding.

9. Concluding remarks

There are numerous reports of mixed-metal complexes in which gold atoms entertain discrete and intimate bonding to other heavy late transition elements (Ir, Pt) and early post-transition elements (Tl, Pb) with a seemingly saturated co-ordination sphere. Many of these interactions have characteristics (M–Au bond lengths, Au–M–Au angles, low binding energies *etc.*) similar to those of aurophilic Au–Au contacts. However, considering the valence state of the second metal M, the interactions cannot be described *bona fide* as metallophilic bonding between "closed-shell" centres in most of these cases. Because of this ambiguity, this area of mixed-metal metallophilic bonding has not been included here, even though it certainly is one of the most interesting, intriguing and rapidly growing fields in the chemistry of compounds with metal–metal bonding.

Finally it is important to mention that results of studies of binary and polynary phases of inorganic gold compounds have led many researchers in solid state chemistry to postulate "weak Au–Au interactions" between Au^+ centres. This is not only true for simple halides,[147] and chalcogenides,[262,263] but also for binary and ternary phosphides[264] and many other systems. In the crystal lattices of these compounds the effect is not always readily discernible owing to the dominance of much stronger forces. The present account has therefore concentrated primarily on the *molecular* chemistry of gold(I), which offers a greater chance to distinguish between the various forces contributing to the mode of assembly of individual units. The impact that "weak forces" like metallophilic bonding may have on macroscopic properties of bulk materials became recently obvious in a study of the temperature dependence of the unit cell parameters of $Ag_3[Co(CN)_6]$: "Colossal" positive and negative expansion coefficients were detected which appear to be based on argentophilic interactions.[265]

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