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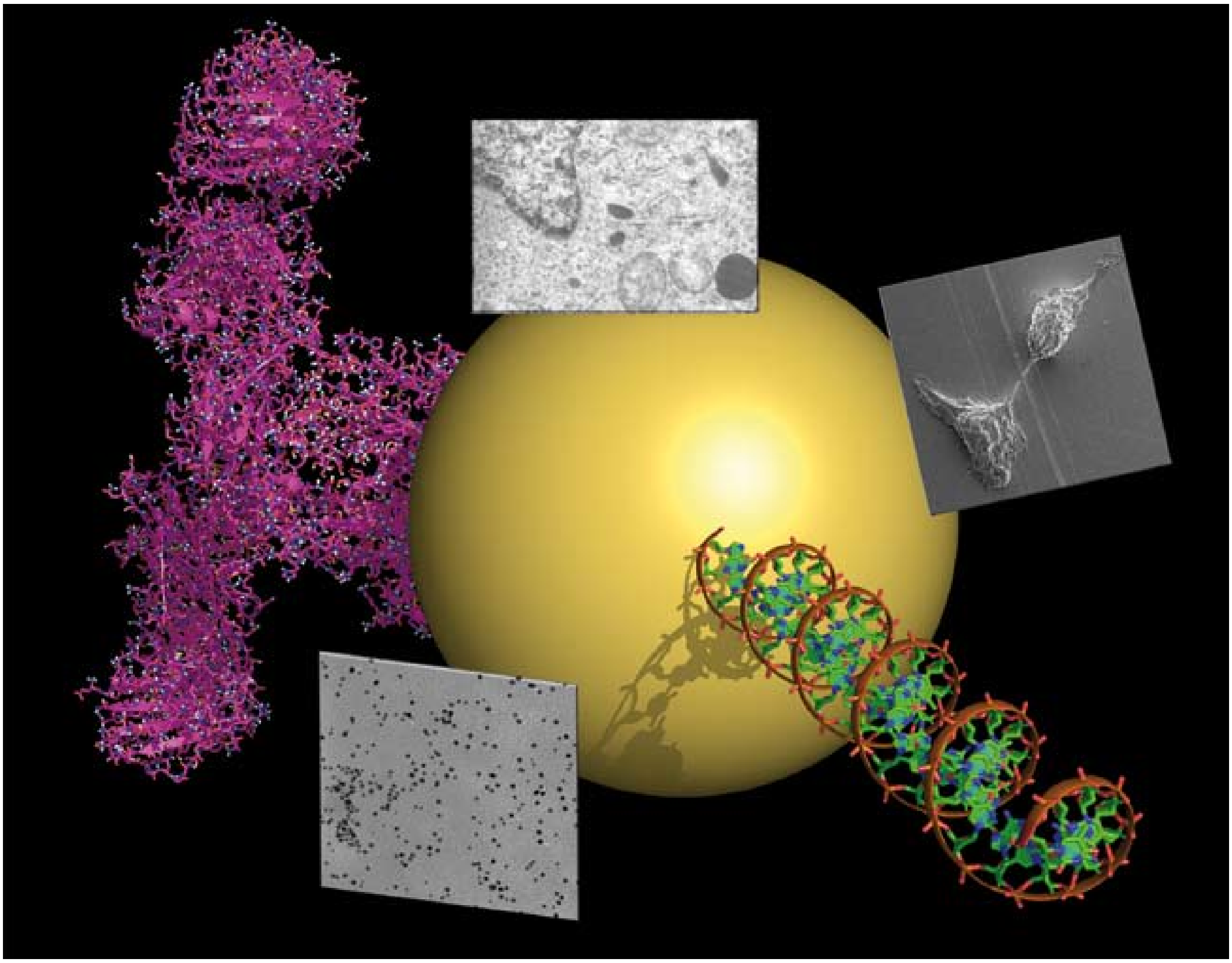

Chalcogenide centred gold complexes†

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Chalcogenide-centred gold complexes are an important class of compounds in which a central chalcogen is surrounded by several gold atoms or gold and other metals. They have special characteristics such as unusual geometries, electron deficiency and properties such as luminescence or non-linear optical properties. The best known species are the trinuclear $[E(AuPR_3)_3]^+$, 'oxonium' type species, that have high synthetic applicability, not only in other chalcogen-centred species, but in many other organometallic derivatives. The aurophilic interactions play an important role in the stability, preference for a particular geometry and luminescence properties in this type of derivatives (*critical review*, 117 references).

1. Introduction

The last two decades have witnessed the development of a fascinating chemistry where phosphino–gold fragments coordinate around a central heteroatom.[1–6] The species formed are exciting not only from the experimental and structural, but also from the theoretical standpoint. Thus interesting hypercoordinated species[7–11] of the type $[C(AuPR_3)_5]^+$, $[C(AuPR_3)_6]^{2+}$, $[N(AuPR_3)_5]^+$, $[P(AuPR_3)_5]^{2+}$, $[P(AuPR_3)_6]^{3+}$, have been described apart from other complexes with more conventional stoichiometry, and all have in common the presence of short gold–gold interactions of *ca.* 3 Å. Usually, the chemistry of the first row elements of the p-block is known to follow classical rules of bonding, and only in cases of extreme electron-deficiency has the traditional electron count to be reconsidered to account for special types of molecular or solid state structures. Many of the heteroatom-centred complexes are electron deficient and the gold–gold interactions provide a significant contribution to their stability. The type of structure adopted is greatly influenced by the existence of gold–gold interactions, and for this reason a great amount of work has dealt with the origin of this gold–gold attraction, called aurophilic attraction. Bonding between closed-shell atoms was successfully traced in several early theoretical investigations by extended Hückel quantum chemical calculations.[12–15] Based on the hybridisation concept, the nature of the bonding interaction could be qualitatively rationalized in the language of chemists. The introduction of relativistic effects in more advanced calculations has shown that bonding between closed-shell metal atoms or ions may be strongly enhanced by these effects.[16–25] Since relativistic effects have been known to reach a local maximum for gold in particular, aurophilicity was accepted as a logical consequence of these contributions. Actually aurophilic bonding is considered as an effect based largely on electron correlation of the closed-shell components, somewhat similar to van der Waals interactions but unusually strong.[21,24,25] All these studies have consistently shown that calculations will reproduce the attractive forces between the gold atoms really well only if relativistic effects are included.

This review focuses on the field of chalcogenide centred gold complexes, and covers the synthesis of the complexes, structural patterns and properties such as luminescence. For

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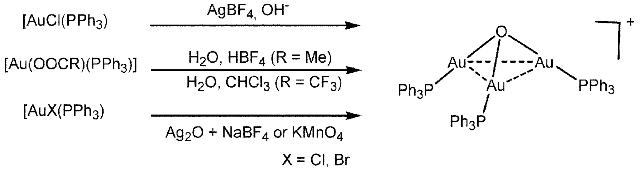
oxygen, the species $[O(AuPR_3)_3]^+$ have revealed a great synthetic applicability, not only in other element-centred species but in many other organometallic derivatives. Sulfur-centred complexes have been the most studied but selenium complexes have been recently developed. So far the telluride derivatives are the most scarcely represented.

2. Oxygen-centred complexes

The chemistry of oxygen-centred complexes has been limited until very recently to the tri(gold)oxonium cations $[O(AuPR_3)_3]^+$ despite the fact that salts of $[O(AuPPh_3)_3]^+$ were the first structurally reported examples of this interesting type of derivatives.[26] Although the AuL^+ moiety is a "soft" Lewis acid and does not usually combine well with oxygen containing ligands, Nesmeyanov *et al.* found that tris(triphenylphosphinegold)oxonium salts could be easily prepared and that they were highly reactive. These salts were obtained in high yield by reaction of water with coordinatively unsaturated $AuPPh_3^+$ cations in an alkaline or acid media. Another convenient method of synthesis, with even higher yield, was the treatment of $[AuCl(PPh_3)]$ with silver(I) oxide in the presence of $NaBF_4$ (Scheme 1).[26]

These procedures for preparing the oxonium salts have been used, sometimes with slight modifications to synthesize this type of complexes with a wide range of phosphine ligands,[27–33] *e.g.* PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$, $P^{i}PrPh_2$, $P(p\text{-}ClPh)_3$, $P(o\text{-}Tol)_3$, $P(OEt)Ph_2$, $P(OMe)_3$, PEt_3, $P^{t}Bu_3$, PMe_3, $P^{i}Pr_3$, $P(NMe_3)_3$, PPh_2py, $PPh_2CH_2CH_2py$. Another preparative route has been reported for PR_3 = PPh_3 or $P(p\text{-}MeOPh)_3$ that consists of the reaction of the acetylacetonate complexes $[Au(acac)(PR_3)]$ with the ammonium salts $(NH_2R'_2)OTf$ (R = Et, Ph) followed by hydrolysis, although the yield is very low compared with other methods.[34]

The tendency of the $AuPR_3^+$ cations to form oxonium species in the reactions that would be expected to lead to the hydrate, $[Au(OH_2)(PR_3)]^+$, hydroxide $[Au(OH)(PR_3)]$ or oxide $[O(AuPR_3)_2]$ suggest the existence of structural factors enhancing the stability of the $[O(AuPR_3)_3]^+$ ion compared to the above complexes, which are not known in the monomeric state. Such a factor could easily be the existence of inter- and intramolecular interactions of gold atoms.



Scheme 1 Synthetic methods for the preparation of $[O(AuPPh_3)_3]^+$.

The solid-state structures of these complexes depend on the size of the phosphine ligand used. Thus, for example, for more sterically demanding phosphines such as $P(o\text{-}Tol)_3$,[27] $P^{i}Pr_3$,[30] or $P(NMe_2)_3$,[31] the structure consists of a trigonal OAu_3 pyramid (Fig. 1, **A**) with the oxygen atom in the apical position. The coordination geometry of the gold atoms is nearly linear and there are intramolecular Au···Au contacts with an average value of 3.086, 3.198 or 3.176 Å, respectively. For phosphine ligands such as PPh_3,[26] $PMePh_2$,[27] or $P(p\text{-}MeOPh)_3$,[34,35] the structure is also based on trigonal pyramidal $[O(AuPR_3)_3]^+$ cations, which undergo intermolecular aggregation to form centrosymmetric dimers (Fig. 1, **B**). The intermolecular interaction between the cations causes the gold atoms to form a rectangular Au_4 subunit, with the six gold atoms of the dimer forming a six-membered ring with a chair conformation. Several crystal structure determinations have been carried out for PPh_3 with different anions and in all the cases the structural framework is the same.[36–40] For the smallest possible tertiary phosphine PMe_3 the monomeric units, which are also OAu_3 pyramids, are aggregated through shared edges to give a tetrahedral Au_4 sub-unit (Fig. 1, **C**).[29] A characteristic that all the structurally determined $[O(AuPR_3)_3]^+$ cations have in common is that the geometry of the monomeric unit shows only small distortions with the size of the phosphine.

The dimerization of the tri(gold)oxonium cations has been studied theoretically by means of the all-electron scalar relativistic linear combination of Gaussian-type orbitals density functional (LCGTO-DFT) theory, examining the model compounds $[OAu_3]^+$ and $[O(AuPH_3)_3]^+$.[41] For $[OAu_3]^+$ the tetrahedral dimerization was calculated to be slightly favourable, while the addition of phosphine ligands leads to a preference for a rectangular dimer structure. Thus, the experimentally observed rectangular dimer structure of $[O(AuPPh_3)_3]_2^{2+}$ is claimed to be determined by steric intermonomer repulsion, and for $[O(AuPMe_3)_3]_2^{2+}$ which dimerizes tetrahedrally, crystal packing effects should play a decisive role because the intermonomer ligand repulsion differs only in a minor way between the rectangular and the tetrahedral structures.

Some studies in solution have been carried out on these trigold oxonium cations, and the complexes show rapid exchange processes with chloro complexes leading to equilibrium mixtures (Scheme 2).[27] The first step could be the dissociation of Cl^- from $[AuCl(PR_3)]$ to produce $AuPR_3^+$ and the exchange could occur through an $[O(AuPR_3)_4]^{2+}$ intermediate.

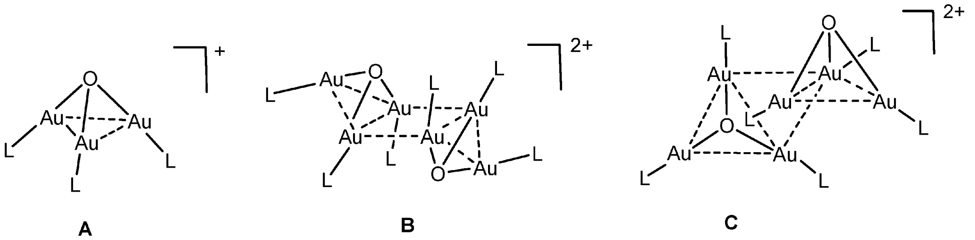
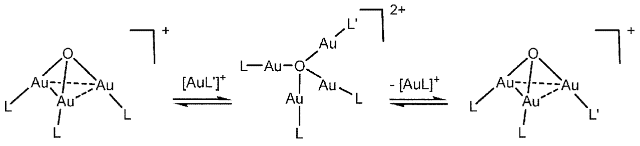


Fig. 1 Structures of the $[O(AuL)_3]^+$ complexes.



Scheme 2 Exchange processes in $[O(AuL)_3]^+$ complexes.

The exchange processes appear to slow down with increasing steric size, suggesting associative pathways.

Hyper-aurated oxygen-centred complexes $[O(AuPR_3)_4]^{2+}$ have been synthesized by Schmidbaur *et al.* in high yield by reaction of the tri(gold)oxonium salts with the aurating agent $[Au(BF_4)(PR_3)]$ (R = Ph, *o*-Tol) (eqn (1)).[42] The complex with R = *o*-Tol was structurally characterized and the central oxygen atom has a crystallographically imposed tetrahedral geometry coordinated by four gold atoms. The gold–gold distances (between the edges of the OAu_4 tetrahedron) are 3.3590(4) Å which, although longer than those found in related complexes with a square-pyramidal geometry, are still much shorter than the sum of the van der Waals radii for Au(I). The unprecedented stability of the $[O(AuPR_3)_4]^{2+}$ unit has been attributed to the significant bonding between the closed-shell gold cations.

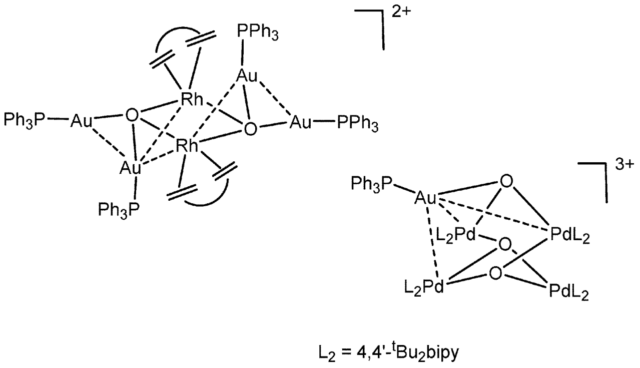
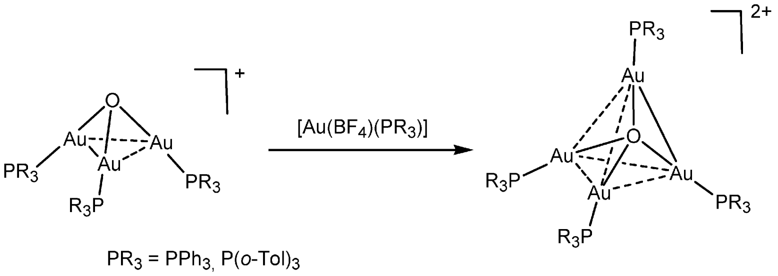
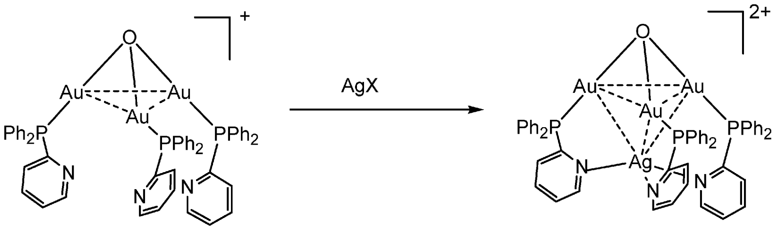


Fig. 2 Some heteronuclear complexes with bridging μ_4-O or μ_3-O ligands.

Another approach to prepare heteronuclear complexes with a central oxide ligand has been the use of the complexes $[O(AuL)_3]^+$, which posses a difunctional phosphine ligand such as PPh_2py, $PPh_2(py\text{-}4\text{-}Me)$ or $PPh_2CH_2CH_2py$, that can coordinate to other metal fragments. The result is different depending on the heterofunctional phosphine and the metal.[32,33] Therefore the reaction of $[O(AuPPh_2py)_3]^+$ with AgOTf or $AgBF_4$ gives the tetranuclear clusters $[O(AuPPh_2py)_3Ag]^{2+}$, which have a tetrahedral Au_3Ag core with short Au···Au and Au···Ag interactions and bridging phosphine ligands (eqn (2)).



(1)



(2)

Heteronuclear μ_3- and μ_4-oxides have been prepared by reaction of $[O(AuPPh_3)_3]^+$ with $[MCl_2L_2]$ (M = Pd, Pt) or $[Rh(\mu\text{-}Cl)(dien)]_2$.[43–46] With palladium and platinum the reaction with the gold complex in different molar ratios gives dinuclear or trinuclear complexes with a μ_3-oxide ligand as shown in Fig. 2. In these complexes there are also short Au···Pd or Au···Pt interactions. The rhodium derivative with dien = norbornadiene (nbd) has been structurally characterized and shows an oxygen atom with an unusual trigonal pyramidal geometry (Fig. 2). The dication consists of a planar $[(nbd)Rh(\mu\text{-}O)Rh(nbd)]$ array in which two $AuPPh_3{}^+$ groups are coordinated to each oxygen atom. Similarly the presence of Au···Au and Au···Rh contacts are observed.

These complexes have been prepared with oxide, sulfide or selenide as bridging ligands.[32] They are all isostructural and, in the case of sulfur and selenium, also isomorphous. The Au···Au interactions in the three complexes are all around 3 Å and the Au···Ag distances lie in the range 2.8–2.96 Å, which are similar to those found in complexes with significant metallophilic interactions. Aurophilic interactions also link two Au_3Ag tetrahedra together (see Fig. 3) with an Au···Au distance of 3.0539 A. The metallophilic interactions and the

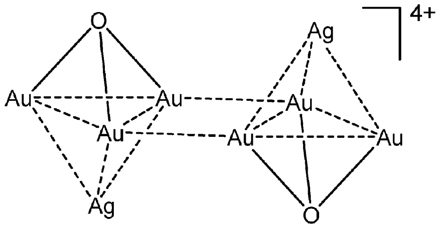
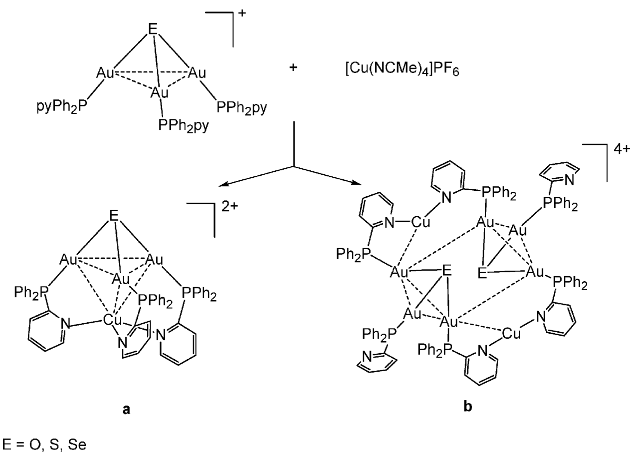


Fig. 3 Association of the $[O(AuPPh_2py)_3Ag]^{2+}$ cations in pairs.

bridging PPh_2py ligands confer greater structural rigidity and stability to these complexes compared with the trinuclear $[E(AuPR_3)_3]^+$ complexes in which the phosphine ligands coordinate as terminal ligands only.

A distinctive feature of these complexes is that they present a extremely bright luminescence. These species exhibit a large variation of λ_{em}^{max} as a function of the μ_3-E capping ligand with values of 466, 554 and 670 nm for E = O, S, Se, respectively. For the oxonium complex the bright blue emission shows single-exponential behaviour with lifetimes of 7 and 49 μs at 295 and 77 K, respectively, indicating that the emission is phosphorescence. The energy of the emissions decreases on going from oxygen (at significantly high energy), to sulfur and to selenium. The large change in λ_{em}^{max} between these complexes clearly indicates involvement of the group 16 capping atom in the excited state. Based on the fact the lone pair orbitals lie lowest in O, next in S, and highest in Se, an assignment consistent with the emission results is that of a ligand-to-metal-metal-charge transfer (^{3}LMMCT).

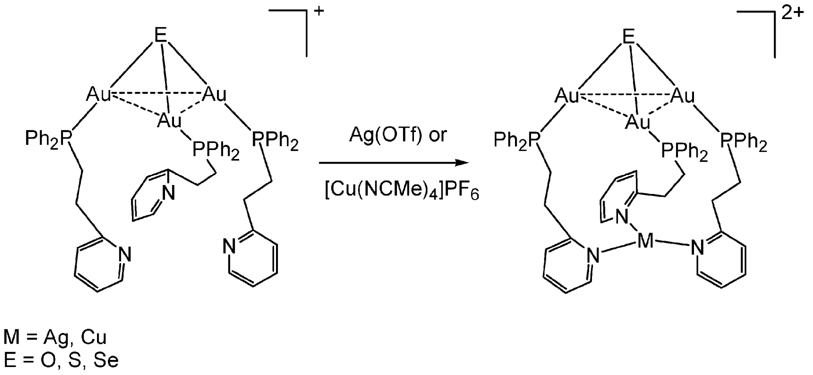
As a consequence of the interesting luminescence properties of this type of complexes the reaction with other metal centres such as copper(I) was investigated.[33] Thus the reaction with $[Cu(NCMe)_4]PF_6$ led to the formation of the species $[E(AuPPh_2py)_3Cu]^{2+}$. They possess the same stoichiometry as the silver derivatives, but in this case, as concluded by NMR and X-ray diffraction studies, they are a mixture of two coordination isomers **a** and **b**, as shown in Scheme 3. At room temperature isomer **a** shows only one resonance for the equivalent phosphorus atoms and isomer **b** two resonances in a approximate ratio 2 : 1 (Scheme 3).



Scheme 3 Coordination isomers of the complexes $[E(AuPPh_2py)_3\text{-}Cu]^{2+}$.

The first isomer **a** is analogous to the silver complexes and in the second, **b**, two $[E(AuPPh_2py)_3]^+$ units bridge two copper atoms through one pyridine group in each unit. For the oxygen and selenium derivatives, isomer **b** is the major component and for sulfur the ratio can be varied changing the counteranion, thus if the starting material is $[S(AuPPh_2py)_3]BF_4$ a higher ratio of isomer **a** is obtained, and if we start from $[S(AuPPh_2py)_3]OTf$ the isomer **b** is favoured. The luminescence behaviour of these complexes has been studied and also show a variation of the energy of the emissions depending on the chalcogenide. Consequently, the emissions have been attributed to a ligand-to-metal charge transfer (LMCT; $E^{2-} \rightarrow Au_3M$) triplet excited state, although a mixed nature, with contribution from a metal-centred (MC, d–s or d–p) state is probable.

The reactivity of $[E(AuPPh_2CH_2CH_2py)_3]BF_4$, which contains a heterofunctional ligand with a longer chain between the donor atoms, towards Ag(OTf) and $[Cu(NCMe)_4]PF_6$ has also been studied (eqn (3)).[33]



(3)

In these complexes the nitrogen atoms bind the silver or copper atoms, but the crystal structure of the copper derivative with sulfur reveals the absence of Au···M interactions, since the larger monophosphine prevents a connection between the three gold atoms and the heterometal. In the lattice the molecules arrange into dimers through intermolecular aurophilic interactions (Fig. 4). These species are also luminescent and the copper complexes exhibit the same pattern as described above, but with a smaller red shift in the emissions.

Gold(III) complexes with a bridging oxide ligand are not well represented; they have been prepared from adducts with bipyridine derivatives, $[Au(HL)Cl_3]$, or the cyclometalated species, [AuLCl], by reaction with silver salts or $MeCO_2Na$

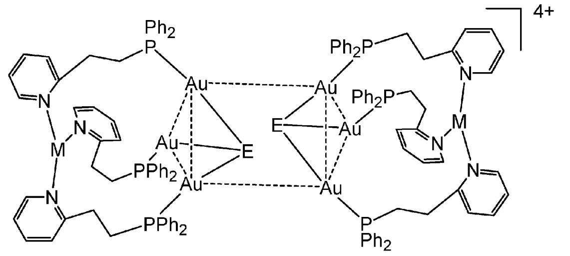


Fig. 4 Association in pairs in the complexes $[E(AuPPh_2CH_2CH_2\text{-}py)_3M]^{2+}$.

(Fig. 5).[47–49] These complexes show antiproliferative effects and DNA and protein binding properties.[50]

Other interesting gold(III) complexes have been prepared by reaction of $AuCl_3$ with metal oxide polytungstate ligands.[51] These complexes, $K_{15}H_2[Au(O)(OH_2)P_2W_{18}O_{68}]\cdot 25H_2O$ and $K_7H_2[Au(O)(OH_2)P_2W_{20}O_{70}(OH_2)_2]\cdot 27H_2O$ are unique because they represent the first examples of terminal Au–oxo complexes that exhibit multiple bonding between gold and oxygen. The gold atom is bonded to six oxygen atoms in a octahedral geometry, the equatorial positions are bridging oxide ligands, at a distance of 1.877(11) Å, and the axial positions are occupied by a terminal Au=O bond, 1.763(17) Å, and a water molecule, Au–O 2.29(4) Å (see Fig. 6).

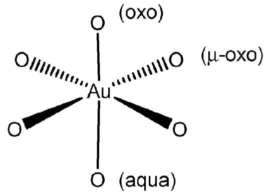


Fig. 6 Environment of the gold(III) atom in $K_7H_2[Au(O)(OH_2)P_2W_{20}O_{70}(OH_2)_2]\cdot 27H_2O$.

3. Sulfur-centred complexes

The chemistry of polynuclear derivatives around a central sulfur ligand has been by far the most widely developed, probably because of the higher stability of the complexes and the readily accessible methods to prepare the starting materials. Species from a doubly bridging to a sextuply bridging sulfide ligand have been reported.

3.1 Doubly bridging sulfide ligands

The complex $[S(AuPEt_3)_2]$ was synthesized by Kowala and Swan a long time ago, in 1966, by reaction of $[AuBr(PEt_3)]$ with Na_2S, however the analogous compound with triphenylphosphine, $[S(AuPPh_3)_2]$, was claimed by the authors to be unstable because it could not be obtained by reaction with Na_2S, or to be an intermediate in the synthesis of $[S(AuPPh_3)_3]Cl$ with H_2S.[52] Other reports deal with the preparation and crystal structure of some doubly bridging sulfide complexes, however, these were not well established procedures and in some cases the sulfur-centred gold complex was obtained as a by-product.[53–56] A high yield synthesis for the gold(I) species $[S(AuPR_3)_2]$ or $[S\{Au_2(\mu\text{-P–P})\}]$ has been developed and involves the reaction of $[AuCl(PR_3)]$ or $[Au_2Cl_2(\mu\text{-P–P})]$ (P–P = 1,1-bis(diphenylphosphine)ferrocene (dppf)) with Li_2S in ethanol; the desired products precipitate in ethanol and are obtained in almost quantitative yield (eqn (4)).[57,58] Complexes with other bridging diphosphines have been obtained by similar reactions (Fig. 7).[59,60]

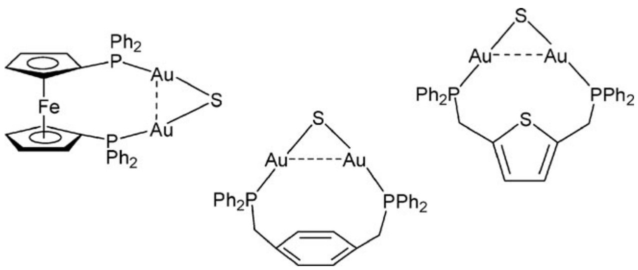
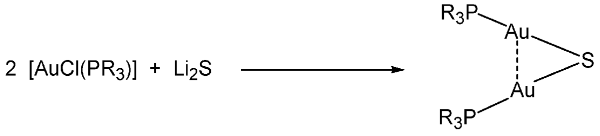


Fig. 7 Complexes of the type $[S\{Au_2(\mu\text{-P–P})\}]$.



$PR_3 = PPh_3,\ PPh_2Me,\ P(p\text{-Tol})_3,\ PPh_2py$

(4)

These complexes are excellent starting materials for the synthesis of highly aurated homoleptic sulfur-centred derivatives. The structures of these complexes consist of two $AuPR_3^+$ or $Au_2(P–P)^{2+}$ units bridged by a sulfide ligand. The main features are short gold–gold distances and an acute Au–S–Au angle. However the differences in the values depending on the ligand are remarkable. For PPh_3 and $C_6H_4(CH_2PPh_2)_2$ these are very similar, with Au···Au distances of 3.081(1) and 3.146(1) Å and Au–S–Au angles of 88.7(1) and 86.7(1)°, respectively, whereas for dppf the Au···Au distance is considerably shorter, 2.882(1) Å, consistent with the narrower Au–S–Au angle of 77.57(9)°.

Following the symmetry rules applied to the frontier orbitals, the proton H^+, carbocations R^+ and $AuPR_3^+$ fragments can be classified as isolobal; then the molecules EH_2, ER_2 and

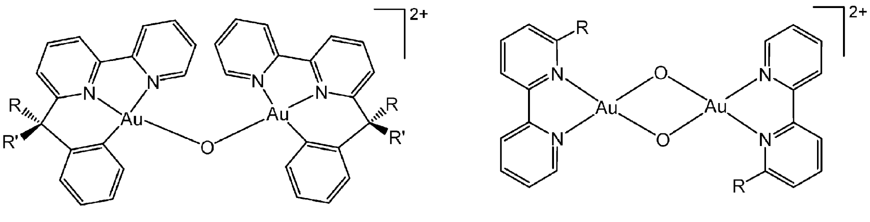


Fig. 5 Gold(III) complexes with a bridging oxo ligand.

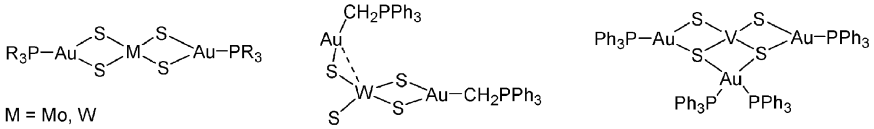


Fig. 8 Heteronuclear complexes with bridging sulfide ligands based on MS_4^{n-} units.

$[E(AuPR_3)_2]$ (E = S, Se) should be isolobal. However their behaviour is very different because no gold complexes with EH_2 are known, usually the ER_2 molecules are weakly coordinating ligands, whereas the sulfur or selenium atom in $[E(AuPR_3)_2]$ acts as a good Lewis base. This is a common feature in this type of complexes. For example, the dications OH_4^{2+}, NH_5^{2+} and CH_5^{2+} are unknown and predicted to be intrinsically unstable, but the corresponding gold complexes have been isolated.

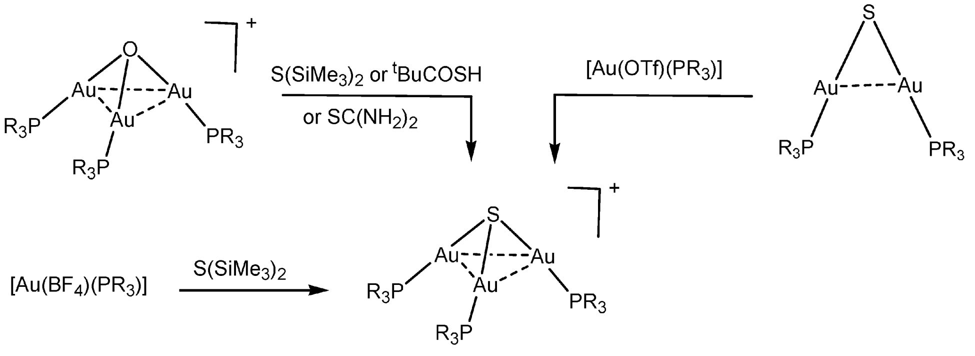
Other types of doubly bridging sulfide complexes are based on the tetrathiometallates, MS_4^{n-} (M = V, Mo, W). Several complexes of stoichiometry $[MS_4(AuL)_2]$ (M = Mo, W) have been reported,[61–68] and they are generally obtained by reaction of the tetrathiometallates with [AuClL]. Other stoichiometries are also possible in this type of complexes such as for example $[Au\{\eta^2\text{-}S_2W(S)Cp\}(AuL)]$ (L = PPh_3, $PPh_2CH_2PPh_2S$),[69,70] $[Mo(O)S_3(AuPPh_3)\{Au(PPh_3)_2\}]$,[62] $[Au_2\{\eta^2\text{-}S_2WS(E)\}(\mu\text{-}P\text{–}P)]$ (E = O, S; P–P = dppe, dppf),[71] $[Au_2\{\mu\text{-}S_2W(E)S\}_2]^{2-}$ (E = S, O),[72,73] $[Au_2(\eta^2{:}\eta^1\text{-}WS_4)(CH_2PPh_3)_2]$,[64] or $[Au_2\{(\eta^2{:}\mu\text{-}WS_3Cp)\}_2]$.[74] Finally a tetrathiometallate derivative has been reported in which the sulfur atoms act as μ_2- and μ_3-bridging ligands, $[Au_3(VS_4)(PPh_3)_3]$, which has been prepared by reaction of $(NH_4)_3[VS_4]$ with three equivalents of $[AuCl(PPh_3)]$.[75] Fig. 8 collects some examples of this type of complexes.

3.2 Triply bridging sulfide ligands

The cationic tri(gold)sulfonium complexes with monodentate ligands are very stable and can be prepared by several procedures as shown in Scheme 4.

Homoleptic species with various phosphine ligands such as PPh_3, PMe_3, P^iPr_3, $PMePh_2$, PPh_2py, $PPh_2CH_2CH_2py$ have been prepared in high yield through one of these methods.[28,32,33,57,76,77] The complexes with the isocyanides, $[S(AuCNR)_3]^+$ (CNR = CNC_7H_{13} or C_6H_{11}), have been obtained by reaction of $[Au(CNR)_2]X$ with a solution of $Na_3[Au(S_2O_3)_2]$ in water.[78] Crystallographic examination of $[S(AuCNC_7H_{13})_3]SbF_6$ shows that it undergoes a reversible phase change from orthorhombic to monoclinic upon cooling. The phase change lowers the symmetry of the gold cations and results in the creation of two different pairs of cations: one with expanded interionic Au···Au separations, the other with contracted interionic Au···Au separations. These complexes are highly luminescent and the luminescence varies with the temperature in agreement with the phase change. The compound $[S\{Au(mbpa)\}_3]Cl$ (mbpa = methyl-4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)-α-D-altropyranoside) has been synthesized in low yield from [AuCl(mbpa)] and L-cysteine.[79] In $[S(AuPPh_3)_3]_2[Fe_5(\mu_3\text{-}S)_2(CO)_{14}]$ the sulfonium cation helps to crystallizes the final compound.[80]

The crystal structures of the homoleptic species resemble those of the tri(gold)oxonium cations. Furthermore, it becomes increasingly obvious that steric and electronic effects play a decisive role in the strength of the Au···Au interaction and in the supramolecular aggregation of the sulfur-centred cations. Again the basic structural framework consists of a trigonal pyramidal SAu_3 with the sulfur atom in the apical position and short gold–gold contacts in the base of the pyramid. However the size of the phosphine influences the further aggregation of the molecules. For the bulky tris(isopropyl)phosphine or mbpa the structure is monomeric and the asymmetric unit contains 1/3 of the cations because they have threefold crystallographic symmetry. The Au–Au distances are almost identical in both cations, 3.253(1) and 3.251(1) Å, and also the Au–S–Au angles are close to 90°, which are indicative of steric repulsion. There is, however, a difference for the complex with the phosphine mbpa because each chloride anion links to three $[S\{Au(mbpa)\}_3]^+$ cations through hydrogen bonds between the OH group of the altropyranose ring to form an infinite two-dimensional net structure. The structures for phosphine ligands such as PPh_3, $PMePh_2$, PPh_2py or $PPh_2CH_2CH_2py$ are dimers related by a centre of symmetry and with little differences between the intra- and inter-molecular gold–gold distances within the dimeric unit. The nature of the anion may also play a significant role because the cation $[S(AuPPh_3)_3]^+$ is a



Scheme 4 Synthesis of $[S(AuPR_3)_3]^+$ complexes.

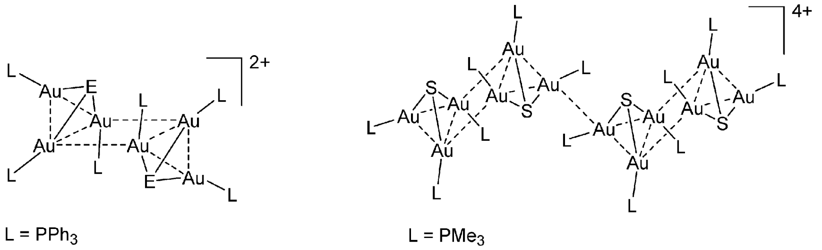


Fig. 9 Structures of $[S(AuL)_3]^+$ complexes.

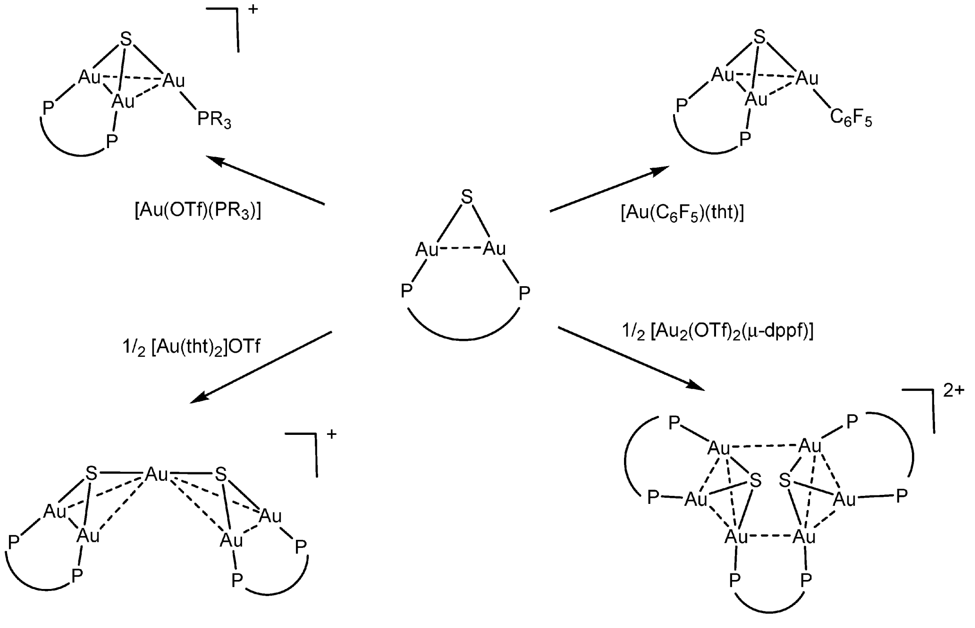
monomer as the tetrafluoroborate salt, but a dimer with the hexafluorophosphate counteranion. For the isocyanide ligands, the trimeric units are related by a mirror plane. The complex $[S(AuPMe_3)_3]BF_4$ crystallizes with two independent formula units (A and B), which are both forming pairs (dimers A_2 and B_2) through a crystallographic centre of inversion. These dimers are aggregated further into strings of dimers (–A–A–B–B–) with short gold–gold contacts (A–B) as links (Fig. 9). Pseudopotential *ab initio* calculations on SAu_3^+ and $S(AuPH_3)_3^+$ have been carried out and they reproduce experimental Au–S–Au angles found in the monomeric $[S(AuPR_3)_3]^+$ cations ($PR_3 = PPh_3$, P^iPr_3) if both correlation and relativistic effects are included.

Another homoleptic compound with a triply bridging sulfide ligand is the anionic $(NEt_4)_2[S\{Au(C_6F_5)\}_3]$, obtained by bubbling H_2S through a solution of $NEt_4[Au(C_6F_5)Cl]$.[81] The structure corresponds to a distorted trigonal pyramidal geometry for the sulfur atom. There are dissimilar Au–Au distances and Au–S–Au angles; two of them are close to those found in other complexes with a μ_3-S ligand whereas the other ones, 3.4772(9) and 97.65(13)°, lie outside of the normal ranges. The complexes $[S(AuPPh_3)_2]$ and $[S(Au_2dppf)]$ serve as building blocks for preparing polynuclear chalcogenide complexes. The reaction of these derivatives with another gold(I) fragment leads to complexes with a μ_3-bridging sulfide ligand as exemplified for the diphosphine complexes shown in Scheme 5.[58]

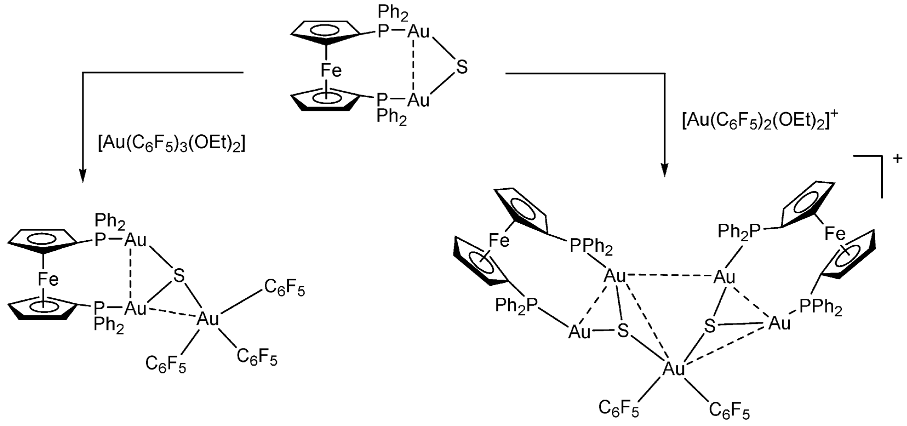
The compound $[\{S(Au_2dppf)\}_2(\mu\text{-}Au_2dppf)](OTf)_2$ has a S_2Au_6 core with short intramolecular gold–gold interactions, with vary from 2.905(2) to 3.272(2) Å. It is worth mentioning that the $^{31}P\{^1H\}$ NMR spectra of these compounds at low temperature show three resonances indicating the inequivalence of all phosphorus atoms, probably as a consequence of the different gold–gold interactions, which can be observed at low temperature. The crystal structure of $[\{S(AuPPh_3)_2\}_2Au][SnMe_3Cl_2]$ has been reported and the atomic arrangement is similar to that found for $[\{S(Au_2dppf)\}_2Au](ClO_4)_2$ with short gold–gold distances between the central gold atom and those of each $S(AuL)_2$ unit.[82]

Mixed gold(I)–gold(III) derivatives have been prepared by reaction of $[E(Au_2dppf)]$ with the gold(III) species $[Au(C_6F_5)_3(OEt_2)]$ or $[Au(C_6F_5)_2(OEt_2)_2]OTf$ (see Scheme 6).[83] In a similar manner and starting from $[S(AuPPh_3)_2]$ the reaction with $[Au(C_6F_5)_3(OEt_2)]$ leads to the mixed gold(I)–gold(III) species $[S(AuPPh_3)_2\{Au(C_6F_5)_3\}]$.

The crystal structures of these complexes show short gold(I)–gold(III) contacts which ranges from 3.2 to 3.6 Å. Theoretical calculations (MP2, DFT and extended Hückel) have been carried out for these complexes and others, supporting the existence of aurophilic gold(I)–gold(III) interactions, though



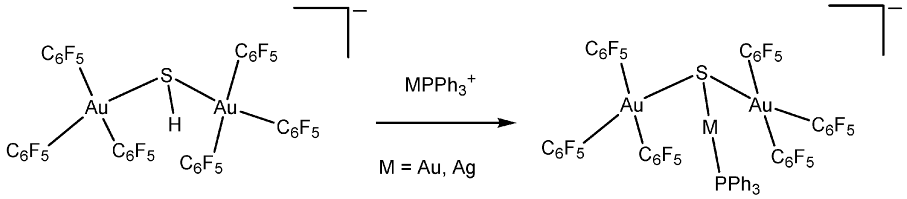
Scheme 5 Synthesis of triply bridging sulfide gold complexes.



Scheme 6 Synthesis of mixed gold(I)–gold(III) complexes.

weaker than the corresponding gold(I)–gold(I) interactions, with bond energies in the range 21–25 kJ mol^{-1}.[83–85]

Taking into account the isolobal relationship between H$^+$, AuPPh$_3$$^+$ and AgPPh$_3$$^+$ the anionic species NBu$_4$[S(MPPh$_3$){Au(C$_6$F$_5$)$_3$}$_2$] (M = Ag, Au) have been prepared by reaction of NBu$_4$[S(H){Au(C$_6$F$_5$)$_3$}$_2$] with MPPh$_3$$^+$ cations in the presence of Na$_2$CO$_3$ (eqn (5)).[86] Both complexes are isostructural and have a trigonal pyramidal geometry at the sulfur atom, although with no short Au···Au or Au···Ag interactions. The Au^{I}–S bond length is 2.303(5) Å and the Ag–S distance 2.374(5), which is in accordance with the observations made by Schmidbaur *et al.* that the covalent radius of gold is smaller than that of silver, as was anticipated on the basis of data obtained in theoretical calculation treatments including relativistic effects.[87–89]



(5)

A series of high-nuclearity gold(I) sulfide complexes have been obtained with bridging diphosphine ligands such as PPh$_2$CH$_2$PPh$_2$ (dppm) or PPh$_2$NRPPh$_2$ (R = alkyl or aryl).[90–92] There are readily accessible through bubbling hydrogen sulfide into a suspension of the complexes [Au$_2$Cl$_2$(μ-P–P)] in ethanol–pyridine. The result is different with each diphosphine and the decanuclear [Au$_{10}$(μ$_3$-S)$_4$-{μ-PPh$_2$N(^{n}Pr)PPh$_2$}$_4$], the dodecanuclear [Au$_{12}$(μ$_3$-S)$_4${μ-dppm}$_6$] or the hexanuclear [Au$_6$(μ$_3$-S)$_2${μ-PPh$_2$N-(*p*-CH$_3$C$_6$H$_4$)PPh$_2$}$_2$] have been obtained (see Fig. 10). The crystal structures have been determined and [Au$_{10}$(μ$_3$-S)$_4${μ-PPh$_2$N(^{n}Pr)PPh$_2$}$_4$] is propeller-shaped with four [Au$_2${μ-PPh$_2$N(^{n}Pr)PPh$_2$}] flaps connected by four sulfur atoms that are further bonded to two interstitial gold atoms, whereas [Au$_{12}$(μ$_3$-S)$_4${μ-dppm}$_6$] shows an interesting "crossroad-sign" structure with the four SAu$_3$ units located at the core and interconnected by six dppm ligands and [Au$_6$(μ$_3$-S)$_2${μ-PPh$_2$-N(*p*-CH$_3$C$_6$H$_4$)PPh$_2$}$_2$] has a distorted heterocubane structure with the sulfur atoms in opposite apices of the cuboid. Intense green and orange emissions were observed upon excitation at $\lambda > 350$ nm both in the solid state and solutions. The green emission has been attributed to originate from excited states derived from the metal-perturbed intraligand (IL) transition while the orange emission arises from the ligand to metal–metal bond charge transfer (LMMCT; S(Au···Au)) states.

Finally, there are heteronuclear derivatives with the triply sulfide ligand bridging gold and platinum atoms.[93–96] They are prepared from the complex [Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] by reaction with [AuCl(PPh$_3$)] or [Au$_2$Cl$_2$(μ-dppf)], or by reaction of the compound [Pt$_2$(μ-S)(CO)(PPh$_3$)$_3$] with AuPPh$_3$$^+$, or by treatment of [Pt(C$_6$F$_5$)$_2$(SH)(PPh$_3$)] with [Au(OTf)(PPh$_3$)] (Fig. 11).

Other heteronuclear μ$_3$-sulfide complexes are those obtained with the heterodifunctional phosphine ligands, [S(AuPPh$_2$py)$_3$]$^+$ and [S(AuPPh$_2$CH$_2$CH$_2$py)$_3$]$^+$, by reaction with silver(I) or copper(I), which have been previously commented on.[32,33]

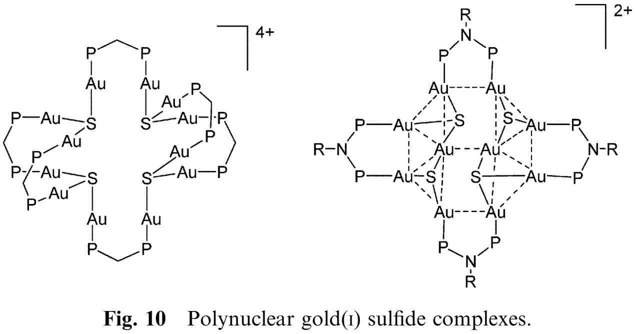


Fig. 10 Polynuclear gold(I) sulfide complexes.

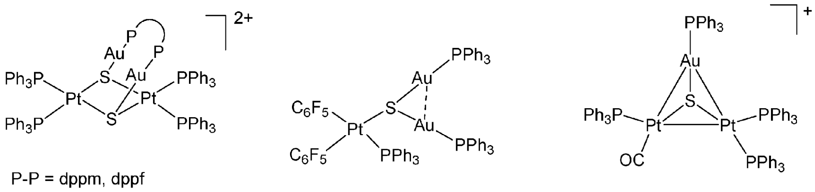
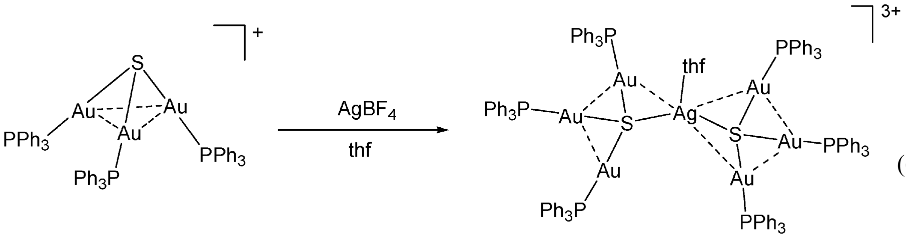


Fig. 11 Mixed platinum–gold complexes with bridging sulfide ligands.

3.3 Quadruply bridging sulfido ligands

The discovery that [S(AuPPh$_3$)$_2$] or [S(AuPPh$_3$)$_3$]$^+$ can add additional AuPPh$_3$$^+$ units led to the preparation of salts of the unprecedented tetra(gold) sulfonium(2+) cation [S(AuPPh$_3$)$_4$]$^{2+}$.[97] The cation has a square pyramidal structure with the sulfur atom occupying the apical position, clearly at variance with any of the classical rules of structure and bonding which demand a sulfur-centred tetrahedral complex similar to [O{AuP(*o*-Tol)$_3$}$_4$]$^{2+}$. There are short metal–metal distances between the gold atoms which are not exactly coplanar, but arranged in a flattened butterfly. The molecules arrange into dimers through aurophilic interactions (Fig. 12). The SAu$_4$ core should be regarded as electron-deficient, considering the sulfide ligand to serve as a six-electron donor. Therefore there exists a lone pair of electrons in the apical position, which means that further coordination of gold around the sulfur atom is conceivable.

There is precedent for such a non-classical pyramidal structure in the analogous tetra(gold)arsonium cations [As(AuPPh$_3$)$_4$]$^+$,[98] which one would expect to be tetrahedral as required for standard arsonium salts AsR$_4$$^+$. The calculations made with *ab initio* or density functional methods, including relativistic effects, show that the system is lower in energy with close contacts between the gold atoms, which is very easy in a square pyramid but impossible in a tetrahedron encapsulating a large sulfur, or arsenic atom.[99]



(6)

Other quadruply bridging species have been synthesized by treatment of [S(Au$_2$dppf)] with two equivalents of [AuX(PR$_3$)] (PR$_3$ = PPh$_3$, PPh$_2$Me; X = ClO$_4$, OTf) which affords the complexes [S(Au$_2$dppf)(AuPR$_3$)$_2$]X$_2$.[58] The structure of [S(Au$_2$dppf)(AuPPh$_2$Me)$_2$](ClO$_4$)$_2$ reveals a new type of structural framework, because it can be regarded as a trigonal bipyramid with one of the apical positions occupied by the lone pair of electrons of the sulfur atom and the other by a gold atom. There are intramolecular gold–gold contacts, the shortest being between the equatorial gold atoms and the gold atom perpendicular to them. The intermolecular aurophilic interactions lead to the formation of dimers (Fig. 13).

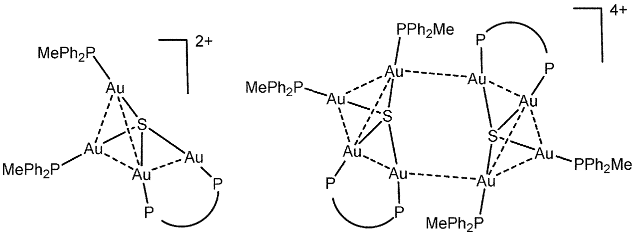


Fig. 13 Structure of the monomer and dimer of [S(Au$_2$dppf)(AuPPh$_2$Me)$_2$](ClO$_4$)$_2$.

The mixed-valence gold(I)–gold(III) derivatives [S(AuPPh$_3$)$_2$ {Au(C$_6$F$_5$)$_3$}$_2$] and [S(Au$_2$dppf){Au(C$_6$F$_5$)$_3$}$_2$] (Fig. 14) have been synthesized by reaction of two equivalents of [Au(C$_6$F$_5$)$_3$(OEt$_2$)] with [S(AuPPh$_3$)$_2$] or [S(Au$_2$dppf)] and structurally characterized.[100] The crystal structure for one of the complexes reveals a tetrahedral coordination at the sulfur centre, in contrast with the square pyramidal geometry obtained for [S(AuPPh$_3$)$_4$](OTf)$_2$. There is a short gold(I)–gold(I) interaction but no gold(III)–gold(III) or gold(I)–gold(III) contacts. The presence of the gold(III) centres causes the geometry around the sulfur to be the expected tetrahedral.

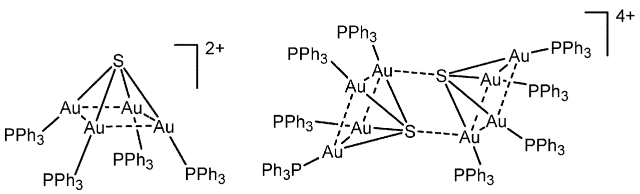


Fig. 12 Monomeric and dimeric structure of [S(AuPPh$_3$)$_4$]$^{2+}$.

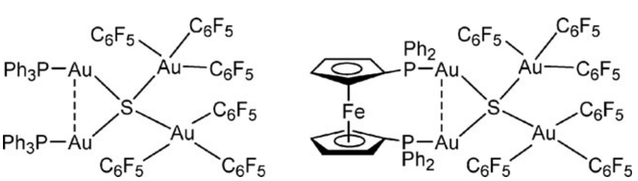


Fig. 14 Mixed gold(I)–gold(III) sulfide complexes.

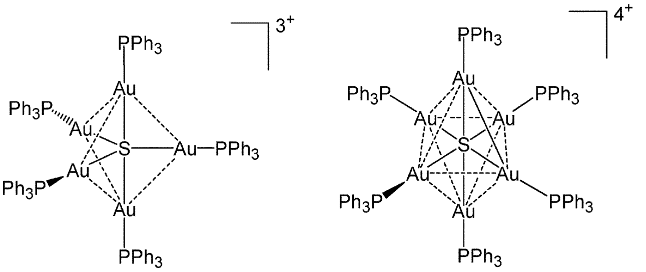


Fig. 15 Hypervalent gold(I) sulfide complexes.

Finally, an heteronuclear μ$_4$-sulfide complex has been reported, $[\{S(AuPPh_3)\}_2Ag](BF_4)_3$, obtained by treatment of $[S(AuPPh_3)_3]BF_4$ with $AgBF_4$ (eqn (6)).[101] The structure consists of two SAu_3Ag square pyramids but more distorted than in the corresponding SAu_4 unit. The silver centre is bonded to the two sulfur atoms and makes close contacts to three adjacent gold atoms.

3.4 Multiply bridging sulfide ligands

The complexes $[S(AuPPh_3)_2]$ can react with three or four equivalents of $[Au(OTf)(PPh_3)]$ to give the penta- or hexa(gold) sulfonium cations $[S(AuPPh_3)_5]^{3+}$ and $[S(AuPPh_3)_6]^{4+}$ (Fig. 15).[57] Unfortunately these complexes could not be characterized by X-ray crystallography and only analytical, conductivity and NMR data are available. The conductivity of the complexes measured in acetone is in agreement with the proposed formulae. Although there is not much data for conductivities of highly charged compounds, the tricationic complexes show values for a 3 : 1 electrolytes, and the values for the tetracationic species also seem appropriate. The $^{31}P\{^1H\}$ NMR spectra for all the homoleptic derivatives $[S(AuPPh_3)_n]^{(n-2)+}$ (n = 2–6) show a sharp single resonance, indicating the equivalence of all phosphine groups. The variable-temperature experiments confirm that all the $AuPPh_3{}^+$ fragments are equivalent, maybe because of a rapid exchange in solution even at low temperature. An upfield displacement is observed when a new gold fragment coordinates to the sulfur centre. This upfield shift has also been reported in the conversion of phosphine–gold compounds to homoleptic hypercoordinated species such as $[C(AuL)_5]^+$ and $[C(AuL)_6]^{2+}$.

4. Selenium-centred complexes

The chemistry of gold selenide complexes has been less developed than that for sulfide species. There are some coincidences in the chemistry of both chalcogens and in fact many compounds are analogous to the sulfur derivatives, but there are also an important number of differences between them.

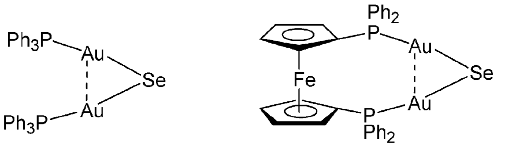


Fig. 16 Doubly bridging selenide gold complexes.

Only two complexes with a doubly bridging selenide ligand have been described so far and are $[Se(AuPPh_3)_2]$[102] and $[Se(Au_2dppf)]$[103] (Fig. 16), which have been obtained in a two-step reaction from $[AuCl(PPh_3)]$ or $[Au_2Cl_2(\mu\text{-dppf})]$ and selenourea followed by treatment with aqueous Na_2CO_3. These complexes are isostructural with the corresponding sulfur derivatives.

Other types of complexes which also have doubly bridging selenide ligands are the heteronuclear derivatives based in tetraselenometallate units. They are prepared by reaction of $[Et_4N]_2[MSe_4]$ with $[AuCl(PR_3)]$ and the most usual stoichiometry is $[Au_2(MS_4)(PR_3)_2]$, in which the gold(I) centres are three-coordinated,[104–106] although the complex $[Au_2(MS_4)(PR_3)_3]$ has also been isolated.[107] These complexes exhibit non-linear optical properties (NLO), with their absorptive and refractive properties being highly sensitive to the heavy atom effect and for the gold derivatives show large NLO absorption and large NLO refraction. The anionic complexes $[Au_2(CN)_2(MSe_4)]^{2-}$ and $[Au(CN)(MSe_4)]^-$ have also been reported.[108] The tetraselenoniobiate anion also reacts with gold compounds to give polynuclear species such as $[Au_3(NbSe_4)(PPh_3)_3]$ or $[Au_2Nb_2Se_4Cl_2(PMe_3)_6]$,[109] in which the selenide ligands are bridging two or three metal atoms. Some examples of these tetraselenometallate–gold complexes are collected in Fig. 17.

The most stable species corresponds to the tri(gold) selenonium cations. The preparative methods are similar to those described for the sulfur complex (Scheme 7). They have been described for phosphines such as PPh_3,[55,102,110] PPh_2py,[33] and $PPh_2CH_2CH_2py$,[33] and the two crystallographic reports for PPh_3 and PPh_2py show that the structures consist of $SeAu_3$ pyramids that further bond to another unit through aurophilic interactions.

The complex $[Se(Au_2dppf)]$ also serves as a building block for preparing polynuclear chalcogenide complexes.[103] The reaction of this derivative with other gold(I) compounds such as $[Au(OTf)(PR_3)]$, $[Au(tht)_2]OTf$ or $[Au_2(OTf)_2(\mu\text{-dppf})]$ leads to complexes with a μ$_3$-bridging chalcogenide ligand $[Se\{Au_2(\mu\text{-dppf})\}(AuPR_3)]OTf$ (PR_3 = PPh_3, PPh_2Me), $[Au\{Se(Au_2dppf)\}_2]OTf$ or $[\{Se(Au_2dppf)\}_2(\mu\text{-}Au_2dppf)](OTf)_2$. The latter has a structure similar to that commented for the sulfur derivative, whereas the crystal structure of $[Au\{Se(Au_2dppf)\}_2]^+$ consists of a dimer in which two

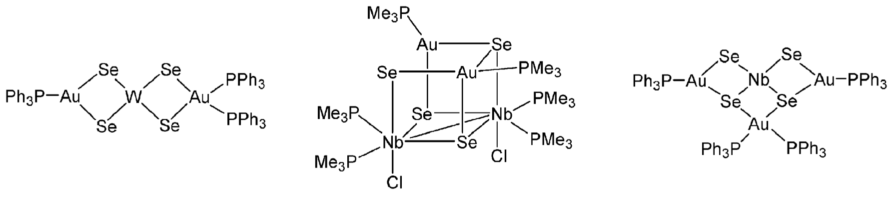
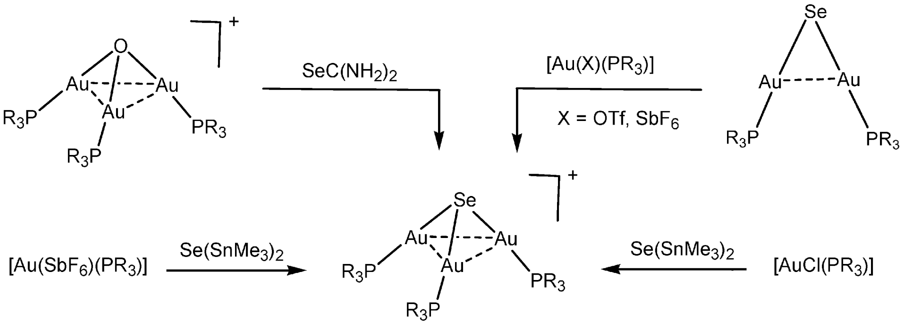


Fig. 17 Tetraselenometallate–gold complexes.



Scheme 7 Synthesis of $[Se(AuPR_3)_3]X$ complexes.

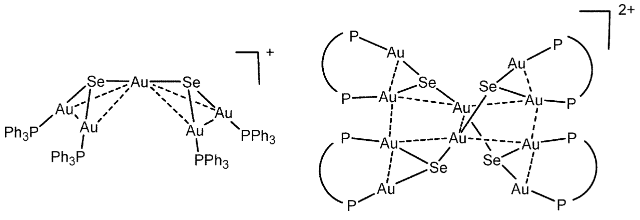


Fig. 18 Monomeric and dimeric structures of $[Au\{Se(AuPPh_3)_2\}_2]^+$ and $[Au\{Se(Au_2dppf)\}_2]^+$.

monomeric units are joined through gold–gold interactions. There are several Au···Au contacts in the range 2.908(4)–3.182(3) Å, the shortest is between the gold atoms bridging the $[Se(Au_2dppf)]$ units (see Fig. 18).[103] The analogous complex with triphenylphosphines as auxiliary ligands has been reported, $[Au\{Se(AuPPh_3)_2\}_2]Cl$, by reaction of $[AuCl(PPh_3)]$ with $^{t}BuSe(SiMe_3)$ but in this case the structure is a monomer.[111]

Polynuclear gold(I) complexes with bridging selenide and diphosphine ligands have also been described. They are prepared by reaction of $[Au_2Cl_2(\mu\text{-}P\text{–}P)]$ (P–P = $PPh_2(CH_2)_nPPh_2$, n = 1 (dppm), 2 (dppe), 5 (dppp), 6 (dpph) with $Se(SiMe_3)_2$ and the result is different depending on the diphosphine; with dppm and dppp the polynuclear derivatives $[Au_{10}Se_4(dppm)_4]Br_2$ or $[Au_{10}Se_4(dppp)_4]InCl_5$ are obtained, although with different structures, with dppe and dpph the complexes $[Au_{18}Se_8(dppe)_6]Cl_2$ and $[Au_6Se_2(dpph)_4]Br_2$ are synthesized.[111,112] The use of other diphosphines or triphosphines such as 1,4-bis(diphenylphosphino)benzene (dppbe), 4,4′-bis(diphenyphosphino)biphenyl (dppbp) or tris(diphenylphosphinoethyl)phosphine (tpep)/1-bis(diphenylphosphinoethyl)-1-(diphenylselenophosphinoethylphosphine) (tpep^{Se}) affords other species with a great variety of stoichiometries and structures, namely $[Au_2Se(dppbe)]_n$, $[(Au_3Se)_2(dppbp)_3]Cl_2$ or $[Au_{34}Se_{14}(tpep)_6(tpep^{Se})_2]Cl_6$.[113] Fig. 19 shows two examples of these polynuclear species with bridging selenide ligands.

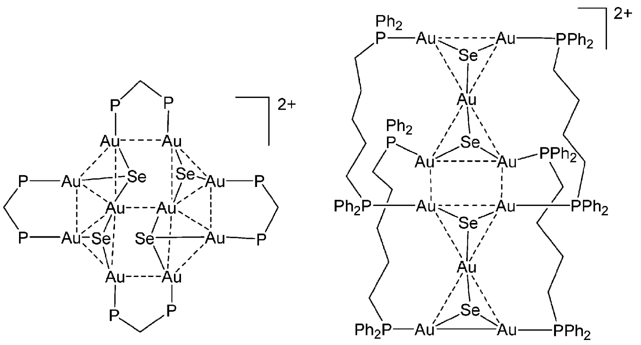
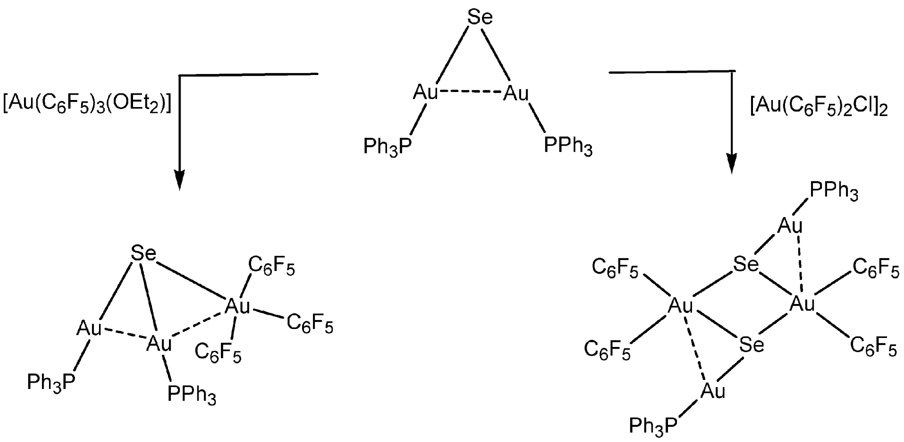


Fig. 19 Polynuclear gold(I) complexes with bridging selenide ligands.

Mixed gold(I)–gold(III) derivatives have been prepared by reaction of $[Se(AuPPh_3)_2]$ with $[Au(C_6F_5)_3(OEt_2)]$ or $[Au(C_6F_5)_2Cl]_2$ (see Scheme 8).[114] Similarly to as commented for the corresponding sulfur derivatives the crystal structures reveal the presence of weak gold(I)–gold(III) interactions.



Scheme 8 Synthesis of gold(I)–gold(III) selenide complexes.

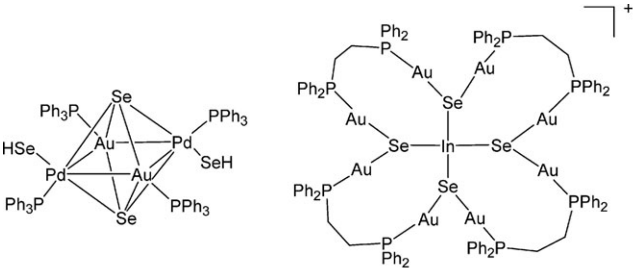


Fig. 20 Heteropolynuclear selenide complexes.

Heteropolynuclear gold derivatives with bridging selenide ligands have also been reported. The reaction of $[AuCl(PPh_3)]$ with $[Pd(acac)_2]$ and $Se(SiMe_3)_4$, in the presence of PPh_3 affords the complex $[Au_2Pd_2Se_2(SeH)_2(PPh_4)_4]$ which has a selenide ligand bridging two palladium and a one gold atom.[115] When the same reactions of gold–diphosphine complexes with $Se(SiMe_3)_2$ are carried out in the presence of $InCl_3$ or $GaCl_3$ the mixed metal selenide complexes $[Au_4(SeInCl_3)(dppp)_2]$, $[Au_4(TeGaCl_3)(dpph)_2]$ or $[Au_8Se_4In(dppe)_4](InCl_4)_3$ are obtained.[111] Finally other type of heteropolynuclear complexes with bridging selenide ligands are those arising from the reaction of the tri(gold) selenonium cations $[Se(AuL)_3]^+$ (L is a heterodifunctional phosphine), with silver or copper compounds which affords the complexes $[Se(AuL)_3M]^{2+}$ (L = PPh_2py, $PPh_2CH_2CH_2py$) and that have been commented on above.[32,33] A selection of these heteronuclear selenide derivatives are shown in Fig. 20.

The number of derivatives with quadruply bridging selenide ligands is very scarce. The homoleptic species $[Se(AuPPh_3)_4](OTf)_2$ has been prepared by reaction of $[Se(AuPPh_3)_2]$ with two equivalents of $[Au(OTf)(PPh_3)]$.[116] The structure is analogous to that of the sulfur derivative and has a square pyramidal geometry with the selenium atom in the apical position. The cations also dimerizes in the solid state through aurophilic interactions. Other quadruply bridging species have been synthesized by treatment of $[Se(Au_2dppf)]$ with two equivalents of $[Au(OTf)(PR_3)]$ (PR_3 = PPh_3, PPh_2Me) or with $[Au_2(OTf)_2(\mu\text{-dppf})]$ which affords the complexes $[Se(Au_2dppf)(AuPR_3)_2]X_2$ or $[Se(Au_2dppf)_2](OTf)_2$ (Fig. 21).[103]

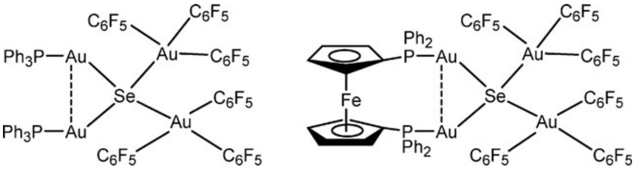


Fig. 22 Mixed gold(I)–gold(III) selenide derivatives.

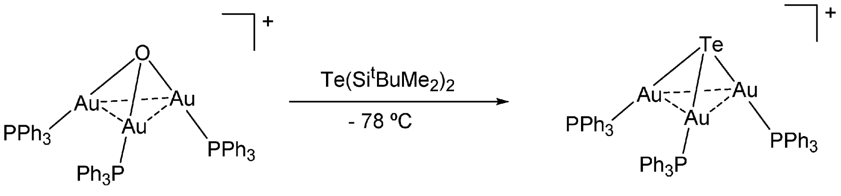
The mixed valence gold(I)–gold(III) derivatives $[Se(AuPPh_3)_2\{Au(C_6F_5)_3\}_2]$ and $[Se(Au_2dppf)\{Au(C_6F_5)_3\}_2]$ (Fig. 22) have also been synthesized by reaction of two equivalents of $[Au(C_6F_5)_3(OEt_2)]$ with $[Se(AuPPh_3)_2]$ or $[Se(Au_2dppf)]$.[114] These complexes are analogous to the sulfur derivatives.

The complexes $[Se(AuPPh_3)_2]$ and $[Se(Au_2dppf)]$ can react with three or four equivalents of $[Au(OTf)(PPh_3)]$ or $[Au_2(OTf)_2(\mu\text{-dppf})]$ to give the penta- or hexa(gold) selenonium cations $[Se(AuPPh_3)_5]^{3+}$, $[Se(AuPPh_3)_6]^{4+}$ or $[Se(Au_2dppf)_3]^{4+}$.[103] These complexes are analogous to the sulfur derivatives and could not be characterized by X-ray crystallography and only analytical, conductivity and NMR data are available. The conductivity of the complexes measured in acetone is in agreement with the proposed formulae. In the $^{31}P\{^1H\}$ NMR spectra for all the derivatives $[Se(AuPPh_3)_n]^{(n-2)+}$ (n = 2–6) an upfield shift is observed when a new $AuPPh_3{}^+$ fragment coordinates to the selenium atom.

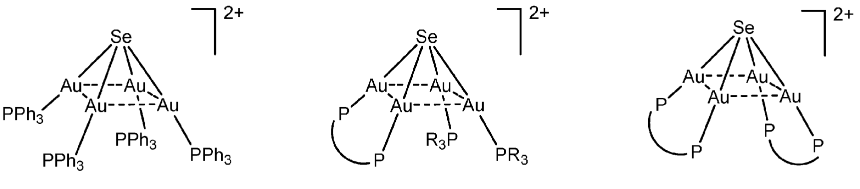
5. Tellurium-centred complexes

The preparative methods to access to poly(gold)telluronium salts are similar to those of the corresponding sulfonium or selenonium salts. The reaction of $[O(AuPPh_3)_3]BF_4$ with $Te(^tBuMe_2Si)_2$ in dichloromethane at −78 °C leads to the trinuclear complex $[Te(AuPPh_3)_3]BF_4$ (eqn (7)), however only in 33% yield.[117] With the ligand PMe_3 only decomposition products were obtained, so it seems that the tellurium complexes are more unstable than the analogous oxygen, sulfur or selenium derivatives.

The structure of $[Te(AuPPh_3)_3]BF_4$ consists of two independent cations in the asymmetric unit, each one with a trigonal

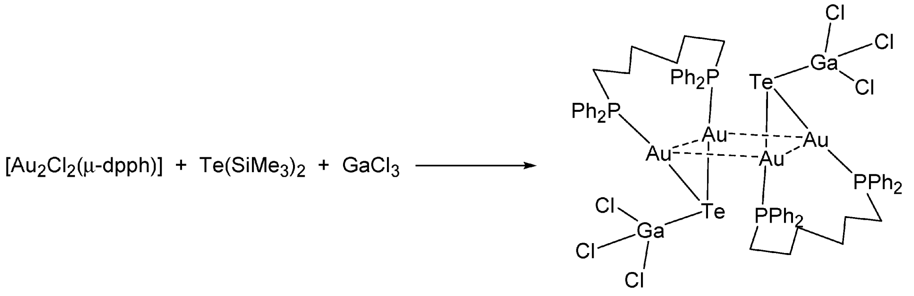


(7)



P-P = dppf; PR3 = PPh3, PPh2Me

Fig. 21 Quadruply bridging gold–selenide complexes.



(8)

pyramidal geometry and associated in centrosymmetric dimers through short aurophilic contacts. The intramolecular Au–Au distances are very dissimilar and range form 3.074(1) to 3.515(1) Å, which indicates a more distorted geometry for this salt compared with the oxonium, sulfonium or selenonium salts. The reaction of $Te(^tBuMe_2Si)_2$ with four equivalents of $[Au(BF_4)(PPh_3)]$ gives $[Te(AuPPh_3)_4](BF_4)_2$, which is also unstable and could not be crystallized, although a square-pyramidal geometry is proposed by the authors.

Another complex with a telluride bridging ligand has been prepared by reaction of $[Au_2Cl_2(\mu\text{-dpph})]$ with $Te(SiMe_3)_2$ in the presence of $GaCl_3$ (eqn (8)).[111] This complex crystallizes also as a dimer through aurophilic interactions.

6. Conclusions

The chemistry of gold chalcogenide-centred complexes has been developed in the last two decades. An important number of derivatives have been synthesized for oxygen, sulfur and selenium, though gold–telluride complexes are poorly represented, probably because of their instability. The complexes have special characteristics such as unusual geometries, *e.g.* the square pyramidal geometry for $[E(AuPPh_3)_4](OTf)_2$ (E = S, Se) instead the expected tetrahedral, electron deficiencies as a consequence of the fact that the chalcogen atoms still possesses the lone pair of electrons in the apical position, or formation of hypervalent species. Another important feature is the general presence of Au(I)···Au(I) interactions that contributes substantially to the stability of the complexes, and also weak Au(I)···Au(III) interactions. Furthermore, these complexes present interesting properties such as luminescence, with absorption originating in chalcogenide to metal charge transfer transitions, modified by the Au···Au interactions. In the species $[E(AuPPh_2py)Ag]^{2+}$ (E = O, S, Se) the change in the chalcogenide provokes a dramatic change in the energy of the emission, or non-linear optical properties.

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