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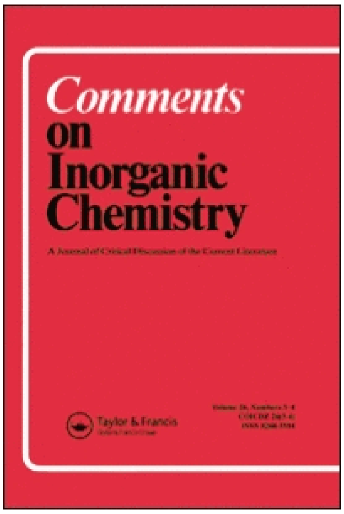

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CHALCOGENIDE CENTERED GOLD COMPLEXES

M. Concepción Gimeno[a]; Antonio Laguna[a]
[a] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, Zaragoza, Spain

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CHALCOGENIDE CENTERED GOLD COMPLEXES

M. CONCEPCIÓN GIMENO
ANTONIO LAGUNA

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, Zaragoza, Spain

INTRODUCTION

The last years have witnessed the development of a fascinating chemistry where phosphino-gold fragments coordinate around a central heteroatom.[1–5] The species formed are exciting not only from the experimental and structural but also from the theoretical standpoint. Thus interesting hypercoordinated species[6–10] 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 or molecular or solid state structures. Many of the heteroatom-centered 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, for these reasons 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

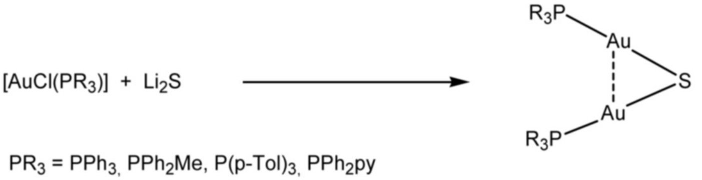
Address correspondence to Antonio Laguna, Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain. E-mail: antlag@yahoo.com

chemical calculations.[11–14] 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 advance calculations has shown that bonding between closed-shell metal atoms or ions may be strongly enhanced by these effects.[15–23] 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.[20,23] All these studies have consistently shown that calculations will reproduce the attractive forces between the gold atoms well only if relativistic affects are included.

Here we present an overview of our results in the synthesis and reactivity of chalcogen-centered derivatives. Most of the work has been developed with sulfur and selenium, and has been divided according to the nuclearity of the bridging chalcogenide ligands. The chemistry of the oxonium complexes is mostly limited to the μ_3-O, although a μ_4-O species have been isolated by Schmidbaur et al.[24] whereas for the sulfide and selenide μ_4-E, μ_5-E and μ_6-E complexes have been isolated. Furthermore, the results obtained with sulfur and selenium are very similar. The chemistry of tellurium-centered derivatives has not been explored because the only complex characterized $[Te(AuPPh_3)_3]BF_4$ is the most unstable of the chalcogenides.[25]

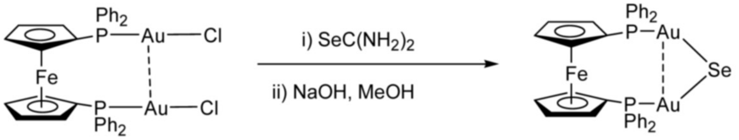
Doubly Bridging Chalcogenide Ligands

The chemistry of doubly bridging chalcogenide ligands is limited to the sulfur and selenium atoms; no gold(I) compound with a μ_2 oxide or telluride ligand is known. The complex $[S(AuPEt_3)_2]$ was synthesized by Kowala and Swan a long time ago 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.[26] We have developed a high yield synthesis for the gold(I) species $[S(AuPR_3)_2]$ or $[S(Au_2dppf)]$ that involves the reaction of $[AuCl(PR_3)]$ or $[Au_2Cl_2(\mu\text{-dppf})]$ with Li_2S in ethanol; the desired products precipitate in ethanol and are obtained in almost quantitative yield (Eq. 1).[27,28]



(1)

The corresponding $[Se(AuPR_3)_2]$ or $[Se(Au_2dppf)]$ have been obtained in a two–step reaction from $[AuCl(PR_3)]$ or $[Au_2Cl_2(\mu\text{-dppf})]$ and selenourea followed by treatment with aqueous Na_2CO_3 (Eq. 2).[29,30] These complexes are excellent starting materials for the synthesis of highly aurated homoleptic sulfur- or selenium-centered derivatives.



(2)

The structures for the sulfur or selenium complexes with the bidentate 1,1′ -bis(diphenylphosphino)ferrocene show the chalcogenide atom bridging both gold centers with a short aurophilic interaction. The angles Au-E-Au are very narrow, 77.57(9) and 79.1(1)° for the sulfur and selenium derivatives, respectively, which favors the presence of a shorter gold-gold contact. 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 $[E(AuPR_3)_2]$ ($E = S$, Se) should be isolobal. However, their behavior is very different because no gold complexes with the 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 good Lewis base. This is a common feature in these type of complexes as, 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.

Triply Bridging Chalcogenide Ligands

The oxonium gold complexes $[O(AuPR_3)_3]^+$ were the first chalcogenide-centered complexes, reported by Nesmejanov et al. many years ago.[31] A convenient synthesis is the reaction of $[AuCl(PR_3)]$ with Ag_2O in the presence of $NaBF_4$. This method has been used to prepare this type of complex with a large number of phosphine ligands.[32–36] We have synthesized the oxonium derivatives with heterofunctional phosphine ligands, $[O(AuPPh_2py)_3]BF_4$ or $[O(AuPPh_2CH_2CH_2py)_3]BF_4$, following the same procedure (Eq. 3).[37]

$$[AuCl(PPh2py)] + Ag_2O + NaBF_4 \longrightarrow [O(AuPPh_2py)_3)]BF_4 \qquad (3)$$

The solid state structure of these derivatives depends on the size of the phosphine ligand used. Thus, for more sterically demanding phosphines, such as $P(C_6H_4Me\text{-}2)_3$,[32] P^iPr_3,[35] or $P(NMe_2)_3$,[36] the structure consists of a trigonal OAu_3 pyramid with the oxygen atom in the apical position. The coordination of the gold atoms is nearly linear and there are intramolecular AučAu contacts. For other phosphine ligands the structure is also based on $[O(AuPR_3)_3]^+$ cations, which undergo dimerization through intermolecular aurophilic interactions (Figure 1).

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 $[O(AuPR_3)_2]$ suggests 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 intra-molecular interactions of gold atoms.

The tri(gold)sulfonium or selenonium cations are very stable complexes than can be prepared by reaction of $[E(AuPR_3)_2]$ with $[Au(OTf)(PR_3)]$ or by treatment of the oxonium species $[O(AuPR_3)_3]^+$ with thiourea or selenourea, respectively (see Scheme 1). We have prepared these compounds with several phosphine ligands, as PPh_2Me, $P(p\text{-}Tol)_3$, $PPh_2py\text{-}R\text{-}4$ ($R = H$, Me). The structure of these sulfur or selenium species is similar to that of the oxonium ones, trigonal EAu_3 that dimerizes through aurophilic interactions.[27,28,30,37,38]

The complexes $[E(AuPPh_3)_2]$ and $[E(Au_2dppf)]$ serve as building blocks for prepararing polynuclear chalcogenide complexes. The reaction of these derivatives with another gold(I) fragment leads to complexes with

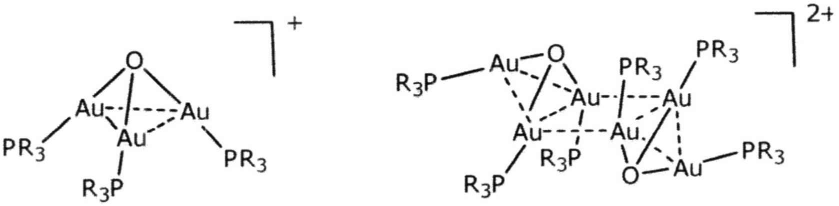
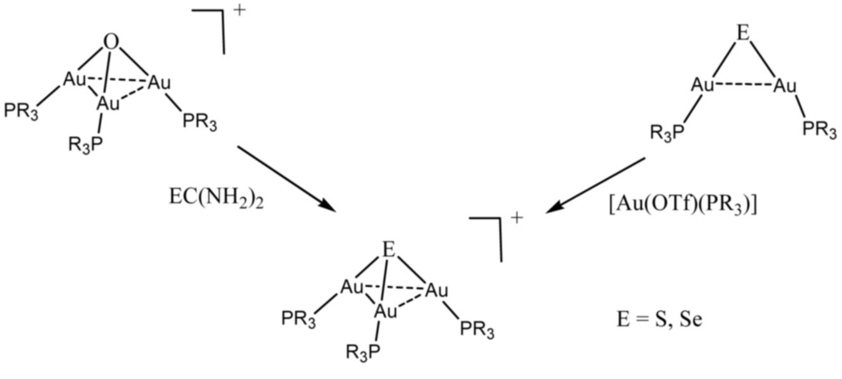


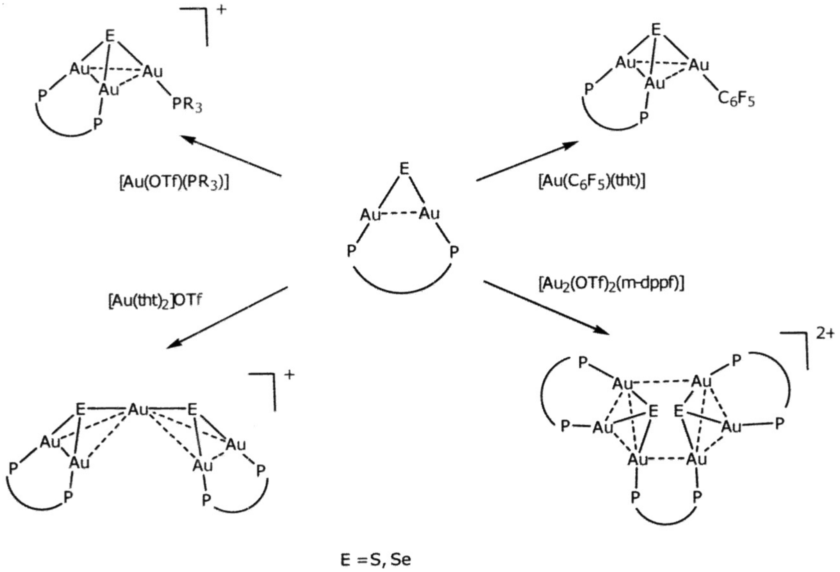
Figure 1.



Scheme 1.

a μ_3-bridging chalcogenide ligand as exemplarized for the diphosphine complexes shown in Scheme 2.[28,30]

The crystal structure of $[Au\{Se(Au_2dppf)\}_2]^+$ consist of a dimer, two monomeric units 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 Figure 2).[30]



Scheme 2.

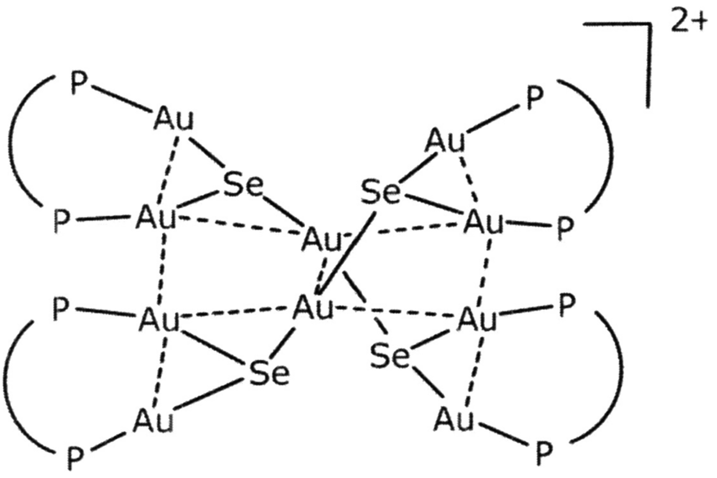


Figure 2.

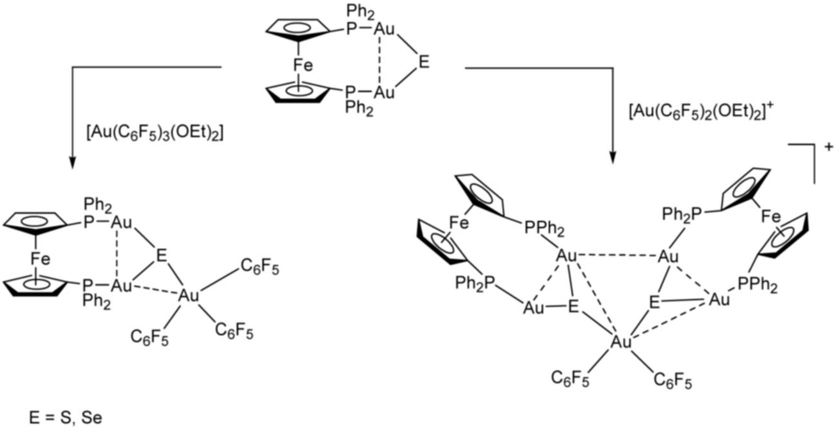
The complexes $[\{E(Au_2dppf)\}_2(\mu\text{-}Au_2dppf)]^{2+}$ have a E_2Au_6 core with short intramolecular gold-gold interactions. It is worth mentioning that the $^{31}P\{^1H\}$ NMR spectra of these compounds at low temperature show three resonances, indicating the inequivalence of all phosphorus atoms, probably as a consequence of the different gold-gold interactions, which can be observed at low temperature.

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 3).[39,40]

The crystal structures of these complexes show short gold(I)-gold(III) contacts, which range 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, also weaker than the corresponding gold(I)-gold(I), and with bond energies in the range 21–25 kJ mol^{-1}.[39–42]

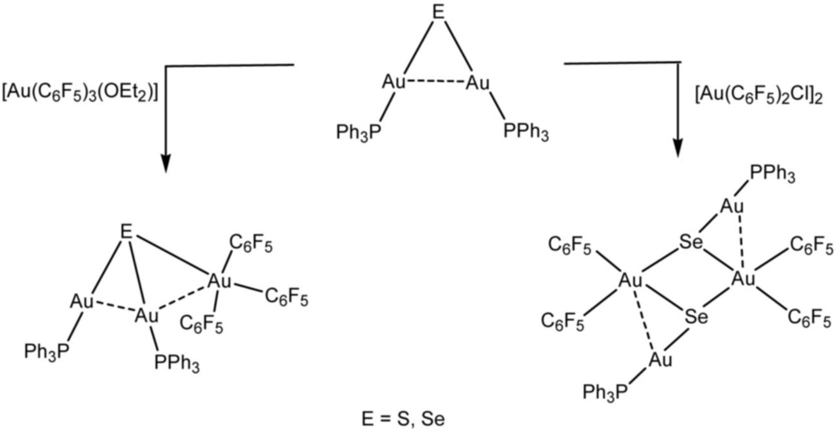
In a similar manner and starting from $[E(AuPPh_3)_2]$ the reaction with $[Au(C_6F_5)_3(OEt_2)]$ or $[Au(C_6F_5)_2Cl]_2$ leads to the mixed gold(I)-gold(III) species $[E(AuPPh_3)_2\{Au(C_6F_5)_3\}]$ or $[\{E(AuPPh_3)\}_2\{\mu\text{-}Au(C_6F_5)_2\}_2]$ (see Scheme 4).[39,40]

Taking into account the isolobal relationship between the H^+, $AuPPh_3^+$ and $AgPPh_3^+$ the anionic species $NBu_4[S(MPPh_3)\{Au(C_6F_5)_3\}_2]$ (M = Ag, Au) have been prepared by reaction of

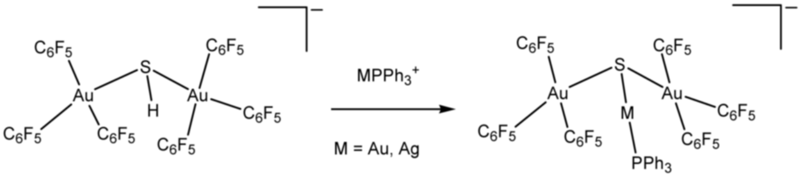


Scheme 3.

$NBu_4[S(H)\{Au(C_6F_5)_3\}_2]$ with $MPPh_3^+$ cations in the presence of Na_2CO_3 (Eq. 3).[43] 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 calculations treatments including relativistic effects.[44–46]

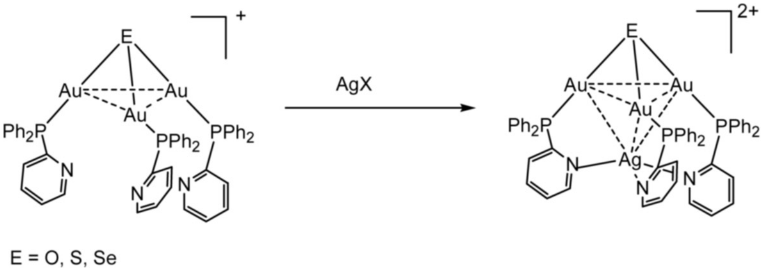


Scheme 4.



(3)

The complexes $[E(AuPPh_2py)_3]^+$ (E = O, S, Se) posses a difunctional ligand, the 2-diphenylphosphinopyridine, which can be also used to coordinate to other metal fragments, for example silver. Therefore the reaction of these trinuclear species with AgOTf or $AgBF_4$ gives the tetranuclear clusters $[E(AuPPh_2py)_3Ag]^{2+}$, which have a tetrahedral Au_3Ag core with short Au···Au and Au···Ag interactions and bridging phosphine ligands (Eq. 4).[38]



(4)

The structures for the three chalcogenides are isostructural, and for sulfur and selenium 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 others found in complexes with appreciably metallophilic bonding. Aurophilic interactions also link two Au_3Ag tetrahedron together (see Figure 3) with an Au···Au distance of 3.0539 A. The metallophilic interactions and the bridging PPh_2py ligands confer greater structural rigidity and integrity 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 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 behavior 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

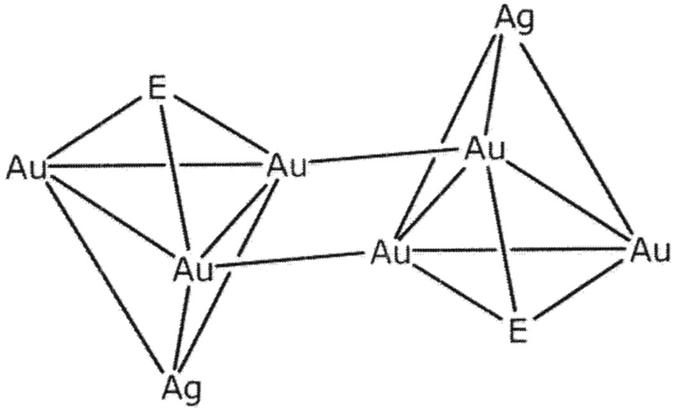
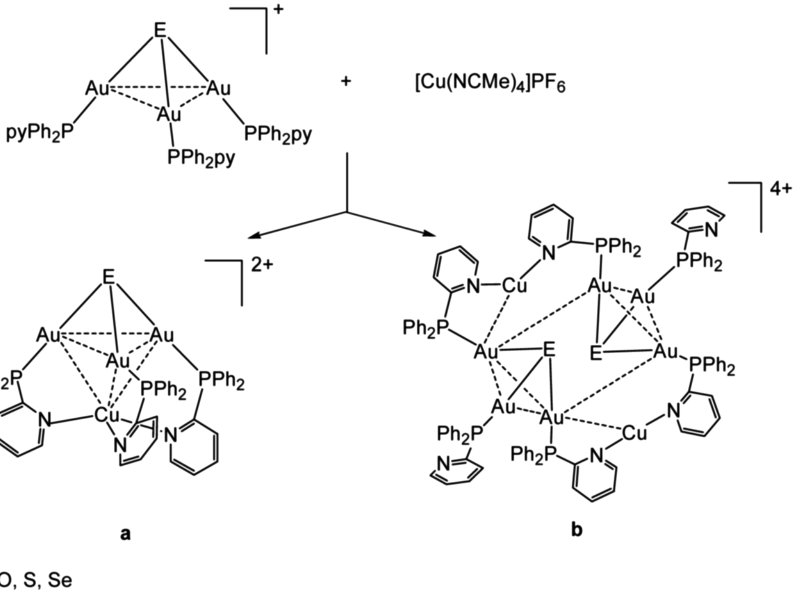


Figure 3.

from oxygen, significantly at higher 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 that the lone pair orbitals lie lowest in O, next in S, and highest in Se, an assignment consistent with the emission results in that of a ligand-to-metal-metal- charge transfer (^{3}LMMCT).

As a consequence of the interesting luminescence properties of this type of complexes, we investigated the reaction with other metal centers such as copper(I).[37] 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 that the silver derivatives possess, but in this case, as concluded by NMR and X-ray diffraction studies, there are a mixture of two coordination isomers **a** and **b**, as shown in Scheme 5. At room temperature isomer **a** shows only one resonance for the equivalent phosphorous atoms and isomer **b** two resonances in an approximate ratio 2:1.

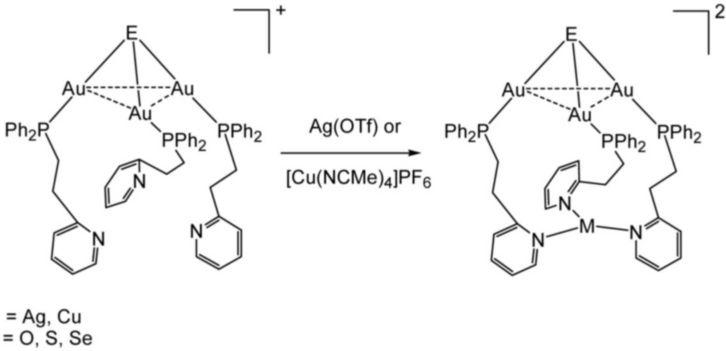
The first isomer **a** is analogous to the silver complexes and in the second, **b**, two $[S(AuPPh_2py)_3]^+$ units bridge two copper atoms through one pyridine group in each unit. For the oxygen and selenium derivatives, isomer **b** is the major component and for sulfur the ratio can be varied changing 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 favored. The luminescence behavior of these complexes has been studied and also shows a variation of the energy of the emissions depending on the chalcogenide. Consequently,



Scheme 5.

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-centered (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 (Eq. 5).[37]



(5)

In these complexes the nitrogen atoms bind the silver or copper atoms but the crystal structure of the copper derivative with sulfur reveals the

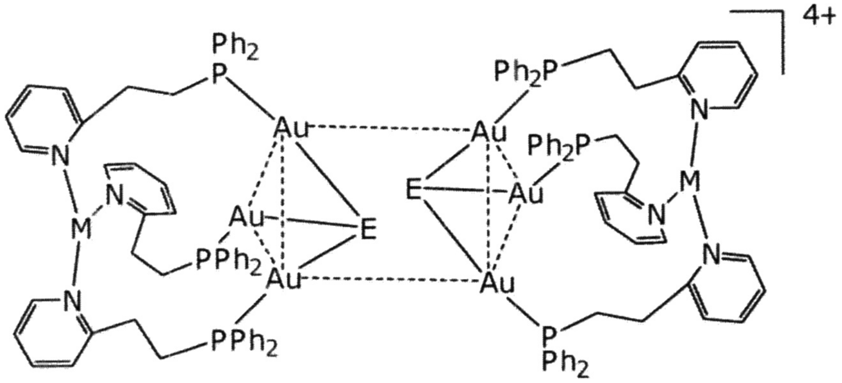


Figure 4.

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 (Figure 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.

Quadruply Bridging Chalcogenide Ligands

The discovery that $[E(AuPPh_3)_2]$ or $[E(AuPPh_3)_3]^+$ can add additional $AuPPh_3^+$ units led to the preparation of the unprecedented tetra(gold) sulfonium or selenonium(2+) salts $[E(AuPPh_3)_4]^{2+}$ ($E = S$, Se).[47,48] Both structures are analogous and have a square pyramidal structure with the sulfur or selenium atoms occupying the apical position, clearly at variance with any of the classical rules of structure and bonding, which demand chalcogenide-centered tetrahedral complexes similar to $[O\{AuP(o\text{-}Tol)_3\}_4]^{2+}$.[24] There are short metal-metal distances between the golds atoms, which are not exactly coplanar, but arranged in a flattened butterfly shape. The molecules arrange into dimers through aurophilic interactions (Figure 5). The EAu_4 core should be regarded as electron-deficient, considering the sulfide or selenide ligands to serve as a six-electron donor. Therefore they still possess a lone pair of electrons in the apical position, which means that further coordination of gold around the sulfur or selenium atoms is conceivable.

There is precedent for a non-classical pyramidal structure in the analogous tetra(gold)arsonium cations $[As(AuPPh_3)_4]^+$,[49] which one

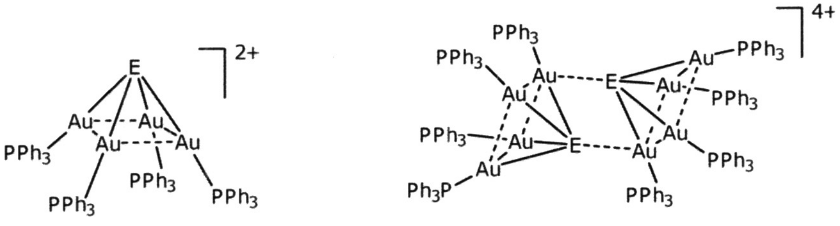


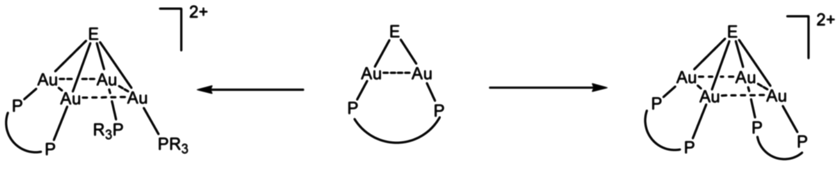
Figure 5.

would expect to be tetrahedral as required for standard arsonium salts of AsR_4^+. The calculations made with *ab initio* or density functional methods, including relativistic effects, show that this system is lower in energy with close contacts between the gold atoms, which is very easy in a square pyramid and impossible in a tetrahedron encapsulating a large sulfur, selenium or arsenic atom.[50]

Other quadruply bridging species have been synthesized by treatment of $[E(Au_2dppf)]$ with two equivalents of $[AuX(PR_3)]$ ($PR_3 = PPh_3$, PPh_2Me; $X = ClO_4$, OTf) or with $[Au_2(OTf)_2(\mu\text{-}dppf)]$, which affords the complexes $[E(Au_2dppf)(AuPR_3)_2]X_2$ or $[E(Au_2dppf)_2](OTf)_2$ (Scheme 6).[28,30]

The structure of $[E(Au_2dppf)(AuPPh_2Me)_2](ClO_4)_2$ 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 (Figure 6).

The mixed valence gold(I)-gold(III) derivatives $[E(AuPPh_3)_2\{Au(C_6F_5)_3\}_2]$ and $[E(Au_2dppf)\{Au(C_6F_5)_3\}_2]$ (Figure 7) have been synthesized by reaction of two equivalents of $[Au(C_6F_5)_3(OEt_2)]$ with



E = S, Se; P-P = dppf; $PR_3 = PPh_3$, PPh_2Me

Scheme 6.

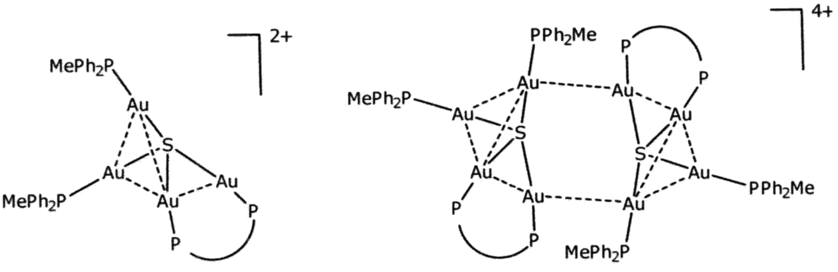


Figure 6.

[$E(AuPPh_3)_2$] or [$E(Au_2dppf)$] and structurally characterized.[40,51] The crystal structure for one of the complexes reveals a tetrahedral coordination at the sulfur center, in contrast with the square pyramidal geometry obtained for [$E(AuPPh_3)_4$]$(OTf)_2$. There is a short gold(I)-gold(I) interaction but no gold(III)-gold(III) nor gold(I)-gold(III) interactions. The presence of the gold(III) centers makes the geometry around the sulfur the expected tetrahedral.

Multiply Bridging Chalcogenide Ligands

The complexes [$E(AuPPh_3)_2$] can react with three or four equivalents of [$Au(OTf)(PPh_3)$] to give the penta or hexa(gold) sulfonium or selenonium cations [$E(AuPPh_3)_5$]$^{3+}$ and [$E(AuPPh_3)_6$]$^{4+}$.[27] 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

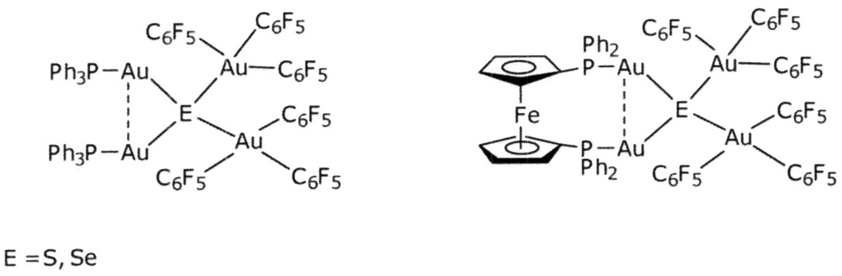
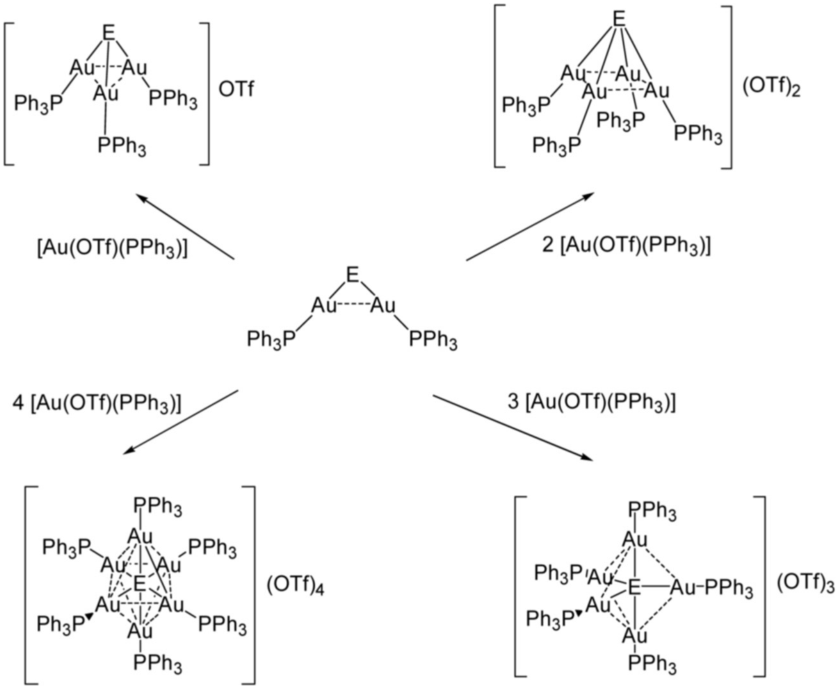


Figure 7.

Table 1. $^{31}P\{^1H\}$ NMR data for $[E(AuPPh_3)_n]^{(n-2)+}$ (n = 2–6)

Complex	S	Se
$[E(AuPPh_3)_2]$	36.3	37.3
$[E(AuPPh_3)_3]OTf$	33.5	34.7
$[E(AuPPh_3)_4](OTf)_2$	32.4	33.5
$[E(AuPPh_3)_5](OTf)_3$	32.2	32.6
$[E(AuPPh_3)_6](OTf)_4$	31.5	31.7

conductivities of highly charged compounds, the tricationic compounds show values for 3:1 electrolytes, and the values for the tetracationic species also seems appropriate. The $^{31}P\{^1H\}$ NMR spectra for all the homoleptic derivatives $[E(AuPPh_3)_n]^{(n-2)+}$ (n = 2–6) show a sharp single resonance, indicating the equivalence of all phosphine groups. The variable-temperature experiments confirm that all the $AuPPh_3^+$



Scheme 7.

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 or selenium center. This upfield shift has also been reported in the conversion of phosphine-gold compounds to homoleptic hypercoordinated species such as $[C(AuL)_5]^+$ and $[C(AuL)_6]^{2+}$. Table 1 shows the chemical shift for the homoleptic sulfur and selenium species.

In Scheme 7 an overview of the synthesis of the hypercooordinated sulfur or selenium-centered species starting from the dinuclear complexes is shown.

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