Metal–metal bonds in a Au_5 chain and other species

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(Received September 29, 1993)

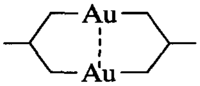
Abstract

The formation of gold–gold bonds in polynuclear compounds having both supported and unsupported bonds is analysed from an electronic point of view, based on results from extended Hückel calculations. The starting point is the complex $[[\{Au(CH_2)_2PPh_2\}_2R]_2AuR_2]^+$ ($R{=}C_6F_5$), containing a pentanuclear gold chain, with two different types of bond: inner bonds have no bridging ligands formed and are between gold atoms in a lower oxidation state; outer, stronger bonds involve gold atoms in higher oxidation state and are spanned by the bidentate ligands. Different factors, such as the nature of the ligand donor atom, the formal oxidation state of the metal atoms, the presence of bulky ligands near them, are discussed. For instance, ligands containing carbon donor atoms lead to stronger Au–Au bonds than those having sulphur donor atoms and the strongest bonds are observed when Au^{III} is involved. Metal-metal bonds are found to be present in a great number of compounds having formally Au^I d^{10} metals, and in some cases distortions take place in order to allow them to form, unless that is forbidden on steric grounds.

Key words: Gold; Extended Hückel calculations; Bridging ligands; Metal–metal bonds

1. Introduction

Many compounds containing more than one gold atom, ranging from simple dinuclear complexes to complicated multinuclear clusters, have been synthesized and structurally characterized [1]. A large number among the compounds of low nuclearity contain gold in a formal oxidation state I, with a d^{10} electronic configuration. In spite of this, short Au–Au bond distances can be found and metal–metal bonds have been shown to exist in many species. A typical environment observed, for instance, in dinuclear molecules, is sketched in **a**, with typical Au ··· Au distances of 2.8 Å.



a

Each gold is bonded to two donor atoms, one of each bidentate ligand, forming a weak metal–metal bond with the second gold atom, therefore achieving a T-type geometry. In this situation, the existence of a metal–metal bond has been explained using the results of extended Hückel calculations, by the mixing of s and p orbitals into the d set [2]. Similar bonds are formed for other d^{10}–d^{10} atoms, such as silver and copper. *Ab initio* calculations have indicated an attractive interaction between gold atoms in $ClAuPH_3$ fragments even at relatively long distances [3]. This theoretical work was prompted by the existence of the remarkable $(AuPPh_3)_6C$ cluster where the carbon atom occupies the centre of an octahedron, but the Au–Au edges are suspiciously long [4]. Recently, a database analysis of Au ··· Au interactions was carried out [5]. In order to achieve a better understanding of the formation of Au–Au bonds, taking into account the electronic aspects of the problem, we looked for different types of these bonds, specially unsupported ones, where the adjoining gold atoms are not bridged, and studied

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0022-328X/94/$7.00
SSDI 0022-328X(93)24230-3

gold–gold interactions using extended Hückel calculations [6].

2. Polynuclear gold complexes: the Au_5 chain

One difficulty in discussing metal–metal interactions is how to define a bond. The Au ··· Au distances in the Cambridge Database [5] range from 2.50 to 4.00 Å, and may be compared with the intermetallic separation of 2.88 Å for metallic gold [7]. The question we want to address is how to find whether there is a bond. Let us consider again the structural type described in a. Calculations of several authors for this and related systems [2,12] have indicated a significant interaction between the two metal atoms, which may be described as a weak bond. What happens is that two formally d^{10} metal atoms interact. This would not lead to a bond, but s and p orbitals can mix into the d set, transforming the repulsive interaction between two closed shells into an attractive one. Such a situation is reminiscent of the extremely weak bond in the Be_2 molecule [8]. The two s^2 beryllium atoms seem to be involved in a 4-electron repulsive interaction. However, mixing of p orbitals into the σ_s anti-bonding orbital relieves part of the antibonding character and allows the formation of a very weak Be–Be bond [8].

Searching for a suitable species which might contain a single Au–Au bond, we looked for compounds having unsupported Au–Au groups, that is, with no bridge between the two (or more) metal atoms and found the pentanuclear chain complex, $[\{[Au(CH_2)_2PPh_2]_2R\}_2AuR_2]^+$ ($R{=}C_6F_5$) [9]. In the structure (Fig. 1), there are two different types of gold–gold bond, the inner ones (i), between the central gold and its neighbours, and the other two, the outer ones (o). They differ, among other factors, because in the latter there are two bidentate ligands bridging the gold atoms, while the first one is an unsupported bond.

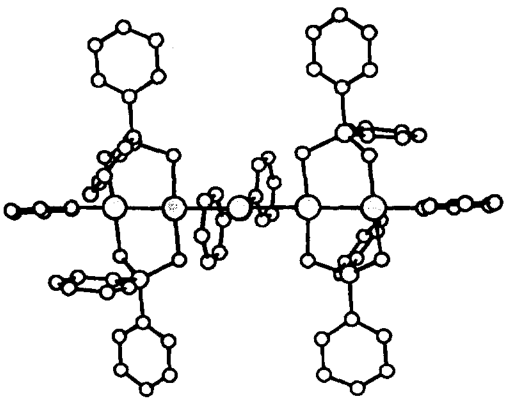


Fig. 1. The structure of the cation $[\{[Au(CH_2)_2PPh_2]_2R\}_2AuR_2]^+$ ($R{=}C_6F_5$). The Au atoms are shaded and both hydrogen and fluorine atoms are omitted for clarity.

The gold distances are 2.755 (inner) and 2.640 Å (outer). Other complexes will be described later, but in order not to lengthen the discussion too much, gold clusters will not be considered systematically. Besides having been the object of many studies on their own [10] and being quite well known, they are not particularly relevant to our purpose.

3. Bonding in the Au_5 chain

In most calculations a model chain for $[\{[Au(CH_2)_2PPh_2]_2R\}_2AuR_2]^+$ ($R{=}C_6F_5$) was used, where both the R and Ph groups were replaced by hydrogen atoms, as the results are not affected significantly. All the gold–gold distances were set to 2.70 Å. A good indicator for the strength of a bond is the overlap population. The two types of bonds have, in the real chain and in the simplified model, overlap populations of 0.139, 0.120 (inner) and 0.177, 0.185 (outer), respectively. These indicate that the inner bond should be weaker than the other, a conclusion which is consistent with the longer Au–Au distance observed. The change introduced by using the simple model does not affect the conclusion qualitatively.

Another factor which has to be taken into account is the formal oxidation state of the metal atoms. It is well known that bond strengths and bond lengths depend on the oxidation state of the elements involved, leading, therefore, to definitions of a radius for each oxidation state of an element. Going back to the Au_5 chain, there is a global 9 + charge for all the gold atoms. Our calculations can be used to assign formal oxidation states to the metals. Indeed, in the model chain, the central gold (Au1) has a -0.017 charge, the adjacent (Au2) a -0.03 charge and finally the outer (Au3) a 0.25 charge. Taking into account Pauling's principle of electroneutrality and the total charge of the gold chain, this result leads us to propose that Au1 and Au2 are formally Au^I, while the two outer Au3 are Au^{III}, but we shall return to this problem later. Au^{III} would be involved in the outer, shorter bond, as intuitively expected.

In order to analyse the bonding in the complex, a possible starting point is the interaction between the central gold fragment AuH_2^{-1} and two $\{AuH(CH_2)_2PH_2\}_2^+$ groups, which is shown in Fig. 2.

The two gold–gold bonds formed can be analysed as two components: combination of the symmetric orbitals of the first fragment, based on non-bonding $d_{x^2-y^2}$ and d_{z^2}, and a σ^* level resulting from interaction with the two hydride hydrogenations with an appropriate symmetric combination of molecular orbitals of the second

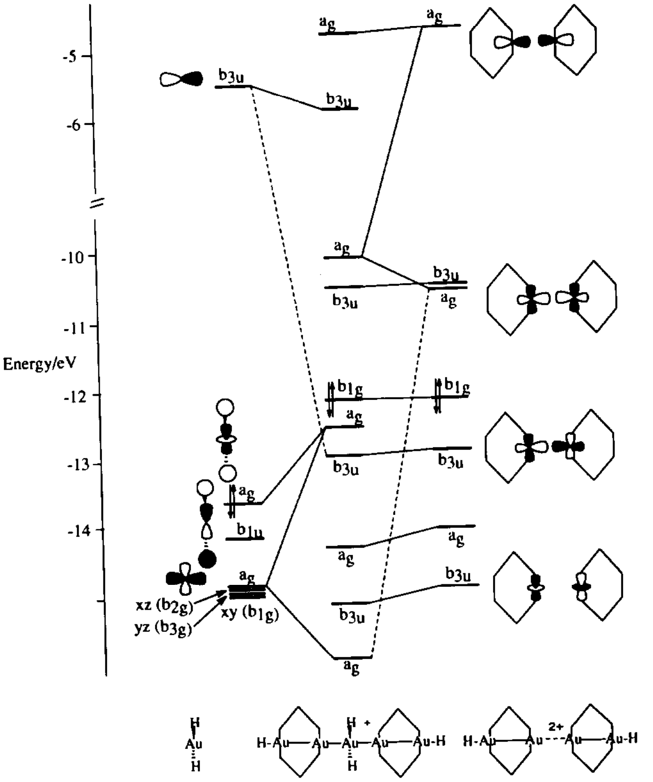
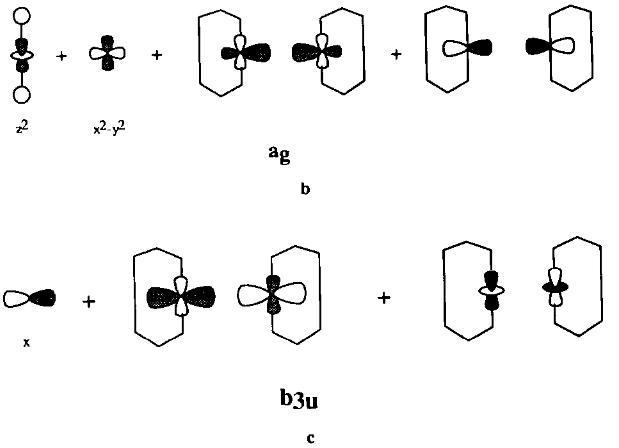


Fig. 2. Diagram of the interaction between the central gold fragment AuH_2^{-1} and the two $AuH_2(CH_2)_2PH_2^+$ groups in the chain. For simplicity only the selected orbitals are shown in the diagram.

fragment, **b**; and combination of an antisymmetric orbital of AuH_2, x, with the antisymmetric linear combination of orbitals from the second fragment, **c**. They can be thought of as single metal–metal bonds.



This is a simplified picture of the bonding in this relatively big molecule. There are many other orbitals of the same symmetry (a_g or b_{3u}) which mix in. Some of them can be seen in the molecular orbital diagram of Fig. 2. In contrast, the interaction between $x(b_{3u})$ and the linear combinations of orbitals belonging to the second fragment (antisymmetric) is much smaller than the other (symmetric), as a result of the very large energy difference between fragment orbitals. Once again, the p orbitals of gold play a big role in the formation of these bonds. This is not surprising since the gold atoms forming the bonds are indeed formally Au^I. Before proceeding, we should study the second type of gold–gold bond in the chain, which we call the outer bonds.

A second model has to be used for this analysis, as the presence of the bidentate $(CH_2)_2PPh_2^+$ without further assumptions prevents the hypothetical decomposition of the chain in the simplest way. For this reason, $[Au_5H_4(CH_3)_8]^{3-}$ was used. The Au–Au overlap populations are not significantly altered, the inner bond being still the weakest (overlap populations 0.131 and 0.218). Now the fragments are $Au_3H_2(CH_3)_4^{3-}$ and two $AuH(CH_3)_2$ groups, and their interaction is represented in a simplified way in Fig. 3.

This diagram is qualitatively different from Fig. 2, because two of the gold atoms are formally Au^{III}, d^8, and therefore one of the d orbitals is empty and can receive electrons from the other fragment. The empty d orbital is $d_{x^2-y^2}$, pushed up in energy by its antibonding interaction with the terminal ligands (H^- or CH_3^- in our model), but by not too much, owing to bonding mixing of high lying p_x.

The two bonds formed, based again on the symmetric and the antisymmetric interactions between appropriate orbitals in each fragment, as sketched in the diagram of Fig. 3, can also be considered single bonds. They are stronger than the first type of bond analysed (the inner bonds) essentially owing to much better

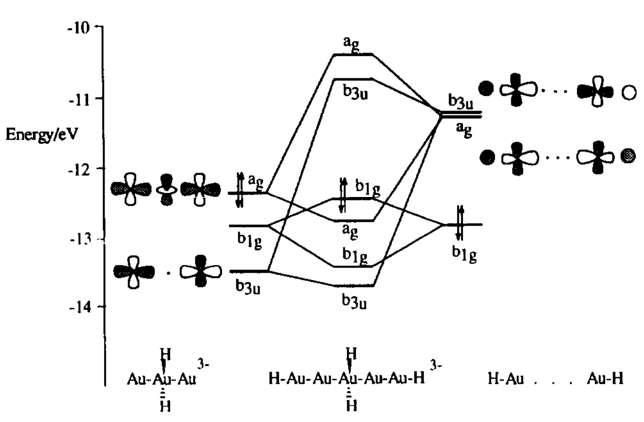
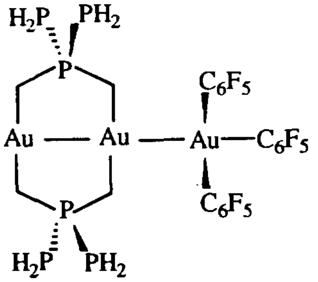


Fig. 3. Diagram of the interaction between the central gold trinuclear fragment $Au_3H_2(CH_3)_4^{3-}$ and the two $AuH(CH_3)_2$ groups in the model $[Au_5H_4(CH_3)_8]^{3-}$ chain. The methyl groups attached to each gold atom are not included in the figure.

energy matching between interacting orbitals. Notice that in spite of the movement of electrons being from the central fragment to the outside fragment, the bonding molecular orbitals are much more localized on the first and the formal oxidation states assigned to each metal should not be reversed. This is, of course, a direct consequence of the σ^* antibonding character of the d orbitals of $AuH(CH_3)_2$ involved.

The analysis of the two types of Au–Au bond shows that stronger bonds occur between Au^{III} and Au^{II}, rather than between Au^I and Au^I, reflecting the availability of a good acceptor orbital in the first case.

There is a related Au_3 chain, $[\{[Au(CH_2)_2PPh_2]_2\}AuR_3]$ ($R=C_6F_5$), represented schematically in **d**, which is at first sight very similar.



d

In this chain, the real Au–Au distances are 2.769 and 2.572 Å for the bond across the ring and the exo-bond, respectively. Calculated overlap populations for these distances are 0.098 and 0.219, respectively, and change to 0.117 and 0.182 when a separation of 2.70 Å is taken for the two bonds. This is the opposite of what was observed for the longer chain, that is, the unsupported bond is stronger. However, the calculated net charges are −0.158, −0.065 and 0.210 from left to right, and this result is understandable as they correspond to Au^I, Au^I and Au^{III}. Again, Au^{III} takes part in the strongest and shortest bond. The presence of a C_6F_5 ligand *trans* to the $\{Au(CH_2)_2PPh_2\}_2$ group indicates that a qualitative analysis of the bond, as in the previous case, can be assumed.

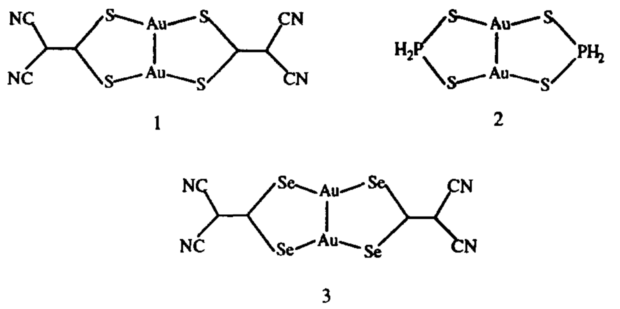
Replacing C_6F_5 by $\{Au(CH_2)_2PPh_2\}_2R$ to form the Au_5 chain changes significantly the gold atom to which these groups are coordinated. We now consider some other compounds, even though other members of this family are available [11].

4. Au–Au bonds in eight-membered rings containing S or Se donor atoms

The type of structure represented in **a** above is very similar to the outer part of the Au_5 chain, if one omits the terminal ligand. The bonds between gold atoms in this class of complex have been well studied [2,12] and the gold–gold overlap populations are much smaller than those calculated above. A few selected values for the complexes indicated in **e** are given in Table 1.

TABLE 1. Au–Au distances and overlap populations in some dimeric complexes

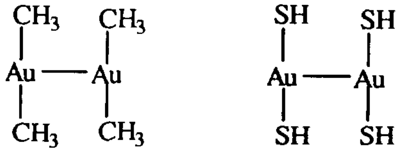
Complex	d(Au–Au) (Å)	OP	Ref.
e1, $[Au_2\{S_2C_2(CN)_2\}_2]^{2-}$	2.78	0.089	This work
	2.70	0.108	
e2, $[Au_2\{S_2PH_2\}_2]$	3.04	0.044	2a
e3, $[Au_2\{Se_2C_2(CN)_2\}_2]^{2-}$	2.81	0.084	12



e

These results should not be directly compared, because different intermetal distances were used in the calculations for the two situations. The calculated Au–Au overlap population for a distance of 3.00 Å drops to 0.059 and 0.069, respectively, in the inner and outer bonds of the Au_5 chain. These differences are relatively small, reflecting the small change in bond lengths for the two types of complex. Therefore, the bonds are stronger in the Au_5 chain than in the eight-membered ring. Since the distances are so similar, one reason may be the different donor atom. The carbon atoms in the chain are replaced by chalcogens in the ring compounds.

In order to gain some insight on the influence of the donor atom, we studied two very simple dimers which contain the basic unit in the gold compounds, $[Au_2L_4]^{2-}$ (L=SH or CH_3) (**f**).



f

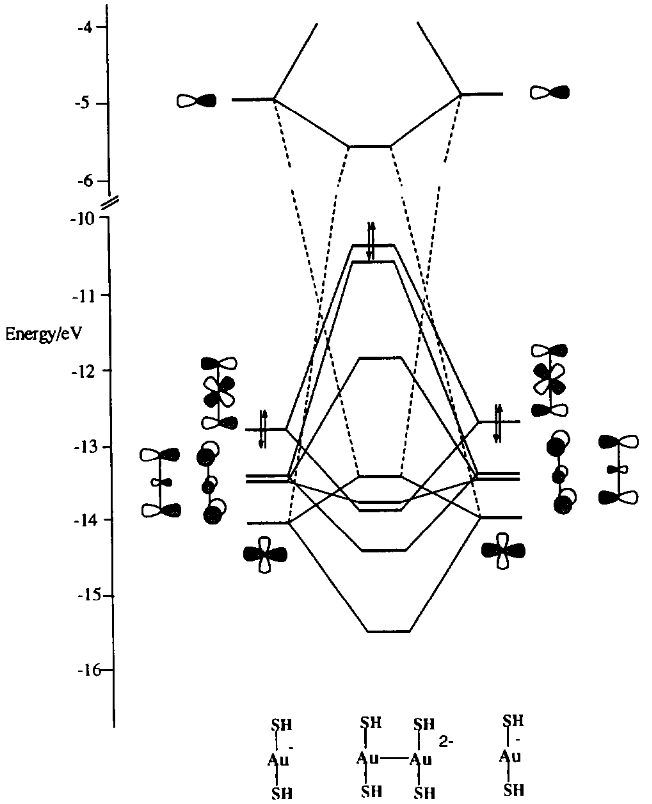
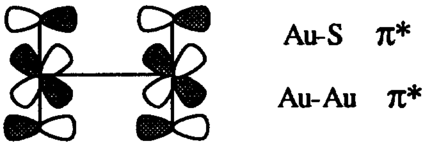


Fig. 4. Diagram of the interaction between two $Au(SH)_2^-$ fragments.

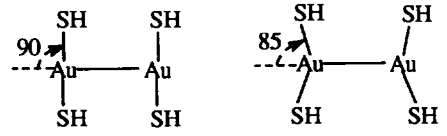
The Au–Au overlap populations, calculated for the same intermetal distance of 2.70 Å, are 0.032 and 0.133 for L=SH and CH_3, respectively, indicating that for these very similar situations the bond strengths are intrinsically different. The basic features of the interaction between two AuL_2^- group are sketched in Fig. 4 (L=SH).

Once again the Au–Au bond results from the four-electron destabilizing interaction between two occupied $d_{x^2-y^2}$ orbitals, one on each gold atom, where empty p has strongly mixed in. This lowers the energy of the antibonding orbital so that the overall interaction is attractive. Although this type of interaction takes place for the two models and is responsible for the bond description in $[Au_2(CH_3)_4]^{2-}$, the p orbitals of the sulphur atoms must be taken into account when L=SH. They enter into a four-electron destabilizing interaction with filled d_{xy} orbital of gold for instance. The resulting π^* orbitals are also gold–gold antibonding and, as they are occupied, the Au–Au bond is weakened, as seen in the HOMO (g).



g

Molecular orbitals such as those shown in g are also S–S antibonding. A distortion moving the two sulphur atoms on each side of the gold atoms away from each other will relieve this repulsion, without affecting significantly the Au–S bonds, and strengthening the Au–Au bonds. This is depicted in h, along with the corresponding Au–Au and S–S overlap populations.



OP			
	Au-Au	0.032	0.079
	S-S	-0.146	-0.051

h

These results help to explain why the coordination geometry around gold in many of these complexes is distorted from a **T** geometry to a **Y** geometry [13]. Real complexes are not as simple as these models and the Au–Au overlap populations do not differ as much as one might expect. This reflects all the other details in the geometry, such as the real metal–ligand distances, the type of donor atom, and steric constraints imposed by the bidentate ligand containing the donor atoms. It is possible to find almost a continuum of values for the overlap populations (calculated in "normalized" conditions, that is, with constant bond length), but we can be sure that a metal–metal bond exists in these complexes.

5. Au–Au bonds in complexes containing hypervalent carbon

There are not many examples, to our knowledge, of such complexes. The most interesting, $[(AuPPh_3)_6C]$ contains an octahedral carbon atom [4] and is shown in Fig. 5.

The discussion of this complex centres around the fact that a carbon atom with six $AuPPh_3$ ligands and an octahedral environment seemed very unusual, even considering the well known presence of carbon atoms (and also hydrogen atoms and many others) inside

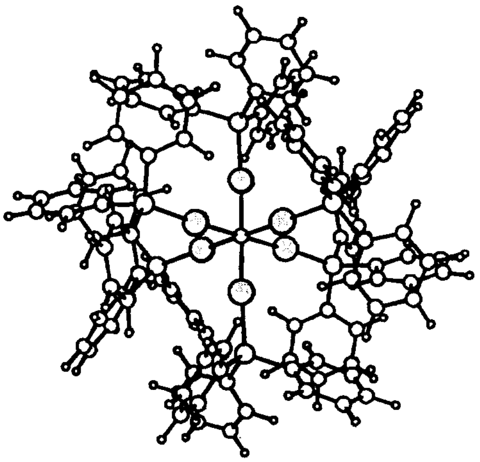
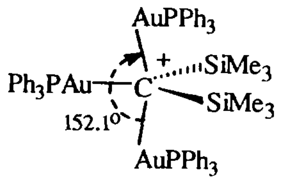


Fig. 5. The structure of $[C(AuPPh_3)_6]$.

octahedral metal clusters [14]. In this complex, the gold–gold distances between adjacent atoms range from 2.910 to 3.090 Å. In the $[(AuPH_3)_6C]$ model, the Au–Au distances were taken as an average of 3.00 Å, and the calculated overlap population was 0.031. Compared to previous values, this low OP suggests very weak interactions between the gold atoms. This was indeed proposed on different grounds by the authors who first described the compound [4], and was supported by theoretical *ab initio* calculations which took into account relativistic effects [3].

More recently, the same group reported the synthesis and structural characterization of a related carbon complex [15], where the carbon occupies the centre of a distorted trigonal bipyramid, **i**.



i

The gold–gold distances (2.720 Å) are much shorter than those found for the Au_6 cluster, and the overlap populations are accordingly much stronger (0.118), when calculated for this distance. In the undistorted trigonal bipyramid with a 180° angle between Au_{ax}–C–Au_{ax}, (α), the gold-gold distances are much longer and the corresponding overlap populations lower, as expected. The drop in energy along this distortion (the Au_{ax}–C–Au_{ax} angle decreases from the initial 180°) is shown in Fig. 6, with the accompanying changes in the Au–Au and Au–C overlap populations.

Even in the absence of a more detailed analysis, it seems that making Au–Au bonds is the cause of the distortion. The C–Au_{ax} bonds become slightly stronger during this process, while the C–Au_{eq} bonds are weakened, but as seen above, the process appears to be energetically favourable. The Au–C overlap populations, calculated for a Au–Au distance of 2.70 and Au–C distance of 2.20 Å, are 0.370 and 0.408 for the axial and equatorial bonds, in agreement with the experimental distances, 2.220 and 2.208 Å (axial) and 2.190 Å (equatorial), and the normal geometry of a trigonal bipyramidal environment.

We should add that the Au–C bonds in the octahedral complex are shorter than in the bipyramid (2.122–2.129, compared to 2.190–2.208 Å). In spite of this, the Au–Au bonds are still too long to allow the formation of a strong metal cluster. As is easy to see from Fig. 5, the great number of phenyl groups in the environment prevents a more drastic shortening of these bonds.

As a conclusion, the two apparently similar compounds differ greatly when the gold–gold interactions are analysed, and one moves from a situation of weak intermetal interactions to another where strong bonds are formed, depending on steric constraints.

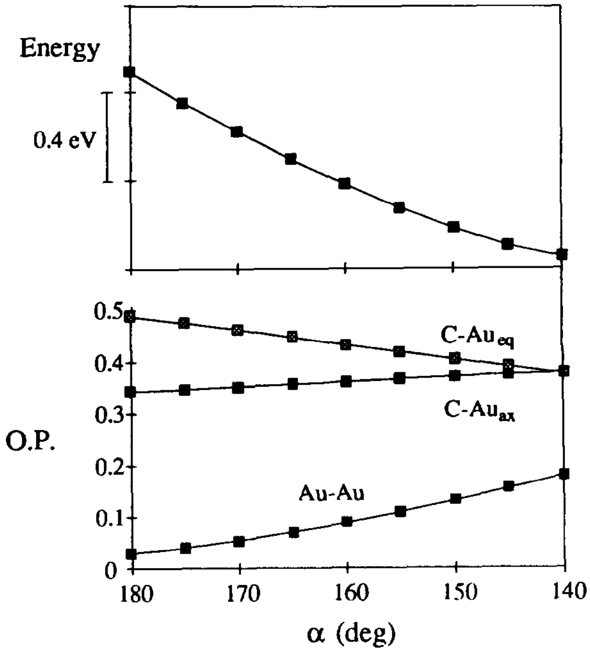
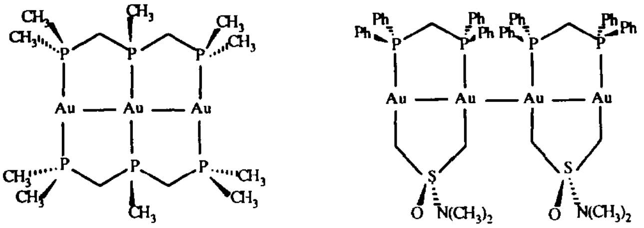


Fig. 6. The change in energy and some relevant overlap populations for the distortion of the trigonal bipyramidal complex $[C(AuPH_3)_3(SiMe_3)_2]$, when the axial $AuPH_3$ ligands approach one another.

6. Other polynuclear gold complexes containing phosphorus ligands

The new class of compound in this section contains only Au–Au and Au–P bonds, being therefore different from all the previous ones, although reminiscent of those containing eight-membered rings. Some examples [16,17] are presented in **j**.



1 2

j

This choice was made to show how arbitrary the representation of structures can be. Indeed, in the first compound, **j1**, a 3 + cation, the Au–Au–Au group is far from linear (136.26°) and no bonds are shown in the figure [16a], although the distances are from left to right, 2.981 and 2.962 Å. Our calculations give overlap populations indicative of non-negligible Au–Au interaction (0.030 and 0.031, respectively, calculated for the same intermetal distance). All the charges are negative (−0.135, −0.175, −0.136) consistent with charges found in formally Au^I for other species. The deviation from linearity in the Au_3 group was explained by the authors as arising from a gold–gold interaction between the two outer gold atoms. The calculated overlap population is 0.0, suggesting that no such interaction exists. More likely, this geometry is adopted because it allows the phosphorus atoms to acquire a coordination environment closer to tetrahedral, as would be preferred. For the related trimetallic complex where the methyl groups have been replaced by phenyls, the Au–Au–Au angle increases to 167.21°, and, although the Au–Au distances are slightly longer (3.013 and 3.005 Å), bonds are now drawn [16b]. A more repulsive interaction between the phenyl substituents may well be at the origin of the different angle.

The second compound, **j2**, is described in the original publication [17] as a binuclear compound with two molecules side by side in the crystal, in such a way that the intermolecular Au–Au bond (the inner bond in our nomenclature) is shorter than the intramolecular bond (the outer bond), their lengths being 2.959 and 2.984 Å, respectively. Although the differences are too small to be significant, they indicate that a tetranuclear compound is a better and much less confusing description for the complex.

The charges on the outer Au atoms are −0.163 and those on the inside Au atoms are −0.153. This is then a chain of four Au^I atoms and the inner bond provides another example of an unsupported metal–metal bond between two formally d^{10} metal atoms. The overlap populations are 0.035 for the outer bonds and 0.047 for the inner (calculated for the same Au–Au distance of 2.97 Å). The central bond is the stronger, as hinted at by the experimental bond lengths.

7. Conclusions

We tried to investigate the gold–gold bonds in some polynuclear gold complexes where a gold atom is closer to other gold atoms (normally two). In most cases, two Au^I d^{10} species form a metal–metal bond, through mixing of p character into the d set of orbitals, unless some extrinsic factor prevents it. This normally arises from bulky groups in the neighbourhood of the metal atoms, which will not allow their approach. The type of the donor atom attached to gold is important in determining the strength of the interaction. As was found when comparing ligands containing carbon and sulphur donor atoms, the first give rise to stronger Au–Au bonds, as four-electron destabilizing interactions are less effective. This effect may be obscured by other factors.

The strongest Au–Au bonds were found when at least one of the gold atoms is Au^{III} and a good acceptor orbital is available for bond formation. The ligand *trans* to the gold chain, seen in Fig. 1 for the Au_5 species, and in one half of the Au_3 derivative in **d**, but absent in the other compounds, plays an important role as it mixes in antibonding fashion with the $d_{x^2-y^2}$ orbital involved in metal–metal bond, pushing its energy to a value closer to that of the other interacting orbital. This is true in the square planar environment observed around these terminal Au^{III} d^8 atoms. For the central gold in the Au_5 chain, however, the orbital responsible for the Au–Au bond does not interact with the other ligands. Finally, gold–gold interactions are quite significant even in compounds in which their existence has not been proposed.

Acknowledgements

We thank JNICT for financial support (PMCT/C/CEN/367/90).

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Appendix

All the calculations were done using the extended Hückel method [6] with modified H_{ij} values [18]. The parameters used were for Au (H_{ii} (eV), ζ): 6s −10.92, 2.601; 6p −5.55, 2.584; 5d −15.07, 6.163, 2.794 (ζ_2), 0.6442 (c_1), 0.5356 (c_2); for Se (H_{ii} (eV), ζ): 4s −20.50, 2.44; 4p −13.20, 2.07. Standard parameters were used for other elements.

The calculations were performed on model complexes with idealized geometries taken from the real structures quoted along the text. The groups R (R = CH_3, C_6H_5, or C_6F_5) were replaced by hydrogen atoms since the results were not qualitatively altered. In the study of the outer Au–Au bonds of the pentamer, two methyl groups replaced each $(CH_2)_2PPh_2$ ligand in order to facilitate the fragment decomposition analysis.