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Can triple bonds exist between gold and main-group elements?

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Abstract. Pseudopotential ab initio calculations of several gold carbides, gold nitrides and their third-row analogues have been performed with the goal of finding species which contain triple bonds with gold. Multiple-bond character has been observed for Cl_2AuCH and Cl_2AuN. Bonding in these and related compounds is analysed and the reasons why gold prefers single bonds are outlined.

Key words: Triple bond – Gold – Pseudopotential – Relativity

1 Introduction

The chemistry of gold [1–4] is dominated by single chemical bonds between a gold atom and the surrounding ligands, as well as inter- and intramolecular gold-gold attractions. With its single 6*s* electron, gold is often considered to be isolobal with the hydrogen atom, even though it easily forms more than one chemical bond with ligands, thus activating the 5*d* and 6*p* shells. The question arising is whether these bonds could be directed towards the same atom in the form of a double or triple bond.

The only experimentally known example of an Au-L multiple bond is in the carbene $AuCH_2^+$, whose corrected experimental Au-C bond energy is 393(8) kJ/mol or 4.08(9) eV [5]. Theoretical calculations [5–7] suggest a partial double bond due to Au $5d\pi$—C $2p\pi$ donations. The calculated Au-C bond lengths are 185–191 pm. The first example of a corresponding, partial triple bond is AuC^+. The bond length, calculated at the CASPT2 level [8], is predicted to be 176.6 pm, and the dissociation energy, 3.815 eV. This is the shortest known Au-C bond. Both of these species are ionic. Could such Au≡L bonds occur in neutral, polyatomic molecules?

2 Methodology

In the present work we examine the possible existence of neutral molecules which have unusually short and strong bonds involving the gold atom. The calculations were performed with Gaussian 94[9] software using the quasi-relativistic Stuttgart effective core potentials and corresponding basis sets [10, 11]. For hydrogen, the Huzinaga non-relativistic $4s/[2s]$ basis set [12] was used. This basis set was augmented with two sets of f-type polarization functions for gold ($\alpha_f = 0.2$ and 1.19) and one set of polarization functions for the other atoms. The exponents were taken from Ref. [13]; for hydrogen $\alpha_p = 0.8$ was used. For carbon we used $\alpha_d = 0.8$.

In order to choose a suitable method for treatment of the correlation effects, a sensitivity study was carried out on the AuC^+ ion. The calculated Au–C bond lengths at various levels of correlation treatment are plotted in Fig. 1. From the difference between Hartree-Fock and second-order Møller-Plesset (MP2) results, when compared to CASSCF and CASPT2, it can be seen that the majority of electron correlation is dynamic, and is treated well at the perturbative level. Therefore, for most of the calculations the correlation effects were treated at the MP2 level, with selected calculations performed at the coupled cluster [CCSD(T)] level as well for improved accuracy.

The species were considered to have C_s or C_{2v} symmetry as appropriate. At the MP2 level, the minima were confirmed by calculating the respective Hessians. At the CCSD(T) level Hessians were not calculated due to limited computer resources.

3 Results and discussion

A selection of the calculated bond lengths is presented in Table 1. Numerous other compounds were also studied, but the resulting bond lengths are longer than those reported. They are not included in Table 1.

The seemingly obvious first candidates for molecules having triple bonds between a main-group element and gold are Au≡CH and Au≡N. If the N atom or CH

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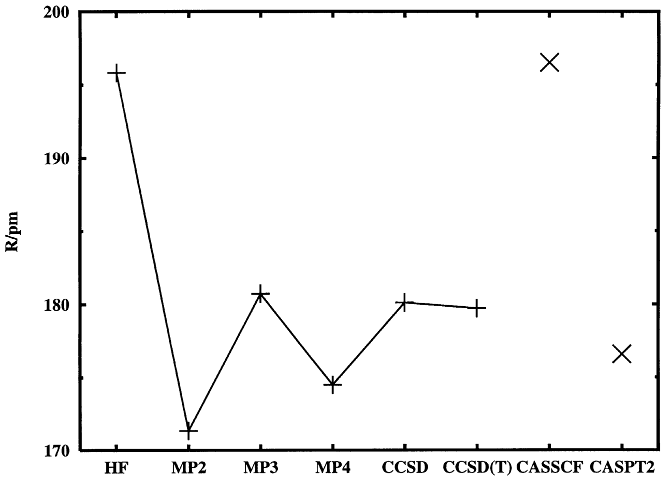

Fig. 1. Dependence of the calculated bond length in AuC^+ on the correlation method. The CASSCF and CASPT2 results use a basis set other than that used in the current work and are taken from Ref. [8]

Table 1. Some calculated bond lengths involving an atom of gold

Bond	Compound	Spin	Bond length (pm)		
			MP2	CCSD(T)	CASPT2
Au-C	$AuCH_3$[a]	0	198.5	203.1	
	AuC^+	0	171.3	179.7	176.6[b]
	Cl_2AuCH	0	178.3	184.8	
	AuCH[c]	0	185.6		
	AuCH	1	188.3		
	$AuCH_2^+$	0	188.3		
	PH_3AuCH	0	195.1		
Au-N	$AuNH_2$[a]	0	196.0	202.0	
	$AuNH^+$	0	180.3		
	AuN^{2+}	0	170.1	181.2	
	AuN[c]	0	175.6		
	AuN	1	186.6		
	Cl_2AuN	0	172.5		
	OAuN	0	187.2		
	SAuN	0	192.6		

[a] Reference value for a single bond
[b] Ref. [8]
[c] The triplet is lower in energy

group involve four electrons from the gold 5*d* π orbitals, in addition to the one in 6*s*, a perfect 8-orbital 10-electron system would be created, analogous to the well-known textbook example of N_2 molecular orbitals (MOs).

However, the symmetry of the atomic orbitals dictates that two gold orbitals (6*s* and $5d_{z^2}$ if the bond is directed along the *z*-axis) will be involved in sigma bonding, and two ($5d_{xz}$ and $5d_{yz}$) in the pi bonding, leaving the remaining two 5*d* orbitals relatively unmodified with delta symmetry. To these σ and π orbitals, gold contributes 7 electrons in addition to 5 from nitrogen, resulting in an 8-orbital 12-electron system, resemblant of the textbook O_2 example (Fig. 2). Two of the electrons involved occupy the degenerate antibonding $2\pi^*$ system, resulting in a considerable net weakening of the overall bond. The AuCH case is analogous, with additional bending of the geometry which removes the degeneracy of the singly occupied π orbitals.

The cases of AuB and AuAl, which do not have excess electrons to fill the antibonding systems, have recently been studied [14, 15]. While these bonds are relatively strong, the electronegativity of boron or aluminium is apparently not sufficient to create the necessary electron density for a true multiple Au≡L bond. Third-row analogues of the CH and N ligands do not yield unusually short chemical bonds either, for similar reasons to those attributed to B and Al.

We therefore set out to find ligands on either side of the bond which would otherwise engage the electrons which tend to occupy the π^* orbitals. Attaching a single ligand, such as PH_3 or its analogues to the other side of the gold atom did not lead to shortening of Au-N or Au-C bonds. Placing oxygen or sulphur on the other side of the gold atom created an 18-electron system analogous to ozone, with its corresponding 1.5-strength chemical bonds. Attaching two electron-withdrawing ligands to gold did, however, withdraw some of the electron density as desired.

The most promising species we have investigated so far appear to be Cl_2AuCH and Cl_2AuN. The Au-C bond length in the former is the shortest known for any neutral molecule, 182 pm at the CCSD(T) level (178.3 pm at the MP2 level), representing a 20 pm decrease from a single bond in $AuCH_3$. The molecule has an unusual non-planar geometry, illustrated in Fig. 3. An estimated heat of formation from metallic gold, graphite and gaseous Cl_2 and H_2 is +427 kJ/mol [CCSD(T), no zero-

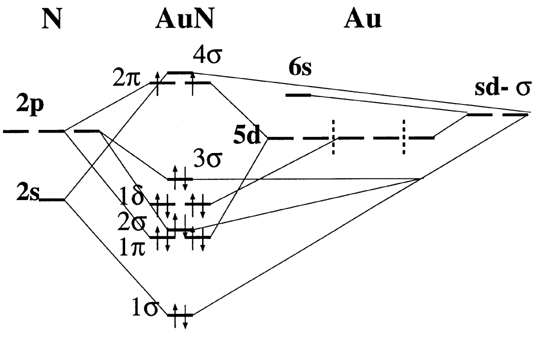

Fig. 2. Orbital energy diagram of AuN

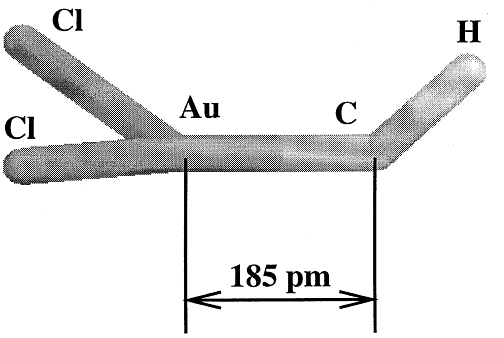

Fig. 3. The geometry of Cl_2AuCH

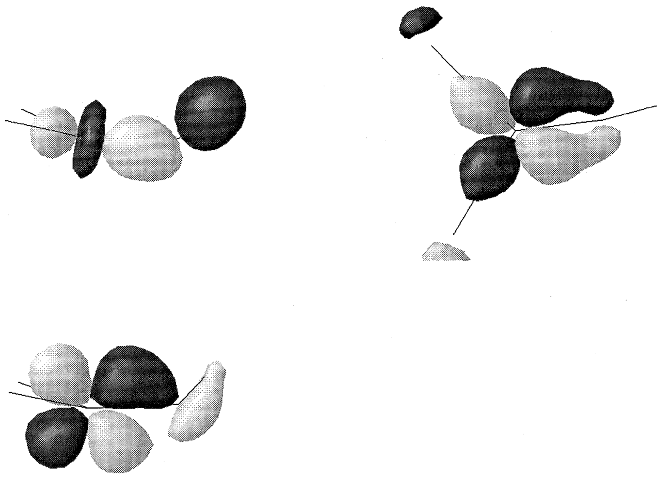

Fig. 4. The three bonding orbitals of Cl_2AuCH

point vibrations included]. The ΔH of the hypothetical reaction

$$\tfrac{1}{2}C_2H_2 + Cl_2 + Au(g) \rightarrow Cl_2AuCH$$

is estimated at −50 kJ/mol with the same assumptions as above. Triplet Cl_2AuCH has a MP2 Au-C bond length of 180 pm and its lowest-energy geometry is 1.28 eV (121 kJ/mol) higher in energy than the singlet. Thus we expect that observation of Cl_2AuCH as a gas-phase or matrix species is not theoretically excluded.

The Cl_2AuN has a very short Au-N bond of 172.5 pm (MP2 level), a 23 pm decrease from $AuNH_2$. The molecule is planar (C_{2v}). Its standard heat of formation is estimated to be +577 kJ/mol [CCSD(T), MP2 geometry of Cl_2AuN, no zero-point corrections]. It is, however, 184 kJ/mol below the Cl_2 + Au(g) + N limit, and 67 kJ/mol above the AuN + NCl limit. Triplet Cl_2AuN has a MP2 Au-N bond length of 190.3 pm and it lies 0.55 eV (54 kJ/mol) above the singlet. Selected single-point calculations at the CCSD(T) level suggest, however, that the singlet-triplet gap may be even smaller. This can be explained by the higher electronegativity of N relative to the CH group, with the chlorine ligands less successful in competing for the electrons in the π system. Such near-degeneracy would also give rise to strong spin-orbit interaction, which the current series of calculations did not account for. In conclusion, the stability of Cl_2AuN as a gas-phase or matrix entity remains an open question. Even if it exists, the π^* system is likely to be partially occupied, with resulting weakening of the Au-N bond.

When the chlorine ligands are replaced with other halogens in Cl_2AuCH, the Au-C bond length increases. Substituting the hydrogen atom with a halogen has a similar effect.

The MP2 MOs of Cl_2AuCH were plotted on a grid and visualized using AVS [16]. The three orbitals which appear to participate in Au-C bonding are illustrated in Fig. 4. The plotted surfaces represent 0.06 a.u. isosurfaces of the corresponding wavefunctions; at this level the multiple-bond features start to appear clearly. For comparison, the multiple-bond character of ethylene starts to become visible at the 0.19 a.u. isosurface level, and is very profound at the 0.06 a.u. level. One should therefore be careful in calling the Au-C bond in this species a triple bond.

4 Conclusions

As the current study shows, any triple bond between a gold atom and a main-group element in a neutral molecule would require a very delicate balance between the electronegativities of the bonding partner and other ligands attached to the gold. These other ligands need to have the "right" electronegativity to pull away electron density from the antibonding orbitals which would otherwise destroy the multiple bond between gold and the primary bonding partner, at the same time not competing for electrons in the bonding orbitals of the multiple bond itself. While artificial examples of such molecules can be constructed (e.g. Cl_2AuCH), in typical chemical environments one would expect only single bonds between gold and its ligands, in agreement with experimental practice.

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