



# Boron as intruder in planar gold clusters. How does its presence modify reactivity?



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## ABSTRACT

In this paper, our main objective is to analyze the effect of one boron atom on the properties of gold clusters. To this end, a density functional study of gold–boron clusters is carried out. Gold–boron clusters are obtained by substituting one gold atom with one boron atom in planar gold clusters consisting of up to nine atoms. The systems being studied ( $\text{Au}_N$  (with  $N = 2\text{--}8$ )) are investigated using the electron donor–acceptor electronegativities and the electrostatic potential surface (EPS). In order to investigate the influence of the boron atom on the reactivity of gold clusters, the reaction of gold–boron clusters with  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{OH}^-$  was analyzed in terms of Gibbs free energies, and compared with the reactivity of pure gold clusters. Generally, gold–boron clusters represent better electron donors than gold clusters, and the presence of the boron atoms enhances the reactivity of the clusters. The active sites of Au clusters are Au while those of  $\text{Au}_N\text{B}$  clusters are the B atoms. This is important for future applications of these systems.

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## 1. Introduction

Gold clusters have been attributed great importance because of their potential applications in medical sciences, for catalysis, and for new materials that may be useful as sensors [1–9]. These applications can be explained with reference to the relativistic effects [10] that denote the unique properties of these systems. Gold atoms have an electron configuration with a closed 5d shell and one electron in 6s shell, similar to that of the alkali metals. The relativistic effect stabilizes the 6s orbital resulting in anomalously high ionization potential (9.225 eV) and electron affinity (2.309 eV) [11]. Likewise, the experimental and theoretical studies indicate that gold clusters can adopt several geometries in two and three-dimensions, for example planar, flat cage, spherical cage or pyramidal structures [12–41]. All these configurations are very close in terms of energy, and are therefore able to be present in these experiments. However, planar structures are clearly the most stable geometries for gold clusters up to 9 atoms [23].

State-of-art research in the context of gold clusters relates to geometric structure, size of clusters, and how these factors affect the chemical properties of these nanostructures [42]. Recently, many researchers have focussed attention on the interaction between gold clusters and other atoms such as boron [43,44]. The boron–gold clusters are particularly interesting, due to the fact that boron and gold are among rare, unique elements, whose elemental clusters possess planar or quasi-planar geometries, up to large

sizes [45]. Several studies exist dealing with the interaction between boron clusters and gold, describing a photoelectron spectra that concurs well with experimental data [46]. In spite of all these investigations, there are no reports focussing on the influence of a boron atom in terms of the properties of planar gold clusters. For this reason, the main goal of this investigation is to study how the electronic properties of small gold clusters are modified, when structures change as a result of the incorporation of a boron atom into the cluster. Most of the reactions involving gold clusters initiate with a charge transfer process and for this reason, the electrodonating ( $\chi^-$ ) and electroaccepting ( $\chi^+$ ) electronegativity of  $\text{Au}_N\text{B}$  (with  $N = 2\text{--}9$ ) clusters are good parameters to analyze the reactivity. The aim of this research is to analyze the electron donor–acceptor properties of planar gold–boron clusters and to study the reactivity of these mixed clusters with  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{OH}^-$ .

## 2. Computational and theoretical details

All calculations related to gold–boron clusters were undertaken using the Gaussian 09 implementation [47]. Calculations involving atomic geometry and electronic structure were carried out by applying the DFT framework for all the stationary points, using the three parameters for B3LYP functional [48–50] and the basis LANL2DZ [51–53]. In order to verify optimized minima, harmonic analyses were performed and local minima were identified, according to the number of imaginary frequencies (NIMAG = 0). In the frame of the DFT, previous studies reproduce equilibrium geometries and relative stabilities with hybrid functionals and many of these functionals include the Hartree–Fock exact

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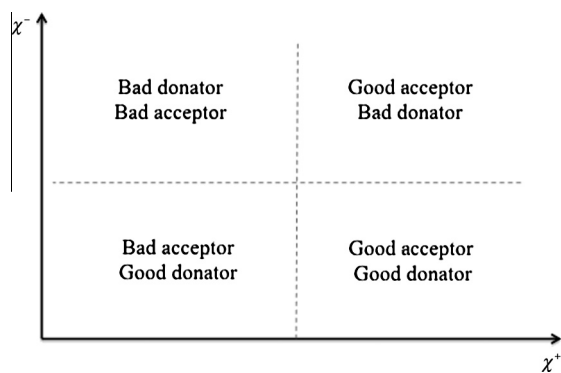


Fig. 1. Donator Acceptor Map in terms of electronegativities.

exchange energy. In previous works, the density functional approximation calculations using LANL2DZ pseudopotentials were reported to provide a good description of Au cluster chemistry. These calculations also included relativistic effects.

In Density Functional Theory, chemical potential ( $\mu$ ) is identified as the first derivative of energy, with respect to the number of electrons at constant external potential and also determining the charge flow direction and the capacity of the system to either donate or accept charge [42]. Gázquez et al. [54–56] proposed a simpler approach that differentiates the response to charge donation, resulting from the response to charge acceptance in terms of vertical ionization energy ( $I$ ) and vertical electron affinity ( $A$ ). They find that the charge donation process and the charge acceptance process can be defined as

$$\mu^- = -\frac{1}{4}(3I + A)$$

$$\mu^+ = -\frac{1}{4}(I + 3A)$$

Apparently  $\mu^-$  focuses more on ionization potential than it does on electron affinity, whereas  $\mu^+$  indicates the opposite. It is possible to define two different electronegativities for the charge transfer process, setting  $\chi$  as the negative of the chemical potential [50]. The charge donation is described with reference to the electrodonating ( $\chi^-$ ) electronegativity, whereas the charge acceptance is described with reference to electroaccepting ( $\chi^+$ ) electronegativity, defined as

$$\chi^+ = \frac{1}{4}(I + 3A)$$

and

$$\chi^- = \frac{1}{4}(3I + A)$$

The relationship between electronegativity with ionization potential and electron affinity indicates that lower values for  $\chi^-$  indicate greater capacity for donating electrons, whereas larger values for  $\chi^+$  imply better electron acceptance. Accordingly, it is possible to draw a Donator Acceptor Map (DAM) indicating electronegativities Fig. 1.

### 3. Results and discussion

Fig. 2 presents the most stable optimized structures for planar gold clusters with a boron atom. The reported structures of planar gold clusters [42] were used as initial geometries for the substitution of one gold atom by one atom of boron. This was achieved taking into account that certain gold atoms are symmetrically

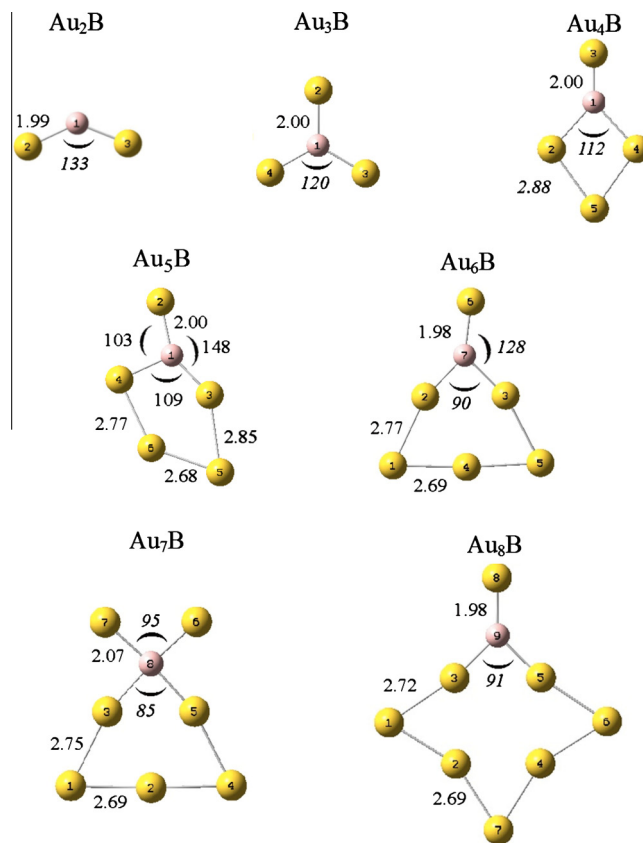


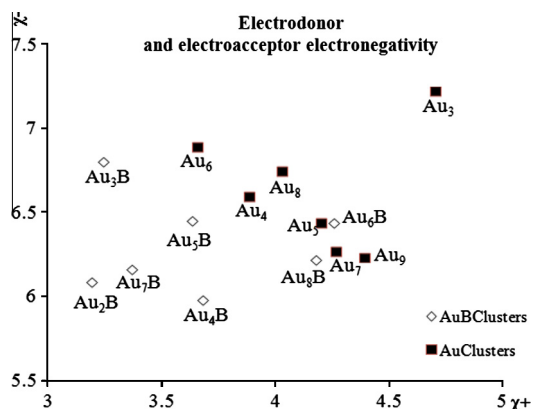
Fig. 2. Optimized structures of  $Au_nB$  (with  $N=2-9$ ) clusters. Distances (Å) and angles ( $^\circ$ ) are included.

equivalent. The most stable optimized structures are planar, with the boron atom bonded to three gold atoms, forming triangle-like geometries. The other gold atoms form a grid-like structure. The only exceptions that present the boron atom bonded to two and four gold atoms are  $Au_2B$  and  $Au_7B$ , respectively.

Bond distances and bond angles are also presented in Fig. 2. The symmetry of the structures is  $C_{2v}$  except for  $Au_5B$  and  $Au_6B$  that are slightly distorted, and  $Au_3B$  that is  $D_{3h}$ . The Au–B bond distance is about 2 Å, whilst there are two Au–Au bond lengths, one short (2.68–2.69 Å) and one long (2.72–2.88 Å). The longest Au–Au bond distance is that between the atoms closer to the boron atom.

The comparison between gold–boron clusters and gold clusters indicate that Au–Au bond lengths are similar, but the presence of boron as intruder modifies their structure and increases their symmetry. These differences are expected to affect electron donor acceptor properties, as well as reactivity.

The chemical properties of clusters depend both on size and shape. We only considered planar clusters due to the fact that planar structures are more stable than three-dimensional structures, with reference to the clusters included in this research. The main goal of this investigation is to analyze the reactivity of gold–boron and to compare it with the reactivity of gold clusters. It would appear that the first step in the reaction involves a charge transfer process between the reactants. If this were the case, donor–acceptor electronegativity would act as a good indicator of reaction capacity. In order to analyze the influence of the boron atom on the reactivity of gold clusters, the electron donor–acceptor electronegativity of gold–boron clusters is compared with the values for gold clusters. The calculated values of  $\chi^+$  and  $\chi^-$  for gold–boron clusters are presented in Fig. 3. The results for gold clusters previously reported are included for comparison. Evidently,  $Au_3$  is the best electron acceptor and the worse electron donor. This result



**Fig. 3.** Electroaccepting ( $\chi^+$ ) and electrodonating ( $\chi^-$ ) electronegativities of gold (black squares) and gold–boron (white squares) clusters.

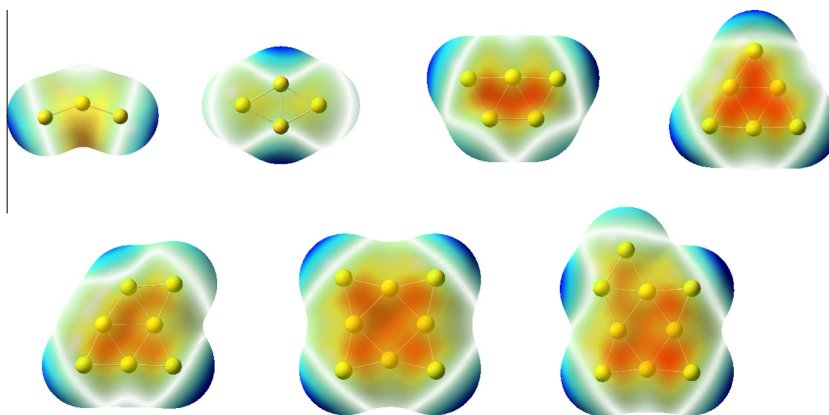
is different compared to the result previously reported. In this case, the trimmer is an obtuse triangle, whereas the previous result manifests an acute triangle. The former is more stable than the latter by almost 4 kcal/mol and for this reason we decided to use the result corresponding to the obtuse angle. The best electron donors are those located down to the left. They are  $\text{Au}_2\text{B}$ ,  $\text{Au}_4\text{B}$  and  $\text{Au}_7\text{B}$ .

Generally, it is possible to see in Fig. 3 that the gold–boron clusters are down to the left with respect to the gold clusters. This means that when boron is the intruder, it increases the ability to donate electrons and reduces the capacity to accept electrons. However, as with the flat gold clusters, [45] the novel flat gold–boron clusters represent effective electron acceptors and electron donors, with respect to other systems.

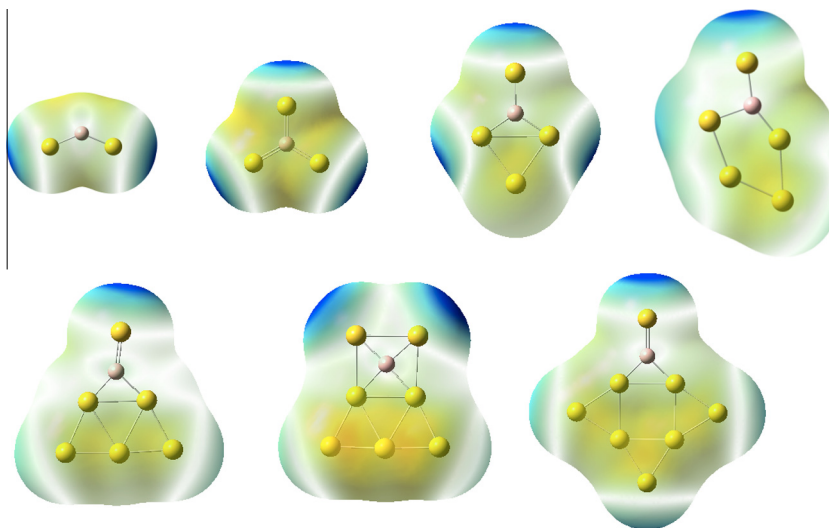
The electron donor–acceptor capacity is a global descriptor for reactivity. Apparently, gold–boron clusters will be better reactants towards electron acceptors than the gold clusters. To realize a deeper analysis of reactivity behavior, it is necessary to include local descriptors of reactivity, such as the electrostatic potential surface (EPS).

The EPS of the systems under study are reported in Figs. 4 and 5, for gold and gold–boron clusters, respectively. The gold clusters have two main important regions; one related to large values, indicating electron density (red–orange region) that corresponds to delocalized electrons pertaining to gold atoms, and the other related to low electron density in the cluster (blue region), localized at the edges of the molecule. The low electron density is an effect that can be explained by the diminished coordination in these gold atoms.

As presented in Fig. 5, the EPS of the gold–boron clusters is different when compared to the EPS of gold clusters. The Mulliken atomic charges are included in Table 1. Boron atom is negatively



**Fig. 4.** EPS of  $\text{Au}_N$  ( $N = 3-9$ ).



**Fig. 5.** EPS of  $\text{Au}_N\text{B}$  ( $N = 2-8$ ).

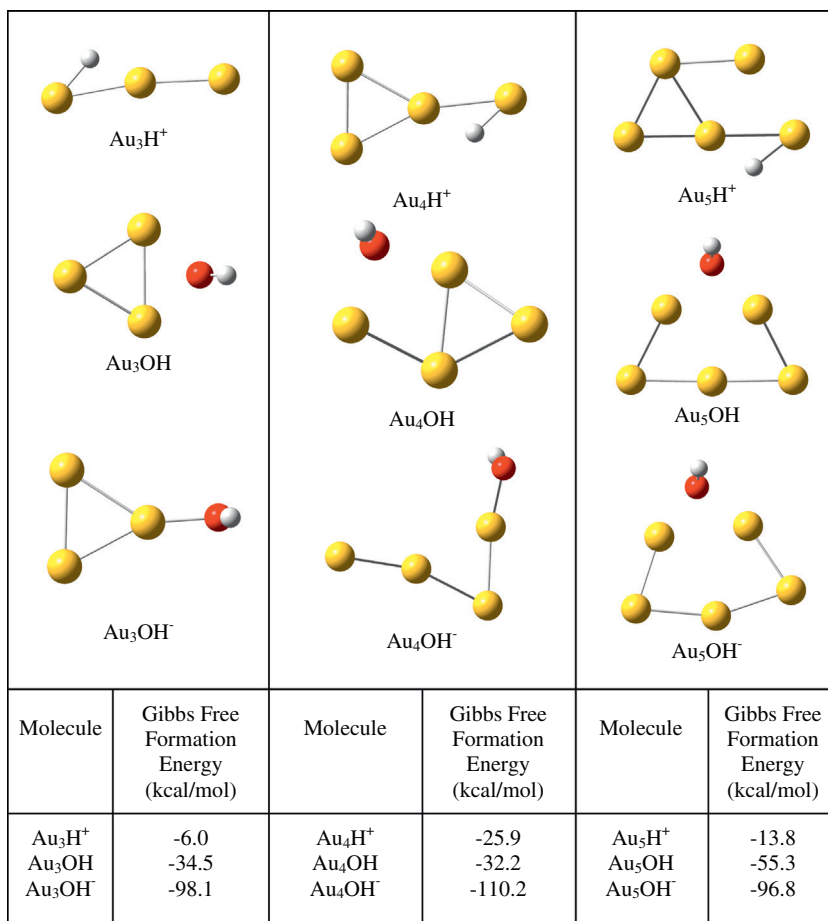
**Table 1**  
Mulliken atomic charges.

Cluster	$q_B$	$q_{Au1}$	$q_{Au2}$	$q_{Au3}$	$q_{Au4}$	$q_{Au5}$	$q_{Au6}$	$q_{Au7}$	$q_{Au8}$
Au <sub>2</sub> B	-0.271	-	0.135	0.135	-	-	-	-	-
Au <sub>3</sub> B	-1.346	-	0.449	0.448	0.448	-	-	-	-
Au <sub>4</sub> B	-1.062	-	0.392	0.396	0.392	-0.118	-	-	-
Au <sub>5</sub> B	-0.625	-	0.280	0.172	0.194	-0.191	0.169	-	-
Au <sub>6</sub> B	-0.505	-0.200	0.119	0.372	0.221	-0.186	0.179	-	-
Au <sub>7</sub> B	-1.040	-0.198	0.109	0.380	-0.197	0.382	0.284	0.280	-
Au <sub>8</sub> B	-0.561	-0.246	0.238	0.316	0.235	0.292	-0.247	-0.154	0.126

charged in all cases. Gold atoms are positive and negatively charged. The boron atom enhances the symmetry and shrinks the electron density of the gold atoms (yellow region). Consequently, in the case of boron a low electron density cluster exists. The boron atom is neutral in the EPS and a low electron density region (blue) is also present at the edges of the clusters. It is expected that variations in electron density will significantly affect reactivity. To verify this hypothesis, the interactions of these clusters with three different reactants, H<sup>+</sup>, OH<sup>-</sup> and OH<sup>-</sup> were analyzed, representing an electrophilic, a free radical attack and a nucleophilic attack respectively. This analysis was undertaken for gold clusters and gold–boron clusters formed with up to 5 atoms, as these clusters are representative of all systems being studied. The optimized structures are presented in Figs. 6 and 7. Gibbs free energies for the reaction are also included.

Optimized geometries for the complexes are different in the case of clusters with and without the boron atom. For gold–boron clusters, H<sup>+</sup>, OH<sup>-</sup> and OH<sup>-</sup> preferentially bind to the boron atom.

When bonded to H<sup>+</sup>, OH<sup>-</sup> and OH<sup>-</sup> gold clusters are planar, whereas the corresponding gold–boron clusters are three-dimensional and highly distorted structures. The first conclusion that emerges from the results presented in Figs. 6 and 7 is that the reactions of gold–boron clusters with all the molecules under study are more exergonic than the reaction for corresponding gold clusters. The only exception is [Au<sub>4</sub>H]<sup>+</sup>. Comparing the donor acceptor electronegativity of Au<sub>4</sub> and Au<sub>3</sub>B, it is evident that the former represents a better electron donor than the latter. For Au<sub>3</sub> and Au<sub>5</sub>, this is not the case. Gold–boron clusters are better electron donors than the corresponding gold–clusters. It is possible to say that electron donor capacity is directly correlated with the reactivity of these systems. In addition and in accordance with the EPS, the reaction is carried out with the atom that manifests least electron density, in any situation. As the presence of boron atoms results in a low electron density cluster, an increment in the reactivity with the presence of boron can be expected, concurring with the results that we report in Figs. 6 and 7.

**Fig. 6.** Optimized structures of gold cluster interacting with H<sup>+</sup>, OH<sup>-</sup> and OH<sup>-</sup>. Formation Gibbs free energies are included.

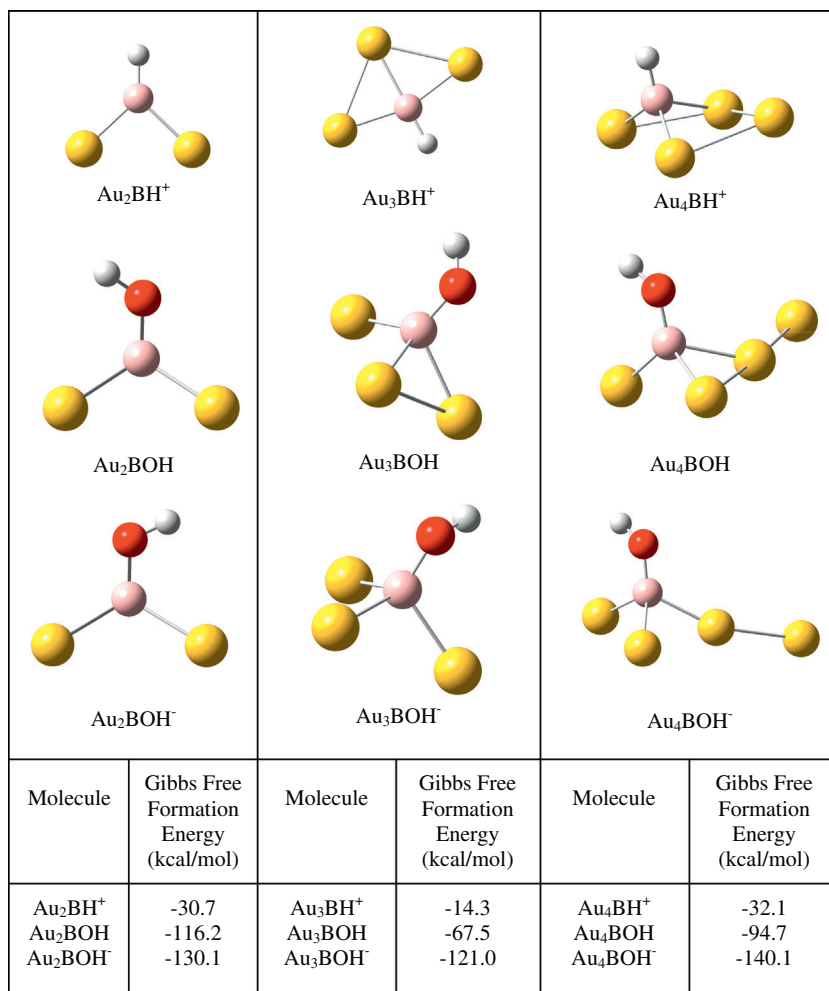


Fig. 7. Optimized structures of gold–boron cluster interacting with  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{OH}^-$ . Formation Gibbs free energies are included.

#### 4. Conclusions

The presence of a boron atom as an intruder in the gold clusters modifies their structure and increases their symmetry in all cases. The modification of the structure and the presence of an atom with different electronegativity affect the electron donor/acceptor capability of the clusters, gold–boron clusters representing better electron donors than corresponding gold clusters. The boron atom is the active site of  $\text{Au}_n\text{B}$  clusters. The EPS changes with the presence of the boron atom. The boron atom enhances the symmetry and shrinks the electron density of the gold clusters. Consequently, the reaction of gold–boron clusters with  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{OH}^-$  is more exergonic than the reaction of the corresponding gold clusters. In summary, the presence of the boron atom enhances the electron donor capability and the reactivity of gold clusters. This will be useful for future applications of these systems.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.comptc.2013.06.016>.

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