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Supporting Information for the article: Phosphine passivated gold clusters: How charge transfer affects electronic structure and stability.

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Comparison of several structure values of the structure optimized cluster systems with X-Ray data

	$Au_6(PPh_3)_6{}^{2+}$	$Au_7(PPh_3)_7{}^{+}$	$Au_8(PPh_3)_7{}^{2+}$	$Au_8(PPh_3)_8{}^{2+}$	$Au_9(PPh_3)_8{}^{3+}$
Av Au-Au	2.80 (2.76)	2.88 (2.83)	2.81 (2.78)	2.78 (2.88)	2.82 (2.78)
Min Au-Au	2.69 (2.65)	2.63 (2.56)	2.65 (2.63)	2.75 (2.72)	2.73 (2.67)
Max Au-Au	2.87 (2.84)	3.13 (3.09)	2.96 (2.94)	2.85 (3.00)	2.92 (2.88)
Av Au-P	2.33 (2.30)	2.34 (2.30)	2.33 (2.30)	2.36 (2.49)	2.33 (2.28)
Min Au-P	2.33 (2.29)	2.30 (2.26)	2.31 (2.24)	2.34 (2.46)	2.32 (2.27)
Max Au-P	2.34 (2.31)	2.36 (2.33)	2.34 (2.36)	2.44 (2.56)	2.35 (2.29)

	$Au_6(PPh_3)_6$	$Au_7(PPh_3)_7$	$Au_8(PPh_3)_7$	$Au_8(PPh_3)_8$	$Au_9(PPH_3)_8$
Av Au-Au	2.82	2.88	2.86	2.84	2.84
Min Au-Au	2.65	2.65	2.60	2.68	2.65
Max Au-Au	3.01	3.09	3.33	3.02	2.98
Av Au-P	2.34	2.34	2.34	2.35	2.33
Min Au-P	2.30	2.29	2.32	2.32	2.32
Max Au-P	2.39	2.38	2.39	2.39	2.34

Local density of states (LDOS) and projected local density of states (PLDOS)

The electronic structure via local density of states (LDOS) is analyzed for both the ligand-protected and naked gold clusters, in the same structure as is stabilized by the ligand-shell. The electronic structure has a molecular character, but for an easier analysis a smearing of 0.2 is applied to aggregate the close lying peaks. Gold *S*-, *P*- and *D*-states are highlighted in different colors for the LDOS spectra. To assess the validity of the electron accounting rule for the global electronic structure of the gold phosphine systems the projected local density of states (PLDOS) has been calculated. This is realized by projecting the Kohn-Sham orbitals onto spherical harmonic functions within a sphere of radius R_c. The origin of this sphere has been chosen as the centre of mass of the gold cluster core. Several radii have been tested, but the radius of 3 Å is consistently used for all cluster systems.

The **electronic structure** of the systems with **6** and **9** atoms contains a single peak as the HOMO state: a mixture of mainly d and p-states. In the case of 7 and 8 atoms there are close lying double peaks which appear due to the smearing as a single peak. The largest separation between this single state (or close lying double states) and the other peaks at lower energies occurs for the system **7**. However, the system **9** displays a double peak with larger separation than for **7** and **8a/8b**, close to the lower energy peaks, thus system **6** presents the exception in this series. Voltammetry studies of **9** in CH_2Cl_2 revealed an energy gap of 1.8 eV between the first one-electron oxidation peak and the first reduction peak. Here we calculate the HOMO-LUMO gap as 1.5 eV using the PBE functional and 2.7 eV using the PBE0 functional, in the gas phase.

For the clusters without ligand shells, LDOS occurs just for the Au_7^+ with the close lying double peak as HOMO. In general, the d-states are observed at higher energies for the naked gold clusters, and are shifted to lower energies in the gold cluster phosphine systems. Furthermore the HOMO states for the naked clusters are based on a hybridization of s and d states instead of p and d as seen in the ligand-protected clusters. The HOMO-LUMO gaps show no correlation with the effective charge as seen previously. Instead the HOMO-LUMO gap decreases systematically with system size (with the exception of **8b**), which is consistent with studies for gold clusters of 1.1 to 1.9 nm.[1] The clusters with an even number of cluster atoms result in higher HOMO-LUMO gaps than those with an odd number. This is also the case for the naked cluster core without structural changes.

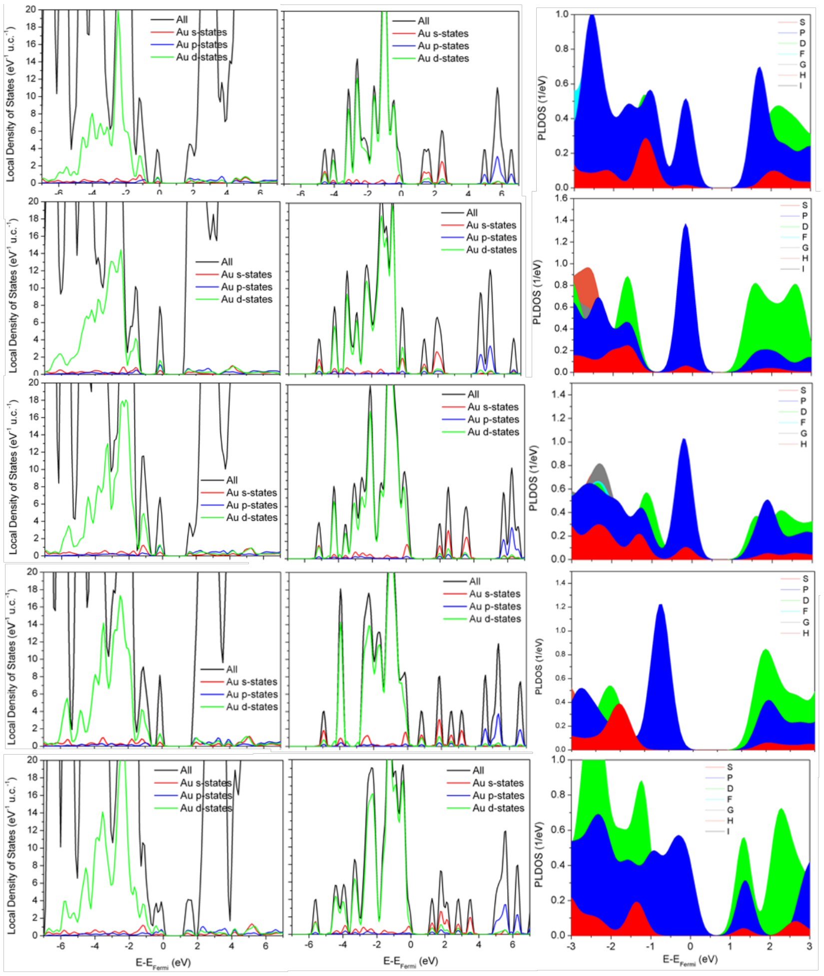

Figure 1: Local density of states (LDOS) and superatomic electronic structures (PLDOS) are calculated for the charged Au_n cluster phosphine (PPh_3) systems (A,C) and the naked cluster without ligand shell (B) at PBE/pw (PAW potentials)//PBE-D3(MARI-J)/cc-pVDZ(-PP, ECP60MDF) level of theory.

The neutral gold cluster series

Analyzing the structure

Reoptimization of the neutral ligand-stabilized gold cluster series results in a change of structure in comparison to the charged ones. An exception here is cluster **7**. The visualization of the results is shown in Fig. 2 and 3.

For the neutral **6n** the central dimer develops with one of the other atoms to a trimer with short bond length. Furthermore, there is another trimer with slightly longer Au-Au distances. The symmetry is close to C_{2v}. The average Au-Au bond length is a bit larger compared to the charged one and there is a larger variation of Au-Au bond lengths. The Au-P bond lengths are slightly enhanced and show a larger range of minimal and maximal values as well. The re-optimized Au_6 cluster without ligands results in a pentagon with one atom above in nearly C_{5v} symmetry, the re-optimized global minimum (taken from literature[2]) is planar and approximately D_{3h} symmetry. Thus, the ligands do not stabilize a local gold cluster minimum for the neutral system, and instead a cluster which is 35 kcal/mol higher in energy than the neutral global minimum is obtained. Comparing the optimized free cluster with the global minimum shows that it is still about 20 kcal/mol higher in energy.

The cluster structure and Au-P bond length of the neutral system **7n** are remarkably similar to the charged cluster structure. An re-optimization of this cluster without the ligand shell results in a similar structure to the optimized free D_{5h}-symmetry cluster for the singly charged cluster system. The global minimum of the neutral Au_7 cluster was determined to be a planar structure similar to the singly charged one. The cluster stabilized by the ligand shell is about 19 kcal/mol higher in energy than the global minimum, and 9 kcal/mol above the optimized free cluster. Thus, similar cluster structures are obtained for the neutral system as for the charged one, but the energy differences between them are about 10 kcal/mol larger.

The cluster structure of the neutral **8an** changes only slightly in structural shape, but more significantly in terms of the Au-Au distances. The average and maximum distances are increased and also the Au-P average distance is slightly larger with increased variance in the values. An re-optimization of this cluster without the ligand shell results in the planar global minimum cluster, which adopts D_{4h} symmetry. The cluster stabilized by the ligand shell is about 45 kcal/mol higher in energy than the global minimum. Similar results have been obtained for the neutral **8bn** system. The only difference occurs for the optmization without the ligand shell for which a 3D cluster about 7 kcal/mol higher than the 2D one has been found.

The neutral sytem **9n** also changes when optimized as a neutral system. The Au_9 cluster contains five atoms which form a planar cross, and two dimer units perpendicular to the plane of the cross. The Au-Au distances are generally enlarged relative to the charged cluster, but some shorter distances than in the charged cluster can be found. The Au-P distances are very similar to the charged system. By re-optimizing the cluster without ligands, one obtains a changed structure (D_{2h} symmetry), which is about 25 kcal/mol about the planar (C_{2v} symmetry) global minimum system. The cluster stabilized by the ligands is 45 kcal/mol higher in energy than the 2D cluster. In all cases, the HOMO-LUMO gap verifies the same order of stability as indicated by the relative energies.

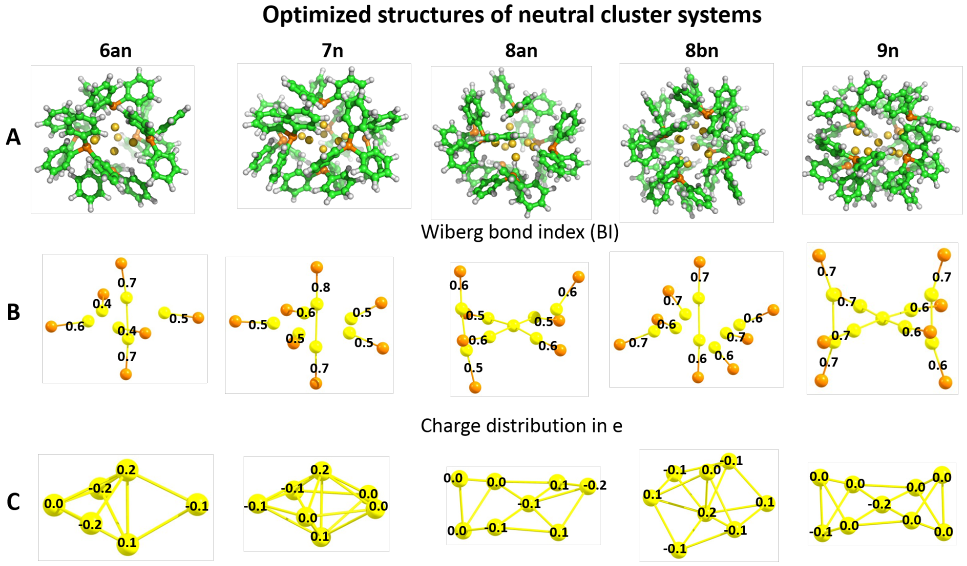

Figure 2: The reoptimized ligand-stabilized neutral gold cluster systems of the gold series n=6-9 are visualized (A). The calculated bond order between the gold cluster and the phosphorous (B) and the charge distribution within the cluster (C) are plotted. The used level of theory is therefore PBE0-D3/cc-pVTZ(-PP, ECP60MDF)//PBE-D3(MARI-J)/cc-pVDZ(-PP, ECP60MDF). The BI for the system **8b** and **9** is based on the calculation with PMe_3 and PH_3 ligands, respectively (for the other systems the BI of the system with different phosphine ligands are very similar).

Analyzing the binding nature

The **ABE** for the neutral Au_n phosphine cluster series are quite similar with around 40 kcal/mol. Compared to the ABE of the charged systems, the ABE is about 1.4 to 2 times weaker for the neutral systems and correlates with the number of cluster atoms. The energetic differences due to structural changes are larger for the neutral systems than for the charged systems. The data can be found in Fig. 4.

The large differences in ABE between the charged and neutral systems does not appear in the **Wiberg BI** between the gold cluster and phosphorus (see Fig. 3). There are very similar values found (0.4 - 0.8) as in the corresponding charged clusters, indicating a half single to a single bond between the ligands and the gold cluster. Thus the ABE is not changing due to changes in orbital overlap, but due to major change in the **CT effects** (see Fig. 3). The total CT is smaller for the neutral systems (0.0 to 0.4 e) than for the charged ones (0.8 to 2.3 e). However, the CT per bond is slightly increasing along the cluster size for the neutral system. The charge distribution in the neutral gold cluster series shows a similar trend as for the charged systems. As for the charged cluster systems the **ligand shell interaction** contributes to the stabilization of the systems.

Looking at the **electronic structure** the evidence occurs that only the neutral system **6an** shows a clear separation in the HOMO-LUMO gap, implying that this should be the most stable one. With the PBE0 functional, all gaps are larger, but still indicate higher stability for the **6an** phosphine system, followed by **8an** and **8bn**. The differences can be explained due to both **6an** and **8a/bn** being systems with even electron numbers, whereas all other systems have an odd number of electrons. This stabilizes the system from the electronic side. Furthermore, as the system **6an** has a smaller number of delocalized 6s electrons, the bright peak in the DOS occurs at higher energies, resulting in a double peak as the HOMO and the bright peak as LUMO. For all other systems the bright peak is the HOMO. This property can already be detected in the LDOS of the cluster without the ligand shell.

Variation of the phosphine ligand shell

The effect of modifying the phosphine ligands on the neutral gold cluster series is analyzed. The data are shown in Fig. 4.

As was observed for the charged systems, it has been found that the PH_3 and PPh_3 ligand-surrounded clusters agree very well with each other on the preferred structures, relative energies and CT effects. There is just (as for the charged systems) a small variation for the system **8an**. For the PMe_3 ligand surrounded clusters the CT is higher than for the other ligands and as a result the structures of **6an**, **8an**, **8bn** and **9n** are slightly distorted (compared to the structures with PPh_3 ligands), with corresponding relative energy differences between 2 and 6 kcal/mol. However, the structure of **7n** is totally changed, to a structure including one trimer and two dimer units (energy change of about 15 kcal/mol). The HOMO-LUMO gap increases for the systems with an even number of cluster atoms from PPh_3 over PMe_3 to PH_3. The same happens for the odd numbered clusters, with the difference that the PMe_3 and PH_3 systems are much more similar. The ABE between clusters with PPh_3 and PMe_3 are very similar, whereas the PH_3 ligands reduce the magnitude of binding by about 10 kcal/mol.

References

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(2) Zanti, G.; Peeters, D. *The Journal of Physical Chemistry A* **2010**, *114*, 10345–10356.

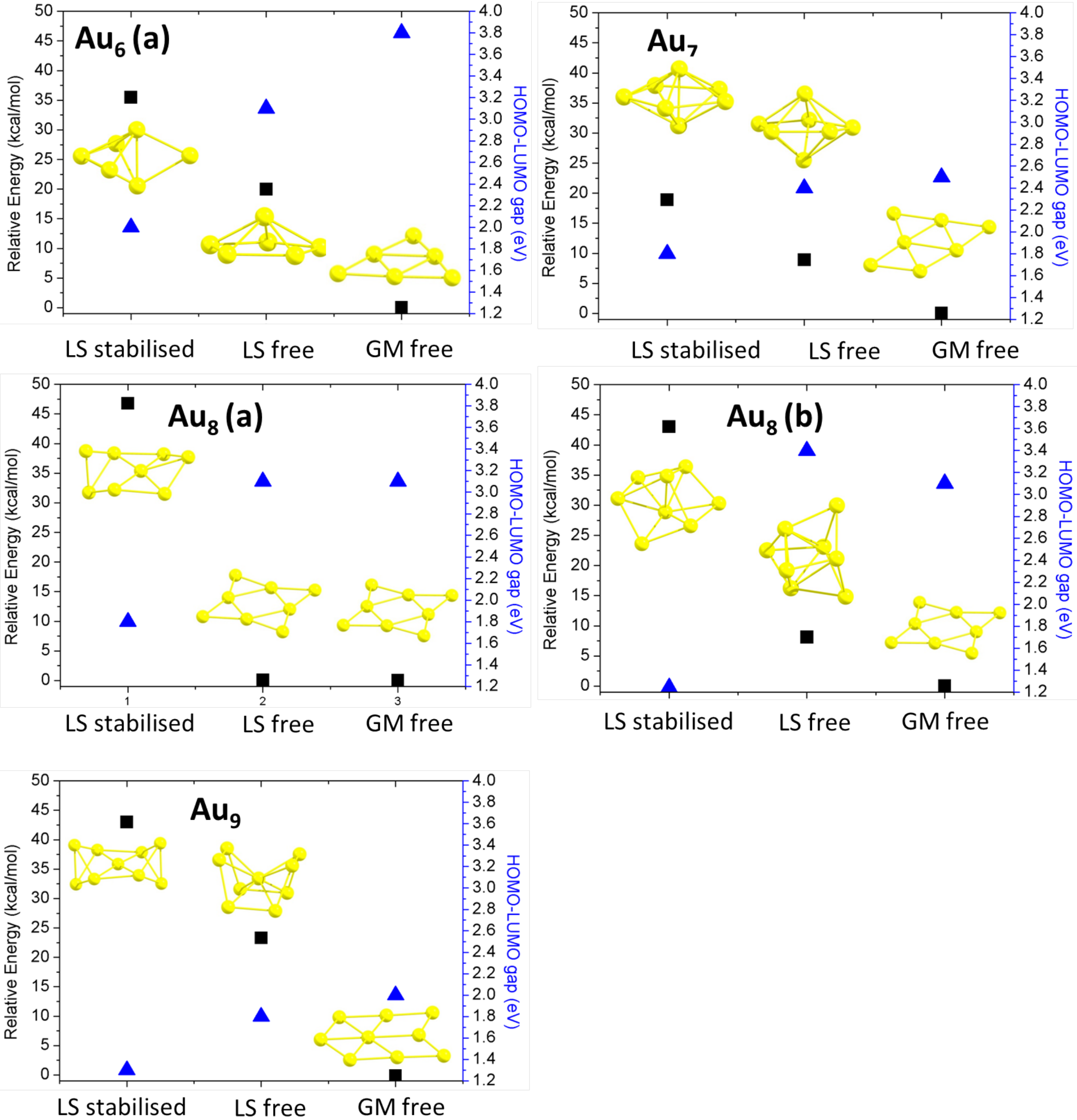

Figure 3: Neutral cluster structures of the ligand-stabilized cluster (LS-stabilized) and the naked re-optimized clusters derived from the LS-stabilized (LS free) or the global minima one (GM free) as well as related relative energies and HOMO-LUMO gaps calculated at PBE0-D3/cc-pVTZ(-PP, ECP60MDF)//PBE-D3(MARI-J)/cc-pVDZ(-PP, ECP60MDF) level of theory.

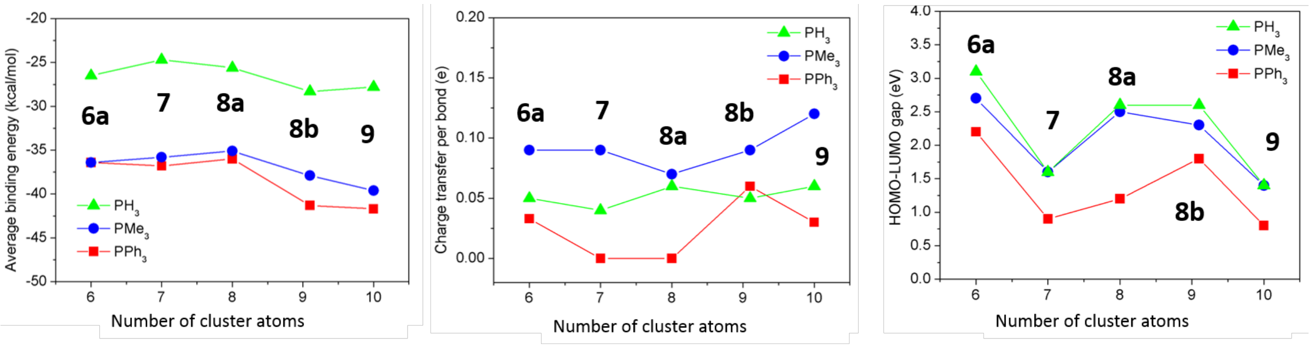

Figure 4: Average binding energies (in kcal/mol), the charge transfer from the ligand shell to the cluster per bond (in e) as well as the HOMO-LUMO gap (in eV) calculated at PBE0-D3/cc-pVTZ(-PP, ECP60MDF)//PBE-D3(MARI-J)/cc-pVDZ(-PP, ECP60MDF) level of theory are given for the neutral Au$_n$ cluster phosphine systems.