

**Supporting Information for:**

**Aromatic Character of  $[\text{Au}_{13}]^{5+}$  and  $[\text{MAu}_{12}]^{4+/6+}$  ( $\text{M}=\text{Pd},\text{Pt}$ ) Core in Ligand Protected Gold Nanoclusters. Interplay Between Spherical and Planar  $\sigma$ -Aromatics**

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Figure S1. Canonical molecular orbitals of  $[\text{Au}_{13}]^{5+}$ .

Figure S2. Chemical bonding pattern for 8-ve  $[\text{Au}_{13}]^{5+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative 5d lone-pairs. ON stands for occupation number.

Figure S3. Chemical bonding pattern for 8-ve  $[\text{PdAu}_{12}]^{4+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative lone-pairs on Pd (similar lone-pairs were found for gold atoms, Figure S2). ON stands for occupation number.

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Figure S4. Chemical bonding pattern for 6-ve  $[\text{PdAu}_{12}]^{6+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative lone-pairs on Pd (similar lone-pairs were found for gold atoms, Figure S2). ON stands for occupation number.

Figure S5. Chemical bonding pattern for 8-ve  $[\text{PtAu}_{12}]^{4+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative lone-pairs on Pt (similar lone-pairs were found for gold atoms, Figure S2). ON stands for occupation number.

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Figure S6. Chemical bonding pattern for 6-ve  $[\text{PtAu}_{12}]^{6+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative lone-pairs on Pt (similar lone-pairs were found for gold atoms, Figure S2). ON stands for occupation number.

Figure S7. Alternative chemical bonding pattern for 6-ve  $[\text{PtAu}_{12}]^{6+}$  as shown by the AdNDP analysis. All the 6 ve are localized only on  $\text{Au}_{10}$  ribbon. ON stands for occupation number.

Figure S8. Molecular orbitals for  $[\text{Au}_{13}]^{5+}$ ,  $[\text{PdAu}_{12}]^{4+}$  and  $[\text{PtAu}_{12}]^{6+}$ , accounting for the respective  $1\text{S}^2 1\text{P}^6$  and  $1\text{S}^2 1\text{P}_{x,y}^4 1\text{P}_z^0$  electronic configuration

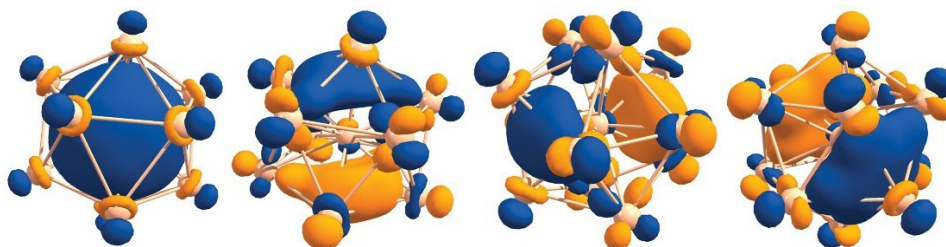


Figure S1. Canonical molecular orbitals (MO) of  $[\text{Au}_{13}]^{5+}$ . One can clearly see that all spherical aromatic multi-centered bonds recovered by the AdNDP analysis originate from these MOs.

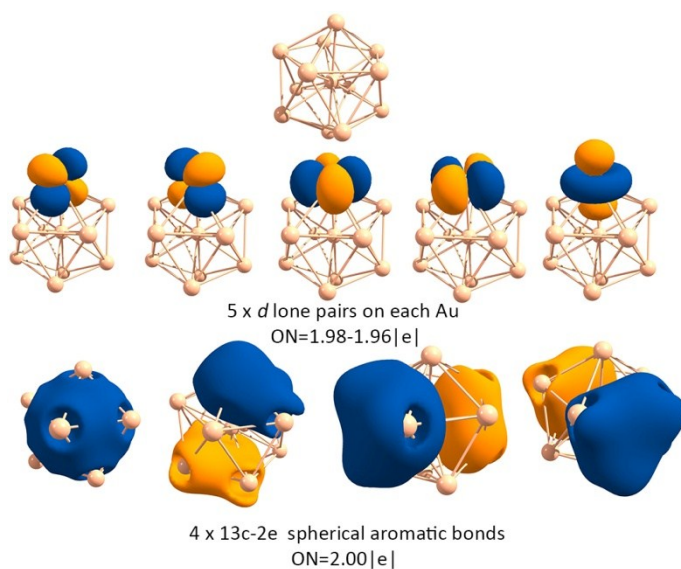


Figure S2. Chemical bonding pattern for 8-ve  $[\text{Au}_{13}]^{5+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative 5d lone-pairs. ON stands for occupation number.

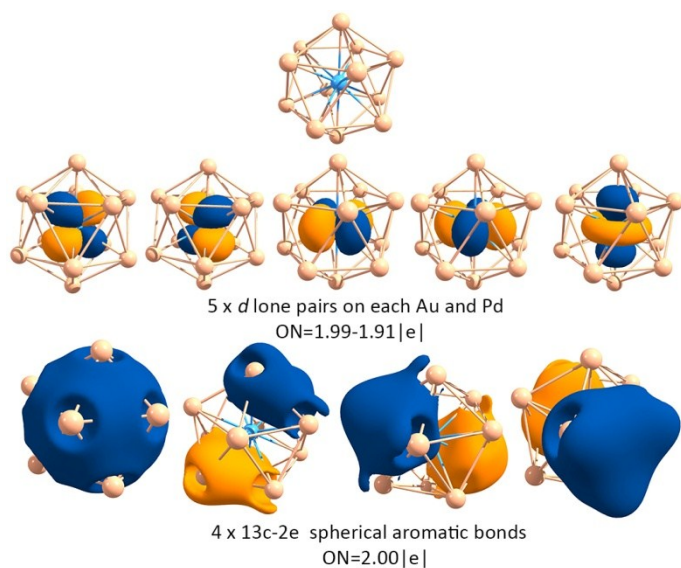


Figure S3. Chemical bonding pattern for 8-ve  $[\text{PdAu}_{12}]^{4+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative lone-pairs on Pd (similar lone-pairs were found for gold atoms, Figure S1). ON stands for occupation number.

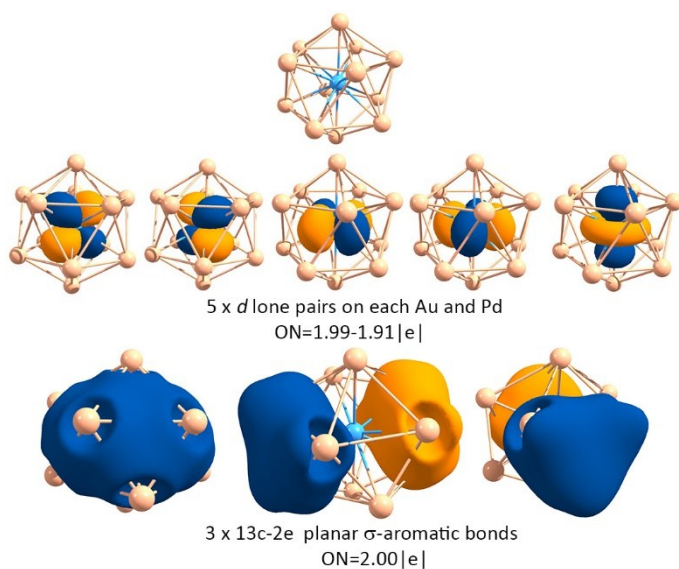


Figure S4. Chemical bonding pattern for 6-ve  $[\text{PdAu}_{12}]^{6+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative lone-pairs on Pd (similar lone-pairs were found for gold atoms, Figure S1). ON stands for occupation number.

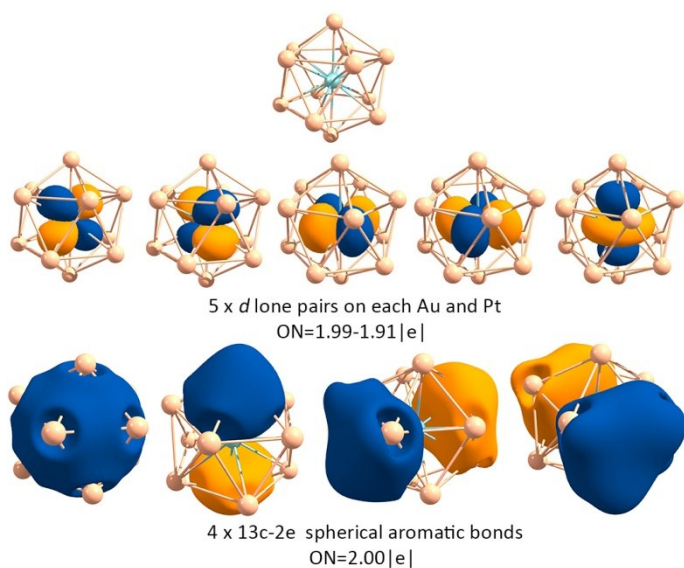


Figure S5. Chemical bonding pattern for 8-ve  $[\text{PtAu}_{12}]^{4+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative lone-pairs on Pt (similar lone-pairs were found for gold atoms, Figure S1). ON stands for occupation number.

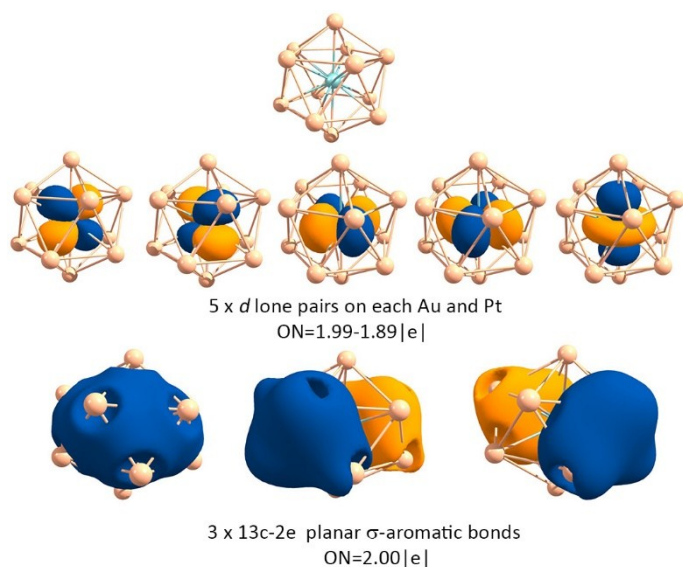


Figure S6. Chemical bonding pattern for 6-ve  $[\text{PtAu}_{12}]^{6+}$  as shown by the AdNDP analysis, denoting 13c-2e bond and representative lone-pairs on Pt (similar lone-pairs were found for gold atoms, Figure S1). ON stands for occupation number.

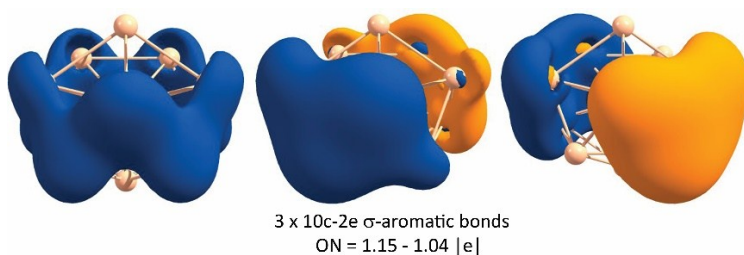


Figure S7. Alternative chemical bonding pattern for 6-ve  $[\text{PtAu}_{12}]^{6+}$  as shown by the AdNDP analysis. All the 6 ve are localized only on  $\text{Au}_{10}$  ribbon. ON stands for occupation number.

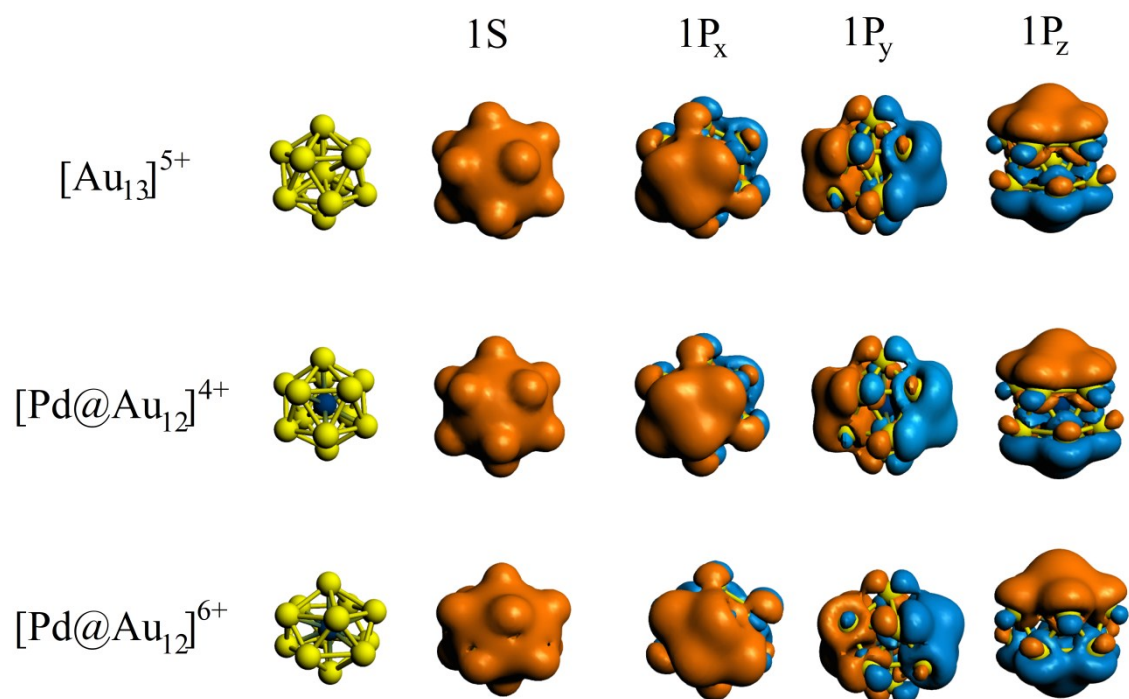


Figure S8. Molecular orbitals for  $[\text{Au}_{13}]^{5+}$ ,  $[\text{PdAu}_{12}]^{4+}$  and  $[\text{PdAu}_{12}]^{6+}$ , accounting for the respective  $1S^2 1P^6$  and  $1S^2 1P_{x,y}^4 1P_z^0$  electronic configuration. For  $[\text{PdAu}_{12}]^{6+}$  the  $1P_z^0$  level remains as LUMO.