

Evaluation of N-Heterocyclic Carbene Counterparts of Classical Gold Clusters; Bonding Properties of Octahedral CAu₆, Icosahedral Au₁₃Cl₂, and Bi-icosahedral Au₂₅Cl₂ Cores from Relativistic DFT Calculations

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Gold clusters are useful templates for nanosized species retaining a distinctive size-dependent behavior. Usually, a ligand-protected shell passivates such clusters, where their properties can be potentially tuned by introduction of versatile ligands. Here, we explored the recent addition to the well-explored gold-phosphine chemistry, introducing N-heterocyclic carbene (NHC) ligands as characterized by the octahedral carbon-centered CAu₆ core, in [CAu₆(NHC)₆]²⁺. Our results show their similar bonding patterns in such discrete clusters, with slight preference for the later ligands, enabling the proposition of medium-sized species featuring the predominant icosahedral Au₁₃ structure. NHC counterparts for Au₁₃Cl₂(dppe) and Au₂₅Cl₂(PPh₃)₁₀(SR)₅ clusters, denoting both icosahedral and bi-icosahedral central cores, where the bonding features patterns and favorable stability, remain similar to that observed for their phosphine parents and [CAu₆(NHC)₆]²⁺ clusters, shedding light on other feasible members for explorative synthetic efforts. Optical properties are modified when NHC is introduced instead of phosphine ligands, inducing a red-shift for the lowest-energy peak with a highest occupied molecular orbital lowest unoccupied molecular orbital character and a blue-shift for higher energy absorptions. Hence, NHC derivatives as a ligand-protected layer for medium-sized clusters can introduce useful alternatives for ligand-protected shells, which can be further explored owing to their recognition for well-established versatility in organometallic chemistry. © 2019 American Chemical Society.