

Toward the Formation of N-Heterocyclic-Carbene-Protected Gold Clusters of Various Nuclearities. A Comparison with Their Phosphine-Protected Analogues from Density Functional Theory Calculations

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Abstract

The structure and bonding of a series of selected phosphine-protected gold clusters (Aun-P) of nuclearity varying from $n = 6$ to 13 were investigated by density functional theory (DFT) calculations and compared to those of the hypothetical homologues in which phosphines were replaced by N-heterocyclic carbene (NHC) analogues (Aun-C). Both the Aun-P and Aun-C series exhibit similar stabilities and structural features, except for $n = 6$, where some differences are noted. The NHC ligands are found to be even slightly more strongly bonded to the gold core (by a few kilocalories per mole per ligand) than phosphines. Investigation of the optical properties of both series using time-dependent DFT calculations indicates similarities in the nature and energies of the UV-vis optical transitions and, consequently, relatively similar shapes of the simulated spectra, with a general blue-shift tendency when going from Aun-P to Aun-C. The fluorescence behavior observed experimentally for some of the Aun-P species is expected to occur also for their Aun-C analogues, which can be extended to other carbene-ligand-protected nanoclusters. Our results show that it should be possible to stabilize gold clusters with NHC ligands, in relation to the seminal Au₁₃-ligand-protected core, offering novel building blocks for the design of nanostructured materials with various properties.