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Impact of Swapping Ethyl for Phenyl Groups on Diphosphine-Protected Undecagold

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1,3-Bis(diethylphosphino)propane (depp) protected gold clusters are synthesized and studied via electrospray ionization mass spectrometry. An undecagold cluster, $[Au_{11}(depp)_4Cl_2]^+$, is observed under soft ionization conditions and is found to persist in solution for at least 1 month. The importance of the Cl ligands is discussed in terms of the electron-donating nature of the depp ligands, and we contrast the core−ligand interactions observed here with those found in the previously reported $[Au_{11}(dppp)_5]^{3+}$ (where dppp = 1,3-bis-(diphenylphosphino)propane). The experimental observations are supported by density functional theory calculations, which suggest that the dppp ligand is a better electron acceptor than depp. Further calculations illustrate some of the subtleties that emerge when attempting to model core−ligand interactions on small clusters. The results demonstrate that a degree of caution is merited when making ligand approximations for modeling of monolayer-protected nanoparticles.

Accurate modeling of real-world nanoparticles is highly desirable as a vehicle for both characterization and prediction of technologically important chemical, electronic, optical, and magnetic properties. Even relatively small nanostructures observed in experiments still pose a challenge to high-level theory, but improvements in density functional theories (DFT) continue to advance the frontiers of computationally tractable systems. Gold clusters have received substantial theoretical attention,[1] and recently several reports have treated relatively small monolayer-protected gold clusters (Au MPCs) by replacing functional groups studied experimentally with smaller approximations;[1,2] for example, $P(C_6H_5)_3$ might be replaced by PH_3. In this manner, calculations can be made much less costly, but the extent to which important ligand properties might be lost in the approximation is unclear.[2c] Herein, we describe experimental and DFT investigations of a system in which a small change to a diphosphine ligand has a pronounced effect on the core−ligand interactions of a MPC.

Two of the authors of this work recently reported[3] the gas-phase fragmentation behavior of several diphosphine-protected Au MPCs first described by Bertino et al.,[4] including $[Au_{11}(dppp)_5]^{3+}$ (dppp = 1,3-bis(diphenylphosphino)propane).[5] We hoped to compare the results of the fragmentation experiments to DFT calculations. Although this particular cluster contains only 11 Au atoms, the moderately bulky ligands expand the computational system to a total of 271 atoms, so attempts at a DFT treatment would be very ambitious. Replacing the phenyl groups with ethyl groups, using the commercially available 1,3-bis(diethylphosphino)propane (depp) ligand would reduce the total number of atoms by 80, while preserving the

essential features; particularly important was the preservation of the three-carbon chain between the two P atoms of the bidentate ligand, which we believed would maintain the good size selectivity of the synthesis. Noting the obvious differences between the two ligands, we were interested to see how the steric differences and the elimination of any potentially stabilizing $\pi-\pi$ interactions from the phenyl rings might affect the clusters. As we describe, however, the substitution of ethyl groups for phenyl groups leads to an important change in the core−ligand interaction by changing the diphosphine ligands from net electron acceptors to net electron donors.[6]

The MPCs were synthesized according to the procedures described previously.[3] $AuClP(C_6H_5)_3$, depp, and borane tert-butylamine complex were dissolved in a 1:1:5 ratio in a 1:1 solution of $CHCl_3/CH_3OH$. The solution was stirred under inert gas overnight, gradually acquiring a dark-red color. UV−vis spectroscopy revealed the formation of a molecular cluster absorbing at ∼415 and ∼300 nm; another peak at ∼515 nm is presumably due to a surface plasmon resonance band from larger gold nanoparticles.

Au/depp solutions were diluted in CH_3OH for analysis via electrospray ionization mass spectrometry (ESI-MS) (Micromass Quattro Micro).[7] In analogy to the observed[3,4] $[Au_{11}(dppp)_5]^{3+}$ cluster, $[Au_{11}(depp)_5]^{3+}$ would be expected to appear at 1089 m/z; however, no such peak was observed. In fact, we were unable to identify any multiply charged MPCs in the m/z range below 2000. Utilizing an instrument (Micromass Quattro II) with capabilities extending to 4000 m/z, we confirmed that the MPCs that appeared in the UV−vis spectrum were actually singly charged, Cl-containing clusters, including the closed-shell (eight electron) $[Au_{11}(depp)_4Cl_2]^+$.[8] Significantly, under conditions that gave a good $[Au_{11}(dppp)_5]^{3+}$ signal, $[Au_{11}(depp)_4Cl_2]^+$ and not $[Au_{11}(depp)_5]^{3+}$ was observed. As Figure 1 shows,

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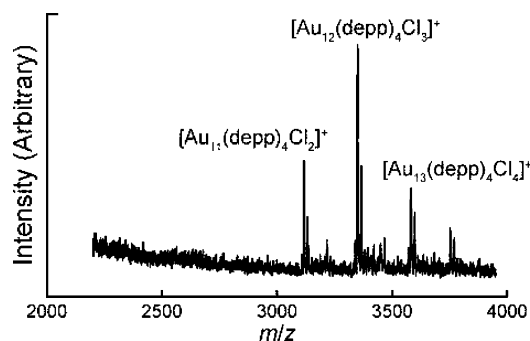 ‡ National Institute of Standards and Technology.

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Figure 1. Mass spectrum obtained via ESI of Au/depp clusters synthesized in 1:1 CHCl₃/CH₃OH and diluted in CH₃OH prior to direct infusion to the ESI source. At a cone voltage of 20 V, no fragmentation of the cluster ions is observed.

Figure 2. Calculated (B3LYP/LANL2DZ) energy required to remove a ligand or Au atom from $[Au_n(dppp)]^+$ and $[Au_n(depp)]^+$. For both ligands, the $[Au_3L]^+$ configuration is particularly stable.

$[Au_{11}(depp)_4Cl_2]^+$ appears prominently at low cone voltages (without fragmentation), and we found that it persists in solution for at least 1 month. Also present are the closed-shell[9] $[Au_{12}(depp)_4Cl_3]^+$ and $[Au_{13}(depp)_4Cl_4]^+$ clusters, which form more slowly than the undecagold species, but then persist in solution for at least 1 month.

Of particular interest here is the preferred stoichiometry of the undecagold cluster: specifically, the electronic necessity for stabilizing pseudohalide Cl ligands. Pseudohalide ligands are fairly common on phosphine-protected gold clusters,[9] and the necessity for pseudohalide ligands in the present example can be simply explained as arising from the electron donating/accepting properties of the diphosphine ligands. Phosphine (PR₃) ligands in organometallic chemistry are both σ donors and π acceptors, and the relative strengths of these interactions is determined by the electronegativity of the R groups.[6] A more electronegative R withdraws electrons from the P so that it is more positive and better able to accept electrons. Our preliminary DFT calculations[10] confirm that the P atoms of depp are less positive than those of dppp, with a natural population analysis giving respective values of 0.72305 e+ and 0.75865 e+.

In light of this behavior, the stoichiometry of the undecagold clusters is readily understood. For $[Au_{11}(dppp)_5]^{3+}$, all 10 exposed Au atoms are coordinated to a P atom, and the ligands pull electron density from the core, enabling Au₁₁ to adopt its preferred 3+ charge state (with an eight electron core configuration). Alternatively, $[Au_{11}(depp)_4Cl_2]^+$, which again features 10 filled coordination sites, shows that the tendency of depp to push electrons onto the Au₁₁ core leads to the necessity for two electron-withdrawing Cl ligands to satisfy the preferred 3+ charge state. Coordination of five depp ligands to the Au₁₁ core is prohibited either by the energetics of the formation reaction or by a destabilization of the core. The absence of $[Au_{11}(depp)_5]^{3+}$ in the experiments demonstrates clearly that depp is a poor approximation for dppp.

To further probe the nature of the core-ligand interaction, we performed additional calculations on small $[Au_n(dppp)]^+$ and $[Au_n(depp)]^+$ complexes ($n = 2-5$), and Figure 2a and b demonstrates that the $[Au_3L]^+$ (L = dppp or depp) are particularly stable with respect to neighboring species. The trimer-based clusters appeared as a fragment ion of each Au MPC considered in our recent CID studies. ($[Au_3(depp)]^+$ was also a ubiquitous fragment of Au/depp MPCs, as we observed at higher cone voltages), which was interpreted as indicative of intrinsic stability.[3]

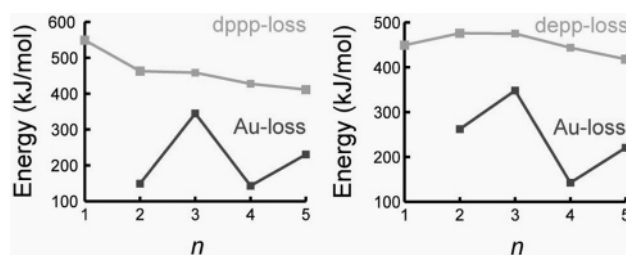Because the calculations reproduced the experimentally determined stability trends, we turned to the calculated electron densities for insight into the donor/acceptor interactions. Although numerous schemes were employed, we found it difficult to reconcile the results with the simple donor/acceptor model. At present, it is enough to note that several intricacies emerge as the size of the cluster system being investigated increases. One important consideration involves "magic numbers", and it is significant that if a ligand has a capacity for electron donation *and* acceptance, then it is possible for the electronic structure of the core to play the determining role in the nature of the core−ligand interaction.

Despite these difficulties, the interpretation of experimental results indicates the importance of considering the complete ligand in the modeling of MPCs. It is difficult to predict the extent to which these results can be generalized for nanoparticles. Certainly, very small MPCs with molecule-like electronic structure will be critically sensitive to small changes in the chemical functionality of protecting ligands. However, the extent to which a change from an electron-accepting to an electron-donating ligand might perturb a larger gold nanoparticle is uncertain. Larger clusters differ from smaller ones in numerous ways, including a smaller surface/volume ratio, a greater diversity of coordination sites, and a closer electronic approximation of bulk band structure. It is possible that a relatively large nanoparticle will not be substantially perturbed geometrically by a change to the chemical character of its ligands; however, if one hopes to model electronic properties, for example a band gap or surface plasmon effect, it is crucial that any approximations used for the ligands do not alter the electronic structure of the core.

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(7) Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

(8) Although this synthesis was not as selective as the dppp synthesis described in refs 3 and 4, we were able to discern a number of small MPCs with both pure-depp and mixed-depp/P(C_6H_5)$_3$ protecting ligands. These results, including a description of fragmentation patterns, will be discussed in a forthcoming disclosure.

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(10) We used density functional theory within two different approximations: the B3LYP hybrid functional and PBE generalized gradient functional. Two basis sets, LANL2DZ and SDD, were used, both with 60 electron core pseudopotentials for Au and differing sized cores for P. Negligible differences were seen in using different basis sets and functionals. All calculations were performed using the Gaussian03 program suite with default criteria for convergence and density grids. In some cases, XQC was needed to converge the single-point energies. See refs 11a–j for details.

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