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Hydride, Chloride, and Bromide Show Similar Electronic Effects in the $Au_9(PPh_3)_8^{3+}$ Nanocluster[†]

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Recent experimental and computational results have suggested that a hydride bound to the $Au_9(PPh_3)_8^{3+}$ gold nanocluster donates its electrons to the metal core, forming an 8-electron cluster. We present electronic absorption spectra of precisely mass-selected $Au_9(PPh_3)_8^{3+}$ clusters featuring a surface hydride, chloride, or bromide. Comparison of these spectra shows that H^-, Cl^-, or Br^- perturb the electronic structure of the $Au_9(PPh_3)_8^{3+}$ core in similar ways. This suggests that hydride and halides play similar roles electronically in this cluster, and thus are either both metallic or both ligand-like.

Atomically-precise metal nanoclusters bearing metal-hydride bonds are studied as homogeneous hydrogenation catalysts, as well as intermediates in the controlled growth of gold nanoclusters (AuNCs) or their alloys.[1–6] The reactivity of cluster-hydrides could be expected to parallel organometallic hydride complexes,[1,7] in that the relative metal-hydride bond strength of clusters will largely determine the reaction mechanism. Classification schemes must thus be sought to predict reactivity, substrate scope, and develop analogous designer catalysts. However, the specific nature of the hydride ligand in AuNCs is ambiguous. Experimental and computational work provide competing explanations over the hydride's function in $Au_9(PPh_3)_8H^{2+}$ – an adduct which exhibits remarkable flexibility as a synthetic intermediate in the formation of alloy clusters.[2] Recent synthetic work indicates that the metal-hydride bond functions as an acidic metal-hydride whereby the nucleophilic metal cage is capable of controlled cluster growth.[2–4] In contrast, computational results suggest that the hydride participates in the gold core as a delocalizing metal center, mimicking the role of a metal dopant in forming a closed-shell "superatom."[2,8] Photoelectron spectra of ligand-free gold clusters containing hydride show strikingly similar spectra

for Au_nH^- and Au_{n+1}^-.[9]

Classifying hydride as a ligand or metal becomes a question over its impact on the $Au_9(PPh_3)_8^{3+}$ electronic structure. As such, comparison of electronic spectra of hydride- and halide-containing $Au_9(PPh_3)_8^{3+}$ clusters could evince the role of the hydride. We hypothesized that the electronic spectrum of a metallic hydride would show qualitative differences from that of a more typical halide-containing cluster. However, purification of $Au_9(PPh_3)_8^{3+}$ clusters with unambiguous hydrides or halides has not yet been achieved. We employed a gas-phase spectroscopy approach that interfaces mass spectrometry with UV/Vis spectroscopy, yielding highly-resolved spectra of atomically-precisely mass-selected clusters from solution-synthesized mixtures.[10] This basic approach has shown the ability to successfully isolate a variety of hydride-containing species, and thus we harness it as an alternate purification method that provides unambiguous speciation of a solution-phase mixture.[2,5,6,11–14]

The triphenylphosphine-protected AuNCs, $Au_9(PPh_3)_8^{3+}$ and structurally-related $Au_8(PPh_3)_7^{2+}$, were prepared by reduction of chloro(triphenylphosphine)gold(I) with sodium borohydride. $Au_9(PPh_3)_8H^{2+}$ was readily prepared by mixing the raw reaction product containing $Au_9(PPh_3)_8^{3+}$ with borane tert-butylamine, in a similar procedure to that already reported, and electrospraying the resulting mixture.[2] The resulting mass spectra, tabulated in the SI, match those presented by Tsukuda and co-workers.[2] The $Au_9(PPh_3)_8Cl^{2+}$ and $Au_9(PPh_3)_8Br^{2+}$ clusters were prepared by the same approach but with the organic salts tetraphenylphosphonium chloride or tetrabutylamonium bromide, respectively, instead of borane tert-butylamine (see SI for synthetic details). All products were introduced into the mass spectrometer by electrospray ionization with no purification, an approach commonly employed in gas-phase chemistry of triphenylphosphine-protected AuNCs.[11,15] The resulting clusters were mass selected such that UV/Vis absorption spectra could be obtained of only the cluster of interest, as outlined in the SI.

Figure 1 compares the published UV/Vis spectra of both $Au_9(PPh_3)_8^{3+}$ and $Au_9(PPh_3)_8H^{2+}$ in solution to those recorded

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for the same clusters in the gas phase. Notable similarities between the gas- and solution-phase spectra of each cluster are apparent, particularly in the position and width of the broad peaks found in $Au_9(PPh_3)_8H^{2+}$ and the position of the intense, sharp feature near 430 nm in $Au_9(PPh_3)_8^{3+}$. This similarity provides strong evidence that the solution-phase species is faithfully transmitted to the gas phase via electrospray. Figure S3 similarly compares the solution phase UV/Vis spectra of the samples used in these experiments to the same spectra reported in the literature, again finding a close match.
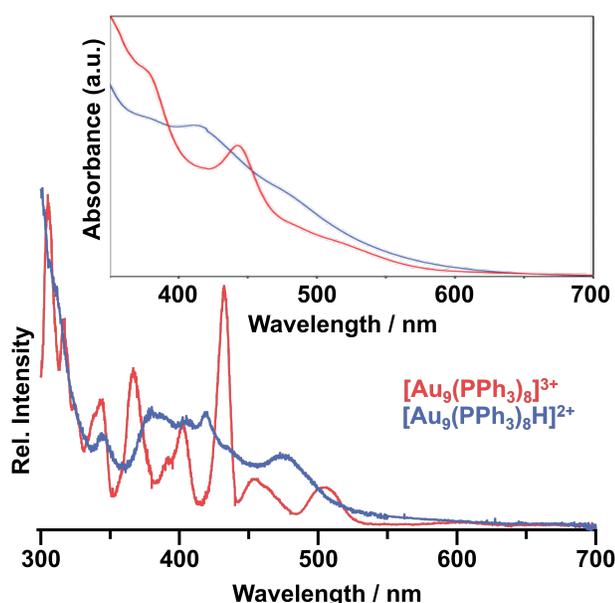
Fig. 1 Comparison of previously-reported solution-phase UV/Vis spectra for $Au_9(PPh_3)_8^{3+}$ and $Au_9(PPh_3)_8H^{2+}$ to those recorded in this study.[2] Both spectra of $Au_9(PPh_3)_8^{3+}$ feature a strong, narrow absorbance near 430 nm and additional features near 370 and 500 nm that are less well-resolved in the solution phase. For $Au_9(PPh_3)_8H^{2+}$, a broad, bimodal feature spanning 400-500 nm is found in both spectra. The close correspondence between the solution- and gas-phase spectra indicates that the electronic structure of these clusters is preserved upon introduction to the mass spectrometer. Adapted with permission from Reference [2]. Copyright 2018 American Chemical Society.

Figure 2 presents the mass-selective UV/Vis spectra of all five ligand-protected AuNCs measured at 3.8 K. The $Au_8(PPh_3)_7^{2+}$ (purple) and $Au_9(PPh_3)_8^{3+}$ (red) spectra highlight the the fact that changing the overall cluster composition need not qualitatively change the electronic spectrum of this cluster. Previous crystallographic characterization of $Au_9(PPh_3)_8^{3+}$ and $Au_8(PPh_3)_7^{2+}$ suggests that the two clusters are geometrically-related (D_{2h} and C_s, respectively), each sharing an analogous mirror plane, with $Au_8(PPh_3)_7^{2+}$ bearing a lower symmetry structure via "loss" of a closed-shell $[Au(I)PPh_3]^+$ fragment.[16,17] We have previously shown that there is essentially a one-to-one correspondence between the peaks in these spectra, suggesting that the electronic structure of the two clusters are very similar.[10]

Addition of the hydride ion to the $Au_9(PPh_3)_8^{3+}$ cluster yields a dramatic, qualitative change to the spectrum, as the blue trace in Figure 2 shows no apparent preservation of the parent clus-
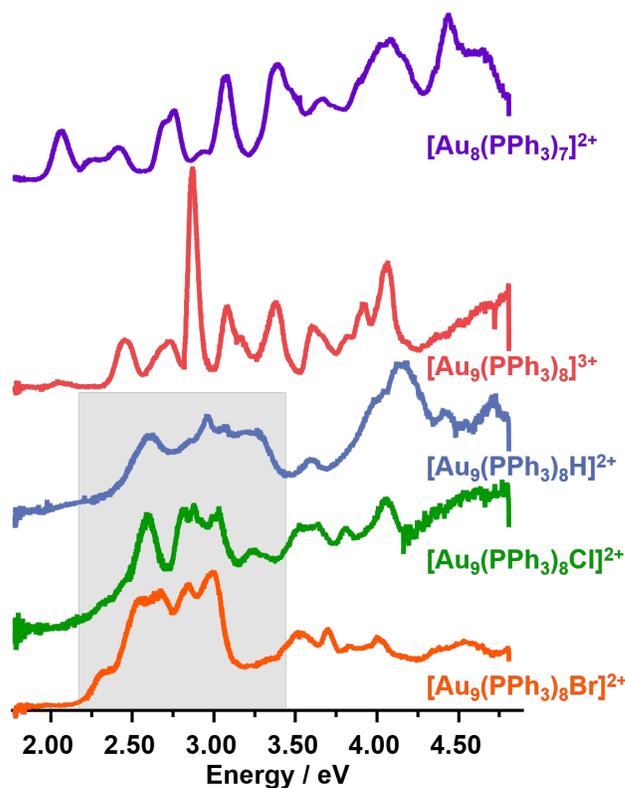
Fig. 2 Response of the electronic absorption spectrum of $Au_9(PPh_3)_8^{3+}$ (red) to compositional modulation. $Au_8(PPh_3)_7^{2+}$ (purple) shows several electronic transitions are preserved between clusters. $Au_9(PPh_3)_8H^{2+}$ (blue), $Au_9(PPh_3)_8Cl^{2+}$ (green), and $Au_9(PPh_3)_8Br^{2+}$ (orange) are presented below.

ter's electronic structure. Subtle features across the spectrum indicate the presence of several unresolved, overlapping transitions with both broader and narrower bands. The dramatic change in the UV/Vis spectrum suggests that addition of a hydride ligand is more perturbative to the electronic structure than loss of a $[Au(I)PPh_3]^+$ fragment, where both the MLCT and intracore transitions notably respond to hydride addition. Comparison to the $Au_9(PPh_3)_8Cl^{2+}$ and $Au_9(PPh_3)_8Br^{2+}$ spectra (green and orange traces, respectively) shows that the spectra closely resemble the $Au_9(PPh_3)_8H^{2+}$ spectrum. Surprisingly, the spectral profile spanning 2.25 – 3.40 eV remains essentially intact (highlighted in gray), despite the substantial electronic differences between these two halides.

We can consider the following interpretations:

1. The hydride ion participates in the metal core as a delocalizing dopant, overall increasing the electron count of the cluster core. If this is true, then it follows that both chloride and bromide also participate in the clusters as metal dopants.

2. Ligating the $Au_9(PPh_3)_8^{3+}$ with H^-, Cl^-, or Br^- similarly isomerize the core geometric structure, thus making structure the strongest factor governing the electronic structure.

3. H^-, Cl^-, or Br^- interface with the cluster as X-type ligands with electrons relatively localized on the ligand.

We have previously reported the gas-phase electronic absorption spectrum of $Au_9(P(p\text{-}OCH_3\text{-}Ph)_3)_8^{3+}$, which features a sim-

ilar core geometry as that predicted by density functional theory calculations for $Au_9(PPh_3)_8H^{2+}$.[2,10,18] There is no obvious correspondence between the two spectra (Fig. S1); indeed the $Au_9(P(p\text{-}OCH_3\text{-}Ph)_3)_8^{3+}$ spectrum bears more resemblance to those of $Au_9(PPh_3)_8^{3+}$ and $Au_8(PPh_3)_7^{2+}$. Thus, it is unlikely that the core reorganization alone drives this spectral change, casting doubt on interpretation 2. Further, recent experimental evidence suggests that the $Au_9(PPh_3)_8^{3+}$ core may take on a more analogous core structure to $Au_9(P(p\text{-}OCH_3\text{-}Ph)_3)_8^{3+}$ than previously shown.[19] The new features between 2.50 and 3.40 eV arise in a region of the spectrum previously predicted (for $Au_9(PPh_3)_8^{3+}$) to show metal-to-ligand charge transfer (MLCT) character by time-dependent density functional theory calculations,[20] suggesting that they may involve final states with substantial contribution from the hydride or halide. Given dissimilar electronic structures amongst these ions, it is unlikely that their MLCT transitions would coincidentally overlap – arguing against interpretation 3. We then converge on the realization that there is no spectroscopic evidence that is inconsistent with interpretation 1; in this case, the new features could be ascribed to particularly intense transitions between well-separated superatomic P and D orbitals in the case of a formally 8-electron core. Recent theoretical work has suggested that 8-electron gold nanoclusters with differing metal dopants and hydride numbers show similar frontier orbitals,[8] which would likely lead to similarities in their spectra.

This analysis suggests that, if hydride behaves as a metal center, then chloride and bromide should also be investigated for metallic character. If chloride and bromide are to be considered as X-type ligands, then it follows that hydride likely behaves as an X-type ligand as well. Lacking a clear framework by which to interpret these complex spectra, we are limited to such qualitative arguments. Detailed comparisons of the reactivity of chloride- and bromide-containing clusters to hydride-containing clusters will likely be clarifying. Quantum chemical support will be required to draw a definitive conclusion, and the relatively high resolution, atomic precision, and minimal environmental broadening of these spectra make them ideal benchmarks for such efforts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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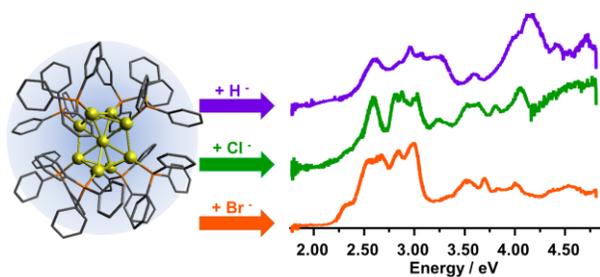
Hydride and halide ligands in gold nanoclusters exhibit an unexpected similar electronic relationship, suggesting an underlying chemical linkage between them.