# Ligand Induced Structural Isomerism in Phosphine Coordinated Gold Clusters Revealed by Ion Mobility Mass Spectrometry

Marshall R. Ligare,[a] Erin S. Baker,[b] Julia Laskin*[a] and Grant E. Johnson*[a]

a Physical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, MSIN K8-88, Richland, WA 99352

b Biological Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352

# Supplemental Information

**Other Gold Clusters Observed in this Study:** Prior to ligand exchange a range of gold clusters was observed; $(8,7)^{2+}$, $(9,8)H^{2+}$, $(10,8)^{2+}$ and $(11,9)H^{2+}$. After ligand exchange with $MePPh_2$, $Au_8$ $Au_{10}$ and $Au_{11}$ formed mixed ligand clusters and $Au_9$ was no longer present in the mass spectrum. $Au_{10}$ clusters exhibited two arrival times before and after ligand exchange but also show mixed ligand $Au_{10}$ clusters with both 8 and 9 ligands attached. One of the arrival times of $Au_{10}$ with 8 ligands coincided with that of $Au_{10}$ with 9 ligands indicating that the $Au_{10}$ 9 ligand cluster may be fragmenting through loss of a $MePPh_2$ ligand leading to one of the two arrival times observed for $Au_{10}$ with 8 ligands. Thus, the choice to focus our analysis on $(8,7)^{2+}$ and $(11,9)H^{2+}$ in this study was based on two considerations; 1) $(8,7)^{2+}$ showed no evidence that the two arrival times were coming from fragmentation of a larger cluster but rather were truly two different isomers of the mixed ligand $(8,7)^{2+}$ clusters and 2) the $(11,9)H^{2+}$ exhibited interesting chemical bonding behavior post ligand exchange which lead to the binding of either H or $Cl^-$ depending on the number of exchanged ligands.

**Gold Cluster Synthesis and Ligand Exchange**: Phosphine-ligated gold clusters were synthesized in solution according to modified versions of literature procedures.[1] All syntheses were 1.05 mL total volume in methanol (HPLC grade Sigma–Aldrich) carried out in 1.5 mL microcentrifuge tubes with final concentrations of each reagent as follows: 50 µM gold precursor, chloro (triphenylphosphine) gold (I) (99.9% Sigma–Aldrich) and 1.0 mM borane tert-butyl amine complex reducing agent (BTBA) (96% Sigma–Aldrich). The gold precursor and BTBA were allowed to react for 30 minutes prior to the addition of exchange ligand, methyldiphenylphosphine ($MePPh_2$). Reactions were analyzed as is without any filtering.

**Ion Mobility-Orthogonal Time of Flight Mass Spectrometer**: The custom-built platform coupling ion mobility spectrometry with a time of flight mass spectrometer (IMS-TOF MS) was used in this study and has previously been described in detail.[2] Briefly, for IMS measurements, samples were infused directly from a syringe pump into a 20 µm inner diameter fused-silica emitter and following electrospray ionization, the ions were passed through a heated stainless steel capillary, focused by a high pressure ion funnel, and accumulated in a lower pressure ion funnel trap. Ions were then pulsed into the 90 cm-long IMS drift tube filled with ~ 4 Torr of nitrogen gas, where they travel under the influence of a weak electric field (10-20 V/cm). Ions exiting the drift tube were refocused by a rear ion funnel prior to TOF MS detection (6224 TOF, Agilent Technologies, Santa Clara CA, USA). The signal from the TOF detector is then routed to an 8-bit Analog-to-Digital converter (ADC) (AP240, Agilent Technologies, Switzerland) and processed using custom control-software written in C#.

**References**

1. Johnson, G. E.; Olivares, A.; Hill, D.; Laskin, J., Cationic gold clusters ligated with differently substituted phosphines: effect of substitution on ligand reactivity and binding. *Physical Chemistry Chemical Physics* **2015,** *17* (22), 14636-14646.
2. Ibrahim, Y. M.; Baker, E. S.; Danielson, W. F.; Norheim, R. V.; Prior, D. C.; Anderson, G. A.; Belov, M. E.; Smith, R. D., Development of a new ion mobility (quadrupole) time-of-flight mass spectrometer. *International Journal of Mass Spectrometry* **2015,** *377*, 655-662.

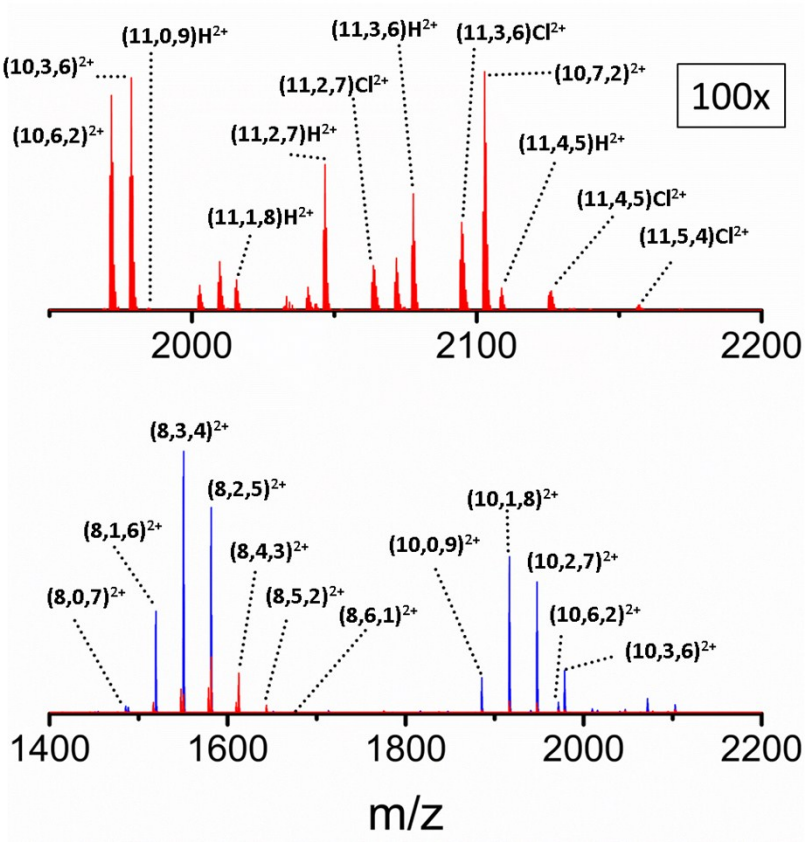


**Figure S1**. Representative positive mode ESI mass spectra of gold clusters formed after the addition of $MePPh_2$ to preformed $Au_x(PPh_3)_y^{2+}$ clusters. **Red trace**, 2.5/1 ratio of $PPh_3$ to $MePPh_2$. **Blue trace**, 2.5/2 ratio of $PPh_3$ to $MePPh_2$. The y-axis of the red trace spectrum is scaled to 100x the blue trace spectrum.