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)$^{2+}$, (10,8)$^{2+}$ and (11,9)$^{2+}$. 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)$^{2+}$ 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)$^{2+}$ 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

Figure S1. Representative positive mode ESI mass spectra of gold clusters formed after the addition of MePPh₂ to preformed Auₓ(PPh₃)ᵧ²⁺ clusters. **Red trace**, 2.5/1 ratio of PPh₃ to MePPh₂. **Blue trace**, 2.5/2 ratio of PPh₃ to MePPh₂. The y-axis of the red trace spectrum is scaled to 100x the blue trace spectrum.