ABSTRACT: We herein investigated collision-induced dissociation (CID) processes of undecagold clusters protected by mixed ligands \([\text{Au}_{11}(\text{PPh}_3)_8\text{X}_2]^+\) (\(X = \text{Cl, } \text{C} \equiv \text{CPh}\)) using mass spectrometry and density functional theory calculations. The results showed that the CID produced fragment ions \([\text{Au}_x(\text{PPh}_3)_y\text{X}_z]^+\) with a formal electron count of eight via sequential loss of PPh3 ligands and AuX(PPh3) units in a competitive manner, indicating that the CID channels are governed by the electronic stability of the fragments. Interestingly, the branching fraction of the loss of the AuX(PPh3) units was significantly smaller for \(X = \text{C} \equiv \text{CPh}\) than that for \(X = \text{Cl}\). We ascribed the effect of \(X\) on the branching fractions of dissociations of PPh3 and AuX(PPh3) to the steric difference.

1. INTRODUCTION

Atomically precise metal clusters protected by organic ligands (thiolates, phosphines, halides, and alkynes) have attracted the attention of material scientists as building units of new functional materials, owing to their unique physicochemical properties.1−4 To understand the origin of their novel properties and to rationally design their functions, characterization of their geometric and electronic structures is of paramount importance. The atomic structures of the clusters that are crystallized have been determined by single-crystal X-ray diffraction. By contrast, high-resolution transmission electron microscopy5−7 and X-ray absorption spectroscopy8,9 have been successfully used for structural characterization of the metal clusters that cannot be crystallized. The electronic structures have been probed by optical spectroscopy,10,11 voltammetry,12−14 and laser photoelectron spectroscopy.15 These studies have demonstrated that the properties of protected metal clusters are strongly dependent on the number and arrangement of the constituent atoms of the metallic core.

Surface modification is another key to tuning the electronic structures, functionality, and stability of metal clusters. Anionic ligands such as thiolates, halides, and alkynes play a role in adjusting the formal number of valence electrons in the metallic core: they take one electron from the metallic core.16 Chiral ligands can impart chiroptical activity in the metal clusters.17−20 It was proposed that circular dichroic activity can be amplified by placing the \(\pi\)-electron system near the metallic cores.21,22 Ligation of alkynes enhanced the catalytic activity23 and allowed electronic conjugation between the metallic core and ligands.24 Geometric structures of the ligands govern the coverage of the metallic core25 and the structures of the interface26 and the metallic core.27 Binding affinity of the ligands affects the thermal stability of metal clusters against aggregation.28 It was reported that \([\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]^+\) and \([\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3]\) showed different reactivity in the ligand-exchange reaction with thiols.29 Recently, collision-induced dissociation (CID) mass spectrometry has proven to be a powerful tool to characterize the bonding nature and stability of the ligand-protected metal clusters in the isolated state in vacuum.30−38 Ligand-protected metal clusters that are internally excited upon collision with rare gas atoms undergo unimolecular dissociation. Mass analysis revealed the dissociation processes.
ation of RH, (RS)$_2$, and Au$_4$(SR)$_4$ in the CID processes of thiolate-protected Au clusters$^{30−32}$ and dissociation of Ag$_2$(SR)$_4$ and Ag(SR) in the CID of thiolate-protected Ag clusters.$^{33,34}$ Ligand loss, ligand activation, and core fission were observed in the CID of phosphine-protected Au clusters.$^{35−38}$

We herein conducted CID mass spectrometry on one of the typical protected gold clusters, [Au$_{11}$(PPh$_3$)$_8$X$_2$]$^+$ [X = Cl, C$≡$CPh (phenyl acetylene, PA)]. These gold clusters can be viewed as Au$_{11}^{3+}$ superatoms having a closed electronic structure with eight electrons protected by neutral (PPh$_3$) and anionic (X$^-$) ligands. The CID of [Au$_{11}$(PPh$_3$)$_8$X$_2$]$^+$ provides molecular level information on how the dissociation of the mixed ligands proceeds from the Au$_{11}^{3+}$ superatom upon collisional excitation.

2. RESULTS AND DISCUSSION

2.1. Characterization of [Au$_{11}$(PPh$_3$)$_8$X$_2$]$^+$ Samples. Figure 1a shows the positive-ion electrospray ionization (ESI) mass spectra of [Au$_{11}$(PPh$_3$)$_8$X$_2$]$^+$ (X = Cl, PA). The single peaks in the mass spectra can be assigned to [Au$_{11}$(PPh$_3$)$_8$X$_2$]$^+$ (X = Cl, PA) by the isotope pattern analysis, indicating high purity of the samples used in this study. Figure 1b shows the optical spectra of [Au$_{11}$(PPh$_3$)$_8$Cl$_2$]$^+$ (X = Cl, PA). The spectrum of [Au$_{11}$(PPh$_3$)$_8$Cl$_2$]$^+$ agreed well with that reported previously.$^{29}$ The spectral profile of the newly synthesized [Au$_{11}$(PPh$_3$)$_8$(PA)$_2$]$^+$ is similar to that of [Au$_{11}$(PPh$_3$)$_8$Cl$_2$]$^+$, suggesting similar structures. Figure 1c shows the optimized structures of [Au$_{11}$(PPh$_3$)$_8$X$_2$]$^+$ (X = Cl, PA) obtained by density functional theory (DFT) calculations. The optimized structure of [Au$_{11}$(PPh$_3$)$_8$Cl$_2$]$^+$ reproduced the crystal structure reported previously,$^{29}$ ten surface Au atoms of the icosahedron-like Au$_{11}$ core are completely capped by eight PPh$_3$ and two Cl ligands. The structure of [Au$_{11}$(PPh$_3$)$_8$(PA)$_2$]$^+$ newly synthesized in this study could not be determined crystallographically, but the optimized structure was obtained by replacing Cl of [Au$_{11}$(PPh$_3$)$_8$Cl$_2$]$^+$ with PA while retaining the motifs of the Au$_{11}$ core. These results illustrate that the effect of anionic ligands on the geometric and electronic structures is rather small.

2.2. Thermal-Induced Dissociation and CID of [Au$_{11}$(PPh$_3$)$_8$Cl$_2$]$^+$. Two fragments, [Au$_{11}$(PPh$_3$)$_7$Cl$_2$]$^+$ and [Au$_{10}$(PPh$_3$)$_7$Cl$_1$]$^+$, were observed in the thermal-induced dissociation (TID) in the temperature range of 94−139 °C (Figure 2). The formation of [Au$_{11}$(PPh$_3$)$_7$Cl$_2$]$^+$ involves loss of one PPh$_3$ ligand.

\[
[Au_{11}(PPh_3)_8Cl_2]^+ \xrightarrow{TID} [Au_{11}(PPh_3)_7Cl_2]^+ + PPh_3
\]  

(1)

To confirm the energetical feasibility of eq 1 and to identify the most weakly bound ligand, we calculated the dissociation energy of the following reaction for all possible ligands. Figure 3 shows the energy diagrams of the dissociation pathways of PPh$_3$. Isomeric structures of [Au$_{11}$(PPh$_3$)$_7$Cl$_2$]$^+$ optimized are shown in Figure S1. The dissociation channels were categorized into three in terms of energies depending on the positions of the ligand lost (as categorized in the inset of Figure 3). It was found that the PPh$_3$ ligand bonded to the bottom site is the most weakly bonded. Although it is not trivial to discuss whether this PPh$_3$ is selectively lost or not, it is safe to conclude that the loss of PPh$_3$ is feasible under our TID conditions.

By contrast, there are two possible routes for the formation of [Au$_{11}$(PPh$_3$)$_7$Cl$_1$]$^+$: loss of an AuCl(PPh$_3$) unit (eq 2) or sequential loss of PPh$_3$ followed by AuCl (eq 3).

\[
[Au_{11}(PPh_3)_8Cl_2]^+ \xrightarrow{TID} [Au_{11}(PPh_3)_7Cl_1]^+ + AuCl(PPh_3)
\]  

(2)

\[
[Au_{11}(PPh_3)_8Cl_2]^+ \xrightarrow{TID} [Au_{10}(PPh_3)_7Cl_1]^+ + PPh_3 + AuCl
\]  

(3)

To identify which route is energetically plausible, the energies for eqs 2 and 3 were calculated by DFT and are summarized in Figure 3. On the basis of the calculation results for reaction 1, we limit ourselves to consider the loss of PPh$_3$ at the bottom. Optimized structures of [Au$_{10}$(PPh$_3$)$_7$Cl$_1$]$^+$
produced by eqs 2 and 3 and other fragments are shown in Figure S2. The results show that the loss of AuCl relative to Cl is energetically more favorable than the sequential loss of PPh3 and AuCl. Namely, the loss of Cl ligands is always accompanied by Au and PPh3 in the form of AuCl(PPh3), which corresponds to the synthetic precursor of the clusters. In conclusion, the TID of [Au11(PPh3)8Cl2]+ proceeds via the competitive loss of neutral fragments of PPh3 and AuCl(PPh3).

The CID mass spectra of [Au11(PPh3)8Cl2]+ recorded at various CID voltages are listed in Figure 4. Monocationic product ions assigned to [Au9(PPh3)6Cl2]+ (peaks 2−11) are observed as a result of the CID of the precursor ions (peak 1), indicating that ligand fission was not involved. The (x, y, z) values for peaks 1−11 are listed in Table 1. The mass assignment was confirmed through isotope pattern analysis. The important finding is that the formal number of valence electrons is eight for all fragments observed. With an increase in the CID voltage (i.e., nominal collision energy), the values of (x, y, z) gradually decreased, as we expected.

According to the TID results, CID of [Au11(PPh3)8Cl2]+ also proceeds via the competitive loss of neutral fragments of PPh3 and AuCl(PPh3). Namely, the ionic fragments observed in Figure 4 can be viewed as the composites of the eight-electron superatomic core of Au9+, neutral PPh3 ligands, and AuCl(PPh3) and can be formulated as Au9+(PPh3)n[AuCl(PPh3)]m (4).

The energetically preferable dissociation pathways of [Au11(PPh3)8Cl2]+ are considered using the (n, m) representation. The populations of fragments (n, m) (Figure 4) are plotted as a function of the CID voltage in Figure S3. In this analysis, we ignore the fragments with populations smaller than 3% at certain CID voltages. The populations of fragments with smaller (n, m) values are increased with the increase of the CID voltage, indicating that the release of neutral species proceeds sequentially with the increase in the collision energy. The fragments of [Au11(PPh3)8Cl2]+ are summarized in Scheme 1. To gain insight into the major dissociation pathways, the maximum value of the population of each fragment (see Figure S3) is represented by the degree of contrast of the gray positions.

Table 1. Peak Assignment of CID Mass Spectra of [Au11(PPh3)8Cl2]+

| peak number | (x, y, z) | (n, m) |
|-------------|----------|--------|
| 1           | (11, 8, 2) | (6, 2) |
| 2           | (11, 7, 2) | (5, 2) |
| 3           | (10, 7, 1) | (6, 1) |
| 4           | (10, 6, 1) | (5, 1) |
| 5           | (10, 5, 1) | (4, 1) |
| 6           | (9, 5, 0)  | (5, 0) |
| 7           | (10, 4, 1) | (3, 1) |
| 8           | (9, 4, 0)  | (4, 0) |
| 9           | (10, 3, 1) | (2, 1) |
| 10          | (9, 3, 0)  | (3, 0) |
| 11          | (9, 2, 0)  | (2, 0) |

Scheme 1. CID Pathway of [Au11(PPh3)8Cl2]+
background: the dominant fragment is indicated by greater contrast. Scheme 1 indicates that the fragmentation of neutral fragments of PPh₃ and AuCl(PPh₃) from [Au₁₁(PPh₃)₈Cl₂]⁺ proceeds competitively.

2.3. CID of [Au₁₁(PPh₃)₈(PA)₂]⁺. Figure 5 shows the CID mass spectra of [Au₁₁(PPh₃)₈(PA)₂]⁺ (peak 1) as a function of the CID voltage. All of fragment peaks 2–10 are assigned to [Au₁₀(PPh₃)₆(PA)]⁺, and the (x, y, z) values are listed in Table 2. The fragments correspond to eight-electron superatoms and sequential loss of PPh₃ ligands was much more favored than that of the Au(PA)(PPh₃) unit.

2.4. Effect of X on CID of [Au₁₁(PPh₃)₈X₂]⁺. As demonstrated in Sections 2.2 and 2.3, eight-electron superatoms Au₉⁺(PPh₃)₆[AuX(PPh₃)]₂ were obtained in the CID of [Au₁₁(PPh₃)₈X₂]⁺ (=Au₉⁺(PPh₃)₆[AuX(PPh₃)]₂) via competitive loss of PPh₃ and AuX(PPh₃). Notably, we observed that the anionic ligand X significantly affects the branching fractions of the two dissociation channels, although it does not affect the electronic and geometric structures of the Au₁₁⁺ superatom. This section focuses on the origin of the effect of ligand X on the branching fractions of the CID processes of [Au₁₁(PPh₃)₈X₂]⁺. We first compared the energetics related to the dissociation of PPh₃ and AuX(PPh₃) from [Au₁₁(PPh₃)₈X₂]⁺. According to the calculation results in Figure S7, the minimal dissociation energies of PPh₃ (−0.14 eV) and Au(PA)(PPh₃) (−0.02 eV) from [Au₁₁(PPh₃)₈(PA)₂]⁺ are comparable to those of PPh₃ (−0.08 eV) and AuCl(PPh₃) (0.19 eV) from [Au₁₁(PPh₃)₈(PA)]⁺ (Figure 3). Thus, the difference in the branching fractions of the CID pathways is not due to the difference in energetics between X = Cl and PA.

The major difference between the fragmentation of PPh₃ and AuX(PPh₃) is that the former proceeds via breaking of the Au–P bond, whereas the latter requires significant rearrangement of the chemical bonds. In order that AuX(PPh₃) is dissociated from collisionally excited [Au₁₁(PPh₃)₈X₂]⁺, the two ligands X and PPh₃ originally bonded to different surface Au atoms must be transferred to a single Au atom. As shown in the space-filling model of [Au₁₁(PPh₃)₈X₂]⁺ (Figure 6), the local environment of X is sterically crowded. Under such circumstances, the formation of AuX(PPh₃) is retarded when X becomes bulkier. Although information on the structure of the transition state is not presently available, we propose that the bulkiness of the PA ligand contributes to the suppression of the dissociation of Au(PA)(PPh₃), thereby preferentially promoting the loss of PPh₃.

3. CONCLUSIONS

We studied the CID processes of undecagold clusters, [Au₁₁(PPh₃)₈X₂]⁺, protected by mixed ligands of PPh₃ and X (=Cl, PA), using mass spectrometry and DFT calculations. Eight-electron superatoms formally described as Au₉⁺(PPh₃)₆[AuCl(PPh₃)]₂ were obtained via competitive loss of PPh₃ and AuX(PPh₃). This result indicates that the CID channels are governed by the electronic stability of the...
product ions. Interestingly, we observed that the anionic ligand X significantly affects the branching fractions of the two competing dissociation channels, although it does not affect the electronic and geometric structures of the \([\text{Au}_{11}X]\)\(^{3+}\) superatom. We ascribed the suppression of dissociation of \(\text{Au}(\text{PA})(\text{PPh}_3)\) to the kinetic retardation of the formation of \(\text{Au}(\text{PA})(\text{PPh}_3)\) because of the steric hindrance of PA.

4. METHODS

4.1. Synthesis and Characterization. Details of the synthesis are provided in the Supporting Information. \([\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]\)\(^{+}\) was synthesized by a method reported previously with slight modifications.\(^{26}\) \([\text{Au}_{11}(\text{PPh}_3)_8(\text{PA})_2]\)\(^{+}\) was newly synthesized by the ligand exchange of \([\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]\)\(^{+}\) with PA under conditions similar to those for the synthesis of \([\text{Au}_{13}(\text{diphosphine})_3(\text{PA})_2]\)\(^{3+}\).\(^{24}\) The product was characterized by UV–vis absorption spectroscopy and ESI mass spectrometry.

4.2. Thermal-Induced Dissociation. Dissociation reaction of \([\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]\)\(^{+}\) was observed in a heated capillary of a home-built ESI mass spectrometer. Details of the apparatus are available elsewhere.\(^{15}\) Briefly, the \(\text{Au}_{11}\) clusters dispersed in acetonitrile (~1 mg/mL) were electrosprayed at a flow rate of 90 \(\mu\)L/h. Dissociation was induced by introducing them into the capillary located at the entrance of the mass spectrometer and resistively heated in the range of 93–139 °C. The cluster ions injected into the capillary were thermalized by a sufficient number of collisions with atmospheric molecules (>\(10^6\)) before the dissociation. The fragments were monitored by a time-of-flight (TOF) mass spectrometer.

4.3. Collision-Induced Dissociation. The CID mass spectra were measured by using a JMS-T100LP (JEOL Ltd.) spectrometer composed of an ESI source, an in-source CID assembly (Figure S8), and a TOF mass spectrometer. Acetonitrile dispersion of the \(\text{Au}_{11}\) clusters (~0.1 mg/mL) was supplied to the source at a flow rate of ~200 Pa. Voltage applied to an electrode in the in-source CID assembly (CID voltage) was adjusted within the range of 80–250 V (Figure S8). Under the above conditions, the collision energy of the ions with a background gas (\(N_2\) in the nebulizer, the atmosphere, and the solvent) is expected to be higher than that in the TID and increases with the CID voltage.

4.4. Theoretical Calculations. The geometric structures of \([\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]\)\(^{+}\) and \([\text{Au}_{11}(\text{PPh}_3)_8(\text{PA})_2]\)\(^{+}\) and possible candidates of the fragments were studied by the DFT calculations on the B3LYP/LanL2DZ (Au) and 6-31G(d) (others) level. The spin multiplicities were fixed to a singlet. Vibrational frequencies were calculated to confirm that the optimized structures corresponded to local minimum structures. In the calculation of the relative energies, the zero-point energies were taken into account. The charge on each atom was estimated using natural population analysis. All calculations were carried out using the Gaussian 09 program.\(^{40}\) The results were visualized through PyMOL.\(^{11}\)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01096.

Full reference of Gaussian09, synthesis procedure of \([\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_2]\)\(^{+}\) and \([\text{Au}_{11}(\text{PPh}_3)_8(\text{PA})_2]\)\(^{+}\), additional calculation results, results of population analysis of CID fragments, the mass spectra related to \([\text{Au}_{11}(\text{PPh}_3)_8(\text{PA})_2]\)\(^{+}\), and schematic image of apparatus (PDF)

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Notes

The authors declare no competing financial interest.

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