

## 論文の内容の要旨

### 論文題目

Combined experimental and theoretical study on the activation of the C–I bond of CH<sub>3</sub>I by coinage metal atoms and clusters

(貨幣金属原子・クラスターによる CH<sub>3</sub>I の C–I 結合の活性化に関する  
実験的・理論的研究)

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### 1. Introduction

The discovery of oxidation catalysis of nano-sized gold by Haruta *et al.* [1] stimulated not only the development of the practical Au catalysts, but also fundamental studies on model systems to gain insights into the size-specific catalysis. Previous studies on bare Au cluster cations and anions isolated in the gas phase revealed that their chemical reactivities toward O<sub>2</sub> are governed by the electronic structures. The Au clusters with low electron affinities are reactive when they are negatively charged, indicating that O<sub>2</sub> can be activated by electron transfer from the Au cluster anions. Motivated by this simple guiding principle, oxidation catalysis of Au clusters stabilized by polyvinylpyrrolidone (Au:PVP) has been studied [2]. It was found that only the small (<3 nm) Au clusters acted as catalysts for aerobic oxidation of alcohols, where the key step was thought to be the activation of O<sub>2</sub> through electron transfer from a negatively-charged Au cluster by the interaction with PVP. The fact that the oxidation of bare Au cluster anions and oxidation catalysis of Au:PVP proceed via common key step demonstrates that cluster-based catalysts can be developed rationally based on the fundamental knowledge on chemical properties of isolated systems [2].

Recently it has been revealed that Au nanoparticles/clusters catalyze a variety of carbon–carbon (C–C) coupling reactions via activation of C(sp or sp<sup>2</sup>)–X bonds by oxidative addition [3]. In contrast, activation of C(sp<sup>3</sup>)–X bonds has been regarded as a challenge due to the more electron-rich nature of the sp<sup>3</sup> carbons [4]. In this thesis, I conducted experimental and theoretical studies on activation of C–I bond of CH<sub>3</sub>I by the atomic Au, Ag, and Cu isolated in the gas phase and trapped in the low-temperature neon matrix to gain basic information on their chemical properties for future development of coinage metal catalysts for coupling reactions.

## 2. Reaction of CH<sub>3</sub>I with Au<sup>−</sup> in the gas phase

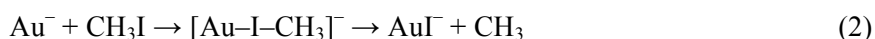
The gas phase reaction of atomic gold anion (Au<sup>−</sup>) with CH<sub>3</sub>I was examined to test the hypothesis that Au<sup>−</sup> is more nucleophilic than Au(0), Au(I) and Au(III) species commonly used in gold-catalyzed coupling reactions. The Au<sup>−</sup> ions generated by laser ablation under helium carrier gas were allowed to react with CH<sub>3</sub>I molecules in a reaction cell. The compositions of the anionic products were determined using a time-of-flight mass spectrometer. Photoelectron spectra of the mass-separated anion of interest were recorded with a magnetic-bottle type energy analyzer using 3rd or 4th harmonic output from a Nd:YAG laser [5].

Figure 1a shows typical mass spectra before and after the reaction of Au<sup>−</sup> and CH<sub>3</sub>I. After the reaction, the reactant Au<sup>−</sup> was disappeared while AuCH<sub>3</sub>I<sup>−</sup> and AuI<sub>2</sub><sup>−</sup> were mainly produced. The photoelectron spectrum of AuCH<sub>3</sub>I<sup>−</sup> shown in Figure 1b exhibits two bands at 2.41 and 3.96 eV. These bands were assigned two isomers since the intensity ratios changed by tuning the ion source conditions. The intense band was assigned to the oxidative addition product [I–Au–CH<sub>3</sub>]<sup>−</sup> whose vertical electron detachment energy (VDE) was calculated to be 4.02 eV by the density functional theory (DFT) calculations (B3LYP/LanL2dz (Au, I), 6-31+G(d,p) (C, H)). The weak band at 2.41 eV was assigned to a less stable isomer, [Au–I–CH<sub>3</sub>]<sup>−</sup>, whose calculated VDE value was 2.59 eV.

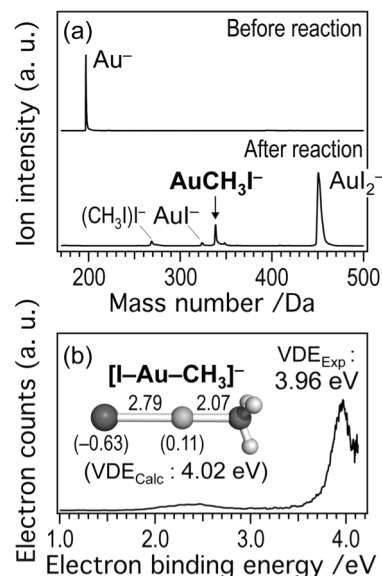
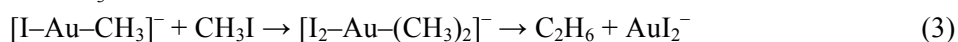
Formation mechanism of [I–Au–CH<sub>3</sub>]<sup>−</sup> was studied theoretically by reaction pathway exploration using Global Reaction Route Mapping (GRRM) program [6]. Figure 2 shows the energy profile along the intrinsic reaction coordinate (IRC), indicating that [I–Au–CH<sub>3</sub>]<sup>−</sup> was formed via barrier-less pathway: S<sub>N</sub>2 attack of Au<sup>−</sup> to CH<sub>3</sub>I from the C atom side, followed by migration of the leaving I<sup>−</sup> to Au site (eq. 1).



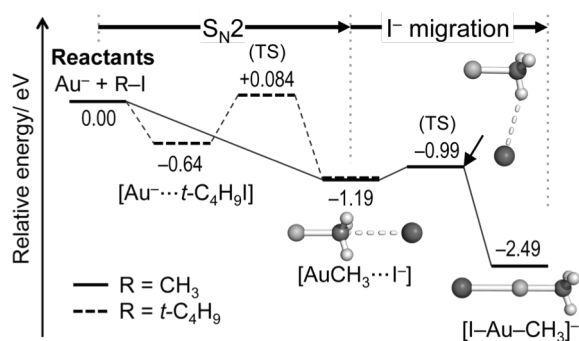
This mechanism was experimentally supported by the retardation of the reaction with *t*-C<sub>4</sub>H<sub>9</sub>I. The product Au<sup>−</sup>·C<sub>4</sub>H<sub>9</sub>I was assigned to an ion-neutral complex [Au<sup>−</sup> ⋯ *t*-C<sub>4</sub>H<sub>9</sub>I] (Figure 2) by photoelectron spectroscopy. The formation of such ion-neutral complex is explained in terms of a potential barrier for the nucleophilic attack associated with bulky substituent groups. In contrast, it was indicated that a minor product AuI<sup>−</sup> (Figure 1) was formed via I abstraction pathway: the attack of Au<sup>−</sup> from the I atom side to form [Au–I–CH<sub>3</sub>]<sup>−</sup>, followed by dissociation of AuI<sup>−</sup> (eq. 2).



Further GRRM calculations suggested that the other major product AuI<sub>2</sub><sup>−</sup> (Figure 1) was generated via barrier-less sequential oxidative addition of another CH<sub>3</sub>I to [I–Au–CH<sub>3</sub>]<sup>−</sup> followed by reductive elimination of C<sub>2</sub>H<sub>6</sub> (eq. 3). These results indicate that Au<sup>−</sup> acts as a nucleophile to activate C(sp<sup>3</sup>)–I bond and mediates the C–C coupling reaction of CH<sub>3</sub>I.



**Figure 1.** (a) Mass spectra before and after the reaction of Au<sup>−</sup> with CH<sub>3</sub>I. (b) Photoelectron spectrum of AuCH<sub>3</sub>I<sup>−</sup>. Inset shows the assigned structure with bond lengths in Å. Numbers in parentheses indicate NBO charges.



**Figure 2.** Calculated energy profiles along IRC of oxidative addition of CH<sub>3</sub>I to Au<sup>−</sup> (solid line) and of S<sub>N</sub>2 step between *t*-C<sub>4</sub>H<sub>9</sub>I and Au<sup>−</sup> (dash line).

### 3. Reaction of CH<sub>3</sub>I with other coinage metal anions, Cu<sup>−</sup> and Ag<sup>−</sup>

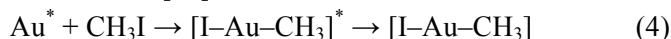
Au<sup>−</sup> anion has a closed electron configuration [Xe](4f)<sup>14</sup>(5d)<sup>10</sup>(6s)<sup>2</sup> similar to conventional nucleophiles such as halides (X<sup>−</sup>) and hydride (H<sup>−</sup>). I examined the reactions of CH<sub>3</sub>I with other coinage metal anions Cu<sup>−</sup> and Ag<sup>−</sup>, which have the analogous closed electronic structures. Mass spectrometry and photoelectron spectroscopy revealed that the adduct species, MCH<sub>3</sub>I<sup>−</sup> (M = Cu, Ag), were commonly formed, whose VDE values were 3.53 and 3.82 eV for M = Cu and Ag, respectively. These VDE values are in good agreement with those calculated for the oxidative addition products [I–M–CH<sub>3</sub>]<sup>−</sup>: 3.43 and 3.78 eV for M = Cu and Ag (B3LYP/aug-cc-pVTZ with pseudopotentials for Cu, Ag, Au and I). The GRRM calculations showed that S<sub>N</sub>2 attack by M<sup>−</sup> to CH<sub>3</sub>I followed by I<sup>−</sup> migration was barrier-less.

Figure 3 compares the thermodynamic stabilities of [I–M–CH<sub>3</sub>]<sup>−</sup> based on their heat of formation. The stability increases in the order of Au < Ag < Cu. It is noteworthy that these [I–M–CH<sub>3</sub>]<sup>−</sup> species are more stable than the typical Grignard reagent, [I–Mg–CH<sub>3</sub>]. The high stability of [I–M–CH<sub>3</sub>]<sup>−</sup> is consistent with a recent report on crystallization of [Br–Au–CF<sub>3</sub>]<sup>−</sup>·(PPh<sub>4</sub>)<sup>+</sup> having the linear Br–Au–C backbone [7].

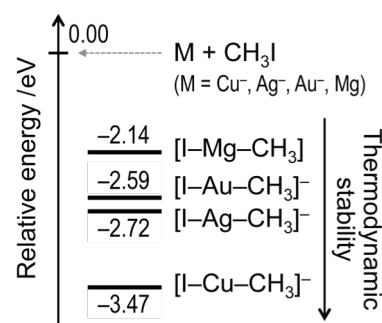
### 4. Reaction of CH<sub>3</sub>I with Au in solid neon matrix

The reaction of Au/Au<sup>−</sup> and CH<sub>3</sub>I was conducted in solid noble gas matrix to provide an evidence for the C–C coupling reaction proposed in eq. 2 by detecting both neutral and ionic products and intermediates by infrared (IR) absorption spectroscopy. Laser-ablated Au atoms in the electronically ground and excited states and anions were co-deposited with CH<sub>3</sub>I (0.05%)/Ne gas mixture onto a CsI substrate kept at ~4 K. Fourier transform IR spectra were recorded after the co-deposition, after annealing of the sample up to 11 K, and after the irradiation of broadband visible light (wavelength > 400 nm) from a high-pressure Hg lamp, respectively [8].

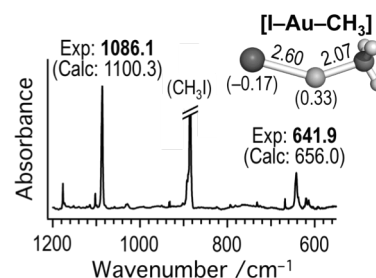
The IR spectrum of the initial reaction products (Figure 4) exhibits intense peaks at 1086.1 and 641.9 cm<sup>−1</sup>. Frequency calculation with anharmonic terms [9] (B3LYP/cc-pVTZ with pseudopotentials for Au and I) revealed that these peaks were not assigned to the anionic oxidative addition product [I–Au–CH<sub>3</sub>]<sup>−</sup>, but to the corresponding neutral species [I–Au–CH<sub>3</sub>]. The energy profile along the IRC to form [I–Au–CH<sub>3</sub>] from the Au in the ground state and CH<sub>3</sub>I showed that the potential barrier was as high as 0.53 eV. This implies that an Au atom in an electronically excited state (Au<sup>\*</sup>) formed in the laser ablation was involved in the reaction (eq. 4), as proposed in a previous report on the reaction of Au in solid Ar [10].



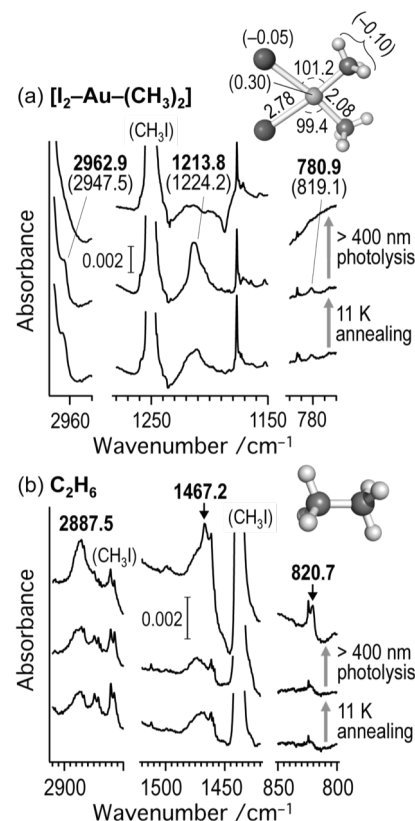
Close inspection of the IR spectra revealed the unprecedented peaks at 2962.9, 1213.8 and 780.9 cm<sup>−1</sup> as shown in Figure 5a. They



**Figure 3.** Total electronic energies of [I–M–CH<sub>3</sub>] (M = Cu<sup>−</sup>, Ag<sup>−</sup>, Au<sup>−</sup>, Mg) with respect to M + CH<sub>3</sub>I.

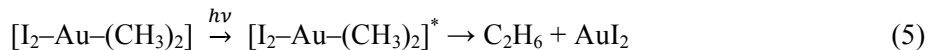


**Figure 4.** IR spectrum after co-deposition of Au and CH<sub>3</sub>I/Ne. Inset shows the optimized structure of [I–Au–CH<sub>3</sub>].



**Figure 5.** Expanded IR spectra of (a) [I<sub>2</sub>–Au–(CH<sub>3</sub>)<sub>2</sub>] and (b) C<sub>2</sub>H<sub>6</sub> with the optimized structures (inset). Peak positions shown in bold and with parentheses represent experimental and calculated frequencies.

were assigned to  $[\text{I}_2\text{-Au-(CH}_3)_2]$ , in which two  $\text{CH}_3\text{I}$  molecules are oxidatively adsorbed on an Au atom. This species can be viewed as the intermediate for the C–C coupling of  $\text{CH}_3\text{I}$ . The IR peaks remained even after annealing at 11 K, but vanished after visible light irradiation. In addition, peaks assigned to  $\text{C}_2\text{H}_6$  [11] appeared at 2887.5, 1467.2 and 820.7  $\text{cm}^{-1}$  (Figure 5b) after visible light irradiation. This spectral change indicates that  $\text{C}_2\text{H}_6$  was produced from  $[\text{I}_2\text{-Au-(CH}_3)_2]$  via photoexcitation (eq. 5).



In summary, photoassisted homocoupling of  $\text{CH}_3\text{I}$  is mediated by Au atom via  $[\text{I}_2\text{-Au-(CH}_3)_2]$  as an intermediate.

## 5. Reaction of $\text{CH}_3\text{I}$ with gold cluster anions, $\text{Au}_n^-$ ( $n = 2\text{--}4$ )

In order to elucidate the cluster size effect on the C–I bond activation, the gas phase reactions of  $\text{CH}_3\text{I}$  with  $\text{Au}_n^-$  ( $n = 2\text{--}4$ ) were investigated. Figure 6 shows the mass spectra before and after the reaction of  $\text{Au}_n^-$  ( $n = 1\text{--}4$ ) with reduced amount of  $\text{CH}_3\text{I}$ . Obviously, the intensity of  $\text{Au}_2^-$  decreases by the reaction more than that of the clusters with other sizes ( $n = 1, 3$ , and 4), implying that  $\text{Au}_2^-$  is most reactive among others. The marked decrease of  $\text{Au}_2^-$  is accompanied by sharp increase of  $\text{Au}_2\text{I}^-$  after the reaction compared to  $\text{Au}_n\text{I}^-$  ( $n = 1, 3$ , and 4) and  $\text{AuCH}_3\text{I}^-$ . These results indicate that  $\text{Au}_2\text{I}^-$  is produced in a reaction of  $\text{Au}_2^-$  with  $\text{CH}_3\text{I}$  as shown in eq. 6.



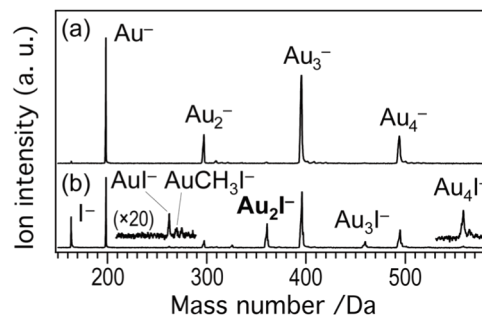
DFT calculations (B3LYP/LanL2dz (Au, I), 6-31+G(d,p) (C, H)) for the reaction of  $\text{Au}_2^-$  with  $\text{CH}_3\text{I}$  predicted that pathways for production of  $[\text{I-Au}_2\text{-CH}_3]^-$  and  $\text{Au}_2\text{I}^-$  via  $\text{S}_{\text{N}}2$  attack and I abstraction, respectively, are both exothermic (1.73 and 0.91 eV, respectively) and barrier-less. However, only  $\text{Au}_2\text{I}^-$  was observed as the products in the mass spectrum. I concluded that the  $\text{S}_{\text{N}}2$  pathway for  $\text{Au}_2^-$  was quenched due to a steric factor;  $\text{Au}_2^-$  only with specific orientations can attack the C atom of  $\text{CH}_3$  group, while it is not significant for I abstraction pathway.

## 6. Conclusion

Reactions of atomic coinage metals toward  $\text{CH}_3\text{I}$  were investigated. In the gas phase, coinage metal anions  $\text{M}^-$  ( $\text{M} = \text{Cu, Ag, Au}$ ) commonly afforded novel oxidative addition products,  $[\text{I-M-CH}_3]^-$ , via  $\text{S}_{\text{N}}2$  attack by  $\text{M}^-$  to  $\text{CH}_3\text{I}$  followed by  $\text{I}^-$  migration. Sequential oxidative addition of  $\text{CH}_3\text{I}$  to  $[\text{I-Au-CH}_3]^-$  to yield  $\text{C}_2\text{H}_6$  and  $\text{AuI}_2^-$  was proposed. In the solid Ne matrix, the Au atom in an electronically excited state afforded the oxidative addition product,  $[\text{I-Au-CH}_3]$ , as well as an intermediate for C–C bond formation,  $[\text{I}_2\text{-Au-(CH}_3)_2]$ . Visible light irradiation on  $[\text{I}_2\text{-Au-(CH}_3)_2]$  triggered the reductive elimination of the coupling product,  $\text{C}_2\text{H}_6$ . In contrast,  $\text{Au}_2^-$  promoted I abstraction to afford  $\text{Au}_2\text{I}^-$  and  $\text{CH}_3$ . These results demonstrate that Au compounds/clusters have a potential to activate C–I bond and to promote C–C coupling reaction, and that the activation mechanism drastically depends on the cluster size.

## 7. References

- [1] Haruta, M. *et al. Chem. Lett.* **1987**, 405. [2] Yamazoe, S. *et al. Acc. Chem. Res.* **2014**, 47, 816. [3] Li, G. *et al. Nanotechnol. Rev.* **2012**, 2, 529. [4] Frisch, A. C.; Beller, M. *Angew. Chem. Int. Ed.* **2005**, 44, 674. [5] Watanabe, T.; Tsukuda, T. *J. Phys. Chem. C* **2013**, 117, 6664. [6] Maeda, S. *et al. Bull. Chem. Soc. Jpn.* **2014**, 87, 1315. [7] S. Martínez-Salvador, *et al. Chem. Sci.* **2015**, 6, 5506. [8] Wang, G. J.; Zhou, M. F. *Int. Rev. Phys. Chem.* **2008**, 27, 1. [9] Barone, V. *J. Chem. Phys.* **2005**, 122, 14108. [10] Cho, H. -G.; Andrews, L. *Inorg. Chem.* **2011**, 50, 10319. [11] Snelson, A. *J. Phys. Chem.* **1970**, 74, 537.



**Figure 6.** Mass spectra (a) before and (b) after the reaction of  $\text{Au}_n^-$  with reduced amount of  $\text{CH}_3\text{I}$ .