

Oxidative Addition of Haloalkanes to Atomic Gold Anion in the Gas Phase

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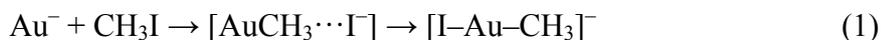
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Recent experimental and theoretical studies have demonstrated that gold nanoparticles and clusters can catalyze a variety of C–C coupling reactions which require activation of C(sp²/sp³)–X (X: halogen) bond via oxidative addition [1]. By contrast, catalytic activation of haloalkanes with C(sp³)–X bonds is considered to be more difficult due to electron-rich nature of sp³ carbon [2]. In this work, we studied simple gas phase reaction of atomic gold anion (Au[−]) by means of mass spectrometry, photoelectron spectroscopy and theoretical calculations, and found that Au[−] can undergo the oxidative addition of haloalkanes [3].

Reaction of laser-ablated Au[−] with methyl iodide (CH₃I) under high-pressure helium carrier gas afforded AuCH₃I[−] and AuI₂[−] as major products (Fig. 1a). Photoelectron spectrum of AuCH₃I[−] exhibited a strong band with the electron binding energy of 3.96 ± 0.03 eV (Fig. 1b). This band was assigned to an oxidative addition product [I–Au–CH₃][−] (Fig. 1b), in which Au is inserted into the C–I bond of CH₃I. Reaction pathway exploration using Global Reaction Route Mapping (GRRM) program [4] indicated that [I–Au–CH₃][−] is formed via S_N2 attack of Au[−] to CH₃I, followed by migration of the leaving I[−] to Au site, as shown in eq. 1.



GRRM calculations suggested that the other product AuI₂[−] (Fig. 1a) was generated via sequential oxidative addition of another CH₃I to [I–Au–CH₃][−] followed by reductive elimination of C₂H₆ (eq. 2).



These findings suggest that Au[−] acts as a nucleophile to activate C(sp³)–I bond of CH₃I and induces the C–C coupling reaction of CH₃I.

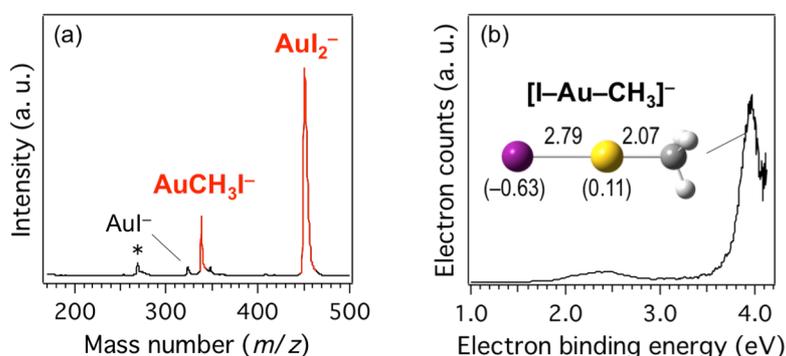


Fig. 1 (a) Typical mass spectrum after the reaction of Au[−] with CH₃I. Asterisk indicates (CH₃I)I[−]. (b) Photoelectron spectrum of AuCH₃I[−]. Inset shows the structure of [I–Au–CH₃][−] with the bond distances in Å and NBO charges of Au and I atoms.