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Facile Method of Halogen Exchange between Au(Cl)(*L*) and MeC(O)*X* (*L* = PPh₃ and IPr; *X* = Br and I) via σ-Bond Metathesis Supported by DFT Calculation

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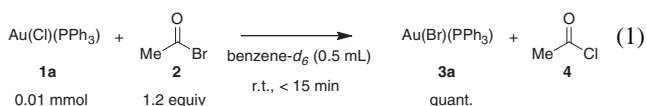[2]*Institute for Molecular Science, Okazaki, Aichi 444-8585*

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Complexes with the formula Au(*X*)(*L*) (*X* = Br and I; *L* = PPh₃ and IPr) were conveniently prepared by a quite simple procedure using the treatment of Au(Cl)(*L*) with MeC(O)*X* and the subsequent evaporation under reduced pressure. The mechanistic study by DFT calculation with M06 functional supported that the reaction proceeded through σ-bond metathesis, where *Cl atom underwent a more roundabout course than Br atom did.*

One of the most common methods of preparation of transition-metal bromides and iodides is the conversion of the corresponding chlorides by the treatment with typical metal salts such as Li*X*, K*X*, and Na*X* (*X* = Br and I). In general, however, due to the necessity of employment of a considerable excess amount of metal salt and the formation of metal chloride as a by-product, a series of procedures such as filtration, extraction, dryness with desiccant, and recrystallization are required to obtain analytically pure products. On the other hand, we have recently reported that Cl-to-Br and Cl-to-I transformations of nickel triad complexes were quite facilely realized by using acetyl bromide and acetyl iodide as the halogen-exchange reagents, and analytically pure products were isolated by just subjection of the reaction mixture in vacuo.[1] Herein, we wish to report that the prototype is also successfully applicable to the aurous complexes with the formula of Au(*X*)(L).[2] In addition, the mechanism is successfully elucidated by theoretical calculation.

Into a Pyrex NMR glass tube were added Au(Cl)(PPh₃) (**1a**, 0.01 mmol), benzene-*d₆* (0.5 mL), and MeC(O)Br (**2**, 0.012 mmol) at 25 °C. The ³¹P NMR spectrum taken right after the sample was prepared showed that **1a** (δ 33.4) was quantitatively converted into Au(Br)(PPh₃) (**3a**) (δ 35.2) (eq 1). To test the utility of the present transformation as the synthetic method, a large-scale reaction was attempted as follows. Into a 100-mL flask were added **1a** (1.0 mmol), **2** (1.2 mmol), and C₆H₆ (50 mL) in a glove box at room temperature. After the solution was stirred for 30 min, the solvent, excess **2** (bp 75–77 °C), and by-product MeC(O)Cl (**4**, bp 52 °C) were removed in vacuo. The ³¹P and ¹H NMR spectra as well as elemental analysis of the product demonstrated that analytically pure **3a** was obtained quantitatively.

Au(Cl)(PPh₃) + [structure: Me–C(=O)–Br] → [benzene-*d₆* (0.5 mL), r.t., < 15 min] → Au(Br)(PPh₃) + [structure: Me–C(=O)–Cl]   (1)

1a   **2**   **3a**   **4**

0.01 mmol   1.2 equiv   quant.

Similarly, Au(I)(PPh₃) (**5a**) was isolated by a treatment of **1a** with MeC(O)I (**6**, bp 108 °C).
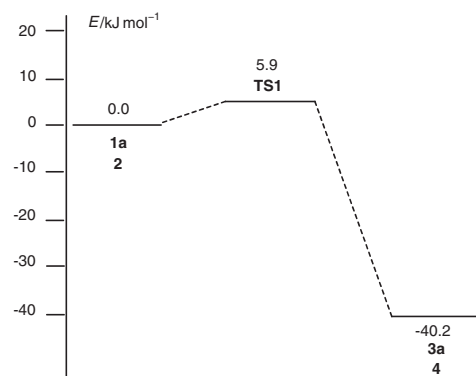
Figure 1. The energy diagram of the reaction of **1a** with **2** via tricoordinated σ-bond metathesis.
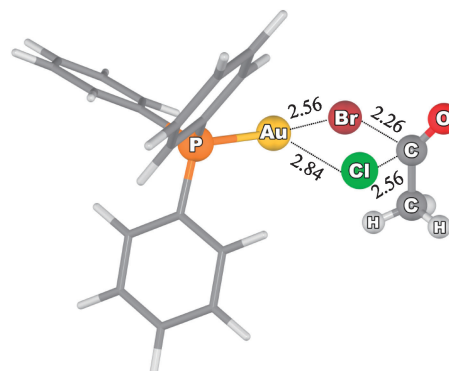

Figure 2. Structure of **TS1** by DFT study with M06 functional.

In the previous study, we succeeded in demonstrating that the Cl-to-Br ligand-exchange reaction between *trans*-M(Cl)-[C(O)Ph](PPh₃)₂ (M = Pt and Pd) and PhC(O)Br took place through σ-bond metathesis by density functional theory (DFT) method. Thus, the reaction mechanism of the reaction of **1a** with **2** was examined with the same calculation method (M06 functional).[3,4] The study successfully located the transition state (**TS1**) of tricoordinated σ-bond metathesis. The energy diagram of the reaction pathway and the structure of **TS1** are shown in Figures 1 and 2, respectively.[5] It should be noted that the **TS1** is only 5.9 kJ mol⁻¹ energetically higher than the starting **1a** and **2**.

The dihedral angle of ∠Au–Cl–Br–C of **TS1** is −174.9°, demonstrating that σ-bond metathesis takes place through a slightly distorted quadrangular geometry. The selected bond lengths of reactants, products, and **TS1** were shown in Figure 3.
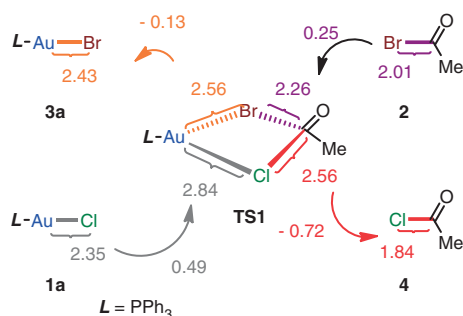
Figure 3. The selected bond lengths (Å) of starting materials, products, and **TS1**.
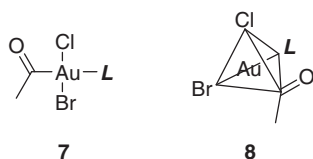
Figure 4. The possible Au(III) complexes.

When the Au–Cl bond distance of **1a** (2.35 Å) is compared with that of **TS1** (2.84 Å), the bond is stretched by 0.49 Å. On the other hand, the C–Br bond length difference between **2** (2.01 Å) and **TS1** (2.26 Å) is only 0.25 Å. The C–Cl bond length difference between **TS1** (2.56 Å) and **4** (1.84 Å) is 0.72 Å, whereas the Au–Br bond in **TS1** (2.56 Å) shrinks by 0.13 Å with respect to that in **3a** (2.43 Å). Therefore, both Au–Cl and C–Cl bonds undergo more dynamic bond changes than C–Br and Au–Br bonds.

In other words, *Cl atom takes a more roundabout route than Br atom does during the course of σ-bond metathesis*, a similar behavior found in the σ-bond metatheses of platinum and palladium complexes.[1]

For the halogen-exchange reaction between **1a** and **2**, the mechanisms through Au(III) complexes such as square planer **7** and tetrahedral **8** are also possible as the intermediate or transition state by the oxidative addition of **2** to **1a** (Figure 4).[6] The DFT study suggested that the complex **7** could exist as an intermediate whose energy is 19.7 kJ mol^{-1} higher than starting **1a** and **2**. However, as we can see from the energy diagram shown in Figure S3,[7] the transition state **TS2** for the formation of **7** and **TS3** from **7** to the products are 47.3 and 44.0 kJ mol^{-1} energetically higher than the reactants, respectively.[5] On the other hand, all the attempts to locate **8** have failed by the DFT calculation. Based on these considerations, we concluded that the Cl-to-Br ligand-exchange reaction between **1a** and **2** proceeded through distorted σ-bond metathesis via **TS1**.

Finally, to demonstrate the generality of the present halogen-exchange reaction with aurous complex, the following were examined. The reactions of Au(Cl)(IPr) (IPr: 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) (**1b**, 0.01 mmol) with 2 equiv of **2** and **6** in CD$_2$Cl$_2$ (0.5 mL) also facilely proceeded to afford Au(Br)(IPr) (**3b**) and Au(I)(IPr) (**5b**) quantitatively after 30 min at 25 °C, respectively (eq 2). Moreover, preparative-scale (0.5 mmol) reactions were successfully performed to afford **3b** and **5b**, respectively (see the Supporting Information).[7]
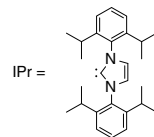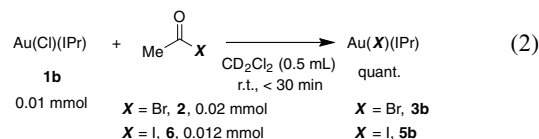
In conclusion, this paper together with our previous study clearly suggested the generality of acetyl bromide (**2**) and iodide (**6**) as the convenient Cl-to-Br and Cl-to-I conversion reagents from metal chlorides through σ-bond metathesis mechanism.[1] Our continuous efforts will be focused on the extension of the σ-bond metathesis to other metal systems.

References and Notes

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7　Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.