## **ORGANOMETALLICS**

# Transformation of Thiolatogold(I) to an Au Complex with an (Arylthio)silyl Ligand. Use of an (Aminosilyl)boronic Ester as a Silylene Precursor

Yoshitaka Tsuchido, Kazuki Okuma, Kohtaro Osakada,\* and Tomohito Ide\*

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**ABSTRACT:** The gold(I) thiolate complex  $[Au(SC_6H_4-4-OMe)-(PCy_3)]$  reacts with an (aminosilyl)boronic ester,  $Et_2N-SiPh_2-BO(CMe_2)_2O$ , to afford a complex with an (arylthio)silyl ligand,  $[Au(SiPh_2(SC_6H_4-4-OMe))(PCy_3)]$ . In the solid state the molecule shows almost linear Si-Au<sup>1</sup>-P coordination. DFT studies revealed that the reaction pathway involves an intermediate having an Au-S bond formed via initial association of the Si center of the substrate with the thiolate ligand. Reaction of  $H_2SiPh_2$  with the thiolate complex also produces the silylgold complex in a lower yield.

**C** ilyl complexes of late transition metals<sup>1,2</sup> have been studied Decause of their relevance to the mechanism of synthetic organic reactions catalyzed by the metal complexes.<sup>3</sup> Oxidative addition of organosilanes with Si-H bonds to low-valent late transition metals<sup>4</sup> provides common and useful routes for formation of a metal-Si bond. The reaction is regarded as a crucial step in the hydrosilylation of olefins catalyzed by latetransition-metal complexes.<sup>5</sup> (Aminosilyl)boronic esters Et<sub>2</sub>N- $SiR_2$ -B(pin) (R = Me, Ph, B(pin) = B(O(CMe\_2)\_2O)) were recently found to function as a source of a disubstituted silylene group in catalytic and stoichiometric reactions using group 10 transition-metal complexes. A Pd(0) phosphine complex catalyzes  $\begin{bmatrix} 1 + 2 + 2 \end{bmatrix}$  cycloaddition of the (aminosilyl)boronic ester to alkynes to yield the corresponding siloles with new regioselectivity, while a similar [1 + 4]reaction using a diene produces the silacyclopentenes.<sup>6</sup> These reactions were proposed to involve an intermediate Pd complex with the disubstituted silylene ligand. Stoichiometric reactions of the (aminosilyl)boronic ester with Pd(0) and Pt(0) complexes afforded the dinuclear complexes of these metals with bridging diphenylsilylene ligands.

The synthesis and properties of silylgold complexes have attracted attention.<sup>8</sup> The reactions of organosilanes with Au(I) complexes are expected to form the corresponding silylgold-(III) complexes,<sup>8c</sup> similar to the complexes of other d<sup>10</sup> metals, such as Pd(0) and Pt(0). Recently, we reported the reaction of H<sub>2</sub>SiPh<sub>2</sub> with [AuCl(PCy<sub>3</sub>)] to form [Au(SiPh<sub>2</sub>Cl)(PCy<sub>3</sub>)], probably via oxidative addition of H<sub>2</sub>SiPh<sub>2</sub> to form an Au(III) intermediate followed by elimination of dihydrogen.<sup>9</sup> This paper presents the reaction of an (aminosilyl)boronic ester



with a thiolatogold(I)  $complex^{10}$  to form a complex with the thio(silyl) ligand.

X-ray crystallography confirmed the molecular structure of  $Et_2N$ -SiPh<sub>2</sub>-B(pin) (1) having a tetrahedral Si center with NEt<sub>2</sub> and pinacolboryl substituents.<sup>11</sup> The Si–N and Si–B bond lengths (1.718(1) and 1.719(1) Å and 2.033(2) and 2.035(2) Å) are similar to those of Me<sub>3</sub>Si-NMe<sub>2</sub> (1.719(1) Å) and PhMe<sub>2</sub>Si–B(pin) (2.028(5) Å), respectively.<sup>12</sup> A gold(I) complex with an arenethiolate ligand, [Au(SC<sub>6</sub>H<sub>4</sub>-4-OMe)-(PCy<sub>3</sub>)] (2), was newly prepared and subjected to the reactions. Scheme 1 summarizes the reactions of an (aminosilyl)boronic ester and of H<sub>2</sub>SiPh<sub>2</sub> with the thiolatogold(I) complex.

Heating a mixture of 1 and 2 in a 1:2 molar ratio at 74 °C for 15 h produces  $[Au(SiPh_2(SC_6H_4-4-OMe))(PCy_3)]$  (3) in 57% isolated yield, as shown in Scheme 1i. A similar reaction of H<sub>2</sub>SiPh<sub>2</sub> also yields complex 3 (Scheme 1ii), and the NMR yield (23%) after the reaction for 20 h at 74 °C is lower than that of 1 (90%). Figure 1 compares the molecular structures of 2 and 3 determined by X-ray crystallography. Both complexes have a two-coordinated linear structure around the Au(I) center with an S1-Au1-P1 angle of 178.84(5)° and an Si1-Au1-P1 angle of 177.98(8)°, respectively. The Au-Si bond distance of complex 3 (2.345(2) Å) is similar to that of



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### Scheme 1. Reactions of (Aminosilyl)boronic Ester and of Ph<sub>2</sub>SiH<sub>2</sub> with an Au(I) Thiolate Complex



Figure 1. ORTEP drawings (30% level of probability). (a) Molecular structure of 2. Bond distances (Å) and angles (deg): Au1–S1 2.310(2), Au1–P1 2.274(2), S1–C19 1.773(6), S1–Au1–P1 178.84(5), Au1–S1–C19 105.7(2). (b) Molecular structure of 3. Bond distances (Å) and angles (deg): Au1–Si1 2.345(2), Au1–P1 2.362(2), Si1–S1 2.187(3), Si1–Au1–P1 177.98(8), Au1–Si1–S1 112.9(1), Si1–S1–C31 103.5(3). Hydrogen atoms are omitted for clarity.

 $\begin{bmatrix} Au(SiPh_2Cl)(PCy_3) \end{bmatrix} (2.343(4) \text{ Å})^9 \text{ and is within the range of those of Au(I) complexes with silvl ligands (2.25–2.58 \text{ Å}).^{8f} \\ The Si–S bond of$ **3**(2.187(3) Å) is shorter than the corresponding bond of*fac* $-[RhH<sub>2</sub>(SiPh<sub>2</sub>(SPh))(PMe_3)_3]$ 

(2.228(1) Å).<sup>13</sup> The Au–P bond of complex 2 (2.274(2) Å) is shorter than the bond of complex 3 (2.362(2) Å) because of the larger trans influence of the silyl ligand in comparison to the thiolate ligand. NMR spectra of the complexes agree with the structures by X-ray crystallography. The <sup>29</sup>Si{<sup>1</sup>H} NMR signal of 3 is observed at 47.1 ppm (SiMe<sub>4</sub> standard) with a J(SiP) value of 186 Hz.

The <sup>1</sup>H NMR spectra during the reaction of Scheme 1i showed the clean formation of complex 3 and no intermediates or byproducts in the reaction mixture. Plots of the reaction of excess amounts of 1 (10–20 equiv with respect to 2) suggested that the reaction rates do not increase linearly depending on the initial concentration of 1. Figure 2 summarizes the plausible pathway and the intermediates for the reaction in Scheme 1i, as shown by DFT calculations. The initial step involves approach of the Si atom to the coordinating sulfur atom of the ligand and an accompanying structural change of the substrate. The formed intermediate I contains an S-coordinated silyl thioether ligand with an amino(pinacol)-borate substituent at the Si atom. The intermediate has a Au–S–Si–B–N linkage but no significant interaction between the Si and Au atoms.

Details of the process were analyzed on the basis of nudged elastic band (NEB) calculations (data are given in the Supporting Information). The transition state (TS1) has the Si and S atoms at close positions (2.85 Å), while the Si-S bond distance of intermediate I is 2.42 Å. A three-membered ring composed of Si, S, and B atoms is formed via attractive interaction of the N and B atoms with an N…B distance of 1.95 Å (the sum of N and B atom radii being 1.58 Å) and an acute N–Si–B angle (60.0°). The Si–N distance of TS1 (1.92 Å) is longer than the corresponding bond length of 1 by X-ray crystallography (1.718(1) and 1.719(1) Å), while the Si-B distance of TS1 (1.97 Å) is similar to those of 1 (2.033(2) and 2.035(2) Å). The Si center of TS1 is bonded with boron, nitrogen, sulfur, and two ipso carbon atoms with a distortedtrigonal-bipyramidal geometry. The sum of the C-Si-C angle (109.8°) and the B-Si-C angles (119.5 and 130.4°) is 359.7°, while N-Si-S angle (153.4°) is the largest among the bond angles around the Si center. Thus, TS1 is expected to undergo a structural change caused by further bond formation between the Si and S atoms and activation of the Si-N bond at the



Figure 2. Pathway and intermediates of the reaction of 1 with 2, on the basis of the results of DFT calculations.

apical sites of the trigonal-bipyramidal coordination. The sum of the C–N–C angle and two Si–N–C angles of TS1 (353.3°) suggests minor pyramidalization of the nitrogen atom.

Elimination of amino(pinacol)borane from intermediate I occurs easily to form the complex with an S-coordinated silyl sulfide anion as the ligand (intermediate II). Further migration of the Au center from S-coordination to S*i*-coordination leads to formation of the thermodynamically stable product with an (arenethiolate)silyl ligand (3). These two reactions from intermediate I to II and from intermediate II to the product occur with much lower activation energies. Formation of intermediate I occurs with an activation energy of 22.5 kcal mol<sup>-1</sup>, which should be the rate-determining step of the total reaction. The transition state (TS1), with a structure similar to that of intermediate I, may account for the results of kinetic measurement.

Another pathway via direct bond formation between the Si and Au atoms can be also considered for formation of complex 3 from the reaction of 1 with 2. Scheme 2 shows a possible

Scheme 2. Possible Au-Si Bond Formation for the Early Stage of the Reaction on the Basis of DFT Calculations



early stage of the reaction on the basis of DFT calculations. An approach of the Si atom of the substrate to the Au(I) center accompanies the formation of an Si…N…B three-membered ring (intermediate III). Further progress of the reaction would form a Au-Si bond and Si-N and N-B bonds of the ligand, accompanied by cleavage of the Si-B bond. The resulting intermediate IV has a (pinacolboryl)amine-coordinated diphenylsilylene ligand, with coordination similar to that of the base-stabilized silylene complexes.<sup>2a-d</sup> Another pathway involving a Au(I) intermediate with a bare diphenylsilylene ligand is not plausible for this reaction. Intermediate III has higher energy in comparison to the substrate by 25.4 kcal mol<sup>-1</sup>. The real transition state was not determined for the formation of III and IV, and the activation for the early stage of the reaction is higher than that for the pathway in Figure 2. Thus, the reaction in Scheme 1i prefers the pathway initiated by S-Si bond formation (Figure 2) rather than the pathway that includes the direct Au-Si bond forming process in Scheme 2.

We already reported that the reaction of 1 with [AuCl- $(PCy_3)$ ] gave [Au $(SiPh_2Cl)(PCy_3)$ ] in 11% yield after heating for 7 days.<sup>9</sup> Attempted DFT calculations on the reaction according to the pathway shown in Figure 2 were not successful. The approach of 1 to [AuCl $(PCy_3)$ ] did not provide a possible intermediate or transition state, and Cl and Si atoms are separated from each other (>3.61 Å). The calculated bond order between Si and Cl atoms is lower than

0.103, while I in Figure 2 shows a bond order of 0.764 between the Si and S atoms. This indicates that the reaction in Scheme 1ii proceeds via a pathway different from that of complex 2.  $H_2SiPh_2$  reacts with [AuCl(PCy<sub>3</sub>)] more smoothly than with thiolate complex 2. The (aminosilyl)boronic ester and  $H_2SiPh_2$  are used as complementary precursors for insertion of the diphenylsilylene group into the Au–SAr and Au–Cl bonds.

In summary, we obtained Au complexes with a thiolatosilyl ligand by using an (aminosilyl)boronic ester as the source of a diphenylsilylene group. The reaction occurs via initial formation of the Si–S bond rather than direct approach of the Si atom to the Au center, as shown by theoretical calculations. The resulting intermediate and proposed pathway of the total reaction were unexpected but account for the smooth formation of the gold complex with the thiolatosilyl ligand.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00294.

- Synthetic procedures, spectroscopic data ( $^{1}H$  and  $^{31}P{}^{1}H$  NMR), and DFT calculations (PDF)
- Coordinates of results of the theoretical calculations (XYZ)

#### **Accession Codes**

CCDC 1999367–1999369 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

#### **Corresponding Authors**

- Kohtaro Osakada Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan; o orcid.org/0000-0003-0538-9978; Email: koskada@res.titech.ac.jp
- Tomohito Ide Department of Chemical Science and Engineering, National Institute of Technology, Tokyo College, Tokyo 193-0997, Japan; Email: ide@tokyo-ct.ac.jp

#### Authors

- Yoshitaka Tsuchido Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan
- Kazuki Okuma Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00294

#### Notes

The authors declare no competing financial interest.

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