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Mechanistic Study on the Gold-Catalyzed C−S Bond Formation of α-Thioallenes To Form 2,5-Dihydrothiophenes

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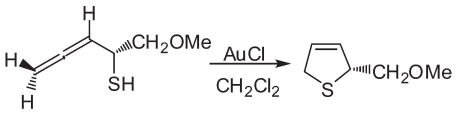

B3LYP/6-31G*, SDD for Au

The reaction mechanism of the AuCl-catalyzed reaction of the α-thioallenes to give 2,5-dihydrothiophenes has been computationally studied using DFT (B3LYP/6-31G*, SDD for Au). Calculations indicate the complexation of α-thioallene with AuCl occurs preferentially at the distal double bond, followed by the C−S bond formation, the proton transfer from the sulfur to the carbon "b", and the [1,2]-hydride shift to give the 2,5-dihydrothiophene gold complex. The proton transfer is the rate-limiting step with very high activation energy in the gas phase. In the presence of one water molecule, the activation free energy of the proton transfer was lowered by as much as 19.9 kcal/mol. Furthermore, one dichloromethane molecule stabilized all of the transition structures by its hydrogen bonds.

Introduction

The use of homogeneous gold catalysts in organic synthesis has received much attention in the first decade of this century. Because of their strong Lewis acidity and their potential to stabilize cationic intermediates, gold catalysts exhibit not only high reactivity but also high selectivity in various transformations.[1] Recently, Krause et al. reported the first gold-catalyzed C−S bond formation of α-thioallenes to give 2,5-dihydrothiophenes with complete axis-to-center chirality transfer (Scheme 1).[2,3] Soon after that, Nakamura and Yamamoto et al. reported gold(I)-catalyzed intramolucular carbothiolation of alkynes,[4] and He et al. reported the gold(I)-mediated hydrothiolation of conjugate olefins.[5] However, it is well-known that organosulfur compounds such as thiols, sulfides, and disufides strongly coordinate to transition metals, particularly to gold.[6] Therefore, the use of gold catalysts in the presence of these functional groups was not expected to be promising. To understand this contradiction and elucidate the reaction mechanism, a computational study was performed. Here we report our results.

Computational Methods

All of the calculations were performed using the Gaussian 03 program.[7] Gibbs free energies are the values at 25 °C (298.15 K) and 1.00 atm obtained from the frequency calculations. Most of the calculations were performed by the B3LYP

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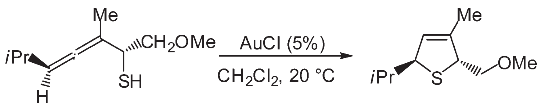
SCHEME 1



hybrid functional[8] together with 6-31G* basis set for all atoms except gold, for which the Stuttgart−Dresden effective core potential (SDD)[9] was used. Since the scaled factor for B3LYP/6-31G* is close to 1.0,[10] the thermal energy corrections are not scaled. Vibrational frequency calculations gave only one imaginary frequency for all transition structures and confirmed that those structures are authentic transition structures. The structures of reactants, products, and intermediates were obtained by the optimization of the last structures on both sides of the IRC calculations.[11] The frequency calculations on their structures gave only harmonic frequencies and confirmed that they are minima. Although the density functional theory was proved to be appropriate for the investigation of gold-catalyzed systems,[12] some calculations were performed at the MP2/6-31G*(Au:SDD) level for comparison.

Results and Discussion

The salts of transition metals can operate as bifunctional Lewis acids activating both carbon−carbon multiple bonds via π-complex formation and heteroatom functional groups via σ-complex formation. Yamamoto calculated the stability of the complexes between AuCl and representative unsaturated compounds (aldehydes, alkynes, and alkenes) to evaluate its applicability to highly selective transformations.[13] The results show AuCl has a preference for the coordination to the carbon−carbon multiple bonds over aldehydes. Since the α-thioallene in Scheme 1 has three functional groups, allene, thiol, and ether, which can coordinate to AuCl, the coordination energies of AuCl with them were calculated. In order to reduce the conformations of the reactant, the α-thioallene **1** was used as a simplified model substrate in this study. The relative energies of the optimized complex structures **2a** (with allene), **2b** (with thiol), and **2c** (with ether) were calculated at the B3LYP/6-31G*(Au:SDD) level (Figure 1). The energy of **2a** is slightly higher than that of **2b** (0.5 kcal/mol) (also see complex **2a′** in Figure 3, which is more stable than **2b** by 0.1 kcal/mol) and much lower than that of **2c**. Thus, the coordination of AuCl to the ether oxygen can be negligible. Although the coordination of AuCl to the proximal double bond of the allene is also possible, the complex was less stable than **2a** by 1.5 kcal/mol and did not give any products. Since the energies of **2a** and **2b** were almost same, we calculated their energies at the MP2 and the QCISD levels of the B3LYP structures. The energy of **2a** is 3.4 and 2.8 kcal/mol lower than that of **2b** at these levels. Also, the effect of the isopropyl group (the structure in Scheme 1) was tested. The energy difference is the same 0.6 kcal/mol at the B3LYP level. For comparison, the structures were also optimized at the MP2/6-31G*(Au:SDD) level, and the relative energies were calculated. At this level, **2a** is the most stable structure, and **2b** and **2c** are 3.9 and 14.1 kcal/mol less stable than **2a**, respectively. Furthermore, the coordination energies ($\Delta G = G_{\text{complex}} - G_{\text{compound}} - G_{\text{AuCl}}$)[14] for the complexes between AuCl with allene, methanthiol, and dimethyl ether **a**−**c** were also calculated in order to compare the more general coordination energy. The allene−AuCl complex **a** is stabilized by 34.4 and 25.8 kcal/mol at the MP2 and the B3LYP levels, respectively. Thus, the complexation reaction is highly exothermic. These stabilization energies are higher than those of the thiol−AuCl complex **b** (29.0 and 24.9 kcal/mol) and the ether−AuCl complex **c** (21.0 and 16.6 kcal/mol). Thus, the coordination of AuCl to the allenyl group is energetically more favorable than that to the thiol and the ether groups.

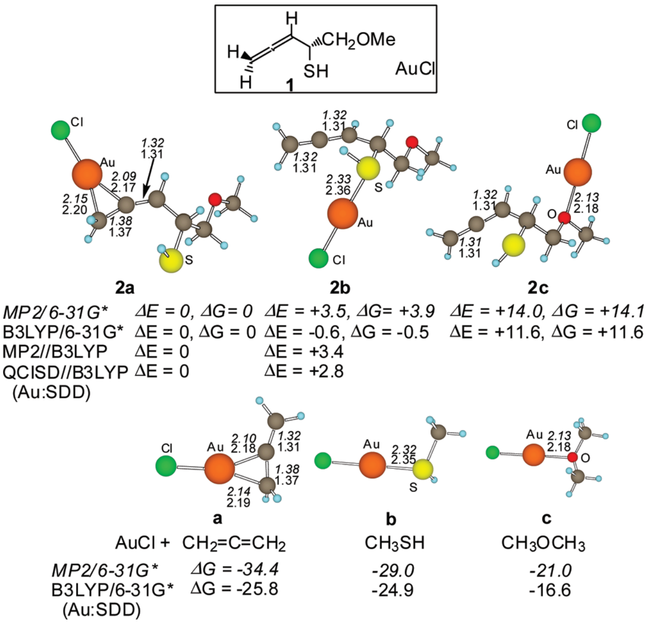


FIGURE 1. Comparison of the complexation energies (kcal/mol).

The transition-state structure **2a-TS1** for the C−S bond formation from the complex **2a** was located at the B3LYP level (Figure 2). The distance of the forming C−S bond is 2.11 Å, and the activation free energy is 15.3 kcal/mol. The IRC analysis gave the intermediate **2a-Int1**, whose energy is almost same as **2a-TS1** and the distance of the C−S bond is also only slightly shorter 2.08 Å. For comparison, the transition structure for the C−S bond formation was reoptimized at the MP2/6-31G*(Au:SDD) level. The activation free energy is slightly higher 17.9 kcal/mol, and the energy of the intermediate **2a-Int1** is 16.5 kcal/mol. Since both the MP2 energies and the optimized MP2 geometries are quite similar to those at the B3LYP level, we performed the rest of the study at the B3LYP level. In order to get the 2,5-dihydrothiophene product, the proton transfer from the sulfur to the carbon "a" in **2a-Int1** should occur. Even after many trials, the transition structure for the direct proton transfer from the sulfur to the

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(14) For **2a**−**c**, the relative energy is equal to the relative coordination energy.

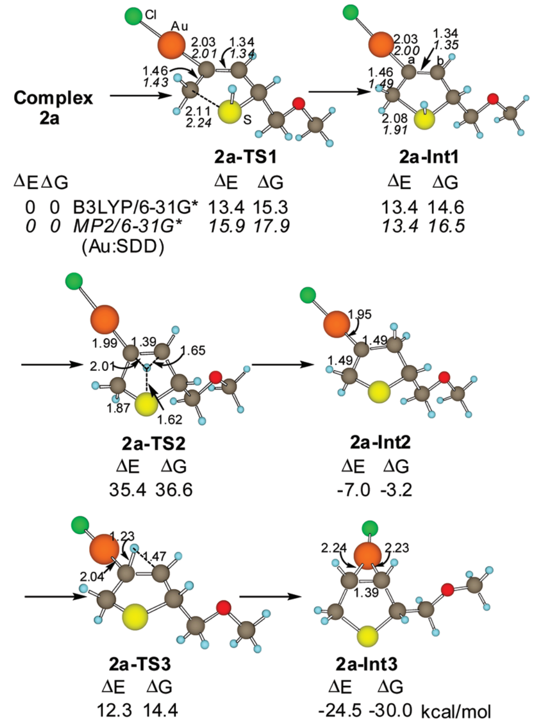
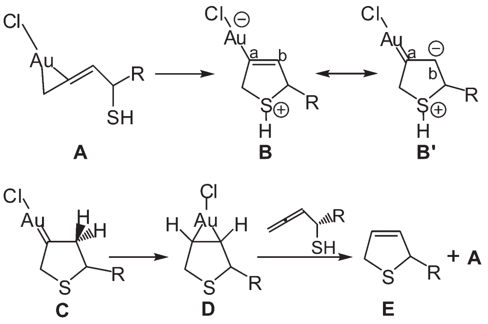


FIGURE 2. Transition structures of the C−S bond formation and the proton transfer reaction (B3LYP/6-31G*,Au:SDD). The italic numbers are the values at the MP2 level.

SCHEME 2



carbon “a” has never been obtained. Instead of that, the transition structure **2a-TS2** for the proton transfer from the sulfur to the carbon “b” was obtained with the relative Gibbs free energy of 36.6 kcal/mol. The activation energy from **2a-Int1** is 22.0 kcal/mol. This can be explained by the reaction mechanism shown in Scheme 2. From complex **A**, intramolecular nucleophilic attack by the sulfur atom occurred to give **B**. The negative charge is delocalized between the gold atom and the carbon atom “b” (**B′**). The proton transfer from the sulfur to the carbon “b” gives the stable intermediate **C**. The [1,2]-hydride shift from the carbon “b” to the carbon “a” will give **D**, from which the ligand exchange reaction of the gold complex gives the product **E** and the substrate **A**. However, the relative Gibbs free energy of **2a-TS2** is too high for the reaction to occur at room temperature. Therefore, it is impossible for the proton to transfer from the sulfur either to the carbons “a” or “b” in the gas phase. The [1,2]-hydride shift from the carbon “b” to the carbon “a” occurred with 14.4 kcal/mol energy to give the much stable intermediate **2a-Int3**. In the hydride shift transition state, **2a-TS3**, the distance of Ca−H is shorter than that of Cb-H (1.23 vs 1.47 Å). Similar unsymmetrical three-membered ring structures were previously reported.[15−17] The decomplexation of **2a-Int3** will give the 2,5-dihydrothiophene and AuCl. We will discuss the decomplexation reaction in Figure 8.

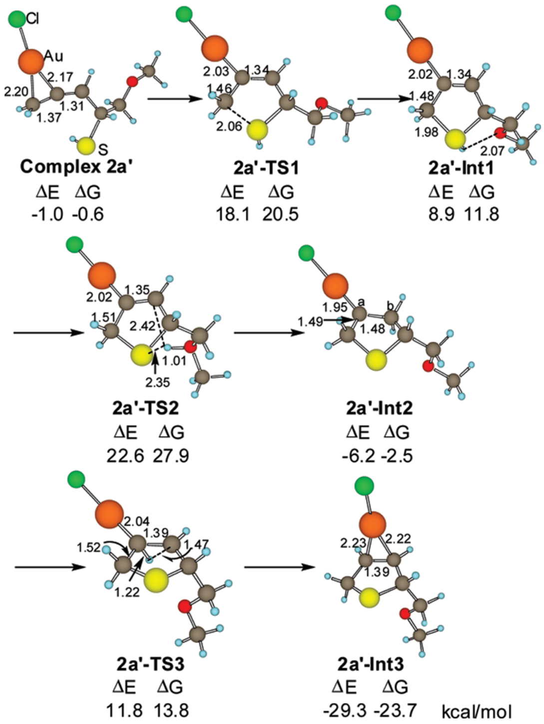


FIGURE 3. Transition structures for the C−S bond formation of complex **2a′** (SH proton down) and the proton transfer reaction.

There is another conformation for the complex of **1** and AuCl. That is, **2a′**, which has SH proton down and is more stable than **2a** by 0.6 kcal/mol (Figure 3). However, the activation energy for the C−S bond formation is 21.1 kcal/mol and higher than that of **2a-TS1** by 2.6 kcal/mol. We focused on the possibility that the proton transfer occurs under the dihydrothiophene ring by the assistance of the side chain oxygen atom. The transition structure **2a′-TS2** was obtained, where the moving proton interacts with the side chain oxygen and moves from the sulfur to the allenyl carbon “b” with the relative Gibbs free energy of 27.9 kcal/mol. This energy is 8.7 kcal/mol lower than that of **2a-TS2**, and the activation energy is 16.1 kcal/mol. From the intermediate **2a′-Int2**, the [1,2]-hydride shift from the carbon “b” to the carbon “a” occurred with 13.8 kcal/mol energy to form the intermediate **2a′-Int3**. The structure of **2a′-TS3** is almost same as **2a-TS3**, and their energies are also similar. Although the activation energy for the proton transfer reaction was much reduced, this is still the rate-limiting step for the overall potential energy surface.

The decrease of the activation energy for the proton transfer reaction from the sulfur to the allenyl carbon “b” by the assistance of the side chain oxygen suggested us the possibility

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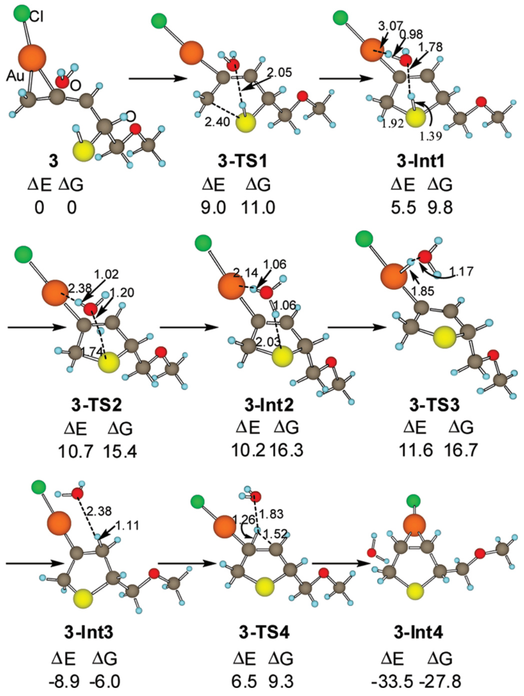

FIGURE 4. Reaction of complex **2a** in the presence of H_2O (kcal/mol).

that a trace amount of water in CH_2Cl_2 can catalyze the proton transfer from the sulfur to the allenyl carbon "b". Recently, Yu et al. reported the DFT study on the Au(I)-catalyzed tandem [3,3]-rearrangement/Nazarov reaction/[1,2]-hydride shift.[15] The reaction discovered by Zhang et al. was initially reported to be performed in dry CH_2Cl_2, and the authors later observed that the reaction was faster in wet CH_2Cl_2 than in dry CH_2Cl_2.[18] Since it is difficult to get perfectly dry CH_2Cl_2, we studied the effect of a trace amount of water to the reaction.[19] The reaction of the complex **2a** in the presence of one water molecule was studied, and the results are shown in Figure 4. The transition structure **3-TS1** for the C−S bond formation was stabilized by the hydrogen bond between the water oxygen and the SH hydrogen. The activation energy is 11.0 kcal/mol, which is 4.3 kcal/mol lower than that in the absence of water in Figure 2. The water molecule interacts with the thiol group, increases the nucleophilicity of the thiol, and decreases the activation energy of the reaction. The intermediate **3-Int1** was also stabilized in the presence of water by 4.8 kcal/mol. The proton-transfer reaction from the sulfur to the water oxygen atom occurred to give the intermediate **3-Int2**. The transition structure **3-TS2** was stabilized by the interaction between the negative gold atom and one of the water hydrogens. Although **3-TS2** is the transition structure on the base of the electronic energy, **3-Int2** is less stable than **3-TS2** by 0.9 kcal/mol on the base of the Gibbs free energy. Therefore, it is not the real transition structure. The transition structure **3-TS3** is the rate-limiting step for the delivery of the proton to the carbon "b". The activation energy is 16.7 kcal/mol, which is lower than that of **2a-TS2** by 19.9 kcal/mol. Even a single water molecule can accelerate the reaction by lowering the barrier significantly. Since the structure of **3-TS3** is interesting, we performed a full IRC analysis of this reaction. Several representative intermediates on the IRC are shown together with those energies in Figure 5. From the starting point of **3-Int2**, the energy increases when a proton "x" of the H_3O^+ moves to the gold. Right after going beyond the transition structure **3-TS3**, the distance between the gold and the proton "x" is the shortest (1.84 Å). After that, the distance Au−H"x" starts to increase, and the proton "y" moves to the carbon "b" to give **3-Int3**. From **3-Int3**, the [1,2]-hydride shift occurred. The relative Gibbs free energy of the transition structure **3-TS4** is 9.3 kcal/mol, which is lower than that of **2a-TS3** by 5.1 kcal/mol. This reduction of the activation energy in the presence of water molecule is consisitent with Yu's previous study, in which 3.8 kcal/mol reduction of the activation energy was reported for the [1,2]-hydride shift.[15] These reactions in the presence of a water molecule are quite similar to the proton-transfer processes in many enzyme-catalyzed reactions.[20]

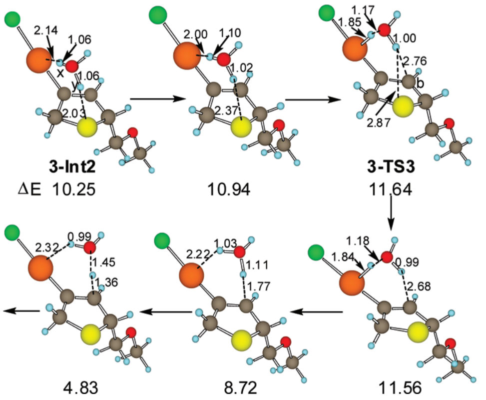

FIGURE 5. Representative intermediates on the IRC (0.1 amu$^{1/2}$ bohr along the path) of the proton-transfer reaction from **3-Int2** to **3-Int3** (kcal/mol).

Krause et al. reported the reaction to proceed smoothly in dichloromethane whereas very slow conversions and low yields were obtained in THF, toluene, or hexane.[2] Since the dielectric constants of dichloromethane and THF are similar (8.93 and 7.58, respectively), we are interested in the effect of dichloromethane for the reaction. The transition structure of the complex **2a** for the C−S bond formation reaction was located in the presence of one dichloromethane molecule. As shown in Figure 6, the activation energy is 2.1 kcal/mol lower than that in the absence of solvent in Figure 2. The dichloromethane proton interacts with the chloride of the gold complex, withdraws an electron from the gold complex, and increases the electrophilicity of the allene part. Since dichloromethane protons are more acidic than those of THF, the activation energy was lowered in CH_2Cl_2.[21]

As mentioned above, both water and dichlomethane can lower the activation energy of the C−S bond formation. The

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[18] Zhang, L.; Wang, S. *J. Am. Chem. Soc.* **2006**, *128*, 1442–1443.

[19] Recently, Zhang and Liu et al. reported their study on the gold-catalyzed cyclization of α-aminoallenes. They concluded that another aminoallene molecule assists proton transfer by a stepwise H-abstraction and H-donation process.[17]

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[21] The relative acidity of molecules X and Y was calculated by the comparison of the optimized energies between $[(X-H)^- Y]$ and $[X(Y-H)^-]$ at the B3LYP/6-31G* level. The results are as follows: THF < NH_3 < CH_3CN < CH_2Cl_2 < AcOEt.

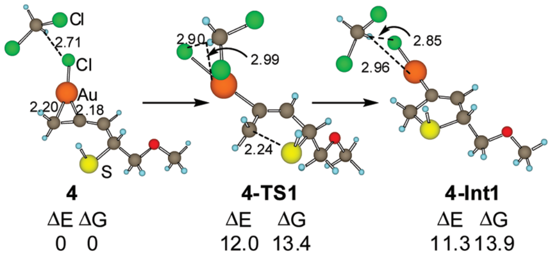

FIGURE 6. AuCl-catalyzed C−S bond formation of **2a** in the presence of CH_2Cl_2.

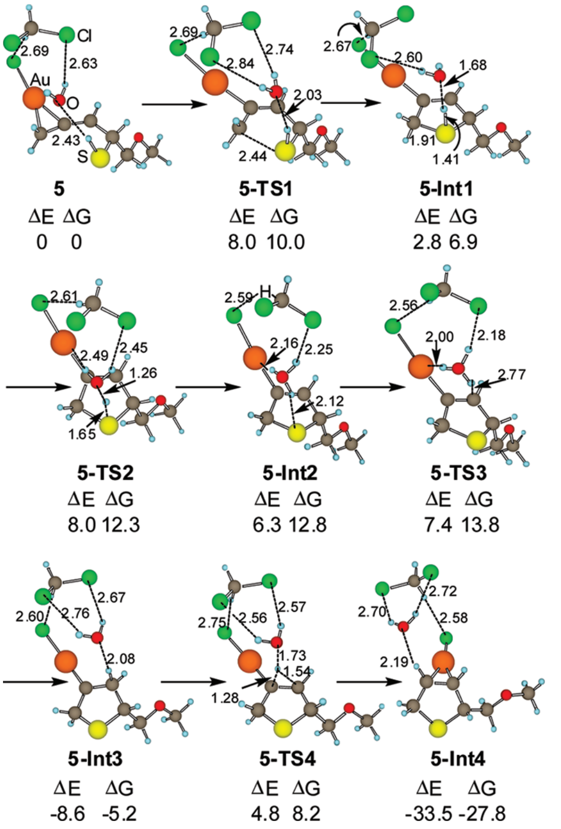

FIGURE 7. Reaction of **2a** in the presence of H_2O and CH_2Cl_2 (kcal/mol).

reaction of the complex **2a** in the presence of one water molecule and one dichloromethane was studied, and the results are shown in Figure 7. The transition-state structure **5-TS1** for the C−S bond formation was stabilized by the hydrogen bond between the water oxygen and the SH hydrogen, and the allene part was activated by the interaction between AuCl and dichloromethane. Also there are two hydrogen bonds between water hydrogens and dichloromethane chlorides. The activation energy is 10.0 kcal/mol, which is 5.3 and 1.0 kcal/mol lower than that of **2a-TS1** and **3-TS1**, respectively. The energy of the intermediate **5-Int1** was 6.9 kcal/mol and also stabilized by 7.7 and 2.9 kcal/mol compared with those of **2a-Int1** and **3-Int1**, respectively. The proton-transfer reaction from **5-Int1** occurred in the same way as that in the presence of water in Figure 4 to give the intermediate **5-Int3**. The relative Gibbs free energy of the rate-limiting **5-TS3** is 13.8 kcal/mol and is lower than those of **2a-TS2** and **3-TS3** by 22.8 and 2.9 kcal/mol, respectively.

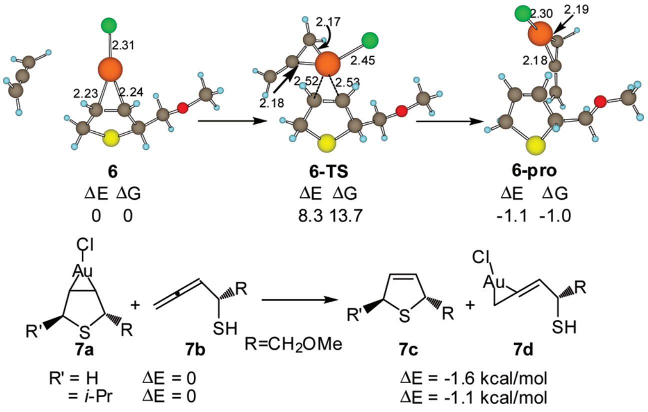

FIGURE 8. Transition structure for the ligand-exchange reaction of **2a-Int3** and allene (kcal/mol).

The structure **5-TS3** was stabilized by the interaction between the negative gold atom and one of the water hydrogens. In addition, there are two hydrogen bonds between water hydrogen and dichloromethane chloride and the chloride of the gold complex and dichloromethane hydrogen. These two hydrogen bonds lower the energy by 2.9 kcal/mol. From **5-Int3**, the [1,2]-hydride shift occurred with 8.2 kcal/mol energy to give the stable intermediate **5-Int4**. The energy of **5-TS4** is lower than that of **2a-TS3** by 6.2 kcal/mol, and **5-TS4** was stabilized by four hydrogen bonds with water and dichloromethane. Thus, the rate limiting step is the proton transfer process in this reaction and both water molecule and dichloromethane molecule can stabilize all the transition structures and reduce the activation energy as high as 22.8 kcal/mol.

Finally, the decomplexation reaction of the intermediate **2a-Int3** to give the 2,5-dihydrothiophene and AuCl was studied (Figure 8). The transition structure **6-TS** for the ligand-exchange reaction of **2a-Int3** with allene was located. The activation energy is 13.7 kcal/mol. Since the activation free energy of the raction is low enough, the allene−AuCl complex and 2,5-dihydrothiophene are readily generated from **2a-Int3** and allene. However, **6-pro** is more stable than **6** by only 1.0 kcal/mol. Therefore, the energies of **7a−d** were calculated. The combined energy of **7c** and **7d** is lower than that of **7a** and **7b** by 1.6 and 1.1 kcal/mol for R = H and isopropyl, respectively. In addition, the whole catalytic cycle is highly exothermic (for example, −27.8 kcal/mol in Figure 7). Thus, the catalytic cycle can be easily continued to complete the reaction.

In summary, the reaction mechanism of the AuCl-catalyzed reaction of the α-thioallenes to give 2,5-dihydrothiophenes has been computationally studied using DFT method (B3LYP/6-31G*, SDD for Au). Calculations indicate the complexation of α-thioallene with AuCl occurred preferencially at the distal double bond to give the complex **2a** or **2a′**. Although the activation energies of the C−S bond formation and the [1,2]-hydride shift are below 20 kcal/mol, the proton transfer from the sulfur to the carbon “b” is the rate-limiting step with activation free energy of 36.6 kcal/mol in the absence of solvent (see Figure 2 and Scheme 2). In the presence of one water molecule, the proton transfer from the sulfur to the carbon b is efficiently catalyzed by water with the activation free energy of 16.7 kcal/mol, which is lower than that in the absence of solvent by 19.9 kcal/mol. Furthermore, the presence of one dichloromethane molecule lowers the activation energies of all the transition structures by hydrogen bonds. These findings are precious and may improve transition-metal-catalyzed reactions.

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Supporting Information Available: Gibbs free energies (hartrees) and the imaginary frequencies of the transition structures at the B3LYP level and the *xyz* coordinates for structures **2a**, **2b**, **2a-TS1**, **2a-TS2**, **2a-TS3**, **2a′-TS2**, **3-TS1**, **3-TS2**, **3-TS3**, **3-TS4**, **4-TS1**, **5-TS1**, **5-TS2**, **5-TS3**, **5-TS4**, and **6-TS**. This material is available free of charge via the Internet at http://pubs.acs.org.