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Mechanism of Rhodium-Catalyzed Carbon−Silicon Bond Cleavage for the Synthesis of Benzosilole Derivatives: A Computational Study

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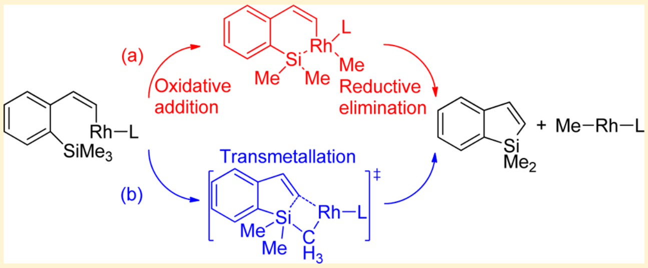
Ⓢ *Supporting Information*



ABSTRACT: Rhodium-catalyzed carbon−silicon bond cleavage reaction is an efficient approach for the synthesis of silole derivates. The newly reported density functional theory method M11 is employed in order to elucidate how to cleave the inactive C(methyl)−Si bond. The computational results indicate that oxidative addition/reductive elimination pathway is favored over direct transmetallation in the C(methyl)−Si bond cleavage step. Alternatively, 1,4-rhodium−silicon exchange could take place before oxidative addition/reductive elimination. The rate-determining step for both pathways has been targeted on the initial transmetallation of 2-trimethylsilylphenyl boronic acid. The active catalytic species is a monomeric hydroxyrhodium complex, which could be regenerated from the hydrolysis of methylrhodium complex. In addition, theoretical calculations show that the hydrolyses of both aryl and vinyl intermediates are inhibited by intramolecular π-coordinated groups.

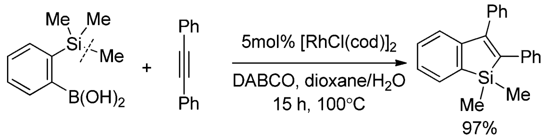
INTRODUCTION

Silole derivates, whose structure contains a silacyclopentadiene framework, have a wide scope of application in making Si-containing materials[1] and have been applied for organic electronic devices, such as light-emitting diodes,[2] field-effect transistors,[3] solar cells,[4] and fluorescent sensors.[5] Due to the interaction between the σ^* orbitals of the two exocyclic Si−C bonds and the π^* orbital of the butadiene moiety, they possess a low-lying LUMO,[6] which leads to a series of unique properties in materials science. In the past two decades, much attention has been paid to develop novel preparative methods for these compounds.[7] Transition-metal catalysts, involving nickel,[8] ruthenium,[9] rhodium,[10] iridium,[11] palladium,[12] and gold complexes,[13] are employed in the synthesis of silole derivates.

Among previous silole syntheses,[14] C−Si bond transformation often acts as a key step.[15] The hybridization status of the carbon atom, directly attached to silicon, manipulates the reactivity of C−Si bond. In general, sp^2-, sp-, and allylic carbons are more active than sp^3-carbon in the C−Si bond cleavage step due to the hyperconjugation between silicon and its neighboring π orbitals. Early work only reported C(sp^3)−Si bond cleavage reactions with strained silanes,[16] SiMe$_4$,[17] $Me_3Si(CH_2)_3SO_3Na$,[18] Me_3SiCF_3,[19] and penta- or hexa-coordinated silicon species.[20]

The successful cleavage of inactive C(sp^3)−Si bonds in trialkylsilyl groups, such as trimethylsilyl, would bring a vast expansion in the synthesis of a variety of substituted silole derivatives.[21] Xi and co-workers reported a series of palladium-catalyzed cleavage of C(sp^3)−Si bond using organolithium reagents for the preparation of silole derivatives.[22,23] Fe(acac)$_3$ can also be used as the catalyst in the synthesis of benzosilole derivatives.[24] Recently, Chatani and co-workers reported a Rh-catalyzed intermolecular coupling of 2-trimethylsilylphenyl boronic acids with alkynes by the cleavage of an inactive C(sp^3)−Si bond (Scheme 1).[25,26] This reaction is insensitive to moisture, and up to a 97% yield can be obtained with 5 mol % catalyst loading.

Scheme 1. Rh-Catalyzed Intermolecular Synthesis of Silole



In this Rh-catalyzed intermolecular coupling reaction, the essential step is the cleavage of the inactive C(sp^3)−Si bond. As shown in Scheme 2, there are two plausible pathways for C(sp^3)−Si bond cleavage: (a) via a sequential oxidative addition and reductive elimination pathway or (b) via direct transmetallation. The pathway for going through oxidative addition/reductive elimination mechanism to break a C−Si bond was reported only for the C(aryl)−Si bond cleavage in an 1,4-rhodium−silicon exchange step.[27] Additionally, Chatani proposed a direct transmetallation for C−Si bond cleavage due to the absence of hydrolyzed side products, which could be generated from plausible rhodium−silicon exchange intermediates.[26] The real mechanism, however, is still unclear. In order to elucidate the ambiguity for this Rh-catalyzed intermolecular

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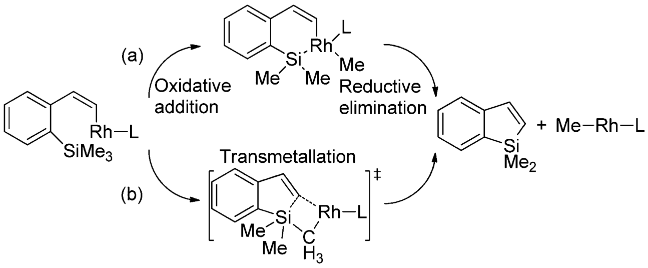
Scheme 2. Two Plausible Pathways for the Cleavage of the C−Si Bond



coupling reaction, density functional theory (DFT) calculations are performed on this reaction.

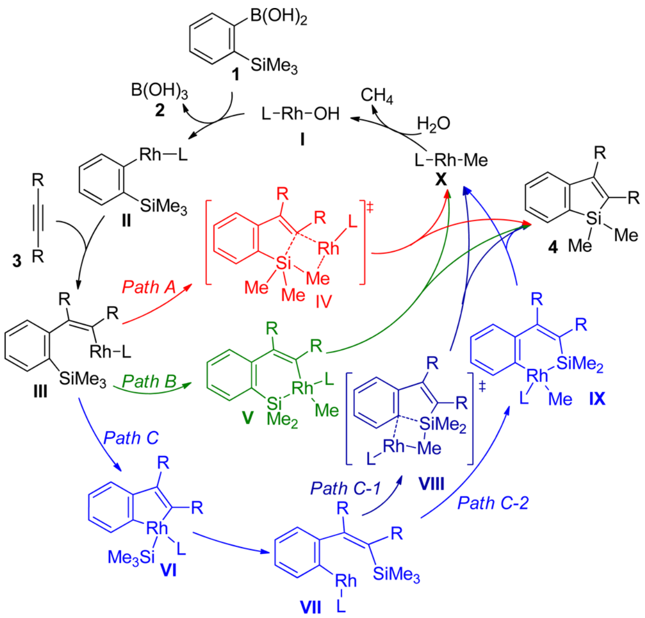
COMPUTATIONAL METHODS

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs.[28] Density functional theory B3LYP[29] with a standard 6-31G(d) basis set (LanL2DZ basis set for rhodium atom) was used for geometry optimizations. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition structures and to derive the thermochemical corrections for the enthalpies and free energies. M11 functional,[30] recently proposed by the Truhlar group, is used to calculate the single point energies, which could give more accurate energetic information.[31] The solvent effects were considered by single point calculations on the gas-phase stationary points with an integral equation formalism polarizable continuum model (IEFPCM).[32] The larger basis set 6-311+G(d,p) (SDD basis set for the rhodium atom) is used in the salvation single point calculations. The energies given in this paper are the M11 calculated Gibbs free energies in the 1,4-dioxane solvent, and the values given in parentheses are the B3LYP calculated Gibbs free energies in the same solvent.

RESULTS AND DISCUSSION

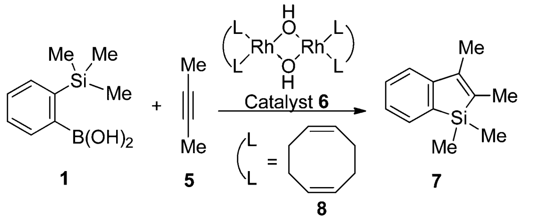
As depicted in the mechanistic map (Scheme 3), four possible pathways are taken into account (paths A, B, C-1, and C-2). All begin with the transmetallation of 2-trimethylsilylphenyl boronic acid **1** on the hydroxyrhodium complex **I**, where the intermediate **II** is formed. Subsequent alkyne **3** insertion gives complex **III**. In path A (red part, Scheme 3), complex **III** undergoes transmetallation via a transition state **IV**, giving complex **X** and product **4**. In path B (green part, Scheme 3), Me−Si bond oxidative addition from complex **III** generates a Rh(III) intermediate **V**. The following reductive elimination gives identical products as in path A. A common intermediate for both paths C-1 and C-2, complex **VII**, is generated from **III** first by 1,4-rhodium−silicon exchange via Rh(III) intermediate **VI**. In path C-1 (dark blue part, Scheme 3), transmetallation occurs via transition state **VIII**; whereas path C-2 (blue part, Scheme 3) undergoes oxidative addition and reductive elimination steps. As a general feature of all four routes, complex **X** is always formed whenever product **4** is out of the catalytic cycle. Hydrolysis of **X** would release one molecular methane and then regenerate complex **I**. All four pathways will be evaluated in the following discussion.

Scheme 3. Proposed Mechanisms for the Rh-Catalyzed Intermolecular Synthesis of Silole



As shown in Scheme 4, the coupling reaction of 2-trimethylsilylphenyl boronic acid **1** with 2-butyne **5**, catalyzed by rhodium dimer **6**, was chosen as the model reaction to study the mechanism of this intermolecular silole synthesis. Cyclooctadiene is chosen as the model ligand, which has also been employed experimentally.[25,26]

Scheme 4. Model Reaction for the Formation of Silole 7



The free-energy profile for the initiation steps of this Rh-catalyzed intermolecular synthesis is shown in Figure 1. After dissociation of dimeric Rh complex **6**, the monomeric Rh complex undergoes transmetallation with reactant **1** via a four-membered-ring transition state **10-ts** with a 16.6 kcal/mol overall barrier, where an aryl-rhodium complex **12** is generated. Subsequent alkyne insertion into the C−Rh bond of complex **12** via a 4-membered-ring transition state and 9.7 kcal/mol barrier produces complex **15** irreversibly. Complex **15** is the key species for all of the four possible pathways, as depicted in Scheme 3. The geometry information of complex **15** is shown in Figure 2, whereby the shortest distance between the aryl carbon and rhodium is only 2.50 Å, indicating a strong π-coordination.

As shown in Figure 3 (red lines), silole product **7** could be formed from complex **15** via a direct transmetallation fashion and through transition state **16-ts** with a 43.8 kcal/mol barrier. Figure 4 provides the geometry information of the square planar transition state **16-ts**, representing the status when the Rh−C(vinyl) bond is almost broken and the new Rh−C(methyl) bond is not yet formed, with the corresponding Rh−C bond lengths of 2.38 Å and 2.55 Å, respectively. Therefore, direct transmetallation via the transition state **16-ts** is unfavorable because of its high activation energy.

As shown in Figure 3 (blue lines), the 1,4-rhodium−silicon exchange from complex **15** to **21** could proceed through a sequential oxidative addition/reductive elimination pathway. An intramolecular oxidative addition of the C(aryl)−Si bond

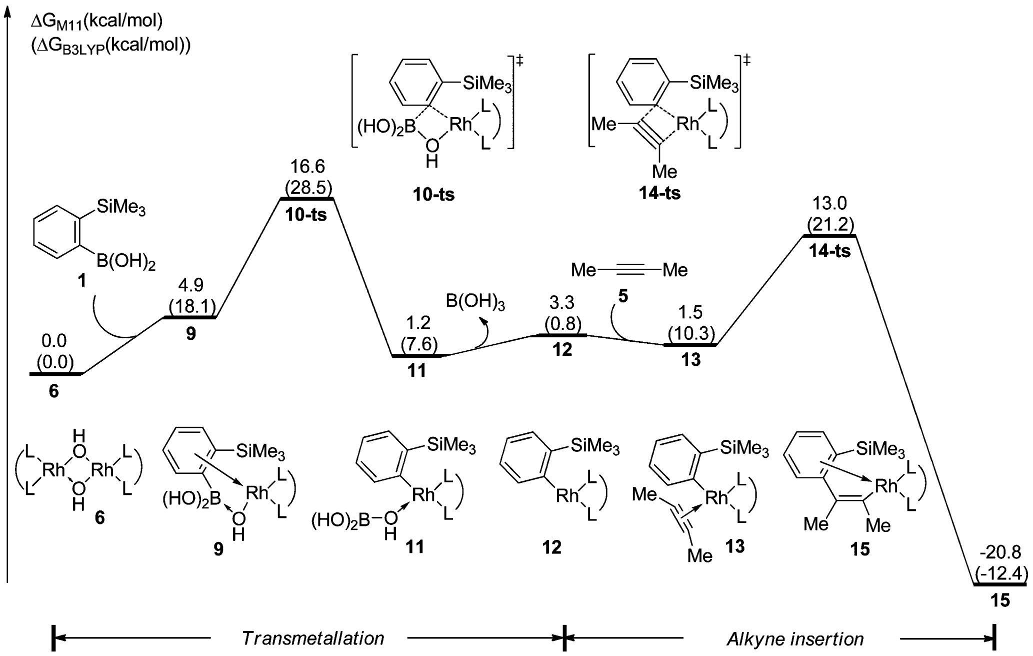


Figure 1. Free-energy profile for the initiation step.

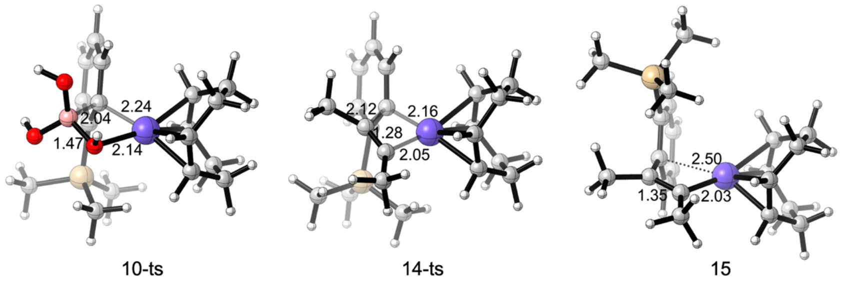


Figure 2. Geometry information for **10-ts**, **14-ts**, and **15**.

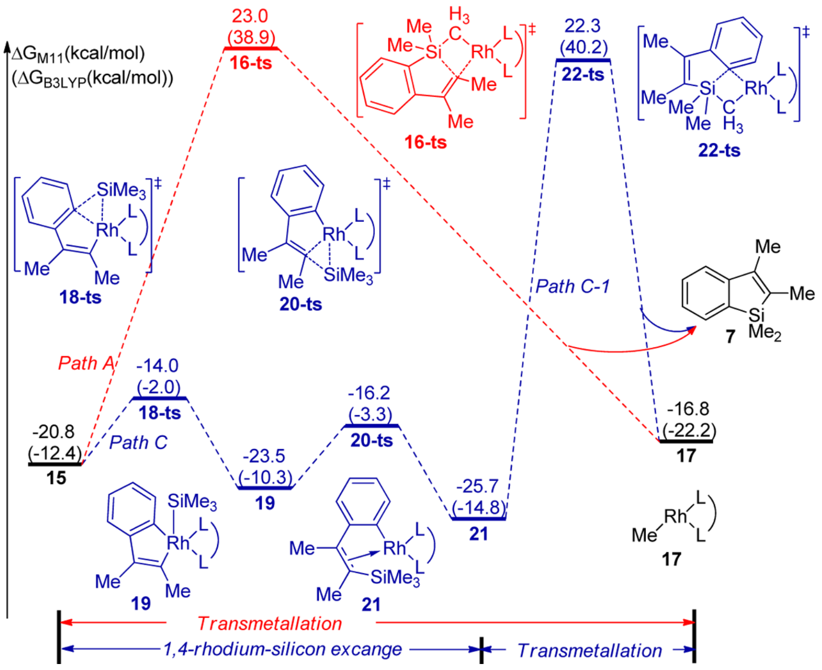


Figure 3. Free energy profile for direct transmetallation mechanism (Path A, red line), and 1,4-rhodium-silicon exchange/transmetallation mechanism (Path C-1, dark blue line).

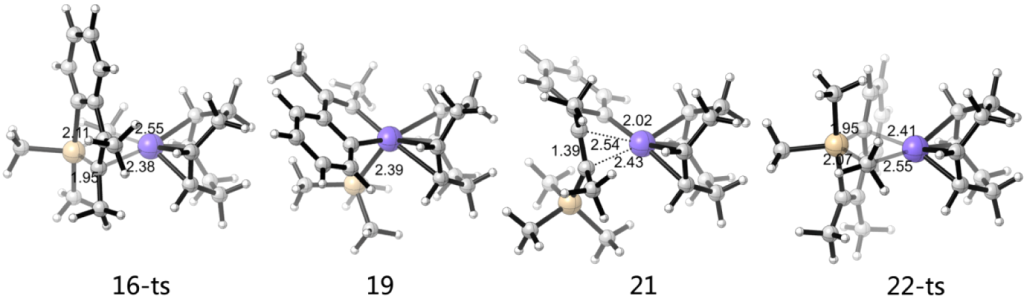


Figure 4. The geometry information of **16-ts**, **19**, **21**, and **22-ts**.

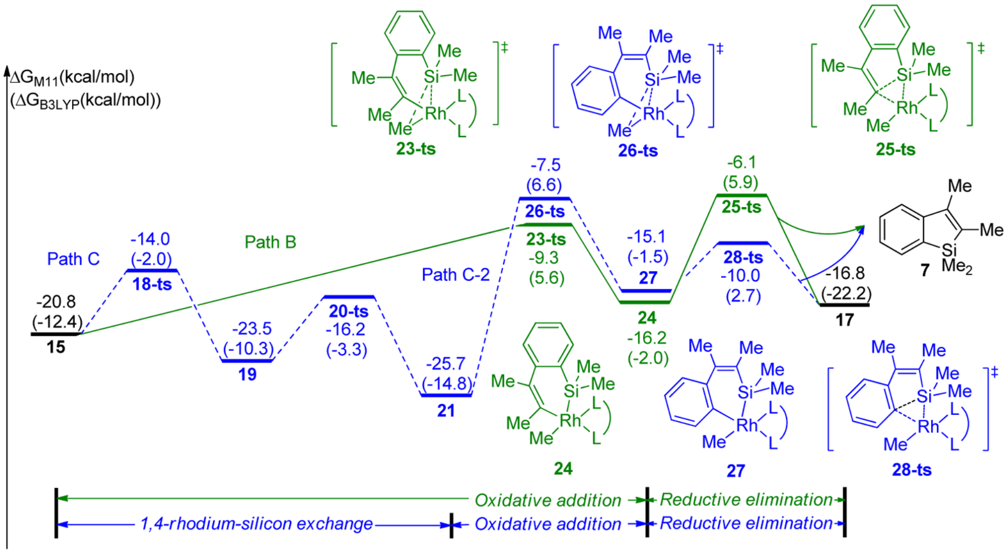


Figure 5. Free energy profiles for the oxidative addition/reductive elimination mechanism (Path B, green line) and the 1,4-rhodium-silicon-exchange/oxidative addition/reductive elimination mechanism (Path C-2, blue line).

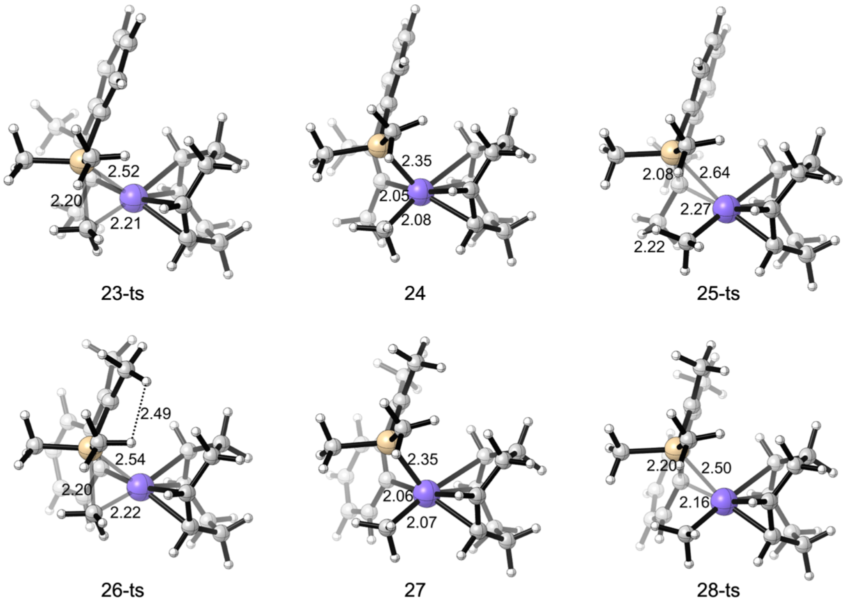


Figure 6. The geometry information of **23-ts**, **24**, **25-ts**, **26-ts**, **27**, and **28-ts**.

could take place reversibly via the transition state **18-ts** with only a 6.8 kcal/mol barrier. The square pyramidal Rh(III) intermediate **19** is then formed with only 2.7 kcal/mol exothermic. The geometry information of intermediate **19** is shown in Figure 4. The trimethylsilyl group is out of the plane with a Rh−Si bond length of 2.39 Å. The following reductive elimination would occur via the transition state **20-ts** with a 7.3 kcal/mol barrier and could reversibly form the C(vinyl)−Si complex **21**. The energy information shows that the reversible 1,4-rhodium−silicon exchange can take place easily, and the aryl−rhodium complex **21** is 4.9 kcal/mol more stable than the vinyl−rhodium complex **15**. The final transmetallation via transition state **22-ts**, however, exhibits a barrier as high as 48.0 kcal/mol in order to produce product **7**. Consequently, this theoretical calculation clearly shows that both transmetallation mechanisms of paths A and C-1 for C(methyl)−Si bond cleavage can be ruled out.

The above calculations indicate that, since the barrier for this process is as high as 43.8 kcal/mol, the C(methyl)−Si bond cleavage is unfavorable via a direct transmetallation pathway. Consequently, the alternative oxidative addition/reductive elimination mechanism (paths B and C-2) with or without 1,4-rhodium−silicon exchange are then examined, respectively. As showed in Figure 5 (green lines), an intramolecular oxidative addition on C(methyl)−Si bond occurs via a three-membered-ring transition state **23-ts** with an 11.5 kcal/mol barrier. The square pyramidal methyl-Rh(III) intermediate **24** is formed, where the silyl group occupies its vertex position. Subsequent reductive elimination via the transition state **25-ts** could afford product **7**. The relative free energy of **25-ts** is 3.2 kcal/mol higher than that of **23-ts**. Therefore, the overall barrier from intermediate **15** to product **7** and intermediate **17** is 29.1 kcal/mol lower than that of the direct transmetallation mechanism.

For comparison, oxidative addition/reductive elimination mechanism from intermediate **21** is also computed (Figure 5, blue lines). The activation free energy of intramolecular oxidative addition on the C(methyl)−Si bond from intermediate **21** is 18.2 kcal/mol via the transition state **26-ts**. Intermediate **27** then undergoes reductive elimination via the transition state **28-ts** to afford product **7** and complex **17**. Comparing the relative free energies between transition states **25-ts** and **26-ts**, path C-2 is only 1.4 kcal/mol more favorable than path B. This result indicates that both pathways are possible.

The relative free energy of **23-ts** is 1.8 kcal/mol lower than that of **26-ts**. On the basis of the geometry information of **23-ts** and **26-ts** (Figure 6), we hypothesized that the higher relative free energy of transition state **26-ts** comes from the repulsion between two eclipsed methyl groups on silicon and another methyl group on its vicinal vinyl carbon because the shortest H⋯H distance within this part is only 2.49 Å. In contrast, the relative free energy of the reductive elimination transition state **25-ts** is 3.9 kcal/mol higher than that of **28-ts**. The geometry information of transition state **25-ts** indicates that the methyl group on vinyl carbon adjacent to rhodium is in close proximity to the methyl group on rhodium. The closest distance between the hydrogen atoms of two methyl groups is only 2.22 Å, which results in a higher activation free energy than that in **28-ts**.

Within all four pathways depicted in Scheme 3, catalyst **8** could be regenerated by the hydrolysis of the methyl−rhodium complex **17** to complete the catalytic cycle. As shown in Figure 7, one water molecule coordinates with complex **17** and complex **29** is formed with only 3.9 kcal/mol exothermic. The C(methyl)-Rh bond is hydrolyzed via a four-membered-ring transition state **30-ts** with 14.2 kcal/mol activation free energy. After releasing one methane molecule, the active catalytic species **8** is regenerated irreversibly to finish the catalytic cycle.

The hydrolyzing probability of the key intermediates **15** and **21** has also been examined (Figure 8). As showed in Figure 2, the aryl group coordinates with rhodium in complex **15**. The coordination of **15** with one water molecule forms intermediate **31** with a 4.4 kcal/mol free-energy increase because the intramolecular aryl coordination would be dissociated first. Therefore, the overall barrier for the hydrolysis of complex **15** is 23.4 kcal/mol via a four-membered-ring transition state **32-ts**. The relative free energy of transition state **32-ts** is 10.1 kcal/mol higher than that of transition state **26-ts**, which is the rate-determining step of pathway C-2 from complex **15**. Consequently, the hydrolysis of complex **15** can rarely take place due to its high-energy barrier. In the case for the hydrolysis of complex **21**, whose geometry is shown in Figure 4, it is the same as complex **15**. The coordination of water forms intermediate **34** with 8.2 kcal/mol endothermic energy. The overall barrier for the hydrolysis of complex **21** is 28.1 kcal/mol via transition state **35-ts**. The relative free energy of transition state **35-ts** is also 9.9 kcal/mol higher than that of transition state **26-ts**. Therefore, the hydrolysis of complex **21** also cannot happen. For comparison, the overall barriers for the hydrolysis of complexes **15** and **21** are 9.2 and 13.9 kcal/mol higher than the hydrolysis of complex **17**, respectively. A comparison with the free-energy profiles shown in Figures 7 and 8, the difference among the barriers mainly comes from the binding of a water molecule. When water coordinates to the vacant site of complex **17**, square planar intermediate **29** is formed only with 3.9 kcal/mol decrease. In contrast, in complexes **15** and **21**, their vacant sites have already been occupied by an intramolecular π-coordinated vinyl or aryl group. The dissociation of the π-coordinated group leads to high relative free energy for water-coordinated intermediates **31** and **34**. The binding of an additional vinyl or aryl group inhibits the hydrolysis of the C(sp^2)−Si bond. Therefore, side product **33** or **36** cannot be observed experimentally.

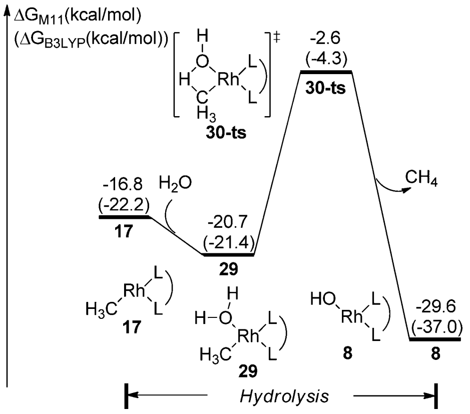


Figure 7. Hydrolysis of **17** for the regeneration of catalyst **8**.

■ CONCLUSION

The newly reported density functional theory method, M11, has been used to clarify the mechanism of the rhodium-catalyzed carbon−silicon bond cleavage reaction reported by Chatani et al. The results favor path B, which undergoes an oxidative addition to insert rhodium into the C(methyl)−Si bond, followed by reductive elimination to generate the C(vinyl)−Si bond. Meanwhile, path C-2 has also been considered as a plausible route, where a reversible 1,4-rhodium−silicon exchange takes place prior to the C(methyl)−Si bond oxidative addition. In both pathways, the rate-determining step is the initial transmetallation of 2-trimethylsilylphenyl boronic acid. The direct transmetallation pathway has also been examined. Comparing with the sequential oxidative addition/reductive elimination pathway,

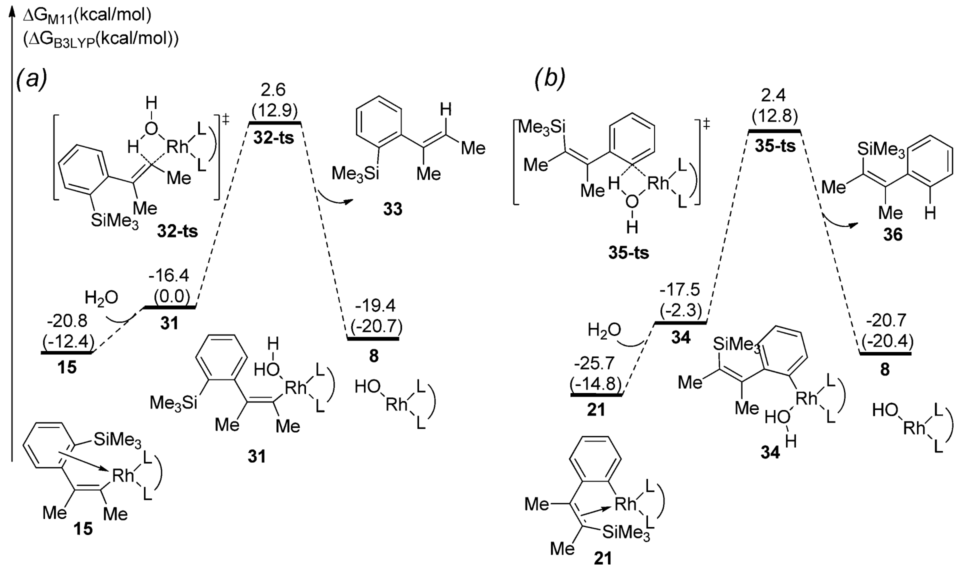


Figure 8. The hydrolysis possibility of the key intermediates (a) **15** and (b) **21**.

the direct transmetallation pathway is 29.1 kcal/mol unfavorable. The hydrolysis of vinylrhodium and arylrhodium complexes has also been examined. The barrier for this hydrolysis is higher than that of the oxidative addition and reductive elimination. Therefore, hydrolysis side products cannot be observed. This result is consistent with the experimental observations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates and energies of all reported structures and full authorship of Gaussian 09. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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