

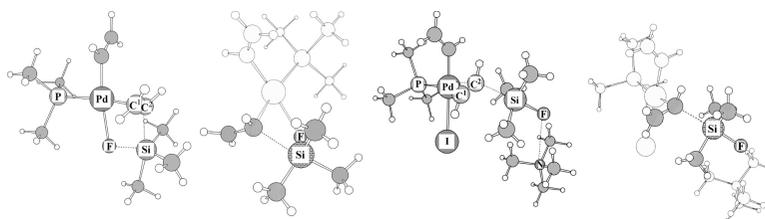
Article

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Why Does Fluoride Anion Accelerate Transmetalation between Vinylsilane and Palladium(II)–Vinyl Complex? Theoretical Study

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Abstract: Transmetalation between palladium(II)–vinyl complex and vinylsilane was theoretically investigated with the DFT and MP2 to MP4 methods to clarify the reaction mechanism and the reasons why fluoride anion accelerates the Pd-catalyzed cross-coupling reaction between vinyl iodide and vinylsilane. This transmetalation occurs with a very large activation barrier (45.8 kcal/mol) and a very large endothermicity (25.6 kcal/mol) in the absence of fluoride anion, where the potential energy change resulting from the solvation effect is evident. This is consistent with the experimental fact that this cross-coupling reaction does not proceed well in the absence of fluoride anion. The effects of fluoride anion were investigated in three possible reaction courses. In the first course, fluorovinylsilicate anion is formed before the transmetalation, and it reacts with the palladium(II)–vinyl complex. In the second course, an iodo ligand is substituted for fluoride anion, and then the transmetalation occurs between the palladium(II)–fluoro–vinyl complex and vinylsilane. In the third course, fluoride anion attacks the Si center of vinylsilane in the transition state of the transmetalation between the palladium(II)–iodo–vinyl complex and vinylsilane. Our theoretical calculation suggests that fluorovinylsilicate anion is not formed in the case of trimethylvinylsilane. In the second and third cases, the transmetalation occurs with a moderate activation barrier (E_a) and a considerably large exothermicity (E_{exo}): $E_a = 25.3$ kcal/mol and $E_{exo} = 5.7$ kcal/mol in the second course, and $E_a = 12.7$ kcal/mol and $E_{exo} = 24.8$ kcal/mol in the third course, indicating that fluoride anion accelerates the transmetalation via the second and third reaction courses. The acceleration of transmetalation by fluoride anion is clearly interpreted in terms of the formation of a very strong Si–F bond and the stabilization of the transition state by the hypervalent Si center, which is induced by the fluoride anion. Our computational results show that hydroxide anion accelerates the transmetalation in a manner similar to that observed with fluoride anion. From these results, we predict that the electronegative anion accelerates this transmetalation because the electronegative group forms a strong covalent bond with the silyl group and facilitates the formation of the hypervalent Si center in the transition state.

Introduction

Transition-metal-catalyzed cross-coupling reactions play important roles in organic synthesis and catalytic chemistry, because a new C–C bond can be produced by the cross-coupling reaction.¹ One good example is the Suzuki–Miyaura coupling reaction, which is a Pd-catalyzed cross-coupling reaction between phenyl iodide and organic boron compounds.¹ Of those cross-coupling reactions, the transition-metal-catalyzed cross-coupling reaction of organic halides and organosilicon compounds is considered very useful, because various organosilicon compounds are available and usually stable in air. However, organosilicon compounds are not very reactive, probably because of the stable and strong Si–C bond. The product yield

was rather low in a Pd-catalyzed cross-coupling reaction between phenyl iodide and trimethylvinylsilane.² Interestingly, Hiyama and co-workers later reported that addition of fluoride anion very much accelerated this cross-coupling reaction and increased the product yield.^{3,4} This cross-coupling reaction can be applied to various synthetic reactions,⁵ including stereoselective syntheses.⁶

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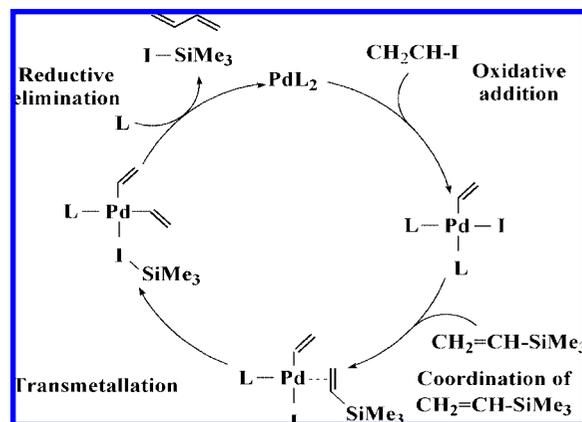
The acceleration by fluoride anion is of considerable interest from the points of view of both theoretical chemistry and synthetic chemistry, because fluoride anion is considered inert in general, but it accelerates this cross-coupling reaction. Thus, it is worth investigating the reasons why fluoride anion accelerates the reaction. It was experimentally proposed that silicate anion was formed by addition of fluoride anion and it was more reactive for transmetalation with palladium(II)–vinyl intermediate than usual silane.^{3,7} Similar suggestions were presented by other groups.^{8–12} Correct knowledge of this transmetalation process is necessary to understand well the cross-coupling reaction with organosilicon compounds, to clarify what roles fluoride anion plays in the reaction, and to further develop this type of cross-coupling reaction.

In this work, we theoretically investigated the Pd-catalyzed cross-coupling reaction between vinyl iodide and trimethylvinylsilane with and without fluoride anion. Here, we focus on the transmetalation process. Our main purposes here are to present theoretical knowledge of the transition state and the activation barrier of the transmetalation with and without fluoride anion, to clarify the reasons why fluoride anion accelerates the transmetalation process, and to investigate whether another anion can be used to accelerate this process.

Computational Details

Geometries were optimized by the DFT method with the B3LYP functional.^{13,14} Energy and population changes were evaluated with DFT and MP2 to MP4(SDQ) methods. Two types of basis set systems, BS-I and BS-II, were employed in this work. In the BS-I, a (541/541/211)^{15,16} basis set was used to represent valence electrons of Pd, where the effective core potentials (ECPs)¹⁵ were employed to replace core electrons (up to 3d). Usual LANL2DZ basis sets were used for P, Si, and I,¹⁷ where one d-polarization function was added to each basis set.¹⁸ For C, O, F, and H, 6-31G(d)

Scheme 1



basis sets were employed,¹⁹ where d-polarization function was omitted in the C atom of the methyl group. This BS-I was used for geometry optimization and MP2 to MP4(SDQ) calculations. In BS-II, a (5311/5311/211/1) basis set^{15,16,20} was used for Pd with the same ECPs as those of BS-I;¹⁵ for I, a (111/111/1) basis set^{17,18} was used with the same ECPs as those of LANL2DZ.¹⁷ For Si, P, O, F, and H, 6-311G(d) basis sets were used.²¹ Diffuse function was not added to F and I because they are very different from the anion but rather similar to negatively charged species. This BS-II was used in DFT calculations. Energy and population changes were mainly discussed on the basis of DFT/BS-II computational results. The reliability of the DFT method was checked by making comparison between DFT- and MP4(SDQ)-calculated energy changes.

To investigate the solvation effect of THF, we employed the PCM method.²² Population analysis was carried out with the method of Weinhold et al.²³ Zero-point energy, thermal energy, and entropy were evaluated by the DFT/BS-I method without scaling factor. All these calculations were carried out with the Gaussian 03 program package.²⁴

In typical experiments,^{3–5} triphenylphosphine, triethoxyphosphine, and tri(*tert*-butyl)phosphine were used as ligand, and vinyl iodide derivatives (RCH=CHI; R = *n*-alkyl group) and vinylsilanes such as trimethylvinylsilane, fluorodimethylvinylsilane, and difluoromethylvinylsilane were used as substrates. We employed vinyl iodide (CH₂=CHI) and trimethylvinylsilane (CH₂=CHSiMe₃) as substrates in this work. PMe₃ was employed as ligand, because the size and the electronic properties of PMe₃ are considered to be intermediate between those of tri(*tert*-butyl)phosphine and triethoxyphosphine.

Results and Discussion

A typical catalytic cycle of the Pd-catalyzed cross-coupling reaction is shown in Scheme 1. The first step is the oxidative addition of vinyl iodide (CH₂=CHI, **1**) to the palladium(0)

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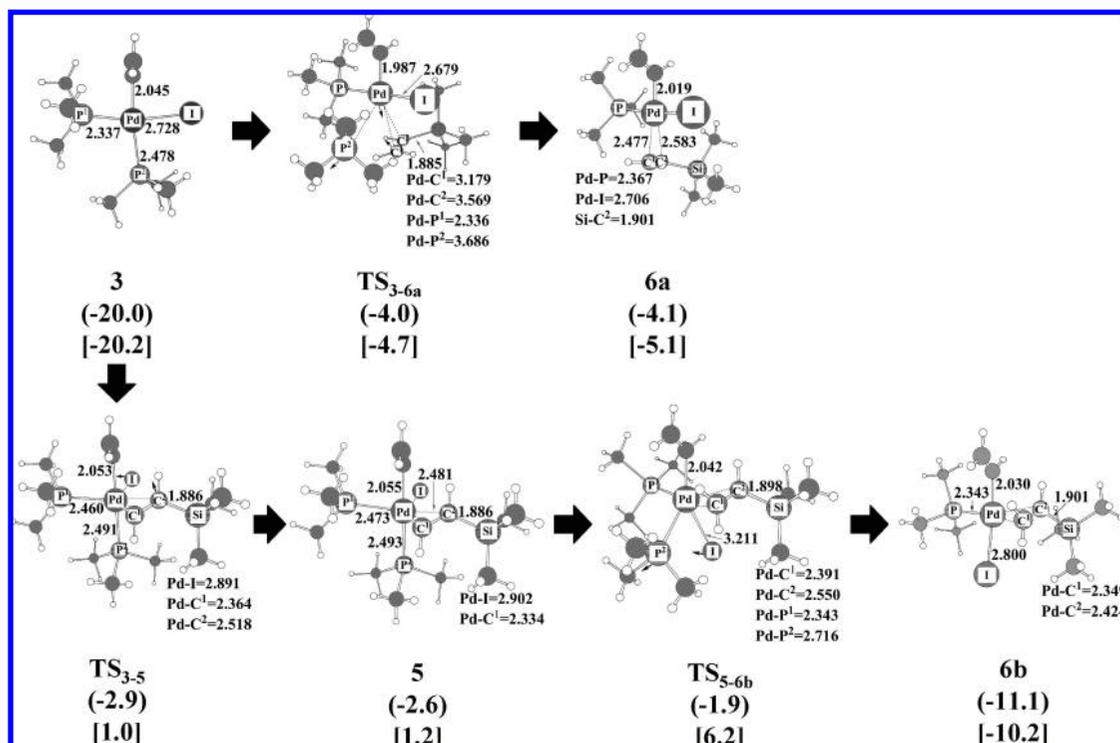


Figure 1. Geometry and energy changes resulting from the associative substitution of phosphine for trimethylvinylsilane. Bond distances in angstroms. In parentheses is the energy change without solvation effect, and in brackets is the energy change with solvation effect, where the DFT/BS-II method was employed. The standard (energy zero) is the sum of Pd(PMe₃)₂ and CH₂=CHI.

complex, Pd(PMe₃)₂ (**2**), to afford *cis*-PdI(CH=CH₂)(PMe₃)₂ (**3**). Because a similar process has been well-investigated theoretically,^{25–30} we omit detailed discussion about this process; see Supporting Information, Figure S1, for geometry and energy changes. The next step is substitution of phosphine for vinylsilane followed by transmetalation. The final step is the reductive elimination of butadiene from the palladium(II)–divinyl complex. Because the reductive elimination is simply the reverse of the oxidative addition which has already been theoretically investigated,^{25–30} we omit detailed discussion but only mention important geometry changes. In this work, we will present a detailed discussion about the transmetalation.

Substitution of Phosphine for Trimethylvinylsilane. Starting from *cis*-PdI(CH=CH₂)(PMe₃)₂ (**3**), which is the product of the oxidative addition of vinyl iodide, substitution of phosphine for vinylsilane occurs to form an intermediate, *cis*-PdI(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃) (**6a**) or its *trans*-isomer **6b**, where “*cis*” means that the vinyl group and the iodo ligand take positions *cis* to each other and “*trans*” means that they take positions *trans* to each other. This substitution reaction occurs via either a dissociative mechanism or an associative one. Here, we present geometry changes resulting from the associative mechanism because the presence of vinylsilane, which is a coordinating species, favors the associative mechanism; see Supporting Information, Figure S2, for dissociative substitution and a comparison of these two mechanisms.

In the associative substitution, trimethylvinylsilane approaches the Pd center in the vinyl–Pd–PMe₃ plane, as shown in Figure 1, leading to transition state **TS_{3-6a}**. This transition state takes a distorted trigonal bipyramidal structure, in which trimethylvinylsilane is approaching the Pd center and PMe₃ on the equatorial plane is dissociating from the Pd center, to form **6a**. The activation barrier of 16.0 (15.5) kcal/mol is somewhat large, where the zero-point energy correction is made and the values presented without and with parentheses are DFT/BS-II-calculated energy changes without and with solvation effect, respectively, unless otherwise noted in text. In the other course, trimethylvinylsilane approaches the Pd center in the I–Pd–PMe₃ plane, to form distorted a trigonal bipyramidal five-coordinate intermediate, PdI(CH=CH₂)(PMe₃)₂(CH₂=CHSiMe₃) (**5**), through transition state **TS₃₋₅**. This step corresponds to the Berry’s pseudorotation. The activation barrier is 17.1 (21.2) kcal/mol, and **5** is less stable than **3** by 17.4 (19.0) kcal/mol, indicating that **5** cannot be experimentally detected. Starting from **5**, PMe₃ on the equatorial plane dissociates from the Pd center, to yield **6b** through transition state **TS_{5-6b}** with a small activation barrier of 0.7 (5.0) kcal/mol.

To conclude this section, we wish to mention that the *trans*-isomer **6b** is more important than the *cis*-isomer **6a**, as follows. Because **6a** is less stable than **6b** and **3** by 7.0 (5.1) and 15.9 (15.1) kcal/mol, respectively, **6a** easily returns to **3** and cannot stay as a stable intermediate. Thus, the equilibrium between **3** and **6b** is more important than that between **3** and **6a**; in other words, mainly **6b** participates in the next step. Also, the endothermicity of the substitution reaction suggests that the transmetalation must occur easily with a small activation barrier and considerable exothermicity to complete the catalytic cycle. If not, this catalytic reaction becomes difficult.

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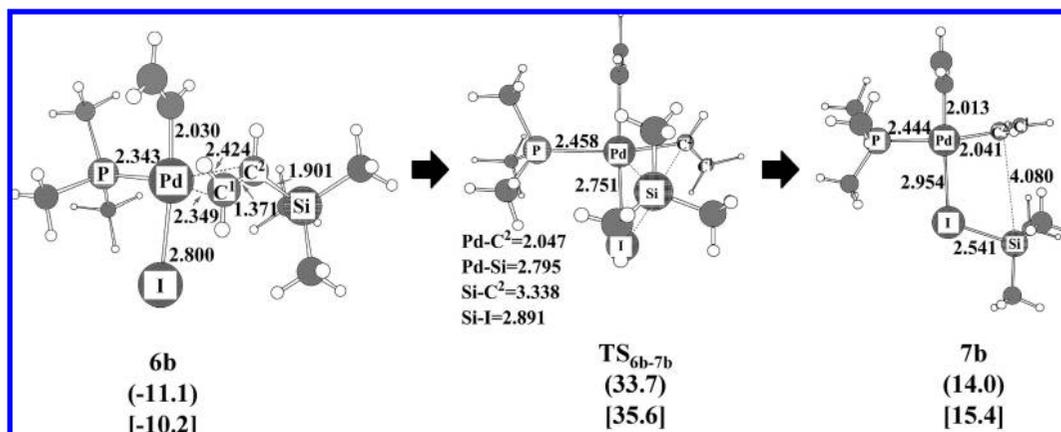


Figure 2. Geometry and energy changes resulting from the transmetalation in *trans*-PdI(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃). Bond distances in angstroms. In parentheses is the energy change without solvation effect, and in brackets is the energy change with solvation effect, where the DFT/BS-II method was employed. The standard (energy zero) is the sum of Pd(PMe₃)₂ and CH₂=CHI.

Transmetalation in *trans*-PdI(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃) (6b**).** We investigated first the transmetalation in **6b** because **6b** is more stable than **6a**, as discussed above. As shown in Figure 2, the vinyl group moves to the Pd center from the Si center through transition state **TS_{6b-7b}**, to afford palladium(II)–divinyl intermediate *cis*-Pd(CH=CH₂)₂(PMe₃)(SiMe₃) (**7b**), in which the two vinyl groups take positions *cis* to each other. In **7b**, the Pd–I distance (2.954 Å) is not very long compared to that of **6b**, suggesting that the coordinate bond is formed between Pd and ISiMe₃. In **TS_{6b-7b}**, the Si–C(vinyl) distance (3.338 Å) is much longer than that of **6b**, and the Si–I distance (2.891 Å) is 0.35 Å longer than that of **7b**. The Pd–C(vinyl) distance (2.047 Å) is similar to that of **7b**. These geometrical features indicate that the Si–vinyl bond is almost broken and the Pd–vinyl bond is almost formed, but the Si–I bond is not completely formed yet. It is also noted that the valence orbital of SiMe₃ seems to expand toward the Pd center in **TS_{6b-7b}** and the Pd–Si distance (2.795 Å) is moderately longer than the experimentally reported Pd(II)–silyl distance by 0.4–0.5 Å.^{31–33} The geometry around the Pd center is understood to be distorted square pyramidal, in which the silyl group takes the axial position and moves toward the iodo ligand from the vinyl group, interacting with the Pd center in **TS_{6b-7b}**. Because of the presence of the Pd–silyl interaction, it is likely that the Pd center takes 4+ oxidation state.

The very large activation barrier of 44.8 (45.8) kcal/mol and considerably large endothermicity of 25.1 (25.6) kcal/mol should be noted here. These results clearly indicate that the transmetalation is very difficult, and therefore, this Pd-catalyzed cross-coupling reaction does not proceed well in the absence of fluoride anion.² We will discuss below the reason why this transmetalation is difficult.

We also investigated the transmetalation in the *cis*-isomer **6a**, because this process would become important if its activation barrier is small. However, the activation barrier is 39.4 (41.9) kcal/mol and the endothermicity is 22.1 (24.6) kcal/mol, indicating that this transmetalation is difficult, too; see Supporting Information, Figure S3. Hereafter, we will stop to discuss the reaction course via **6a**.

We ascertained that the DFT method presents reliable results in this transmetalation and the solvation effect is not large,

because this is the first theoretical study of the transmetalation between an organosilicon compound and the palladium(II)–vinyl complex; see Supporting Information, Figure S4.

Reductive Elimination of Butadiene from Palladium(II)–Divinyl Complex. The last step is the reductive elimination of butadiene from *cis*-palladium(II)–divinyl complex. In *cis*-Pd(CH=CH₂)₂(PMe₃)(SiMe₃), which is the product of the transmetalation, ISiMe₃ easily dissociates from the Pd center to yield a three-coordinate intermediate, *cis*-Pd(CH=CH₂)₂(PMe₃) (**8b**), with a small destabilization energy of 4.9 (2.6) kcal/mol, as shown in Figure 3. This is because ISiMe₃ is not a good coordinating species. The entropy effect favors this dissociation; actually the Gibbs free energy change (ΔG^0) is -7.8 kcal/mol when it is evaluated in gas phase.³⁴ Because of the presence of coordinating species such as vinylsilane and PMe₃ in the solution, *cis*-Pd(CH=CH₂)₂(PMe₃)₂ and *cis*-Pd(CH=CH₂)₂(PMe₃)(CH₂=CHSiMe₃) should be considered as plausible intermediates. In these complexes, reductive elimination from *cis*-Pd(CH=CH₂)₂(PMe₃)₂ occurs the easiest; see Supporting Information, Figures S5 and S6 and Scheme S1, for the reductive eliminations starting from the other complexes. Important geometry and energy changes are summarized as follow: PMe₃ easily coordinates with the Pd center of **8b** to yield four-coordinate complex *cis*-Pd(CH=CH₂)₂(PMe₃)₂ (**11**), with a considerably large stabilization energy of 20.4 (18.0) kcal/mol and Gibbs free energy change of -7.3 kcal/mol,³⁴ indicating that PMe₃ easily coordinates with the Pd center. The reductive elimination easily occurs through planar transition state **TS₁₁₋₁₂**, to produce Pd(PMe₃)₂(C₄H₄) (**12**).³⁵ The activation

(34) (a) The partition functions of translation and rotation movements are very large in the gas phase, but they are considered to be small in solution; in other words, the entropy due to translation and rotation movements is already small in solution. This means that the entropy decrease induced by the formation of adduct from two molecules in solution is smaller than the value evaluated in the gas phase; in other words, the ΔG^0 value evaluated in the gas phase is the upper limit for the ΔG^0 value in solution.^{34b–e} (b) Sakaki, S.; Takahama, T.; Sumimoto, M.; Sugimoto, M. *J. Am. Chem. Soc.* **2004**, *126*, 3332. (c) Sumimoto, M.; Iwane, N.; Takahama, T.; Sakaki, S. *J. Am. Chem. Soc.* **2004**, *126*, 10457. (d) Ohnishi, Y.-y.; Nakao, Y.; Sato, H.; Sakaki, S. *J. Am. Chem. Soc.* **2005**, *127*, 4021. (e) Ohnishi, Y.-y.; Nakao, Y.; Sato, H.; Sakaki, S. *Organometallics* **2006**, *25*, 3352.

(35) IRC calculation starting from **TS₁₁₋₁₂** stopped when the Pd–C distance became 2.07 Å. This structure exhibits one imaginary frequency, which involves slide motion of the new C–C bond (Supporting Information, Scheme S2). The geometry optimization along this imaginary frequency led to formation of **12**.

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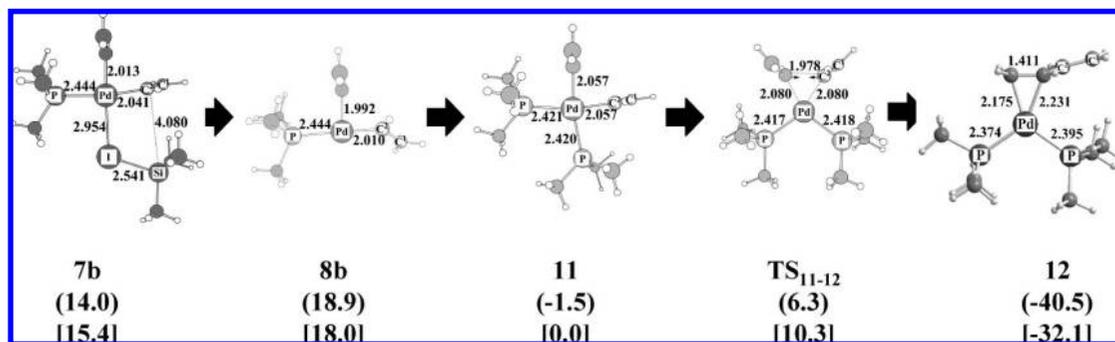


Figure 3. Geometry and energy changes resulting from the reductive elimination of butadiene from Pd(II)-divinyl complex after dissociation of I-SiMe₃, followed by coordination of PMe₃. Bond distances in angstroms. In parentheses is the energy change without solvation effect, and in brackets is the energy change with solvation effect, where the DFT/BS-II method was employed. The standard (energy zero) is the sum of Pd(PMe₃)₂ and CH₂=CHI.

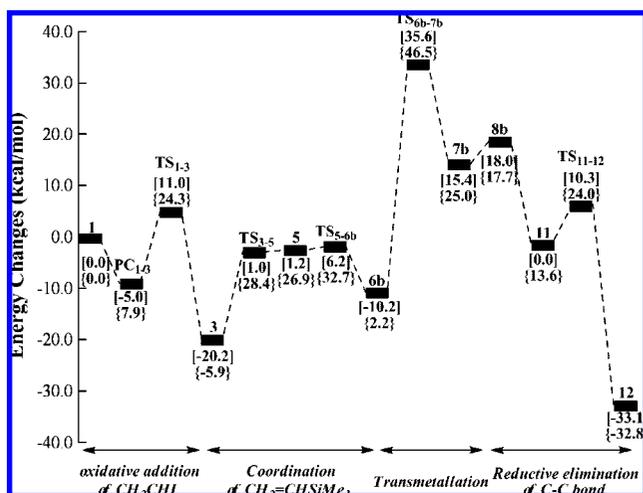


Figure 4. Energy changes (in kcal/mol) along the whole catalytic cycle in the absence of fluoride anion. Top values, potential energy change with solvation effect; bottom values, Gibbs free energy change with solvation effect. The DFT/BS-II method was employed.

barrier is 7.8 (10.3) kcal/mol, and the exothermicity is 39.0 (32.1) kcal/mol, where **11** is taken to be a standard. This small activation barrier arises from the fact that the d orbital energy of Pd is low.^{36,37}

Energy Changes along the Whole Catalytic Cycle in the Absence of Fluoride Anion. Summarizing the above results, the energy changes in the absence of fluoride anion along the whole catalytic cycle are shown in Figure 4. The associative substitution of PMe₃ for trimethylvinylsilane in *cis*-PdI(CH=CH₂)(PMe₃)₂ (**3**) and the reductive elimination of butadiene from Pd(PMe₃)₂(CH=CH₂)₂ (**11**) are involved in these energy changes. Apparently, the rate-determining step is the transmetalation, the activation barrier of which is 45.8 (48.7) kcal/mol, where in this section the values without and with parentheses are the potential energy change and Gibbs free energy change including the solvation effect, respectively. The activation barrier to complete the catalytic cycle corresponds to the energy difference between TS_{6b-7b} and **3**, which is the most stable intermediate before the transmetalation. This value is very large, 55.8 (52.4) kcal/mol, indicating that the reaction is very difficult.

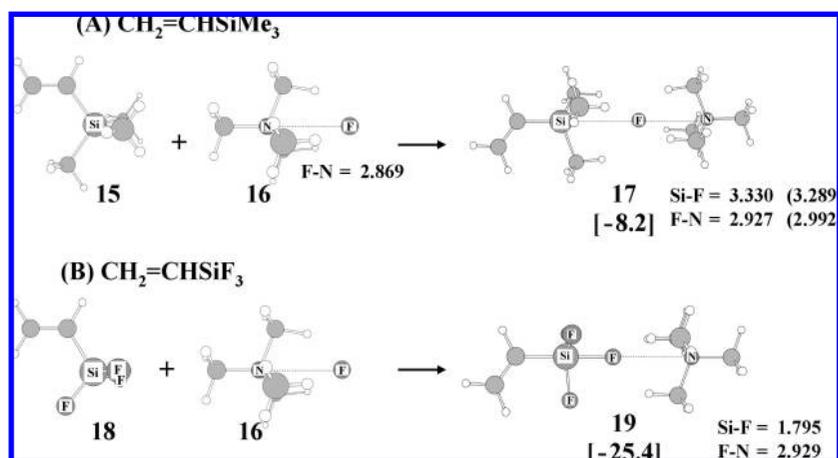
Thus, it is crucially important to lower the activation barrier of the transmetalation to accelerate this catalytic reaction. The same conclusion is presented on the basis of Gibbs free energy change; see Supporting Information, p S12. From these energy changes, it is likely that fluoride anion accelerates the catalytic reaction by facilitating the transmetalation process. In the latter half of this work, therefore, we focus on the transmetalation.

Three Possible Transmetalation Processes in the Presence of Fluoride Anion. Because the transmetalation is the rate-determining step, it is likely that fluoride anion participates in the transmetalation to accelerate this cross-coupling reaction. In the presence of fluoride anion, three reaction courses are considered possible. In the first case, fluorosilicate anion is formed from trimethylvinylsilane and fluoride anion, which then reacts with the palladium(II)-vinyl complex. In the second case, an iodo ligand is substituted for the fluoro ligand, and the transmetalation occurs between the Pd(II)-fluoro-vinyl complex and trimethylvinylsilane. In the third case, fluoride anion participates in the transition state of the transmetalation between palladium(II)-iodo-vinyl complex and trimethylvinylsilane. We investigated all these possibilities.

Formation of Silicate Anion with Fluoride Anion and Trimethylvinylsilane. As shown in Scheme 2A, addition of tetramethylammonium fluoride to trimethylvinylsilane yields a stabilization energy of 8.2 kcal/mol, where only the potential energy change resulting from the solvation effect is presented in this section because the solvation effect is important in anion-exchange reactions. However, the geometry around the Si center is still tetrahedral, indicating that the Si center does not take hypervalency. On the other hand, addition of tetramethylammonium fluoride to trifluorovinylsilane yields a typical silicate anion, as shown in Scheme 2B, in which the geometry around Si becomes trigonal bipyramidal. Also, the energy stabilization is much larger than that of trimethylvinylsilane. These results suggest that the silicate anion is formed not from trimethylvinylsilane but from trifluorovinylsilane.³⁸ However, it was experimentally found that the cross-coupling reaction between trifluorovinylsilane and vinyl iodide did not yield the product at all.^{4a} The combination of these experimental and theoretical results suggests that formation of silicate anion is not key in this cross-coupling reaction.

(36) Low, J. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1986**, *108*, 6115.
 (37) (a) Sakaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *Inorg. Chem.* **1994**, *33*, 1660. (b) Sakaki, S.; Ogawa, M.; Kinoshita, M. *J. Phys. Chem.* **1995**, *99*, 9933. (c) Sakaki, S.; Kai, S.; Sugimoto, M. *Organometallics* **1999**, *18*, 4825.

(38) One of the authors (T.H.) found experimentally that the NMR chemical shift of trimethylvinylsilane little changes upon addition of tetramethylammonium fluoride, suggesting that pentacoordinate silicate anion is not formed well in the case of trimethylvinylsilane.

Scheme 2^a

^a In parentheses are bond distances (in angstroms) optimized with the PCM method at the DFT/BS-I level. In brackets are relative energies (in kcal/mol) calculated with the PCM method at the DFT/BS-II level.

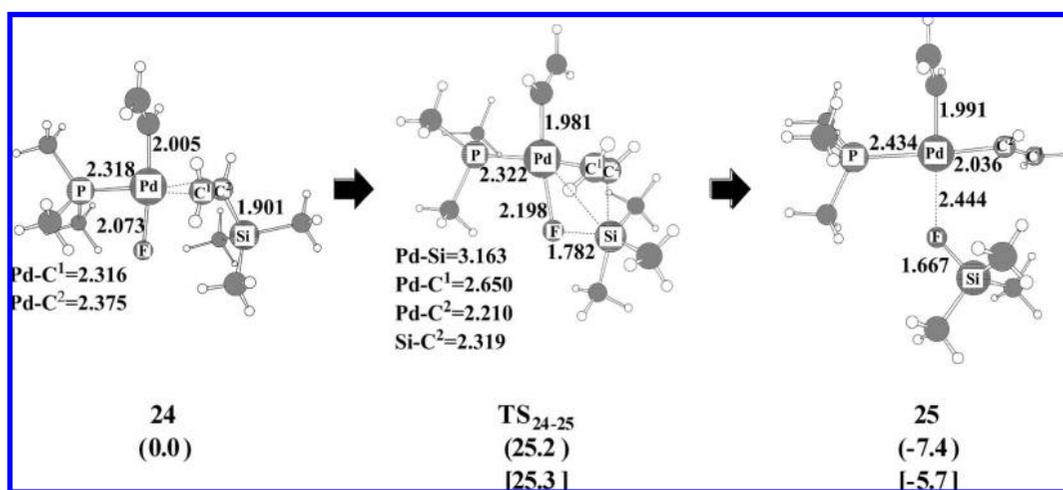


Figure 5. Geometry and energy changes in the transmetalation in the palladium(II)–vinyl–fluoro complex, PdF(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃) (**24**). Bond distances in angstroms. In parentheses is the energy change without solvation effect, and in brackets is the energy change with solvation effect, where the DFT/BS-II method was employed.

Transmetalation of Palladium(II)–Fluoro–Vinyl Complex, PdF(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃). We investigated the substitution of iodide for fluoride with the PCM method at the DFT/BS-II level, because this is an anion-exchange reaction. This reaction occurs easily, with a moderate activation barrier (5.0 kcal/mol) and a moderate exothermicity (5.6 kcal/mol), to yield *cis*-PdF(Ph)(PMe₃)₂ (**23**), where the Gibbs free energy change with solvation effect is given; see Supporting Information, Figure S7, for detailed geometry and energy changes. Here, only the associative substitution reaction was investigated in the presence of tetramethylammonium cation because the anion dissociation from cation species is very difficult in organic solvent.

The next step is the substitution of phosphine for trimethylvinylsilane in **23**. This process occurs in a similar manner to that observed with **3**, to yield PdF(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃) (**24**) with a moderate activation barrier of 21.1 (30.0) kcal/mol and a moderate endothermicity of 3.1 (4.6) kcal/mol; see Supporting Information, Figure S8A,B, for geometry and energy changes of associative and dissociative substitution reactions.

Transmetalation in **24** occurs through geometry and potential energy changes shown in Figure 5. In the transition state

TS_{24–25}, the Si–C distance is 2.319 Å and the Si–F distance is 1.782 Å, which are moderately longer than those in trimethylvinylsilane and fluorotrimethylsilane, respectively, indicating that the silyl group starts to interact with the fluoro ligand, keeping the Si–vinyl bonding interaction. The Pd–Si distance is much longer than that of **TS_{6b–7b}** in the reaction by the iodo complex, indicating that the silyl group interacts little with the Pd center in **TS_{24–25}**. In other words, the silyl group is moving toward the fluoro ligand without the help by the Pd–silyl interaction, and thus, **TS_{24–25}** is characterized to be a typical four-center transition state. In **25**, fluorotrimethylsilane is considered to coordinate with the Pd center because the Pd–F distance (2.444 Å) is in the range of the usual coordinate bond distance.

The activation barrier is 25.2 (25.3) kcal/mol and the exothermicity is 7.4 (5.7) kcal/mol, where **24** is taken as a standard, as shown in Figure 5. However, the activation barrier to complete this catalytic reaction is the energy difference between **TS_{24–25}** and **23**, because **23** is the most stable intermediate before the transmetalation, as shown in Figure 6, where the transmetalation reactions of PdI(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃), PdI(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃), and PdI(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃) with [NMe₄]F are named path 1, path 2, and path 3, respectively, for brevity. This activation

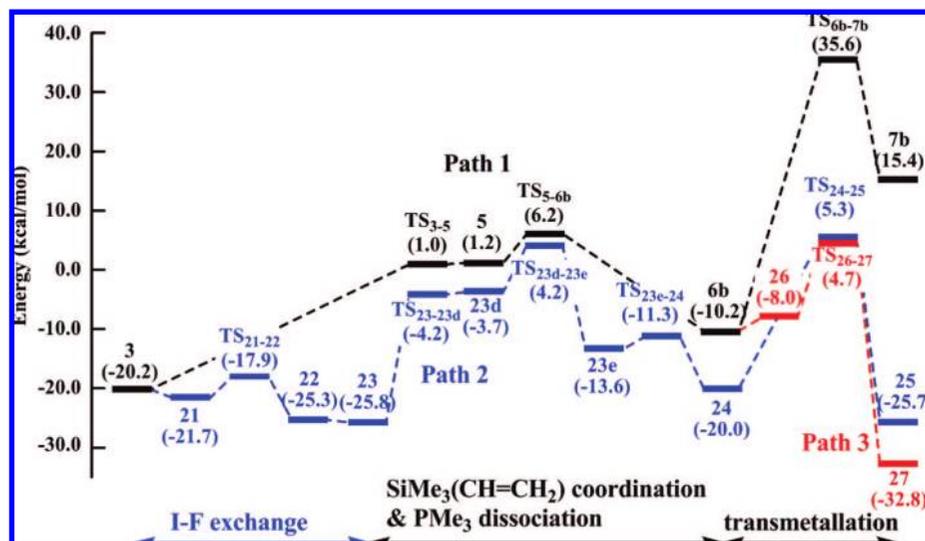


Figure 6. Potential energy changes (in kcal/mol) in the transmetalation starting from $\text{PdI}(\text{CH}=\text{CH}_2)(\text{PMe}_3)_2$ (path 1), $\text{PdF}(\text{CH}=\text{CH}_2)(\text{PMe}_3)_2$ (path 2), and $\text{PdI}(\text{CH}=\text{CH}_2)(\text{PMe}_3)_2$ with $[\text{NMe}_4]\text{F}$ (path 3). The solvation effect is involved.

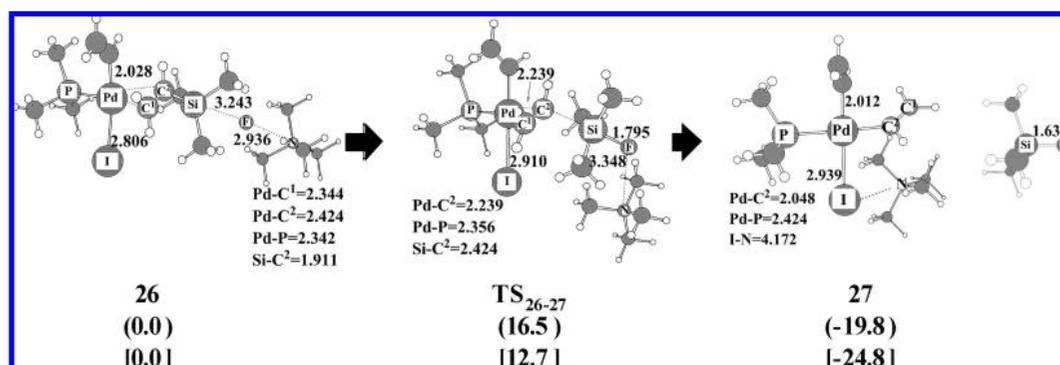


Figure 7. Geometry and energy changes in the fluoride-assisted transmetalation in the palladium(II)-vinyl-iodo complex, $\text{PdI}(\text{CH}=\text{CH}_2)(\text{PMe}_3)(\text{CH}_2=\text{CHSiMe}_3) + \text{F}[\text{NMe}_4]$ (**26**). Bond distances in angstroms. In parentheses is the energy change without solvation effect, and in brackets is the energy change with solvation effect, where the DFT/BS-II method was employed.

barrier is 30.0 kcal/mol, where we employed the potential energy difference with solvation effect.³⁹ This moderate activation barrier clearly indicates that the transmetalation occurs much more easily in the fluoro complex than in the iodo complex. The reason will be discussed below.

In this transmetalation, the entropy effect is not large because this is a unimolecular process. The MP2 to MP4(SDQ) methods present almost the same energy changes as the DFT method, similar to the energy changes in the transmetalation of the iodo complex; see Supporting Information, Figure S9. Also, the solvation effect little influences the energy changes.

Fluoride-Assisted Transmetalation in *trans*- $\text{PdI}(\text{CH}=\text{CH}_2)(\text{PMe}_3)(\text{CH}_2=\text{CHSiMe}_3)$ (6b**).** It is of considerable interest to investigate the possibility that the fluoride anion participates in the transition state of transmetalation. As shown in Figure 7, tetramethylammonium fluoride approaches the Si center from the back side of trimethylvinylsilane in the intermediate **26**,

though the Si–F distance is very long (3.243 Å). In the transition state TS_{26-27} , the fluoride anion is approaching the Si center and the vinyl group is moving toward the Pd center from the Si center, where the Pd–C distance is 2.239 Å. This distance is moderately longer than that of the product $[\text{PdI}(\text{CH}=\text{CH}_2)_2(\text{PMe}_3)][\text{NMe}_4]$ (**27**) + F–SiMe₃ by about 0.2 Å, indicating that the Pd–vinyl bond is formed to a considerable extent. It is noted that the trimethylsilyl moiety becomes almost planar in TS_{26-27} , which clearly shows the hypervalent character of the Si center. The Si–F distance (1.795 Å) is moderately longer than that of fluorotrimethylsilane (1.632 Å). From these geometrical features, this reaction is characterized as nucleophilic attack of fluoride anion to the Si center, in which the fluoride anion approaches the Si center to weaken the Si–vinyl bond and induces the transfer of the vinyl group to the Pd center. These features indicate that this is similar to an S_N2 substitution reaction.

The activation barrier of 16.5 (12.7) kcal/mol is much smaller and the exothermicity of 19.8 (24.8) kcal/mol is much larger than those of the transmetalation of the iodo complex **6b** (path 1); see Supporting Information, Figure S10, for basis set effect and comparison of computational methods. These values clearly show that the transmetalation is accelerated very much by nucleophilic attack of fluoride anion to the Si center. This reaction easily occurs in the fluoro analogue PdF–

(39) The activation barrier corresponds to the energy difference between TS_{24-25} and *cis*- $[\text{PdI}(\text{CH}=\text{CH}_2)(\text{PMe}_3)(\text{CH}_2=\text{CHSiMe}_3)\cdots\text{F}]^-$ (**22**), which is the most stable species before the transmetalation, when the solvation effect is not included. Its value is 49.5 kcal/mol. It is likely that the energy stabilization of **22** is overestimated without the solvation effect because **22** is formed between two polarized species. Thus, the activation barrier with solvation effect should be used for discussion instead of that without solvation effect.

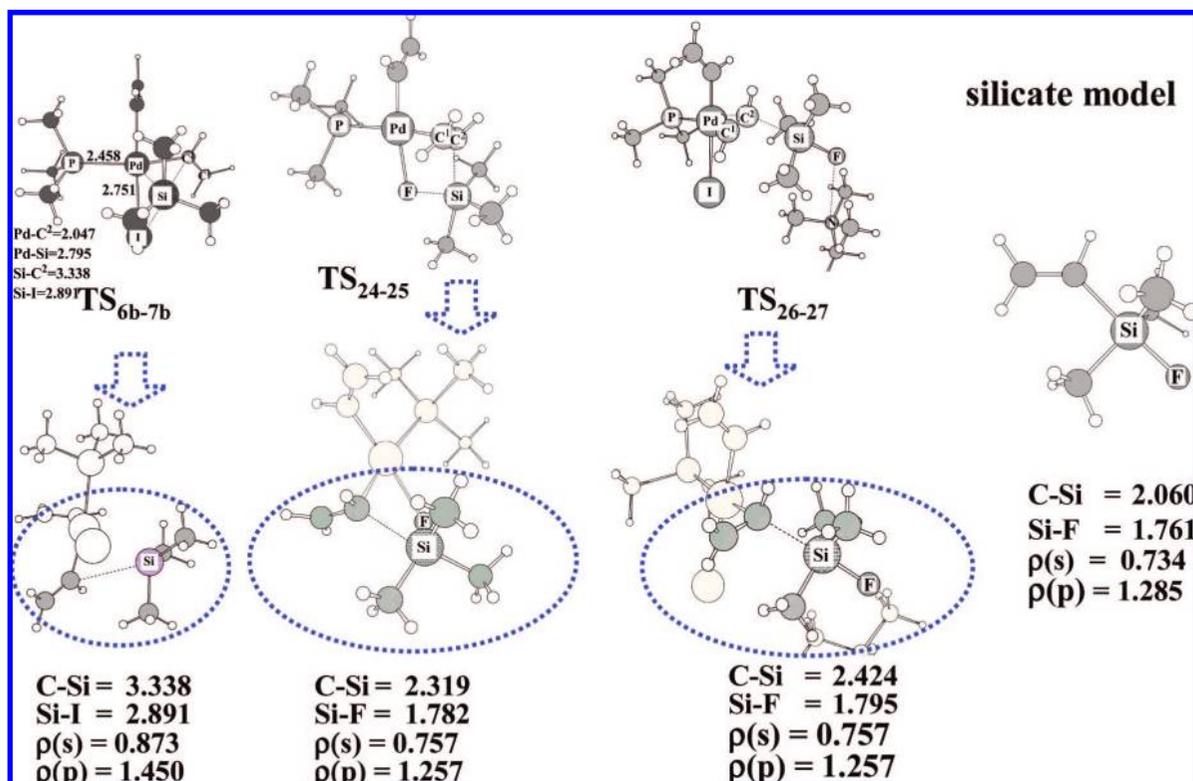


Figure 8. Transition-state structures of **TS₂₄₋₂₅** and **TS₂₆₋₂₇** in comparison with the typical silicate anion trimethylvinylfluorosilicate.

(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃), too; see Supporting Information, Figure S11.

Because **3** is the most stable and **TS_{5-6b}** is the most unstable in the path 3, as shown in Figure 6, the activation barrier to complete the catalytic cycle is the energy difference between **3** and **TS_{5-6b}**; in other words, the rate-determining step changes to the substitution of PMe₃ for CH₂=CHSiMe₃. This value is 26.4 kcal/mol, which is much smaller than the activation barrier of path 1.

Also, the solvation effect considerably decreases the activation barrier and somewhat increases the exothermicity. This solvation effect on the activation barrier arises from the polarized transition state **TS₂₆₋₂₇**, as follows. In this transition state, the fluoride anion is approaching the Si center and the vinyl group is leaving from the Si center, like the usual S_N2 substitution reaction. Also, the fluoride anion is becoming distant from the tetramethylammonium cation in **TS₂₆₋₂₇**. In other words, positively charged tetramethylammonium cation [NMe₄]⁺ is more distant from negatively charged fluoride anion in **TS₂₆₋₂₇** than in **26**. This transition state is therefore more stabilized by polar solvent than the reactant **26**, indicating that the polar solvent should be used.

Here, we wish to mention that the reductive elimination step becomes slightly different because the product of the transmetalation is **27**. However, reductive elimination from **27** easily occurs⁴⁰ because **27** is a palladium(II) complex.^{36,37}

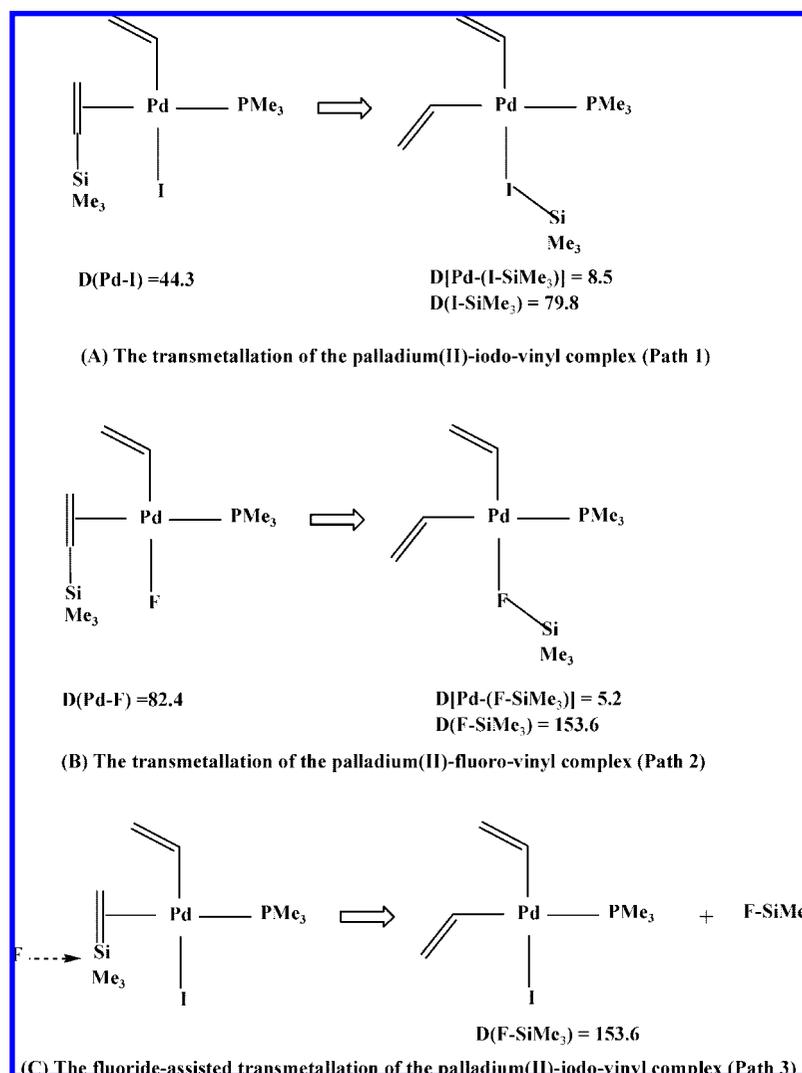
The Reason Why Fluoride Anion Accelerates the Transmetalation. Apparently, path 1 is very difficult, and paths 2 and 3 are much easier than path 1, as clearly compared in Figure 6.

It is noted that, though the Si–vinyl distance is considerably longer in **TS₂₄₋₂₅** and **TS₂₆₋₂₇** of paths 2 and 3 than that of a typical silicate anion [(CH₂=CH)SiF₄][−], the Si center takes five-coordinate trigonal bipyramidal structure in **TS₂₄₋₂₅** and **TS₂₆₋₂₇**, as shown in Figure 8. Also, the electron distribution in **TS₂₄₋₂₅**

and **TS₂₆₋₂₇** is similar to that of silicate anion; see electron populations $\rho(s)$ and $\rho(p)$ in Figure 8. On the other hand, the geometry and electron distribution of **TS_{6b-7b}** (path 1) are considerably different from those of silicate anion (Figure 8). These results suggest that the Si center takes the hypervalency in **TS₂₄₋₂₅** and **TS₂₆₋₂₇** to stabilize these transition states but does not in **TS_{6b-7b}**. This is because fluoride is sufficiently electronegative but iodide is not very much electronegative.

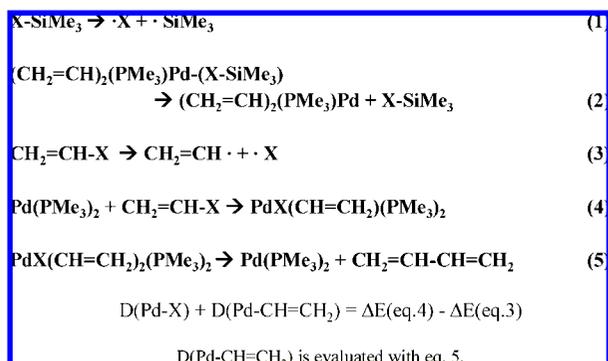
The other reason is found in the bond energy. In all paths 1–3, the Si–vinyl bond is broken but the Pd–vinyl bond is formed. Besides these bond changes, the Pd–I bond changes to the Pd–(I–SiMe₃) bond and the Si–I bond is formed in path 1 (Scheme 3). In path 2, the Pd–F bond changes to the Pd–(F–SiMe₃) bond and the Si–F bond is formed. In path 3, the Pd–I bond changes little but the Si–F bond is formed. We evaluated Pd–X, Pd–(X–SiMe₃), and X–SiMe₃ (X = I or F) bond energies with the DFT/BS-II method employing several equations (Scheme 4). Though the strong Pd–F bond changes to the weak Pd–(F–SiMe₃) bond in path 2, the F–SiMe₃ bond is much stronger than the I–SiMe₃ bond, as is well known; see Scheme 3A,B. This is one of the important reasons why the fluoride anion accelerates the transmetalation in path 2. In path 3, the Pd–I bond changes little and the very strong Si–F bond

(40) It is likely that the reductive elimination from **27** occurs similar to that from **7b**, as follows: Though the iodo ligand coordinates with the Pd center in **27**, the Pd–I coordinate bond becomes weaker in the reaction, and [NMe₄]⁺ cation, which exists near the iodo ligand, facilitates the dissociation of the iodo ligand from the Pd center. Actually, the activation barrier was calculated to be 8.6 kcal/mol with the DFT/BS-II//DFT/BS-I method. However, we omit detailed discussion about this reductive elimination for brevity. Also, we believe that systematic theoretical study of reductive elimination from various palladium(II) complexes including **27** should be carried out in a separate work, because such theoretical study is necessary to provide detailed knowledge of the ligand effect on the reductive elimination but needs a lot of computations.

Scheme 3^a

^a Bond energies (in kcal/mol) were evaluated with the DFT/BS-II method.

Scheme 4



is formed (Scheme 3C). Thus, this reaction course is the best. From these results, it should be concluded that the fluoride anion accelerates the transmetalation because of the formation of the very strong Si-F bond.

The covalent bond energy is approximately represented with eq 6 based on Hückel theory.

$$\Delta E_{\text{cov}} = \sqrt{(\epsilon_A - \epsilon_B)^2 + 4\beta^2} \quad (6)$$

Because the valence orbital energy of the silyl group is high due to its electropositive nature, the electronegative group bearing valence orbital at low energy leads to a large $\epsilon_A - \epsilon_B$ value: $\epsilon_{\text{SOMO}} = -9.1$ eV for SiMe₃, -11.9 eV for I, and -14.4 eV for F. Therefore, the electronegative group is expected to form a strong covalent bond with the silyl group. Also, the electronegative group is necessary for the Si center to take hypervalency. From these results, we predict that the electronegative group accelerates this transmetalation.

Is the Transmetalation Accelerated by an OH Group? If the above discussion is correct, the hydroxy (OH) group accelerates the transmetalation, because the SOMO of hydroxy is calculated at very low energy like that of fluorine: $\epsilon_{\text{SOMO}} = -14.9$ eV for OH. Actually, it was experimentally reported that addition of KOH to the solution led to acceleration.^{5c} It is worth theoretically investigating if the transmetalation reaction occurs easily in the palladium(II)-hydroxy-vinyl complex Pd(OH)-(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃) (**28**). As shown in Figure 9, the transmetalation occurs easily with a moderate activation barrier, 15.4 (14.9) kcal/mol, which is much smaller than that of the palladium(II)-iodo-vinyl complex **6b** (path 1) and moderately smaller than that of the palladium(II)-fluoro-vinyl complex **24** (path 2). The exothermicity is 17.5 (15.7) kcal/

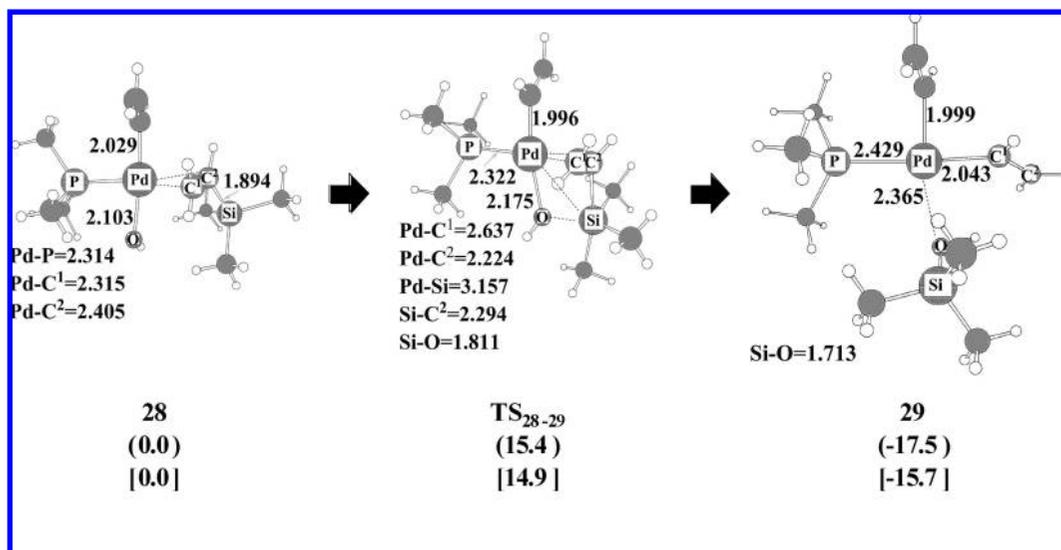


Figure 9. Geometry and energy changes in the transmetalation in the palladium(II)–vinyl–fluoro complex, Pd(OH)(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃) (**28**). Bond distances in angstroms. In parentheses is the energy change without solvation effect and in brackets is the energy change with solvation effect, where the DFT/BS-II method was employed.

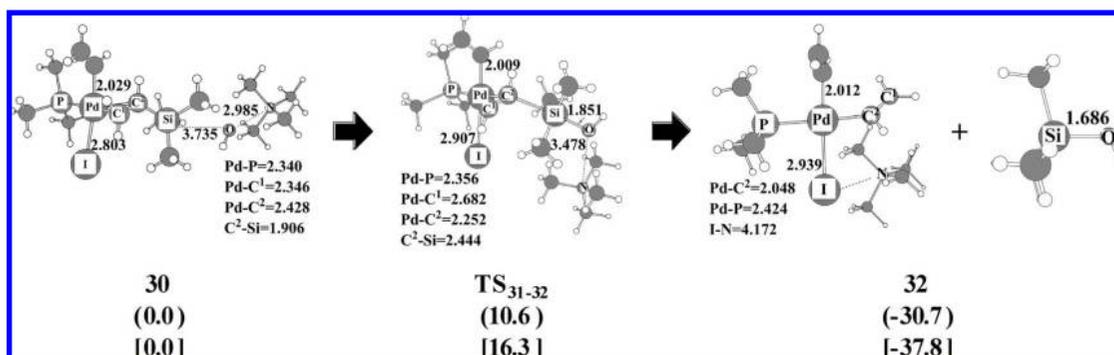


Figure 10. Geometry and energy changes in the fluoride-assisted transmetalation in the palladium(II)–vinyl–iodo complex, Pd(CH=CH₂)(PMe₃)(CH₂=CHSiMe₃) + F[NMe₄] (**30**). Bond distances in angstroms. In parentheses is the energy change without solvation effect and in brackets is the energy change with solvation effect, where the DFT/BS-II method was employed.

mol, which is much larger than that of path 1. When the nucleophilic attack of hydroxide occurs at the Si center in the transition state **TS₃₁₋₃₂**, the activation barrier is 10.6 (16.3) kcal/mol and the exothermicity is 30.7 (37.8) kcal/mol, as shown in Figure 10. The activation barrier without solvation effect is moderately smaller and that with solvation effect is moderately larger than those of path 3. The exothermicity is moderately larger than that of path 3. From these results, it is clearly concluded that not only fluoride anion but also hydroxide anion accelerates the transmetalation. This result agrees well with the experimental result.^{5e} Thus, we propose that the valence orbital energy of the X group is useful to predict whether the transmetalation is accelerated by the X group.

Conclusions

The Pd-catalyzed cross-coupling reaction between vinyl iodide and trimethylvinylsilane was theoretically investigated with the DFT and MP2 to MP4(SDQ) methods. The first step is the oxidative addition of vinyl iodide to Pd(PMe₃)₂, which occurs easily with a moderate activation barrier. The next is the associative substitution of PMe₃ for trimethylvinylsilane, which also occurs with moderate activation barrier and moderate endothermicity. The transmetalation between the palladium(II)–iodo–vinyl complex and vinylsilane occurs with a very large

activation barrier (45.8 kcal/mol) and very large endothermicity (25.6 kcal/mol) in the absence of fluoride anion, where the potential energy change with solvation effect is presented. The final step is the reductive elimination of butadiene, which occurs from Pd(CH=CH₂)₂(PMe₃)₂ with a small activation barrier. It should be clearly concluded that the rate-determining step is transmetalation in the absence of fluoride anion.

Three possible reaction courses were investigated in the presence of fluoride anion. In the first case, vinylsilicate anion is formed before the transmetalation, and it reacts with the palladium(II)–vinyl complex. However, theoretical calculation suggests that fluorovinylsilicate anion is not formed in the case of trimethylvinylsilane. Also, combination of experimental and theoretical results suggests that formation of vinylsilicate anion is not key in this cross-coupling reaction.³⁸ In the second case, an iodo ligand is substituted for the fluoro ligand, followed by the transmetalation between the palladium(II)–fluoride–vinyl complex and vinylsilane. This process occurs with a moderate activation barrier (25.2 kcal/mol) and considerable exothermicity (7.4 kcal/mol). In the third case, fluoride anion attacks the Si center of vinylsilane in the transition state of the transmetalation. This process proceeds with a small activation barrier (16.5 kcal/mol) and a large exothermicity (19.8 kcal/mol). It is concluded

that fluoride anion accelerates the transmetalation through the second and third reaction courses.

The acceleration of transmetalation by fluoride anion is easily interpreted in terms of the formation of a very strong Si–F bond and the stabilization of the transition state by the hypervalent Si center which is induced by fluoride anion. We also investigated the acceleration by hydroxide anion. Interestingly, hydroxide anion accelerates the transmetalation in a manner similar to that observed with fluoride anion. From these results, we propose that the electronegative anion accelerates this transmetalation, because the electronegative anion forms a strong covalent bond with the silyl group and facilitates the formation of hypervalent Si center. Also, we propose that theoretical prediction can be made by evaluating the valence orbital energy of the X group which is added to the reaction solution. We believe that a similar prediction can be made for many transmetalation processes which are very important in the transition-metal-catalyzed cross-coupling reactions.

Acknowledgment. This work was financially supported by Grant-in-Aids on basic research (No. 15350012), Priority Areas for “Molecular Theory for Real Systems” (No.461), NAREGI project from the Ministry of Education, Science, Sports, and Culture. Some of theoretical calculations were performed with SGI Altix4700 workstations at the Institute for Molecular Science (Okazaki, Japan), and some of them were carried out with PC cluster computers in our laboratory.

Supporting Information Available: Complete ref 24; geometry and energy changes resulting from oxidative addition of **1** to **2** to form **3**, dissociative substitution of PMe_3 for trimethylvinylsilane, and transmetalation in **6a**; basis set and solvation effects for the transmetalation in **6b**; geometry and energy changes resulting from reductive elimination of butadiene from three Pd(II) complexes; second transition-state geometry found in IRC calculation of the reductive elimination from $\text{Pd}(\text{CH}=\text{CH}_2)_2(\text{PMe}_3)_2$; discussion based on the Gibbs free energy change along the whole catalytic cycle geometry and energy changes resulting from substitution of I for F and dissociative and associative substitutions of PMe_3 for trimethylvinylsilane in the fluoro complex **23**; basis set and solvation effects for the transmetalation in **24**; geometry and energy changes in transmetalation of $[\text{PdI}(\text{CH}=\text{CH}_2)(\text{PMe}_3)(\text{CH}_2=\text{CHSiMe}_3)] + [\text{NMe}_4]\text{F}$; comparison of three reaction courses of transmetalation in the Gibbs free energy change; and Cartesian coordinates of important species with total energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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