Mechanistic Study on the Platinum-Catalyzed Reaction between Disilacyclobutene and Acetylene

Song-Yun Kang,[†] Tokio Yamabe,[‡] Akinobu Naka,[§] Mitsuo Ishikawa,[*,§] and Kazunari Yoshizawa[*,||]

Department of Molecular Engineering, Kyoto University, Kyoto 606-8501, Japan, Nagasaki Institute of Applied Science, Nagasaki 851-0193, Japan, Department of Chemical Technology, Kurashiki University of Science and the Arts, Kurashiki, Okayama 712-8505, Japan, and Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka 812-8581, Japan

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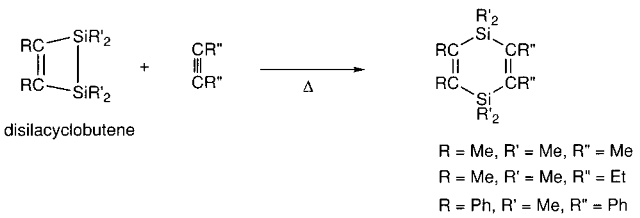
The mechanism and energetics of the $Pt(PPh_3)_2$-catalyzed reaction between disilacyclobutene and acetylene are considered from density functional theory calculations at the B3LYP/6-31G**+LanL2DZ level using reasonable models. The catalytic cycle involves the following elementary processes: (1) oxidative addition of the Si−Si bond of disilacyclobutene to Pt, (2) release of one phosphine ligand, (3) coordination of acetylene to form a π-complex, (4) migratory insertion of acetylene into a Pt−Si bond leading to an Si−C bond, (5) coordination of acetylene, and (6) elimination of product disilacyclohexadiene. The rate-determining step is the insertion of acetylene into a Pt−Si bond. Its activation energy of 23.0 kcal/mol is lower than that of the ring opening of disilacyclobutene, 41.5 kcal/mol, in the thermal reaction between disilacyclobutene and acetylene, which occurs at 250 °C (Yoshizawa, K.; Kang, S.-Y.; Yamabe, T.; Naka, A.; Ishikawa, M. *Organometallics* **1999**, *18*, 4637). Therefore this Pt-catalyzed reaction should proceed under milder conditions. There are two possible reaction pathways in the initial stages of this catalytic cycle; one is the addition of disilacyclobutene, and the other is the addition of acetylene, the former being energetically more preferred than the latter in the initial stages of this reaction. Our calculations demonstrate that this Pt-catalyzed reaction should proceed stereospecifically.

Introduction

Small ring compounds involving two silicon atoms are interesting because of their high-strain energy and reactivity. The reactions of 1,2-disilacyclobutenes reported so far are summarized in Scheme 1, where Ph is C_6H_5.[1−7] Shiina studied the synthesis and reactions of 3,4-benzo-1,1,2,2-tetramethyl-1,2-disilacyclobut-3-ene.[8] Ishikawa et al. have extensively studied thermal,[9] photochemical,[10,11] and transition-metal-catalyzed[12−20] reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene, as shown in Scheme 2. This silicon compound is rather stable at room temperature, but it undergoes various reactions with substituted acetylenes at 250 °C to yield 1,4-disilacyclohexa-2,5-dienes. The reaction takes place under mild conditions using platinum

Scheme 1



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[*] To whom correspondence should be addressed. E-mail: kazunari@ms.ifoc.kyushu-u.ac.jp; mishika@chem.kusa.ac.jp.

[†] Kyoto University.

[‡] Nagasaki Institute of Applied Science.

[§] Kurashiki University of Science and the Arts.

[||] Kyushu University.

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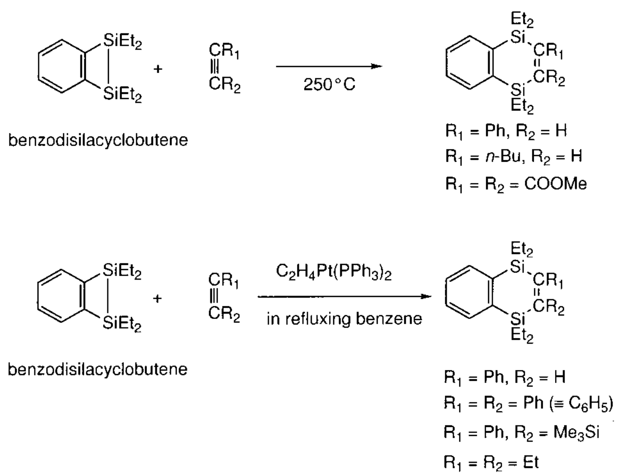
Scheme 2

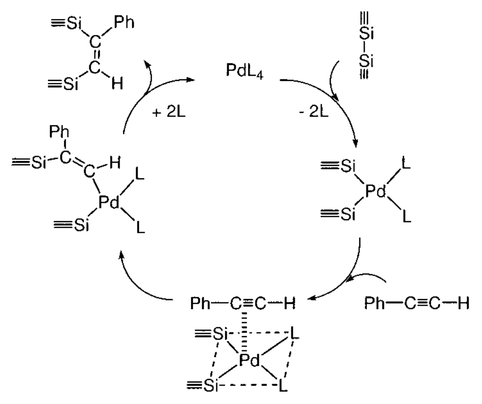


catalyst $C_2H_4Pt(PPh_3)_2$ to give products arising from the insertion of the triple bond of acetylene into the silicon–silicon bond of benzodisilacyclobutene.

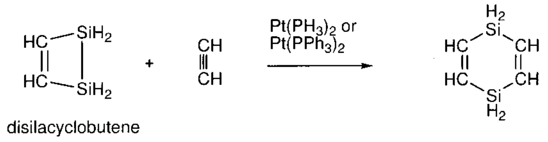
Possible reaction mechanisms for the thermal addition of disilacyclobutene and acetylene have been suggested by Barton and Kilgour.[1] Disilabutadiene with silicon–carbon double bonds, which can be formed from the ring opening of disilacyclobutene, undergoes Diels–Alder reactions with acetylenes. However, disilabutadiene is an unstable intermediate and has not yet been detected experimentally. Our knowledge of the reactivity of these silicon compounds is increased from quantum chemical calculations as reliable information. Recently, we demonstrated from detailed analyses of the potential energy surfaces that disilabutadienes formed by the thermal ring opening of disilacyclobutenes should play a central role in the addition reactions as intermediates in a manner similar to usual Diels–Alder reactions.[21,22]

Bis-silylation of unsaturated hydrocarbons catalyzed by group 10 metals is a useful method for synthesizing organosilicon compounds, in which two Si–C bonds are created in a single chemical process. Although several elementary processes of bis-silylation have been investigated experimentally[23–34] and theoretically,[35–39] the mechanism of the metal-catalyzed reaction has not yet been fully understood. According to Nagai and co-workers,[24] the bis-silylation of acetylene proceeds in the sequence of the elementary processes shown in Scheme 3. The first step of this catalytic cycle is the oxidative addition of disilane to a low-valent metal species to form a bis-silyl complex, and the insertion of a carbon–carbon multiple bond into a resulting metal–silicon bond provides an organosilyl metal intermediate, which reductively eliminates a bis-silylation product. Sakaki and co-workers[38] investigated the Pt-catalyzed bis-silylation of ethylene using molecular orbital calculations and proposed that the rate-determining step is the insertion of ethylene into a Pt–Si bond.

Scheme 3



Scheme 4



The purpose of our theoretical work is to investigate the mechanism of the Pt-catalyzed reaction between benzodisilacyclobutene and acetylene as well as the structures and energetics of the assumed intermediates and transition states involved in this reaction. We consider the $Pt(PPh_3)_2$-catalyzed reaction between disilacyclobutene and acetylene using a reasonable model; see Scheme 4.

Method of Calculation

Detailed calculations for the reactants, products, transition states (TSs), and intrinsic reaction coordinate (IRC)[40,41] were carried out using the B3LYP density functional theory method,[42–44] which consists of the nonlocal exchange functional of Becke's three-parameter set[42,43] and the nonlocal correlation functional of Lee, Yang, and Parr.[44] It has been successfully applied to Pt-catalyzed reactions to give better results with experiment than the CCSD(T) method, with respect to molec-

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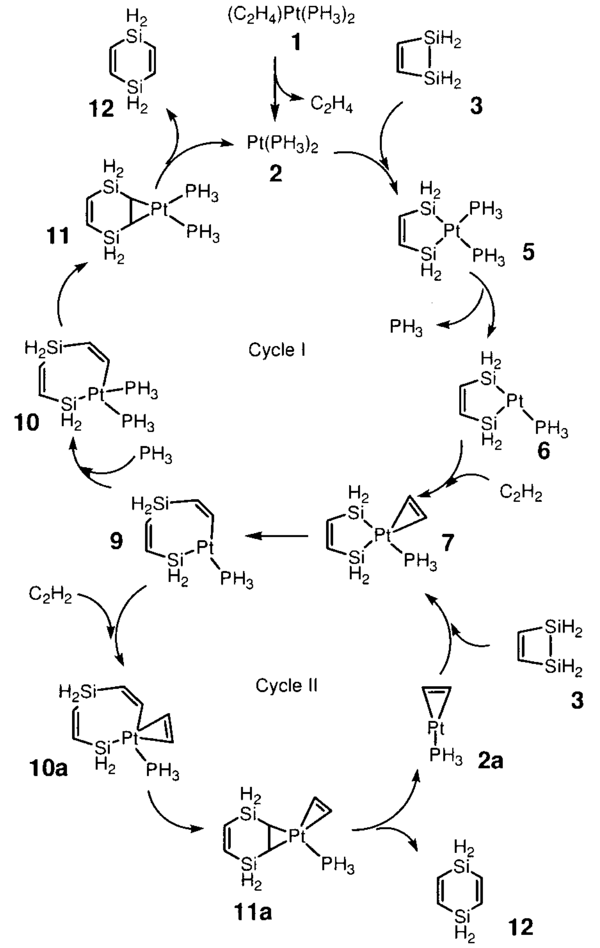
ular structures and energetics.[45] We used two kinds of basis sets. The smaller one is the LanL2DZ[46−48] basis set, which is associated with the relativistic effective core potential (ECP) for Pt and nonrelativistic ECP for Si and P and the D95 double-ζ basis set[49] for C and H; the larger one (6-31G**+LanL2DZ) is a combination of the 6-31G** basis set,[50−52] a standard double-ζ basis set with polarization functions for C, H, Si, and P, and the LanL2DZ basis set for Pt. Vibrational mode analyses were systematically carried out to confirm that on potential energy surfaces optimized geometries correspond to a local minimum that has no imaginary frequency mode or a saddle point that has only one imaginary mode. Corrections of zero-point vibrational energies were taken into account in stationary structures obtained. The Gaussian 98 ab initio program was used throughout this work.[53]

Results and Discussion

Release of Ethylene from (η^2-C_2H_4)Pt(PH_3)$_2$. In our calculations, we used disilacyclobutene and PH_3 to model 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene and PPh_3 (Ph ≡ C_6H_5), respectively. The model is small, but we will consider ligand effects coming from PPh_3 later in this paper. We show in Scheme 5 our final conclusion, a possible reaction pathway for this Pt-catalyzed reaction. Computed total energies and zero-point vibrational energies for the reaction species are summarized in Table 1. The first step of the catalytic cycle is the release of ethylene from (η^2-C_2H_4)Pt(PH_3)$_2$ (**1**); computed structures and energy diagram are shown in Figure 1. The C−C bond length of **1** was calculated to be 1.425 Å, which is shorter than the standard C−C single bond length, 1.530 Å,[54] and longer than the C═C double bond length of ethylene, 1.339 Å.[54] The Pt−C bond of **1** was calculated to be 2.158 Å, which is longer than a Pt−C bond length, 2.11 Å, of Pt(PPh_3)$_2$(C_2H_4).[55,56] In the chemical process via $\mathbf{TS_{1-2}}$, the C═C double bond is finally formed and the Pt−C bond is cleaved to give ethylene and **2**. The activation energy for this process is 14.7 kcal/mol. As discussed by Goddard and coworkers,[57,58] the dissociation reaction involves a change in the effective electronic configuration of Pt from the s^1d^9 configuration to the d^{10} configuration. The d^{10} configuration is not capable of forming two covalent bonds, while the s^1d^9 configuration with two singly occupied orbitals can form two covalent bonds. The dissociation energy of **1** into ethylene and Pt(PH_3)$_2$ (**2**) is 10.7 kcal/mol, while the C═C, C−C, and Pt−C bond dissociation energies are 174.1,[54] 89.9,[54] and 32.3 kcal/mol,[59,60] respectively. Thus, the energy for the promotion from s^1d^9 to d^{10} is required in the dissociation process.

Scheme 5



Addition of Disilacyclobutene to Pt(PH_3)$_2$. The second step in the catalytic cycle is the coordination of disilacyclobutene (**3**) to Pt(PH_3)$_2$ (**2**), leading to a weakly bound reactant complex, **4**, as shown in Figure 2, where the Si−Si and the P−Pt−P axes are perpendicular to each other and the Si−Si bond is 0.011 Å shorter, the Pt−P bond is 0.006 Å longer, and the P−Pt−P angle is 4.8° smaller than the corresponding bonds and angles of free **2** and **3**. The two Pt−Si distances are 3.719 and 3.534 Å, and the energy is 1.2 kcal/mol higher than the energy of **2** *plus* **3**. Thus, the interaction between the two species is weak and the structure of **3** remains almost unchanged upon complexation. The complex with the Si−Si axis parallel to the P−Pt−P axis was not found, which suggests that such a complex is energetically unfavorable due to steric repulsion. The Si−Si bond of **4** is activated in the reaction via $\mathbf{TS_{4-5}}$, and complex **5** is formed as a result. Note that the Si−Pt−

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Table 1. Energetics for the Reaction Species and the Transition States at the B3LYP/6-31G+LanL2DZ Level of Theory**[a]

	energy (au)	ZPE (kcal/mol)
1	−884.12778	68.0
TS$_{1-2}$	−884.10290	67.0
ethylene	−78.59381	32.1
2	−805.51476	34.5
3	−658.76974	41.4
4	−1464.28322	76.3
TS$_{4-5}$	−1464.28298	76.1
5	−1464.34709	76.6
PH$_3$	−343.14507	15.1
6	−1121.17232	59.1
acetylene	−77.32957	16.8
7	−1198.52039	77.8
TS$_{7-8}$	−1198.51666	77.9
8	−1198.51474	78.0
TS$_{8-9}$	−1198.48089	78.2
9	−1198.54923	79.8
10	−1541.71410	97.2
TS$_{10-11}$	−1541.68540	96.3
11	−1541.73142	97.6
TS$_{11-12}$	−1541.70603	97.3
12	−736.20214	62.6
10a	−1275.88785	97.4
TS$_{10-11a}$	−1275.87643	98.2
11a	−1275.91401	99.1
TS$_{11-12a}$	−1275.89243	98.1
2a	−539.69601	35.0
TS$_{2-13}$	−882.83731	51.4
13	−882.86921	52.8
TS$_{4-5a}$	−1198.46326	76.7

[a] 1 au = 27.21 eV = 627.5 kcal/mol.

Table 2. Energetics for the Reaction Species and the Transition States at the B3LYP/LanL2DZ[a] **and B3LYP/6-31G**+LanL2DZ**[b] **Levels of Theory**[c]

	energy (au)	ZPE (kcal/mol)
5	−223.33389[a]	75.2[a]
6	−215.03369[a]	58.5[a]
PH$_3$	−8.26987[a]	14.6[a]
5′	−1609.43999[a]	
6′	−908.09605[a]	
PPh$_3$	−701.32332[a]	
3m	−816.09212[b]	113.9[b]
7m	−1355.82943[b]	150.1[b]
TS$_{7-8m}$	−1355.82884[b]	150.1[b]
8m	−1355.83379[b]	150.1[b]
TS$_{8-9m}$	−1355.79209[b]	150.4[b]
9m	−1355.86832[b]	152.0[b]

[a] The B3LYP/LanL2DZ method. [b] The B3LYP/6-31G**+LanL2DZ method. [c] 1 au = 27.21 eV = 627.5 kcal/mol.

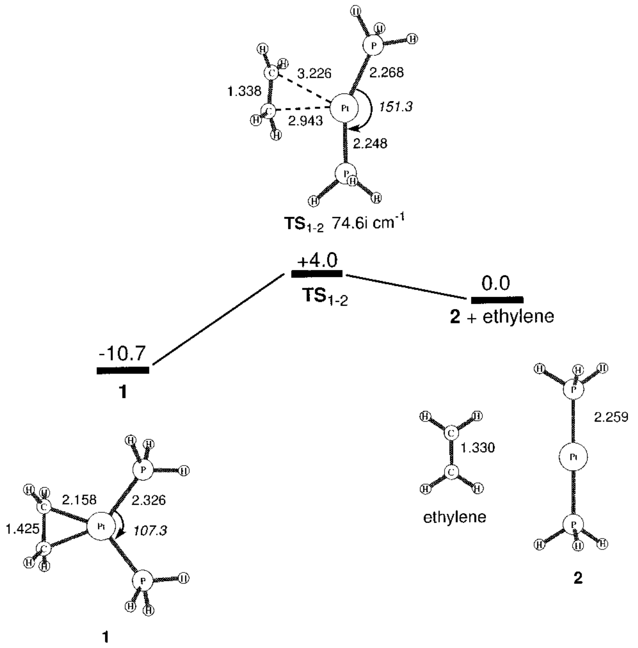


Figure 1. Optimized geometries and energetics for the release of acetylene from **1** at the B3LYP/6-31G**+LanL2DZ level. Bond lengths are in Å and angles are in deg.

Si plane rotates with respect to the P−Pt−P plane as the reaction proceeds from **4** to **5**. The activation barrier is 0.0 kcal/mol relative to **4**. Computed bond distances of **TS$_{4-5}$** are similar to those of **4** except for the Pt−Si bond distances, which are decreased from 3.719 and 3.534 Å to 3.249 and 3.227 Å, respectively.

Release of PH$_3$. The third step of the catalytic cycle is the release of PH$_3$ from complex **5** and the coordination of acetylene. The release of a PH$_3$ ligand leads to an unsaturated three-coordinate complex **6**, which has a well-defined T-shaped structure. The Pt−Si bond *trans* to the open site in complex **6** is decreased from 2.398 Å in **5** to 2.315 Å, while the Pt−Si bond *cis* to the open site remains almost unchanged. The energy required for the release of PH$_3$ in the process from **5** to **6** was calculated to be 16.3 kcal/mol. We could not obtain the transition state for this electronic process despite detailed investigations of the potential energy surface. The computed energetics suggest that the release of PH$_3$ will easily occur.

Addition of Acetylene. After the release of PH$_3$, acetylene directly coordinates to **6** at its open site to form complex **7**, as shown in Figure 3. Chart 1 indicates that the LUMO of **6** is directed to the open site and can significantly interact with the π HOMO of acetylene. Since the Pt−Si σ* orbital is partially occupied, the Pt−Si bonds are increased to 2.398 and 2.425 Å in **7**. We could not find the transition state for the addition of acetylene. The energy change in the addition of acetylene is similar to that in the release of PH$_3$. The Pt−C distances in **7** were calculated to be 2.259 and 2.279 Å, being slightly long in comparison with an experimental value of 2.127 Å.[32] The C−C bond distance was calculated to be 1.242 Å, which is close to a calculated C−C distance of 1.205 Å in free acetylene. These results suggest that **7** is a weakly bound π-complex. Its binding energy is 9.7 kcal/mol, which is lower than the energy required for the release of PH$_3$ in **5**. Thus, PH$_3$ binds to Pt more strongly than acetylene. Although the addition of acetylene is likely to occur before the release of PH$_3$, no six-coordinate complex was found in our calculations, and we therefore think that this process can take place in a dissociative fashion.

Insertion of Acetylene. The next step is the insertion of acetylene into a Pt−Si bond via **TS$_{8-9}$** leading to complex **9**, as shown in Figure 3. Before the insertion of acetylene, the acetylene group in complex **7** rotates to form complex **8**, in which the C−Pt−P plane is perpendicular to the Si−Pt−Si plane. In complex **9**, one of the carbon atoms forms a bond with the Pt atom with a Pt−C distance of 2.086 Å, and the other carbon atom forms a bond with Si with an Si−C distance of 1.872 Å. Thus, the Pt−Si bond and the C−C π-bonds are broken. The Pt−Si bond is shortened from 2.405 to 2.319 Å in **9**. The acetylene insertion process is exothermic by 18.2 kcal/mol relative to complex **8**. In view of the transition

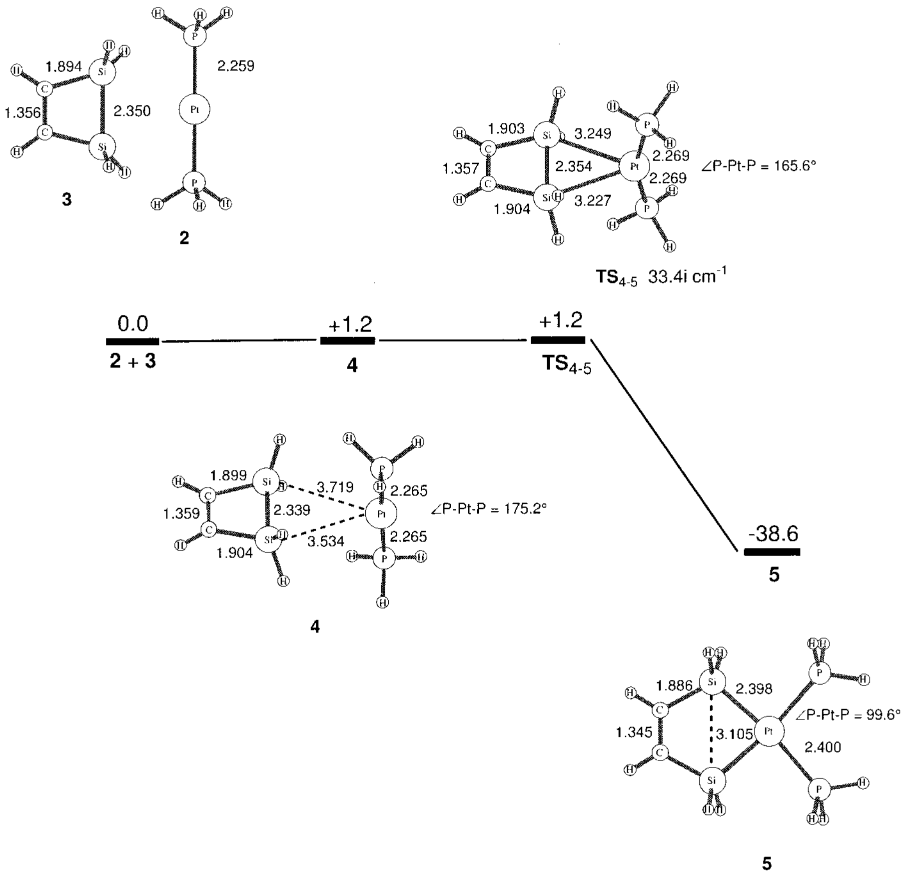


Figure 2. Optimized geometries and energetics for the reaction of **2** and **3** at the B3LYP/6-31G**+LanL2DZ level. Bond lengths are in Å.

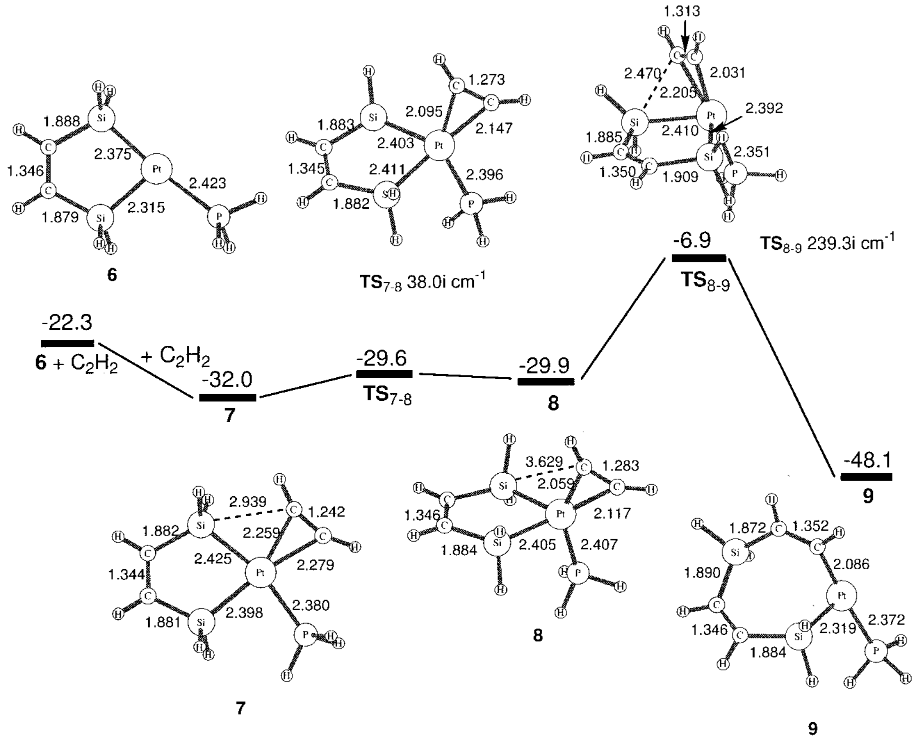
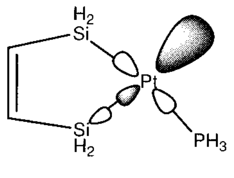


Figure 3. Optimized geometries and energetics for the insertion of acetylene at the B3LYP/LanL2DZ level. Bond lengths are in Å.

state for the insertion of acetylene into the Pt−Si bond, one of the Pt−C bonds with respect to the coordinated acetylene group is 2.205 Å and the other Pt−C bond is 2.031 Å. The C−C bond is increased to 1.313 Å. In $\mathbf{TS_{8-9}}$ the distance of the C−Si bond being formed is 2.470 Å and the distance of the Pt−Si bond being broken is 2.410 Å. The barrier height of $\mathbf{TS_{8-9}}$ is 23.0 kcal/mol relative to **8**.

Chart 1



LUMO of **6**

To look at whether $\mathbf{TS_{8-9}}$ is the transition state that connects **8** and **9**, we performed an IRC analysis at the B3LYP/LanL2DZ level of theory. Figure 4 presents the energy profile and the change in the Pt−Si, Si−C, and Pt−C distances along the IRC. The IRC was traced from $\mathbf{TS_{8-9}}$ ($s = 0$) toward both directions to **8** ($s < 0$) and **9** ($s > 0$). When we follow the reaction pathway from **8** to $\mathbf{TS_{8-9}}$, the Si−C distance gradually decreases, and after passing $\mathbf{TS_{8-9}}$ the Si−C single bond is formed. On the contrary, after passing $\mathbf{TS_{8-9}}$ the Pt−Si and Pt−C bond distances are gradually increased and finally cleaved in **9**. These geometrical features demonstrate that $\mathbf{TS_{8-9}}$ is the true transition state for the conversion of **8** to **9**.

Re-Coordination of $\mathbf{PH_3}$. The re-coordination of PH_3 to **9**, which is a barrierless process, leads to complex **10**. The Pt−P bond of 2.447 Å *trans* to an Si atom of **10** is longer than the Pt−P bond of 2.360 Å *trans* to a C atom, which reflects the weaker *trans* influence. The binding energy of PH_3 in the reaction from **9** to **10** is 10.2 kcal/mol. This process takes place at no cost of energy, and it is similar to the release of PH_3 from **5**.

Release of Disilacyclohexadiene. On complex **10**, the Si−C bond is formed via $\mathbf{TS_{10-11}}$ to lead to complex **11**, as shown in Figure 5. A normal-mode analysis for $\mathbf{TS_{10-11}}$ shows that this transition state is a true saddle point that has only one imaginary frequency of 231.1i cm^{-1}. The activation barrier for this process is 17.1 kcal/mol relative to **10**. The resultant complex **11** is a typical π-complex with a Pt−C bond of 2.165 Å. From complex **11**, final products **12** and **2** are formed in the reaction via $\mathbf{TS_{11-12}}$. The activation energy relative to **11** is 15.7 kcal/mol, and the binding energy relative to **12** plus **2** is 8.6 kcal/mol, which is in good agreement with the energy for the release of ethylene from **1**.

Coordination of Acetylene to 9. We assumed that re-coordination of PH_3 occurs in the Si−C reductive elimination, but acetylene can also coordinate to the Pt atom of complex **9** because acetylene exists in excess in the reacting system. Sakaki and co-workers[39] showed that ethylene coordination can accelerate the reductive elimination in Pt complexes more than PH_3. We thus examined the acetylene coordination reaction starting from complex **9**, in which acetylene coordinates to complex **9** to form **10a**, as shown in Figure 6. The binding energy is 4.9 kcal/mol, being 5.3 kcal/mol lower than the binding energy of PH_3. On complex **10a**, the Si−C bond is formed via $\mathbf{TS_{10-11}a}$, leading to π-complex **11a**, the activation energy for this process being 8.0 kcal/mol, which is about half as large as the value in the PH_3 case. Complexes **12** and **2a** are released from complex **11a** through $\mathbf{TS_{11-12}a}$, and **2a** reacts with **3** to enter the next catalytic cycle. The activation energy is 12.5 kcal/mol, which is lower than that in the PH_3 case. Thus, acetylene should accelerate the reductive elimination more than PH_3 from complex **11a**, and this reaction pathway is more favorable than the re-coordination of phosphine.

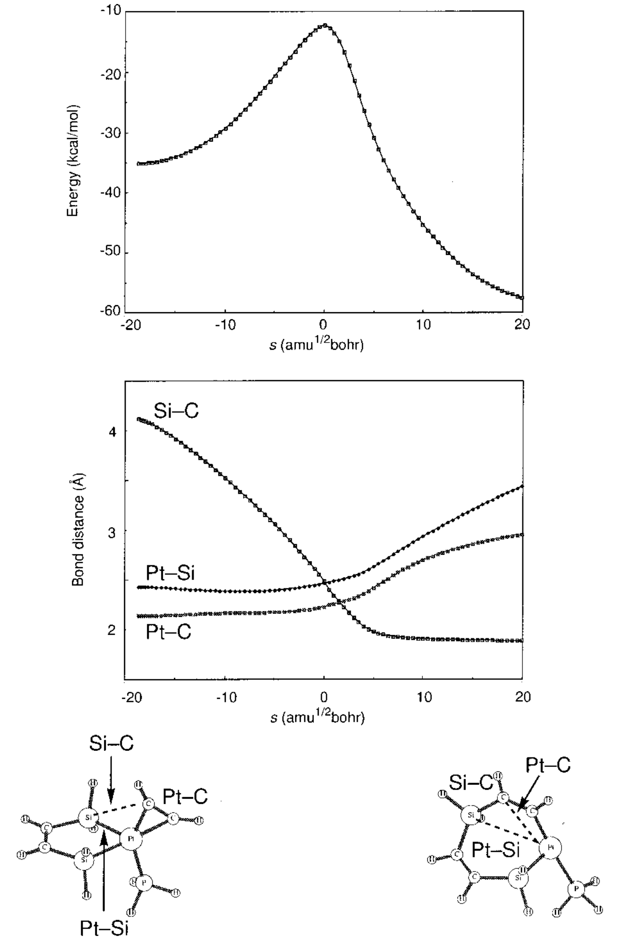


Figure 4. Changes in potential energy and internal coordinates along the IRC with respect to the insertion of acetylene at the B3LYP/LanL2DZ level.

Solvent Effect. Figure 7 shows that the entire reaction from **2**, **3**, and acetylene to **2a**, **12**, and PH_3 is exothermic by 59.3 kcal/mol, which is of course consistent with our previous calculation for the thermal cycloaddition of disilacyclobutene and acetylene.[22] The rate-determining step is clearly the migratory insertion of acetylene into a Pt−Si bond. The activation energy (23.0 kcal/mol) is lower than that of the ring-opening step of disilacyclobutene (41.5 kcal/mol) in the thermal addition of disilacyclobutene and acetylene. Moreover, the energies of the stationary points, except for **4** and $\mathbf{TS_{4-5}}$, the highest energy points in the course of this reaction, are lower than that of the dissociation limit of **2**, **3**, and acetylene. Therefore this Pt-catalyzed reaction is predicted to proceed under milder conditions.

To confirm this result to be correct in solution, we performed polarized-continuum-model calculations based on the self-consistent reaction field theory (SCRF/CPCM)[61] at the B3LYP/6-31G**+LanL2DZ level of theory. We used benzene as a solvent and estimated $\Delta G_{\text{solution}}$ values at 298.15 K. The essential features of the energetics for the reaction pathway remain unchanged by the free energy calculations. The dissociation and coordination steps are slightly affected by

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[61] Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.

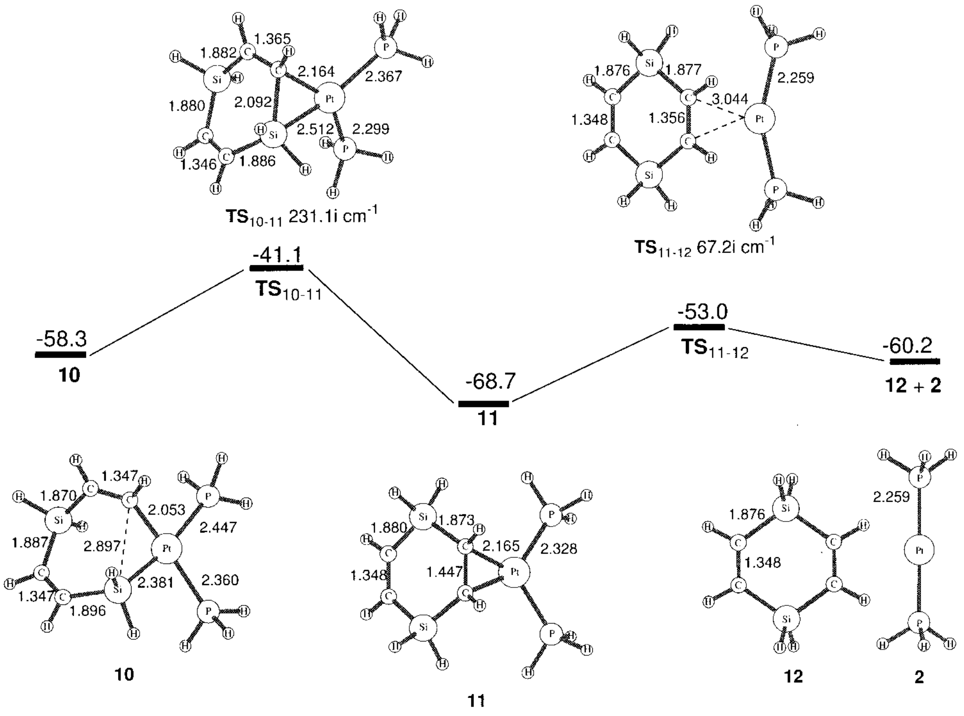


Figure 5. Optimized geometries and energetics for the release of **12** and **2** at the B3LYP/6-31G**+LanL2DZ level. Bond lengths are in Å.

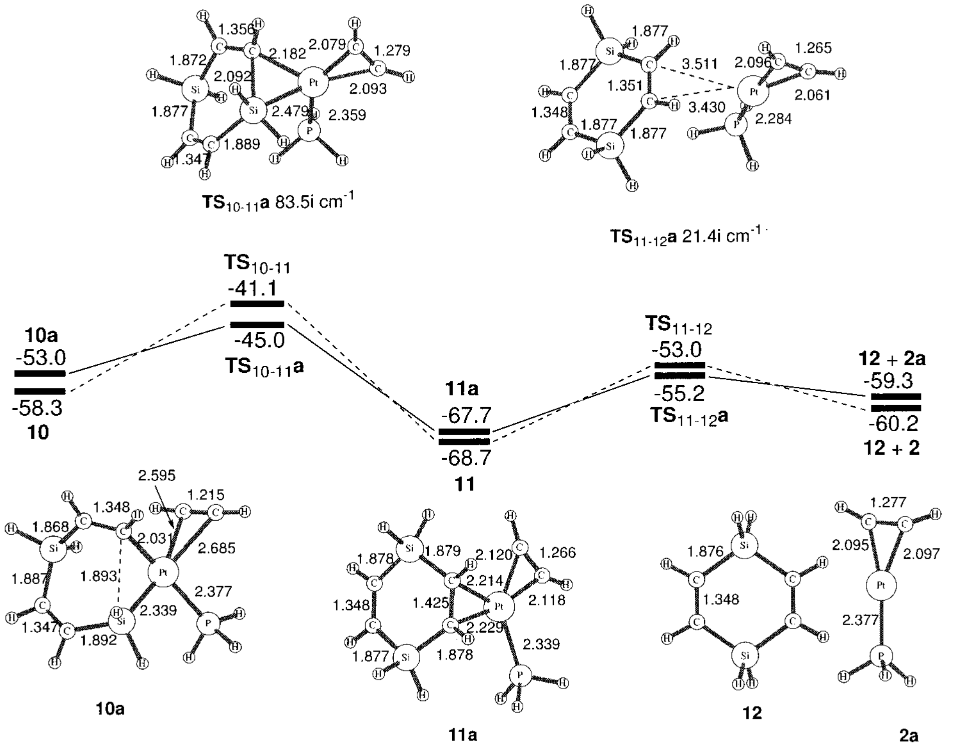


Figure 6. Optimized geometries and energetics for the release of **12** and **2a** at the B3LYP/6-31G**+LanL2DZ level. Bond lengths are in Å.

solution, while the other steps remain unchanged. For example, a computed $\Delta G_{\mathrm{solution}}$ value for the dissociation of PH_3 from **5** to **6** is 11.6 kcal/mol (ΔE = 16.3 kcal/mol), a $\Delta G_{\mathrm{solution}}$ value for the coordination of acetylene in **7** is 4.3 kcal/mol (ΔE = 9.8 kcal/mol), a $\Delta G_{\mathrm{solution}}$ value for the coordination of acetylene in **10a** is −4.3 kcal/mol (ΔE = 4.9 kcal/mol), and a $\Delta G_{\mathrm{solution}}$ value for the activation for the release of disilacyclohexadiene (**12**) from **11a** is 14.6 kcal/mol (ΔE = 12.5 kcal/mol). The differences between the $\Delta G_{\mathrm{solution}}$ and ΔE values for the dissociation and coordination steps are calculated to be 1.8−10.0 kcal/mol, while those of the other steps fall in the range 0.1−3.5 kcal/mol. The most important step for this catalytic reaction is the acetylene insertion into the Si−Pt bond, the difference between $\Delta G_{\mathrm{solution}}$ and ΔE being 2.3 kcal/mol. Thus, the effect of entropy on the reaction steps is not significant. We can therefore characterize from energy calculations the essential

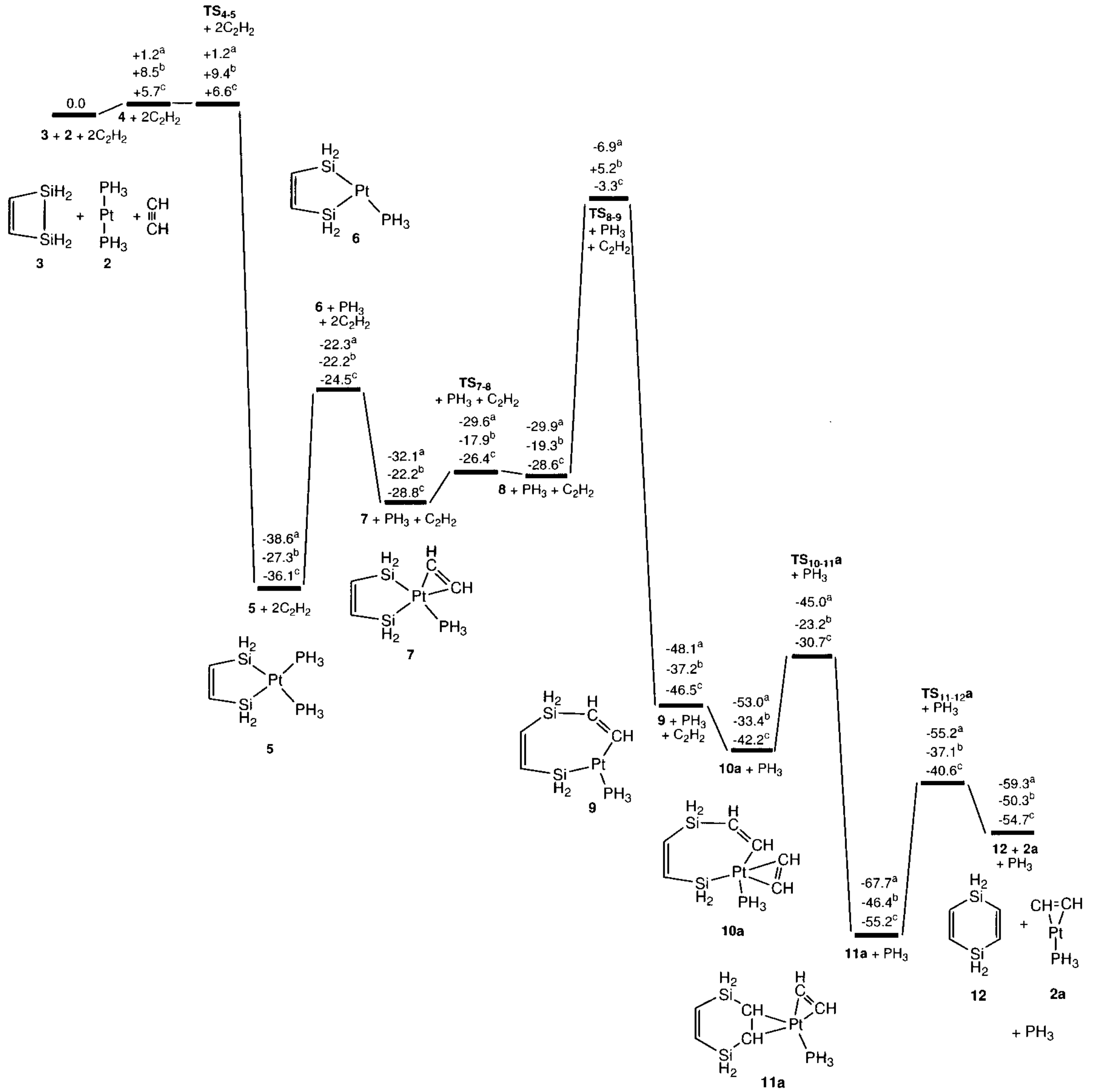
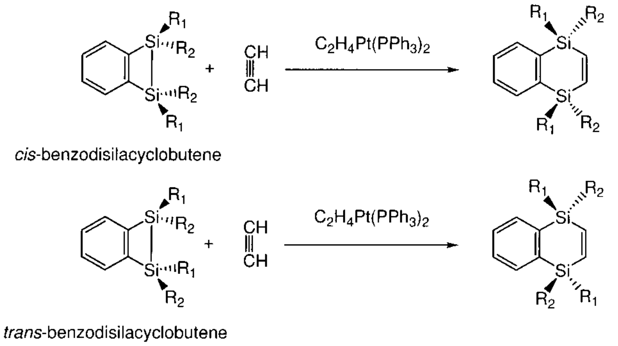


Figure 7. Energy diagram of the entire reaction pathway at the B3LYP/6-31G**+LanL2DZ level: (a) Relative energies (ΔE) with zero-point energy corrections, (b) free energies (ΔG) in the gas phase, and (c) free energies ($\Delta G_{\text{solution}}$) in benzene solution.

energetic features of the Pt-catalyzed reaction between disilacyclobutene and acetylene. Considering that the relative energy of **TS$_{8-9}$** from complex **5** is increased from 31.7 kcal/mol to 32.8 kcal/mol, complex **5** is stabilized in solution. On the other hand, the energies of complexes **10a** and **11a** are significantly increased in solution. In this electronic process, the SiH_2 group of disilabenzene does not rotate; in other words, this Pt-catalyzed reaction takes place stereospecifically. Therefore, as shown in Scheme 6, the reaction of *cis*-benzodisilacyclobutene with acetylene will give *cis*-benzodisilacyclohexadiene, and the reaction between *trans*-benzodisilacyclobutene and acetylene will give *trans*-benzodisilacyclohexadiene. These predictions will be tested by appropriate experiments.

Scheme 6



Another Reaction Pathway. Apart from the reaction pathway explored above, we considered another possible branch of the catalytic cycle (path B), in which acetylene coordination takes place in the first step. As Figure 8 shows, acetylene can directly coordinate to $Pt(PH_3)_2$ to give complex **13** via **TS$_{2-13}$**. The activation energy and coordination energy measured from $Pt(PH_3)_2$ and acetylene are 4.5 and 14.1 kcal/mol, respectively. In complex **13**, the Pt−C bond distance is 2.073 Å, which is shorter than that in complex **7**, and the C−C bond distance is 1.304 Å, which is longer than that in complex **7**. Indeed, acetylene in complex **13** coordinates to Pt more strongly than in complex **7**, but the total energy of complex **13** is higher than that of complex **5**. The

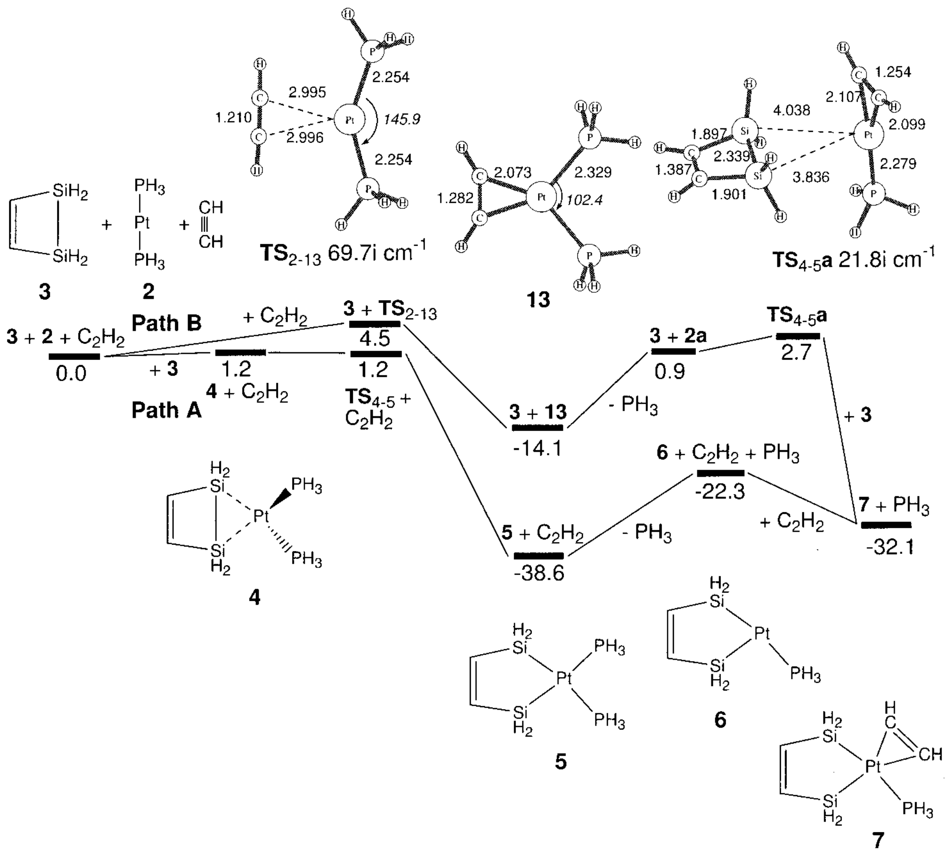


Figure 8. Optimized geometries and energetics for the reaction of **2** and acetylene at the B3LYP/6-31G**+LanL2DZ level. Bond lengths are in Å and angles are in deg.

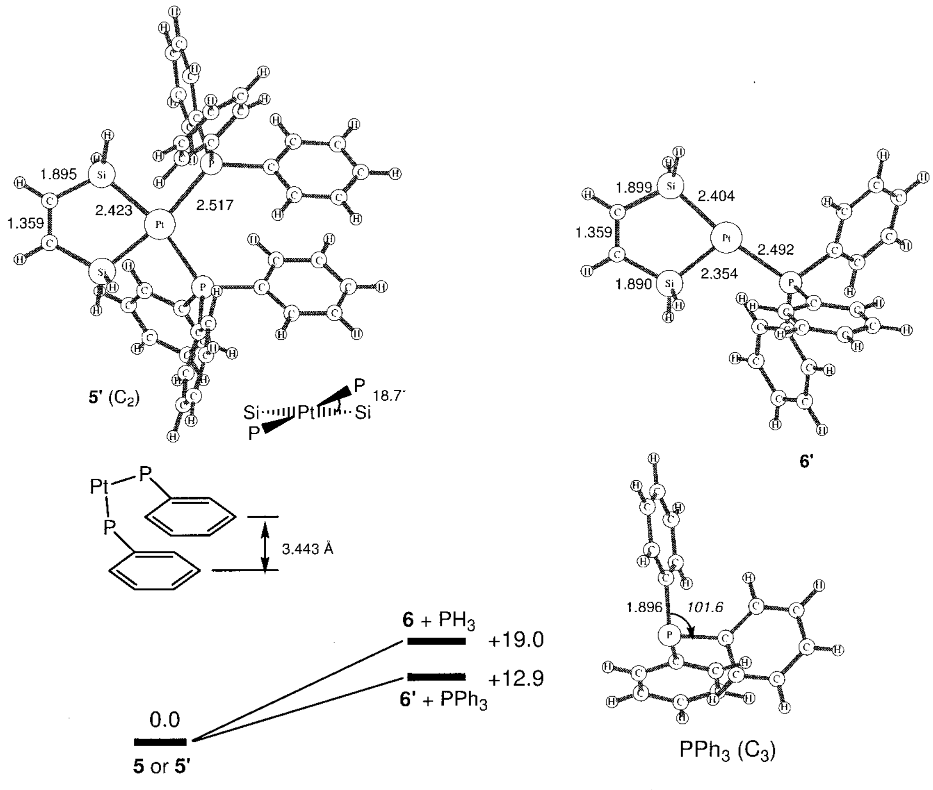


Figure 9. Optimized geometries and energetics for the release of PPh_3 from **5′** at the B3LYP/LanL2DZ level. Bond Lengths are in Å and angle are in deg. Zero-point vibrational correction is not included in the energy diagram.

Pt–P bond length is increased to 2.329 Å in complex **13**, and PH_3 dissociates from **13** to form complex **2a**. Complex **2a** binds to **3** to form complex **7** via $\mathbf{TS_{4-5}a}$.

As shown in the energy diagram in Figure 8, the stationary points along path B lie above those along the original reaction pathway (path A), in which disilacy-

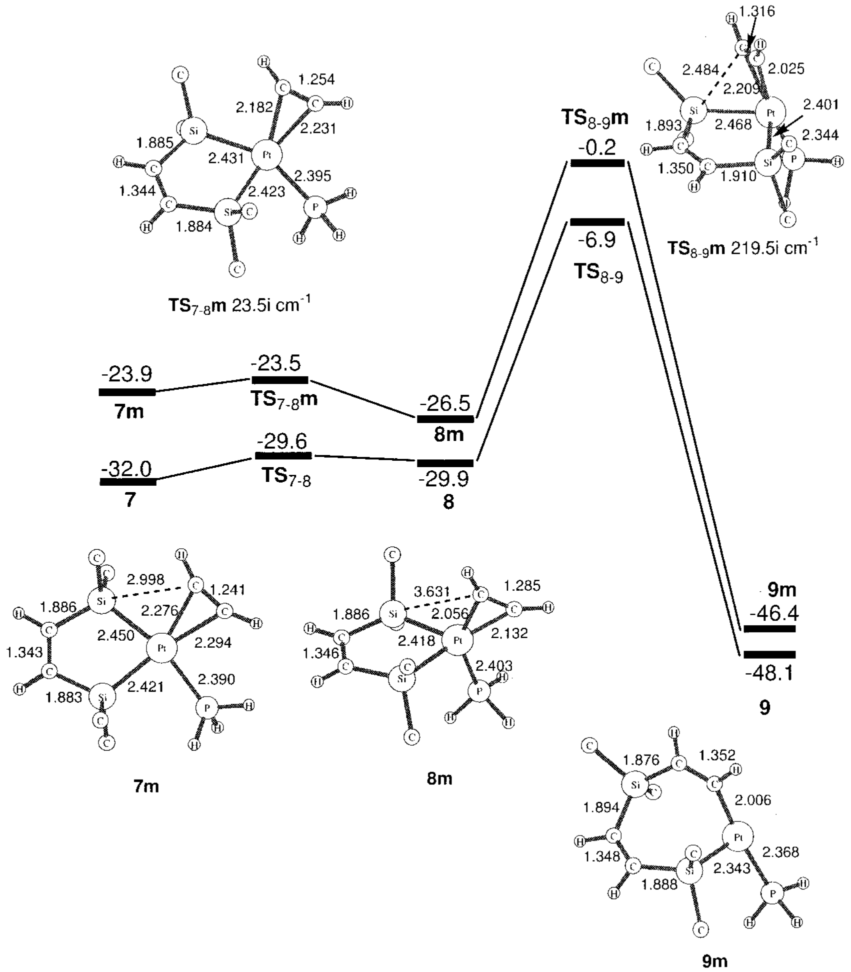


Figure 10. Optimized geometries and energetics around $\mathbf{TS_{8-9}}$ replaced by the $SiMe_2$ group at the B3LYP/6-31G**+LanL2DZ level. Bond lengths are in Å. The H atoms of methyl groups are omitted for the sake of clarity.

clobutene reacts with $Pt(PH_3)_2$ at first. Therefore path A is energetically more favorable; the coordination of acetylene is very unlikely to occur in the initial stages of this catalytic reaction.

Size Effect 1. Release of PPh_3. We have used $Pt(PH_3)_2$ to consider the catalytic reaction that actually occurs with $Pt(PPh_3)_2$. To better understand the mechanism of this catalytic reaction, we finally calculated the release of PPh_3 (Ph ≡ C_6H_5) from **5′** at the B3LYP/LanL2DZ level. Optimized structures and an energy diagram are illustrated in Figure 9. The Si−Pt−Si plane and the P−Pt−P plane in **5′** are not on the same plane and are slightly twisted around the Pt atom with a dihedral angle of 18.7°. Two benzene rings of the two phosphine ligands lie close in space with a distance of 3.443 Å, as indicated in the illustration. Thus, the two phosphine ligands have a steric repulsion, which can increase the Pt−P distance to 2.517 Å, while the other molecular parts remain almost unchanged from **5**. On the other hand, the Pt−P bond distance is decreased from 2.601 Å in **6** to 2.492 Å in **6′**. These results suggest that the Pt−P bonds of **5′** are weaker than the Pt−P bonds of **5**, whereas the Pt−P bond of **6′** is stronger than the Pt−P bond of **6**. In fact, the energy required for the release of phosphine ligand is decreased from 19.0 kcal/mol in **6** to 12.9 kcal/mol in **6′**. Therefore the release of PPh_3 from the Pt complex can take place more easily than in our PH_3 model. This is an important difference between the actual catalytic system and our model.

Size Effect 2. Effect of $SiMe_2$ Group. The energetically most important point is $\mathbf{TS_{8-9}}$ because it is the rate-determining step in this Pt catalytic system. The size effect around the Si atom in $\mathbf{TS_{8-9}}$ is interesting. To increase our understanding of the size effect, we replaced the SiH_2 group with a $SiMe_2$ group in $\mathbf{TS_{8-9}}$ and performed calculations at the B3LYP/6-31G**+LanL2DZ level. Optimized structures and their energetics are shown in Figure 10. Complex **7m** is destabilized by the steric repulsion of the $SiMe_2$ groups, and optimized Pt−C bond lengths are increased relative to those of complex **7**. Complex **8m** is rather stable in comparison with **7m**. The activation energy for the acetylene insertion is 26.3 kcal/mol relative to **8m**, which is 3.3 kcal/mol higher than that in the SiH_2 case. Therefore the activation energy for the acetylene insertion will be higher in real systems with bulky silyl groups.

Conclusions

We have investigated the mechanism and energetics of the $Pt(PPh_3)_2$-catalyzed reaction between disilacyclobutene and acetylene using reasonable models at the B3LYP/6-31G**+LanL2DZ level of density functional theory. Detailed descriptions of the total energies of the reaction species (stable points) and the transition states (saddle points) calculated are presented in Table 1. The catalytic cycle involves the following elementary processes: (1) oxidative addition of the Si−Si bond of disilacyclobutene to Pt, (2) release of one phosphine ligand, (3) coordination of acetylene to form a π-complex, (4) migratory insertion of acetylene into a Pt−Si bond to form an Si−C bond, (5) coordination of acetylene, and (6) elimination of product disilacyclohexadiene. The rate-determining step was found to be the migratory insertion of acetylene into a Pt−Si bond, i.e., the process from **6** to **7**. Its activation energy (23.0 kcal/mol) is lower than that of the ring-opening step of disilacyclobutene (41.5 kcal/mol) in the thermal addition between disilacyclobutene and acetylene, which occurs at 250 °C. Therefore the Pt-catalyzed reaction between disilacyclobutene and acetylene should proceed at lower temperature. We compared two reaction branches in the initial stages of the catalytic cycle; one is the addition of disilacyclobutene, and the other is the addition of acetylene. We found that the addition of disilacyclobutene is energetically more preferred than the addition of acetylene. Finally, we proposed that this Pt-catalyzed reaction should proceed stereospecifically. The reaction of *cis*- and *trans*-benzodisilacyclobutenes with acetylene will give *cis*- and *trans*-benzodisilacyclohexadienes, respectively.

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