JOC The Journal of Organic Chemistry

Article

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Quantum Chemical Study of $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Carbonyl Group

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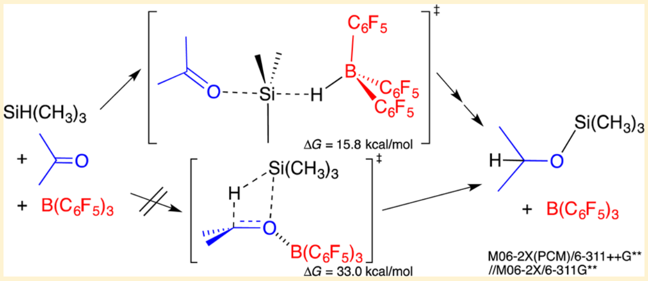
Ⓢ *Supporting Information*

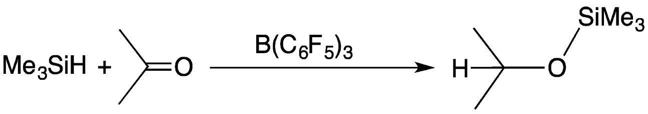


ABSTRACT: The hydrosilylation reaction of a carbonyl group catalyzed by tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, is investigated by using the DFT method. M06-2X level calculations suggest the presence of a stable complex between trimethylsilane and $B(C_6F_5)_3$. The attack of the carbonyl group in acetone from the back side of the Si−H bond prompts the abstraction of the hydride ion by $B(C_6F_5)_3$. This reaction path is lower in free energy than the conventional carbonyl-activation path via a four-membered cyclic transition state. The silane-activation mechanism is supported in this case, in agreement with experimental results reported by Piers and by Oestreich. The calculations show, on the other hand, that the silane-activation mechanism does not apply to the reaction catalyzed by BF_3. This difference in mechanisms arises from a stronger electrophilicity of the boron center in $B(C_6F_5)_3$ than in BF_3 toward a hydride ion, as demonstrated by an analysis of reactive orbitals. Attractions between the silane part and the fluorine atoms at the *ortho* positions of C_6F_5 groups in the Lewis acid assist the path by making up for the destabilization of the reacting system that is caused by the distortion of the $B(C_6F_5)_3$ framework in forming a bond with the hydrogen of silane.

INTRODUCTION

Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$,[1,2] has been utilized not only as the co-catalyst in the metallocene-catalyzed polymerization of olefins[3] but also as the Lewis acid catalyst for organic reactions, such as the Aldol-type reaction of silyl enol ethers.[4−8] Recently, the combination of the Lewis acid and bulky Lewis bases, which is called the *frustrated Lewis pairs* (FLP), has attracted much attention since the metal-free hydrogen activation was reported.[9,10] Many theoretical studies have been made of the Lewis acidity of fluoroarylboranes[11] and of the role of the Lewis acid catalysts in olefin polymerizations[12] and in hydrogenation reactions.[13]

One of the organic reactions catalyzed by $B(C_6F_5)_3$ is hydrosilylation of a variety of carbonyl and imine compounds.[5a,b,14] Piers and co-workers reported the $B(C_6F_5)_3$-catalyzed reactions between hydrosilane and the aromatic aldehydes, ketones, and esters.[5a] They examined in detail the reaction mechanism and proposed that the role of the Lewis acid is not to activate the carbonyl or imine group but to activate the hydrogen of silane.[5b] That is, the proposed mechanism consists of three steps: (1) silane activation by the coordination of $B(C_6F_5)_3$, (2) the transfer of a silyl group to the carbonyl oxygen atom, and (3) hydride ion transfer from the Lewis acid to the carbonyl carbon atom (Scheme 1). The $B(C_6F_5)_3$-catalyzed reactions of carbonyl groups reported by Piers and co-workers was apparently an example of reactions catalyzed by FLP that became well-known later.[9,10,13] Yamamoto and co-workers also proposed the silane-activation mechanism for the $B(C_6F_5)_3$-catalyzed reduction of alcohols and ethers.[6a,b] Gevorgyan developed the hydrosilylation of olefins based on this mechanism.[6d] Recently, Oestreich examined $B(C_6F_5)_3$-catalyzed hydrosilylation of acetophenone by employing a silicon-stereogenic silane as a stereochemical probe and observed the Walden inversion that strongly suggests the S_N2 mechanism at Si (Scheme 1).[14] Enantioselective reactions with chiral Lewis acids have also been explored.[15] In the present study, we examine a model reaction system that consists of trimethylsilane and acetone to reveal how the silane is activated by $B(C_6F_5)_3$. We study also the system catalyzed by BF_3 to see whether or not the silane-activation mechanism is common in a variety of hydrosilylation of C═O bonds.



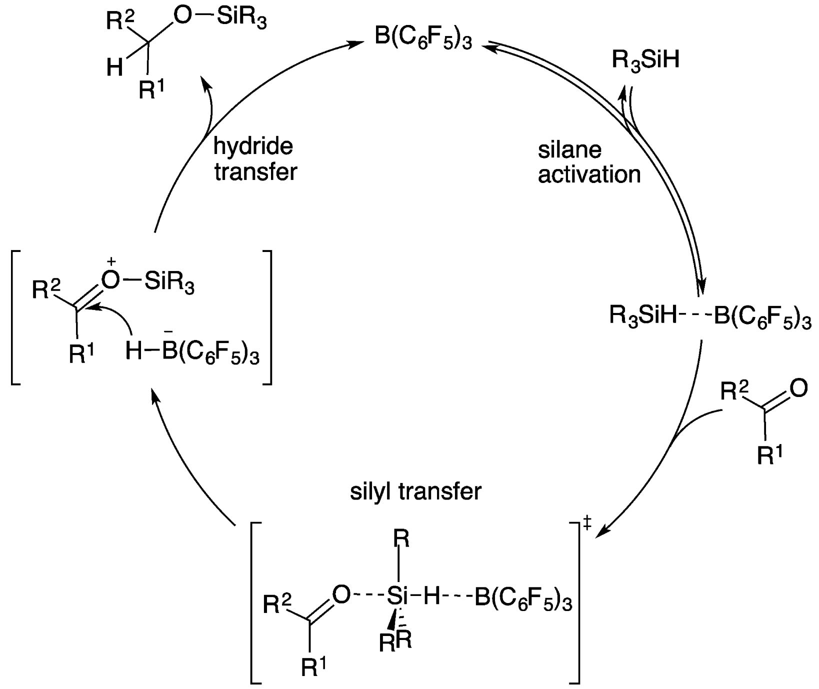
COMPUTATIONAL DETAILS

The quantum chemical calculations were carried out with the Gaussian 09[16] program package. Geometry optimization and analytical vibrational frequency analysis were performed by the M06-2X Kohn−Sham DFT

Received: October 2, 2013
Published: October 29, 2013

dx.doi.org/10.1021/jo402195x | *J. Org. Chem.* 2013, 78, 12505−12512

Scheme 1



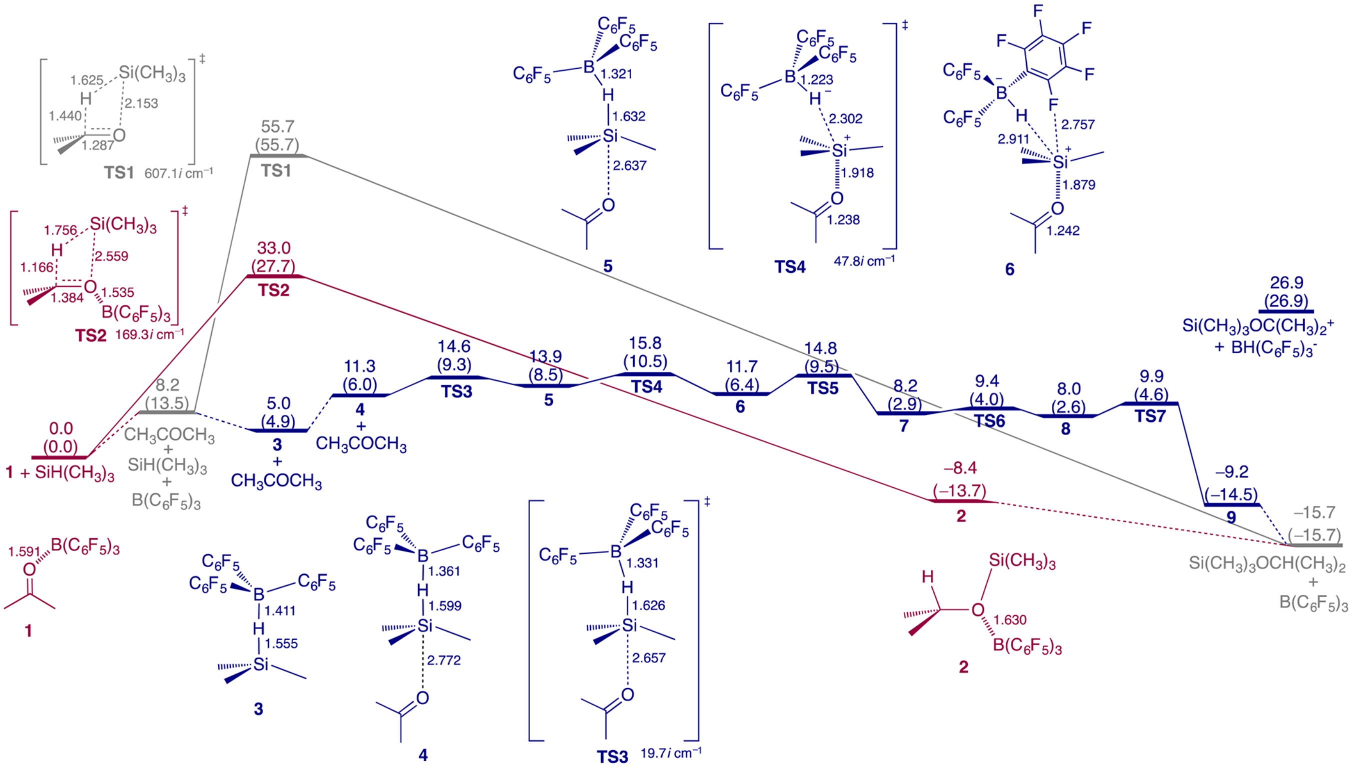


Figure 1. Gibbs free energy diagram at the M06-2X(PCM)/6-311++G**//M06-2X/6-311G** level of theory (kcal/mol) for hydrosilylation reaction catalyzed by $B(C_6F_5)_3$. Relative free energies with the translational entropy evaluated by the Whitesides method[22−24] are in parentheses.

method[16−19,10] with the 6-311G** basis set[20] (M06-2X/6-311G**). The solvent effects of toluene were estimated by the polarizable continuum model (PCM)[21] for the gas-phase optimized structures. For the PCM calculations, the M06-2X functional was used with the 6-311++G** basis set[20] (M06-2X(PCM)/6-311++G**//M06-2X/6-311G**). The free energy in solution was estimated by the PCM solvation free energy and the gas-phase thermal free energy. Since gas-phase calculations are known to overestimate the translational entropy in the solution, we evaluated the entropy of the $B(C_6F_5)_3$-catalyzed reactions by not only using the usual method but also applying the Whitesides method.[22−24]

■ RESULTS AND DISCUSSION

Carbonyl Activation in $B(C_6F_5)_3$-Catalyzed Reaction. We examine first the hydrosilylation reaction catalyzed by

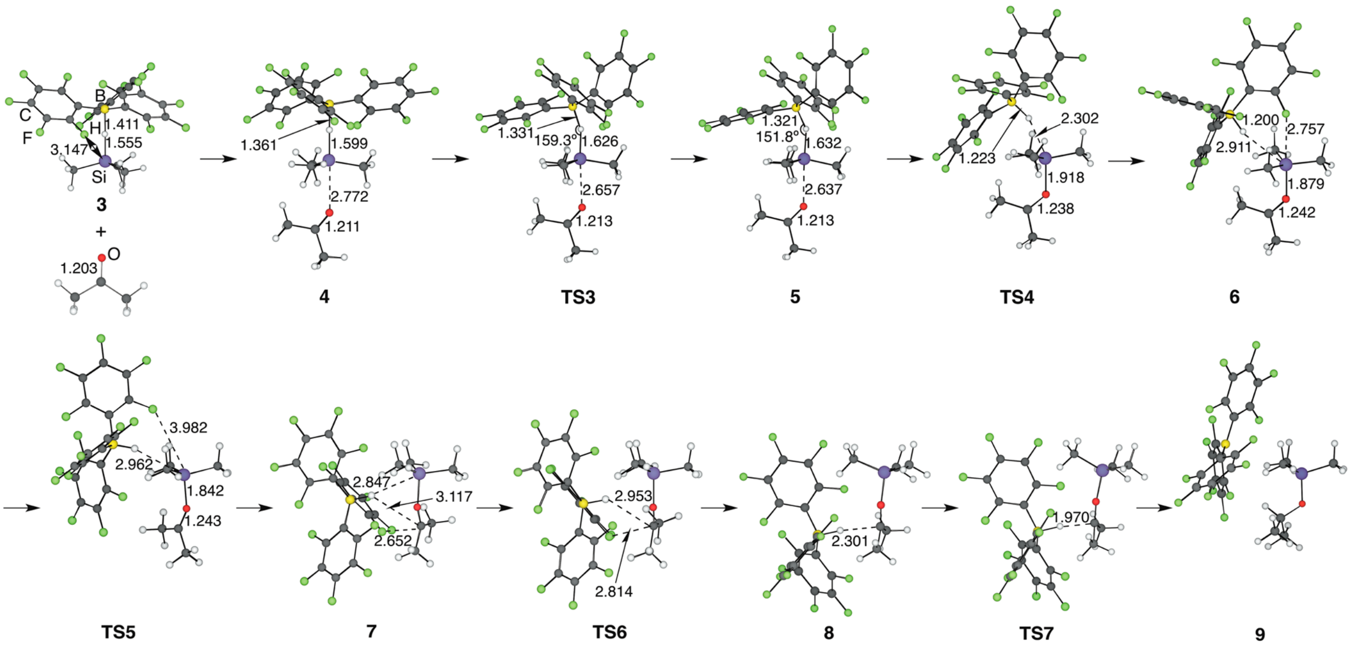


Figure 2. Structures for the silane-activation path at the M06-2X/6-311G** level of theory. Bond lengths are given in Å. The hydrogen atoms are colored in white, the boron atom in yellow, the carbon atoms in black, the oxygen atom in red, the fluorine atoms in green, and the silicon atom in purple.

$B(C_6F_5)_3$, assuming that the Lewis acid activates the carbonyl group of acetone.[25,26] The relative free energy diagram is shown in Figure 1. In the absence of $B(C_6F_5)_3$, the transition state, **TS1**, with a four-membered cyclic structure has been located on the potential surface. At the M06-2X(PCM)/6-311++G**//M06-2X/6-311G** level of theory, the activation free energy of **TS1** has been evaluated relatively high, 47.5 kcal/mol above the initial state that consists of trimethylsilane and acetone, and the reaction energy is exothermic, −23.9 kcal/mol.

In the presence of $B(C_6F_5)_3$, the Lewis acid was attached to the carbonyl oxygen atom of acetone. The free energy of the complex **1** is lower than that of the dissociated state of the two species, (acetone + $B(C_6F_5)_3$), by 8.2 kcal/mol. The attack of trimethylsilane to the C=O bond in the complex **1** gives the product complex **2** via **TS2**. The transition state also has a four-membered cyclic structure, and the activation free energy is calculated to be 33.0 kcal/mol, being considerably lower than that of **TS1**. This shows that $B(C_6F_5)_3$ can activate the carbonyl group toward trimethylsilane. The product complex **2** easily dissociates to give the product $Si(CH_3)_3OCH(CH_3)_2$ and $B(C_6F_5)_3$, reducing the repulsion between the bulky C_6F_5 groups in the latter.

In the path accompanied by the cleavage of a $B(C_6F_5)_2-C_6F_5$ bond in complex **1**, a six-membered cyclic transition state (**TS8**) is formed (see Figure S1 of the Supporting Information). The free energy of this transition state is calculated to be higher, however, than that of **TS2** by 6.4 kcal/mol. The mechanism involving the migration of a C_6F_5 group seems to be unfavorable in this system.[2d,27]

Silane Activation in $B(C_6F_5)_3$-Catalyzed Reaction. A silane-activation pathway was proposed by Piers.[5b] Although the complex between $B(C_6F_5)_3$ and silane molecules has not been observed experimentally,[28] some theoretical examinations have been reported.[2d,5b,29] Piers and co-workers studied complexes between $B(C_6F_5)_3$ and triphenylsilane or triethylsilane using the semiempirical MO AM1 method.[5b] They reported that the distance between the boron atom and the hydrogen atom, r(B−H), is 1.3938 and 1.3929 Å in the triphenylsilane and triethylsilane complexes, respectively. On the other hand, B3LYP level calculations showed that the interaction between triethylsilane or trimethylsilane and the Lewis acid is relatively weak, r(B−H) being 2.6−2.8 Å.[2d,29] In the present study, our M06-2X level calculations give the complex **3**, which shows a relatively strong interaction between $B(C_6F_5)_3$ and trimethylsilane.[30] The bond length between the silicon atom and the hydrogen atom, r(Si−H), and r(B−H) are 1.555 and 1.411 Å, respectively, and the Si−H−B bond arrangement is linear, as illustrated in Figure 2. The complexation free energy has been calculated to be 3.2 kcal/mol.

In line with the experimental results reported by Oestreich,[14a] let us examine here the attack of the carbonyl oxygen in acetone from the back side of the Si−H bond in trimethylsilane. In the reactant complex **4**, the distance between the silicon and the carbonyl oxygen is 2.772 Å, and r(B−H) has been shortened, 1.361 Å, while the r(Si−H) has been lengthened, 1.599 Å. The linear Si−H−B arrangement is retained also in **4**, but becomes bent at the transition state **TS3** to give another complex, **5**. Further approach of the carbonyl oxygen to the silicon atom gives the complex **6** via the transition state **TS4**. The Si−H bond is further lengthened, r(Si−H) being 2.302 Å in **TS4** and 2.911 Å in **6**. The free energies of these transition states, **TS3** and **TS4**, relative to the state (**1** + trimethylsilane) are 14.6 and 15.8 kcal/mol, respectively. They are much lower than that of **TS2** calculated above, assuming that the Lewis acid activates the carbonyl group. The hydrogen atom in silane is easily pulled away by $B(C_6F_5)_3$, carrying a negative charge, when the Si−H bond is pushed by acetone from the back side.[31]

The dissociation of the complex **6** into $Si(CH_3)_3OC(CH_3)_2^+$ and $BH(C_6F_5)_3^-$ requires 15.2 kcal/mol. The dissociated state ($Si(CH_3)_3OC(CH_3)_2^+$ + $BH(C_6F_5)_3^-$) is still lower in free energy than **TS2**, as shown in Figure 1. In the reacting system, the two ionic species are not likely to be separated, but should keep on interactions to yield the final product.[32] Actually, we have located a path involving three transition states, **TS5** (rotation of

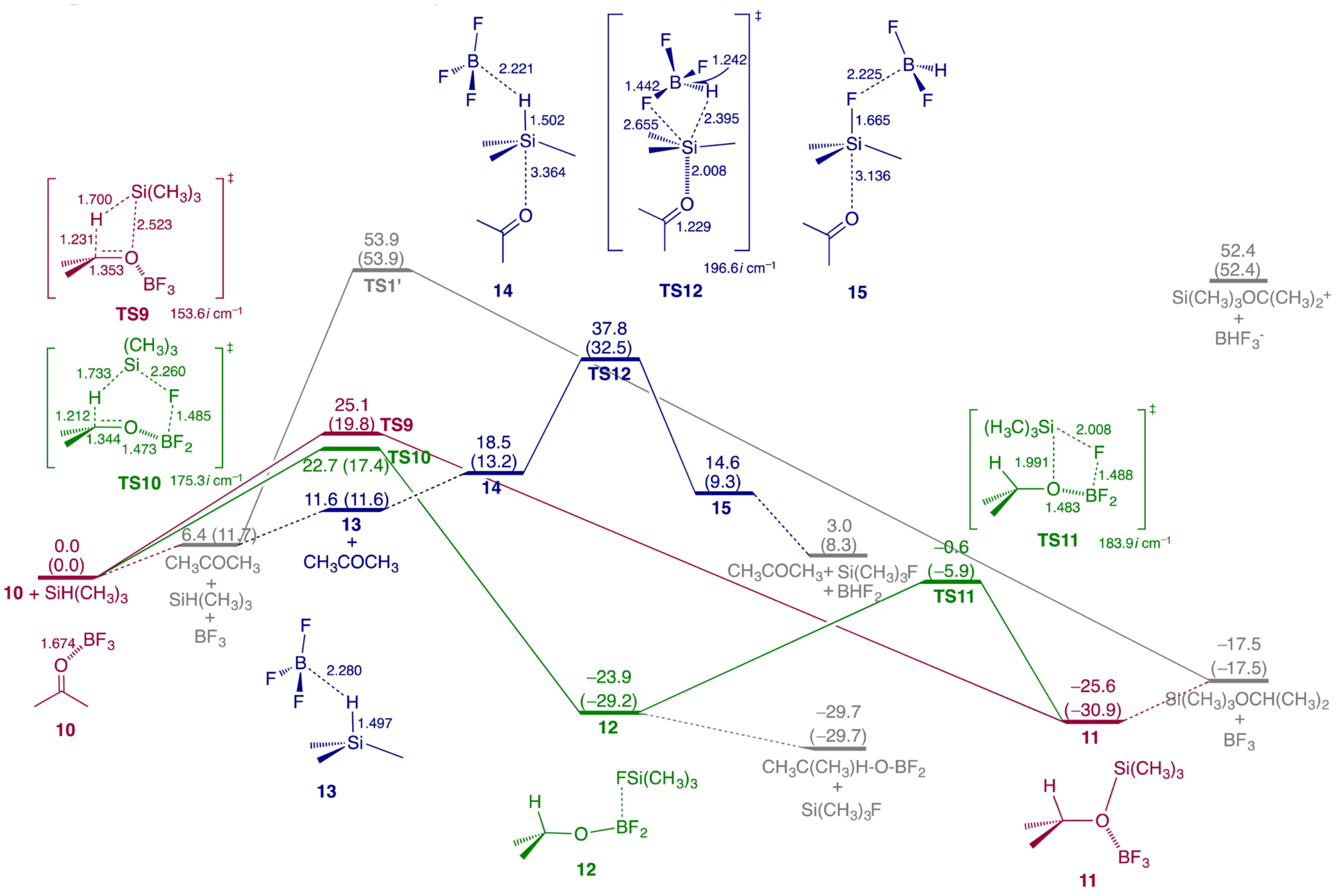


Figure 3. Gibbs free energy diagram at the M06-2X(PCM)/6-311++G**//M06-2X/6-311G** level of theory (kcal/mol) for the hydrosilylation reaction catalyzed by BF_3. Relative free energies with the translational entropy evaluated by the Whitesides method[22−24] are in parentheses. Note that **TS1′** corresponds to **TS1** in Figure 1, the free energy value of **TS1′** being given here relative to (**10** + trimethylsilane).

the acetone plane), **TS6** (transformation into another arrangement of the ion-pair complex), and **TS7** (hydride transfer), and three reaction intermediates, **7**, **8**, and **9** (see Figure S2 of the Supporting Information). All of them are lower in free energy than the dissociated state. Accordingly, the silane-activation pathway is preferred over the carbonyl-activation pathway, although the Lewis acid $B(C_6F_5)_3$ initially coordinates to the carbonyl oxygen atom to give the complex **1**. This complex may undergo a thermally induced frustration as proposed by Pápai and co-workers prior to interaction with trimethylsilane.[33]

Hydrosilylation Catalyzed by BF_3. To see whether or not silane activation is preferred in hydrosilylation reactions of the carbonyl group catalyzed by boron Lewis acids, we study next the reaction in the presence of BF_3 in place of $B(C_6F_5)_3$. Doyle and co-workers investigated organosilane reductions of aldehydes and ketones in the presence of $BF_3{\cdot}Et_2O$, suggesting the carbonyl-activation mechanism.[25a]

The relative free energy diagram is shown in Figure 3. In the path via a four-membered cyclic transition state, **TS9**, which corresponds to **TS2** in the reaction catalyzed by $B(C_6F_5)_3$, the activation energy is calculated to be 25.1 kcal/mol, which is much lower than that of **TS2**. Furthermore, we have observed another carbonyl-activation path that goes through a six-membered cyclic transition state, **TS10**, involving a boron and a fluorine within the ring. The barrier height for this path is even lower in free energy than the path that goes through **TS9** by 2.4 kcal/mol. A B−F bond is loosened in this lowest-energy path.

On the contrary, the interaction between trimethylsilane and BF_3 is not so strong as that between trimethylsilane and $B(C_6F_5)_3$, r(B−H) being as long as 2.280 Å. We found the transition-state structure, **TS12**, which corresponds to **TS4** in the reaction catalyzed by $B(C_6F_5)_3$. However, **TS12** connects in this case to a complex, **15**, in which the hydrogen atom in silane is replaced by one of the fluorine atoms in BF_3, as illustrated in Figure 3. The free energy of **TS12** is much higher than those of **TS9** and **TS10**. The state $(Si(CH_3)_3OC(CH_3)_2^+ + BHF_3^-)$ is also very high in free energy, 52.4 kcal/mol, relative to the state (**10** + trimethylsilane). Thus, silane activation is unlikely in the BF_3-catalyzed reactions. It appears to be rather specific to the $B(C_6F_5)_3$-catalyzed cases.

The calculations show that one of the reasons why silane activation is preferred over carbonyl activation in $B(C_6F_5)_3$-catalyzed reactions is the lower reactivity of B−C bonds. One of the B−F bonds is loosened in the most favorable pathway of the BF_3-catalyzed reaction, whereas the cleavage of a B−C bond in $B(C_6F_5)_3$ costs a larger amount of energy. Let us try to find other reasons why silane activation is favored in the $B(C_6F_5)_3$-catalyzed reaction.

Electron-Acceptor Strength of B. The results of calculations obtained above are in agreement with the experimental findings reported so far. Then, for a better understanding of FLP-catalysis that is of use in organic syntheses, it is important to investigate characteristics of the $B(C_6F_5)_3$-catalyzed reaction. We begin by estimating the Lewis acidity of the boron center in $B(C_6F_5)_3$. Park observed the NMR chemical shift of trimethylamine adducts of Lewis acids and suggested that the electron-accepting strength of $B(C_6F_5)_3$ is almost the same as that of BF_3.[1b] Later, many experimental and theoretical studies of Lewis acidity in $B(C_6F_5)_3$ have been reported.[11,34] Let us look at here electrophilicity of the boron center in several Lewis acids, comparing with that in the smallest boron compound BH_3 as a reference.[35] In electron delocalization from the donor species to BH_3 at an early stage of interaction, the lowest unoccupied (LU) MO (Kohn−Sham orbital) plays a dominant part. The LUMO is located at −0.83 eV at the M06-2X/6-311G** level. We projected then the boron components in the LUMO of BH_3, δ_r, onto the unoccupied orbitals of other boron compounds in an isolated state to generate the orbital in each of them that is closest in character to the LUMO of BH_3.[35] The energy expectation value of the orbital, $\lambda_{\mathrm{unoc}}(\delta_r)$, is presented in Table 1. It is −0.50 eV in $B(C_6F_5)_3$, being considerably lower than those in BF_3 and BCl_3, +2.44 and +0.70 eV, respectively. This result implies that the electrophilicity of boron in $B(C_6F_5)_3$ is significantly stronger than those in BF_3 and BCl_3. It is −0.70 eV in $B(C_6Cl_5)_3$, indicating that the boron in $B(C_6Cl_5)_3$ has an electrophilicity similar to or even stronger than that in $B(C_6F_5)_3$. The electrophilicity of boron centers appears to correlate neither with the Mulliken charge[36] nor with the natural population analysis (NPA) charge[37] on B in these cases.

Table 1. Electrophilicity of Lewis Acids at the M06-2X/6-311G Level of Theory**

	BF_3	BCl_3	$B(C_6H_5)_3$	$B(C_6F_5)_3$	$B(C_6Cl_5)_3$
electron-accepting level $\lambda_{\mathrm{unoc}}(\delta_r)$[a]	+2.44	+0.70	+1.25	−0.50	−0.70
Mulliken charge on B	+0.531	+0.225	+0.665	+0.832	+0.467
NPA charge on B	+1.422	+0.390	+0.929	+0.887	+1.190

[a] In eV.

We have calculated the dissociation energies of the complexes between these Lewis acids and some donor molecules (see Table S2 of the Supporting Information). In the adducts with NH_3, the dissociation energy is calculated to be 39.7 kcal/mol in $B(C_6F_5)_3$, which is larger than that in BF_3, 27.7 kcal/mol, and in BCl_3, 33.9 kcal/mol, at the M06-2X/6-311G** level of theory. This result is reasoned in terms of the difference in electrophilicity of B presented in Table 1. On the contrary, the dissociation energy of the adduct between trimethylamine and $B(C_6F_5)_3$, 28.5 kcal/mol, is smaller than those of the adducts of trimethylamine with BF_3 and BCl_3, 37.8 and 39.6 kcal/mol. The deformation in the $B(C_6F_5)_3$ part that is brought about by the attachment of $N(CH_3)_3$ makes the adduct less stable and easier to dissociate, relative to the BF_3 and BCl_3 adducts. The acid makes a strong bond with H^-, as already reported by Frenking and co-workers.[11a] The stronger Lewis acidity of the boron center toward the H−Si bond as compared with that in BF_3 must be the key factor that makes the silane-activation mechanism prevail in $B(C_6F_5)_3$-catalyzed hydrosilylation. The coordination to the carbonyl group of acetone, on the other hand, makes $B(C_6F_5)_3$ deform to lessen the strong overlap repulsion from the lone pairs of electrons and the π electrons on oxygen. In $B(C_6Cl_5)_3$, which has recently been synthesized,[38] the boron center has an electrophilicity similar to or even higher than that in $B(C_6F_5)_3$, as indicated in Table 1. A large amount of energy is needed, however, to deform $B(C_6Cl_5)_3$ in forming the adduct with Lewis bases. In fact, the calculations indicate that the adduct with NH_3 is less stable than the adduct between $B(C_6F_5)_3$ and NH_3 and that $B(C_6Cl_5)_3$ does not give an adduct with $N(CH_3)_3$.

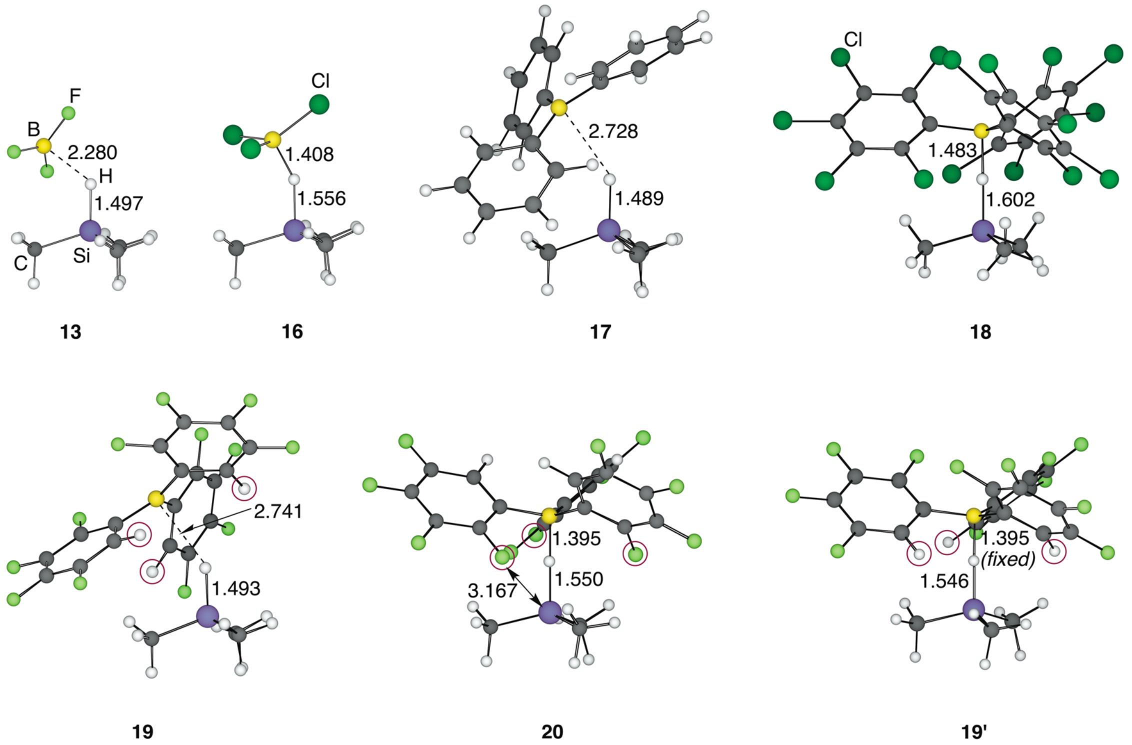


Figure 4. Structures of complexes between boron Lewis acids and trimethylsilane at the M06-2X/6-311G** level of theory. Bond lengths are given in Å. The hydrogen atoms are colored in white, the boron atom in yellow, the carbon atoms in black, the fluorine atoms in green, the silicon atom in purple, and the chlorine atoms in dark green.

An analysis using the interaction frontier orbitals (IFOs)[39] showed that a pair of orbitals, (ϕ'_1; ψ'_1) is crucial in electron delocalization from the acetone fragment to the (trimethylsilane·$B(C_6F_5)_3$) complex fragment in complex **4** (see Figure S3 of the Supporting Information). The orbital ϕ'_1 is given by a linear combination of the occupied Kohn−Sham orbitals of the acetone part, appearing to be one of the lone-pair orbitals of the carbonyl oxygen. The orbital ψ'_1, which consists of the unoccupied orbitals of the $B(C_6F_5)_3$-coordinated trimethylsilane part, shows a large amplitude on the back side of the Si−H bond and is *out-of-phase* between the Si atom and the H atom. The orbitals ϕ'_1 and ψ'_1 are located at −11.53 and +0.61 eV, respectively.

When $B(C_6F_5)_3$ is removed with the geometry of the remaining system frozen to the same as that in complex **4**, a pair of orbitals, (ϕ''_1; ψ''_1), are obtained that look very much the same as (ϕ'_1; ψ'_1). This means that electron delocalization from acetone to silane is not altered in nature in the absence and presence of the Lewis acid. The electron-accepting orbital, ψ''_1, is elevated, however, to +2.28 eV, while the electron-donating orbital, ϕ''_1, remains almost the same in energy level, −11.46 eV. The strong electrophilicity of $B(C_6F_5)_3$ in an isolated state has been transferred to the reactive orbital of silane, and consequently, electron delocalization from acetone to silane is strengthened. Formation of the Si−O bond and cleavage of the Si−H bond have thus been accelerated.

Subsidiary Attractions. Complex **3** has been shown above to be one of the key intermediates in the silane-activation mechanism. The Lewis acid that has a lower electron-accepting ability, i.e, an electron-accepting orbital placed at a higher energy, BF_3 or $B(C_6H_5)_3$ in Table 1, gives a loose complex, **13** or **17**, with trimethylsilane in which r(B−H) is 2.280 and 2.728 Å, respectively, as shown in Figure 4. On the other hand, a Lewis acid having a higher electrophilicity yields the adduct in which the B−H length is relatively short, 1.408 Å in **16** and 1.483 Å in **18**. Let us replace here one of the *ortho*-fluorine atoms in each C_6F_5 group in $B(C_6F_5)_3$ by a hydrogen atom to give B(*o*-$HC_6F_4)_3$.[40] Then, two structures, **19** and **20**, are possible for the complex with silane. The *ortho*-H atoms come on the opposite side of silane in **20**, while the *ortho*-H atoms stay on the same side of trimethylsilane in **19**. The r(B−H) in **19** is 2.741 Å, whereas that in **20** is much shorter, 1.395 Å. To see where this difference comes from, we examined an imaginary complex structure, **19′**, in which the r(B−H) is shortened to 1.395 Å in **19**, relaxing other structural parameters in the two fragments. Although the deformation energy (*DEF*) of **19′** is almost the same as that of **20**, the interaction energy (*INT*) of **19′** was found to be much smaller than that of **20** in absolute value (see Table S4 of the Supporting Information). The electron-accepting energy level of the boron center in the fragment B(*o*-$HC_6F_4)_3$ in **19′** is higher than that in **20**, but only by a small margin. The orbital analysis indicates that weak, but direct, interactions between the fluorine atoms at the *ortho*-positions in the HC_6F_4 substituent and the Si center in silane molecule are the source of the difference in r(B−H) in **19** and in **20**. Attractive interactions between *ortho*-fluorines of the C_6F_5 substituents and silane should stabilize **3** presented in Figure1. The attractions amount to ca. 14 kcal/mol. This is considerable to make up for the deformation energy of the reactants to favor the silane-activation mechanism.

CONCLUSION

We have examined the hydrosilylation reaction of the carbonyl group in acetone catalyzed by $B(C_6F_5)_3$ and by BF_3, applying the M06-2X DFT method. In the BF_3-catalyzed reaction, the Lewis acid coordinates to the carbonyl oxygen of acetone. An attack of trimethylsilane to the C═O bond leads to a four-membered cyclic transition state to complete the conventional carbonyl-activation mechanism. This path does not encounter a high-energy barrier. The calculations show that another path via a six-membered cyclic transition state in which a B−F bond has inserted into the O−Si bond of the four-membered cyclic transition state shows even a lower barrier height. These two have much lower activation free energies than that for the path with silane activation. These results are in agreement with the experiments reported by Doyle.[25a] In clear contrast, the calculations located a stable complex between $B(C_6F_5)_3$ and trimethylsilane in which the boron species abstracts very easily the hydrogen atom of silane in cooperation with the back-side attack of acetone. The activation of silane is preferred in the $B(C_6F_5)_3$-catalyzed reaction to the path that involves carbonyl activation via a four-membered cyclic transition state. The six-membered cyclic transition state is much higher in free energy. The B−C bonds tend to remain unloosened in the $B(C_6F_5)_3$-catalyzed reaction. This contrasting result is in line with the mechanism of the $B(C_6F_5)_3$-catalyzed reaction proposed by Piers.[5b]

The present analysis demonstrates that the major reason for the difference in mechanism between the $B(C_6F_5)_3$- and BF_3-catalyzed reactions is the electrophilic nature of the boron center that has turned out to be much stronger in $B(C_6F_5)_3$ than in BF_3. The former interacts more strongly with small electron-donating species than the latter does. Thus, the hydride-ion abstraction, the key step of the silane-activation mechanism, should be facilitated in the $B(C_6F_5)_3$-catalyzed hydrosilylation reaction. It has also been shown that there arise attractive interactions between some *ortho*-fluorine atoms in $B(C_6F_5)_3$ and the trimethylsilane part. The attractions cover whole or some part of the energy that is required to deform $B(C_6F_5)_3$ along the reaction path. This should also make the silane-activation mechanism preferable in the $B(C_6F_5)_3$-catalyzed hydrosilylation. The calculations suggest that $B(C_6Cl_5)_3$ shows an electrophilicity similar to or larger than that of $B(C_6F_5)_3$, but its stronger structural resistance against the deformation in giving an adduct with trimethylsilane will make $B(C_6Cl_5)_3$ less usable as a catalyst in the hydrosilylation reaction.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables listing energies, geometries, and dissociation energies, and figures of interaction frontier orbitals. 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.
§H. F. is an Emeritus Professor.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Advanced Molecular Transformations by Organocatalysts” from The Ministry of Education, Culture, Sports, Science and Technology (Japan). Some of the calculations were made at the Research Center for Computational Science, Okazaki, Japan. K. S. is grateful to the Center for generous permission to use its computing facilities.

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(32) The relative free energy of the dissociated state, ($Si(CH_3)_3OC(CH_3)_2^+$ + $BH(C_6F_5)_3^-$), depends on the contribution from the translational entropy term. Involving the entropy term evaluated by the Whitesides method, the dissociated state is comparable to **TS2** in free energy.

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