Possible Nitrogen Fixation by Disilabutadiene

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Received July 1, 1997[⊗]

A possible nitrogen fixation based on a Diels−Alder reaction of 1,4-disila-1,3-butadiene and N_2 is discussed. The activation energy from the reactants to the product, a six-membered ring of $C_2Si_2N_2$, was computed to be only 5.1 kcal/mol at the B3LYP/6-311G** level of density functional theory. QCISD(T)/6-31G**//CASSCF/6-31G** calculations also gave 8.0 kcal/mol comparable to the B3LYP value. These computed activation energies are smaller than that of the well-known Diels−Alder reaction of butadiene and ethylene, 24.8 kcal/mol at the B3LYP/6-31G* level (Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036), and consequently, this unique reaction would proceed under mild conditions if this reactive species, disilabutadiene, is prepared. The triple bond of N_2 is partially cleaved in a reductive manner to lead to the formation of an N=N double bond. Orbital interaction analyses suggest that one of the degenerate π^* LUMOs of N_2 has a good interaction with the high-lying HOMO of disilabutadiene, and this interaction should contribute to significant electron transfer from disilabutadiene to N_2. 1,4-Disila-1,3-butadiene, could be prepared by thermal ring opening of 1,2-disilacyclobutene; the activation barrier for a symmetry-allowed conrotatory process of the two silylene groups was calculated to be 40.9 kcal/mol at the B3LYP/6-311G** level and 47.6 kcal/mol at the QCISD(T)/6-31G**//CASSCF/6-31G** level. We, thus, expect the artificial nitrogen fixation to occur when 1,2-disilacyclobutene and N_2 gas are heat-treated in a sealed tube.

Introduction

Dinitrogen (N_2) is activated and converted into ammonia in biological systems under physiological conditions. N_2-fixing enzymes in general contain transition metals such as Fe, Mo, and V at their catalytically active centers.[1] Toward the development of synthetic N_2-fixing systems, extensive research has been made on model complexes that bind N_2 as a ligand and can convert it to nitrogenous compounds.[2] Many N_2 complexes have been prepared and characterized so far, usually terminal end-on bonding between a single metal active center and an N_2 ligand, as represented by an M−N≡N linkage. The NN distance in this binding mode remains almost unchanged from that of free N_2, due to little electron transfer. Linear μ-η^1:η^1-N_2 complexes with an M−N−N−M linkage are also available; such complexes can be formally classified into those containing $(N{\equiv}N)^0$, $(N{=}N)^{2-}$, and $(N{-}N)^{4-}$ ligands.[2a] The NN distances in these complexes significantly depend on the atomic charge of N. Cummins and co-workers[3] recently showed a reductive cleavage of N_2 by a three-coordinate Mo(III) complex to provide a terminal nitride Mo complex. Moreover, samarium complexes with a side-on μ-η^2:η^2-N_2 mode were synthesized.[4,5]

Silicon and carbon are strikingly different, in spite of their similarities in electronic structure:[6] an Si=Si double bond is usually unstable in contrast to a C=C double bond. Graphite, which consists of honeycomb hexagons formed by three sp^2 hybridized orbitals of carbon, is the most stable carbon allotrope, but there is no such planar network in silicon. Barton and co-workers[7] recently examined thermal isomerization of olefins to carbenes via a [1,2]-silyl shift, which does not occur in all-carbon systems, both experimentally and theoretically. Recent ab initio calculations[8] showed that the [1,3]-sigmatropic silyl shift in allylsilane proceeds in a way that is very different from the corresponding methyl shift in 1-butene. We now have numerous examples of π-bonded silicon compounds including Si=C, Si=N, and Si=Si double bonds. These structures are highly reactive and used as reagents and reaction intermediates for organic synthesis. Organosilicon reagents have recently become major tools in organic synthesis,[6] but the reactivity of organosilicon compounds is not understood in detail. The chemistry of disilabutadiene, which is generated by pyrolysis of the corresponding disilacyclobutene,[9,10] has been an interesting subject due to its high reactivity as a transient reaction species. From this intermediate many [4 + 1],

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[†] Kyoto University
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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

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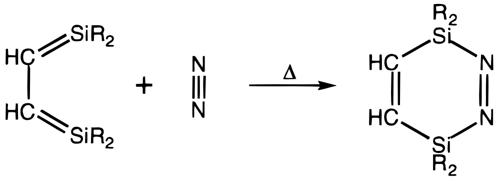
S0276-7333(97)00553-0 CCC: $14.00

Scheme 1



[4 + 2], and [4 + 4] cycloadditions have been observed by Ishikawa and colloborators.[10]

In this paper, we predict from high-level density-functional and configuration-interaction (CI) computations that 1,4-disila-1,3-butadiene, including two Si=C bonds, should react with N_2 to form a six-membered ring with a bent $Si_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ mode, as shown below in Scheme 1, just like the well-known Diels−Alder reaction of butadiene and ethylene. The partial cleavage of the triple bond of N_2 is likely to be chemically significant from the viewpoint of nitrogen fixation by a synthetic system.

Method of Calculation

We computed a concerted reaction pathway for a possible Diels−Alder reaction of 1,4-disila-1,3-butadiene and N_2. Detailed analyses for the reactants, product, transition state (TS), and intrinsic reaction coordinate (IRC)[11] of the unique N_2-fixing reaction were carried out using a hybrid Hartree−Fock/density-functional-theory (HF/DFT) method (the so-called B3LYP method).[12,13] This method consists of the nonlocal exchange functional of Becke's three-parameter set[12] and the nonlocal correlation functional of Lee, Yang, and Parr.[13] It has been successfully applied to the Diels−Alder reaction of butadiene and ethylene, giving structures and energetics reasonably well.[14] We performed geometry optimizations and IRC analyses with the 6-311G**[15] and 6-31G**[16] basis sets, respectively. Vibrational mode analyses were systematically carried out to confirm that on a potential-energy surface all optimized geometries correspond to a local minimum that has all real frequencies or a saddle point that has only one imaginary frequency. Corrections of the zero-point vibrational energies were taken into account in calculating total energies. In order to support B3LYP calculational results, we performed geometry optimizations with the CASSCF[17] method, followed by QCISD(T)[18] single-point calculations. The B3LYP and QCISD(T)//CASSCF methods are suggested to yield a comparable activation energy that is consistent with the experimental value.[14] We carried out fragment molecular orbital (FMO) analyses using the extended Hückel method[19] in the vicinity of the TS to look at significant electron transfer from Si to N atoms and the governing orbital interactions. This approximate molecular orbital method models general orbital energy trends, orbital interactions, and major charge shifts well. In this study, Gaussian 94[20] and YAeHMOP[21] were used.

Diels−Alder Reaction of Disilabutadiene and Dinitrogen

First, we show, Figure 1, the geometries of the reactant (1,4-disila-1,3-butadiene), final product, and TS connecting the reactants and product, optimized at the B3LYP/6-311G** level of theory. The NN distance of free N_2 was also optimized to be 1.095 Å. We can see that the NN distance of 1.247 Å in the product lies in the range of N=N double bond distances.[20,22] The CC distance of 1.434 Å in the reactant changes to 1.349 Å in the product, an appropriate value for a C=C double bond distance. Moreover, the CSi distance of 1.740 Å in the reactant increases to 1.873 Å in the product. One can expect that such significant bond-length changes should reasonably occur in a Diels−Alder reaction. In the TS on the concerted pathway, which has C_s symmetry, the SiN bond of 2.474 Å that is being formed is 1.4 times as long as that of 1.826 Å in the product, which is typical for a TS structure. The transition vector indicated in the TS structure in Figure 1 ensures that this TS correctly connects the reactants and the final product.

One of the most interesting changes along the reaction pathway is, of course, the conversion of the N≡N triple bond of N_2 to an N=N double bond. Since the primary energetic barrier to N_2 activation is, in general, its strong triple bond and that subsequent reduction of the double and single bonds is relatively easy, the partial cleavage of the triple bond occurring in this Diels−Alder reaction is chemically significant, we think. The changes in the NN and CC distances along the IRC carried out at the B3LYP/6-31G** level are shown in Figure 2. The geometries optimized at the B3LYP/6-31G** and 6-311G** levels had essentially no differences: bond distances at the 6-311G** level were only 0.001−0.004 Å shorter. Starting from the reactants (theoretically, $s = -\infty$), the NN distance slowly increases and after passing the TS ($s = 0$) it starts to significantly increase. In fact, the NN distance of 1.130 Å in the TS (Figure 1) is only 0.035 Å longer than that of free N_2, but the difference between the NN distances of the TS and product is 0.117 Å. In contrast, the CC distance is gradually shortened along the reaction coordinate, leading to the formation of a C=C double bond.

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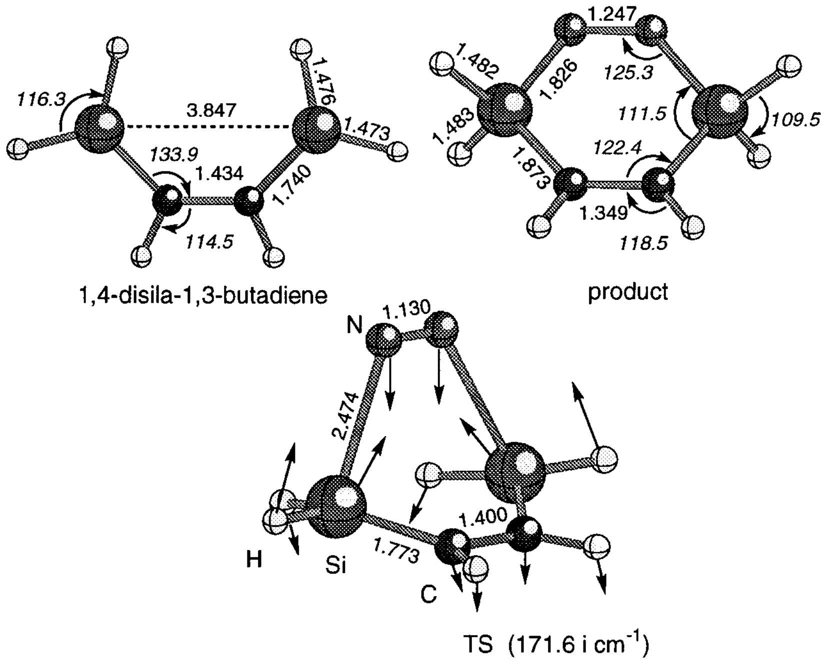

Figure 1. Optimized geometries of the reactant, product, and transition state (TS) for a Diels–Alder reaction, $C_2H_6Si_2 + N_2 \rightarrow C_2H_6N_2Si_2$, at the B3LYP/6-311G** level. The arrows in the TS indicate the transition vector.

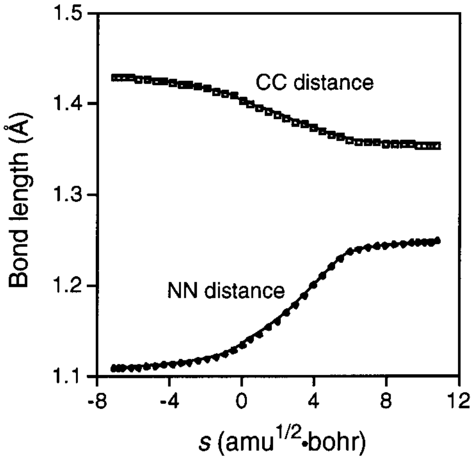

Figure 2. NN and CC distance changes along the intrinsic reaction coordinate (IRC) for a Diels–Alder reaction, $C_2H_6Si_2 + N_2 \rightarrow C_2H_6N_2Si_2$, at the B3LYP/6-31G** level. s is the length of the IRC; $s = 0$, the transition state.

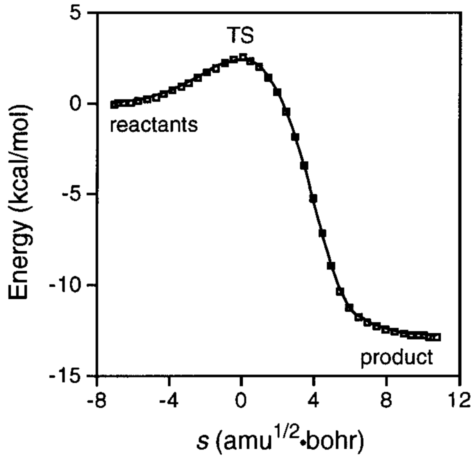

Figure 3. Energy profile along the intrinsic reaction coordinate for a Diels–Alder reaction, $C_2H_6Si_2 + N_2 \rightarrow C_2H_6N_2Si_2$, at the B3LYP/6-31G** level.

In Figure 3 the energy profile of this Diels–Alder reaction along the IRC at the B3LYP/6-31G** level is shown. Surprisingly, this reaction can proceed almost without any cost of activation energy. By zero-point-energy corrections, the activation energy was computed to be only 5.1 kcal/mol at the B3LYP/6-311G** level and 3.3 kcal/mol at the B3LYP/6-31G** level. This barrier height is much lower than 24.8 kcal/mol for that of the well-known Diels–Alder reaction of butadiene and ethylene at the B3LYP/6-31G* level.[14] Moreover, the reaction of disilabutadiene and N_2 was calculated to be 6.4 kcal/mol exothermic at the B3LYP/6-311G** level. Hybrid HF/DFT methods have been proposed to provide, in general, excellent descriptions of Diels–Alder[14] and other reaction profiles,[23] particularly in geometries, heats of reaction, and barrier heights. The B3LYP and QCISD(T)//CASSCF methods were suggested by Houk et al.[14] to yield comparable, excellent energetics for the barrier height of the chemical reaction. Although the CASSCF/6-31G** method[17] overestimated the barrier height to be 17.0 kcal/mol, QCISD(T)/6-31G**//CASSCF/6-31G** calculations[18] yielded 8.0 kcal/mol, comparable to the value by the B3LYP method. Therefore, this N_2-fixing reaction is likely to occur under mild conditions, judging from the computed low barrier height if we have this organosilicon compound in hand.

The atomic (Mulliken) charge of the N atom changes from 0 in the reactant to −0.27 in the product, and that of the Si atom changes from +0.23 to +0.58. It is quite clear from Table 1 that this significant electron transfer occurs directly from the Si to N atoms because the atomic charge of the C atom is nearly constant (−0.23 to −0.26) throughout the reaction pathway. This electron transfer is the main reason why the N≡N triple bond is partially cleaved in a reductive manner. For comparison, changes in atomic charge along the reaction pathway for a similar Diels–Alder reaction of disila-

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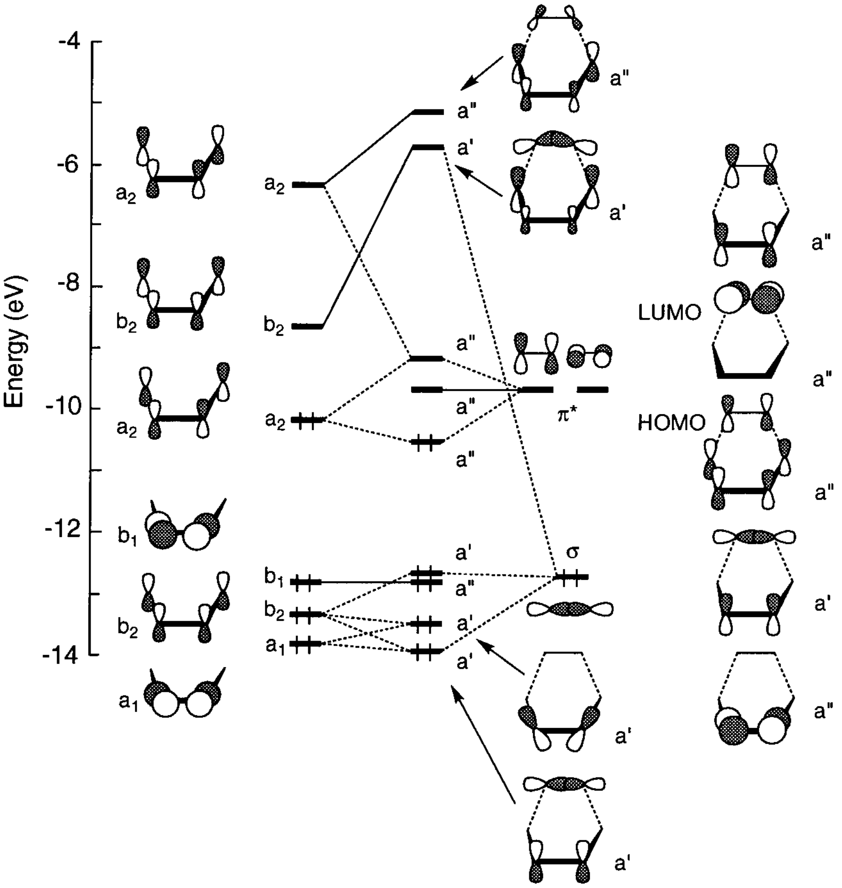

Figure 4. Orbital interaction diagram for the TS, partitioned into disilabutadiene and N_2 fragments, with the extended Hückel method.

Table 1. Atomic (Mulliken) Charges for the Reactants, TS, and Product along the Reaction Pathway for the Reaction of Disilabutadiene and N_2

atom	reactants	TS	product
C	−0.23	−0.24	−0.26
Si	0.23	0.34	0.58
N	0	−0.08	−0.27

Table 2. Atomic (Mulliken) Charges for the Reactants, TS, and Product along the Reaction Pathway for the Reaction of Disilabutadiene and Acetylene

atom or fragment	reactants	TS	product
C	−0.23	−0.22	−0.24
Si	0.23	0.22	0.48
CH(acetylene)	0	0.02	−0.14

butadiene and acetylene are listed in Table 2. The reactions of disilabutadienes and acetylenes occur[24−26] in a manner quite similar to the Diels−Alder reaction of butadiene and ethylene, but the activation energy is very small. Charge transfer is found to be larger in the reaction of disilabutadiene and N_2.

To understand the electron transfer and the governing orbital interactions, we performed an FMO analysis (based on the extended Hückel method) for the TS of this reaction. We partitioned the optimized geometry of the TS into disilabutadiene and N_2 fragments. Figure 4 shows that one of the degenerate π^* LUMOs of N_2 has a good interaction with the HOMO of disilabutadiene and greatly contributes to the HOMO of the TS structure. On the other hand, the counterpart of the π^* LUMO has no interaction with orbitals of the disilabutadiene fragment. If one of the π^* orbitals is occupied by a pair of electrons, the NN triple bond is reductively cleaved to lead to the formation of a double bond from a simple bond-order consideration. The a_2 HOMO and one of the π^* LUMOs are mixed in approximately equal weights and contribute to the formation of the a″ HOMO of the TS,[27] as seen in Figure 4. As the reaction proceeds, the contribution of one of the π^* LUMOs of N_2 to the HOMO of the united system becomes greater and greater and, therefore, the atomic charge of N becomes larger and larger in negative charge. As a consequence, the NN triple bond is partially cleaved in a reductive manner in the final stage of the reaction.

As shown in Figure 4, the HOMO (a_2) of the disilabutadiene fragment is high-lying at −10.2 eV and, accordingly, the energy difference between the a_2 HOMO and π^* LUMO of the N_2 fragment is very small (∼0.5 eV). This situation is favorable for the interactions between the two orbitals from second-order perturbation theory viewpoint. For comparison, we carried out an FMO analysis for the TS of a hypothetical Diels−Alder reaction of butadiene and N_2 (not shown here). The a_2 HOMO of the butadiene fragment lies at −12.1 eV, and consequently, the electron-donating ability of butadiene

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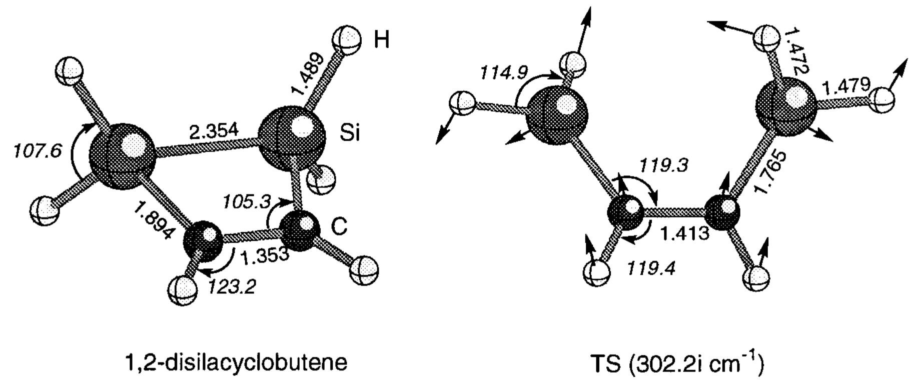

1,2-disilacyclobutene TS (302.2i cm^{-1})

Figure 5. Optimized structure of 1,2-disilacyclobutene and TS toward 1,4-disila-1,3-butadiene at the B3LYP/6-311G** level. The arrows in the TS indicate the transition vector.

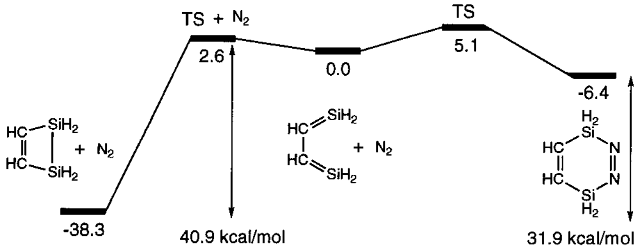

Figure 6. Potential-energy diagram for the entire reaction pathway at the B3LYP/6-311G** level. Values are in units of kcal/mol.

is much weaker than that of disilabutadiene. Therefore, the high reactivity of disilabutadiene is derived mainly from its high-lying HOMO that ensures strong electron-donating ability.

The σ HOMO of the N_2 fragment also interacts with some orbitals of the disilabutadiene fragment, as shown in Figure 4. In particular, the interaction between the σ HOMO of N_2 and the LUMO (b_2) of disilabutadiene could lead to back-donation of an electron from N_2 to disilabutadiene, but it is not important compared with the electron transfer from disilabutadiene to N_2 because the energy difference between the two orbitals is quite large. As mentioned above, the interaction between the HOMO of disilabutadiene and the π^* LUMO of N_2 plays an essential role in the reductive cleavage of the triple bond of N_2 in this possible N_2-fixing reaction.

We will finally discuss how we prepare such a highly reactive silicon species, disilabutadiene. 1,4-Disila-1,3-butadienes can be generally formed by thermal ring opening of 1,2-disilacyclobutenes.[26] We, thus, calculated 1,2-disilacyclobutene at the B3LYP/6-311G** level; the optimized geometry is shown in Figure 5. The CC bond of 1,2-disilacyclobutene is 1.353 Å in length, and it is clearly a double bond. This species lies 38.3 kcal/mol below disilabutadiene, so that the ring opening is a quite important step for the possible nitrogen fixation discussed above. The TS connecting 1,2-disilacyclobutene and 1,4-disila-1,3-butadiene is also shown in Figure 5. The transition vector indicated in the TS structure exhibits a conrotatory process of the two silylene groups. It is theoretically clear that the conrotation of the two silylene groups should lead to the symmetry-allowed TS (with C_2 symmetry) toward 1,4-disila-1,3-butadiene.[27]

In Figure 6, we show the potential-energy diagram for the entire reaction pathway. The activation energy for the ring opening of 1,2-disilacyclobutene was calculated to be 40.9 kcal/mol at the B3LYP/6-311G** level and 47.6 kcal/mol at the QCISD(T)/6-31G**//CASSCF/6-31G** level. Such a ring opening was observed by Ishikawa et al.[10] to occur as a reactive intermediate: thermolysis of 3,4-dibenzo-1,1,2,2-tetraethyl-1,2-disilacyclobutene at 250 °C produces 1,2-bis(diethylsilylene)-cyclohexa-3,5-diene, *o*-quinodisilane. Thus, the ring opening of 1,2-disilacyclobutene is a highly probable process in the laboratory for generating disilabutadiene. The overall reaction was calculated to be endothermic by 31.9 kcal/mol, as shown in Figure 6. From the energy profile of the entire reaction pathway, highly reactive disilabutadiene can be viewed as a reaction intermediate. If this reactive species is formed from 1,2-disilacyclobutene, then the Diels–Alder reaction of disilabutadiene and N_2 is concluded to readily occur. We, thus, expect that the artificial nitrogen fixation should occur when 1,2-disilacyclobutene is heat-treated in a sealed tube filled with N_2 gas. The calculated barrier heights at the different levels of theory for both the ring opening of 1,2-disilacyclobutene and the Diels–Alder reaction of disilabutadiene and dinitrogen are summarized in Table 3.

Table 3. Calculated Activation Barriers (Δ*E*) for the Symmetry-Allowed Ring Opening of 1,2-Disilacyclobutene and the Diels–Alder Reaction of Disilabutadiene and Dinitrogen (units in kcal/mol)

method	Δ*E* (ring opening)	Δ*E* (Diels–Alder)
B3LYP/6-311G**	40.9	5.1
QCISD(T)/6-31G**//CASSCF/6-31G**	47.6	8.0

Summary and Conclusions

We have studied the concerted reaction pathway for a Diels–Alder reaction of 1,4-disila-1,3-butadiene and N_2 using the density-functional B3LYP and CI methods. The activation energy of this reaction was calculated to be 5.1 kcal/mol at the B3LYP/6-311G** level and 8.0 kcal/mol at the QCISD(T)/6-31G**//CASSCF/6-31G** level, and we, therefore, think that this reaction should reasonably occur under mild conditions. This value is much smaller than that of the well-known Diels–Alder reaction of butadiene and ethylene. The triple bond of N_2 is suggested to be partially cleaved in a reductive manner by this unique N_2-fixing reaction. Detailed IRC analyses suggest that the partial cleavage of the triple bond of N_2 occurs after passing the TS. Orbital-interaction analyses suggest that one of the π^* LUMOs of N_2 has a good interaction with the high-lying HOMO

Table 4. Extended Hückel Parameters for Si, C, N, and H Atoms[a]

orbital	H_{ii} (eV)	ζ
Si 3s	−17.30	1.383
Si 3p	−9.20	1.383
C 2s	−21.4	1.625
C 2p	−11.4	1.625
N 2s	−26.0	1.950
N 2p	−13.4	1.950
H 1s	−13.6	1.3

[a] H_{ii}, orbital energy; ζ, Slater exponent.

of disilabutadiene and that this interaction greatly contributes to the reductive cleavage of the triple bond of N_2, due to the significant electron transfer from disilabutadiene to N_2. The high reactivity of disilabutadiene is mainly due to its very high-lying HOMO, which is about 2 eV above the HOMO of butadiene. In order to prepare highly reactive disilabutadiene, thermal ring opening of 1,2-disilacyclobutene is possible in the laboratory. The activation energy for the ring opening, which is related to a symmetry-allowed conrotatory process of the two silylene groups, was calculated to be 40.9 kcal/mol at the B3LYP/6-311G** level and 47.6 kcal/mol at the QCISD(T)/6-31G**//CASSCF/6-31G** level, so that this unique Diels−Alder reaction is likely to occur when 1,2-disilacyclobutene and N_2 gas are heat treated in a sealed tube. We think that this reaction would be chemically significant as a first step of nitrogen fixation in a synthetic system if it is possible under mild conditions, as we expect.

Acknowledgment. We are grateful to a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan and to the Research for the Future Program from the Japan Society for the Promotion of Science (JSPS-RFTF96P00206) for their support of this work.

Appendix

Extended Hückel parameters used for Si, C, N, and H atoms appear in Table 4.

OM970553R