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SiH_3 Radical Mechanisms for Si–N Bond Formation

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Abstract: Ab initio quantum chemical calculations have been performed to elucidate the Si–N bond formation processes in the chemical vapor deposition (CVD) of silicon nitride Si_3N_4. Among the silicon reactive species likely to be present in the silicon CVD system, SiH_3 radical is found to be relatively stable with respect to other silicon reactive species, such as silylene. A two-step chain reaction mechanism, $H + SiH_4 \rightarrow H_2 + SiH_3$ plus $SiH_3 + NH_3 \rightarrow SiH_3NH_2 + H$, is suggested to be the most favorable reaction path for the Si–N bond formation. To form an Si–N bond in appreciable yield via this reaction pathway, the recombination of SiH_3 radicals must be slowed by keeping the SiH_3 concentration low. This is in effect achieved via the high NH_3/SiH_4 mixing ratio of about 12:1 in the actual CVD system.

Introduction

Silicon-based substances including ceramics, silicon carbide, and silicon nitride are outstanding examples of high-temperature structural materials. During the last decade, a fair amount of effort has been made toward improving the purity, range of particle sizes, etc. of such substances. In particular, the laser chemical vapor deposition technique (CVD) has become one of the ideal production methods for silicon-containing ceramics.[1-6]

In the application of the laser CVD process on silicon nitride, silane gas has been used as the silicon source, and ammonia gas as the nitrogen source. The dependency of the CVD process on external parameters such as pressure and temperature has been closely examined,[3-5] yet the mechanism for bond formation in this process remains unknown.

Many models have been presented for the silane CVD processes.[6-19] The bond dissociation of the silane Si–H bond is believed to be the initial step in the process. Silylene has been shown to be the initial product of silane decomposition.[7] The reactivity of silylene has been investigated and reported in the literature.[10-15] There is general agreement that silylene is quite reactive and that it is likely to rapidly undergo insertion,[12] $^1SiH_2 + SiH_4 \rightarrow SiH_3SiH_3$, and hydrogen abstraction reactions, $^3SiH_2 + SiH_4 \rightarrow 2SiH_3$, in the early stage of the CVD process.[16]

Recently, a high concentration of SiH_3 radicals in silane plasma has been observed by infrared diode laser absorption spectroscopy.[17,18] Other products such as SiH and SiH_2 species are likely to undergo rapid reaction with other species, thus leaving the relatively stabler SiH_3 radicals behind.[17] This observation provides some indication of the relative reactivity of these silyl species.

In this study, we have examined computationally some basic reactions of the SiH_3 radical. The SiH_3 radical appears relatively stable and somewhat unreactive except in the recombination reaction. In all cases, the reactions involving the SiH_3 radical are predicted to be endothermic. Other radical species can be converted into the SiH_3 radical with fairly low activation energies (E_a) via hydrogen abstraction from silane as will be discussed in a later section. Since the SiH_3 radical can be accumulated in relatively high concentrations without undergoing recombination, it may be regarded as the dominant reactive species in the CVD process rather than silylene. This appears to be in agreement with the experimental results.[17,18] Along this line, we suggest here a novel CVD mechanism with the SiH_3 radical as a key reactive species.

Computational Methods

Ab initio quantum chemical calculations were performed using GAUSSIAN 82[20a] and GAUSSIAN 86[20b] programs. Optimized structures at the stable state and at the transition state (TS) were determined via the energy gradient method[21] at the HF/6-31G* level.[22] As a characteri-

Table I. Energetics for Elementary Reactions in Kilocalories/Mole

reaction no.	reactants	products	E_a	ΔH	$\Delta H_{\rm exptl}$/ $\Delta H_{\rm BAC}$
1	[a]$SiH_4 + NH_3$	$SiH_3NH_2 + H_2$	55.4	−2.8	−6.4[h,i]/−5.5[j]
2	[b]SiH_4	$SiH_2 + H_2$	56.9	55.2	57.1[h,i]
3	[c]$SiH_2 + NH_3$	SiH_3NH_2	13.2	−60.0	−63.5[h,i]/−63.7[j]
4	[d]$SiH_2 + SiH_4$	SiH_3SiH_3	0.0	−54.5	−54.3[h]
5	[e]$SiH_2\ (^1A_1)$	$SiH_2\ (^3B_1)$	15.7	15.7	18.0 or 21.0[k]
6	[f]$^3SiH_2 + SiH_4$	$2SiH_3$	15.9	2.8	1.3 or −1.7[h,k]
7	[g]SiH_4	$SiH_3 + H$	91.6	91.6	90.3[h]
8	[g]NH_3	$NH_2 + H$	107.5	107.5	103.3[i]

[a] From ref 8 on the CISD+SCC/6-31G**//HF/6-31G* level. [b] From ref 19 on the MP4/MC-311++G//MP2/MC-311G level. [c] From ref 15 on the MP4/6-31G**//HF/6-31G* level. [d] From ref 12 on the MP3/6-31G*//HF/3-21G level. [e] From ref 19 on the MP2/6-311G(2d,2p)//MP2/MC-311G (2d,2p) level. [f] From ref 16 on the MP3/6-31G**//HF/3-21G level. [g] Present work on the CISD+SCC/6-31G**//HF/6-31G* level. [h] Experimental results from ref 29. [i] Experimental results from ref 28. [j] Empirically corrected theoretical value at BAC-MP4(SDTQ) level from ref 30. [k] Experimental results from ref 31.

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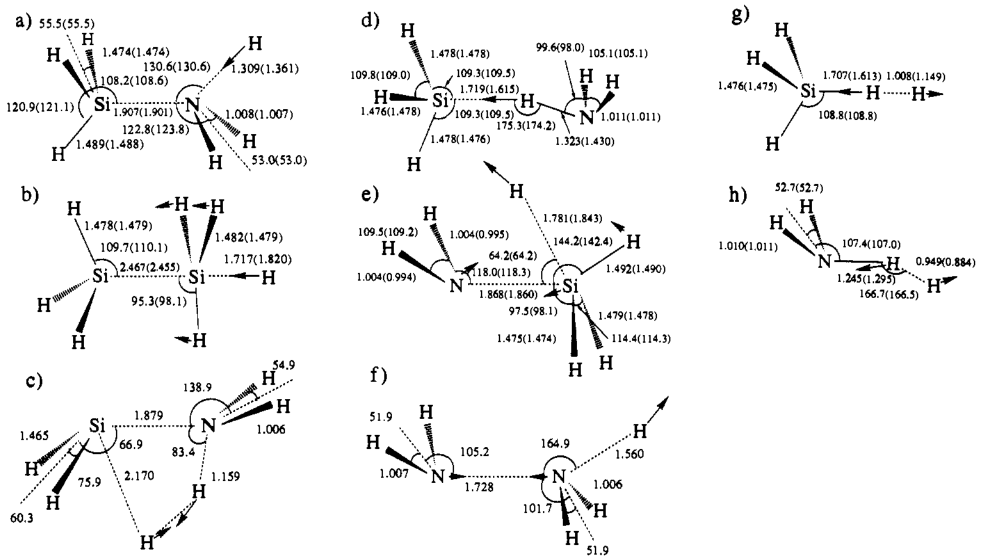

Figure 1. HF/6-31G* optimized geometries with transition vectors of (a) reaction 9 at the TS, (b) reaction 10 at the TS, (c) reaction 11 at the TS, (d) reaction 13 at the TS, (e) reaction 14 at the TS, (f) reaction 15 at the TS, (g) reaction 16 at the TS, and (h) reaction 17 at the TS. (Distances are in angstroms, angles in degrees.) The values in parentheses are the geometries for the corrected TSs.

zation of the equilibrium geometries, vibrational analysis was carried out with the aid of analytical second derivatives based on the HF method.[23] As confirmation that the HF TS geometries obtained in this manner are approximately the same as the correct ones calculated at the post HF level, the following procedure was performed. Searches of the intrinsic reaction coordinate (IRC)[24] in the proximity of the HF TS for some of the reaction pathways were performed using the HONDO[25] program using the 6-31G* basis set at the HF level. For each geometry obtained along the IRC in this manner (at the HF/6-31G* level), the electron correlation effect was estimated by the single- and double-substituted configuration interaction method (CISD) within the frozen core approximation using the 6-31G** basis set.[26] The unlinked cluster quadruple correction proposed by Pople et al.[27] was added to allow for the size-consistency correction (SCC). The energies at the CISD+SCC/6-31G** level obtained in this manner were plotted for each reaction pathway. The energy curve had a maximum at a point that was different from the TS at the HF level. The differences in geometries and energies between these maximums and the HF level TSs were found to be small in all cases as will be shown in a later section. This makes our identification of the TSs credible.

Results and Discussion

1. Elementary Reactions. The elementary reactions in the gas-phase reaction system $SiH_4 + NH_3$ are shown in Table I. There are three possible types of elementary reactions: (1) the direct reaction, (2) the reaction involving silylene formation, and (3) the reactions involving radical formations. The energetics calculated are listed in Table I together with the experimental results.

The experimental dissociation energy of the Si–N bond in $R_3Si{-}NR'R''$ is available;[29] therefore we have estimated the $\Delta H_{\rm exptl}$ for reactions 1 and 3 by using the data for $(CH_3)_3Si{-}NHCH_3$.[29] The experimental bond additivity correction (BAC) for the theoretical value of the heat of formation of SiH_3NH_2 is also available.[30] The corrected value at the BAC-MP4(SDTQ) level[30] was used for the calculation of the heats of the reactions 1 and 3 designated as $\Delta H_{\rm BAC}$.

Table II. CISD+SCC/6-31G**//HF/6-31G* Energetics for Si–N Radical Reactions in Kilocalories/Mole

reaction no.	reactants	products	E_a	ΔH	$\Delta H_{\rm exptl}$/ $\Delta H_{\rm BAC}$
9	$SiH_3 + NH_3$	$SiH_3NH_2 + H$	31.3 (32.2[a])	11.4	7.5[b,c]/8.4[d]
10	$SiH_3 + SiH_4$	$SiH_3SiH_3 + H$	30.3 (31.7[a])	19.5	16.7[b]
11	$SiH_3 + NH_3$	$SiH_2NH_2 + H_2$	55.3	−2.9	−5.4[d]
12	$2SiH_3$	SiH_3SiH_3	0.0	−72.1	−73.6[b]
13	$NH_2 + SiH_4$	$NH_3 + SiH_3$	9.7 (11.3[a])	−15.9	−13.0[b,c]
14	$NH_2 + SiH_4$	$SiH_3NH_2 + H$	14.4 (14.8[a])	−4.5	−5.5[b,c]/−9.4[d]
15	$NH_2 + NH_3$	$NH_2NH_2 + H$	59.2	45.3	35.2[c]
16	$SiH_4 + H$	$SiH_3 + H_2$	7.7 (8.7[a])	−14.2	−13.9[b,c]
17	$NH_3 + H$	$NH_2 + H_2$	16.4 (16.5[a])	1.7	−0.9[c]
chain I in figure 3			17.1 (18.0[a])	−2.8	−6.3[b,c]/−5.5[d]
chain II in figure 3			16.1 (17.5[a])	5.3	2.9[b,c]

[a] The values in parentheses are calculated using the highest energy point search at the CISD+SCC/6-31G** level along the HF/6-31G* level IRC. [b] Experimental values taken from ref 29. [c] Experimental values taken from ref 28. [d] Empirically corrected theoretical values from ref 30.

Reaction 1 in Table I is the direct bond formation reaction without reactive species. This reaction was examined in our previous paper[8] and was shown to have 66.4 kcal/mol of E_a at the CISD+SCC/6-31G**//HF/6-31G* level.

Reaction 2 in Table I is the silylene formation reaction, the E_a of which is 56.9 kcal/mol at the MP4/MC-311++G//MP2/MC-311G level. Since this E_a is comparable with that of the direct reaction, both reactions 1 and 2 are competitive. It should be noted here that silylene has the ability to insert into N–H bonds and Si–H bonds, as in reactions 3 and 4 in Table I, respectively. Reaction 4 has no energy barrier. Thus, silylene is expected to be consumed instantaneously in reaction 4 forming a Si–Si bond. Therefore, the direct reaction is more plausible than silylene formation plus insertion as a candidate for the Si–N bond formation reaction.

The third possibility involves the formation of radicals. There are several possible initiation steps. Triplet silylene abstracts a hydrogen atom from silane to form SiH_3 radicals, as in reactions

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5 and 6 in Table I. Reaction 7 in Table I is the homolysis of silane to yield a SiH_3 radical and a hydrogen radical. Reaction 8 in Table I is the dissociation of an N–H bond of ammonia. The enthalpy change (ΔH) for reactions 7 and 8 are estimated to be 91.6 and 107.5 kcal/mol, respectively, at the CISD+SCC/6-31G** level. The experimental dissociation energy values, $\Delta H_{\mathrm{exptl}}$ values in Table I for reactions 7 and 8, 90.3 and 103.3 kcal/mol, respectively, are consistent with the calculations and illustrate the order of bond strength as N–H > Si–H. As a consequence, it is likely that the SiH_3 radical would form more readily than the NH_2 radical. For this reason, we will focus on the reactions of SiH_3 radical in the following subsections.

2. Reactions of Radicals. The radical reactions considered here are shown in Table II with their energetics. The $\Delta H_{\mathrm{exptl}}$ and ΔH_{BAC} values in Table II are obtained in the same way as in Table I. Corrections to the TS geometries at the HF level were calculated in the manner mentioned in Computational Methods for every reaction except reactions 11 and 15, which were considered unlikely to take place. The energies of activation (E_a) at the CISD+SCC/6-31G** level calculated for the corrected TSs at the post HF level are shown in parentheses in Table II. The energy values without parentheses are the Ea values calculated for the HF level TSs. The TS geometries are shown in the same manner in Figure 1a–h (The values in parentheses are the corrected TS geometries, and those without parentheses are the HF level TS geometries). We examine first the reactions involving SiH_3 radicals (reactions 9, 10, 11, and 12 in Table II).

Reaction 9 proposes Si–N bond formation by substitution of a hydrogen atom on ammonia with the SiH_3 radical. The geometry at the TS of reaction 9 is shown in Figure 1a. For reaction 9, the E_a and ΔH values are calculated to be 32.2 and 11.4 kcal/mol, respectively, at the CISD+SCC/6-31G** level. Reaction 10 proposes Si–Si bond formation by substitution of a hydrogen atom of silane with the SiH_3 radical to produce disilane. For reaction 10, the E_a and ΔH values are calculated to be 31.7 and 19.5 kcal/mol, respectively, at the CISD+SCC/6-31G** level. The geometry at the TS of reaction 10 is shown in Figure 1b. Si–N and Si–Si bond formation through reactions 9 and 10, respectively, is considered to be competitive because both have E_a values of similar magnitude.

Reaction 11 represents Si–N bond formation via elimination of H_2, which closely resembles the direct reaction between silane and ammonia we described earlier.[6] For reaction 11, the E_a and ΔH values are estimated to be 55.3 and −2.9 kcal/mol, respectively, at the CISD+SCC/6-31G** level. The $\Delta H_{\mathrm{exptl}}$ for reaction 11 is not given in Table II since it cannot be deduced from the dissociation energy of the Si–N bond of $(CH_3)_3SiNHCH_3$, which has saturated bonds. The ΔH_{BAC} for reaction 11, −5.4 kcal/mol, is consistent with the ΔH, −2.9 kcal/mol. The HF/6-31G* optimized geometry at the TS of reaction 11 is shown in Figure 1c. Since the E_a of reaction 11 is much greater than those of the other reactions, reaction 11 should be regarded as unlikely.

The SiH_3 radical is likely to be consumed in reaction 12, that is, via recombination with another SiH_3 radical, rather than in reactions 9 and 10, because of their relatively large endothermicity. However, an obstacle to the recombination is that the probability of collision between two SiH_3 radicals is small and is heavily dependent on the experimental environment, e.g., the NH_3/SiH_4 mixing rate and temperature.

Although the NH_2 radical is an unlikely reactant, we examined the reaction involving the NH_2 radical for the sake of reference. Reactions 13–15 in Table II are the reactions involving the NH_2 radical. Reaction 13 represents the hydrogen atom abstraction from silane by the NH_2 radical. The E_a and ΔH values for reaction 13 are calculated to be 11.3 and −15.9 kcal/mol, respectively, at the CISD+SCC/6-31G** level. Thus, the NH_2 radical, if present, would likely produce the SiH_3 radical via hydrogen abstraction from silane spontaneously. The geometry of the TS of reaction 13 is shown in Figure 1d. Reaction 14 represents Si–N bond formation by substitution of a hydrogen atom of silane with the NH_2 radical. The geometry of the TS of reaction 14 is shown in Figure 1e. A characteristic feature of reaction 14 is its TS structure, which indicates a front side attack as shown in Figure 1e. The E_a and ΔH values for reaction 14 are estimated to be 14.8 and −4.5 kcal/mol, respectively, at the CISD+SCC/6-31G** level. Reaction 15 represents N–N bond formation by substitution of a hydrogen atom of ammonia with NH_2. The HF/6-31G* optimized TS geometry of reaction 15 is shown in Figure 1f. The E_a and ΔH values for reaction 15 are predicted to be 59.2 and 45.3 kcal/mol, respectively, at the CISD+SCC/6-31G** level. The highly endothermic reaction 15 is the least favorable among the bond formation reactions considered here. Among the reactions 13–15, the hydrogen atom abstraction from silane by the NH_2 radical, reaction 13, is concluded to be the most favorable both kinetically and thermodynamically.

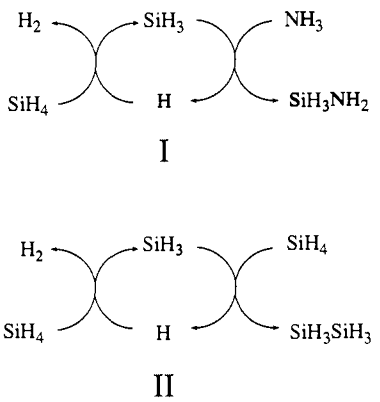

Figure 2. Reaction scheme of chains I and II.

The hydrogen radical, a product of reactions 9 and 10, is expected to react with the saturated species. In Table II, reactions 16 and 17 represent the abstraction of a hydrogen atom from silane and ammonia by the H radical. For reaction 16, E_a and ΔH are calculated to be 8.7 and −14.2 kcal/mol, respectively, at the CISD+SCC/6-31G** level. The geometry of the TS of reaction 16 is shown in Figure 1g. For reaction 17, the E_a and ΔH values are estimated to be 16.5 and 1.7 kcal/mol, respectively, at the CISD+SCC/6-31G** level. The geometry of the TS of reaction 17 is shown in Figure 1h. Reaction 16 is considered to be more favorable than reaction 17 both kinetically and thermodynamically, and this is likely due to the fact that the bond strength of Si–H is weaker than that of N–H. Hence the product of reactions 9 and 10, a hydrogen atom, is probably consumed via reaction 16, forming the SiH_3 radical.

Thus, all the radical species except the SiH_3 radical are predicted to produce the SiH_3 radical via hydrogen abstraction from SiH_4. SiH_3 is an extraordinarily stable radical, which is consistent with the experimental observation.[17,18]

3. Radical Chain Reaction Mechanisms. Any chain reaction mechanism in this system must include the reaction of the SiH_3 radical as a chain element, since all the other radicals end up producing the SiH_3 radical via hydrogen abstraction from silane.

The SiH_3 radical can undergo reactions 9 and 10 if it does not undergo recombination, reaction 12. Reactions 9 and 10 are competitive radical substitution reactions as discussed in subsection 2, and represent the propagation steps.

As a product of reactions 9 and 10, a hydrogen atom is obtained and probably helps to generate the SiH_3 radical via reaction 16. This SiH_3 radical can also be considered part of the propagation step.

From calculated results thus far, we find it reasonable to propose two-step chain reactions for (I) Si–N bond formation (composed of reactions 16 and 9) and (II) Si–Si bond formation (composed of reactions 16 and 10). The reaction schemes of these chains I and II are tabulated in Table II and shown in Figure 2. It is found that the E_a of chain I is comparable to that of chain II, thus, kinetically these Si–N and Si–Si bond formation chains are competitive. Thermodynamically chain II is less favorable than chain I. Chain I is predicted to be 2.8 kcal/mol exothermic and expected to repeat spontaneously, while chain II is slightly en-

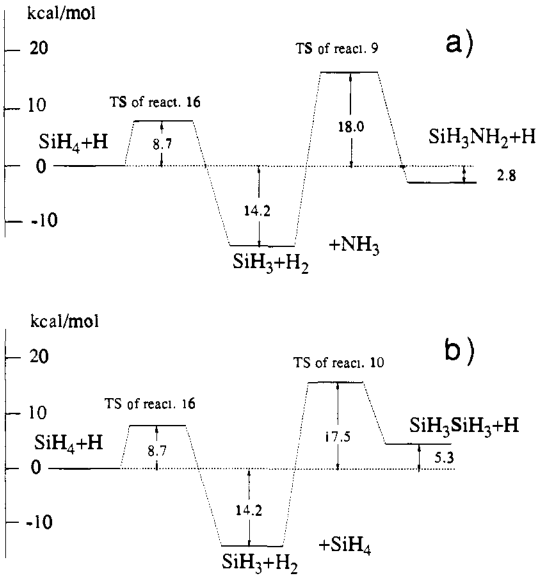

Figure 3. Energy diagrams for (a) chain I and (b) chain II.

dothermic. The ΔH_{exptl} values for chain I and II are consistent with the corresponding ΔH values (See Figure 3).

Some side chain reactions can be derived from the combination of basic reactions we discussed previously, e.g., reactions 17 and 14 (Si–N bond formation chain). However, all such side chain reactions include the formation of the particularly unstable NH_2 radical, and hence their contribution to the Si–N bond formation is likely negligible.

The radical chain reaction mechanism I gives the most reasonable explanation for selective Si–N bond formation and the lowest energy surface for the bond formation compared with other reaction mechanisms.

Conclusions

The following new points emerge from this study.

1. The SiH_3 radical is confirmed to be an extraordinarily stable reactive species in the silane CVD system. This is consistent with the observation of a high concentration of SiH_3 radicals in actual CVD experiments.[17,18]

2. As a method for the Si–N bond formations, the radical substitution reactions turn out to be more favorable energetically than any other bond formation reactions, namely, the silylene insertion or the direct bond formation, assuming that the radical substitution reaction is more likely to occur than the recombination. Under the conditions of real CVD experiments,[1,5] this assumption seems to be satisfied.

3. In the reaction of silane and ammonia, the order of reactivity of bond formation is predicted to be Si–N > Si–Si ≫ N–N. In the CVD experiments,[1,5] it has been observed that the formation of Si–N and Si–Si bonds in the heated gas mixture of silane and ammonia occurs under comparable reaction conditions and that the N–N bond formation is unlikely to occur. These are consistent with the theoretical prediction.

In the case of the laser CVD process of silicon ceramics, the surface reaction is said to play a role.[3,6] Evaluating such a complex surface reaction is beyond the scope of the present study. This present study represents a preliminary attempt toward a better understanding of the complex CVD reaction mechanism.

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Registry No. Si_3N_4, 12033-89-5; SiH_3, 13765-44-1; SiH_4, 7803-62-5; NH_3, 7664-41-7; H, 12385-13-6.

Σ Metathesis Reactions Involving Group 3 and 13 Metals. $Cl_2MH + H_2$ and $Cl_2MCH_3 + CH_4$, M = Al and Sc

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Abstract: Correlated ab initio theoretical calculations at the valence double zeta plus polarization level are used to study the degenerate exchange processes involving metal–hydrogen, metal–carbon, hydrogen–hydrogen, and carbon–hydrogen σ bonds observed for early transition metal complexes (groups 3 and 4). In agreement with Rooney's hypothesis, we find that an empty p orbital can rehybridize with a bonding p orbital to permit four-center 2 + 2 reactions to occur with relatively low activation energies for aluminum–hydrogen and aluminum–carbon σ bonds. However, the greater directionality of a d orbital permits the reactions to occur with substantially lower barriers for the transition metal cases (for hydrogen exchange, the Al barrier is 32.2 kcal/mol higher than for Sc; for methane exchange, the Al barrier is 33.7 kcal/mol higher than for Sc). Further, we present computational evidence for the hypothesis that metal fragment orbitals can be tuned to either stabilize transition states of preferred reactions or destabilize transition states for pathways that are not desired. We calculate a barrier for methane exchange of 28.0 kcal/mol for $Cl_2Sc(CH_3) + CH_4$. Further, we determine the methyl plus methane exchange process to occur with a barrier of less than 25.1 kcal/mol.

I. Introduction

In the past several years it has become apparent that early transition metal complexes possess unique reactivity patterns[1-3] that have been attributed to quite small activation energetics for four-center 2 + 2 reactions. Several members of this class of reactions have been studied theoretically,[4-9] and these studies led us[8,9] to propose (as an extension of the orbital phase continuity principle[4,8,10]) that the essential electronic factor was the presence

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