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Theoretical Study of the Reaction Mechanism of Abstraction Reactions of Disilenes and Digermenes with Haloalkanes

Ming-Der Su*

School of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan, R.O.C.

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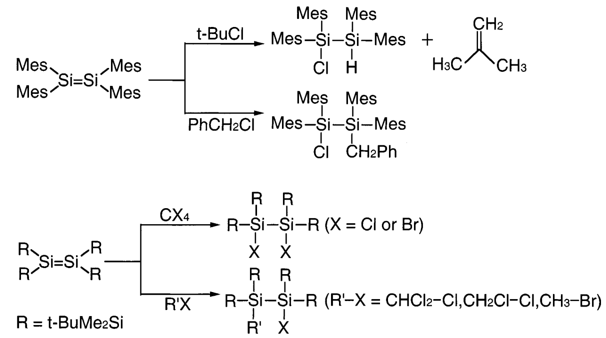
The potential energy surfaces for the abstraction reactions of disilenes and digermenes with carbon tetrachloride have been characterized in detail using density functional theory (B3LYP/6-311G(d)), including zero-point corrections. Ten substituted disilene and digermene species, $R_2X{=}XR_2$ (X = Si, Ge; R = H, F, Cl, CH_3, and SiH_3), have been chosen in this work as model reactants. Of the two possible reaction paths, the Cl abstraction (path 1) and the CCl_3 abstraction (path 2), the former is found to be more favorable, with a very low activation energy and a larger exothermicity. This is in accordance with available experimental observations. The activation barriers and enthalpies of the reactions are compared to determine the relative reactivity of disilene and digermene as well as the influence of substitution on the reaction potential energy surface. Our theoretical investigations indicate that, irrespective of disilene and digermene species, the more electropositive and/or the more bulky the substituents, the lower the activation barrier and the more exothermic the haloalkane abstraction. In short, electronic as well as steric factors play a dominant role in determining the chemical reactivity of the disilene or digermene species kinetically as well as thermodynamically. Furthermore, a configuration mixing model based on the work of Pross and Shaik is used to rationalize the computational results. The results obtained allow a number of predictions to be made.

I. Introduction

Since the first isolation of a stable disilene species with a silicon−silicon double bond, by West, Fink, and Michl in 1981,[1] the chemistry of disilenes has attracted widespread interest owing to their unusual properties, structures, and bonding. Many reviews have been written on the subject of silicon−silicon double bonds.[2] A number of chemical reactions of these doubly bonded silicon compounds have been investigated.[3,4] Typically, disilenes react by 1,2-addition or by cycloaddition to give products in which the π bond between the silicon atoms is broken but the σ bond remains.[5] The reactions of disilenes therefore resemble those of olefins, except that disilenes are much more reactive.[6,7] Nevertheless, an understanding of the various facets of disilene chemistry is still far below the level of what we know about alkenes. It therefore remains a major challenge, both in the experimental arena and in the theoretical domain, to construct a logical framework that allows us to view factors determining the fundamental chemical properties of doubly bonded silicon compounds, e.g., molecular geometries, mechanistic information, and reactivity.

Recently, through the elegant studies performed by West, Kira, and many co-workers,[2i,8] it was found that disilenes can react smoothly with various haloalkanes in the dark to give several types of disilane products in high yields as shown in Scheme 1. Apparently, the formation of these products suggests a radical nature for the reactions. Indeed, as evidenced by an ESR observation of an intermediate radical, these disilene reactions are quite unusual, forming neutral radical pairs from two closed shell molecules in the first step.[8b] In contrast to the wealth of experimental information on the halogen abstraction of disilenes from haloalkanes, no similar direct reaction of a C═C double bond with a haloalkane has been observed so far.

SCHEME 1



Besides these, attention is also naturally directed toward the reactions of digermenes,[9] $R_2Ge{=}GeR'_2$, with haloalkanes. To the best of our knowledge, until now neither experimental nor theoretical work has been devoted to the study of digermene abstraction reactions. It is therefore believed that, in view of recent dramatic developments in disilene chemistry,[2j,8] analogous extensive studies of digermenes should soon be forthcoming and will open up new areas.

Because the abstraction reactions mentioned above are both unusual and useful, we were curious about exactly how they occur and wanted detailed mechanistic knowledge in order to exercise greater control over them. In fact, a detailed understanding of disilene as well as digermene reactivity is of interest not only for the advancement of basic science but also for the continued development of their applications. To our knowledge, detailed mechanistic studies of the abstraction reactions of disilenes and digermenes with haloalkanes and a comparison between these processes are still lacking. Indeed, it is very difficult to detect the intermediate and the transition state due to the limitations in current experimental techniques. Theory is therefore a potentially useful partner in the investigation of the

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* To whom correspondence should be addressed. E-mail: midesu@cc.kmu.edu.tw.

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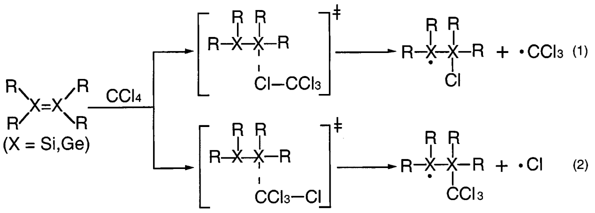
mechanism of such abstraction reactions by the heavier ethylene analogues.

As a result of recent experiments,[2j,8] two competitive reaction pathways have been proposed for the initial reactions of disilenes or digermenes with haloalkanes[10] (vide infra). In principle, they are radical mechanisms proceeding via either a chlorine atom (eq 1) or a CCl_3 group abstraction (eq 2).



To examine the generality of the disilene and digermene abstractions, we have now undertaken a systematic investigation of the abstraction reactions of $R_2Si{=}SiR_2$ and $R_2Ge{=}GeR_2$ (R = H, F, Cl, CH_3, and SiH_3) species using density functional theory (DFT). These reactions have been chosen because they represent various kinds of disilene abstractions for which experimental results have been reported by Kira and coworkers.[8b] Moreover, it was found that carbon tetrachloride was the most reactive toward these disilenes, of all the haloalkanes investigated, producing only the corresponding 1,2-dichlorodisilanes.[8b] As a result, through this theoretical study, we hope (i) to clarify the reaction mechanism and to determine the possible transition-state structures and the relative energetics for eq 1 and eq 2, (ii) to investigate the thermodynamics of the disilene and digermene abstraction reactions with the CCl_4 molecule, (iii) to estimate their activation barriers and to understand the reasons why Cl abstraction becomes the favored path of the radical reaction, and (iv) to establish general trends and predictions for the abstraction reactions of heavy ethylene analogues with haloalkanes. We anticipate that the results obtained in this work may allow one to predict the reaction pathway for some known and/or as yet unknown systems and shed some light on optimal designs of further related synthesis and catalytic processes.

II. Theoretical Methods

All geometries were fully optimized without imposing any symmetry constraints, although in some instances the resulting structure showed various elements of symmetry. For our DFT calculations, we used the hybrid gradient-corrected exchange functional proposed by Becke,[11a,b] combined with the gradient-corrected correlation functional of Lee, Yang, and Parr.[11c] This functional is commonly known as B3LYP, the results of which have been shown to be closer to the QCISD(T) reference than the MP2 value.[12] For C, H, F, Si, Ge, and Cl, the standardized 6-311G(d) basis sets were used. We thus denote our B3LYP calculations by B3LYP/6-311G(d). The spin-unrestricted (UB3LYP) formalism used for the open-shell (triplet) species and their $\langle S^2 \rangle$ values were all nearly equal to the ideal value (2.00). All critical points were further characterized by analytic computations of harmonic vibrational frequencies at the same level/basis set. Transition states were located by using synchronous transit-guided quasi-Newton (STQN) methods, implemented in the Gaussian program by Schlegel et al.[13,14] Following this stage, the structures were fully optimized at the B3LYP/6-311G(d) level by traditional transition state optimization, using the Berny algorithm[13] with the application of the read FC option for specifying curvature information. All transition structures were checked by intrinsic reaction coordinate (IRC) computations[15] at the same level of theory. Relative energies are corrected for vibrational zero-point energies (ZPE, not scaled), i.e., B3LYP/6-311G(d) + ZPE (B3LYP/6-311G(d)). All calculations were performed using the Gaussian 98/DFT package.[16]

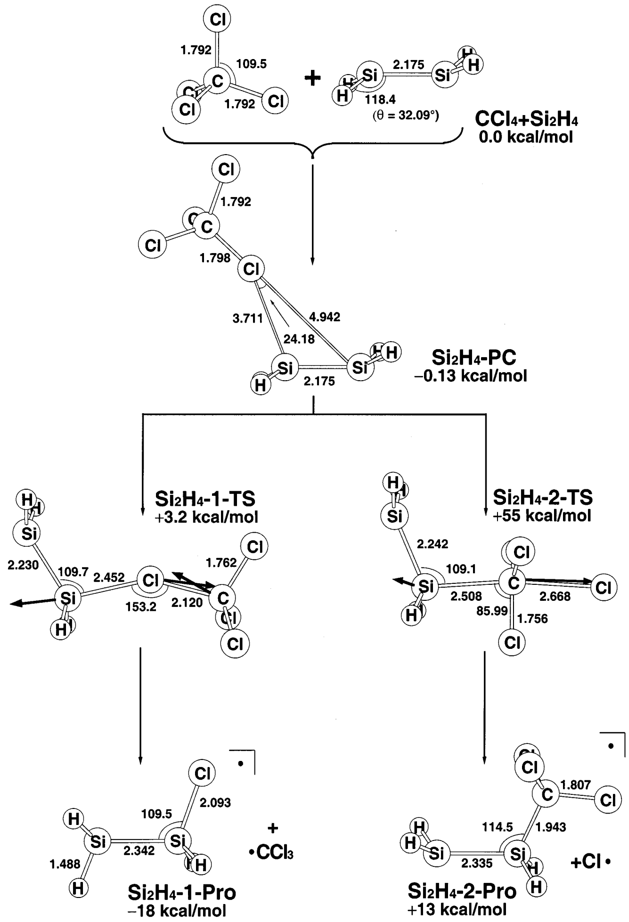


Figure 1. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of Si_2H_4 with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

III. Geometries and Energetics of $R_2Si{=}SiR_2 + CCl_4$

The model reactions that we adopt in this paper are already shown in eq 1 (Cl abstraction) and eq 2 (CCl_3 abstraction). Despite its simplicity, when comparing our model with the realistic systems, we believe that the reactivities of the various substituted disilenes can be reproduced by this model system. In this section, the results for four regions on the potential energy surfaces will be presented: the reactants ($R_2Si{=}SiR_2 + CCl_4$; R = H, F, Cl, CH_3, and SiH_3), the precursor complex (PC), the transition state (TS), and the abstraction product (Pro; either $R_2Si{=}SiR_2Cl^\bullet + CCl_3^\bullet$ or $R_2Si{=}SiR_2CCl_3^\bullet + Cl^\bullet$). The fully optimized geometries for those stationary points calculated at the B3LYP/6-311G(d) level are given in Figures 1–5, respectively. The corresponding relative energies at the DFT level of theory are collected in Table 1. The B3LYP/6-311G(d) geometrical parameters and energies are used throughout the text unless otherwise noted.

A. Reactants. Let us first discuss the reactant–disilene. It is well established that the heavier analogues of olefins ($R_2X{=}XR_2$) do not exhibit classical planar geometry (**1**) but rather have a trans-bent structure (**2**), with pyramidalization of both

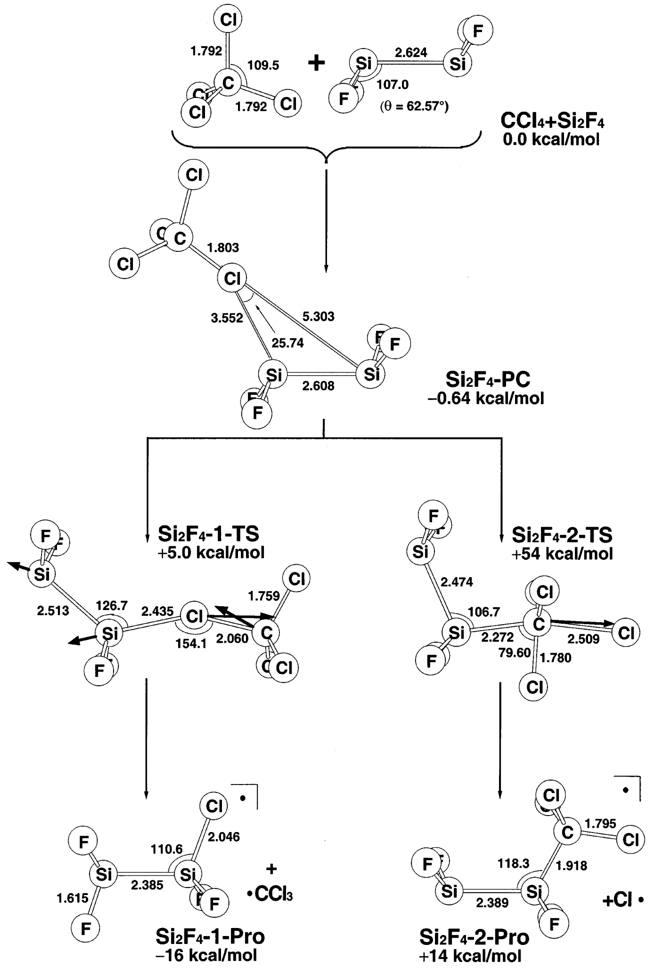


Figure 2. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of Si_2F_4 with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

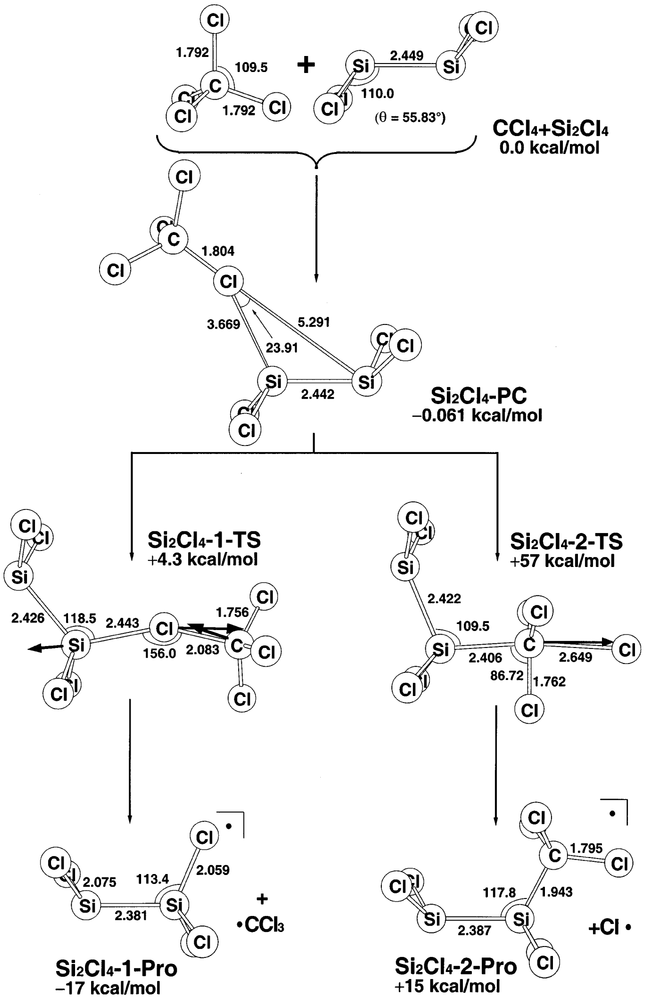
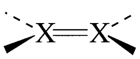


Figure 3. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of Si_2Cl_4 with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

XR_2 groups. Indeed, these compounds, containing so-called "nonclassical double bonds", have been proved to be the preferred arrangements for disilene and digermene and are local minima on the potential energy surface for all of the heavier analogues of ethylene. There is currently much discussion concerning these phenomena in the literature. Interested readers can find excellent reviews in ref 2. Substituent effects on the structure of disilenes have been discussed by several theoretical groups.[17,18] It was suggested that the geometries of disilenes are determined by the substituents' electronegativities. That is to say, the more electronegative substituents induce larger deviations from planarity and a longer Si═Si bond, whereas disilenes with more electropositive substituents (or more bulky groups) will suffer less distortion and the Si═Si bond length is similar to or slightly longer than that in the parent disilene (R = H).[17,18]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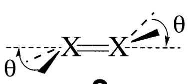

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Our computational results based on the present study have confirmed these predictions. For instance, as can be seen in Figures 1−5, the B3LYP/6-311G(d) calculations indicate that both the bending angle θ (see **2**) and the Si═Si bond length r are larger for the more electronegatively substituted disilenes than for the less electronegative systems. Namely, R = F (θ = 62.6°, r = 2.62 Å) > R = Cl (55.8°, 2.45 Å) > R = H (32.1°, 2.18 Å) > R = CH_3 (28.1°, 2.18 Å) > R = SiH_3 (6.64°, 2.17 Å). In particular, one thing that should be mentioned here is that earlier theoretical calculations had predicted that the introduction of a silyl group into disilene would force a planar arrangement around the Si═Si bond.[18(b,c)] Our theoretical results based on the DFT study are not consistent with this prediction, but strongly in accordance with the experimental findings.[19] Kira, Sakurai, and co-workers have reported that a series of trialkylsilyl substituents at the central silicon atoms are trans to each other and bent out of the plane of the double bond by 8.1−10.2°.[20] In other words, severe steric repulsion among the trialkylsilyl groups could be responsible for the deformation from planarity,[20] even if the distortion is slight. In any event, the good agreement between our computational results and available experimental results is quite encouraging. We are therefore confident that the computational methods used in this study are reliable and useful for further investigations of molecular geometries and energetic features of the bimolecular abstraction reactions, for which experimental data are not available.

B. Precursor Complexes. When we searched the potential energy surfaces of the abstraction of disilenes with CCl_4 for transition structures, we noticed an initial decrease in the total

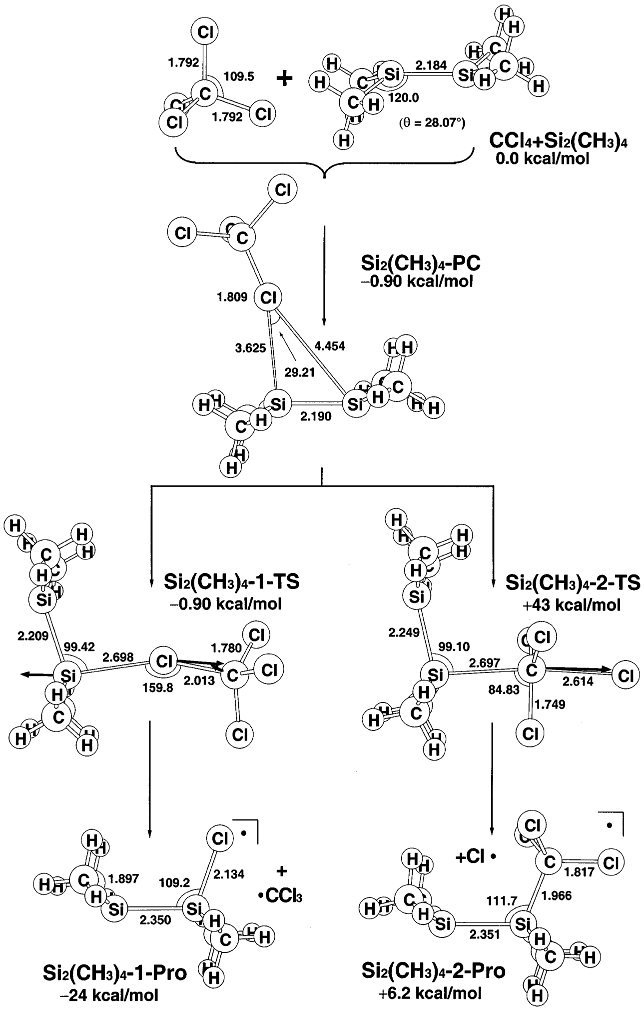


Figure 4. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of $Si_2(CH_3)_4$ with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

energy as compared with the isolated molecules at large separation. As one can see in Figures 1−5, the abstraction of CCl_4 by disilenes initiates the formation of a precursor complex. All five precursor complexes (i.e., Si_2H_4-PC, Si_2F_4-PC, Si_2Cl_4-PC, $Si_2(CH_3)_4$-PC, and $Si_2(SiH_3)_4$-PC) adopt very similar $R_2Si{=}SiR_2\cdots CCl_4$ bonding characteristics. They are best described as π-bonded complexes, in which one chlorine atom of CCl_4 is interacting with the π system of the disilene, with the Cl⋯Si bond length ranging from 3.55−5.30 Å. We describe these species as complexes, because there are only minor differences between their bond lengths and those of the free reactants. The calculated bond distances for the disilene⋯CCl_4 contacts are much longer than those calculated for the corresponding products (vide infra). It is not surprising that such long bond distances are reflected in the calculated complexation energy. As shown in Figures 1−5, the energy of the precursor complex relative to its corresponding reactants is less than 1.0 kcal/mol at the DFT level of theory, and there are only small distortions of the intramolecular bond lengths relative to the free reactants. Calculated vibrational frequencies for the precursor complexes reveal that these structures are true minima on the potential energy surface of the disilene + CCl_4 reaction. Consequently, our theoretical calculations show that these complexes are weakly bound and fall in a very shallow minimum at a large distance on the reaction surface.

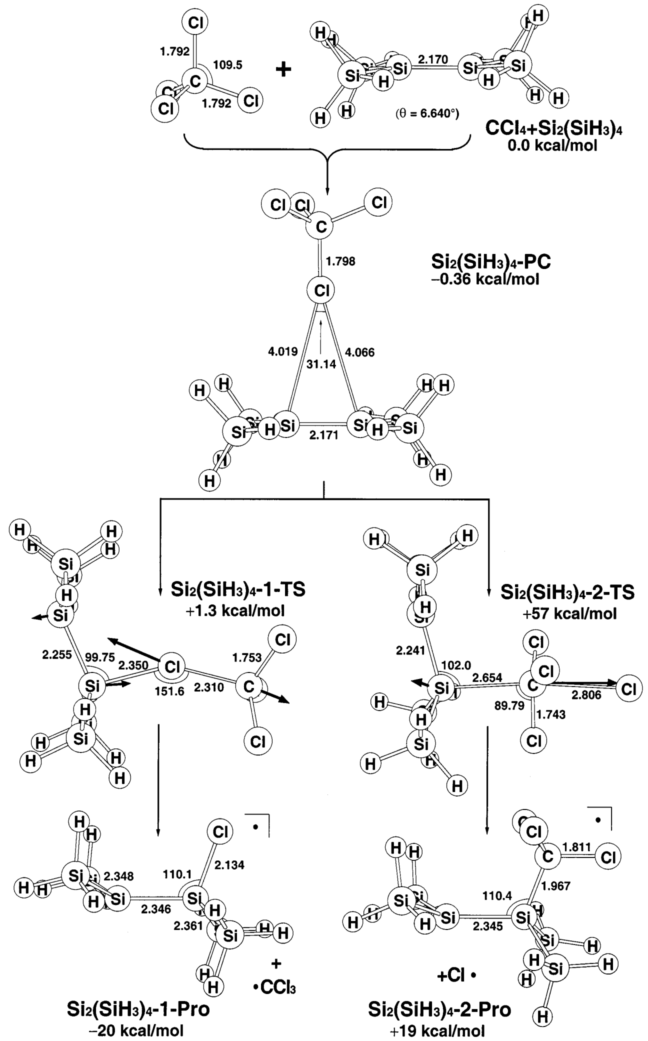


Figure 5. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of $Si_2(SiH_3)_4$ with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

Finally, an intriguing question to be asked is whether the disilene abstraction reaction gives a complex with CCl_4. According to these theoretical results, it appears unlikely that the π-bonded complexes can be isolated experimentally at room temperature because their stabilization energies are too low. Indeed, to the best of our knowledge, no experimental detection of disilene-haloalkane complexes formed during the reactions has been reported yet.[2j,8]

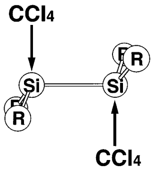
C. Transition States. As mentioned in the Introduction, the initial reaction of disilene with carbon tetrachloride via radical mechanisms can take place from two directions: the abstraction of a chlorine atom from CCl_4 to produce $R_2Si{=}SiR_2Cl^\bullet$ and $CCl_3^\bullet$ (shown in eq 1) and the $CCl_3^\bullet$ radical transfer to $R_2Si{=}SiR_2$ leading to the formation of $R_2Si{=}XSi_2CCl_3^\bullet$ and $Cl^\bullet$ (shown in eq 2). In both pathways, CCl_4 is considered to attack the silicon atom from the less hindered side as depicted in **3** in order to avoid steric repulsion between CCl_4 and the two substituents (R). The third reaction pathway with a single electron transfer (SET) process is not considered in this study. The reason for this is that, according to the experimental work,[8b] the relatively high oxidation potentials of the various disilenes renders the mechanism unlikely. In addition, the results for the transition states of the disilene abstraction reactions might

TABLE 1: Relative Energies (All in kcal/mol) for Singlet and Triplet Disilenes (or Digermenes) and for the Process: Disilenes (or Digermenes) + CCl_4 → Precursor Complex → Transition State → Abstraction Products[a,b]

system	ΔE_{st}[c]	ΔE_{cpx}[d]	$\Delta E^{\ddagger}$[e] (path 1)	ΔH[f] (path 1)	$\Delta E^{\ddagger}$[e] (path 2)	ΔH[f] (path 2)
Si_2H_4	+20.88	−0.1286	+3.155	−18.09	+55.27	+12.71
Si_2F_4	+34.91	−0.6400	+5.018	−16.27	+54.40	+13.55
Si_2Cl_4	+28.95	−0.0608	+4.350	−16.83	+56.78	+15.10
$Si_2(CH_3)_4$	+20.09	−1.326	−0.8992	−24.38	+43.34	+6.246
$Si_2(SiH_3)_4$	+20.62	−0.3608	+1.306	−20.82	+57.37	+19.17
Ge_2H_4	+21.72	−0.1562	+6.520	−6.386	+55.11	+24.57
Ge_2F_4	+52.40	−0.6834	+11.54	+13.69	+70.11	+43.13
Ge_2Cl_4	+37.58	−0.4003	+11.71	+7.861	+66.22	+38.55
$Ge_2(CH_3)_4$	+20.66	−1.144	+0.6049	−15.52	+44.81	+15.72
$Ge_2(SiH_3)_4$	+21.24	−0.3213	+5.566	−7.653	+55.45	+21.30

[a] At the B3LYP/6-311G(d) level of theory. The B3LYP optimized structures of the stationary points see Figures 1−10. [b] Energies differences have been zero-point corrected. See the text. [c] Energy relative to the corresponding singlet state. A positive value means the singlet is the ground-state. [d] The stabilization energy of the precursor complex, relative to the corresponding reactants. [e] The activation energy of the transition state, relative to the corresponding reactants. [f] The reaction enthalpy of the product, relative to the corresponding reactants.

perhaps be one of the most interesting results of the present study since very little is known about the barrier heights.



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The main geometrical parameters of the transition states corresponding to abstraction reactions as well as their appearance are shown in Figures 1−5, together with the meaningful components of their transition vector. These transition states will be referred to as Si_2H_4-1-TS, Si_2F_4-1-TS, Si_2Cl_4-1-TS, $Si_2(CH_3)_4$-1-TS, and $Si_2(SiH_3)_4$-1-TS and Si_2H_4-2-TS, Si_2F_4-2-TS, Si_2Cl_4-2-TS, $Si_2(CH_3)_4$-2-TS, and $Si_2(SiH_3)_4$-2-TS for eq 1 (Cl abstraction) and eq 2 (CCl_3 abstraction), respectively. Regarding the Cl abstraction, one can observe that the main components of the transition vector correspond to the motion of the chlorine atom between the silicon and the carbon atoms, whose eigenvalue gives an imaginary frequency of 187i (Si_2H_4-1-TS), 170i (Si_2F_4-1-TS), 195i (Si_2Cl_4-1-TS), 130i ($Si_2(CH_3)_4$-1-TS), and 79i ($Si_2(SiH_3)_4$-1-TS) cm^{-1}. Indeed, inspection of the transition vector shows clearly that the reaction proceeds toward formation of $R_2Si{=}SiR_2Cl^{\bullet}$ and $CCl_3^{\bullet}$. It should be mentioned here that the three atoms (Si, Cl′, and C; Cl′ = the migrating chlorine atom) involved in the bond-breaking and bond-forming processes are not collinear along the Cl′−C axis as displayed in Figures 1−5. The silicon atom of the Si_2R_4 molecule makes an angle, with respect to the Cl′−C bond, of 153°, 154°, 156°, 160°, and 152° for Si_2H_4, Si_2F_4, Si_2Cl_4, $Si_2(CH_3)_4$, and $Si_2(SiH_3)_4$, respectively. One of the interesting points to emerge from calculations of TS geometries is the extent to which the Si−Cl′ bond is formed in the transition state. Relative to its value in the product (vide infra), the Si−Cl bond length in Si_2H_4-1-TS, Si_2F_4-1-TS, Si_2Cl_4-1-TS, $Si_2(CH_3)_4$-1-TS, and $Si_2(SiH_3)_4$-1-TS is 17%, 19%, 19%, 26%, and 20% longer than in the corresponding products, respectively. Additionally, the distance of the Cl′−C bond to be broken is 18%, 15%, 16%, 12%, and 12% longer than that of the corresponding reactant CCl_4, respectively. All of these data point out the fact that the $Si_2(CH_3)_4$ and $Si_2(SiH_3)_4$ abstraction reactions arrive at the TS relatively early, whereas the Si_2F_4 and Si_2Cl_4 abstraction reactions reach the TS relatively late. Consequently, the barriers are encountered earlier in the abstractions of the former than of the latter. As will be shown below, this is consistent with the Hammond postulate[21] which associates an earlier transition state with a smaller barrier and a more exothermic reaction.

Next we consider the CCl_3 abstraction (eq 2). A search for the transition state did show that the energy profile for this reaction exhibits a maximum. The transition states located for the CCl_3 abstractions by various disilenes are also presented in Figures 1−5, respectively. Those transition structures are characterized by one imaginary frequency of 567i, 535i, 591i, 485i, and 527i cm^{-1} for Si_2H_4-2-TS, Si_2F_4-2-TS, Si_2Cl_4-2-TS, $Si_2(CH_3)_4$-2-TS, and $Si_2(SiH_3)_4$-2-TS, respectively. The normal coordinate corresponding to the imaginary frequency is primarily located at the Cl'_3C−Cl bond cleavage, followed by the formation of the Si−CCl'_3 bond. Accordingly, the reaction coordinate is fundamentally an asymmetric stretch at the conventional transition state. Besides, to avoid the steric repulsion with the substituents of disilene, the Si···C···Cl is slightly bent in these TSs. Moreover, the transition structures show that the newly formed Si−C bond length is 2.51 Å (Si_2H_4-2-TS), 2.27 Å (Si_2F_4-2-TS), 2.41 Å (Si_2Cl_4-2-TS), 2.70 Å ($Si_2(CH_3)_4$-2-TS), and 2.65 Å ($Si_2(SiH_3)_4$-2-TS), compared to that in the final radical product (vide infra) of 1.94 Å (Si_2H_4-2-Pro), 1.92 Å (Si_2F_4-2-Pro), 1.94 Å (Si_2Cl_4-2-Pro), 1.97 Å ($Si_2(CH_3)_4$-2-Pro), and 1.97 Å ($Si_2(SiH_3)_4$-2-Pro), respectively. Again, taken together these features indicate that the transition structures for $Si_2(CH_3)_4$ and $Si_2(SiH_3)_4$ take on a more reactant-like character than in the Si_2F_4 and Si_2Cl_4 cases. These observations will be related to the predicted energetics below.

In the Cl abstraction, examination of the energy values collected in Figures 1−5 and Table 1 shows that at the B3LYP/6-311G(d) level the $Si_2(CH_3)_4$ and $Si_2(SiH_3)_4$ abstractions are favored. The present calculations predict that the energies of Si_2H_4-1-TS, Si_2F_4-1-TS, and Si_2Cl_4-1-TS are above those of the reactants by 3.2, 5.0, and 4.3 kcal/mol, respectively. In contrast, the DFT results suggest that the energies of $Si_2(CH_3)_4$-1-TS (−0.90 kcal/mol) and $Si_2(SiH_3)_4$-1-TS (+1.3 kcal/mol) are below or close to those of the reactants, so that no net barrier to reaction exists. Moreover, the B3LYP results show that the overall barrier heights are determined to be in the order $Si_2(CH_3)_4 < Si_2(SiH_3)_4 < Si_2H_4 < Si_2Cl_4 < Si_2F_4$. In any event, the above reflects the greater ease of abstracting a chlorine atom by $Si_2(CH_3)_4$ and $Si_2(SiH_3)_4$ over abstraction by Si_2F_4 and Si_2Cl_4. Namely, our theoretical findings suggest that the more electropositive and/or the more bulky the substituents attached to the disilene, the more facile the abstraction of chlorine from CCl_4 becomes. On the other hand, the energetics of reactions of the type $R_2Si{=}SiR_2 + CCl_4$ via eq 2 (CCl_3 abstraction) are also summarized in Figures 1−5 and in Table 1. The B3LYP calculations indicate that the overall barrier heights with respect to the corresponding reactants for CCl_3 abstraction are 55 (Si_2H_4-2-TS), 54 (Si_2F_4-2-TS), 57 (Si_2Cl_4-2-TS), 43 ($Si_2(CH_3)_4$-2-TS), and 47 ($Si_2(SiH_3)_4$-2-TS) kcal/mol. Consequently, our theoretical results predict that the process of CCl_3 abstraction by $Si_2(CH_3)_4$ and $Si_2(SiH_3)_4$ is more facile than that by Si_2F_4 and Si_2Cl_4. That is, the trend is similar to that for the Cl abstraction reactions described above.

Furthermore, from the computational data discussed above, one can readily see that, for a given disilene species, the barrier to Cl abstraction is always smaller than that for CCl_3 abstraction. This may be due to the fact that the site of the disilene fragment attacked in the CCl_3 abstraction path is more congested. As a result, it is easier for CCl_4 to approach the disilene through the Cl abstraction path rather than through the CCl_3 abstraction one, and therefore, the former is kinetically more favorable than the latter. These theoretical results are in good agreement with experimental observations that substituted disilenes react with haloalkanes via halogen abstraction rather than carbon trihalide abstraction.[2i,8] We shall discuss more about the origin of the barrier heights in a later section.

D. Abstraction Products. The B3LYP/6-311G(d) geometries of the abstraction productsfor both reaction pathways (Si_2H_4-1-Pro, Si_2H_4-2-Pro; Si_2F_4-1-Pro, Si_2F_4-2-Pro; Si_2Cl_4-1-Pro, Si_2Cl_4-2-Pro; $Si_2(CH_3)_4$-1-Pro, $Si_2(CH_3)_4$-2-Pro; and $Si_2(SiH_3)_4$-1-Pro, $Si_2(SiH_3)_4$-2-Pro) are displayed in Figures 1−5, respectively. To simplify comparisons and to emphasize the trends, the calculated reaction enthalpies for abstraction are also collected in Table 1. Unfortunately, experimental structures for these abstraction products are not yet known.

As discussed earlier, a disilene with a more electropositive and/or a more bulky substituent reaches the transition state relatively early, whereas a disilene with a more electronegative group arrives relatively late. The former is therefore predicted to undergo a more exothermic abstraction, which is borne out by our theoretical calculations. For instance, the order of enthalpy follows a similar trend to the activation energy: $Si_2(CH_3)_4$-1-Pro (−24 kcal/mol) < $Si_2(SiH_3)_4$-1-Pro (−20 kcal/mol) < Si_2H_4-1-Pro (−18 kcal/mol) < Si_2Cl_4-1-Pro (−17 kcal/mol) < Si_2F_4-1-Pro (−16 kcal/mol) and $Si_2(CH_3)_4$-2-Pro (+6.2 kcal/mol) < Si_2H_4-2-Pro (+13 kcal/mol) < Si_2F_4-2-Pro (+14 kcal/mol) < Si_2Cl_4-1-Pro (+15 kcal/mol) < $Si_2(SiH_3)_4$-1-Pro (+19 kcal/mol). Note that the energies of the CCl_3-abstraction products are all above those of their corresponding reactants. This strongly indicates that the CCl_3 abstraction reactions by disilene are energetically unfavorable and would be endothermic. Namely, our computational results suggest that the abstraction products $R_2Si{=}SiR_2CCl_3^{\bullet}$ are not produced from a CCl_3 group transfer reaction as in $R_2Si{=}SiR_2 + CCl_4 \rightarrow R_2Si{=}SiR_2CCl_3^{\bullet} + Cl^{\bullet}$ but possibly exist if these radicals ($R_2Si{=}SiR_2CCl_3^{\bullet}$) are produced through other reaction paths.

In summary, the present calculations suggest the following about the radical mechanism for the $R_2Si{=}SiR_2 + CCl_4$ reaction: (1) The Cl abstraction pathway is more favorable than the CCl_3 abstraction pathway from both kinetic as well as thermodynamic considerations. This is consistent with the experimental observation that only the Cl abstraction products are formed.[2(i),8] (2) One of the reasons for the smaller activation energy of eq 1 is presumably the smaller repulsion between the chlorine atom and the substituents of the disilene. Namely, the site of the disilene moiety attacked in eq 2 is more congested. As a result, it is easier for CCl_4 to approach the Si atom of disilene through Cl abstraction than through CCl_3 abstraction. (3) Our model calculations demonstrate that the more electropositive and/or the more bulky the substituents attached to the disilene, the earlier the transition state is formed, the lower the barrier to abstraction, and the greater the exothermicity.

IV. Geometries and Energetics of $R_2Ge{=}GeR_2 + CCl_4$

The fully optimized B3LYP/6-311G(d) geometries of the reactants, precursor complexes, transition states, and products for the $R_2Ge{=}GeR_2 + CCl_4$ (R = H, F, Cl, CH_3, and SiH_3) reactions are shown in Figures 6−10, respectively. Also, their relative energies, calculated at the B3LYP/6-311G(d) level, are given in Table 1.

A. Reactants. By analogy with the disilene systems discussed earlier, similar bonding properties, in which π bonding is weakened and lone pair character is enhanced, can also be found in digermene systems. According to our DFT calculations, a decreasing trend in both bending angle θ and the Ge=Ge bond length r (see **2**) can be represented as follows: R = F (θ = 63.6°, r = 3.33 Å) > R = Cl (60.3°, 2.88 Å) > R = H (43.9°, 2.31 Å) > R = CH_3 (41.1°, 2.34 Å) > R = SiH_3 (28.0°, 2.29 Å). Again, our theoretical results have confirmed the previous predictions.[17,18] That is, the more electronegative substituents will decrease the strength of the π bond and increase the distortion from planarity, whereas the more electropositive substituents will increase the strength of the π bond and give rise to less distortion. Indeed, our calculations are corroborated by some available experiments. X-ray-crystallographic studies of tetraalkyl- and tetraaryldigermenes have in each case revealed some degree of trans pyramidalization (θ = 12−36°).[9,22] From these analyses, because the computed structures of the substituted digermene are in reasonable agreement with the available experimental data, it is therefore believed that the current method (B3LYP/6-311G(d)) employed in this study will provide reliable information for the further discussion of the reaction mechanisms.

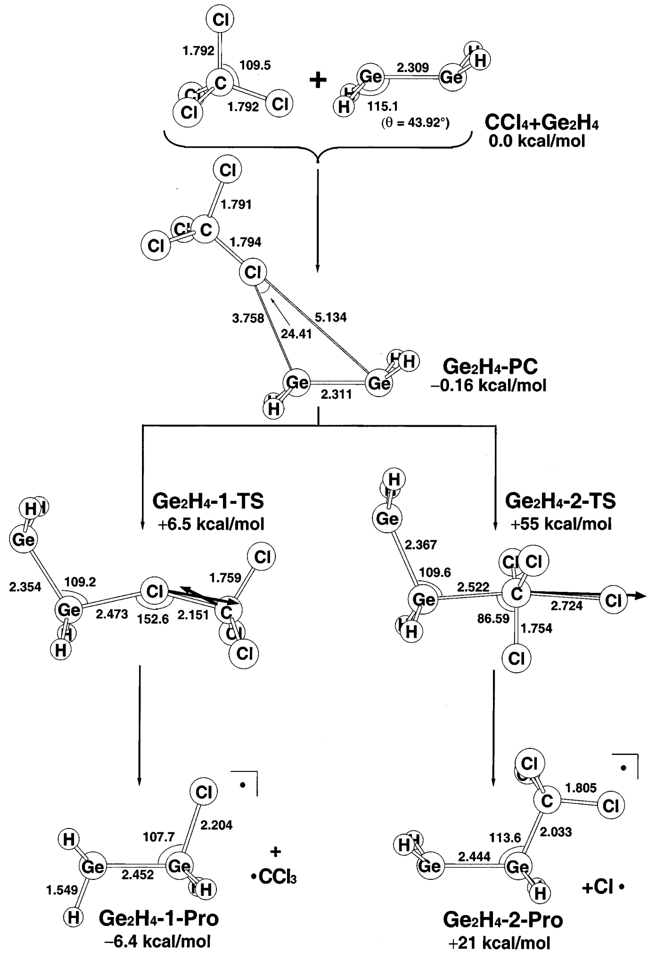

Figure 6. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of Ge_2H_4 with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

B. Precursor Complexes. Like the disilene abstraction discussed earlier, precursor complexes (Ge_2H_4-PC, Ge_2F_4-PC, Ge_2Cl_4-PC, $Ge_2(CH_3)_4$-PC, and $Ge_2(SiH_3)_4$-PC) for digermene abstraction with CCl_4 were also located at the B3LYP level. These complexes were confirmed to have no imaginary frequencies, indicating that they are true minima on the potential energy

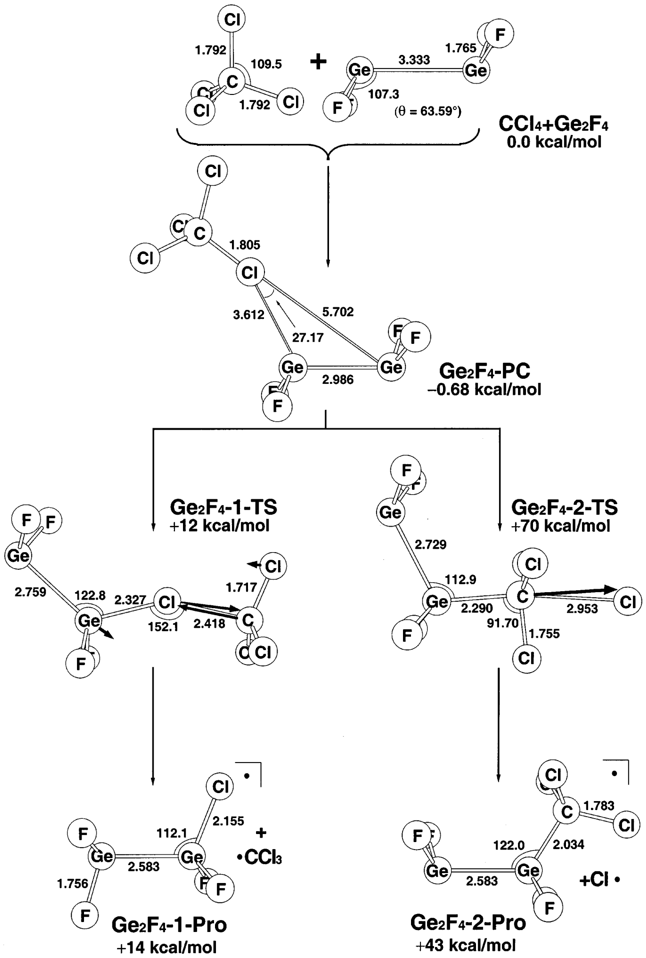

Figure 7. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of Ge_2F_4 with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

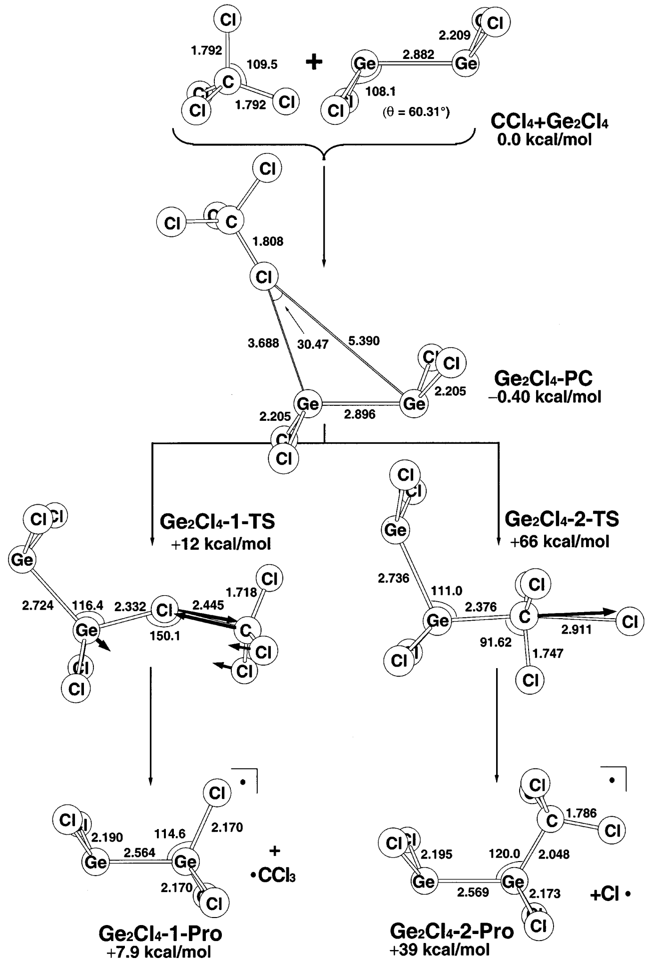

Figure 8. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of Ge_2Cl_4 with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

surfaces. As can be seen in Figures 6−10, all five precursor complexes adopt a similar structure in which the chlorine atom of CCl_4 interacts with the π system of digermene. These species can be described as π-bonded complexes and as such are quite similar to the complexes formed between disilenes and CCl_4. Furthermore, our B3LYP calculations indicate that they all have very long Cl···Ge bond distances (3.61−5.70 Å) compared with those in their corresponding abstraction products. We attribute this to the electronic repulsion between the chlorine atoms and the π bond in the digermene. Moreover, we should stress that long Cl···Ge distances should correlate with small values for the intermediate stabilization energy. For instance, as presented in Table 1, the complexation energies of the five precursor complexes are estimated to be less than 1.1 kcal/mol at the B3LYP/6-311G(d) level. Our attempt to locate molecular complexes at much shorter Cl···Ge distances was not successful. Thus, the present calculations indicate that the $R_2Ge{=}GeR_2\cdots CCl_4$ precursor complex exists only as a shallow minimum and any experimental detection of such an intermediate formed during the reaction is highly unlikely. As there are no relevant experimental and theoretical data on such systems, the above result is a prediction.

C. Transition Sates. Our calculations of the transition structure for the digermene abstractions closely parallel those for the reactions of disilenes with CCl_4. That is to say, there are also two paths for the abstraction reactions of digermenes. Starting from the 1-TS (eq 1), this leads apparently to Cl atom abstraction and the formation of $R_2Ge{=}GeR_2Cl^\bullet + CCl_3^\bullet$. On the other hand, the CCl_3 abstraction reactions through the 2-TS (eq 2) result in $R_2Ge{=}GeR_2CCl_3^\bullet + Cl^\bullet$ products. In all cases, we have found that both Cl and CCl_3 abstractions proceed in one step and that the three atoms involved in the process are in a nonlinear arrangement due to steric repulsion between CCl_4 and substituents on digermene. These phenomena are quite similar to those found for disilene abstractions as discussed earlier. Moreover, all of these transition states possess one imaginary frequency and are true first-order saddle points. For all of the transition structures, frequency analysis has shown that the transition vector associated with the imaginary frequency is a linear combination of the breaking and forming bonds as shown in Figures 6−10.

Considering the effects of substitution, our results suggest that, from a kinetic viewpoint, the abstraction reactions of digermene systems bearing electropositive and/or bulky substituentsare more facile than those of digermenes with electronegative groups. For example, the B3LYP barrier height for Cl abstraction by digermenes increases in the order: $Ge_2(CH_3)_4$-1-TS (0.61 kcal/mol) < $Ge_2(SiH_3)_4$-1-TS (5.6 kcal/mol) < Ge_2H_4-1-TS (6.5 kcal/mol) < Ge_2Cl_4-1-TS (12 kcal/mol) ∼ Ge_2F_4-1-TS (12 kcal/mol). The same effect can also be found in the CCl_3 abstractions as follows: $Ge_2(CH_3)_4$-2-TS (45 kcal/mol) < $Ge_2(SiH_3)_4$-2-TS (55 kcal/mol) ∼ Ge_2H_4-2-TS (55 kcal/

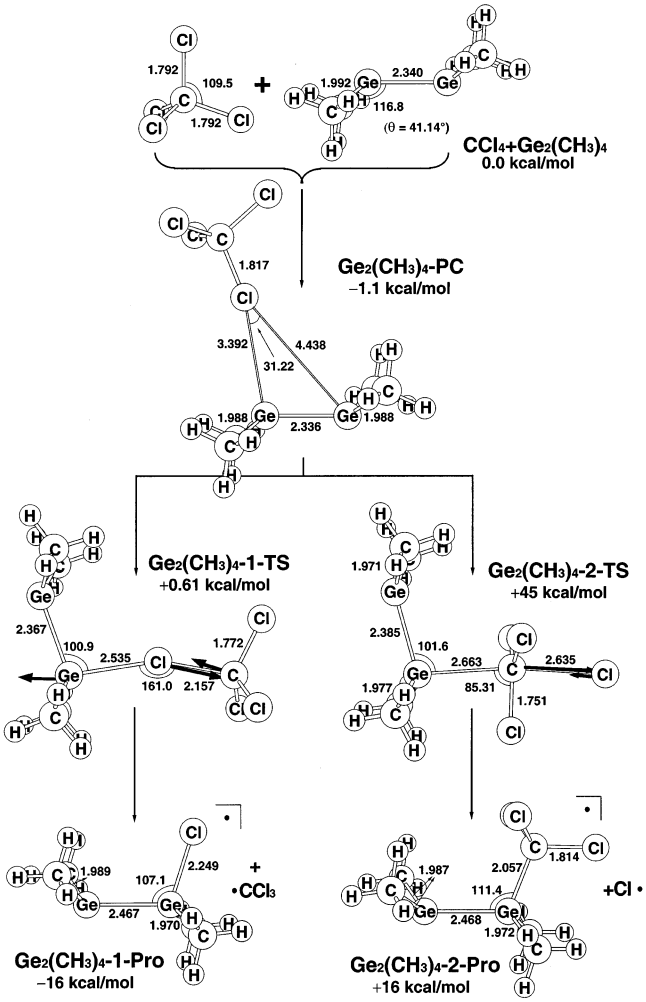

Figure 9. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of $Ge_2(CH_3)_4$ with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

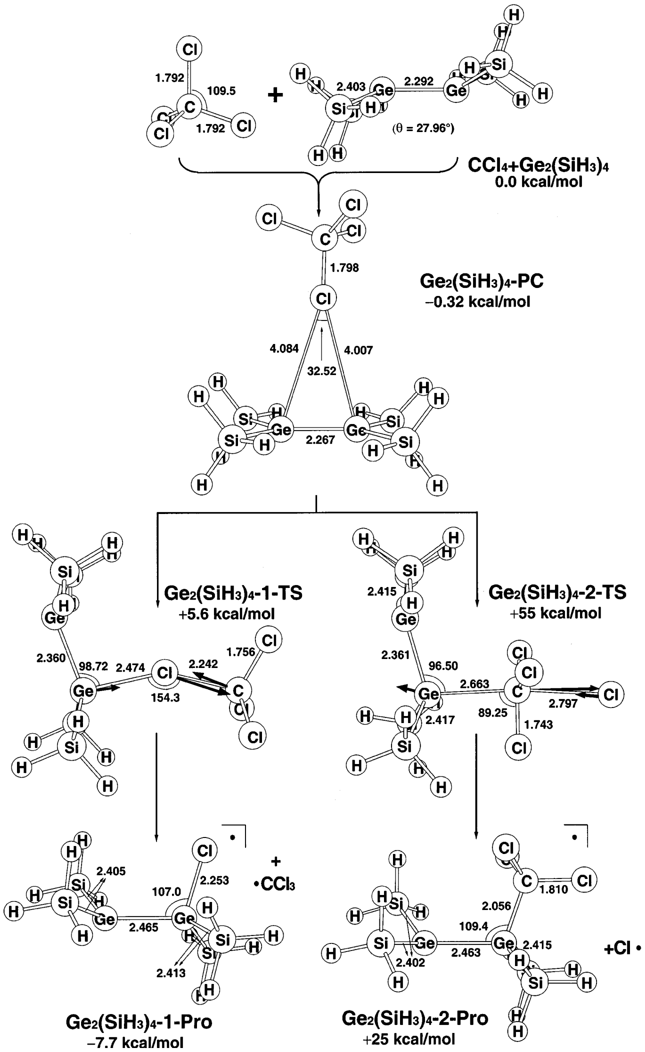

Figure 10. Optimized geometries (in Å and deg) for the precursor complexes (PC), transition states (TS), and abstraction products (Pro) of $Ge_2(SiH_3)_4$ with CCl_4. All were calculated at the B3LYP/6-311G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

mol) < Ge_2Cl_4-2-TS (66 kcal/mol) < Ge_2F_4-2-TS (70 kcal/mol). Furthermore, as also found in disilene abstractions, it is clear that the calculated activation energy is substantially lower for Cl than for CCl_3 abstraction, indicating that in all cases the halogen abstraction process is highly favored.

D. Abstraction Products. As mentioned earlier, the expected products of the abstraction reactions of digermenes with CCl_4 are radicals containing a Ge−Ge bond, i.e., $R_2Ge{=}GeR_2Cl^•$ or $R_2Ge{=}GeR_2CCl_3^•$. The theoretical results depicted in Figures 6−10 reveal that all of these germanium radical products adopt a staggered ethane-like structure. It is of interest to note that, for the Cl abstraction (eq 1), the newly formed Ge−Cl bond in the transition structures is stretched by an average 10% relative to their final equilibrium values in $Ge_2(CH_3)_4$ and $Ge_2(SiH_3)_4$ abstractions and about 7.2% in Ge_2F_4 and Ge_2Cl_4 abstractions. Again, these features indicate that the electropositively substituted digermene abstraction reaction reaches the TS relatively early, whereas the halogen-substituted digermene abstraction arrives at the TS relatively late. Thus, one may anticipate a larger exothermicity for the former than the latter. As demonstrated in Table 1, the energetic ordering of the Cl abstraction of substituted digermene with CCl_4 shows that the reaction enthalpy for the process is $Ge_2(CH_3)_4$-1-Pro (−16 kcal/mol) < $Ge_2(SiH_3)_4$-1-Pro (−7.7 kcal/mol) < Ge_2H_4-1-Pro (−6.4 kcal/mol) < Ge_2Cl_4-1-Pro (+7.9 kcal/mol) < Ge_2F_4-1-Pro (+14 kcal/mol). Again, this is consistent with the observations shown earlier that the electropositively substituted digermene saddle point lies much closer to the reactants than the products. On the other hand, our theoretical investigations suggest that the energies of CCl_3 abstraction products are always above those of their corresponding reactants. This strongly indicates that this type of reaction is energetically very unfavorable, and that, if they did occur, the reactions would be endothermic as opposed to exothermic for the corresponding Cl abstractions.

In brief summary, two intriguing conclusions are worth noting: (1) Figures 6−10 show that every interaction component has an absolute value larger for path 2 (CCl_3 abstraction) than for path 1 (Cl abstraction). This is probably because the transition state for path 2 is later, tighter, and thus more strongly interacting than that for path 1. In other words, as in the disilene cases, chlorine abstraction is intrinsically more favorable than CCl_3 abstraction by digermene ($R_2Ge{=}GeR_2$), regardless of the electronegativity of the substituent R. (2) Our theoretical findings suggest that the abstraction of digermene with electropositive and/or bulky substituents is feasible from both a kinetic and a thermodynamic viewpoint.

V. Overview of Disilene and Digermene Abstraction

From our study of the mechanisms of the reactions of disilenes and digermenes with CCl_4, the major conclusions that can be drawn are as follows:

(1) For both disilene and digermene systems, a precursor complex for the haloalkane abstraction reaction should not be observable.

(2) The reaction proceeds in one step through a transition state characterized by a nonlinear arrangement of the three atoms involved in the process.

(3) Regardless of whether disilene or digermene is considered, the Cl abstraction is highly favored with respect to the CCl_3 abstraction from both kinetic and thermodynamic viewpoints.

(4) The magnitudes of the Cl abstraction barriers are not high. This strongly implies that the radical reactions of disilenes or digermenes with haloalkane should be facile processes at room temperature.

(5) It should be emphasized that, although both disilene and digermene abstractions are energetically feasible, the former reaction is more energetically as well as more kinetically favorable.

(6) Given identical reaction conditions the reaction of a disilene with a haloalkane should be more exothermic than that of a digermene. In consequence, the production of silaalkyl compounds is more thermodynamically favored than germanalkyl molecules.

(7) Irrespective of disilene or digermene species, the more electropositive and/or the more bulky the substituents, the lower the activation barrier and the more exothermic the haloalkane abstraction.

(8) Electronic as well as steric factors should play a significant role in determining the chemical reactivity of disilene and digermene species, kinetically as well as thermodynamically.

In brief, considering both the activation barrier and enthalpy, based on the model calculations presented here, we conclude that the disilene and digermene reactivity order should be as follows: $X_2(CH_3)_4 > X_2(SiH_3)_4 > X_2H_4 > X_2Cl_4 \approx X_2F_4$ (X = Si and Ge). In other words, electropositive substituents (or electron donating groups) on the disilene or digermene accelerate the abstraction reaction, whereas elentronegative substituents (or electron withdrawing groups) on the disilene or digermene will retard the reaction.

VI. Origin of the Barrier Height and the Reaction Enthalpy for Abstraction of Disilene and Digermene

In this section, an intriguing model for interpreting the reactivity of disilene and digermene abstractions is provided by the so-called configuration mixing (CM) model, which is based on Pross and Shaik's work.[23] Based on the CM model for barrier formation in heavy ethylene abstraction reactions, we are now in a position to provide some insight into the parameters that are likely to affect reactivity in these systems. It is readily seen that the barrier height ($\Delta E^{\ddagger}$) as well as the reaction enthalpy (ΔH) may be expressed in terms of the initial energy gap between the reactant and product configurations. That is to say, the anchor point for $^3[R_2X{=}XR_2]^3[CCl_4]$ in the reactant geometry, will be governed by the singlet−triplet energy gap for both disilene (or digermene) and carbon tetrachloride, that is, ΔE_{st} (= $E_{triplet} - E_{singlet}$ for $R_2X{=}XR_2$) + $\Delta E_{\sigma\sigma^*}$ (= $E_{triplet} - E_{singlet}$ for CCl_4). We thus conclude that both the order of the singlet and triplet states as well as their energy separation are responsible for the existence and the height of the energy barrier. Namely, the smaller the value of $\Delta E_{st} + \Delta E_{\sigma\sigma^*}$, the lower the activation barrier and the larger the exothermicity.[23,24]

Bearing these analyses in mind, we shall now explain the origin of the following observed trends:

(a) Given Identical Reaction Conditions, Why Is the Abstraction Reaction of Disilene More Favorable than That of Digermene both Kinetically and Thermodynamically? The reason for this can be traced to the singlet−triplet energy gap (ΔE_{st}) of $R_2X{=}XR_2$. As analyzed above, if $\Delta E_{\sigma\sigma^*}$ is a constant, the smaller the ΔE_{st} of $R_2X{=}XR_2$, the lower the barrier height and the larger the exothermicity, and, in turn, the faster the abstraction reaction. Indeed, our B3LYP calculations confirm this prediction and indicate an increasing trend in ΔE_{st} for $(CH_3)_2Si{=}Si(CH_3)_2$ (20.09 kcal/mol) < $(CH_3)_2Ge{=}Ge(CH_3)_2$ (20.66 kcal/mol), $(SiH_3)_2Si{=}Si(SiH_3)_2$ (20.62 kcal/mol) < $(SiH_3)_2Ge{=}Ge(SiH_3)_2$ (21.24 kcal/mol), $H_2Si{=}SiH_2$ (20.88 kcal/mol) < $H_2Ge{=}GeH_2$ (21.72 kcal/mol), $Cl_2Si{=}SiCl_2$ (28.94 kcal/mol) < $Cl_2Ge{=}GeCl_2$ (37.58 kcal/mol), and $F_2Si{=}SiF_2$ (34.91 kcal/mol) < $F_2Ge{=}GeF_2$ (52.40 kcal/mol). For this reason, haloalkane abstraction is much easier and more exothermic for the disilene system than for its digermene counterpart.

(b) Why Are the Electropositively and/or Bulkily Substituted Disilenes (or Digermenes) Much More Favorable than the Electronegatively Substituted Disilenes (or Digermenes) toward Abstraction Reactions with Haloalkanes? Again, the driving force for this may be traced to the singlet−triplet energy gap (ΔE_{st}) of $R_2X{=}XR_2$. As mentioned previously, our DFT results suggest an increasing trend in ΔE_{st} for $(CH_3)_2Si{=}Si(CH_3)_2$ (20.09 kcal/mol) < $(SiH_3)_2Si{=}Si(SiH_3)_2$ (20.62 kcal/mol) < $H_2Si{=}SiH_2$ (20.88 kcal/mol) < $Cl_2Si{=}SiCl_2$ (28.94 kcal/mol) < $F_2Si{=}SiF_2$ (34.91 kcal/mol) and $(CH_3)_2Ge{=}Ge(CH_3)_2$ (20.66 kcal/mol) < $(SiH_3)_2Ge{=}Ge(SiH_3)_2$ (21.24 kcal/mol) < $H_2Ge{=}GeH_2$ (21.72 kcal/mol) < $Cl_2Ge{=}GeCl_2$ (37.58 kcal/mol) < $F_2Ge{=}GeF_2$ (52.40 kcal/mol). From Table 1, it is seen that these results are in accordance with both the activation energy as well as the enthalpy ($\Delta E^{\ddagger}$, ΔH) trends for Cl abstractions by disilenes which are $(CH_3)_2Si{=}Si(CH_3)_2$ (−0.90, −24), $(SiH_3)_2Si{=}Si(SiH_3)_2$ (1.3, −20), $H_2Si{=}SiH_2$ (3.2, −18), $Cl_2Si{=}SiCl_2$ (4.3, −17), and $F_2Si{=}SiF_2$ (5.0, −16) kcal/mol. Likewise, the same phenomenon can also be found in the Cl abstractions by digermenes as follows: $(CH_3)_2Ge{=}Ge(CH_3)_2$ (0.61, −15), $(SiH_3)_2Ge{=}Ge(SiH_3)_2$ (5.6, −7.7), $H_2Ge{=}GeH_2$ (6.7, −6.4), $Cl_2Ge{=}GeCl_2$ (11, 7.9), and $F_2Ge{=}GeF_2$ (12, 14) kcal/mol.

(c) For a Given Disilene (or Digermene) Species, Why Is the Cl Abstraction Favored over the CCl_3 Abstraction? The reactivity order for both Cl and CCl_3 abstractions can be easily understood from the bonding energy point of view. Let us expand on the effect of the difference in the strength of the Si−Cl bond (i.e., abstraction of Cl, see eq 1) and the Si−C bond (i.e., abstraction of CCl_3, see eq 2) on the reactivity. Based on the bonding dissociation energy in $(CH_3)_3Si{-}Cl$ and in $(CH_3)_3Si{-}CH_3$, the difference in these bond strength amounts to be about 25 kcal/mol, in favor of the Si−Cl bond. This is almost the entire difference in the disilene reaction energies between eqs 1 and 2, which are estimated to be 31, 30, 32, 30, and 40 kcal/mol for R = H, F, Cl, CH_3, and SiH3, respectively. This is what we observed in the disilenes, which are in excellent agreement with the known experimental results.[2i,8] The same explanation can also be applied to the digermene systems as shown in Table 1.

VII. Conclusion

In this paper, we have reported the results of a theoretical study of the halogen abstraction reactions by various disilenes and digermenes from carbon tetrachloride using density functional theory. Our model calculations have shown that the B3LYP/6-311G(d) level is an appropriate theory with which to investigate heavier ethylene abstraction processes because it can reproduce the available experimental results accurately. In fact, the good agreement between our computational results and experimental observations is quite encouraging. Moreover, we have demonstrated that the computational results can be rationalized using a simple CM model. Although the relative reactivity of various heavy olefins is determined by the entire potential energy surface, the concepts of the CM model, focusing on the singlet−triplet splitting in the reactants, allows one to assess quickly the relative reactivity of a variety of disilenes or digermenes without specific knowledge of the actual energies of the interactions involved. Therefore, not only have we given explanations of the experimental results for the disilene abstraction reactions, but we have also made predictions of some unknown digermene abstraction reactions.

Finally, these approaches have proved to be rather effective and can provide chemists with mechanistic insights into the factors controlling the radical reactions of the heavier analogues of olefins. Despite the fact that the estimated magnitude of the energy barrier and the predicted enthalpy of such abstraction reactions may appear to be dependent on the calculational level applied, we would emphasize that the trends, rather than the precise values, are more accurate and more valuable. This, in turn, will allow a better understanding of the nature of such systems as well as a number of predictions to be made.

It is hoped that our study will provide stimulation for further research into the subject.

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(6) There is growing evidence from both theory and experiment that the unsaturated disilenes exhibit chemical features that are quite dissimilar from analogous carbon-containing compounds. This is not altogether surprising indeed−rather simple qualitative arguments indicate that p-type atomic orbitals play a more important role than s orbitals in hybridization in silicon hydrides (see ref 7). This is in contrast to carbon hydrides in which s and p functions are comparably balanced in the formation of sp-, sp^2-, and sp^3-hybrid orbitals. As a result, certain chemical properties, such as equilibrium geometries and reactivity, can exhibit striking features in these compounds.

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