Mechanism of Abstraction Reactions of Heavy Cyclopropenes with Carbon Tetrachloride

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The potential energy surfaces for the abstraction reactions of heavy cyclopropenes (X−Y−Z) with carbon tetrachloride have been characterized in detail using density functional theory (B3LYP), including zero-point corrections. Five cyclopropene analogues including **A(C−C−C)**, **B(Ge−Si−Si)**, **C(Si−Si−Si)**, **D(Si−Si−Ge)**, and **E(Ge−Ge−Ge)**, have been chosen in this work as model reactants. Two reaction paths, the Cl abstraction I and the CCl_3 abstraction II, have been considered in the present study. Our theoretical findings strongly suggest that the former is more favorable, with a very low activation energy and a large exothermicity. This is in accordance with available experimental observations. Moreover, our theoretical investigations also indicate that the more electropositive the elements making up the double bond of a heavy cyclopropene, the lower its activation barrier and the more exothermic the haloalkane abstraction. That is, electronic factors play a dominant role in determining the chemical reactivity of the heavy cyclopropene 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

The development of the chemistry of multiply bonded systems involving elements in higher periods is generally regarded as a renaissance of main group chemistry.[1] In particular, small ring systems consisting of the heavy group 14 elements (such as Si, Ge, and Sn) have been synthesized and isolated in the past decade thanks to the use of bulky stabilizing groups.[2] That is, it has now been possible to characterize these reactive species due to their kinetic and thermodynamic stabilization by appropriate substitution. Among them, cyclotrimetallenes, processing a metal−metal double bond in the three-membered ring skeleton, have only recently been synthesized.[2] In spite of the much greater difficulties in the preparation of such compounds, due to their high reactivity and great ring strain, compared with their carbon analogue (cyclopropene),[3] they are constituting a new highly promising and quickly developing class of organometallic compounds, i.e., heavy cyclopropene analogues. Indeed, the chemistry of heavy cyclopropenes is starting to bring about both novel insights into structural and physical properties as well as possibilities for the synthesis of new and interesting systems.[2] For instance, heavy cyclopropenes can give access to cyclic and bicyclic compounds via addition and cycloaddition reactions.[4] Besides these, available experimental evidence has demonstrated that highly strained heavy cyclopropenes[2] exhibit enhanced reactivity over analogous cyclopropenes,[3] particularly in chemical reactions with halogenated hydrocarbons.[2] As such, many novel reactions can be carried out with heavy cyclopropenes that are not feasible or at least cannot be carried out under mild conditions with analogous cyclopropenes.

In this work, we shall focus on the chemical reactions of heavy cyclopropenes with haloalkanes. The reactions of heavy cyclopropenes with CCl_4 have been reported in the case of cyclotrisilenes and mixed cyclotrimetallenes.[2] In this study, cyclotrisilene **1**, 1-disilagermirene **2**, and 2-disilagermirene **3** were reacted with an excess of CCl_4 to form the corresponding *trans*-1,2-dichloro derivatives, even at low temperature, in nearly quantitative yield (see reactions 1−3 in Scheme 1).[5] Also, cyclotrisilene **4** reacted with CCl_4 to produce the *trans*-1,2-dichloro derivative (reaction 4 in Scheme 1).[6] Moreover, the reaction of cyclotrisilene **5** with 1,2-dibromoethane yields quantitatively the corresponding *trans*-1,2-dibromocyclotrisilane (reaction 5 in Scheme 1),[5] and the 1-disilagermirene **6** reacts with MeI with quantitative formation of *trans*-1-iodo-2-methyldisilagermirane (reaction 6 in Scheme 1).[2b] All these available experiments strongly suggest that these reactions proceed selectively to produce only the trans isomers. In fact, Sekiguchi and co-workers proposed that these experimental results should be explained by steric requirements as well as by the single-electron-transfer (SET) mechanism.[2b]

It is these fascinating experimental results that inspire this study. The key questions are how the trans products are formed and why they show a significant abundance in the formation process. Knowledge of the features of potential energy surfaces is in general of great value in understanding the roles of various possible processes. Although the above experimental results help in understanding the potential energy surfaces in heavy cyclopropene systems, they are at present not capable of providing complete mechanistic detail. Indeed, it is very difficult to detect the intermediate and the transition state due to the limitations in current experimental techniques. Theory, a primary source of reliable fundamental information, is therefore an extremely valuable tool with which to study the heavy cyclopropene species. According to the above available experimental results,[2b] two competitive reaction pathways have been considered for the reactions of heavy cyclopropenes with halocarbons. Basically, they are both abstraction mechanisms proceeding via either a chlorine atom (reaction I) or a CCl_3 group (reaction II).

To examine the generality of the heavy cyclopropene (X−Y−Z) abstractions, we have thus undertaken a systematic

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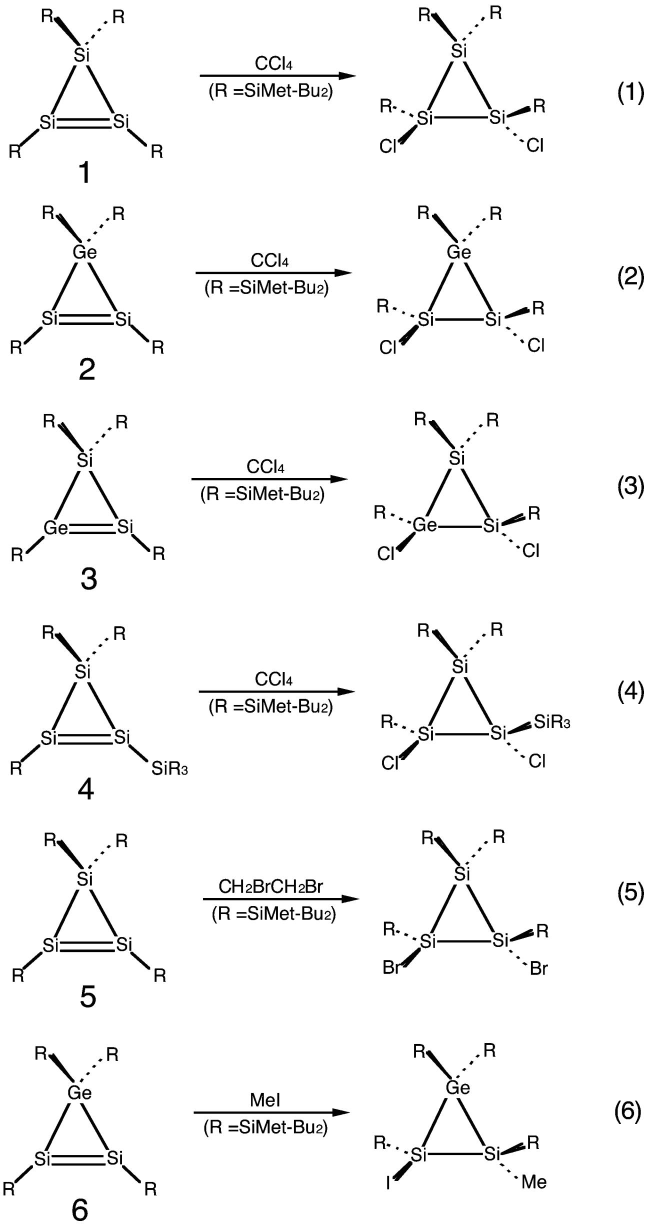

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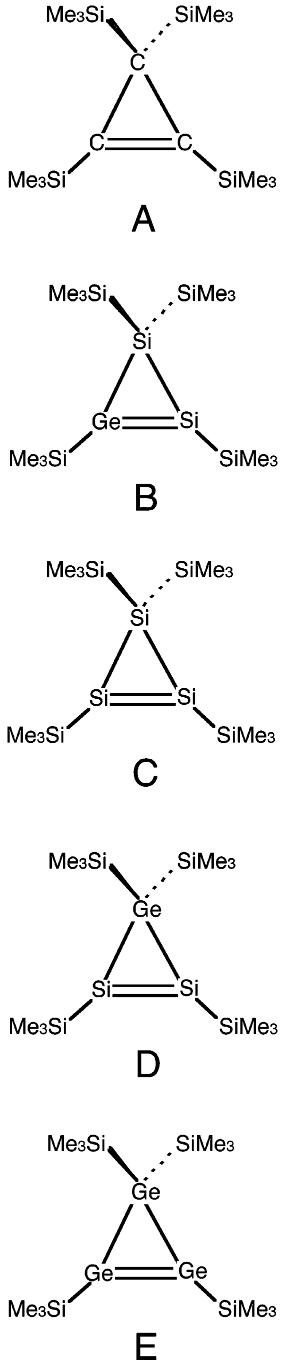
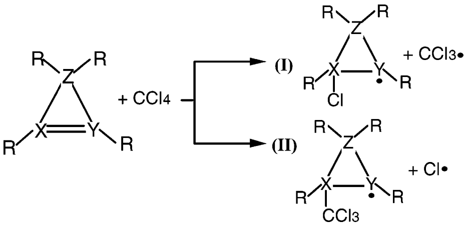


investigation of the abstraction reactions of model compounds **A(C−C−C)**, **B(Ge−Si−Si)**, **C(Si−Si−Si)**, **D(Si−Si−Ge)**, and **E(Ge−Ge−Ge)** (see Scheme 2) and CCl_4. The reason for choosing these model reactions is because they represent various kinds of heavy cyclopropene abstractions for which experimental results have been reported by Sekiguchi and co-workers.[2] Indeed, only through a thorough systematic study of heavy cyclopropene abstractions can we understand trends in their reactivity.[6−8]



(X, Y, Z = C, Si, and Ge; R = $SiMe_3$) (1)

Our primary aim in this work is to explain the trend of the reactivities in numerous variations in the group 14 elements and to bring out the definitive factors that control the activation barrier for the heavy cyclopropene abstraction reactions. To the best of our knowledge, this is the first theoretical study on the abstraction of heavy cyclopropenes and the first application of DFT to the majority of these molecules. Thus, the present calculations can provide comprehensive energetic information on the abstraction potential energy surface for all the reactions. It is believed that a better understanding of the thermodynamic and kinetic aspects of such abstractions may suggest further synthetic applications involving heavy cyclopropene compounds.

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. The geometries and energetics of the stationary points on the potential energy surface were calculated using the DFT (B3LYP)[9] method in conjunction with the 6-31G(d) basis set.[10] We denote our B3LYP calculations by B3LYP/6-31G(d). Thus, the model compounds (see Scheme 2) have at least 182 (for A) electrons and 373 basis functions. The spin-unrestricted (UB3LYP) formalism used for the open-shell (doublet) species, and their $<S^2>$ values were nearly all equal to the ideal value (0.75). Vibrational frequency calculations at the B3LYP/6-31G(d) level were used to characterize all stationary points as either minima (the number of imaginary frequencies (NIMAG) = 0) or transition states (NIMAG = 1). The relative energies are thus corrected for vibrational zero-point energies (ZPE, not scaled). All the stationary points were positively identified as equilibrium structures (the number of imaginary frequency (NIMAG = 0) or transition states (NIMAG = 1)). It should be pointed out that our theoretical findings suggest that singlet state chemistry should be dominant because of their high reactivity toward heteroatom lone pairs. Therefore, only the singlet potential energy surface was considered throughout this work. All of the DFT calculations were performed with the GAUSSIAN 03 package of programs.[11]

III. Results and Discussion

In this section the results for four regions on the potential energy surfaces will be presented: heavy cyclopropene (X−Y−Z; X, Y, Z = C, Si, and Ge) + CCl_4, the precursor complex (**PC**), the transition state (**TS**), and the abstraction products (**AP**). The fully optimized geometries for those stationary points calculated at the B3LYP/6-31G(d) level are given in Figures 1−5, respectively. The selected geometrical parameters and relative energies at the B3LYP level of theory are collected in Tables 1 and 2, together with some known experimental results. The Cartesian coordinates calculated for the stationary points at the B3LYP level are available as Supporting Information.

(1) Geometries and Energetics of Heavy Cyclopropenes. As one can see in Table 1, the computed structures of the singlet heavy cyclopropene compound (X−Y−Z) are in good agreement with the available experimental data (in parentheses).[6,7] In particular, it is of interest to note that some of the calculated bond lengths (such as model **C**) are in perfect agreement with the experimental values.[6] This thus gives us confidence that the present models with the current method (B3LYP/6-31G(d)) employed in this study should provide reliable information for the discussion of the reaction mechanism.

By analogy with all other known dimetallenes ($R_2E{=}ER_2$; E = C, Si, Ge, Sn, and Pb),[8] it is expected that the two lowest states of heavier cyclopropene analogues (**A**−**E** in Scheme 2) are singlet and triplet.[12] These states are derived from the ground state HOMO, an essentially bonding π orbital based on the central doubly bonded X=Y atoms, and the LUMO, an antibonding π orbital on the X=Y atoms. As one can see in Table 1, the triplet state of heavy cyclopropene (X−Y−Z) has a significantly larger double bond distance (X=Y) and a wider bond angle (∠XZY) than its closed shell singlet state. This can be easily understood from the simple orbital results.[12,13] Indeed, this is usually the case in group 14 cyclopropene compounds, in accordance with expectations of the Walsh rules.[14] Additionally, the X=Y double bond distance for both singlet and triplet states shows a monotonic increase down the group from C to Ge. For instance, the X=Y double bond distance increases in the order **A** (1.310 Å) < **C** (2.143 Å) < **D** (2.159 Å) < **B** (2.178 Å) < **E** (2.261 Å). This trend is also the same in the triplet state.

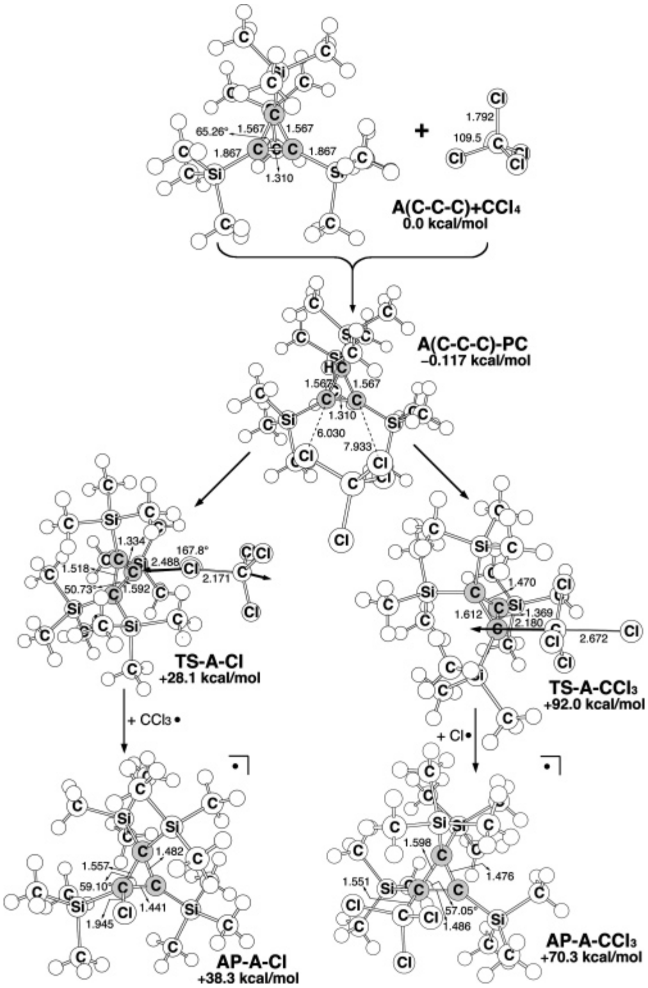


Figure 1. The optimized geometries (in Å and deg) for the precursor complexes (**PC**), transition states (**TS**), and abstraction products (**AP**) of cyclotricarene (C−C−C) with CCl_4. All were calculated at the B3LYP/6-31G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

Furthermore, the singlet−triplet energy separations ($\Delta E_{st} = E_{triplet} - E_{singlet}$) of group 14 heavy cyclopropenes is one of the most important parameters in the present study. Our theoretical results as given in Table 2 show a decreasing trend in the singlet−triplet energy splitting, ΔE_{st}, for **A**(46.3 kcal/mol) > **B**(20.7 kcal/mol) > **C**(18.0 kcal/mol) > **D**(16.9 kcal/mol) > **E**(14.1 kcal/mol) at the B3LYP/6-31G(d) level of theory. This is quite analogous to previous ΔE_{st} results observed for dimetallenes.[8] Since the HOMO−LUMO energy difference for a dimetallene decreases rapidly from carbon down to lead, so, in turn, does its ΔE_{st}.[8] Similarly, our theoretical investigations also confirm that the heavier the group 14 elements participating in the heavy cyclopropene system, the smaller its singlet−triplet energy splitting ΔE_{st} is. The reason for this is primarily because of the interaction of the high-lying π orbitals of the endocyclic X=Y double bonds in the framework and the low-lying σ*-orbitals of the exocyclic Z−Si (Z = C, Si, and Ge) bonds.[15] Besides this, from a binding energy point of view, it is well-established that the π bond strength of a double bond decreases from carbon to lead owing to the longer bond length down with the group 14 elements.[15] Combining all these important factors, one may obtain the following conclusion: the greater the atomic weight of group 14 elements involved in the double bond of a heavy cyclopropene, the weaker its π bond strength, and the smaller the singlet−triplet energy gap, ΔE_{st}. We shall use this

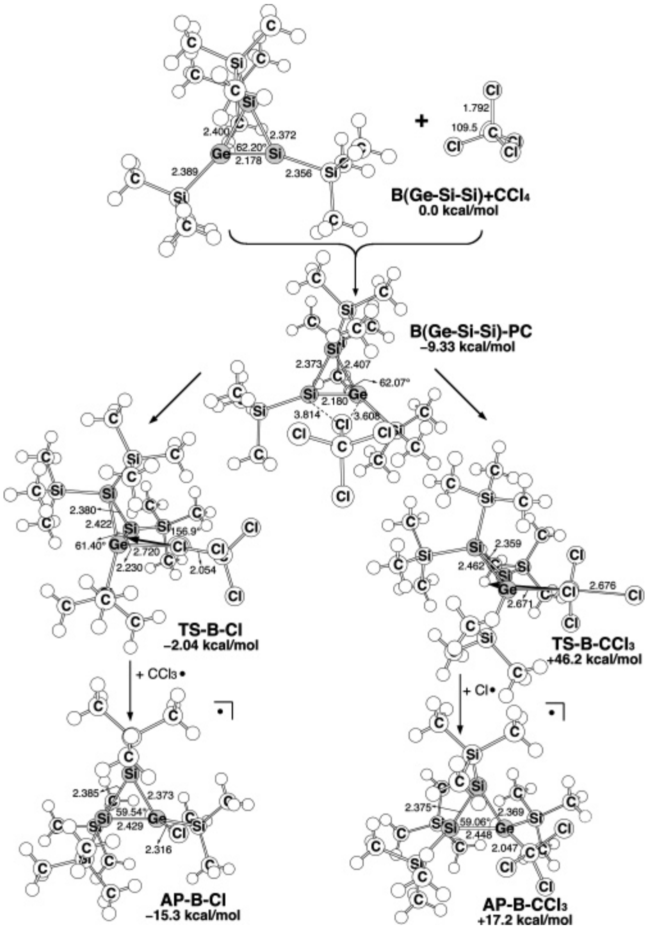


Figure 2. The optimized geometries (in Å and deg) for the precursor complexes (**PC**), transition states (**TS**), and abstraction products (**AP**) of 2-disilagermirene (Ge−Si−Si) with CCl_4. All were calculated at the B3LYP/6-31G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

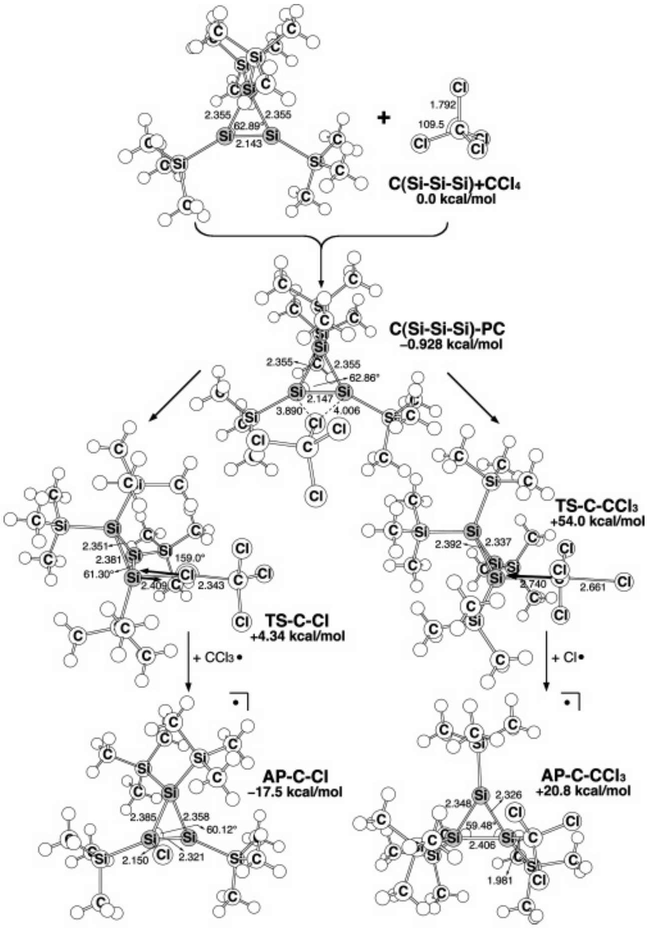


Figure 3. The optimized geometries (in Å and deg) for the precursor complexes (**PC**), transition states (**TS**), and abstraction products (**AP**) of cyclotrisilene (Si−Si−Si) with CCl_4. All were calculated at the B3LYP/6-31G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

conclusion to explain the origin of barrier heights for heavy cyclopropene abstractions in a later section.

(2) Precursor Complexes. In fact, when we searched the potential energy surfaces of the abstraction of heavy cyclopropenes with CCl_4 for transition structures, we noticed an initial decrease in the total energy as compared with the isolated molecules at large separations. That is to say, the abstraction of CCl_4 by heavy cyclopropenes initiates the formation of a precursor complex. The optimized geometries of complexation of heavy cyclopropenes with CCl_4, i.e., **A(C−C−C)−PC, B(Ge−Si−Si)−PC, C(Si−Si−Si)−PC, D(Si−Si−Ge)−PC,** and **E(Ge−Ge−Ge)−PC** are shown in Figures 1−5, respectively. For convenience, the energies are given relative to the two reactant molecules, i.e., heavy cyclopropene (X−Y−Z) and CCl_4, which are also summarized in Figures 1−5 and Table 2. We describe these species as complexes, because there are only minor differences between their bond lengths and those of the free reactants.

As seen in Figures 1−5, all these five precursor complexes adopt very similar X−Y−Z----CCl_4 bonding characteristics. They are best described as π-bonded complexes, in which the CCl_4 molecule is interacting with the π system of the heavy cyclopropene (X−Y−Z), the X═Y----Cl bond length ranging from 3.55 Å to 7.93 Å. Namely, the calculated bond distances for (X−Y−Z)----CCl_4 contacts are much longer than those calculated for the corresponding products (vide infra). Accordingly, it is not surprising that such long bond distances are reflected in the calculated complexation energy. Indeed, as shown in Figures 1−5 and Table 2, the energy of the precursor complex relative to its corresponding reactants is less than 10 kcal/mol at the present DFT level of theory. Calculated vibrational frequencies for the precursor complexes reveal that these structures are true minima on the potential energy surface of the heavy cyclopropene + CCl_4 reaction. Note that there are only very small distortions of the intramolecular bond lengths relative to the free reactants. In consequence, 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.

Furthermore, one may wonder whether any experiments can detect the precursor complex formed by heavy cyclopropene with CCl_4 or not. According to the present theoretical results, it appears unlikely that the π-bonded complexes can be isolated experimentally at room temperature because their stabilization energies are too low to be detected. Indeed, to the best of our knowledge, no experimental detection of heavy cyclopropene−haloalkane complexes formed during the reactions has been reported yet.[2]

(3) Transition States. As mentioned in eq 1, there are two reaction pathways for the abstraction reactions of heavy cyclopropenes (X−Y−Z). One is the Cl abstraction I. That is, starting from the **TS−Cl**, this leads apparently to Cl atom abstraction and the formation of $(X{-}Y{-}Z)Cl^{\bullet} + CCl_3^{\bullet}$. On the other hand, the CCl_3 abstraction reaction II via the **TS−CCl₃** results in (X−

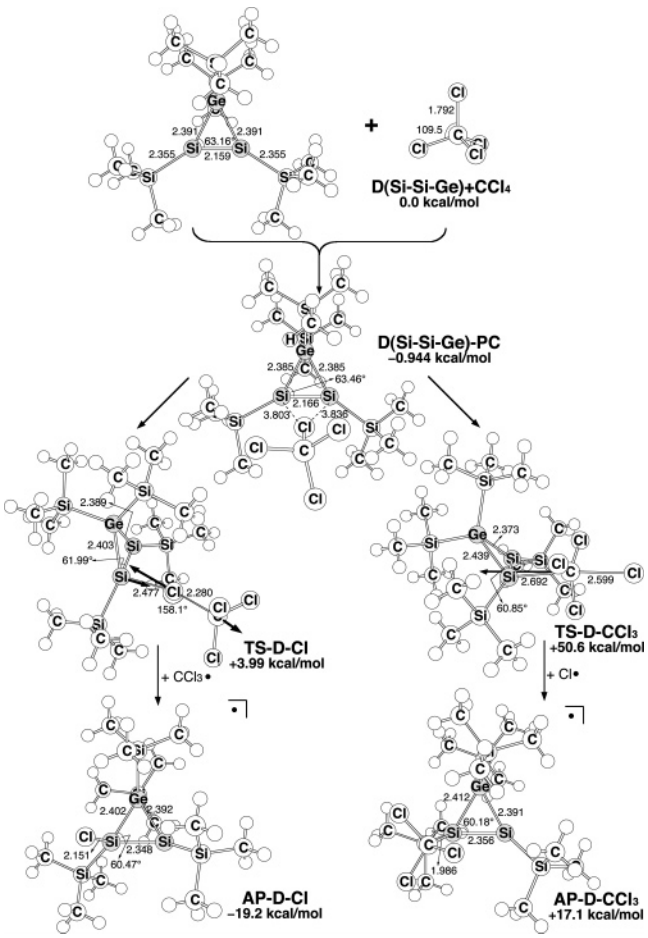


Figure 4. The optimized geometries (in Å and deg) for the precursor complexes (**PC**), transition states (**TS**), and abstraction products (**AP**) of 1-disilagermirene (Si−Si−Ge) with CCl_4. All were calculated at the B3LYP/6-31G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

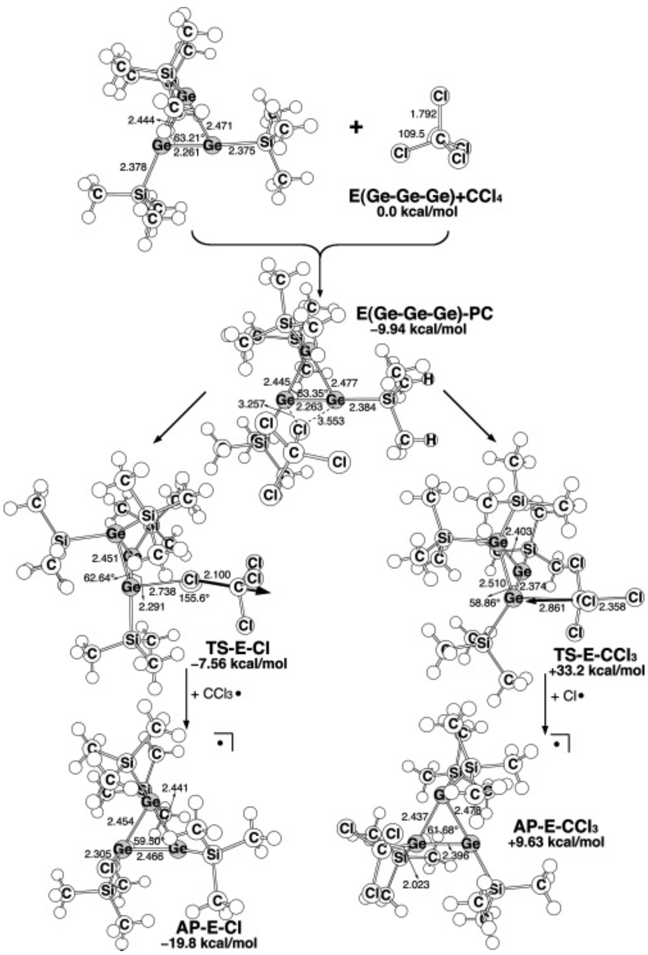


Figure 5. The optimized geometries (in Å and deg) for the precursor complexes (**PC**), transition states (**TS**), and abstraction products (**AP**) of cyclotrigermene (Ge−Ge−Ge) with CCl_4. All were calculated at the B3LYP/6-31G(d) level of theory. The heavy arrows indicate the main components of the transition vector.

TABLE 1: Selected Geometrical Parameters for Singlet and Triplet Heavy Cyclopropenes (X−Y−Z)[a,b]

system (X−Y−Z)	X=Y (Å)	X−Z and Y−Z (Å)	∠XZY (deg)	X−Si and Y−Si (Å)
		singlet		
A (C−C−C)	1.310	1.567	49.43	1.867
B (Ge−Si−Si)	2.178	2.400, 2.372	54.29	2.389, 2.356
C[c] **(Si−Si−Si)**	2.143	2.355	54.15	2.363
	(2.138)	(2.358)		(2.369)
D (Si−Si−Ge)	2.159	2.391	53.67	2.355
E[d] **(Ge−Ge−Ge)**	2.261	2.458	54.78	2.377
	(2.239)	(2.522)	(52.7)	(2.448)
		triplet		
A (C−C−C)	1.487	1.475	60.51	1.835
B (Ge−Si−Si)	2.420	2.431, 2.362	60.64	2.411, 2.370
C (Si−Si−Si)	2.343	2.375	59.12	2.375
D (Si−Si−Ge)	2.377	2.397	59.45	2.368
E (Ge−Ge−Ge)	2.504	2.480	61.40	2.417

[a] At the B3LYP/6-31G(d) level of theory. For the B3LYP optimized structures of the singlet reactants see Figures 1−5. Experimental data are in parentheses. [b] The abbreviation "X−Y−Z" is taken from eq 1. See the text. [c] See ref 6. [d] See ref 7.

Y−Z)$CCl_3^\bullet$ + $Cl^\bullet$ products. In both pathways, CCl_4 is considered to attack the less electronegative atom of the double bond. 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 **TS−A−Cl**, **TS−B−Cl, TS−C−Cl, TS−D−Cl**, and **TS−E−Cl** for (I) (Cl abstraction) and **TS−A−CCl$_3$, TS−B−CCl$_3$, TS−C−CCl$_3$, TS−D−CCl$_3$,** and **TS−E−CCl$_3$** for (II) (CCl_3 abstraction), respectively. It should be noted that the results for the transition states of the heavy cyclopropene abstraction reactions might perhaps be one of the most interesting results of the present study since very little is known about the barrier heights.[2]

Regarding the Cl abstraction, one can observe that the main components of the transition vector correspond to the motion of the chlorine atom between X (the attacked atom on the double bond) and the carbon atoms, whose eigenvalue gives an imaginary frequency of 105i (**TS−A−Cl**), 73.5i (**TS−B−Cl**), 93.9i (**TS−C−Cl**), 125i (**TS−D−Cl**), and 71.2i (**TS−E−Cl**) cm^{-1}. In fact, inspection of the transition vector shows clearly that the reaction proceeds toward formation of (X−Y−Z)$Cl^\bullet$ and $CCl_3^\bullet$. In addition, decreasing the electronegativity of the attacked atom X in the heavy cyclopropene (X−Y−Z) causes a large increase in the (X−Y−Z)−Cl′ (Cl′ = the migrating chlorine atom) distance. That is, the newly forming X−Cl′ bond length increases in the order **TS−A−Cl** (2.39 Å) < **TS−C−Cl** (2.41 Å) < **TS−D−Cl** (2.48 Å) < **TS−B−Cl** (2.72 Å) < **TS−E−Cl** (2.74 Å). It is noted that the three atoms (X, Cl′, and C) involved in the bond-breaking and bond-forming processes are not collinear along the Cl′−C axis as displayed in Figures 1−5. For instance, the X atom of the heavy cyclopropene (X−Y−Z)molecule makes an angle, with respect

TABLE 2: Relative Energies for Singlet and Triplet Heavy Cyclopropenes (X−Y−Z) and for the Process Heavy Cyclopropene + CCl_4 → Precursor Complex → Transition State → Abstraction Products[a]

system	ΔE_{st}[b] (kcal mol^{-1})	ΔE_{cpx}[c] (kcal mol^{-1})	$\Delta E^{\ddagger}$[d] (kcal mol^{-1})	ΔH[e] (kcal mol^{-1})
		for Cl abstraction		
A (C−C−C)	+46.29	−0.1167	+28.07 (+28.19)	+38.26
B (Ge−Si−Si)	+20.66	-9.326	−2.043 (+7.283)	−15.29
C (Si−Si−Si)	+18.03	−0.9281	+4.337 (+5.265)	−17.49
D (Si−Si−Ge)	+16.91	−0.9444	+3.993 (+4.937)	−19.16
E (Ge−Ge−Ge)	+14.14	−9.938	−7.559 (+2.339)	−19.76
		for CCl_3 abstraction		
A (C−C−C)	+46.29	−0.1167	+92.01 (+92.13)	+70.34
B (Ge−Si−Si)	+20.66	−9.326	+46.24 (+55.57)	+17.15
C (Si−Si−Si)	+18.03	−0.9281	+54.02 (+54.95)	+20.78
D (Si−Si−Ge)	+16.91	−0.9444	+50.60 (+51.55)	+17.05
E (Ge−Ge−Ge)	+14.14	−9.938	+33.16 (+43.10)	+9.613

[a] At the B3LYP/6-31G(d) levels of theory. For the B3LYP optimized structures of the stationary points see Figures 1−5. [b] Energy relative to the corresponding singlet state. A positive value means the singlet is the ground state. [c] The stabilization energy of the precursor complex, relative to the corresponding reactants. [d] The activation energy of the transition state, relative to the corresponding reactants (relative to the precursor complex in parentheses). [e] The enthalpy of the product, relative to the corresponding reactants.

to the X−Cl′−C bond of 168°, 157°, 159°, 158°, and 156° for model molecules **A**, **B**, **C**, **D**, and **E**, respectively.

Next we consider the CCl_3 abstraction II. 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 heavy cyclopropenes are also presented in Figures 1−5, respectively. These transition structures are characterized by one imaginary frequency of 589i, 493i, 515i, 526i, and 483i cm^{-1} for model molecules **A**, **B**, **C**, **D**, and **E**, 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 $X{-}CCl'_3$ bond. If one examines these bond distances for the attacking CCl_4 molecule in Figures 1−5, one may easily find that the reaction coordinate is fundamentally an asymmetric stretch at the conventional transition state. Besides, to avoid the steric repulsion with the substituents of heavy cyclopropene (X−Y−Z), the X····C····Cl angle is slightly bent in these TS's, as observed in Figures 1−5. For example, our theoretical findings demonstrate that the angle ∠X−C−Cl of **TS−CCl$_3$** for **A−E** five model molecules is 178°, 175°, 174°, 173°, and 175°, respectively.

Considering the effects of substitution, our results suggest that, from a kinetic viewpoint, the abstraction reactions of heavy cyclopropene systems bearing electropositive elements on the double bond are more facile than that with more electronegative elements. As seen in Table 2, for instance, the B3LYP barrier height for Cl abstraction by heavy cyclopropenes decreases in the order (relative to the precursor complex) **TS−A−Cl** (28 kcal/mol) > **TS−B−Cl** (7.3 kcal/mol) > **TS−C−Cl** (5.3 kcal/mol) > **TS−D−Cl** (4.9 kcal/mol) > **TS−E−Cl** (2.3 kcal/mol). The same effect can also be found in the CCl_3 abstractions as follows (relative to the precursor complex): **TS−A−CCl$_3$** (92 kcal/mol) > **TS−B−CCl$_3$** (56 kcal/mol) > **TS−C−CCl$_3$** (55 kcal/mol) > **TS−D−CCl$_3$** (52 kcal/mol) > **TS−E−CCl$_3$** (43 kcal/mol). In other words, our theoretical work strongly indicates that the lower the electronegativity of the substituent group 14 elements, the lower its barrier to abstraction with CCl_4. Moreover, as already found in dimetallene abstractions,[8] 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.

(4) Abstraction Products. The expected products of the abstraction reactions of heavy cyclopropenes with CCl_4 are either **AP−Cl** and $CCl_3^{\bullet}$ or **AP−CCl$_3$** and $Cl^{\bullet}$. Accordingly, the optimized product structures are named as **AP−A−Cl**, **AP−B−Cl, AP−C−Cl, AP−D−Cl**, **AP−E−Cl**, **AP−A−CCl$_3$**, **AP−B−CCl$_3$**, **AP−C−CCl$_3$**, **AP−D−CCl$_3$**, and **AP−E−CCl$_3$**, which are collected Figures 1−5, and the calculated reaction enthalpies for the abstractions are given in Table 2. Again, as Figures 1−5 show, the order of the X−Cl (X is the attacked atom) bond length follows the same trend as the atomic weight of the atom X: **AP−A−Cl** (1.95 Å) < **AP−C−Cl** (2.15 Å) ≈ **AP−D−Cl** (2.15 Å) < **AP−B−Cl** (2.32 Å) ≈ **AP−E−Cl** (2.32 Å). The same effect can also be found in the CCl_3 abstraction reactions: **AP−A−CCl$_3$** (1.55 Å) < **AP−C−CCl$_3$** (1.99 Å) ≈ **AP−D−CCl$_3$** (1.99 Å) < **AP−E−CCl$_3$** (2.02 Å) < **AP−B−CCl$_3$** (2.05 Å).

As demonstrated earlier, a heavy cyclopropene with more massive and less electronegative atoms on the double bond reaches the transition state relatively early, whereas a cyclopropene analogue with less massive but more elecronegative atoms on the double bond arrives at the transition state relatively late. The former is therefore predicted to undergo a more exothermic abstraction, which is borne out by our DFT calculations. For instance, our theoretical findings indicate that the enthalpy for the Cl atom abstraction of heavy cyclopropenes decreases in order **AP−A−Cl** (+38.3 kcal/mol) > **AP−B−Cl** (−15.3 kcal/mol) > **AP-C−Cl** (−17.5 kcal/mol) > **AP−D−Cl** (−19.2 kcal/mol) > **AP−E−Cl** (−19.8 kcal/mol). On the other hand, our theoretical results demonstrate 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 heavy cyclopropene are endothermic, which would be energetically unfavorable. That is to say, the abstraction products $(X{-}Y{-}Z)CCl_3^{\bullet}$ are not produced from a CCl_3 group transfer reaction as in (II) but possibly exist if these radicals ($(X{-}Y{-}Z)CCl_3^{\bullet}$) are produced through other reaction paths.

IV. Overview of Heavy Cyclopropene Abstraction

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

(1) For the heavy cyclopropene systems studied in the present work a precursor complex for the CCl_4 abstraction reaction should not be observable.

(2) The abstraction reactions of the heavy cyclopropenes proceed via a two-step abstraction-recombination path (formation of the two radicals and then abstraction of another atom in a subsequent step collapsing to the final product). Moreover, such abstraction reactions should occur via a transition state characterized by a nonlinear arrangement of the three atoms involved in the process.

(3) During the competition between Cl- and CCl_3-abstraction, the magnitudes of the Cl abstraction barriers are much lower

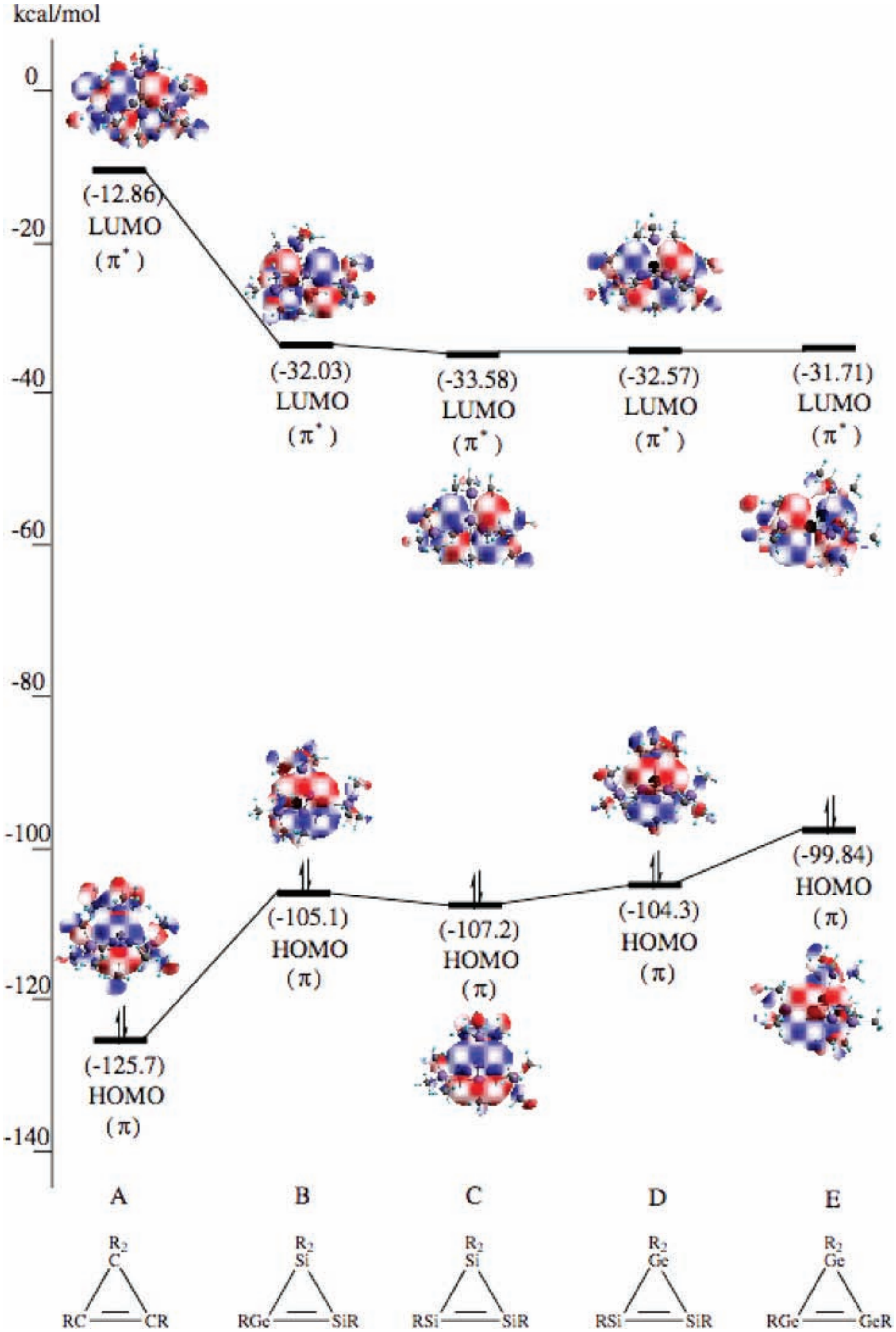


Figure 6. Calculated frontier molecular orbitals for model molecules **A** (C−C−C), **B** (Ge−Si−Si), **C** (Si−Si−Si), **D** (Si−Si−Ge), and **E** (Ge−Ge−Ge). The abbreviation R stands for the SiMe$_3$ group. For details see the text.

than those of the CCl$_3$ abstractions. This strongly implies that the one-chlorine-atom-abstraction reaction should be the most energetically favorable path for heavy cyclopropene abstractions. In consequence, one-chlorine-atom-abstraction will be the first step in the initial reaction of a heavy cyclopropene and a halocarbon, and halogen-abstraction products will dominate. Our model conclusions are consistent with some available experimental findings.^{2}

(4) For a given haloalkane, the more massive and less electronegative the doubly bonded atoms of a given heavy cyclopropene are, the easier the abstraction reaction with haloalkane will be. That is to say, the present theoretical findings suggest that the reactivity of heavy cyclopropenes increases in the order model molecule **A** (C−C−C) < model molecule **C** (Si−Si−Si) < model molecule **E** (Ge−Ge−Ge). It is thus presumably concluded that heavy cyclopropenes containing either the Sn═Sn or the Pb═Pb double bond can readily abstract halogen atoms from halocarbons, while heavy cyclopropenes containing the C═C double bond are unreactive toward them.

(5) Electronic as well as steric factors should play a pivotal role in determining the chemical reactivity of heavy cyclopropene species, kinetically as well as thermodynamically.

In brief, based on the model calculations presented here, it is found that a heavy cyclopropene should undergo first one atom (Cl) abstraction and then proceed to the second atom (Cl) abstraction. Finally, one may thus obtain the *trans*-1,2-dichlorocyclotrimetallane products. This is consistent with what we found in the Sekiguchi's experimental observations.[2]

V. The Configuration Mixing Model

Based on our theoretical study, all our computational results can be rationalized on the basis of a configuration mixing (CM) model which was developed by Pross and Shaik.[8,17,18] According to this model, it is readily seen that the barrier height ($\Delta E^{\ddagger}$) as well as the reaction enthalpy (ΔH) should be expressed in terms of the singlet−triplet splitting ΔE_{st} ($=E_{triplet} - E_{singlet}$) of the reactant, i.e., the heavy cyclopropene (X−Y−Z). That is to say, the reactivity of such abstraction reactions will be governed by the singlet−triplet excitation energies for each of the reactants, i.e., ΔE_{st} ($=E_{triplet} - E_{singlet}$ for heavy cyclopropene) and $\Delta E_{\sigma\sigma^*}$ ($=E_{triplet} - E_{singlet}$ for CCl_4). The stabilization of the transition state of an abstraction reaction depends on the singlet−triplet splitting ΔE_{st} ($=E_{triplet} - E_{singlet}$) of the reactant heavy cyclopropene.[17,18] Accordingly, if $\Delta E_{\sigma\sigma^*}$ is a constant, then the smaller the value of ΔE_{st} of the heavy cyclopropene is, the lower its barrier height is, and the larger its exothermicity is, and, in turn, the faster the abstraction reaction with haloalkanes is. In other words, understanding the singlet−triplet splitting ΔE_{st} of the heavy cyclopropene can be used to predict the relative reactivity of the various reactants. We shall see that the calculated results support these predictions below.

From the above analysis, a strong correlation between ΔE_{st} and the activation energy as well as the reaction enthalpy is expected.[17,18] For instance, our B3LYP calculations suggest that ΔE_{st} (kcal/mol) decreases in the order **A**(46.3) > **B**(20.7) > **C**(18.0) > **D**(16.9) > **E**(14.1), while the barrier height for Cl abstraction by the heavy cyclopropene also decreases in the order **TS−A−Cl** (28) > **TS−B−Cl** (7.3) > **TS−C−Cl** (5.3) > **TS−D−Cl** (4.9) > **TS−E−Cl** (2.3). Again, the enthalpy follows the same trend as for ΔE_{st}: **AP−A−Cl** (+38.3 kcal/mol) > **AP−B−Cl** (−15.3 kcal/mol) > **AP−C−Cl** (−17.5 kcal/mol) > **AP−D−Cl** (−19.2 kcal/mol) > **AP−E−Cl** (−19.8 kcal/mol). Namely, the DFT calculations indicate that there exists a linear correlation between the activation energy and the reaction enthalpy. This investigation makes it quite obvious that, in order to find a good model for the facile abstraction of heavy cyclopropene with halocarbons, an understanding of the singlet−triplet gap ΔE_{st} of the coordinatively unsaturated heavy cyclopropene is crucial. That is to say, abstraction reactions in which heavy cyclopropenes have smaller singlet−triplet gaps will have smaller barriers as well as larger exothermicity than reactions whose corresponding cyclopropenes have large singlet−triplet gaps.

Finally, one may wonder why the abstraction reaction of a heavy cyclopropene formed by less electronegative atoms (such as model molecule **E**) is preferable to that formed by more electronegative atoms (such as model molecule **A**). The reason for this can be traced directly to electronic factors within the heavy cyclopropene. From Figure 6, it is apparent that the magnitude of the energy difference between HOMO and LUMO for the heavy cyclopropene systems decreases as one proceeds along the series from model molecule **A** to **E**. These results strongly imply that heavy cyclopropenes formed by less electronegative atoms prefer to remain in high-spin states, whereas heavy cyclopropenes formed by more electronegative atoms favor low-spin states. It is reasonable to expect that the promotion energy from the singlet state to the triplet state should be smaller for the former than for the latter. Accordingly, these observations can explain why model molecule **E** has a smallest singlet−triplet splitting (ΔE_{st}=14.1 kcal/mol), whereas the other model molecule **A** species has comparatively a largest singlet−triplet separation (ΔE_{st}=46.3 kcal/mol). Our B3LYP/6-31G(d) results as shown earlier are consistent with the above prediction. For this reason, abstraction by halocarbons is easier and more exothermic for the heavy cyclopropene systems than for their cyclopropene counterpart. In other words, our theoretical findings strongly suggest that the singlet−triplet splitting of a heavy cyclopropene species can be used as a diagnostic tool to predict the reactivities of various cyclopropene analogues in abstraction reactions with haloalkanes.[19]

VI. Conclusion

In this work, we have studied the mechanisms of heavy cyclopropene abstraction reactions with carbon tetrachloride by density functional theory. It should be mentioned that this study has provided the first theoretical demonstration of the reaction trajectory and theoretical estimation of the activation energy and reaction enthalpy for these abstraction processes. However, it should be pointed out that the calculated DFT barrier heights are, if anything, too low.[20] Those barrier heights therefore quoted here might be underestimated by several kilocalories per mole. Nevertheless, the energies obtained at the B3LYP/6-31G(d) level can, at least, provide qualitatively reliable conclusions. In particular, our study has shown that the singlet−triplet gap ΔE_{st} ($=E_{triplet} - E_{singlet}$) based on the CM model can provide a useful basis for understanding and rationalizing the relative magnitude of the activation barriers as well as reaction enthalpies for the abstraction of haloalkanes by heavy cyclopropenes.

Consequently, not only have we given an explanation for the available experimental observations but also our approach provides chemists with important insights into the factors controlling heavy cyclopropene abstraction reactions with halocarbons and thus permits them to predict the reactivity of several, as yet unknown, heavier cyclopropene species.

We encourage experimentalists to carry out further experiments to confirm our predictions.

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Supporting Information Available: B3LYP/6-31G(d) optimized geometries and B3LYP energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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