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Abstraction Reactions of Heavy Cyclobutenes with Carbon Tetrachloride. A Theoretical Study

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The potential energy surfaces for the abstraction reactions of heavy cyclobutenes with CCl_4 have been characterized in detail by using density functional theory (B3LYP/LANL2DZdp), including zero-point corrections. Seven heavy cyclobutene species including **A** (C—C—C=C), **B** (Si—Si—Si=Si), **C** (Ge—Ge—Ge=Ge), **D** (Si—Si—Ge=Ge), **E** (Si—Si—Ge=Sn), **F** (Sn—Sn—Sn=Sn), and **G** (Pb—Pb—Pb=Pb) have been chosen in this work as model reactants. All the interactions involve a Cl or CCl_3 shift via a two-center transition state. The activation barriers and enthalpies of the reactions were compared in order to determine the relative heavy cyclobutene reactivity as well as the influence of substituents on the reaction potential energy surface. As a result, our theoretical investigations suggest that a heavy cyclobutene species that contains more massive and less electronegative atoms in the double bond should undergo radical abstraction reactions with CCl_4 more readily than one containing less massive and more electronegative atoms. Moreover, we show that having undergone an initial chlorine atom abstraction, a heavy cyclobutene will then proceed to undergo a second abstraction to give a tetrachloro derivative. Furthermore, a configuration mixing model based on the work of Pross and Shaik is used to rationalize the computational results. The results obtained allow us to make several predictions.

I. Introduction

The chemistry of unsaturated four-membered ring compounds of heavier group-14 elements (or heavy cyclobutenes) is one of the most fascinating topics discovered just 10 years ago.[1−4] Via probe techniques and sophisticated synthetic methodologies, Sekiguchi, Lee, and co-workers reported that the heavier group-14 cyclobutene complex, *trans*-1,2-dichloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-$^3\Delta$-1,2,3,4-disiladigermetene (**1**), could be synthesized and characterized.[1] The crystal structure of **1** was determined by X-ray crystallography to be a four-membered ring skeleton composed of two silicon and two germanium atoms in the sequence Si—Si—Ge=Ge.[1] See Scheme 1. Besides this, Sekiguchi, Lee, and co-workers also synthesized an interesting unsaturated four-membered ring molecule **2**, *trans*-1,2-dichloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-$^3\Delta$-1,2,3,4-disilagermastannetene (Si—Si—Ge=Sn).[1] In spite of being stable at room temperature, this compound exhibited high reactivity toward addition reactions across the Ge=Sn double bond. As a result, it can be smoothly chlorinated with carbon tetrachloride to form qualitatively the *trans*,*trans*,*trans*-tetrachloro derivative **3**, as shown in Scheme 2.[2]

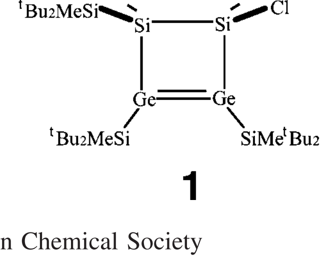
This fascinating experimental result inspired this study. If compound **2** can be used as a reagent for chlorine abstraction reactions of organic molecules, would it be possible to extend this to other heavier unsaturated four-membered ring analogues? In this theoretical work, we have now undertaken a systematic investigation of the abstraction reactions of seven unsaturated four-membered ring molecules (see Scheme 3)
with carbon tetrachloride by using density functional theory (DFT). That is, we present a DFT study of the following reactions:

$$\mathbf{A}\text{—}\mathbf{G} + CCl_4 \rightarrow [\mathbf{A}\text{—}\mathbf{G}\text{—}CCl_3]\bullet + Cl\bullet \qquad (2)$$

As can be seen above, these reactions can be classified into two types based on the order of chemical events in each pathway: (a) the chlorine (Cl) abstraction and (b) the CCl_3 abstraction. Each of these pathways was examined computationally, and each is described in detail below. To the best of our knowledge, until now, neither experimental nor theoretical studies have been performed on these systems, except for the case of (**2**) species.[1,2]

One referee asked what the basis for exclusively considering radical based mechanisms is. The reason for this could be due to the available experimental observations. As one can see in refs 1 and 2, no insertion and other kinds of products have been found in the experimental work. Nevertheless, the formation of the product suggested that the reaction is of a radical nature. Indeed, the involvement of radicals in such reactions should be verified through electron paramagnetic resonance studies. However, little definitive information (such as activation energies and reaction mechanisms) has been obtained about the abstraction reactions because of difficulties in probing these reactions experimentally. Consequently, the currently accepted mechanism involves forming neutral radical pairs from two closed-shell molecules in the first step.[5]

SCHEME 1



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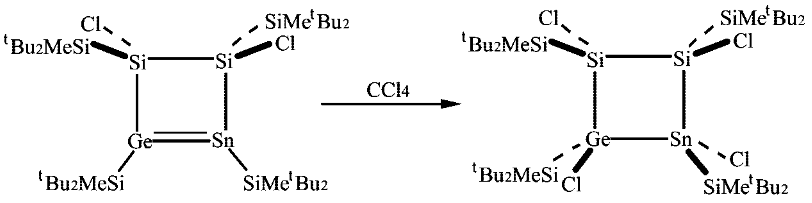
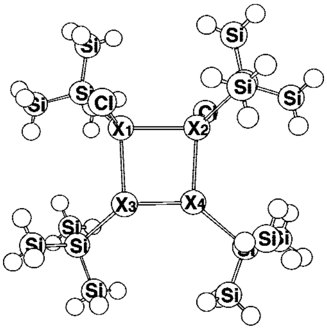
SCHEME 2



2 **3**

SCHEME 3



A. X_1-X_2-X_3=X_4 = C-C-C=C
B. X_1-X_2-X_3=X_4 = Si-Si-Si=Si
C. X_1-X_2-X_3=X_4 = Ge-Ge-Ge=Ge
D. X_1-X_2-X_3=X_4 = Si-Si-Ge=Ge
E. X_1-X_2-X_3=X_4 = Si-Si-Ge=Sn
F. X_1-X_2-X_3=X_4 = Sn-Sn-Sn=Sn
G. X_1-X_2-X_3=X_4 = Pb-Pb-Pb=Pb

$$\mathrm{(SiMe_3)ClC{-}CCl(SiMe_3){-}C(SiMe_3){=}C(SiMe_3)} \qquad \mathrm{(A)}$$

$$\mathrm{(SiMe_3)ClSi{-}SiCl(SiMe_3){-}Si(SiMe_3){=}Si(SiMe_3)} \qquad \mathrm{(B)}$$

$$\mathrm{(SiMe_3)ClGe{-}GeCl(SiMe_3){-}Ge(SiMe_3){=}Ge(SiMe_3)} \qquad \mathrm{(C)}$$

$$\mathrm{(SiMe_3)ClSi{-}SiCl(SiMe_3){-}Ge(SiMe_3){=}Ge(SiMe_3)} \qquad \mathrm{(D)}$$

$$\mathrm{(SiMe_3)ClSi{-}SiCl(SiMe_3){-}Ge(SiMe_3){=}Sn(SiMe_3)} \qquad \mathrm{(E)}$$

$$\mathrm{(SiMe_3)ClSn{-}SnCl(SiMe_3){-}Sn(SiMe_3){=}Sn(SiMe_3)} \qquad \mathrm{(F)}$$

$$\mathrm{(SiMe_3)ClPb{-}PbCl(SiMe_3){-}Pb(SiMe_3){=}Pb(SiMe_3)} \qquad \mathrm{(G)}$$

$$\mathbf{A{-}G} + \mathrm{CCl_4} \rightarrow [\mathbf{A{-}G}{-}\mathrm{Cl}]\bullet + \mathrm{CCl_3}\bullet \qquad (1)$$

The object of this study is thus to reach a more thorough understanding of unsaturated four-membered ring compounds of the heavier group-14 elements. With this theoretical study, we hope (1) to ascertain whether the Cl radical or CCl_3 radical abstraction reaction is preferred, (2) to find potential unsaturated four-membered ring analogues that can facilitate the radical transfer reactions, (3) to predict trends in the activation and reaction enthalpies, (4) to obtain a better understanding of the origin of the barrier heights for such abstraction reactions, and (5) to provide experimentalists with a theoretical basis for predicting the relative reactivities of unsaturated four-membered ring compounds of the heavier group-14 elements.

II. Theoretical Methods

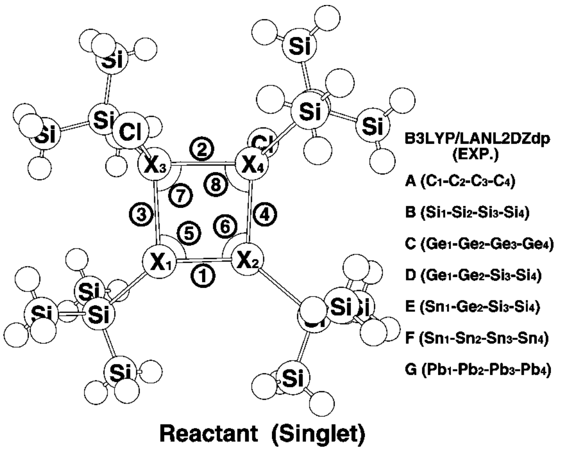
All the geometries were fully optimized without imposing any symmetry constraints, although several optimized structures showed various elements of symmetry. For our DFT calculations, we used the hybrid gradient-corrected exchange functional proposed by Becke,[6] combined with the gradient-corrected correlation functional of Lee, Yang, and Parr.[7] Thus, the geometries of all the stationary points were fully optimized at the B3LYP level of theory. These B3LYP calculations were carried out with pseudorelativistic effective core potentials on the group-14 elements modeled by using the double-ζ (DZ) basis sets[8] augmented by a set of d-type polarization functions.[9] The DZ basis set for the hydrogen element was augmented by a set of p-type polarization functions (p exponents 0.356). The d exponents used for C, Si, Ge, Sn, and Pb are 0.587, 0.296, 0.246, 0.186, and 0.179, respectively. Accordingly, we denote our B3LYP calculations by B3LYP/LANL2DZdp, which has been shown to be quite reliable both for geometries and energies.[10] It is noted that the model compounds $\mathrm{(SiMe_3)ClX{-}XCl(SiMe_3){-}X(SiMe_3){=}X(SiMe_3)}$ and CCl_4 have 584 (162 electrons) and 580 (154 electrons) basis functions for X = C, Si, Ge, Sn, and Pb. The spin-unrestricted (UB3LYP) formalism was used for the open-shell (triplet) species. The computed expectation values of the spin-squared operator $\langle S^2 \rangle$ were in the range of 2.001−2.032 for all triplet species considered here, and they were therefore very close to the correct value of 2.0 for pure triplets, so that their geometries and energetics are reliable for this study.

Frequency calculations were performed on all the structures to confirm that the reactants and products had no imaginary frequencies and that the transition states (TSs) possessed only one imaginary frequency. The relative energies at 0 K were thus corrected for vibrational zero-point energies (not scaled). All of the DFT calculations were performed by using the GAUSSIAN 03 package of programs.[11]

III. Results and Discussion

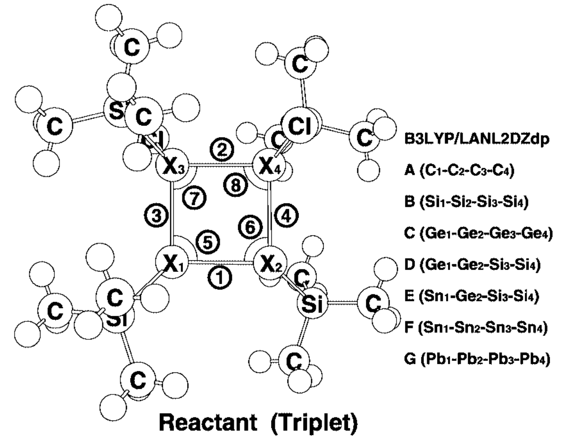
1. Geometries and Electronic Structures of Heavy Cyclobutenes. Before discussing the geometrical optimizations and the potential energy surfaces for the chemical reactions of unsaturated four-membered ring compounds of the heavier group-14 elements with carbon tetrachloride, we shall first examine the geometries of the reactants, that is, **A**−**G**. The optimized geometries for these group-14 reactants based on the singlet and triplet states were calculated at the B3LYP/LANL2DZdp level of theory, and their selected geometrical parameters are collected in Figures 1 and 2, respectively. The relative energies obtained from the B3LYP calculations are summarized in Table 1. Their Cartesian coordinates are included in the Supporting Information.

Unfortunately, as mentioned in the Introduction, only one stable unsaturated four-membered ring compound (**1**) with a Ge=Ge double bond has been isolated and characterized unequivocally by Sekiguchi, Lee, and co-workers.[1,2] For convenience, we have optimized its similar structure, $\mathrm{(SiMe_3)ClSi{-}SiCl(SiMe_3){-}Ge(SiMe_3){=}Ge(SiMe_3)}$ (**D**), by using the B3LYP/LANL2DZdp calculations. Selected geometric parameters for the theoretically calculated (**D**) model compound are given in Figure 1, along with the corresponding values experimentally observed for the molecule (**1**). As one can see in Figure 1, in principle, the agreement for both bond lengths and bond angles



	A	B	C	D	E	F	G
①	1.380	2.166	2.324	2.335 (2.291)	2.545	2.715	2.910
②	1.580	2.357	2.521	2.360 (2.372)	2.370	2.896	3.045
③	1.525	2.314	2.475	2.393 (2.357)	2.592	2.876	3.024
④	1.525	2.314	2.474	2.390 (2.385)	2.399	2.877	3.024
⑤	92.86	91.88	92.10	89.89 (88.75)	85.26	91.07	91.05
⑥	92.86	91.88	92.10	89.98 (89.63)	90.30	91.06	90.88
⑦	85.46	87.20	87.55	89.30 (87.72)	89.82	87.51	88.36
⑧	85.46	87.20	87.58	89.37 (86.84)	93.71	87.50	88.49

Figure 1. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of the reactants **A**−**G** (singlet). The experimental values (see ref 1) are in parenthesis. The relative energies for each species are in Table 1. Hydrogens are omitted for clarity.



	A	B	C	D	E	F	G
①	1.580	2.380	2.554	2.541	2.728	2.936	3.170
②	1.568	2.358	2.523	2.363	2.365	2.878	3.031
③	1.508	2.340	2.533	2.447	2.654	2.899	3.063
④	1.508	2.340	2.533	2.448	2.446	2.899	3.216
⑤	88.48	88.69	89.63	87.66	82.42	89.15	91.24
⑥	88.48	88.69	89.64	87.77	89.05	89.15	84.84
⑦	88.91	89.24	90.35	91.96	92.58	90.30	89.97
⑧	88.91	89.24	90.35	91.79	94.95	90.30	90.94

Figure 2. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of the reactants (triplet). The relative energies for each species are in Table 1. Hydrogens are omitted for clarity.

TABLE 1: Relative Energies for Singlet and Triplet Silylenes and for the Process Heavy Cyclobutene + CCl_4 → TS → Abstraction Products[a,b]

system	ΔE_{st}[c] (kcal mol^{-1})	$\Delta E^{\ddagger}$[d] (kcal mol^{-1})	ΔH[f] (kcal mol^{-1})
	For Cl Abstraction		
A	+61.59	+39.54	+47.35
B	+31.09	+10.15	−7.024
C	+22.65	+3.520	−7.999
D	+22.44	+2.538	−9.296
E	+17.12	+3.046	−13.09
F	+14.26	+1.428	−15.02
G	+12.03	+0.6978	−19.97
	For CCl3 Abstraction		
A	+61.59	+96.53	+85.39
B	+31.09	+64.84	+27.41
C	+22.65	+59.29	+25.77
D	+22.44	+59.09	+25.45
E	+17.12	+55.95	+24.04
F	+14.26	+52.41	+20.75
G	+12.03	+41.24	+15.83

[a] At the B3LYP/LANL2DZdp levels of theory. For the B3LYP optimized structures of the stationary points, see Figure 4 and Table 2. [b] Energies differences have been zero-point corrected. See text. [c] Energy relative to the corresponding singlet state. A positive value means that the singlet is the ground state. [d] Activation energy of the TS, relative to the corresponding reactants. [f] Exothermicity of the product, relative to the corresponding reactants.

TABLE 2: Selected Geometrical Parameters for the Process Reactant (A−G) + CCl_4 → TS → Abstraction Products[a]

	system						
	A	B	C	D	E	F	G
1	1.380	2.166	2.324	2.335	2.545	2.715	2.910
2	1.525	2.314	2.475	2.393	2.592	2.876	3.024
3	2.528	2.510	2.876	3.017	2.817	3.017	2.975
4	2.435	2.258	2.352	2.405	2.545	2.737	2.919
5	1.929	2.149	2.266	2.270	2.297	2.433	2.534
6	1.502	2.323	2.493	2.449	2.639	2.888	3.087
7	2.151	2.754	2.792	2.453	2.875	2.849	2.804
8	1.426	2.224	2.398	2.453	2.583	2.793	3.077
9	1.928	1.968	2.070	2.072	2.259	2.252	2.337
10	1.546	2.323	2.506	2.510	2.641	2.890	3.051

[a] All at the B3LYP/LANL2DZdp level of theory. For the B3LYP optimized structures of the stationary points, see Figure 4.

in (**D**) between the B3LYP results and the available experimental data for (**1**)[1,2] for the singlet state is quite good, with the bond lengths and angles in agreement to within 0.044 Å and 2.5°, respectively. As a result of this encouraging agreement, we therefore believe that the present models with the current method (B3LYP/LANL2DZdp) employed in this study should provide reliable information for the discussion of the reaction mechanism, for which experimental data are still not available.

One of the most interesting features of these group-14 metal substituted unsaturated four-membered ring compounds is the substantial effects of metal substituents on the electronic structures. As demonstrated in Table 1, the singlet−triplet energy splitting generally decreases as the atomic number of atom X increases. That is, a decreasing trend in the singlet−triplet energy splitting ($\Delta E_{st} = E_{triplet} - E_{singlet}$) for **A** (62 kcal/mol) > **B** (31 kcal/mol) > **C** (23 kcal/mol) > **D** (22 kcal/mol) > **E** (17 kcal/mol) > **F** (14 kcal/mol) > **G** (12 kcal/mol) is observed at the DFT level of theory. The reason for this is due to the electron-donating effect of substituents such as the silyl group, which raises the π orbital energy with respect to the π^* level. This, in turn, causes a decrease in the $\pi \rightarrow \pi^*$ transition energy

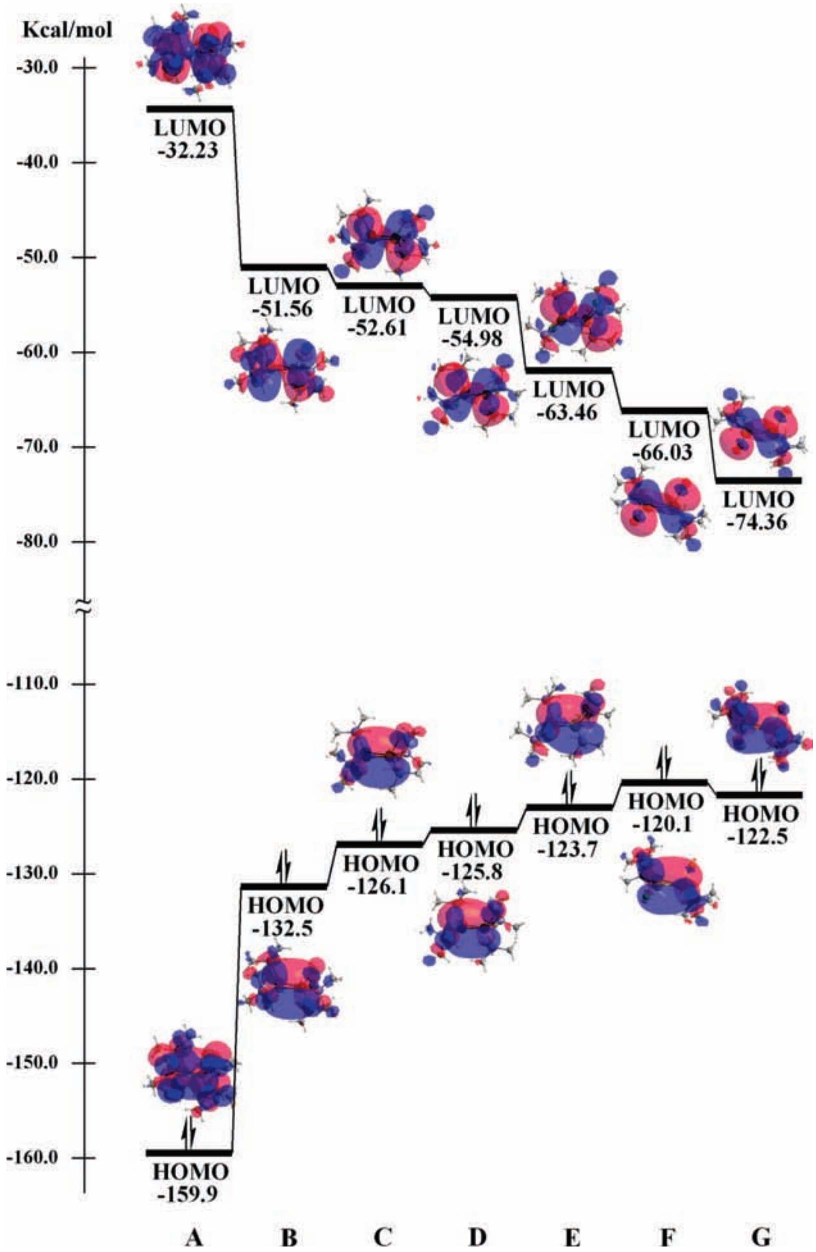


Figure 3. Calculated frontier molecular orbital for the reactants **A**−**G** species. For more information, see the text.

as well as in the singlet−triplet energy gap, which is especially noticeable when the atoms involved in the cyclobutene double bond are less electronegative. Further supporting evidence can be found in Figure 3. Namely, the HOMO and LUMO energy gap reduces from the cyclobutene to the heavier cyclobutene systems.

In addition to this, it is well known that the π-bond strength of a double bond decreases from carbon to lead owing to the greater bond lengths of the heavier group-14 elements.[12] Combining all these important factors, one comes to the following conclusion: the greater the atomic weight of the group-14 elements involved in the double bond of a heavy cyclobutene, the weaker its π bond, and the smaller the singlet−triplet energy gap ΔE_{st} becomes. We shall use the above results to explain the origin of barrier heights for the radical transfer reactions in a later section.[13]

2. TSs. Next, let us consider the mechanisms which proceed via eqs 1 and 2, focusing on the TSs as well as on the abstraction products themselves. In Cl abstraction (eq 1), the system passes through a TS, **TS−Cl**, which leads to the formation of [**A**−**G**−Cl]• + CCl_3•. On the other hand, in the CCl_3 abstraction reaction (eq 2), the system passes through the TS, **TS−CCl$_3$**, resulting in [**A**−**G**−CCl_3]• + Cl• products. The main geometrical parameters of the TSs corresponding to the abstraction reactions as well as their appearances are shown in Figure 4. These TSs will be referred to as **A−TS−Cl**, **B−TS−Cl**, **C−TS−Cl**, **D−TS−Cl**, **E−TS−Cl**, **F−TS−Cl**, and **G−TS−Cl** for (eq 1, Cl abstraction) and **A−TS−CCl$_3$**, **B−TS−CCl$_3$**, **C−TS−CCl$_3$**, **D−TS−CCl$_3$**, **E−TS−CCl$_3$**, **F−TS−CCl$_3$**, and **G−TS−CCl$_3$** for (eq 2,CCl_3 abstraction). Several intriguing features may be picked up from Figures 4 and Tables 1 and 2 and are worth noting.

First, when considering the Cl abstraction, 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 CCl_3 group, the eigenvalue of which gives an imaginary frequency of 125i (**A−TS−Cl**), 163i (**B−TS−Cl**), 181i (**C−TS−Cl**), 124i (**D−TS−Cl**), 143i (**E−TS−Cl**), 131i

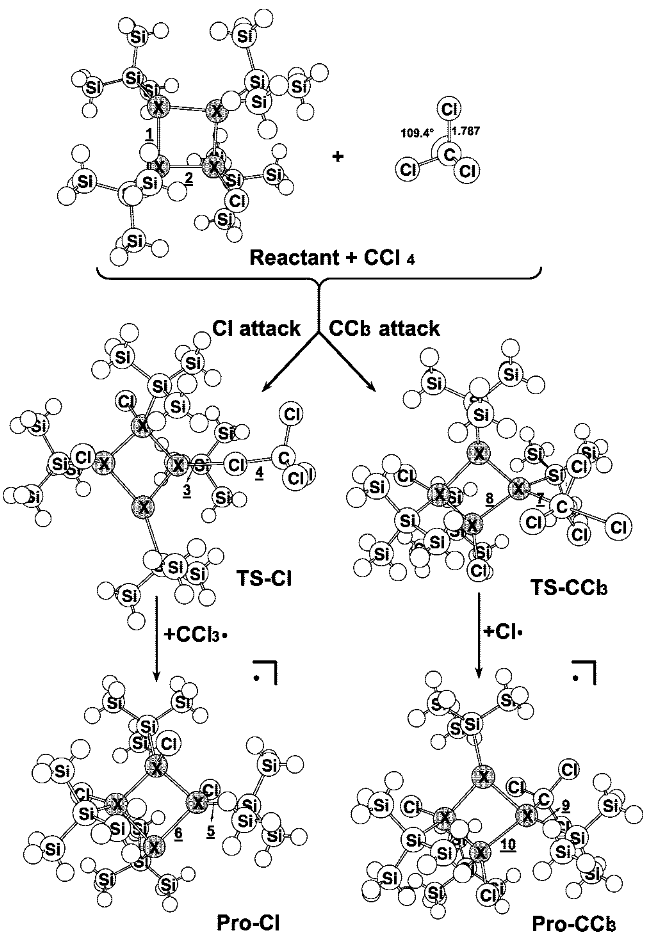


Figure 4. Optimized geometries (in Å and deg) for the TSs and abstraction products (Pro) of **A**−**G** with CCl_4. All were calculated at the B3LYP/LANL2DZdp level of theory. Hydrogens are omitted for clarity. For the selected geometrical parameters, see Table 1.

(**F**−**TS**−**Cl**), and 122i (**G**−**TS**−**Cl**) cm^{-1}. In fact, inspection of the transition vector shows clearly that the reaction proceeds toward formation of [**A**−**G**−Cl]• and CCl_3•. Basically, it seems that decreasing the electronegativity of the attacked atom X in the heavy cyclobutene causes a large increase in the **A**−**G**−Cl′ (Cl′ = the migrating chlorine atom) distance. As seen in Figure 4 and Table 2, the newly forming X−Cl′ bond length are as follows: **A**−**TS**−**Cl** (2.53 Å), **B**−**TS**−**Cl** (2.51 Å), **C**−**TS**−**Cl** (2.88 Å), **D**−**TS**−**Cl** (3.02 Å), **E**−**TS**−**Cl** (2.82 Å), **F**−**TS**−**Cl** (3.02 Å), and **G**−**TS**−**Cl** (2.98 Å).[14] Besides this, it should be 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 shown in Figure 4. For example, the X atom of the heavy cyclobutene molecule makes an angle, with respect to the Cl′−C bond of 169, 163, 160, 162, 166, 163, and 164° for the model molecules **A**−**TS**−**Cl**, **B**−**TS**−**Cl**, **C**−**TS**−**Cl**, **D**−**TS**−**Cl**, **E**−**TS**−**Cl**, **F**−**TS**−**Cl**, and **G**−**TS**−**Cl**, respectively.

On the other hand, regarding the CCl_3 abstraction reaction (eq 2), a search for the TS confirmed that the energy profile for this reaction does exhibit a maximum. The TSs located for the CCl_3 abstractions by various heavy cyclobutenes are also presented in Figure 4. These transition structures are characterized by one imaginary frequency of 322i, 489i, 480i, 471i, 477i, 506i, and 432i cm^{-1} for CCl_3 abstraction TSs **A**−**TS**−**CCl$_3$**, **B**−**TS**−**CCl$_3$**, **C**−**TS**−**CCl$_3$**, **D**−**TS**−**CCl$_3$**, **E**−**TS**−**CCl$_3$**, **F**−**TS**−**CCl$_3$**, and **G**−**TS**−**CCl$_3$**, respectively. As one can see in Figure 4, 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. Additionally, to avoid steric repulsion with the substituents of the heavy cyclobutene, the X•••C•••Cl is slightly bent in these TSs, as observed in Figure 4. For instance, our theoretical findings demonstrate that the angle ∠ X−C−Cl of **TS**−**CCl$_3$** for **A**−**G** seven model molecules is 180, 179, 175, 179, 179, 179, and 177°, respectively.[15]

In principle, our computational results suggest that, from a kinetic viewpoint, the abstraction reactions of heavy cyclobutene systems bearing more electropositive elements in the double bond are more facile than those with more electronegative elements. As can be seen in Table 1, the B3LYP barrier height for Cl abstraction by heavy cyclobutenes decreases in the order **A**−**TS**−**Cl** (40 kcal/mol) > **B**−**TS**−**Cl** (10 kcal/mol) > **C**−**TS**−**Cl** (3.5 kcal/mol) > **E**−**TS**−**Cl** (3.0 kcal/mol) > **D**−**TS**−**Cl** (2.5 kcal/mol) > **F**−**TS**−**Cl** (1.4 kcal/mol) > **G**−**TS**−**Cl** (0.70 kcal/mol).[16] The same phenomenon can also be found in the CCl_3 abstractions as follows: **A**−**TS**−**CCl$_3$** (97 kcal/mol) > **B**−**TS**−**CCl$_3$** (65 kcal/mol) > **C**−**TS**−**CCl$_3$** (59 kcal/mol) ≈ **D**−**TS**−**CCl$_3$** (59 kcal/mol) > **E**−**TS**−**CCl$_3$** (56 kcal/mol) > **F**−**TS**−**CCl$_3$** (52 kcal/mol) > **G**−**TS**−**CCl$_3$** (41 kcal/mol). In other words, a heavy cyclobutene with more massive and less electronegative atoms in the double bond reaches the TS relatively early, whereas a cyclobutene analogue with less massive but more elecronegative atoms in the double bond arrives at the TS relatively late. Namely, our theoretical calculations strongly indicate that the lower the electronegativity of the substituent group-14 elements, the lower the barrier to abstraction with CCl_4. Moreover, it is worth noting that the calculated activation energy is substantially lower for Cl than for CCl_3 abstraction, indicating that, in all cases, the chlorine abstraction process (eq 1) is highly favored.

3. Abstraction Products. The expected products of the abstraction reactions of heavy cyclobutenes with CCl_4 are either **Pro**−**Cl** and CCl_3• or **Pro**−**CCl$_3$** and Cl•. As a result, the optimized product structures are named as **A**−**Pro**−**Cl**, **B**−**Pro**−**Cl**, **C**−**Pro**−**Cl**, **D**−**Pro**−**Cl**, **E**−**Pro**−**Cl**, **F**−**Pro**−**Cl**, **G**−**Pro**−**Cl**, **A**−**Pro**−**CCl$_3$**, **B**−**Pro**−**CCl$_3$**, **C**−**Pro**−**CCl$_3$**, **D**−**Pro-CCl$_3$**, **E**−**Pro**−**CCl$_3$**, **F**−**Pro**−**CCl$_3$**, and **G**−**Pro**−**CCl$_3$**. These are all collected in Figure 4, and the calculated reaction enthalpies for the abstractions are given in Table 1. As seen in Figure 4 and Table 2, the order of X−Cl (X is the attacked atom) bond lengths follows the same trend as the atomic weight of the atom X. That is, the X−Cl bond length increases in the order **A**−**Pro**−**Cl** (1.93 Å) < **B**−**Pro**−**Cl** (2.15 Å) ≈ **E**−**Pro**−**Cl** (2.15 Å) < **C**−**Pro**−**Cl** (2.27 Å) ≈ **B**−**Pro**−**Cl** (2.27 Å) < **F**−**Pro**−**Cl** (2.43 Å) < **G**−**Pro**−**Cl** (2.53 Å). The same phenomenon can also be found in the CCl_3 abstraction reactions: **A**−**Pro**−**CCl$_3$** (1.58 Å) < **B**−**Pro**−**CCl$_3$** (1.97 Å) < **C**−**Pro**−**CCl$_3$** (2.07 Å) ≈ **D**−**Pro-CCl$_3$** (2.07 Å) < **F**−**Pro**−**CCl$_3$** (2.25 Å) < **E**−**Pro**−**Cl** (2.27 Å) < **G**−**Pro**−**CCl$_3$** (2.34 Å).

Furthermore, from Table 1, it is apparent that only Cl abstractions are exothermic, whereas the energies of the CCl_3-abstraction products all lie above those of their corresponding reactants. This strongly indicates that the CCl_3 abstraction reactions by heavy cyclobutene are endothermic and, therefore, energetically unfavorable. Nevertheless, their order of exothermicity follows a trend similar to that of their activation energy. For example, our theoretical investigations indicate that the enthalpy for the Cl atom abstraction of heavy cyclobutene decrease in order **A**−**Pro**−**Cl** (+47 kcal/mol) > **B**−**Pro**−**Cl** (−7.0 kcal/mol) > **C**−**Pro**−**Cl** (−8.0 kcal/mol) > **D**−**Pro**−**Cl** (−9.3 kcal/mol) > **E**−**Pro**−**Cl** (−13 kcal/mol) > **F**−**Pro**−**Cl**

(−15 kcal/mol) > **G—Pro—Cl** (−19 kcal/mol). Again, our computational results suggest that the enthalpy for the CCl_3 group abstraction also decreases in order **A—Pro—CCl_3** (+85 kcal/mol) > **B—Pro—CCl_3** (+27 kcal/mol) > **C—Pro—CCl_3** (+26 kcal/mol) > **D—Pro—CCl_3** (+24 kcal/mol) > **E—Pro—CCl_3** (+21 kcal/mol) ≈ **F—Pro—CCl_3** (+21 kcal/mol) > **G—Pro—CCl_3** (+16 kcal/mol). Therefore, the Cl-abstraction path is predicted to be more exothermic than the equivalent CCl_3-abstraction process.

IV. Overview of Heavy Cyclobutene Abstractions

The major conclusions that can be drawn from Figure 4 and Tables 1 and 2 are as follows:

1. For a given unsaturated four-membered ring compound of a heavier group-14 element, a precursor complex for both Cl and CCl_3 abstraction should not exist.
2. The activation barrier for the Cl abstraction is much smaller than that for the CCl_3 abstraction, indicating that the former is kinetically more favorable than the latter. In other words, providing reaction conditions remain the same, the unsaturated four-membered ring molecule of a heavier group-14 element is more susceptible to a Cl than a CCl_3 abstraction reaction. Consequently, a one-atom abstraction will be the first step in the initial reaction of a heavy cyclobutene and CCl_4, and one-chlorine abstraction products will dominate. This is consistent with some available experimental findings.[1,2]
3. The Cl abstraction reaction is also more exothermic than the equivalent CCl_3 abstraction. In consequence, the production of chlorine-abstraction compounds is clearly more thermodynamically favored than CCl_3-abstraction products. This strongly suggests that the one-atom-abstraction reaction should be the most energetically favorable path for heavy cyclobutene abstractions.
4. Abstraction of chlorine from CCl_4 by a singlet heavy cyclobutene should produce a one-chlorine-abstraction product in a single step (i.e., in a concerted manner), thus stereospecifically. Namely, such heavy cyclobutene abstractions should be favored for producing stereoretention products.
5. The abstraction reactions of heavy cyclobutenes proceed via a two-step abstraction−combination path (formation of the two radicals and then abstraction of another atom in a subsequent step collapsing to the final product). In addition, such abstraction reactions should occur via a TS characterized by a nonlinear arrangement of the three atoms involved in the process.[17]
6. Given identical reaction conditions, the more massive and less electronegative the doubly bonded atoms in a given heavy cyclobutene are, the easier the abstraction reaction with CCl_4 will be. We therefore predict that heavy cyclobutenes containing either the Sn═Sn or the Pb═Pb double bond can readily abstract chlorine atoms from CCl_4, whereas heavy cyclobutenes containing the C═C double bond are unreactive toward CCl_4.
7. Our theoretical findings suggest that the double bond strengths (X═X) of cyclobutenes increase in the order **A** (1.380 Å) < **B** (2.166 Å) < **C** (2.324 Å) < **D** (2.335 Å) < **E** (2.545 Å) < **F** (2.715 Å) < **G** (2.910 Å). From Table 1, it is easy to see that these X═X double bond strengths agree well with the trend in their reaction barriers and enthalpies calculated. That is, the greater the atomic weight of X, the weaker the π bond strength of X═X, and the more facile the abstraction reaction becomes.
8. The mechanisms of the reactions of heavy cyclobutenes with CCl_4 we studied in this work are quite similar to the case of heavy cyclopropenes.[18] That is, the Cl abstraction is more favorable than the CCl_3 abstraction. Also, the reactions of heavier group-14 elements are easier than those of lighter elements.
9. Electronic as well as steric factors should play an important role in determining the chemical reactivity of heavy cyclobutene species from both a kinetic and thermodynamic viewpoint.[19]

In short, considering both the activation barrier and exothermicity based on the model calculations presented here, we conclude that the reactivity of heavy cyclobutenes increases in the order **A** (C—C—C═C) < **B** (Si—Si—Si═Si) < **C** (Ge—Ge—Ge═Ge) < **D** (Si—Si—Ge═Ge) < **E** (Si—Si—Ge═Sn) < **F** (Sn—Sn—Sn═Sn) < **G** (Pb—Pb—Pb═Pb). This may be the reason that compounds **D** and **E** have been synthesized and characterized successfully in laboratory experiments.[1,2] On the basis of the present theoretical conclusions, we predict that the heavy cyclobutene molecules **A**, **B**, and **C** should also be synthesized in the laboratory. Our theoretical models also demonstrate that the heavy cyclobutenes should undergo first one chlorine-atom abstraction and then proceed to a second chlorine-atom abstraction.[20] Finally, one may thus obtain the *trans*,*trans*,*trans*-tetrachloro products as given in the present work. Our model conclusions are in good agreement with what we found in Sekiguchi's experimental observations.[1,2]

V. 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.[21,22] According to this model, the barrier height ($\Delta E^{\ddagger}$) as well as the reaction enthalpy (ΔH) can be expressed in terms of the singlet−triplet splitting ΔE_{st} (= $E_{triplet} - E_{singlet}$) of the reactants, that is, ΔE_{st} (= $E_{triplet} - E_{singlet}$ for heavy cyclobutene) and $\Delta E_{\sigma\sigma^*}$ (= $E_{triplet} - E_{singlet}$ for CCl_4). Accordingly, if $\Delta E_{\sigma\sigma^*}$ is a constant, then, the smaller the value of ΔE_{st} of the heavy cyclobutene, the lower its barrier height, the larger its exothermicity, and, in turn, the faster the abstraction reaction with carbon tetrachloride will be. In other words, understanding the singlet−triplet splitting ΔE_{st} of the heavy cyclobutene can be used to predict its relative reactivity. Bearing the above analysis in mind, we shall explain the origin of the previously observed trends.

a. Why does a heavy cyclobutene containing heavier and less electronegative elements in its double bond undergo a more favorable abstraction reaction with CCl4 than one containing less massive and more electronegative elements?

   The reason for this can be traced to the singlet−triplet energy gap (ΔE_{st}) of the heavy cyclobutene. As analyzed above, if $\Delta E_{\sigma\sigma^*}$ is a constant, the smaller the ΔE_{st} of the heavy cyclobutene, the lower the barrier height and the larger the exothermicity, and, in turn, the faster the abstraction reaction. Indeed, our theoretical calculations confirm this prediction and suggest a decreasing trend in ΔE_{st} for **A** (62 kcal/mol) < **B** (31 kcal/mol) < **C** (23 kcal/mol) < **D** (22 kcal/mol) < **E** (17 kcal/mol) < **F** (14 kcal/mol) < **G** (12 kcal/mol). From Table 1, it is readily seen that this result agrees well with the trend in activation energy and enthalpy ($\Delta E^{\ddagger}$, ΔH) for Cl abstraction, which is **A** (+40, +47), **B** (+10, −7.0), **C** (+3.5, −8.0), **D** (+2.5, −9.3), **E** (+3.0, −13), **F** (+1.4, −15), and **G** (+0.70, −19) kcal/mol, respectively. Likewise, the same phenomenon can also be found in CCl_3 abstraction as follows: **A** (+97,

+85), **B** (+65, +27), **C** (+59, +26), **D** (+59, +25), **E** (+56, +24), **F** (+52, +21), and **G** (+41, +16) kcal/mol, respectively. That is to say, the heavy cyclobutenes formed by less electronegative atoms have a preference for high-spin states, whereas the heavy cyclobutenes formed by more electronegative atoms favor low-spin states. As a result, our theoretical findings strongly suggest that the singlet−triplet splitting of a heavy cyclobutene species can be used as a diagnostic tool to predict the reactivities of various cyclobutene analogues in abstraction reactions with haloalkanes.

b. For a given heavy cyclobutene species, why is Cl abstraction favored over CCl_3 abstraction?
Again, the reason for this can be traced to the singlet−triplet energy gap of carbon tetrachloride. For more information, interested readers can find a discussion in ref 23.

VI. Conclusion

Our DFT investigations present the first theoretical evidence that electron-donating substituents (such as the silyl group) on the double bond of an unsaturated four-membered ring compound will result in a smaller ΔE_{st}. We have also shown that a heavy cyclobutene species containing more massive and less electronegative atoms in the double bond also has a smaller ΔE_{st} than one containing less massive and more electronegative atoms. Both these effects facilitate the radical abstraction reaction with CCl_4. It should be emphasized that although both Cl and CCl_3 abstraction reactions are competing processes, the former is more exothermic as well as more kinetically favorable. Additionally, the present model calculations demonstrate that a concerted process, which does not involve intermediates, should play a dominant role in such abstraction reactions. That is to say, these chlorine atom transfer reactions by heavy cyclobutenes will proceed stereospecifically, leading to a *trans*,*trans*,*trans*-tetrachloro derivative with retained stereochemistry.

Furthermore, as our analysis demonstrates, the CM approach adds additional facets and insights into this relatively poorly understood area of mechanistic study. Although the relative reactivity of various heavy cyclobutenes 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 heavy cyclobutenes without specific knowledge of the actual energies of the interactions involved. In spite of its simplicity, our approach can provide chemists with important insights into the factors controlling the activation energies for radical transfer reactions and thus permit them to predict the reactivity of some unknown heavy cyclobutenes. The predictions may be useful as a guide to future synthetic efforts and to indicate problems that merit further study by both theory and experiment.

It is hoped that this study can stimulate further research into the subject.

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Supporting Information Available: B3LYP/LANL2DZdp optimized geometries and B3LYP energies. This material is available free of charge via the Internet athttp://pubs.acs.org.

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(13) As suggested by reviewers, we also calculated the model system (**D**) by using the B3LYP/6-31G(d) level of theory. Basically, our calculated bond lengths and bond angles are in agreement to within 0.083 Å and 3.2°, respectively, compared with the available experimental data. Besides these, we calculated its abstraction−addition process (see eq 1) with CCl_4. Our theoretical findings suggest that its barrier height and reaction energy are 10.52 and−16.72 kcal/mol, respectively. All these results are consistent with the present study based on the B3LYP/LANL2DZdp method (see Table 1). We thus feel confident that the current method (B3LYP/LANL2DZdp) employed in this study should provide reliable information for the discussion of the nature of such abstraction−addition reactions.

(14) However, in case of **D**, **F**, and **G** (X = Si, Sn, and Pb), the X−Cl′ bond lengths are almost identical. The reason for such phenomena could be the weak $\pi-\sigma^*$ effect. That is, the heavier central atom X has a larger atomic radius. This, in turn, can cause the weak $\pi-\sigma^*$ effect between the central X atom and chlorine, which makes X−Cl′ (X = Si, Sn, and Pb) bond lengths almost identical.

(15) Compound **E** has a Ge=Sn double bond; reactions at two atoms, Ge and Sn, are possible. According to our present calculations, however, we only found the Cl attack on the Ge atom and the CCl_3 attack on the Sn atom. The reason for this is could bethe electronic origin rather than the steric effect.

(16) However, one reviewer indicates that barrier heights for **D**, **E**, **F**, and **G** are probably on the limit of the accuracy of the computational method used. It is believed that using the more sophisticated theoretical level would increase their barrier heights. Nevertheless, this is beyond the scope of the present work.

(17) As suggested by one reviewer, when one Cl adds to one center of the X═X bond to give Cl—X—X• and CCl_3• radicals, it could be possible that the opposite face of the cyclobutene analogue reacts with another CCl_4 to yield a trans Cl—X/X—Cl product. However, such a consideration needs at least two CCl_4 molecules to be involved in these model systems. As one can see, this would increase the complexity and difficulty of the questions we asked as well as enlarge the calculation systems that we studied in this work. We thus have no choice but to decide to use one CCl_4 molecule in our present model systems.

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(19) One reviewer mentioned that it could be possible yhatthese reactions progress via charged intermediates. However, such a case can yield many kinds of products. As suggested by the experimental work,[1] only one product has been found. We thus feel confident that no charged intermediates are involved in such reactions.

(20) Although the second step was never analyzed theoretically in this manuscript, it is presumably assumed that Cl-abstraction path would be favored over the CCl_3-abstraction one. The reason for this is the steric factor.

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