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A Quantum Mechanical Study of the Abstraction Reactions of Fused Bicyclic Dimetallenes

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The potential energy surfaces for the abstraction reactions of fused bicyclic dimetallene species with carbon tetrachloride have been characterized in detail by using density functional theory including zero-point corrections. All the stationary points were determined at the B3LYP/LANL2DZdp level of theory. Five fused bicyclic dimetallene species including fused bicyclic diethylene, fused bicyclic disilene, fused bicyclic digermene, fused bicyclic distannene, and fused bicyclic diplumbene have been chosen in this work as model reactants. Comparisons of the activation barriers and reaction enthalpies were used to determine the relative reactivity of the fused bicyclic dimetallenes on the reaction potential energy surface. As a result, our theoretical investigations suggest that, irrespectively of the fused bicyclic dimetallene, the Cl-abstraction pathway is more favorable than the CCl_3-abstraction pathway from both kinetic and thermodynamic considerations. Moreover, our model calculations indicate that the heavier the group 14 element in the fused bicyclic dimetallenic species, the lower the activation barrier and the more exothermic the haloalkane abstraction. 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 report of a stable disilene by West and coworkers in 1981,[1] the chemistry of doubly bonded compounds of heavier group 14 elements is one of the most fascinating topics in organometallic field. Over the past two decades, dramatic progress has been made in the synthetic chemistry of stable disilenes, cyclotrisilenes, cyclotetrasilabutenes, and spirocyclic disilenes.[2] Despite the much greater difficulties in the preparation of such stable molecules compared with their carbon analogue, they are becoming increasingly available, constituting a new highly promising and quickly developing class of organometallic compounds.

Recently, Iwamoto, Kira, and co-workers reported the first example of a fused bicyclic disilene, namely, bicyclo[3,3,0]octasil-1(5)-ene **1**,[3] which can be considered topologically as a partial structure of Si(001), up to the third layer. They also investigate the reactions of **1** with various small molecules, which should be useful in predicting the reactivity of the silicon surface. For instance, compound **1** reacted with carbon tetrachloride to give *trans*-1,5-dichlorobicyclooctasilane similar to other stable disilenes,[4] whereas the reaction of the Si(001) surface with carbon tetrachloride has never been reported.[5] Apparently, the formation of these products suggests a radical nature for the reactions.[6]

It is these fascinating synthetic results that inspired this study. If a fused bicyclic disilene can undergo an abstraction reaction with carbon tetrachloride, would it be possible to extend this to other group 14 containing species? If this is possible, which abstraction group, either the chlorine atom or the carbon trichloride, has the lowest activation energy and therefore can undergo abstraction the fastest? As far as we know, until now, no theoretical studies have been carried out on these abstraction reactions, let alone a systematic study of the effect of substitution on the reactivities of the heavier fused bicyclic dimetallene species.

We therefore present a density functional theory (DFT) study of the following reactions (dimetallenes = C, Si, Ge, Sn, and Pb):

$$\text{fused bicyclic dimetallene} + CCl_4 \rightarrow [\text{fused bicyclic dimetallene-Cl}]\bullet + CCl_3\bullet \quad (1a)$$

$$\text{fused bicyclic dimetallene} + CCl_4 \rightarrow [\text{fused bicyclic dimetallene-}CCl_3\bullet + Cl\bullet \quad (1b)$$

In this theoretical work, five typical fused bicyclic dimetallenes (dimetallenes = C, Si, Ge, Sn, and Pb) were selected as model systems for investigating the geometry and energetics of abstraction reactions. The reason for choosing these compounds is because they are isoelectronic species and might therefore be expected to show similar chemical behavior. Moreover, as mentioned previously,[3] two plausible mechanisms are suggested for the reactions of fused bicyclic disilenes with carbon tetrachloride, which can be classified into two types based on the order of chemical events in each pathway: (a) the chlorine abstraction and (b) the CCl_3 abstraction. Each of these pathways was examined computationally, and each is described in detail below. Besides this, because most fused bicyclic dimetallene molecules have not yet been synthesized and characterized, it is reasonable to infer that they may serve as potential molecules for making further development in the chemistry of halogen atom abstractions.

II. Computational Details

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,[7] combined with the gradient-corrected correlation functional of Lee, Yang, and Parr.[8] This functional is commonly known as B3LYP and has been shown to be quite reliable both for geometries and energies.[9] These

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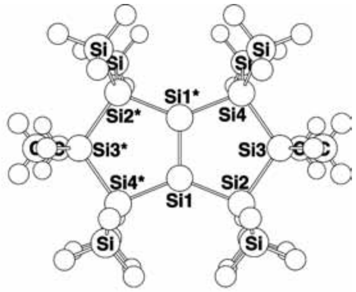


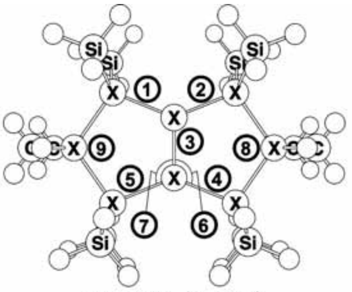
		B3LYP /LANL2DZdp	EXP.
Si1* - Si1	=	2.152	(2.180)
Si1 - Si2	=	2.315	(2.330)
Si1 - Si4*	=	2.315	(2.323)
Si2 - Si3	=	2.377	(2.380)
Si3 - Si4	=	2.377	(2.360)
Si1* - Si1 - Si2	=	111.8	(112.4)
Si1 - Si1* - Si4	=	111.5	(110.2)
Si2 - Si1 - Si4*	=	136.0	(137.3)
Si1 - Si2 - Si3	=	103.4	(100.0)
Si2 - Si3 - Si4	=	108.8	(111.6)
Si1* - Si4 - Si3	=	103.4	(100.0)

Figure 1. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of bicyclo[3,3,0]octasil-1(5)-ene **1**, compared with the experimental data. See ref 3.

B3LYP calculations were carried out with relativistic effective core potentials on the group 14 elements modeled by using the double-ζ (DZ) basis sets[10] augmented by a set of d-type polarization functions.[11] 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 Cl, C, Si, Ge, Sn, and Pb are 0.648, 0.587, 0.296, 0.246, 0.186, and 0.179, respectively. Accordingly, we denote our B3LYP calculations by B3LYP/LANL2DZdp. The spin-unrestricted (UB3LYP) formalism was used for the open-shell (doublet) species. The S^2 expectation values of the doublet states for the radical products all showed an ideal value (0.750) after spin annihilation, so that their geometries and energetics are reliable for this study. Frequency calculations were performed on all structures to confirm that the reactants, intermediates, and products had no imaginary frequencies and that transition states possessed only one imaginary frequency. The relative energies were thus corrected for vibrational zero-point energies (ZPE, not scaled). All of the DFT calculations were performed by using the GAUSSIAN 98 package of programs.[12]

III. Results and Discussion

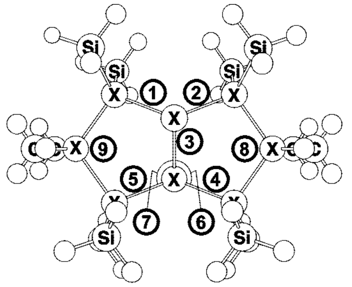
1. Geometries and Energetics of Fused Bicyclic Dimetallenes. Before discussing the geometrical optimizations and the potential energy surfaces for the abstraction reactions, we shall first discuss the geometry and energy of the fused bicyclic disilene reactant (**1**). The optimized geometries for **1** were calculated at the B3LYP/LANL2DZdp level of theory, and their selected geometrical parameters are collected in Figure 1, where they are compared with some available experimental data.[3] Their Cartesian coordinates are included in the Supporting Information.



Reactant (Singlet)

X	C	Si	Ge	Sn	Pb
①	1.534	2.318	2.482	2.855	3.005
②	1.536	2.319	2.483	2.855	3.004
③	1.363	2.153	2.308	2.727	2.975
④	1.535	2.316	2.481	2.885	3.046
⑤	1.534	2.316	2.481	2.885	3.046
⑥	112.7	112.0	110.7	97.16	91.65
⑦	113.0	112.1	110.7	97.12	91.61
⑧	104.6	108.7	109.4	107.5	105.9
⑨	104.8	108.8	109.4	107.4	105.8

Figure 2. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of the reactants (singlet) fused bicyclic dimetallene (M = C, Si, Ge, Sn, and Pb). Hydrogens are omitted for clarity.



Reactant (Triplet)

X	C	Si	Ge	Sn	Pb
①	1.510	2.334	2.498	2.890	3.046
②	1.510	2.334	2.498	2.890	3.046
③	1.540	2.358	2.542	2.906	3.265
④	1.512	2.332	2.496	2.877	3.047
⑤	1.512	2.332	2.496	2.876	3.048
⑥	110.1	108.9	104.6	109.4	95.63
⑦	110.0	108.9	104.5	109.3	95.56
⑧	106.1	108.2	109.0	108.3	106.2
⑨	105.9	108.3	109.0	108.4	106.3

Figure 3. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of the reactants (triplet) fused bicyclic dimetallene (M = C, Si, Ge, Sn, and Pb). Hydrogens are omitted for clarity.

Reactant **1** was calculated as both singlet and triplet species. As mentioned in the Introduction, only one substituted fused bicyclic disilene (**1**) has been synthesized and characterized unequivocally.[3] Although only a few details concerning its geometrical parameters are as yet available, we may compare some of our results with those obtained for this substituted fused bicyclic disilene. As can be seen in Figure 1, the agreement between the B3LYP results and the available experimental data[3] for the singlet state is quite good, with the bond lengths and angles in agreement to within 0.028Å and 3.4°, respectively. The latter values may be attributed to steric effects that cause the substituted fused bicyclic disilene to have larger bond angles than the parent fused bicyclic disilene itself. In any event, because of this this agreement,[3] one would therefore expect that the same relative accuracy should also apply to the geometries as well as energetics predicted for the other fused bicyclic dimetallenes species.

Furthermore, as one can see in Figures 2 and 3, both singlet and triplet structures are quite similar to each other. The biggest difference between these two structures is the M=M (M = C,

TABLE 1: Relative Energies for Singlet and Triplet Fused Bicyclic Dimetallenes with Carbon Tetrachloride and for the Process Fused Bicyclic Dimetallene + CCl_4 → Transition State → Abstraction Product[a]

systems	ΔE_{st}[b] (kcal/mol)	ΔE_{act}[c] (kcal/mol)	ΔH[d] (kcal/mol)
	Fused Bicyclic Ethylene		
Cl-attack	+74.7	+82.4	+64.2
CCl3-attack	+74.7	+95.4	+86.4
	Fused Bicyclic Disilene		
Cl-attack	+29.2	+9.51	−8.71
CCl3-attack	+29.2	+61.4	+24.7
	Fused Bicyclic Digermene		
Cl-attack	+23.4	+6.83	−9.21
CCl3-attack	+23.4	+54.9	+25.3
	Fused Bicyclic Distnnene		
Cl-attack	+12.1	+5.15	−11.7
CCl3-attack	+12.1	+50.7	+23.0
	Fused Bicyclic Diplumbene		
Cl-attack	+7.132	+2.789	−15.75
CCl3-attack	+7.132	+50.57	+11.56

[a] At the B3LYP/LANL2DZdp level. See the text. [b] Energy relative to the corresponding singlet state. A negative value means the triplet is the ground state. [c] Activation energy of the transition state, relative to the corresponding reactants. [d] Reaction enthalpy of the product, relative to the corresponding reactants.

Si, Ge, Sn, and Pb) double-bond length. That is to say, the triplet state of a fused bicyclic dimetallene has a significantly greater bond distance (M═M) than its equivalent closed-shell singlet state. Indeed, this is usually the case in group 14 doubly bonded compounds, in accordance with the expectations of the frontier orbital theory.[13] For instance, our theoretical results indicate that 1.363 Å $(C{=}C)_1$ < 1.540 Å $(C{=}C)_3$, 2.153 Å $(Si{=}Si)_1$ < 2.358 Å $(Si{=}Si)_3$, 2.308 Å $(Ge{=}Ge)_1$ < 2.542 Å $(Ge{=}Ge)_3$, 2.727 Å $(Sn{=}Sn)_1$ < 2.906 Å $(Sn{=}Sn)_3$, and 2.975 Å $(Pb{=}Pb)_1$ < 3.265 Å $(Pb{=}Pb)_3$. Besides this, no matter what multiplicity the group 14 fused bicyclic dimetallenes adopts, our computations suggest that the M═M bond distance shows a monotonic increase down the group from C to Pb. The reason for this is mainly due to the increase of atomic radius of M from C to Pb.

The singlet−triplet energy separations of the group 14 fused bicyclic dimetallenes have also been investigated in the present study. These results are perhaps one of the most interesting results of this work, because very little is known about these energy splittings. As one can see in Table 1, the stability of the triplet state increases along with the atomic number of the group 14 atom in the fused bicyclic dimetallene. That is, the singlet−triplet energy splitting generally decreases as the atomic number of the group 14 atom increases. As given in Table 1, our theoretical results suggest that a decreasing trend in singlet−triplet energy splitting should be as follows: fused bicyclic diethylene (75 kcal/mol) > fused bicyclic disilene (29 kcal/mol) > fused bicyclic digermene (23 kcal/mol) > fused bicyclic distannene (12 kcal/mol) > fused bicyclic diplumbene (7.1 kcal/mol) at the B3LYP level of theory. Indeed, it is well-known that spin−orbit effects will grow as one proceeds down the periodic table because of the relativistic effect,[14] so that for M = Pb, its triplet state would be the most stable. We shall use the above results to explain the origin of barrier heights for the abstraction reactions in a later section.

2. Transition States. As already mentioned in the Introduction, the initial reaction between fused bicyclic dimetallene and carbon tetrachloride can take place from two directions: the abstraction of a chlorine atom from CCl_4 to produce [fused bicyclic dimetallene-Cl]• and CCl_3• (shown in eq 1a) and the CCl_3• radical transfer to produce fused bicyclic dimetallene leading to the formation of [fused bicyclic dimetallene-CCl_3]• and Cl• (shown in eq 1b). In both pathways, CCl_4 is considered to attack the central M═M double bond from the less hindered side in order to avoid steric repulsion with any substituents.

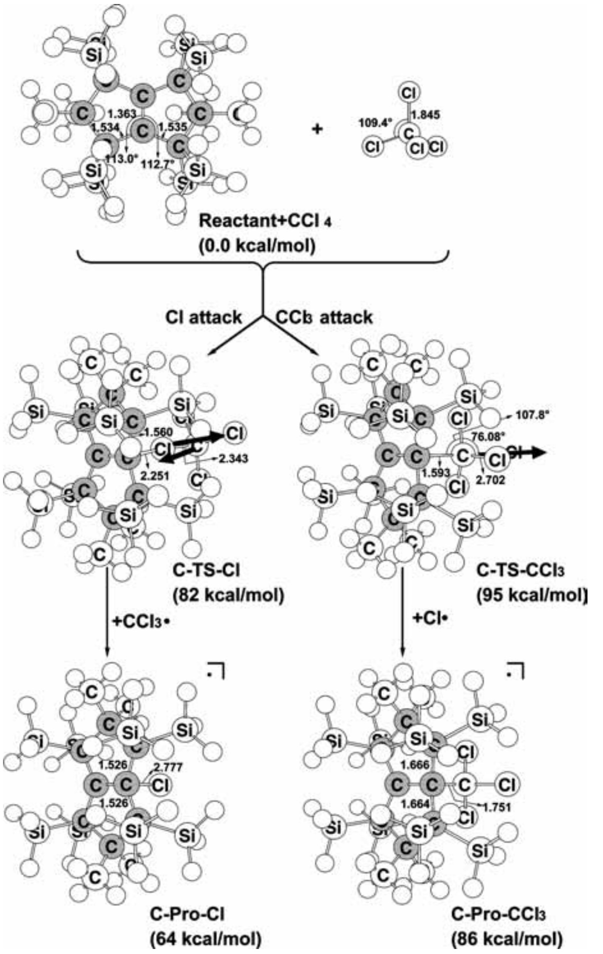


Figure 4. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of the reactants (singlet), transition states, and abstraction products of fused bicyclic dimetallene (M = C) and CCl_4. The relative energies for each species are in Table 1. The thick arrows indicate the main atomic motions in the transition state eigenvector. Hydrogens are omitted for clarity.

The main geometrical parameters of the transition states corresponding to abstraction reactions as well as their appearance are shown in Figures 4−8, together with the meaningful components of their transition vectors. These transition states will be referred to as **C−Cl−TS**, **Si−Cl−TS**, **Ge−Cl−TS**, **Sn−Cl−TS**, **Pb−Cl−TS**, and **C−CCl_3−TS**, **Si−CCl_3−TS**, **Ge−CCl_3−TS**, **Sn−CCl_3−TS**, **Pb−CCl_3−TS**, for eq 1a (Cl abstraction) and eq 1b (CCl_3 abstraction), respectively. Starting from eq. 1, this leads apparently to Cl atom abstraction and the formation of [fused bicyclic dimetallene-Cl]• and CCl_3•. In all cases, we have found that the Cl abstractions proceed in one step and that the three atoms (M, Cl′, and C; Cl′ = the migrating chlorine atom) involved in the process are in a nonlinear arrangement because of steric repulsion between CCl_4 and substituents on the fused bicyclic dimetallene. The group 14 atom (M) of the fused bicyclic dimetallene molecule makes an angle with respect to the Cl′−C bond of 170, 161, 173, 165, and 166° for **C−Cl−TS**, **Si−Cl−TS**, **Ge−Cl−TS**, **Sn−Cl−TS**, and **Pb−Cl−TS**, respectively. Moreover, all these transition

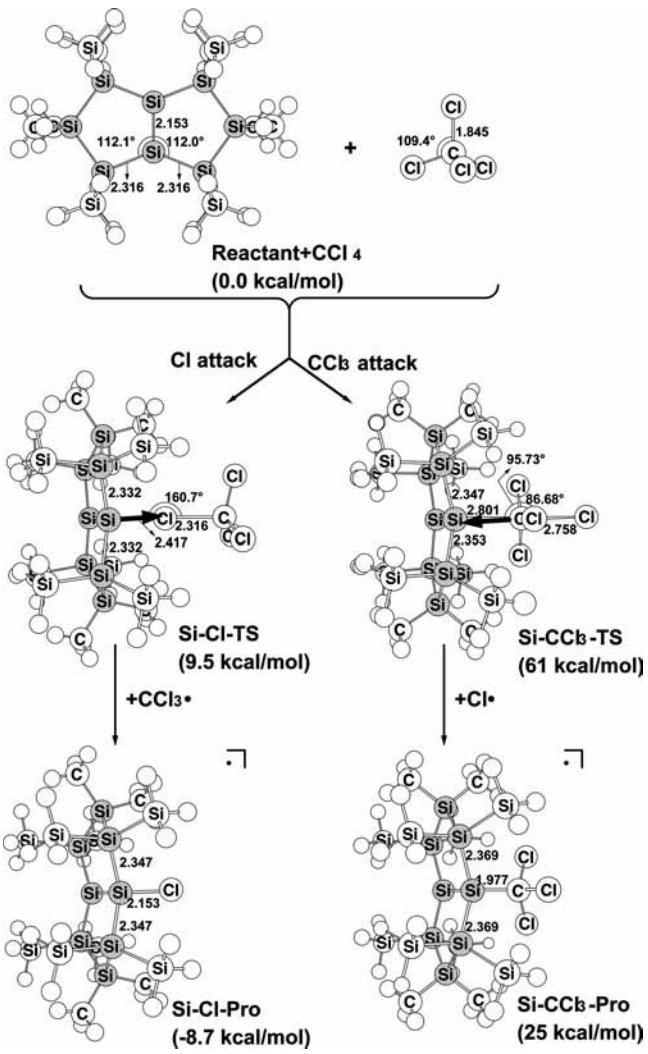


Figure 5. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of the reactants (singlet), transition states, and abstraction products of fused bicyclic dimetallene (M = Si) and CCl_4. The relative energies for each species are in Table 1. The thick arrows indicate the main atomic motions in the transition state eigenvector. Hydrogens are omitted for clarity.

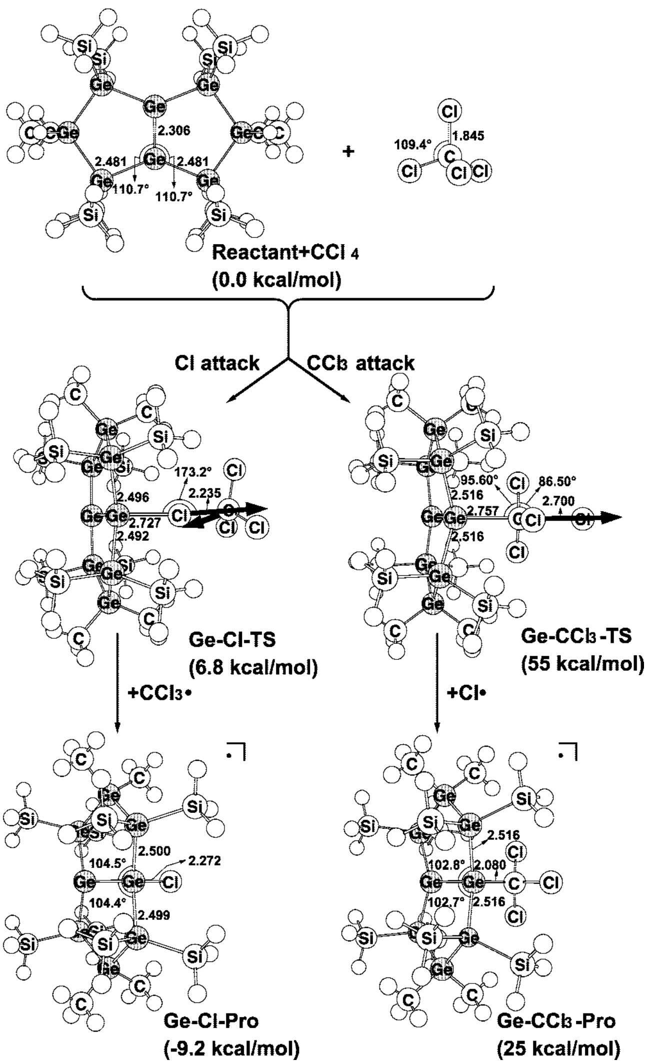


Figure 6. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of the reactants (singlet), transition states, and abstraction products of fused bicyclic dimetallene (M = Ge) and CCl_4. The relative energies for each species are in Table 1. The thick arrows indicate the main atomic motions in the transition state eigenvector. Hydrogens are omitted for clarity.

states possess one imaginary frequency and are true first-order saddle points. Our computational results demonstrate that the eigenvalue gives imaginary frequencies of 167*i* (**C−Cl−TS**), 99.9*i* (**Si−Cl−TS**), 162*i* (**Ge−Cl−TS**), 138*i* (**Sn−Cl−TS**), and 96.6*i* (**Pb−Cl−TS**) cm^{-1}. For all 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 4−8.

One of the interesting points to emerge from these calculations of transition state geometry is the extent to which the X−Cl′ bond is formed in the transition state. Our computations indicate that the Cl′−C bond length in **C−Cl−TS**, **Si−Cl−TS**, **Ge−Cl−TS**, **Sn−Cl−TS**, and **Pb−Cl−TS** is 27, 26, 21, 19, and 17% longer than that of the corresponding reactant CCl_4, respectively. This demonstrates that the fused bicyclic diplumbene abstraction reaction arrives at the transition state relatively early, whereas the fused bicyclic diethylene abstraction reaction reaches the transition state relatively late. In consequence, 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,[15] which associates an earlier transition state with a smaller barrier and a more exothermic reaction.

Next, we consider the CCl_3 abstraction (eq 1b). A search for transition states indicates that the energy profile for this reaction exhibits a maximum. The transition states thus located are also presented in Figures 4−8. Those transition structures are characterized by one imaginary frequency of 349*i*, 500*i*, 500*i*, 495*i*, and 435*i* cm^{-1} for **C−CCl$_3$−TS**, **Si−CCl$_3$−TS**, **Ge−CCl$_3$−TS**, **Sn−CCl$_3$−TS**, and **Pb−CCl$_3$−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 M−CCl_3 bond. That is to say, the reaction coordinate is fundamentally an asymmetric stretch at the conventional transition state. Moreover, the transition structures show that the newly formed M−C bond length is 1.59 Å (**C−CCl$_3$−TS**), 2.80 Å (**Si−CCl$_3$−TS**), 2.76 Å (**Ge−CCl$_3$−TS**), 2.85 Å (**Sn−CCl$_3$−TS**), and 2.78 Å (**Pb−CCl$_3$−TS**), compared to that in the final radical product (vide infra) of 1.75 Å (**C−CCl$_3$−Pro**), 1.98 Å (**Si−CCl$_3$−Pro**), 2.08 Å (**Ge−CCl$_3$−Pro**), 2.86 Å (**Sn−CCl$_3$−Pro**), and 2.37 Å (**Pb−CCl$_3$−Pro**), respectively. Again, taken together these features indicate that the transition structure for the fused bicyclic diplumbene is more reactant-like than that in the fused

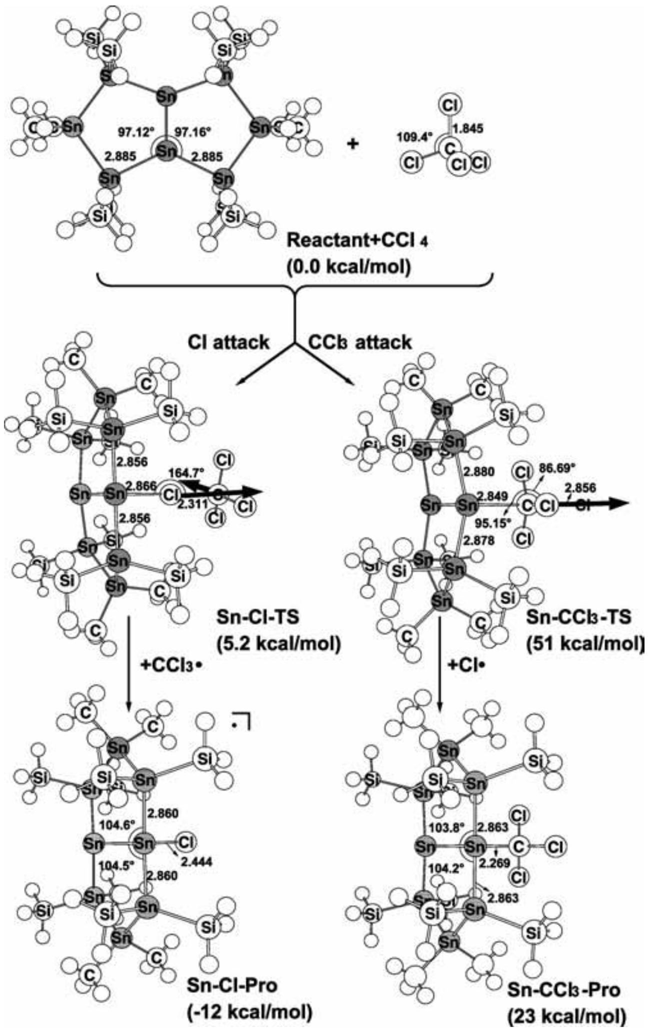


Figure 7. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of the reactants (singlet), transition states, and abstraction products of fused bicyclic dimetallene (M = Sn) and CCl_4. The relative energies for each species are in Table 1. The thick arrows indicate the main atomic motions in the transition state eigenvector. Hydrogens are omitted for clarity.

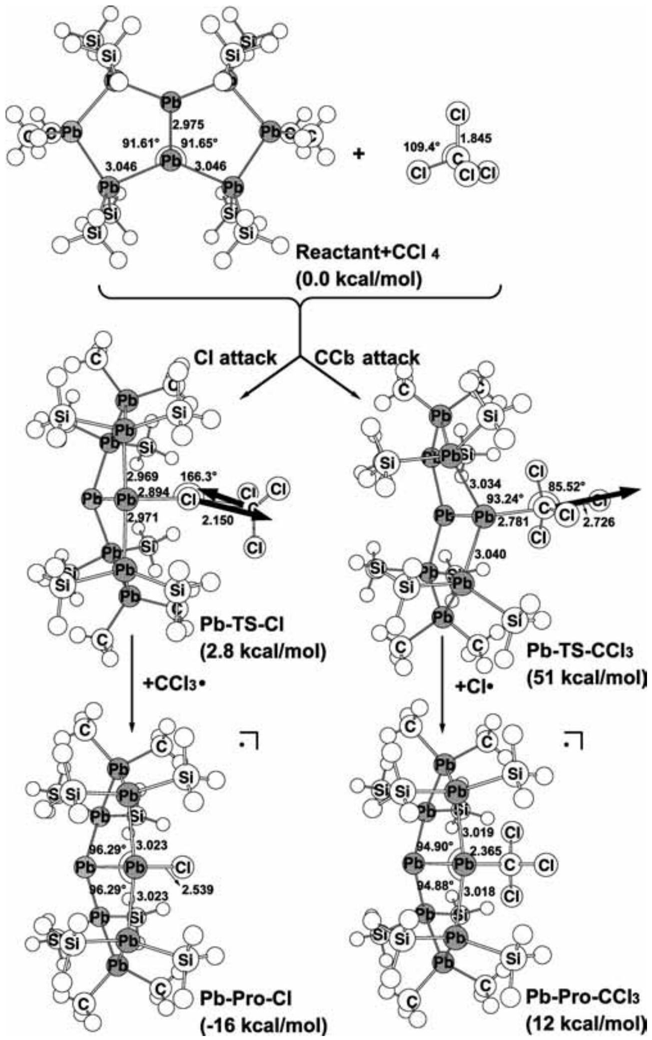


Figure 8. B3LYP/LANL2DZdp optimized geometries (in Å and deg) of the reactants (singlet), transition states, and abstraction products of fused bicyclic dimetallene (M = Pb) and CCl_4. The relative energies for each species are in Table 1. The thick arrows indicate the main atomic motions in the transition state eigenvector. Hydrogens are omitted for clarity.

bicyclic diethylene case. These observations will be related to the predicted energetics below.

In the Cl abstraction, examination of the energy values collected in Figures 4−8 and Table 1 shows that, at the B3LYP/LANL2DZdp level, the fused bicyclic distannene and diplumbene abstractions are favored. The present calculations predict that the energies of the transition states of the fused bicyclic diethylene, fused bicyclic disilene, fused bicyclic digermene, fused bicyclic distannene, and fused bicyclic diplumbene reactions are above those of the reactants by 82, 9.5, 6.8, 5.2, and 2.8 kcal/mol, respectively. Namely, our DFT calculations show that the overall barrier heights are determined to be in the order fused bicyclic diethylene > fused bicyclic disilene > fused bicyclic digermene > fused bicyclic distannene > fused bicyclic diplumbene. In any event, the above order reflects the greater ease of abstracting a chlorine atom by fused bicyclic diplumbene over abstraction by fused bicyclic diethylene. That is to say, our theoretical findings suggest that the more electropositive the element attached to the fused bicyclic dimetallene species, the more facile the abstraction of chlorine from CCl_4 becomes.

On the other hand, the energetics of reactions of the type fused bicyclic dimetallene + CCl_4 via eq 1b (CCl_3 abstraction) are also summarized in Figures 4−8 and in Table 1. The B3LYP calculations indicate that the overall barrier heights with respect to the corresponding reactants for CCl_3 abstraction are 95 (**C−CCl$_3$−TS**), 61 (**Si−CCl$_3$−TS**), 55 (**Ge−CCl$_3$−TS**), 51 (**Sn−CCl$_3$−TS**), and 51 (**Pb−CCl$_3$−TS**) kcal/mol. Accordingly, our theoretical results suggest that the process of CCl_3 abstraction by fused bicyclic distannene and fused bicyclic diplumbene is more facile than that by fused bicyclic diethylene. That is, the trend is similar to that for the Cl abstraction reactions described above. Our theoretical results also predict that, for the same reactant species, the barrier height for CCl_3 abstraction is much higher that that for Cl abstraction. In other words, Cl abstraction should be much easier than CCl_3 abstraction. The supporting experimental evidence comes from the fact that fused bicyclic disilene reacted with carbon tetrachloride to give *trans*-1,5-dichlorobicyclooctasilane similar to other stable disilenes,[4,6] without giving the CCl_3 abstraction product.[3]

3. Abstraction Products. The B3LYP/LANL2DZdp geometries of the abstraction products for both reaction pathways (**C−Cl−Pro**, **Si−Cl−Pro**; **Ge−Cl−Pro**, **Sn−Cl−Pro**; **Pb−Cl−Pro**, **C-CCl$_3$-Pro**, **Si-CCl$_3$-Pro**, **Ge-CCl$_3$-Pro**, **Sn-CCl$_3$-Pro**, and **Pb-CCl$_3$-Pro**) are displayed in Figures 4−8, 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 fused bicyclic dimetallene with a more electropositive element reaches the transition state relatively early, whereas one with a more electronegative element 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 that of activation energy: **C−Cl−Pro** (+64 kcal/mol) > **Si−Cl−Pro** (−8.7 kcal/mol) > **Ge−Cl−Pro** (−9.2 kcal/mol) > **Sn−Cl−Pro** (−12 kcal/mol) < **Pb−Cl−Pro** (−16 kcal/mol), and **C-CCl$_3$-Pro** (+86 kcal/mol) > **Si−CCl$_3$−Pro** (+25 kcal/mol) ≈ **Ge−CCl$_3$−Pro** (+25 kcal/mol) > **Sn−CCl$_3$−Pro** (+23 kcal/mol) > **Pb−CCl$_3$−Pro** (+12 kcal/mol). Note that our theoretical investigations suggest that the energies of CCl$_3$-abstraction products are always above those of their corresponding reactants, whereas the Cl-abstraction products are below those of their corresponding reactants (except for the case of M = C). This strongly indicates that the CCl$_3$-abstraction reaction is energetically very unfavorable and that, if it did occur, the reactions would be endothermic as opposed to exothermic for the corresponding Cl abstractions. As there are no relevant experimental and theoretical data on the fused bicyclic dimetallenic systems, the above result is a prediction.

IV. Overview of Fused Bicyclic Dimetallene Abstraction

From our study of the mechanisms of the reactions of fused bicyclic dimetallenes with CCl$_4$, the major conclusions that can be drawn are as follows.

(1) For fused bicyclic dimetallenic systems, a precursor complex for the haloalkane abstraction reaction does not exist.

(2) Irrespectively of the species abstracted, the abstraction 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 which fused bicyclic dimetallene is considered, the Cl-abstraction pathway is more favorable than the CCl$_3$-abstraction pathway from both kinetic and thermodynamic considerations. This is consistent with the experimental observation that only the Cl-abstraction products are formed.[3]

(4) One of the reasons for the smaller activation energy of the Cl abstraction is presumably the relatively small amount of repulsion between the chlorine atom and the substituents attached to the fused bicyclic dimetallene. Namely, the site of the fused bicyclic dimetallene moiety attacked in CCl$_3$ abstraction is more congested. In addition, another reason for the smaller activation energy of the Cl-abstraction reaction is the difference in electronegativity between Cl and Si, Ge, as opposed to the CCl$_3$ abstraction. This factor lowers the energy of the products and hence also lowers the barrier.

(5) Our model computations conclude that it is easier for CCl$_4$ to approach the M atom of the fused bicyclic dimetallene through Cl abstraction than through CCl$_3$ abstraction. Indeed, it is well-known that the M−Cl bond energy is much larger than the M−C bond energy and that this is why M−CCl$_3$ species would not exist.[16]

(6) The magnitudes of the Cl abstraction barriers are not high (except for the case of M = C) on the basis of our model calculations. This strongly implies that the radical reactions of the fused bicyclic dimetallenes with haloalkanes should be facile processes at room temperature. This is consistent with the available experimental finding.[3]

(7) The heavier the group 14 element in the fused bicyclic dimetallenic species, the lower the activation barrier and the more exothermic the haloalkane abstraction.

(8) Electronic as well as steric factors play a crucial role in determining the chemical reactivity of the fused bicyclic dimetallenic species, kinetically as well as thermodynamically.

In brief, by considering both the activation barrier and enthalpy, on the basis of the model calculations presented here, we conclude that the fused bicyclic dimetallenic reactivity order should be as follows: fused bicyclic diethylene < fused bicyclic disilene < fused bicyclic digermene < fused bicyclic distannene < fused bicyclic diplumbene.

V. Origin of the Barrier Height and Reaction Enthalpy for Abstraction of Fused Bicyclic Dimetallene

In this section, an interesting model for interpreting the reactivity of halogen abstraction reactions is provided by the so-called configuration mixing (CM) model.[17,18] According to the conclusions of this model, the energy barriers governing processes as well as the reaction enthalpies should be proportional to the energy gap ΔE_{st} (= $E_{\mathrm{triplet}} - E_{\mathrm{singlet}}$) between the singlet and the triplet states of the fused bicyclic dimetallene and $\Delta E_{\sigma\sigma^*}$ (= $E_{\mathrm{triplet}} - E_{\mathrm{singlet}}$ for CCl$_4$). In other words, the smaller the ΔE_{st} of a fused bicyclic dimetallene (when keeping the $\Delta E_{\sigma\sigma^*}$ constant) or the lower the value of $\Delta E_{\sigma\sigma^*}$ (when keeping the ΔE_{st} constant), the lower the barrier height and the larger the exothermicity and, in turn, the faster the halogen abstraction reaction.

Our model calculations confirm the above prediction. For the B3LYP/LANL2DZdp calculations on the aforementioned five systems, a plot of activation barrier versus ΔE_{st} is given: the best fit is $\Delta E^{\ddagger} = -14.7\Delta E_{\mathrm{st}} + 1.23$ and $\Delta E^{\ddagger} = 42.2\Delta E_{\mathrm{st}} + 0.696$ for Cl abstraction and CCl$_3$ abstraction cases, respectively. Likewise, the linear correlation between ΔE_{st} and the reaction enthalpy (ΔH), also obtained at the same level of theory, are $\Delta H = -32.0\Delta E_{\mathrm{st}} + 1.22$ and $\Delta H = 3.81\Delta E_{\mathrm{st}} + 1.06$, respectively. This investigation provides strong evidence that the singlet−triplet gap plays a key role in determining the reactivity of the reactants.

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 the fused bicyclic dimetallene with heavier elements more favorable than that with lighter elements both kinetically and thermodynamically?

The driving force for this can be traced to the singlet−triplet energy gap (ΔE_{st}) of the fused bicyclic dimetallene. According to the CM model, the barrier height ($\Delta E^{\ddagger}$) as well as the reaction enthalpy (ΔH) can be expressed in terms of the initial energy gap between the reactant and product configurations. That is to say, if $\Delta E_{\sigma\sigma^*}$ is a constant, the smaller ΔE_{st} of the fused bicyclic dimetallene, the lower the barrier height and the larger the exothermicity. Indeed, our theoretical calculations confirm this prediction and suggest a decreasing trend in ΔE_{st} for fused bicyclic diethylene (75 kcal/mol) > fused bicyclic disilene (29 kcal/mol) > fused bicyclic digermene (23 kcal/mol) > fused bicyclic distannene (12 kcal/mol) > fused bicyclic diplumbene (7.1 kcal/mol). From Table 1, it is readily seen that this result agrees with the trend in both activation energy and enthalpy ($\Delta E^{\ddagger}$, ΔH) for the Cl abstraction and CCl$_3$ abstraction cases as shown above.

(b) For a given fused bicyclic dimetallene species, why is the Cl abstraction favored over the CCl$_3$ abstraction?

According to the CM model discussed above, it is apparent that the reactivity order for both Cl and CCl$_3$ abstractions is governed by the magnitude of ΔE_{st} of a fused bicyclic dimetallene species. Comparing Cl with CCl$_3$, one may easily see that the latter should be more strongly repulsive than the former when it attacks the fused bicyclic dimetallene species. This, in turn, leads to a smaller barrier height and a larger exothermicity for the Cl than for the CCl_3 abstraction.[6] Interested readers can find more details in ref 6. This is what we observed in the bicyclo[3,3,0]octasil-1(5)-ene **1** molecule, which is in excellent agreement with the available experimental results.[3]

VI. Conclusion

With the above analysis in mind, we are confident in predicting that electropositive group 14 elements on the fused bicyclic dimetallene will result in a smaller ΔE_{st} and, in turn, will facilitate the halogen abstraction reaction. It should be emphasized that no matter what the fused bicyclic dimetallene, the Cl-abstraction pathway is always more favorable than the CCl_3-abstraction pathway from both kinetic and thermodynamic viewpoints. Besides, the present model calculations demonstrate that a concerted process, which does not involve a precursor complex, should play a crucial role in such abstraction reactions. That is to say, these halogen abstraction reactions will proceed stereospecifically, leading to radical products with retained stereochemistry.

On the other hand, 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 the various fused bicyclic dimetallenes 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 fused bicyclic dimetallenes without specific knowledge of the actual energies of the interactions involved.

We eagerly await experimental results to confirm our predictions.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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