Reprinted from Organometallics, 1993, 12.

High Coordinate Germanium and Tin Complexes in the Allylation Reactions of Aldehydes

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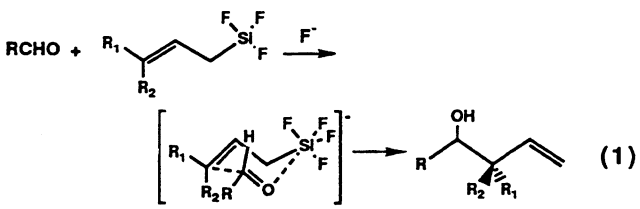
Received March 23, 1993

Allylation reactions of CH_2O by germanium and tin complexes, $AF_4(CH_2CH{=}CH_2)^-$ (A = Ge, Sn), are studied by ab-initio MO calculations and compared with the similar reactions of silicon complex, $SiF_4(CH_2CH{=}CH_2)^-$ reported previously. We determine fully optimized geometries of the tetra-, penta-, and hexacoordinate compounds, $AF_{3+n}(CH_2CH{=}CH_2)^{n-}$ and $AF_4(OCH_2)$-$(CH_2CH{=}CH_2)^-$ (A = Ge, Sn; n = 0, 1), along the reaction path. Pentacoordinate $AF_4(CH_2CH{=}CH_2)^-$ complexes have enhanced nucleophilicity at the allylic γ-carbon and significant Lewis acidity to form hexacoordinate complexes by the addition of CH_2O. These hexacoordinate complexes $AF_4(OCH_2)(CH_2CH{=}CH_2)^-$ are predicted to exist as stable intermediates before the transition state, so that they may be detected experimentally. The structures of the hexacoordinate transition state in the allylation reactions are also determined, assuming that the cyclic chair form is preferable to the linear form, as reported in the previous investigation on the Si compounds. The reactivity of the Ge and Sn complexes is expected to be greater than that of the Si compound because of the lowering of the potential energy barriers. When $CH(CH_3)O$ reacts with $AF_4(CH_2CH{=}CH_2)^-$, the energy differences between the axial and equatorial forms of the transition state are 2 and 5 kcal/mol for Ge and Sn, respectively, in comparison with 13.6 kcal/mol for the Si compounds, so that the stereoselective control, which is observed in the Si complexes, may be diminished in the Ge and Sn complexes.

1. Introduction

High coordinate silicon compounds have received much attention in recent years since they are moderately stable and show high reactivity and unique stereoselectivity. They frequently serve as useful intermediates in synthetic methods, although the mechanism of their reactions is not necessarily clear despite the many experimental investigations. Recently, reactions of pentacoordinate allylsilanes with various carbonyl compounds have been studied as a unique allylation method.[1-3] It is known that allylation of carbonyl compounds with allylsilanes can be promoted by the fluoride ion.[4,5] Majetich et al.[5] proposed that pentacoordinate intermediates are formed by the addition of the fluoride ion to silicon as an ambient nucleophilic species. Deiters and Holmes discussed the enhanced reactivity of pentacoordinate silicon species using ab-initio molecular orbital calculations.[6] Hexacoordinate complexes have also been suggested to exist as intermediates or transition states in the course of the reactions.[7,8]

The allylation of aldehydes by allyltrifluorosilanes and F^- proceeds without catalyst, and its stereoselectivity has been well characterized.[9] This reaction is believed to proceed as follows:



(1)

Tetra-, penta-, and hexacoordinate complexes are involved in the course of this reaction, as the initial compound, intermediate, and the transition state, respectively. The high reactivity and unique stereoselectivity of this reaction

(1) Sato, K.; Kira, M.; Sakurai, H. *J. Am. Chem. Soc*, **1989**, *111*, 6429.
(2) Hosomi, A.; Kohara, S.; Tominaga, Y. J. *Synth. Org. Chem. Jpn.* **1989**, *47*, 831.
(3) Becker, B.; Corriu, R.; Guerin, C.; Henner, B.; Wang, Q. *J. Organomet. Chem.* **1989**, *359*, C33. Brefort, J. L.; Corriu, R.; Guerin, C.; Henner, B. *J. Organomet. Chem.* **1989**, *370*, 9.
(4) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedoron Lett.* **1978**, 3043.
(5) Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *J. Org. Chem.* **1986**, *51*, 1745.
(6) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 7197.
(7) Boudin, A.; Cerveau, G.; Chuit, C.; Curriu, R. J. P.; Reye, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *25*, 473 and 265.
(8) Fujita, M.; Hiyama, T. *Tetrahedron Lett.* **1987**, *28*, 2263.
(9) Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1988**, *110*, 4599. Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1990**, *112*, 257.

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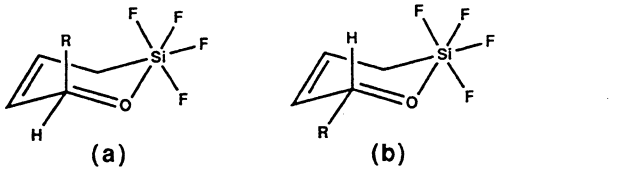
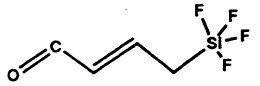
have been ascribed to two factors[9]: one is the significant Lewis acidity of the silicon center which facilitates formation of penta- and hexacoordinate silicates, and the second is the enhanced nucleophilicity of the γ-carbon of the allyl group due to the $\sigma-\pi$ conjugation. As the coordination number of the silicon center increases, its Lewis acidity decreases and the γ-carbon nucleophilicity increases. A cyclic transition state which is responsible for the stereochemistry of the products has been suggested as a result of these two factors.

Previously, we have reported ab-inito MO calculations for the tri-, tetra-, and pentafluoroallylsilanes and the transition state for the allylation reaction of formaldehyde by tetrafluoroallylsilicate (R = R_1 = R_2 = H in reaction 1).[10] The results were consistent with the experimental observations as a whole and supported the proposition that the cyclic chair form (i) is much preferable to the linear one (ii) as the transition state of the reaction.



(i) cyclic chair form



(ii) linear form

In this paper, we examine theoretically for the same reactions what happens when the Si center is replaced by Ge and Sn atoms. Generally speaking, penta- and hexacoordinate Ge and Sn complexes are more stable than the analogous Si complexes, so that different behaviors as intermediates and transition states are to be expected in the reactions involving the Ge and Sn complexes. As a first step of studying the chemistry of the Ge and Sn complexes, we carry out ab-initio MO calculations for hypothetical allylation reactions of Ge and Sn, the same as those which have already been observed experimentally for the Si compounds. Then, we compare the structures of the intermediates and the transition states, the reactivities, and the stereoselectivities among the Si, Ge, and Sn compounds.

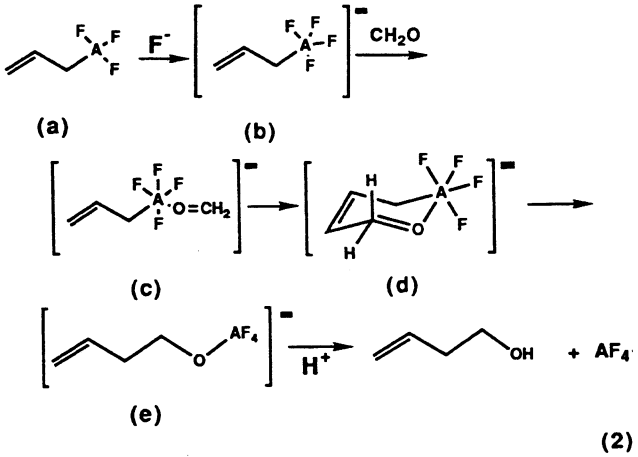
2. Brief Review of the Investigation for the Si Compounds

Previously, we have performed ab-initio MO calculations on the role of the penta- and hexacoordination in the allylation reaction of CH_2O by $SiF_3(CH_2CH{=}CH_2)$ and the fluoride ion F^-.[10] From the analyses of the Mulliken populations and the orbital energies, we have found that the nucleophilicity of the allylic γ-carbon is much enhanced in the pentacoordinate allylsilane $SiF_4(CH_2CH{=}CH_2)^-$, which appears as an intermediate before the transition state. Two transition states have been found in this reaction. One is a cyclic chair form (i), and the other is a linear form (ii). The geometrical parameters were fully optimized for the two forms in the case of R = H. The cyclic chair form is much preferable to the linear one. The cyclic boat form was not examined. The energy barrier for the reaction going through the cyclic chair form is 13.6 kcal/mol, while the energy of the linear form is 50.2 kcal/mol higher than the cyclic one. We therefore have examined the reaction which proceeds through the transition state of the cyclic chair form.

In the cyclic chair form, there are two possible forms when R $\neq$ H: the R group may occupy an axial (i)–(a) or an equatorial position (i)–(b). This selection of the position determines the stereochemistry of the products. For R = CH_3, the equatorial position is shown to be preferable by 18.7 kcal/mol to the axial one. This energy difference, compared with the energy barrier of the reaction, 13.6 kcal/mol, seems to be sufficient to control the stereoselectivity of the reaction. This explains the experimental observations for stereoselectivity.

3. Compounds and Methods of Calculation

Now, we study what happens when Si in the above reaction is replaced by Ge and Sn. The compounds studied in this paper are $AF_3(CH_2CH{=}CH_2)$, $AF_4(CH_2CH{=}CH_2)^-$, and $AF_4(OCH_2)(CH_2CH{=}CH_2)^-$ (A = Ge and Sn), which are tetra-, penta-, and hexacoordinate complexes. They appear in the course of the following chemical reactions:



(2)

Simple tetra-, penta-, and hexafluorides, AF_n^{4-n} (n = 4–6; A = Si, Ge, Sn) are also calculated in the next section in order to determine their relative stabilities. The existence of the stable hexacoordinate complexes c is then examined. We compare the geometries and the electronic structures of the compounds a–c. On the basis of the structures and stabilities of the transition states d, we investigate the reactivity and the stereoselectivity of the reactions involving Ge and Sn, in comparison with those involving Si. The summary of the present study is given in the last section.

In this paper, the geometrical parameters of the complexes described above are fully optimized by the method explained below, except for some auxiliary compounds described in section 8. The complexes which appear in the course of the allylation reactions are shown in Figures 1 and 2. Some of the optimized bond lengths and bond angles are also shown. For studying the stereoselectivity in the allylation reaction, we have replaced one H of CH_2O with CH_3, fixing the other geometrical parameters.

All calculations in this paper are in the framework of the ab-initio Hartree–Fock method. The programs used

(10) Kira, M.; Sato, K.; Sakurai, H.; Hada, M.; Izawa, M.; Ushio, J. *Chem. Lett.* **1991**, 387.

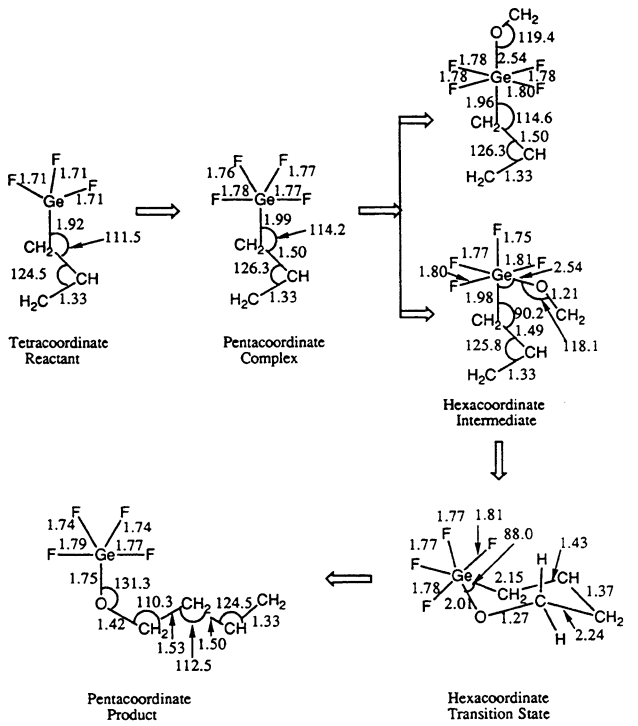


Figure 1. Optimized geometries of the Ge complexes along the allylation reaction path. Bond lengths are in angstroms and bond angles in degrees. Some other bond angles and dihedral angles are shown in Table II.

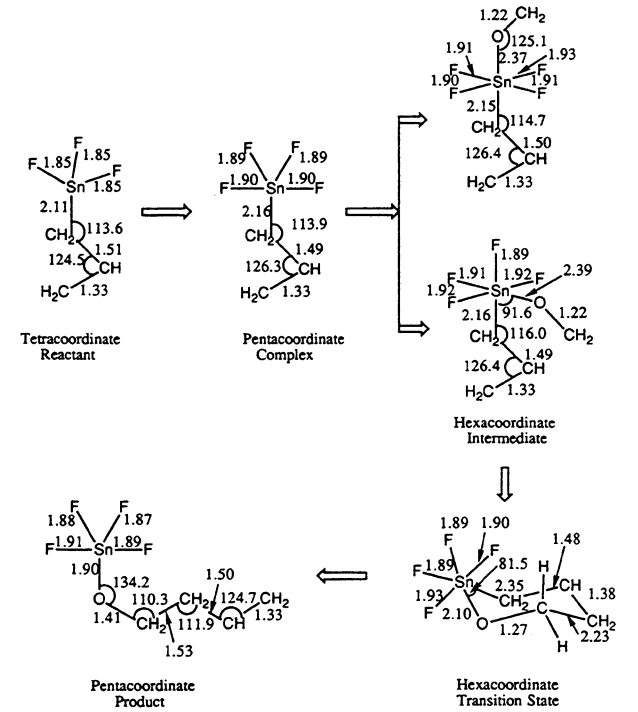


Figure 2. Optimized geometries of the Sn complexes along the allylation reaction path. Bond lengths are in angstroms and bond angles in degrees. Some other bond angles and dihedral angles are shown in Table III.

are HONDO7[11] and Gaussian 82.[12] We use double-ζ basis sets for Ge, Sn,[13] C, O, and F[14] and add polarization d functions to Ge and Sn.[14] STO-3G is used for H atoms.[15] Core electrons of Ge and Sn are replaced by the effective core potentials.[13] Although we used anion p basis sets[16] on F of the Si compounds in the previous paper, we have not included these basis sets in the present computation. We explore in the next section how this reduction in the basis set affects the relative stability and the structures of the penta- and hexacoordinate complexes of AF_n^{4-n} (A = Ge, Sn; n = 5, 6). We use the anion p basis set only when we calculate the stereoselectivities of the Ge and Sn complexes in comparison with that of the Si complex.

Table I. Relative Energies[a] and Internuclear Distances of AF_n^{4-n} (n = 5, 6; A = Si, Ge, Sn)

	present basis set		present basis set + anion p		
molecule	rel energy (kcal/mol)	R_{A-F} (Å)	rel energy (kcal/mol)	R_{A-F} (Å)	exptl R_{A-F} (Å)
SiF_5^-		1.688 (ax)		1.694 (ax)	1.660 (ax)[c]
		1.649 (eq)		1.652 (eq)	1.622 (eq)[c]
SiF_6^{2-}	11.0	1.727	29.6	1.732	1.685[d]
GeF_5^-		1.767 (ax)		1.775 (ax)	
		1.734 (eq)		1.740 (eq)	
GeF_6^{2-}	5.1	1.808	24.3	1.817	
SnF_5^-		1.887 (ax)		1.896 (ax)	
		1.870 (eq)		1.877 (eq)	
SnF_6^{2-}	−11.3	1.931	7.6	1.941	

[a] Relative energy is defined by $E(AF_6^{2-}) - E(AF_5^-) - E(F^-)$ (A = Si, Ge, Sn). [b] For Si, a double-ζ basis set is added a polarization d function is used.[13,14] [c] Schomburg and Krebs.[18] [d] Denne, Mathieson, and Mackay.[19]

4. Relative Stability of AF_{4+n}^{n-} (A = Si, Ge, Sn; n = 0–2)

First we examine the relative stability of AF_{4+n}^{n-} with A = Si, Ge, Sn and n = 0–2. It is well established that high coordinate complexes of Ge and Sn are more stable than the corresponding ones of Si.[17] For SiF_5^- and SiF_6^{2-}, Schomburg and Krebs[18] and Denne *et al.*[19] have reported the crystal data, respectively. Deiters and Holmes have theoretically investigated the structures and reactivities of some pentacoordinate Si species, and they discussed the enhanced Lewis acidity of pentacoordinate Si species.[6] Gutsev treated theoretically the existence of the hexacoordinate SiF_6^- anion.[20]

Table I shows the relative energies and the internuclear distances of AF_n^{4-n} (A = Ge, Sn; n = 5, 6). The expansion of the basis set by adding the anion p functions does not much affect the internuclear distances R_{A-F}. The relative stability between the hexacoordiante Si, Ge, and Sn species is not much affected also, although all hexacoordinate species AF_n^{4-n} (A = Si, Ge, Sn; n = 5, 6) are evenly destabilized by 18–19 kcal/mol by adding the anion p functions. Calculated distances R_{Si-F} are larger by 0.03–0.04 Å than the experimental ones in the present basis set.

(11) Dupuis, M.; Watts, J. D.; Villar, H. O.; Hurst, G. J. B. HONDO (Version 7). IBM Corp., Scientific Engineering Computations, Kingston, New York 12401; QCPE No. 544, Indiana University, Bloomingston, IN.
(12) Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; DeFrees, D. J.; Rahagavachari, K.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Gaussian 82. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.
(13) Waldt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
(14) *Gaussian basis sets for molecular calculations—physical data 16*; Huzinaga, S., Ed.; Elsevier Science Publishing Co. Inc.: New York, 1984.
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(20) Gutsev, G. L. *Chem. Phys. Lett.* **1991**, *184*, 305.

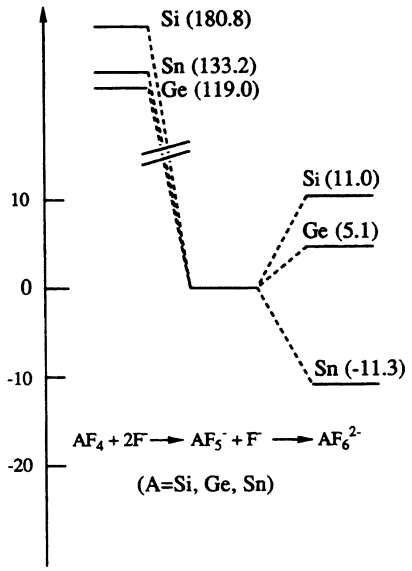


Figure 3. Energy diagrams of the tetra- and hexacoordinate fluorides AF_{4+n}^{n-} (A = Si, Ge, Sn; n = 0, 2) relative to the pentacoordinate fluorides AF_5^- (A = Si, Ge, Sn). Values in the parentheses are in kcal/mol.

Figure 3 shows the energy diagrams of SiF_{4+n}^{n-}, GeF_{4+n}^{n-}, and SnF_{4+n}^{n-} (n = 0, 2) relative to the pentacoordinate fluorides SiF_5^-, GeF_5^-, and SnF_5^-. Formation of pentacoordinate SiF_5^-, GeF_5^-, and SnF_5^- from SiF_4, GeF_4, and SnF_4 in each case is exothermic. In the hexacoordinate complexes, only the formation of SnF_6^{2-} from pentacoordinate SnF_5^- is exothermic. The formation of SiF_6^{2-} and GeF_6^{2-} is endothermic, although SiF_6^{2-} and GeF_6^{2-} have local stable structures. From the results of Figure 3, the stability of the hexacoordinate complexes is in the order of Sn > Ge > Si, as already known in many reports. Variation of the relative energy in the hexacoordinate Si, Ge, and Sn complexes is moderate and comparable with the energy of the transition state of the allylation reaction (13.6 kcal/mol[10]) for the Si compound summarized in the previous section. So it is of much interest to examine the effect of the stability in high coordinate Ge and Sn complexes in the allylation reactions.

5. Hexacoordinate Intermediates

Next, we examine the possibility of the formation of hexacoordinate complexes; $AF_4(OCH_2)(CH_2CH{=}CH_2)^-$ (A = Ge, Sn) in the reaction path. In the system of $SiF_4(CH_2CH{=}CH_2)^-$ and CH_2O, a weak interaction exists between F and H of CH_2O and so the system becomes 5 kcal/mol more stable. The shortest H—F distance between the Si compound and CH_2O is 2.17 Å, and the next shortest one is 2.90 Å; the oxgen atom does not coordinate to the Si atom.

We found that the hexacoordinate Ge and Sn complexes, $GeF_4(OCH_2)(CH_2CH{=}CH_2)^-$ and $SnF_4(OCH_2)(CH_2CH{=}CH_2)^-$ are stable compared with the corresponding pentacoordinate complexes and CH_2O. The stabilization energies are 5.1 and 10.6 kcal/mol for the Ge and Sn complexes, respectively. These results suggest that the pentacoordinate Ge and Sn complexes have significant Lewis acidity which enables them to accept an additional ligand and to form stable hexacoordinate *intermediates* in the course of the reaction. By adding anion basis functions, these hexacoordinate intermediates may become unstable, as shown in Table I. Two types of stable

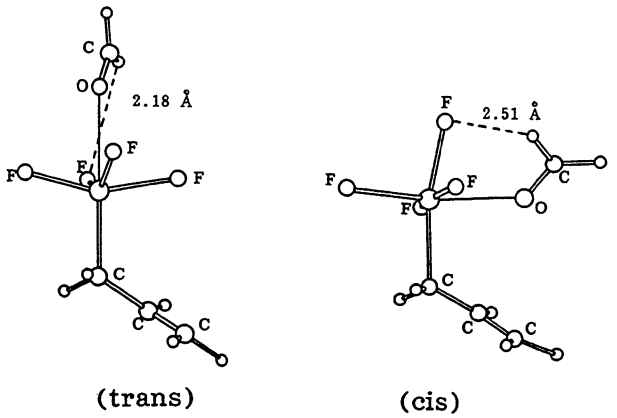


Figure 4. Optimized geometries of the hexacoordinate Sn intermediates before the transition state; $SnF_4(OCH_2)(CH_2CH{=}CH_2)^-$. The cis form is 1 kcal/mol more stable than the trans form.

structures are found for $AF_4(CH_2CH{=}CH_2)(OCH_2)^-$ (A = Ge, Sn). The structures of $SnF_4(OCH_2)(CH_2CH{=}CH_2)^-$ are shown in Figure 4. CH_2O occupies a *trans* position or a *cis* position with respect to the allyl group. The *cis* form is 1 kcal/mol more stable than the *trans* form. From the figure, there seems to be an interaction between F and H of CH_2O. The shortest distances between H of CH_2O and F are 2.18 and 2.51 Å in the *trans* and *cis* complexes, respectively, so the interaction seems to be larger in the *trans* form than in the *cis* form. Since the transition state of the reaction forms a six membered ring, only the cis complex in Figure 4 can give the product directly, while the *trans* complex must undergo a pseudorotation of the ligands to permit the reaction to occur.

$GeF_4(CH_2CH{=}CH_2)(OCH_2)^-$ also has two different arrangements at the Ge atom. They are essentially the same as those of the Sn complexes, so the above discussion is also valid for the Ge complexes. The shortest distance between H and F is 2.19 and 2.35 Å in the Ge complexes corresponding the *trans* and *cis* forms in Figure 4, respectively. Considering that GeF_5^- is not energetically stable compared with the sum of the energies of GeF_4^- and F^-, this interaction between H and F might be important for stabilizing the complexes.

6. Comparison of the Tetra-, Penta-, and Hexacoordinate Complexes

We compare the geometries and the electronic structures of the tetra-, penta-, and hexacoordinate complexes for the following compounds. The tetracoordinate compounds are $AF_3(CH_2{=}CHCH_2)$, and the pentacoordinate ones are $AF_4(CH_2{=}CHCH_2)^-$ (A = Ge, Sn). The hexacoordinate complexes are $AF_4(OCH_2)(CH_2{=}CHCH_2)^-$ (A = Ge, Sn) which are formed by the addition of CH_2O to the Ge and Sn atoms and which correspond to the *cis* form in Figure 4. Fully optimized geometrical parameters are summarized in Tables II and III. From the $C_\alpha AF$ angles (A = Ge, Sn), the geometries around the Ge and Sn atoms are approximately described as tetrahedral, trigonal bipyramidal (TBP), and octahedral for tetra-, penta-, and hexacoordinate complexes, respectively. The allyl group in the pentacoordinate compounds occupies an equatorial position of TBP, and the F atoms the two axial positions, as expected from the apicophilicity of negative ligands.[21]

(21) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1692.

Table II. Geometrical Parameters, Net Atomic Charges of the Ge and C Atoms, and Relative Energies of $GeF_3(CH_2{=}CHCH_2)$ (1), $GeF_4(CH_2{=}CHCH_2)^-$ (2), and $GeF_4(OCH_2)(CH_2{=}CHCH_2)^-$ (3)

	1 (tetracoordinate)	2 (pentacoordinate)	3 (hexacoordinate)
	Bond Lengths (Å)		
Ge–F	1.71	1.76–1.78	1.75–1.81
Ge–C_α	1.92	1.99	1.98
C_α–C_β	1.51	1.50	1.49
C_β–C_γ	1.33	1.33	1.33
Ge–O			2.54
O–C(aldehyde)			1.21[a]
	Bond Angles (deg)		
C_αGeF	112.4–114.3	90.5, 91.9, 121.8	87.4, 96.1, 93.7
		120.3	164.9
$GeC_\alpha C_\beta$	111.5	114.2	117.3
$C_\alpha C_\beta C_\gamma$	124.5	126.3	125.8
	Dihedral Angle (deg)		
$GeC_\alpha C_\beta C_\gamma$	−109.6	−118.8	−123.6
	Net Atomic Charges		
C_α	−0.39	−0.42	−0.41
C_β	−0.11	−0.08	−0.05
C_γ	−0.17	−0.31	−0.34
Ge	1.57	1.58	1.70
	Relative Energy (kcal/mol)[b]		
		94.5	5.1

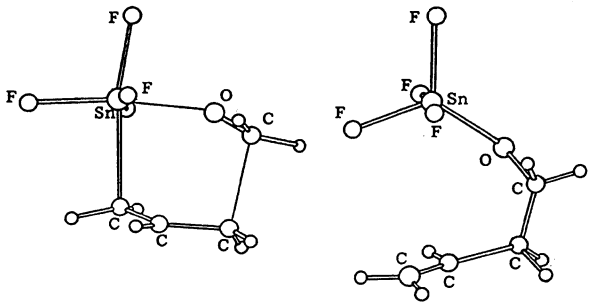
[a] The C–O distance in a free CH_2O calculated by the same basis set is 1.20 Å. [b] Relative energies are defined by $\Delta E(2) = E(2) - E(1) - E(F^-)$, $\Delta E(3) = E(3) - E(2) - E(CH_2O)$, where $E(n)$ denotes the total energy of compound **n**.

Table III. Geometrical Parameters, Net Atomic Charges of the Sn and C Atoms, and Relative Energies of $SnF_3(CH_2{=}CHCH_2)$ (1), $SnF_4(CH_2{=}CHCH_2)^-$ (2), and $SnF_4(OCH_2)(CH_2{=}CHCH_2)^-$ (3)

	1 (tetracoordinate)	2 (pentacoordinate)	3 (hexacoordinate)
	Bond Lengths (Å)		
Sn–F	1.85	1.89–1.90	1.89–1.93
Sn–C_α	2.11	2.16	2.16
C_α–C_β	1.51	1.49	1.49
C_β–C_γ	1.33	1.33	1.33
Sn–O			2.39
O–C(aldehyde)			1.22[a]
	Bond Angles (deg)		
C_αSnF	112.6–113.9	91.2, 92.0, 122.4	89.6, 95.1, 92.3
		121.8	167.7
$SnC_\alpha C_\beta$	113.6	113.9	116.0
$C_\alpha C_\beta C_\gamma$	124.5	126.3	126.4
	Dihedral Angle (deg)		
$SnC_\alpha C_\beta C_\gamma$	−113.6	−107.6	−109.8
	Net Atomic Charges		
C_α	−0.51	−0.60	−0.61
C_β	−0.10	−0.06	−0.05
C_γ	−0.18	−0.31	−0.34
Sn	2.00	2.00	2.14
	Relative Energy (kcal/mol)[b]		
		108.9	10.6

[a] The C–O distance in a free CH_2O calculated by the same basis set is 1.20 Å. [b] Relative energies are defined by $\Delta E(2) = E(2) - E(1) - E(F^-)$, $\Delta E(3) = E(3) - E(2) - E(CH_2O)$, where $E(n)$ denotes the total energy of compound **n**.

The Ge—F and Sn—F bond lengths increase with the increasing number of ligands at Ge and Sn, while the Ge—C and Sn—C bonds are almost the same in the respective penta- and hexacoordinate complexes. In the same coordination number, the order of bond distances is always Ge—F < Sn—F and Ge—C < Sn—C, as expected: the Si—F and Si—C bond lengths are shorter than these.[10]



Transition State Product

Figure 5. Optimized geometries in the transition state and the product in the course of the allylation reaction; $SnF_4(CH_2CH{=}CH_2)^- + CH_2O \rightarrow SnF4(OCH_2)(CH_2{-}CH{=}CH_2)^-$.

The bond distance of the allyl group does not change with the change of the coordination number at Ge and Sn. However, only the dihedral angle of $GeC_\alpha C_\beta C_\gamma$ changes markedly with increasing coordination number at Ge and Sn. This suggests that the preferable conformation of the allyl group is mainly determined by the stabilization due to the hyperconjugation between the Ge—C σ-bond and the C=C π-bond of the allyl group. In the Sn complexes, the structures of the allyl group seem not to be largely affected by the variation in the coordination of Sn.

Net atomic charges, calculated from the Mulliken population analysis, are summarized in Tables II and III. The Ge and Sn atoms are positively charged, and the carbons are negative. The net charge of C_γ increases markedly with increasing coordination number at Ge and Sn. In contrast, the net charge of C_β decreases in the same order. This tendency is similar to that for the Si complexes previously reported. The σ-bonds of Ge–C and Sn–C donate electrons to the allylic C_γ through σ–π hyperconjugation in the penta- and hexacoordinate complexes. The reason the net charges at C_α and C_γ increase in the high coordinate complexes is understood by considering that the second π-MO of the allyl radical has a node at C_β and has amplitudes only at C_α and C_γ. Net charges of the free allyl radical are 0.20, 0.16, and 0.20 for C_α, C_β, and C_γ, respectively, and those of free allyl anion are 0.68, 0.04, and 0.68 for C_α, C_β, and C_γ, respectively. Net charges at C_γ of penta- and hexacoordinate Ge and Sn complexes are larger than those of the free allyl radical. The orbital energies of the allylic π-orbitals in the penta- and hexacoordinate complexes become higher than that in the tetracoordinate silane, suggesting that the nucleophilicity of the allylic C_γ increases with the increasing number of ligands at Ge and Sn.

7. Transition States and Energetics

Next, we investigate the transition states. The six membered ring is formed by nucleophilic attack of the allylic C_γ to the carbonyl C. This is due to the enhanced nucleophilicity of the allylic C_γ in the hexacoordinate complexes. We do not consider the boat form, since Li and Houk reported that the boat forms are unstable compared with the chair form in similar reactions.[22]

The structures of the transition state and the product in the case of Sn are shown in Figure 5. Potential energy

(22) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 1236.

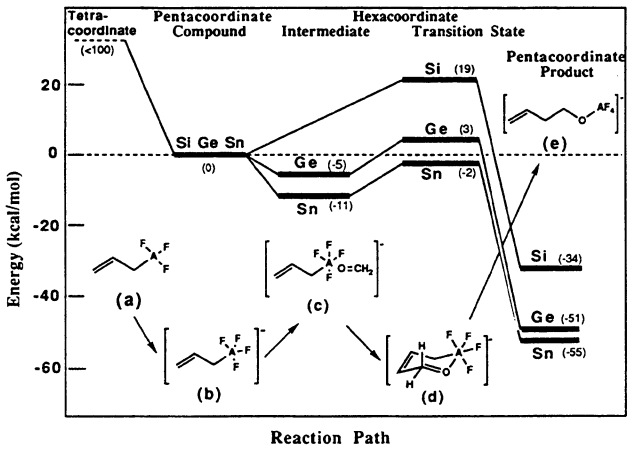


Figure 6. Energy diagrams for the allylation reactions of CH_2O by $AF_4(CH_2CH{=}CH_2)^-$ (A = Si, Ge, Sn). The transition states of the reactions are assumed to be in the cyclic chair form which is preferable for the Si compound. Numbers in the parentheses indicate energies (kcal/mol) relative to the pentacoordinate complexes. The relative energies for the tetracoordinate compounds $AF_3(CH_2CH{=}CH_2)$ (A = Ge, Sn) are shown in Tables II and III.

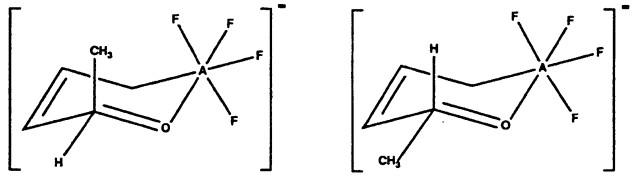
Table IV. Bond Lengths in the Cyclic-Chair Transition States of the Allylation Reactions of CH_2O by $AF_4(CH_2CH{=}CH_2)^-$ (A = Si, Ge, Sn) (Å)

bond	Si	Ge	Sn
A–C_α	2.134	2.152	2.350
C_α–C_β	1.422	1.430	1.484
C_β–C_γ	1.376	1.368	1.380
C_γ–C	2.224	2.240	2.225
A–O	1.902	2.013	2.100
O–C(aldehyde)	1.267	1.260	1.269
A–F	1.686–1.732	1.761–1.808	1.887–1.932

barriers of the reactions measured from the intermediate are 8 and 9 kcal/mol for the Ge and Sn cases, respectively. These energy barrier heights are smaller than that for the Si compound, suggesting that the Ge and Sn compounds are more reactive than the Si one. It is suggested from the results of Table I that these transition states may be destabilized by adding the anion basis on F. However, the relative stability between the Si, Ge, and Sn species would not be affected by adding these basis functions. Table IV shows some of the bond lengths for the transition states. They are similar to those of the hexacoordinate complexes shown in Tables II and III: these transition states are early transition states. The structures of the allyl group and CH_2O are not much influenced by replacing Si with Ge and Sn, while the A–F and A–O lengths increase in the order of Sn > Ge > Si.

The energy diagram for the overall reaction is shown in Figure 6, in which the results for the Si compound are also shown for comparison. First, the pentacoordinate complexes are formed from the trifluoroallyl compounds by the addition of F^-: the energies of the pentacoordinate complexes are taken as a standard in the figure. The energy levels of the tetracoordinate compounds $AF_3(CH_2CHCH_2)$ are shown by a broken line, since they are greater by more than 100 kcal/mol than the standard level: the pentacoordinate Si, Ge, and Sn complexes are all very stable complexes. The hexacoordinate Ge and Sn intermediates are formed by the addition of CH_2O, and they are 5 and 11 kcal/mol more stable, respectively. We therefore think that these intermediates may be detected experimentally.

The transition states are formed from the hexacoordinate intermediates in the cases of Ge and Sn. In the case



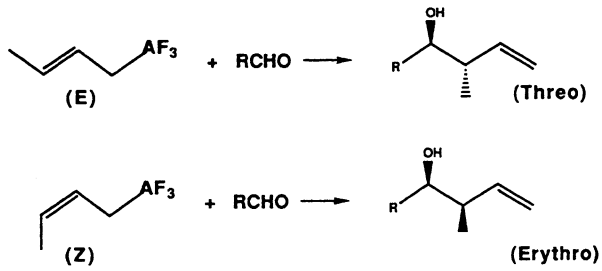
(a) axial (b) equatorial

Figure 7. Transition states having the methyl group in axial and equatorial positions (A = Si, Ge, and Sn).

of Si, it is formed directly from the pentacoordinate intermediate. The activation energies for the Ge and Sn reactions relative to the energy levels of the intermediates are lower by 10–11 kcal/mol than that of the Si reaction. The energy levels of the transition states relative to the energy levels of the pentacoordinate complexes are 19, 3, and −2 kcal/mol for the Si, Ge, and Sn compounds, respectively. The products are much more stable than the initial pentacoordinate intermediates in all cases. These results suggest that the reactivities of the Ge and Sn complexes are moderately greater than that of the Si compound.

8. Stereoselectivity of the Allylation Reaction

Next, we examine the selectivity of the reaction. These allylation reactions are expected to have the following stereoselectivity: [8]



This selectivity can be explained by the assumption that the R group prefers the equatorial position to the axial one in the transition state. These two positions are shown in Figure 7. We replace one of the two hydrogen atoms of CH_2O by a CH_3 group in order to estimate the relative stability between the axial and equatorial methyl positions in the allylation reaction with $CH(CH_3)O$. Other geometrical parameters are fixed to those of the transition states of $AF_4(CH_2CH{=}CH_2)^-$ (A = Ge, Sn) and CH_2O. In the Si case, the relative energy between the axial and equatorial positions is 13.6 kcal/mol. This value is large enough to control the selectivity of the reaction, considering that the height of the potential barrier from the initial compounds is 18.7 kcal/mol in the case of Si. In the Ge and Sn cases, the energy differences between the axial and equatorial positions are 3.5 and 1.2 kcal/mol, respectively. The six membered rings in the transition states are larger for Ge and Sn than for Si, so that the repulsion between CH_3 and F at the axial position decreases in the Ge and Sn transition states. Thus, the stereoselectivity in the Ge and Sn compounds should be smaller than that in the Si compound.

We also examined, for comparison, the allylboration reaction of $BH_2(CH_2CH{=}CH_2)$ with $CH(CH_3)O$ in the same manner. Several transition states of the reaction were calculated by Li and Houk, and they suggested that

the cyclic chair form is preferable.[19] We used the geometry calculated in their paper and obtained 5.5 kcal/mol as the relative energy by exchanging an axial or equatorial hydrogen with CH_3. From these results, allyltrifluorosilane and $CH(CH_3)O$ have higher stereoselectivities than the tetracoordinate allylborane, which has only two hydrogen atoms at B and has small steric repulsion. From the comparison of axial–equatorial relative energies, $AF_4(CH_2CH{=}CH2)^-$ (A = Ge and Sn) and $CH(CH_3)O$ may have lower stereoselectivities than allylborane.

9. Conclusion

We have investigated the reactivity and the stereoselectivity of the allylation reactions of aldehydes involving high coordinate Ge and Sn complexes along the reaction formula 2.

(1) The formation of the pentacoordinate compounds $AF_4(CH_2CH{=}CH_2)^-$ from $AF_3(CH_2CH{=}CH_2)$ by the addition of F^- is exothermic. The nucleophilicity of the allylic γ-carbon is much enhanced when the pentacoordinate $AF_4(CH_2CH{=}CH_2)^-$ is formed. These results are qualitatively similar to those found previously for the reaction of the corresponding Si compound.

(2) The pentacoordinate Ge and Sn complexes still have a significant Lewis acidity which allows them to form stable hexacoordinate intermediates in the course of the reaction. It is expected that these intermediates can be detected experimentally as $AF_4(OCH_2)(CH_2CH{=}CH_2)^-$.

(3) The reactivity of the Ge and Sn complexes may be enhanced because the energy barriers for the transition states are 3–4 kcal/mol lower than that for the Si compound.

(4) The stereoselectivity of the reaction may be diminished in the case of the Ge and Sn complexes in comparison with the Si complex. Although the experimental observation of reactions involving highly coordinate Ge and Sn complexes has not yet been reported, we expect such reactions will be performed in the near future.

Acknowledgment. We thank Prof. M. Kira and Prof. H. Sakurai for their kind interest in this work. Part of the calculations have been carried out with the computers at the Data Processing Center of Kyoto University and the Institute for Molecular Science. We thank the IMS computer center for grants of computing time. Part of this study has been supported by the Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, and Culture and by CIBA-GEIGY Foundation (Japan) for the Promotion of Science.

OM930178C