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An ab Initio Computational Study on the Reaction of Organotin Enolates: Comparison of Highly Coordinated Tin Reagent with Noncoordinated Reagent

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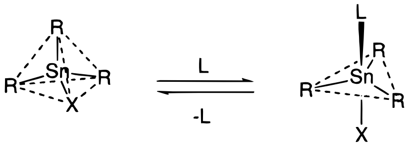
Abstract: An ab initio computational study revealed the mechanism of the reaction between tin enolates and aldehydes or organic halides in both cases with and without a bromide anion as a coordinating ligand to tin. The calculations showed the stabilization of tin compounds by complexation with the bromide anion. The order of stabilization is tin bromide > tin enolate > tin alkoxide. In the reaction of tin enolate with aldehyde, a noncoordinated tin enolate gave the cyclic transition state in sled-form while the acyclic transition state which leads to deactivation of the reaction process is shown in the use of a highly coordinated enolate. This open structure is ascribed to the bromide anion-coordinated tin which is reluctant to coordination by carbonyl oxygen in aldehyde. In both cases with and without ligands, synclinal arrangements between carbonyl C═O in aldehyde and vinyl C═C in enolate are observed. The reaction of tin enolates with organic halides proceeds through two steps involving alkylation in S_N2 mode and destannylation with formation of bromostannane. The system of high-coordinated tin enolate is favored both kinetically and thermodynamically. The high nucleophilicity of high-coordinated tin enolate is due to coordination of an anionic ligand.

Introduction

A high coordination of organometallic reagents often leads to a change in their reactivity and/or selectivity. In that case, the highly coordinated species could have a totally different character from that of the original noncoordinated species, partly because of the change in the hybridization states of relevant metals. This phenomenon, while not exactly comprehended, is generally considered and understood to be a solvent effect or an additive effect. We chose tin compounds to discuss comparison between highly coordinated species and noncoordinated species for our computational study since high coordination of tin compounds has been extensively examined.

Organotin(IV) compounds could be easily coordinated by an appropriate ligand, giving a highly coordinated species.[1,2] This fact, of course, shows significant contrast between tin and carbon from the point of view of high coordination. A five-coordinated carbon, which is well-known as a transition state in S_N2 reactions, lies on the top of the potential energy surface. On the contrary, a five-coordinated organotin compound could lie at the bottom of the energy surface due to the contribution of their d-orbitals to be rehybridized to a hyper coordination state (Scheme 1). Then the highly coordinated tin(IV) could be used as a unique reagent which has far different properties from those of the noncoordinated tin.

Scheme 1



In fact, we have recently reported the unusual reactivity of highly coordinated tin compounds such as organotin(IV) enolates[3] or organotin(IV) hydrides.[4] NMR studies disclose the existence of five-coordinated tin enolate arising from the addition of certain ligands.[3a,c] In particular, the coordination to tin enolates by a bromide anion (from Bu_4NBr) shows novel types of selective reactions,[3a] which are summarized in eqs 1−4. In general, organotin enolates readily add to aldehydes[5] (eq 1) and are inert to organic halides[6] (eq 2). On the contrary, the highly coordinated tin enolates, which attained a marked change in chemoselectivity, have higher nucleophilicity to organic halides (eq 4). However, they show low reactivity toward

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[†] Osaka Univerity.

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(6) A high temperatrue is required for halide-coupling with tin enolates. Odic, Y.; Pereyre, M. *J. Organomet. Chem.* **1973**, *55*, 273.

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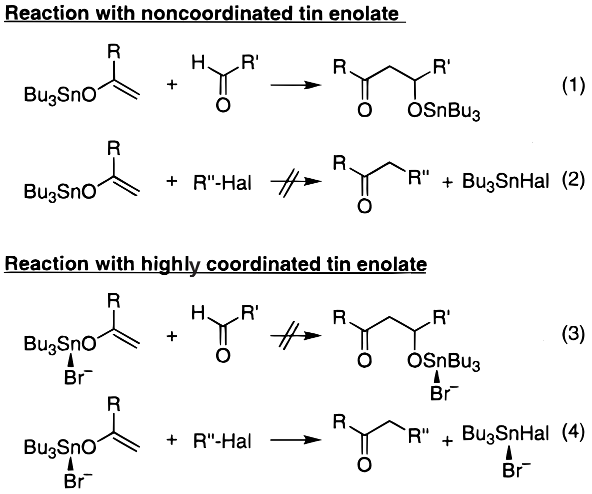


carbonyl compounds (eq 3).[3a] Thus, this high coordination method accomplishes significant change in chemoselectivity even in a competitive reaction system which includes both carbonyl compounds and organic halides.[3a]

The highly coordinated silyl enolates have been studied more than tin enolates and they are reported to accelerate both reactions with organic halide[7] and carbonyls.[8] Compared to the silyl system, the system using highly coordinated tin enolate has a unique character and can be applied to a chemoselective reaction. In this paper, we report a computational study of the difference between non- and high-coordinated tin enolates and their reactivities toward organic halides or carbonyl compounds.

Results and Discussion

Computational Method. We applied an ab initio LCAO-SCF-MO method based on Hartree–Fock–Roothaan[9] approximation. The electronic structure program, Turbomole,[10] was used to carry out our all calculations for geometry optimization. To obtain natural bond orbital charges, the NBO program[11] in Gaussian98[12] was applied to the optimized structures. A valence double-ζ quality basis set made by Schäfer et al.[13] and for Sn atoms an effective core potential proposed by LaJohn et al.[14] were employed. All molecular structures including transition states were fully optimized to evaluate reaction paths and activation energies of those paths. To make a torsional potential curve for the tin enolate complex, constrained optimization calculations were carried out on seven structures by changing 30° of the Sn–O–C–C torsion angle. Model tin compounds **1**–**3** which are representative of triorganotin enolates, triorga-

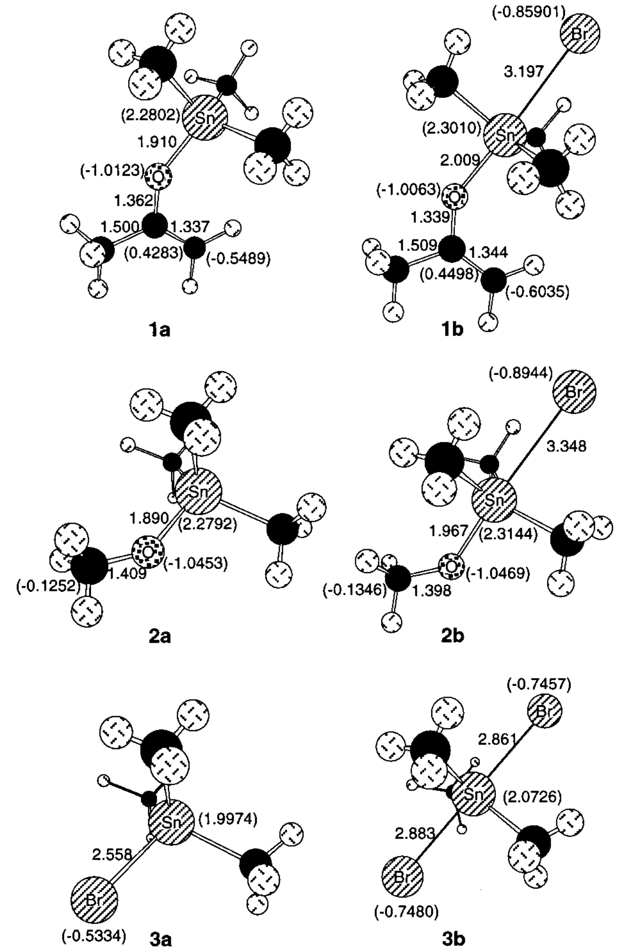
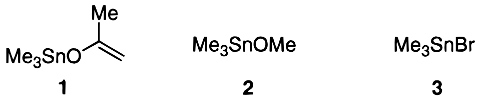
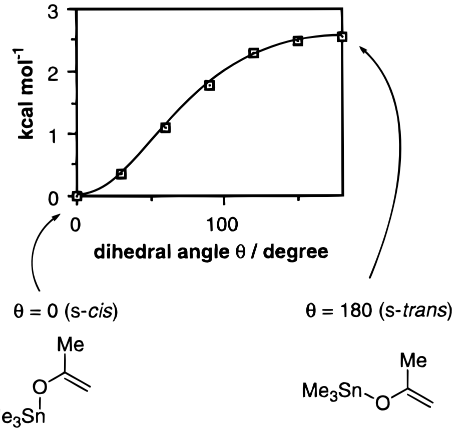


Figure 1. Structures of tin compounds **1**–**3** (distances in Å, numbers in parentheses are NBO charges): (**a**) four-coordinated species and (**b**) five-coordinated species.

Scheme 2



Scheme 3



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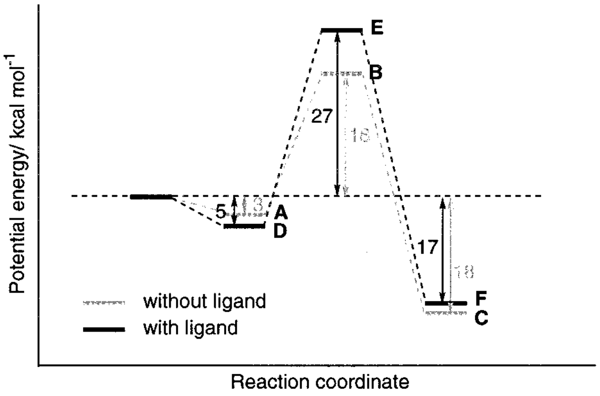


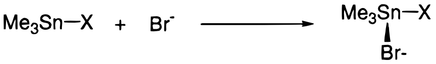
Figure 2. Potential energy profile for the reaction of **1** with benzaldehyde.

notin alkoxides, and triorganotin bromides, respectively, were chosen to mimic the structural and electronic features of the tin compounds we studied.

Optimized Structure of Tin Enolate. The geometry of tin enolate was optimized and the results are illustrated in Scheme 3, which shows the correlation between dihedral angle θ ($\angle$C$-$C$-$O$-$Sn) and potential energy. The optimized structure of tin enolate gave 0° of dihedral angle θ, although it is only 2.5 kcal/mol more stable than the antiperiplanar structure ($\theta = 180°$) which has the highest energy.[15]

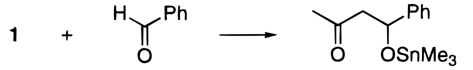
Model Reaction System. Equations 5 (**1** + benzaldehyde) and 6 (**1** + 1-bromopropane) are chosen as a model system for investigation of the reaction of tin enolates with aldehydes and organic halides, respectively.

Table 1

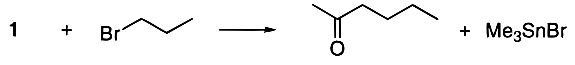


$$Me_3Sn{-}X + Br^- \longrightarrow \underset{Br^-}{\overset{}{Me_3Sn{-}X}}$$

Tin compound	ΔE/ kcal mol^{-1}
1	-20
2	-17
3	-31



(5)



(6)

High Coordination of Tin Compounds by Bromide (Br$^-$). Since three types of tin compounds are employed in eqs 1$-$4, namely, tin enolate, tin alkoxide (aldol-adduct), and tin halide with or without coordination by a bromide, it would be important to have information on these tin compounds with or without highly coordinated structures. Three tin compounds (trimethyltin enolate **1**, trimethyltin methoxide **2**, and trimethyltin bromide **3** in Scheme 1) were chosen to investigate the degree of stability by bromide coordination to the tin center. For all cases, the

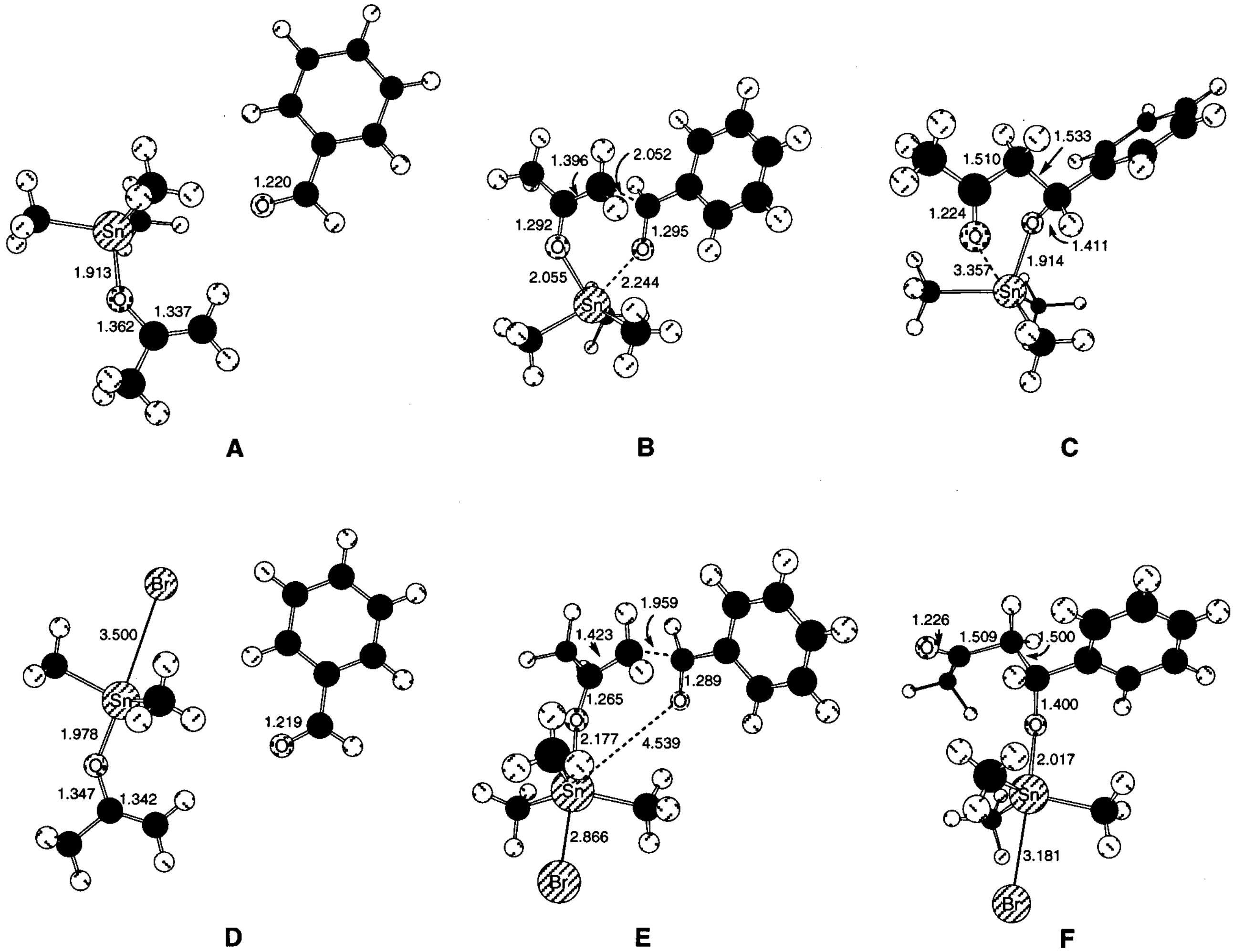
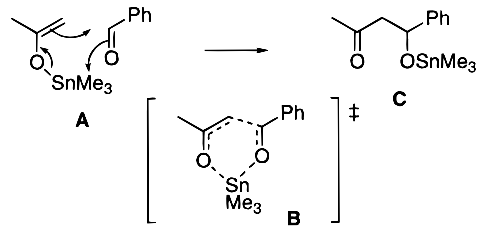


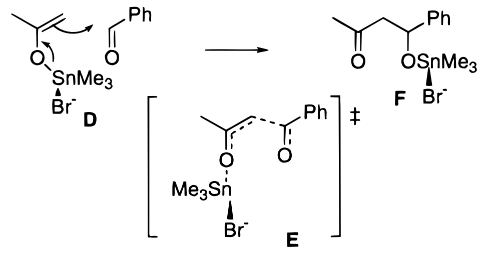
Figure 3. Structures along the reaction between **1** and benzaldehyde with or without ligand (distances in Å).

Scheme 4

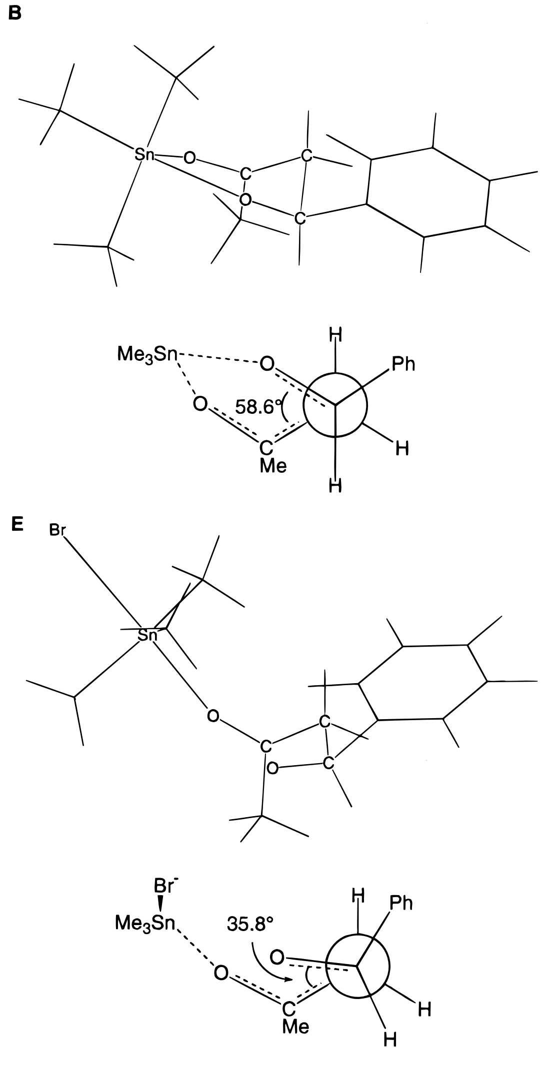
(a) The reaction of **1** with benzaldehyde without ligand



(b) The reaction of **1** with benzaldehyde with ligand



Scheme 5



computational calculations showed the stabilization by high coordination. As shown in Table 1, the order of stabilization is **3** > **1** > **2**. The results of the order are in good agreement with those of ^{119}Sn NMR chemical shifts: stronger coordination of tin compounds causes higher-field shift in ^{119}Sn NMR,[16] and their shifts of $|\Delta\delta(^{119}\mathrm{Sn})|$ also show the same order (**3** > **1** > **2**) of high-field shift.[3a] In fact, the high coordination of the bromide (Br$^-$) changes the structure of the tin species from a tetrahedral to a trigonal bipyramidal structure as shown in Figure

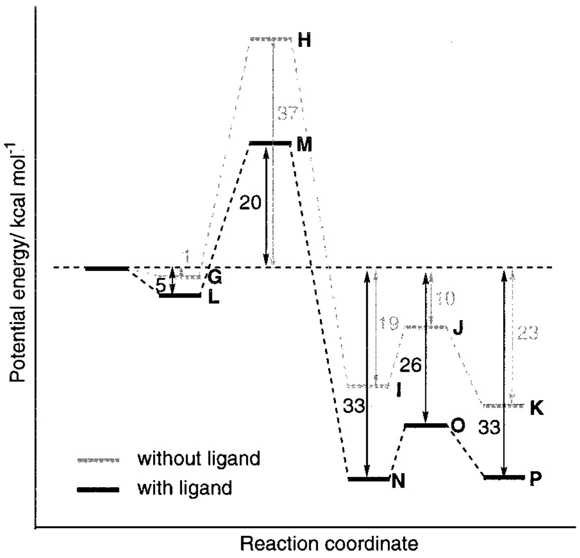
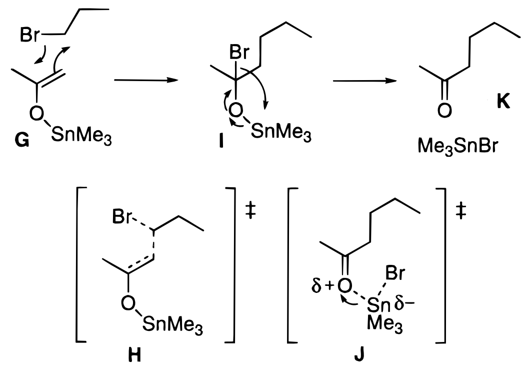


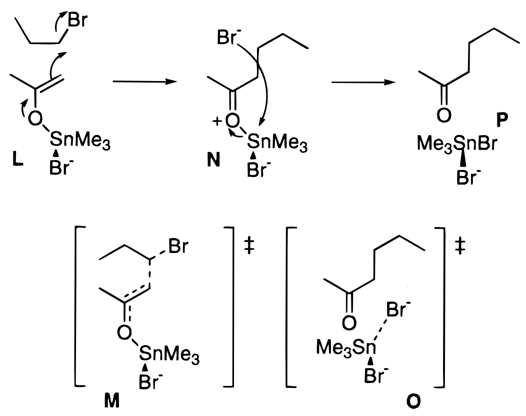
Figure 4. Potential energy profile for the reaction of **1** with bromopropane.

Scheme 6

(a) The reaction of **1** with bromopropane without ligand



(b) The reaction of **1** with bromopropane with ligand



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(15) The optimized geometry of silyl enolate has been reported. Takahashi, M.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 8597.

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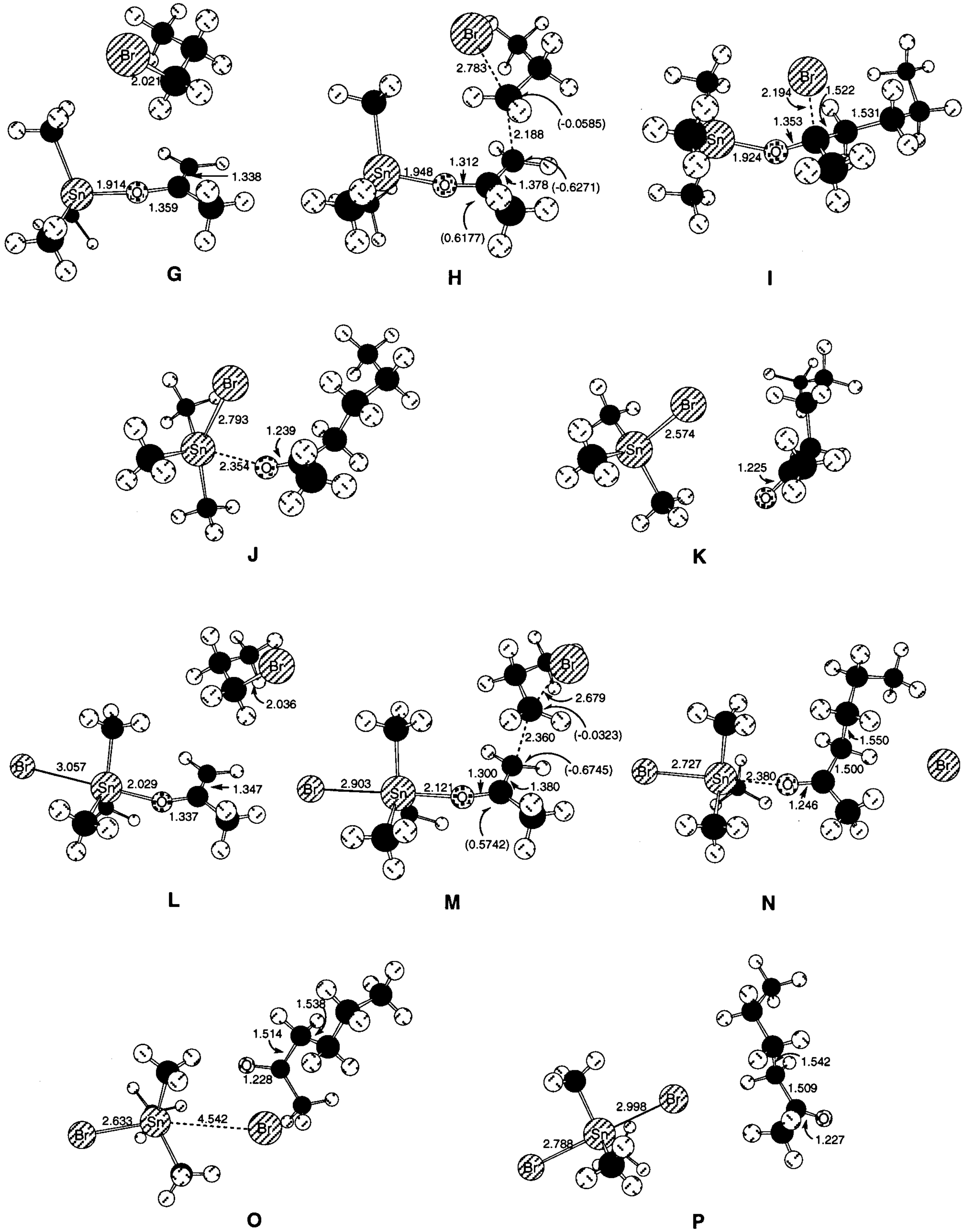
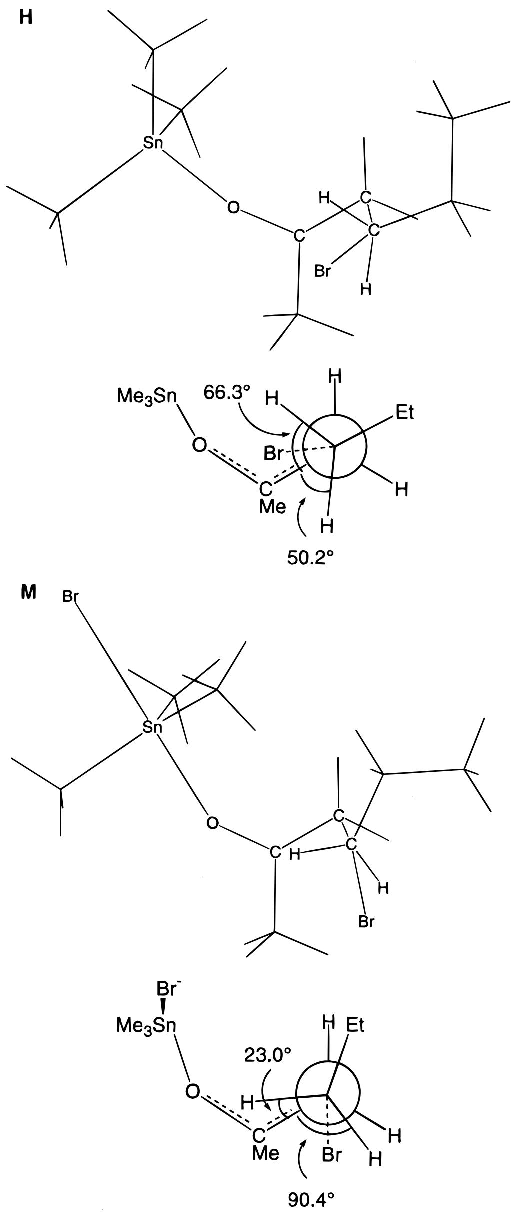


Figure 5. Structures along the reaction between **1** and bromopropane with or without ligand (distances in Å, numbers in parentheses are NBO charges).

1. The tin and three methyl carbons on the tin lie in the same plane for all cases (**1**−**3b**). It is apparent that bromine can receive a negative charge better than oxygen since tin bromide **3** is the most strongly stabilized. The increment of the negative charge [−0.5334 (**3a**) → −0.7480 (**3b**)] on bromine in **3** by bromide coordination is much larger than that on oxygen in **1** [−1.0123 (**1a**) → −1.0063 (**1b**)] or **2** [−1.0453 (**2a**) → −1.0469 (**2b**)].

It is notable that the tin enolate **1** is stabilized more than tin alkoxide **2**. This high-stabilization effect for **1** would be due to

Scheme 7



the delocalization of the negative charge through the carbon skeleton, and the terminal vinyl carbon can be charged negatively. In fact, the terminal vinylic carbon in **1** accepts the negative charge from the ligand [−0.5489 (**1a**) → −0.6035 (**1b**)], while the methyl carbon in **2** has almost no ability to accept the negative charge [−0.1252 (**2a**) → −0.1346 (**2b**)]. The polarity of the vinylic C=C bond can be estimated by the difference in partial charge Δq on those carbons. The larger polarity occurs in highly coordinated tin enolate rather than in noncoordinated enolate due to increase of Δq [−0.9772 (**1a**) → −1.0533 (**1b**)], which means elevation of nucleophilicity.

Reaction with Aldehyde. The calculated potential energy profiles for the reaction of four-coordinated and five-coordinated tin enolate with aldehyde (eq 5) are shown in Figure 2. The optimized geometries for their pathways and the detailed reaction schemes are illustrated in Figure 3 and Scheme 4. While both systems are exothermic, the reaction with four-coordinated tin enolate has less activation energy (18 kcal/mol) than that with five-coordinated tin enolate (27 kcal/mol). This contrast can be explained by comparison of their transition states **B** and **E**. In the structure **B**, the cyclic transition state, which is established[17] in the aldol reaction between metal enolates with aldehydes, is found because of the appropriate bond length (2.24 Å) between Sn and oxygen (Figure 3). It should be noted that the six-membered cyclic transition state **B** has a unique shape which deviates from either chair- or boat-types. Five atoms other than the methylene carbon are on the same plane (sled-type) probably because of the steric hindrance of trialkylstannyl group (Scheme 5). The transition state **E** shows an acyclic structure in which the bond length (4.54 Å) of Sn−O is too long to have interaction. This open structure is ascribed to the bromide-coordinated tin which is reluctant to coordination by another ligand. In both cases, the synclinal arrangement between carbonyl C=O in aldehyde and vinyl C=C in enolate is observed with the dihedral angles 58.6° in **B** and 35.8° in **E** (Scheme 5).

Reaction with Halides. The energy diagrams for the reactions of four-coordinated and five-coordinated tin enolate with organic halide (eq 6) are shown in Figure 4. The optimized geometries for their pathways and the detailed reaction schemes are illustrated in Figure 5 and Scheme 6. These reactions proceed through two steps involving alkylation in the S_N2 mode (to **I** or **N**) and destannylation with formation of bromostannane (to **K** or **P**) as shown in Scheme 6. The system using bromide-coordinated tin enolate is favored both thermodynamically and kinetically, showing (1) higher stabilization of products and (2) lower activation energy than the system using four-coordinated species. The significant stabilization of organotin bromide by high coordination as discussed in Table 1 allows this thermodynamically favored feature. On comparing the transition states **H** and **M** (Figure 5), the carbon at which the atom displacement occurs is found to be more neutral [partial charge; −0.0323 (**M**)] in the high coordination system than in the four-coordination system [−0.0585 (**H**)]. Furthermore, the positive charge on the carbon bonding to oxygen in **M** (0.5742) is closer to neutral than that in **H** (0.6177). These neutralization effects caused by an anionic ligand lead to stabilization of the structure of the transition state.

It is also notable that the high coordination on the tin center significantly influences the approaching direction of bromopropane to the enolate. To avoid the steric hindrance to the methyl groups on tin, the bromine in bromopropane in **M** resists the tin center. As shown in Scheme 7, the antiperiplanar arrangement between the ethyl group and C=C in enolate is observed in **H** (dihedral angle $\angle$C−C−O−H = 66.3°). The structure **M** is near the eclipsed conformation (dihedral angle = 23.0°), in which Br is away from the internal vinyl carbon in enolate. Therefore, the following intermediate **I** has Br bounded to the carbon which is an internal vinyl moiety while bromine in **N** exists as an anion that is far away from the substrates. In the next steps including the formation of 2-hexanone and bromostannane from **I** or **N**, five-coordinated tin species are formed in both transition states **J** and **O**. The tin in **J** is bound to three methyl groups, bromine, and oxygen while the tin in **O** has three methyl groups and two bromines without interaction of oxygen. The high coordination seriously affects this halide coupling in each step and leads to the strong acceleration.

Conclusion

The computational study revealed the mechanism of the reaction between trialkyltin enolates and aldehydes or organic halides in both cases with and without coordinating ligands.

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[17] Zimmerman, H. E.; Traxler, M. D. *J. Am. Chem. Soc.* **1957**, *79*, 1920.

High coordination of trialkyltin enolates causes an increase of their nucleophilicity and decrease of Lewis acidity of tin center. The reaction courses are ascribed to the balance of these factors.[18] In the reaction of tin enolate with aldehydes, noncoordinated tin enolate gives the cyclic transition state in sled-form while the acyclic transition state which leads to deactivation of the reaction process is shown in the case of a high-coordinated enolate. As calculated and experimental results of our system using trialkyltin enolates, the factor of diminished Lewis acidity is found to be more important than that of enhanced nucleophilicity in the reaction with aldehydes. This is probably because the Lewis acidity is effectively reduced by high coordination with elevation of nucleophilicity.[19] In the reaction with organic halides, on the contrary, the system of highly coordinated tin enolate is favored both kinetically and thermodynamically. The bromide-coordination to tin enolate increases the high nucleophilicity to promote the reaction kinetically.[20] The complexation of a bromide (Br^-) with bromostannane strongly affects the stabilization which leads to a thermodynamically favored reaction course.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research, the Ministry of Education, Science, Sports, and Culture, of the Japanese Government.

Supporting Information Available: Listings of absolute energies and geometries for calculated species (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] The nucleophilicity and Lewis acidity of pentacoordinated allylsilicates have been discussed. Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1988**, *110*, 4599.

[19] High coordination of trichlorosilyl or dimethylsilyl enolates accelerates the addition to aldehydes probably because metal centers still have enough Lewis acidity to accept carbonyl oxygen owing to electronic or steric reasons. In those cases, the increase of nucleophilicity would be much more important than the change of acidity. For example: (a) Denmark, S. E.; Winter, S. B. D.; Su, W. X.; Wong, K.-T. *J. Am. Chem. Soc.* **1996**, *118*, 7404. (b) Miura, K.; Sato, H.; Tamaki, K.; Ito, H.; Hosomi, A. *Tetrahedron Lett.* **1998**, *39*, 2585.

[20] The Lewis acidity is not significant in this S_N2 type reaction course as shown in Figure 5 and Scheme 6.