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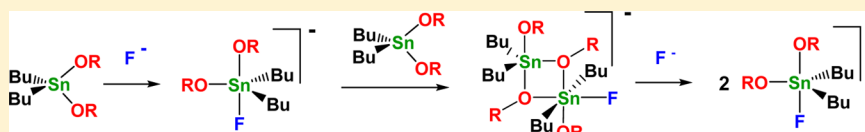
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# How Do Nucleophiles Accelerate the Reactions of Dialkylstannylene Acetals? The Effects of Adding Fluoride to Dialkoxydi-*n*-butylstannanes

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## S Supporting Information



**ABSTRACT:** Dialkylstannylene acetals are organotin intermediates widely used to facilitate regioselective monofunctionalization of diols or polyols by electrophiles. Alkylation is both the slowest and the most useful reaction of these intermediates, and this reaction is markedly accelerated by the addition of nucleophiles to the reaction media, usually cesium fluoride in dimethylformamide (DMF) or tetrabutylammonium iodide or bromide in toluene. The regioselectivity may be influenced by aggregation of the dialkylstannylene acetals into dimers and higher oligomers, and by the addition of these nucleophiles. The stabilities and the geometries of the species potentially involved in these processes were examined by using theoretical chemistry methods with di-*n*-butyldialkoxytin derivatives as examples and fluoride as the nucleophile. Geometry optimizations were performed at B3LYP/6-31G(d,p) level, and single point energies obtained at the MP2/6-311G(2d,p) level with diffuse functions added for fluorine. The LANL2DZdp basis set with diffuse and polarization functions and its effective core potential were used to describe tin. The addition of fluoride to monomeric di-*n*-butyldialkoxytin derivatives to give fluoridated monomers is predicted to be strongly exothermic, by 187 to 209 kJ/mol, depending on the alkoxy group. The fluoridated monomers are calculated to react with monomers exothermically to give monofluorinated dimers, except for the di-*t*-butoxy derivative. Dimer formation on average is about 20 kJ mol<sup>-1</sup> more exothermic than for the nonfluoridated monomers alone. Monofluorinated monomers strongly prefer to exist as monomers because the difluorinated dimers are estimated to be 209 to 278 kJ mol<sup>-1</sup> less stable at 298 K.

## INTRODUCTION

Organotin derivatives are extensively used as intermediates that facilitate regioselective monofunctionalization of diols or polyols, particularly carbohydrates.<sup>1–3</sup> Two types of intermediates have been used, trialkylstannyl ethers and dialkylstannylene acetals,<sup>1,2</sup> but the latter are used more commonly and the studies reported herein relate to these dialkoxytin derivatives. The dialkylstannylene acetal intermediates react with a wide variety of electrophiles, and reactions proceed at higher rates and under milder conditions than with the parent diols. The principal advantage of these reactions, which include acylation, sulfonylation, alkylation, and oxidation, is that monosubstitution is obtained, often with high regioselectivity.<sup>1–3</sup> One complicating factor that may influence the regioselectivity of monosubstitution is the fact that dialkylstannylene acetals aggregate into dimers, and higher oligomers in solution,<sup>4–8</sup> and into polymers in the solid state if the substituents are small.<sup>9–12</sup> The nature of the substituents on the alkoxy groups and the alkyl groups on tin have been identified as factors that affect dimerization of stannylene acetals.<sup>2,3</sup> A second complicating factor is the presence of nucleophiles in alkylation reactions, the most important of these regioselective monosubstitutions. It is known that the addition of nucleophiles increases the rates of reaction of alkylation and allows these reactions to proceed under much

less forcing conditions.<sup>13–18</sup> In addition, the presence of added nucleophiles sometimes changes the regiochemistry of substitution markedly.<sup>19–21</sup>

Previous computational and experimental work on the dimerization of acyclic dialkoxydialkylstannanes revealed these compounds were less aggregated than their cyclic analogues derived from diols; only dimers and monomers were present and the size of alkoxy group affected the geometries and the magnitudes of the thermodynamic parameters associated with dimerization.<sup>5,22</sup> For di-*n*-butyltin derivatives, the dimer was thermodynamically favored at room temperature except when the carbons bearing the oxygen atoms were tertiary.<sup>22</sup>

In the present work, computational chemistry is employed to examine how the presence of added nucleophiles affects the geometries and thermodynamics of dialkoxydi-*n*-butylstannane dimerization. In addition, the study also examines how the steric volume of the alkoxy alkyl group influences the degree of dimerization. This is accomplished using high-level computational chemistry techniques, which have been shown in previous work to accurately calculate the geometric structures and thermodynamic properties associated with the dimerization

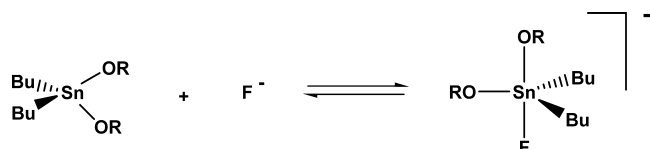
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of these organotin intermediates.<sup>22</sup> Computational methods are appropriate tools to study such organotin systems,<sup>22–26</sup> where the low populations and the short-lived nature of critical species can make it difficult for them to be examined experimentally.

The previously examined dialkoxydi-*n*-butylstannanes,<sup>22</sup> namely, di-*n*-butyltin dialkoxides, were chosen for the present study because their aggregation equilibria only involved monomers and dimers. Cesium fluoride is the nucleophile used most commonly in reactions of stannylene acetals, and thus fluoride ions are used to study the effects of nucleophiles on dimerization. A fluoride ion ( $F^-$ ) was coordinated to each monomer (M), creating a monofluorinated monomer ( $MF^-$ )



1 R = Me 2 R = Et 3 R = Pr 4 R = Bu 5 R = iPr 6 R = *t*-Bu

Figure 1. Fluorination of di-*n*-butyltin dialkoxide monomer.

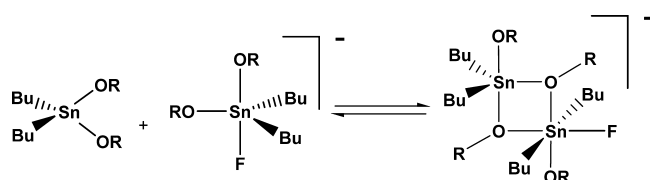
(Figure 1) and theoretical methods were employed to calculate the thermodynamic parameters of fluorination (eqs 1–3).

$$\text{Relative energy of monofluorination} = E_{MF^-} - E_{F^-} - E_M \quad (1)$$

$$\Delta H_{\text{Reaction}} = \Delta H_{MF^-} - \Delta H_{F^-} - \Delta H_M \quad (2)$$

$$\Delta G_{\text{Reaction}} = \Delta G_{MF^-} - \Delta G_{F^-} - \Delta G_M \quad (3)$$

Because this initial equilibrium was found to lie overwhelmingly on the side of the fluorinated monomer, we chose to examine the stability of products in which fluoride is added to the dimer by initially considering the equilibrium in which this fluorinated monomer ( $MF^-$ ) was bound to a non-fluorinated monomer (M) to form a monofluorinated dimer ( $DF^-$ ), shown in Figure 2. This reaction is referred to as



1 R = Me 2 R = Et 3 R = Pr 4 R = Bu 5 R = iPr 6 R = *t*-Bu

Figure 2. Monofluorinated dimerization of di-*n*-butyltin dialkoxides.

monofluorinated dimerization and theoretical methods were used to calculate the thermodynamic parameters associated with the reaction (eqs 4–6).

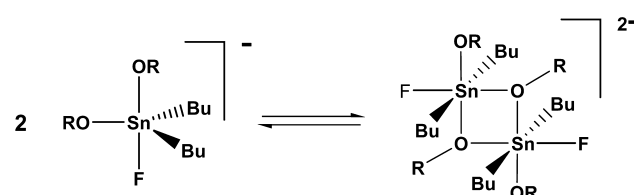
$$\text{Relative energy of monofluorinated dimerization}$$

$$= E_{DF^-} - E_{MF^-} - E_M \quad (4)$$

$$\Delta H_{\text{Reaction}} = \Delta H_{DF^-} - \Delta H_{MF^-} - \Delta H_M \quad (5)$$

$$\Delta G_{\text{Reaction}} = \Delta G_{DF^-} - \Delta G_{MF^-} - \Delta G_M \quad (6)$$

Lastly, the energetics of difluorinated dimerization were examined (Figure 3), where two monofluorinated monomers



1 R = Me 2 R = Et 3 R = Pr 4 R = Bu 5 R = iPr 6 R = *t*-Bu

Figure 3. Difluorinated dimerization of di-*n*-butyltin dialkoxides.

( $MF^-$ ) coordinate to form the difluorinated dimer ( $DF_2^{2-}$ ). The thermodynamic parameters associated with the reaction are defined in eqs 7–9.

$$\text{Relative energy of difluorinated dimerization}$$

$$= E_{DF_2^{2-}} - 2(E_{MF^-}) \quad (7)$$

$$\Delta H_{\text{Reaction}} = \Delta H_{DF_2^{2-}} - 2(\Delta H_{MF^-}) \quad (8)$$

$$\Delta G_{\text{Reaction}} = \Delta G_{DF_2^{2-}} - 2(\Delta G_{MF^-}) \quad (9)$$

This work investigates the geometric and thermodynamic effects of fluorination on di-*n*-butyltin dialkoxides and how fluorination can influence dimerization. This entails comparing monofluorinated monomers to mono or difluorinated dimers. Furthermore, the effects of fluorination on dimerization are examined by comparing the geometric and thermodynamic parameters of the fluorinated species with those of their nonfluorinated precursors.<sup>22</sup> A variety of di-*n*-butyltin dialkoxides (1–6) are examined to determine the importance of the size of alkoxy alkyl group, R, on the aforementioned geometric and thermodynamic effects and if steric effects contribute to fluorination effects. Examining these may reveal potential implications for the suggested mechanism of regioselective monosubstitution reactions of stannylene acetals, and the role of both dimerization and added nucleophiles in these complex reactions.

## COMPUTATIONAL METHODS

Gas-phase geometry optimizations and frequency calculations were performed using the B3LYP<sup>27–29</sup> hybrid functional followed by MP2 single point calculations within the Gaussian 03 program suite.<sup>30</sup> The Los Alamos National Laboratory double- $\zeta$  basis set (LANL2DZdp) with diffuse and polarization functions<sup>31</sup> and the associated effective core potential developed by Hay and Wadt<sup>32</sup> were employed for tin atoms, while all non-tin atoms in this study (H, C, and O) were treated at the MP2/6-311G(2d,p)//B3LYP/6-31G(d,p) level, with diffuse functions added for F. This combination of basis sets and effective core potentials has been shown to accurately predict the geometries<sup>33</sup> and energies<sup>34</sup> of organotin species, as well the thermodynamics of dimerization for di-*n*-butyltin dialkoxides.<sup>22</sup> Frequency analysis confirmed that all structures were minima on the potential energy surface. Basis set superposition error (BSSE)<sup>35</sup> and zero point vibrational energy corrections were included in relative energies, enthalpies, and Gibbs energies.

## RESULTS AND DISCUSSION

**Geometries of Fluorinated Monomers ( $MF^-$ ).** The geometries of the fluorinated monomers were constructed by

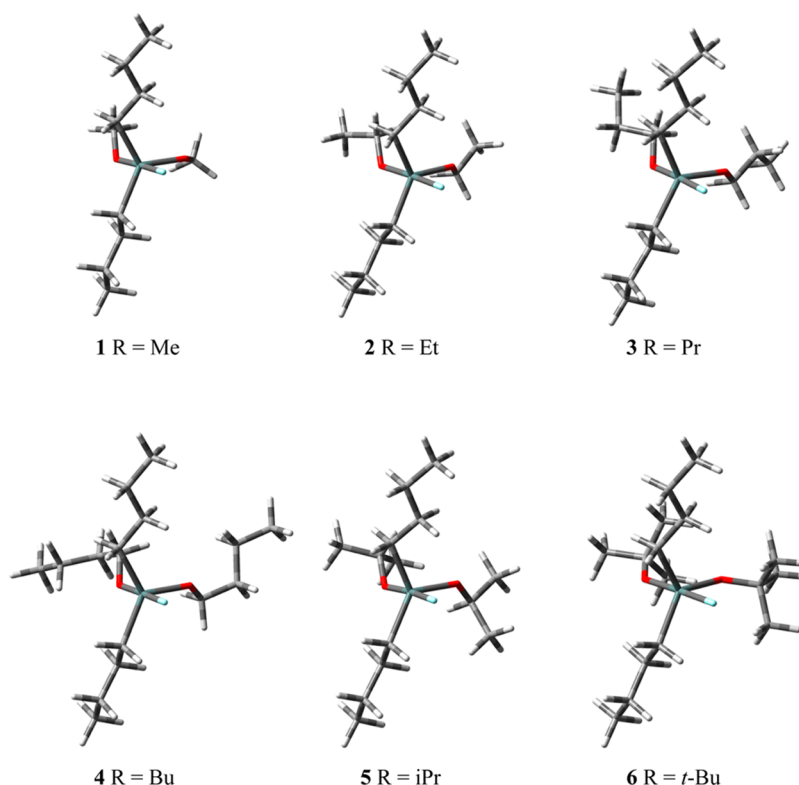


Figure 4. Structures of the fluorinated di-*n*-butyltin dialkoxide monomers (1–6).

using the previously optimized monomers of di-*n*-butyltin dialkoxides,<sup>22</sup> coordinating a fluoride ion to the tin center, and reoptimizing. It should be noted that coordination of a fluoride to a monomer creates five potential geometric isomers for each fluorinated dialkoxydi-*n*-butylstannane. These were all optimized and analyzed for compounds 1–6, and while the results are not discussed at length here, the thermodynamics are included in the Supporting Information. For 1–6, the monomer is a trigonal bipyramid, where both butyl groups and one OR are equatorial, while the fluorine and the other OR group are axial. This structure is one of the lowest-energy geometric isomers for the 1–6; therefore this geometry was used to study the thermodynamics of monofluorinated dimerization of di-*n*-butyltin dialkoxide. Further details about these geometric isomers are available in the Supporting Information.

The relative geometries are consistent for all of the fluorinated di-*n*-butyltin dialkoxide monomers 1–6 (Figure 4). While the individual geometric parameters (Table 1) in the di-*n*-butyltin dialkoxide vary, bond angles and bond lengths differ by less than 7.1° and 0.032 Å. The largest differences were between Me and *t*-Bu monomers, where  $\angle(\text{C},\text{Sn},\text{C})$  and  $r(\text{Sn},\text{F})$  increase with steric bulk. The *n*-butyl groups in the fluorinated monomers have the same conformation, as dihedral angles are approximately equal for 1–6.

The general structures of the di-*n*-butyltin dialkoxide monomers<sup>22</sup> differ from their respective fluorinated derivatives. Addition of the fluoride ion results in five-coordinate tin centers, where R and Bu groups reposition to accommodate the anion (Figure 4). The most drastic effect is on  $\text{dih}(\text{C},\text{Sn},\text{C},\text{C})$ , where fluorination of monomers can cause them to change by up to 37.2° in di-*n*-butyltin dialkoxides. Upon fluorination, all bonds in the monomer lengthen, most dramatically with  $r(\text{Sn},\text{O}')$  (the equatorial oxygen) increasing by as much as

0.138 Å. In addition, fluorination results in  $\angle(\text{O},\text{Sn},\text{O})$  decreasing by up to 16.5° and  $\angle(\text{C},\text{Sn},\text{C})$  increasing by up to 10.8°.

Interestingly, the effects of fluorination on the geometry of the monomers are not affected by the size of R. That is, as the volume of R increases in the di-*n*-butyltin dialkoxides, the change in geometric parameters as a result of fluorination is constant.

**Thermodynamics of Monomer Fluorination.** The relative energies, enthalpies, and Gibbs energies of fluorination (eqs 1–3) in Table 2 reveal that the fluorinated monomers are preferred to the free monomer and fluoride. These trends are consistent with the reactions of  $\text{Sn}(\text{CH}_3)_2\text{X}$  with  $\text{Y}^-$ .<sup>36</sup> Interestingly, based on the calculated thermodynamic parameters in Table 2, the fluorination of monomers is calculated to be much more favored than the dimerization of nonfluorinated di-*n*-butyltin dialkoxides.<sup>22</sup> As R increases in size in the di-*n*-butyltin dialkoxides, fluorination also becomes more favored. Solvation would be expected to stabilize the localized charge in fluoride more than the delocalized charge in the fluorinated monomer. Therefore, the energetic preference for fluorinated monomer would be expected to decrease in solution, but it was so large in the gas phase that it is expected that the preference would still be very large in solution.

**Geometries of Monofluorinated Dimers ( $\text{DF}^-$ ).** The relative geometries are consistent for all six monofluorinated di-*n*-butyltin dialkoxide dimers (Figure 5). Within each dimer, one of the tin centers adopted a distorted trigonal bipyramid and the other a distorted octahedral geometry. The two intermolecular bonds between the monomer and the fluorinated monomer are unequal, with intermolecular bonds and angles differing by as much as 0.638 Å and 19.0°, respectively, in each fluorinated dimer (Table 1).

Table 1. Geometric Parameters of Fluorinated di-*n*-Butyltin Dioxides Species 1–6 ( $r$  in Å,  $\angle$  and Dihedrals in Degrees)<sup>a</sup>

	R											
	dimethoxy			diethoxy			di-1-proxopoxy			di-1-butoxy		
	MF <sup>b</sup>	DF <sup>c</sup>	DF <sub>2</sub> <sup>2-d</sup>	MF <sup>b</sup>	DF <sup>c</sup>	DF <sub>2</sub> <sup>2-d</sup>	MF <sup>b</sup>	DF <sup>c</sup>	DF <sub>2</sub> <sup>2-d</sup>	MF <sup>b</sup>	DF <sup>c</sup>	DF <sub>2</sub> <sup>2-d</sup>
$r(\text{Sn}, \text{O})_{\text{F}}$	1.981	2.027	2.079	1.983	2.034	2.092	1.984	2.040	2.095	1.986	2.030	2.091
$r(\text{Sn}, \text{O}')_{\text{F}}$	2.077	2.250	2.203	2.081	2.264	2.207	2.082	2.261	2.201	2.080	2.276	2.206
$r(\text{Sn}, \text{O})_{\text{M}}$		2.032			2.037			2.035			2.046	
$r(\text{Sn}, \text{O}')_{\text{M}}$		2.023			2.019			2.021			2.024	
$r(\text{Sn}, \text{C})_{\text{F}}$	2.174	2.173	2.190	2.173	2.177	2.185	2.173	2.175	2.185	2.171	2.171	2.185
$r(\text{Sn}, \text{C})_{\text{M}}$		2.167			2.167			2.168			2.168	
$r(\text{Sn}, \text{F})$	2.013	2.001	2.030	2.015	1.993	2.034	2.014	1.994	2.034	2.016	1.994	2.034
$r(\text{Sn}, \text{M} \cdots \text{O}')_{\text{F}}$		2.158	2.232		2.178	2.238		2.178	2.243		2.192	2.242
$r(\text{Sn}, \text{F} \cdots \text{O}')_{\text{M}}$		2.397			2.374			2.367			2.451	
$\angle(\text{O}, \text{Sn}, \text{O}')_{\text{F}}$	93.0	92.5	95.2	92.4	96.2	93.7	92.2	95.8	93.2	92.4	96.0	93.6
$\angle(\text{O}, \text{Sn}, \text{O}')_{\text{M}}$		91.7			90.5			90.3			93.1	
$\angle(\text{C}, \text{Sn}, \text{C})_{\text{F}}$	124.5	169.4	176.1	125.2	173.5	173.8	125.1	173.2	173.5	126.0	171.4	173.8
$\angle(\text{C}, \text{Sn}, \text{C})_{\text{M}}$		120.1			119.4			119.2			124.4	
$\angle(\text{O}', \text{Sn}, \text{O}')_{\text{F}}$		65.2	69.5		65.7	69.6		65.9	69.8		67.0	69.4
$\angle(\text{O}', \text{Sn}, \text{O}')_{\text{M}}$		73.6			73.6			73.6			76.5	
$\angle(\text{Sn}, \text{O}', \text{F}, \text{Sn}, \text{M})$		110.4	110.5		109.1	110.2		109.0	110.1		108.2	110.4
$\angle(\text{Sn}, \text{M}, \text{O}', \text{M}, \text{Sn}, \text{F})$		109.7			110.6			110.7			107.6	
$\angle(\text{F}, \text{Sn}, \text{O}')_{\text{F}}$	86.7	105.2	104.2	87.7	106.2	103.9	87.9	106.0	103.7	88.5	103.3	104.6
$\angle(\text{F}, \text{Sn}, \text{O}')_{\text{M}}$	178.1	162.3	160.5	177.8	157.6	162.4	177.6	158.1	163.0	179.0	160.7	133.2
$\text{dih}(\text{C}, \text{Sn}, \text{C}, \text{C})_{\text{F}}$	153.9	138.0	20.6	155.8	125.0	16.8	148.6	133.2	20.2	160.0	131.2	17.0
$\text{dih}(\text{C}, \text{Sn}, \text{C}, \text{C})_{\text{M}}$	137.4	131.0	-137.9	122.8	111.7	-138.4	132.7	117.4	-140.1	125.1	110.0	-140.5
$\text{dih}(\text{C}, \text{Sn}, \text{C}, \text{C})_{\text{M}}$		144.8	21.4		126.0	16.6		126.2	20.2		145.7	17.0
$\text{dih}(\text{C}, \text{Sn}, \text{C}, \text{C})_{\text{M}}$		-177.6	-137.7		-179.0	-138.2		178.9	-140.1		-169.4	-140.4
$\text{dih}(\text{Sn}, \text{C}, \text{C}, \text{C})_{\text{M}}$	-174.8	179.9	176.9	-174.5	176.9	176.9	-174.3	177.1	176.1	-175.2	176.2	176.9
$\text{dih}(\text{Sn}, \text{C}, \text{C}, \text{C})_{\text{F}}$	-176.4	175.1	-176.4	-176.0	176.2	177.1	-175.8	174.5	177.5	-174.5	173.6	177.1
$\text{dih}(\text{Sn}, \text{C}, \text{C}, \text{C})_{\text{M}}$		-174.4	177.8		-175.7	176.9		-176.1	176.1		-172.1	176.9
$\text{dih}(\text{Sn}, \text{C}, \text{C}, \text{C})_{\text{M}}$		-178.9	-177.7		-178.9	177.1		-179.6	177.5		177.5	177.1

<sup>a</sup>The  $r(\text{Sn}, \text{O})$  and  $r(\text{Sn}, \text{O}')$ , respectively, refer to the intramolecular bonds between tin and dicoordinate (O) and tricoordinate oxygen (O'), while  $r(\text{Sn} \cdots \text{O}')$  refers to the intermolecular bond between tin and tricoordinate oxygen. Furthermore, geometric parameters involving atoms from the fluorinated and nonfluorinated monomers are labeled as subscript F and M, respectively. Values that are not applicable to the species are left blank. <sup>b</sup>Monofluorinated monomer. <sup>c</sup>Monofluorinated dimer. <sup>d</sup>Diffluorinated dimer.



**Table 2. Energetics and Thermodynamics of the Monofluorination of di-*n*-Butyltin Dialkoxide Monomers (Figure 1)**

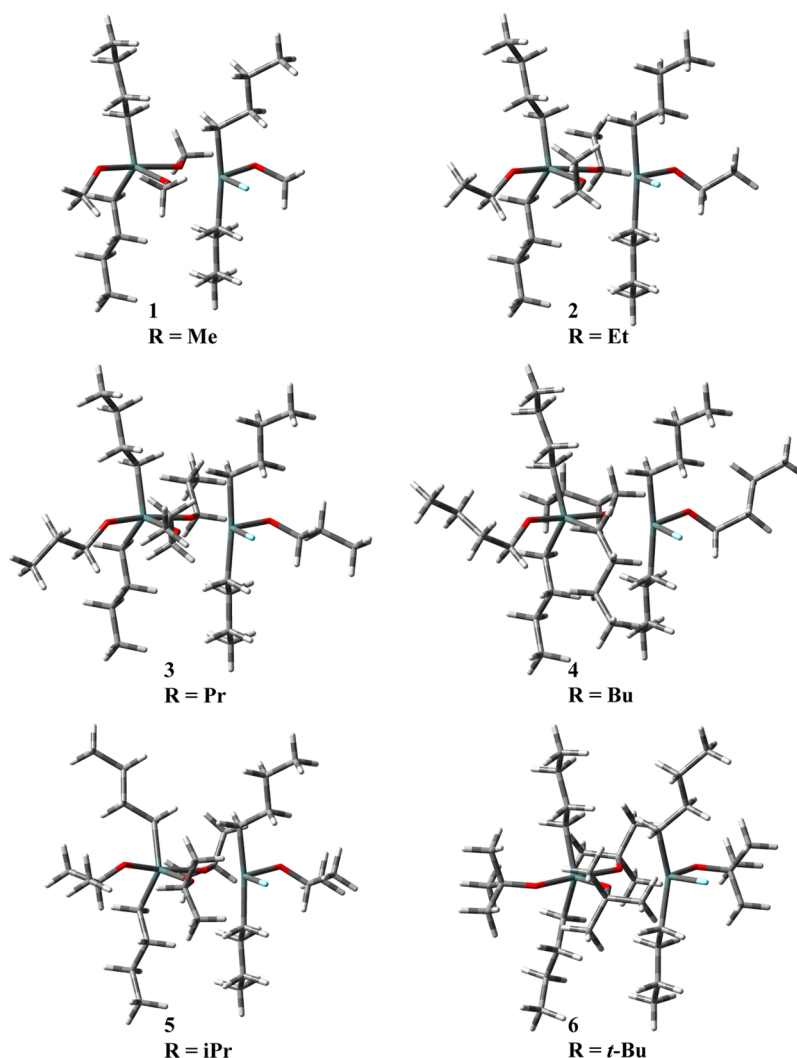
	R	relative energies (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^{298}$ (kJ mol <sup>-1</sup> )
1	Me	-226.2	-225.5	-127	-187.5
2	Et	-229.7	-229.0	-129	-190.5
3	Pr	-234.0	-233.3	-136	-192.6
4	Bu	-235.0	-234.0	-133	-194.5
5	iPr	-230.4	-228.9	-123	-192.3
6	<i>t</i> -Bu	-241.8	-240.0	-103	-209.3

Interesting trends include the relative magnitude of intramolecular Sn–O bonds in the fluorinated dimer. In the monomer,  $r(\text{Sn},\text{O})_{\text{M}} > r(\text{Sn},\text{O}')_{\text{M}}$  by 0.019 Å, while in the fluorinated monomer  $r(\text{Sn},\text{O})_{\text{F}} < r(\text{Sn},\text{O}')_{\text{F}}$  by 0.336 Å. As expected, the coordination number of tin affects bond angles in the fluorinated dimer; the trigonal bipyramid and octahedral tins have  $\angle(\text{C},\text{Sn},\text{C})_{\text{F}} > \angle(\text{C},\text{Sn},\text{C})_{\text{M}}$  by 54.0°. However, some geometric parameters remain relatively consistent between the monomer and the fluorinated monomer within the dimer, such as  $r(\text{Sn}–\text{C})$  bonds and  $\angle(\text{O},\text{Sn},\text{O})$ . It is important to note that the relative conformations of the butyl groups are equal in all

six monofluorinated di-*n*-butyltin dialkoxide monomers, with all dihedral angles (C,Sn,C,C) differing by less than 33.0°.

The steric effects of the alkoxides alkyl groups (R) on the geometries of the fluorinated dimers are variable. As R gets larger, bond lengths and angles inconsistently increase and decrease, by relatively small amounts. That is, for the fluorinated dimers 1–5, the individual geometric parameters vary by less than 0.021 Å and 7.0°. In fact, the size of R only notably affects intramolecular Sn–O bonds and intermolecular Sn–O' bonds. As R increases,  $r(\text{Sn}_{\text{M}}\cdots\text{O}'_{\text{F}})$  and  $r(\text{Sn}_{\text{F}}\cdots\text{O}'_{\text{M}})$  increase by as much as 0.184 Å and 0.606 Å, respectively. Table 1 reveals that only when  $R = t\text{-Bu}$  does the size of R affect the geometries of the fluorinated dimers. When 1–5 are compared to the *t*-Bu monofluorinated dimers (6), bond angles and intramolecular bonds can differ by 0.083 Å and 26.0°.

The effects of dimerization on geometries are revealed by examining the geometric differences of the free monomer and its fluoride adduct with the corresponding structures in the dimer complex. Upon dimerization, all bond lengths in the monomers and fluorinated monomers increase to accommodate the new intermolecular bonding. The Sn–O bonds are most affected, increasing by 0.280 Å. The greatest change is seen for  $r(\text{Sn}–\text{O}')$ , as the O' atom moves away from the fluorinated monomer and closer to the nonfluorinated tin. The

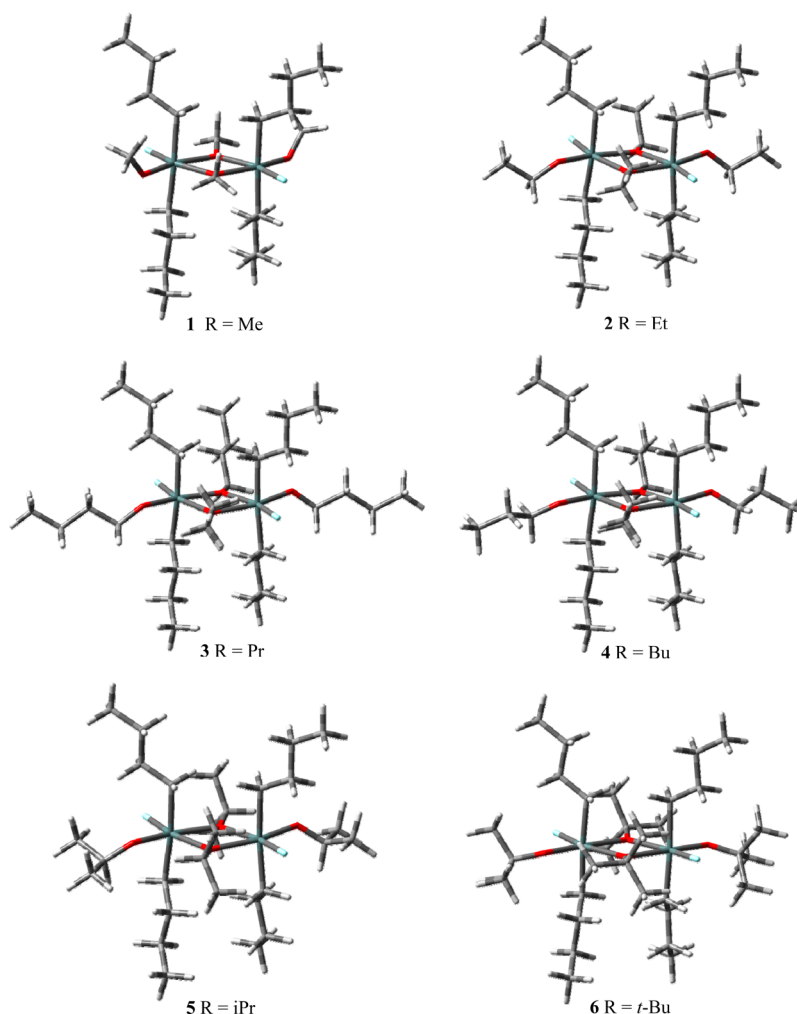


**Figure 5.** Structures of the monofluorinated di-*n*-butyltin dialkoxide dimers (1–6).

Table 3. Energetics and Thermodynamics of the Monofluoridated Dimerization of di-*n*-Butyltin Dialkoxides (Figure 2)

	R	relative energies (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^{298}$ (kJ mol <sup>-1</sup> )	$\Delta G^{298a}$ (kJ mol <sup>-1</sup> )
1	Me	-107.0	-106.4	-212	-43.2	-21.6
2	Et	-100.5	-100.8	-236	-30.6	-19.6
3	Pr	-103.9	-103.7	-240	-32.3	-14.1
4	Bu	-102.4	-102.2	-244	-29.6	-13.7
5	iPr	-88.3	-89.1	-244	-16.4	11.7
6	<i>t</i> -Bu	-54.0	-55.1	-257	21.7	4.1

<sup>a</sup>Gibbs energies calculated for dimerization of monomeric, nonfluoridated di-*n*-butyltin dialkoxides.<sup>22</sup>

Figure 6. Structures of the difluoridated di-*n*-butyltin dialkoxide dimers (1–6).

changes in bond angles reflect the change in tin's coordination, with  $\angle(\text{C}, \text{Sn}, \text{C})_{\text{F}}$  increasing by  $48.3^\circ$  in the fluoridated dimer. Furthermore, the position of the fluorine atom shifts in the fluoridated dimer, altering  $\angle(\text{F}, \text{Sn}, \text{O})_{\text{F}}$  and  $\angle(\text{F}, \text{Sn}, \text{O}')_{\text{F}}$ . In the fluoridated monomer,  $\angle(\text{O}, \text{Sn}, \text{O})_{\text{F}}$  decreases  $18.4^\circ$  to accommodate new intermolecular bonding.

The dimerization effects become more pronounced as the size of alkoxy group R increases. The steric bulk of R emphasizes the increase in bond lengths and angles as it increases from methyl to isopropyl. The dimerization effects on the *t*-Bu fluoridated species are distinct from these, and the aforementioned geometric trends are not observed. For example, in the monofluoridated dimer 6, the large *t*-Bu groups hinder the fluorine mobility in the dimer and prevent increased  $\angle(\text{C}, \text{Sn}, \text{C})_{\text{F}}$ , thus butyl carbons are in a distorted axial position.

### Thermodynamics of Monofluoridated Dimerization.

The steric bulks of the alkoxy groups have been shown to influence the geometries of the monofluoridated dimers of di-*n*-butyltin dialkoxides and may dictate the degree of geometric change upon dimerization. The energetics and thermodynamics associated with monofluoridated dimerization reflect these aforementioned geometric trends.

The relative energies, enthalpies, and Gibbs energies (defined in eqs 4–6) for the monofluoridated dimerization of di-*n*-butyltin dialkoxides are reported in Table 3. The relative energies of the species reveal that all di-*n*-butyltin dialkoxides have monofluoridated dimers that are more stable than their respective fluoridated and nonfluoridated monomers. Similarly, the  $\Delta H$  values for the reaction indicate that fluoridated dimerization is favored. The size of R affects both the relative

energies and the enthalpies. The relative energies and  $\Delta H$  for monofluorinated dimers with straight chain R (1–4) differ by less 3.1 kJ mol<sup>-1</sup>; however as R becomes larger, the values begin to deviate. As R increases from methyl to *t*-butyl, the energies and enthalpies increase by 53.0 kJ mol<sup>-1</sup> and 51.3 kJ mol<sup>-1</sup>, respectively, thus decreasing the likelihood of dimerization. The changes in entropy ( $\Delta S$ ) in Table 3 suggest the order of the system increases in the monofluorinated dimerization of di-*n*-butyltin dialkoxides. In addition, the change in entropy becomes larger as the size of R increases from Me to *t*-Bu.

The Gibbs energies indicate that the monofluorinated dimer is thermodynamically favored for all di-*n*-butyltin dialkoxides, excluding the di-*t*-butoxy dimer 6. The preference for the monofluorinated dimer decreases markedly as R increases in bulk. Changing from methyl to primary alkyl groups destabilizes the dimer by 10.9 to 13.6 kJ mol<sup>-1</sup>, changing from primary to secondary alkyl groups destabilizes by 13.2 to 15.9 kJ mol<sup>-1</sup>, and from secondary alkyl to tertiary alkyl groups destabilizes by a further 38.1 kJ mol<sup>-1</sup>. Over the whole range, as R increases from Me to *t*-Bu, the Gibbs energy increases by 64.9 kJ mol<sup>-1</sup>. Solvation would be expected to have little effect on this equilibrium because charges are delocalized in both species and there is little change in dipole moments on dimer formation.

**Geometries of Difluorinated Dimers (DF<sub>2</sub><sup>2-</sup>).** All six difluorinated di-*n*-butyltin dialkoxide dimers have the same relative geometries, (Figure 6) where each dimer has two, eight-coordinated tin centers. The difluorinated dimers have symmetric intermolecular bonding because of the two monofluorinated monomers present; thus the geometric parameters for the difluorinated di-*n*-butyltin dialkoxide dimers in Table 1 refer to the averages of two monomers in the complex.

Examining the geometries of the di-*n*-butyltin dialkoxide difluorinated dimers reveals that the effects of R are variable, with bond lengths and angles inconsistently increasing and decreasing. However, it should be noted that in general these differences are minimal, where the difluorinated dimers 1–5 geometric parameters vary by less than 0.032 Å and 3.9°. The only notable parameter affected by R is the intermolecular bond, where  $r(\text{Sn} \cdots \text{O}')$  increases by as much as 0.184 Å as R is increased to *t*-Bu. It appears only in 6 do sterics affect geometry of the difluorinated dimers and when compared to 1–5 difluorinated dimers, bond angles and intramolecular bonds can differ by 0.131 Å and 12.0°.

Comparing the fluorinated monomer structures to that of its difluorinated dimer (Table 1) reveals the effects of dimerization on the geometries of the di-*n*-butyltin dialkoxides. As a result of dimerization, all bonds lengthen, with the Sn–O bonds most affected. These bonds can increase by as much as 0.287 Å for  $r(\text{Sn}–\text{O}')$ , as they adjust to new intermolecular interactions. In addition, tin's increase coordination from trigonal bipyramid to distorted octahedral requires the  $\angle(\text{C}, \text{Sn}, \text{C})_{\text{F}}$  angle to increase by as much as 54.4°. In addition, the fluoride position shifts in the octahedron, thus increasing and decreasing  $\angle(\text{F}, \text{Sn}, \text{O})_{\text{F}}$  and  $\angle(\text{F}, \text{Sn}, \text{O}')$ , respectively. Interestingly, the  $\angle(\text{O}, \text{Sn}, \text{O})_{\text{F}}$  is not affected by dimerization, and it is only for R = *t*-Bu is there any effect, as it increases by 13.7° upon dimerization. It should also be noted that the steric bulk of R does not dictate the size of the geometric effect of dimerization. That is, as R increases, the dimerization effects on the bond lengths and angles are generally consistent. The only deviation arises for the difluorinated di-*n*-butyltin di-*t*-butoxide.

**Thermodynamics of Difluorinated Dimerization.** The thermodynamics of the difluorinated di-*n*-butyltin dialkoxide dimerization are reported in Table 4 as relative energies,

**Table 4. Energetics and Thermodynamics of the Difluorinated Dimerization of di-*n*-Butyltin Dialkoxide (Figure 3)**

	R	relative energies (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^{298}$ (kJ mol <sup>-1</sup> )
1	Me	156.7	158.8	–197	217.6
2	Et	147.0	147.8	–238	218.6
3	Pr	139.0	140.2	–232	209.3
4	Bu	139.0	139.0	–271	219.8
5	iPr	143.2	142.7	–250	217.3
6	<i>t</i> -Bu	193.1	191.7	–289	277.8

enthalpies, and Gibbs energies (defined in eqs 7–9). The calculated relative energies show that for all di-*n*-butyltin dialkoxides, difluorinated dimers are unstable and the two fluorinated monomers are preferred instead. The size of R has interesting effects on the thermodynamics of dimerization, with the relative energies and enthalpies all similar for species 2–5 and for 1–5 for the Gibbs energies. The only large effect of R size occurs when R is largest (*t*-Bu); thus the difluorinated di-*n*-butyltin di-*t*-butoxide is the least favored dimer, consistent with the nonfluorinated results.<sup>22</sup> Solvation might be expected to increase this preference because the two Sn–F bond moments are opposed in the dimer, decreasing the overall dipole moment and hence increasing the relative stability of the fluorinated monomer.

As expected, the negative changes in entropy ( $\Delta S$ ) on dimerization listed in Table 4 are consistent with loss of entropy of translation. As R increases in steric volume, the change in entropy becomes larger.

**Effects of Fluorination on the Geometry of Dimerization.** The general structures of the di-*n*-butyltin dialkoxide dimers from the previous study<sup>22</sup> differ from their respective monofluorinated dimers in the present work. Inspection of Figure 5 reveals that the R and Bu groups severely twist to accommodate the fluoride anion. In addition, the fluorinated dimers contain a six-coordinate tin center, thus altering all intramolecular and intermolecular geometric parameters in the fluorinated dimers. Generally, for the di-*n*-butyltin dialkoxides, all bonds are up to 0.114 Å longer in the monofluorinated dimers compared to the respective nonfluorinated dimers. One notable exception is  $r(\text{Sn}_{\text{M}} \cdots \text{O}'_{\text{F}})$ , which decreases upon fluorination. Some bond angles may increase while others decrease; however, the most affected bond angle is  $\angle(\text{C}, \text{Sn}, \text{C})_{\text{F}}$ , which fluorination increases at least 30°.

It should be noted that the di-*n*-butyltin di-*t*-butoxide (6) dimer is the most affected by fluorination, with changes up to 1.789 Å and 19.1° that are attributed to the distinct geometry of the nonfluorinated dimer.<sup>22</sup> The geometry of the monofluorinated dimer of di-*n*-butyl di-*t*-butoxystannane is much closer to that expected for a dimer than that of its nonfluorinated parent.<sup>22</sup> In the former, the intramonomer Sn–O bond lengths were calculated to be 1.998, 1.977, 2.333, and 2.072 Å while the intermonomer bond lengths were 2.342 and 2.981 Å. In the latter symmetrical structure, the two intramonomer Sn–O bond lengths were calculated to be 1.958 and 1.950 Å while the two intermonomer bond lengths were both 4.131 Å.<sup>22</sup> Therefore, in the case of 6, addition of a



fluoride facilitates dimer formation by decreasing the intermolecular bond lengths by  $\sim 2$  Å.

It should be noted that unlike the monomers, the size of R influences the fluorination effects on the geometric parameters. Generally, increasing R emphasizes the geometric differences between dimers and monofluorinated dimers. This may suggest that fluorination alters the intermolecular bonding of the dimerization of stannylene acetals.

The geometric structure of the difluorinated dimer can be compared to the monofluorinated dimer in the present work, as well as nonfluorinated dimers previously examined.<sup>22</sup> Visual inspection of the geometries of these nonfluorinated dimers of di-*n*-butyltin dialkoxides from the previous study<sup>22</sup> compared to those in Figure 6 reveals that difluorination has resulted in the R and Bu groups becoming severely twisted. The once five-coordinate tins have become six-coordinate because of new bonds with fluoride, and this affects all the intramolecular and intermolecular geometric parameters in the fluorinated dimers. When comparing difluorinated dimers to their respective nonfluorinated dimers,<sup>22</sup> the bonds increase by as much as 0.204 Å upon fluorination of the di-*n*-butyltin dialkoxides. However, it should be noted that intermonomer bonds in the dimers complex decrease as fluorides are added, by up to 0.252 Å for 1–5. This decrease is even larger for di-*n*-butyltin di-*t*-butoxide (6), at 1.786 Å. Again, the geometry of the difluorinated dimer of di-*n*-butyl-di-*t*-butoxystannane is much closer to that expected for a dimer than that of its nonfluorinated parent.<sup>22</sup> In the former  $C_2$ -symmetric structure, the intramonomer Sn–O bond lengths were calculated to be 2.201 and 2.341 Å while the intermonomer bond length was 2.363 Å. The latter structure had only slightly associated monomer units with intermonomer Sn–O distances of 4.131 Å.<sup>22</sup>

All of the aforementioned effects of fluorination become more pronounced as the size of R increases, and the largest changes occur when  $R = t\text{-Bu}$ . The effects of difluorination are small for bond angles of the di-*n*-butyltin dialkoxides, changing by less than  $2.7^\circ$ . However, increasing the tin coordination does substantial increase the  $\angle(\text{C}, \text{Sn}, \text{C})$ , by  $49.3^\circ$  to  $60.7^\circ$ , the largest when  $R = t\text{-Bu}$ .

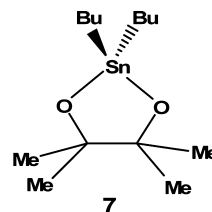
**Effects of Fluorination on the Thermodynamics of Dimerization.** For  $\text{Bu}_2\text{Sn}(\text{OR})_2$ , the thermodynamics of difluorinated dimerization (Table 4) are compared to the thermodynamics of monofluorinated dimerization (Table 3) as well as the thermodynamics of the previously calculated dimerization of  $\text{Bu}_2\text{Sn}(\text{OR})_2$ .<sup>22</sup>

Based on the calculated thermodynamic parameters (Tables 3 and 4), for 1–5, the tendency to dimerize is greater if one monomer is fluorinated (Figure 2), but less if both bear fluorides. Specifically, the last column of Table 3 gives the Gibbs energies for dimerization of nonfluorinated di-*n*-butyltin dialkoxides from our previous work,<sup>22</sup> and comparing the last two columns indicates that adding a fluoride atom to one monomer favors the dimerization reaction by 21.6, 11.0, 18.2, 15.9, and 28.1  $\text{kJ mol}^{-1}$ , for 1 to 5, respectively. The impact of fluorination on the position of the equilibrium is most pronounced for  $R = i\text{Pr}$ . Previous experimental and computational results<sup>22</sup> of  $\text{Bu}_2\text{Sn}(\text{OiPr})_2$  dimerization indicate that the monomer is slightly favored at 298 K. Conversely, the calculated thermodynamics results in the present study indicate the monofluorinated dimer is favored, with a  $\Delta G^{298}$  of  $-16.4$   $\text{kJ mol}^{-1}$ .

It should also be noted that for  $\text{Bu}_2\text{Sn}(\text{Ot-Bu})_2$  (6) comparison of the thermodynamic parameters suggest that monofluorination does not increase the tendency to dimerize. However, the nonfluorinated dimerization<sup>22</sup> had a  $\Delta G^{298}$  of 4.1  $\text{kJ mol}^{-1}$  but a geometry that suggests two individual monomers separated by 4.131 Å. The addition of one fluoride decreases intermonomer bond lengths to values consistent with a real dimer, and dimerization has a calculated  $\Delta G^{298}$  of 21.7  $\text{kJ mol}^{-1}$ . This suggests that the nonfluorinated dimer structure with intermonomer bond lengths typical of stannylene acetal dimers is so unstable that it is not a minimum on the potential energy surface. Addition of fluoride stabilizes the typical dimer structure sufficiently that it is now a minimum, albeit still less stable than the separated monomers.

The dimerization of two monofluorinated monomers to a difluorinated dimer (Table 4) is very unfavorable thermodynamically in contrast to nonfluorinated<sup>22</sup> and monofluorinated dimerizations (Table 3). Compared to nonfluorination, the presence of two fluorides decreases the energetic tendency to dimerize as measured by the Gibbs energies at 298 K by very large amounts, 239.2, 238.2, 223.4, 233.5, 205.6, and 273.7  $\text{kJ mol}^{-1}$ , for 1 to 6, respectively. Similarly, compared to monofluorination, the presence of an additional fluoride decreases the energetic tendency to dimerize ( $\Delta G^{298}$ ) by 260.8, 249.2, 241.6, 249.4, 233.7, and 256.1  $\text{kJ mol}^{-1}$ , for 1 to 6, respectively.

When the two alkoxy groups in the dialkylstannylene acetal are joined to make five- or six-membered rings, the tendency to form dimers (and oligomers) is greatly increased,<sup>5,6,11</sup> because the O–Sn–O bond angle is forced to be less than  $90^\circ$  by the long Sn–O bonds in the rings.<sup>37</sup> 2,2-di-*n*-butyl-4,4,5,5-tetramethyl-1,3,2-dioxastannolane (7) is the five-membered ring analogue of di-*n*-butyl-di-*t*-butoxystannane (6). Compound 7 is a dimer both in solution and in the solid state.<sup>10</sup> In both its  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra, the four methyl groups appear as two doublets in its room temperature spectra due to the  $C_{2v}$  symmetry of the dimer. These signals coalesce as the temperature is raised, and line shape analysis gave 61.9  $\text{kJ mol}^{-1}$  as the Gibbs energy of activation for this process.<sup>6</sup> The transition state for this process is probably the monomer, giving an estimate of the difference in stability of these two structures for 7. In comparison to the results herein, this value suggests that for cyclic di-*n*-butyldialkoxystannanes, all monofluorinated dimers would be present in the dimer form, but the very large destabilization of the difluorinated dimers ensures that they would also exist as fluorinated monomers.



**Implications for Suggested Mechanisms.** Two mechanisms have been proposed to explain the effects of added nucleophiles on the reactions of di-*n*-butylstannylene acetals.<sup>2,3,17</sup> Both of these mechanisms involve the nucleophile binding to the tin monomer, and the reaction proceeds through the coordinated monomer. Because monocoordinated stannylene acetal dimers would yield different regioselectivity, they

have not been suggested as potential reactive intermediates in these regioselective reactions.

The results in the present work indicate that the reaction may proceed through the monocoordinated dialkylstannylene acetal monomer or the monocoordinated dialkylstannylene acetal dimer. The calculated thermodynamics indicate that monofluoridated monomers and monofluoridated dimers are favored for di-*n*-butyltin dialkoxides. While the magnitudes of the thermodynamic parameters are influenced by the size and volume of the acetal substituent R, these findings indicate that fluoridation increases the tendency for di-*n*-butyltin dialkoxides to dimerize. It should be noted that the difluoridated dimer is not thermodynamically favored, and therefore low populations are likely at equilibrium.

Recent experimental results on the kinetics of reactions of di-*n*-butylstannylene acetals indicate that rates of reaction do not increase as the concentration of added nucleophile is increased beyond 0.5 equiv.<sup>18</sup> This result could be interpreted as indicating that the intermediate is the monofluoridated dimer. It could also be interpreted as indicating that the monofluoridated monomer is a much more reactive intermediate than the monofluoridated dimer.

## CONCLUSIONS

This study used high-level computational chemistry methods to investigate the geometric and thermodynamic effects of fluoridation on the dimerization of various di-*n*-butyltin dialkoxides. Based on the thermodynamics, the species present will vary as the mole fraction of fluoride to dialkoxydialkyltin derivative changes. For mole fractions up to 0.5, mixtures of nonfluoridated dimer and monofluoridated dimer are present. For mole ratios between 0.5 and 1, mixtures of monofluoridated dimers and fluoridated monomers will be present. After the mole ratio passes 1, only monofluoridated monomers will be present for the species investigated here. The effects of solvation were discussed in the sections on the thermodynamics of the three equilibria. No significant effects of solvation on these conclusions are anticipated.

The acetal substituent (R) has geometric and thermodynamic influences on the monofluoridated dimerization of di-*n*-butyltin dialkoxides. The calculated thermodynamic parameters indicate that dimerization becomes less favored as R increases in steric bulk. Furthermore, for di-*n*-butyltin dialkoxides, the magnitudes of the effects of fluoridation increase as the steric volume of R increases. For some di-*n*-butyltin dialkoxides (R = *i*Pr) the effects of fluoridation are so large that they change the direction of equilibrium and facilitate the presence of the monofluoridated dimer. These trends provide promise for mechanistic studies of monosubstitution reactions, where the proposed mechanism may proceed through a monofluoridated stannylene acetal dimer intermediate.

## ASSOCIATED CONTENT

### Supporting Information

Archive entries for all of the geometry optimizations, as well as any Supporting Information referred to in this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

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