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Mechanistic Studies on the $B(C_6F_5)_3$ Catalyzed Allylstannation of Aromatic Aldehydes with *Ortho* Donor Substituents

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Abstract: Mechanistic studies on the $B(C_6F_5)_3$ catalyzed allylstannation of isomeric substituted benzaldehydes are reported. Confirming a report by Maruoka et al., good (5:1) to excellent (>20:1) selectivities for *ortho* over *para* isomers are observed when 1:1 mixtures (X = OMe, Cl, F, OTBS) are allylstannated with $C_3H_5SnBu_3$ in the presence of $B(C_6F_5)_3$ (2.5% per CHO). The best selectivities are observed for the anisaldehydes. Multinuclear NMR studies on solutions of $B(C_6F_5)_3$ and $C_3H_5SnBu_3$ (1:1 to 1:5) show that the borane abstracts the allyl group from the organotin reagent, forming an adduct $(C_6F_5)_3B\cdots CH_2CHCH_2SnBu_3$, **1**, or ion pair $[(C_6F_5)_3BCH_2CH{=}CH_2]^-[Bu_3SnCH_2CHCH_2SnBu_3]^+$, **2**, depending on the reagent ratio. These compounds are important in the mechanism of Lewis acid catalyzed 1,3-isomerization of substituted allyl stannanes. When allyltin reagent is added to solutions of $B(C_6F_5)_3$ and *ortho*-anisaldehyde (1:5) at −60 °C, conversion to the stannylium ion pair $[Bu_3Sn(ortho\text{-anisaldehyde})_2]^+[o\text{-ArCH(allyl)OB}(C_6F_5)_3]^-$, ***o,o*-4**, is observed. The structure of this species was confirmed by ^1H, ^{11}B, ^{19}F, and ^{119}Sn NMR spectroscopy and by forming related ion pairs (***o*-5** and ***o,o*-5**) utilizing the $[B(C_6F_5)_4]^-$ counteranion via reaction of $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ with aldehyde. The anion in ***o,o*-4** is formed via direct allylation of the *ortho*-anisaldehyde/$B(C_6F_5)_3$ adduct ***o*-3**, while the cation arises upon aldehyde ligation of the resulting tributylstannylium ion. The crystal structure of the related derivative *ortho*-$C_6H_4(OMe)CHO{\bullet}SnMe_3BF_4$, **6**, showed that the aldehyde binds the tin nucleus only through the carbonyl oxygen. Similar reactions using *para*-anisaldehyde show that formation of ***p,p*-4** occurs at a much slower rate, again demonstrating the preference for the *ortho* substituted substrates. For similar experiments using benzophenone, however, formation of the ion pair $[Bu_3Sn(Ph_2CO)_2]^+[(C_3H_5)B(C_6F_5)_3]^-$, **8**, was observed, illustrating the differences subtle changes in substrate can bring. Ion pair **8** is formed via the trapping of **1** by the benzophenone substrate. In the presence of excess aldehyde and allyltin reagent, ion pair ***o,o*-4** catalyzes the allylstannation of aldehyde to give the product stannyl ether. Several lines of experimental evidence suggest this is the true catalyst in the system. The chemoselectivity observed thus does not rely on classical chelation control in any way. Rather, we propose that the *ortho* donor group stabilizes the developing positive charge at the β carbon of the allyl group and the tin atom during the allylation event. This stabilization renders the *ortho* substituted substrates kinetically favored toward allylation irrespective of the Lewis acid employed.

Introduction

Over the past two decades, the Lewis acid (LA) catalyzed allylstannation of aldehydes has become an important carbon−carbon bond forming reaction in organic synthesis.[2] In addition to forming a new C−C bond, the reaction adds functionality which can be elaborated in further transformations. This reaction has found particular utility for stereocontrol in reactions mediated by acyclic transition states; as such, it has been described as a surrogate for the aldol reaction.[3] Diastereoselective additions of substituted derivatives, such as crotylstannanes[4] and chiral alkoxy-substituted allylstannanes,[5] lead to important building blocks for natural product synthesis. Chiral α- and β-substituted aldehydes can be allylated with impressive stereocontrol of the newly formed chiral center,[6] while the use of chiral LAs has also given enantioenriched products.[7]

While the utility of this methodology is clear, the reactions are mechanistically complex; despite a number of studies, a clear consensus on the mechanism has been slow to emerge. In part

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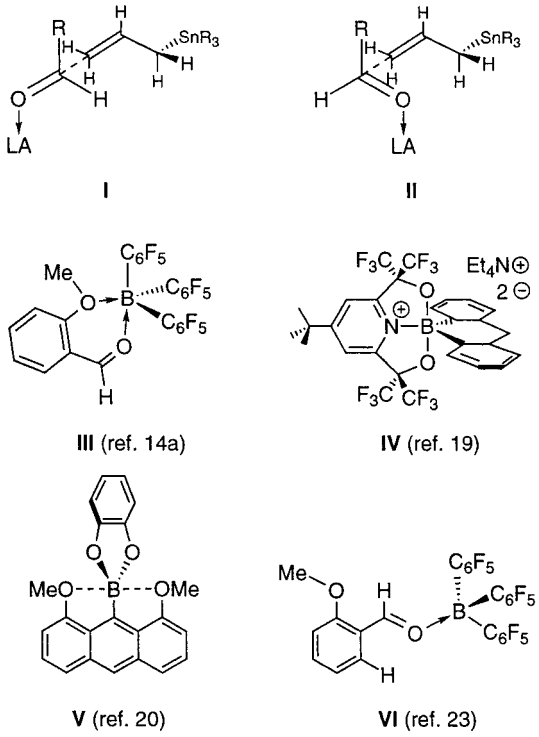
Chart 1



this stems from the convincing evidence for several mechanistic alternatives, depending on the substrate, the LA employed and the reaction conditions.[2a,8] Studies by Yamamoto on the nature of attack of the allylstannnane on LA complexed carbonyl functions has led to the conclusion that, most commonly, an acyclic, antiperiplanar transition state **I** is favored.[9] On the other hand, Denmark,[3,10] Keck,[4d] and others[2a] have provided compelling evidence that an alternative synclinal transition state **II** can be predominant under certain conditions. The role of common LAs such as $SnCl_4$, $TiCl_4$, and BF_3 has also been studied extensively. Although the normal role of the LA is to activate the carbonyl,[11] competitive transmetalation reactions between the LA and the allylstannane (e.g., $SnCl_4$ + allyl$SnBu_3$ → allyl$SnCl_3$ + Bu_3SnCl) can occur; which role the LA plays depends highly on the reaction conditions.[12] The related LA catalyzed isomerization of allylstannanes (and allenyl- and propargylstannanes[5]) has also attracted attention, but with relatively little mechanistic study.[5,8,10,13]

More recently, Maruoka and co-workers reported[14] the remarkably chemoselective allylstannation of *ortho*-anisaldehyde over *para*-anisaldehyde, catalyzed by the LAs Me_3Al and $B(C_6F_5)_3$.[15] To account for this impressive selectivity, these authors proposed the involvement of a hypercoordinate organoboron species **III** which, via chelation of the borane by the *ortho*-anisaldehyde substrate, leads to selective allylstannation of this substrate.[16] While hypercoordination is plausible for the aluminum based LA in Maruoka's studies, for the much smaller boron nucleus (atomic radius = 0.50 Å) the involvement of hypercoordinate structures such as **III** seem less likely for a few reasons. Five-coordinate aluminum compounds are abundant,[17] but only two examples of compounds where boron is apparently five-coordinate in the ground-state structure have been reported.[18] Furthermore, both of these (**IV**[19] and **V**[20]) contain fairly contrived ligand systems aimed at enforcing hypercoordination, and alternative formulations which do not involve hypercoordinate boron are conceivable. A recent computational study[21] has shown that 2:1 adducts between NH_3 and BH_3 are disfavored not only for steric reasons, but also because of the primarily covalent nature of the initial $H_3N \rightarrow BH_3$ dative bond, which discourages the addition of a second Lewis base. By contrast, the N−Al bond of the adduct $H_3N \rightarrow AlH_3$ has a more significant electrostatic component, which favors coordination of a second Lewis base since the Al center is still somewhat electropositive.[22] Even if "L_2BR_3" were a viable species, the ligands L would undoubtedly occupy opposing axial sites for steric reasons and by virtue of the directionality of the unhybridized p-orbital utilized in the bonding. A chelating structure such as **III** would not be able to attain this geometry. Finally, chelation control in this fashion is intuitively unsatisfying, since it might be expected that the activation of the carbonyl toward nucleophilic attack is diminished because the Lewis acidity of the catalyst is now spread over two sites. This would seem to work against the selectivity observed for the *ortho*-anisaldehyde substrate in the Maruoka reaction.

The above discussion suggests that **III** is improbable even as a transition-state structure and these issues led us to consider

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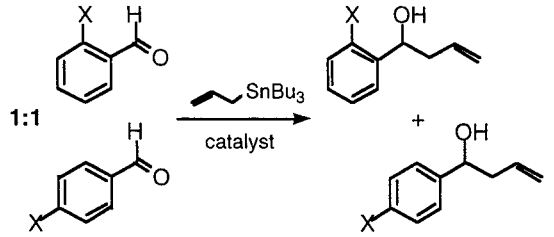
Table 1. *Ortho:Para* Selectivity in the Catalytic Allylstannation of Benzaldehydes



entry[a]	catalyst	X	ratio (*o*:*p*)
1	$B(C_6F_5)_3$	OMe	>20:1
2	$B(C_6F_5)_3$	F	5:1
3	$B(C_6F_5)_3$	Cl	3:1
4	$B(C_6F_5)_3$	OTBS	18:1
5	$B(C_6F_5)_3$	Me	1.1:1
6	$[Bu_3Sn]^+[B(C_6F_5)_4]^-$	OMe	12.5:1
7[b]	$BF_3{\bullet}OEt_2$	OMe	7.1

[a] Conditions: toluene, −40 °C, 2.5% catalyst loading. [b] Reaction done in CH_2Cl_2 at −78 °C.

other explanations for the chemo- and regioselectivities reported by Maruoka in $B(C_6F_5)_3$ catalyzed allylstannations.[23] In these preliminary studies, we showed that the adduct formed between $B(C_6F_5)_3$ and *ortho*-anisaldehyde has a ground-state structure **VI** both in solution and the solid state. Furthermore, using multinuclear NMR spectroscopic studies, we showed that the borane is capable of activating the allylstannane reagent via allyl group abstraction. Unanswered questions include the tin speciation in these catalytic reactions, the role and nature of the borate counteranion, and the ultimate source of the selectivities observed. Herein we report our attempts to answer these questions. Although we stop at generalizing these results to other systems, this study raises questions concerning the role of the LA in other reactions involving allylstannanes with surprising selectivities.[24] Indeed, these results argue against generalizations and suggest that the mechanisms of these reactions should be evaluated on a case-by-case basis.

Results and Discussion

Reaction Selectivities. The selectivity for *ortho*-anisaldehyde over *para*-anisaldehyde in the $B(C_6F_5)_3$ catalyzed allylstannation reported by Maruoka was >20:1.[14a] We repeated this reaction and found the same selectivities for this pair of substrates (entry 1, Table 1), although separate experiments show that the *para*-anisaldehyde isomer is more basic toward $B(C_6F_5)_3$ than the *ortho* substituted substrate.[25] For other *ortho* and *para* substituted benzaldehydes, various levels of selectivity were observed (entries 2−4). For the fluoro-[26] and chloro-substituted substrate pair, only moderate preference for the *ortho* isomer was exhibited, while negligible selectivity was observed in the reaction involving a 1:1 mixture of *ortho* and *para*-tolualdehydes. Interestingly, a high preference for *ortho*-*tert*-butyldimethylsiloxybenzaldehyde relative to the *para* isomer is observed (entry 5); typically, silyl ethers have been considered to be poor chelating groups because of the decreased oxygen basicity and increased steric requirements of this base.[27] This substrate would be hard-pressed to chelate $B(C_6F_5)_3$ (or any other Lewis acid) in the fashion proposed by Maruoka (**III**).

Thus, to achieve selectivity in these reactions, the X group requires a lone pair, while the level of selectivity appears to be loosely associated with the donor ability of the *ortho*/*para* group in place. The last two entries in the Table show that high selectivities are also observed when other LA catalysts are employed. The stannylium cation $[Bu_3Sn]^+[B(C_6F_5)_4]^-$, generated in situ from Bu_3SnH and $[Ph_3C]^+[B(C_6F_5)_4]^-$[28,29] provides excellent selectivity for allylation of *ortho*-anisaldehyde, while even the more traditional LA $BF_3{\cdot}OEt_2$ also gives positive results in this regard. Thus, in line with Maruoka's observations, where $[AlMe_3]_2$ also provided selective allylation, the selectivity is substrate specific and not a function of the nature of the Lewis acid employed.

If hypercoordinate boron structures are not responsible for the selectivity observed in the reactions summarized in Table 1, then what is its origin? Previously, we have shown that in the $B(C_6F_5)_3$ catalyzed hydrosilation of aromatic carbonyl functions,[30] imines[31] and the silation of alcohols,[32] the borane serves to activate the silane reagent rather than the carbonyl group as is traditionally surmised. Since it is well established that allyl groups are abstractable from tin by carbocations[33] and silylium ions,[34] which are isoelectronic with $B(C_6F_5)_3$,[35] we hypothesized that the borane may be interacting with the allylstannane reagent in some way to generate cationic stannylium ions which serve as the actual LA catalysts in this reaction.[23] The efficacy of $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ as a catalyst for chemoselective allylstannation (entry 6, Table 1) supports this notion. Carbonyl dissociation from the borane is facile and thus "free" borane is kinetically accessible even though the $B(C_6F_5)_3{\cdot}$ carbonyl compound adducts are thermodynamically favored.[36,37] We thus began our mechanistic experiments with stoichiometric reactivity studies between $B(C_6F_5)_3$ and $C_3H_5SnBu_3$.

Interaction between $B(C_6F_5)_3$ and Allyltributylstannane. Prolonged stirring of a 1:1 mixture of $B(C_6F_5)_3$ and $C_3H_5SnBu_3$ at room temperature results in a $-C_6F_5$ transfer reaction where the primary tin-containing product is $C_6F_5SnBu_3$ (Scheme 1).[38]

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(25) In a competitive situation, ^{19}F NMR experiments showed that the *para*−anisaldehyde adduct ***p*-3** is favored over ***o*-3** by a 2.2: 1.0 margin.
(26) The solid-state structure of the adduct between *ortho*-fluorobenzaldehyde and $B(C_6F5)_3$ reveals a ground-state structure identical to that found for the *ortho*−anisaldehyde/$B(C_6F_5)_3$ adduct (***o*-3**). Thus, no evidence for a chelated structure involving hypercoordinate boron was found in this species. Details of this structure determination can be found in the Supporting Information.
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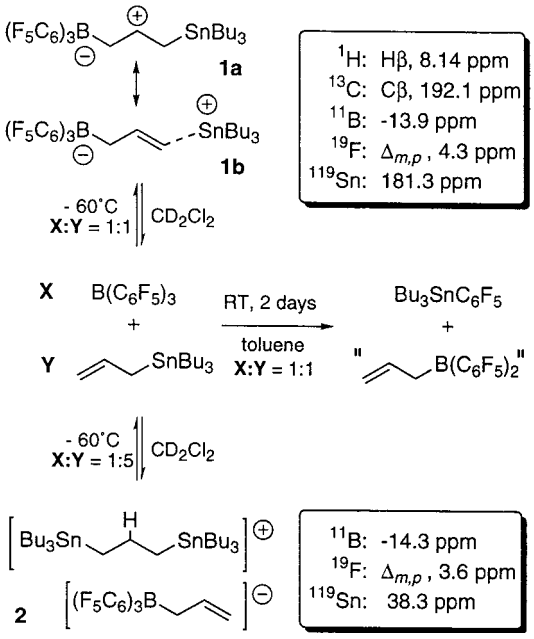
(36) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369.
(37) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 12379.
(38) There is also some evidence for minor amounts of allylstannation of the allyl carbon−carbon double bond, producing $CH_2{=}CHCH_2CH(CH_2SnBu_3)_2$.

Scheme 1



The allyl borane which must be produced to balance the equation undergoes further uncharacterized reactivity. Clearly, then, there is some chemical interaction between these two partners, as exemplified by the broad, featureless signals apparent in the room-temperature proton NMR spectroscopic data obtained. More concrete evidence is obtained if toluene solutions of $B(C_6F_5)_3$ and $C_3H_5SnBu_3$ are cooled to −60 °C, where the multinuclear NMR data is supportive of formation of an adduct **1a/b**; key spectroscopic data is given in Scheme 1. Although the character of these spectra is similar in toluene,[23] the ionization process is facilitated in the more polar solvent CD_2Cl_2 and the spectra are cleaner in this medium. The ^{11}B shift is characteristic of anionic, four-coordinate boron[39] and the difference in the chemical shifts of the *meta* and *para* fluorine nuclei, $\Delta_{m,p}$, is also indicative of significant borate character, but with some residual association with the stannylium center ($\Delta_{m,p}$ values of less than 3 are found for solvent-separated ion pairs where $[RB(C_6F_5)_3]^-$ is not coordinated to its cation).[40]

Formation of adduct **1** occurs when the two reagents are mixed in a 1:1 ratio. Under conditions more closely related to those found in the catalytic reactions, that is, with excess $C_3H_5SnBu_3$ present, a new species is observed to form, which we assign as the ion pair **2** on the basis of the ^1H NMR spectra (Figure 1). A sample containing $B(C_6F_5)_3$ and $C_3H_5SnBu_3$ in a 1:2 ratio gives the spectrum in Figure 1a. The allyl group of the borate counteranion appears with a typical pattern, while the signals for the allyl group bridging the tin centers have been symmetrized into two signals at 3.27 and 6.63 ppm in a 4:1 ratio ($^3J_{HH}$ = 11.0 Hz). Positive charge is stabilized at the central carbon (^{13}C NMR = 161.2 ppm, $^1J_{CH}$ = 154.9 Hz) by the two β-tin atoms,[41] which give rise to a resonance at 90.8 ppm in the ^{119}Sn NMR spectrum. When the allyltin:borane ratio is increased to 5:1 (Figure 1b), these two signals in the ^1H NMR spectrum increase in intensity relative to those for the allyl borate

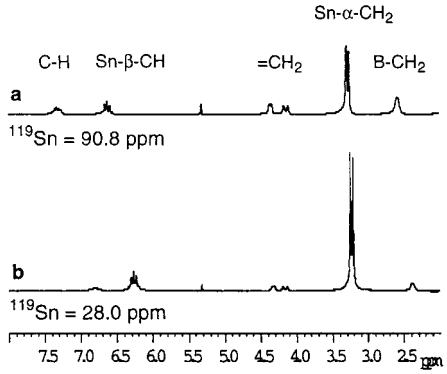


Figure 1. 400 MHz ^1H NMR spectra (−60 °C, CD_2Cl_2) of (a) a 2:1 mixture of $C_3H_5SnBu_3$ and $B(C_6F_5)_3$ and (b) a 5:1 mixture of of $C_3H_5SnBu_3$ and $B(C_6F_5)_3$.

while signals for free allyltributylstannane are absent. These observations suggest that the allyl moieties in free allylstannane and the cation of **2** are rapidly exchanging on the NMR time scale, while involvement of the allyl group of the borate counteranion in the exchange is minimal in this medium.[42] This is also supported by the observed changes in the ^{119}Sn chemical shift of the sample; as more allyltributylstannane is added, the shift progresses toward the value for free allyltributylstannane in CD_2Cl_2 at −60 °C (−17.7 ppm).

LAs catalyze the isomerization of allyl and crotyl tin reagents.[5] Early mechanistic proposals accounting for this 1,3-isomerization[13b] did not invoke LA abstraction of the allyl group, but a more plausible pathway involving such a path was hinted at by Denmark et al.[12g] The direct spectroscopic observation of **2**, and the observed exchange processes, along with some recent investigations by Marshall and Gill,[43] put this latter proposal on much firmer footing. Formal allyl group abstraction by the LA to form an ion pair like **2** results in the rapid exchange of allyl groups between **2** and free allylstannane; the extent of allyl borate counteranion participation in this exchange depends on the temperature, the solvent polarity, and the amount of excess allylstannane present.

Boron and Tin Speciation in Catalytic Allylation Reactions. The above discussion establishes that $B(C_6F_5)_3$ is capable of abstracting an allyl group from the organotin reagent in the presence of as weak a Lewis base as allyltributylstannane, a process which may be pertinent to the mechanism of $B(C_6F_5)_3$ catalyzed allylstannation. To determine the chemical nature of the boron and tin reagents under conditions more relevant to allylstannation catalysis, multinuclear NMR spectroscopy was conducted on solutions of $B(C_6F_5)_3$ (20% relative to allyltin/substrate), $C_3H_5SnBu_3$, and anisaldehyde substrates under conditions where the rate of allylation of the substrate is negligible (−60 °C). Separate experiments show that the borane forms isolable and spectroscopically definable adducts with both *ortho*-

(39) Kidd, R. G. in *NMR of Newly Accessible Nuclei*; Laszlo, P. Ed.; Academic Press: New York, 1983; Vol. 2.
(40) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424.
(41) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183.

(42) The chemical shifts of the allylborate protons are dependent on the equivalency of the allylstannane added, suggesting that the allylborate may be involved in the exchange process on a slower time scale; indeed, upon warming to −30 °C, the signals for the allyl borate are observed to undergo coalescence behavior. In toluene, the allyl group of the borate appears to participate in allyl group scrambling at −40 °C, since only one set of allyl signals is observed under these conditions. The process may be partially frozen out in toluene at temperatures below −40 °C, but the presence of detectable quantities of **1a/b** complicates the spectra. Evidently, in the more polar solvent, the allylborate counteranion is more effectively solvated away from the cation, whereas in toluene an equilibrium mixture of **1a/b** and **2** is observed.
(43) Marshall, J. A.; Gill, K. *J. Organomet. Chem.* **2001**, *624*, 294.

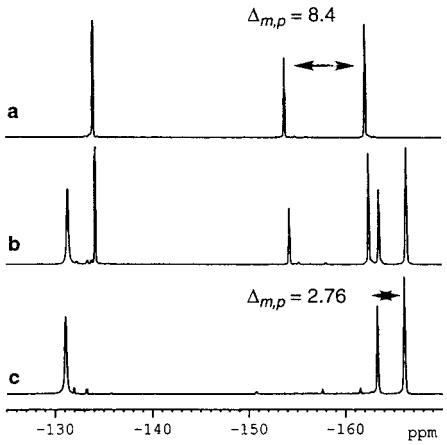


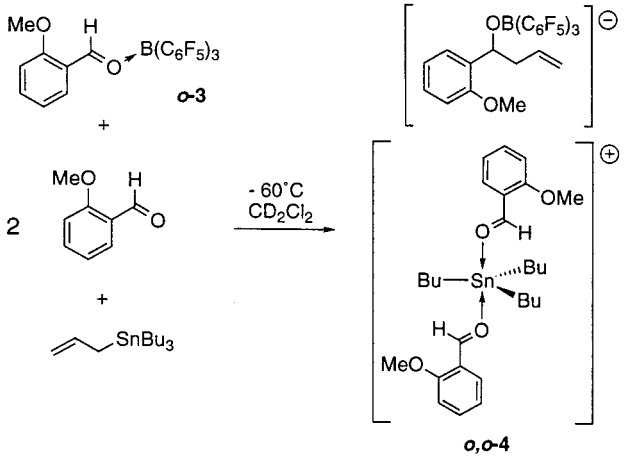
Figure 2. 282 MHz ^{19}F NMR spectra (−60 °C, C_7D_8) of (a) a solution of *ortho*-anisaldehyde and 20% $B(C_6F_5)_3$ prior to addition of allyltributylstannane (spectrum of ***o*-3**); (b) spectrum taken 3 min after addition of one equivalent of allyltributylstannane (based on aldehyde); and (c) spectrum taken 15 min after addition of allyltributylstannane (spectrum of ***o,o*-4**).

anisaldehyde (***o*-3**, i.e., **VI** from Chart 1) and *para*-anisaldehyde (***p*-3**); essentially all of the $B(C_6F_5)_3$ is sequestered in this form prior to addition of $C_3H_5SnBu_3$. However, on the basis of the observation of exchange between free and bound aldehyde in these systems at −60 °C, these adducts are kinetically labile, and free $B(C_6F_5)_3$ should be accessible under these conditons. Since the preparative catalytic reactions are generally performed by premixing the borane and the substrate to form the ***o*-3** or ***p*-3** adducts and then adding the organotin allylating agent at low temperature, samples for NMR spectroscopy were prepared in this fashion. The relatively high catalyst loading of 20% was necessary to produce samples amenable to study by a variety of NMR techniques, but we presume that the results of these experiments are germane to the lower catalyst loadings as well.

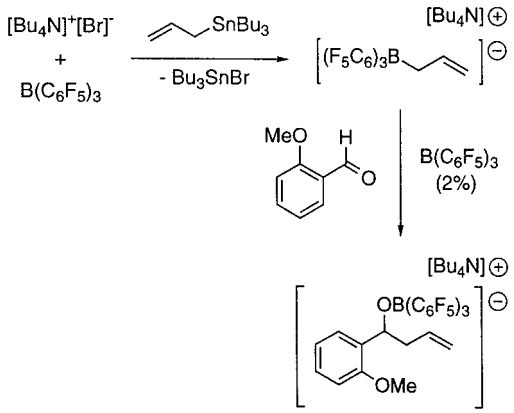
In our preliminary communication, we reported the production of an ion pair upon addition of allylstannane to a solution of *ortho*-anisaldehyde and 20% $B(C_6F_5)_3$. On the basis of the observed chemistry between allylstannane and $B(C_6F_5)_3$ described above and of the ^{19}F NMR spectra of this reaction while in progress (Figure 2), we assigned this species the structure $[(L)SnBu_3]^+[(C_3H_5)B(C_6F_5)_3]^-$, where the *ortho*-anisaldehyde substrate serves as the base which displaces the allylborate counteranion to form the stannylium cation ligated by substrate. While the ^{19}F NMR spectra are certainly consistent with this proposal, full examination of the ^{11}B, ^{119}Sn, and particularly the ^1H NMR spectra of this ion pair shows that, in fact, it has the structure shown in Scheme 2. Ion pair ***o,o*-4** is formed via direct allylation of adduct ***o*-3**, where the tributylstannylium ion produced is stabilized by two *ortho*-anisaldehyde substrate molecules. This is supported by the following spectroscopic data.

The ^{11}B NMR spectrum for ***o,o*-4** exhibits a resonance at −4.5 ppm, which is consistent with anionic, four-coordinate boron, but shifted about 10 ppm downfield from the position of the resonance typically observed for the $[(C_3H_5)B(C_6F_5)_3]^-$ anion. The tetrabutylammonium salt of this latter ion can be prepared separately via treatment of a 1:1 mixture of allyltributylstannane and $B(C_6F_5)_3$ with $[Bu_4N]^+[Br]^-$ as shown in Scheme 3. The ^{11}B chemical shift of this species is −14.4 ppm in CD_2Cl_2 at −60 °C and the ^1H NMR is similar to that observed for this counteranion in Figure 1 above. In addition to the markedly different ^{11}B chemical shift, in the ^1H NMR spectrum of ion

Scheme 2



Scheme 3



pair ***o,o*-4**, a set of resonances associated with the alkoxyborate anion $[o\text{-ArCH(allyl)OB}(C_6F_5)_3]^-$ (*o*-Ar = *ortho*-anisyl) is apparent; this assignment was again verified by separate synthesis of the $[Bu_4N]^+$ salt of this alkoxyborate as shown in Scheme 3. The ^1H NMR spectra of the resulting salt and the anion in ***o,o*-4** are nearly identical, as are the ^{13}C NMR spectra, indicating that the anions in ***o,o*-4** and $[Bu_4N]^+[o\text{-ArCH(allyl)OB}(C_6F_5)_3]^-$ are chemically the same. No reaction between $ArCH(allyl)OB(C_6F_5)_3]^-$ $[Bu_4N]^+$ and the Bu_3SnBr byproduct is observed over the course of a few hours. A similar analysis of the experiment using *para*-anisaldehyde also leads to the conclusion that the anion produced is an alkoxyborate species arising from allylation of ***p*-3**, although this process occurs at a much slower rate (vide infra).

To ascertain the precise nature of the cationic portion of ion pairs ***o,o*-4**, ^{119}Sn NMR spectroscopic measurements were conducted. Samples of ***o,o*-4** which were free of excess allyltin reagent were generated by mixing *ortho*-anisaldehyde, $B(C_6F_5)_3$, and allyltributylstannane in a 3:1:1 ratio in CD_2Cl_2 at −60 °C. A clean ^{119}Sn NMR spectrum of this material was obtained, showing a single resonance at 90.0 ppm, which the following experiments show is consistent with a cationic $[R_3Sn]^+$ fragment ligated by two donors.[44]

Strong evidence for this formulation was obtained by probing the reactions of in situ generated $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ with *ortho*-anisaldehyde. This stannylium species, first reported by Lambert and co-workers, forms a colorless oil in toluene solution[29,45] and NMR experiments can be conducted directly on this oil. Although we write this species as "$[Bu_3Sn]^+$-

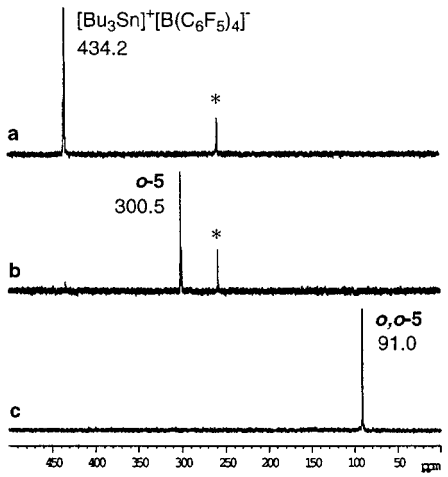
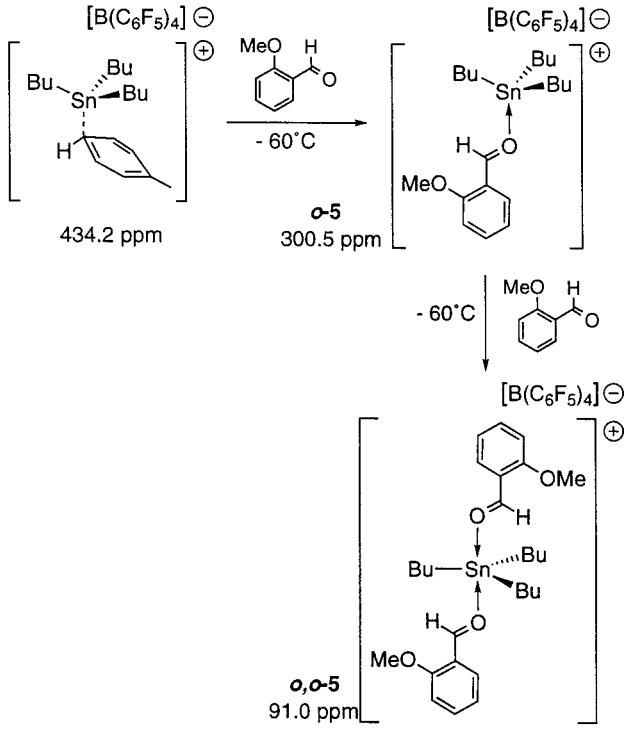


Figure 3. 149.2 MHz ^{119}Sn NMR spectra (−60 °C, C_7D_8) of (a) $[Bu_3Sn]^+[B(C_6F_5)_4]^-$; (b) $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ plus one equivalent of *ortho*-anisaldehyde to form ***o*-5**; and (c) $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ plus two equivalents of *ortho*-anisaldehyde to form ***o,o*-5**. The peak marked by (*) in spectra (a) and (b) is an unidentified species (see footnote 47).

$[B(C_6F_5)_4]^-$", it is more accurately decribed as the toluene coordinated species $[Bu_3Sn(\eta^1\text{-}C_7D_8)]^+[B(C_6F_5)_4]^-$.[46] Since the $[B(C_6F_5)_4]^-$ counteranion is highly inert, the resulting stannylium cations are free from potential complications arising from allylation by the counteranion. Figure 3 shows a series of ^{119}Sn NMR spectra acquired on these samples at −60 °C. Spectrum 3a is simply that of $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ in the absence of added aldehyde and shows a singlet at 434.2 ppm.[47] Upon addition of ≈0.5 equivalents of *ortho*-anisaldehyde to the oil, a new signal appears upfield at 300.5 ppm; at this temperature, both peaks are sharp. After addition of a full equivalent of aldehyde, the peak at 300.5 ppm dominates the spectrum (Figure 3b). In light of the well-documented tendency of LAs to coordinate aldehydes syn to the aldehydic proton,[11] the higher field chemical shift of 300.5 ppm, which is consistent with the presence of four-coordinate tin cation,[48,49] and the crystal structure of a related derivative (vide infra), we assign this species as the mono-*ortho*-anisaldehyde adduct of $[Bu_3Sn]^+$, with an unchelated structure (***o*-5**, Scheme 4). As a second equivalent of *ortho*-anisaldehyde is added, a third signal at 91.0 ppm emerges (Figure 3c), which can be ascribed to the bis-*ortho*-anisaldehyde adduct ***o,o*-5**;[50] addition of >2 equivalents of aldehyde results in no further change to the spectrum. Further support for these assignments is found in the observed $^1J_{Sn-C}$ coupling constants. For ***o*-5**, the ^{117} and ^{119}Sn satellites were not resolved, and the observed coupling of 286 Hz is thus an average of the two values. For ***o,o*-5**, the two couplings were resolved and found to be $^1J_{119Sn-C}$ = 408 Hz and $^1J_{117Sn-C}$ = 392 Hz, both substantially larger than that found in the four-coordinate ***o*-5**. This is consistent with larger s character in the Sn−C bonds of the five-coordinate structure and is a phenomenon which has been observed and interpreted in this way for the silicon congeners $[R_3Si(L)_n]^+[A]^-$.[44]

Scheme 4



***o,o*-5** differs from ***o,o*-4** (derived from $B(C_6F_5)_3$) only in the nature of the counteranion, and the similarity in the ^{119}Sn NMR data is strongly suggestive that the cationic portions of these species are the same. A similar series of spectra are obtained when $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ is treated with *para*-anisaldehyde at −60 °C, giving ***p*-5** (291.9 ppm) and ***p,p*-5** (81.4 ppm). The slightly higher field chemical shifts for the adducts of *para*-anisaldehyde are consistent with its greater basicity in comparison to the *ortho* isomer. The coordinated aldehydes in these compounds are kinetically labile at −60 °C, since exchange with free aldehyde is observed on the ^{1}H NMR time scale.

(44) To our knowledge, a systematic ^{119}Sn NMR study of $[R_3Sn(L)_n]^+[A]^-$ compounds has not been undertaken. However, a detailed ^{29}Si NMR study has been done for the silylium analogues, and progressive upfield shifts are observed for the series $[R_3Si(arene)]^+[A]^- \rightarrow [R_3Si(L)]^+[A]^- \rightarrow [R_3Si(L)_2]^+[A]^-$: Arshadi, M.; Johnels, D.; Edlund, U.; Ottosson, C.−H.; Cremer, D. *J. Am. Chem. Soc.* **1996**, *118*, 5120.

(45) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729.

(46) Arshadi, M.; Johnels, D.; Edlund, U. *Chem. Commun.* **1996**, 1279.

(47) Lambert et al have reported[29,45] a chemical shift of 262 ppm for this species at room temperature. As seen in Figure 3a and 3b, a small peak at this chemical shift (263) appears in our experiments. We find that, at room temperature, the signal at 434 ppm is severely broadened, while that at 263 remains sharp. We do not know what this latter signal is due to, although spiking samples with small amounts of water indicate that it is *not* due to the water adduct $[Bu_3Sn{\bullet}OH_2]^+[B(C_6F_5)_4]^-$. In light of the substantially downfield shifted resonance of 434 ppm for $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ in toluene, this species has more cationic character than originally supposed on the basis of the chemical shift of 262 ppm. Likely, the broadening observed at room temperature is due to rapid exchange of coordinated and free toluene.

(48) (a) The ^{29}Si chemical shift of a related silylium ion, $[Et_3Si(sulfolane)]^+[B(C_6F_5)_4]^-$, was reported to be 58.4 ppm.[48b] ^{29}Si chemical shifts may be related empirically to ^{119}Sn chemical shifts by the relation $\delta_{Sn} = 5.2\delta_{Si} - 46$,[46,48b−d] which gives a ^{119}Sn chemical shift of ≈258 for the analogous tin species, indicating that the observed shift of 300.5 ppm for ***o*-5** is characteristic of a mono-ligated tin cation. (b) Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383. (c) Mitchell, T. N. *J. Organomet. Chem.* **1983**, *255*, 279. (d) Watkinson, P. J.; Mackay, K. M. *J. Organomet. Chem.* **1984**, *275*, 39.

(49) Kira et al. have reported a ^{119}Sn chemical shift of 165 for "$[Bu_3Sn(OEt_2)]^+[B(3, 5\text{-}(CF_3)_2C_6H_3)_4]^-$".[28] However, this sample was prepared with over 10 equivalents of diethyl ether present and is in all likelihood the bis-ether adduct $[Bu_3Sn(OEt_2)_2]^+[B(3, 5\text{-}(CF_3)_2C_6H_3)_4]^-$.

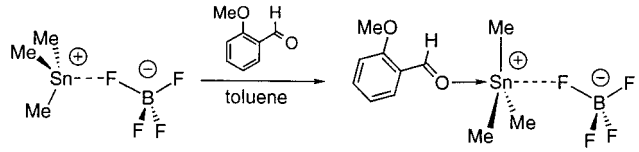
(50) Bis-adducts of R_3Sn^+ are well precedented. Several examples where L = R_nE = O have been crystallographically characterized: (a) Hiemisch, O.; Henschel, D.; Blaschette, A.; Jones, P. G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1391. (b) Lange, I.; Krahl, J.; Jones, P. G.; Blaschette, A. *J. Organomet. Chem.* **1994**, *474*, 97. (c) Wirth, A.; Lange, I.; Henschel, D.; Moers, O.; Blaschette, A.; Jones, P. G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1308. (d) Lange, I.; Henschel, D.; Wirth, A.; Krahl, J.; Blaschette, A.; Jones, P. G. *J. Organomet. Chem.* **1995**, *503*, 155. (e) The structure of an ion pair containing the $[Bu_3Sn{\bullet}(OH_2)_2]^+$ cation has been reported: Davies, A. G.; Goddard, J. P.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem Soc., Dalton Trans.* **1986** 1873. The ^{119}Sn chemical shift reported was 57.5 ppm in $CDCl_3$.

Table 2. Summary of Data Collection and Refinement Details for **6**

formula	**6** $C_{11}H_{17}F_4BO_2Sn$
fw	386.75
cryst syst	monoclinic
space group	*C*2/*c*
a, Å	32.3199(19)
b, Å	7.3722(4)
c, Å	28.0359(17)
β, °	113.5282(11)
V, Å^3	6124.7(6)
Z	16
d_{calc}, mg m^{-3}	1.678
μ, mm^{-1}	1.704
T, °C	−80
crystal dimensions, mm^3	0.34 × 0.12 × 0.04
rel. transmission factors	0.9349−0.5949
2θ (max), deg	52.82
total data	14122
independent reflections	6271
number of observations[a]	4308
no. of variables	349
restraints	0
R_1 $F_O^2 > 2\sigma(F_O^2)$	0.0402
wR_2 $F_O^2 > 2\sigma(F_O^2)$	0.0928
gof	0.993
residual density, e/Å^3	−0.561 to 0.809

[a] $F_O^2 \geq 2\sigma(F_O^2)$.

Scheme 5



6

The structure of mono-*ortho*-anisaldehyde adduct ***o*-5** with *ortho*-anisaldehyde in a nonchelating bonding mode is supported by the results of an X-ray structural investigation on the related species *ortho*-C_6H_4(OMe)CHO•$SnMe_3BF_4$, **6**. This material was prepared as shown in Scheme 5,[51] and single crystals were obtained from toluene. The compound crystallizes as two independent molecules which mainly differ in the metrical parameters associated with the Sn−F−B linkage; parameters within the $[LSnMe_3]^+$ fragment are essentially the same for each molecule so Figure 4 shows an ORTEP diagram of molecule A, along with selected metrical data for this species only. In this structure, the *ortho*-anisaldehyde binds to the tin center through the lone pair of the carbonyl oxygen which is syn to the aldehydic proton (Sn−O(10)−C(10) = 128.7(3)°) in a geometry nearly identical to that observed for adduct ***o*-3**.[23] This geometry may be partially induced by a weak hydrogen bond between the aldehydic proton and the methoxy group.[52] The tin center is distorted trigonal pyramidal in geometry and the $[BF_4]^-$ counteranion occupies the second axial site via a weak F→Sn interaction (F(1)−Sn-O(10) = 175.21(11)°; Sn−F(1) = 2.387(2) Å), cf. the Sn−F distance of 1.974(8) Å in the related five-coordinate organotin compound **VII**[53]). The B−F(1) distance of 1.431(7) Å is elongated by

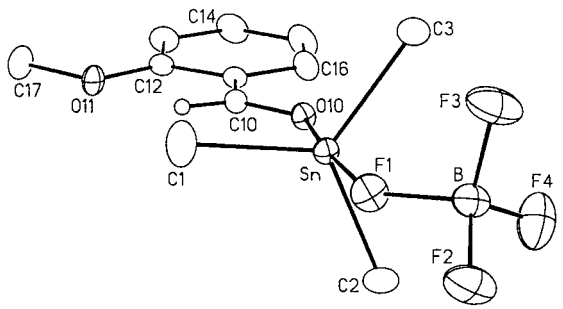
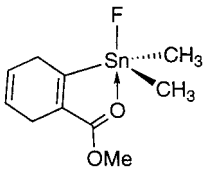


Figure 4. ORTEP diagram of molecule A of *ortho*-C_6H_4(OMe)CHO•$SnMe_3$-BF_4, **6**. Metrical parameters are for molecule A only and the butyl groups have been partially removed for clarity; full details are given in the Supporting Information. Selected bond distances (Å): Sn−F(1), 2.387(2); Sn−O(10), 2.231(3); F(1)−B, 1.431(7); F(2)−B, 1.370(6); F(3)−B, 1.345-(6); F(4)−B, 1.357(7); O(10)−C(10), 1.233(5); O(11)−C(12), 1.341(5); C(10)−C(11), 1.436(5); C(11)−C(12), 1.408(6); C(11)−C(16), 1.396(6); C(12)−C(13), 1.392(6); C(13)−C(14), 1.369(8); C(14)−C(15), 1.387(8); C(15)−C(16), 1.369(6). Selected bond angles (°): F(1)−Sn-O(10), 175.21-(11); F(1)−Sn-C(1), 87.30(17); F(1)−Sn-C(2), 87.17(14); F(1)−Sn-C(3), 85.94(14); O(10)−Sn-C(1), 97.36(17); O(10)−Sn-C(2), 91.56(15); O(10)−Sn-C(3), 90.78(14); C(1)−Sn-C(2), 118.2(2); C(1)−Sn-C(3), 119.5(2); C(2)−Sn-C(3), 121.4(2); Sn−F(1)−B, 130.9(3); Sn−O(10)−C(10), 128.7-(3); O(10)−C(10)-C(11), 123.2(4); C(10)−C(11)-C(12), 119.5(4); C(10)−C(11)-C(16), 120.8(4).



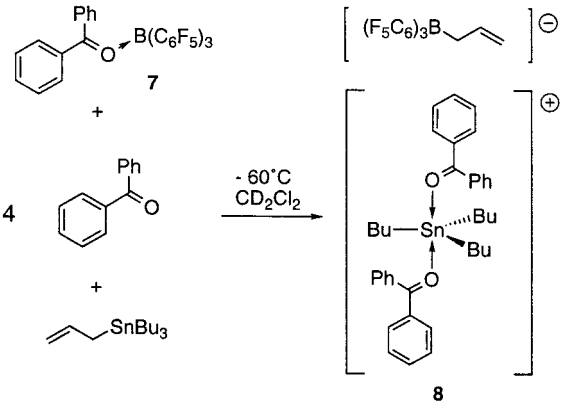
VII

≈0.08−0.09 Å relative to those to the nonbridging fluorine atoms. The parameters within the aldehyde ligand, (i.e., C(10)−O(10) = 1.233(5) Å vs 1.262(4), and C(10)−C(11) = 1.445(7) Å vs 1.418(5) Å) in comparison to the same ones in ***o*-3**, indicate that $B(C_6F_5)_3$ is perhaps slightly more activating than the $SnMe_3$•••FBF_3 species. To the extent that $[BF_4]^-$ is more coordinating than $[RB(C_6F_5)_3]^-$ or $[B(C_6F_5)_4]^-$, this compound is not a perfect model for the ion pair ***o*-5**, but it is clear that $[BF_4]^-$ coordination is favored over chelation by OMe in the ground state of this species. However, ^{119}Sn spectroscopy shows that addition of excess *ortho*-anisaldehyde to solutions of this compound yields the bis-aldehyde adduct of $[Me_3Sn]^+$ (^{119}Sn = 106 ppm) where presumably the BF_4^- anion is displaced.[54]

It thus appears that our initial postulate concerning the nature of this ion pair was inaccurate in a subtle way. For the relatively basic anisaldehyde substates, production of substrate stabilized tributylstannylium ions is indeed occurring but via allylation of borane activated substrate rather than borane abstraction of the allyl function from the tin reagent as originally proposed.[23] For these substrates, which bind the borane with equilibrium constants on the order of 10^4, there is not enough "free" borane present to activate the tin reagent in a kinetically efficient way. Furthermore, in aldehydes, the carbonyl carbon is more sterically open to nucleophilic attack. However, ion pair formation by borane activation of the allylstannane is a viable pathway for

(51) Me_3SnFBF_3 was generated in situ from Me_3SnCl and $AgBF_4$.
(52) Corey, E. J.; Lee, T. W. *Chem. Commun.* **2001**, 1321.
(53) Kolb, U.; Dräger, M.; Jousseaume, B. *Organometallics* **1991**, *10*, 2737. A detailed analysis in this paper fixes the Sn−F single bond distance at 1.96 Å.
(54) Addition of *ortho*-anisaldehyde to **6** results in a gradual upfield shift of the tin signal, indicating that the BF_4^- anion competes to some extent with the aldehyde for the second coordination site. The chemical shift of 106 assigned $[Me_3Sn(ortho\text{-anisaldehyde})_2]^+[BF_4]^-$ was recorded in the presence of a large excess of L and did not change with additional L.

Scheme 6



ionization for other, less basic (more sterically hindered) carbonyl functions such as ketones, as exemplified by benzophenone (Scheme 6). Here, the equilibrium constant for formation of **7** is estimated to be about 100[36] and the carbonyl carbon is less prone to nucleophilic allylation on a steric basis as well. Indeed, addition of allyltributylstannane to solutions of **7** in CD_2Cl_2 at −60 °C cleanly yields solutions of ion pair **8** where the ^{11}B resonance of −14.4 ppm and the ^1H NMR spectrum both match very closely those found for the anion in $[Bu_4N]^+[(C_3H_5)B(C_6F_5)_3]^-$. A sharp signal at 149.0 ppm in the ^{119}Sn NMR spectrum is consistent with a bis-ligated Bu_3Sn^+ cation, the downfield shift relative to ***o,o*-4** indicative of the lower basicity of benzophenone compared to *ortho*-anisaldehyde. Thus, the precise nature of the anion (the boron speciation) in the ion pairs generated under these conditions varies significantly depending largely on the Lewis base behavior and the steric properties of the substrate. Examination of these species using the full battery of NMR experiments available is necessary to accurately evaluate each case.

Relative Rates of Ion Pairs 4. Analogous experiments to those described above (Scheme 2) can be performed with *para*-anisaldehyde and a 1:1 mixture of the two substrate isomers and the rate of ion pair formation followed qualitatively by ^{19}F NMR spectroscopy. As summarized in Scheme 7, these experiments reveal that formation of ***o,o*-4** is much more facile than formation of ***p,p*-4**, that is, allylation of the coordinated aldehyde in ***o*-3** is significantly faster than that in ***p*-3**. Thus, for the *ortho* isomer, ion pair formation is complete after only 15 min at −60 °C (Figure 2 above, Scheme 7a), whereas the analogous reaction with the *para* isomer has only gone to 10% completion after 2 h under the same conditions (Scheme 7b). Even upon warming to −40 °C, a temperature at which the catalytic allylstannation of the *ortho* isomer ensues, ionization to ***p,p*-4** is slow, with about 60% conversion observed after 3 h. Furthermore, allylation catalysis for the *para* isomer is extremely slow in this temperature regime. At −20 °C, allylation ensues, albeit at a much slower rate than observed for *ortho*-anisaldehyde. Since the ion pair forming reaction occurring here is initiated by an allyation event, these observations again show that allylation of the substrate with the *ortho* donor substituent is substantially kinetically favored over that of the *para* isomer, even though the latter is actually the stronger Lewis base.

This is underscored by the results of the third experiment (Scheme 7c), where the initially observed mixture of ***o*-3** and ***p*-3** is completely converted to the mixture of aldehyde solvated stannylium/borate ion pairs ***o,o*-4**, ***o,p*-4**, and ***p,p*-4** over the course of 2 h. This is supported by the ^{119}Sn NMR spectrum of this sample, which shows three signals in a 1:2:1 ratio as would be expected for a statistical distribution of adducts (Figure 5).[55] However, while the cations produced are comprised of a mixture, the anion is, within the detection limits of ^1H NMR, solely derived from allylation of ***o*-3**; no alkoxyborate species arising from the *para*-isomer is observed. Thus, the ion pair formation is initiated by selective allylation of ***o*-3** and is driven to completion because the lability of the system allows for reestablishment of the equilibrium between ***o*-3** and ***p*-3** under these conditions.

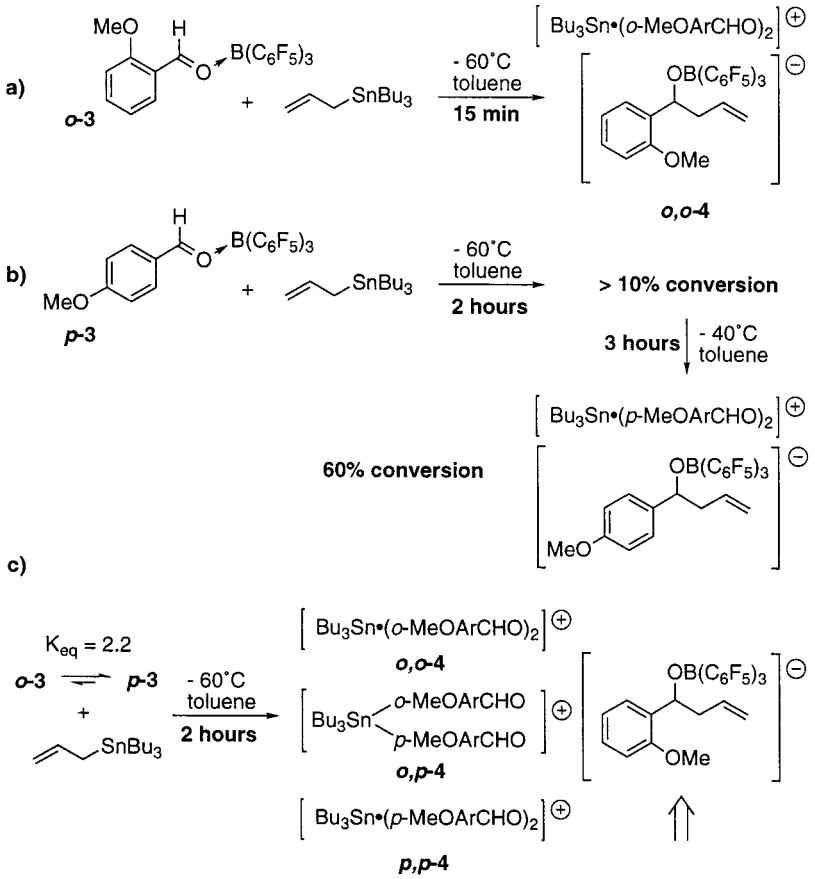
In our previous communication,[23] we speculated that the more rapid ionization observed for the *ortho*-substituted substrate might find its origin in a greater basicity of *ortho*-anisaldehyde toward "Bu_3Sn^+", possibly because of chelation, providing the basis for an explanation of the remarkable chemoselectivity observed for this reaction. However, in light of the more detailed tin and boron speciation studies described above, this initial postulate is something of a "red herring". As the ^{119}Sn NMR spectrum in Figure 5 shows, there is little if any bias for either of the two substrates in the coordination of "Bu_3Sn^+". Also, the selective formation of the *ortho*-anisyl substituted alkoxyborate anion illustrates that the bias toward substrates with *ortho* donor substitutents is independent of whether the Lewis acid is $B(C_6F_5)_3$ or "Bu_3Sn^+"; therefore, an explanation for selective allylation which does not feature chelation control of any stripe must be proffered.

Mode of Product Formation and the Role of the Alkoxyborate Counteranion. Before addressing the origin of the chemoselectivity, one more aspect of the catalytic cycle for allylation needs to be considered, namely, the product-generating step in the reaction. The small $\Delta_{m,p}$ values of 2.8−3.1 ppm in the ^{19}F NMR spectra for ion pairs **4** suggest that the alkoxyborate counteranion is not associated with the stannylium cation in a significant way, that is, it is effectively insulated from the tin center by the two aldehyde substrate molecules. The question arises as to whether **4** is *directly* involved in the dominant catalytic cycle for production of the allylated stannyl ether product. That is, does the ion pair ***o,o*-4** collapse to give product and regenerate the borane adduct ***o*-3** via an alkoxide group exchange, or does the anion essentially remain a spectator during the course of catalysis, with "Bu_3Sn^+" serving as the "true" Lewis acid catalyst in the reaction. This question was addressed by allowing solutions of ***o,o*-4**, generated as described above, to warm to temperatures where allylation is facile both in the presence and absence of excess allyltin reagent.

In the presence of excess allyl tin reagent, which is obviously most reflective of the conditions under which catalysis occurs, stannyl ether product formation turns over smoothly upon warming to −40 °C in CD_2Cl_2. As this reaction is monitored by ^{19}F NMR spectroscopy, no change is observed in the signals because of the alkoxyborate anion, and no other signals for either $B(C_6F_5)_3$ or ***o*-3** appear. When ***o,o*-4** is generated without excess allylstannane present and allowed to warm to −40 °C, no product formation is observed even after several hours, that is, this ion pair is stable in the absence of allyltin reagent. Further warming to −20 °C results in some formation of stannyl ether product, but only slowly (≈60% complete after 60 min). The

(55) The lower temperature is required to fully resolve the three different adducts, which are exchanging on the NMR time scale at −60 °C.

Scheme 7



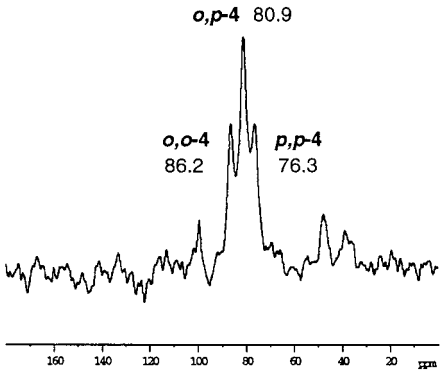
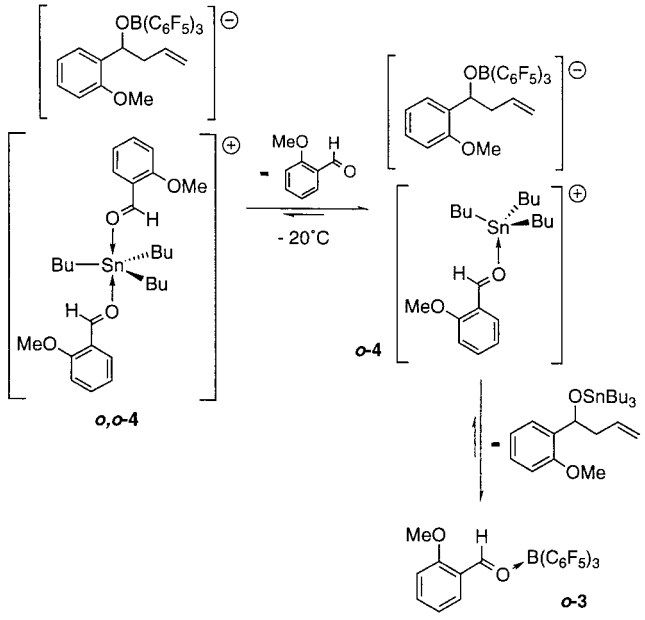


Figure 5. 149.2 MHz ^{119}Sn NMR spectrum (−80 °C, C_7D_8, 2 h) of a 1:1 mixture of *ortho*-anisaldehyde and *para*-anisaldehyde and $B(C_6F_5)_3$ after treatment with one equivalent of $C_3H_5SnBu_3$ at −60 °C for 2 h. Under identical conditions, the chemical shifts for separately prepared samples of ***o,o*-4** (86.5 ppm) and ***p,p*-4** (76.1 ppm) closely match those found for these species in the mixture.

mode of product formation under these conditions is not known precisely, but likely involves dissociation of a coordinated *ortho*-anisaldehyde ligand, followed by transfer of the alkoxide group from the borate to the stannylium cation[56] (Scheme 8). The observation of ***o*-3** in the ^{19}F NMR spectrum at these higher temperatures is consistent with this notion. We also observed that when these solutions of ***o,o*-4** are treated with a further five equivalents of *ortho*-anisaldehyde, the rate of stannyl ether product generation by this route is significantly inhibited at −20

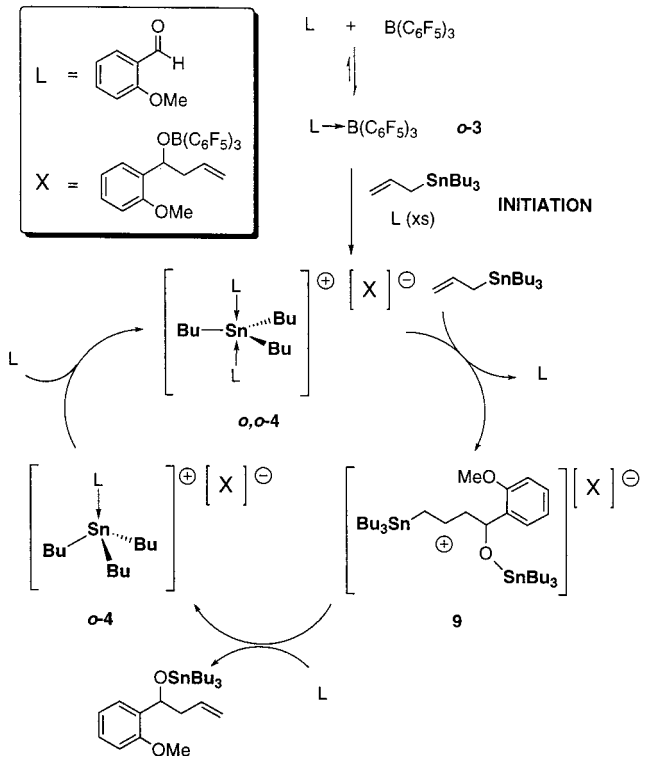
Scheme 8



°C (≈6% complete after 60 min). Taken together, these results show that the rate of stannyl ether formation via this route is much slower than direct allylation of substrate coordinated to "Bu_3Sn^+" and suggest that the bulk of the allylation catalysis is mediated by the substrate-coordinated stannylium ion when excess allylstannane is present. The alkoxyborate anion, formed upon initiation, apparently remains a spectator through the reaction under these conditions, that is, low temperatures and excess allyltin reagent.

(56) Transfer of an alkoxide group to electrophilic metallocenium cations is a common decomposition pathways for ion pairs of general formula $[Cp_2Zr(R)]^+[R'OB(C_6F_5)_3]^-$. See, for example, Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Schroepfer, J. N. *Polyhedron* **1990**, *9*, 301.

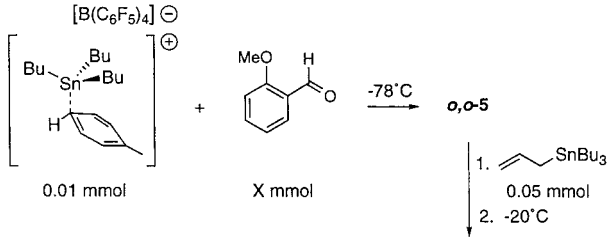
Scheme 9



A mechanistic picture for the Lewis acid catalyzed allylstannation of substituted aromatic aldehydes such as *ortho*-anisaldehyde akin to that shown in Scheme 9 has emerged from these studies. The reaction is initiated by allylation of adduct ***o*-3** to form stannylium ion pair ***o,o*-4**. As demonstrated for benzophenone, less basic or more sterically hindered substrates may induce direct allyl abstraction by the borane to form ion pairs with $[(C_3H_5)B(C_6F_5)_3]^-$ anions (i.e., **8** above); however, the cationic species produced is of the same general type, namely, the bis-ligated $[R_3Sn(L)_2]^+$ cation. It is this species which undergoes further allylation, giving the ion pair **9** which generates product stannyl ether via reaction with *ortho*-anisaldehyde as shown in the Scheme. The mono-ligated intermediate ***o*-4**, for which the spectroscopically characterized ***o*-5** provides support, is probably very short-lived in the presence of excess substate, capturing another substrate L to regenerate the bis-ligated stannylium catalyst. This rapid capture of ***o*-4** also prevents collapse of the ion pair via alkoxide transfer from boron to tin (Scheme 8).

Experimental support for ion pair **9** was obtained by allowing ***o,o*-4** to react with two equivalents of allyltributyltin, a reaction which produces one equivalent of stannyl ether product and a new ion pair which is stable in CD_2Cl_2 solution at room temperature for several hours. ^{1}H, ^{19}F, and ^{11}B NMR spectroscopy show that the anion is the alkoxyborate species $[o\text{-ArCH(allyl)OB}(C_6F_5)_3]^-$ (*o*-Ar = *ortho*-anisyl) analogous to that found in ***o,o*-4**. The cation appears to be the $[Bu_3Sn]^+$ stannylium ion ligated by the other equivalent of stannyl ether product formed in this reaction, that is, the cation of **9**. This is supported by the ^{119}Sn NMR spectrum observed for this reaction, which, in addition to exhibiting a somewhat broadened signal for the stannyl ether product at 104.5 ppm, shows two very broad signals for the tin nuclei in the cation at 211−229 and 240−266 ppm.[57] Interestingly, this ion pair can also be generated

Scheme 10



time (min)	percentage completion X = 0.1	0.2	0.3	1.0
10	30	33	38	24
15	37	40	45	36
20	42	46	51	44
25	48	51	56	48
30	53	56	61	52

cleanly by reacting the stannyl ether product with 0.5 equivalents of $B(C_6F_5)_3$ supporting its formulation as $[o\text{-ArCH(allyl)OB}(C_6F_5)_3]^-[Bu_3Sn\bullet o\text{-ArCH(allyl)OSn}Bu_3]^+$.[58] Addition of further substrate/allyltin to a cooled (−60 °C) solution of **9** results in rapid regeneration of ***o,o*-4**, which is stable at this temperature; upon warming to −40 °C stannyl ether product formation resumes smoothly as the catalytic allylation ensues. The precise structure of **9** is unknown and the structure shown in Scheme 9, though reasonable, is speculative.

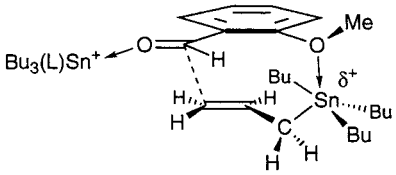
Origin of Selectivity for *Ortho*-Substituted Substrates. While it is tempting to invoke some sort of chelation control to account for the superb selectivity for *ortho*-substituted aldehydes, several observations discredit such a rationale. Most importantly, the selectivity is general for several Lewis acids, including boron-based reagents where chelation is not likely an option as discussed in the Introduction. Second, on the basis of NMR and structural studies for adduct ***o*-3** and ion pairs **4**, **5,** and **6**, these substrates do not appear to readily engage in chelating bonding modes in the ground state even for larger tin-based Lewis acids. It is possible, of course, that chelation is an important feature of a transition structure. For example, a mechanistic alternative to Scheme 9 would involve ligand dissociation from ***o,o*-4** or ***p,p*-4** to form the mono-ligated ion pairs, which are allylated selectively because of the greater activation of the substrate when only one ligand is coordinated. We considered the possibility that such a dissociative event might be more facile for the *ortho*-substituted substrates. Full kinetic analysis to determine the rate dependence on [*ortho*-anisaldehyde] was experimentally difficult, but a qualitative sense of this feature was obtained via the series of experiments depicted in Scheme 10. Using Lambert's stannylium ion $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ as a catalyst (20% based on added allyltributyltin), allylation reactions using various amounts of added *ortho*-anisaldehyde were monitored by ^{1}H NMR spectroscopy over time. As indicated in the Table in Scheme 10, the rate of product formation was not significantly affected by excess

(57) The broadening of these signals is likely due to dynamic exchange between free and bound stannyl ether; when **9** is generated in the absence of free stannyl ether product, the signals centered around 220 and 240 ppm are much sharper.

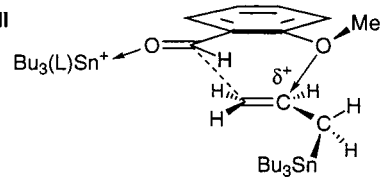
(58) This observation also shows that this ion pair is thermodynamically favored over free stannyl ether and $B(C_6F_5)_3$ *in the absence* of substrate *ortho*-anisaldehyde, at least in methylene chloride. Thus, the transfer of RO^- from this non-nucleophilic alkoxyborate anion to the stannylium cation is thermodynamically disfavored when there are no Lewis bases present to drive the reaction by formation of, in this case, ***o*-3**. The remarkable thermal stability of **9** at room temperature also attests to this notion.

substrate, the reactions being about 57(4)% complete after 30 min in all cases. In other words, it is unlikely that (chelation-assisted) ligand dissociation is required for allylation of ***o,o-5*** to occur.[59]

Assuming that this bimolecular allylation reaction occurs via an antiperiplanar transition state (**I**),[9] we propose that the *ortho* donor group in these substrates plays a role in stabilizing the developing positive charge either at tin (**VIII**) or at the allyl β-carbon (**IX**) as the allyl group is delivered.[60] This selectivity



VIII



IX

argument accounts for the nonspecific nature of this chemoselectivity vis-à-vis the Lewis acid. The actual mode of stabilization of developing positive charge may be a combination of **VIII** and **IX**; however, we favor structure **IX** since it is less chemically cumbersome in that this mode of stabilization involves a six-membered ring as opposed to the eight-membered ring of structure **IX**. Also in structure **IX**, in addition to the stabilization provided by the *ortho* methoxy group, the transition state may be further stabilized via the hyperconjugation mechanism which is a key feature of antiperiplanar allyl addition.[9] Although plausible, these structures are to a large extent speculative and await computational studies to place them on firmer footing.

Conclusions

Although the LA catalyzed allylstannation of carbonyls is an established and versatile method for C−C bond formation, it is a mechanistically complex process for which general mechanistic schemes are difficult to construct. The studies described herein underscore the complicated nature of even prototype reactions with a well defined and behaved LA such as $B(C_6F_5)_3$. We have shown that, within this system, even small changes in substrate or reaction conditions can alter the chemistry in subtle but significant ways. A full study using all the analytical techniques available is therefore required to determine what is happening in reacting solutions. Thus, while it is tempting to make general conclusions, it is clear that these reactions need to be examined on a case-by-case basis to make accurate assessments concerning the operative mechanism. Nonetheless, for the $B(C_6F_5)_3$ catalyzed reactions, these studies have brought to light various possibilities for boron and tin speciation during the reactions, information which is valuable in, for example, the design of stereoselective reactions of this type.

In terms of practical utility, the selectivity observed toward substrates with *ortho* donor substituents is potentially exploitable for organic synthesis. Its origin remains somewhat obscure, but we can conclude that it likely does not have anything to do with a chelating function for this *ortho* donor group, at least not in the classical sense as originally proposed by Maruoka et al.[14,16] In our opinion, the donor group most likely plays a stabilizing role in the transition state for C−C bond formation by dampening positive charge build-up within the allyl tin reagent as it is delivered, and the invoking of hypercoordinate boron structures must be received with caution.

Experimental Section.

General. All manipulations of air- and moisture-sensitive materials were undertaken using standard vacuum and Schlenk techniques or in a glovebox under an atmosphere of nitrogen. All solvents were dried and purified by passing through suitable drying agents (alumina and Q5)[61] and stored in evacuated pots over titanocene[62] or Na/benzophenone. ^{1}H NMR spectra (300 or 400 MHz) in CD_2Cl_2 were referenced versus residual $CHDCl_2$ (5.32 ppm at all temperatures). ^{13}C NMR spectra (100 MHz) were referenced versus CD_2Cl_2 (54.0 ppm at all temperatures). ^{119}Sn NMR spectra (149.2 MHz) were referenced externally versus Me_4Sn (0.0 ppm at all temperatures). ^{11}B NMR spectra (128 MHz) were referenced externally versus BF_3•OEt_2 (0.0 ppm at all temperatures). ^{19}F NMR spectra (282 MHz) were referenced externally versus C_6F_6 (−163 ppm at all temperatures). CD_2Cl_2 and C_7D_8 were purchased from Cambridge Isotopes and rigorously dried then distilled from CaH_2 and Na/benzophenone, respectively. $B(C_6F_5)_3$ was purchased from Boulder Scientific and dried and sublimed prior to use. Both *ortho*- and *para*-anisaldehyde were purchased from Aldrich and distilled before use. $Ph_3CB(C_6F_5)_4$ was received as a generous gift from NOVA Chemicals (Calgary, Alberta). $AgBF_4$, Bu_4NBr, Me_3SnCl, Bu_3SnH, and $C_3H_5SnBu_3$ were purchased from Aldrich and used as received.

Preparation of Ion-Pair *o,o*-4. An NMR tube was charged with $B(C_6F_5)_3$ (34 mg, 0.067 mmol) and *ortho*-anisaldehyde (27 mg, 0.20 mmol) and CD_2Cl_2 (approximately 500 μL). The sample was cooled to −78 °C and allyl$SnBu_3$ (10 μL, 0.67 mmol) was added via syringe. The reaction mixture was shaken once and placed in the NMR probe precooled to −60 °C. ^{1}H and ^{19}F NMR spectra were obtained. ^{119}Sn, ^{11}B, and ^{13}C NMR spectra were obtained at −60 °C on a sample prepared analogously. Very minor resonances can be observed for the stannyl ether, (*ortho*-anisyl)CH(allyl)O$SnBu_3$, and *ortho*-anisaldehyde, $B(C_6F_5)_3$, but one set of signals attributed to ***o,o*-4** dominates the spectra. ^{1}H NMR: (cation) 10.10 (br s, 2H, C*H*O), 7.87 (d, 2H, J = 8.0 Hz), 7.78 (app. t, 2H, J = 7.7 Hz), 7.12−7.05 (m, 4H), 3.95 (s, 6H), 1.70−1.20 (m, 18H), 0.87 (t, J = 6.8 Hz); (anion) 7.29 (d, 1H, J = 7.3 Hz), 6.91 (app. t, 1H, J = 7.2 Hz), 6.72 (app. t, 1H, J = 7.3 Hz), 6.44 (d, 1H, J = 8.0 Hz), 5.54 (ddd, 1H, J = 7.0, 10.1, 17.0 Hz), 4.87−4.68 (m, 3H), 3.53 (s, 3H), 2.80−2.68 (m,1H), 2.38−2.25 (m, 1H); ^{13}C NMR: (cation) 195.5 (br., *C*HO), 164.2 (br.), 141.5 (br.), 129.3 (br.), 121.7 (br), 120.9 (br), 112.3 (br), 56.1 (br), 27.7 ($^2J_{C-Sn}$ = 29.2 Hz), 26.9 ($^3J_{C-Sn}$ = 76.6 Hz), 18.2 ($^1J_{C-Sn(119)}$ = 391.0 Hz, $^1J_{C-Sn(117)}$ = 408 Hz, *C*H_2Sn), 13.6 (*C*H_3); (anion) 154.7, 147.4 (dm, C−F), 137.5 (dm,

(59) (a) A reviewer has suggested that preferential trimerization of *para*-anisaldehyde to form the trioxane may account for the difference in the rates of allylation observed. While we were aware that Denmark had observed this phenomenon for acetaldehyde,[12g] we observed no spectroscopic evidence for such a trimerization under any of the conditions employed. In particular, ^{1}H NMR spectroscopy showed only the presence of monomeric aldehydes (free and bound); no signals in the region 4.7−4.9 ppm were observed. Furthermore, very little literature precedent exists for the trimerization of benzaldehydes.[59b] Therefore, it is extremely unlikely that this occurs to the extent necessary to explain the large difference in allylation rates for these two substrates. (b) Zhu, Z.; Expenson, J. H. *Synthesis* **1998**, 417.

(60) This proposal is related to one first put forward by Yamataka and coworkers in a related study in which the observed rates of allylation were higher for *ortho* halogen substituted benzaldehydes: Yamataka, H.; Nishikawa, K.; Hanafusa, T. *Chem. Lett.* **1990**, 1711.

(61) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(62) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.

C−F), 136.3, 135.7 (dm, C−F), 134.9, 127.6, 126.0−123.5 (br m, *ipso* Ar_f), 125.7, 119.1, 114.8, 107.7, 67.4, 54.3, 44.7; ^{19}F NMR: −133.0, −164.0, −167.1; ^{119}Sn NMR: 90.5; ^{11}B NMR: −4.5 ppm.

Preparation of Mono- and Bis-*ortho*-Anisaldehyde Adducts of $[Bu_3Sn]^+[B(C_6F_5)_4]^-$, *o*-5 and *o,o*-5. A solution of *ortho*-anisaldehyde was prepared by dissolving aldehyde (54 mg, 0.4 mmol) in 200 μL of C_7D_8. 100 μL (0.2 mmol of *ortho*-anisaldehyde) of this solution was added via syringe to an NMR tube containing ion pair $[Bu_3Sn]^+$-$[B(C_6F_5)_4]^-$ prepared as above. NMR analysis of the oily layer at −60 °C shows a ^{119}Sn NMR signal at 300.5 ppm. The remainder of the solution (0.4 mmol of *ortho*-anisaldehyde total) was then added and a ^{119}Sn NMR shift of 91.0 ppm was observed. Further NMR characterization by ^1H and ^{13}C NMR spectroscopy was carried out at −60 °C on the mono- and bis-*ortho*-anisaldehyde adducts of "Bu_3Sn^+" by adding CD_2Cl_2 solutions of *ortho*-anisaldehyde to $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ prepared analogously but starting with 0.10 mmol of $Ph_3CB(C_6F_5)_4$. ***o*-5**: ^{119}Sn NMR: 298.6; ^1H NMR: 10.0 (C*H*O), 8.05 (br s), 7.94 (br s), 7.20 (br s), 7.07 (br d, J = 6.7 Hz), 4.00 (s, 3H, OCH_3), 1.94−1.45 (m, 18H), 1.20−1.09 (br m, 9H); ^{13}C NMR: 198.3 (*C*HO), 166.8 (br), 148.2 (d, J = 241 Hz, C−F), 145.4 (br), 142.0 (br), 138.4 (d, J = 245 hz, C−F), 136.4 (d, J = 246 Hz), 130.3 (br), 126.0−122.0 (br, *ipso* Ar_f), 121.8 (br), 121.3 (br), 113.0, 56.5, 27.7, 27.4 ($^3J_{C-Sn}$ = 72.0 Hz), 19.9 (br, *C*H_2Sn), 13.8 (*C*H_3). ***o,o*-5**: ^{119}Sn NMR: 91.1; ^1H NMR: 10.30 (s, 2H, C*H*O), 8.08 (d, 2H, J = 7.7 Hz), 7.88 (app. t, 2H, J = 8.0 Hz), 7.23 (app. t, 2H, J = 7.2 Hz), 7.10 (d, 2H, J = 8.5 Hz), 4.02 (s, 6H), 1.97−1.85 (6H), 1.79−1.69 (6H), 1.69−1.55 (6H), 1.17 (t, 9H, J = 7.4 Hz); ^{13}C NMR: 195.7 (*C*HO), 164.5, 148.3 (d, J = 240 Hz), 141.5, 138.5 (d, J = 245 Hz), 136.6 (d, J = 245 Hz), 129.5 (br), 126.0−122.0 (br, *ipso* Ar_f), 122.2, 121.3, 112.5, 56.1, 28.2 ($^2J_{C-Sn}$ = 29.2 Hz), 27.3 ($^3J_{C-Sn}$ = 75.2 Hz), 18.6 ($^1J_{C-Sn(119)}$ = 390.2, $^1J_{C-Sn(117)}$ = 408.0, *C*H_2Sn), 13.9 (*C*H_3).

Preparation of Ion-Pair 9. (a) Addition of $B(C_6F_5)_3$ to Stannyl Ether. $B(C_6F_5)_3$ (51 mg, 0.10 mmol) in CD_2Cl_2 was added slowly via syringe to an NMR tube (at −78 °C) containing stannyl ether (0.20 mmol) prepared as described above. The sample was placed in the NMR probe at −60 °C and ^1H and ^{19}F NMR spectra showed that reaction occurred immediately leading to a new ion pair with the following spectral data measured at −60 °C. ^1H NMR: (cation) 7.50 (t, 1H, J = 8.0 Hz), 7.07 (app. t, 1H, J = 7.3 Hz), 6.99 (d, 1H, J = 8.3 Hz), 5.77−5.64 (m, 1H), 5.30−5.20 (m, 3H), 3.88 (s, 3H), 2.82−2.52 (m, 2H), 2.65−2.50 (m, 1H), 2.37−2.22 (m, 1H), 1.50−1.10 (m, 36H, 0.86 (t, 18H, J = 7.2 Hz, CH_3); (anion) 7.30 (app. t, 2H, J = 7.0 Hz), 6.91 (app. t, 1H, J = 7.8 Hz), 6.72 (app. t, 1H, J = 7.3 Hz), 6.43 (d, 1H, J = 8.2 Hz), 5.59−5.45 (m, 1H), 4.87−4.68 (m, 3H), 3.52 (s, 3H); ^{13}C NMR: (cation) 158.4, 127.7, 124.4, 121.1, 120.6, 111.4, 77.0, 55.7, 38.5, 27.6 ($^2J_{C-Sn}$ = 21.6 Hz), 27.4 ($^3J_{C-Sn}$ = 82.8 Hz), 20.1 ($^1J_{C-Sn(119)}$ = 303.6 Hz, $^1J_{C-Sn(119)}$ = 317.4 Hz, *C*H_2SnBu$_3$), 13.6 (*C*H_3); (anion) 154.9, 147.5 (d, J = 239 Hz), 137.7 (d, J = 240 Hz), 136.4, 135.1, 135.8 (d, J = 245 Hz), 127.5, 126.0−122.0 (br, *ipso* Ar_f), 125.7, 119.2, 114.8, 107.8, 67.5, 54.4, 44.7; ^{19}F NMR: −133.2, −163.6, −166.8; ^{119}Sn NMR: 266−240 (br), 229−211 (br); ^{11}B NMR: −4.4.

(b) Addition of AllylSnBu$_3$ to *o,o*-4. An NMR tube was charged with $B(C_6F_5)_3$ (34 mg, 0.67 mmol) and *ortho*-anisaldehyde (27 mg, 0.20 mmol) and CD_2Cl_2 (approximately 500 μL). The sample was cooled to −78 °C and allylSnBu$_3$ (31 μL, 0.20 mmol) was added via syringe. The NMR tube was shaken and allowed to warm to room temperature briefly. The sample was then placed in the NMR probe cooled to −60 °C. ^1H, ^{13}C, ^{19}F, and ^{11}B NMR analysis at −60 °C all supported the presence of the anion [(*ortho*)-anisylCH(allyl)OB-$(C_6F_5)_3]^-$. ^1H and ^{13}C NMR spectroscopy for stannyl ether were extremely broad indicating that free and bound stannyl ether are in rapid exchange. ^1H NMR: (cation) 7.50−7.25 (br s, 4H), 7.00 (br s, 2H), 6.90 (br s, 2H), 5.85 (br s, 2H, C*H*=CH_2), 5.12 (br s, 6H, CH=CH_2, C*H*OSn), 3.83 (br s, 6H, OCH_3), 2.75−2.30 (br, 4H), 1.60−1.10 (br, 36H), 0.86 (t, 18H, J = 6.6 Hz); (anion) 7.33 (d, 1H, J = 7.3 Hz), 6.93 (app. t, 1H, J = 8.2 Hz), 6.75 (app. t, 1H, J = 7.2 Hz), 6.45 (d, 1H, J = 8.0 Hz), 5.55 (ddd, 1H, J = 7.0, 10.1, 17.1 Hz, C*H*=CH_2), 4.87−4.68 (m, 3H, CH=CH_2, C*H*OB), 3.54 (s, 3H, OCH_3), 2.85−2.73 (m, 1H, C(H_a)H_bCH=CH_2), 2.40−2.26 (m, 1H, C(H_b)-H_aCH=CH_2); ^{13}C NMR: (cation) 156.0, (br), 126.9 (br), 120.5 (br), 110.0 (br), 55.3 (br), 27.8, 27.5, 20.0 (br), 13.7 (4 C's missing); (anion) 154.9, 147.5 (dm, J = 240 Hz, C−F), 137.7 (dm, J = 245 Hz, C−F), 136.5, 135.9 (dm, J = 246 Hz, C−F), 135.1, 127.8, 126.0−123.5 (m, *ipso* Ar_f), 125.8, 119.2, 114.9, 107.8, 67.6, 54.4, 44.8; ^{119}Sn NMR: 267−244 (br), 229−210 (br), 105.3; ^{11}B NMR: −4.5.

Other Procedures. A complete description of all the procedures used can be found in the Supporting Information, along with all spectroscopic characterization data for the compounds reported herein.

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Supporting Information Available: Complete experimental details, tables of crystal data, atomic coordinates, and bond lengths and angles and anisotropic displacement parameters for *ortho*-$C_6H_4(F)CHO{\bullet}B(C_6F_5)_3$ and *ortho*-$C_6H_4(OMe)CHO{\bullet}SnMe_3$-$BF_4$, **6** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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