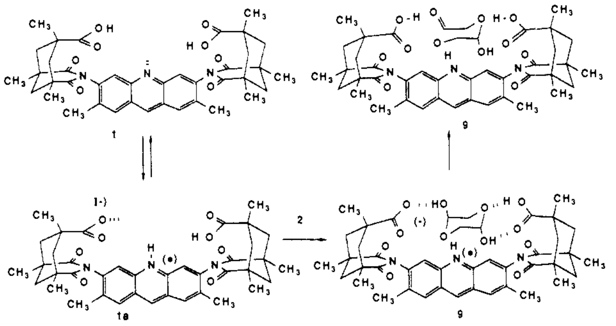
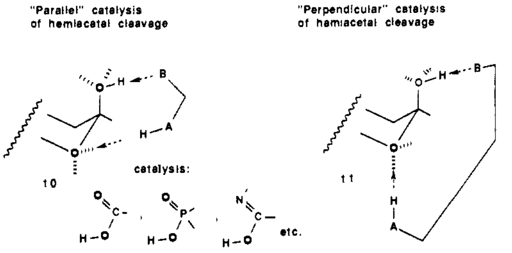
a catalyst, and the dimerization rate is first order in the catalyst. Again, the other acids and bases of Table I are quite ineffective for the dimerization reaction.

Why is **1** such an effective catalyst for this reaction? One possibility, suggested in eq 4, involves complexation before reaction in a micromolecular version of enzymatic catalysis. Binding of a hemiacetal function to a carboxylic acid of **1** brings the other hemiacetal into contact with both acidic and basic groups. The latter are poised for general acid–base catalysis in the concerted sense suggested in **8** → **9**.



(4)

Since **1** is known[2b] to exhibit zwitterionic character (as in **1a**), the assignment of acid and base roles is ambiguous. Even so, the proposal of eq 4 incorporates favorable stereoelectronic effects at carboxyl oxygen.[9] Specifically, the syn lone pair of the carboxylate can accept the proton of the hydroxyl while the ethereal oxygen accepts a proton from acridine nitrogen. Alternatively, the carboxylic acid protonates the ethereal oxygen, while the acridine nitrogen acts as the general base. Conventional concerted catalysis of mutarotation is likely to involve parallel approaches of acid (A–H) and base (B), as in **10**. While this mechanism may be operating in the case at hand, an intriguing additional possibility exists in **1** for the *perpendicular* approach of the two components as in **11**. Such an arrangement is expected to reduce the anomeric effect and thereby weaken the endocyclic C–O bond. In any event, the convergence of acid and base sites is unique to **1**. Other model systems for such reactions are constrained by their shapes to involve the less basic anti lone pair of the carboxylate.[10]



While the present system provides appropriate molecular shape, its activity may be specifically suited to **2** (or other substrates which can be bound within the cleft). For example, **1** shows no activity in the mutarotation of tetramethyl glucose beyond that expected for typical carboxylic acids, and CPK models show that binding a substrate of this size within the cleft of **3** does not favor the convergence of the acid–base functions in an appropriate sense for reaction. Indeed a complex is formed with **1** and tetramethyl glucose which is unreactive, i.e., modest inhibition is observed. This result underlines the importance of having the correct orientation of functional groups in the substrate–catalyst complex. Our present efforts are directed toward the construction of systems that are more general in which molecular recognition and stereoelectronic effects are appropriately combined.

Acknowledgment. We are grateful for financial support from the National Institutes of Health and the Spanish State of Valencia for a fellowship to A.C. We are also pleased to acknowledge helpful commentary from Professor Rich Gandour.

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On the Lewis Acid Induced Addition of Allylstannanes to Aldehydes: A Spectroscopic Investigation

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The addition of allylic stannanes to aldehydes,[2] ketones,[3] acetals,[4] enones,[5] imines,[6] allylic alcohols,[7] and other functions[8] is a powerful carbon–carbon bond-forming reaction. The process is also of current interest in the context of acyclic stereoselection.[2a,9] In all of these reactions a Lewis acid (e.g., $BF_3{\cdot}OEt_2$, $TiCl_4$, $MgBr_2$, or $SnCl_4$) is employed presumably to activate the electrophilic function toward nucleophilic attack by the allylic organometallic reagent. Our previous studies in this area have served to illustrate the importance of the structure of the Lewis acid–aldehyde complex in determining the stereochemical course of intramolecular allylmetal–aldehyde condensations.[10] Nonetheless, the possibility that the Lewis acid first reacts with the allylmetal generating a new species prior to addition could not be ruled out, Scheme I. Indeed the possibility of metathetical processes has been discussed by Tagliavini,[11a] Keck,[11b] and Yamamoto[11c] based on product analysis. Furthermore, Tagliavini[11a,12a] and Gambaro[12b] have extensively studied ligand exchange to prepare allylchlorostannanes for additions to aldehydes and ketones. Herein, we report the first *direct evidence* for interaction between the *Lewis acid and the allylic stannane in the presence of the substrate aldehyde*.

All of the studies involved direct ^{13}C NMR (75.5 MHz) observation of reactions carried out in $CDCl_3/CD_2Cl_2$ 1:1 at 0.5 M between −80 and +20 °C. As control experiments we first carried out the reactions between allyltrimethylstannane (**1**) and the Lewis acids $BF_3{\cdot}OEt_2$ and $SnCl_4$. It has been known for some time that both Me_4Sn[13a] and $(allyl)_4Sn$[13b] undergo ligand exchange with $SnCl_4$ rapidly at 25 °C. However, we have found that *metathesis of either **1** or $(allyl)_4Sn$ with $SnCl_4$ is instantaneous and quantitative at −80 °C*. The only detectable products are $allylSnCl_3$ and Me_3SnCl. On the other hand, the reaction of **1** with $BF_3{\cdot}OEt_2$ proved to be an enigma. Already at −80 °C the resonances for

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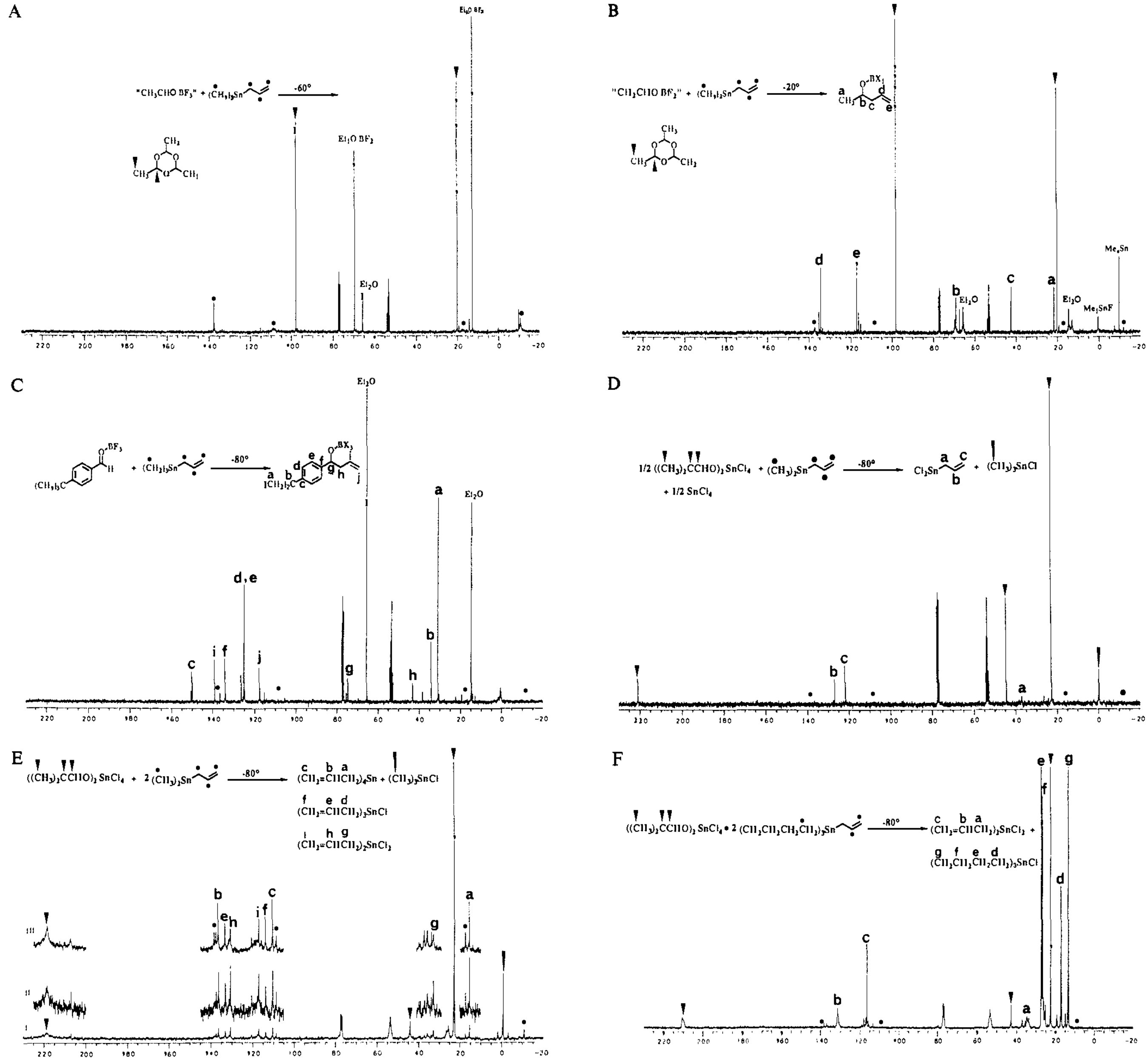
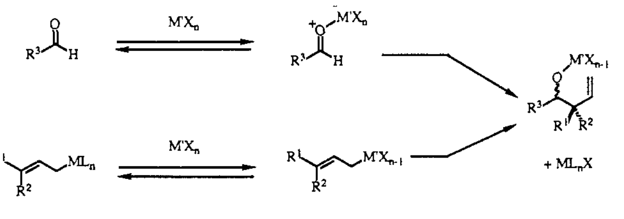


Figure 1. ^{13}C NMR spectra of reaction of **1** with **2** in the presence of BF$_3$·OEt$_2$ (A–C) and SnCl$_4$ (D–F).

Scheme I



C(3), C(1), and (CH$_3$)$_3$Sn– (108.49 δ, 17.41 δ, and −10.78 δ) broadened while that for C(2) (137.74 δ) remained sharp. At −20 °C only signals for C(2) (137.34 δ), Et$_2$O, and Me$_4$Sn (−9.71 δ) were visible. Upon recooling to −80 °C the ^{13}C NMR spectrum showed that the sample had undergone redistribution of the allyl groups. Thus signals for three different allyl species could be seen along with methyl resonances for Me$_4$Sn (−9.71 δ), **1** (−10.77 δ), and (allyl)$_n$Me$_{4-n}$Sn (−11.85 δ).[14] The identical spectrum could be obtained by reaction of Me$_4$Sn and (allyl)$_4$Sn with BF$_3$·OEt$_2$ (−80 °C → +20 °C → −80 °C). The absence of formation of Me$_3$SnF·BF$_3$ (0.7 δ) excludes the possibility of extensive metathesis to allylBF$_2$. The available data[15] are most consistent with a rapid 1,3-shift of the Me$_3$Sn group by a process involving BF$_3$·OEt$_2$ which also labilizes the allyls for bimolecular exchange to another tin center.

Reference spectra were also obtained for the Lewis acid complexation of the three test aldehydes, acetaldehyde (**2a**), pivaldehyde (**2b**), and 4-*tert*-butylbenzaldehyde (**2c**) (Table I). The complexation with SnCl$_4$ was quantitative; no free **2** was detected at −80 °C.[10b] The results with BF$_3$·OEt$_2$ were surprisingly dependent upon aldehyde structure. For example, in the presence of BF$_3$·OEt$_2$, **2a** existed in a highly temperature dependent equilibrium with its trimer, paraldehyde ((**2a**)$_3$). At −80 °C only the trimer was detected, which began to dissociate at ca. −40 °C. At +20 °C only monomeric species were detected. Trimerization of **2b** was also seen at −80 °C (ca. 10%). Interestingly, the remaining **2b** was not associated with BF$_3$. Aromatic aldehyde **2c** represented a third case as it existed as a ca. 1:1 mixture of free and BF$_3$-complexed monomers.

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(14) The methyl resonances for $n = 2$ and 3 may be coincident with other signals. Three different sets of allyl groups were clearly visible.

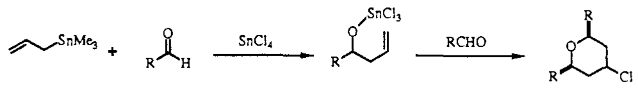
(15) ^{1}H NMR spectra revealed the same behavior in which the terminal methylenes broadened to the base line, while H–C(2) remained a clean quintuplet centered at 5.87 δ. This behavior is reminiscent of the "permanent" allylic rearrangement in allylboranes: Mikhailov, B. M. *Russ. Chem. Rev.* **1976**, *45*, 557.

Table I. Control Experiments with **2a**, **2b**, and **2c**[a]

aldehyde	Lewis acid	temp, °C	
		−80	20
2a	$BF_3{\cdot}OEt_2$	100% trimer[b]	free and complexed **2a**,[c] no trimer
2a	$SnCl_4$	100% complexed **2a**	100% complexed **2a**
2b	$BF_3{\cdot}OEt_2$	10% trimer,[d] free **2b**	weakly complexed **2b**
2b	$SnCl_4$	100% complexed **2b**	100% complexed **2b**
2c	$BF_3{\cdot}OEt_2$	complexed **2c**/**2c** (44:56)[e]	[f]
2c	$SnCl_4$	100% complexed **2c**	100% complexed **2c**

[a] All reactions were run at 0.5 M in $CDCl_3/CD_2Cl_2$ (1:1) with 1 equiv of Lewis acid. [b] Paraldehyde. [c] Trace contamination by crotonaldehyde. [d] Obtained by integration of the ^1H NMR signals for trimer ($\delta(CH_3)_3C$ 0.78 ppm) versus **2b** (υ $(CH_3)_3C$ 0.97 ppm). [e] Obtained by integration of the ^1H NMR signals for the complex (δ CHO 9.93 ppm) versus **2c** (δ CHO 9.55 ppm). [f] Signals broad due to rapid exchange.

Scheme II



3

The condensation reactions were performed by addition of **1** (neat) to a −80 °C solution of precomplexed **2a–c**. In all reactions equimolar amounts of **1** and **2** were used. The results are shown in Figure 1; spectra A–C are the $BF_3{\cdot}OEt_2$-induced reactions. For **2a** the −80 °C spectrum was a clean superposition of **1** and $(\mathbf{2a})_3$. At −60 °C (spectrum A) the redistribution of **1** is clearly occurring in the presence of $(\mathbf{2a})_3$ without reaction. The product, 4-penten-2-ol,[16] was first evident at −20 °C (as $(\mathbf{2a})_3$ began to dissociate) and was the dominant species at 0 °C (spectrum B). It is noteworthy that the product was formed as diastereomeric boron ethers; Me_3Sn ethers were never detected. In contrast, reaction of **1** with **2b** showed immediate formation of products at −80 °C, together with $(\mathbf{2b})_3$ which persisted to 20 °C. Finally reaction of **1** with **2c** (spectrum C) was complete upon mixing at −80 °C! Thus, the extent of reaction depends upon the degree of trimerization at −80 °C (**2a** > **2b** > **2c**), which in turn affects the extent of $BF_3{\cdot}OEt_2$-catalyzed redistribution of **1**.

The results of reaction of **1** with $SnCl_4$-complexed aldehydes fundamentally differed from those with $BF_3{\cdot}OEt_2$. These reactions are highly sensitive to temperature and stoichiometry.[17] The first series of experiments employed a 1:1 stoichiometry of **2** and $SnCl_4$ which by ^1H, ^{13}C, and ^{119}Sn NMR analysis constituted an equimolar mixture of $(\mathbf{2})_2$ $SnCl_4$ and free $SnCl_4$.[18] For **2a**, **2b**, and **2c** the *metathesis of **1** to allyl$SnCl_3$ was instantaneous and quantitative at −80 °C with little evidence of addition.* The reaction with **2b** (spectrum D) is illustrative. The presence of Me_3SnCl and the unreacted aldehyde was clearly seen in all cases. Only in the case of **2a** could signals due to the addition product be detected at −80 °C. As the samples were warmed signals for the addition product appeared and were replaced (−40 °C → 20 °C) by signals for the chloropyrans **3**, Scheme II.[12b] A second series of experiments using a 2:1 stoichiometry of **2** and $SnCl_4$ (no free $SnCl_4$) gave different results. With **2a**, complete addition was observed as low as −95 °C. Thus, while traces of metathesis products were also observed, their intermediacy in the addition cannot be established. For **2b** and **2c** *only metathesis of **1** without addition was observed as evidenced by the immediate formation of Me_3SnCl.* Now, however, the metathesis products were different ((allyl)$_4$Sn, (allyl)$_3$SnCl, (allyl)$_2$SnCl$_2$)).[19] Spectrum E (**2b**) clearly shows the conversion of **1** to Me_3SnCl within 3–4 min (traces i and ii (4×)). After 10 min (trace iii) the allylchlorostannanes and **2b** are still present. A final series of experiments with $(\mathbf{2b})_2{\cdot}SnCl_4$ and $(\mathbf{2c})_2{\cdot}SnCl_4$ and allyltributylstannane (allylBu_3Sn) was performed at −90 °C to confirm our observations. In both cases the allylBu_3Sn was instantaneously consumed, and only allyl$_2SnCl_2$ and Bu_3SnCl were detected (within 5 min) as products (see spectrum F for $(\mathbf{2b})_2{\cdot}SnCl_4$).

In summary we have demonstrated that (1) with $BF_3{\cdot}OEt_2$, a ligand redistribution of **1** may occur depending upon the amount of trimeric aldehyde present under the reactions conditions and (2) with $SnCl_4$, **1** is not involved in aldehyde additions when free $SnCl_4$ is present, and metathesis with fully complexed $SnCl_4$[20] is demonstrably faster than addition in most if not all cases. Studies on the behavior of allylic silanes and (*E*)- and (*Z*)-2-butenylmetals with $SnCl_4$ and other Lewis acids will be the subject of future reports.

Acknowledgment. We are grateful to the National Science Foundation (Grants NSF CHE 82-08565 and 85-15371) for support of this research. We thank Professor Gary E. Keck (University of Utah) for informative discussions.

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[16] Authentic samples of all homoallylic alcohol products as well as their Me_3Si, Me_3Sn, and Cl_3Sn ethers were prepared.

[17] (a) Similar observations have been made by Professor Gary E. Keck (University of Utah). (b) To assure full complexation of $SnCl_4$ a 5–10% excess of **2** was used. To assure temperature control the precooled solution (2 mL) of the complex $(\mathbf{2})_2{\cdot}SnCl_4$, in a 10-mm NMR tube, was carefully layered with neat **1**, then reintroduced to the probe, the equilibrated at the desired temperature without spinning. Reaction was initiated by vortexing the solution at 70 rps. The results of these experiments did not differ from externally shaking the solution. We thank Professor Keck for suggesting this technique and for providing the experimental details.

[18] This is seen in the ^{119}Sn NMR spectrum which shows signals for both $SnCl_4$ (−156 ppm) and $(\mathbf{2a})_2{\cdot}SnCl_4$ (−571 ppm), $(\mathbf{2b})_2{\cdot}SnCl_4$ (−572 ppm), or $(\mathbf{2c})_2$ $SnCl_4$ (−585 ppm).

[19] The same mixture could be generated by mixing (allyl)$_4$Sn and $SnCl_4$ at room temperature in a 3:1 ratio. Only upon standing at room temperature for 3 days did (allyl)$_3$SnCl form completely. Mixing these reagents in a 1:1 ratio produced only (allyl)$_2$SnCl$_2$.

[20] For a thorough study of the mechanism of ligand exchange in L_2SnCl_4 complexes, see: Knight, C. T. G.; Merbach, A. E. *Inorg. Chem.* **1985**, *24*, 576.

[Th^{III}{η^5-$C_5H_3(SiMe_3)_2$}$_3$], an Actinide Compound with a 6d^1 Ground State

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The free ion of trivalent thorium [Th(III)] has a 5f^1 ground state electronic configuration whose center of gravity is 9897 cm^{-1} below the center of gravity of the excited state 6d^1 configuration. The 7s^1 level is at 23 120 cm^{-1} while the 7p$_{1/2,3/2}$ levels are found at energies greater than 60 000 cm^{-1} above the ground state.[1] Although the free ion spectrum of the isoelectronic ion Pa(IV) is not known, the difference between the centers of gravity of the ground state 5f^1 configuration and the excited state 6d^1 configuration for this ion is estimated to be ~50 000 cm^{-1} from the interpolation of the known free ion data for the isoelectronic series Ra(I), Ac(II), Th(III), and U(V).[2,3] Optical spectra of Pa(IV)/$ThBr_4$ and [$PaCl_6^{2-}$] showed that the lowest 5f^1 → 6d^1 crystal field transition appeared at ~20 000 cm^{-1}.[4,5] Two factors con-

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