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Spectroscopic Studies on the Structure and Conformation of Lewis Acid–Aldehyde Complexes

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Abstract: The complexation of aldehydes with $SnCl_4$ and BF_3 has been studied spectroscopically. It was determined by HOESY analysis that the aldehyde·$SnCl_4$ complexes examined prefer the *E* geometry. This preferential complexation is likely due to steric influences from the substituents on the aldehyde. A qualitative assessment of the relative basicity of various substituted aldehydes was also determined. It was found that both 2-heptynal and *n*-heptanal were significantly weaker Lewis bases than either (*E*)-2-heptenal or 4-*tert*-butylbenzaldehyde. The difference in basicity between (*E*)-2-heptenal and 2-heptynal is thought to arise from the electronegativity of the sp carbon atom. Finally the conformation of Lewis acid complexed and neutral (*E*)-2-heptenal was studied in solution. When complexed to either BF_3 or $SnCl_4$ or even uncomplexed, (*E*)-2-heptenal was determined by 1D-NOE studies to be in the s-trans conformation.

Introduction

The formation of a complex between a donor and an acceptor is one of the most fundamental processes in chemistry. In 1923 G. N. Lewis provided the framework for understanding this process in modern terms and it remains the best definition 70 years hence "... with complete generality we may say that a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom, and that an acidic substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms."[1] Indeed, the domain of coordination chemistry is founded on this principle and consequently the concepts of Lewis acidity and basicity have been exhaustively studied and quantified.[2] Within the domain of organic chemistry this process is most commonly associated with the complexation of (basic) heteroatomic functional groups by main group, transition metal, and lanthanide-based Lewis acids. Because of its central role in organic structure and reactivity the family of carbonyl functional groups (aldehyde, ketone, acid, ester, amide, etc.) has been scrutinized in some detail.

It has been known for many years that coordination of the Lewis basic carbonyl group by a Lewis acid enhances the electrophilic reactivity of the carbonyl carbon.[3] This phenomenon has played a crucial role in the development of mild nucleophilic reagents (e.g. organosilanes) for carbon–carbon bond formation.[4] Further, the dramatic accelerating effect of Lewis acids on the powerful Diels–Alder reaction of α,β-unsaturated carbonyl compounds[5] has stimulated enormous interest in the stereochemical and reactivity consequences of carbonyl complexation.

Our interest in this area began a number of years ago in our studies on the origins of stereocontrol in the allylmetal–aldehyde condensation.[6] The pronounced dependence of stereochemistry on the nature of the Lewis acid activator emphasized the importance of understanding, in detail, the structure of the Lewis acid carbonyl complex. This paper describes the solution structure and relative stability of Lewis acid complexes of various types of aldehydes (aliphatic, aromatic, olefinic, etc.) by variable-temperature, heteronuclear NMR spectroscopy. In addition, we have established the solution conformation of a complexed α,β-unsaturated aldehyde.

Background

Preparative. The complexation of carbonyl compounds by Lewis acids is an important prerequisite for many carbon–carbon bond forming reactions containing those functional groups.[7] In addition to serving an electronic activating function, the Lewis acid moiety can also provide a sterically significant component to the stereochemical outcome of the reaction. In both of these capacities, the geometry of the complex is critical. In most transformations it is assumed that the Lewis acid will coordinate to the carbonyl compound in an anti fashion in simple aldehydes and in a syn fashion in α-heterosubstituted aldehydes.[8] The stereochemical consequences of the geometry of Lewis acid complexation have been invoked to explain the observed selectivities in several reactions including the following: (1) the addition of nucleophiles to substituted cyclohexanones,[9] (2) intramolecular allylsilane and allylstannane additions to aldehydes,[6] (3) the addition of enolsilanes[10] and allysilanes[11] to α-heterosubstituted

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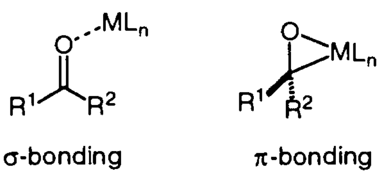

Figure 1. Bonding modes for Lewis acid–carbonyl complexes.

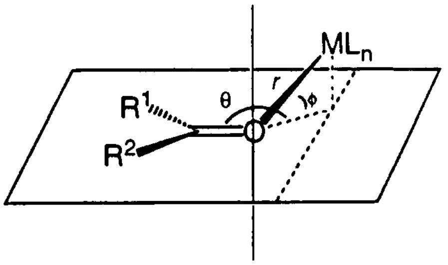

Figure 2. Geometrical descriptors for Lewis acid–carbonyl complexes.

aldehydes, (4) the addition of α-alkoxystannanes to aldehydes,[12] (5) hetero-Diels–Alder reactions,[13] (6) asymmetric Diels–Alder reactions,[14] and (7) a recently developed Lewis acid mediated asymmetric aldol reaction.[15]

Structural.[16] The structure of the Lewis acid–carbonyl complex influences the local environment of the reactive carbonyl carbon in a number of ways: (1) mode of coordination, (2) location of the Lewis acid, and (3) conformational preferences for the groups adjacent to the carbonyls. There are two limiting modes of complexation of carbonyl groups: σ-type or π-type (Figure 1). In general π-type complexation is only found for electron rich transition metal complexes,[17] though the σ–π equilibrium is influenced by the electronic nature of the aldehyde.[17b] One exception is the $TiCl_4$ complex of acryloyllactate in which chelation enforces a π-complexation of the ester.[18] For the most part main group, early transition, and lanthanide-based Lewis acids are believed to coordinate in a σ-fashion. In the σ-mode, the Lewis acid can be located in many different positions, e.g. in-plane bent, in-plane linear, out-of-plane, etc. The position of the Lewis acid can be defined by the three variables r, the Lewis acid–oxygen distance, and two angles, θ and ϕ (Figure 2).[16] The angle ϕ represents the elevation of the Lewis acid with respect to the plane of the aldehyde. The angle θ is the C–O–M angle or the projection of the M–O vector onto the carbonyl plane.

All crystallographically defined σ-complexes of aldehydes with Lewis acids are planar ($\phi = 0$) and bent.[19] The structures shown in Figure 3 represent the various classes of complexes. In all cases, the observed coordination geometry corresponds to an (*E*)-type complex wherein the Lewis acid is trans to the aldehyde residue (Table I).

The uniformity of geometrical details of complexation is remarkable considering the diversity of central atoms (B, Sn, In, W), coordination geometries (tetrahedral, trigonal bipyramidal, octahedral), and stoichiometries (1:1, 2:1, 3:1). The *p*-(dimethylamino)benzaldehyde Ph_2SnCl_2 complex **4** was the first reported structure and is the only trigonal-bipyramidal complex.[20] The 1:1 complexation is common for complexes of alkyl and aryl tins.[21]

The X-ray crystallographic analysis of $SnCl_4 \cdot$(4-*tert*-butylbenzaldehyde)$_2$ (**5**) has been determined in our laboratories.[6c] Unlike the 1:1 complex of Ph_2SnCl_2, the complex with $SnCl_4$ consists of two aldehydes disposed cis to one another around the octahedrally coordinated tin atom. The tin atom lies in the plane of the carbonyl group for both of the aldehydes and is in the (*E*)-complex geometry with each aldehyde (i.e. anti to the aromatic ring). This 2:1 stoichiometry was also observed in solution by ^{119}Sn, ^{1}H, ^{13}C NMR spectroscopy. Only one species was observed spectroscopically which corresponds to the 2:1 complex. A recent disclosure from our laboratories has demonstrated (with *n*-heptanal and 4-*n*-heptylbenzaldehyde) that the 2:1 complexes are the only observable species even in the presence of excess $SnCl_4$. The X-ray crystal structure of $SnCl_4 \cdot$(benzaldehyde)$_2$ has been determined by Reetz.[22] This 2:1 complex has a distorted octahedral geometry similar to that exhibited by **5**. The (*E*)-complexation geometry was again observed and the two aldehydes are cis disposed on the octahedral geometry.

The X-ray structure of $BF_3 \cdot$benzaldehyde (**6**) clearly shows the BF_3 unit to be located syn to the hydrogen of benzaldehyde.[23] The boron atom lies in the same plane of the almost planar benzaldehyde molecule with a B–O bond length of 1.591 Å. Very recently, the X-ray structure of $BF_3 \cdot$2-methylacrolein was reported and it too conforms to the general trends identified here, namely a planar B–O–C unit in the (*E*)-configuration ($\theta = 123.8°$).[24]

The tungsten-based complex $[(Me_3P)(CO)_3(NO)(acrolein)W]^+SbF_6^-$ (**7**)[25] is one of several structurally defined transition metal complexes of an α,β-unsaturated aldehyde.[26] The carbonyl is σ-coordinated with geometrical features similar to those of the main group complexes ($\theta = 137.1°$). Moreover, the structure provides clear evidence for the preferred s-trans conformation of the α,β-unsaturated aldehyde unit in the solid state. This corroborates an ab initio computational study of the conformation of complexed enals (vide infra).

The indium complex $InCl_3 \cdot$(benzaldehyde)$_3$ (**8**) has three benzaldehyde molecules bonded in an octahedral geometry.[27] Each of the three aldehyde molecules is unique, though the variation in bonding details is small.

Surprisingly, few studies have addressed the structure of Lewis acid–aldehyde complexes in solution. In one of the most extensive studies on record, Childs has evaluated the complexation of α,β-unsaturated aldehydes with various Lewis acids and established a relative Lewis acidity scale from an analysis of the chemical

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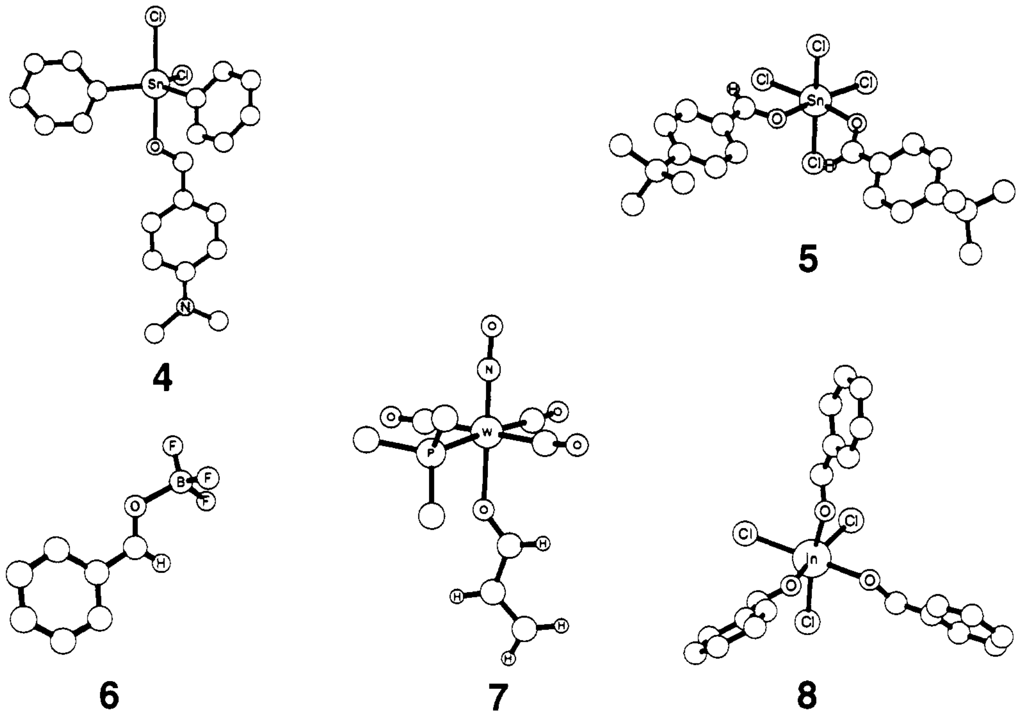


Figure 3. X-ray crystal structures of Lewis acid–aldehyde σ-complexes.

Table I. Geometric Data for X-ray Structures

angle	4	5	6	7	8
ϕ, deg	5.2	3.2[a]	3.1	0.7	2.5[b]
θ, deg	121.7	127.1[a]	118.2	137.0	126.1[b]

[a] Average of two values. [b] Average of three values.

shifts.[28] These authors assumed an s-trans, (E)-complex conformation, though this was not explicitly established. A landmark study by Forsén established the nonlinear complexation of cyclic ketones by the use of low-temperature ^{13}C NMR spectroscopy.[29] In addition, Azzaro has examined the complexation of conformationally rigid α,β-unsaturated ketones.[30] These investigations established that complexation occurs in a nonlinear fashion on the sterically least encumbered side of the oxygen.

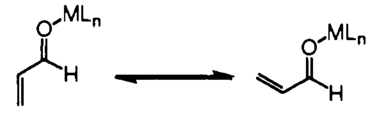
The structure of the BF_3·benzaldehyde complex (**6**) was also studied in solution by the use of a heteronuclear Overhauser experiment (HOESY).[22] In this experiment, the fluorine atoms were irradiated, leading to a 5% enhancement of the aldehyde proton resonance, but causing no affect on the aromatic protons. This result suggests that the (E)-complex was preferred, but it does not rule out small amounts of the syn isomer which may be in equilibrium with the trans isomer.

In a recent study, Faller has shown that the equilibrium of syn/anti complexation geometries in $[HC(py)_3M(NO)_2(\eta_1\text{-aldehyde})](SbF_6)_2$ (M = M, W) is dependent on the aldehyde structure. On the basis of the magnitude of $^3J_{W-H}$ it was concluded that the concentration of the (Z)-complex is greater for α,β-unsaturated aldehydes than for aromatic aldehydes.[26]

The structure of aldehyde complexes has been extensively examined computationally.[31] In general, the ground-state conformation has a bent geometry, though it has been noted that linear complexes are preferred for cationic Lewis acids or Lewis acids capable of π-type overlap. Wiberg has studied, inter alia, the complex of propanal with BH_3 by ab initio methods and has determined that the (E)-complex is favored over the (Z)-complex by 2.5 kcal/mol.[32] The structures of BF_3·acetaldehyde and BF_3·benzaldehyde (**6**) were examined by MNDO methods.[22] For both, the bent anti geometry was found to be the ground state (θ = 133.6° and 132.9°, respectively) with the bent syn geometry slightly higher in energy, 1.8 and 2.5 kcal/mol, respectively.

In an attempt to shed light on some anomalous results obtained in the reaction of α-alkoxyallylstannanes with aldehydes,[12] Gung has recently re-examined the structure of several BF_3·aldehyde complexes using ab initio molecular orbital methods.[33] The results from this study indicate that the syn complex of BF_3 and acetaldehyde is only 1.22 kcal/mol less stable than the corresponding anti complex. For benzaldehyde the syn complex was found to be 5.31 kcal/mol less stable than the corresponding anti complex.

The final factor to be addressed is the effect of the Lewis acid upon the ground-state conformational preference of the carbonyl group. Although this issue has been considered in the context of sp^3-sp^2 conformational preferences for α-substituted aldehydes,[34] our interest focused on the sp^2-sp^2 conformational preferences in α,β-unsaturated carbonyl compounds where the possibility of s-cis or s-trans conformers exists.



Free acrolein is found to prefer the s-trans over the s-cis conformation by approximately 2 kcal/mol according to microwave[35] and ultraviolet[36] spectroscopy and ultrasonic[37] studies.

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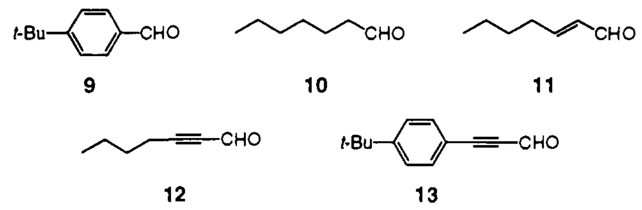
Chart I



This has also been found computationally using molecular mechanics[38] as well as ab initio methods.[39] The rotational barrier between the s-trans and the less stable s-cis conformer has been measured to be between 4.0 and 6.6 kcal/mol by ultrasonic[34] and microwave[40] studies, though a higher number (8.9 kcal/mol) was found computationally.[36c] When complexed (H^+, Li^+, BH_3, BF_3) the conformation of acrolein does not change. Indeed, the s-trans conformation was preferred even more strongly (3.2 kcal/mol) and the rotational barrier also increases to 12 kcal/mol.

The X-ray crystal structure of the tungsten acrolein complex **6** clearly illustrates the preference for the s-trans conformation in the solid state.[23] The same s-trans conformation was found for the $SnCl_4\cdot$(ethyl cinnamate)$_2$ complex.[41] In this structure a trans-octahedral 1:2 complex was observed. In the complex the cinnamate group was found to adopt an s-trans conformation and the Sn was located syn to the double bond. However, the acrylate group in the $TiCl_4$ complex of acryloyllactate[18] exists in an s-cis conformation. The most recently reported study by Corey has established the s-trans conformation of the $BF_3\cdot$2-methylacrolein complex persists in solution at −70 °C.[24]

The goal of this study was to provide a thorough investigation of the solution structure of Lewis acid–aldehyde complexes. We hoped to determine if the (*E*)-complexes were preferred both in solution and the solid state for a variety of aldehydes. We were also interested in establishing the relative strength of the complexes formed between various aldehydes and $SnCl_4$ and to obtain therefrom a qualitative assessment of the relative basicity of the various aldehydes.

Results

Solution Structure and Geometry of Lewis Acid–Aldehyde Complexes. The solution structure of Lewis acid–aldehyde complexes was studied using $SnCl_4$ and BF_3 as the Lewis acids and the various aldehydes shown in Chart I. These aldehydes were chosen because they represent a wide range of substrates from simple aliphatic to aromatic. A solution of the aldehyde in dichloromethane-d_2 was cooled to −80 °C and 0.5 equiv. of $SnCl_4$ was added to form the 2:1 complex. In all of the experiments with $SnCl_4$, the 2:1 complex (aldehyde to $SnCl_4$) was the only species observed. In a recently published study we showed by ^{13}C NMR spectroscopy that the 2:1 complex is the only coordinated species present upon combination of **9** and **10** with 0.25–1.0 equiv of $SnCl_4$.[6e] Further evidence for the presence of only the 2:1 complex was obtained from the ^{119}Sn NMR spectra. For all of the aldehydes studied the chemical shift of the tin resonance indicated that an octahedrally coordinated tin atom was present. The following chemical shifts were recorded for the $SnCl_4$ complexes: 4-*tert*-butylbenzaldehyde (**9**) 582.5 ppm; *n*-heptanal (**10**), 572 ppm; (*E*)-2-heptenal (**11**), 582.6 ppm; 2-heptynal (**12**), 582.5 ppm; and 3-(4-(1,1-dimethylethyl)phenyl)-2-propynal (**13**), 573.4 ppm. To establish the geometry of the Lewis acid–aldehyde complexes, a 2D heteronuclear Overhauser experiment (HOESY)[42] was used. In this experiment (closely related to the NOESY experiment) one nucleus undergoes excitation and evolution. A mixing period then follows where cross-relaxation with a second nucleus can occur. The change in *z*-magnetization of this second nucleus is then sampled by the spectrometer.

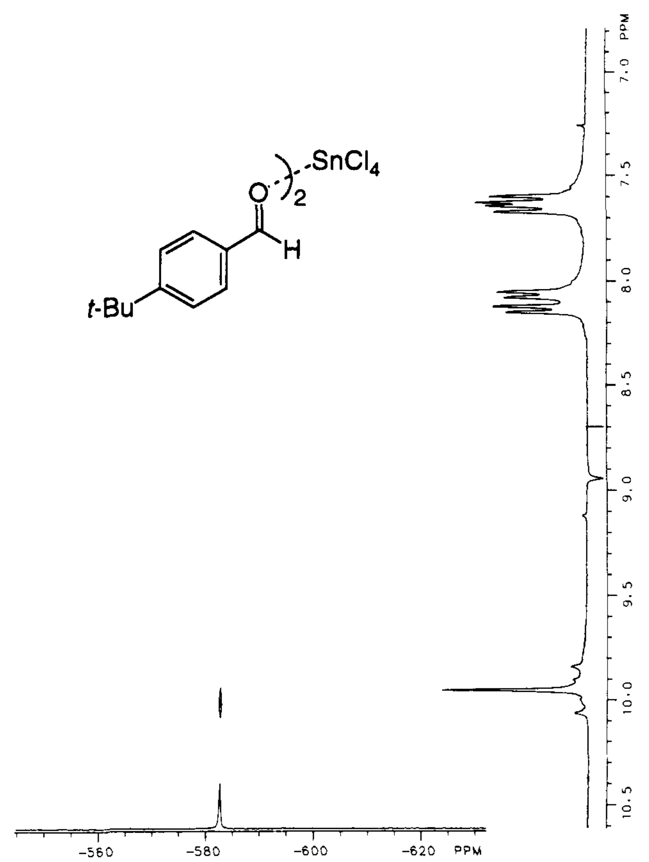


Figure 4. HOESY spectrum of $(9)_2\cdot SnCl_4$.

The HOESY spectra were all recorded at −100 °C. At this temperature (the lowest temperature accessible on our spectrometer) the ^{119}Sn resonances all appeared as relatively sharp lines. The aromatic (**9**), aliphatic (**10**), and (*E*)-olefinic (**11**) aldehydes exhibited a strong positive correlation between the ^{119}Sn resonance and the aldehyde proton. A representative 2D HOESY spectrum of $(9)_2\cdot SnCl_4$ is shown in Figure 4. Surprisingly, no correlations were observed with the acetylenic aldehyde **12** and $SnCl_4$. Since an octahedral 2:1 complex was detected by ^{119}Sn NMR, the lack of a correlation can be due to (1) a weak, dynamic complexation of **12** with $SnCl_4$, (2) strong complexation of a different geometry, or (3) strong complexation with rapid geometrical permutation. To distinguish these possibilities, we employed a deficiency of $SnCl_4$. When only 0.25 equiv of $SnCl_4$ was used with the acetylenic aldehyde **12**, a static 1:1 mixture of both complexed and uncomplexed aldehyde was observed as distinct sharp resonances by ^1H and ^{13}C NMR spectroscopy. This indicated that the complex formed with the acetylenic aldehyde **12** and $SnCl_4$ was of 2:1 stoichiometry and did not readily dissociate on the NMR time scale. Thus, the lack of a positive HOESY correlation suggests that species other than the

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Table II. Chemical Shift Differences on Complexation[a]

	$(\mathbf{9})_2SnCl_4$[d]			$(\mathbf{10})_2SnCl_4$[e]			$(\mathbf{11})_2SnCl_4$[f]			$(\mathbf{12})_2SnCl_4$[g]		
temp, °C	complex	neutral	$\Delta\delta$[c]	complex	neutral	$\Delta\delta$[c]	complex	neutral	$\Delta\delta$[c]	complex	neutral	$\Delta\delta$[c]
−100	199.72	192.61	7.11	219.89	204.23	15.66		195.38		187.96	178.33	9.63
−80	199.76	192.46	7.30	219.66	203.99	15.67		195.16		187.90	178.14	9.76
−60	199.77	192.29	7.48	219.42	203.66	15.76	202.51	194.89	7.62	187.71	177.84	9.87
−40	199.75	192.13	7.62	219.14	203.38	15.76	202.45	194.62	7.83	187.20	177.61	9.59
−20	199.67	191.97	7.70	218.68	203.08	15.60	202.36	194.35	8.01	186.08	177.37	8.71
0	199.44	191.79	7.65	217.83	202.81	15.02	202.25	194.10	8.15	184.25	177.15	7.10
20	198.86	191.63	7.23	215.93	202.51	13.42	202.07	193.81	8.26	181.43	176.90	4.53
40				213.66	202.58	11.38	201.75	193.58	8.17	179.33	176.70	2.63

[a] All complexes were prepared with 2 equiv of the aldehyde and 1 equiv of $SnCl_4$. [b] In CD_2Cl_2. [c] $\Delta\delta = \delta(\text{complex}) - \delta(\text{neutral})$; positive numbers are downfield shifts. [d] 0.10 M in aldehyde. [e] 0.30 M in aldehyde. [f] 0.30 M in aldehyde. [g] 0.15 M in aldehyde.

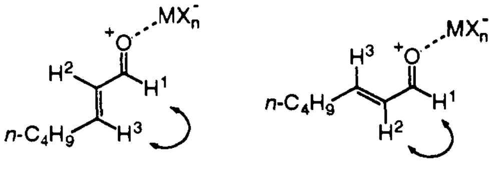
(*E*)-complex are present in solution. We then studied the complexation of acetylenic aldehyde **13**. This substrate was easily prepared from 4-*tert*-butylbenzaldehyde using a Corey–Fuchs reaction.[43] The complex formed with $SnCl_4$ and the aldehyde **13** now behaved like all of the other aldehydes. We observed a strong positive HOESY correlation with this aldehyde from the tin nucleus to the aldehyde proton. From these results we can conclude that complexation of $SnCl_4$ to the various aldehydes will occur exclusively in a trans relationship of $SnCl_4$ to the substituents on the aldehyde ((*E*)-complex).

Studies on the Magnitude of Complexation of Aldehyes with $SnCl_4$. Because of the importance of the aldehyde function we attempted to determine the relative basicity of the various aldehydes employed in this study. In these experiments, a solution of the aldehyde (**9**, **10**, **11**, and **12**) in CD_2Cl_2 was cooled to −80 °C and 0.5 equiv of $SnCl_4$ was added. The aldehyde–$SnCl_4$ complexes were cooled to −100 °C and ^{13}C NMR spectra were recorded at 10 or 20 deg C intervals. Shown in Table II is a compilation of the resonances for the neutral and complexed aldehydes as well as the chemical shift differences ($\Delta\delta$) of the carbonyl carbon (C(1)) from −100 to 40 °C. Assuming a linear relationship between change in chemical shift and the concentration of the complex it should be possible to determine the equilibrium constants for complexation. By plotting the temperature dependence of the chemical shift differences ($\Delta\delta$), we had hoped to obtain thermochemical data (K_{eq}) from these spectra. However, this was not possible because either (1) the complexes were too strong (**9**, **11**) and showed no temperature dependence or (2) the plots were nonlinear (**10**, **12**), indicating the other processes are occurring in solution. Nonetheless, the relative basicity of the complexes could still be estimated from these data by inspection of the onset temperature of dissociation.

For both 4-*tert*-butylbenzaldehyde (**9**) and (*E*)-2-heptenal (**11**), the chemical shift differences were temperature independent. At no time did either of these complexes (in dichloromethane) show any indication of dissociation as the temperature was increased. To extend the accessible temperature range, the solvent was changed to toluene. *Remarkably, even at 120 °C the complex* $(\mathbf{9})_2 \cdot SnCl_4$ *showed no signs of dissociation.* On the other hand, the complex $(\mathbf{11})_2 \cdot SnCl_4$ appeared to dissociate slightly when the temperature was raised above 40 °C in toluene. Unfortunately, when the temperature was raised above 60 °C the complex decomposed. A brown solid appeared and the signal-to-noise ratio of the ^{13}C resonances decreased dramatically.

The complexes formed between $SnCl_4$ and heptanal (**10**) or 2-heptynal (**12**) behaved qualitatively differently. For $(\mathbf{10})_2 \cdot SnCl_4$, a decrease in the chemical shift differences ($\Delta\Delta\delta$) of the carbonyl carbon (C(1)) was observed beginning at −20 to 0 °C. This decrease is indicative of a shift in the complexation equilibrium toward the free aldehyde. The acetylenic aldehyde **12** was examined next. For this complex, $(\mathbf{12})_2 \cdot SnCl_4$, the change in the chemical shift difference ($\Delta\Delta\delta$) for the carbonyl carbon (C(1)) was first observed between −40 and −20 °C.

Chart II



On the basis of onset-temperature for dissociation, as reflected in the decrease in chemical shift, the relative basicity for the various aldehydes could be estimated. The aromatic aldehyde, 4-*tert*-butylbenzaldehyde (**9**), and the α,β-unsaturated aldehyde, (*E*)-2-heptenal (**11**), were much stronger Lewis bases than the other two aldehydes. No appreciable change in the chemical shift differences ($\Delta\Delta\delta$) of the carbonyl carbons (C(1)) was observed even at 60 °C. For the aliphatic aldehyde **10** the dissociation began at a much lower temperature (−20 °C) and for the acetylenic aldehyde **12** lower still (−40 °C). We thus conclude the relative basicity order to be the following: $\mathbf{9} \approx \mathbf{11} >> \mathbf{10} > \mathbf{12}$.

Complexation of (*E*)-2-Heptenal with $SnCl_4$ and BF_3. The complexation of (*E*)-2-heptenal (**11**) with $SnCl_4$ was shown in the previous section to occur in a trans fashion ((*E*)-complex). The conformation of the α,β-enol unit (s-cis versus s-trans) remained to be established. By the use of difference NOE measurements, the conformation around the single bond can be determined (Chart II). When the complex is in an s-trans conformation the protons labeled H^1 and H^3 should exhibit a strong mutual NOE. If, instead, the complex is in an s-cis conformation the protons labeled H^1 and H^2 should exhibit a strong NOE between one another. Of course, a positive NOE will only indicate that the majority of the complex is in one conformation. The other conformer may still be present at low concentration in solution.

First, the difference NOE spectra were obtained for uncomplexed (*E*)-2-heptenal at −95 °C. Irradiation of H^1 resulted in a 14.0% NOE to H^3. Irradiation of H^2 resulted in no NOE to either H^1 or H^3. When H^3 was irradiated an NOE of 16.4% was observed to H^1. Therefore, at −95 °C the uncomplexed (*E*)-2-heptenal must reside primarily in the s-trans conformation (Chart III). All of the NOE results are collected in Table III.

The difference NOE spectra of (*E*)-2-heptenal complexed with $SnCl_4$ and BF_3(g) were then recorded. As before, to a solution of (*E*)-2-heptenal in dichloromethane-d_2 was added 0.5 equiv of $SnCl_4$. The three protons labeled H^1, H^2, and H^3 were individually irradiated and the resulting NOE's were measured. Irradiation of H^1 resulted in a strong −29.2% NOE to H^3. When H^2 was irradiated no NOE to either H^1 or H^3 was observed. Irradiation of H^3 again led to a strong NOE of −38.0% to H^1. These results indicate that the complex of $SnCl_4$ and (*E*)-2-heptenal is primarily in the s-trans conformation (Chart III). It is not unreasonable to expect negative NOE's in small molecules at low temperature where the solution may become viscous. Negative NOE's are

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(43) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.

Chart III

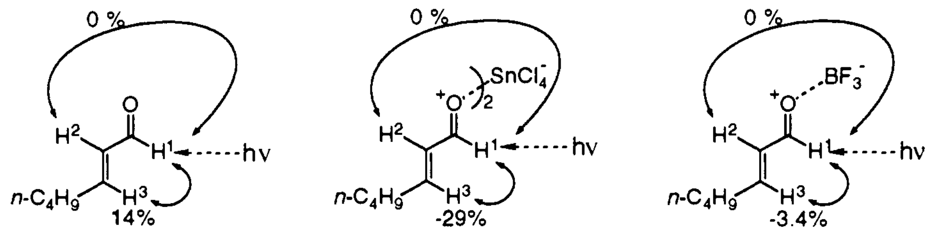

Table III. Summary of the NOE Data for *trans*-2-Heptenal

complex	temp.[b] °C	NOE (saturate/observe), %			
		H^1/H^3	H^3/H^1	H^2/H^1	H^2/H^3
11[a]	-95	14.0	16.4	0	0
$(\mathbf{11})_2 \cdot SnCl_4$[c]	-95	-29.2	-38	0	0
$(\mathbf{11}) \cdot BF_3$[d]	-95	-3.4	-3.3	0	0

[a] In CD_2Cl_2. [b] Calibrated probe temperature. [c] Complex formed by addition of 0.5 equiv of $SnCl_4$ to the aldehyde. [d] Complex formed by addition of $BF_3(g)$ (1.0 equiv) to the aldehyde.

often observed with a viscous solvent at low temperatures as they affect the rotational correlation time, τ_c, of the molecule.[44]

To determine the generality of this result the complexation of (*E*)-2-heptenal with 1.0 equiv of $BF_3(g)$ was studied. Irradiation of H^1 resulted in an NOE of -3.4% to H^3. When H^2 was irradiated no NOE was observed to either H^1 or H^3. Irradiation of H^3 resulted in an NOE of -3.3% to H^1 (Chart III). The magnitude of the NOE observed with $BF_3(g)$ was appreciably lower than that observed with $SnCl_4$. This is a result of the lower molecular weight of the BF_3–aldehyde complex. A lower molecular weight complex will have a smaller radius and will be able to tumble rapidly, changing the rotational correlation time, τ_c. From the results obtained with BF_3 and $SnCl_4$ it can be concluded that the (*E*)-2-heptenal–Lewis acid complex is in the s-trans conformation in solution.

Discussion

The solution structure of various $SnCl_4$–aldehyde complexes has been determined. In all of the aldehydes studied except the acetylenic aldehyde **12** (*E*)-complexation geometry was observed. The $SnCl_4$ is thought to complex the lone pair on oxygen adjacent to the aldehyde hydrogen in order to minimize steric repulsion. We had thought that the acetylenic aldehyde might not be as selective for the (*E*)-complex because of a lack of steric bias. Because of the weak nature of this complex we are unable to rule out the formation of both the (*E*)- and (*Z*)-complexes. In fact, a syn complex may be formed with this aldehyde, but it would not be possible to observe this by the HOESY experiment. No protons are located close to the carbonyl unit on the same side as the alkyne, therefore no correlations would be possible. In the complex formed with the aryl-substituted acetylenic aldehyde **13** the ortho protons on the aromatic ring may prevent cis complexation by interaction with the $SnCl_4$. Therefore, the complex formed with this aldehyde may not be a good representation of an alkynal·$SnCl_4$ complex.

The results obtained with $SnCl_4$ should be general for other Lewis acids, although the effective bulk of the $SnCl_4$ 2:1 complex would be greater. The hypothetical geometry of the (*Z*)-complexes with $SnCl_4$ and the various aldehydes could be approximated by importing the parameters from the crystal structure of **5**.[6c] It is clear that formation of a (*Z*)-complex in the more highly substituted aldehydes would be sterically unfavorable. The ortho protons would be ca. 4.6 Å away from the tin atom in the (*E*)-complex, while they are only ca. 1.8 Å away from the tin atom in the (*Z*)-complex.

For the acetylenic aldehyde **12**, complexation to either lone pair of the carbonyl group appears feasible by a similar analysis. The (*Z*)-complex of this aldehyde would not have the same steric interactions that are present in any of the other aldehydes studied. The effective bulk of the alkyne would not be much larger than a hydrogen.[45] The α-carbon of the acetylene is 3.4 Å from the tin atom in the (*Z*)-complex, while it is 4.6 Å away in the (*E*)-complex.

The relative basicity of the various aldehydes was established by a variable-temperature ^{13}C NMR study and the results provided some unexpected surprises. Both 2-heptynal (**12**) and *n*-heptanal (**10**) were found to be significantly weaker Lewis bases than (*E*)-2-heptenal (**11**) and 4-*tert*-butylbenzaldehyde (**9**). It is possible that the basicity of the acetylenic aldehyde is lower than the other aldehydes because of the electronegativity of the sp carbon atom.[46] Due to the greater percentage of s-character, an sp carbon atom is more electronegative than the corresponding sp^2 and sp^3 carbon atoms.[47] In addition, the alkynyl unit may inductively destabilize the partial positive charge on the carbonyl carbon compared to the vinyl or phenyl moieties. This is reflected in the lower stabilization energy of propargyl cation compared to allyl or benzyl cations as manifest in the higher heterolytic bond dissociation energy of the parent hydrocarbons (propyne, 271 kcal/mol; propene, 256 kcal/mol; toluene, 238 kcal/mol).[48] It is interesting to note that the heterolytic bond dissociation energy of *n*-propane (268 kcal/mol) is only slightly less than that of propyne. This supports the idea that the weak cation stabilizing effect of an alkyl chain is responsible for the low basicity of *n*-hexanal.

Through extensive spectroscopic studies Rabinovitz has shown that boron trifluoride forms a stable 1:1 σ-complex with a variety of aromatic aldehydes.[28a,49] This complex can act as a pseudosubstituent which can stabilize resonance forms containing a high π-bond character between the substituent and the ipso carbon in the ground state. Rabinovitz demonstrated that this pseudosubstituent ($-CHO \cdot BF_3$) is in fact an extremely strong electron withdrawing group. On the basis of these results it seems reasonable to assert that the aromatic and trans-olefinic aldehydes will be stabilized by resonance delocalization. No resonance stabilization is possible with the aliphatic aldehyde and it should thus be less Lewis basic as is observed. The qualitative scale established by these studies provides experimental support for

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(45) Taft and others have compiled an extensive set of data on the kinetics of ester hydrolysis. From these data a scale of steric effects has been developed which can be used to correlate rates of various reactions (E_s). Unfortunately, alkynes were not studied, but the nitrile group would be a close approximation. As an example, in this scale hydrogen is defined as 0, nitrile is -0.54, *n*-hexyl is -1.54, vinyl (CH=CH) is -2.84, and phenyl is ~3.8. For more E_S values see: (a) Unger, S. H.; Hansch, C. *Prog. Phys. Org. Chem.* **1976**, *12*, 91–118. (b) Gallo, R. *Prog. Phys. Org. Chem.* **1983**, *14*, 115–163. (c) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1952**, *74*, 3120. (d) Taft, R. W., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 4538. (e) Taft, R. W., Jr. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; John Wiley & Sons: New York, 1956; pp 556–675.

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the relative complex stabilities calculated by Gung.[30] According to theory, the complex formed with BF_3 and acetaldehyde is less stable than the corresponding complex formed with benzaldehyde.

Caveat. The results of this study are unambiguous in the establishment of the preferred conformation of Lewis acid–aldehyde complexes in solution, namely (*E*)-complexed and s-trans for α,β-enals. However, for precisely this reason it is essential to stress that this information should not be imported into transition state rationalizations nor designs for new Lewis acid catalysts.

The Curtin–Hammett principle[50] teaches us to consider the reactive conformation of the substrates and reagents as they might appear in the transition state ensemble. This is particularly relevant to several aspects of the Lewis acid–aldehyde complexes studied herein. First is the issue of σ-type vs π-type complexation. In a cleverly designed model, Corcoran has recently provided the first experimental evidence that additions to complexed carbonyls do not proceed through a small concentration of a highly reactive π-complexed isomer.[51a] However, these workers did find that Diels–Alder reaction of an enone may proceed faster through a π-complexed intermediate.[48b] This conclusion may not be general and there will need to be more experimentation for other reactions. Second, Gung[30] has proposed, on the basis of ab initio calculations, that the less stable syn isomer of BF_3·acetaldehyde is still energetically accessible and may be more reactive for certain types of additions. This, too, must be tested. Finally, a recent computational study by Houk[36b] showed that acrolein adopts the s-cis conformation upon Diels–Alder reaction with a diene thus overriding the ground-state preference for the s-trans conformation. This has also been suggested by Corey for catalyzed Diels–Alder reactions of 2-bromoacrolein.[52]

Our objective in this study was to call attention to the stereochemical significance of the Lewis acid moiety in promoted and catalyzed reactions. Although we examined equilibrium structures we want to stress the importance of (1) evaluating how these structures may change in going to transition state and (2) designing models to test the kinetic competence of various alternative structures.

Conclusions

The complexation of aldehydes with $SnCl_4$ has been studied spectroscopically. It was determined that the aldehydes examined prefer to form an (*E*)-complex with $SnCl_4$. This preferential complexation is likely due to steric influences from the substituents on the aldehyde. The relative basicity of the aldehydes was determined as follows: **9** ~ **11** > **10** >> **13** > **12**. The difference in basicity between (*E*)-2-heptenal and 2-heptynal is thought to arise from the electronegativity of the sp carbon atom. Finally the conformation of (*E*)-2-heptenal was studied in solution. When complexed to either BF_3 or $SnCl_4$ the α,β-unsaturated aldehyde moiety was observed by 1D-NOE studies to be in the s-trans conformation.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 200, 300, 400, or 500 MHz in $CDCl_3$ with $CHCl_3$ as an internal reference (7.26 ppm). ^{13}C NMR spectra were recorded at 75.5, 100.6, or 125.8 MHz in $CDCl_3$ solutions with $CHCl_3$ (77.0 ppm) as internal reference. Chemical shifts are reported in ppm (δ) and coupling constants (J) are reported in Hz. The NMR probe was calibrated for the VT experiments, thus the reported temperatures are corrected.[53] 2-Heptynal[54] and 3-(4-(1,1-dimethylethyl)-phenyl)-2-propynal[40] were prepared by literature methods.

NMR Studies. General Procedure for the Formation of $SnCl_4$–Aldehyde Complexes. Into an oven-dried 10-mm NMR tube sealed with a septum was added the aldehyde (0.8 mmol) by syringe. The tube was charged with $CDCl_3$ (2.0 mL) and CD_2Cl_2 (2.0 mL). The resulting solution was cooled to −80 °C and then placed into the probe of the NMR. Reference spectra at −80 °C were obtained and then freshly distilled, neat $SnCl_4$ was added to the solution, and the tube was gently swirled and shaken in a 80 °C cooling bath. The sample was inserted into the probe of the NMR and ^{13}C spectra were recorded. After accumulation of the FID was complete the probe was warmed in either 10 or 20 deg C increments and allowed to equilibrate for 10–15 min. A spectrum was again acquired. This process was repeated at 10 or 20 deg C intervals until the desired temperature was reached.

General Procedure for the Formation of BF_3–Aldehyde Complexes. Into an oven-dried 10-mm NMR tube sealed with a septum was added the aldehyde (0.8 mmol) by syringe. The tube was charged with $CDCl_3$ (2.0 mL) and CD_2Cl_2 (2.0 mL). The NMR tube was placed in a gas-transfer line (Cajon Ultra-Torr fittings). The solution was cooled to −196 °C in a liquid nitrogen bath. Boron trifluoride gas (1.0 equiv) was condensed on top of the frozen aldehyde–solvent mixture and the NMR tube was sealed. The NMR tube was allowed to gradually warm to −80 °C and then the solution was placed into the probe of the precooled NMR. The 1D difference NOE experiments were all performed on a General Electric GN-500 spectrometer using 64K data files. In these experiments a 90° pulse width was used with an irradiation time corresponding to $5 \times T1$.

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Supplementary Material Available: Complete tabular listings of all of the ^{13}C NMR chemical shift data for the aldehydes and their complexes, stacked plots of the actual spectra, the HOESY spectra for the $SnCl_4$ complexes of **9**, **10**, **11**, **and 13**, and the NOE spectra for (*E*)-2-heptenal and its $SnCl_4$ and BF_3 complexes (18 pages). Ordering information is given on any current masthead page.

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