for $C_{14}H_{12}Cl_2N_4$: C, 54.74; H, 3.94; N, 18.24. Found: C, 55.03; H, 4.20; N, 18.14.

Arylazo(α,α-dimethyl-*p*-methoxybenzyl)malononitriles (3e–g). The azo compounds **3e–g** were prepared by the reaction of diazotized anilines with (α,α-dimethyl-*p*-methoxybenzyl)malononitrile which was obtained from methylmagnesium iodide and 1,1-dicyano-2-(*p*-methoxyphenyl)-propene.[22] These were recrystallized from benzene–hexane to afford yellow prisms, which underwent methanolysis very rapidly when dissolved in methanol. **3e**: mp 77 °C; NMR δ 1.83 (s, 6 H), 3.77 (s, 3 H), 6.82 (d, *J* = 9 Hz, 2 H), 7.39 (d, *J* = 9 Hz, 2 H), 7.4–7.85 (m, 5 H). Anal. Calcd for $C_{19}H_{18}N_4O$: C, 71.68; H, 5.70; N, 17.60. Found: C, 71.89; H, 5.70; N, 17.50. **3f**: mp 81 °C; NMR δ 1.83 (s, 6 H), 3.78 (s, 3 H), 6.84 (d, *J* = 9 Hz, 2 H), 7.40 (d, *J* = 9 Hz, 2 H), 7.2–7.7 (m, 4 H). Anal. Calcd for $C_{19}H_{17}ClN_4O$: C, 64.68; H, 4.86; N, 15.88. Found: C, 64.62; H, 5.04; N, 15.87. **3g**: mp 83 °C; NMR δ 1.88 (s, 6 H), 3.78 (s, 3 H), 6.87 (d, *J* = 9 Hz, 2 H), 7.50 (d, *J* = 9 Hz, 2 H), 7.2–7.4 (m, 3 H). Anal. Calcd for $C_{19}H_{16}Cl_2N_4O$: C, 58.93; H, 4.16; N, 14.47. Found: C, 58.97; H, 4.45; N, 14.60.

Thionbenzoates 7a and 7b. The thionbenzoates were prepared according to the literature procedure.[19,20] **7a** (yellowish-orange oil): NMR δ 2.32 (s, 3 H), 7.0–7.6 (m, 12 H), 7.75 (s, 1 H), 8.15–8.35 (m, 2 H). **7a** gave **8a** exclusively in aprotic solvents except pyridine. The pyridiniuim salt, which showed characteristic signals in the aromatic region of the NMR spectrum, was formed in the ratio of the salt to **8a** of ca. 40:60 in pyridine-d_5 at 85 °C. **7a** gave ca. equal amounts of **8a** and the substitution product in methanol-d_4. **8a** (colorless prisms): mp 73 °C; NMR δ 2.31 (s, 3 H), 6.11 (s, 1 H), 6.95–7.5 (m, 12 H), 7.85–8.05 (m, 2 H). **7b** (yellowish-orange oil): NMR δ 1.53 (d, *J* = 6 Hz, 3 H), 5.1–6.4 (m, 4 H), 7.2–7.6 (m, 3 H), 8.1–8.3 (m, 2 H). **7b** was converted to **8b** nearly quantitatively in any solvent. **8b** (colorless oil): NMR δ 1.4–1.8 (m, 3 H), 3.65 (d, *J* = 6 Hz, 2 H), 5.25–6.0 (m, 2 H), 7.2–7.6 (m, 3 H), 7.8–8.1 (m, 2 H).

Kinetics. Kinetic experiments were carried out as described in the preceding paper.[5] The rates of rearrangement and solvolysis were determined by following the decrease of the methyl peak on the allyl or phenyl group except for the cases of **1j** and **7a**, in which the increase of the methyl peak of **2j** and the methine peak of **8a** was monitored. 9,10-Dihydroanthracene, anisole, *p*-xylene, or *p*-nitrotoluene was used as an internal standard.

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Structure and Electronic Nature of the Benzaldehyde/Boron Trifluoride Adduct

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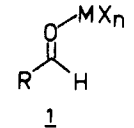
Abstract: The structure of the benzaldehyde/boron trifluoride adduct (**6**) has been determined by X-ray crystallography. Accordingly, the Lewis acid BF_3 is complexed anti to the phenyl group in benzaldehyde. The B–O–C–C fragment lies essentially in a common plane. Anti complexation also pertains in solution, as shown by a heteronuclear Overhauser experiment. MNDO calculations of the acetaldehyde/BF_3 adduct show that anti complexation does indeed lead to the lowest energy species. However, the syn adduct lies only 1.8 kcal/mol higher in energy. The linear form does not represent a minimum on the energy surface but rather the lowest energy transition state for intramolecular anti ⇄ syn isomerization. The calculations of CH_3CHO/BF_3, of **6**, and of the free aldehydes clearly point to LUMO lowering and to an increased positive charge at the carbonyl carbon atom upon complexation. The results are discussed in light of Lewis acid mediated aldehyde additions involving allyl and enolsilanes, stannanes, and cyanotrimethylsilane as well as such processes as Diels–Alder, ene, and Grignard reactions.

A wide variety of C–C bond-forming reactions of carbonyl compounds are mediated by Lewis acids such as BF_3, $AlCl_3$, $EtAlCl_2$, $TiCl_4$, $SnCl_4$, and ZnX_2. They include carbonyl additions of allylsilanes, enosilanes, cyanotrimethylsilane, and other silyated[1] and stannylated[2] carbon nucleophiles, as well as ene reactions,[3] Diels–Alder additions,[4] and hetero-Diels–Alder cyclocondensations.[5] It is generally accepted that the Lewis acid activates the carbonyl component by forming an adduct prior to C–C bond formation.

Whereas X-ray crystallographic data of a $TiCl_4$ adduct of a chiral acrylic acid ester has recently been reported and discussed with regard to stereoselective Diels–Alder reactions,[6] precise structural information concerning complexes of aldehydes with the above-mentioned Lewis acid remains to be presented. NMR, UV, and IR data of common aldehyde/Lewis acid complexes are available, but they do not answer the question of anti vs. syn complexation (**1** vs. **2**; MX_n = Lewis acid).[7] A great deal of experimental and theoretical work concerning the interaction of formaldehyde with Li^+ and other Lewis acids has accumulated



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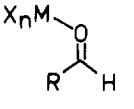

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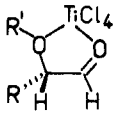

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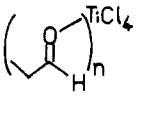

4 (n=1,2)

over the years.[8,9] For example, the geometries and energies of complexes between CH_2O and first- and second-row cations such

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as H^+, CH_3^+, BH_2^+, and Li^+ were recently investigated by ab initio MO calculations.[9] The preferred geometries of the complexes are either bent (e.g., $CH_2{=}O{-}H^+$, $CH_2{=}O{-}CH_3^+$) or linear (e.g., $CH_2{=}O{-}Li^+$, $CH_2{=}O{-}BH_2^+$), depending on the nature of the Lewis acid. A bent geometry is preferred if the major interaction is a charge transfer from the carbonyl oxygen to a σ-type acceptor orbital on the Lewis acid. A linear geometry results if an additional π-type acceptor orbital is available on the Lewis acid that can interact with the lone-pair p orbital of the carbonyl oxygen. If electrostatic interactions predominate, linear coordination is again preferred.[9]

Ketone/Lewis acid adducts, particularly those involving BF_3, have been studied by IR, UV, and NMR techniques, the latter showing that mixtures of syn and anti adducts exist.[10] Recently, an X-ray crystallographic structure determination of a ketone/Ag^+ adduct has been published.[11] In particular, it shows that (*p*-methylacetophenone)$_2AgBF_4$ is a molecule in which Ag^+ is tetracoordinated to two carbonyl oxygens (n donation) and to two aromatic rings (π donation). Complexes between carbonyl compounds and Lewis acids play an important role in other organic and biological reactions, including O-protonation and alkylation,[12] lanthanide ion interactions,[13] and cation binding in polypeptides.[14]

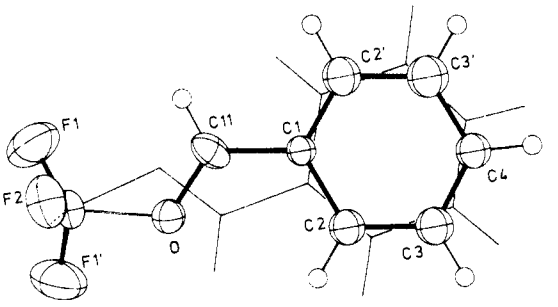
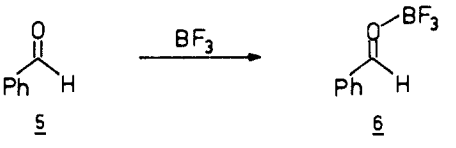


Figure 1. ORTEP drawing of **6** with thermal ellipsoids for the non-hydrogen atoms at the 50% probability level. The alternative orientation of the disordered adduct is shown by thin lines. Selected interatomic distances (Å) and angles (deg): C1–C11, 1.455 (7); C11–O, 1.244 (5); O–B, 1.591 (6); mean C–C in the phenyl ring, 1.387; angle C1–C11–O, 122.8 (5); C11–O–B, 118.7 (3); mean of bond angles in phenyl ring, 120.0.

In the C–C bond-forming reactions mentioned at the outset, anti complexation of aldehydes by a Lewis acid MX_n according to **1** rather than the isomeric syn form **2** is usually *assumed*. For example, the stereochemical outcome of MX_n-promoted crotylstannane additions to aldehydes[2] (simple diastereoselectivity) and enosilane additions to α-chiral aldehydes[15] (diastereofacial selectivity) as well as intramolecular allylsilane and stannane additions have been explained on this basis.[16] In contrast, chelation control in $TiCl_4$ or $SnCl_4$-mediated allyl and enolsilane additions to chiral α-alkoxyaldehydes probably involves syn complexation **3**.[17] For example, prochiral enolsilanes undergo aldol additions not only with complete chelation control (diastereofacial selectivity) but also with excellent simple diastereoselectivity.[18] The latter is unexpected, because normal aldehydes such as 1-propanal react essentially stereorandomly in Mukaiyama-type aldol additions.[18,19] The "discrepancy" was rationalized on the basis of syn complexation (**3**) vs. anti complexation (**4**),[17,18] a model which has been applied in related reactions.[20] Recently, chelates of the type **3** were also implicated in a series of intriguing cyclocondensations with siloxydienes, whereas the same reactions involving normal aldehydes were explained in terms of anti complexation **1**.[5] Inspite of the plausibility of many of these postulates, insight into the actual structure and electronic nature of such aldehydeLewis acid adducts would be desirable.

In this paper we report (a) an X-ray crystallographic structure determination of the benzaldehyde/BF_3 adduct **6**, (b) NMR evidence for the structure of **6** in solution, and (c) molecular orbital calculations of **6** and of the acetaldehyde/BF_3 analogue.



5 **6**

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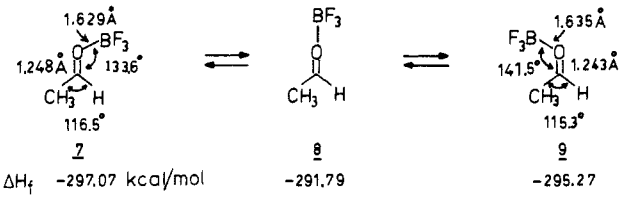
Scheme I. MNDO-Optimized Parameters



Experimental Section

X-ray Measurements. A dilute solution of **6**[21] in dichloromethane was allowed to stand in the refrigerator for several days, resulting in the formation of crystals. A colorless needle (about 0.08 × 0.2 × 0.7 mm³) was measured on a 4-circle diffractometer. The measurement was performed by using a CAD 4 (Enraf-Nonius) instrument with graphite-monochromated Mo Kα radiation at 158 K: space group *Pnma*, $Z = 4$, $a = 17.036$ (3) Å, $b = 9.582$ (1) Å, $c = 4.667$ (3) Å; 497 independent reflections, 399 with $F_o < 3\sigma$, were collected in the range $1° < \theta < 22°$. The structure was solved by direct methods (MULTAN 80) and difference Fourier techniques. Due to orientational disorder, all atoms except the B and F1 atoms had to be split. The two possible orientations of the adduct are related by the mirror plane at $y = 1/4$. Attempts to describe the structure without disorder in the noncentrosymmetric space group $Pn2_1a$ were not successful. The hydrogen atoms have been included at calculated positions (d(C–H) = 0.95 Å) with fixed temperature factors. The split C atoms with C atoms of the phenyl group were refined with isotropic temperature factors, the remaining atoms with anisotropic temperature factors. To avoid strong correlations, the y parameter of F2 was fixed at the final cycles. The refinement by a weighted full-matrix least-squares method (SHELX76) converged well at R values $R_g = \{\sum w(|F_o| - |F_c|)^2/\sum w f_o^2\}^{1/2} = 0.0387$ and $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o| = 0.0396$. The anomalous temperature factor components of F1 as well as geometrical reasons suggest the F1 atoms to be also disordered, but the two neighboring split positions could not be refined separately. Thus, the geometry of the BF_3 group itself is falsified. Despite the high degree of disorder, the benzaldehyde atoms and boron could be located with a high degree of precision.

NOE Measurements. Compound **6** was dissolved in dry CD_2Cl_2 so that a ~0.06 M solution was obtained. Cyclohexane was added as an internal integration standard and the mixture degassed. The ^{19}F NMR spectrum shows an absorption signal at 150.5 ppm upfield from $CFCl_3$. Irradiation at this signal using a Varian XL-100 instrument led to a 5% enhancement of the aldehyde proton absorption. This value is an average of five measurements.

Results and Discussion

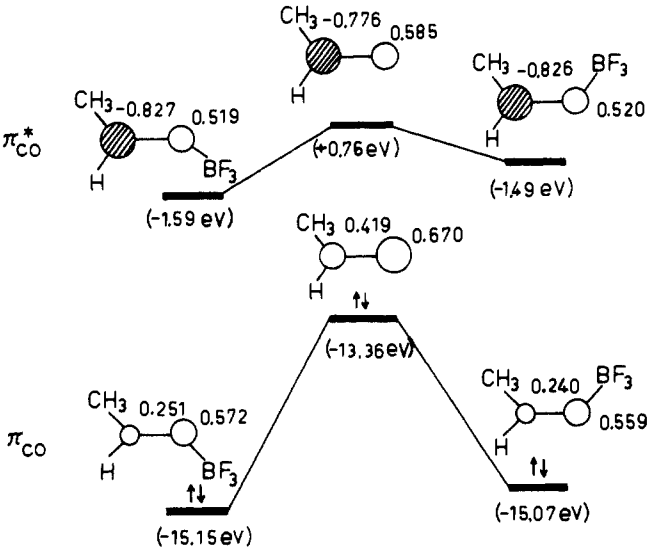
The most interesting features of the X-ray crystallographic structure are shown in Figure 1. The boron atom lies in the plane of the almost planar benzaldehyde molecule (maximum deviation from the least-squares plane is 0.04 Å), anti to the phenyl group. The oxygen–boron bond length (1.591 Å) is longer than in such compounds as orthoboric acid (1.361 Å)[22] or in potassium tetraacetatoborate (1.472 Å).[23]

The question whether anti complexation also pertains in *solution* was resolved by performing a heteronuclear Overhauser experiment. Irradiation of the fluorine atoms led to a 5% enhancement of the aldehyde proton absorption, whereas the aromatic protons remained unaffected. This speaks for the anti geometry **6**.[24]

In order to understand the bonding of aldehyde/BF_3 adducts, resort to MNDO calculations[25] was made.[26] Minimum energy geometries were first determined for acetaldehyde/BF_3 (Scheme I). The anti form **7** in which the C–C–O–B skeleton lies in a common plane turned out to be more stable than the syn isomer **9** by 1.8 kcal/mol. The linear form **8** is not a minimum on the energy surface. However, it represents the least energy transition state for possible internal anti ⇄ syn isomerization.[27] The computed energy required for this process amounts to 5.3 kcal/mol. Calculations of species in which boron is not in the C–C–O plane (π complexation) show that alternative isomerization pathways require more energy.

Scheme II. MNDO-Computed Charge Values

Scheme III. MNDO-Computed Effects of Complexation of Acetaldehyde by BF_3[a]



[a] The numbers in parentheses refer to π-MO energy levels; the others to the atomic coefficients. MO's of the type σ and n have been left off for clarity.

The charges at the carbonyl carbon atom in **7** and **9** are +0.363 and +0.374, respectively (Scheme II), which are more positive than the calculation value of +0.242 in noncomplexed acetaldehyde. This lends support to the traditional postulate that Lewis acid complexation activates the carbonyl compound by increasing the partial positive charge at the carbon atom.[28] Scheme II shows that negative charge flows to the fluorine atoms (the calculated charge at fluorine in noncomplexed BF_3 is only −0.176). Interestingly, the charge at oxygen does not change much upon complexation (−0.286 in neutral acetaldehyde).

BF_3 complexation also lowers the energy of the π_{CO}* orbital (Scheme III), rendering the molecule more susceptible to nucleophilic attack.[29] The extent of LUMO lowering is a little greater in the anti complex than in the syn isomer. Finally, the coefficient of the orbital at the carbonyl C atom in π_{CO}* increases in magnitude upon complexation, a phenomenon which also enhances the ease of nucleophilic addition. It should be mentioned that π_{CO} (Scheme III) is not the actual highest occupied molecular orbital of the acetaldehyde/BF_3 adducts. The HOMO is in fact the n_O orbital (lying at 13.25 eV in the case of the anti complex).

The results of MNDO calculations of **6** follow similar lines: $\Delta H_f = -266.7$ kcal/mol; B–O bond distance = 1.607 Å; C–O = 1.255 Å; B–O–C angle = 132.9°; C–C–O = 121.9°; charge at carbonyl C atom = +0.433 (vs. +0.306 in benzaldehyde). Thus, the computed and experimental B–O bond distances agree well. However, the calculation does not reproduce the B–O–C bond angle precisely. This is not necessarily of great concern, since the optimum geometry of **6** and of other crystalline Lewis acid

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(24) The NOE experiment does not rule out small amounts of the syn isomer which may be in equilibrium with **6**.
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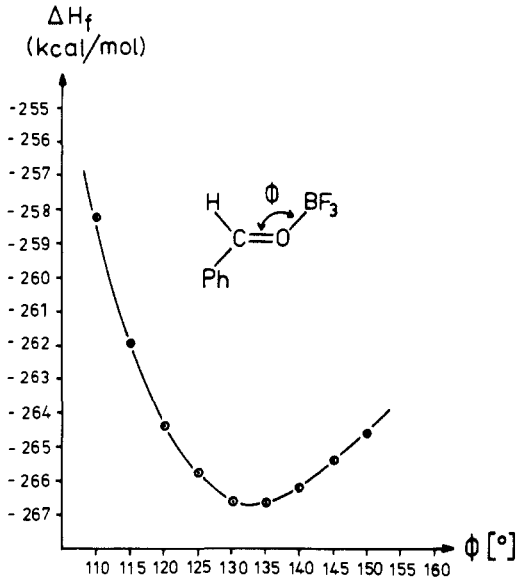
(26) In a previous MO study of PhCHO/BF_3 using the CNDO/2 technique, syn complexation was assumed; i.e., the isomer **6** was not considered.[8c]
(27) Syn/anti isomerization may also occur via dissociation/recombination.
(28) The ^{13}C NMR data of **6** (carbonyl C atom at 199.8 ppm vs. 191.8 ppm of benzaldehyde)[7c] and similar adducts also point to this effect.
(29) LUMO lowering of dienophiles as a consequence of Lewis acid complexation (or protonation) is well-known in Diels–Alder reactions, e.g.: Houk, K. N.; Strozier, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4094.

Scheme IV. Effect of Varying the Angle ϕ in the Adduct **6**. Planarity of Ph–C–O–B Has Been Assumed



complexes is expected to be the result of a combination of orbital, steric, and electrostatic effects as well as crystal packing forces.[30] In fact, the effect of varying the B–O–C bond angle ϕ within reasonable bounds is not all that dramatic (Scheme IV). As in CH_3CHO/BF_3, the linear form of **6** does not represent a minimum on the energy surface but rather the lowest energy transition state (ΔH_f = −260.5 kcal/mol) for anti ⇄ syn isomerization. The calculations also show that **6** is 2.5 kcal/mol more stable than the syn isomer. These adducts are inherently different from linear $CH_2{=}O{-}BH_2^+$ because the latter has an empty p orbital at boron.[9]

The above experimental and computational data may well be representative of aldehyde/BF_3 adducts in general and of electronically similar aldehyde/Lewis acid complexes. The traditional assumption of anti complexation in BF_3-mediated C–C bond-forming reactions is thus no longer a matter of pure speculation. Alternative π complexation at the carbonyl function plays no role in these reactions. However, the present results do not strictly rule out the participation of a syn adduct, since the energy barrier of anti ⇄ syn isomerization is not that great. Nevertheless, there is no current experimental evidence which speaks for the syn adduct being the actual reacting species; i.e., there is no reason to assume an inherent greater reactivity. Our results also have a bearing on such reactions as the stereoselective aldol addition of enolboronates to aldehydes. Experimental[31] and computational[32] results are in line with initial anti complexation followed by C–C bond-forming rearrangement.[33] This model also explains the stereochemical course of the addition of N-titanated hydrazones to aldehydes,[34] although this remains to be proven. Other organometallic additions such as the Grignard reaction may also be initiated by similar modes of complexation.[35] We are making use of the present information in designing chiral Lewis acids.

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Supplementary Material Available: Tables of atomic positional and thermal parameters, observed and calculated structure factors, additional interatomic distances, and angles and distances to the least-square plane (7 pages). Ordering information is given on any current masthead page.

(30) We thank Prof. D. J. Raber for emphasizing this point.

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(33) The stereochemistry of the addition of (*Z*)- and (*E*)-dialkylboron enolates to aldehydes has been explained by Evans on the basis of a cyclic transition state (Zimmermann–Traxler postulate); it is not clear whether aldehyde/boron complexation precedes this transition state. Anti complexation of the type **1** has been invoked in the aldol addition of zirconium enolates: Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1.

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