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Quantum Chemical Modeling of Chiral Catalysis. Part 14. On the Coordination of Carbonyl Compounds to Diaza-, Oxaza- and Dioxaluminolidines of Potential Use as Chiral Controllers in Organic Synthetic Chemistry

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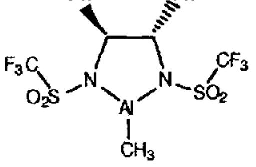
Abstract: - Conformers of 4-coordinate adducts of carbonyl compounds and diaza-, oxaza- and dioxaluminolidines were investigated by means of *ab initio* MO methods (RHF). Formaldehyde was used as a model of carbonyl compounds. Relative stabilities of the conformers indicate formation of *syn* adducts of carbonyl compounds and aluminolidines ($C_{C=O}$ and aluminolidine ring *syn* about the Al-$O_{C=O}$ bond) to be favoured over that of the corresponding *anti* ones (all *syn*/*anti* ratios higher than 99:1, 6-31G//6-31G). The energetic preference for the formation of *syn* adducts of oxazaaluminolidines was about twice as high as that of diaza- or dioxaluminolidines of which the *syn*/*anti* selectivities were found to be practically equal.

INTRODUCTION

For more than one decade, catalytic properties of boron, aluminum, zinc, titanium, rhodium, europium etc. containing chiral Lewis acids for a variety of asymmetric reactions have drawn the attention of those involved in the development of asymmetric reactions in the field synthetic organic chemistry.[1] Also reports describing the use of magnesium, copper and iron containing Lewis acids have been recently published.[2] Many of the known catalysts could be regarded as chelates of the above mentioned metal(oid)s with polydentate oxygen and/or nitrogen bases. Structurally perhaps the most simple of those are derivatives of oxazaborolidines[1a,c,i] of which the mechanism of action in the enantioselective reduction of ketones[3] and asymmetric Diels-Alder reactions[4] has been studied computationally in this laboratory. Diazaaluminolidines **1** are structurally analogous to oxazaborolidines and are used also as efficient catalysts in the asymmetric Diels-Alder reaction (enantioselectivities higher than 95 % can be achieved).[1i,5]



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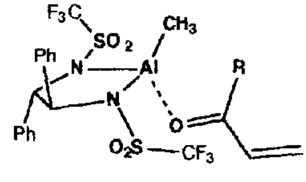
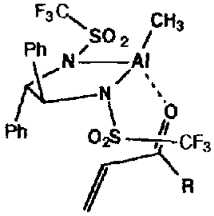


2 (*anti* adduct)



2' (*syn* adduct)

Complexes **2** (the dienophile and catalyst moieties *anti*) and **2'** (the dienophile and catalyst moieties *syn*) have been regarded as plausible reactive intermediates of the Diels-Alder reaction of cyclopentadiene and 3-acryloxazolidin-2-one or acrylate ester of (-)-menthol.[1i,5] Determination of the 3-dimensional structure of **1** by means of X-ray crystallography has revealed that **1** can exists as a head to tail dimer consisting of two Al-N-S-O sequences.[5a] In the dimer the acidic aluminum is bound to one of the basic oxygens of the sulfonyl group.[5] A related role of the sulfonyl oxygens has been proposed also in the case of an *ab initio* study on a formaldehyde complex of *N*-sulfonyl-1,3,2-oxazaborolidine (one O_{SO2} was found to coordinate to $C_{C=O}$ of the formaldehyde while $O_{C=O}$ was bound to the boron of the oxazaborolidine ring).[4] NMR-Spectrometric studies on the complex of 3-acryloxazolidin-2-one and **1** indicate formation of a monocoordinate 1:1 adduct.[5a] Orientation of the reacting counterparts was predicted to correspond best to that of **2'** (*syn* orientation).[5a] In the case of coordination of formaldehyde to borane adducts of oxazaborolidines (a computational study) both ways of coordination have been predicted to be possible.[6] Furthermore, formation of the *syn* adducts appeared to be enthalpically more advantageous.[6] As diazaaluminolidines resemble borane - oxazaborolidines adducts in that they both have an acidic center between nitrogen/oxygen atoms in a five-membered ring system it could be interesting to determine what these systems have in common with respect to binding Lewis bases (e.g. carbonyl compounds).

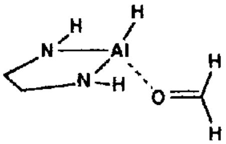
In addition to diazaaluminolidines (**1**), other related systems which could be best regarded as oxazaaluminolidines have been reported by Sartor *et al.*[7] to catalyze asymmetric Diels-Alder reactions (aluminolidines not characterized but proposed as catalysts generated *in situ*). Enantioselective reductions of ketones by using boron and aluminum containing catalysts (prepared from chiral aminoalcohols and H_3B or H_3Al) have been reported by Itsuno *et al.*[8] However, in both of these cases the performance of the aluminum-based systems was found to be clearly inferior to that of the corresponding boron-based ones.[7,8] The lower catalytic performance of aluminum chelates might be attributable to the propensity of trigonal aluminum alkoxides and amides to form aggregates[9] containing 4-coordinate tetrahedral and/or 6-coordinate octahedral aluminum centers (one aggregate may contain several metals centers of different coordination states).[10-12] Aggregates, or systems serving as models of aggregates, containing 5-coordinate (trigonal-bipyramidal and square pyramidal)[13] and 7-coordinate (pentagonal-bipyramidal)[14] aluminum are also known. Furthermore, formation of aggregates of aluminum containing chelates may not always emanate only from propensities of aluminum but aggregates can be bound, for example, by hydrogen bonds.[15]

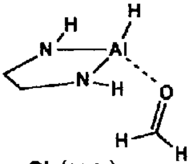
The properties of some rather simple aluminum containing systems (e.g. AlH_3 and its adducts to Lewis bases) have been lately studied also by means of *ab initio* and related theoretical methods.[16] However, although chemistry of aluminum has been extensively studied there are cases in which experimental confirmation of fundamental structural information related to aluminum complexes has not been achieved until very recently. For example, structural characterization of alkylalumoxanes by Mason, Smith, Bott, and Barron;[17] determination of structures of AlH_3 adducts of common solvents (e.g. tetrahydrofuran by Gorrell, Hitchcock, and Smith);[18] and coordination of two or more Lewis acids to a carbonyl oxygen at the same time [two Al-O bonds simultaneously to an oxygen of ketone as reported by Sharma, Simard and Wuest,[10b] and two, or even four, Hg-$O_{C=O}$ bonds (to the oxygen of dimethylformamide) at once as discovered by Simard, Vaugeois and Wuest[19]]. Nevertheless, although significant progress has been made on the advanced level of understanding aluminum chemistry, these works do not throw much light on the field of aluminolidines.

Although the chemical literature discussed above clearly indicates that various aluminum complexes containing diaza-, oxaza- and dioxaluminolidine systems (some of which already have shown catalytic activity[5]) development of catalytic applications of aluminum chelates related to the preparation of fine chemicals is still on its early stage. Except for the pioneering work of Corey *et al.*,[5a] the rational basis for predicting orientational selectivities of the coordination of Lewis bases to aluminolidines (e.g. *syn/anti* selectivity in the case of **2** and **2'**), as well as the role of higher coordination states in the catalytic function of aluminolidines, is still unrevealed. Understanding the factors which control the coordination process may help one to develop new and better enantioselective catalysts of which the activity is based on the Lewis acidic aluminum centers. Therefore, the aim of this work was to compare properties of *syn* and *anti* adducts of carbonyl compounds to diaza-, oxaza- and dioxaluminolidines (systems configurationally analogous to 2 and 2'). As it could be rational to predict trigonal 3-coordinate aluminum chelates to be more acidic than the 4-, 5- or 6-coordinate analogs, carbonyl adducts of the 3-coordinate chelates would be the most rational starting point for studies on the coordination of carbonyl compounds to Lewis acidic aluminolidine type of catalysts.

MODELS AND COMPUTATIONAL METHODS

Standard *ab initio* MO calculations (RHF) were carried out by using the Gaussian 90 series of programs at the 3-21G, 6-31G and 6-31G* levels.[20] Modelling techniques similar to those applied in the case of previous reports of this series were employed.[3,4] Adducts **3** - **5** and **3'** - **5'** of formaldehyde to diazaaluminolidine, oxazaaluminolidine and dioxaluminolidine were used as models of ketone/aldehyde adducts of aluminolidines. In adducts **3** - **5** configuration of the formaldehyde moiety is *anti* with respect to the aluminolidine ring whereas the configuration of **3'** - **5'** is *syn*. As involvement of polarization functions would have given rise to highly demanding calculations adducts **3** - **5** and **3'** - **5'** were studied at the 3-21G and 6-31G levels only. Importance of the polarization functions was determined by studying a related water adduct (**6**) at the 3-21G, 6-31G and 6-31G* levels. Symmetry (C_s) was used in the case of adducts **3**, **3'**, **5**, **5'** and **6**. The torsion angle H-Al-O_{CO}-C_{CO} of **4** was fixed to 0° in order to prevent the carbonyl moiety from tumbling around the Al-O axis. Apart from one preliminary report[21] no other calculations on **3** - **5**, **3'** - **5'** or **6** appear to have been published.


3 (*anti*)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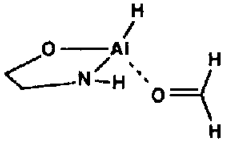
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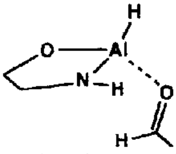
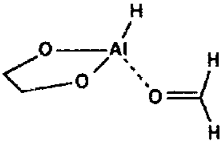
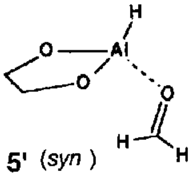
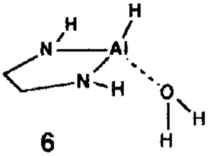

4' (*syn*)


5 (*anti*)


5' (*syn*)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RESULTS AND DISCUSSION

Total energies, dipole moments, Al-O and C=O bond lengths, Al-O-C bond angles and charge transfer values of the optimized structures of **3** - **6** and **3'** - **5'** are presented in Table 1. The optimized (6-31G//6-31G) structures of **3** and **3'** are shown in Figure 1, **4** and **4'** in Figure 2, and **5** and **5'** in Figure 3. The optimized structure (6-31G*//6-31G*) of **6** is shown in Figure 4. The LUMO energies and degrees of hybridization of aluminum and nitrogen centers of **3** - **6**, **3'** - **5'** are presented in Table 2 and the relative energies of conformers in Table 3. As in the case of water -

borane adducts of aminoborane[22] it again turned out to be difficult to find a minimum for the *anti* configuration of the corresponding adduct (**6**) of diazaaluminolidine.[23]

Characterization of aluminum centers

The coordination chemistry of aluminum in tetrahedral environments of adducts **3** - **5** and **3'** - **5'** could be characterized by reference to the Al-O and Al-N bond lengths and angles (Figures 1-3) and the degrees of hybridization of aluminum and its adjacent nitrogens presented in Table 2. One of the first conclusions to be drawn when inspecting the structural parameters of these adducts is related to the tight binding of all ligands of aluminum. In contrast to the corresponding formaldehyde - oxazaborolidine complexes,[22] the oxygen of the formaldehyde moiety is clearly bound to the aluminum in all **3** - **5** and **3'** - **5'** [all $Al-O_{CO}$ bond lengths in the range of 2.033 ± 0.051 Å, 6-31G//6-31G, Figures 1-3]. Also the sp^2 degrees of hybridization of nitrogens are very high in all **3** - **5** and **3'** - **5'** [all $sp^2/sp^3(N)$ values in the range of 96.5 - 99.7 %, 6-31G//6-31G, Table 2]. This result is well consistent with that of another related study on the dimer of **1** which contains two 4-coordinate aluminum centers.[5a] The nitrogen centers of the dimer have been found to be highly sp^2 hybridized.[5a] Lengths of all the Al-N bonds of **3** - **5** and **3'** - **5'** are closely similar (all within the range of 1.810 ± 0.009 Å, Figures 1-2) as are those of the $Al-O_{rng}$ bonds of **4**, **5** and **5'** (all within the range of 1.765 ± 0.008 Å, Figures 2-3). The $Al-O_{rng}$ bond of **4'** (1.794 Å, Figure 2) is, however, clearly longer.

Table 1. Total energies (**E**), dipole moments (**D**) and the most important bond lengths (**r**), bond angles (ϑ) and the charge transfer values of formaldehyde (**Q**) of the optimized structures of **3** - **6**, **3'** - **5'**.[a,b]

Structure[b]	3-21G//3-21G						6-31G//6-31G					
	E[a]	D[a]	$r(Al\text{-}O_{co})$[a]	$r(C=O)$[a]	$\vartheta(Al\text{-}O\text{-}C_{co})$[a]	$Q(H_2CO)$[c]	E	D	$r(Al\text{-}O_{co})$	$r(C-O)$	$\vartheta(Al\text{-}O\text{-}C_{co})$	$Q(H_2CO)$
3	-541.55442	6.27	2.000	1.220	131.0	+0.149	-544.37982	6.19	2.084	1.219	131.0	+0.094
3'	-541.56063	5.22	1.981	1.223	121.6	+0.145	-544.38508	5.11	2.060	1.221	123.5	+0.098
4 [d]	-561.30291	6.74	1.965	1.220	132.8	+0.154	-564.22338	6.82	2.032	1.219	133.4	-0.100
4'	-561.31561	4.90	1.954	1.229	123.0	+0.136	-564.23417	4.70	2.012	1.226	125.5	+0.097
5	-581.04482	7.05	1.940	1.221	135.0	+0.158	-584.06095	7.18	1.999	1.220	135.8	+0.103
5'	-581.05057	5.74	1.928	1.225	124.0	+0.154	-584.06619	5.80	1.982	1.223	127.8	-0.108
6 [e]	-503.93988	3.94	1.954	-	-	+0.170	-506.56985	4.18	2.026	-	-	+0.105 [f]

[a] Total energies (E) given in hartrees, dipole moments (D) in debyes, lengths of the $Al-O_{co}$ bonds in ångströms and $Al-O_{co}-C_{co}$ angles in degrees. [b] C_s symmetry was used except in the case of **4** and **4'**. [c] Positive charge of $H_2C=O$. [d] Torsion angle $H-Al-O_{co}-C_{co}$ of **4** fixed to 0°. [e] Values related to water given in place of those of formaldehyde. [f] The corresponding 6-31G*//6-31G* values are: E = -506.67926, D = 2.61, $r(Al-O_{H2O})$ = 2.054; $Q(H_2O)$ = -0.137.

The degrees of sp^2 hybridization of aluminum centers of **3** - **5** and **3'** - **5'** are lower than those of nitrogens [all $sp^2/sp^3(Al)$ values in the range of 61.1 - 70.3 %, 6-31G//6-31G, Table 2]. Interestingly, the $sp^2/sp^3(Al)$ values are the higher the more nitrogens are bound to aluminum [e.g. values of **3** and **3'** are higher than those of **4** and **4'**, which in turn are higher than those of **5** and **5'**, Table 2]. The rational basis of this serial change could be found by taking into account the nature of the neighbours of aluminum atoms. Namely, the more an aluminum atom would have sp^2 hybridized neighbours able to donate π-electrons the more sp^2 hybridized the aluminum would also be; i.e. the more π-resonating [$Al-N <-> Al^-=N^+$] neighbours the higher sp^2 degree of aluminum. Nevertheless, importance of the π-resonance could be predicted to be lower in the case of aluminum than in the case of boron because, in contrast to aluminolidines, oxazaborolidines cannot bind[22] formaldehyde. The π-resonance [$B-N <-> B^-=N^+$] deactivates the ring boron of oxazaborolidines.[22]

The considerably high degree of sp^2 hybridization of the aluminum centers indicates that the centers are still acidic. That prediction is supported by the high dipole moments (Table 1) and low LUMO energies (Table 2) of the adducts **3** - **5** and **3'** - **5'**. The dipole moments are clearly higher than those of borane - oxazaborolidine adducts[22] capable to bind Lewis bases [e.g. at the 6-31G level moments of formaldehyde - aluminolidine adducts are all in the range of 4.70 - 7.18 D, (Table 1) whereas the moment of borane adduct of 1,3,2-oxazaborolidine[22] is 4.89 D]. Also the LUMO energies of formaldehyde - aluminolidine adducts are much lower than those of borane - oxazaborolidine adducts[24] [e.g. the highest LUMO energy of the formaldehyde - aluminolidine adducts is 1.82 eV (**5**, 6-31G//6-31G, Table 2) whereas the LUMO energy of borane adduct of 1,3,2-oxazaborolidine[24] is 4.06 eV]. Interestingly, the LUMO energy of the water adduct (**6**) is much higher than that of any of the formaldehyde adducts (Table 2). Therefore, the water adduct (**6**) should be clearly less Lewis acidic than the formaldehyde adducts (**3** - **5** and **3'** - **5'**). However, preliminary studies on the coordination of one more water to the aluminum of **6** reveal that the aluminum is still Lewis acidic (studies indicate coordination two waters to diazaaluminolidine to be possible). Consequently, one could predict that the formaldehyde adducts (**3** - **5** and **3'** - **5'**) would be highly Lewis acidic and that the adducts would form 5- or perhaps even 6-coordinate adducts with Lewis basic solvents or aggregate in the absence of such solvents. This implies isolation and experimental studies on these formaldehyde adducts to be hardly possible under normal conditions.

Table 2. LUMO energies[a] and degrees of hybridization[b] of aluminum and nitrogen centers of aluminolidines **3** - **6**, **3'** - **5'**.

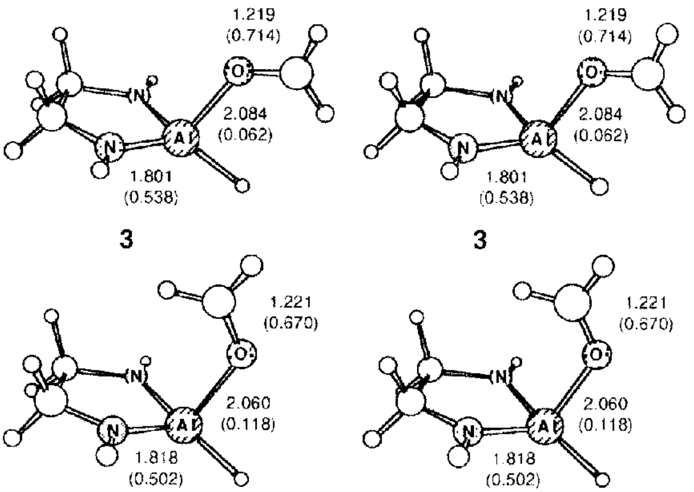
Structure	E_{LUMO}	sp^2/sp^3(N)	sp^2/sp^3(Al)
3	+1.63	99.4	69.0
3'	+1.82	96.5	70.3
4	+1.30	99.4	65.5
4'	+1.66	99.7	62.3
5	+0.97	-	62.0
5'	+1.15	-	61.1
6	+3.77	95.9	69.3
$\mathbf{6}^{6\text{-}31G^*//6\text{-}31G^*}$	+3.95	82.9	74.7

[a] LUMO energies (6-31G//6-31G) given in eV. [b] The sp^2/sp^3 values (6-31G//6-31G) given in percentages are calculated by summing the three angles of the trigonal center and converting the sum to the relative scale between the fully planar (360°; corresponds to 100 % of sp^2/sp^3) and the fully tetrahedral (328.4°; corresponds to 0 % of sp^2/sp^3) systems.

The lengths of Al-N and Al-O_{rng} bonds of **3** - **5** and **3'** - **5'** are similar to those of other diazaaluminolidine analogs or related compounds (some of which are shown in Scheme I) containing 4-coordinate aluminum centers reported in the literature. For example, on the basis of an X-ray crystallographic study on a system of aluminum phenoxides bound to a ketocarbonyl (an intramolecular adduct of two aluminum phenoxides to oxygen of a ketone) Al-$O_{phenoxide}$ bonds have been found to be about 1.78 Å long (structure <u>A</u>, Scheme I).[10b] The lengths of Al-N bonds of the diazaaluminolidine radical (<u>B</u>, Scheme I) of which the aluminum is partially sp^2 hybridized [sp^2/sp^3 (Al) = 54.1 %)] are in the range of 1.813 - 1.839 Å.[10g] In the case of the intramolecular amine adduct of dichloroamino aluminum derivative (<u>C</u>, Scheme I), the Al-N bonds are somewhat shorter and the degree of sp^2 hybridization [sp^2/sp^3 (Al) = 56.0 %] slightly higher than the corresponding values of <u>B</u> (presumably the aluminum of <u>C</u> is more Lewis acidic and sterically less hindered than that of <u>B</u>). The lengths of Al-O_{CO} bonds of **3** - **5** and **3'** - **5'** are all in the range of 2.033 ± 0.051 Å (Figures 1-3). The bonds are somewhat longer than those of <u>A</u> (1.96 Å, Scheme I) or the Al-O_{CO} bond of benzophenone complex of aluminum phenoxide.[10b]

Bond and torsion angles	3
N-Al-N	93.0°
N-Al-O$_{CO}$	107.2°
H-N-C-C	175.8°
Al-N-C-C	2.5°
H-Al-N-C	150.6°
H-Al-N-H	27.2°

Bond and torsion angles	3'
N-Al-N	91.0°
N-Al-O$_{CO}$	100.9°
H-N-C-C	173.8°
Al-N-C-C	4.4°
H-Al-N-C	142.0°
H-Al-N-H	-25.0°

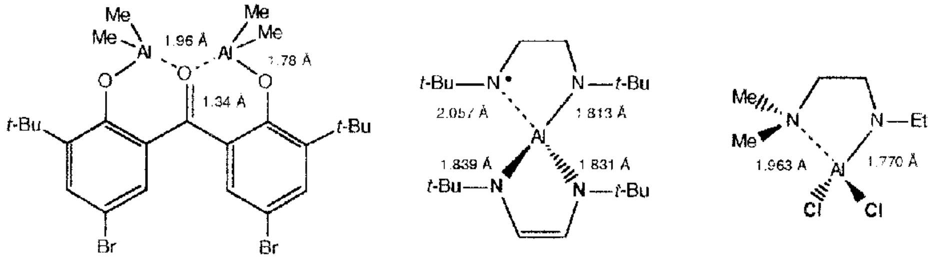


3 3

3' 3'

Figure 1. Stereo representations of the optimized (6-31G//6-31G) structures of formaldehyde - diazaaluminolidine *anti* and *syn* adducts (**3** and **3'**). Some of the most important bond lengths [in Å] and angles, as also Mulliken overlap populations (in parentheses), are shown.

Scheme I



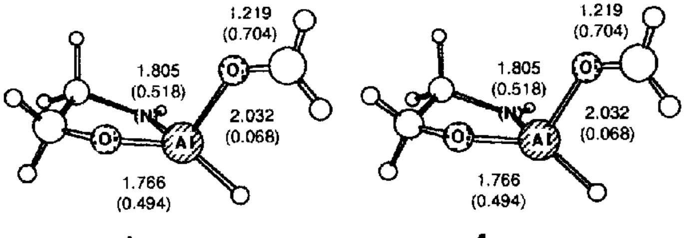
A (ref. 10b) **B** (ref. 10g) **C** (ref. 11g)

The N-Al-N bond angles of adducts **3** and **3'** are 93.0° and 91.0° (Figure 1). These values are similar to those of the diazaaluminolidine rings of **B** (86.7° and 92.4°)[10g] and **C** (91.3°)[11g] (Scheme I). Values of the N-Al-O$_{rng}$ and O$_{rng}$-Al-O$_{rng}$ angles are also practically in the same range (i.e. 91.5 ± 1.5°, Figures 2 - 3). Altogether, in the light of lengths of Al-N and Al-O bonds of several 4-coordinate aluminum complexes determined by X-ray crystallography[10-11] the structural parameters of models **3** - **5** and **3'** - **5'** are clearly in the range of values typical to this class of structures.

The lengths of Al-N (1.810 ± 0.009 Å, 6-31G//6-31G, Figures 1-2) bonds of **3** - **4** and **3'** - **4'** are also near the length of Al-N bond of aminoalane[16i] (H_2Al-NH_2, Al-N = 1.771 Å, 6-31G*//6-31G*) and that of tris-(dimethylamino)alane[16k] [$(Me_2N)_3Al$, Al-N = 1.778 Å, STO-3G (partial optimization)]. These Al-N bonds are considerably shorter than that of the alane adduct of H_3N[16e] (H_3Al-NH_3, Al-N = 2.095 Å, 6-31G*//6-31G*) or aluminum trichloride adduct of H_3N[16e] (Cl_3Al-NH_3, Al-N = 2.025 Å, 6-31G*//6-31G*). The lengths of Al-O$_{rng}$ (1.765 ± 0.008 Å, 6-

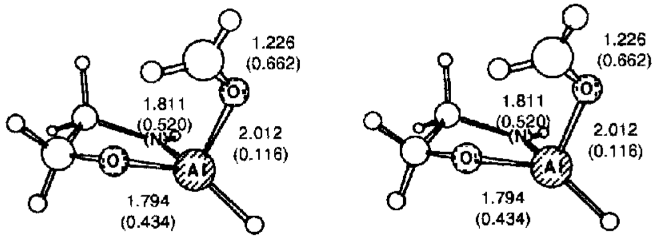
31G//6-31G) and Al-O_{CO} (2.033 ± 0.051, 6-31G//6-31G) bonds of models 3 - 5 and 3' - 5' are somewhat longer than Al-O bonds of hydroxy- and methoxyalane[16c] ($H_2Al\text{-}OH$ and $H_2Al\text{-}OCH_3$, Al-O = 1.665 and 1.649 Å, 3-31G*//3-31G*) and 4-coordinate phosphine adducts of hydroxy- and methoxyalane[16c] (Al-O = 1.690 and 1.665 Å, 3-31G*//3-31G*). The lengths of Al-O_{CO} (2.033 ± 0.051) and C=O_{Al} (1.222 ± 0.004, Figures 1-3) bonds of models 3 - 5 and 3' - 5' are closely similar to those of the alane - formaldehyde adduct[16g] ($H_3Al{\bullet}O{=}CH_2$, Al-O_{CO} = 2.046 Å and C=O_{Al} = 1.119 Å, 6-31G*//6-31G*), Al^+ adduct of formaldehyde[16l] ($H_2C{=}O{\bullet}Al^+$, Al-O_{CO} = 1.928 Å and C=O_{Al} = 1.234 Å, 3-21G//3-21G) and formaldehyde - aluminum trichloride adduct[16b] ($Cl_3Al{\bullet}O{=}CH_2$, Al-O_{CO} = 1.947 Å and C=O_{Al} = 1.205 Å, 6-31G*//6-31G*). Therefore, also in the light of the comparison of lengths of Al-N and Al-O bonds of models 3 - 5 and 3' - 5' with those of 4-coordinate aluminum complexes studied earlier by computational methods[16] the structural parameters of models 3 - 5 and 3' - 5' are clearly in the range of values typical to alkoxy- and aminoalanes.

Bond and torsion angles	**4**
N-Al-O_{mg}	92.7°
N-Al-O_{CO}	110.8°
O-Al-O_{CO}	101.0°
H-N-C-C	157.8°
Al-N-C-C	-25.4°
H-Al-N-C	155.6°
H-Al-N-H	-28.4°
N-C-C-O	32.0°
N-Al-O-C	8.7°



4 4

Bond and torsion angles	**4'**
N-Al-O_{mg}	91.0°
N-Al-O_{CO}	112.7°
O-Al-O_{CO}	90.4°
H-N-C-C	158.4°
Al-N-C-C	-23.7°
H-Al-N-C	150.7°
H-Al-N-H	31.9°
N-C-C-O	34.5°
N-Al-O-C	14.5°



4' 4'

Figure 2. Stereo representations of the optimized (6-31G//6-31G) structures of formaldehyde - oxazaaluminolidine *anti* and *syn* adducts (4 and 4'). Some of the most important bond lengths [in Å] and angles, as also Mulliken overlap populations (in parentheses), are shown.

Table 3. Relative energies of *anti* (3 - 5) and *syn* (3' - 5') adducts.[a]

	3-21G	6-31G
Structures	E_{anti} / E_{syn}[b]	E_{anti} / E_{syn}[b]
3 / 3'	0 / -16.3	0 / -13.8
4 / 4'	0 / -33.4	0 / -28.4
5 / 5'	0 / -15.1	0 / -13.8

[a] Energies given in kJ mol^{-1}. [b] Energies of *syn* adducts relative to energies of *anti* adducts. Energies of the *anti* adducts set to zero.

Comparison of syn and anti adducts of formaldehyde to aluminolidines

A comparison of structural parameters of free formaldehyde and those of adducts **3** - **5** and **3'** - **5'** (Figures 1-3) reveals that the C=O bond of formaldehydes lengthens as the carbonyl oxygen coordinates to aluminum. The length of the C=O bond of free formaldehyde is 1.210 Å (6-31G//6-31G) whereas the corresponding values of **3** - **5** and **3'** - **5'** are in the range of 1.222 ± 0.004 (Figures 1-3). Interestingly, the lengths of C=O bonds of **3** - **5** and **3'** - **5'** are closely similar to those of formaldehyde - borane complexes of oxazaborolidines[3] [e.g. in the formaldehyde - borane adduct of 1,3,2-oxazaborolidine[3] the C=O (*syn* to the oxazaborolidine ring) bond is 1.220 Å long, 6-31G//6-31G]. On the other hand, the C=O bonds of **3** - **5** and **3'** - **5'** are shorter than the C=O bond of a formaldehyde adduct of *N*-sulfonylated 1,3,2-oxazaborolidine[4] (1.355 Å, 6-31G//6-31G). In this light one could predict that C=O of a carbonyl compound bound to the aluminum of a diaza-, oxaza-, or dioxaluminolidine system would be activated as much as that bound to the ring boron of a borane - oxazaborolidine adduct.

Bond and torsion angles	5
O_{rng}-Al-O_{rng}	93.0°
O_{rng}-Al-O_{CO}	105.0°
H-Al-O-C	146.0°
Al-O-C-C	1.5°
C-O_{rng}-Al-O_{rng}	-2.0°

Bond and torsion angles	5'
O_{rng}-Al-O_{rng}	90.7°
O_{rng}-Al-O_{CO}	99.5°
H-Al-O-C	133.9°
Al-O-C-C	7.3°
C-O_{rng}-Al-O_{rng}	-9.8°

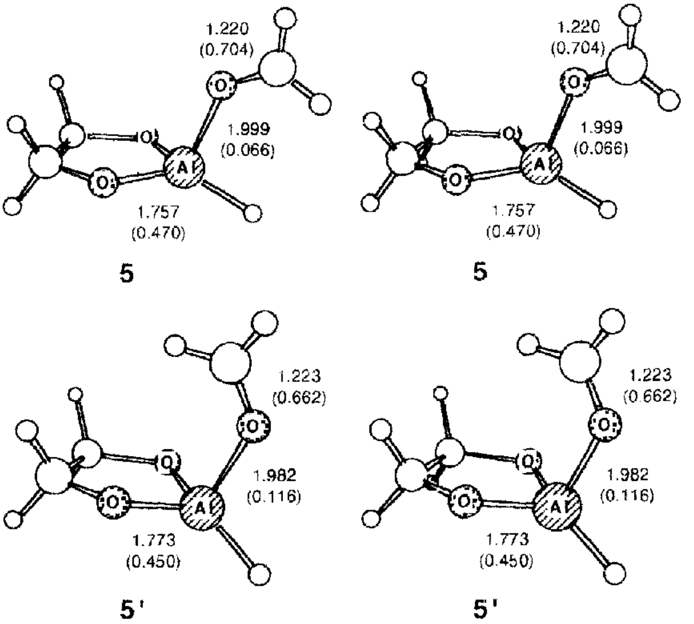


Figure 3. Stereo representations of the optimized (6-31G//6-31G) structures of formaldehyde - dioxaluminolidine *anti* and *syn* adducts (**5** and **5'**). Some of the most important bond lengths [in Å] and angles, as also Mulliken overlap populations (in parentheses), are shown.

A comparison of structural parameters of *anti* adducts (**3** - **5**) with those of *syn* ones (**3'** - **5'**) reveals that the *syn* coordinated formaldehydes are more tightly bound to aluminum than the *anti* coordinated ones. The Al-O_{CO} bonds of *anti* adducts (**3** - **5**) are 0.024 , 0.020 and 0.017 Å longer and the corresponding Mulliken overlap populations 0.056, 0.048 and 0.050 lower than those of the *syn* adducts (**3'** - **5'**, Figures 1-3). A similar observation has been made in the case of formaldehyde - borane adducts of oxazaborolidines; formaldehyde *syn* to the oxazaborolidine ring about the B-O_{CO} bond was found to be more tightly bound than the corresponding *anti* one (e.g. the Mulliken B-O_{CO} overlap population of a formaldehyde - borane *syn* adduct of an oxazaborolidine system derived from prolinol was 0.122 whereas that of the corresponding *anti* adduct was only 0.070).[3]

As formaldehyde coordinates to diaza-, oxaza- or dioxaluminolidine to form adducts **3** - **5** and **3'** - **5'** it donates electron density to the aluminolidine system [Q(H_2CO) values, Table 1]. The positive charge gained by formaldehyde does not vary much [all charge transfer values in the range of 0.094 - 0.108 (6-31G//6-31G, Table 1)]. Interestingly, the positive charges of formaldehyde moieties of diaza- and dioxaluminolidine *syn* adducts (**3'** and **5'**) are slightly higher than those of the corresponding *anti* adducts (**3** and **5**) whereas the relative order of these values is opposite in the case of oxazaaluminolidine adducts (**4** and **4'**). Comparison of the charge transfer values of **3** - **5** and **3'** - **5'** with those of formaldehyde - borane adducts of oxazaborolidines[3] reveals that the values of oxazaborolidine adducts are considerably higher than those of aluminolidine systems [e.g. inspected at the 6-31G level the charge transfer values of formaldehyde - borane *syn* and *anti* adducts of 1,3,2-oxazaborolidine[3] are in the range of 0.122 - 0.156 whereas those of oxazaaluminolidine adducts (**4** and **4'**) are near 0.100, Table 1]. This indicates that C=O of a carbonyl compound coordinating to a borane adduct of oxazaborolidine could be activated more than that coordinating to an aluminolidine. This prediction is different from that presented on the basis of the comparison of bond lengths discussed above (both of these coordination processes were predicted to activate the coordinating carbonyl by about the same amount).

As the charge transfer values and lengths of the C=O bonds (1.222 ± 0.004 Å, Figures 1-3) of adducts **3** - **5** and **3'** - **5'** are closely similar one could predict that also the related Mulliken overlap populations of the C=O bonds would be similar. However, that is not the case. Namely, Mulliken C=O overlaps of *anti* adducts **3** - **5** are considerably higher than those of *syn* adducts **3'** - **5'** (e.g. C=O overlap of **3** is 0.714 whereas that of **3'** is 0.670). This implies more tight binding / less activation of C=O of the carbonyl compound bound *anti* to an aluminolidine system (the looser the C=O bond the more active the carbonyl, and *vice versa*). The formation of *syn* adducts is also considerably more enthalpically advantageous than that of *anti* adducts (relative energies of all adducts correspond to *syn*/*anti* ratios higher than 99:1, 6-31G//6-31G, Table 3). Furthermore, the energetic preference of the formation of *syn* adducts of oxazaaluminolidines could be predicted to be twice as high as that of diaza- and dioxaluminolidines (Table 3).

Although the C=O overlaps of *syn* adducts were lower than those of *anti* ones differences of overlaps between the *anti*/*syn* pairs **3** / **3'**, **4** / **4'**, **5** / **5'**, are 0.044, 0.042 and 0.042 (i.e. the differences are almost equal). It looks as if the relative differences of C=O overlaps between *syn* and *anti* adducts would not depend on the nature of the aluminolidine system the carbonyl is bound to. Therefore, if better *syn*/*anti* selectivities would be observed in the case of reactions involving oxazaaluminolidines than in the case of related reactions of diaza- or dioxaluminolidines that would not emanate from the higher difference of activation of the *syn* and *anti* bound C=O groups of the adducts but be related to energetics.

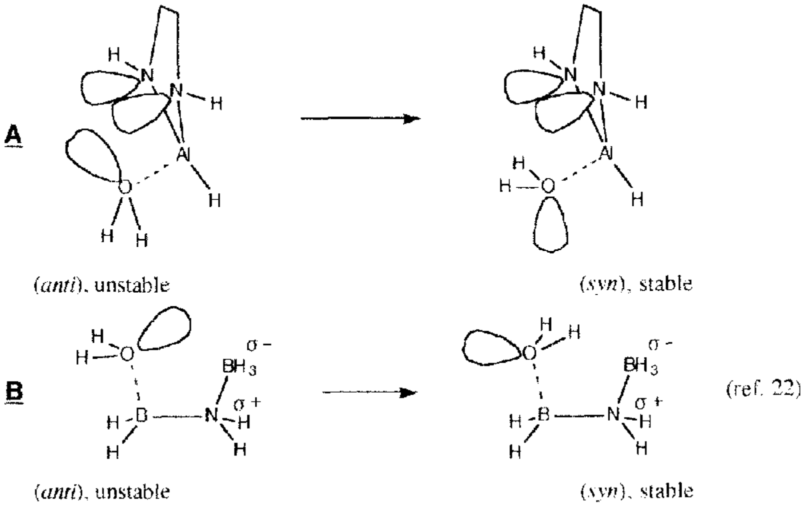
A comparison of Al-O_{CO}-C_{CO} bond angles of *syn* adducts (**3'**, **4'** and **5'**) with those of the corresponding *anti* ones (**3**, **4** and **5**) reveals that the angles of *syn* adducts are closer to 120° (all between 123.5° - 127.8°, Table 1) than those of the *anti* adducts (all between 131.0° - 135.8°, Table 1). This result is somewhat surprising because one could have predicted the angles of less sterically crowded *anti* systems to be closer to 120° than those of the more crowded *syn* ones. On the other hand, the same relative order of bond angles of *syn* and *anti* adducts has been observed also in the case of formaldehyde - borane adducts of 1,3,2-oxazaborolidine. The B-O_{CO}-C_{CO} bond angle of the *syn* adduct (H_2C=O *syn* to the oxazaborolidine about the B-O_{CO} bond) was 123.9° whereas that of the corresponding *anti* adduct was 126.2° (6-31G//6-31G).[3]

The Al-O_{CO}-C_{CO} bond angles increase in the series of **3** -> **4** -> **5** and **3'** -> **4'** -> **5'**. It looks as if changing heteroatoms of the diazaaluminolidine ring to oxygens would broaden the Al-O_{CO}-C_{CO} angle. At first glance the Al-O_{CO}-C_{CO} bond angle of **5** (135.8°, 6-31G//6-31G, Table 1) might look too obtuse already. However, even more obtuse angles have been observed in the case of aluminum aryloxides (Al-O-C_{Aryl} in the range of 140° - 164°).[16c] Furthermore, as compared with the Al-O_{CO}-C_{CO} angle (132.4°, 6-31G*//6-31G*) of aluminum trichloride - formaldehyde adduct[10c] the Al-O_{CO}-C_{CO} angles of **3** - **5** and **3'** - **5'** are not particularly large.

Water - diazaaluminolidine adduct (6)

The optimized structure (6-31G*//6-31G*) of the water - diazaaluminolidine adduct (**6**) is shown in Figure 4. Orientation of the water moiety of **6** corresponds to that of the formaldehyde *syn* adduct **3'** (the lone pair of oxygen *anti* to the aluminolidine ring). Despite several attempts no optimum was found for the corresponding *anti* adduct of water.[23] Similar behaviour of water coordinated to a borane adduct of aminoborane has been observed earlier.[22] The preference of the *syn* conformation could be rationalized as shown in Scheme II.

Scheme II



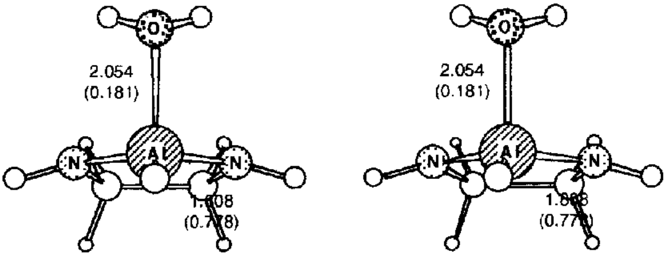
In the case of the *anti* conformation of **6** (A, Scheme II) the free electron pair of water (or ether, ketone etc.) would be placed close to the lone pairs of ring nitrogens. In other words, in the case of the *syn* adduct basic counterparts of the adduct are taken as far from one another as possible (low repulsion) whereas in the case of the *anti* adducts basic sites reside close together (high repulsion). In the borane - water adduct of aminoborane the free electron pair of oxygen of the *anti* conformation (**B**, Scheme II) is oriented towards the negatively charged H_3B group (high repulsion) whereas in the *syn* conformation the free electron pair points away from the H_3B group (low repulsion). As the free electron pair of formaldehyde of the *anti* adducts **3** - **5** would point towards the free electron pairs of the ring nitrogens [as does the lone pair in the water - diazaaluminolidine *anti* adduct (A, Scheme II)] the same repulsive destabilizing interaction could play a role also in the case of the formaldehyde adducts. Indeed, *anti* adducts are (**3** - **5**) less stable than the corresponding *syn* ones (**3'** - **5'**), Table 3.

A comparison of bond lengths of the water - diazaaluminolidine adduct (**6**, Figure 4) with those of the corresponding formaldehyde analog (**3'**) indicates that an sp^3 hybridized oxygen could coordinate somewhat tighter to aluminolidines than an sp^2 hybridized one. The Al-O bond of **6** (2.026 Å, 6-31G//6-31G, Figure 4) is 0.034 Å shorter than that of **3'** (Figure 1). On the other hand, the Mulliken Al-O overlap of **6** (0.080, 6-31G//6-31G, Figure 4) is lower than that of **3'** (0.118, Figure 1) but the charge transfer value of the water moiety of **6** is, however, only 0.007 units higher than that of formaldehyde of **3'** (6-31G//6-31G, Table 1). The N-Al-O bond angles of **3'** (100.9°, Figure 1) and **6** (99.6°, Figure 4) are closely similar, as are the hybridization degrees of the ring Al and N atoms (values of Al differ only by 0.6 % and those of N by 1 %, Table 2). The energy of formation of **6** is 20 kJ mol^{-1} more negative than that of its formaldehyde analog (**3'**, 6-31G//6-31G, Table 1). This indicates that the formation of complexes of Lewis basic ethers and diazaaluminolidines would be enthalpically more advantageous than that of carbonyl compounds. Consequently, aluminolidines could be predicted to be most acidic in noncoordinating solvents (not surprisingly, reactions catalyzed by diazaaluminolidines are normally run in CH_2Cl_2).[5,7]

On the relative performance of 3-21G, 6-31G and 6-31G basis sets*

On the basis of the comparison of structural parameters of **3'** and **6** discussed above one could conclude that **3'** and **6** are rather close relatives in the group of adducts of diazaaluminolidines and Lewis basic oxygen containing compounds. Therefore, a comparison of structural parameters of **6** optimized at the 6-31G level with those optimized at the 6-31G* level would reveal whether inclusion of polarization functions would be necessary for a study on the relative properties of these closely analogous compounds. As shown in Figure 4 the lengths of Al-N and Al-O bonds of **6** do not change much in consequence of inclusion the polarization functions. The Al-N bond shortens by 0.007 Å whereas the Al-O bond lengthens by 0.029 Å. However, as the Al-O bond lengthens also the degrees of hybridization of the ring Al and N atoms should change. This is indeed what is observed to take place. The sp^2/sp^3 (Al) value increases by 5.4 % whereas that of N decreases by 13 % (Table 2).

Bond and torsion angles	**6**	
N-Al-N	93.2°	(92.9°)
N-Al-O_{H2O}	96.9°	(99.6°)
H-N-C-C	162.8°	(168.2°)
Al-N-C-C	5.8°	(-0.5°)
H-Al-N-C	142.4°	(148.0°)
H-Al-N-H	-9.3°	(-18.0°)



6 **6**

Figure 4. Stereo representation of the optimized (6-31G*//6-31G*) structure of diazaaluminolidine - water adduct (**6**). Some of the most important bond lengths [in Å] and angles, as also Mulliken overlap populations (in parentheses below bond lengths), are shown. The Al-N and Al-O bond lengths of **6** optimized at the 6-31G level were 1.815 (overlap 0.518) and 2.026 Å (overlap 0.080). The bond and torsion angles optimized at the 6-31G level are shown in parentheses (right column).

A comparison of properties calculated at the 6-31G level with those obtained at the 3-21G level could be useful too. Namely, the changes of structural parameters of **6** in consequence of inclusion of polarization functions are less significant that those observed in consequence of moving from the 3-21G basis to the 6-31G one. For example, lengths of Al-O_{CO} bonds calculated at the 3-21G level (Table 1) are 0.069±0.015 Å shorter than those calculated at the 6-31G level. The rationale of inspection of relative differences of properties on the basis of results provided with no inclusion of polarization functions could be illustrated also by comparing the relative energies of *syn/anti* pairs shown in Table 3 or the charge transfer values shown in Table 1. The relative energies obtained at the 3-21G level are not much different from those provided at the 6-31G level [the largest difference of 3-21G and 6-31G energies is only 5 kJ mol^{-1} (in the case of **4/4'**), Table 3].

The charge transfer values calculated on the basis of results provided at 3-21G level are higher than those provided at the 6-31G level (Table 1). However, if the difference of charge transfer values of each pair (**3/3'**, **4/4'** and **5/5'**) is determined (0.004, 0.018, 0.004 at the 3-21G level and 0.004, 0.003, 0.005 at the 6-31G level, Table 1) it turns out that the differences are closely similar. Again, conclusions similar to those discussed above can be drawn; i.e. the relative values are not sensitive to the selection basis sets. Although this does not mean that stabilities of Lewis acid - base adducts would not be sensitive to the selection basis sets (some complexes of which the stationary point has been found when studied at the 3-21G level have turned out to be unstable when studied at the 4-31G or 6-31G levels or with inclusion of polarization functions)[25] problems with predicting stabilities arise only in the cases in which the systems inspected are very weakly bound; i.e. in the case of systems which could be regarded as labile, borderline cases. Adducts of carbonyl compounds to aluminolidines do not belong to the class of weakly bound systems.

Altogether, none of the results of the comparison of performance of basis sets would give rise to changes in any of the conclusions drawn above on the basis of comparisons of relative properties of adducts **3** - **5** and **3'** - **5'** determined with no inclusion of polarization functions. Computational studies on aluminolidines and related catalysts continue.

CONCLUSIONS

All results of this study indicated the formation of *syn* adducts of aluminolidines and carbonyl compounds (as those of ethers and related Lewis bases) to be favoured over that of the corresponding *anti* ones (C_{CO} *syn/anti* to the aluminolidine moiety about the Al-O_{CO} bond). The energetic preference for the formation of *syn* adducts of diazaaluminolidines was predicted to be closely similar to that of the corresponding *syn* adducts of dioxaluminolidines. The highest energetic preference for the formation of *syn* adducts was observed in the case of formaldehyde adduct to oxazaaluminolidines.

Activation of a carbonyl coordinated *syn* to the Lewis acidic aluminum of aluminolidines could be predicted to be higher than that of the corresponding *anti* coordinated one. On the other hand, the relative difference of the levels of activation of *syn* and an *anti* coordinated C=O groups could be predicted to be equal in the case of analogous diaza-, oxaza- and dioxaluminolidine adducts.

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