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A New Class of Oxazaborolidine Derivatives Discovered. Ketones and Aldehydes as Bidentate Ligands

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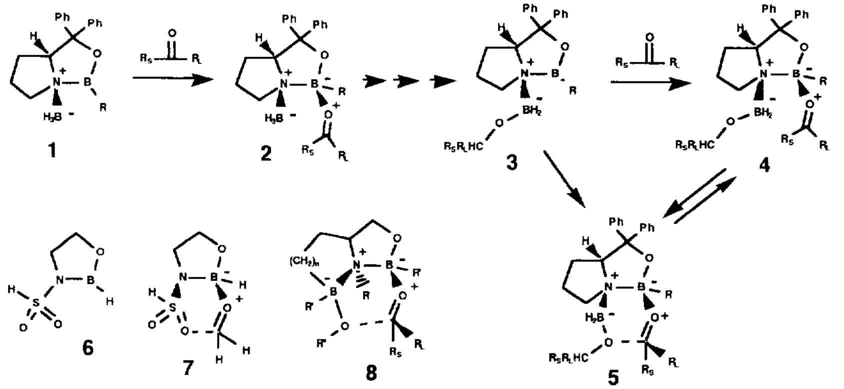
Abstract: - Novel adducts (**5'a-f**) of H_2CO / Me_2CO and H_2BOR (R = H, Me) to aminoborane (**1'a**), aminohydroxy-borane (**1'b**) and 1,3,2-oxazaborolidine (**1'c**) were studied by means of *ab initio* MO (RHF) methods. Energies of the formation of the adducts were clearly exothermic [e.g. -140 and -134 kJ mol^{-1} (MP2/6-31G*//MP2/6-31G*) in the case of H_2CO - H_2BOH adduct of **1'a** and **1'c**]. All the Me_2CO adducts were found to be slightly less stable than the corresponding H_2CO adducts. In all the adducts (**5'a-f**) studied the carbonyl system was found to behave as a bidentate ligand. All the bidentate adducts were found to be significantly more stable than the related monodentate adducts (**4'a-c**). Activation of the carbonyl moiety of the bidentate adducts resembles that of the related adducts of *N*-sulfonylated oxazaborolidines (**7**).

INTRODUCTION

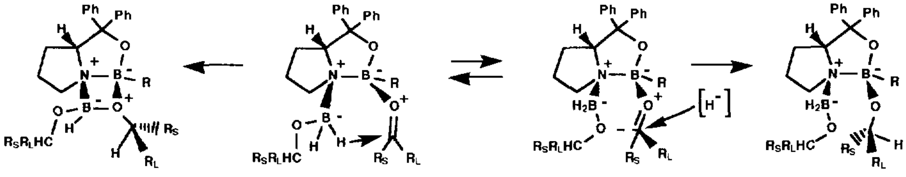
Chiral oxazaborolidines capable of forming borane adducts (e.g. **1**, Scheme I) have been shown to be efficient catalysts for the enantioselective reduction of ketones.[1,2] Computational studies[1,3,4] on the mechanism of the reduction indicate[4d] that the hydride transfer in **2** may lead to the formation of alkoxyborane adducts (**3**). These adducts (**3**) have been proposed to bind ketones to form alkoxyborane - ketone complexes (**4**, Scheme I).[4a,4e] Cai *et al.* suggest that alkoxyborane adducts (e.g. **3**) may perform less well in the enantioselective reduction of ketones than the corresponding borane adducts (e.g. **1**).[5]

Scheme I



Ab initio studies on the models of **3** indicate[4a] that the conformation of the alkyl tail of the borane moiety would greatly influence the nature of the $\text{N-B}_{\text{H}_2\text{BOCHR}_\text{L}\text{R}_\text{S}}$ interaction. If the alkoxy tail would be flexible enough its oxygen could interact with the carbonyl compound coordinated to the ring boron (e.g. the reaction **4** -> **5**). It is not known whether **3** could have this type of propensities of bidentate complexation agents. Nevertheless, they could be expected on the basis of the structural analogy between **3** and the *N*-sulfonylated oxazaborolidine **6**. *Ab initio* calculations indicate **6** to react with H_2CO to form chelates **7** (bidentate behaviour of H_2CO).[6] The structure and formation of **5** and its analogs could be of interest because formation of **5** could influence the catalytic performance of **1**. Namely, a hydride delivering agent could approach the carbonyl of **5** best from a direction opposite (hydride addition by an S_{N2} mechanism, Scheme II) to that of the desired reduction. Furthermore, as analogs of **6** are known as highly efficient catalysts for enantioselective reactions (e.g. asymmetric Diels - Alder reaction),[7] analogs of **5** (e.g. **8**, or other related systems in which the *N*-coordinated alkoxyborane group would be bound to the skeleton of the catalyst by an inert and rigid spacer) could be used as tools for controlling the activation of π-systems of C=O of ketones and aldehydes (e.g. for addition reactions analogous to those catalyzed by *N*-sulfonylated oxazaborolidines).

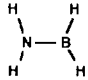
Scheme II

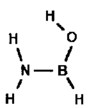

(Formation of the **desired** enantiomer)
4
5
(Formation of the **undesired** enantiomer)

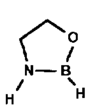
MODELS AND METHODS

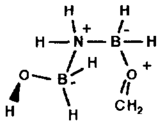
In order to study the structure and energetics of the formation of **5** (Scheme I) standard *ab initio* MO calculations (RHF) were carried out using the Gaussian packages[8] of programs (G80,[8a-b] G90,[8c] G92[8d] under VAX/VMS systems) at the 3-21G, 6-31G (G80) and 6-31G* (G80, G90, G92) levels. The influence of electron correlation was taken into account by performing single-point second-order Møller-Plesset calculations (G90, G92)[8c-d] on the structures optimized at the 6-31G* levels (denoted as MP2/6-31G*//6-31G*).

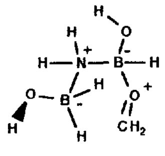
Models used in this study were as follows: **1'a-c** (for **1**); **4'a-c** (for **4**); and **5'a-f** (for **5**). The structure[6b] of **7** was reoptimized with inclusion of polarization functions. Although the goals of this study could have been achieved by inspecting the models **1'c**, **4'c** and **5'c**, the other models (**1'a-b** and the related hydroxyborane - formaldehyde adducts) were involved for purposes of comparisons (this work *vs* the previous studies[4]). Properties of the models **1'a-c** have been discussed in the literature[7] whereas no previous calculations on **4'a-c** or **5'a-f** appear to have been published.

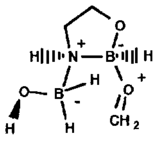

1'a

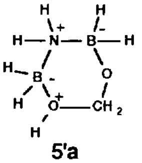

1'b

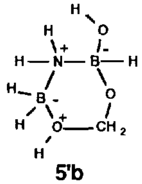

1'c


4'a


4'b


4'c


5'a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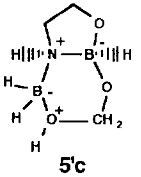
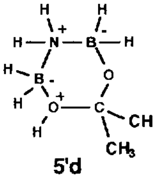
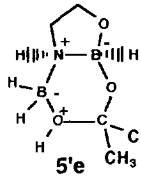
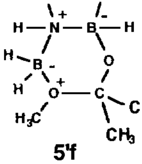

5'c


5'd


5'e


5'f

In order to determine the influence of electron correlation on the structural parameters selected mono- and bidentate adducts (**4'a**/ **5'a** and **4'c**/ **5'c**) were fully optimized (using G92 on Cray X-MP / EA 464 / Unicos for **4'c**/ **5'c**) at the MP2 level (with inclusion of polarization functions; denoted as MP2/6-31G*//MP2/6-31G*). Furthermore, to assess the overall quality of the optimized structures of the novel bidentate chelates, IR spectrum of the best $H_2C{=}O$ chelate model (**5'c**; MP2/6-31G*//MP2/6-31G*) was calculated. The absence of imaginary frequencies in the spectrum was considered to confirm the geometry of the model to represent a true energy minimum. Electronic charges and bonding properties of the model were analyzed with the help of the NBO program, which is a subprogram in G92.[8d]

It has been lately shown that density function (LDF) theories[9] perform well for small polarized molecules [results compatible with high level *ab initio* (MP2/6-31G*//MP2/6-31G*) calculations have been reported by Llamas-Saiz *et al.*].[10] Therefore, in order to probe the utility of LDF methods in the case of the highly polarized adducts studied in this work, structures of the best bidentate $H_2C{=}O$ chelate model (**5'c**) and the related monodentate analog (**4'c**) were optimized using the LDF method (using DMol[11] on a Convex C3840 main frame computer). The DNP basis set used in the LDF calculations corresponds to the 6-31G** basis in the Gaussian terminology.

RESULTS AND DISCUSSION

Total energies and dipole moments of the optimized structures are shown in Table 1. Energies of the formation of the adducts are shown in Table 2. Observations related to the (un)stability of **4'c** are summarized in Table 3. Charge transfer values related to the formation of **5'a-f** and **7** are presented in Table 4 and the degrees of *sp*^{2} - *sp*^{3} hybridization (% of pyramidalization) of the $C_{C=O}$ of **5'a-f** and **7** in Table 5.

Table 1. Total energies and dipole moments of the models.[a]

Structure	3-21G//3-21G		6-31G//6-31G		6-31G*//6-31G*		MP2/6-31G*//6-31G*	MP2/6-31G*//MP2/6-31G*	
	E[a]	D[a]	E	D	E	D	E	E	
1'a	-81.04343	2.01	-81.46276	1.76	-81.48910	1.82	-81.73077	-81.73122	1.81
1'b	-155.55682	3.27	-156.35434	3.23	-156.40862	2.96	-156.82606	-	
1'c	-232.01452	3.16	-233.19703	3.21	-233.29859	2.67	-233.96562	-233.96765	2.74
4'a	295.04789	4.58	296.54686	4.27	-	-[b]	-	-[b]	
4'b	-369.55717	4.15	-371.43266	4.01	-371.58315	3.53	-372.57755	-	
4'c	-446.01955	3.28	-448.27888	2.87[c]	-448.47665	2.90	-449.72473	-[b]	
5'a	-295.09939	3.63	-296.58227	3.71	-296.70263	3.41	-297.52669	-297.53002	3.17
5'b [d]	-369.61129	3.43	-371.47330	3.33	-371.61755	2.75	-372.61782	-	
5'c	-446.06774	4.84	-448.31276	4.97	-448.50654	4.02	-449.75952	-449.76389	3.88
5'd	-372.75270	3.74	-374.63489	3.67	-374.78125	3.46	-	-	
5'e	-523.72117	4.58	-526.36555	4.84	-	-	-	-	
5'f	-411.56028	4.77	-413.63538	4.51	-413.80140	4.19	-	-	
6	-779.25546	5.60[e]	-780.07042	5.67[e]	-780.44814	4.88	-	-	
7	-889.47817	4.54[e]	-893.87650	4.41[e]	-894.29290	3.42	-	-	
H_2B-OH	-100.76196	1.91	-101.27793	1.89	-101.32139	1.68	-101.57685	-101.57769	1.71
H_2B-OMe	-139.57090	21.6	-140.28052	2.06	-140.54684	1.71	-	-	
$H_2C{=}O$	-113.22182	2.66	-113.80836	3.04	-113.86633	2.67	-114.16525	-114.16775	2.84
$Me_2C{=}O$	-190.88722	3.14	-191.87503	3.59	-191.96224	3.12	-192.52160	-	

[a] Total energies (E) given in Hartrees and dipole moments (D) in Debyes (ref. 12). [b] The complex was found to be unstable (mimicking the reduction catalyzed by oxazaborolidines a hydride of H_2BOH was transferred to the carbon of H_2CO). [c] See notes (ref. 13). [d] Orientation of the O-H bond of the off-ring OH group better described as *syn* to the adjacent B-H bond (than *syn* to the B-N bond). [e] From ref. 6b.

Monodentate adducts

Structural parameters of the monodentate adducts (**4'a-c**) compared with those of the related borane adducts[4] indicate that alkoxyborane adducts of oxazaborolidines resemble the corresponding borane adducts. The energies of formation of monodentate alkoxyborane adducts (Table 2) compared with those[4] of the related borane adducts indicate that the former adducts seemingly should not be much less stable than the latter ones. Neither the dipole moments of **4'a-c** (Table 1) are much higher than the moments[4] of the related borane adducts. The energies of formation (Table 2) of these monodentate adducts (**4'a-c**) were, however, much less favorable than the corresponding values of the bidentate adducts (**5'a-c**).

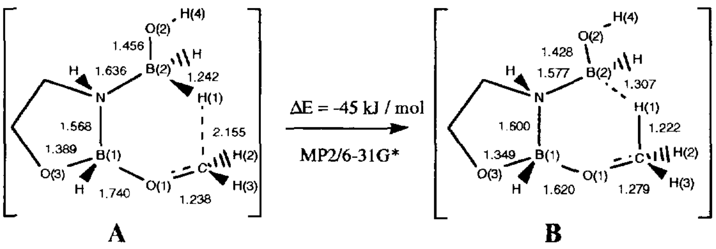
Table 2. Energies (ΔE)[a,b] of the coordination of $H_2C{=}O$ / $Me_2C{=}O$ and $H_2B\text{-}OH$ to aminoboranes (**1'a-c**).

Structure	3-21G//3-21G	6-31G//6-31G	6-31G*//6-31G*	MP2/6-31G*//6-31G*	MP2/6-31G*//MP2/6-31G*
4'a	-54	+6	-[c]	-[c]	-[c]
4'b	-44	+21	+35	-25	-
4'c	-56	+12 [c]	+25	-45	-[c]
5'a	-190	-87	-68	-141	-140
5'b [c]	-178	-76	-48	-123	
5'c	-183	-77	-53	-136	-134
5'd	-158	-50	-22	-	-
5'e	-151	-41	-	-	-
5'f	-154	-45	-	-	-
7	-62	+26	+57	-	-

[a] Energies (ΔE, relative to **1'a-c** + $H_2B\text{-}OH$ + H_2CO/Me_2CO) given in kJ mol^{-1}. [b] These energies should not be considered as absolute reaction enthalpies but used only for comparisons between closely related analogs or series of analogs. [c] See Table 1.

In spite of the similarities described above, results of this work indicate a difference between the (kinetic) stability of the borane and alkoxyborane adducts. Namely, in the case of optimization of structures of H_2BOH - H_2CO adducts the hydride (of H_2BOH) residing spatially close to the $C_{C=O}$ of H_2CO was drawn so close to the $C_{C=O}$ that a new (C-H) bond was formed. The newly formed C-H bond could be best described as a normal covalent C-H bond. The "reduction" of the H_2CO moiety by the hydride of H_2BOH was observed at both 6-31G* and MP2/6-31G* levels in the case of **4'a** (Table 1).[13] In the case of **4'c** the same phenomenon was seen at the MP2/6-31G* level (Tables 1 and 3).[13] The LDF calculations (on **4'c**) corroborate the results obtained at the MP2/6-31G* level (Table 3).

Table 3. The most important structural parameters of two intermediate structures (**A** and **B**)[a] obtained during optimization of the geometry of **4'c** at the MP2/6-31G* level.



#	(torsion)angles:	**A**	**B**	Δ (**B**-**A**)	#	(torsion)angles:	**A**	**B**	Δ (**B**-**A**)
1	H(1)-C-H(3)	100.5°	98.3°	-2.2°	12	B(1)-O(1)-C-H(2)	-169.0°	-172.6°	-3.6°
2	H(1)-B(2)-H	110.0°	103.0°	-7.0°	13	B(1)-O(1)-C-H(1)	-62.4°	-59.6°	-2.8°
3	H(1)-C-O(1)	97.6°	111.8°	+14.2°	14	N-B(2)-H(1)	106.0°	102.0°	-4.0°
4	H(1)-C-H(2)	75.8°	91.5°	+15.7°	15	N-B(2)-O(2)	101.4°	106.3°	+4.9°
5	H(1)-B(2)-N-B(1)	-49.9°	-31.0°	-18.9°	16	N-B(1)-O(1)	100.5°	100.6°	+0.1°
6	H(1)-B(2)-O(2)	114.4°	110.5°	-3.9°	17	N-B(1)-O(3)	108.0°	105.4°	-2.6°
7	H(1)-B(2)-O(2)-H	78.6°	80.2°	+1.6°	18	N-B(2)-O(2)-H(4)	-167.7°	-169.4°	-1.7°
8	B(1)-N-B(2)	122.0°	117.8°	-4.2°	19	N-B(1)-O(1)-C	75.8°	55.0°	-20.8°
9	B(1)-O(1)-C	115.3°	111.8°	-3.5°	20	O(1)-C-H(2)	121.6°	120.9°	-0.7°
10	B(1)-N-B(2)-O(2)	-169.6°	-148.0°	-21.6°	21	O(1)-C-H(3)	119.2°	118.2°	-0.4°
11	B(1)-O(1)-C-H(3)	15.6°	46.2°	+30.6°					

[a] Neither **A** nor **B** represents a minimum in the potential energy surface.

In the light of the results (Table 3) and that what is known about the related borane adducts,[4] it looks as if the energy barrier preventing the hydride from spontaneously "falling down" onto the carbonyl would be lower in the case of alkoxyborane adducts than in the case of the related borane adducts [so low that it was not recognized when the energy gradients (relative to the structural parameters of **4'c**) were calculated]. On the other hand, this is not a surprising result because it has been experimentally observed that alkoxyborane adducts (sp^3 hybridized boron) are stronger reducing agents than the related borane adducts. Unfortunately, a thorough comparative study on borane and alkoxyborane adducts of oxazaborolidines would be a very demanding (computationally) task [plausible conformers of alkoxyborane adducts need to be generated (by rotating the O-B bond of alkoxyborane, the N-B bond between the catalyst and alkoxyborane and the B-O_{CO} bond), stabilities of all the (numerous) conformers evaluated, and finally, all the transition states (between the conformers found stable) determined]. Therefore, further analyses in this direction were considered to be beyond the scope of this work (describing novel bidentate chelates). Only very preliminary results obtained (at the MP2/6-31G*) in the case of **4'c** are summarized in Table 3. The results imply that simple rotations of the N-$B_{alkoxyborane}$ (#5 and #10, Table 3) and B-$O_{C=O}$ bonds (#11, Table 3) accompanied by predicted changes of bond lengths[3,4] and minor changes of most bond angles [e.g. in both the **A** and **B** systems the $C_{C=O}$ is still sp^2-hybridized and the B(2) sp^3-hybridized (#20, #21, Table 3)] allow the hydride to approach very close to the $C_{C=O}$ (H-$C_{C=O}$ distance 1.222 Å in **B**) and the total energy of the system to decrease substantially [e.g. -45 kJ mol^{-1} (Table 3)]. On the basis of an analogous study on **4'c** (using DMol at the DNP level) and **4'a** (MP2/6-31G*) continued optimization of **B** (Table 3) would shorten the newly formed C-$H_{hydride}$ bond further and lead, eventually, to the formation of a structure in which the $C_{C=O}$ center would be fully sp^3-hybridized.

Bidentate adducts

Structural parameters of the adducts (**5'a**, **5'c** and **7**, Fig. 1) imply that the mechanism of binding of the carbonyl would be similar in the case of both **5** and **7**. This similarity could be illustrated as follows:

a) The carbonyl moiety is planar neither in **5'a-f** nor in **7** [e.g. the degree of pyramidalization (6-31G*//6-31G*) of the $C_{C=O}$ of **7** is 55 %; the corresponding values of **5'a-c** are all 67 %, Table 5];
b) The C=O bond of **7** (Fig. 1) is 1.315 Å long, the C=O bonds of **5'a-d** are 1.331 ± 0.005 Å long;
c) The distance between the Lewis basic oxygen (donating electron pair to the carbonyl) and the $C_{C=O}$ in **7** (1.556 Å, Fig. 1) is only 0.070 Å longer than the corresponding distances (1.487 ± 0.005 Å) of **5'a-c**;
d) The B-$O_{C=O}$ bond of **7** (Fig. 1) is only slightly weaker than the B-$O_{C=O}$ bonds (1.484 ± 0.005 Å) of **5'a-d**;
e) Differences of the positive charges of $C_{C=O}$ of **5'a-c** (+0.248 ± 0.008, Table 5) and **7** (+0.285) are small.
f) Dipole moments of the adducts (**5'a-f** and **7**, Table 1) are all rather high [e.g. D(6-31G*//6-31G*) of **5'a-d** and **7** are all within 3.4 ± 0.7 D, Table 1].

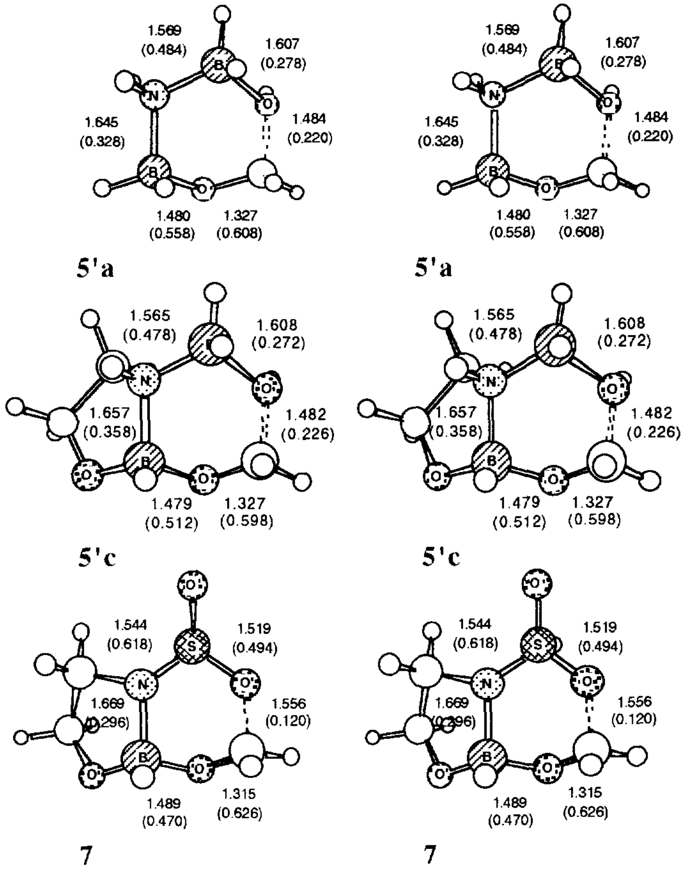
Table 4. Charge transfer (Q_T) related to the formation of adducts **5'a-f** and **7**.[a]

Structure		6-31G//6-31G			6-31G*//6-31G*		
		$Q_T(R_2C{=}O)$	$Q_T(H_2BOH)$	Q_T(1'a-c or 6)	$Q_T(R_2C{=}O)$	$Q_T(H_2BOH)$	Q_T(1'a-c or 6)
5'a	(R=H)	-0.048	+0.037	+0.011	0.000	-0.012	+0.012
5'b[b]	(R=H)	-0.067	+0.044	+0.023	-0.024	-0.006	+0.030
5'c	(R=H)	-0.074	+0.055	+0.019	-0.025	+0.008	+0.017
5'd	(R=Me)	-0.019	+0.007	+0.012	+0.043	-0.051	+0.008
5'e	(R=Me)	-0.043	+0.032	+0.011	-	-	-
5'f	(R=Me)	-0.012	-0.004 [c]	+0.016	-	-	-
7	(R=H)	-0.043	-	+0.043	+0.047	-	-0.047

[a] The negative (positive) sign indicates that the species has received (donated) negative charge. [b] See Table 1. [c] The value of H_2BOMe given instead.

The energies of formation (ΔE, Table 2) indicate that the bidentate adducts (analogous to **5**) could be much more stable than the related monodentate adducts (analogs of **4**). The ΔE values (Table 2) of bidentate adducts (**5'a-c**) are clearly lower [e.g. 91 kJ mol^{-1} in the case of 4'c/5'c-(MP2/6-31G*//6-31G*), Table 2] than those of the related monodentate adducts (**4'a-c**). Furthermore, these conclusions are consistent with those one could draw on the basis of the following two observations: 1) the IR spectrum of **5'c** calculated at the MP2/6-31G*//MP2/-6-31G* level did not show imaginary frequencies; 2) **4'a** and **4'c** were found to be unstable[13] when optimized at the MP2/6-31G* level. On the other hand, the ΔE values of monodentate adducts (**4'a-c**) appeared to be less positive than ΔE of **7** (Table 2).

Results of this work indicate that the nature of the aminoborane derivative (**1'a-c**) has only a minor influence on the ΔE values of the bidentate adducts. Namely, although the relative ΔE values of the adducts are rather similar (e.g. **5'a-c** of which all the values are within $\Delta E_{average}$ ± 10 kJ mol^{-1}, Table 2) the values decrease slightly with the decreasing electron withdrawing nature of the Lewis acidic center of the catalyst model. The nature of the complexing carbonyl counterpart has, however, a larger influence on the energies. The ΔE values of the H_2CO complexes are significantly more negative than those of the related Me_2CO complexes [e.g. ΔE of **5'a** is 46 kJ mol^{-1} (MP2/6-31G*//6-31G*) more negative than that of **5'd**, Table 2]. Structural changes related to this energy difference could be inspected as shown in Figure 2.



5'a 5'a

5'c 5'c

7 7

Figure 1. The optimized (6-31G*//6-31G*) structures of 5'a, 5'c (6-rings chairs) and 7 (6-ring a boat). Some of the most important bond lengths [in Å] and the corresponding Mulliken overlap populations (values in parentheses) are presented.

The structural changes (Fig. 2) indicate that the substitution (H -> Me) on the $C_{C=O}$ affects interactions between the carbonyl and the adjacent oxygen of the alkoxy/hydroxyborane (more than the others). In consequence of the substitution (Fig. 2) the C=O bonds lengthen slightly (the corresponding overlaps decrease) but, the B-$O_{C=O}$ bonds, however, are hardly affected. Therefore, as the electron donating interaction (from the oxygen of alkoxy/hydroxyborane to the carbonyl carbon) weakens (Fig. 2), charge transfer (from the oxygen of the alkoxy/hydroxyborane) to the C=O system should be lower in the case of ketones. Furthermore, as the bond providing sp^3 nature to the carbonyl carbon lengthens (Fig. 2) the degree of sp^2 hybridization of the carbon should increase (ketones should be more activated than aldehydes). This is indeed what was observed. The charge transfer values [$Q_T(R_2C=O)$, Table 4] of **5'd** and **5'e** are more positive / less negative [the % of pyramidalization slightly lower (Table 5)] than those of **5'a** and **5'c**.

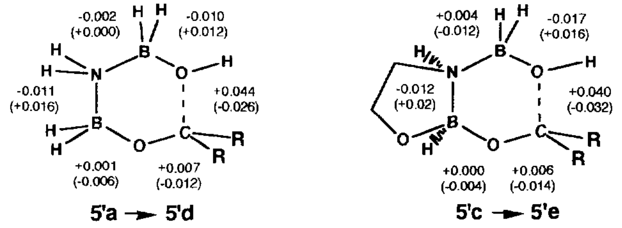


Figure 2. Changes of bond lengths (in Å) and Mulliken overlap populations (values in parentheses) related to the hypothetical reactions 5'a -> 5'd and 5'c -> 5'e (replacement of the hydrogens of the H_2CO moiety by methyls) calculated on the basis the 6-31G//6-31G optimized structures.

Table 5. The degree of sp^2 - sp^3 hybridization and the total atomic charge of the carbonyl carbon in the formaldehyde and acetone adducts 5'a-f and 7.[a]

Structure	$sp^2 : sp^3$		$Q(C_{CO})$	
	6-31G/6-31G	6-31G*/6-31G*	6-31G/6-31G	6-31G*/6-31G*
5'a	36 : 64	33 : 67	+0.327	+0.249
5'b [b]	33 : 67	33 : 67	+0.321	+0.245
5'c	33 : 67	33 : 67	+0.318	+0.240
5'd	37 : 63	32 : 68	+0.591	+0.589
5'e	35 : 65	-	+0.574	-
5'f	29 : 71	-	+0.639	-
7	50 : 50	45 : 55	+0.315	+0.285
H_2CO	100 : 0	100 : 0	+0.159	+0.134
Me_2CO	100 : 0	100 : 0	+0.477	+0.524

[a] Calculated on the basis of the sum of the R_1-C=O, R_2-C=O and R_1-C-R_2 angles of the $R_1R_2C=O$ system. The value 328.4° corresponds to the ratio of 0:100 (% of pyramidalization 100) and 360° to 100:0 (% of pyramidalization 0) of the sp^2 - sp^3 nature. [b] See Table 1.

As described above, adducts analogous to 5 could be predicted to posses properties similar to those of 7. Taking into account that many catalysts (*N*-sulfonylated 1,3,2-oxazaborolidines analogous to 6)[1,7] for the asymmetric Diels - Alder reaction are known and computational studies on 7[6b] and the related acrolein analogs[6a] imply the activation of the carbonyl carbon of the aldehyde to increase (e.g. the positive charge of $C_{C=O}$ of the formaldehyde moiety in 7 and 5'a-c is about two times as high as that of an uncomplexed formaldehyde molecule, Table 5) one could predict that the carbonyl carbon of 5 would react with strong nucleophiles (e.g. hydride, delivered by some of the borane derivatives present in the reaction mixture of the CBS reduction, Scheme II). Furthermore, the potentiality of formation of intramolecular borane adducts (e.g. 8) could be used for adjusting the electrophilic character of (conjugated) carbonyl π-systems of ketones and aldehydes to better meet requirements of (enantio)selective addition reactions (i.e. for purposes of design of active sites of new chiral catalysts). A brief preliminary evaluation of the prospect of this approach could be done on the basis of the analysis of the electron structure (NBO and electrostatics) of **5'c** (MP2/6-31G*//MP2/6-31G*) summarized in Figure 3.

The NBO analysis of **5'c** (MP2/6-31G*//MP2/6-31G*) reveals, that **5'c** has neither clearly Lewis acidic centers nor double bonds. Nevertheless, the $C_{C=O}$ [natural electron configuration 1s(1.00), 2s(1.00), 2p(2.62), 3p(0.02), 3d(0.01)] of **5'c** has partially vacant *2p* orbitals. Furthermore, the first antibonding orbital is located on the $C_{C=O}$ - O_{H_2BOH} interaction (Figure 3) indicating that, if a Lewis base donates electron density to a chelate such as **5'c** the $C_{C=O}$ - O_{H_2BOH} bond would be the first one being weakened or broken (both the bonding and antibonding orbitals located on the $C_{C=O}$ - O_{H_2BOH} interaction would be occupied). An inspection of the natural bonding orbitals (Figure 3) reveals that, neither the $C_{C=O}$ - O_{H_2BOH} nor $C_{C=O}$ - $O_{C=O}$ bond is much less polarized that the B-O or B-N bonds. This is somewhat surprising, because the B-O and B-N bonds (Figure 3) are so highly polarized that they could be considered almost as ionic bonds. The bonding NAO contributions of the oxygen and boron in the $(B\text{-}O)_{H_2BOH}$ bond are 86 and 14 %, respectively. Therefore, although no highly Lewis acidic centers were found in **5'c** the high ionic nature of the C-O bonds of $C_{C=O}$ (also the positive charge of $C_{C=O}$ of the formaldehyde of **5'c** is substantially higher than that of free formaldehyde, Table 5) could allow the carbonyl counterpart to react with basic species (e.g. a hydride, Scheme II). Further studies on the properties and mechanisms of formation of analogs of **5** / **8** an their reactions (e.g. Scheme II) are in progress.

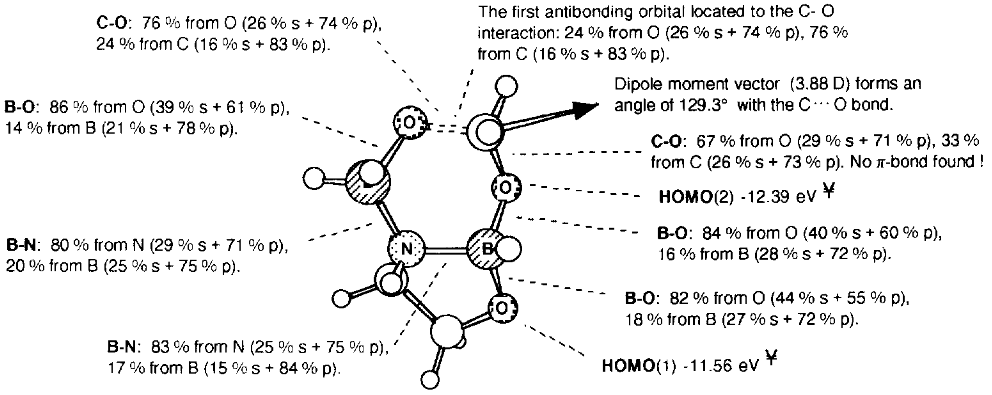


Figure 3. A summary of results of a natural bond orbital analysis (NBO) of the electron structure of 5'c (MP2/6-31G*//MP2/6-31G*). ¥ 1-Center valence electron lone pair.

On the performance of the methods

The performance of MP2/6-31G* and LDF[9,10] methods was evaluated in the case of the models **4'c** and **5'c**. Because the novel nature of the bidentate adducts (**5**) the reliability of results obtained at the MP/6-31G* level was assessed by calculating the IR spectrum of **5'c**. The absence of imaginary frequencies [only one insignificant imaginary vibration (at -2.8 cm^{-1}) was observed] confirms the (MP2/6-31G*//MP2/6-31G*) stucture of **5'c** to represent a true energy minimum.

In order to compare the performance of MP2/6-31G* and LDF[9,10] methods the structures (6-31G*//6-31G*) of **4'c** and **5'c** were reoptimized at the DNP level of LDF theory (DMol[11]). Although all the bonds of the chelate ring (of **5'c**) shortened (Fig. 4) the optimized structure was highly superimposable with that obtained at the MP2/6-31G*//MP2/6-31G* level. In the case of **4'c** both the methods gave similar results; the spontaneous reduction[13] of the formaldehyde moiety took place (e.g. Table 3). Therefore, it looks as if, in the case of these highly polarized chelates, the LDF methods at the DNP level would give results compatible with those achieved using MP2/6-31G*.

Results calculated at the different levels of the *ab initio* theory indicate that the absolute ΔE values (Table 2) vary much with the level of goodness of the method. Until the 6-31G* level the (ΔE) values become continuously more positive (less negative) with the increasing quality of basis sets [e.g. in the case of 5'c the ΔE values calculated (3-21G//3-21G, 6-31G//6-31G, 6-31G*//6-31G*) were: -183, -77 and -53 kJ mol^{-1} (Table 2). Then, effects related to electron correlation (at the 6-31G* level) decrease the values substantially [e.g. ΔE of 5'c (MP2/6-31G*/6-31G*) is -136 kJ mol^{-1}]. Interestingly, reoptimization of the 6-31G*//6-31G* structures at the MP2/6-31G* level hardly changed the relative ΔE values of the bidentate chelates [e.g. ΔE of 5'c (MP2/6-31G*//MP2/6-31G*) was only 1 kJ mol^{-1} lower that the MP2/6-31G*//6-31G* value, Table 2]. Interestingly, in the case of the models of 5 it looks as if ΔE values obtained at the 3-31G level would be more close to those obtained at the significantly more expensive MP2/6-31G*//MP2/6-31G* level than the ΔE values provided using other basis sets (Table 2). This conclusion appears to apply also in the case of bond lengths of the models of 5 (Fig. 4). At the MP2/6-31G*//MP2/6-31G* level the bond lengths of the chelate ring [except the length of N-B(1), Fig. 4] turn back towards the values obtained using the 3-21G basis. In the case of the models of 4 the results, however, were significantly dependent on the models and methods.[13] Altogether, it looks as if, in the case of these polar molecules (analogs of 1 - 5), the best computational methods could be found on the basis of trial and error, case by case.

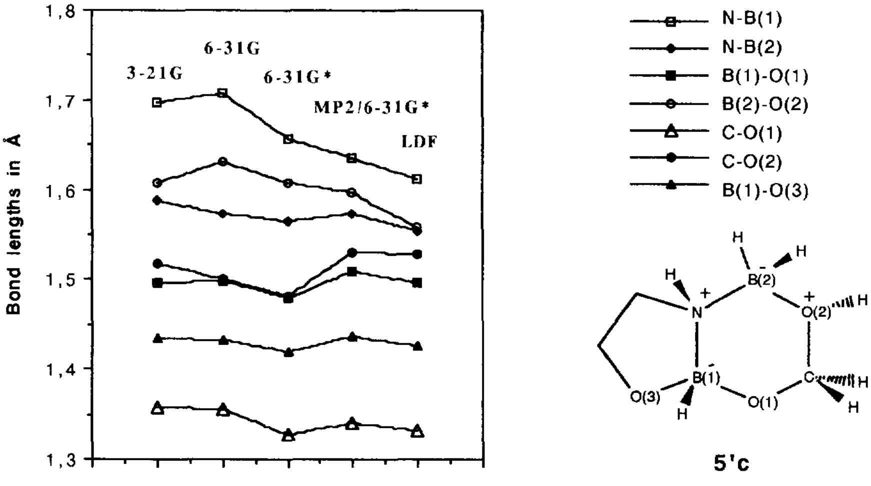


Figure 4. Correlation of bond lengths of 5'c with the quality of computational methods.

CONCLUSIONS

Bidentate chelates (5) of aldehydes/ketones and alkoxy/hydroxyboranes with aminoboranes, alkoxy/hydroxyboranes and oxazaborolidines were predicted to be significantly more stable than the related monodentate chelates (4). The bidentate chelates were found to be structurally analogous to aldehyde complexes (e.g. 7) of *N*-sulfonylated oxazaborolidines. In both of these systems (5 and 7) formaldehyde was found to behave as a bidentate ligand.

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12. Units: 1 Hartree = 4.359 7482 10^{-18} Joules (627.5095 kcal mol^{-1}); 1 Debye = 3.336 10^{-30} Cm.
13. The structure of **4'c** was found stable at the 3-21G and 6-31G levels when optimized using the G80 package. Reoptimization of the 6-31G//6-31G structure of **4'c** (from G80) using the more recent version of the package (i.e. using G90 and G92) indicated that the structure (**4'c**) should be unstable (interactions between the carbonyl oxygen and boron of the oxazaborolidine ring were loose; the formaldehyde was expelled from the H_2BOH - oxazaborolidine adduct. However, being optimized with inclusion of polarization functions (6-31G* level using G92) the structure (**4'c**) turned stable again (both the H_2BOH and H_2CO counterparts decently bound to the oxazaborolidine system). Then, when the structure (**4'c**; 6-31G*//6-31G*) was submitted for further optimization with inclusion of electron correlation (i.e. in order to determine the MP2/6-31G*//MP2/6-31G* structure and energy of **4'c**) another type of instability turned up. One of the hydrides of the H_2BOH counterpart fell to the carbonyl carbon leading to the "reduction" of the carbonyl (Table 3). The same results were observed when the structure (**4'c**; 6-31G*//6-31G*) was optimized further at the DNP level using DMol. In the case of **4'a** this "reduction" was observed at both the 6-31G* and MP2/6-31G* levels.

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