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Quantum Chemical Modeling of Chiral Catalysis. Part 17. On the Diborane Derivatives of Chiral Oxazaborolidines Used as Catalysts in the Enantioselective Reduction of Ketones

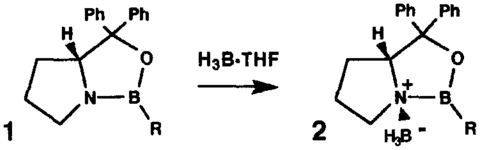
Vesa Nevalainen

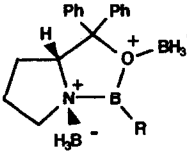
Division of Organic Chemistry, P.O. Box 6, SF-00014 University of Helsinki, Finland

Abstract: - Relative stabilities of isomers of borane (H_3B) diadducts of oxazaborolidines (**1**) were investigated by means of *ab initio* MO (RHF) methods [1,3,2-oxazaborolidine (**1'**) as a model of **1**]. Three isomers (**4'**, **5'** and **6'**, all hydride-bridged) were found to be (51, 24 and 69 kJ mol^{-1}; MP2/6-31G*//6-31G*) more stable than the borane *N,O*-diadduct (**3'**) of **1'**. The most stable isomer (**6'**) could be described as a system in which two bridges ("-H_2B-H-BH_2-" and "-H_2B-") connect the *O*- and *N*-ends of the 2-aminoethoxy moiety. The other two isomers (**4'** and **5'**) could be both considered as (amino)diborane derivatives. In the former (**4'**) the diborane system is fused to the B-N bond of borane *O*-adduct of **1'** (one hydride bridge) whereas in the latter the B-H bond of the boron of the oxazaborolidine ring of borane *N*-adduct of **1'** is involved in the diborane structure (two hydride bridges). A new plausible regeneration pathway for the CBS reduction was proposed.

INTRODUCTION

Chiral oxazaborolidines **1** are known to induce a highly enantioselective catalytic reduction of ketones as borane is used as a source of hydrogen (the CBS reduction). Two review articles summarize the present status of oxazaborolidines in the field of enantioselective synthesis.[1] Formation of the borane adducts **2** has been proposed to be the first step in the mechanism of the catalysis.[1,2]





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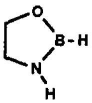
The formation of **2** ($R=CH_3$) has been recently confirmed by means of X-ray crystallography.[3] NMR-Spectrometric studies on borane adducts of oxazaborolidines derived from ephedrine have been reported by Tlahuext and Contreras.[4] Those studies indicate that oxazaborolidines **1** (R=H) may undergo a hydrogen - deuterium exchange if treated with D_3B. The exchange was proposed to involve a formation of diborane type of 4-membered ring system (one of the deuteriums of the *N*-coordinated D_3B suggested to form a deuteride bridge to the boron of the oxazaborolidine moiety). Conclusions different from those of Tlahuext and Contreras[4] were drawn as aggregation of oxazaborolidines and borane adducts of oxazaborolidines was studied by means of theoretical methods [*ab initio* MO studies on simple models of **1** and **2** and their aggregates].[5] A related *ab initio* study on plausible isomers of borane adducts of 1,3,2-oxazaborolidine was published simultaneously.[6] Results of these studies[5,6] imply diborane systems fused to the B-N bond of oxazaborolidines to be unstable (although the structure of borane *N*-adduct of aminoborane is known to be analogous to that of diborane[7,8]). On the other hand, results of computational studies indicate that borane *O*-adducts of oxazaborolidines could be stable (although the energies of formation of *O*-adducts were found to be less advantageous than those of the corresponding *N*-adducts).[9] Therefore, as the results of *ab initio* (RHF) studies indicate that oxazaborolidines have two Lewis basic centers capable of binding Lewis acids a question arises whether both of these basic centers could bind borane to give borane *N,O*-diadducts (e.g. **3**), and if so, what type of other related structures could be formed (isomerism) and what role those structures could play in the reactions catalyzed by oxazaborolidines. The goal of the present work was to answer these questions.

MODELS AND COMPUTATIONAL METHODS

Standard *ab initio* MO calculations (RHF) were performed using the Gaussian-80 program system at the 3-21G, 4-31G, 6-31G and 6-31G* levels.[10] Modeling techniques similar to those applied in the case of previous reports of this series[11] were employed. Inclusion of electron correlation was handled to second order with Moller-Plesset perturbation theory by performing single-point calculations on the optimized 6-31G* structures (MP2/6-31G*//6-31G*). These (MP2) energies were determined using the Gaussian-90 package.[10c] 1,3,2-Oxazaborolidine (**1'**) was used as a model of the catalysts (**1**) and **2'** as a model of the corresponding borane *N*-adducts (**2**). Structures **3'** - **12'** were used as models of plausible borane diadducts of oxazaborolidines. No other calculations on **3'** - **12'** appear to have been published. Properties of models **1'** and **2'** have been described in the literature.[5,6,12]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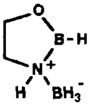
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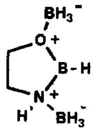
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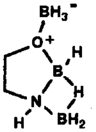
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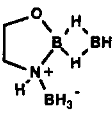
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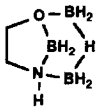
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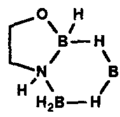
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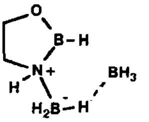
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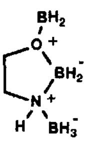
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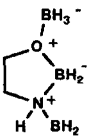
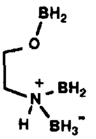

10'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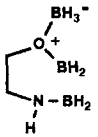

12'

RESULTS AND DISCUSSION

The model **10'** was stable only at the 3-21G level whereas **7'** appeared to be unstable also at the 3-21G level.[13] Total energies and dipole moments of the optimized structures of **1'** - **6'** and **8'** - **12'** are shown in Table 1. Energies of the isomers [relative to **3'**, **1'** plus 2($R_2O\cdot BH_3$; R = H, CH_3)[14] and H_6B_2 (diborane)[15]] are shown in Table 2.

Table 1. Total energies and dipole moments of the optimized structures of **1'** - **6'** and **8'** - **12'**.[a]

Structure	3-21G//3-21G		4-31G//4-31G		6-31G//6-31G		6-31G*//6-31G*		MP2/6-31G*//6-31G*
	E[a]	D[a]	E	D	E	D	E	D	E
1'	-232.01452	3.16	-232.95883	3.18	-233.19703	3.21	-233.29859	2.67	-233.96562
2'	-258.28393	5.22	-259.32696	4.93	-259.59052	4.89	-259.70944	4.97	-260.47119
3'	-284.54857	6.16	-285.69495	5.81	-285.98452	5.79	-286.10543	5.31	-286.95364
4'	-284.54865	7.73	-285.69450	7.34	-285.98499	7.34	-286.11045	6.92	-286.97290
5'	-284.51093	5.13	-285.66059	4.88	-285.95337	4.81	-286.09678	4.92	-286.96292
6'	-284.55913	5.19	-285.69964	4.96	-285.98871	4.94	-286.11276	4.81	-286.98005
8' [b]	-284.52830	7.06	285.67971	6.79	-285.97025	6.75	-286.10339	6.77	-286.95225
9'	-284.54501	9.30	-285.69196	8.88	-285.98168	8.80	-286.10030	8.39	-286.94995
10' [b]	-284.53828	9.10	-	-	-	-	-	-	-
11'	-284.52523	4.59	-285.68106	4.27	-285.97229	4.22	-286.09995	4.42	-286.94150
12' [b]	-284.54364	3.29	-285.69923	3.21	-285.99238	2.93	-286.10848	1.85	-286.94430
H_6B_2 (diborane)	-52.49780	0	-52.71938	0	-52.77542	0	-52.81239	0	-52.99254
Aminodiborane	-107.31010	3.03	-107.74728	2.83	-107.85816	2.87	-107.90701	2.92	-108.25203
$H_2B\text{-}N(H_2)\cdot BH_3$ [c]	-107.29823	4.35	-107.73575	3.84	-107.84578	3.78	-107.88689	4.24	-108.21634
$H_3B\cdot OH_2$	-101.86336	5.28	-102.28057	4.92	-102.38267	4.86	-102.41525	4.26	-102.68773
$H_3B\cdot O(CH_3)_2$	-179.49234	5.61	-180.21470	5.28	-180.39623	5.20	-180.47171	4.77	-181.00085
H_2O	-75.58596	2.39	-75.90864	2.49	-75.98536	2.51	-76.01075	2.20	-76.19597
$(CH_3)_2O$	-153.21319	1.85	-153.83833	1.97	-153.99468	1.97	-154.06457	1.49	-154.50188

[a] Total energies (E) given in hartrees and dipole moments (D) in debyes. [b] See ref. 13. [c] An isomer of aminodiborane of which the 4-membered ring is kept open by forcing (by symmetry) the N-BH_3 group to a staggered conformation.

Energetics of the formation of borane diadducts of oxazaborolidines

The isomers (**3'** - **12'**) can be divided into three groups on the basis of their energies (E_R relative to **3'**; Table 2). One group could consist of the most stable isomers (**4'** - **6'**). These isomers (all hydride-bridged) contain only tetracoordinate boron centers. Inclusion of electron correlation enhances the stabilities of the isomers (**4'** - **6'**) substantially. Another group could cover those isomers of which each has one tricoordinate boron center (i.e. **3'**, **8'** and **9'**). These isomers are significantly less stable than the members of the first group. The MP2/6-31G*//6-31G* energies of **3'**, **8'** and **9'** compared with the corresponding 6-31G*//6-31G* values indicate that the relative stabilities of these isomers are not affected by inclusion of electron correlation. In contrast to that, stabilities of the rest of the isomers (**11'** and **12'**, the third group) decrease with inclusion of electron correlation. Both of these isomers have two tricoordinate boron centers. The relative (MP2) energies of **11'** and **12'** are also higher than those of the other isomers.

The relative stabilities of **3'**, **4'** and **5'** (Table 2) are interesting. Namely, in contrast to that observed[6] in the case of diborane type of isomer of **2'** (found unstable)[6] the hydride-bridged adducts **4'** and **5'** are stable (and considerably more stable than **3'**). In this respect the behaviour of **3'** resembles more that of $H_2B\text{-}N(H_2){\bullet}BH_3$ [94 kJ mol^{-1} less stable than its hydride-bridged isomer (aminodiborane);[7] MP2/6-31G*//6-31G*, Table 2]. These results lead to an interpretation of diboranes as potentially important intermediates in the hydrogen - deuterium exchange observed by Tlahuext and Contreras.[4]

Table 2. Relative energies (E_R)[a] of **3'**- **6'**, **8'** - **12'**, $H_2B\text{-}N(H_2){\bullet}BH_3$ and aminodiborane.[b]

E_R relative to:	**3'**[b]					$1'+2(H_3B{\bullet}OR_2)$		$1'+H_6B_2$
	3-21G	4-31G	6-31G	6-31G*	MP2/6-31G*	MP2/6-31G*		
Structure						R=H	$R=CH_3$	
3'	0 (55/64)[c]	0 (20/44)[c]	0 (19/41)[c]	0 (5/20)[c]	0 (-12/26)[c]	-12	26	-12
4'	0	1	-1	- 13	-51	-62	-25	-63
5'	99	90	82	23	-24	-36	2	-36
6'	-28	-12	-11	-19	-69	-81	-43	-81
8'[d]	53	40	38	5	4	-8	30	-8
9'	9	8	8	13	10	-2	36	-2
10'[d]	27	-	-	-	-	-	-	-
11'	61	37	32	14	32	20	58	20
12'[d]	13	-11	-21	- 8	25	13	51	13
$H_2B\text{-}N(H_2){\bullet}BH_3$	0	0	0	0	0	-	-	-
Aminodiborane	-31	-30	-33	-53	-94	-	-	-

[a] Energies (E_R) given in kJ mol^{-1}. [b] Values relative to the energy of **3'** (set zero) except in the case of aminodiborane of which the energy is given relative to that of $H_2B\text{-}N(H_2){\bullet}BH_3$ (set zero). [c] In parentheses are shown ΔE values of the reaction $1' + 2(H_3B{\bullet}OR_2) \text{->} 3' + 2(R_2O)$; R = H, CH_3. [d] See ref. 13.

Energies of all the borane diadducts relative to **1'** plus 2 eq. of $H_3B{\bullet}OMe_2$ are rather low [the most positive of the E_R values is +58 kJ mol^{-1} (that of **11'**; MP2/6-31G*//6-31G*, Table 2)] as compared with the ΔE of the elimination reaction $(2')_2$ -> $(1')_2$ plus H_6B_2 (+49 kJ mol^{-1}; on the basis of MP2/6-31G*//6-31G*, Table 1). This elimination could be, particularly as the energies of all the borane diadducts relative to **1'** plus H_6B_2 are much more negative (less positive) than those relative to **1'** plus 2 eq. of $H_3B{\bullet}OMe_2$ (Table 2), a reasonable reference for assessing relations between the calculated energies and experimental observations. Namely, Mathre *et al.* have found out that in noncoordinating solvents an equilibrium exists between **2** and **1** plus diborane (H_6B_2).[3b] At room temperature about 10 % of the material exists as free **1** and diborane. In this light (i.e. ΔE of the observed reaction is more positive than the corresponding values of most of the isomerization reactions) the mechanism of the hydrogen - deuterium exchange[4] could be explained by involvement of any of borane diadducts analogous to **3'** - **12'**. Although a simple exchange mechanism could be deduced, for example, on the basis of the formation of **5'** [e.g. **2'** + D_3B -> deuterated **5'** -> 2-deuterated **2'** + D_2BH; mechanisms involving the most stable isomers (**4'** and **6'**) would be more complicated] only a full characterization of the transition states interconnecting the intermediates would reveal the main reaction pathway(s) behind the exchange. Because a complete transition state search would be a highly demanding task (computationally) in the case of these intermediates (**3'** - **12'**) no transition state studies were attempted.[13b]

Some of these isomers (**3'** - **12'**) are Lewis acidic. Therefore, the relative order of stabilities of the isomers could be predicted to change in the presence of coordinating solvents (e.g. THF). The following Lewis acidic centers can be identified: the ring boron in **3'** and **8'** (Fig. 1), the boron of the BH_2 group adjacent to the oxygen in **9'** (Fig. 1) and **12'** (Fig. 2) and the boron of the BH_2 group adjacent to the nitrogen in **10'** and **11'** (Fig. 2). Energies of the coordination of Lewis bases to **9'** and **10'** are difficult to assess but the values of the other adducts could be estimated on the basis of the results of earlier studies of this series.[9,14] The energies of coordination (6-31G*//6-31G*) of water (water as a model of Lewis basic solvents) to a borane *O*-adduct of $HO\text{-}BH_2$ (-40 kJ mol^{-1}),[9] borane *N*-adduct of $H_2N\text{-}BH_2$ (-60 kJ mol^{-1})[14] and borane *N*-adduct **2'** (-20 kJ mol^{-1})[14] reported in the literature[9,14] imply that the isomers **3'** and **8'** could be stabilized by about 20 kJ mol^{-1} in the presence of a Lewis basic solvent (e.g. THF). The corresponding stabilization of **11'** could be 60 kJ mol^{-1} and that of **12'** about 40 kJ mol^{-1}. Thus, in the presence of a Lewis basic solvent (e.g. THF) the positive energies of formation of **3'** and **8'** - **12'** [from **1'** plus $2(H_3B{\bullet}OMe_2)$, Table 2] could decrease to the nearness of zero. Interestingly, the recent discoveries of Mathre *et al.*[3b] indicate that borane *N*-adducts of oxazaborolidines can be stored for years as crystalline solids (i.e. in the absence of coordinating solvents) without noticeable degradation.[3b]

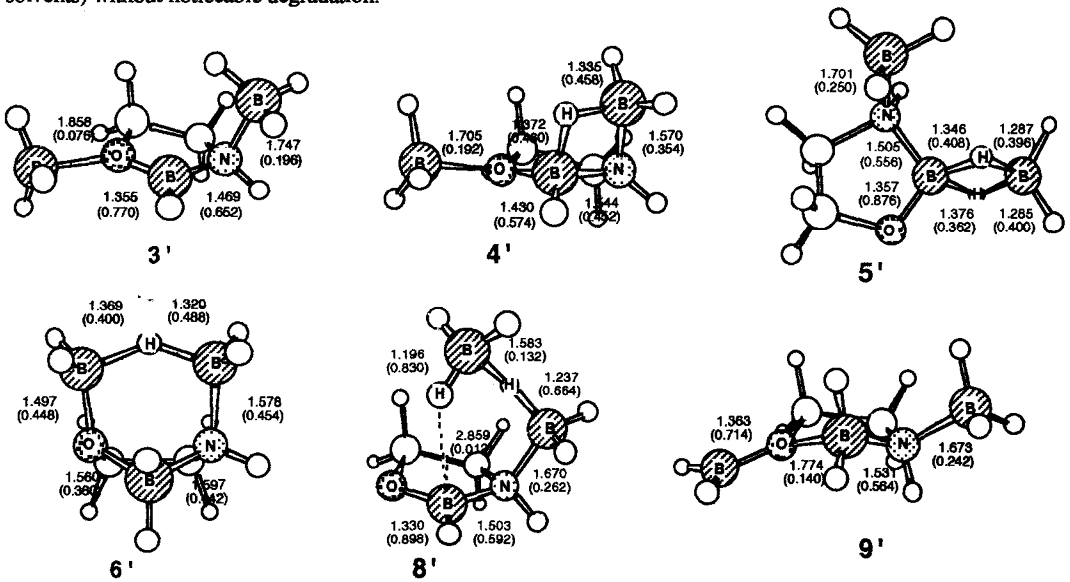


Figure 1. Optimized (6-31G*//6-31G*) structures of isomers (**3'**- **6'** and **8'**-**9'**) of borane diadducts of 1,3,2-oxazaborolidine. Some of the most important bond lengths [in Å] and the corresponding Mulliken overlap populations (in parentheses) are shown.

The most stable isomer **6'** (Fig. 1) represents a common product of two different intramolecular addition reactions (**11'** -> **6'** and **12'** -> **6'**). In the former case an alkoxyborane coordinates to a borane adduct of an aminoborane liberating 102 kJ mol^{-1} energy (on the basis of MP2/6-31G*//6-31G*, Table 2) whereas in the latter case an aminoborane coordinates to a borane adduct of an alkoxyborane liberating 94 kJ mol^{-1} energy. These reactions could be involved as oxazaborolidines are prepared from the corresponding aminoalcohols.

Structure, bonding and Lewis acid - base properties

The LUMO and HOMO energies decrease and the positive charge of the ring boron increases as borane coordinates to **1'** (LUMO energies become less positive and HOMO energies more negative, Fig. 3). The changes arising from the *O*-coordination are less significant than those of *N*-coordination. Both the HOMO/LUMO energies and the charges (Fig. 3) indicate that the more borane coordinates to **1'** the more Lewis acidic the boron of the oxazaborolidine ring and the less basic the coordinated boranes would become.

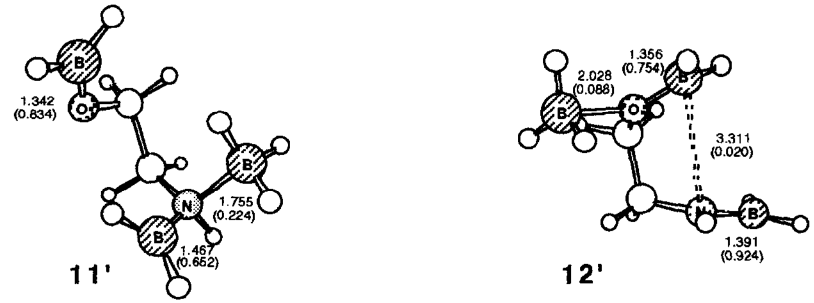
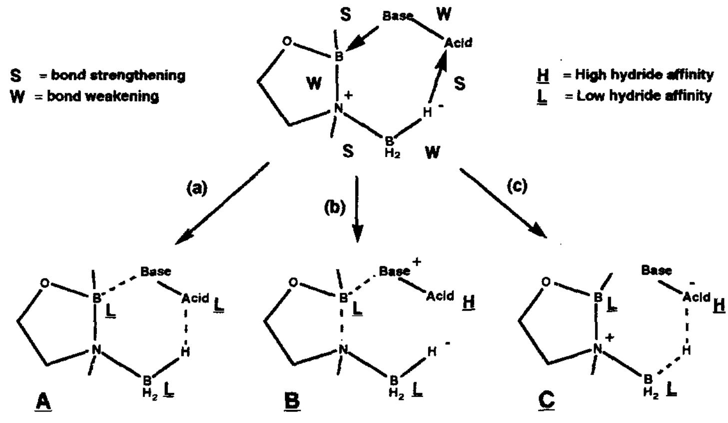


Figure 2. Optimized (6-31G*//6-31G*) structures of the open-chain isomers (11' and 12') of borane diadducts of 1,3,2-oxazaborolidine. Some of the most important bond lengths [in Å] and the corresponding Mulliken overlap populations (in parentheses) are shown.

The structural changes related to the coordination (reactions **a** - **c**, products A , B and C; Scheme I) of different Lewis dipoles (molecules which contain adjacent Lewis acidic and basic centers connected by a chemical bond)[5] to **2'** have all the same pattern. In the case of the pathway (**a**; Scheme I) the coordinating Lewis dipole[5] can be an aminoborane (the boron of R_2B-NR'_2 regarded as an acid and the nitrogen as a base),[5] alkoxyborane (the boron of R_2B-OR' regarded as an acid and the oxygen as a base)[16] or oxazaborolidine (the boron of the oxazaborolidine ring regarded as an acid and the nitrogen as a base).[5] As complexes A form both ends of the Lewis dipole would be clearly bound to the borane adduct moiety. None of the bonds of the 6-membered ring formed is significantly weaker than the others related bonds (e.g. the bridging hydride in A is bound tightly to both ends of the bridge). The formation of complexes A would not be limited to the borane adducts of oxazaborolidines. Aldehyde complexes of *N*-sulfonylated oxazaborolidines have been predicted to exist in a form structurally analogous to A.[17]

Scheme I



Results of this and all earlier studies of this series[12,16,17] indicate that complexes analogous to A may be formed in the case of Lewis dipoles of which the acidity (basicity) of one end would not be significantly different from the basicity (acidity) of the other and of which the hydride affinity of the acid end of the Lewis dipole would be at the same level as that of the boron of the borane coordinated to the ring nitrogen (i.e. low, Scheme I). Borane does not belong to this class of Lewis dipoles. Interestingly, the adduct **10'** (analogous to A) was found to be unstable.[13]

In the case of the reaction pathway (**b**; Scheme I) the coordinating Lewis dipole[5] can be a carbonyl compound[5,7,12] or water/ether.[5,14] Results of this work indicate that borane would not form (basicity of the hydrogens of borane is apparently too low) complexes analogous to B. None of the diadducts involved in this study can be assigned to this class of Lewis dipole adducts.

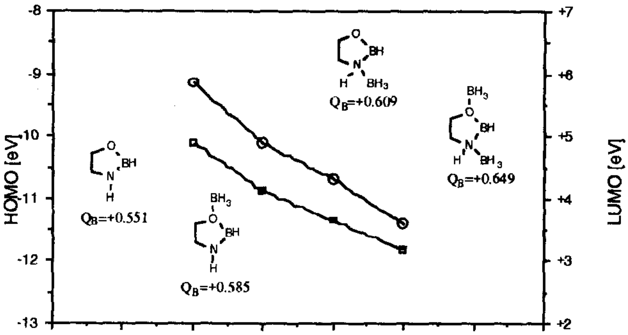


Figure 3. HOMO (——■——) and LUMO (——⊖——) energies (6-31G*//6-31G*) of 1,3,2-oxazaborolidine (1') and its borane *O*-, *N*-, and *N,O*-adducts accompanied with the charges of the ring boron (Q_B; below the structures).

The reaction pathway (c; Scheme I) has not been discussed in the literature. The adduct **8'** (Fig. 1) is structurally analogous to C (Scheme I). In consequence of the coordination of borane to **2'** (formation of **8'**) the B-N bond of the oxazaborolidine ring lengthens by 0.018 Å (overlap decreases by 0.030), the $N\text{-}B_{H_3B}$ bond shortens by 0.048 Å (overlap increases by 0.032), the $H\text{-}B_{H_3B}$ bond bridging the two boranes lengthens by 0.030 Å (overlap decreases by 0.176) and one of the B-H bonds of the coordinating borane lengthens by 0.009 Å (overlap unchanged). These structural changes correspond to those shown in Scheme I.

The structure of **5'** is interesting in that there are two ligands (hydrogens) on the boron of the oxazaborolidine ring. The ligands are *cis/trans* to the borane bound to the ring nitrogen. Results of earlier studies of this series indicate that any *trans*-coordinated Lewis basic ligand would be less tightly bound to the boron of the oxazaborolidine ring than the corresponding *syn*-coordinated ligand.[5,7,14] However, the *syn*-coordinated hydrogen is more tightly bound to the boron of the oxazaborolidine ring that the *trans*-coordinated one [e.g. the B-H bond related to the *cis* interaction is 0.030 Å shorter (overlap 0.046 higher) than the *trans* B-H bond, Fig. 1]. Interestingly, structural changes related to the reaction **2'** + borane -> **5'** are smaller than those observed in the case of the formation of any other related complex (in which the Lewis base and *N*-bound H_3B has been *cis* about the oxazaborolidine ring).

The hydride-bridged system of **6'** (Fig. 1) is structurally analogous to borane - alkoxyborane (and borane - aminoborane) adducts of oxazaborolidines and aminoboranes studied recently.[5,16] The lengths of the B-N, B-O and B-H bonds (and related overlap populations) of the hydride-bridged ring of **6'** are similar to those of the recently studied more simple analogs[16] although the oxazaborolidine ring of **6'** is considerably distorted. The torsion angles C-O-B-N and O-C-C-N of **6'** are 51.2° and -0.8° (6-31G*//6-31G*) indicating that the boron of the oxazaborolidine ring is clearly out of the plane of the other atoms of the ring. Consequently, it would be rational to predict that hydride-bridged systems analogous to **6'** may not form in the case of rigid and/or strained oxazaborolidines (e.g. **1**).

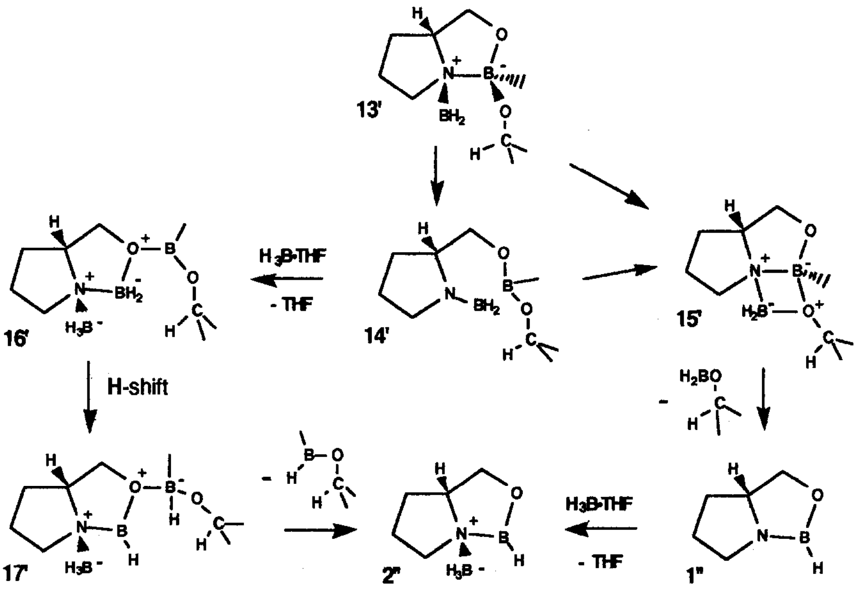
Structures of the adducts **11'** and **12'** (Fig. 2) resemble those of alkoxy- and aminoboranes and borane adducts of alkoxy- and aminoboranes. The $O\text{-}BH_2$ bond of **11'** is only 0.003 Å shorter than the corresponding bond of hydroxyborane.[11,16] Also the $O\text{-}BH_2$ bond of **12'** is only 0.005 Å shorter and the $O\text{-}BH_3$ bond 0.113 Å longer than the corresponding bonds of the borane *O*-adduct[9] of hydroxyborane (6-31G*//6-31G*). The $N\text{-}BH_2$ bond of **11'** is 0.018 Å longer (and the $N\text{-}BH_3$ bond 0.071 Å shorter) than that of $H_2B\text{-}N(H_2)\bullet BH_3$ whereas the $N\text{-}BH_2$ bond of **12'** is only 0.002 Å shorter than the B-N bond of $H_2B\text{-}NH_2$ (6-31G*//6-31G*).[7]

The structure of **9'** (Fig. 1) is interesting in that **9'** represents a Lewis base - borane complex of an aminoborane in which the base (oxygen of the alkoxyborane end) and the borane are *trans* about the B-N bond of the aminoborane (the B-N bond of the oxazaborolidine ring). The B-O distance is surprisingly short in **9'**, only 1.774 Å [Mulliken overlap 0.140 (Fig. 1)]. Earlier studies of this series[5,714] indicate that the base counterpart of Lewis base - borane *trans* adducts of oxazaborolidines would be less tightly bound to the oxazaborolidine than that of the corresponding *cis* adducts. For example, the B-O distance in the water - borane *trans* adduct of $H_2B\text{-}NH_2$ has been calculated to be 2.088 Å (Mulliken overlap 0.068, 6-31G*//6-31G*)[14] whereas the corresponding value of the *cis*-adduct is 1.643 Å

(Mulliken overlap 0.250).[14] If the distance between the Lewis acidic center of the borane *N*-adduct of oxazaborolidine and the *trans* coordinated Lewis base (or the corresponding Mulliken overlap) is used as a measure of tightness of the acid - base binding it turns out that in **9'** the Lewis base (oxygen of the alkoxyborane end) is more tightly bound to the acidic boron of the aminoborane moiety than in any other related system studied so far [Lewis bases such as water,[14] formaldehyde[7,12] and oxazaborolidine[5] have been studied recently]. Also dipole moments of the *trans* adducts are higher[5,14] than those of the corresponding *cis* adducts [e.g. the water - borane *trans* adduct of H_2N-BH_2 has a dipole moment of 8.47 D (6-31G*//6-31G*) whereas the moment of the corresponding *cis* adduct is only 1.98 D].[14] The dipole moment of **9'** is high (8.39 D, 6-31G*//6-31G*, Table 1); clearly compatible with the values of the other *trans* adducts studied earlier.[5,14] The moment of **9'** is also much higher than that of its open-chain isomer (**11'**, 4.42 D).

In part IV of this series of reports[11] mechanisms potentially involved in the regeneration of CBS catalysts were discussed.[11] Two reactions (**13'** -> **14'** and **13'** -> **15'** -> **1''**) were proposed to occur in the reactive intermediate **13'** (Scheme II). The formation of **15'** was predicted to be essential for the catalytic performance of oxazaborolidines [elimination of the alkoxyborane moiety from **15'** would lead to the regeneration of the catalyst (**1''**)]. Also the reaction of borane with **14'** leading to the formation of **16'** (Scheme II) has been predicted to be an advantageous process.[11] However, if it would be possible to convert **16'** (structurally analogous to **9'**; Fig. 1) to **17'** (structurally analogous to **3'**; Fig. 1) an elimination of the alkoxyborane moiety from **17'** would lead to the formation of the borane *N*-adduct **2''**. Therefore, the pathway **13'** -> **14'** -> **16'** -> **2''** would represent a new regeneration mechanisms for the CBS reduction. Interestingly, at the MP2/6-31G*//6-31G* level ΔE of the conversion **9'** -> **3'** (analogous to **16'** -> **17'**) is -10 kJ mol^{-1}. Although the ΔE value is negative it is rather low. Nevertheless, the low ΔE implies that the probability of the hydride transfer (i.e. **16'** -> **17'**) to occur would depend more on the factors related to kinetics. Computational studies on the properties of oxazaborolidines and enantioselective reactions catalyzed by chiral oxazaborolidines continue.

Scheme II



CONCLUSIONS

On the basis of results of this work one could predict that adducts consisting of oxazaborolidine and two equivalents of borane could exist (if formed) under conditions of the CBS reduction. Two of these diadducts could be predicted to be more stable than the corresponding *N*-monoadducts (in the absence of coordinating solvents). On the other hand, as the results of this work indicate that the borane *N,O*-diadduct of oxazaborolidine could be more Lewis acidic (potentially also more reactive) than the corresponding *N*- or *O*-monoadducts it would be rational to expect the relative stabilities of the adducts (in solution) to be dependent on the nature (e.g. Lewis basicity) of the solvent.

New mechanisms explaining why hydrogen - deuterium exchange could take place as oxazaborolidines are treated with deuteroborane (D_3B) delivering agents could be proposed on the basis of the enthalpically advantageous formation of diborane type of hydride-bridged systems consisting of two borane molecules and one oxazaborolidine. Results of this work indicate also that exchange of borons between borane and oxazaborolidines could be possible. On the basis of the boron exchange a new regeneration mechanism for the CBS reduction was proposed. In the case of 2-substituted oxazaborolidines the borane exchange would result in the "loss" of the substituent.

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