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The first N,N'-ditosyl-substituted cyclic boron cation, stabilized by neighboring-group participation by two sulfonyl groups, and the alternative, stabilized by polar solvents

Syun-ichi Kiyooka,^{a,*} Ryoji Fujiyama,^a Md. Khabir Uddin,^b Kazuki Goh,^a Yoshiya Nagano,^b Mizue Fujio^b and Yuho Tsuno^b

^aDepartment of Material Science, Faculty of Science, Kochi University, Akebono-cho 2-5-1, Kochi 780-8520, Japan ^bInstitute of Materials Chemistry and Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan

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Abstract—When 2-bromo-1,3-ditosyl-1,3,2-diazaborolidine was treated with AgSbF₆, a novel cyclic boron cation was formed in CD_2Cl_2 , the ¹¹B NMR chemical shift of which appeared at 8.7 ppm. Ab initio calculations were consistent with the cationic boron center being stabilized by neighboring-group participation of the two sulfonyl functions. The reaction in CD_3NO_2 resulted in an alternate formation of a cyclic boron cation species (16.2 ppm), stabilized by coordination to the basic solvents. © 2004 Elsevier Ltd. All rights reserved.

Although a limited number of reports dealing with boron cation species as catalysts in organic synthesis¹ have appeared, in regard to utilizing their extreme Lewis acidity, our understanding of the electrophilicity of such boron cations is not necessarily sufficient, even at the present stage of development. We are continuing our ¹¹B NMR and ab initio calculation studies of boron cations, involving the historical diphenylboron cation, in order to clarify the fundamental properties of boron cations in solution.² Tetracoordinate and tricoordinate boron cations by coordination to electrophiles, owing to their inherent high Lewis acidity have been detected and are classified as boronium and borenium ions, respectively.³ While dicoordinate borinium ions (1)would be expected to be stable if the boron atom is sp hybridized, π -bonding, using two vacant p orbitals of the boron with other heteroatoms, should certainly be necessary for producing stable borinium ions, which correspond to borylenes (2), as shown in Figure 1. Some interesting borylenes involving transition metals, instead of heteroatoms, have recently been reported.⁴ Taking into account the fact that $BN \pi$ -back-bonding is efficient, bis(amino)boron cations (3) represent an adequate system for stable borinium cations. Stable diamino bori-

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* Corresponding author. Tel.: +81 888448295; fax: +81 888448359; e-mail: kiyooka@cc.kochi-u.ac.jp



Figure 1.

nium ions can be isolated when the bulkiness of the amino substituents is increased⁵ or extended conjugation is allowed, such as $-P=N=B-N=P-.^{6}$ However, the expected stable borinium ions were not formed and only tricoordinate boron (borenium ion) adducts were produced in the cyclic system **4**, and no linear NBN skeletons with BN π -bonding were detected.⁷ For the first time, we report here that the use of cyclic *N*,*N'*-ditosyl-diazaborolidines readily facilitate to the formation of stable cyclic boron cations.

A precursor, 2-bromo-1,3-ditosyl-1,3,2-diazaborolidine 5, of cyclic boron cations was prepared according to Corey's procedure.⁸ Preparation of 5: A solution of

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bis(*N*-*p*-toluenesulfonyl)-ethylenediamine $(37 \, \text{mg})$ 0.1 mmol) in anhydrous CH_2Cl_2 (1 mL) was treated with 1 equiv of 1 M BBr₃ in CH₂Cl₂ (100 µL, 0.1 mmol) at rt under Ar. After stirring for 30min, the solution was evaporated in vacuo in order to eliminate HBr completely.⁹ Ionization of 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine by Lewis acids in the presence of a coordinative base is known to result in the corresponding 1,3-dimethyl-1,3,2-diazaborolidinium ion as borenium.⁷ Based on this observation, it is possible that the ditosyl homolog 5 would also ionize in the presence of BBr₃ or AlBr₃ but such a reaction was not observed. The abstraction of the bromine atom from 5 can be regarded as being retarded by the ditosyl substituents due to their greater electron-withdrawing character. The use of $AgSbF_6$, which contains a SbX_6 anion to be effective as a counter ion of boron cations was considered.^{2c} Procedure for ionizing 5 to 6: The AgSbF₆ salt (49 mg,0.15 mmol) in dry CD₂Cl₂ was added to a solution of 5 (0.1 mmol) in an NMR tube at rt under Ar, resulting in the precipitation of AgBr. The reaction mixture was allowed to stand for 15min.9 An interesting up-field shift, from 26.6 to 8.7 ppm (from a BF₃·OEt₂ standard), in ¹¹B NMR spectra (CD_2Cl_2) was observed (Scheme 1). This is the first observation of a cyclic boron cation without coordination by solvent and/or base, as depicted in Figure 2. The optimized geometry of the cyclic boron cation 6 at the B3LYP/6-31+G(d) level indicates that the cationic boron center is stabilized by intramolecular coordination with two oxygen atoms of both the tosyl substituents where the B-O bond length is 1.50Å, as shown in Figure 3. In conclusion, this boron cation exists as a tetracoordinate species of boronium ion. The ¹¹B chemical shift was calculated to be 7.5 ppm using the GIAO-HF/6-311+G(2d,p) method¹⁰ on the basis of the optimized geometry. The agreement between the calculated and found values suggests that the actual structure of 6 may be close to the theoretical structure. On the other hand, treatment of 5 with $AgSbF_6$ in CD_3NO_2 led to the formation of different species of cyclic boron cations (7 and 7'). The procedure for 7 and 7': A solution of compound 5 (37mg,



Scheme 1. Cyclic boron cations stabilized by neighboring groups and by polar solvents.



Figure 2. Observed peaks in ¹¹B NMR spectra of the starting borane 5 and the cyclic boron cation 6.



Figure 3. Optimized structure of 6 [B3LYP/6-31+G* basis sets].

0.1 mmol) in dry CH₂Cl₂ (1 mL) was treated with 1 equiv of 1 M BBr₃ in CH₂Cl₂ (100 µL, 0.1 mmol) at rt under Ar. After stirring for 30min, the solution was evaporated in vacuo in order to eliminate HBr completely.¹¹ The ¹¹B NMR signal of the species in CD₃NO₂ appeared at 16.2 ppm, which is 11.1 ppm higher than that (27.3 ppm) of the starting 5 in the solvent. Ab initio calculations of the ¹¹B chemical shift were performed using two models corresponding to mono-solvent and di-solvent coordinate species. The calculated ¹¹B chemical shifts were 27.1 and 7.0 ppm, respectively. The preferential structure for the cyclic boron cation in CD_3NO_2 should be an equilibrium mixture of the mono-solvent coordinate 7 and the di-solvent coordinate 7' in comparison of their simply averaged value (17.1 ppm) with the observed one (Scheme 1). The existence of 7 as a trico-



Scheme 2. Chiral cyclic boron cations of the (R,R)-stien system.

ordinate species is inferred by analogy with the comparable ¹¹B chemical shifts of the neutral perchlorate **8**, derived from **5** and AgClO₄ (Scheme 1). As mentioned above, two types of N,N'-ditosyl-substituted cyclic boron cations can be formed in both nonpolar and polar aprotic solvent systems. The procedures were then applied to the chiral congeners **9**, prepared from bis(*N*-*p*-toluenesulfonyl)-(*R*,*R*)-1,2-diphenylethylenediamine, (*R*,*R*)-stien. The expected corresponding cyclic boron cations were observed, as shown in Scheme 2.

A preliminary experimental result on the utilization of these chiral cyclic boron cations in a Lewis acid catalyzed asymmetric aldol reaction is as follows. The effectiveness of precursor 9a to 10a and 10b was examined in advance for the reaction. The neutral chiral borane 9a underwent an asymmetric aldol reaction of hydrocinnamaldehyde with a trimethylsilvlketene acetal, derived from S-phenyl thioacetate, in nitroethane to give the corresponding aldol with 40% ee (S) but in only 10%yield, which is corresponding to the loading quantity (10mol%) of the catalyst. Under similar conditions the two different chiral boron cations, 10a and 10b, were examined in the reaction with expectations based on the development of new chiral catalysts. Unfortunately, these reactions did not proceed at all. These results can be assigned significance in terms of the sufficient, coordinative saturation of the boron cations in being stabilized by intramolecular and/or intermolecular interactions with electrophiles, where such tight complexes no longer exchange the present ligands with an external substrate aldehyde. Thus, for the purpose of the effective use of the chiral boran cations as catalysts for asymmetric reactions the species must have more labile ligands, which are exchangeable with external substrates in solution, where ample time is allowed for activation of the substrates.12

In conclusion novel cyclic boron cation 6 formed by treatment with AgSbF₆ in an aprotic nonpolar solvent,

 CD_2Cl_2 , was found to be stabilized by intramolecular coordination to the oxygen atoms at the both sides of the boron cationic center. On the other hand, in an aprotic polar solvent, CD_3NO_2 , an equilibrium mixture of different cyclic boron cation species, 7 and 7', was detected. The latter can be attributed to stabilization of the nitromethane solvated cations by electron donor O-atoms of the solvent. The corresponding chiral cyclic boron cations, **10** and **11**, could also be prepared.

Method of calculation: The calculations were performed with a Gaussian 98 rev. A.11, using the B3LYP methods with 3-6-31+G* basis sets for geometry optimizations.¹³

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- 9. Compound **5**: ¹¹B NMR (160.35MHz, CD₂Cl₂, ppm): δ 26.5 ppm. ¹H NMR (500MHz, CD₂Cl₂, ppm): δ 2.44 (s, 6H, *p*-Me), 3.72 (br s, 4H), 7.35 (d, *J* = 8.6 Hz, 4H, Ar), 7.99 (d, *J* = 8.6 Hz, 4H, Ar). ¹³C NMR (125.77 MHz, CD₂Cl₂, ppm): δ 21.7, 46.7, 127.6, 130.2, 136.1, 145.4. **6**: ¹¹B NMR (160.35 MHz, CD₂Cl₂, ppm): δ 8.7 ppm. ¹H NMR (500 MHz, CD₂Cl₂, ppm): δ 2.46 (s, 6H, *p*-Me), 3.17 (br s, 4H), 7.44 (br s, 4H, Ar), 7.82 (br s, 4H, Ar). ¹³C NMR (125.77 MHz, CD₂Cl₂, ppm): δ 21.8, 43.7, 128.1, 130.9, 147.0.
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- 11. Compound 7: ¹¹B NMR (160.35 MHz, CD₃NO₂, ppm): δ 16.16 ppm. ¹H NMR (500 MHz, CD₃NO₂, ppm): δ 2.50 (s, 6H, *p*-Me), 3.37 (br s, 4H), 7.53 (d, *J* = 8.0 Hz, 4H, Ar), 7.85 (d, *J* = 8.0 Hz, 4H, Ar). ¹³C NMR (125.77 MHz, CD₃NO₂, ppm): δ 21.9, 44.1, 129.6, 131.8, 134.6, 148.6.
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