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Preparation and characterization of diphenylboron cation in solution

Md. Khabir Uddin,[a] Ryoji Fujiyama,[b] Syun-ichi Kiyooka,[a] Mizue Fujio[a,*] and Yuho Tsuno[a]

[a] *Institute for Materials Chemistry and Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan*
[b] *Department of Material Science, Faculty of Science, Kochi University, Akebono-cho 2-5-1, Kochi 780-8520, Japan*

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Abstract—The electrophilic abstraction of chloride ion by $SbCl_5$ from diphenylchloroborane in CD_3NO_2 resulted in a transient species of which ^{11}B NMR chemical shift appeared at 20 ppm. This was indicative of diphenylboron cation, stabilized with electron donor O-atom of two nitromethane molecules. The experimental ^{11}B chemical shift for the solvated diphenylboron cation is in good agreement with that calculated by GIAO-HF/6-311+G(2d,p)//B3LYP/6-31+G(d).

The expected Lewis acidity of the boronium ion, available in organic reactions, is of interest in connection with the long-standing question of the nature of the ionic species.[1] Davidson and French[2] reported the observation of diphenylboron cation, $Ph_2B^+AlCl_4^-$, by the treatment of diphenylchloroborane and aluminum trichloride in ethyl methyl ketone and also $Ph_2B^+ClO_4^-$ prepared by metathesis of Ph_2BCl and $AgClO_4$ in nitromethane or sulfolane. However, the cationic boron species could be isolated only as the 2,2′-bipyridyl salt, $[(C_6H_5)_2B(bpy)]^+\ ClO_4^-$.[2b] Recently, we found that diphenylboron perchlorate (Ph_2BClO_4) was characterized to possess a covalent character in the B–O bond.[3] It is reported that diphenylboryl hexachloroantimonate (Ph_2BSbCl_6) was used to be an effective catalyst for Friedel–Crafts acylation of aromatic compounds with acid chlorides, acid anhydrides, and acyl enolates.[4] Although the catalyst, Ph_2BSbCl_6, was prepared from diphenylchloroborane and $SbCl_5$ in dichloromethane for 1 h stirring, we measured ^{11}B NMR spectra of the above mixture that showed only a characteristic signal of starting diphenylchloroborane at 64.2 ppm. Furthermore, it should also be noted that $SbCl_5$ alone catalyzed the acylation reaction of veratrole with acetyl enolate to give 3,4-dimethoxyacetophenone in quantitative yield in the present study. Actually, in our experiments the electrophilic abstraction of chloride ion by $AlCl_3$, BCl_3, and $SbCl_5$ from diphenylchloroborane did not proceed in nonpolar solvents such as benzene, chloroform, and dichloromethane and, furthermore, ionization did not occur by $AlCl_3$ even in polar nitromethane. This nonreactivity evidently reflects the lack of ionization necessary for B–Cl bond of diphenylchloroborane. Therefore, it should be noted that the diphenylboron cation reported in the literatures is unclear with respect to the cationic character. Figure 1 shows several structures of the historical boron cations[2,5] based on the studies on its conductance, UV spectra, ^1H NMR spectra, and MO calculation at a lower level. As described above, it has not been yet clear whether the historical boron cation could be formed by S_N1 pathway. In this meaning it is important to observe the transient cationic species including the structural information. We disclose herein evidence of novel boron cationic reaction of diphenylchloroborane with strong Lewis acid $SbCl_5$ in nitromethane at room temperature

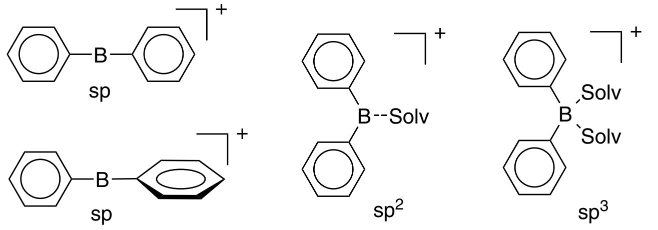

Figure 1.

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* Corresponding author. Tel.: +81-92-642-2724; fax: +81-92-642-2715; e-mail: fujio@ms.ifoc.kyushu-u.ac.jp

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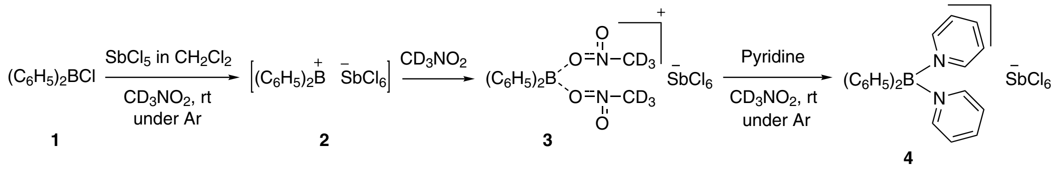


Scheme 1. A boron cationic reaction of diphenylchloroborane in nitromethane.

as shown in Scheme 1, which is monitored in situ by using ^{11}B and ^{13}C NMR spectroscopy, and the cationic species is confirmed by a correlation between the calculated and the experimental ^{11}B NMR chemical shifts.

^{11}B and ^{13}C NMR spectra were measured on a JEOL JNM-A500 FT-NMR spectrometer operating at 160.35 and 125.65 MHz, respectively. Chemical shifts are expressed in ppm downfield from external $BF_3{\cdot}OEt_2$ for ^{11}B and internal TMS for ^{13}C NMR. All experimental manipulations were conducted in NMR tube under rigorously anhydrous conditions in a dry glove box equipped with an oxygen free argon atmosphere at room temperature. When 1.0 M $SbCl_5$ solution in CH_2Cl_2 (0.13 mmol, 130 μL) was added to a solution of diphenylchloroborane **1** (0.1 mmol, freshly prepared in a NMR tube with molecular sieves 4A) in CD_3NO_2, a dark yellow color appeared from the solution. When ^{11}B and ^{13}C NMR spectra were measured, the ^{11}B NMR signal for one species was found at δ 19.8 ppm, shifted to considerably lower frequency relative to Ph_2BCl **1**. The $^{13}C_{para}$ NMR signal of this species was observed at δ 129.5 ppm, shifted by 5.1 ppm to lower frequency relative to **1**, as compared in Table 1. This low frequency shift is inconsistent with the expected cationic character, which would be accompanied by a decrease in electron density.[5e,6] It may be considered that the cleavage of B–Cl bond in diphenylchloroborane in CD_3NO_2 by the strong Lewis acid $SbCl_5$ resulted in a solvated cation containing sp^3 hybridized boron atom rather than in a cation containing an sp hybridized boron atom. Two equivalents of pyridine (0.2 mmol) in CD_3NO_2 were added to the dark solution of the cation **3** of which the ^{11}B NMR chemical shift was observed at 11.1 ppm to give the pyridine-complex (Scheme 1). The relative intensity of ^{13}C NMR spectra of the complex was obtained 1:1 for phenyl and pyridine carbons. The chemical shift of *para*-carbon of pyridine ring in pyridine-complex shifted 8.7 ppm lower frequency than that of the pyridine, and is closer to pyridinium ion (entry 4 in Table 1). These results confirmed the structure of the complex as the four coordinate boronium salt **4**. While addition of 2 equiv of acetonitrile to the solvated cation **3** moved the ^{11}B chemical shift to be 0.9 ppm. This again moved on forming boronium salt **4** at 11.1 ppm with the further addition of pyridine. When two equivalents of THF were added to the solvated cation **3**, the ^{11}B NMR spectra was shifted to 17.5 ppm to give the THF-solvated diphenylboron cation.

An ab initio calculation of the ^{11}B chemical shift was carried out by using the method GIAO-HF/6-311+G(2d,p)//B3LYP/6-31+G(d).[7] All quantum chemical calculations were carried out with the GAUSSIAN 98 program suite.[8] The results are summarized in Table 2. As reported previously, the optimized structure of the free diphenylboron cation **2** at B3LYP/6-31+G(d) level was found to be a linear structure, where two phenyl rings are perpendicular,[3a] and the ^{11}B chemical shift was calculated to be 85.5 ppm (from the standard of $BF_3{\cdot}OEt_2$).[9] The calculated ^{11}B chemical shift of the solvent-coordinated species, starting from the free diphenylboron cation **2** and one nitromethane, found to be 54.5 ppm, which is far from the observed value of 19.8 ppm while the calculation on the species involving two solvent molecules could be converged to give optimized structure **3** with ^{11}B of 20.7 ppm. The agreement between the calculated and found values suggests that the actual structure of diphenylboron cation observed may not be far from the optimized structure where boron cation was stabilized by dative interaction of each O-atom of two nitrometanes. The B–O bond length (1.637 Å) of **3** is longer than the former value of 1.545 Å (entries 1 and 2 in Table 2) and the N–O bond remains comparable to that of neutral nitromethane. The boronium salt **4** was calculated using the same procedure and a good correlation between the calculated and experimental ^{11}B NMR chemical shifts was obtained (entry 4

Table 1. ^{13}C NMR (125.65 MHz) spectra concerning the reaction of diphenylchloroborane with $SbCl_5$ in CD_3NO_2

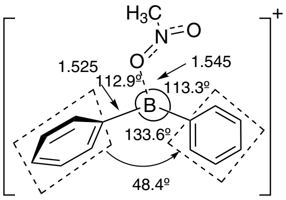
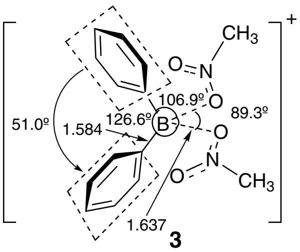
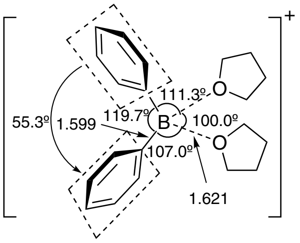
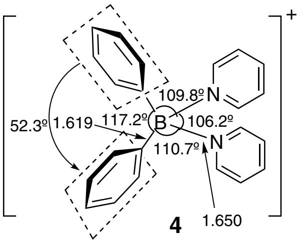
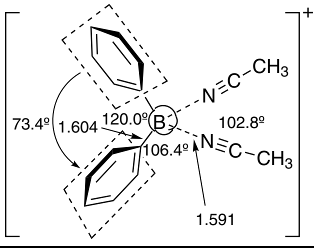
Entry	Compound	δ (^{13}C)/ppm: phenylboron[a]			δ (^{13}C)/ppm: pyridine moiety		
		C_{ortho}	C_{meta}	C_{para}	C_{ortho}	C_{meta}	C_{para}
1	Ph_2BCl	138.3	129.4	134.6			
2	$Ph_2B(CD_3NO_2)_2^{+}\ SbCl_6^{-}$	134.6	129.1	129.5			
3	Pyridine = Py				151.1	125.1	137.3
4	$Ph_2B(Py)_2^{+}\ SbCl_6^{-}$	135.3	128.7	129.2	148.3	129.5	146.0
5	$Ph_2B(THF)_2^{+}\ SbCl_6^{-}$[b]	133.6	129.1	128.1			
6	$Ph_2B(CH_3CN)_2^{+}\ SbCl_6^{-}$[c]	132.9	129.3	129.7			

[a] The chemical shifts δ ^{13}C(*ipso*) are not given. Most likely these NMR signals are broad.

[b] The chemical shift of THF was found 73.6 ppm for $C_{2,5}$ and 26.4 ppm for $C_{3,4}$.

[c] The chemical shift of CH_3CN was found 120.4 ppm for CN and 4.0 ppm for CH_3.

Table 2. Optimized structures and the correlation of experimental and calculated ^{11}B NMR shifts

Entry	Structure[a]	Expt.[b] in CD_3NO_2		Calcd[c] δ (ppm)
		δ (ppm)	Line width (Hz)	
1		—	—	54.5
2	 **3**	19.8	740	20.7
3		17.5	430	15.5
4	 **4**	11.1	250	9.0
5		0.9	470	−0.2

[a] Optimized structures using B3LYP/6-31+G(d).

[b] The chemical shifts are expressed in ppm downfield from BF_3OEt_2.

[c] Calculated using GIAO-HF/6-311+G(2d,p) for B3LYP/6-31+G(d) optimized structures.

in Table 2). The THF and acetonitrile coordinated cations were also optimized and found a good agreement between the calculated and observed values (entries 3 and 5 in Table 2). These results suggest that the structure of all solvated cations may not be far from the optimized structures shown in Table 2. The ^{13}C chemical shifts in Table 1 and their intensities are well explicable by the optimized structures in Table 2.

Successful capture of diphenylboron cation in nitromethane solvent is due to the rather large Lewis acidity ($\alpha = 0.22$) and the relatively small Lewis basicity ($\beta = 0.22$) of the solvent[10] in order to cause the ionization and coordination, respectively. Namely solvents such as dichloromethane and chloroform, which have solely acidic properties could not promote any reaction, while solvents with pronounced basic character such as acetonitrile and pyridine form 1:1 adducts with **1**.[11] Thus, the subtle balance of both abilities of respective solvents is important in order to obtain the diphenylboron cation species.

In conclusion, the heterolysis of diphenylchloroborane by the strong Lewis acid $SbCl_5$ in nitromethane provides convincing evidence of a novel boron cationic reaction. The observed diphenylboron cation is most reasonably ascribed to the nitromethane solvated cation **3** stabilized by electron donor O-atom of two nitromethane molecules. It is converted easily to the coordination of two molecules of MeCN or THF solvent from $MeNO_2$ and finally to the dipyridine salt **4**.

Acknowledgements

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References and notes

1. (a) *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley-VCH: Weinheim, 2000; (b) Sanrelli, N.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis*; CRC: Boca Raton, 1996.
2. (a) Davidson, J. M.; French, C. M. *J. Chem. Soc.* **1958**, 114–117; (b) Davidson, J. M.; French, C. M. *Chem. Ind.* **1959**, 750.
3. (a) Kiyooka, S.-i.; Fujiyama, R.; Kawai, T.; Fujimoto, H.; Goh, K. *Tetrahedron Lett.* **2001**, *42*, 4151–4153; (b) Kiyooka, S.-i.; Fujimoto, H.; Mishima, M.; Kobayashi, S.; Uddin, M. K.; Fujio, M. *Tetrahedron Lett.* **2003**, *44*, 927–930.
4. Mukaiyama, T.; Nagaoka, H.; Ohshima, M.; Murakami, M. *Chem. Lett.* **1986**, 165–168.
5. (a) Davidson, J. M.; French, C. M. *J. Chem. Soc.* **1962**, 3364–3368; (b) Douglass, J. E. *J. Am. Chem. Soc.* **1962**, *84*, 121–122; (c) Moodie, R. B.; Ellul, B.; Connor, T. M. *Chem. Ind.* **1966**, 767; (d) Armstrong, D. R.; Perkins, P. G. *J. Chem. Soc. A* **1966**, 1026–1031; (e) Noth, H.; Staudigl, R.; Wagner, H.-U. *Inorg. Chem.* **1982**, *21*, 706–716; (f) Higashi, J.; Eastman, A. D.; Parry, R. W. *Inorg. Chem.* **1982**, *21*, 716–720; (g) Kolle, P.; Noth, H. *Chem. Rev.* **1985**, *85*, 399–418.
6. (a) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61–200; (b) Siedle, A. R. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 205–314.
7. (a) London, F. *J. Phys. Radium, Paris* **1937**, *8*, 397; (b) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789; (c) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.
8. GAUSSIAN 98, Revision A.11: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN, Pittsburgh, PA, 2002.
9. The absolute shielding value was obtained for $BF_3{\cdot}OEt_2$, which was optimized according to the same procedures GIAO-HF/6-311+G(2d,p)//B3LYP/6-31+G(d).
10. (a) Kamlet, M. J.; Abboud, J. M.; Abraham, H. M.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877–2887; (b) Lee, I.; Sung, D. D.; Uhm, T. S.; Ryu, Z. H. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1697–1701.
11. The pyridine adduct did not give **4** by further addition of pyridine but gave tricoordinate cation by the reaction with $SbCl_5$. To be published.