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Tricoordinate diphenylboron cation prepared in solution

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Abstract—Treatment of diphenylchloroborane with 1 equiv of pyridine or pyridine-*N*-oxide in CD_2Cl_2 formed the corresponding 1:1 adduct, which gave tricoordinate diphenylboron cation by electrophilic abstraction of chloride ion with the strong Lewis acid, $SbCl_5$. The experimental ^{11}B chemical shifts were in good agreement with the ab initio calculation results and the optimized structures were well explicable by ^{11}B, ^{13}C, and ^{121}Sb NMR spectroscopy.

The expected Lewis acidity of the boron cation, proposed as an intermediate in organic reactions, is of interest in connection with the long-standing question of the nature of the ionic species.[1] Related cationic species derived from diphenylborane derivative have been mentioned in early reports, but none have been either convincingly characterized or properly isolated.[2] We have been seeking for the capture of the diphenylboron cation as an effective reaction intermediate during asymmetric synthesis.[3–5] We found[4] that the diphenylboron perchlorate possesses a covalent B–O bond in contrast to the literatures.[2] We have recently found evidence for the nitromethane-solvated diphenylboron cation, containing an sp^3 hybridized boron atom, by the reaction of diphenylchloroborane **1** with $SbCl_5$ in nitromethane and its conversion to MeCN- or THF-solvated one and the boronium cation $[Ph_2B(pyridine)_2]^+$.[5] The next target is to obtain diphenylboron cations, containing an sp or sp^2 hybridized boron atom. This requires a less basic solvent than nitromethane such as dichloromethane. However, the electrophilic abstraction of the chloride ion by $AlCl_3$ and $SbCl_5$ from diphenylchloroborane does not proceed in nonpolar dichloromethane.[5,6] The addition of pyridine and pyridine-*N*-oxide into the dichloromethane solution of **1** surely gives the corresponding 1:1 adducts with **1**. We disclose herein the evidence for the formation of tricoordinate diphenylboron cations from the reactions of these adducts with the strong Lewis acid $SbCl_5$ in dichloromethane at room temperature (Scheme 1). The new species were continuously monitored in situ by using ^{11}B, ^{13}C, and ^{121}Sb NMR spectroscopy, and their existence was further confirmed by comparing calculated and experimental ^{11}B chemical shifts.

^{11}B, ^{13}C, and ^{121}Sb NMR spectra were measured on a JEOL JNM-ECA500 FT-NMR spectrometer operating at 160.47, 125.77, and 119.69 MHz, respectively. Chemical shifts are expressed in ppm downfield from external $BF_3{\cdot}OEt_2$ for ^{11}B, internal TMS for ^{13}C, and external NH_4SbCl_6 for ^{121}Sb NMR. All experimental manipulations were conducted in quartz NMR tube under rigorously anhydrous conditions under Ar in a glove box at room temperature. By the addition of 1 equiv of pyridine (0.1 mmol), the ^{11}B NMR signal at δ 62.7 ppm ($\Delta\nu^{1/2}$ = 300 Hz) of Ph_2BCl **1** (0.1 mmol) in CD_2Cl_2 is shifted to δ 8.2 ppm, indicating the formation of the 1:1 adduct with pyridine (**2a**, Scheme 1), also identified by its ^{13}C NMR spectrum, as follows. The $^{13}C_{para}$ NMR signal of the Ph_2B moiety of **2a** (entry 3 of Table 1) is observed at δ 125.9 ppm, 7.5 ppm to lower frequency relative to **1**, while $\delta(^{13}C)_{para}$ is shifted by 6.2 ppm to higher frequency than that of pyridine. The relative intensity of ^{13}C NMR signals for **2a** show a 2:1 ratio for phenyl groups and pyridine. Further addition of pyridine (0.1 mmol) to the adduct solution did not lead to the boronium cation **5a**, since free pyridine

Keywords: Diphenylboron cation; ^{11}B NMR; Ab initio calculation.

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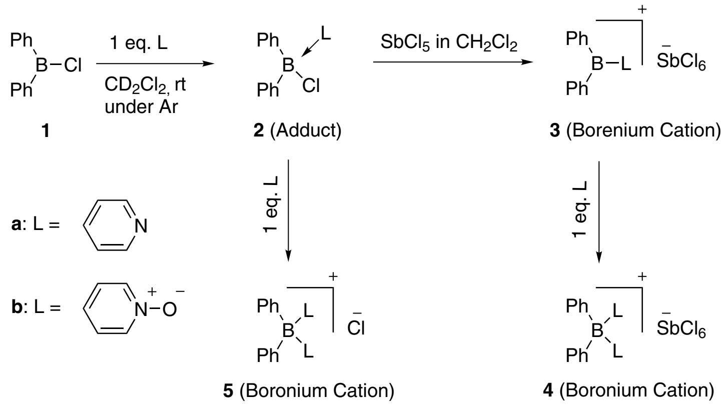


Scheme 1. Adduct and cation forming reactions of diphenylchloroborane with pyridine and pyridine *N*-oxide in dichloromethane.

Table 1. ^{13}C NMR (125.77 MHz) spectra concerning the reaction of adduct of diphenylchloroborane with $SbCl_5$ in CD_2Cl_2

Entry	Compound	$\delta(^{13}C)$/ppm: phenylboron[a]			$\delta(^{13}C)$/ppm: pyridine moiety		
		C_{ortho}	C_{meta}	C_{para}	C_{ortho}	C_{meta}	C_{para}
1	Ph_2BCl **1**	137.4	128.3	133.4			
2	Pyridine = Py				150.2	124.0	136.1
3	Ph_2BPyCl **2a**	133.7	127.7	125.9	147.2	127.0	142.3
4	$[Ph_2BPy]^+\ SbCl_6^-$ **3a**	140.4	129.6	136.6	148.6	128.6	150.1
5	$[Ph_2B(Py)_2]^+\ SbCl_6^-$ **4a**	134.2	128.9[b]	128.8	147.1	128.1[b]	145.1
6	Pyridine-*N*-oxide				139.5	126.4	125.2
7	Ph_2B(Py-*N*-oxide)Cl **2b**	133.1	127.4	126.7	142.6	128.2	140.1
8	$[Ph_2B(\text{Py-}N\text{-oxide})]^+\ SbCl_6^-$ **3b**	135.7[c]	129.1	134.0[c]	141.1	130.2	146.1
9	$[Ph_2B(\text{Py-}N\text{-oxide})_2]^+\ SbCl_6^-$ **4b**	132.7	128.1[b]	127.8	141.6	127.8[b]	140.8
10	$[Ph_2B(\text{Py-}N\text{-oxide})_2]^+\ Cl^{-}$[d] **5b**	133.0	127.7[b]	127.5	142.7	127.8[b]	140.3

[a] The chemical shifts of $^{13}C_{ipso}$ are not given. Most likely these NMR signals are broad.

[b] Interconvertible.

[c] Broad signal.

[d] Two equivalents of pyridine-*N*-oxide were added into the solution of diphenylchloroborane.

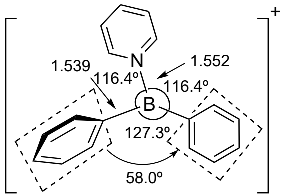
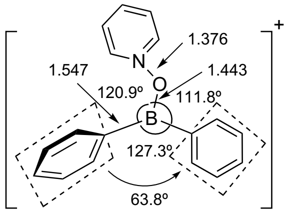
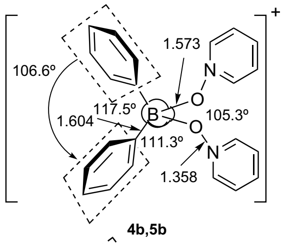
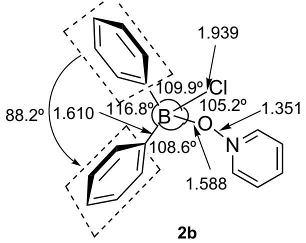
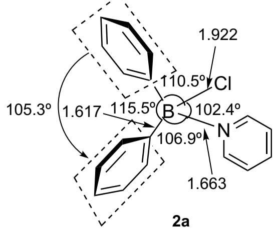
can be observed by the ^{13}C NMR spectrum of the reaction solution. When a solution of $SbCl_5$ in CH_2Cl_2 (1.0 M, 0.10 mmol, 100 μL) was added to the solution of the adduct **2a**, a dark yellow color appeared. The ^{11}B NMR signal of this solution is found at δ 58.2 ppm, shifted by 50 ppm to higher frequency relative to the adduct **2a**. This is consistent with the presence of tricoordinate boron[7,8] in the cationic species **3a**. The $^{13}C_{para}$ NMR signal of the Ph_2B moiety (entry 4 in Table 1) is observed at δ 136.6 ppm, shifted by 10.7 ppm to higher frequency relative to **2a**. The $^{13}C_{para}$ NMR signal of the pyridine moiety is also shifted to higher frequency, 7.8 and 14.0 ppm relative to those for **2a** and pyridine, respectively, and is identical to that of the pyridinium ion.[9] The ^{121}Sb NMR signals at δ 0 ppm assignable to $SbCl_6^-$ anion is a further indication of the ionic structure **3a**, as compared with 425 ppm of $SbCl_5$ in CD_2Cl_2. The color of the solution faded by further addition of pyridine (0.1 mmol) and the ^{11}B NMR signal moves to δ 8.6 ppm, indicating tetracoordinate boron in the boronium cation **4a**, while the ^{121}Sb NMR chemical shift remains constant at δ 0 ppm for $SbCl_6^-$ anion.

The analogous experiment was carried out using pyridine-*N*-oxide. When 1 equiv of pyridine-*N*-oxide was added to a CD_2Cl_2 solution of **1** (0.1 mmol), the ^{11}B NMR signal appears at δ 12.0 ppm, indicating the formation of the pyridine-*N*-oxide adduct **2b**. When the adduct **2b** was allowed to react with $SbCl_5$, the solution turned dark yellow to yield the borenium cation **3b**, for which the ^{11}B NMR signal at δ 49.6 ppm is consistent. The ^{13}C NMR signal at δ 134.0 ppm for C_{para} of the Ph_2B moiety is shifted by 7.3 ppm to higher frequency relative to **2b** (entries 7 and 8 in Table 1). Similarly, the $^{13}C_{para}$ NMR signal of pyridine-*N*-oxide ring is observed at δ 146.1 ppm, 6.0 and 20.9 ppm at higher frequencies than those of **2b** and pyridine-*N*-oxide, respectively, and is identical to that of protonated pyridine *N*-oxide.[9] By further addition of pyridine-*N*-oxide (1 equiv), **3b** is converted to the boronium salt **4b**, for which the ^{11}B NMR signal is found at δ 12.0 ppm. The presence of the $SbCl_6^-$ anion of **3b** and **4b** is confirmed by the ^{121}Sb NMR signal at δ 0.6 ppm. The addition of one more equivalent of pyridine-*N*-oxide to the adduct **2b** solution yielded boronium salt **5b**, in contrast to the reaction of pyridine with **2a** (vide supra).

An ab initio calculation of the ^{11}B nuclear magnetic shielding was done by using the method,[10] GIAO-HF/6-311+G(2d,p)//B3LYP/6-31+G(d). All quantum chemical calculations were carried out with the GAUSSIAN 98 program suite.[11] The calculated ^{11}B chemical shifts[12] are summarized in Table 2 together with the experimental data. The reasonable agreement between calculated and experimental values of all species in Table 2 as well as **4a**[13] suggests that the actual structures of the adducts and borenium 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. The optimized structure of the diphenylborenium cation **3a** was found to be a planar structure around boron atom, where the planes of the three aromatic rings are twisted against the central C_2BN plane by 30° (phenyl) and 45° (pyridine), comparable to the situation in the trityl cation (twisted angle 32°). The B–N bond length (1.552 Å) of **3a** is expectedly shorter than for the pyridine adduct **2a** (1.663 Å) and boronium cation **4a** (1.650 Å).[5]

In conclusion, the electrophilic abstraction of the chloride ion by the strong Lewis acid $SbCl_5$ from pyridine

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

Entry	Structure[a]	Expt.[b] in CD_2Cl_2		Calcd.[c] δ (ppm)
		δ (ppm)	Line width (Hz)	
1	 **3a**	58.2	740	56.4
2	 **3b**	49.6	720	49.4
3	 **4b,5b**	12.0 (**4b**) 11.9 (**5b**)	350 290	12.1
4	 **2b**	12.0	240	11.7
5	 **2a**	8.2	160	8.9

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

[b] The chemical shifts are expressed in ppm downfield from $BF_3 \cdot OEt_2$.

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

and pyridine-*N*-oxide adducts **2** is indicated by ^{11}B nuclear magnetic deshielding, typical of tricoordinate boron atoms in the surroundings assigned for the borenium cations **3**. Apparently, the pyridine ring in **3a** and the B–O bond in **3b** help to stabilize the borenium cations to some extent by π back-bonding to boron, thus delocalizing the positive charge.

Acknowledgements

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12. 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).
13. Theoretical ^{11}B chemical shift (9.0 ppm) and the optimized structure of **4a** were reported in Ref. 5.