Boron Cations derived from BH^{2+}

By G. E. RYSCHKEWITSCH,* M. A. MATHUR, and T. E. SULLIVAN
(*Department of Chemistry, University of Florida, Gainesville, Florida* 32601)

Summary The boron cations reported represent the first examples of mononuclear 2+ species with B–H bonds and show a surprising deactivation of the boron–hydrogen bond towards electrophilic reagents.

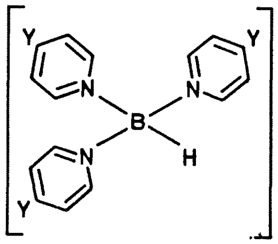
A GENERAL synthesis was reported recently of ions containing BH_2^+ in which boron was co-ordinated to two similar[1] or to two different[2] nitrogen bases. We now report the preparation of cations in which a BH^{2+} group is co-ordinated to three pyridine bases to form tetrahedral ions.

On heating trimethylamine dibromoborane[3] under reflux in dry pyridine a yield of 96% of the anhydrous bromide salt of (Ia) was obtained. Precipitation of this ion from water solution by addition of acetone gave the dihydrate, $(C_5H_5N)_3BH^{2+}$, $2Br^-\cdot 2H_2O$ in 86% yield, m.p. 222—224°, (decomp.). Precipitation with aqueous NH_4PF_6 gave $(C_5H_5N)_3BH^{2+}$, $2PF_6^-$ in 96% yield, m.p. 248—250°.

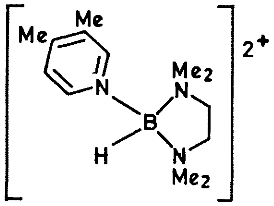
Similarly, the analogous 4-methylpyridine (Ib) derivative was isolated as the PF_6^- salt in 68% yield, m.p. 234—236°. The same cation was also produced in 85% yield as the iodide salt by the rection of 4-methylpyridine di-iodoborane with 4-methylpyridine at room temperature in toluene solution.

The iodide of the chelated ion (II) was obtained by a similar procedure from 3,4-dimethylpyridine di-iodoborane and *NNN'N'*-tetramethylethylenediamine. Subsequent conversion into the PF_6^- salt gave an overall yield of 45% of crude product, which after two recrystallizations had m.p. 228—234° (decomp.).

The i.r. spectra of the salts have a single B–H stretching vibration between 2540 and 2545 cm^{-1}, a frequency which is about 50—70 cm^{-1} higher than is observed for analogous BH_2^{2+} salts.[2] The ^{11}B n.m.r. spectrum for the pyridine derivative in water gives the expected doublet at δ 13·0 ± 0·5 p.p.m., J_{B-H} 120 ± 10 Hz [external $B(OCH_3)_3$ standard] whereas the PF_6^- salts in nitromethane exhibit at room temperature only broad singlets with a width of about 120 Hz. The doublet structure is apparently broadened because of quadrupole relaxation. The ^1H n.m.r. spectra show the number and multiplicity of resonances at the relative intensities expected for the attached ligands. Relative to the free nitrogen bases, the chemical shifts of the protons are displaced to lower field, an observation which has also been made for BH_2^+ salts.[2] The downfield shifts are, however, more pronounced in BH^{2+} compounds, as would be expected from the de-shielding effect of the greater positive charge. Boron-attached hydrogens were not observed,[4] nor was there long-range coupling between boron and carbon-attached hydrogens.[5] This again is attributed to quadrupole relaxation.[4,5]



(I)a; Y = H
b; Y = Me



(II)

The 2+ cations are more resistant to halogenation than singly charged species.[6] Thus the ion (Ib) was recovered unchanged as the PF_6^- salt after 12 hr. at reflux with 2M-Br_2 in 1,2-dichloroethane. In contrast, an excess of 0·5 M-Br_2 in dichloromethane substituted one boron-attached hydrogen in $(4\text{-}CH_3C_5H_4N)_2BH_2^+$ within 40 min. at room temperature, and 1·5 M-Br_2 replaced both hydrogens after 4 hr. at reflux in dichloromethane. The 2+ cations are also significantly more resistant to hydrolytic degradation than are analogous 1+ species.[2] No evidence of hydrolysis was observed when the bromide of (Ib) was heated for 8 hr. in water or 0·5 M-HCl at 100°. Although stable towards 0·5 M-NaOH at room temperature or at 80°, boiling base degraded the cation fairly rapidly.

The introduction of two positive charges appears to strengthen the B–H bond, as suggested by the shifts in the i.r. spectrum and by the low reactivity towards bromine or acid. Resistance to degradation by base is also high, but most likely involves nucleophilic displacement of the nitrogen base rather than reaction at the B–H bond.

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