Some New Tetra-coordinated Complexes of Boron

A S KOTHIWilliam, A SINGH, A K RAI & R C MEHROTRA*
Department of Chemistry, University of Rajasthan, Jaipur 302004
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New molecular adducts of the type \( \text{G} \text{OBO} \text{L} \) [where (i) \( \text{G} = \text{C}_6\text{H}_4, \text{R} = \text{Bu}^\alpha \); (ii) \( \text{G} = \text{C}_6\text{H}_4, \text{C}_6\text{H}_4\text{CH}_2; \text{R} = \text{Pr}^\dagger \) and \( \text{Bu}^\alpha \); and \( \text{L} = \text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3(\alpha-, \text{m-} \) and \( \text{p-} \) ) and \( \text{p-Me}_2\text{N}\text{C}_6\text{H}_4\text{COCH}_3 \)] have been synthesised and characterised by elemental analyses, molecular weight measurements and a tetracoordination environment around boron atom in these complexes has been established on the basis of spectral (UV, IR, \( ^1\text{H} \) and \( ^11\text{B} \) NMR) data. Orthorhombic symmetry is indicated for crystalline \( \text{OC}_6\text{H}_4\text{OBO} \text{Bu}^\alpha \cdot \text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3 \).

In contrast to alkoxyboranes, the aryloxyboranes in general\(^1\) and 2-alkoxy-1, 3, 2-benzodioxaborole\(^3\) and 2-alkoxy-4H-1, 3, 2-benzodioxaborin\(^4\) have been shown to form stable addition complexes with nitrogen-containing organic bases but the nature of the complexes and their stereochemistry have not been investigated.

In this paper we report the preparation and characterisation of adducts of aryloxyboranes, such as \( \text{OC}_6\text{H}_4\text{OBO} \text{Bu}^\alpha \) and \( \text{OC}_6\text{H}_4\text{CH}_2\text{OBO} \text{Bu}^\alpha \) with aminoacetophenones (\( \alpha, \text{m} \) and \( \text{p} \)) and \( \text{p-dimethylamino} \text{benzaldehyde} \). Due to the presence of two potential donor sites (oxygen and nitrogen) in these ligands, they may form addition complexes involving either of the donor sites.

\( \text{X} = \text{Y} = \text{O} \); or \( \text{X} = \text{O}, \text{Y} = \text{OCH}_2 \)
\( \text{R}^\alpha = \text{H} \) or \( \text{Me} \)
\( \text{R}^\beta = \text{H} \) or \( \text{Me} \)

**Materials and Methods**
Rigorous precautions were taken to exclude moisture from the reaction system. Benzene and ether were dried over sodium and distilled before use. Aryloxyboranes used were prepared by the method reported earlier\(^3\). Ligands (commercially available) were purified by standard methods prior to use.

**Table 1 — Analytical and Physical Data of Some Boron Adducts**

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Compound</th>
<th>Yield ((%))</th>
<th>Physical state</th>
<th>m.p.</th>
<th>Mol. wt.</th>
<th>Analysis*</th>
<th>NMR ((\delta), p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td></td>
<td>( % \text{N} )</td>
<td>( % \text{B} ) ( ^1\text{H} )</td>
</tr>
<tr>
<td>1</td>
<td>( \text{OC}_6\text{H}_4\text{OBO} \text{Bu}^\alpha \cdot \text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3 )</td>
<td>68</td>
<td>Yellow powder</td>
<td>151</td>
<td>315</td>
<td>4.21</td>
<td>3.31</td>
</tr>
<tr>
<td>2</td>
<td>( \text{OC}_6\text{H}_4\text{OBO} \text{Bu}^\alpha(m) \cdot \text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3 )</td>
<td>67</td>
<td>Yellow powder</td>
<td>126</td>
<td>309</td>
<td>(4.28)</td>
<td>(3.30)</td>
</tr>
<tr>
<td>3</td>
<td>( \text{OC}_6\text{H}_4\text{OBO} \text{Bu}^\alpha(p) \cdot \text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3 )</td>
<td>74</td>
<td>Yellow powder</td>
<td>118</td>
<td>333</td>
<td>(4.28)</td>
<td>(3.30)</td>
</tr>
<tr>
<td>4</td>
<td>( \text{OC}_6\text{H}_4\text{OBO} \text{Bu}^\alpha(p) \cdot \text{NMe}_2\text{C}_6\text{H}_4\text{CHO} )</td>
<td>83</td>
<td>Yellow powder</td>
<td>100</td>
<td>351</td>
<td>(4.28)</td>
<td>(3.30)</td>
</tr>
<tr>
<td>5</td>
<td>( \text{OC}_6\text{H}_4\text{CH}_2\text{OBO} \text{Bu}^\alpha(p) \cdot \text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3 )</td>
<td>80</td>
<td>Yellow powder</td>
<td>128</td>
<td>—</td>
<td>4.02</td>
<td>3.13</td>
</tr>
<tr>
<td>6</td>
<td>( \text{OC}_6\text{H}_4\text{CH}_2\text{OBO} \text{Bu}^\alpha(m) \cdot \text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3 )</td>
<td>77</td>
<td>Yellow powder</td>
<td>120</td>
<td>353</td>
<td>(4.12)</td>
<td>(3.17)</td>
</tr>
<tr>
<td>7</td>
<td>( \text{OC}_6\text{H}_4\text{CH}_2\text{OBO} \text{Bu}^\alpha(n) \cdot \text{NH}_2\text{C}_6\text{H}_4\text{COCH}_3 )</td>
<td>65</td>
<td>Yellow powder</td>
<td>120</td>
<td>353</td>
<td>(4.12)</td>
<td>(3.17)</td>
</tr>
<tr>
<td>8</td>
<td>( \text{OC}_6\text{H}_4\text{CH}_2\text{OBO} \text{Pr}^\beta(p) \cdot \text{NMe}_2\text{C}_6\text{H}_4\text{CHO} )</td>
<td>90</td>
<td>Red oily liquid</td>
<td>144</td>
<td>360</td>
<td>4.17</td>
<td>3.11</td>
</tr>
</tbody>
</table>

*The calculated values are in parentheses.  "Relative to TMS.
"The corresponding ligand absorptions are in parentheses recorded in 2\("\text{H}\) CDCl\(_3\) solution.
"Relation to BF\(_3\), OEt\(_2\).
Nitrogen was estimated by Kjeldahl’s method and boron as methyl borate. IR spectra were recorded as nujol mulls on a Perkin-Elmer 577 spectrophotometer, PMR spectra on a Perkin-Elmer R-12 B spectrometer in acetone-<sup>d6</sup> and UV spectra on a Pye-Unicam SP-8-100 spectrophotometer. Molecular weights were measured in refluxing benzene on a semi-micro ebulliometer (Gallenkamp) using a thermistor sensor.

**Synthesis of addition complexes**

The adducts were prepared by the following general methods. Further details are listed in Table 1.

Addition of appropriate aminoacetophenone (or dialkylaminobenzaldehyde) dissolved in benzene or ether to the aryloxyboranes in the same solvent in equimolar amounts resulted in an exothermic reaction with immediate precipitation of a coloured solid. The reaction mixture was stirred for ~3 hr, the supernatant liquid decanted off, the residue washed well with benzene or ether and dried under reduced pressure to yield the corresponding boron derivative which was recrystallised from hot benzene.

**Results and Discussion**

The interaction of aryloxyboranes with appropriate aminoacetophenone in benzene or ether afforded 1:1 addition complexes of the type (I). It is interesting to note that complexes of 1:1 stoichiometry are formed irrespective of the molar ratios of the reactants employed. Further, there is no reaction between 2-isopropoxy-4,4,6-trimethyl-1,3,2-dioxaborinane and aminoacetophenones, indicating weaker electrophilic nature of the boron in the above derivative.

All the resulting complexes are coloured, sharp melting solids, monomeric, hydrolytically stable and soluble in common organic solvents. The complexes undergo decomposition on attempted distillation or sublimation under reduced pressure.

The facile reaction of aryloxyboranes used as precursors in this investigation with aminoacetophenones or p-dimethylaminobenzaldehyde and non-formation of addition complexes with acetophenone or benzaldehyde even on prolonged stirring is indicative of the coordination through the amino-nitrogen atom.

PMR spectra

A comparison of the PMR spectra of the ligands and the corresponding adducts, indicates no appreciable shift in the signals due to phenyl and COCH<sub>3</sub> protons. However, a significant lowering (δ 3.40 ± 0.40 ppm) in the position of the signals due to the amino protons provides an evidence for the coordination through the amino-nitrogen atom.

The PMR spectrum of the p-dimethylaminobenzaldehyde displays a sharp singlet at δ 9.75 ppm due to the aldehydic proton. Another singlet at δ 3.05 ppm is assigned to NMe<sub>2</sub> protons. In the spectra of the corresponding boron derivatives the singlet due to NMe<sub>2</sub> protons shifts to lower field (δ 3.25) suggesting the formation of B←N dative bond, whereas the position (δ 9.75) of aldehydic protons remains unchanged in the region characteristic of aromatic aldehydes bearing a strong electron-withdrawing group at the para position (cf. p-nitrobenzaldehyde displays aldehydic proton at δ 9.99 ppm).

**UV spectra**

Three maxima are observed in the UV region in the free ligands. The highest energy band appearing at 208 ± 5 nm can be ascribed to I<sub>0</sub> transitions of the benzenoid ring. Further, the bands appearing at ~232 nm and 318 nm have been assigned to π-π* transition of the C=O chromophore and π-π* of the NH auxochrome respectively. These free ligand bands remain almost unaltered in the UV spectra of the adducts, except the one due to the n-π* transition which shows a blue shift due to the elimination of p-π conjugation (as observed in the case of anisole-BF<sub>3</sub> complex) on complexation. The shift to lower frequency by ~5 nm in all the derivatives, though rather small, may be taken as a corroborative evidence of the coordination through ‘nitrogen’ of the amino group to the boron atom.

**IR spectra**

The lowering of νNH<sub>2</sub> and the presence of new absorption bands in the region 680-720 cm<sup>-1</sup> which could tentatively be assigned to νB←N modes indicate the coordination of the ligand through nitrogen to the boron atom. Moreover, the presence of a strong band in the region 1700-1800 cm<sup>-1</sup> is indicative of the free unligated carbonyl group in these derivatives. The strong bands characteristic of tricoordinated B-O in the region 1310-1380 cm<sup>-1</sup> in the parent boron compounds are virtually absent in the spectra of the adducts, again confirming the change of boron coordination state from three to four.
oxygen compound) and the appearance of sharp singlets at δ 14.15 and 19.13 ppm in two representative derivatives \( \text{OC}_6\text{H}_4\text{OBOBu}^\text{a-o-NH}_2\text{C}_6\text{H}_4\text{COCH}_3 \) and \( \text{OC}_6\text{H}_4\text{CH}_2\text{OBOPr}^\text{1-p-NMe}_2\text{C}_6\text{H}_4\text{CHO} \) respectively provide convincing evidence for tetracoordination around the boron atom in the complexes studied herein.

Additionally, the \(^{11}\text{B} \) NMR chemical shift value (δ 19.13 ppm) in the complex \( \text{OC}_6\text{H}_4\text{CH}_2\text{OBOPri.p-NMe}_2\text{C}_6\text{H}_4\text{CHO} \) may be due to the combined effect of the weaker electrophilic nature of \( \text{OC}_6\text{H}_4\text{CH}_2\text{OB} \) and steric factors (two methyl groups attached to the nitrogen atom of the coordinating ligand).

The X-ray powder diffraction analysis of the compound, \( \text{OC}_6\text{H}_4\text{OBu}^\text{a-o-NH}_2\text{C}_6\text{H}_4\text{COCH}_3 \) has been carried out in order to throw some light on its lattice dimensions. The complex is orthorhombic with \( a = 11.84 \) Å, \( b = 23.25 \) Å, \( c = 11.46 \) Å; \( \alpha = \beta = \gamma = 90^\circ \).

Acknowledgement

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References