Role of Catechol in the Radical Reduction of $B$-Alkylcatecholboranes in Presence of Methanol

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General Informations: Unless otherwise stated, all reagents were obtained from commercial sources and used without further purification. All glassware was oven-dried at 130 °C or flame dried under vacuum, assembled hot and allowed to cool under nitrogen. $^1$H and $^{11}$B NMR spectra were recorded on a Bruker Avance II 400 spectrometer ($^1$H: 400.12 MHz, $^{11}$B: 128.38 MHz). The $^{13}$C and some $^1$H NMR spectra were recorded on a Bruker Avance 300 ($^1$H: 300.18 MHz, $^{13}$C: 75.48 MHz). Chemical shifts are reported in units of $\delta$ (ppm) using the internal standard residual ($\text{C}_6\text{H}_6 \delta = 7.16$ ppm for $^1$H NMR spectra and $\text{C}_6\text{D}_6 \delta = 120.06$ ppm for $^{13}$C NMR spectra) or Et$_2$OBF$_3$ as an external standard ($\delta = 0$ ppm) for $^{11}$B NMR spectra. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. GC analyses were carried out on a CE instruments MEGA Series HRGC fitted with an Optima delta-3 (Macherey-Nagel) capillary column (30 m and 10 m). GC/MS analyses were carried out on a Finnigan Trace GC/MS fitted with an Optima delta-3 (30 m).

General Procedure for the preparation of NMR samples

C$_6$D$_6$ was purchased from Cambridge Isotopes and degassed by 5 cycles freezing / vacuum / nitrogen then stored on MS 4A in the glove box under Argon (MBRAUN Uni-Lab (1200/780)). Commercially available $B$-n-propylcatecholborane (PrBCat) and catecholborane (CatBH) were distilled under reduced pressure prior to use (respectively 73 °C, 1 mbar and 50 °C, 67 mbar). Catechol was recrystallised from benzene then sublimed under reduced pressure. Commercial anhydrous methanol (Aldrich) was used without further purification. All the samples were prepared in the glove box and readily sealed under vacuum.

$B$-Methoxy-1,2,3-benzodioxaborole (4)

To a solution of CatBH (15 mmol, 1.6 mL) in C$_6$H$_6$ (10 mL), MeOH (1 equiv, 15 mmol, 0.6 mL) was added dropwise. The resulting solution was stirred until no more H$_2$ evolution was visible (c.a. 15 min). After evaporation of the solvent, the residue was distilled under reduced pressure to yield MeOBCat 4 as a colorless oil. $^1$H-NMR (400 MHz, C$_6$D$_6$): 6.88-6.93 (m, 2H), 6.71-6.77 (m, 2H). 3.37 (s, 1H). $^{13}$C-NMR (75 MHz, C$_6$D$_6$): 148.6, 122.5, 112.2, 53.1. $^{11}$B-NMR (128 MHz, C$_6$D$_6$): 23.5.
Dimethyl-propylboronic ester (7b)
Propylboronic acid (5 mmol, 0.44 g) was dissolved in C₆D₆ (2 mL) with MeOH (5 equiv., 25 mmol, 1 mL). After 5 min stirring, the resulting solution was distilled at atmospheric pressure. 0.550 g of an azeotropic mixture (T = 45 – 55 °C) of B(OMe)₃, PrB(OMe)₂ and MeOH (1:10:50 determined by integration of ¹H NMR spectra) was obtained as a colorless liquid. This mixture was readily dissolved in C₆D₆ over MS 4 Å to trap the excess of MeOH. The resulting solution was used as obtained for NMR experiments.

¹H-NMR (400 MHz, C₆D₆): 3.36 (s, 6H), 1.53-1.62 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H), 0.69 (t, J = 7.6 Hz, 2H). ¹³C-NMR (75 MHz, C₆D₆): 51.2, 17.8, 17.4. ¹¹B-NMR (128 MHz, C₆D₆): 31.9. NMR data are in good accordance with the literature.[1]

B-isopinocampheyl-1,2,3-benzodioxaborole (3a)
Catecholborane (1.2 mL, 9 mmol) was added dropwise to α-pinene 1a (5 mmol). The reaction mixture was heated neat at 100 °C for 12 h. Distillation of the crude material furnished pure 3a (80 °C, 10⁻³ mbar) as a colorless oil. ¹H-NMR (300 MHz, C₆D₆): 7.09-7.03 (m, 2H), 6.85-6.76 (m, 2H), 2.44-2.10 (m, 4H), 1.93-1.87 (m, 1H), 1.65-1.56 (m, 1H), 1.19 (d, J = 7.2 Hz, 1H), 1.16 (s, 3H), 1.03 (s, 3H), 0.92 (d, J = 9.7 Hz, 1H). ¹³C-NMR (75 MHz, C₆D₆): 149.1, 122.8, 112.6, 48.3, 41.6, 38.9, 38.8, 34.4, 29.0, 28.6, 23.3, 23.0.

cis-Pinane (2a)
From α-pinene 1a: Catecholborane (0.4 ml, 3 mmol) was added dropwise at 0 °C to a solution of 1a (1.5 mmol) and N,N-dimethylacetamide (14 µl, 0.15 mmol) in CH₂Cl₂ (2.0 ml) under N₂. The reaction mixture was heated under reflux for 5 h. After cooling down to 0 °C, MeOH (0.24 ml, 6 mmol) was added. The solution was heated under reflux and air (60 ml, 0.5 mmol O₂) was introduced over 1.5 h using a syringe pump (needle placed just below the surface of the reaction mixture).

From B-isopinocampheylcatecholborane (3a): To a solution of 3a (1.5 mmol, 384 mg) in CH₂Cl₂ (2.0 ml) under N₂, MeOH (0.24 ml, 6 mmol) or catechol (1.5 mmol, 249 mg) was added. The solution was heated under reflux and air (60 ml, 0.5 mmol O₂) was introduced over 1.5 h with a syringe. GC yield was determined using phenylcyclohexane as internal standard. The retention time (t = 2.57 min, 60°C-280 °C, rate: 6 °C/min, 45 KPa, helium, l = 10 m) and CG/MS analysis of the reduced product were found to be identical with commercially available (1R)-(+-) cis-pinane.

$B$-cis-$\alpha$-Piny1-1,2,3-benzodioxaborole (3a)
MeOBCat/MeOH NMR study
Determination of the equilibrium constant: $K_3$

$$
\begin{equation}
\begin{aligned}
\ce{B(OMe)_3 + catechol + MeOH &<=> B(OMe)_3[MeOBCat] + MeOH^2} \\
K_3 &= \frac{[B(OMe)_3][\text{catechol}]}{[MeOBCat][MeOH]^2}
\end{aligned}
\end{equation}
$$

<table>
<thead>
<tr>
<th>$[\text{MeOBCat}]$</th>
<th>$[\text{MeOH}]$</th>
<th>$[B(\text{OMe}_3)][\text{MeOBCat}]$</th>
<th>$[\text{MeOH}]$</th>
<th>$[B(\text{OMe}_3)]$</th>
<th>$[\text{BOMe}_3]$</th>
<th>$[\text{MeOBCat}][\text{MeOH}]^2$</th>
<th>$[B(\text{OMe}_3)][\text{catechol}]$</th>
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<td>0.24</td>
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<td>0.0013</td>
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<td>$[B\text{(OMe}_3)]$</td>
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<td>$[B(\text{OMe}_3)][\text{MeOBCat}]$</td>
<td>$[\text{MeOH}]$</td>
<td>$[B(\text{OMe}_3)]$</td>
<td>$[\text{BOMe}_3]$</td>
<td>$[\text{MeOBCat}][\text{MeOH}]^2$</td>
<td>$[B(\text{OMe}_3)][\text{catechol}]$</td>
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<td>0.5</td>
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<td>0.131</td>
<td>0.281</td>
<td>0.399</td>
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<td>0.136</td>
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</table>

$K_3$ from $^{11}$B-NMR integration:

$$
y = 13.912x + 0.0083
$$

$R^2 = 0.9949$
PrBCat/MeOH NMR study
$^{13}$B
PrB(COMe)$_3$

$^1$H
PrB(COMe)$_3$
+ traces of B(COMe)$_3$
$^{13}$C
PrB(O\text{Me})$_2$
+ traces of B(O\text{Me})$_3$

$^1$H
PrB(O\text{Me})$_2$
+ traces of B(O\text{Me})$_3$
**Determination of the equilibrium constant: K₅**

\[
K₅ = \frac{[\text{Pr } B(\text{OMe})₂][\text{catechol}]}{[\text{Pr } B\text{Cat}][\text{MeOH}^2]}
\]

### **¹H-NMR**

<table>
<thead>
<tr>
<th>[PrBCat]</th>
<th>[MeOH]</th>
<th>[PrB(OMe)₂]/[PrBCat]</th>
<th>[PrB(OMe)₂]/[MeOH]</th>
<th>[PrBCat]</th>
<th>[MeOH]</th>
<th>[PrB(OMe)₂]/[Catechol]</th>
<th>[PrBCat]/[MeOH]²</th>
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<tbody>
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<td>0.1</td>
<td>0.55</td>
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<td>0.064</td>
<td>0.018</td>
<td>0.0007</td>
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<tr>
<td>0.2</td>
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<td>0.6</td>
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<td>0.54</td>
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<td>0.175</td>
<td>0.1166</td>
<td>0.0307</td>
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</tbody>
</table>

**K₅ from ¹H-NMR integration**

\[
y = 0.251x + 0.0007 \\
R² = 0.9638
\]

### **¹B-NMR**

<table>
<thead>
<tr>
<th>[PrBCat]</th>
<th>[MeOH]</th>
<th>[PrB(OMe)₂]/[PrBCat]</th>
<th>[PrB(OMe)₂]/[MeOH]</th>
<th>[PrBCat]</th>
<th>[MeOH]</th>
<th>[PrB(OMe)₂]/[Catechol]</th>
<th>[PrBCat]/[MeOH]²</th>
<th>[PrB(OMe)₂]/[Catechol]</th>
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<tbody>
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<td>0.1</td>
<td>0.09</td>
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<td>0.2</td>
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<td>0.0070</td>
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<tr>
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<td>0.0159</td>
</tr>
<tr>
<td>0.5</td>
<td>0.95</td>
<td>0.6</td>
<td>0.313</td>
<td>0.188</td>
<td>0.1875</td>
<td>0.133</td>
<td>0.0392</td>
<td>0.0392</td>
</tr>
</tbody>
</table>

**K₅ from ¹B-NMR integration**

\[
y = 0.3169x + 0.0027 \\
R² = 0.9814
\]
$^1$H NMR

PrBCat 0.5 M
MeOH 0.45 M

$^3$B NMR

PrBCat 0.5 M
MeOH 0.95 M
Catechol / MeOH $^1$H-NMR study: Evidence for strong H-bonding in benzene solution
Effective concentrations of borane species in the reaction conditions:
PrBCat + catechol: O$_2$ free

PrBCat 0.33 M
Catechol 0.1 M
O$_2$ free
PrBCat + catechol: O$_2$ (2 hours)

PrBCat 0.33 M
Catechol 0.1 M
O$_2$ (2 hours)