

## A new type of B-podand catalysts for solid–liquid phase transfer reactions

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**Abstract**—Boron podands **1–4** (B-podands) were studied as strong complexing agents of alkali metal cations and very powerful catalysts in typical anion promoted reactions under solid–liquid conditions, even in chlorobenzene and acetonitrile. The results were comparable with the catalytic activity of classical phase transfer catalysts: crown ethers, polyethylene glycols (PEG) and previously studied Si-podands.

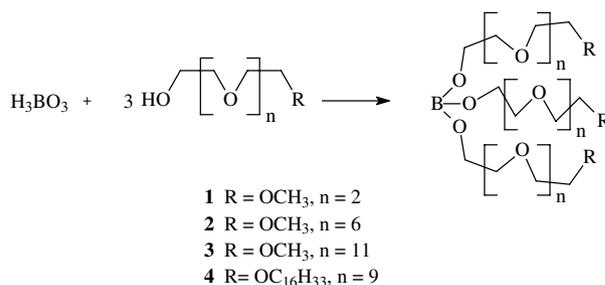
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Phase transfer catalysis (PTC) is a very important technique used in organic synthesis when the reagents differ in physical properties (like polarity) or occur as two immiscible phases, for example, in immiscible liquids (solvents), LL-PTC (liquid–liquid phase transfer catalysis) or in the solid and liquid phase SL-PTC (solid–liquid phase transfer catalysis). Addition of a catalyst would improve the reaction rate or simply permit its occurrence. Such a catalyst, most often being a salt of a complex with a metal cation (e.g., a crown ether), transfers one of the reagents (frequently the anion) to the other phase in which the reaction takes place. PTC in a solid–liquid system has attracted a lot of attention.<sup>1–5</sup>

A fundamental and essential problem of SL-PTC processes is to find an appropriate and effective catalyst. Podands are non-cyclic structures in which several polyether chains are linked to the same binding centre being either an atom (N, P, Si, S), or a multibranch structural arrangement. The number of oxygen atoms and different length of polyoxaalkyl chains determine the complex-forming ability of podands. As a result of their specific properties, they are called open-chain analogues of crown ethers and cryptands. In comparison

with typical phase transfer catalysts, such as open-chain PEGs, cryptands or crown ethers, they are characterized by low cost and easy synthesis, virtual non-toxicity and high complex forming ability.<sup>6–8</sup> These reasons make podands highly promising as anion activators in organic reactions. Recently, we reported on a successful use of Si-podands as particularly suitable ligands for solid–liquid phase transfer catalysis.<sup>9–11</sup>

In this letter, we report a systematic study of boron polypodands **1–4**, obtained in high yields by the reaction presented in **Scheme 1** between boric acid and an appropriate polyethylene glycol according to the procedure described previously.<sup>12</sup> The formulas of podands **1–4** were confirmed by <sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C NMR spectroscopy.<sup>13</sup> B-podands are thermally stable under the reaction conditions. On the basis of calorimetric



**Scheme 1.** Reaction between boric acid and polyethylene glycols.

**Keywords:** Boron podands; Solid–liquid phase transfer catalysis; Anion promoted reaction.

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**Table 1.** The complex stoichiometry (catalyst: M<sup>+</sup>) determined by calorimetric measurements

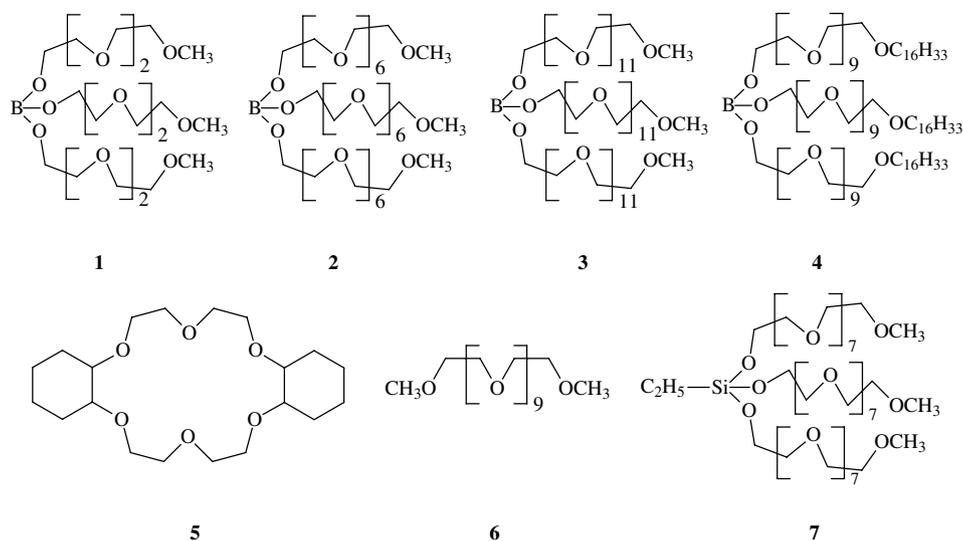
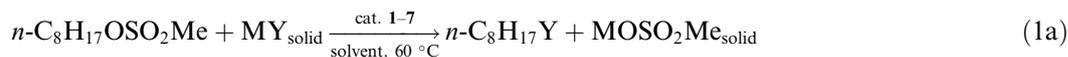
Catalyst	Complex stoichiometry (catalyst: M <sup>+</sup> )	
	Na <sup>+</sup>	K <sup>+</sup>
1	1:1	1:1
2	1:3	1:2
3	1:5	1:3
4	1:4	1:3
5	1:1	1:1
6	1:1	1:1
7	1:4	1:2

M<sup>+</sup> = Na<sup>+</sup>, K<sup>+</sup>.

titrations<sup>14</sup> of B-podands with NaClO<sub>4</sub> or KClO<sub>4</sub> in acetonitrile, we observed that the number of complexed

M<sup>+</sup> metal cations by the ligand mainly depends on the topology of the B-podand and increases with the number of oxygen atoms. The data reported in Table 1 show that the number of complexed Na<sup>+</sup> atoms increases from one for ligand 1 to four to five for ligands 3 and 4. The highest complexation values (about 4 or 5 mol of Na<sup>+</sup>) were always obtained with B-podands 3 and 4, which possess the highest number of donor atoms, 39 and 33 oxygens, respectively. On average, one Na<sup>+</sup> cation is coordinated by six oxygen atoms from the polyoxaalkyl chain of the podand. The analogous situation occurred for calorimetric measurements of B-podands with KClO<sub>4</sub>.

We used B-podands as catalysts in phase transfer catalysis processes and they were found to be excellent catalysts in some anion promoted reactions (nucleophilic

**Scheme 2.** Phase-transfer catalysts: boron podands 1–4, crown ether 5, PEG 6, and silicon podand 7.**Table 2.** The catalytic activity of B-podands 1–4, 5 (DCH18C6), 6 (PEG400Me<sub>2</sub>) and Si-podand 7 in (1a): *n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>2</sub>Me; MY = NaI, KI, NaBr under SL-PTC conditions in chlorobenzene or acetonitrile at 60 °C and (1b) *n*-C<sub>8</sub>H<sub>17</sub>Br; NaI under SL-PTC conditions in chlorobenzene at 60 °C

Catalyst	Reaction time (min) <sup>a</sup>			
	NaI <sup>b</sup>	KI <sup>b</sup>	NaBr <sup>c</sup>	NaI <sup>d</sup>
—	>4300	—	—	—
1	302.0	1250.0	—	440.1
2	46.6	220.0	1650.0	66.8
3	25.9	107.0	1507.0	33.8
4	37.2	130.0	1750.0	50.0
5	43.1	203.0	3400.0	59.8
6	308.0	369.0	3500.0	420.7
7	36.9	130.0	1800.0	51.1

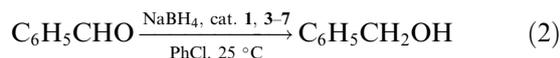
<sup>a</sup> Conversion = 90% (by HPLC).<sup>b</sup> A chlorobenzene solution (10 ml) of substrate *n*-C<sub>8</sub>H<sub>17</sub>OSO<sub>2</sub>Me (3.5 mM), catalyst (0.35 mM) with one molar equivalent of MY as the solid phase.<sup>c</sup> An acetonitrile solution (10 ml) of substrate *n*-C<sub>8</sub>H<sub>17</sub>X (3.5 mM), catalyst (0.35 mM) with one molar equivalent of MY as the solid phase.<sup>d</sup> For reaction (1b), a chlorobenzene solution (10 ml) of substrate *n*-C<sub>8</sub>H<sub>17</sub>Br (3.5 mM), catalyst (0.35 mM) with one molar equivalent of MY as the solid phase.

substitution, reduction, alkylation, etc.) under solid–liquid conditions in chlorobenzene as a low polarity medium and acetonitrile as a polar aprotic solvent. A comparison of the results of the catalytic activity of B-podands **1–4** with the well known PTC catalysts: crown ether DCH18C6 (**5**), PEG400Me<sub>2</sub> (**6**) and Si-podand (**7**), (Scheme 2), studied previously by us<sup>9–11</sup> is collected in Tables 2–4.

We measured the typical S<sub>N</sub>2 nucleophilic substitution reaction of *n*-octyl methanesulfonate or 1-bromooctane with a series of alkali metal salts M<sup>+</sup>Y<sup>−</sup> (M<sup>+</sup> = Na<sup>+</sup>, K<sup>+</sup>; Y<sup>−</sup> = I<sup>−</sup>, Br<sup>−</sup>) in a two phase solid–liquid system (salt–chlorobenzene or salt–acetonitrile) in the presence of a catalytic amount of catalysts **1–7**. The data reported in Table 2 show that under identical conditions, the reaction times (at conversion = 90%) decrease in the following order **6** > **1** ≫ **2** > **5** > **4** = **7** > **3**. The best results were obtained for the B-podands **3** and **4** possessing 13 and 11 oxygen atoms in each polyoxaalkyl chain, respectively (Table 2).

It is particularly interesting to note that in the reduction reactions of benzaldehyde to benzyl alcohol under the

**Table 3.** The catalytic activity of B-podands **1**, **3**, **4**, PHDCH18C6 (**5**), PEG400Me<sub>2</sub> (**6**) and Si-podand (**7**) in the reduction of benzaldehyde under SL-PTC conditions

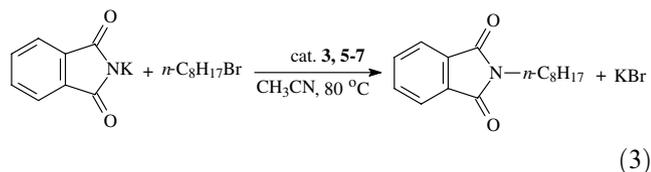


Catalyst	Reaction time (min) <sup>a,b</sup>
—	2900.0
<b>1</b>	13.4
<b>3</b>	12.9
<b>4</b>	15.7
<b>5</b>	109.7
<b>6</b>	138.4
<b>7</b>	20.9

<sup>a</sup> Conversion = 90% (by HPLC).

<sup>b</sup> A chlorobenzene solution (10 ml) of substrate C<sub>6</sub>H<sub>5</sub>CHO (3.5 mM), catalyst (0.35 mM) with one molar equivalent of NaBH<sub>4</sub> as the solid phase.

**Table 4.** The catalytic activity of B-podands **3**, **5** (DCH18C6), **6** (PEG400Me<sub>2</sub>) and Si-podand **7** in the N-alkylation of potassium phthalimide under SL-PTC conditions



Catalyst	Reaction time (min) <sup>a</sup>
—	1980.0
<b>3</b>	75.0
<b>5</b>	202.4
<b>6</b>	668.2
<b>7</b>	238.0

<sup>a</sup> Conversion = 90% (by HPLC).

same SL-PTC conditions (NaBH<sub>4</sub> (salt)–chlorobenzene), the catalytic activity of boron polypodands **1–4** was much better than the classical PT catalysts DCH18C6 (**5**), PEG400Me<sub>2</sub> (**6**) and Si-polypodand (**7**) (Table 3). We observed that the SL-PTC reduction was about 10 times faster with all the B-podands than for catalysts **5** and **6**, and was twice as fast as the reaction with **7**.

We also studied the alkylation reaction of potassium phthalimide with 1-bromooctane, performed in a C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NK (salt)–acetonitrile two-phase system in the presence of catalytic amounts of the ligands **3**, **5–7**. Hitherto, we have performed measurements only for boron podand **3**, but the results look promising. We obtained 90% reaction conversion three times faster with **3** than with the other ligands (Table 4).

In conclusion, the catalytic activity of boron podands in the studied reactions increases with increasing number of polyoxaethylene units in the polyoxaalkylchains and depends on their complexing ability. The obtained data show that the complexing ability of boron polypodands is similar to or even higher than those of typical PTC catalysts such as crown ethers, and much higher than those of open chain ligands (PEGs). B-podands are also more effective than the Si-podand studied by us before.<sup>9–11</sup> Boron podands are a new class of phase transfer catalysts that combine easy availability and good stability with high catalytic activity being a valid alternative to the more sophisticated crown ethers as catalysts in solid–liquid phase-transfer reactions, particularly on a large scale.

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13. B-podands (**1**): 88% yield; bp 256–260/0.5 (°C/mmHg) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.93 (t, *J* = 6.8 Hz, 6H), 3.58 (m, 30H), 3.38 (s, 9H); (**2**) 80% yield; bp 280–282/0.5 (°C/mmHg) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.99 (t, *J* = 7.0 Hz, 6H), 3.55 (m, 78H), 3.26 (s, 9H); (**3**) 78% yield; bp 300–310/0.5 (°C/mmHg) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.01 (t, *J* = 6.9 Hz, 6H), 3.56 (m, 138H), 3.25 (s, 9H); (**4**) 78% yield; mp 40 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.00 (t, *J* = 7.0 Hz, 6H), 3.50 (m, 114H), 3.41 (t, *J* = 7.0 Hz, 6H), 1.25–1.50 (m, 84H), 0.90 (s, 9H).
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