Application of a new class B-podands in solid–liquid phase transfer catalysis

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Abstract

As a continuation of our earlier systematic study, this paper reports on the performance of boron polypodands **1–8** (B-podands) as catalysts in a series of anion promoted reactions (nucleophilic substitution, reduction, *N*- and *O*-alkylation) in chlorobenzene, toluene and acetonitrile solutions carried out in the solid–liquid (SL) phase transfer catalysis (PTC) conditions. Comparison of the catalytic efficiency (expressed by observed rate constants) of **1–8** with that of well known classical phase transfer catalysts: crown ethers, polyethylene glycols (PEG) (**9**, **10**) and previously studied Si-podands (**11**, **12**) is also included.
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Keywords: Boron podands; Solid–liquid phase transfer catalysis; Anion promoted reaction
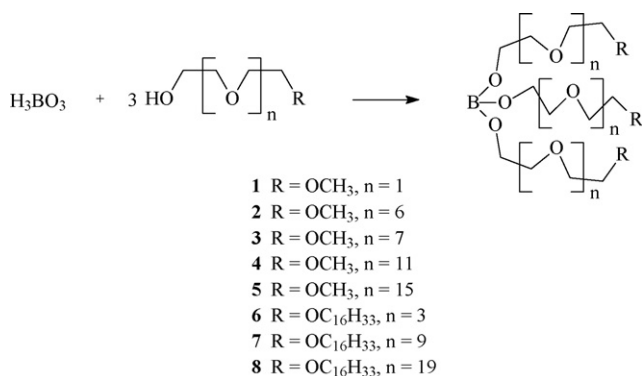
1. Introduction

Phase transfer catalysis (PTC) is now a well-established method of organic synthesis applicable to reactions of inorganic and organic anions and other active species with organic compounds. Phase transfer catalysis has been widely used in organic chemistry and is usually, but not always, based on the reactions involving transfer of anion from an aqueous or solid phase into an organic phase, followed by the reaction of the anion with the substrate in the organic phase. The reacting anions are continuously introduced into the non-polar organic phase as ion pairs with complexed cations supplied by the catalyst. Further reactions of these ion pairs proceed in the organic phase. Nowadays the term "phase transfer catalysis" refers to several effective techniques attractive for their simplicity, mild conditions required, high reaction rates and rather inexpensive reagents, and belonging to the most versatile preparative methods. The search for new catalysts to be used in PTC asymmetric synthesis and the attempts to understand their mechanistic role are current topics of investigation. The PTC technique was introduced almost 40 years ago by the three independent research groups of Mąkosza [1], Bränsdtröm and Gustavii [2] and Starks [3]. Since then there has been great interest in organic reactions carried out using PTC catalysts, most often tetra-alkylammonium salts, crown ethers, cryptands, etc. The most important problems in PTC are to find the optimum reaction conditions and the most effective catalysts [4–8].

We have been interested in the class of simple compounds—podands, distinguished from crown ethers and known as the open-chained analogues of cryptands. In recent years, polypodands being open chain ligands with several polyether chains linked to the same binding centre, have attracted increasing interest as anion activators in homogeneous and heterogeneous systems. They represent a valid alternative to the cyclic analogues of crown ethers and cryptands because of their substantially lower cost, relative non-toxicity and high effectiveness. Several important applications of podands are given [9–13], including their use in phase transfer catalysis. The first application of podands in PTC was reported by Lehmkuhl et al. [14], who studied a variety of nucleophilic substitution of benzyl bromide with different potassium salts.

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$$H_3BO_3 \quad + \quad 3 \; HO\text{-}[\text{-}O\text{-}]_n\text{-}R \quad \longrightarrow$$

1 R = OCH$_3$, n = 1
2 R = OCH$_3$, n = 6
3 R = OCH$_3$, n = 7
4 R = OCH$_3$, n = 11
5 R = OCH$_3$, n = 15
6 R = OC$_{16}$H$_{33}$, n = 3
7 R = OC$_{16}$H$_{33}$, n = 9
8 R = OC$_{16}$H$_{33}$, n = 19

Scheme 1. Reaction between boric acid and polyethylene glycols.

The use of silicon polypodands as phase-transfer catalysts was first reported by us a few years ago [15–17] and further developments were made thanks to the application of boron polypodands. Relative to the traditional classical phase transfer catalysts such as crown ethers, cryptands and polyethylene glycols, which have been by far the most studied phase transfer catalysts, polypodands are easy to prepare and much cheaper.

Recently, boron polypodands (**1–8**), synthesised by our group in high yields in the reaction presented in Scheme 1 between boric acid and an appropriate polyethylene glycol, according to the procedure described previously [18], have enjoyed particular interest. Preliminary data have shown that some B-podands have been successfully used for different reactive phase transfer catalysis systems, such as: classical nucleophilic substitution reactions S$_N$2, i.e., OSO$_2$Me–I exchange [reaction (1a)] and Br–I exchange [reaction (1b)] or sodium borohydride reductions [reaction (2)] [19]. In the light of these promising results we have decided to continue studying a series of modified six boron polypodands (**1–8**) with a different number of polyether chains, binding sites (oxygen atoms) and two types of alkyl end groups of polyoxaalkyl chains in the earlier mentioned SL-PTC system reactions (1a), (1b) and (2), and also *N*-alkylation process [reaction (3)] and *O*-alkylation [reaction (4)]. The ligands used are labelled as: B3.3, B8.3, B9.3, B13.3, B17.3, B5.3H, B11.3H and B21.3H. The capital B stands for a boron ligand, the first digit after this letter stands for the number of oxygen atoms in the polyoxaethylene chain, the second digit is the number of these chains in a given podand. In ligands (**1–5**) the polyoxaethylene chain is terminated with a methyl group (–CH$_3$), while in ligands **6–8**, with a longer alkyl group (–C$_{16}$H$_{33}$) denoted with letter H (an abbreviation from hexodecane). The results have been compared with those obtained, under the same conditions, by using silicon podands (**9** and **10**) studied previously, traditional ligands such as the macrocyclic polyether DCH18C6 (**11**) and simple, open-chain PEG400Me$_2$ (**12**) (Scheme 2).

2. Experimental

2.1. Instrumental methods

HPLC data were obtained with a Dionex ASI-100 equipped with P680 HPLC pump using Thermo BDS Hypersil C18

column and as well as Dionex PDA-100 Photodiode Array Detector. As a mobile phase we used mixtures of acetonitrile, methanol and water at the ratios depending on particular analysis.

2.2. Materials and solvents

2.2.1. B-podands

Boron polypodands **1–8** were prepared following a previously reported procedure [18] and confirmed by the ^{1}H NMR spectroscopy. The B-podands used are thermally stable under the reaction conditions.

B-podand, yield (%), boiling point (°C/mmHg) are as follows: B-podands (**1**): 86% yield; b.p. 252–254/0.5 (°C/mmHg), colourless oil, ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.91 (t, *J* = 6.8 Hz, 6H), 3.56 (m, 18H), 3.40 (s, 9H); (**2**) 80% yield; b.p. 280–282/0.5 (°C/mmHg) colourless oil, ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.99 (t, *J* = 7.0 Hz, 6H), 3.55 (m, 78H), 3.26 (s, 9H); (**3**) 79% yield; b.p. 285–288/0.5 (°C/mmHg) colourless oil, ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.97 (t, *J* = 7.0 Hz, 6H), 3.57 (m, 90H), 3.25 (s, 9H); (**4**) 78% yield; b.p. 300–310/0.5 (°C/mmHg) colourless oil, ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.01 (t, *J* = 6.9 Hz, 6H), 3.56 (m, 138H), 3.25 (s, 9H); (**5**) 75% yield; m.p. 30–32 °C; white wax ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.04 (t, *J* = 6.8 Hz, 6H), 3.55 (m, 186H), 3.3 (s, 9H) 6H); (**6**) 77% yield; m.p. 30 °C; white wax ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.02 (t, *J* = 7.1 Hz, 6H), 3.50 (m, 42H), 3.40 (t, *J* = 7.0 Hz, 6H), 1.25–1.50 (m, 84H), 0.92 (s, 9H); (**7**) 78% yield; m.p. 40 °C; white wax ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.0 (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); (**8**) 73% yield; m.p. 40–45 °C; white wax ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.96 (t, *J* = 7.0 Hz, 6H), 3.50 (m, 234H), 3.39 (t, *J* = 7.1 Hz, 6H), 1.3–1.5 (m, 84H), 0.91 (s, 9H).

The NMR data obtained for ligands **2**, **5** and **9** were published previously [19].

Boron polypodands **1–8** were also confirmed by the elementary analysis carried out on Perkin-Elmer CHN 240.

B-podands—(**1**) calculated: C 48.93%, H 9.03%; found: C 49.12%, H 9.07%; (**2**) calculated: C 53.30%, H 9.42%; found: C 53.67%, H 9.49%; (**3**) calculated: C 52.75%, H 9.11%; found: C 53.11%, H 9.17%; (**4**) calculated: C 53.31%, H 9.13%; found: C 53.68%, H 9.19%; (**5**) calculated: C 53.60%, H 9.13%; found: C 53.98%, H 9.19%; (**6**) calculated: C 68.82%, H 12.02%; found: C 69.37%, H 9.16%; (**7**) calculated: C 63.43%, H 10.93%; found: C 63.96%, H 11.19%; (**8**) calculated: C 60.0%, H 10.25%; found: C 60.54%, H 10.33%.

2.2.2. The other materials and solvents

Silicon polypodands **9** and **10** were synthesised via the reaction of trichloroethyl-silane (EtSiCl$_3$) with an appropriate polyethyleneglycol monomethylether according to the procedure described previously [15].

DCH18-crown-6 (mixture of isomers) **11**, PEG **12** were used as purchased. Octylbromide **14** and benzaldehyde **16** were commercial products (Aldrich), used as purchased.
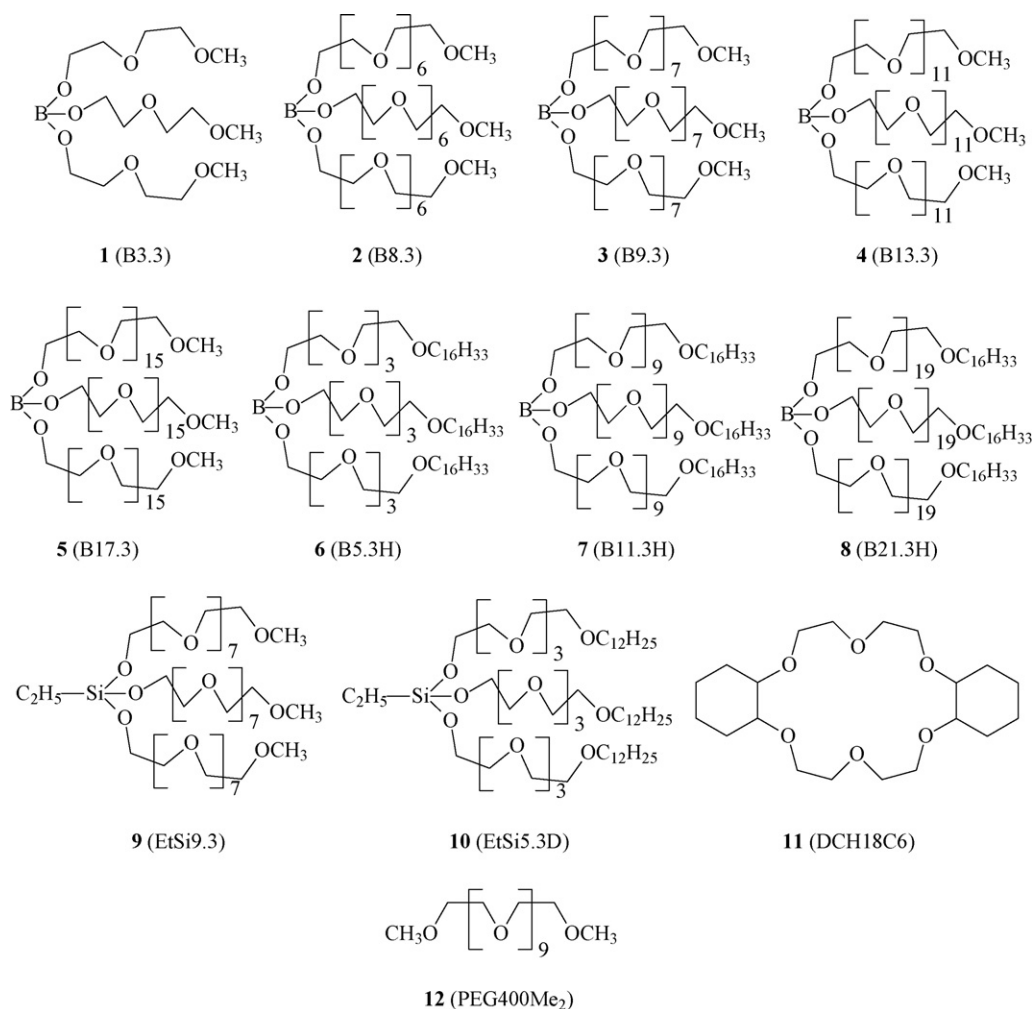
Scheme 2. Phase-transfer catalysts: boron podands **1–8**, silicon podand **9**, **10**, crown ether **11** and PEG **12**.

Alkali metal halides (NaI, KI, NaBr), sodium perchlorate ($NaClO_4$), potassium perchlorate ($KClO_4$), potassium carbonate (K_2CO_3), sodium borohydride ($NaBH_4$) and potassium phthalimide ($C_6H_4(CO)_2NK$) **18** were Fluka and Aldrich commercial products, kept in a desiccator under vacuum.

Dry chlorobenzene (Fluka), toluene (Aldrich), methanol (Aldrich) and acetonitrile (Aldrich) ($H_2O \leq 20$ ppm) were kept over molecular sieves.

Octyl methanesulphonate **13**, b.p. 94–97 °C at 0.003 mmHg, n_D^{20} 1.4392, 78% yield was prepared according to a literature method (b.p. 98 °C at 1.5 mmHg, n_D^{20} 1.4390) [20].

2.3. General procedure for the reactions (**1–4**) under SL-PTC conditions

Solid salt MY (10.0–12.5 mmol) was added to a chlorobenzene, toluene or acetonitrile solution (10 ml) of the substrate (3.0–3.5 mmol) and the catalyst (0.3–0.35 mmol). The heterogeneous mixture was heated at the appropriate temperature (25, 60, 80 or 110 °C) (see Tables 2–5) on vigorous magnetic stirring. The reaction progress was monitored by HPLC analysis of the organic phase.

2.4. Kinetic measurements under SL-PTC conditions

The reaction rates were measured by following the disappearance of the substrate and the appearance of the reaction product. The pseudo-first order rate constants (k_{obsd}) were computer generated by plotting log[substrate] versus time and determining the slope of the straight lines obtained.

3. Results and discussion

3.1. Complexing ability by calorimetric measurements and PM5 semiempirical calculations

In anion promoted reactions, a significant role of the solvent in determining both the solubilization of the salt, source of a nucleophile or a base, and the anionic reactivity is well recognised. The rate of the process depends mainly on the interactions between the anion and the solvent molecules increasing, even by several orders of magnitude, on going from polar protic media, that specifically solvate the anion through hydrogen bonds, to solvents where this interaction is minimised (aprotic dipolar solvents) [21]. The use of lipophilic quaternary onium

salts or complexes of polyether ligands with inorganic salts in anhydrous low polar solvents (toluene, chlorobenzene, etc.) was shown particularly effective for studying the reactivity of anions under conditions approaching those of the gas phase. Indeed in such media the reactivity of the anion is remarkably high due to the low interactions with the bulky ion paired cation as well as with the poor solvating medium [12]. Anion promoted reactions are extensively used in organic synthesis, particularly under heterogeneous (liquid–liquid (LL) or solid–liquid (SL)) conditions, such as phase transfer catalysis (PTC).

In order to select the best catalysts for the anion promoted PTC reaction we began with testing the complexing ability of the B-podands studied versus those of the ligands used in the earlier studies of the PTC reactions.

On the basis of the results of calorimetric titrations [22] of B-podands with $NaClO_4$ or $KClO_4$ in acetonitrile and semiempirical calculation, we found that the number of M^+ metal cations complexed by the ligand depended mainly on the topology of the B-podand and increased with the number of oxygen atoms. We also noted the influence of the length of the alkyl group ($-CH_3$ or $-C_{16}H_{33}$) terminating the polyoxaalkyl chain on the complexation properties of the ligands. An analogous dependence was established on the basis of the semiempirical study (ΔHOF were slightly greater for the podand complexes terminating with $-CH_3$). As shown in Table 1, the number of complexed Na^+ cations increases from one in ligand **1**, three in ligands **2** and **3**, four in ligands **5** and **7**, and to five to six in ligands **5** and **8**. The highest complexation values (about 5 or 6 Na^+ cations) were obtained for B-podands **4**, **5** and **8**, comprising the highest number of donor atoms, 39, 51 and 63 oxygen atoms, respectively. Similar values were obtained as a result of semiempirical calculations. As in the previous paper [19] presenting our preliminary data, we suggested that on average one Na^+ cation is coordinated by six to nine oxygen atoms from the polyoxaalkyl chains of the podand. A similar tendency was observed analysing the calori-

Table 1
The complex stoichiometry (catalyst:M^+) determined by calorimetric measurements as well as by semiempirical studies

Catalyst	Complex stoichiometry (catalyst:M^+)	
	Na^+	K^+
1	1:1	1:1
2	1:3	1:2
3	1:3	1:2
4	1:4	1:3
5	1:5	1:4
6	1:2	1:1
7	1:4	1:3
8	1:6	1:4
9	1:4	1:2
10	1:2	1:1
11	1:1	1:1
12	1:1	1:1

$M^+ = Na^+$ and K^+.

metric measurements of B-podands with $KClO_4$. Taking into regard the presence of 63 oxygen atoms in ligand **8** (B21.3H) it was expected that this podand would be able to complex a greater number of sodium and potassium cations, which was not the case. In our opinion the reason is the presence of a dodecyl ($-C_{12}H_{25}$) or hexododecyl alkyl group ($-C_{16}H_{33}$) ending the polyoxaethylene chain in the ligand preventing the contact of Na^+ or K^+ and the oxygen atoms. This also explains worse complexing properties of these podands relative to those with shorter methyl groups at the end of the chain. Interestingly, a comparison with the corresponding "simple" podand reveals a cooperative effect of the pendant arms in the complexation process. This suggestion is visualised by the PM5 semiempirical study of selected B-podands (Figs. 1 and 2). PM5 semiempirical calculations were performed using the Mopac 2002 Program [23]. In all cases full geometry optimisation was carried out without any symmetry constraints.
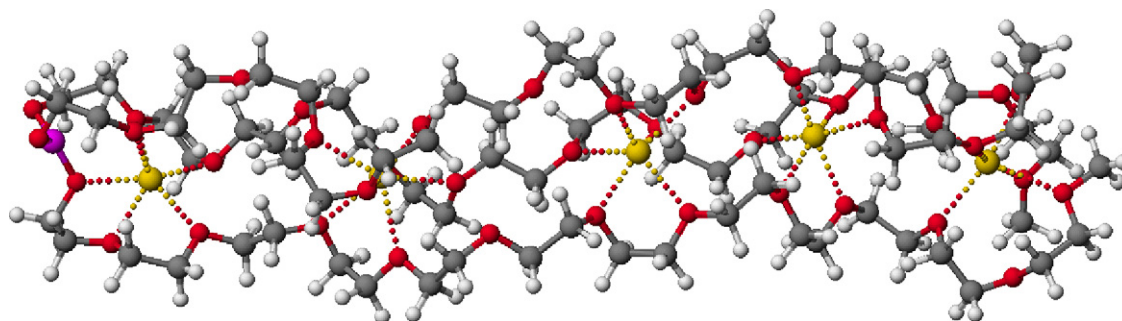

Fig. 1. Calculated structure of the complex of **4** (B13.3) with 5Na^+ cations.
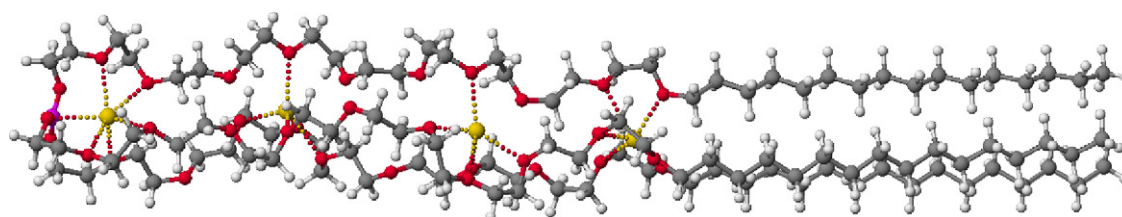

Fig. 2. Calculated structure of the complex of **7** (B11.3H) with 4Na^+ cations.

Catalytic activity of the podands studied strongly depends on the complex stoichiometry (catalyst:M$^+$) determined by calorimetric measurements as well as by semiempirical studies. The exemplary value of ΔHOF for **5** with 5 Na$^+$ cations is 1295.80 kJ mol^{-1}, other examples of calorimetric and semiempirical data for B-podands are given in [24].

3.2. Catalytic activity of B-polypodands **1–8** in SL-PTC reactions

The calorimetric and semiempirical results described above have proved B-polypodands as good catalysts in some standard reactions carried out under phase-transfer catalysis (PTC) conditions. B-podand complexation possibilities increase in the following order **1 < 6 < 2 < 3**, **7 ≪ 4**, **5**, **8** and are largely determined by the size of the cation and the nature of the ligand. Due to the presence of 63 oxygen atoms in the ligand molecule, podand **8** (B21.3H) would be expected the best complex medium in the ligand order. In agreement with these results we found that polypodands **1–8** acted as an excellent phase-transfer catalysts in a number of typical anion-promoted reactions. The results are compared with those obtained by using other ligands, i.e., Si-polypodands, crown ether and PEG.
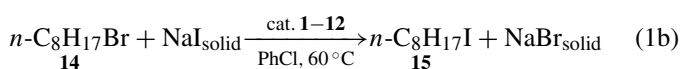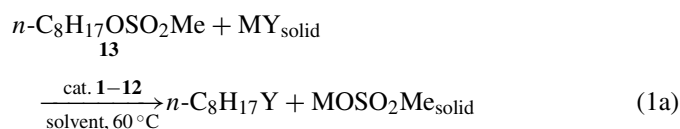
3.3. The catalytic efficiencies of PTC catalysts

The catalytic efficiencies of boron polypodands **1–8** and the well known classical PTC catalysts were studied in a series of anion promoted reactions (nucleophilic substitution, reduction, N- and O-alkylation, etc.) in chlorobenzene, toluene and acetonitrile solutions carried out under solid–liquid (SL) phase transfer catalysis (PTC) conditions. The kinetic determinations were performed (HPLC analysis) by following the disappearance of the substrates or the appearance of the products. In all cases the reactions were found to obey a pseudo-first-order kinetic equation up to at least 90%:

$$\text{rate} = k_{\text{obsd}} \, [\text{substrate}]$$

3.4. Nucleophilic substitution reactions

The catalytic activity of B-polypodands **1–8** was measured in typical S_N2 nucleophilic substitution reactions of *n*-octyl methanesulfonate **13** or 1-bromooctane **14** in organic solvent-solid MY two phase systems (organic solvent: chlorobenzene, acetonitrile; MY: NaI, NaBr, KI) and compared with that exhibited by catalytic amount of ligands **9–12** under the same conditions (reactions (1a) and (1b)).

$$n\text{-C}_8\text{H}_{17}\text{OSO}_2\text{Me} + \text{MY}_{\text{solid}}$$
$$\underset{\mathbf{13}}{}$$

$$\xrightarrow[\text{solvent, }60\,^\circ\text{C}]{\text{cat. }\mathbf{1-12}} n\text{-C}_8\text{H}_{17}\text{Y} + \text{MOSO}_2\text{Me}_{\text{solid}} \qquad (1a)$$

$$n\text{-C}_8\text{H}_{17}\text{Br} + \text{NaI}_{\text{solid}} \xrightarrow[\text{PhCl, }60\,^\circ\text{C}]{\text{cat. }\mathbf{1-12}} n\text{-C}_8\text{H}_{17}\text{I} + \text{NaBr}_{\text{solid}} \qquad (1b)$$
$$\underset{\mathbf{14}}{} \qquad\qquad\qquad\qquad\qquad\qquad \underset{\mathbf{15}}{}$$

The nucleophilic substitution reaction is described by the pseudo-first order kinetics. The presence of the substrate (mesylat) and the catalyst in the solution excludes the possibility of the reaction taking place on the crystal surface. The stage determining the reaction rate is the nucleophilic attack of Y$^-$ on the substrate in the organic solvent, occurring if dissolution of MY salt over a catalyst and the release of the group from MeSO$_3^-$ are relatively fast processes. The phenomenon taking place at the interface is of little importance. The anion reactivity is significantly dependent on the degree of its association with an appropriate cation. The cation–anion interactions are responsible for enhanced stability of the anion and smaller increase in the energy of the coulomb interactions in the active complex.

The reactions were followed by the HPLC method up to ≥90% conversions, on the basis of the substrate disappearance (**13**, **14**) and the reaction products appearance. The catalytic efficiency of these ligands is most likely related to their complex-forming ability, estimated by the calorimetric method and reported in Table 2. Indeed, the values of the observed rate constants (k_{obsd} [s^{-1}]) of the nucleophilic substitution reaction were found to depend on the ligand, progressively increasing in the following order **1**, **12 ≪ 6**, **10 ≪ 2**, **3**, **11 < 7**, **9 < 4 < 8 < 5** under analogous conditions (for reaction with NaI in chlorobenzene). As expected, the best catalysts (shortest reaction times and the highest k_{obsd} values) are polypodands **5** and **8** with the three longest polyether chains, containing 17 and 21 oxygen atoms in each polyoxaalkyl chain, respectively (Scheme 2; Table 2). A comparison with the traditional and earlier known PTC catalysts **9–12** (Table 2) has shown that the catalytic activity of boron polypodands **2–8** is always higher than that of Si-podand **10** and also that of a simple podand PEG400Me$_2$ **12**. This result is in line with their complexation values (Table 1), and this catalytic activity is comparable or even higher than those of more efficient catalysts such as Si-podand **7** and the crown ether DCH18C6 **11**, the latter is the catalyst of choice for many solid–liquid phase-transfer reactions.

The values of k_{obsd} determined for all nucleophilic substitution reactions involving NaBr studied are similar and vary in the range 0.5×10^{-5} to 1.3×10^{-5} [s^{-1}]. In the PTC reactions involving alkali metals halogens, the anions' reactivity decreases in the series: I$^-$ > Br$^-$ > Cl$^-$. It is related to increasing deactivation of the anion in the ionic pair with growing charge density. In agreement with the above, the reactivity of the anions increases with their decreasing solvation and association with the cation [4].

It is worth noting that this tendency is observed in both nucleophilic substitution reactions, with *n*-octyl methanesulfonate **13**, 1-bromooctane **14** and NaI or KI (Table 2). For these reactions we observed a dramatic decline in the reaction times, on changing from ligands **1** to **5** (i.e., to 21.7 min from about 400 min) and increasing of values of k_{obsd}.

3.5. Reduction reactions

The reduction of benzaldehyde **16** to the corresponding benzylic alcohol **17** with NaBH$_4$ was performed in a chlorobenzene-solid NaBH$_4$ two-phase system by using

Table 2
The catalytic efficiency of B-podands: **1–8**; Si-podands: **9** (EtSi9.3), **10** (EtSi5.3D), **11** (DCH18C6) and **12** (PEG400Me$_2$) in (1a): n-C$_8$H$_{17}$OSO$_2$Me; MY = NaI, KI, NaBr under SL-PTC conditions in chlorobenzene or acetonitrile at 60 °C and (1b) n-C$_8$H$_{17}$Br; NaI under SL-PTC conditions in chlorobenzene at 60 °C

Catalyst	Reaction time [min][a]				$10^5\, k_{obsd}$ [s^{-1}]			
	NaI[b]	KI[b]	NaBr[c]	NaI[d]	NaI[b]	KI[b]	NaBr[c]	NaI[d]
–	>4300	–	–	–	–	–	–	–
1	388	>2500	–	502.3	4.3	–	–	3.3
2	46.6	220.0	1650.0	66.8	35.8	7.6	1.0	25.0
3	44.5	199.4	1570.0	59.8	37.5	8.4	1.1	27.9
4	25.9	107.0	1507.0	33.8	64.4	15.6	1.1	49.3
5	21.7	98.4	1312.0	28.2	76.8	16.9	1.3	59.1
6	74.3	378.2	1608.0	105.2	22.4	4.4	1.0	15.8
7	37.2	130.0	1750.0	50.0	44.8	12.8	1.0	33.3
8	22.3	98.2	1305.0	29.1	74.7	17.0	1.3	57.3
9	36.9	130.0	1800.0	51.1	45.2	12.8	0.9	32.6
10	80.0	426.8	1650.0	119.7	20.8	3.9	1.0	13.9
11	43.1	203.0	3400.0	59.8	38.7	8.2	0.5	27.9
12	308.0	369.0	3500.0	420.7	5.4	4.5	0.5	4.0

See Eqs. (1a) and (1b).
[a] Conversion: 90% (by HPLC).
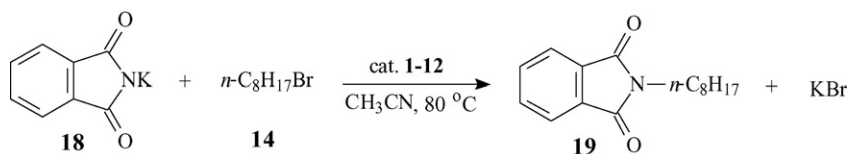[b] A chlorobenzene solution.
[c] An acetonitrile solution.
[d] For reaction (1b), a chlorobenzene solution.

Table 3
The catalytic efficiency of B-podands: **1–8**; Si-podands: **9** (EtSi9.3), **10** (EtSi5.3D), **11** (DCH18C6) and **12** (PEG400Me$_2$) in the reduction of benzaldehyde under SL-PTC conditions
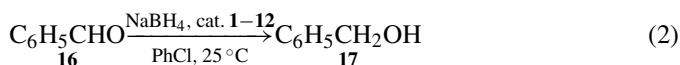
Catalyst	Reaction time [min][a]	$10^5\, k_{obsd}$ [s^{-1}]
–	2900.0	0.6
1	14.3	116.6
2	15.3	108.9
3	14.9	111.9
4	12.9	129.2
5	10.7	155.8
6	17.9	93.1
7	15.7	106.2
8	11.4	146.2
9	20.9	79.7
10	128.7	13.0
11	109.7	15.2
12	138.4	12.0

See Eq. (2).
[a] Conversion: 90% (by HPLC).

B-polypodands **1–8** used, in particular with ligands: **4**, **8** and **5** (10–13 min instead of about 3000 min). Interestingly, the reaction times are even shorter than those with Si-podands (**9**, **10**) and crown ether **11** (110 min.). The same tendency we observed in the k_{obsd} values. They are vary in the range 12.0×10^{-5} to 155.8×10^{-5} [s^{-1}] and the ligand **5** has proved the particular good catalyst for reduction of benzaldehyde **16** to the benzylic alcohol **17** in PTC condition.

3.6. N-Alkylation reaction

The *N*-alkylation reaction of potassium phthalimide **18** by 1-bromooctane **14** was carried out at 80 °C in an acetonitrile-solid C$_6$H$_4$(CO)$_2$NK two-phase system in the presence of catalytic amounts (0.1 mol/mol substrate) of ligands **1–12** and with a 1:1 molar ratio potassium phthalimide (**18**) to alkylbromide **14** (reaction (3)) in acetonitrile as a solvent. The reactions were followed by evaluating the disappearance of alkylbromide in the organic phase, up to conversions ≥90%, observed by HPLC analysis:

(3)

catalytic amounts (0.1 mol equiv) of polypodands **1–8** and comparative ligands **9–12** (reaction (2)) at 25 °C:

$$\text{C}_6\text{H}_5\text{CHO} \xrightarrow[\text{PhCl, 25 °C}]{\text{NaBH}_4,\ \text{cat. } \mathbf{1–12}} \text{C}_6\text{H}_5\text{CH}_2\text{OH} \qquad (2)$$
$$\mathbf{16} \qquad\qquad\qquad\qquad\qquad \mathbf{17}$$

The reaction was followed by evaluating the disappearance of benzaldehyde **16** in the organic phase by HPLC. The results, presented in Table 3, show that the reduction is very fast with all

The catalytic activities of all ligands **1–12** are collected in Table 4. Boron polypodands **2–8** were shown to be better PT catalysts of this *N*-alkylation reaction than the other ligands **9–12**, which are well known as typical of the phase transfer processes. The B-podand's activity increases with the number of donor atoms in the order: **8** > **5** > **4**, **3**, **7**, **2** > **6** (from 38.1 to 98.7 min), while the times of the analogues reaction catalysed by the other catalysts ligand **9–12** ranges 238–668 min, and without any catalyst the reaction lasts till 2000 min. The k_{obsd} values have

Table 4

The catalytic efficiency of B-podands: **1–8**; Si-podands: **9** (EtSi9.3), **10** (EtSi5.3D), **11** (DCH18C6) and **12** (PEG400Me$_2$) in the *N*-alkylation of potassium phthalimide reactions under SL-PTC conditions

Catalyst	Reaction time [min][a]	$10^5 k_{obsd}$ [s^{-1}]
–	1980.0	0.8
1	845.0	2.0
2	80.4	20.7
3	79.0	21.1
4	75.0	22.2
5	42.3	39.4
6	98.7	16.9
7	79.6	20.9
8	38.1	43.7
9	238.0	7.0
10	443.0	3.8
11	202.4	8.2
12	668.2	2.5

See Eq. (3).

[a] Conversion: 90% (by HPLC).

changed in the range 2.0×10^{-5} to 43.7×10^{-5} [s^{-1}] (Table 4) and the ligand **8** has proved the particular useful catalyst for that *N*-alkylation reaction in PTC condition.

3.7. O-Alkylation reaction

We also studied the *O*-alkylation reaction of phenol **20** by 1-bromooctane **14** (with a 1:1 molar ratio) performed at 110 °C in toluene-solid K$_2$CO$_3$ two-phase system in the presence of catalytic amounts (0.1 mol/mol substrate) of ligands 1–10 (reaction (4)) and analysed the reaction's courses by HPLC. We obtained 90% conversion three times faster with some B-podands (**2–8**) as PT catalysts than with the other ligands (Table 5):
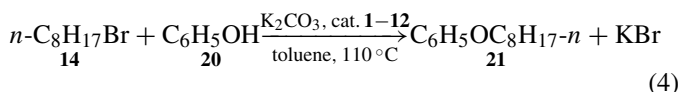
$$n\text{-}C_8H_{17}Br + C_6H_5OH \xrightarrow[\text{toluene, 110 °C}]{K_2CO_3,\ \text{cat. } \mathbf{1-12}} C_6H_5OC_8H_{17}\text{-}n + KBr$$
$$\mathbf{14} \qquad \mathbf{20} \qquad\qquad\qquad\qquad \mathbf{21}$$

(4)

Table 5

The catalytic efficiency of B-podands: **1–8**; Si-podands: **9** (EtSi9.3), **10** (EtSi5.3D), **11** (DCH18C6) and **12** (PEG400Me$_2$) in the *O*-alkylation of phenol reactions under SL-PTC conditions

Catalyst	Reaction time [min][a,b]	$10^5 k_{obsd}$ [s^{-1}]
–	>3500.0	
1	606.0	2.8
2	200.6	8.3
3	187.3	8.9
4	95.5	17.5
5	75.2	22.2
6	147.5	11.3
7	102.0	16.3
8	46.3	36.0
9	182.4	9.1
10	489.3	3.4
11	240.0	6.9
12	720.0	2.3

See Eq. (4).

[a] Conversion: 90% (by HPLC).

[b] A toluene solution and K$_2$CO$_3$ as the solid phase.

It is particularly interesting to note that in the *O*-alkylation reaction of phenol studied under the same SL-PTC conditions, the catalytic activity of boron polypodands **2–8**, was much better than that of the classical PT catalysts DCH18C6 (**11**) and PEG400Me$_2$ (**12**) and also Si-polypodands (**9**, **10**) (Table 5). The described *O*-alkylation reaction was about 10–20 times faster with ligands **8** and **5**, than with catalysts **10** and **12**, and about four times faster than the reaction with **9**. The k_{obsd} values have changed in the range 2.3×10^{-5} to 36.0×10^{-5} [s^{-1}] (Table 5) and the ligand **8** has also proved the particular useful catalyst for that *O*-alkylation reaction in PTC condition.

4. Conclusions

The results provide strong evidence of boron polypodands **1–8** as powerful complexing agents of alkali metal salts in acetonitrile, toluene and in low polarity media such as chlorobenzene. The complex forming ability of boron polypodands increases with the number of oxaethylenic units. As shown in Table 1, the highest complexation values are obtained with polypodand **5** and **8** having the highest number of binding sites (51 and 63 oxygen atoms). The catalytic effect also depends strongly on the topology and the length of the alkyl group (–CH$_3$ or –C$_{16}$H$_{33}$), terminating the polyoxaalkyl chain.

In line with their complexation values, polypodands **1–8** are found to be excellent catalysts in a number of anion-promoted reactions (1)–(4) in solid–liquid two-phase systems. The catalytic activity reflects their complexing ability, increasing in the same order. In particular B-polypodands are better catalysts for reduction of benzaldehyde to the corresponding benzylic alcohol with NaBH$_4$ in SL-PTC process (reaction (2)), because their use has significantly shortened the reaction time, on average by up to 10–20 times and k_{obsd} values for these reactions were also significantly increased (Table 3).

It is also worth noting that the catalytic efficiency of these polypodands is remarkably higher than that of DCH18C6 **11** and PEG **12** in *N*-alkylation of potassium phthalimide and *O*-alkylation reactions of phenol with 1-bromooctane under SL-PTC conditions. In comparison with traditional PT catalysts the data obtained for all B-ligands show a dramatic decrease in the reaction times (from 2 to 20 times), especially for ligands **5**, **7** and **8**.

In summary, we have shown that the new class of boron polypodands, combining easy availability and good stability with excellent complexing properties and high catalytic activity, make a valid alternative to more sophisticated crown ethers as catalysts in solid–liquid phase-transfer reactions, particularly in large scale processes. B-podands **1–8** behave as efficient phase-transfer (PT) agents under SL-PTC conditions and they are more stable and insensitive to water, with their catalytic activity being generally superior to those of Si-podands.

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