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### Silicon polypodands: a new class of efficient solid-liquid phase-transfer catalysts

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Abstract—Silicon polypodands 1-7 were found to be powerful complexing agents of alkali metal salts, even in low polarity media (chlorobenzene) and hence very efficient phase-transfer catalysts. Their catalytic activity was measured in typical anion-promoted reactions under solid–liquid phase-transfer catalysis (SL-PTC) conditions. It is mainly determined by the complexing ability of the ligand, increasing with the number of silicon atoms and binding sites. Comparison with traditional phase-transfer catalysts showed that these polypodands are better catalysts not only than open-chain PEG400Me<sub>2</sub> and TRIDENT, but even than more sophisticated macrocyclic polyethers such as DCH18C6. © 2004 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Polypodands are acyclic ligands in which several polyether chains are linked to the same binding centre. These compounds represent a valid alternative not only to the simple podands but also to the cyclic analogues (crown ethers and cryptands) due to their much lower cost combined with comparable complex-forming properties and almost non-toxicity.<sup>1–8</sup> The above reasons explain the growing interest in these open-chain polyethers and their extensive use as anion activators in the past few years.<sup>1–8</sup>

Silicon polypodands **3** and **5**, recently synthesized by our group via reaction of trichloroethyl- (EtSiCl<sub>3</sub>) and dichlorodimethylsilane (Me<sub>2</sub>SiCl<sub>2</sub>) with the appropriate polyethyleneglycol monomethylether are of particular interest (Scheme 1).<sup>9</sup> Preliminary data showed in fact that they are remarkable complexing agents of alkali metal salts even in low polarity media (chlorobenzene) with complexation extent values up to 4 mol of salt per mole of ligand. As a consequence, polypodands **3** and **5** were found to be very efficient catalysts in representative anion-promoted reactions (e.g. nucleophilic substitutions, reductions, alkylations) under solid–liquid phase-transfer catalysis (SL-PTC) conditions.<sup>9</sup>

In the light of the promising results obtained, we have

extended the study to a new series of silicon polypodands 1, 2, 4, 6, and 7 with a different number of silicon atoms, polyether chains and binding sites (oxygens).<sup>10</sup> The complexing ability of these ligands has been evaluated together with their catalytic activity in a number of typical reactions under SL-PTC conditions. The results have been compared with those obtained, under the same conditions, by using traditional ligands such as the open-chain podands 9 and 10, the tris (polyoxaalkyl) amine 'TRIDENT' 8 and the macrocyclic polyether dicyclohexano-18-crown-6 (DCH18 crown 6) (11).

#### 2. Results and discussion

# **2.1.** Complexation extent of silicon polypodands 1–7 and ligands 8–11, under SL-PTC conditions

The complexing abilities of 1–7, PEGs 9 and 10, TRIDENT 8 and crown ether 11 were evaluated for a series of alkali metal salts  $M^+Y^-$  ( $M^+=Na^+$ ,  $K^+$ ;  $Y^-=I^-$ ,  $Br^-$ , Ph(CO)<sub>2</sub>N<sup>-</sup>, BH<sub>4</sub><sup>-</sup>) by stirring a chlorobenzene or acetonitrile solution of ligand with 10–30 molar equiv of salt as a solid phase at 25, 60 and 80 °C (Table 1). The data reported in Table 1 show that the complexation extent, defined as moles of MY complexed per mole of ligand, mainly depends on the topology of the polypodand, increasing with the number of silicon atoms and oxygens. The salt being the same, the highest complexation values (up to 5.6 mol of NaI) were always obtained with the polypodand 7 which has the highest number of donor atoms (54 oxygens).

*Keywords*: Silicon polypodands; Complexing agents; Phase-transfer catalysts; Solid–liquid phase-transfer catalyzed reactions.

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Scheme 1. Silicon polypodands 1–7 and polyethers 8–11.

Interestingly, comparison with the corresponding simple podand reveals a 'cooperative effect' of the pendant arms in the complexation process. This is particularly evident for the shortest PEG **10**. As shown in Table 1, the complexation extent of polypodand **6** (with six polyether chains) is about 22 (for NaI) and 60 (for KI) times higher than that of the corresponding podand **10**.

# **2.2.** Catalytic activity of polypodands 1–7 and ligands 8–11 in SL-PTC reactions

As expected on the basis of their high complexation values, polypodands 1-7 were shown to be excellent phase-transfer catalysts in a number of typical anion-promoted reactions

such as: nucleophilic substitution reactions, reductions, alkylations, oxirane ring opening reactions.

**2.2.1.** Nucleophilic substitution reactions. The catalytic activity of 1-7 was evaluated in typical nucleophilic substitution reactions in organic solvent-solid MY two phase systems (organic solvent=chlorobenzene, acetonitrile; MY=NaI, NaBr, KI) and compared with that exhibited by ligands 8-11 under the same conditions (reaction 1).

$$1 - 11_{ca}$$

$$n-C_8H_{17}X + MY_{solid} \xrightarrow{\qquad} n-C_8H_{17}Y + MX_{solid}$$
12, 13 PhCl (CH<sub>3</sub>CN), 60°C  
X = OSO<sub>2</sub>Me (12), Br (13) ; MY = NaI, NaBr, KI
(1)

Table 1. Complexation extent<sup>a</sup> of silicon polypodands 1–7 and polyethers8-11 under SL-PTC conditions, at 25, 60 and 80 °C

Ligand	NaI	KI	NaBr	KPh(CO) <sub>2</sub> N	NaBH <sub>4</sub>
4	1.20	0.48		0.02	
4	1.20	0.46	0.26	0.03	
2	1.20	0.80	0.20	0.12	
6	3.45	1.20	0.01	0.10	
5	2.50	1.30	1.70	0.18	1.00
3	4.00	1.70	1.80	0.18	1.10
7	5.60	3.70	2.40	0.47	1.75
10 (PEG)	0.16	0.02			
<b>9</b> (PEG400Me <sub>2</sub> )	0.86	0.47	1.00	0.13	0.20
8 (TRIDENT)	0.95	0.55	1.50	1.10	0.09
11 (DCH18C6)	1.00	1.00	1.10	0.80	0.84

<sup>a</sup> Defined as moles of salt MY complexed per mole of ligand.

The reactions were followed up to conversions  $\geq 90\%$  by GLC analysis of the organic phase evaluating the disappearance of the substrate and/or the appearance of the reaction product with respect to an internal standard (dodecane). The data concerning these reactions are reported in Table 2 and Figure 1. The catalytic activity is mainly related to the complex-forming ability of the podands. The salt MY being the same, the reaction times diminish in the order 4>1>2>6 and 5>3>7 in agreement with the ligand complexation extent values (Table 1). As expected, the best catalysts (shortest reaction times) are polypodands 6 and 7 with two silicon atoms and six pendant arms, but the catalysts with two and three long polyether chains (3 and 5) also have good catalytic activities (Table 2).

The comparison with traditional polyethers 8-11 (Table 2) shows that the catalytic activity of silicon polypodands 1-7 is always higher than that of simple podands 9 and 10, in line with their complexation values (Table 1), and comparable with or even better than that of more efficient catalysts such as the crown ether DCH18C6 11 and TRIDENT 8, the latter being the catalyst of choice for many solid–liquid phase-transfer reactions.

It is worth noting that in the case of alkali iodides NaI and KI, the catalytic activity remarkably decreases (longer

Table 2. Catalytic activity of polypodands 1-7 and polyethers 8-11 in the reaction (1) where X=OSO<sub>2</sub>Me; MY=NaI, KI, NaBr under SL-PTC conditions, at 60 °C

Catalyst	Reaction time (h) <sup>a</sup>				
	NaI	KI	NaBr <sup>b</sup>		
_	>70.00	c	113		
4	2.50		28		
1	1.40		22		
2	1.20	6.60	27		
6	0.61				
5	0.90	3.00	31		
3	0.60	2.20	29		
7	0.42	0.95	7		
10 (PEG)	12.00	18.00			
9 (PEG6400Me <sub>2</sub> )	5.00	6.00	57		
8 (TRIDENT)	2.30	7.00	47		
11 (DCH18C16)	0.70	3.30	57		

<sup>a</sup> Conversion  $\geq 90\%$  GLC.

<sup>b</sup> In CH<sub>3</sub>CN.

<sup>c</sup> Twenty four percent of reaction after 4 days.



Figure 1. Reaction times (h) for the Br/I nucleophilic substitution reaction (1) catalyzed by 6, 3, 7–9, 11.

reaction times) on changing from the sodium iodide to the corresponding potassium salt, according with the lower complexation extent found (Tables 1 and 2). We cannot exclude, however, that the metal ion is involved in the transition state of the reaction ('metal ion electrophilic catalysis') as previously found.<sup>11</sup> Indeed, the reaction time for crown ether DCH18C6 **11** is noticeably lower with the sodium salt (0.7 instead of 3 h) even if the complexation extent is the same (1 mol of complexed salt) in both cases (Table 1).

**2.2.2. Reduction reactions.** The reduction of benzaldehyde (14) (1 mol) to the corresponding benzylic alcohol (15) with NaBH<sub>4</sub> (0.3 mol) was carried out at 25 °C in a chlorobenzene-solid NaBH<sub>4</sub> two-phase system by using catalytic amounts (0.01 molar equiv) of polypodands **3**, **5** and **7** (reaction 2). The reaction was followed by evaluating (GLC analysis) the disappearance of the benzaldehyde (14) in the organic phase with respect to an internal standard (anisole). The results, reported in Figure 2 together with those of ligands **8**, **9** and **11** for sake of comparison, show that the reduction is very fast with all the three polypodands **3**, **5** and **7**. Interestingly, the reaction times are even shorter than those with crown ether **11** (10–30 min instead of about 2 h) in line with their high complexation values reported in Table 1.

 $C_{6}H_{5}CHO + NaBH_{4 \text{ solid}} \xrightarrow{\text{catalyst}} C_{6}H_{5}CH_{2}OH$ (2) 14  $C_{6}H_{5}Cl, 25^{\circ}C$  15



Figure 2. Reaction times (h) for the reduction reaction (2) with catalysts 3, 5, 7–9, 11.

**2.2.3.** Alkylation reaction. The N-alkylation reaction of potassium phthalimide (16) by 1-bromooctane (13) was performed at 80 °C in an acetonitrile-solid  $C_6H_4(CO)_2NK$  (16) two-phase system in the presence of catalytic amounts (0.1 mol/mol of substrate) of ligands 3, 5, 7, 9, 11 and with a 1/1 molar ratio of potassium phthalimide: alkylbromide (reaction 3). The reactions were followed (up to conversions  $\geq$ 90%, GLC analysis) by evaluating the disappearance in the organic phase of the alkylbromide 13 with respect to dodecane as an internal standard.

$$catalyst$$

$$C_{6}H_{4}(CO)_{2}NK_{solid} + nC_{8}H_{17}Br \xrightarrow{} C_{6}H_{4}(CO)_{2}NC_{8}H_{17}n + KBr_{solid}$$
**16 13**

$$CH_{3}CN, 80^{\circ}C$$
**17**
(3)

As shown in Table 3, the catalytic activity of silicon polypodands 3, 5 and 7 is higher than that of  $PEG400Me_2 9$  and comparable with or in the case of 7 even better than that of crown ether DCH18C6 11. The comparison with the uncatalyzed reaction provides evidence for the crucial role of the ligand in reducing the reaction times (32 h without any catalyst and only 2 h for polypodand 7).

**Table 3.** Catalytic activity of polypodands **3**, **5**, **7** and ligand **9** and **11**, N-alkylation (3) and epoxide opening (4) reactions under SL-PTC conditions

Catalyst	Reaction time (h) <sup>a</sup>			
	N-alkylation (3)	Epoxide opening (4)		
	32.0	56.0		
5	4.5			
3	3.8	1.0		
7	2.0	0.75		
9 (PEG6400Me <sub>2</sub> )	10.7	6.0		
11 (DCH18C6)	3.3	31.5		

<sup>a</sup> Conversion  $\geq 90\%$  (by GLC or TLC).

**2.2.4. Oxirane ring opening reactions.** The ring-opening reaction of 1,2-phenylglycidol (**18**) with LiI to give the corresponding iodohydrine  $C_6H_5OCH_2CHOHCH_2I$  (**19**) as the main product (reaction 4) was performed in a chlorobenzene-solid lithium iodide two-phase system in the absence (SL) and in the presence (SL-PTC) of catalytic amounts of polypodands **3** and **7**.

#### Catalyst

$$C_{6}H_{5}OCH_{2}CH(O)CH_{2} + LiI_{solid} \xrightarrow{\phantom{aaaa}} C_{6}H_{5}OCH_{2}CHOHCH_{2}I$$

$$18 \qquad C_{6}H_{5}Cl, 60^{\circ}C \qquad 19$$

$$(4)$$

In this reaction the catalytic activity of silicon polypodands was also found to be noticeably higher not only than PEG400Me<sub>2</sub> 9 but even than crown ether 11 (31.5 h with DCH18C6 11 and only 0.75-1 h with polypodands 7 and 3, respectively). On the other hand, the same reaction performed without any catalyst (solid-liquid SL conditions) is up to 75 times slower than that catalyzed by the polypodand 7 (Table 3).

In addition, it is worth noting that this reaction is faster (about 5 times) with  $PEG400Me_2$  9 than with crown ether 11. Such behaviour can be explained by assuming a lithium

ion participation (metal ion electrophilic catalysis) in the activation process of reaction (4) in analogy with previous results obtained by our group in ring opening reactions of epoxides.<sup>12</sup> The cation being the same, 'electrophilic catalysis' is found to increase, in the order: cyclic<openchain polyether depending on the ability of the ligand to shield the metal ion charge in the transition state. Whereas good complexing agents, such as cyclic polyethers, activate the ion-paired anion but inhibit metal ion catalysis, less efficient anion activators (PEGs) favor the catalysis. In the latter case, the lower anion activation realized by the ligand is largely compensated for by a higher participation of the cation in the activation process.<sup>12</sup>

#### 3. Conclusion

Silicon polypodands 1-7 are powerful complexing agents of alkali metal salts in acetonitrile and in low polarity media such as chlorobenzene. Their complex forming ability increases with the number of silicon atoms and oxaethylenic units. As reported in Table 1, the highest complexation values are always obtained with polypodand 7 which has the highest number of binding sites (54 oxygens).

In line with their complexation values, polypodands 1-7 are found to be excellent catalysts in a number of anionpromoted reactions (1-4) in solid–liquid two-phase systems. The catalytic activity reflects their complexing ability, increasing in the same order. The polypodands **6** and 7 in particular are better catalysts not only than open-chain PEG400Me<sub>2</sub> **9** and TRIDENT **8**, but even than crown ether DCH18C6 **11**. It is worth noting that the catalytic efficiency of these polypodands is remarkably higher than that of DCH18C6 **11** in ring opening reactions of epoxides (up to 42 times) and in the reduction of benzaldehyde (**14**) to the corresponding benzylic alcohol (**15**) with NaBH<sub>4</sub> (more than 10 times) under SL-PTC conditions.

The data as a whole show that this new class of silicon polypodands that combine easy availability and good stability with excellent complexing properties and high catalytic activity represent a valid alternative to the more sophisticated crown ethers as catalysts in solid–liquid phase-transfer reactions, particularly on a large scale.

#### 4. Experimental

#### 4.1. General methods

GLC data were obtained with a Hewlett-Packard 6890 by using a HP-5.5% phenylmethylsiloxane column  $(30 \text{ m} \times 320 \text{ } \mu \text{m} \times 0.25 \text{ } \mu \text{m}).$ 

Potentiometric titrations were carried on with a Metrohm 751 GPD Titrino using a combined silver electrode isolated with a potassium nitrate bridge or a glass electrode isolated with a potassium chloride bridge. Karl Fisher determinations were performed with a Metrohm 684 KF coulometer. <sup>1</sup>H NMR spectra were performed on a Bruker AC 300 spectrometer using TMS as an external reference.

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#### 4.2. Materials and solvents

Silicon polypodands 1-7 were prepared following a previously reported procedure.<sup>10</sup> Their structures were proved by <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectroscopy.<sup>10</sup> Polypodand, yield (%), boiling point (°C)/mm Hg are as follows: **1**, 56, 254–256/1.1; **2**, 51, 258–260/1.1; **3**, 60, 255–258/0.2; **4**, 55, 254–255/1.1; **5**, 75, 113–115/10; **6**, 78, 249–252/1.1; **7**, 79, 243–247/1.1.

Ligands DCH18C6 (mixture of isomers) **11**, PEG **9**, PEG400Me<sub>2</sub> **10** and TRIDENT **8** were utilized as purchased. Octylbromide (**13**), benzaldeyde (**14**), *p*-toluene-sulfonamide (**20**), dodecane and anisole were commercial products, utilized as purchased. Alkali metal halides (NaI, KI, NaBr, LiI), NaBH<sub>4</sub>, NaIO<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>(CO)<sub>2</sub>NK (**16**), were AnalaR grade commercial products, kept in a dessiccator under vacuum.

Dry (Fluka) chlorobenzene and acetonitrile ( $H_2O \leq 20$  ppm) were used. 1,2-Phenylglycidol **18** was a commercial product, purified by distillation and kept over molecular sieves.

Octyl methanesulfonate **12**, bp 92–94 °C at 0.003 mm Hg,  $n_{\rm D}^{20}$  1.4392, was prepared according to the literature (bp 98 °C at 1.5 mm Hg,  $n_{\rm D}^{20}$  1.4390).<sup>13</sup>

#### 4.3. Extent of complexation

The extent of complexation of polypodands 1-7 and polyethers 8-11 under SL-PTC conditions was determined by stirring a standardized chlorobenzene (or acetonitrile) solution (10-20 ml) of ligand (0.02-0.05 M) with 10-50 molar equiv of salt MY, as a solid phase, in a flask thermostatted at 60, 80 °C. The system was stirred for 4-12 h, then kept without stirring for an additional 10 min to allow good separation of the two phases. Aliquots (5-8 ml) of the organic phase were centrifuged, samples (2-3 ml) were withdrawn and titrated with 0.01 M AgNO<sub>3</sub> or 0.01 M HCl (potentiometric titration). In the complexation of NaBH<sub>4</sub> a chlorobenzene solution of ligand (0.01 M) was stirred for 10-12 h with 30 molar equiv of NaBH<sub>4</sub> as a solid phase in a flask thermostatted at 25 °C. Aliquots (3-5 ml) of the organic phase were centrifuged and samples (2-3 ml) were withdrawn and added to an aqueous solution of NaIO<sub>3</sub> (1.2 mol/mol of  $BH_4^-$ ).<sup>14</sup>

After magnetic stirring for about 20 m the iodide formed by the reaction:

 $3BH_4^- + 4IO_3^- \rightarrow 4I^- + 3H_2BO_3^- + 3H_2O$ 

was potentiometrically titrated with 0.01 M AgNO<sub>3</sub>.<sup>14</sup>

### **4.4.** General procedure for the reactions (1–3) under SL-PTC conditions

Solid salt MY (2.5-12.5 mmol) was added to a chlorobenzene or acetonitrile solution (5 ml) of substrate (1-2.5 mmol), catalyst (0.1-0.25 mmol) and an internal standard (0.5-1.25 mmol). The heterogeneous mixture was heated at the appropriate temperature (see Tables 1-3) under vigorous magnetic stirring. The reaction

progress was monitored by GLC analysis of the organic phase, with respect to an internal standard. Dodecane was used in all reactions except for the reduction of benzaldehyde, where anisole was employed. In all cases the mass balance was  $\geq 95\%$ .

## **4.5.** General procedure for the epoxide opening reaction (4)

Solid LiI (10 mol/mol of catalyst) was added to a chlorobenzene solution of catalyst (0.003 M) and the heterogeneous mixture stirred for about 2 h. An aliquot (3-5 ml) of the organic phase was withdrawn and the complex titrated with 0.01 M AgNO<sub>3</sub>. The remaining solution was added with *p*-toluenesulfonamide **20** (0.5 mmol) and 5 ml of a chlorobenzene solution of epoxide (0.06 M). The reaction progress was monitored by TLC (eluant PE/Et<sub>2</sub>O 7/3).

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