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Silicon polypodands: powerful metal cation complexing agents and solid–liquid phase-transfer catalysts of new generation

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Abstract—Silicon polypodands **5**–**7** are found to be powerful complexing agents of alkali metal salts in low polarity solvents and very efficient catalysts in anion-promoted reactions under solid–liquid PTC conditions. The catalytic activity is comparable with that of the cyclic polyether PHDB18C6 **8**. © 2003 Elsevier Science Ltd. All rights reserved.

In recent years, polypodands, open-chain ligands in which several polyether chains are linked to the same binding centre, have attracted increasing interest as anion activators in homogeneous and heterogeneous systems.[1–6] They represent a valid alternative to the cyclic analogues crown ethers and cryptands due to their substantially lower cost, relative non-toxicity and high efficiency.[1–6] In addition, the possibility of regulating their complex-forming properties by altering their structure make them particularly suitable ligands for phase-transfer catalyzed (PTC) processes.[1–6] Here we report that silicon polypodands **5**–**7**, obtained in high yields, by reacting trichloroethyl- (**1**) or dichlorodimethylsilane (**2**) with the appropriate polyethyleneglycol monomethylether **3** and **4** (Scheme 1),[7] revealed powerful complexation of alkali metal salts even in low polarity solvents and hence are very efficient catalysts in a number of anion-promoted reactions (nucleophilic substitution, reduction, alkylation, …) under solid–liquid (SL) PTC conditions. Typical examples of complexation extent and catalytic activity in PTC reactions are collected in Tables 1–3. The data of Table 1 highlight the remarkable complexing ability of polypodands **5**–**7**, increasing in the order **5**<**7**≤**6**. The complexation value (up to 4 mol of salt per mol of ligand) mainly depends on the total amount of donor atoms (oxygens) and, to a lesser extent, on the number of polyether chains linked to the central silicon atom. Catalytic activity of **5**–**7** parallels their complexing ability. Indeed, as reported in Table 2 for typical S_N2 reactions under SL–PTC conditions, the shortest reaction times are always found for polypodands **6** and **7** in line with their high complexation values (Table 1). Comparison with classical polyether ligands reveals that the catalytic efficiency of polypodands **6** and **7** (Table 2) is comparable with that of perhydrodibenzo-18-crown-6 PHDB18C6 (**8**), whereas that of **5**, with shorter chains and a lower number of binding sites, is similar to that of open-chain tris(polyoxaalkyl)amine TRIDENT (**10**), considered to be the catalyst of choice for many SL–PTC reactions,[8] or PEG400Me$_2$ **9**. Analogously, **6** and **7** behave like crown ether **8** in alkylation reactions (2) and (3) (Scheme 2), where PEG400Me$_2$ **9** requires reaction times remarkably longer, close to those of the uncatalyzed reaction (Table 3). In addition, the SL–PTC reduction with NaBH$_4$ of benzaldehyde to the corresponding alcohol is three times faster with **6** and **7** than with crown **8**.

Accordingly, the complexing ability of these silicon podands is similar or even higher than that of the cyclic polyether **8**, and much higher than that of open-chain ligands **9** and **10** (Table 1).

Silicon podands **5**–**7** are found to be thermally stable, almost up to the distillation temperature (250°C, 2

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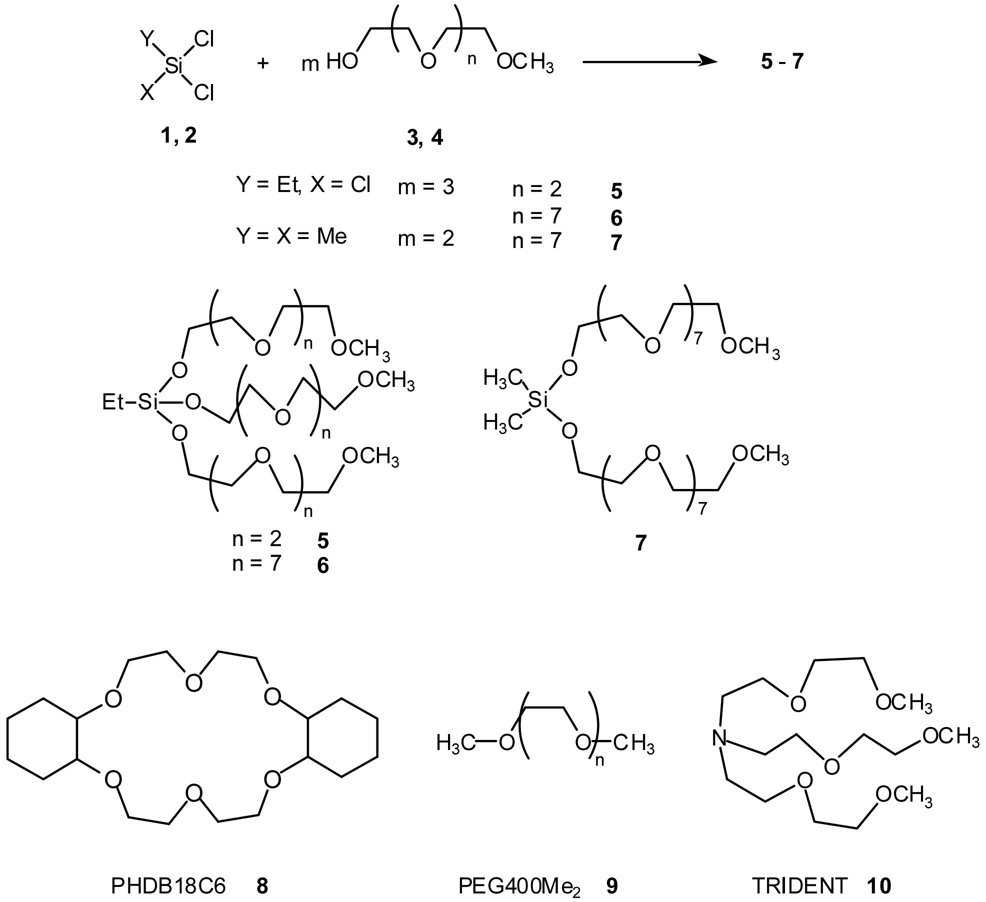

Scheme 1.

mmHg) and stable for long times (almost 3 days) under reaction conditions. The results as a whole reveal the remarkable complexing ability of this new class of open-chain ligands. The presence of more than one polyether chain linked to the same binding centre makes these silicon polypodands complexing agents more efficient than the simple podand PEG400Me$_2$ **9**. As a consequence, the catalytic activity in SL–PT reactions is much higher, even comparable with that of cyclic polyethers such as PHDB18C6 **8**.

Table 1. Complexation extent[a,b] of silicon polypodands **5**–**7** and polyether ligands **8**–**10** under SL–PTC conditions at 60°C

MY	Ligand					
	5	6	7	8	9	10
NaI[a]	0.47	4.0	2.5	1.0	0.86	0.95
KI[c]	0.22	1.7	1.3	1.0	0.47	0.55
NaBr[c,d]	0.35	1.8	1.7	1.1	1.0	1.5
KPh(CO)N[e,f]	0.05	0.18	0.18	0.8	0.13	1.1
KPhO[e,g]	2.0	3.6	3.4	1.2	1.7	2.6

[a] Defined as complexed MY mol/ligand mol.

[b] Average of at least four titrimetric determinations. The error is estimated to be 10%.

[c] A chlorobenzene solution (25 ml) of ligand (0.01 M) and 50 molar equiv. of salt MY, as solid phase.

[d] In CH_3CN.

[e] In CH_3CN at 80°C.

[f] A CH_3CN solution (25 ml) of ligand (0.02 M) and 10 molar equiv. of $KPh(CO)_2NY$, as solid phase.

[g] A CH_3CN solution (25 ml) of ligand (0.02 M), phenol (0.2 M) and 5 mmol equiv. of solid K_2CO_3.

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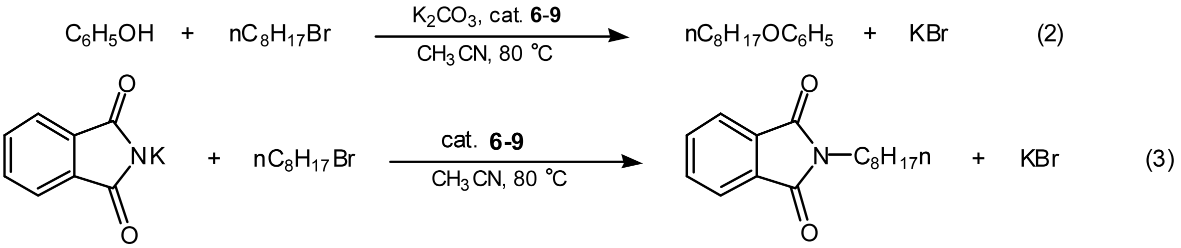
Table 2. Catalytic activity of silicon polypodands **5**–**7** and polyether ligands **8**–**10** in S_N2 reactions (1) under SL–PTC conditions[a]

$$n\text{-}C_8H_{17}X + MY_{solid} \xrightarrow[\text{PhCl, 60 °C}]{\text{cat. } \mathbf{5 - 10}} n\text{-}C_8H_{17}Y + MX_{solid} \qquad (1)$$

X	MY	Reaction time[b] (h)						
		No cat.	**5**	**6**	**7**	**8**	**9**	**10**
OSO_2CH_3	NaI	>70	2.1	0.6	0.9	0.7	5.0	2.3
OSO_2CH_3	KI	[c]	~10	2.2	3	3.3	6	7
Br	NaI	[d]	8	1.8	4.5	1.2	4.2	6
OSO_2CH_3[e,f]	NaBr	113	32	29	31	57	57	47

[a] A chlorobenzene solution (5 ml) of substrate n-$C_8H_{17}X$ (1 M), catalyst (0.05 M) and internal standard (0.5 M) with 12.5 mmol of MY as solid phase.
[b] A conversion ≥90% by GLC.
[c] 24% conversion after 4 days.
[d] 4% conversion after 6 days.
[e] In CH_3CN.
[f] A CH_3CN solution (5 ml) of substrate (0.2 M), catalyst (0.02 M), internal standard (0.1 M) and 5 mmol of solid NaBr.



Scheme 2.

Table 3. Catalytic activity of silicon polypodands (**6** and **7**) and polyether ligands (**8** and **9**) in alkylation reactions (2) and (3) under SL–PTC conditions, at 80°C

Catalyst	Reaction time[a] (h)	
	Reaction (2)[b]	Reaction (3)[c]
–	8	32
6	3	3.8
7	3	4.5
8	2.3	3.3
9	7	10.7

[a] For conversion ≥90%.
[b] A CH_3CN solution (5 ml) of substrate (0.2 M), ligand (0.02 M), internal standard (0.1 M), phenol (0.2 M) and 1 mmol of K_2CO_3.
[c] A CH_3CN solution (5 ml) of substrate (0.2 M), ligand (0.02 M), internal standard (0.1 M), and 1 mmol of $C_6H_4(CO)_2NK$.

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