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New non-hydrolysing poly(oxyethylene) silicon compounds as ligands for phase-transfer catalysis

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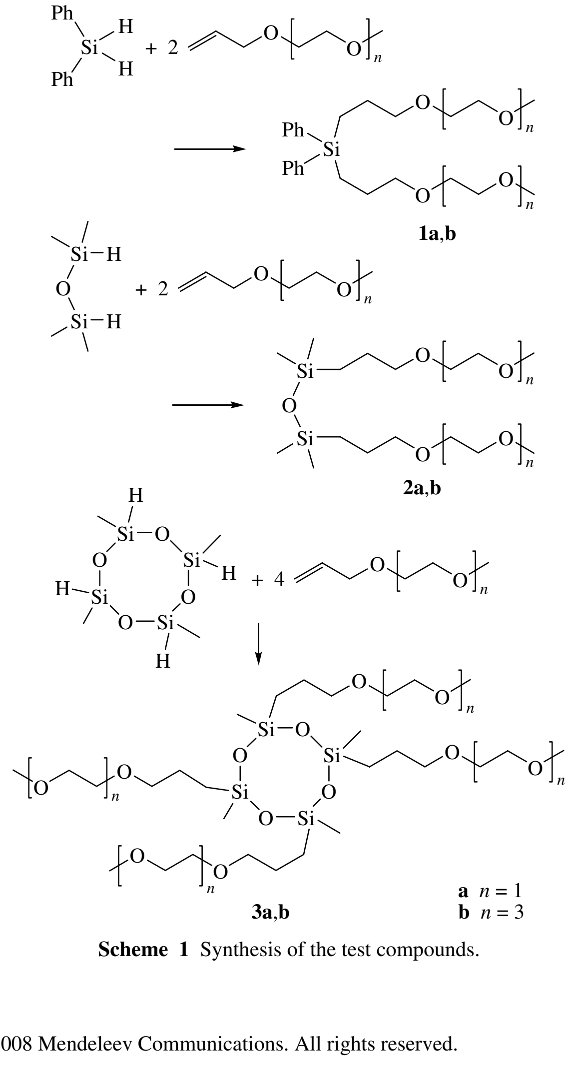
The non-hydrolysing silicon-containing ligands have been synthesised *via* hydrosilylation and studied as catalysts for liquid–liquid and solid–liquid phase-transfer catalysis.

Podands are interesting ligands showing unique properties.[1,2] Previously, we characterised the complex forming abilities of podands being inorganic esters of poly(ethylene glycol) monoalkyl ethers.[3,4] The compounds were also tested in phase-transfer catalysis (PTC).[5–7] Unfortunately, most of them are hydrolytically unstable, so that their applicability to liquid–liquid PTC (LL-PTC) is strongly limited. Their excellent catalytic activity in solid–liquid PTC (SL-PTC) has inspired the synthesis of water-resistant podands containing Si–C bonds, differing in the number of poly(oxyethylene) chains, their length and the structure of the binding centre.

Although the most popular mechanism of LL-PTC assumes a transfer of the ion pair (onium salt, crown ether complex) from organic to aqueous layer, the ion exchange and the back transfer (‘extraction’ mechanism), there are many premises indicating that the LL-PTC does not require the concomitant transfer of the organic (or a supramolecular complex) cation (‘interfacial’ mechanism). In the case of SL-PTC, differences between the mechanisms proposed are significantly more pronounced. Two basic mechanisms, proposed in literature, are the homogeneous solubilization (requires some finite solubility of the solid reagent in the organic phase) and the heterogeneous solubilization (involves the transfer of an anion from the surface of the solid reagent directly to the organic phase by the PT catalyst).



Scheme 1 Synthesis of the test compounds.

The test compounds were prepared using a hydrosilylation reaction (Scheme 1).[†] The starting hydrosilane (1 mmol) was dissolved in dry benzene (150 ml) and a stoichiometric amount of allyl 2-methoxyethyl ether ($n = 1$, **a**) or triethylene glycol allyl methyl ether ($n = 3$, **b**) was added. To the vigorously stirred mixture, the catalyst was added (0.2 mol% per mole of SiH bonds). Tris(triphenylphosphine)rhodium(I) chloride (Wilkinson

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[†] **1a**: colourless liquid, bp 178–180 °C (0.1 mmHg), yield 85%. ^{1}H NMR ($CDCl_3$) δ: 1.08 (t, 2H, $SiCH_2$), 1.77 (qu, 2H, $CH_2C\mathit{H}_2CH_2$), 3.43 (t, 2H, $CH_2CH_2C\mathit{H}_2O$), 3.51 (m, 4H, OCH_2CH_2O), 3.30 (s, 3H, OMe), 7.38 (m, 3H, Ar*H*), 7.58 (m, 2H, Ar*H*). Found (%): C, 69.38; H, 8.67. Calc. for $C_{24}H_{36}O_4Si$ (%): C, 69.19; H, 8.71.

1b: colourless liquid, bp 245–248 °C (0.08 mmHg), yield 80%. ^{1}H NMR ($CDCl_3$) δ: 1.07 (t, 2H, $SiCH_2$), 1.76 (qu, 2H, $CH_2C\mathit{H}_2CH_2$), 3.35 (s, 3H, OMe), 3.43 (t, 2H, $CH_2CH_2C\mathit{H}_2O$), 3.49 (m, 12H, OCH_2CH_2O), 7.38 (m, 3H, Ar*H*), 7.58 (m, 2H, Ar*H*). Found (%): C, 64.97; H, 9.00. Calc. for $C_{32}H_{52}O_8Si$ (%): C, 64.83; H, 8.84.

2a: colourless liquid, bp 208–209 C (0.12 mmHg), yield 90%. ^{1}H NMR ($CDCl_3$) δ: –0.01 (s, 6H, SiMe), 0.47 (t, 2H, $SiCH_2$), 1.54 (qu, 2H, $CH_2C\mathit{H}_2CH_2$), 3.29 (s, 3H, OMe), 3.51 (t, 2H, $CH_2CH_2C\mathit{H}_2O$), 3.62 (m, 4H, OCH_2CH_2O). Found (%): C, 52.11; H, 10.44. Calc. for $C_{16}H_{38}O_5Si_2$ (%): C, 52.41; H, 10.45.

2b: slightly yellow liquid, yield 95%. ^{1}H NMR ($CDCl_3$) δ: –0.01 (s, 6H, SiMe), 0.46 (t, 2H, $SiCH_2$), 1.53 (qu, 2H, $CH_2C\mathit{H}_2CH_2$), 3.37 (s, 3H, OMe), 3.50 (t, 2H, $CH_2CH_2C\mathit{H}_2O$), 3.60 (m, 12H, OCH_2CH_2O). Found (%): C, 53.31; H, 10.08. Calc. for $C_{24}H_{54}O_9Si_2$ (%): C, 53.10; H, 10.03.

3a: slightly yellow viscous liquid, yield 95%, stochastic mixture of stereoisomers. ^{1}H NMR ($CDCl_3$) δ: 0.03 (br., 3H, SiMe), 0.41 (br., 2H, $SiCH_2$), 1.48 (br., 2H, $CH_2C\mathit{H}_2CH_2$), 3.31 (br. s, 3H, OMe), 3.51 (br. t, 2H, $CH_2CH_2C\mathit{H}_2O$), 3.60 (br., 4H, OCH_2CH_2O). Found (%): C, 47.77; H, 9.29. Calc. for $C_{28}H_{64}O_{12}Si_4$ (%): C, 47.69; H, 9.15.

3b: slightly yellow viscous liquid, yield 92%, stochastic mixture of stereoisomers. ^{1}H NMR ($CDCl_3$) δ: 0.03 (br., 3H, SiMe), 0.40 (br., 2H, $SiCH_2$), 1.48 (br., 2H, $CH_2C\mathit{H}_2CH_2$), 3.31 (br. s, 3H, OMe), 3.51 (br. t, 2H, $CH_2CH_2C\mathit{H}_2O$), 3.61 (br., 12H, OCH_2CH_2O). Found (%): C, 50.13; H, 9.33. Calc. for $C_{44}H_{96}O_{20}Si_4$ (%): C, 49.97; H, 9.15.

Table 1 Complexation extent, complex stoichiometry and stability constants of the test compounds.

Compound	Complexation extent[a]	^{23}Na NMR titration results	
		Stoichiometry of complexes observed[b]	Stability constant
1a	0.76	1:1	120±10
1b	1.1	1:1	200±30
		2:1	40±10
2a	0.69	1:1	65±5
2b	0.93	1:1	130±20
		2:1	10±5
3a	0.73	1:1	150±30
3b	1.21	1:1	300±30
		2:1	100±25

[a] Defined as complexed NaI [mol]/ligand [mol]. [b] Defined as metals cation/ligand ratio.

catalyst) was used for the synthesis of **1**, while 1,3-divinyl-1,1,3,3-tetramethyldisiloxane-platinium(0) complex (Karstedt catalyst) was used for the synthesis of **2** and **3**. The solution was heated in an inert atmosphere at 50 °C until no allyl and SiH hydrogen atoms were detected (^{1}H NMR), which happened after 60–100 h. Then, the reaction mixture was filtered thought Celite and the solvent was evaporated in a vacuum. Compounds **1a**,**b** and **2a** were purified by vacuum distillation (final purity of ~98%, GC), while the other ones were used without purification (purity of ~92–95%, NMR).

Table 2 Catalytic activity of the podands and reference compounds in the reaction between *n*-octyl methanesulfonate with sodium iodide under SL- and LL-PTC conditions.[a]

$n\text{-}C_8H_{17}OSO_2Me + NaI_{solid} \rightarrow n\text{-}C_8H_{17}I + MeSO_3Na$ SL-PTC

$n\text{-}C_8H_{17}OSO_2Me + NaI_{solution} \rightarrow n\text{-}C_8H_{17}I + MeSO_3Na$ LL-PTC

Compound	Reaction time[b]/h	
	SL-PTC	LL-PTC
—	200	110
1a	24.1	17.9
1b	6.0	5.5
2a	30.5	25.2
2b	15.0	10.3
3a	6.8	6.0
3b	4.2	3.1
DCH18C6[c]	0.8	0.9
PEG400Me$_2$[c]	6.9	5.2
PEG150Me$_2$[c]	70	95

[a] For SL-PTC experiments: 1 cm^3 of 1 M solution of substrate (n-$C_8H_{17}OSO_2Me$) and 0.01 M of catalyst in chlorobenzene, 5 mmol of solid NaI; for LL-PTC experiments: 1 cm^3 of 1 M solution of substrate (n-$C_8H_{17}OSO_2Me$) and 0.01 M of catalyst in chlorobenzene and 5 cm^3 of 1 M aqueous solution of NaI. 0.1 mmol of *n*-dodecane, as internal standard, was added in both cases. Such mixtures were vigorously stirred and thermostated to 333 K. [b] A conversion equal to 90%, from GC measurements. [c] DC18C6 is dicyclohexano-18-crown-6; PEG400Me$_2$ is nonaethylene glycol dimethyl ether; PEG150Me$_2$ is triethylene glycol dimethyl ether.

The complex-forming abilities of the compounds were tested by ^{23}Na NMR titration experiments carried out at a constant concentration of the sodium ion (1 mM) and changing the ligand/metal ratio from 0.1 to 25. All of the ^{23}Na NMR spectra were measured at 293 K using [^{2}H]$_3$-acetonitrile as a solvent and anhydrous $NaClO_4$ as a sodium salt. The ^{23}Na NMR acquisition parameters were as follows: sfrq, 79.373 MHz; pw, 8.0 μs; pw90, 11.5 μs; tpwr, 55 dB; at, 1.5 s; np, 16k; sw, 3000 Hz; d1, 0.5 s; nt, 512. The stoichiometry and stability constants of the complexes formed in solution were determined from the fit to the titration curves using the WinEQNMR software. Additionally, the complexation extent was determined by the conductometric titration (argentometry) of a saturated solution of sodium iodide in a 0.1 M solution of the test ligands in anhydrous chlorobenzene (Table 1) (2 ml of the solution obtained was dissolved in 50 ml of methanol and titrated with a 0.01 M aqueous $AgNO_3$ using an Eurosensor EPS-2 conductometric probe). The reaction of *n*-octyl methanesulfonate with NaI in PhCl was chosen for catalytic tests (S_N2 nucleophilic substitution). The results of these experiments are summarised in Table 2.

The ligands were stable up to 250 °C; ligands **1** and **2** were hydrolytically stable, while compound **3** polymerised spontaneously in acidic media. After the reaction completion, the podands were isolated and used again without a decrease in the activity. No catalyst decomposition during the activity tests was observed (^{1}H NMR).

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