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CYCLOPHOSPHAZENIC POLYPODANDS: A NEW CLASS OF POWERFUL METAL CATION COMPLEXING AGENTS AND PHASE-TRANSFER CATALYSTS

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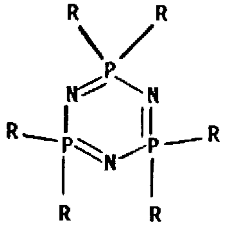
Abstract. Cyclophosphazenic polypodands are found to be powerful complexing agents of alkali metal salts and very efficient phase-transfer catalysts in nucleophilic substitution, alkylation, reduction and oxidation reactions.

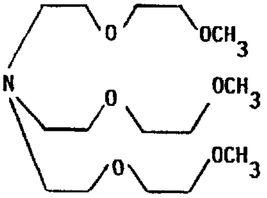
Open-chain ligands (podands) show the ability to form stable complexes with alkali and alkaline-earth metal salts even in low polarity solvents and hence are extensively used as solid-liquid phase-transfer catalysts.[1] However their catalytic activity is always lower than that exibited by their cyclic analogues (crown ethers, cryptands) due to the higher complexation extent of these latter.[1a-d,2]

Recently some of us realized the synthesis of cyclophosphazenic polypodands **1a-c**.[3]

Here we report that polypodands **1a-c**, according to their particular topology, are powerful complexing agents of alkali metal salts in low polarity solvents, and behave as very efficient catalysts in anion promoted reactions (e.g. nucleophilic substitution, alkylation, reduction, oxidation reactions) under solid-liquid and liquid-liquid phase-transfer catalysis (PTC) conditions. Representative examples of the complexation extent[4] and PTC catalytic activity in nucleophilic substitution[5] and reduction reactions are reported in Tables I and II respectively.[6]

The complexation ability of **1a-c** increases in the order **1a** $<$ **1b** $\leq$ **1c** and seems to be related to the number of donor atoms as well as to the nature of the end groups. The ligand being the same, the extent of complexation is largely determined by both the size of the cation and the nature of the counter anion (Table I). The values found in the series of alkali metal iodides clearly indicate the very high complexing ability of these ligands, especially for Na^+ and Li^+. For this latter cation a stoichiometry of 17 moles of





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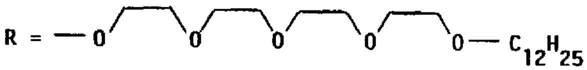
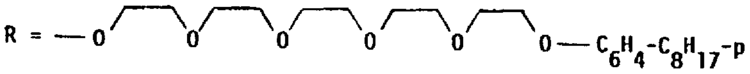
1a 

1b 

1c 

inorganic salt LiI per mole of ligand is found in the case of polypodands **1b** and **1c**. Results also indicate the great selectivity of these ligands to the size of the cation, typical for cyclic compounds such as crown ethers or cryptands.[1a-d,2] Such a trend is likely due to the spatial crowding of the ligand that diminishes its conformational mobility producing a different wrapping around the cation, depending on its size.[1a,7]

Catalytic activity under PTC conditions of **1a-c** reflects their different complexing capability. Indeed in the series of alkali metal iodides the highest reaction rates are found for **1b** and **1c** with the lithium cation, in agreement with the maximum values of complexation measured (Table I).

The effect of the nature of the anion on the complexation extent is also important. In the case of sodium halides NaHal (Hal = Br, I) a noticeable drop in the complexing tendency is observed on going from the iodide to the corresponding bromide. In parallel with this the rate for reaction (1) decreases in the same order (see footnotes d-g of Table I).

In Table I the complexation ability of **1a-c** is compared with that exhibited by the tris(polyoxaalkyl)amine "TRIDENT"-**2** an open-chain ligand considered till now, to be the catalyst of choice in many reactions performed under solid-liquid PTC conditions.[8] Our results clearly indicate the less powerful complexing ability of **2**. In agreement with these results the catalytic activity of polypodands **1a-c** is remarkably higher than that exhibited by

Table I. Catalytic activity and complexation percent of polypodands **1a-c, 2** in the reaction:[6]

$$n\text{-}C_8H_{17}OSO_2CH_3 + M^+I^-_{sol} \xrightarrow[C_6H_5Cl,\ 60^\circ C]{cat} n\text{-}C_8H_{17}I + CH_3SO_3^-M^+_{sol} \tag{1}$$

cat[a]	LiI		NaI		KI		RbI	
	React. time[b]	% compl.[c]	React. time[b]	% compl.[c]	React. time[b]	% compl.[c]	React. time[b]	% compl.[c]
1a	0.7	70	1.50	192	4	39	12	15
1b	$\leq$ 0.015	1700	0.75[d]	390[e]	2	72	3	47
1c	$\leq$ 0.015	1700	0.5[f]	420[g]	2	97	2.5	58
2	3	5	2.5	95	7	9	22	3

[a] 0.05 mol.equiv. [b] Reaction time (hours) for conversions $\geq$ 95%. [c] Defined as complexed M^+I^- moles/ligand moles x100. [d] 93% Conversion was reached after 32h by using NaBr. [e] 22% In the case of NaBr. [f] 92% Conversion was reached after 32h by using NaBr. [g] 21% In the case of NaBr.

Table II. Catalytic activity of polypodands **1a-c, 2** in the reaction:[6]

$$n\text{-}C_6H_{13}COCH_3 \xrightarrow[C_6H_5Cl,\ 60^\circ C]{NaBH_4,\ cat} n\text{-}C_6H_{13}CHOHCH_3 \tag{2}$$

cat	Reaction time (h)	Conversion (%)
1a	12	98
1b	8	98
1c	6	96
2	38	99

"TRIDENT" **2** (Tables I and II).[9] Furthermore, unlike TRIDENT **2**, the more lipophilic polypodands **1b,c**[10] can be utilized as phase-transfer agents also under liquid-liquid PTC conditions.[11] In this case their catalytic efficiency is slightly lower than that observed under anhydrous conditions due to the lower complexation extent in the presence of an aqueous phase.[12] In addition we have found that in the presence of catalytic amounts (0.05 molar equiv.) of **1b,c** alkylations of carbanions and oxidations can be as easily performed. Thus, benzyl methylketone was mono-alkylated with n-butylbromide in 50% aqueous NaOH to give 3-phenyl-2-heptanone (5 h, 20°C, 97%).[10] 1-Dodecene in chlorobenzene solution was oxidized to n-undecanoic acid in the presence of a saturated aqueous solution of $KMnO_4$ at room temperature (40 min., $\geqslant$ 95%).

The experimental results demonstrate the powerful complexing ability of this new class of open-chain ligands and their high catalytic activity in anion promoted reactions, particularly under solid-liquid PTC conditions.

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4) The complexation extent, defined as moles of complexed M^+Hal^-/moles of ligand x 100, was evaluated by stirring for 2-3 h a chlorobenzene solution of ligands **1a-c**, **2** (1-4x10^{-2}M) with an excess (100 molar equiv.) of inorganic salt as solid phase, at 60°C and by argentometrically titrating samples of organic solution.

5) Similar results were found when n-bromooctane was used instead of methanesulphonate.

6) In a typical procedure a chlorobenzene solution (5 ml) of substrate (5 mmol) and catalyst **1a-c** (0.25 mmol) was magnetically stirred with the appropriate inorganic salt (25 mmol) as solid phase, at 60°C. In the reduction (2) a 2:1 $NaBH_4$/substrate molar ratio was used. The reaction progress was monitored by GLC analysis.

7) Attempts at obtaining crystalline alkali metal complexes of **1a-c** are in progress.

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9) Under the same conditions reaction (1) with NaI[6] catalyzed by dicyclohexano-18-crown-6 was complete in 1.5 h, whereas in the presence of tetraethylene glycol monododecyl ether (see b) 98% conversion was reached after 6 h.

10) A similar behaviour was previously found for **1a**.[3]

11) Blank experiments showed that in a chlorobenzene-aqueous NaHal two-phase system (Hal = I, Br) the polypodands **1b,c** are entirely partitioned in the organic phase, in part as free ligands.

12) For example in the chlorobenzene-5M aqueous NaI two-phase system the complexation extent of **1c** at 60°C became 72%, and the reaction (1) was complete in 6 hours.

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