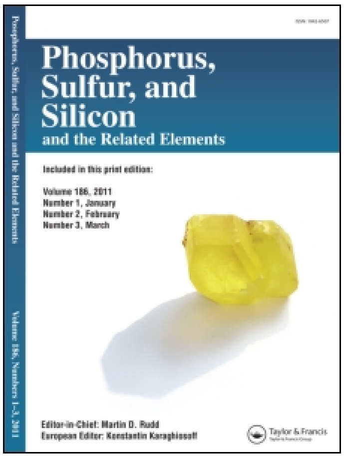

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1,4,7-Tris-(4-Pyridylmethyl)-1,4,7-Triazacyclononane, a New Target Molecule for the Self-Assembly of 3-D Cage Molecules

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Reaction of 1,4,7-triazacyclononane with 4-(chloromethyl)pyridine in the presence of triethylamine in acetonitrile yields a new ligand (**L**) having three pyridyl arms connected to the macrocycle through methylene chains. Owing to its hemi-cage structure, **L** constitutes a target molecule for the self-assembly of 3-D cage molecules.

Keywords: Triazacyclononane; N-ligand; armed macrocycle; pre-organisation; self-assembly; 3-D cage molecule

INTRODUCTION

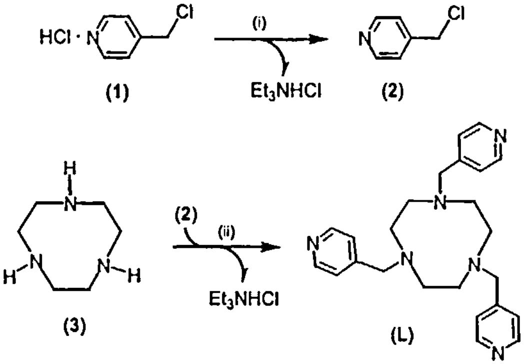
Three-dimensional cage molecules represent a very interesting class of supramolecular compounds with host-guest properties. Such compounds can be used to encapsulate molecular species which are otherwise unstable. Since the development of cryptands has opened the door to the chemistry of three-dimentional receptors, various cage-like molecules with 3-D voids have been prepared.[1-7] The strategy used to construct such three-dimensional systems is based on the coordination of divergent polydentate ligands to *protected* transition metal fragments. Recently several well-detailed reviews focus on recent progress in metal-directed self-assembly.[8-10]

To construct metallosupramolecular capsules, we designed a ligand based on the triazamacrocycle 1,4,7-triazacyclononane with three N-pendent coordinating pyridyl arms. The 1,4,7-tris-(4-pyridylmethyl)-1,4,7-triazacyclononane (**L**) ligand, which was prepared from the reaction of 4-(chlormethyl)pyridine hydrochloride and 1,4,7-triazacyclononane in acetonitrile, shows indeed an interesting pre-organisation for achieving a three-dimentional cage molecule.

RESULT AND DISCUSSION

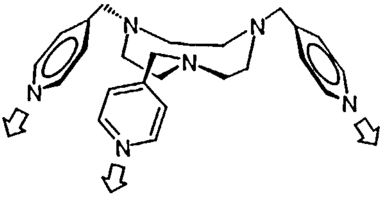
The synthetic method considered for the construction of a 3-D cavity consists of the connection by three transition metal fragments of two organic ligands, which present a hemi-cage pre-organisation. Here we report preliminary work which details the synthesis and the characterisation of a new pyridine-armed triazacyclononane ligand (**L**).

4-(Chloromethyl)pyridine hydrochloride (**1**) suspended in acetonitrile was treated with the stoichiometric amount of triethylamine. $[Et_3NH]Cl$ was filtered off and the solution containing the free 4-(chloromethyl)pyridine (**2**) was added dropwise to a stirred solution of 1,4,7-triazacyclononane (**3**) in presence of triethylamine. The mixture was stirred under reflux for one day. After removal of the precipitate [Et_3NH]Cl, the solvent was evaporated and the oily residue was purified by column chromatography on alumina with CH_2Cl_2/hexane/methanol (8:2:0.5) as eluent (Scheme 1). Finally 1,4,7-tris-(4-pyridylmethyl)-1,4,7-triazacyclononane (**L**) was isolated as a yellow oil in 32 % yield and characterised by its proton and ^{13}C NMR spectra, and a FAB MS.



Scheme 1. Synthesis of 1,4,7-tris-(4-pyridylmethyl)-1,4,7-triazacyclononane (**L**).
Reagents and conditions: (i) Et_3N, MeCN, room temperature; (ii) Et_3N, MeCN, reflux (one day).

The molecular structure of 1,4,7-tris-(4-pyridylmethyl)-1,4,7-triazacyclononane shows an interesting pre-organisation for achieving a three-dimensional cage molecule. The three pyridyl substituents form claw like arms oriented in a calix arrangement (Scheme 2).



Scheme 2. Representation of the molecular structure of **L**.

As palladium(II) is well-known to coordinate two pyridine ligands in a *trans*-position, we plan to connect two 1,4,7-tris-(4-pyridylmethyl)-1,4,7-triazacyclononane ligands using three ethylendiamine or 1,3-bis(diphenylphosphino)propane palladium(II) units. The resulting edifice would be a cationic cage molecule presenting a suitable cavity to encapsulate anionic guests. This study of self-assembly is currently in progress.

EXPERIMENTAL

The NMR spectra (^{1}H and ^{13}C) were recorded on a JEOL JNM-GX-400 spectrometer. All chemical shifts are reported with respect to TMS. Mass spectra were taken on a Micromass ZabSpec (Cs^+) spectrometer.

1,4,7-tris-(4-pyridylmethyl)-1,4,7-triazacyclononane (**L**). Yellow oil; 32% yield; ^{1}H-NMR (400 MHz, CD_3CN, 298 K) δ = 2.77 (12 H, s, 3 × NCH_2CH_2N), 3.63 (6 H, s, 3 × CH_2-pyridine) and 7.29, 7.30, 8,46 and 8.48 (12 H, each m, 3 × pyridine-H); ^{13}C-NMR (100.40 MHz, CD_3CN, 298 K) δ = 150.52, 125.02, 61.91, 55.68; FAB-MS (*m*-Nitrobenzylalkohol): *m*/*z* (%): 403 (100, $[M + H]^+$).

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