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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Plasseraud, Laurent and Saalfrank, Rolf W.(2001) '1,4,7-Tris-(4-Pyridylmethyl)-1,4,7-Triazacyclononane, a New Target Molecule for the Self-Assembly of 3-D Cage Molecules', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 168: 1, 85 – 87

To link to this Article: DOI: 10.1080/10426500108546534

URL: <http://dx.doi.org/10.1080/10426500108546534>

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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-dimensional 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

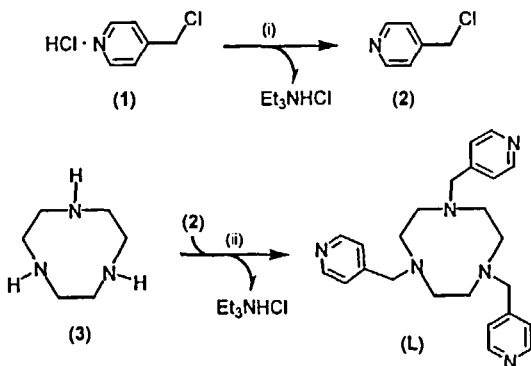
To construct metallosupramolecular capsules, we designed a ligand based on the triazamacrocycle 1,4,7-triazacyclononane with three N-pendent coordinating pyridyl arms. The 1,4,7-tris-(4-pyridylmethyl)-1,4,7-triazacyclononane (L) ligand, which was prepared from the reaction of 4-(chloromethyl)pyridine hydrochloride and 1,4,7-triazacyclononane in acetonitrile, shows indeed an interesting pre-organisation for achieving a three-dimensional 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. $[\text{Et}_3\text{NH}]\text{Cl}$ 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

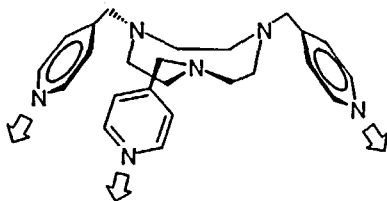
for one day. After removal of the precipitate $[\text{Et}_3\text{NH}]\text{Cl}$, the solvent was evaporated and the oily residue was purified by column chromatography on alumina with $\text{CH}_2\text{Cl}_2/\text{hexane}/\text{methanol}$ (8:2:0.5) as eluent (Scheme 1). Finally 1,4,7-tris-(4-pyridylmethyl)-1,4,7-triazacyclononane (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

ethylenediamine 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 (^1H 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; ^1H -NMR (400 MHz, CD_3CN , 298 K) δ = 2.77 (12 H, s, $3 \times \text{NCH}_2\text{CH}_2\text{N}$), 3.63 (6 H, s, $3 \times \text{CH}_2$ -pyridine) and 7.29, 7.30, 8.46 and 8.48 (12 H, each m, $3 \times$ pyridine-H); ^{13}C -NMR (100.40 MHz, CD_3CN , 298 K) δ = 150.52, 125.02, 61.91, 55.68; FAB-MS (*m*-Nitrobenzylalcohol): m/z (%): 403 (100, $[\text{M} + \text{H}]^+$).

ACKNOWLEDGEMENTS

L. P. thanks the *Alexander von Humboldt* and the *EU* (contract Nr HPMF-CT-1999-00003) for a post-doctoral fellowship.

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