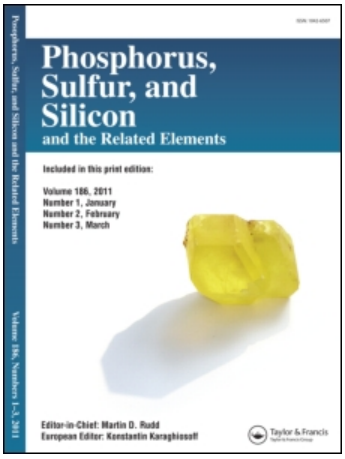

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Synthesis of Main Group Elements Containing Macrocycles

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SYNTHESIS OF MAIN GROUP ELEMENTS CONTAINING MACROCYCLES

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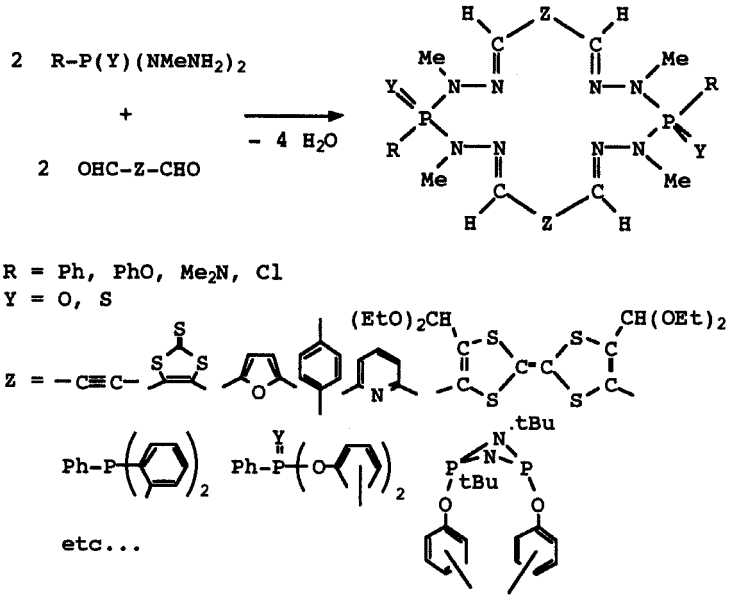
Abstract: Two general approaches allow the facile synthesis of main group elements (phosphorus, silicon...) containing macrocycles.

INTRODUCTION

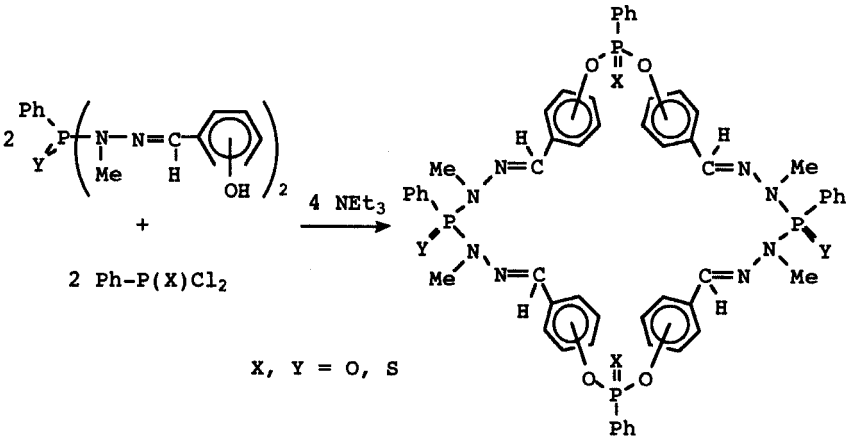
Extensive work has been developped for the synthesis and study of the properties of organic macrocycles since the discovery of crown ethers by Pedersen.[1] However, the synthesis of main group elements containing macrocycles has been much less investigated.

We have already reported a simple, high yield and general method for the synthesis of macrocycles containing two[2-6], three[7], four[8,9], five or six[10] phosphorus atoms, obtained by [2+2] cyclocondensations of phosphodihydrazides with dialdehydes (Scheme 1). Some of these compounds were also obtained by reaction of diphenols with phosphorus dihalide compounds (Scheme 2).[9]

We report here that this reaction is not limited to phosphorus compounds, but may also be applied to the synthesis of various main group elements containing macrocycles.



Scheme 1

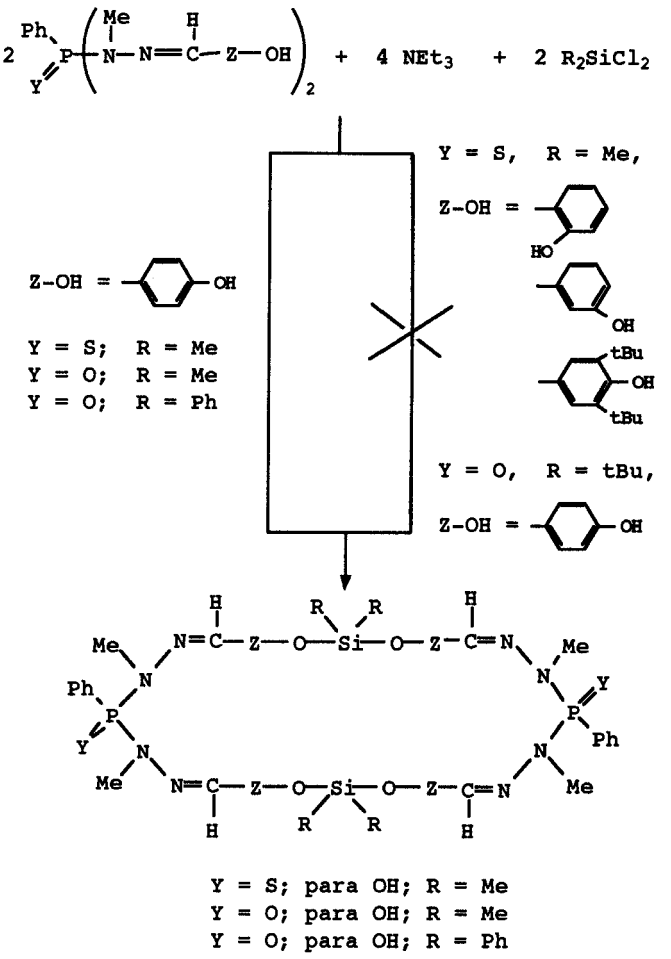


Scheme 2

SYNTHESIS OF MIXED SILICON-PHOSPHORUS CONTAINING MACROCYCLES

The phosphorus phenols used in scheme 2 react with different types of difunctionalized compounds, for example

with dichlorosilanes, in the presence of a base such as triethylamine (Scheme 3).



Scheme 3

The main factor which influences this reaction is the steric hindrance. Indeed, no reaction is observed when *tertio*Butyl groups are linked either to phenoxy rings or to silicon. Furthermore, the position of the OH substituent on the phenoxy ring has an important influence

on the reaction rate: the reaction is over in 1 to 3 days at room temperature when the hydroxy groups are in para position, whereas the reaction is not completed after one week in refluxing THF for ortho or meta OH. We did not succeed in isolating the macrocycles in these later cases, however, macrocycles obtained in the former case were isolated in more than 90% yield and fully characterized. In particular, mass spectroscopy confirmed the formation of 36-memberred rings, including two phosphorus and two silicon atoms.

Work is in progress to apply this reaction to other types of macrocycles. Preliminary results indicate that this method is also convenient to synthesize mixed phosphorus-early transition metals containing macrocycles as well as mixed phosphorus-boron containing macrocycles.

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