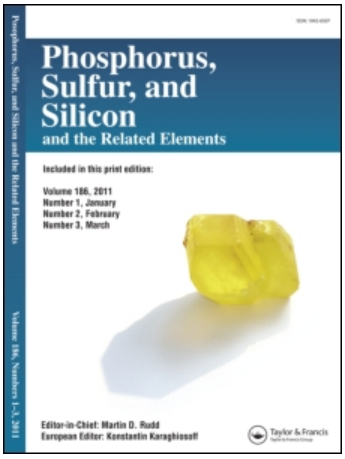


## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Polyazaphosphorus macrocycles

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# Polyazaphosphorus macrocycles

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Abstract : A general way of preparation of phosphorus macrocycles is reported. Their chemical properties are described.

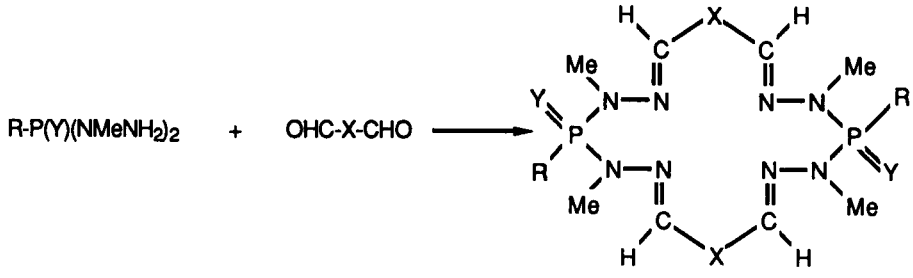


Phosphorus containing macrocycles have not evoked a very large interest probably because of the complexities and low yields of multistage macrocyclic syntheses. Indeed the development of synthetic methods has been slow and concern mainly phosphorus macrocycles possessing P-C, P-O or P-S bonds. Moreover very few investigations were devoted to the preparation of aza or polyazaphosphomacrocycles.

We will report the high yield one pot synthesis of stable functionalized P-N derivatives of this type, the X-ray structure determination of some of them, the preparation of related complexes as well as some examples of their reactivity : reduction of hydrazone moities, 1,2 addition on carbon carbon double or triple bonds, substitution reactions, ring contraction, transmetallations etc ...

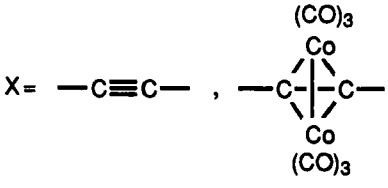
Stable macrocycles of type I are formed when phosphodihydrazides $RP(X)(NCH_3NH_2)_2$ are reacted with dialdehydes OCH-X-CHO (scheme 1). Their constitutions were deduced from $^{31}P$, $^{1}H$, $^{13}C$ NMR, IR, mass spectroscopies.

Noteworthy is the fact that, in contrast with most of the reported synthesis of macrocycles, no template procedures were necessary in these cases.

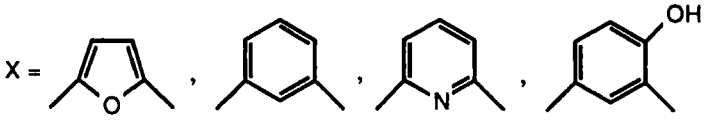



I

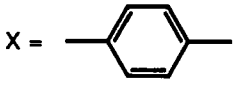
18 membered ring :




20 membered ring :



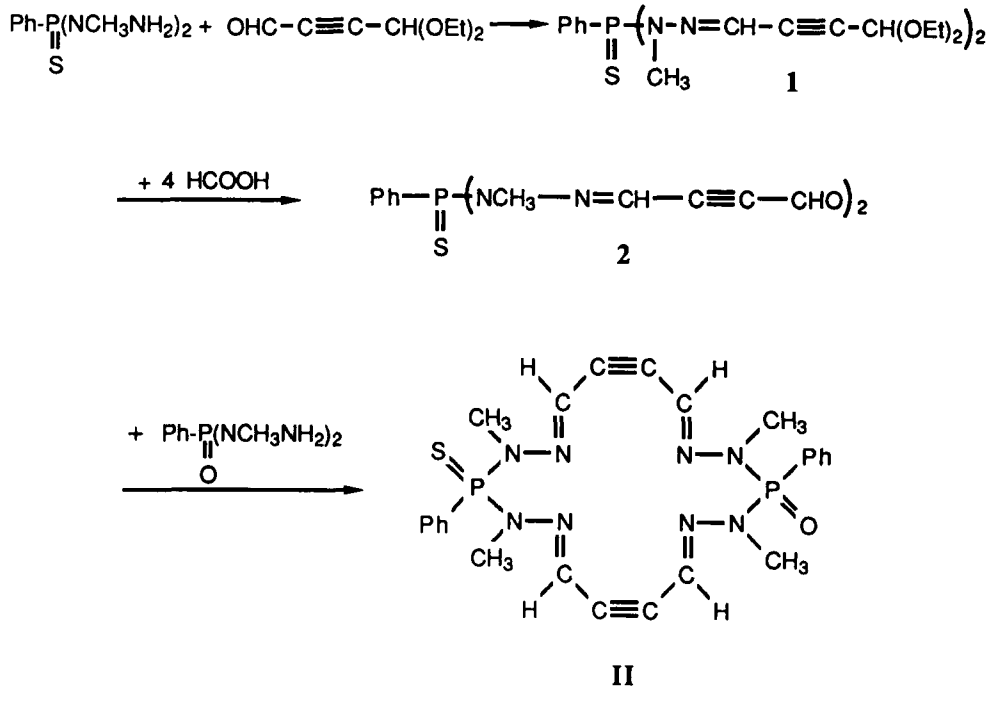

22 membered ring :




Y = O, S R = Ph, PhO, $(CH_3)_2N$

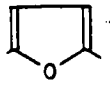
Scheme 1

The strategy used for the synthesis of unsymmetrical macrocycles is illustrated in scheme 2 and involved the preliminary formation of the isolated new polyfunctionalized phosphodihydrazides 1 and 2.



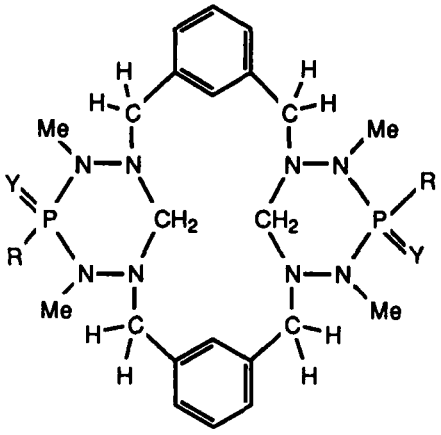

Scheme 2

Stable complexes were obtained either from the direct addition of salts to the free macrocycle or by a template reaction involving phosphodihydrazide, dialdehyde and the desired salt. The obtention of a twelwe coordinated $Ba^{2+}$ sandwich complex Ba $L_2$ $[ClO4^-]_2$ (L=macrocycle with

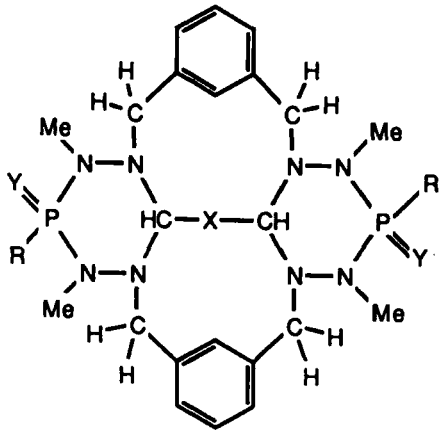
X=  Y=O, R=Ph) examplified these reactions.

Methathetical methods and transmetallation reactions allowed to prepare some other new complexes.

Reduction of the "imine" fonctions of the free 20 (or 22) macrocycles (X= $C_6H_4$) with lithium aluminium hydride followed by addition of formaldehyde or dialdehyde OCH-X-CHO afforded the new polycyclic derivatives III and IV.



III



IV