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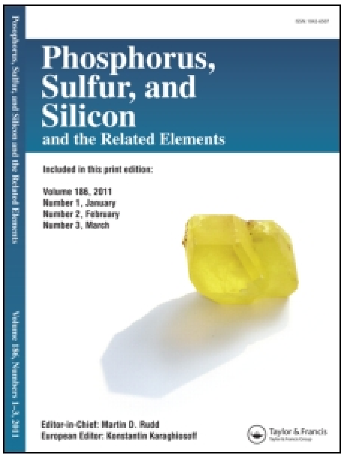

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New Carbon-Phosphorus Macrocycles

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The synthesis of several phosphole and phosphinine-based macrocycles is described. The first ones are flexible as a result of the low inversion barrier of phosphorus. The mixture of isomers can be directly used in coordination chemistry. The second ones are not plagued by conformational problems and display strong π-acceptor properties.

Keywords: Phosphole; Phosphinine; Macrocycles

INTRODUCTION

As a result of the high pyramidal inversion barrier of P, several diastereomers exist for any polyphosphorus macrocycle. They display different coordination behaviors and are difficult to separate. In order to circumvent this problem, we have developed two approaches :

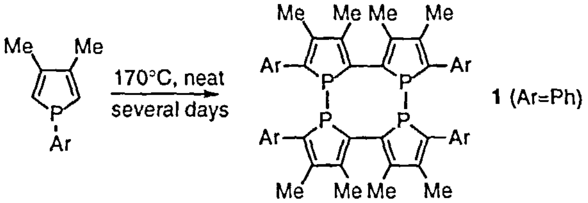
1) The incorporation of phosphorus into phosphole cycles induces an equilibrium between the various

diastereomers of the macrocycle slightly above R.T. (inversion barrier of P *ca.* 16 kcal mol^{-1}).[1] No separation is needed since the macrocycle selects its best geometry to accomodate the metallic center.

2) The second approach consists in the development of a new range of macrocycles based on dicoordinated phosphorus. In practice, the sp^2-P center must be incorporated in an aromatic system for stability. This has led to the synthesis of phosphinine-based macrocycles.

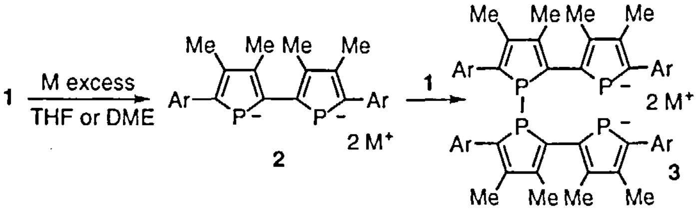
RESULTS AND DISCUSSION

In the first case, two possibilities are available for the incorporation of the phosphole cycle into the macrocycle, *i.e.* via its phosphorus and one of the α-carbons of the cycle, or via its α and α'-carbons. For practical reasons, we have initially developed the first approach. The thermolysis of 1-aryl-3,4-dimethylphospholes under rather drastic conditions (*ca* 170°C, neat, several days) affords easily separable tetramers (Scheme 1). When Ar=Ph, yields as high as 45% can be obtained in the presence of 4-bromo-*N*, *N*-dimethylaniline as a catalyst. This tetramer is a convenient source for two types of phospholide anions[2] (Scheme 2).



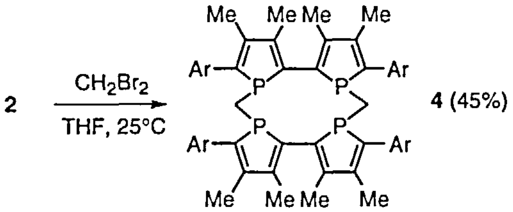
Scheme 1 : Ar=Ph, bithienyl, phosphininyl

The structure of these anions has been investigated by X-ray analysis when Ar=Ph. The potassium salt of the diphosphorus dianion displays a kalocene-type structure when crystallized in the presence of 0.5 eq. of [18]-crown-6.[3]



Scheme 2 : M=Li, Na, K

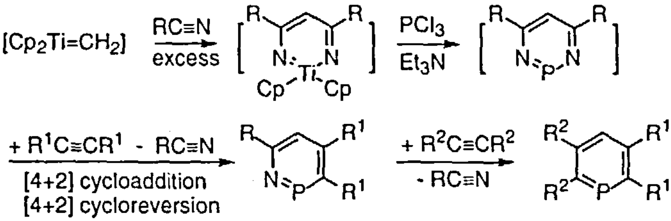
From these anions, it is possible to prepare a series of tetraphosphole macrocycles of various sizes (9 to 16-membered). [2] Up to now, we have only studied the coordination chemistry of the 10-membered species 4 (Scheme 3)



Scheme 3

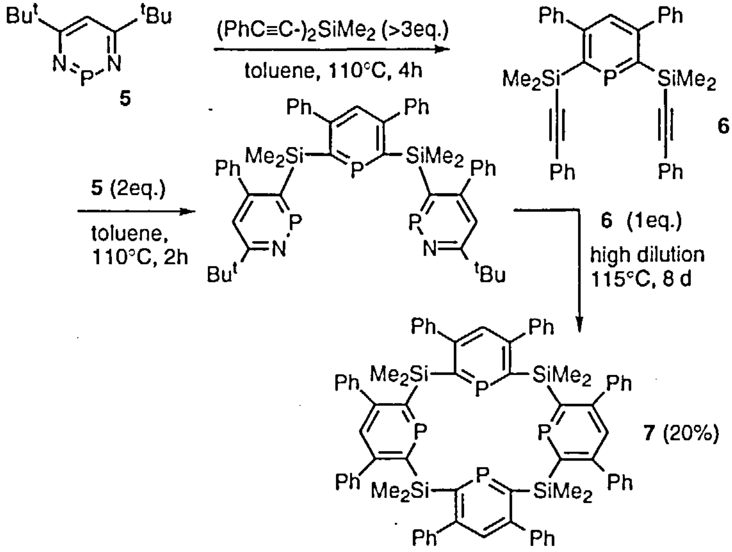
We have checked that 4 is indeed flexible, the equilibrium between the various isomers taking place below 60°C. Diagonal mono- and bis- chelation of one or two identical or different transition metal centers is possible. The Pd(0) complex appears to have an exceptional lifetime as a catalyst of the Heck and Stille cross-coupling reactions.[4] The development of α, α'-connected polyphosphole macrocycles must await an access to α, α'-difunctional phospholes. Such species might become easily accessible since the discovery of a 2,5-dilithiophosphole.[5]

The successful synthesis of polyphosphinine macrocycles first needed the development of a new versatile route to phosphinines.[6] This route is depicted in Scheme 4.



Scheme 4 : R = Ph, Bu^t; R^1, R^2= Ph, SiMe$_3$, COOEt, 2-Py, PPh$_2$, etc.

The conversion of the Tebbe reagent into 1,3,2-diazatitanacyclohexadienes by reaction with nitriles was described by Doxsee and coll.[7] On that basis, we were able to devise an approach to 12-P$_3$ and 16-P$_4$ polyphosphinine macrocycles.[8] The synthesis of the 16-membered ring is given as an example (Scheme 5).



Scheme 5

A preliminary study of the coordination chemistry of 7 has been carried out. The geometry of 7 is ideally suited to the coordination of Rh(I), Ir (I), etc. The reduction of the $[RhP_4]^+$ square planar complex is easy and reversible : $[Rh]^+$ - 0.95V $[Rh]^\circ$ - 1.33V $[Rh]^-$ (*vs* SCE). Diagonal chelation is observed with Au^+ and a fast exchange takes place between the coordinated and non-coordinated P atoms even at -80°C.[9] Other macrocycles incorporating two thiophene and two phosphinine or two furan and two phosphinine rings have been also synthesized. We are on the eve of important advances in the field of macrocyclic P chemistry.

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