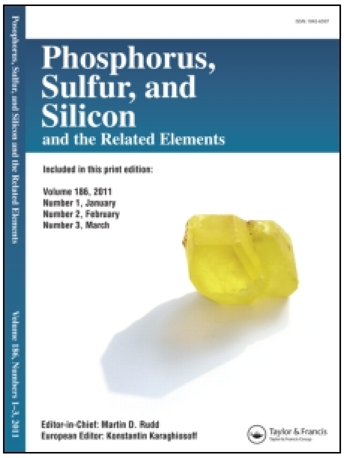

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Latest Advances in Phosphole Chemistry

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LATEST ADVANCES IN PHOSPHOLE CHEMISTRY

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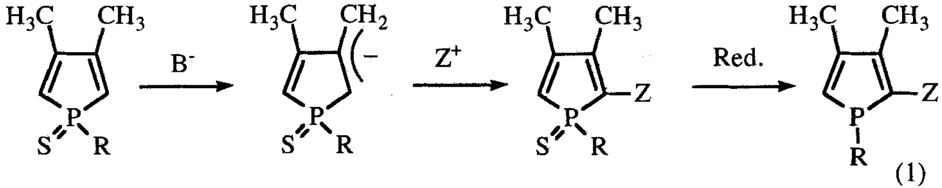
The chemistry of pyramidal phospholes is governed by their low aromaticity and the strong σ,π overlap between the P-R exocyclic bond and the dienic system. Hence, functionalisation of the ring is difficult but [1,5] sigmatropic shift of R is easy. These two complementary aspects of phosphole chemistry are explored. Two routes to α-functional phospholes are described. They involve either a C-Br to C-Li exchange reaction or the allylic metallation of 3,4-dimethylphosphole-borane complexes. The influence of the atom connected to P (sp^2C, spC, N, O, S) and the substitution pattern of the phosphole ring upon the [1,5] sigmatropic migration is discussed. Finally, several applications of this chemistry for the synthesis of water-soluble phosphines and polyphospha-macrocycles are described.

Key words: Phospholes, 1-phosphanorbornadienes, [1,5] shifts, water-soluble phosphines, polyphospha-macrocycles

Phospholes are pyramidal at phosphorus.[1] This fact has two consequences: 1) The electronic delocalisation is weak, hence the functionalisation of phospholes is difficult (no aromatic chemistry); 2) A significant overlap exists between the σ-orbital of the P-R exocyclic bond and the π-dienic system. Hence, [1,5] sigmatropic shifts of R around the phosphole ring are relatively easy. In this report, we shall develop these two aspects of phosphole chemistry.

Recently, we have devised two routes to functional phospholes, which both rely upon the metallation of appropriate phosphole derivatives. The first one is an extension of a previous work describing the allylic metallation of 3,4-dimethylphosphole sulfides.[2] (eq.1)

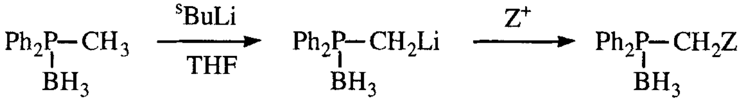


(1)

$B^- = {}^tBuLi, {}^iPr_2NLi$

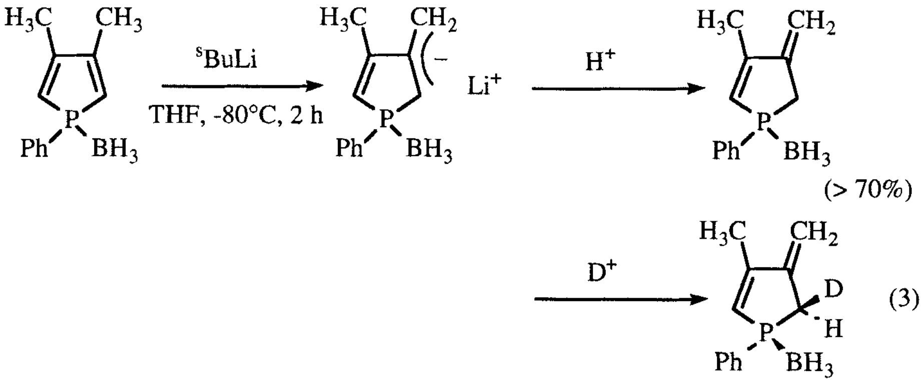
$Z = CO_2H, CO_2Et, C(O)Me, PPh_2$

The reaction of the resulting anions with selected electrophiles gives the corresponding functional phosphole sulfides, which can be reduced to the tervalent species. However, the overall yields are always rather poor (<30%). Our attention was caught by a recent report of Imamoto[3] describing the metallation-functionalisation of phosphine-boranes. (eq. 2)



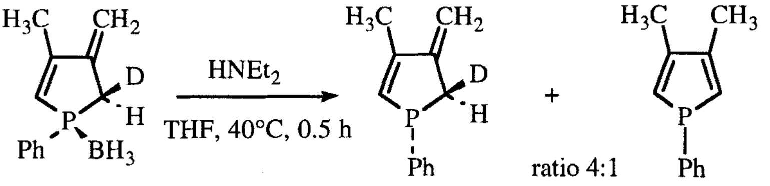
$$\underset{BH_3}{Ph_2P}-CH_3 \xrightarrow[THF]{^sBuLi} \underset{BH_3}{Ph_2P}-CH_2Li \xrightarrow{Z^+} \underset{BH_3}{Ph_2P}-CH_2Z \qquad (2)$$

Thus, we wondered if it was possible to perform the allylic metallation of 3,4-dimethylphosphole-boranes and to use the products for the preparation of functional phospholes.[4] This is indeed the case, as is shown in eq. (3)



(3)

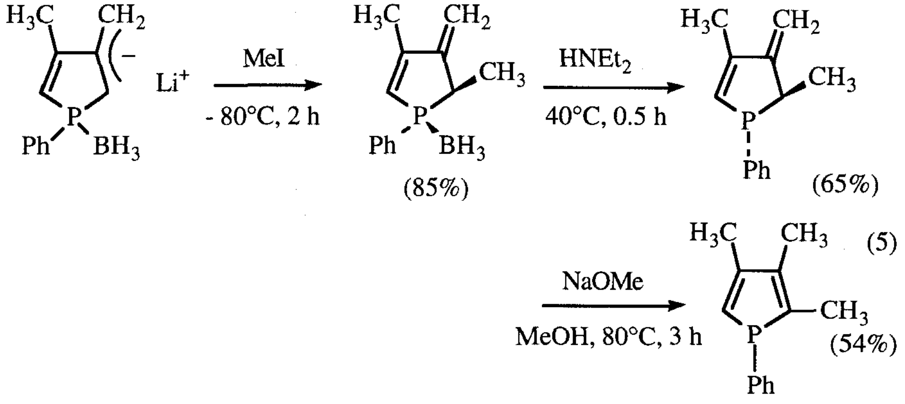
The hydrolysis of the resulting anion yields the corresponding exocyclic phosphole isomer almost quantitatively . The deuterolysis selectively gives the α-deuterated product with deuterium *cis* to BH3. This stereochemistry was proven by decomplexation. (eq. 4)



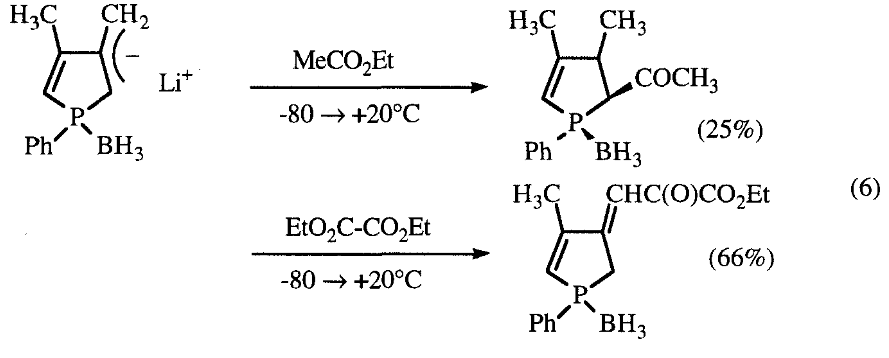
(4)

$^2J(H\text{-}P) = 5.4$ Hz, H *trans* to the lone pair

The decomplexation of phosphine-boranes is known to proceed with retention of configuration at phosphorus,[3] and the fact that deuterium is selectively introduced in *cis* to BH_3 suggests the existence of a stabilizing interaction between the anion and the complexing group. This chemistry can be used to graft a chain onto the α-positions of the phosphole . An example of a 2-alkylphosphole is shown in eq. (5).

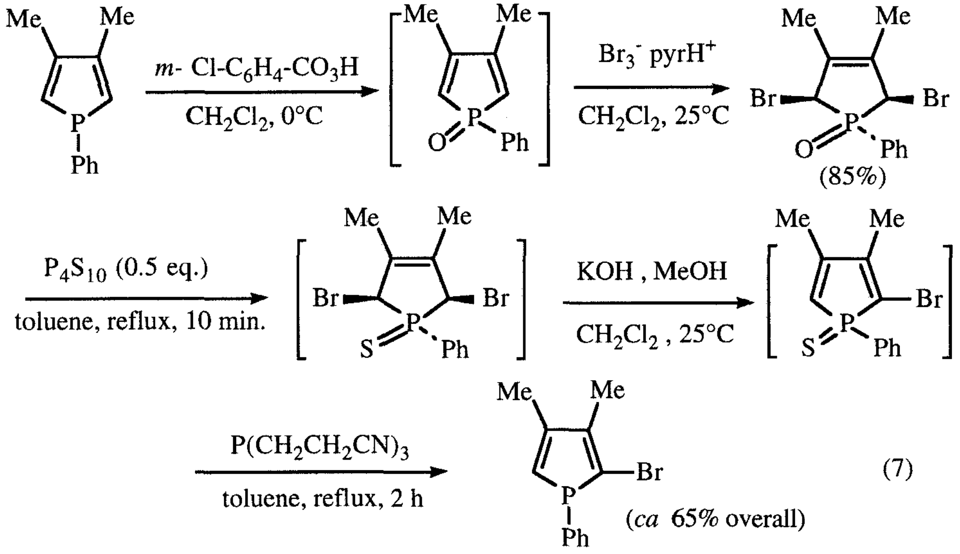


Under mild conditions, the exo-isomer of an α-methylated phosphole is obtained while, under more drastic conditions, the α-methylphosphole is the final result. Using this kind of chemistry, we plan to prepare polyphospholes bonded by polymethylene chains for use in coordination chemistry. α-Silylated and -stannylated derivatives can also be obtained easily. However, the reaction with carboxylic esters gives more erratic results, as is shown in two cases. (eq. 6)

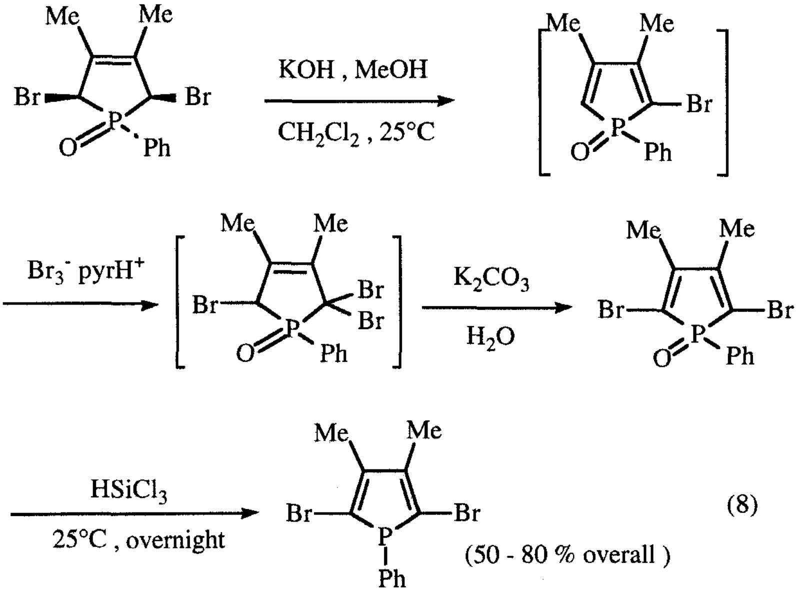


The reduction of the α,β-unsaturated ketone is observed in the first case, the phosphine-borane acting as the hydride carrier. In the second case, a γ-attack of the electrophile takes place.

The second route to functional phospholes involves a bromine to lithium exchange performed on α-bromophospholes.[5] The crucial point appears to be the synthesis of these α-bromophospholes. Our experiments have been made with two such species whose syntheses are depicted in eqs. (7) and (8).

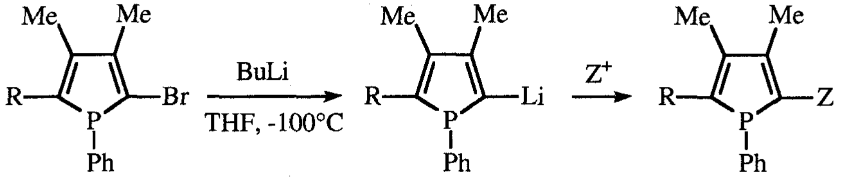


(7)



(8)

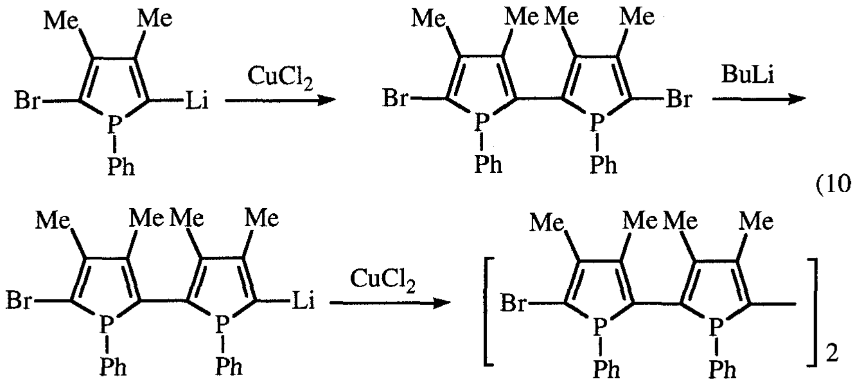
The metallation of these bromophospholes can be carried out at -100°C in THF using butyllithium. The resulting anions are extremely reactive and must be kept below -90°C. They react quickly with a variety of electrophiles as shown in eq. (9).



(9)

R = H, Br ; Z = CO_2H, CO_2R, CHO, C(O)Ph, $SiMe_3$

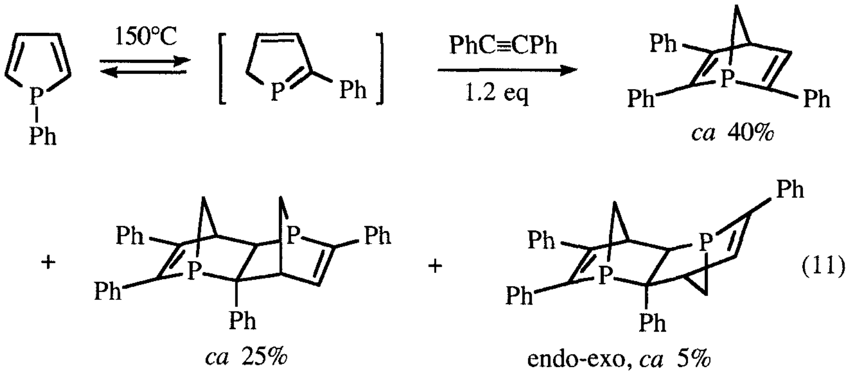
Using this kind of chemistry, we have been able to prepare a tetraphosphole, as depicted in eq. (10).



(10)

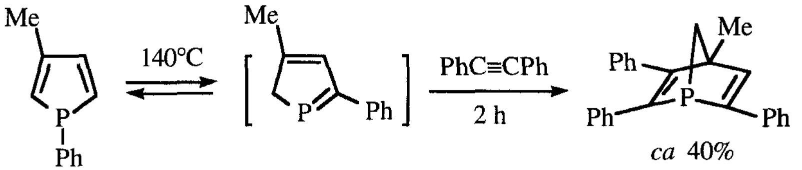
At the moment, this species has been characterized by ^{31}P NMR, elemental analysis and electrospray MS. We are currently trying to get good crystals for X-ray analysis. Our ultimate goal is the synthesis of polyphospholes, which could be of some interest as organic conductors.

As was mentioned in the introduction, concerted [1,5] sigmatropic shifts of the phosphorus substituents are one of the main characteristics of phosphole chemistry. Recently, we have undertaken a systematic study of these shifts, which encompassed different substitution patterns and different migrating groups.[6] Up to now, only hydrogen and aryl groups had been shown to migrate, mainly with phospholes having a 3,4-dimethyl substitution pattern. The influence of the substitution pattern of the phosphole ring carbons was established in a study using Ph as the migrating group and tolane as the trapping reagent. We first studied the case of 1-phenylphosphole. No competition between 2*H*- and 3*H*- phospholes was observed. The reaction exclusively produces mono- and bis adducts derived from the 2*H*- species. (eq. 11)



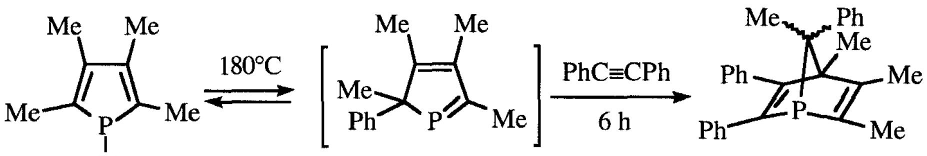
(11)

The minor endo-exo bis-adduct has been characterized by X-ray crystal structure analysis. The case of 1-phenyl-3-methylphosphole is also interesting. The migration exclusively takes place on the side opposite to the methyl group. (eq. 12)



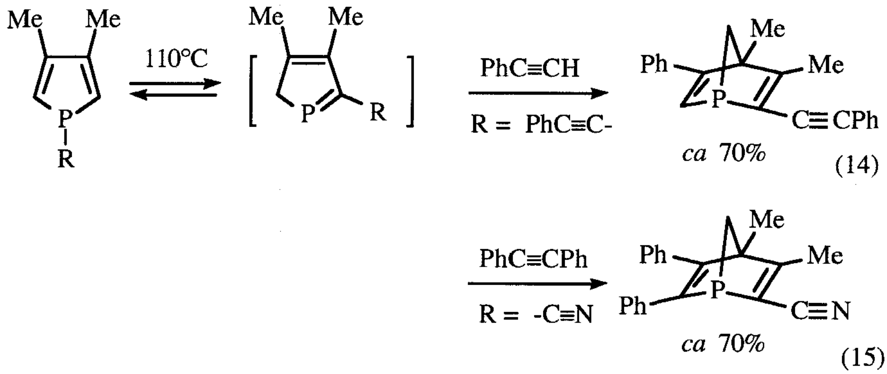
(12)

We feel that steric reasons alone are not sufficient to explain this selectivity. Finally, the migration also takes place with 1-phenyl-2,3,4,5-tetramethylphosphole, although with some difficulty. (eq. 13)



ca 40% (2 isomers) (13)

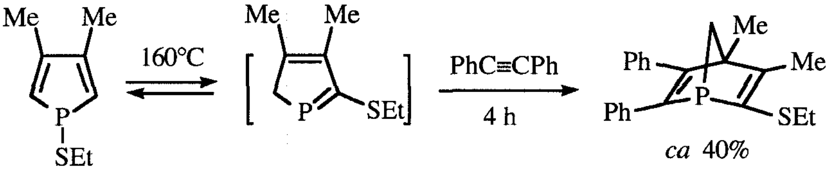
In our studies which concern the nature of the migrating group, we have employed sp carbon, nitrogen, oxygen and sulfur in addition to sp^2 carbon and H. sp-Carbon substituents migrate easily around 110°C, which is a lower temperature than is found for sp^2 carbon. (eqs. 14,15)



(14)

(15)

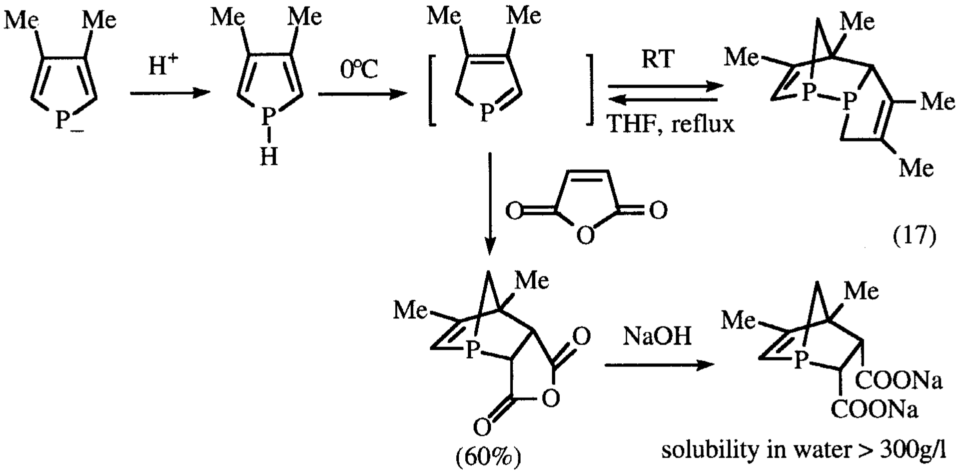
Oxygen does not shift, probably because the P-O bond is too strong; sulfur does migrate. (eq. 16)



(16)

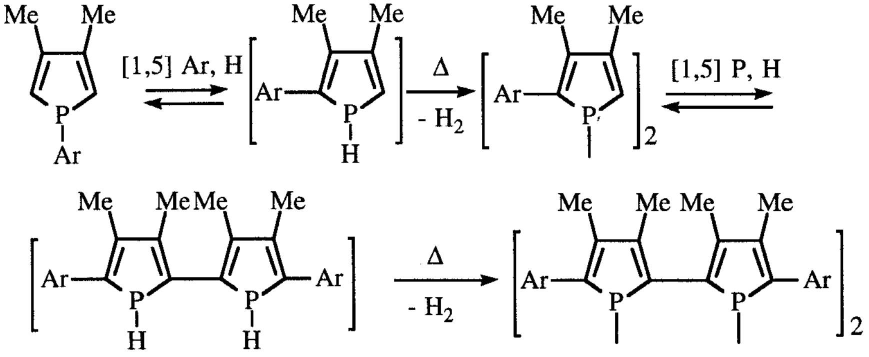
Dismutation takes place with nitrogen substituents: 2 P-N → P-P + N-N.

The scope of these migrations is thus rather large and several applications can be envisaged. Two such applications are currently being developed. The first one concerns the synthesis of a new type of water-soluble phosphine for biphasic catalysis.[7] (eq. 17) This kind of phosphine can be prepared in optically active form for asymmetric catalysis. Preliminary experiments have shown that they perform rather well in the cobalt carbonyl-catalysed hydroformylation of olefins.



(17)

Another application concerns the synthesis of new, fully flexible, phosphorus crowns. From the work of Mislow and coll.[8], it is known that the pyramidal inversion barrier of phospholes is low, *ca* 16 kcal / mol. Hence, as a consequence of the rapid inversion at phosphorus around room temperature, phosphorus crowns involving the phosphole nucleus are able to adapt their conformation to the stereochemical requirements of the metal . Our starting points were phosphole tetramers which are easily obtained by thermolysis of 1-aryl-3,4-dimethylphospholes.[9] The mechanism of their synthesis has been investigated recently[10] and is depicted in eq. (18).

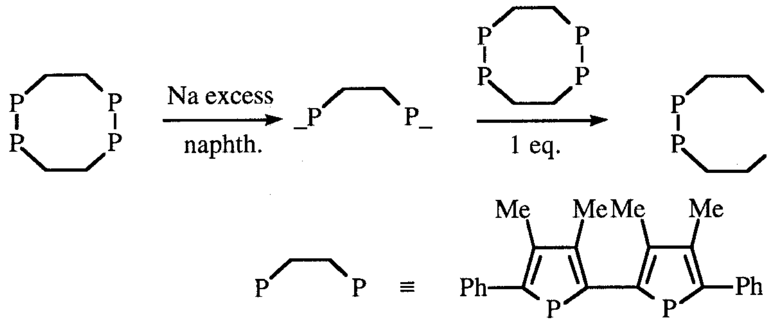


Ar = Ph : 5 days, 170°C, 20-25%

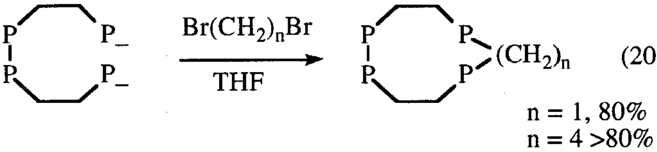
(18)

with 4-Br-C_6H_4-NMe_2 : 18 h, 40-45%

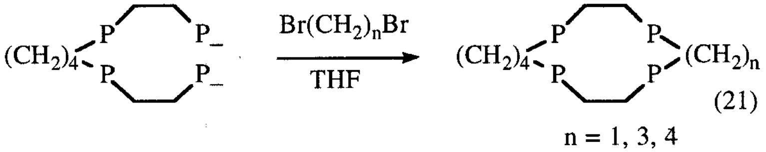
We have made the serendipitous discovery that the presence of *p*- bromo-*N*,*N*- dimethylaniline dramatically enhances both the speed and the yield of the tetramerisation.[6] Thus, from a practical standpoint, these tetramers can be used for the synthesis of macrocycles. The various possible syntheses of these rings are depicted in eqs. (19-23).



(19)



(20)



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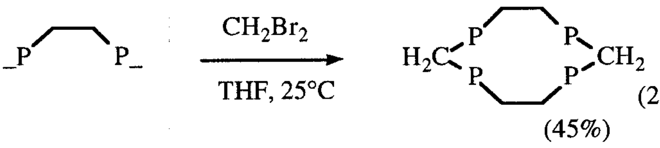

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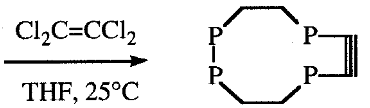
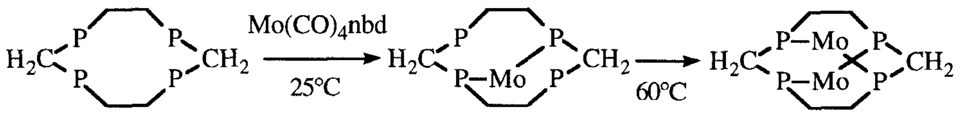


(23)

The acetylenic ring depicted in eq. (23) has been characterized by X-ray crystal structure analysis. Preliminary investigations on the coordination chemistry of these macrocycles have been performed. As an example, the bis-methylene macrocycle can chelate either one or two Mo(CO)4 units. (eq. 24)



(24)

$Mo \equiv Mo(CO)_4$

This diagonal coordination offers the possibility of building either cradle- or cage-like complexes which could show some potential for the activation of small molecules. In one Mo_2 complex, the Mo-Mo distance has been found to be 5.9 Å.

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