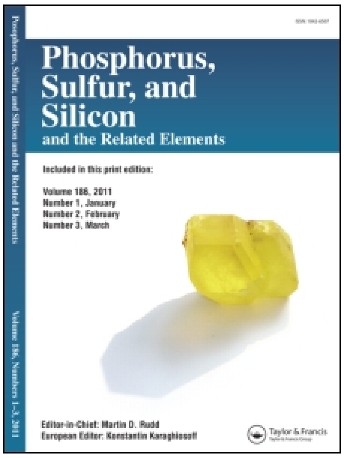


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Formation and Structural Aspects of Four-, Five-, and Six-Membered Phosphorus Nitrogen Ring Compounds

Manfred Meisel[a]; Christiane Donath[a]
[a] Zentralinstitut für anorganische Chemie, Berlin, FRG

To cite this Article Meisel, Manfred and Donath, Christiane(1992) 'Formation and Structural Aspects of Four-, Five-, and Six-Membered Phosphorus Nitrogen Ring Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 64: 1, 63 — 69

To link to this Article: DOI: 10.1080/10426509208041129
URL: http://dx.doi.org/10.1080/10426509208041129

Phosphorus, Sulfur, and Silicon, 1992, Vol. 64, pp. 63–69
Reprints available directly from the publisher
Photocopying permitted by license only

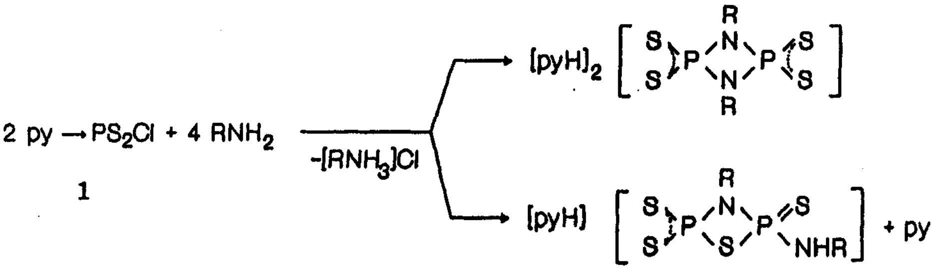
FORMATION AND STRUCTURAL ASPECTS OF FOUR-, FIVE-, AND SIX-MEMBERED PHOSPHORUS NITROGEN RING COMPOUNDS

MANFRED MEISEL and CHRISTIANE DONATH

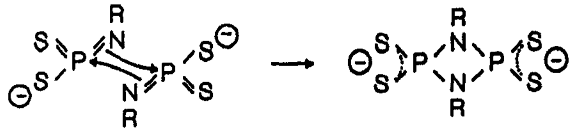
Zentralinstitut für anorganische Chemie, Rudower Chaussee 5,
0-1199 Berlin, FRG

Abstract The donor-stabilized dithiomonometaphosphoryl chloride py→PS_2Cl (py = pyridine) reacts with primary amines, RNH_2, in defined molar ratios to four-ring heterocycles. Whether diaza - or azathiadiphosphetidines are formed depends on the rest R, the basicity of the amines and the reaction conditions. In a similar way the ring size of the P-N heterocycles obtained from py→PS_2Cl and monosubstituted hydrazines is determined by the substituents at hydrazine. The influence of steric factors on the probable reaction mechanisms and some structural features of the obtained heterocycles are discussed.

An extended study of the reaction of py→PS_2Cl with primary amines has shown that in molar ratios 1:amine = 1:2 or 1:1 in the presence of triethylamine four-ring heterocycles are formed in high yields[1-3]. Depending on the steric and electronic effects of the rest R in RNH_2 either diaza - or azathiadiphosphetidines are obtained:



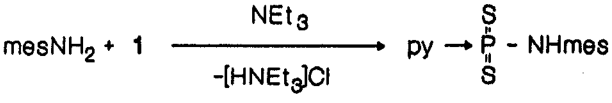
It is assumed that the reaction in both cases proceeds via an instable tricoordinated monometaphosphate intermediate which is stabilized by a [2+2] cycloaddition with formation of the phosphetidine[1], e.g.:



In the case of electron-withdrawing groups R at the nitrogen the formation of diazadiphosphetidines is preferred[3] whereas electron-releasing and bulky groups at the nitrogen lead to the formation of azathiadiphosphetidines[2].

The assumption of a "monometaphosphate mechanism" during the course of nucleophilic substitution at **1** in solution is supported by the following thermal reactions of donor-stabilized amido dithiomonometaphosphates.

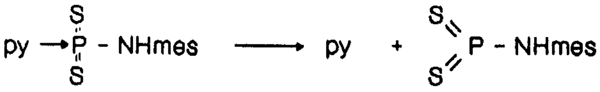
Starting with mesitylamine **2** is obtained as the up to now only stable primary product of the reaction of **1** with primary amines:



$$\mathrm{mesNH_2} + \mathbf{1} \xrightarrow[-[\mathrm{HNEt_3}]\mathrm{Cl}]{\mathrm{NEt_3}} \mathrm{py} \rightarrow \overset{\mathrm{S}}{\underset{\mathrm{S}}{\mathrm{P}}} - \mathrm{NHmes}$$

2

The mass spectrum of **2** shows that a simple dissoziation into pyridine and dithiophosphoryl mesitylamide takes place as main fragmentation step:

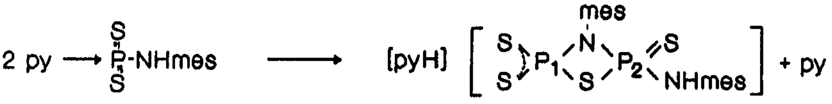


$$\mathrm{py} \rightarrow \overset{\mathrm{S}}{\underset{\mathrm{S}}{\mathrm{P}}} - \mathrm{NHmes} \longrightarrow \mathrm{py} + \mathrm{S_2P{-}NHmes}$$

3

m/z 79 m/z 229

On heating of **2** in a preparative scale the corresponding azathiadiphosphetidine is the main reaction product (80 % yield):

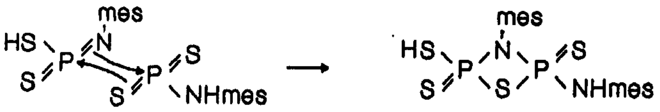


$\delta^{31}P$ 113,9 ppm

$\delta^{31}P_1$ 78,3 ppm (d)

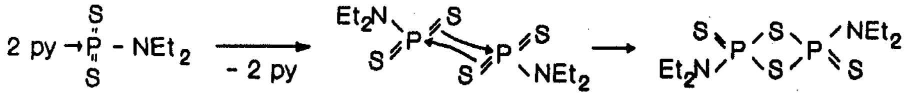
$\delta^{31}P_2$ 60,0 ppm (d)

This result suggests that the monometaphosphate analogue **3**, liberated by thermal dissoziation of **2**, exists in an equilibrium of the amido and imido form which react by [2+2] cycloaddition to the azathiaphosphetidine **4** :



3 **4**

Further evidence for the "monometaphosphate mechanism" is seen in the formation of the dithiaphosphetane **5** starting from the pyridine-stabilized dithiomonometaphosphoryl diethylamide. When this compound is heated, in the first step the corresponding monometaphosphate derivative is produced which is then immediately stabilized in a second step by [2+2] cycloaddition:

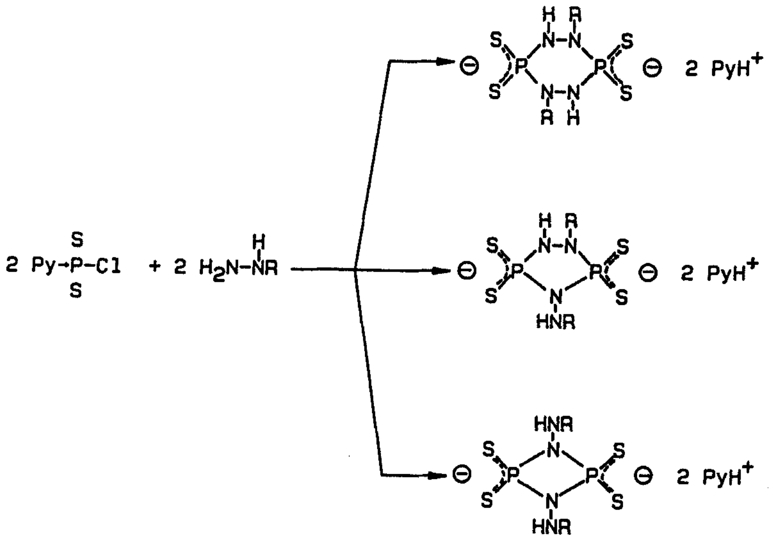


5

$\delta^{31}P$ 122,9 ppm

$\delta^{31}P$ 21,8 ppm

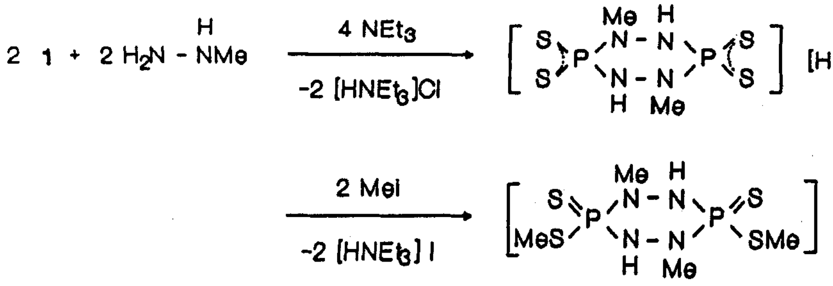
To extend the knowledge of the reaction behaviour of py→PS_2Cl (1) with respect to nucleophilic reagents, especially with regard to the formation of cyclic compounds, it was also of interest to study the raction with hydrazines. In the following scheme the principal possibilities of the formation of phosphorus-nitrogen ring systems during the reaction of 1 with monosubstituted hydrazines are given:



In many cases the reactivity of 1 is comparable to that of phosphorus dichloro compounds because of the two reactive centers at the P-Cl and P-N bonds, respectively. From the literature it is known that phosphorus dichlorides react with hydrazines usually to six-membered ring systems[4]. It was found that in the reaction of 1 with monosubstituted hydrazines depending on the rest R all the possibilities shown in the scheme (see above) can be realized.

In a general procedure 1 and the substitued hydrazine in the presence of triethylamine were heated in acetonitrile or benzene solution for about one hour (molar ratio 1:hydrazine:NEt_3 = 1:1:2). The obtained salts of the corresponding dithiolates (v. scheme) were methylated by methyl iodide yielding normally a mixture of cis/trans isomers of methyl esters, which were separated by column chromatography.

The reaction of **1** with methylhydrazine leads only to the six-membered ring (60 % yield):

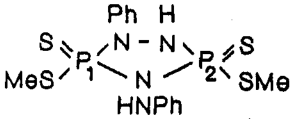


6

cis/trans (87 % yield)

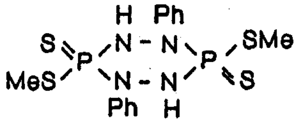
1,4-dimethyl-3,6-dimethylthio-3,6-dithioxo-1,2,4,5-tetraaza-$3\lambda^5 6\lambda^5$-diphosphorinan

With phenylhydrazine besides small amounts of the six-membered ring as main product a five membered ring system (3,5-dimethylthio-1-phenyl-4-phenylamino-3.5-dithioxo-1,2,4-triaza-$3\lambda^5$,$5\lambda^5$-diphospholane, **8**) is obtained.



8

(70 % yield)



7

cis/trans (4 % yield)

The ^{31}P-NMR spectrum of **8** shows the typical AB pattern with doublets at $\delta\,P_1$ 87.3 ppm and $\delta\,P_2$ 84.8 ppm (J_{P-P} 57 Hz). The five-ring structure follows from the ^1H-NMR spectrum. The two different NH protons are characterized by two distinctly separated signal groups. The exocyclic NH proton is coupling across three bonds with the two P atoms giving a triplet ($\delta^{31}P$ 6.02 ppm, J_{PNNH} 2.2 Hz), whereas the endocyclic NH proton couples across two bonds giving a doublet fine structure ($\delta^{31}P$ 4.77 ppm, J_{PNH} 13.4 Hz). The coupling constants are quite different from those found in the six-membered systems (Table I). These structure proposals are confirmed by the X-ray structures of the cis-isomer of **7**[5] and the five-membered ring **8**[6] (Figures A and B). The P_2N_4 ring of **7** shows a distorted twist conformation, the pseudoaxial substituents at the P atoms are arranged in cis positions with respect to the P_2N_4 ring. Fig. B shows the two different kinds of molecules of the P_2N_3 ring which are found in the unit cell of **8**. In both cases the substituents at the P atoms are in trans positions but in one of the molecules the SMe group is directed towards the doubly-bonded S atom and in the other one (above) the methyl group is bent to the opposite direction.

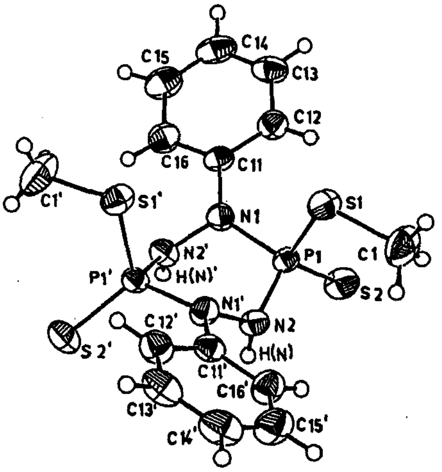


FIGURE A. Molecular structure of the cis isomer of **7**

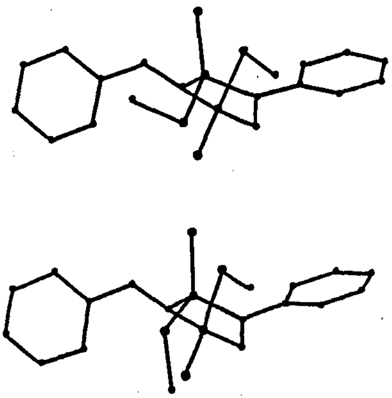


FIGURE B. Arrangement of the substituents in the two molecular forms of **8**

TABLE I ^{1}H and ^{31}P NMR data of the P-N rings **6** - **9**

compound	δ ^{1}H [ppm]		J [Hz]		δ ^{31}P [ppm]
	SMe	NH	J_{PNH}	J_{PNNH}	
6a (trans)	1.954 (d)	4.77 (d)	27.1	1.7	91.5 (s)
6b (cis)	1.95 (d)	6.33 (d)	29.9	1.9	99.6 (s)
7a (trans)	1.87 (d)	5.02 (d)	31.3		85.5 (s)
7b (cis)	1.79 (d)	6.1 (d)	30.5		89.6 (s)
8	1.55 (d)	4.77 (d)	13.4		P_1 87.3 (d)
	1.82 (d)	6.02 (t)		2.2	P_2 84.8 (d)
9	2.32 (m)	3.91 (t)		10.2	107.5 (s)

solvent: C_6D_6

The reaction of **1** with t-butylhydrazine leads to 1,3-diphenylamido-2,4-dimethylthio-2,4-dithioxo-1,3-diaza-2λ^5, 4λ^5-diphosphetidine **9**. The formation of the four-membered ring is caused by the bulky t-butyl group. The four-ring structure is evidenced by the ^{1}H-NMR spectrum which shows a triplet fine structure for the NH protons in accordance with their exocyclic positions.

Possible mechanisms of formation of the different ring systems are discussed.

REFERENCES

1. M. Meisel and Ch. Donath, Phosphorus and Sulfur, 30, 451 (1987)
2. Ch. Donath, B. Wallis, M. Meisel and P. Leibnitz, Z. anorg. allg. Chem., 576, 33 (1989)
3. Ch. Donath and M. Meisel, to be published
4. cf. U. Engelhardt and B. Stromburg, Phosphorus, Sulfur and Silicon, 41, 235 (1989); T. Bünger and U. Engelhardt, Z. Naturforsch., 37b, 24 (1982)
5. B. Wallis, Ch. Donath, M. Meisel and J. Fuchs, Acta Cryst., in press
6. M.-T. Averbuch-Pouchot, Ch. Donath, A. Durif and M. Meisel, to be published