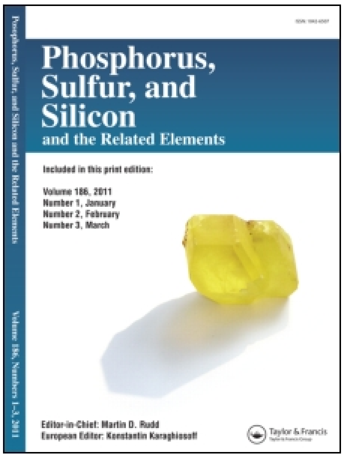


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Derivatives Of Npcl$_2$ (Nsoci)$_2$ And (Npcl$_2$)$_2$Nsocl$_2$ Part Xxv[1]. Reactions Of Npcl$_2$(Nsox)$_2$ (X = Ph, Cl, F) With Bifunctional Reagents

W. Hoeve[a]; K. S. Dhathathreyan[a]; J. C. van de Grampel[a]; F. Van Bolhuis[b]
[a] Department of Inorganic Chemistry, University of Groningen, Nijenborgh 16, AG Groningen, The Netherlands [b] Department of Chemistry, University of Groningen, Nijenborgh 16, AG Groningen, The Netherlands

To cite this Article Hoeve, W. , Dhathathreyan, K. S. , van de Grampel, J. C. and Van Bolhuis, F.(1986) 'Derivatives Of Npcl$_2$ (Nsoci)$_2$ And (Npcl$_2$)$_2$Nsocl$_2$ Part Xxv[1]. Reactions Of Npcl$_2$(Nsox)$_2$ (X = Ph, Cl, F) With Bifunctional Reagents', Phosphorus, Sulfur, and Silicon and the Related Elements, 26: 3, 293 — 298

To link to this Article: DOI: 10.1080/03086648608084583

URL: http://dx.doi.org/10.1080/03086648608084583

Phosphorus and Sulfur, 1986, Vol. 26, pp. 293–298
0308-664X/86/2603-0293/\$15.00/0

DERIVATIVES OF NPCl$_2$(NSOCl)$_2$ AND (NPCl$_2$)$_2$NSOCl, PART XXV[1]. REACTIONS OF NPCl$_2$(NSOX)$_2$ (X = Ph, Cl, F) WITH BIFUNCTIONAL REAGENTS

W. HOEVE, K. S. DHATHATHREYAN and J. C. VAN DE GRAMPEL

Department of Inorganic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

F. VAN BOLHUIS

Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

(*Received August 29, 1985*)

Reactions of NPCl$_2$(NSOX)$_2$ (X = Ph, Cl, F) with 1,2-diaminoethane or 2-aminoethanol in a molar ratio 1:2 afford spirocyclic compounds with formula NP[NH(CH$_2$)$_2$Y][NSOX]$_2$ (Y = NH,O). Using the corresponding propane analogues as reagents, compounds NP[NH(CH$_2$)$_3$Y][NSOX]$_2$(Y = NH,O) are obtained. The size of the spiro ring appears to affect the ^{31}P NMR shift of the spiro phosphorus nucleus to a large extent. The crystal structure of NP[NH(CH$_2$)$_2$O](NSOCl)$_2$ has been determined by X-ray analysis. All the three oxygen atoms are on one side of the mean NPS-plane.

INTRODUCTION

Reaction of bifunctional reagents with the trimeric chloride, N$_3$P$_3$Cl$_6$ yields spirocyclic derivatives.[2-10] In only one case the formation of a mixed *ansa-spiro* compound, *viz.* N$_3$P$_3$Cl$_2$(O(CH$_2$)$_3$O)$_2$ has been demonstrated.[11] An *ansa* derivative[12] and a spirocyclic phosphazene with a P—Fe—Fe three membered ring[13] have also been reported. Two phosphazene rings bridged by a bifunctional reagent is also known.[14]

Recently, we have shown[6] that the sulfur containing ring systems NPCl$_2$(NSOX)$_2$ and (NPCl$_2$)$_2$NSOX (X = Ph, Cl) undergo a geminal replacement of chlorine atoms, when reacted with N,N'-dimethylethylenediamine. In this paper we report about the reactivity of systems NPCl$_2$(NSOX)$_2$ (X = Ph, Cl, F) towards aliphatic bifunctional reagents, varying the nature of the active groups as well as the number of bridging carbon atoms. A correlation between the ^{31}P NMR chemical shift of the spiro-bound phosphorus atom and the size of the spiro ring is briefly discussed.

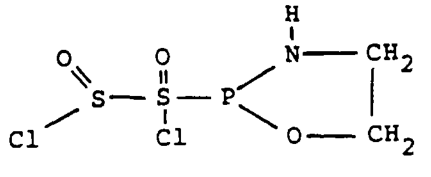
RESULTS AND DISCUSSION

Reaction of *trans*-NPCl$_2$(NSOPh)$_2$ (**1**), *cis*-NPCl$_2$(NSOCl)$_2$ (**2**) and *cis*-NPCl$_2$(NSOF)$_2$ (**3**) with 1,2-diaminoethane in acetonitrile yield the expected spirocyclic compounds NPR$_2$(NSOX)$_2$ [X = Ph(*trans*), Cl(*cis*), F(*cis*)] [R$_2$ =

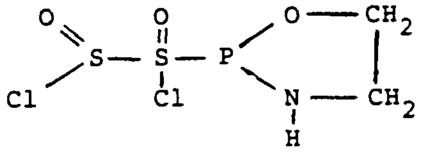
—$NH(CH_2)_2$—NH—]. The product obtained from the reaction of **2** and the diamine is highly moisture sensitive and decomposes to give an insoluble amorphous substance when exposed to atmospheric moisture. The decomposition is accompanied by the evolution of chlorine gas (qualitative test). The IR spectrum of this amorphous substance shows the retention of the characteristic frequency of the inorganic ring (1140, 1180 cm^{-1}), thus showing that the ring is not destroyed during reaction. A similar air-sensitive amorphous solid is obtained when **2** is treated with N,N'-dimethylethylenediamine in acetonitrile.[6]

Interestingly, the reaction of 1,3-propanediamine yields a stable product when reacted with **2**. Analogous, well-defined spirocyclic compounds could be isolated from the reaction of **1** and **3** with 1,3-propanediamine.

We have also carried out the reactions of $NPCl_2(NSOX)_2$ (X = Ph, Cl, F) with 2-aminoethanol and 3-aminopropanol. Although well-defined crystalline products *trans*-$NPR_2(NSOPh)_2[R_2 = NH(CH_2)_nO]$ [$n = 2, 3$] could be isolated from **1**, the reactions with **3** always yielded a resinous mixture of products. However, *cis*-$NPCl_2(NSOCl)_2$ (**2**) yields a crystalline product (**10**) when reacted with 2-aminoethanol. Two structures A & B (as depicted below) are possible for this compound.



[A]



[B]

In order to determine the correct structure for this compound, a single crystal X-ray determination was carried out. The results are given in Figure 1 and in Table I. As can be seen from Figure 1 and Table I, the compound **10** has the structure [B] depicted above, with all the oxygen atoms on one side of the mean plane.

It is known from the reaction of **2** with primary and secondary amines that the first chlorine replaced is the one *cis* to the oxygen atoms on sulfur.[15] So it is reasonable to assume that in the reaction of **2** with 2-aminoethanol, the first nucleophilic attack takes place on the oxygen side of the ring by means of the —NH_2 dent [—NH_2 being a better nucleophile than —OH]. This is followed by inversion about the phosphorus with the concurrent attack by the —OH group, on the oxygen side of the inorganic ring to form **10**.

Similarly, 3-aminopropanol gives the spirocyclic compound

$$NP[NH(CH_2)_3O](NSOCl)_2$$

(**11**)

when reacted with **2** in diethyl ether. Reaction in acetonitrile yields only a resinous material. By analogy, **11** is also expected to have the structure **B** with a six membered ring on phosphorus.

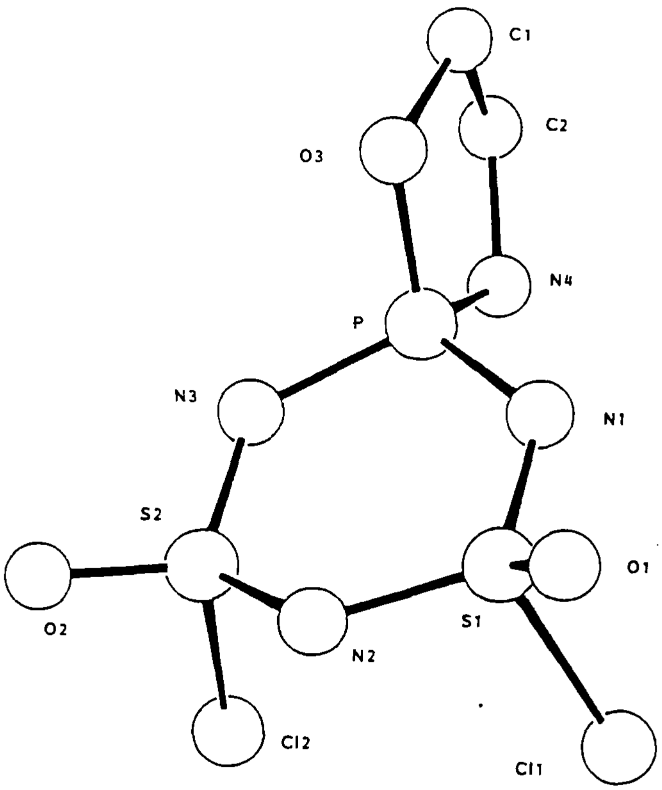


FIGURE 1. Molecular structure and adopted numbering scheme of $NP[NH(CH_2)_2O](NSOCl)_2$ (**10**).

TABLE I

Selected structural data for $NP[NH(CH_2)_2O](NSOCl)_2$ (**10**)

P—N1	1.608(5) Å	N1—P—N3	111.1(3)°
P—N3	1.613(6)	N1—S1—N2	116.6(3)
S1—N1	1.512(6)	N2—S2—N3	116.0(3)
S1-N2	1.574(6)	P—N1—S1	126.0(4)
S2—N2	1.584(5)	S1—N2—S2	119.8(4)
S2—N3	1.511(6)	P—N3—S2	125.6(4)
P—N4	1.613(7)	N4—P—03	98.0(3)
P—03	1.567(6)	01—S1—Cl1	104.0(3)
S1—01	1.433(5)	02—S2—Cl2	104.0(3)
S2—02	1.413(6)		
S1—Cl1	2.037(3)		
S2—Cl2	2.028(3)		

Distances of 01, 02 and 03 to the least-squares plane through PN1S1N2S2N3 (equation in orthogonal coordinates $-0.8741X' + 0.2977Y' - 0.3877Z' + 6.1143 = 0$).
01 −0.749, 02 −0.598, 03 −1.398 Å.

TABLE II

^{31}P NMR data of spirocyclic and primary-amino derivatives of $NPCl_2(NSOX)_2$ [X = Ph, Cl, F]

		δ_P	Ref.
trans-$NPCl_2(NSOPh)_2$	**(1)**	22.1^a	
$NP[NH(CH_2)_2NH](NSOPh)_2$	**(4)**	20.0^b	
$NP[NH(CH_2)_3NH](NSOPh)_2$	**(5)**	3.6^b	
$NP[NH(CH_2)_2O](NSOPh)_2$	**(6)**	22.5^c	
$NP[NH(CH_2)_3O](NSOPh)_2$	**(7)**	4.6^b	
$NP[MeN(CH_2)_2NMe](NSOPh)_2$		15.0^a	[6]
cis-$NPCl_2(NSOCl)_2$	**(2)**	28.6^a	
$NP[NH(CH_2)_2NH](NSOCl)_2$	**(8)**	18.7^c	
$NP[NH(CH_2)_3NH](NSOCl)_2$	**(9)**	8.0^c	
$NP[NH(CH_2)_2O](NSOCl)_2$	**(10)**	27.0^c	
$NP[NH(CH_2)_3O](NSOCl)_2$	**(11)**	5.2^c	
$NP[MeN(CH_2)_2NMe](NSOCl)_2$		14.5^a	[6]
cis-$NPCl_2(NSOF)_2$	**(3)**	31.9^a	
$NP[NH(CH_2)_2NH](NSOF)_2$	**(12)**	27.0^c	
$NP[NH(CH_2)_3NH](NSOF)_2$	**(13)**	10.6^a	
trans-$NP(NH_2)_2(NSOPh)_2$		7.1^c	[20]
$NP(NHEt)_2(NSOPh)_2$		6.7^a	[15]
$NP(NHPr^n)_2(NSOPh)_2$		7.0^a	[15]
cis-$NP(NH_2)_2(NSOCl)_2$		7.9^c	[20]
$NP(NHMe)_2(NSOCl)_2$		10.9^a	[15]
$NP(NHEt)_2(NSOCl)_2$		7.2^a	[15]
cis-$NP(NH_2)_2(NSOF)_2$		10.3^c	[20]
$NP(NHMe)_2(NSOF)_2$		13.0^a	[15]
$NP(NHEt)_2(NSOF)_2$		9.7^a	[15]

$^a CDCl_3$; ^{b}DMSO-d_6; $^c CD_3CN$

The ^{31}P NMR data for the known spirocyclic derivatives of the ring system $NPCl_2(NSOX)_2$ [X = Ph, Cl, F] along with their primary amino derivatives are summarized in Table II. As can be seen clearly, the chemical shift of the phosphorus nuclei incorporated in a five membered ring occurs at a much lower field than observed for the primary amino derivatives. The chemical shift of $\equiv$ P (spiro) in derivatives containing a six membered spiro ring is equal or slightly upfield (X = Ph). Similar observations have been made for the spirocyclic derivatives of $(NPCl_2)_3$ and $(NPCl_2)_4$.[3] These observations can be explained from the steric strain in the five-membered ring leading to a decrease of the π-electron release from the exocyclic groups to the phosphorus atom.[3] Similar arguments have also been advanced by Westheimer [16] to explain the rapid hydrolysis of five membered cyclic phosphate esters.

EXPERIMENTAL

General. All experiments were carried out under dry nitrogen. Solvents were purified and dried by conventional methods. 1,2-diaminoethane, 1,3-diaminopropane, 2-aminoethanol, and 3-aminopropanol were purified by distillation, the former two over KOH pellets, the latter two over molecular sieves. *trans*-$NPCl_2(NSOPh)_2$[17], *cis*-$NPCl_2(NSOCl)_2$[18] and *cis*-$NPCl_2(NSOF)_2$[19] were prepared by previously reported methods. Elemental analyses (on C, H, N and S) were performed in the Microanalytical Department of this University under supervision of Mr. A. F. Hamminga. All compounds isolated gave satisfactory analytical data. Infrared spectra were recorded on a Hitachi-EPI-9 spectrometer using KBr discs. ^{31} P NMR spectra (proton-noise decoupled) were recorded on a Nicolet 283 A FT spectrometer

TABLE III

Reaction conditions, melting points of the products

Starting compound	$H_2N(CH_2)_nX$		Product	Solvent for crystallization	Yield %	M. P. °C
	n	X				
(1)	2	NH_2	(4)	MeCN	24	300-303
(1)	3	NH_2	(5)	MeCN	40	288-290
(1)	2	OH	(6)	CH_2Cl_2	27	193-194
(1)	3	OH	(7)	CH_2Cl_2	21	166-168
(3)	2	NH_2	(12)	Et_2O-nC_5H_{12} (3:1)	16	185-187
(3)	3	NH_2	(13)	Et_2O-nC_5H_{12} (2:1)	17	140-142
(2)	2	NH_2	(8)	(a)		
(2)	3	NH_2	(9)	Et_2O-nC_5H_{12} (2:1)	15	153-155
(2)	2	OH	(10)	CH_2Cl_2	13	155-157
(2)	3	OH^b	(11)	CH_2Cl_2	20	168-169

[a] Could not be crystallized from common solvents, decomposition at 154°C (DTA); $m/e = 297$ ($M^{35}Cl$ 2%), 262 ($M^{35}Cl$—^{35}Cl, 100%).

[b] Reaction carried out in Et_2O.

operating at 80.9 MHz using 85% H_3PO_4 as an external reference. Low field shifts are positive. Proton NMR spectra were recorded with a Jeol C60-HL instrument using TMS as internal standard. Mass spectra were taken on an AEI MS9 spectrometer at 70 eV with an accelerating voltage of 8 kV. Single crystal X-ray studies at 298° K were performed on an Enraf-Nonius CAD4-SDP23M diffractometer, using graphite monochromated MoKα radiation ($\lambda = 0.7107$ Å). All calculations were carried out on a PDP-11/23, making use of Enraf-Nonius CAD4-SDP programs.

Preparation. 3.5 mmoles of $NPCl_2(NSOX)_2$ were dissolved in 30 ml acetonitrile. The solution was stirred and cooled to -17°C. 7.0 mmoles of the bifunctional reagent $H_2N(CH_2)_nY[n = 2, 3, Y = NH_2, OH]$ dissolved in 20 ml acetonitrile was added dropwise and the reaction mixture allowed to warm to room temperature and stirred for a further 17 hrs. After filtration of the aminehydrochloride under dry conditions, the solvent was evaporated under vacuum. The residue was recrystallized from a suitable solvent or solvent mixture. The results are summarized in Table III.

Structure determination of **10**. A suitable crystal (0.25 × 0.23 × 0.50 mm) grown from CH_2Cl_2 was glued on top of a glass fiber. 24 reflections with $14.6° \leqslant \theta \leqslant 18.7°$ were used to refine the cell parameters. The intensities of 2294 unique reflections ($1° \leqslant \theta \leqslant 35°$) were collected by the ω-2θ scan technique, 1683 reflections having $I \geqslant 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects. No absorption corrections were applied. The structure was solved by direct methods (Multan 82) and refined on F by full matrix least-squares techniques with anisotropic thermal parameters. Hydrogen atoms were not included in the refinement. Convergence was reached at R = 0.067, $R_w = 0.073$ (w = 1). The atoms O(3) and N(4) could be discerned unambiguously. A refinement with O(3) = N led to a lower temperature factor, than that found for N(4) while the final difference fourier map showed two peaks at 0.2Å from N with an electron density 1.42 $eÅ^{-3}$ (peak height elsewhere $\leqslant 0.6eÅ^{-3}$).

Crystal data. $C_2H_5N_4O_3PS_2Cl_2$. M = 299.10. Orthorhombic spacegroup $Pna2_1$, a = 10.534(7), b = 8.892(1), c = 10.703(1) Å, V = 1002.6 $Å^3$, Z = 4, $D_c = 1.986$ gcm^{-3}, $\mu(MoK\alpha) = 11.95$ cm^{-1}, F(000) = 600.

Note. Positional and anisotropic thermal parameters, a listing of bond lengths and angles and a table of least-squares planes of the molecule are deposited with the Cambridge Crystallographic Data Centre (CCDC), UK.

REFERENCES

1. F. J. Viersen, E. Bosma, B. de Ruiter, K. S. Dhathathreyan and J. C. van de Grampel, *Phosphorus and Sulfur*, submitted for publication.
2. S. S. Krishnamurthy, K. Ramachandran, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *J. Chem. Soc. Dalton Trans.*, 840 (1980).
3. V. Chandrasekhar, S. S. Krishnamurthy, A. R. Vasudeva Murthy, R. A. Shaw and M. Woods, *J. Chem. Soc. Dalton Trans.*, 621 (1984); V. Chandrasekhar, S. Karthikeyan, S. S. Krishnamurthy and M. Woods, Unpublished results.
4. Y. Sudhakar Babu, H. Manohar, K. Ramachandran and S. S. Krishnamurthy, *Z. Naturforsch.*, **33B**, 588 (1978).
5. S. R. Contractor, M. B. Hursthouse, L. S. Shaw (Nee Gözen), R. A. Shaw and H. Yilmaz, *Acta Cryst.*, **B41** (Part 2), 122 (1985).
6. B. de Ruiter, G. Kuipers, J. H. Bijlaart and J. C. van de Grampel, *Z. Naturforsch.*, **37B**, 1425 (1982).
7. T. Chivers and R. Hedgeland, *Can. J. Chem.*, **50**, 1017 (1972).
8. H. R. Allcock, *Phosphorus Nitrogen Compounds, Cyclic, Linear and High Polymeric Systems*, Academic Press, New York and London (1972).
9. K. Brandt and Z. Jedlinski, *J. Org. Chem.*, **45**, 1672 (1980).
10. N. E. Murr, R. Lahana, J. F. Labarre and J. P. Declereq, *J. Mol. Str.*, **117**, 73 (1984) and references cited therein.
11. S. R. Contractor, M. B. Hursthouse, H. G. Parkes, L. S. Shaw, R. A. Shaw and H. Yilmaz, *J. Chem. Soc. Chem. Commun.*, 675 (1984).
12. P. J. Harris and K. B. Williams, *Inorg. Chem.*, **23**, 1495 (1984).
13. P. P. Greigger and H. R. Allcock, *J. Am. Chem. Soc.*, **101**, 2492 (1979).
14. G. Guerch, J. F. Labarre, R. Lahana, R. Roques and F. Sournies, *J. Mol. Str.*, **99**, 275 (1983).
15. C. Cnossen-Voswijk and J. C. van de Grampel, *Z. Naturforsch.*, **34B**, 550 (1979); C. Cnossen-Voswijk and J. C. van de Grampel, unpublished results.
16. F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968).
17. J. B. van den Berg, B. de Ruiter and J. C. van de Grampel, *Z. Naturforsch.*, **31B**, 1216 (1976).
18. B. de Ruiter, Ph.D Thesis, University of Groningen (1981).
19. H. H. Baalmann and J. C. van de Grampel, *Rec. Trav. Chim. Pays-Bas*, **92**, 716 (1973).
20. H. Winter and J. C. van de Grampel, *Z. Naturforsch.*, **38B**, 1652 (1983)