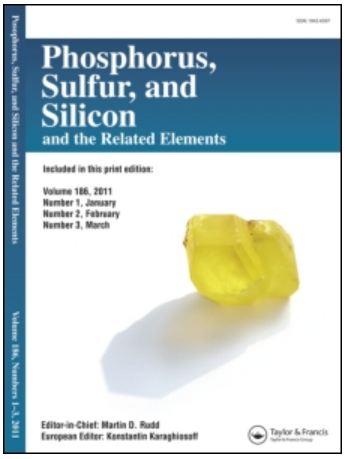

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CYCLENPHOSPHINE SELENIDE: THE STRONGEST P INTERACTION IN THE CHALCOGENIDE (O,S,Se) DERIVATIVES

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CYCLENPHOSPHINE SELENIDE: THE STRONGEST N→P INTERACTION IN THE CHALCOGENIDE (O,S,Se) DERIVATIVES

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The cyclenphosphine selenide is prepared by reaction of molecular selenium on cyclenphosphorane. Its physicochemical properties are compared to those of oxygen and sulfur analogues.

Keywords: cyclenphosphine oxide; cyclenphosphine sulfide; cyclenphosphine selenide; benzylselenophosphorane; benzoylcyclenphosphine selenide

INTRODUCTION

The interest in N-substituted tetraazamacrocycles owing to their many applications in imaging and radioimmunotherapy considerably increased during the past decade[1]. In previous paper, we showed that the phosphoryl and thiophosphoryl group is able to bind three nitrogen atoms of cyclic tetramines to give intermediates where the free nitrogen remains available for alkylation[2,3]. By comparison with triprotected derivatives of higher homologues the behavior of cyclenphosphine oxide and cyclenphosphine sulfide is rather unusual, but consistent with a transannular N→P interaction[3,4].

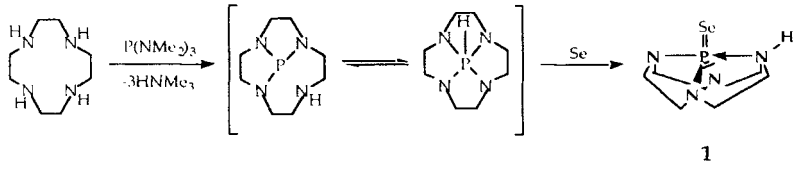
In this paper we describe the synthesis and reactivity of cyclenphosphine selenide, and we report on the preparation of some derivatives. In addition, cyclenphosphine oxide and cyclenphosphine sulfide are compared to cyclenphosphine selenide.

* Corresponding Author.

RESULTS AND DISCUSSION

Synthesis and reactivity

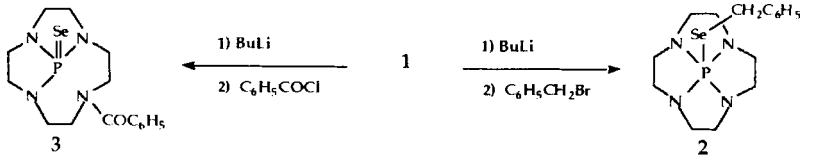
Cyclenphosphine selenide **1** was obtained in good yields after the transamination of hexamethylphosphorous triamide with cyclen followed by the reaction of molecular selenium (scheme 1).



1

SCHEME 1

Cyclenphosphine selenide and sulfide[5] have a very similar reactivity. So, when **1** was treated with one equivalent of BuLi in THF, subsequent addition of an alkylating reagent led either to Se-alkylated or to N-alkylated derivatives, depending on the electrophile. As the first step of the reaction obviously consists in the formation of the anion, we can conclude that an electronic delocalization on the Se-P-N chain occurs. Like sulfur, selenium is a soft nucleophilic center, able to react with soft electrophiles such as benzylbromide to give cyclen benzylselenophosphorane **2**. The nitrogen of the secondary amine reacts with benzoylchloride as a hard nucleophilic center to give N-benzoyl cyclenphosphine selenide **3** (scheme 2).



3 2

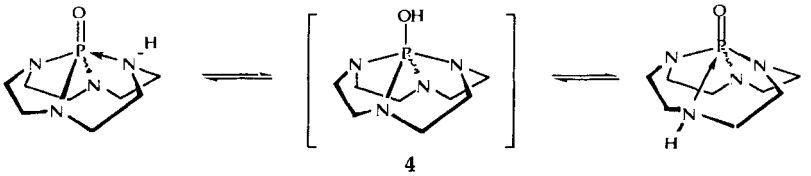
SCHEME 2

IR and NMR analysis

The spectroscopic data of cyclenphosphine selenide and of its oxide and sulfide homologues are summarized in table I. The infrared spectrum in CH_2Cl_2 shows a notable decrease of the free N-H stretching band of cyclenphosphine chalcogenides (cyclenPX with X = O, S, Se) in the following order O > S > Se. Compared to secondary amines[6] and cyclamPX derivatives[7] ($\upsilon_{N\text{-}H}$ = 3330 cm^{-1}), the low free N-H band frequency suggests a strong transannular interaction between nitrogen and the phosphorus atom when X = Se. It is more limited when X = S and nearly non-existent when X = O.

Further evidences in support of an N→P interaction were obtained from NMR data. In any case, the ^{31}P NMR spectrum in $CDCl_3$ exhibited a signal within the two extreme values corresponding to the pentacoordinated and tetracoordinated phosphorus species in which the N→P interaction is not structurally allowed. So for monomeric cyclenPO (in diluted solution) a signal at 10 ppm is consistent with a relatively weak N→P interaction. For cyclenPS, the ^{31}P signal appears halfway between P=S and P-S-R derivatives indicating a more marked interaction. The ^{31}P NMR chemical shift of cyclenPSe, much more shielded at 2 ppm, is in favor of a strong N→P interaction[8]. For this last compound, the weakening of the coupling constant (J_{PSe} = 774 Hz) supports this statement.

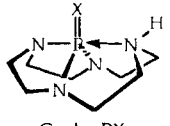
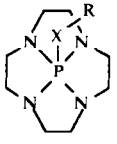
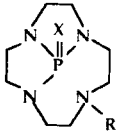
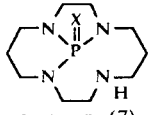
The ^{13}C NMR spectrum of cyclenPX compounds depends strongly on temperature and solvent. For cyclenPO, Richman and Kubale[4] have observed four distinct carbons variously coupled with phosphorus at −39°C in chloroform-*d*. At higher temperatures a collapse occured and, when heating up to 52°C the spectrum exhibited a doublet. The intermediacy of hydroxyphosphorane **4** was suggested for the carbon exchange process (scheme 3).



4

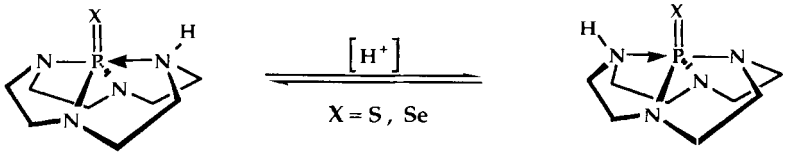
SCHEME 3

TABLE I IR and ^{13}C NMR Data

X	 CyclenPX			*$XP(NMe_2)_3$*	 CyclamPX(7)	
	$\nu_{N\text{-}H}$ *(Cm^{-1})*	$\delta^{31}P$ *(ppm)*	$\delta^{31}P$ *(ppm)*	$\delta^{31}P$ *(ppm)*	$\delta^{31}P$ *(ppm)*	$\delta^{31}P$ *(ppm)*	$\nu_{N\text{-}H}$ *(cm^{-1})*
O(2,4)	3330	+10[a]	-20.4[b]	+25[c]	+25	+26.4	3330
S(5)	3280	+31.5	-18.8[c]	+84.2[d]	+81.4	+79.4	3330
Se	3230	+4 J(PSe)= 774 Hz	-23.3[c] J(pse)= 270 Hz	+79.3[d] $J_{(PSe)}$= 841 Hz	+83.5 $J_{(PSe)}$= 823 Hz	+77.7 $J_{(PSe)}$= 812 Hz	3330

a : Chemical shift extrapolated for monomeric cyclenPO[4].
b : R = CH_3
c : R = $CH_2C_6H_5$
d : R = COC_6H_5.

A similar fluxional behaviour was described for cyclenPS, except that two well resolved peaks slightly split are observed at 60°C; they correspond to a proton transfer between the two apical nitrogen atoms in a pseudotrigonal bipyramidal structure (scheme 4). For cyclenPSe, four distinct carbons at 42.9, 45.1 (d, $J_{PC} = 115.8$ Hz), 46.5, 47.8 ppm were also observed at −10°C, but at 60°C two broad signals were displayed at 44.4 and 47.0 ppm, therefore the exchange process is notably slower.



SCHEME 4

In CD_3OD, the exchange was fast and two signals were observed at low temperature for the three derivatives. This is in agreement with a rapid exchange involving a proton tranfer between apical nitrogen atoms, and the participation of the protic solvent. At higher temperature the signals remained sharp for cyclenPS and cyclenPSe while the spectrum of cyclenPO evolved to a single doublet in ^{13}C NMR as observed in aprotic medium.

CONCLUSION

Our results establish a transannular N→P interaction for cyclenphosphine chalcogenides, increasing from oxygen to selenium. CyclenPSe and cyclenPS are very similar; from this point of view, the behavior of cyclenPS and cyclenPSe on the one hand, and of CyclenPO on the other hand is notably different. Whereas a rapid prototropy (catalyzed by protic solvent) which exchanges apical nitrogen atoms and maintains the uniqueness of carbon sites adjacent to axial and equatorial nitrogen position is only involved for, cyclenPS and cyclenPSe, the tautomeric cyclenhydroxyphosphorane form participates in the further carbon scrambling process which rapidly exchanges the four positions at higher temperature. Similar tautomeric cyclenthiophosphorane and cyclenselenophosphorane were not

detected in our experiments; however the corresponding anion was easily obtained, leading with soft electrophiles to alkylthio- or alkylselenophosphorane derivatives.

In a further step, we will investigate the coordination properties of these compounds. They should be able to act like bidentate ligands[9].

EXPERIMENTAL SECTION

Instrumentation

Infrared spectra were obtained on a Bomem Michelson 100 spectrophotometer. All ^{1}H and ^{13}C NMR were recorded on Brucker AC300 spectrometer (75.47 MHz for C) (d:doublet, m: multiplet, w: wide) ; chemical shifts are given in ppm downfield from external TMS reference. ^{31}P NMR spectra were recorded on JEOL FX 100 spectrometer (40.26 MHz) and Brucker AC300 spectrometer (121.49 MHz) ; chemical shifts are given in ppm downfield from external 85% H_3PO_4. Mass spectra were obtained on a Hewlet Packard GC/MS HP 5995C. All the reactions were run under nitrogen using freshly distilled and dry solvents.

Cyclenphosphine selenide 1

1 mmol of cyclen (1,4,7,10-tetraazacyclododecane) in toluene (30 mL) was refluxed with hexamethylphosphorus triamide (1 mmol) until dimethylamine evolution ceased, and 1 mmol of selenium was added to the solution. The resulting mixture was then refluxed for two hours. After filtering the solution and cooling it at room temperature, white spangles were obtained. The solution was removed and the solid **1** was dried (90% yield). ^{31}P NMR : ($CDCl_3$) 4 ppm (J_{PSe} = 774 Hz) ; (CD_3OD) −8 ppm (J_{PSe}= 650 Hz). ^{13}C NMR ($CDCl_3$, −10°C) : 42.9 (2 N-$\underline{C}H_2$), 45.1 (d, 2 N-$\underline{C}H_2$, J_{PC} = 115.8 Hz), 46.5 (2 N-$\underline{C}H_2$), 47.8 ppm (2 N-$\underline{C}H_2$). ^{13}C NMR (CD_3OD, −10°C) : 44.4 (br, 4 N-$\underline{C}H_2$), 47.3 ppm (br, 4 N-$\underline{C}H_2$), ^{1}H NMR ($CDCl_3$, −10°C) : 2.4 (m, 2H), 2.6 (m, 2H), 2.7 (m, 1H), 3 (m, 7H), 3.3 (m, 2H), 3.4 (m, 2H), 3.9 ppm (N-H). ^{1}H NMR (CD_3OD, -10°C) : 2.6 (br, 4H), 2.9 (br, 6H), 3.1 (br, 2H), 3.3 (br, 4H). IR (CH_2Cl_2) : υ_{N-H} = 3230 cm^{-1}. Mass spectrum m/z (%) : M+1 = 280 (56) ; 279 (11) ; 199 (100). Anal. calc. for $C_8H_{17}N_4PSe$: C, 34.41 ; H, 6.10 ; N, 20.07 ; P, 11.11; Se, 28.31 ;

found : C, 34.5 ; H, 6.1; N, 19.6 ; P, 10.6 ; Se, 28.3. The same procedure can give cyclamphosphine selenide.

General procedure for N- and Se-alkylation

After cooling at –30°C a mixture of **1** (1 mmol) in THF (30 mL), n-butyllitium (1 mmol) was added and allowed to react for 20 min. The alkylating reagent (1 mmol) was added and the mixture stirred at room temperature for about one night. The solvent was removed under reduced pressure and the residue solubilized with CH_2Cl_2. After filtration and evaporation of solvent, **2** and **3** were obtained.

Cyclen(benzylseleno)phosphorane 2

95% yield. ^{31}P NMR ($CDCl_3$) : –23.6 ppm (J_{PSe} = 270 Hz). ^{13}C NMR ($CDCl_3$) : 30.3 (d, Se-$\underline{C}H_2$ J_{PC} = 5 Hz), 44.4 (d, 8 N-$\underline{C}H_2$, J_{PC} = 9.8 Hz), 125.6 (1C, Φ), 128.1 (2C, Φ), 128.5 (2C, Φ), 142.5 ppm (d, 1C Φ, J_{PC} = 3,2 Hz). ^1H NMR ($CDCl_3$) : 2.7–3 (m, 16 H), 3.8 (d, Se-C$\underline{H}_2$, $^3J_{PH}$ = 10.2 Hz), 7.1–7.4 ppm (m, 5H, Φ). Mass spectrum m/z (%) : 199 (100); 91 (72).

N-benzoylcyclenphosphine selenide 3

96% yield. ^{31}P NMR ($CDCl_3$) : 79.3 ppm (J_{PSe} = 841 Hz). ^{13}C NMR ($CDCl_3$) : 45.2 (d, 1 N-$\underline{C}H_2$, J_{PC} = 5.2 Hz), 47.3 (d, 1 N-$\underline{C}H_2$, J_{PC} = 5.6 Hz), 50.8 (1 N-$\underline{C}H_2$), 51 (m, 3 N-$\underline{C}H_2$), 51.5 (d, 1 N-$\underline{C}H_2$, J_{PC} = 14.2 Hz), 51.8 (1 N-$\underline{C}H_2$), 126 (2 C, Φ), 128.3 (2 C, Φ), 128.9 (1 C, Φ), 137.2 (1 C, Φ), 172.4 ppm (C=O). 1H NMR ($CDCl_3$) : 2,6 (m, 1H), 2.7–3.2 (m, 7H), 3.4–3.7 (m, 6H), 4 (m, ^1H), 4.2 (m, 1H), 7.3 (m, 3H, Φ), 7.60 ppm (m, 2H, Φ). IR (CH_2Cl_2) : $\upsilon_{C=O}$=1630 cm^{-1}. Mass spectrum m/z (%) : M+1 = 384 (17) ; 303 (48) ; 199 (100) ; 77(19).

Acknowledgements

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References

[1] R.B. Lauffer, *Chem. Rev.* **87,** 901 (1987). X. Wang, ;T. Jin, V. Comblin, A. Lopez-Mut, E. Merciny and J.F. Desreux, *Inorg. Chem.*. **31**, 1095 (1992).

[2] A. Filali, J.J. Yaouanc and H. Handel, *Angew. Chem. Int. Ed. Engl.*. **30**, 560 (1991).

[3] I. Gardinier, A. Roignant, N. Oget, H. Bernard, J.J. Yaouanc and H. Handel, *Tetrahedron Lett.* **37**, 7711 (1996).

[4] J.E. Richman and J.J. Kubale, *J. Am. Chem. Soc.* **105,** 749 (1983).
[5] N. Oget, F. Chuburu, J.J. Yaouanc and H. Handel, *Tetrahedron* **52,** 2995 (1996).
[6] F. Jeanneaux, J.G. Riess , J. Wachter, *Inorg. Chem.* **19,** 2169 (1980).
[7] F. Bouvier and J.M. Dupart, *Synth. React. Inorg. Met. Org. Chem.* **17,** 301 (1987).
[8] D.V. Kashnis, M. Lattman and U. Siriwardane, *Organometallics* **10,** 1326 (1991).
[9] M. Bochmann, G. C. Bwembya, N. Whilton, X. Song, M. B. Hursthouse, S. J. Coles and A. Karavlov, *J. Chem. Soc. Dalton Trans.*, 1887 (1995).