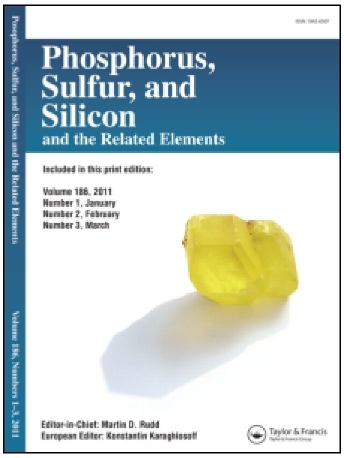

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Ring Transformations of Phosphorus-Selenium Heterocycles

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The compounds $(PhP)_3Se_2$ **I** and $[\{PhPSe(\mu\text{-}Se)\}_2]$ **II**, prepared by selenium oxidation of the homocycle $(PhP)_5$, react with simple unsaturated organic substrates to give highly unusual P-Se-C-N containing heterocycles.

Keywords: Phosphorus; Selenium; Heterocycles

Introduction

The pentaphosphorus homocycle $(PhP)_5$ is a convenient precursor to mixed phosphorus-selenium heterocycles such as $(PhP)_3Se_2$ **I** and $[\{PhPSe(\mu\text{-}Se)\}_2]$ **II**.[1,2] However, little attention has been paid to these molecules as potential synthetic reagents, for example in selenation reactions.[3,4] We describe here some results of our investigations in the reactivity of **I** and **II** with dialkyl cyanamides and norbornene.

Results and Discussion

An X-ray crystallographic analysis has finally confirmed the structure of **II** as a diselenadiphosphetane diselenide (Fig. 1). The central $P_2(\mu\text{-}Se)_2$ ring is planar with a *trans* arrangement of the exocyclic P=Se bonds. Thus **II** is a structural analogue of Lawesson's Reagent, $[\{(p\text{-}MeOC_6H_4)PS(\mu\text{-}S)\}_2]$.

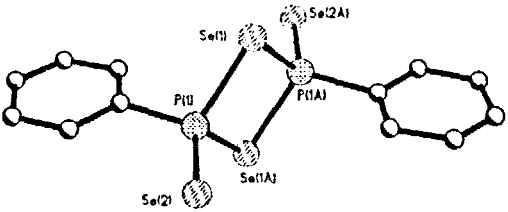

Figure 1 X-Ray crystal structure of [{PhPSe(μ-Se)}$_2$] **II**

The reaction between **II** and R_2N-CN (R_2N = Me_2N, -$(CH_2)_5$- or -$CH_2CH_2OCH_2CH_2$-) gives 1,6,6aλ^4-triselena-3a-phospha-3,4-diazapentalenes in low yields, which contain two fused PSe_2CN rings (Fig. 2).[5] The Se-Se distances in the *N*-morpholino compound are approximately equal [2.621(1), 2.648(1) Å], but differ markedly in the (isostructural) dimethylamino derivative [2.578(1), 2.703(1) Å]. The P^V=Se distances, *ca.* 2.22 Å, are exceptionally long, reflected by the very low ^1J(P-Se) coupling of 320 Hz.

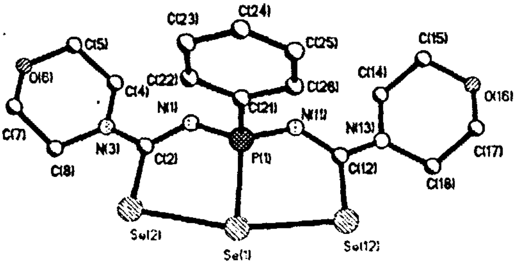

Figure 2 X-Ray crystal structure of
[O(CH$_2$CH$_2$)N-C(Se)=N]$_2$P(Se)Ph

The reaction of **II** with norbornene gives an orange compound characterised crystallographically as $PhP(Se)Se_2(C_7H_{10})$, which contains a saturated 1,2-diselena-3-phospholane (PSe_2C_2) ring (Fig. 3).

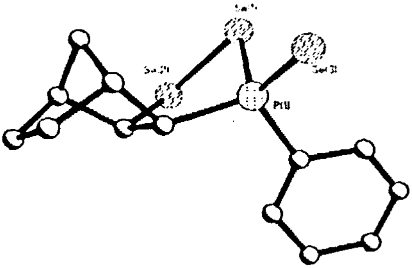

Figure 3 X-Ray crystal structure of $PhP(Se)Se_2(C_7H_{10})$

The C_2PSe_2 ring has an envelope conformation with Se(1) displaced by 1.1 Å from the (approximately planar) P(1)-C(1)-C(2)-Se(2) chain, with P(1)-Se(1) 2.232(2) Å and P(1)-Se(3) 2.117(2) Å. The ${}^1J$(P-Se) couplings, 353 and 773 Hz, confirm the presence of both single and double phosphorus-selenium bonds.

The triphospholane $(PhP)_3Se_2$ **I** reacts with the nitrile group in R_2N-CN ($R_2N = Me_2N$, $-(CH_2)_5-$ or $-CH_2CH_2OCH_2CH_2-$) with retention of the P-P bond to give mixed P(III)-P(V) species containing a non-planar P_2SeNC ring (Fig. 4). These compounds can be considered as special cases of "true" heterocycles, the two phosphorus atoms being in different oxidation states. The P(1)-P(2) distance is 2.2379(14) Å, in the ${}^{31}P\{{}^1H\}$ NMR the ${}^1J$(P-P) coupling is 270 Hz.

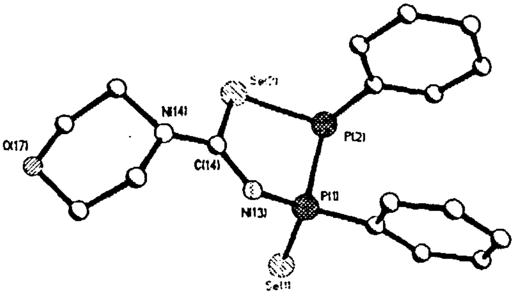

Figure 4 X-Ray crystal structure of PhP-P(Se)(Ph)-N=C(*N*-morph)-Se

Conclusions

Unusual P-Se-C-N containing heterocycles are generated from the reactions between $(PhP)_3Se_2$ or $[\{PhPSe(\mu\text{-}Se)\}_2]$ with simple organic molecules.

Acknowledgements

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