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Ring Transformations of Phosphorus-Selenium Heterocycles

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The compounds $(\text{PhP})_3\text{Se}_2$ **I** and $[\{\text{PhPSe}(\mu\text{-Se})\}_2]$ **II**, prepared by selenium oxidation of the homocycle $(\text{PhP})_5$, react with simple unsaturated organic substrates to give highly unusual P-Se-C-N containing heterocycles.

Keywords: Phosphorus; Selenium; Heterocycles

Introduction

The pentaphosphorus homocycle $(\text{PhP})_5$ is a convenient precursor to mixed phosphorus-selenium heterocycles such as $(\text{PhP})_3\text{Se}_2$ **I** and $[\{\text{PhPSe}(\mu\text{-Se})\}_2]$ **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 $\text{P}_2(\mu\text{-Se})_2$ ring is planar with a *trans* arrangement of the exocyclic $\text{P}=\text{Se}$ bonds. Thus **II** is a structural analogue of Lawesson's Reagent, $[\{(\text{p-MeOC}_6\text{H}_4)\text{PS}(\mu\text{-S})\}_2]$.

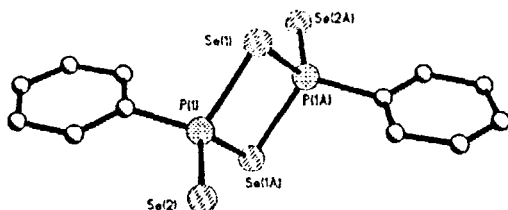


Figure 1 X-Ray crystal structure of $[(\text{PhPSe}(\mu\text{-Se}))_2] \text{ II}$

The reaction between **II** and $\text{R}_2\text{N-CN}$ ($\text{R}_2\text{N} = \text{Me}_2\text{N}$, $-(\text{CH}_2)_5-$ or $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$) gives 1,6,6a λ^4 -triseleno-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 $\text{P}^{\text{V}}=\text{Se}$ distances, *ca.* 2.22 Å, are exceptionally long, reflected by the very low $^1J(\text{P-Se})$ coupling of 320 Hz.

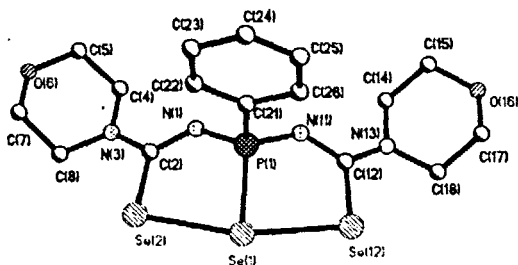


Figure 2 X-Ray crystal structure of $[\text{O}(\text{CH}_2\text{CH}_2\text{N}-\text{C}(\text{Se})=\text{N})]_2\text{P}(\text{Se})\text{Ph}$

The reaction of **II** with norbornene gives an orange compound characterised crystallographically as $\text{PhP}(\text{Se})\text{Se}_2(\text{C}_7\text{H}_{10})$, which contains a saturated 1,2-diselena-3-phospholane (PSe_2C_2) ring (Fig. 3).

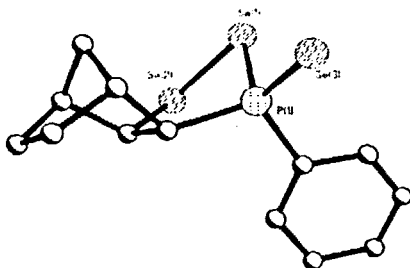


Figure 3 X-Ray crystal structure of $\text{PhP}(\text{Se})\text{Se}_2(\text{C}_7\text{H}_{10})$

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 $^1J(\text{P-Se})$ couplings, 353 and 773 Hz, confirm the presence of both single and double phosphorus-selenium bonds.

The triphospholane $(\text{PhP})_3\text{Se}_2$ **I** reacts with the nitrile group in $\text{R}_2\text{N-CN}$ ($\text{R}_2\text{N} = \text{Me}_2\text{N}$, $-(\text{CH}_2)_5-$ or $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$) 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 $^{31}\text{P}\{^1\text{H}\}$ NMR the $^1J(\text{P-P})$ coupling is 270 Hz.

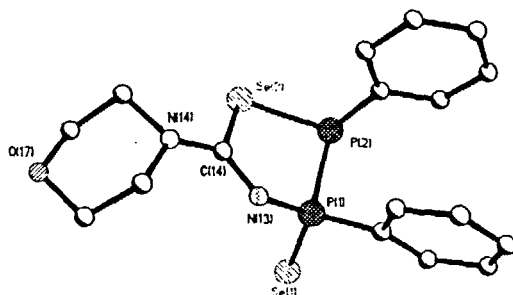


Figure 4 X-Ray crystal structure of
 $\text{PhP-P(Se)(Ph)-N=C(N-morph)-Se}$

Conclusions

Unusual P-Se-C-N containing heterocycles are generated from the reactions between $(\text{PhP})_3\text{Se}_2$ or $[\{\text{PhPSe}(\mu\text{-Se})\}_2]$ with simple organic molecules.

Acknowledgements

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