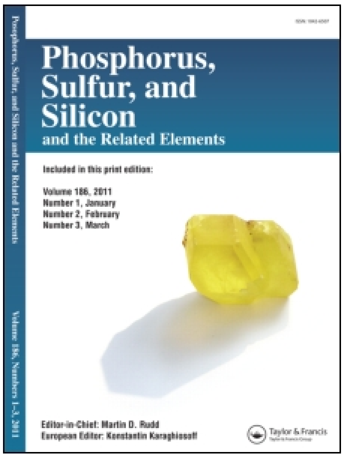

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Phosphorus-Nitrogen-Selenium Ring Systems

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PHOSPHORUS-NITROGEN-SELENIUM RING SYSTEMS

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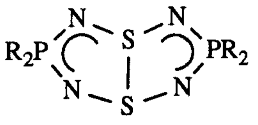
T2N 1N4

Abstract Diphosphadiselenatetrazocines, 1,5-$R_4P_2N_4Se_2$ (R = Me, Et, Ph) and 1,3-$R_4P_2N_4Se_2$ (R = Me, Et), have been prepared in good combined yields from the cyclocondensation of $R_2PN_2(SiMe_3)_3$ with '$SeCl_3$'. The compound 1,5-$Ph_4P_2N_4Se_2$ dissociates into $Ph_2PN_2Se\bullet$ radicals identified by ESR spectroscopy. Metal complexes $(Ph_3P)_2M(Se_2N_4P_2Ph_4)$ (M = Pt, Pd) have been prepared from the reaction of 1,5-$Ph_4P_2N_4Se_2$ with $(Ph_3P)_2PtC_2H_4$ and $(Ph_3P)_4Pd$, respectively. The Se,Se'-dialkyl derivatives 1,5-$Ph_4P_2N_4Se_2R_2$ undergo isomerization to produce 1,3-$Ph_4P_2N_4Se_2R_2$ in the solid-state (R = Me, Et) or, more rapidly, in solution (R = Me, Et, Ph).

INTRODUCTION

The preparation and characterization of cyclophosphathiazenes (P-N-S rings) containing two or three coordinate sulfur have been studied extensively. These heterocycles include 1,5-$R_4P_2N_4S_2$, 1, a butterfly or folded shaped ring with the unusual feature of a transannular S-S bond, and 1,3-$R_4P_2N_4S_2$, 2, a structural isomer of 1.



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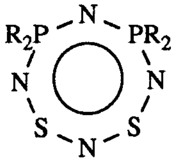
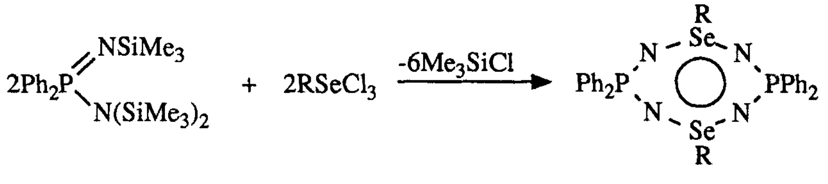


2

Cyclophosphaselenazenes with three coordinate selenium have been previously reported.[1] Eight-membered rings of the type 1,5-$Ph_4P_2N_4Se_2R_2$, 3 (R = Me, Et, Ph) were prepared via the cyclocondensation of $Ph_2PN_2(SiMe_3)_3$ with $RSeCl_3$. In the cases where R = Me or Et the reaction also produces 1,5-$Ph_4P_2N_4Se_2$ (Se analogue of 1) in low yields.

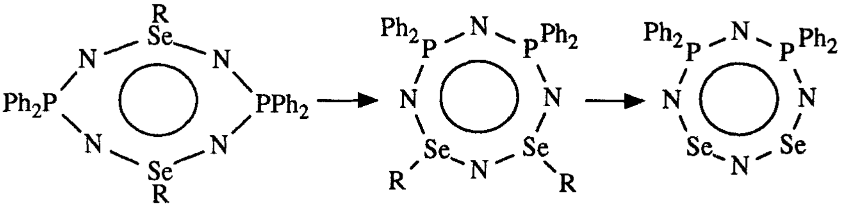

(1)

3

New aspects of the chemistry of P-N-Se rings that will be discussed herein include (a) the isomerization of 1,5-$Ph_4P_2N_4Se_2R_2$, (b) the synthesis and characterization of Se analogues of 1 and 2, (c) the dissociation of 1,5-$Ph_4P_2N_4Se_2$ into Ph_2PN_2Se• radicals, and (d) the formation of Pt and Pd complexes of 1,5-$Ph_4P_2N_4Se_2$.

ISOMERIZATION OF 1,5-$Ph_4P_2N_4Se_2R_2$

When pure 1,5-$Ph_4P_2N_4Se_2R_2$, 3 (R = Me, Et) is left under an inert, dry atmosphere at room temperature (glove box) for a few weeks it undergoes a slow transformation *in the solid state* to produce 1,3-$Ph_4P_2N_4Se_2R_2$, 4, (ca. 90%), and 1,3-$Ph_4P_2N_4Se_2$, 5, (ca. 10%). The sequence of formation is as shown in equation (2) based on the observation that 5 is slowly produced from pure 4 under similar conditions. The Se,Se'-diphenyl derivative, 3 (R = Ph), is stable towards isomerization in the solid state.

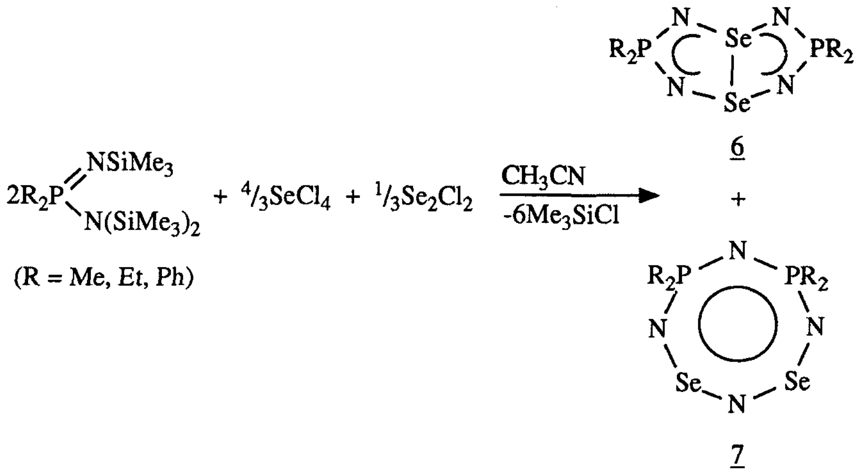

(2)

3 (white) 4 (peach) 5 (yellow)

During the course of these transformations a color change from white (3) to peach (4 + 5) was observed. The combined yields of (4 + 5) are quantitative, and 5 can be easily separated from 4 by washing with acetonitrile. Compounds 3 and 4 can be stored at -20°C to prevent these transformations from occurring. Quantitative isomerization of 3 into 4 also takes place when a CH_2Cl_2 solution of 3 (R = Me, Et) is left at 25°C for 3-5 days or when a toluene solution of 3 is heated at reflux for 15 min (R = Et), 2h (R = Me) or 60h (R = Ph).

SYNTHESIS OF $R_4P_2N_4Se_2$ ISOMERS

In view of the low yields of both 1,3- and 1,5-$Ph_4P_2N_4Se_2$ as described above, a new synthetic route was developed. This procedure involves the cyclocondensation of six molecules of $R_2PN_2(SiMe_3)_3$ with four molecules of $SeCl_4$ and one molecule of Se_2Cl_2.

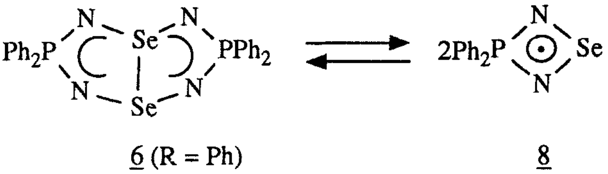


(R = Me, Et, Ph)

(3)

The selenium halides are mixed in this proportion to yield an average stoichiometry of '$SeCl_3$', which is required for the condensation of Me_3SiCl to be quantitative. In this way one R_2PN_2 'building block' is created for each selenium atom. The compounds 6 and 7 are easily identified on the basis of ^{31}P NMR chemical shifts, which are remarkably similar to those of the sulfur analogues, 1 and 2. The ^{31}P chemical shifts of 1 and 6 occur at unusually low field (112-136 ppm) for cyclophosphazenes. This has been tentatively attributed[2] to the relatively small angles at phosphorus imposed by the cross-ring chalcogen-chalcogen bond. In the case where R = Ph, 6 is formed preferentially (~80%) and is readily isolable. For the R = Me or Et derivatives, 7 is produced in more significant quantities (30-50%).

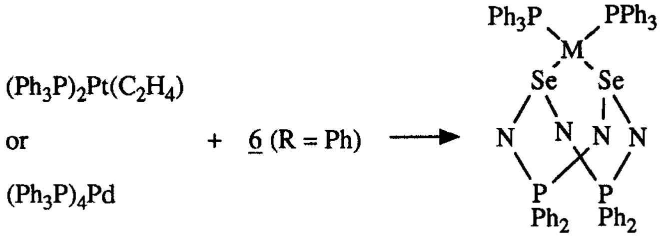
It should be noted that 6, a yellow solid, is thermochromic in solution, being deep green at room temperature, and yellow at -20°C. The ESR spectrum of 6 (R = Ph) yields a quintet, suggesting the formation of a radical with two equivalent nitrogens, as in 8.



(4)

METAL COMPLEXES OF 1,5-$Ph_4P_2N_4Se_2$

The 1,5-diphosphadiselenatetrazocine, 6 (R = Ph) forms monomeric complexes with zerovalent platinum or palladium complexes (equation 5) which, on the basis of ^{77}Se NMR spectra and a comparison of ^{31}P NMR data with those of the corresponding complexes of 1 (R = Ph),[3] involve the novel η^2-Se,Se' coordination mode, as in 9.



(5)

9 (M = Pt, Pd)

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