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PHOSPHORUS-NITROGEN-SELENIUM RING SYSTEMS

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Abstract Diphosphadiselenatetrazocines, 1,5-R₄P₂N₄Se₂ (R = Me, Et, Ph) and 1,3-R₄P₂N₄Se₂ (R = Me, Et), have been prepared in good combined yields from the cyclocondensation of R₂PN₂(SiMe₃)₃ with 'SeCl₃'. The compound 1,5-Ph₄P₂N₄Se₂ dissociates into Ph₂PN₂Se• radicals identified by ESR spectroscopy. Metal complexes (Ph₃P)₂M(Se₂N₄P₂Ph₄) (M = Pt, Pd) have been prepared from the reaction of 1,5-Ph₄P₂N₄Se₂ with (Ph₃P)₂PtC₂H₄ and (Ph₃P)₄Pd, respectively. The Se,Se'-dialkyl derivatives 1,5-Ph₄P₂N₄Se₂R₂ undergo isomerization to produce 1,3-Ph₄P₂N₄Se₂R₂ 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 $1.5-R_4P_2N_4S_2$, $\underline{1}$, a butterfly or folded shaped ring with the unusual feature of a transannular S-S bond, and $1.3-R_4P_2N_4S_2$, $\underline{2}$, a structural isomer of $\underline{1}$.

Cyclophosphaselenazenes with three coordinate selenium have been previously reported. Eight-membered rings of the type 1,5-Ph₄P₂N₄Se₂R₂, $\underline{3}$ (R = Me, Et, Ph) were prepared via the cyclocondensation of Ph₂PN₂(SiMe₃)₃ with RSeCl₃. In the cases where R = Me or Et the reaction also produces 1,5-Ph₄P₂N₄Se₂ (Se analogue of $\underline{1}$) in low yields.

$$2Ph_{2}P \xrightarrow{NSiMe_{3}} + 2RSeCl_{3} \xrightarrow{-6Me_{3}SiCl} Ph_{2}P \xrightarrow{N} \stackrel{R}{\underbrace{Se}_{N}} PPh_{2}$$

$$1)$$

$$\frac{3}{2}$$

New aspects of the chemistry of P-N-Se rings that will be discussed herein include (a) the isomerization of 1,5-Ph₄P₂N₄Se₂R₂, (b) the synthesis and characterization of Se analogues of $\underline{1}$ and $\underline{2}$, (c) the dissociation of 1,5-Ph₄P₂N₄Se₂ into Ph₂PN₂Se• radicals, and (d) the formation of Pt and Pd complexes of 1,5-Ph₄P₂N₄Se₂.

ISOMERIZATION OF 1,5-Ph₄P₂N₄Se₂R₂

When pure 1,5-Ph₄P₂N₄Se₂R₂, $\underline{3}$ (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-Ph₄P₂N₄Se₂R₂, $\underline{4}$, (ca. 90%), and 1,3-Ph₄P₂N₄Se₂, $\underline{5}$, (ca. 10%). The sequence of formation is as shown in equation (2) based on the observation that $\underline{5}$ is slowly produced from pure $\underline{4}$ under similar conditions. The Se,Se'-diphenyl derivative, $\underline{3}$ (R = Ph), is stable towards isomerization in the solid state.

$$Ph_{2}P \xrightarrow{N} PPh_{2} \xrightarrow{Ph_{2}} N \xrightarrow{Ph_{2}} Ph_{2} \xrightarrow{Ph_{2}} N \xrightarrow{Ph_{2}} N \xrightarrow{N} PPh_{2} \xrightarrow{N} PPh_{2} \xrightarrow{N} PPh_{2} \xrightarrow{N} N \xrightarrow{N} N \xrightarrow{N} N \xrightarrow{N} N \xrightarrow{Se} N \xrightarrow{Se} N \xrightarrow{Se} N \xrightarrow{N} Se \xrightarrow{N} Se$$

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 R₄P₂N₄Se₂ ISOMERS

In view of the low yields of both 1,3- and 1,5-Ph₄P₂N₄Se₂ as described above, a new synthetic route was developed. This procedure involves the cyclocondensation of six molecules of R₂PN₂(SiMe₃)₃ with four molecules of SeCl₄ and one molecule of Se₂Cl₂.

$$R_{2}P \xrightarrow{N} Se \xrightarrow{N} PR_{2}$$

$$2R_{2}P \xrightarrow{NSiMe_{3}} + \frac{4}{3}SeCl_{4} + \frac{1}{3}Se_{2}Cl_{2} \xrightarrow{CH_{3}CN} + \frac{6}{6}$$

$$(R = Me, Et, Ph)$$

$$R_{2}P \xrightarrow{N} PR_{2}$$

$$+ \frac{6}{6}$$

$$+ \frac{6}{6}$$

$$+ \frac{1}{3}SeCl_{4} + \frac{1}{3}Se_{2}Cl_{2} \xrightarrow{CH_{3}CN} + \frac{6}{6}$$

$$+ \frac{1}{3}SeCl_{4} + \frac{1}{3}Se_{2}Cl_{2} \xrightarrow{CH_{3}CN} + \frac{6}{6}$$

$$+ \frac{1}{3}SeCl_{4} + \frac{1}{3}Se_{2}Cl_{2} \xrightarrow{CH_{3}CN} + \frac{6}{6}SeCl_{4} + \frac{1}{3}Se_{2}Cl_{2} \xrightarrow{CH_{3}CN} + \frac{1}{3}Se_{2}C$$

The selenium halides are mixed in this proportion to yield an average stoichiometry of 'SeCl₃', which is required for the condensation of Me₃SiCl to be quantitative. In this way one R₂PN₂ 'building block' is created for each selenium atom. The compounds <u>6</u> and <u>7</u> are easily identified on the basis of ³¹P NMR chemical shifts, which are remarkably similar to those of the sulfur analogues, <u>1</u> and <u>2</u>. The ³¹P chemical shifts of <u>1</u> and <u>6</u> occur at unusually low field (112-136 ppm) for cyclophosphazenes. This has been tentatively attributed² to the relatively small angles at phosphorus imposed by the cross-ring chalcogen-chalcogen bond. In the case where R = Ph, <u>6</u> is formed preferentially (~80%) and is readily isolable. For the R = Me or Et derivatives, <u>7</u> is produced in more significant quantities (30-50%).

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

$$Ph_{2}P \bigvee_{N=Se}^{N} PPh_{2} \longrightarrow 2Ph_{2}P \bigodot_{N}^{N} Se$$

$$\underline{6} (R = Ph) \qquad \underline{8}$$
(4)

METAL COMPLEXES OF 1,5-Ph₄P₂N₄Se₂

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

$$(Ph_3P)_2Pt(C_2H_4)$$
or
$$(Ph_3P)_4Pd$$

$$Ph_3$$

$$Se$$

$$Se$$

$$Se$$

$$N$$

$$N$$

$$N$$

$$N$$

$$P$$

$$Ph_2$$

$$Ph_2$$

$$Ph_2$$

$$Ph_2$$

$$9 (M = Pt, Pd)$$

$$(5)$$

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