Articles

Preparation and Spectroscopic Characterization of 1,5- and 1,3-Diphosphadiselenatetrazocines: X-ray Structure of $[N(PMe_2NH_2)_2]_2Se$

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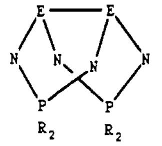
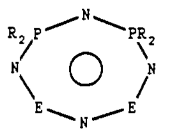
The cyclocondensation of $R_2PN_2(SiMe_3)_3$ (R = Me, Et, Ph) with a mixture of selenium monochloride and selenium tetrachloride that gives a Se:Cl ratio of 1:3 in acetonitrile at 23 °C produces 1,5-$Ph_4P_2N_4Se_2$, **2a**, in 85% yield or mixtures of 1,5- and 1,3-$R_4P_2N_4Se_2$ in combined isolated yields of 79% (R = Me) or 96% (R = Et). The heterocycles 1,3-$Me_4P_2N_4Se_2$, **4b**, and 1,5-$Et_4P_2N_4Se_2$, **2c**, were separated from these mixtures by fractional crystallization and gel permeation chromatography, respectively. The pure compounds **2a,c** and **4b** were characterized by elemental analyses, IR spectroscopy, FAB mass spectrometry, and ^{31}P and ^{77}Se NMR spectroscopy. A solution of **2a** in dichloromethane is pale yellow at −20 °C and green at 23 °C. This green solution exhibits visible absorption bands at 634 and 653 nm and a five line (1:2:3:2:1) ESR signal ($g = 2.011$, $a_N = 0.67$ mT) tentatively attributed to the cyclic radical $Ph_2PN_2Se^•$. Density functional calculations for the model anion $H_2PN_2Se^-$ indicate that the corresponding radical is a planar five π-electron ring system. The singly occupied molecular orbital of $H_2PN_2Se^•$ is based mainly on selenium with strong antibonding interactions with both nitrogen atoms. The decomposition of **4b** in dichloromethane yields $[N(PMe_2NH_2)_2]_2Se$, **5**, in which the selenide ion is involved in strong Se- -NH hydrogen bonding to four NH_2 groups of the surrounding cations. The crystals of **5** are tetragonal, space group $P4_12_12$ with $a = 8.532(2)$ Å, $c = 14.869(3)$ Å, $V = 1082.4$ Å^3, and $Z = 2$. The final R and R_w values were 0.055 and 0.061, respectively.

Introduction

The eight-membered heterocycles 1,5-$Ph_4P_2N_4S_2$, **1a,b**, and their 1,3-isomers, **3a,b**, were first prepared and structurally characterized about ten years ago.[1] More recently an improved synthesis of the 1,5-isomers, including **1c**, by the cyclocodensation of $R_2PN_2(SiMe_3)_3$ with sulfur halides[2,3] has facilitated investigations of the chemistry of this interesting heterocycle. Subsequently, studies of the Lewis base behavior[4,5] and of reactions of **1a–c** with electron-rich metal complexes[6] or organolithium reagents[7] have been added to an earlier investigation of the oxidative addition of halogens.[8] In contrast to the structurally related S_4N_4 cage,[9] the integrity of the $P_2N_4S_2$ ring is retained in all these reactions. In many cases the transannular S–S bond [d(S–S) ~ 2.5 Å][1,2] is destroyed and ^{31}P NMR spectroscopy provides an excellent probe for this structural feature. The loss of the S–S interaction is invariably associated with a large change in the ^{31}P NMR chemical shift from the anomalously high frequency values (110–140 ppm) observed for the folded rings in **1a–c**[3,10] compared to typical cyclophosphazene values of 20–40 ppm for derivatives with open $P_2N_4S_2$ rings.



1a, E = S, R = Ph
1b, E = S, R = Me
1c, E = S, R = Et
2a, E = Se, R = Ph
2b, E = Se, R = Me
2c, E = Se, R = Et



3a, E = S, R = Ph
3b, E = S, R = Me
3c, E = S, R = Et
4a, E = Se, R = Ph
4b, E = Se, R = Me
4c, E = Se, R = Et

About three years ago we reported the formation of 1,5-$Ph_4P_2N_4Se_2$, **2a**, as a minor product (<10% yield) from the reaction of $Ph_2PN_2(SiMe_3)_3$ with alkylselenium trichlorides.[11] Since **2a**, and the related tetraalkyl derivatives **2b,c**, could serve as informative models for the reactions of the dangerously explosive Se_4N_4,[12] a high-yield synthesis of **2a–c** is desirable. Furthermore, it would be interesting to compare the chemistry of these Se–N heterocycles with that of their sulfur analogues, **1a–c**. In this paper we describe (a) a much improved synthesis of **2a**, (b) the formation and spectroscopic characterization of **2b,c** and the 1,3-isomers **4a–c**, (c) ESR evidence for the dissociation of **2a** into the cyclic radical $Ph_2PN_2Se^•$, (d) density functional MO calculations for the model system $H_2PN_2Se^-$, and (e) the X-ray structure of the hydrogen-bonded selenide $[N(PMe_2NH_2)_2]_2Se$ formed by decomposition of **4b**.

Experimental Section

Reagents and General Procedures. The reagents $R_2PN_2(SiMe_3)_3$ (R = Ph, Me, Et) were prepared by the reaction of the corresponding $R_2PN(SiMe_3)_2$ with trimethylsilyl azide (Aldrich) using the procedure

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described for $Me(Ph)PN_2(SiMe_3)_3$.[13] Selenium monochloride was purchased from Aldrich and used as received. Selenium tetrachloride was prepared by exhaustive chlorination of gray selenium with Cl_2 gas in acetonitrile, and the product was washed with carbon tetrachloride.

All manipulations were carried out under a dry atmosphere of purified nitrogen (Ridox, P_4O_{10}, silica). Acetonitrile was freshly distilled over CaH_2, then P_4O_{10}, and finally CaH_2 again. Dichloromethane was distilled from P_4O_{10}. Chemical analyses were performed by the Analytical Services of the Department of Chemistry, The University of Calgary, and by the Canadian Microanalytical Service, Vancouver, BC, Canada.

Instrumentation. Infrared spectra were recorded as Nujol mulls with KBr or CsI windows on a Nicolet 5DX FT-IR spectrometer. UV–visible spectra were obtained by using a Cary 219 spectrometer. ^{31}P NMR spectra were obtained either on a Varian XL200 spectrometer or on a Bruker AM400 spectrometer, using external 85% H_3PO_4 as reference. ^1H NMR spectra were determined on a Bruker ACE200 spectrometer using various deuterated solvents as internal reference. ^{77}Se NMR spectra were recorded on a Bruker AM400 spectrometer using PhSeSePh in $CDCl_3$ as external reference assigned at +461 ppm (reference Me_2Se). Fast atom bombardment mass spectra were obtained at the Institute of Sedimentary and Petroleum Geology, Calgary, Canada. ESR spectra were measured by using a Bruker ER console and a Varian V3600 12-in. magnet equipped with a V/FR2503 FielDial field controller. The microwave cavity was a Bruker Model 4102ST operating in the TE 102 mode. Microwave frequencies were measured with a Hewlett-Packard X532B absorption wave meter, and the magnetic field was determined with an Alpha Scientific 3093 digital NMR gaussmeter.

Preparation of 1,5-$Ph_4P_2N_4Se_2$ (2a). A solution of $Ph_2PN_2(SiMe_3)_3$ (9.29 g, 21.5 mmol) in acetonitrile (100 mL) was added dropwise (60 min), via cannula, with stirring, to a mixture of selenium tetrachloride (3.16 g, 14.3 mmol) and selenium monochloride (0.82 g, 3.6 mmol) suspended in acetonitrile (ca. 150 mL) at 23 °C. After the addition of ca. 15% of the phosphorus(V) reagent the $SeCl_4$ dissolved in the orange solution. When the addition approached the halfway point, the color became paler orange and a large amount of yellow precipitate was formed. As the addition continued to completion, the color of the solution became intense red. The reaction mixture was then stirred for a further 16 h to give a yellow-brown precipitate and a yellow solution. The volume of the solution was reduced to ca. 50 mL under vacuum. The precipitate was separated by using a filter cannula, dried under vacuum, and extracted with dichloromethane (3 × 40 mL) to give essentially pure 1,5-$Ph_4P_2N_4Se_2$ (5.34 g, 9.1 mmol, 85%) identified by comparision of the ^{31}P NMR and IR spectra with those of an authentic sample.[11] IR (cm^{-1}): 1435 s, 1120 s, 1112 s, 1032 m, 1016 m, 999 w, 987 m, 957 vs, 858 w, 850 w, 751 m, 693 s, 672 s, 628 m, 620 m, 536 s, 513 s, 508 s. The filtrate exhibited a ^{31}P NMR resonance at 18.3 ppm, attributed to 1,3-$Ph_4P_2N_4Se_2$, in addition to the signal at 113.4 ppm for 1,5-$Ph_4P_2N_4Se_2$.

Preparation of 1,5- and 1,3-$Me_4P_2N_4Se_2$ (2b, 4b). A solution of $Me_2PN_2(SiMe_3)_3$ (8.41 g, 27.2 mmol) in acetonitrile (150 mL) was added dropwise (60 min), via cannula, to a stirred suspension of selenium tetrachloride (4.01 g, 18.2 mmol) and selenium monochloride (1.04 g, 4.5 mmol) in acetonitrile (200 mL) at 23 °C. The color changes during the addition were similar to those observed during the preparation of **2a**. After the completion of the addition, the lime green solution was separated from the red precipitate by filter cannula. Removal of solvent under vacuum gave an approximately equimolar mixture of 1,3-$Me_4P_2N_4Se_2$ ($\delta(^{31}P)$ 27.9 ppm) and 1,5-$Me_4P_2N_4Se_2$ ($\delta(^{31}P)$ 119.5 ppm) (3.62 g, 10.8 mmol, 79%) [relative yields were determined by ^{31}P NMR spectroscopy]. Fractional recrystallization of this mixture of isomers from dichloromethane at −20 °C produced pure 1,3-$Me_4P_2N_4Se_2$ as yellow crystals (0.32 g, 7%). Anal. Calcd for $C_4H_{12}N_4P_2Se_2$: C, 14.29; H, 3.61; N, 16.68. Found: C, 14.01; H, 3.44; N, 16.39. ^1H NMR (in $CDCl_3$): 1.70 ppm [d, $^2J(H–P)$ = 18 Hz]. ^{31}P NMR (in CH_2Cl_2): δ 28.3 ppm. ^{77}Se NMR (in CH_2Cl_2): δ 1193 ppm (m).

Subsequent crops produced only mixtures of the 1,5- and 1,3-isomers as determined by ^{31}P NMR spectroscopy. Attempts to separate these isomers by chromatography on a Bio-beads S-X8 column using toluene as an eluant were unsuccessful.

Preparation of 1,5- and 1,3-$Et_4P_2N_4Se_2$ (2c, 4c). A solution of $Et_2PN_2(SiMe_3)_3$ (6.43 g, 19.1 mmol) in acetonitrile (175 mL) was added dropwise (75 min), via cannula, with stirring to a suspension of selenium tetrachloride (2.81 g, 12.7 mmol) and selenium monochloride (0.73 g, 3.2 mmol) in acetonitrile (200 mL) at 23 °C. The color changes during the addition were similar to those observed in the corresponding reaction of $Me_2PN_2(SiMe_3)_3$. The mixture was stirred for 4 h at 23 °C after the completion of the addition, and then the lime green solution was separated from the red precipitate by filter cannula. The solvent was removed under vacuum to give a mixture of 1,3- and 1,5-$Et_4P_2N_4Se_2$ (3.59 g, 9.2 mmol, 96% yield) in the approximate molar ratio 1:2 based on integration of the ^{31}P NMR resonances at 35.2 and 135.7 ppm, respectively. A portion (1.72 g) of this mixture of isomers was eluted on a Bio-beads S-X8 column using toluene as the solvent. Aliquots (ca. 15 mL) of the colored eluant were collected and analyzed by ^{31}P NMR spectroscopy. Fraction 5 was shown to contain pure 1,5-$Et_4P_2N_4Se_2$, while all other fractions comprised a mixture of 1,3- and 1,5-isomers. Anal. Calcd for $C_8H_{20}N_4P_2Se_2$: C, 24.50; H, 5.15; N, 14.29. Found: C, 23.96; H, 5.53; N, 14.10. ^{31}P NMR (in CH_2Cl_2): δ 135.7 ppm, $^2J(P–Se)$ = 78 Hz. ^{77}Se NMR (in CH_2Cl_2): δ 1065 ppm [t, $^2J(P–Se)$ = 78 Hz].

Table I. Crystallographic Data for $[N(PMe_2NH_2)_2]_2Se$

formula	$C_8H_{32}N_6P_4Se$	Z	2
fw	415.24	T, K	165
cryst system	tetragonal	λ, Å	0.71069
space group	$P4_12_12$ (No. 92)	ρ_{calcd}, g cm^{-3}	1.274
a, Å	8.532 (2)	μ, mm^{-1}	2.029
c, Å	14.869(3)	R	0.055
V, Å^3	1082.4(4)	R_w	0.061

Table II. Final Fractional Coordinates (×10^4 for Se, P, N, and C; ×3 for H) and Equivalent Isotropic Temperature Factors U_{eq} (Å^2 × 10^3) for $[N(PMe_2NH_2)_2]_2Se$

atom	x	y	z	U_{eq}[a]
Se	7878(2)	7878(2)	0	45(1)
P	3463(2)	5827(2)	177(1)	25(1)
N(1)	4118(5)	4118(5)	0	27(2)
N(2)	4108(5)	7307(6)	−398(4)	35(2)
C(1)	1429(7)	5764(7)	−52(5)	43(2)
C(2)	3769(9)	6363(9)	1330(4)	56(2)
H(1)	389(3)	717(3)	−108(3)	79(3)
H(2)	492(3)	762(3)	−36(3)	79(3)
H(11)	87(3)	528(3)	34(3)	89(3)
H(12)	121(3)	538(3)	−75(3)	89(3)
H(13)	105(3)	673(3)	4(3)	89(3)
H(21)	341(3)	564(3)	165(3)	89(3)
H(22)	309(3)	733(3)	144(3)	89(3)
H(23)	472(3)	650(3)	139(3)	89(3)

[a] U_{eq} is one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray Structural Analysis. Yellow, prismatic crystals of $[N(PMe_2NH_2)_2]_2Se$ were obtained from solutions of 1,3-$Me_4P_2N_4Se_2$ in dichloromethane. Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf-Nonius CAD4 diffractometer by a least-squares fit of the setting angles of 25 reflections. Crystal data are given in Table I, and final fractional coordinates and equivalent isotropic temperature factors are compiled in Table II. Data were corrected for Lorentz, polarization, and absorption effects;[14] transmission factors were in the range 0.931–1.089. The structure was solved by direct methods in SHELXS-86.[15] Refinement of the structure was by full-matrix least-squares calculations, using SHELX-76[16] initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms. At an intermediate stage in the refinement, a difference map revealed maxima consistent with the positions of hydrogen atoms which were included in the subsequent cycles of refinement with overall isotropic temperature factors. Refinement converged with $R = 0.055$ and $R_w = 0.061$. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann[17] and Stewart, Davidson, and Simpson[18] and allowance was made for anomalous dispersion.[19] A difference map calculated at the conclusion of the refinement has no chemically significant features. The computer programs

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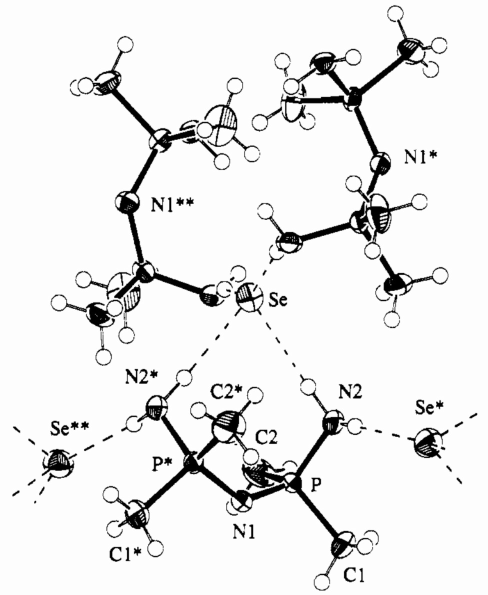


Figure 1. ORTEP plot for $[N(PMe_2NH_2)_2]_2Se$, **5**. Asterisks and double asterisks refer to symmetry-related atoms. The following symmetry operations apply: P* and N2*, y, x, $-z$; Se*, $^1/_2 + x - 1$, $^1/_2 - y + 1$, $^3/_4 - z - 1$; N1*, $^1/_2 + x$, $^1/_2 - y + 1$, $^3/_4 - z - 1$; Se** and N1**, $^1/_2 - y + 1$, $^1/_2 + x$, $^1/_4 + z$.

used for data reduction were part of TEXSAN[20] installed on a Silicon Graphics Personal Iris 4D/35, and Figure 1 was plotted using ORTEP II.[21]

Calculations. The density functional calculations were all carried out by utilizing the HFS-LCAO (Hartree–Fock–Slater linear combination of atomic orbitals) program A-MOL, developed by Baerends and co-workers[22] and vectorized by Ravenek.[23] The numerical integration procedure applied for the calculations was developed by Boerrigter and co-workers.[24] The molecular structure was optimized on the singlet energy surface within the C_{2v} symmetry group. The electronic configuration of $H_2PN_2Se^-$ was described by an uncontracted double-ζ STO (Slater-type Orbital) basis set for N, P, and Se, as well as a double-ζ STO basis set for H.[25,26] A set of auxiliary d STO functions on N, P, and Se,[27] and p functions on H, centered on all nuclei, were used in order to fit the molecular density and present Coulomb and exchange potentials accurately in each SCF (self-consistent field) cycle. The frozen-core approximation was used.[22]

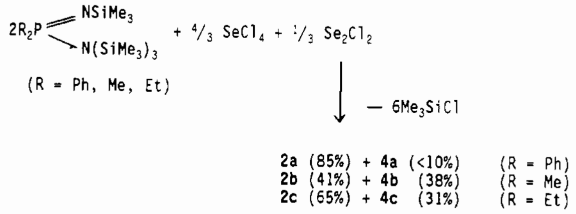
Results and Discussion

Synthesis of 1,5- and 1,3-$R_4P_2N_4Se_2$ (R = Ph, Me, Et). The reaction of $Ph_2PN_2(SiMe_3)_3$ with a mixture of selenium monochloride and selenium tetrachloride designed to give a Se:Cl ratio of 1:3[28] produces 1,5-$Ph_4P_2N_4Se_2$, as a yellow solid in 85% yield. On the basis of ^{31}P NMR spectroscopic evidence (vide infra), the 1,3-isomer, **4a**, is also formed in small amounts, but this minor product could not be isolated. By contrast, the corresponding reaction with $R_2PN_2(SiMe_3)_3$ (R = Me, Et) gives substantial amounts of both the 1,5- and 1,3-isomers (eq 1).

Table III. ^{31}P NMR Data for 1,5- and 1,3-$R_4P_2N_4E_2$ (E = S, Se)

1,5-isomers	$\delta(^{31}P)$ (ppm)[a,b]	1,3-isomers	$\delta(^{31}P)$ (ppm)[a,b]
1a[c]	113.9	**3a**[d]	18.7
2a	113.4 [^2J(PSe) = 81 Hz]	**4a**	18.3[e]
1b[c]	119.7	**3b**[d]	28.3
2b	119.5 [^2J(PSe) = 82 Hz]	**4b**	27.9[e]
1c[c]	136.1	**3c**[d]	34.5
2c	135.7 [^2J(PSe) = 78 Hz]	**4c**	35.2[e]

[a] In CH_2Cl. [b] Relative to external 85% H_3PO_4. [c] Data taken from ref 3. [d] Data taken from refs 1b and 2. [e] ^2J(P–Se) was not resolved for the AA′X spin system.



(1)

The combined isolated yields (≥80%) of the two isomers in these cyclocondensation reactions are remarkably high[29] and significantly better than those obtained (50–60%) for the corresponding sulfur systems.[3] The 1,5-isomer, **2a**, is readily isolated as a pure compound. However, the separation of the isomeric pairs **2b**/**4b** and **2c**/**4c** poses problems because these 1,5- and 1,3-isomers are formed in comparable amounts. A low yield of pure **4b** was isolated by fractional crystallization from dichloromethane at −20 °C, and small quantities of pure **2c** were separated from **4c** by gel permeation chromatography. However, pure samples of **2b** or **4c** could not be obtained. Consequently, the 1,5-isomer **2a** was used in most of the subsequent investigations of the $P_2N_4Se_2$ ring system.

In contrast to their sulfur analogues, the heterocycles **2a,b** display thermochromic behavior in solution. At −20 °C a solution of **2a** or **2b** in CH_2Cl_2 is pale yellow whereas at 25 °C it is lime green. A lime green solution of **2a** in CH_2Cl_2 exhibits absorption bands in the visible spectrum at 634 and 653 nm. This thermochromicity is not observed for **2a** or **2b** in the solid state or for the 1,3-isomer **4b** in solution.

In general the eight-membered rings **2a–c** and **4a–c** are more sensitive to moisture and less thermally stable than their sulfur analogues, but they can be stored for extended periods under a nitrogen atmosphere at −20 °C without decomposition.

Spectroscopic Characterization of 1,5- and 1,3-$R_4P_2N_4Se_2$ (R = Ph, Me, Et). As indicated in Table III, the ^{31}P NMR chemical shifts of **2a–c** and **4a–c** display a remarkable congruence with those of their sulfur analogues. The ^{31}P NMR chemical shifts for the 1,5-isomers **2a–c** occur at anomalously high frequencies (113–136 ppm) compared to those of the 1,3-isomers **4a–c** (18–35 ppm), which, by analogy with their sulfur analogues, is attributable to a transannular Se–Se interaction.[4] Although we have been unable to verify this conclusion by an X-ray structural analysis of **2a** (vide infra), the N-bonded platinum(II) adduct of **2a**, $[PtCl_2(PEt_3)]_2(\eta^1\text{-}N\text{-}Ph_4P_2N_4Se_2)$ has been shown by X-ray crystallography to exhibit a cross-ring Se–Se bond of 2.594(2) Å.[30] The two-bond P–Se coupling constants for **2a–c** fall within the narrow range of 80 ± 2 Hz; cf. values of 28–87 Hz for ^2J(PSe) in other unsaturated PNSe systems.[11,31]

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Table IV. ^{77}Se NMR Data for 1,5- and 1,3-$R_4P_2N_4Se_2$

R	1,5-$R_4P_2N_4Se_2$[a] $\delta(^{77}Se)$[b]	1,5-$R_4P_2N_4Se_2$[a] ^2J(P–Se)[c] (Hz)	1,3-$R_4P_2N_4Se_2$[a] $\delta(^{77}Se)$[b]
Ph	1066	81, t	1356[d]
Me	1076	82, t	1193[d]
Et	1065	78, t	1257[d]

[a] In CH_2Cl_2. [b] In ppm relative to external Ph_2Se_2 in $CDCl_3$ set at +461 ppm relative to Me_2Se (0 ppm). [c] t = triplet (A_2X spin system). [d] Poorly resolved virtual triplet (AA′X spin system).

Table V. Bond Distances (Å) and Bond Angles (deg) for $[N(PMe_2NH_2)_2]_2Se$, **5**

	Bond Distances		
N(1)–P	1.584(3)	C(1)–P	1.769(6)
N(2)–P	1.621(5)	C(2)–P	1.793(6)
	Bond Angles[a]		
N(2)–P–N(1)	120.6(2)	C(2)–P–N(2)	104.8(3)
C(1)–P–N(1)	106.7(3)	C(2)–P–C(1)	109.6(3)
C(1)–P–N(2)	104.8(3)	P–N(1)–P′	132.7(4)
C(2)–P–N(1)	110.0(2)		
	Geometry around Se[a]		
Se···H(1)″	2.28(2)	Se···H(2)	2.59(2)
H(1)″···Se···H(2)	102(2)	H(1)″···Se···H(1)‴	150(2)
H(1)″···Se···H(2)′	100(2)	H(2)···Se···H(2)′	83(2)

[a] The symmetry-related atoms are generated from the reference atoms by the following transformations: prime, $y, x, -z$; double prime, $^1/_2 - y + 1, {}^1/_2 + x, {}^1/_4 + z$; triple prime, $^1/_2 + x, {}^1/_2 - y + 1, {}^3/_4 - z - 1$.

The ^{77}Se NMR data for **2a–c** and **4a–c** are summarized in Table IV. The ^{77}Se NMR spectra of **2a–c** consist of well-resolved 1:2:1 triplets with ^2J(P–Se) values in excellent agreement with those found from the ^{31}P NMR spectrum. By contrast, the ^{77}Se NMR spectra of the 1,3-isomers, **4a–c**, are comprised of poorly resolved virtual triplets corresponding to AA′X spin systems [the phosphorus atoms are magnetically inequivalent since the most abundant isotopomer has only one ^{77}Se atom (^{77}Se, natural abundance 7.7%)].

The FAB mass spectrum of **2a** displays the molecular ion at *m/e* 585 with the appropriate isotopic distribution for a compound containing two selenium atoms.

Crystal Structure of $[N(PMe_2NH_2)_2]_2Se$. Attempts to grow X-ray-quality crystals of **4b** from dichloromethane over several weeks produced colorless crystals of the decomposition product $[H_2NPMe_2NPMe_2NH_2]_2Se$, **5**, identified by X-ray crystallography. The molecular geometry and atomic numbering scheme for **5** are shown in Figure 1, and pertinent bond lengths and bond angles are listed in Table V. The structure consists of $H_2NPMe_2NPMe_2NH_2^+$ cations which are strongly hydrogen-bonded to the Se^{2-} anion. Specifically, two NH_2 groups of one cation and one NH_2 group of two other cations are hydrogen-bonded to Se^{2-} in a highly distorted tetrahedral arrangement ∠H- -Se- -H = 83(2)–150(2)°. The Se–N separation of 330.5 pm in **5** is significantly shorter than the corresponding Se- -H–N distances in selenoureas[32] or 2,4-diselenouracil,[33] which are in the range 347–383 pm. As far as we can ascertain, the structure of **5** represents the first example of hydrogen bonding involving the Se^{2-} ion.

The identification of the $H_2NPMe_2NPMe_2NH_2^+$ cation in **5** provides indirect evidence for the presence of the NPNPN unit in its precursor **4b**. No attempt was made to identify the other product(s) formed in the conversion of **4b** into **5**.

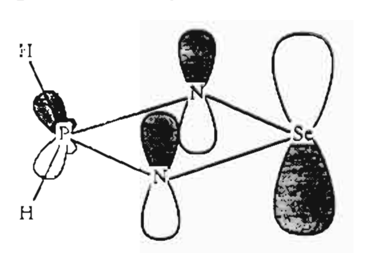


Figure 2. SOMO of $H_2PN_2Se^•$.

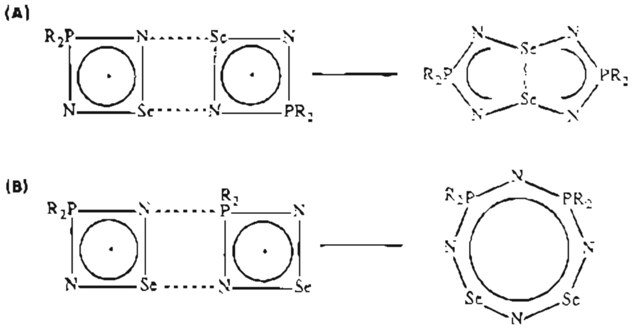
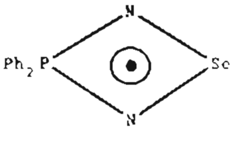
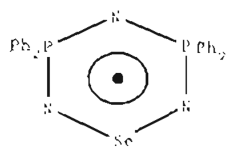


Figure 3. Formation of (A) 1,5-$R_4P_2N_4Se_2$ and (B) 1,3-$R_4P_2N_4Se_2$ by the dimerization of $R_2PN_2Se^•$.

Dissociation of 1,5-$Ph_4P_2N_4Se_2$, 2a, into $Ph_2PN_2Se^•$ Radicals. The ESR spectrum of a green solution of **2a** in dichloromethane at 25 °C consists of a somewhat distorted[34] five-line (1:2:3:2:1) signal with $g = 2.011$ and $a_N = 0.67$ mT. The five-line ESR signal implies that the unpaired electron is coupled to two equivalent nitrogen atoms (and not to phosphorus; vide infra). The data available for cyclic Se–N radicals indicate that g-values of 2.01–2.02 are observed for coupling to one selenium,[35] while g-values of 2.04–2.05 are found when the unpaired electron is coupled to two selenium atoms.[36] Thus it seems reasonable to propose that the radical observed in this work is the four-membered ring $Ph_2PN_2Se^•$, **6**, formed by the dissociation of **2a** in CH_2Cl_2 solution and that this radical (a blue species?) is responsible for the visible absorption bands at 634 and 653 nm exhibited by such solutions (vide supra). We note that the six-membered cyclic radical $Ph_4P_2N_3Se^•$, **7**, a higher homologue of **6** (by addition of a Ph_2PN unit), has a g-value of 2.016 with $a_N = 0.48$.[35b]



6



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In order to determine the composition of the SOMO for **6**, density functional calculations were performed for the model anion $H_2PN_2Se^-$. These calculations indicate that the corresponding radical $H_2PN_2Se^•$ is a planar, 5π-electron system. Consistent with the ESR data, the SOMO of $H_2PN_2Se^•$ is a π-orbital based largely on selenium with strong antibonding interactions with both nitrogen atoms and insignificant contributions from the phosphorus atom (see Figure 2).

Mechanism of Ring Formation. The formation of both 1,3- and 1,5-isomers of $R_4P_2N_4S_2$ in the cyclocondensation reaction

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(33) Shefter, E. S.; James, M. N. G.; Mautner, H. G. *J. Pharm. Sci.* **1966**, *55*, 643.

(34) The distortion is manifested in lower than expected intensities for the fourth and fifth lines suggesting radical decay during the recording of the spectrum.

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(36) (a) Awere, E. G.; Passmore, J.; White, P. S.; Klapotke, T. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1415. (b) Belluz, P. D. B.; Cordes, A. W.; Kristof, E. M.; Kristof, P. V.; Liblong, S. W.; Oakley, R. T. *J. Am. Chem. Soc.* **1989**, *111*, 9276.

of $R_2PN_2(SiMe_3)_3$ with selenium chlorides (eq 1) is puzzling. In the light of the identification of **6** we hypothesized that this reaction might generate radicals of the type $R_2PN_2Se^\bullet$, which could subsequently dimerize in two ways to give either 1,5- or 1,3-$R_4P_2N_4S_2$ (see Figure 3). The formation of the 1,5-isomer, which would involve two Se–N interactions, would be the favored process in view of the composition of the SOMO of $H_2PN_2Se^\bullet$ (Figure 2). Indeed the ESR spectrum of the reaction mixture represented in eq 1 (R = Et) exhibited a poorly resolved five-line pattern consistent with the formation of $Et_2PN_2Se^\bullet$.

The proposed involvement of the radicals $R_2PN_2Se^\bullet$ in the formation of 1,3-$R_4P_2N_4Se_2$ implies that 1,5-$Ph_4P_2N_4Se_2$, **2a**, should isomerize to 1,3-$Ph_4P_2N_4Se_2$, **4a**, via the radical **6** in dichloromethane at room temperature. However, solutions of **2a** slowly deposit red selenium and there is no evidence for the formation of the 1,3-isomer **4a**. The homologous radical **7** also undergoes decomposition to red selenium in solution.[35b] Thus the involvement of the radicals $R_2PN_2Se^\bullet$ in the formation of the $R_4P_2N_4Se_2$ isomers remains an open question.

Conclusions

The cyclocondensation reaction of $R_2PN_2(SiMe_3)_3$ (R = Me, Et, Ph) with a mixture of selenium chlorides (Se:Cl = 1:3) produces both 1,5-and 1,3-$R_4P_2N_4Se_2$ in excellent combined yields. These Se–N heterocycles have much higher moisture-sensitivity and lower thermal stability than those of their sulfur analogues. The observed dissociation of 1,5-$Ph_4P_2N_4Se_2$ into the five π-electron radical $Ph_2PN_2Se^\bullet$ in CH_2Cl_2 solution at room temperature suggests the possible formation of the corresponding sulfur radicals $R_2PN_2S^\bullet$ from the thermal decomposition of 1,5-$Ph_4P_2N_4S_2$.

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Supplementary Material Available: Tables listing crystallographic experimental details, bond distances and bond angles (including hydrogen atoms), anisotropic temperature factors, and parameters for hydrogen atoms (5 pages). Ordering information is given on any current masthead page.