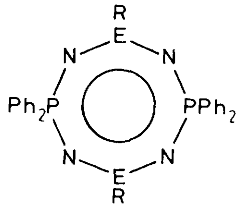
Diphosphadiselenatetrazocines: Preparation and Structural Characterization of a $P^{V}_2N_4Se_2$ Ring

Tristram Chivers,* Daniel D. Doxsee, and James F. Fait

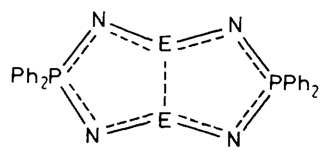
Department of Chemistry, The University of Calgary, Calgary, Alberta T2N 1N4, Canada

The reaction of $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ with $RSeCl_3$ (R = Ph, Me, Et) in acetonitrile produces 1,5-$Ph_4P_2N_4Se_2R_2$ [R = Ph, (**1a**); Me, (**1b**); Et, (**1c**)] and 1,5-$Ph_4P_2N_4Se_2$, (**2a**) when R = Me or Et; *X*-ray crystallography shows that (**1b**) is an eight-membered chair with the two selenium atoms displaced on either side of the P_2N_4 plane by 1.073(2) Å.

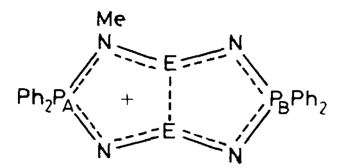
The preparation, molecular and electronic structures, and reactivity of cyclophosphathiazenes containing two-co-ordinate sulphur, $(R_2PN)_x(SN)_2$ (x = 1,2,4),[1,2] or three-co-ordinate sulphur, $(R_2PN)_x(NSX)_y$,[1,3] have been investigated extensively, but the corresponding cyclophosphaselenazenes are unknown. We report here the synthesis of the eight-membered rings (**1a**—**c**) by the cyclocondensation reaction of $RSeCl_3$ (R = Ph, Me, Et) with $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ and the *X*-ray structure of (**1b**). When R = Me or Et this reaction also produces (**2a**), and ^{31}P NMR data for (**2a**) and the



(**1a**) E = Se, R = Ph
(**1b**) E = Se, R = Me
(**1c**) E = Se, R = Et



(**2a**) E = Se
(**2b**) E = S



(**3a**) E = Se
(**3b**) E = S

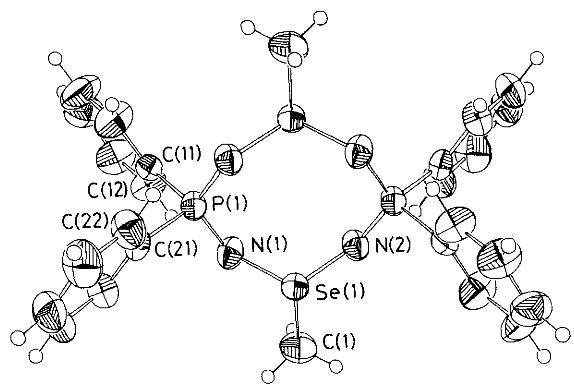


Figure 1. ORTEP plot for 1,5-$Ph_4P_2N_4Se_2Me_2$ (**1b**); selected bond lengths (Å) and bond angles (°): P(1)–N(1) 1.623(3), N(1)–Se(1) 1.778(3), Se(1)–N(2) 1.776(3), N(2)–P(1) 1.592(3), Se(1)–C(1) 1.913(5), P(1)–C(11) 1.804(4), P(1)–C(21) 1.814(4); N(2′)–P(1)–N(1) 120.8(1), P(1)–N(1)–Se(1) 116.0(2), N(1)–Se(1)–N(2) 105.0(2), Se(1)–N(2)–P(1′) 118.3(2), N(1)–Se(1)–C(1) 94.9(2), N(2)–Se(1)–C(1) 95.8(2), C(11)–P(1)–C(21) 104.5(2).

Table 1. ^{31}P NMR data for 1,5-diphospha-dithiatetrazocines and -diselenatetrazocines and their methylated derivatives.

	$\delta(^{31}P)^a$	$^4J(^{31}P_A-^{31}P_B)$
$Ph_4P_2N_4Se_2$, (**2a**)[b]	113.0	
$Ph_4P_2N_4S_2$, (**2b**)[c]	113.8	
$Ph_4P_2N_4Se_2Me^+$, (**3a**)[d]	81.8, 131.6[e]	—[f]
$Ph_4P_2N_4S_2Me^+$, (**3b**)[g]	83.5, 129.3[e]	16.1[h]

[a] Chemical shifts are in p.p.m. relative to external 85% H_3PO_4. [b] In CH_2Cl_2. [c] Ref. 2k. [d] In MeCN. [e] The downfield signal is tentatively assigned to P_A (ref. 2o). [f] Not resolved, $\nu_{1/2}$ ~40 Hz. [g] Ref. 2o. [h] Doublet of doublets.

methylated derivative (**3a**) indicate the presence of a trans-annular Se–Se bond.

The slow addition of $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ (5.9 mmol) in acetonitrile (130 ml) to a solution of phenylselenium trichloride (5.9 mmol) in acetonitrile (150 ml) at 23 °C produces a white precipitate of $Ph_4P_2N_4Se_2Ph_2$ (**1a**) (2.7 mmol, 91%).† In a similar manner, compounds (**1b**)† and (**1c**)† were obtained as white solids from $MeSeCl_3$ or $EtSeCl_3$ in *ca.* 50% yields. The ^{31}P NMR spectra (in CH_2Cl_2) for (**1a**), (**1b**), and (**1c**) exhibit singlets at 33.6, 32.5, and 21.7 p.p.m. respectively. The ^{77}Se NMR spectrum of (**1b**) in CH_2Cl_2 shows a poorly resolved 1:2:1 triplet at 453 p.p.m. (ref. Ph_2Se_2 in $CDCl_3$), ^2J (^{31}P–^{77}Se) 45 Hz [*cf.* ^2J (^{31}P–^{77}Se) 27—87 Hz for related P–N–Se compounds];[4,5] ^1H NMR: (**1b**) δ 2.82 (s, 6H), 7.3—7.6, and 7.8—8.0 (m, 20H); (**1c**) δ 1.40 (t, 6H), 3.15 (q, 4H), 7.3—7.6, and 7.8—8.0 (m, 20H). The mass spectra (electron impact, EI, 70 eV) of (**1a**), (**1b**), and (**1c**) are dominated by the peaks for $R_2Se_2^+$ and its fragment ions. All three derivatives decompose on heating to give a red melt: (**1a**) (decomp. 225—230 °C), (**1b**) (164—168 °C), (**1c**) (148—155 °C). Compounds (**1a—c**) are stable in air for a few days, but (**1b**) undergoes decomposition in the solid state after several weeks under an inert atmosphere.

The sulphur analogue of (**1b**) has been reported[3a] but no structural information is available. Crystals of (**1b**) were obtained by recrystallization from CH_2Cl_2 at 0 °C and the structure was determined by *X*-ray crystallography.‡ The molecular geometry and atomic numbering scheme are shown in Figure 1. The molecule is an eight-membered chair in which the two phosphorus and four nitrogen atoms are planar to within 0.054(3) Å. The two selenium atoms are displaced on either side of the centrosymmetric ring by 1.073(2) Å and the two exocyclic methyl groups occupy axial positions (*cf.* 1,5-$Ph_4P_2N_4S_2Br_2$).[3f] The average Se–N bond length of 1.777(3) Å is close to the values found for related unsaturated ring systems containing three-co-ordinate selenium, *e.g.* $Ph_2C_2N_3SeCl$ [*d*(Se–N) 1.757(8) Å][6] and $[N_2S_2SeCl]^+$ [*d*(Se–N) 1.788(7)[7] or 1.741(4) Å[8]].

The yellow filtrate from the reaction of $MeSeCl_3$ and $Ph_2P(NSiMe_3)[N(SiMe_3)_2]$ produces yellow needles of (**2a**) in *ca.* 6% yield.† Compound (**2a**) was also isolated in low yield from the synthesis of (**1c**). The ^{77}Se NMR spectrum of (**2a**) in CH_2Cl_2 exhibits a well resolved 1:2:1 triplet at 19.1 p.p.m., ^2J (^{31}P–^{77}Se) 87 Hz. The ^{31}P NMR signal of (**2a**) occurs at an unusually low field (113.0 p.p.m.) for a cyclophosphazene.[9] Similar low-field chemical shifts for (**2b**)[2k] and related 1,5-diphosphadithiatetrazocines[10] have been attributed[2o,11] to the relatively small angles at phosphorus imposed by the cross-ring S- -S interaction [(**2b**), *d*(S–S) 2.53 Å].[2g] This interaction is strengthened significantly in (**3b**) [*d*(S–S) 2.44 Å][2o] and the ^{31}P NMR spectrum of (**3b**) shows two doublets with chemical shifts on either side of that of the parent heterocycle and a well resolved four-bond coupling between the two inequivalent phosphorus atoms (Table 1). The treatment of (**2a**) with $MeSO_3CF_3$ (1:1 molar ratio) in MeCN

† Satisfactory elemental analyses were obtained for new compounds.

‡ *Crystal data* for $C_{26}H_{26}N_4P_2Se_2$ (**1b**): M = 614.4, triclinic, space group $P\bar{1}$; at 298 K a = 8.697(2), b = 8.934(2), c = 10.163(2) Å, α = 81.36(2), β = 68.46(1), γ = 65.69(2)°, U = 669.3 Å^3, Z = 2, μ(Mo-K_α) = 28.42 cm^{-1}, $F(000)$ = 324, D_c = 1.524 g cm^{-3}. Intensity data were collected at 298 K on an Enraf-Nonius CAD-4F diffractometer operating in the ω–2θ mode and using Mo-K_α radiation (λ = 0.71069 Å, graphite monochromator). Total number of unique reflections 5879, of which 3513 had $I > 2.0\sigma(I)$. Crystal dimensions 0.23 × 0.37 × 0.31 mm^3. The structure was solved by symbolic addition and was refined by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms to R 0.073 and R_w 0.044. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

at 0 °C produces (**3a**) with similar ^{31}P NMR parameters (Table 1) to those of (**3b**). Thus the ^{31}P NMR data strongly suggest the presence of a cross-ring Se - - Se interaction in (**2a**) and (**3a**). However, (**2a**) deposits selenium slowly in the solid state and more rapidly in solution at 25 °C and this decomposition has thwarted attempts to obtain crystals of (**2a**) suitable for *X*-ray crystallography.

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