Our attempt to prepare the mononuclear species $WCl_3(PMe_2Ph)_3$ from the dinuclear edge-sharing compound $W_2Cl_6(PMe_2Ph)_4$ in the presence of excess phosphine ligand was unsuccessful. Recently, it was reported[15] that the opposite reaction does not proceed either. We find this result puzzling and are reexamining it.

We carried out the ^{31}P NMR experiment for **1** to determine whether we could observe an equilibrium between the edge-sharing and face-sharing dinuclear complexes as reported[7] by Chisholm et al. for the PEt_3 ligand. We have not yet been able to observe such an equilibrium, but the work is continuing. The $^{31}P\{^1H\}$ NMR spectrum of **3** is similar to that of the face-sharing compound[7] $W_2Cl_6(PEt_3)_3$ (**6**) in equilibrium with the corresponding edge-sharing compound, and the $^2J_{P-P}$ values are 44.7 and 44.0 Hz for **3** and **6**, respectively.

The crystal structures of these complexes allow us to make some interesting comparisons with those of related molybdenum and tungsten compounds, as shown in Table XI. The W–W bond lengths in compounds **2** and **4b** are the shortest in any neutral halogen-bridged dinuclear W(III) complexes so far reported. Another striking feature in the bromo-bridged complexes **4a** and **4b** is that the average $W-Br_b-W$ angles are only 56.28 (for **4a**) and 55.32° (for **4b**). In general, the $M-X_b$ distances are shorter than the $M-X_t$ distances in the edge-sharing compounds while the opposite is true in the face-sharing compounds.

Acknowledgment. We thank Professor M. H. Chisholm for providing unpublished information and Dr. Lee M. Daniels for very helpful discussion and aid with graphics. We also thank the Robert A. Welch Foundation for financial support.

Registry No. **1**, 139376-26-4; **2**, 139376-27-5; **3**, 139376-28-6; **4a**, 139376-29-7; **5**, 139376-30-0; W, 7440-33-7.

Supplementary Material Available: Full tables of hydrogen atom parameters, bond distances, bond angles, and anisotropic displacement parameters for **1**, **2**, **4a**, and **4b** and a least-squares planes for **1** (26 pages); tables of observed and calculated structure factors for **1**, **2**, **4a**, and **4b** (81 pages). Ordering information is given on any current masthead page.

---

[15] Hills, A.; Hughes, D. L.; Leigh, G. L.; Prieto-Alcon, R. *J. Chem. Soc., Dalton Trans.* **1991**, 1515.

[16] Chisholm, M. H. Private communications, 1991.

[17] Jackson, R. B.; Strieb, W. E. *Inorg. Chem.* **1971**, *10*, 1760.

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

Reactions of $Ph_2PN_2(SiMe_3)_3$ with Organochalcogen Halides: Preparation, X-ray Structure, and Reactions of $Ph_2PN_2(SiMe_3)_2(SPh)$ with E_2Cl_2 (E = S, Se) and PhSeCl

Tristram Chivers,* Santhanathan S. Kumaravel, Masood Parvez, and M. N. Sudheendra Rao

Received October 15, 1991

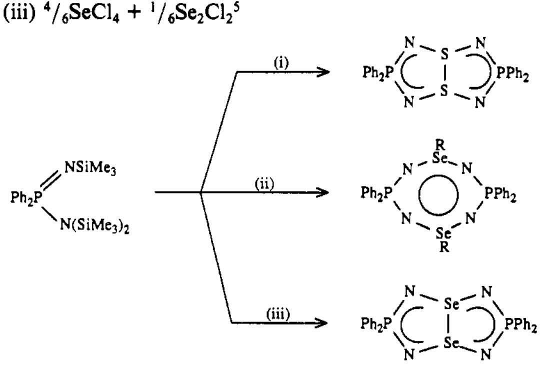
The reactions of $Ph_2PN_2(SiMe_3)_3$ with arenesulfenyl chlorides in a 1:1 or 1:3 molar ratio in methylene dichloride produces the metathetical products $Ph_2PN_2(SiMe_3)_2(SAr)$ [**1a**, Ar = Ph; **1b**, Ar = 2,4-$(NO_2)_2C_6H_3$] or $Ph_2PN_2(SAr)_3$ (**2d**, Ar = 2,4-$(NO_2)_2C_6H_3$), respectively. Compound **2d** is thermally stable below ca. 80 °C whereas the trisubstituted derivatives $Ph_2PN_2(EPh)_3$ (E = S, Se) decompose above 0 °C to give the eight-membered rings 1,5-$Ph_4P_2N_4E_2Ph_2$ with the elimination of Ph_2E_2. The structure of **1a** was determined by X-ray crystallography. The crystals of **1a** are monoclinic, space group $P2_1$ with $a = 9.824$ (4) Å, $b = 10.322$ (3) Å, $c = 13.425$ (7) Å, $\beta = 102.75$ (4)°, $V = 1327.8$ Å^3, and $Z = 2$. The three-coordinate (amino) nitrogen atom in **1a** is attached to three consecutive third-row elements (Si, P, and S). The reaction of **1a** with 2 molar equiv of PhSeCl or with Se_2Cl_2 produces 1,5-$Ph_4P_2N_4S_2Ph_2$ in 65–75% with the elimination of Ph_2Se_2 and selenium, respectively. The reactions of **1a** or $Ph_2PN_2(SiMe_3)_3$ with S_2Cl_2 under a variety of conditions yield the heterocycles 1,5-$Ph_4P_2N_4S_2Cl_2$ and $Ph_4P_2N_3SCl$ as the major products.

Introduction

The readily prepared reagents $R_2PN_2(SiMe_3)_3$[1] provide a fertile source of eight-membered phosphorus–nitrogen (P–N) ring systems containing sulfur or selenium in a low oxidation state (see Scheme I).[2-5] These cyclocondensation reactions with polyfunctional reagents must involve a number of steps. In an attempt to gain a better understanding of these systems, we have investigated the reactions of $R_2PN_2(SiMe_3)_3$ (R = Ph, Me) with *mono*functional reagents of the type PhECl (E = S, Se). When these reactions are carried out in a 1:3 molar ratio (eq 1) the eight-membered rings 1,5-$Ph_4P_2N_4E_2Ph_2$ are obtained in good yields, with the elimination of Ph_2E_2, as described in a preliminary communication.[6]

In this account we provide further details of these investigations, including (a) the preparation of the monosubstituted derivatives $R_2PN_2(SiMe_3)_2(SAr)$ (**1a**, R = Ar = Ph; **1b**, R = Ph, Ar = 2,4-$C_6H_3(NO_2)_2$; **1c**, R = Me, Ar = Ph), (b) the X-ray structure of **1a**, (c) the preparation of the trisubstituted derivative $Ph_2PN_2(SAr)_3$ [Ar = 2,4-$C_6H_3(NO_2)_2$], (d) the formation of the eight-membered rings 1,5-$R_4P_2N_4E_2Ph_2$ (R = Me, Ph, E = S; R = Ph, E = Se) by the decomposition of $R_2PN_2(EPh)_3$; (e) the preparation of 1,5-$Ph_4P_2N_4S_2Ph_2$ by the reaction of **1a** with PhSeCl (1:2 molar ratio) or Se_2Cl_2, and (f) the reactions of **1a** or $Ph_2PN_2(SiMe_3)_3$ with S_2Cl_2.

Scheme I. Preparation of $P_2N_4E_2$ Rings (E = S, Se) from $Ph_2PN_2(SiMe_3)_3$: (i) SCl_2[2] or $SOCl_2$;[3] (ii) $RSeCl_3$ (R = Me, Et, Ph);[4] (iii) $^4/_6SeCl_4$ + $^1/_6Se_2Cl_2$[5]



---

[1] (a) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1977**, *16*, 2519. (b) Wilburn, J. C.; Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 1429.

[2] Chivers, T.; Dhathathreyan, K. S.; Liblong, S. W.; Parks, T. *Inorg. Chem.* **1988**, *27*, 1305.

[3] Chivers, T.; Edwards, M.; Parvez, M. *Inorg. Chem.*, in press.

[4] Chivers, T.; Doxsee, D. D.; Fait, J. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1703.

[5] Chivers, T.; Doxsee, D. D. Unpublished observations.

[6] Chivers, T.; Kumaravel, S. S.; Meetsma, A.; van de Grampel, J. C.; van der Lee, A. *Inorg. Chem.* **1990**, *29*, 4591.

Exerimental Section

Reagents and General Procedures. All reactions and the manipulation of moisture-sensitive compounds were carried out under an atmosphere of dry N_2 by using Schlenk techniques or a Vacuum Atmospheres drybox.

The following reagents were prepared by literature procedures: $R_2PN_2(SiMe_3)_3$ (R = Ph, Me)[2] and PhSCl.[7] The commercially available compounds Ph_2S_2, 2,4-$(NO_2)_2C_6H_3SCl$, S_2Cl_2, Ph_2Se_2, PhSeCl, and Se_2Cl_2 (all from Aldrich) were used as received. The reagents CCl_3SCl (Aldrich) and SO_2Cl_2 (Aldrich) were distilled before use. All solvents were dried and distilled before use: CH_3CN (P_4O_{10} and CaH_2), CH_2Cl_2 (P_4O_{10}), and pentane and hexanes (CaH_2).

Instrumentation. Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls (KBr windows) on a Nicolet 5DX FT-IR spectrophotometer. Mass spectra were measured on a Kratos MS80RFA instrument (EI/70 eV). ^1H NMR spectra were obtained on a Bruker ACE 200 spectrometer, and chemical shifts are reported relative to Me_4Si in $CDCl_3$. ^{31}P NMR spectra were recorded on a Varian XL 200 spectrometer, and chemical shifts are reported relative to external 85% H_3PO_4.

Chemical analyses were performed by the Analytical Services Division, Department of Chemistry, The University of Calgary, and the Canadian Microanalytical Service, New Westminster, B.C.

Preparation of $Ph_2PN_2(SiMe_3)_2(SPh)$ (1a). A solution of PhSCl (1.2 g, 8.3 mmol) in CH_2Cl_2 (20 mL) was added dropwise (90 min) to a stirred solution of $Ph_2PN_2(SiMe_3)_3$ (3.5 g, 8.1 mmol) in CH_2Cl_2 (30 mL) at 25 °C. After 20 h, solvent was removed under vacuum, and the residual oil was dissolved in CH_3CN (30 mL) and cooled at −20 °C for 1 day to give moisture-sensitive, colorless needles of $Ph_2PN_2(SiMe_3)_2(SPh)$ (**1a**) (2.9 g, 76%), mp 104–105 °C. Anal. Calcd for $C_{24}H_{33}N_2PSSi_2$: C, 61.50; H, 7.10; N, 5.98. Found: C, 61.52; H, 7.37; N, 5.96. IR (Nujol, cm^{-1}): 1584 m, 1478 m, 1437 s, 1292 vs, 1257 s, 1243 s, 1115 s, 1106 m, 923 s, 900 vs, 890 s, 861 vs, 841 vs, 749 s, 735 s, 721 m, 695 s, 552 s, 526 s. ^1H NMR ($CDCl_3$): δ 7.17–7.83 [m, $P(C_6H_5)_2$, 10 H], 6.59–6.95 (m, SC_6H_5, 5 H), 0.49 [s, $>NSi(CH_3)_3$, 9 H], −0.11 [$=NSi(CH_3)_3$, 9 H]. ^{31}P NMR (CH_2Cl_2): δ +15.8.

Preparation of $Ph_2PN_2(SiMe_3)_2[SC_6H_3(NO_2)_2$-2,4] (1b). A solution of 2,4-$(NO_2)_2C_6H_3SCl$ (0.55 g, 2.35 mmol) in CH_3CN (20 mL) was added dropwise (1 h) to a stirred solution of $Ph_2PN_2(SiMe_3)_3$ (1.0 g, 2.32 mmol) in CH_3CN (20 mL) at 25 °C. After 4 h, solvent was removed from the dark red solution under vacuum, and the oily residue was extracted with pentane (30 mL) and cooled to −20 °C for 2 days to give moisture-sensitive, dark red crystals of $Ph_2PN_2(SiMe_3)_2[SC_6H_3(NO_2)_2$-2,4] (**1b**) (0.52 g, 40%), mp 126–128 °C. Anal. Calcd for $C_{24}H_{31}PN_4SSi_2O_4$: C, 51.58; H, 5.60; N, 10.03. Found: C, 50.42; H, 5.21; N, 10.35. IR (Nujol, cm^{-1}): 1594 m, 1576 s, 1498 s, 1440 s, 1346 m, 1329 vs, 1296 s, 1254 s, 1147 m, 1139 m, 1118 s, 1095 s, 1071 vs, 1052 s, 1029 m, 952 m, 857 m, 845 m, 736 m, 720 m, 529 m. ^1H NMR ($CDCl_3$): δ 8.13–9.10 [$SC_6H_3(NO_2)_2$, 3 H], 7.40–7.95 [$P(C_6H_5)_2$, 10 H], 0.17 [$NSi(CH_3)_3$, 18 H]. ^{31}P NMR (CH_2Cl_2): δ +24.4.

The CH_3CN extract of the pentane-insoluble residue was cooled to 0 °C to give [2,4-$(NO_2)_2C_6H_3S]_2$ (100 mg) as a yellow powder. Anal. Calcd for $C_{12}H_6N_4O_8S_2$: C, 36.18; H, 1.52; N, 14.07. Found: C, 36.20; H, 1.42; N, 14.02.

Preparation of $Me_2PN_2(SiMe_3)_2(SPh)$ (1c). A solution of PhSCl (1.05 g, 7.3 mmol) in CH_2Cl_2 (5 mL) was added dropwise to $Me_2PN_2(SiMe_3)_3$ (2.20 g, 7.1 mmol) in CH_2Cl_2 (20 mL) with stirring at 0 °C. Afer 16 h the solvent was removed under vacuum and the residue was distilled to give $Me_2PN_2(SiMe_3)_2(SPh)$ (**1c**) as a very pale green oil (0.75 g, 2.2 mmol), bp 105–106 °C (0.25 Torr). Anal. Calcd for $C_{14}H_{29}N_2PSSi_2$: C, 48.80; H, 8.48; N, 8.13. Found: C, 48.92; H, 8.52; N, 7.73. IR (liquid, cm^{-1}) 3075 m, 3061 m, 2950 s, 2896 m, 1583 m, 1478 m, 1439 m, 1419 m, 1408 m, 1384 m, 1316 s, 1283 s, 1247 s, 1024 m, 954 s, 927 s, 915 s, 896 m, 872 s, 855 s, 838 s, 761 s, 737 s, 691 m, 678 m, 649 m, 634 m, 401 m. ^1H NMR ($CDCl_3$): δ 7.55–7.05 (m, C_6H_5, 5 H), 1.53 [d, CH_3, 3 H, $^2J(^1H-^{31}P)$ = 13 Hz], 1.34 [d, CH_3, 3 H, $^2J(^1H-^{31}P)$ = 13 Hz], 0.37 [s, $Si(CH_3)_3$, 9 H], 0.05 [s, $Si(CH_3)_3$, 9 H], ^{31}P NMR (CH_2Cl_2): δ +27.7.

Preparation of $Ph_2PN_2[SC_6H_3(NO_2)$-2,4]$_3$ (2d). A solution of $Ph_2PN_2(SiMe_3)_3$ (1.0 g, 2.31 mmol) in CH_3CN (20 mL) was added dropwise (90 min) to a stirred solution of 2,4-$(NO_2)_2C_6H_3SCl$ (1.63 g, 6.95 mmol) in CH_3CN (30 mL) at 25 °C. After 16 h, an orange-yellow precipitate (1.26 g, 67%) was separated from the red solution by filtration and recrystallized from CH_3CN-CH_2Cl_2 (3:2) at −20 °C to give orange-red plates of $Ph_2PN_2[SC_6H_3(NO_2)_2$-2,4]$_3$ (**2d**). *Caution!* A small sample decomposed explosively at ca. 200 °C during a melting point determination. Anal. Calcd for $C_{30}H_{19}PN_8S_3O_{12}$: C, 44.44; H, 2.37; N, 13.82. Found: C, 43.35; H, 2.20; N, 13.48. IR (Nujol, cm^{-1}): 1595 s, 1519 s, 1365 m, 1340 vs, 1300 m, 1117 s, 1087 m, 1077 m, 1052 m, 831 m, 734 m, 725 m. ^1H NMR ($CDCl_3$): δ 7.45–9.22 (m). ^{31}P NMR (CH_2Cl_2): δ +39.5.

A small amount (50 mg) of [2,4-$(NO_2)_2C_6H_3S]_2$ was obtained upon keeping the CH_3CN filtrate at 0 °C for 7 days.

Attempted Synthesis of $Ph_2PN_2(SCCl_3)_3$. A solution of $Ph_2PN_2(SiMe_3)_3$ (2.70 g, 6.25 mmol) in CH_2Cl_2 (45 mL) was added slowly (2.5 h) to a stirred solution of Cl_3CSCl (3.50 g, 18.8 mmol) in CH_2Cl_2 (30 mL) at −5 °C. After 20 h at 25 °C, solvent was removed under vacuum to give a viscous, yellow oil. A CCl_4 extract of this residue gave a single ^{31}P NMR resonance at +39.8 ppm, but it was not possible to obtain an analytically pure sample of this product.

Preparation of 1,5-$Ph_4P_2N_4(SPh)_2$ (3a). Benzenesulfenyl chloride (1.80 g, 12.6 mmol) was added dropwise to a stirred solution of $Ph_2PN_2(SiMe_3)_3$ (1.80 g, 4.20 mmol) in CH_2Cl_2 (50 mL) at 0 °C. After 16 h, the removal of solvent under vacuum followed by extraction of the solid residue with pentane gave Ph_2S_2 (0.55 g, 2.50 mmol). Recrystallization of the residue from CH_2Cl_2 afforded colorless crystals of 1,5-$Ph_4P_2N_4(SPh)_2$ (**3a**) (0.81 g, 1.26 mmol, 60%), mp 238–240 °C. Anal. Calcd for $C_{36}H_{30}N_4P_2S_2$: C, 67.07; H, 4.69; N, 8.69. Found: C, 66.73; H, 4.71; N, 8.63. IR (Nujol, cm^{-1}): 1437 s, 1116 m, 1110 s, 1097 s, 1077 m, 1067 m, 1035 s, 1019 s, 993 m, 749 m, 739 m, 719 m, 694 m, 556 m, 534 m, 516 m, 478 m, 455 m, 430 m. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ +29.3.

When this reaction was carried out *in the absence of a solvent* the yield of 1,5-$Ph_4P_2N_4(SPh)_2$ was 80%.

Preparation of 1,5-$Me_4P_2N_4(SPh)_2$ (3c). Liquid $Me_2PN_2(SiMe_3)_3$ (2.01 g, 6.50 mmol) was added dropwise by syringe to a solution of PhSCl (2.84 g, 19.7 mmol) in CH_2Cl_2 (30 mL) at 23 °C. After 30 min, the solvent was removed under vacuum, and the residue was extracted with hexanes to give Ph_2S_2 (1.42 g, 6.50 mmol). Recrystallization of the residue from CH_2Cl_2 gave colorless crystals of 1,5-$Me_4P_2N_4(SPh)_2$ (**3c**) (0.32 g, 0.81 mmol), mp 218–220 °C. Anal. Calcd for $C_{16}H_{22}N_4P_2S_2$: C, 48.47; H, 5.59; N, 14.13. Found: C, 48.16; H, 5.61; N, 14.12. IR (Nujol, cm^{-1}): 1444 s, 1412 m, 1303 m, 1294 s, 1287 s, 1102 s, 1090 s, 1061 s, 1018 s, 1000 s, 979 s, 943 s, 925 s, 873 s, 854 m, 751 s, 739 m, 711 m, 692 s, 653 s, 616 m, 500 s, 490 m, 442 s, 432 s, 400 m. ^1H NMR ($CDCl_3$): δ 7.9–7.8 and 7.55–7.35 (m, C_6H_5, 10 H), 1.75 [d, CH_3, 12 H, $^2J(^1H-^{31}P)$ = 13.0 Hz]. ^{31}P NMR (CH_2Cl_2): δ +46.6.

Preparation of 1,5-$Ph_4P_2N_4(SePh)_2$ (3b). The reaction of $Ph_2PN_2(SiMe_3)_3$ with PhSeCl in a 1:3 molar ratio in CH_2Cl_2 at 0 °C produced 1,5-$Ph_4P_2N_4(SePh)_2$ (**3b**) (60%), which was identified by comparison of IR and NMR spectra with those of an authentic sample [$\delta(^{31}P)$ NMR (in CH_2Cl_2): δ +33.2; cf. literature value of δ +33.6[4]]. Ph_2Se_2 was isolated in 54% yield by extraction of the crude product with hexanes.

Reaction of $Ph_2PN_2(SiMe_3)_2(SPh)$ with 2PhSeCl. A solution of PhSeCl (0.56 g, 2.92 mmol) in CH_2Cl_2 (15 mL) was added dropwise (30 min) to a stirred solution of $Ph_2PN_2(SiMe_3)_2(SPh)$ (**1a**) (0.67 g, 1.43 mmol) in CH_2Cl_2 (15 mL) at 25 °C. After 60 h, solvent was removed under vacuum, and the yellow residue was extracted with hexane to give Ph_2Se_2 (0.30 g, 0.96 mmol). The hexane-insoluble solid was washed with CH_3CN (3 × 5 mL) to give 1,5-$Ph_4P_2N_4(SPh)_2$ (**3a**) (0.30 g, 65%) identified by comparison of IR and ^{31}P NMR spectra with those of an authentic sample. An additional 60 mg of 1,5-$Ph_4P_2N_4(SPh)_2$ was obtained from the CH_3CN solution after 5 days at 0 °C.

Reaction of $Ph_2PN_2(SiMe_3)_2(SPh)$ with Se_2Cl_2. A solution of Se_2Cl_2 (0.50 g, 2.18 mmol) in CH_2Cl_2 (50 mL) was added very slowly (3.5 h) to a stirred solution of $Ph_2PN_2(SiMe_3)_2(SPh)$ (1.0 g, 2.14 mmol) in CH_2Cl_2 (50 mL) at 25 °C. After 20 h, the precipitate of red selenium (0.325 g, 94%) was removed by filtration. Solvent was removed from the filtrate under vacuum and the yellow, semisolid residue was washed with CH_3CN (20 mL) to give 1,5-$Ph_4P_2N_4(SPh)_2$ (**3a**) (0.45 g, 65%) as an insoluble white solid.

Reaction of $Ph_2PN_2(SiMe_3)_2(SPh)$ with S_2Cl_2. (i) A solution of S_2Cl_2 (0.44 g, 3.26 mmol) in CH_2Cl_2 (70 mL) was added very slowly (5 h) to a stirred solution of $Ph_2PN_2(SiMe_3)_2(SPh)$ (1.0 g, 2.14 mmol) in CH_2Cl_2 (50 mL) at 25 °C. After 16 h solvent was removed under vacuum and the residue was extracted with CH_3CN (25 mL). The pale yellow residue was shown to be slightly impure 1,5-$Ph_4P_2N_4S_2Cl_2$ (0.20 g) by comparison of the IR spectrum with that reported in the literature.[8] The CH_3CN filtrate was reduced in volume to ca. 15 mL and cooled to −20 °C for 2 days to give highly moisture-sensitive, colorless crystals of 1,5-$Ph_4P_2N_4S_2Cl_2$ (0.10 g), mp 155–156 °C dec (cf. lit. mp 156–158 °C dec[8]). Anal. Calcd for $C_{24}H_{20}Cl_2N_4P_2S_2$: C, 51.34; H, 3.60; N, 9.98. Found: C, 50.74; H, 3.61; N, 9.85. ^{31}P NMR (CH_2Cl_2): δ +2.2.

The CH_3CN filtrate was further reduced in volume to ca. 5 mL and then cooled to −20 °C for 3 days to give a mixture of $Ph_4P_2N_3SCl$ (80 mg) as very pale yellow, rectangular crystals and an unidentified phos-

---

(7) Mueller, W. H. *J. Am. Chem. Soc.* **1968**, *90*, 2075.

(8) Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1946.

Table I. Crystallographic Data for $Ph_2PN_2(SiMe_3)_2(SPh)$ (**1a**)

formula	$C_{24}H_{33}N_2PSSi_2$	Z	2
fw	468.75	T, K	165
space group	$P2_1$	λ, Å	0.710 69
a, Å	9.824 (4)	ρ_{calcd}, g cm^{-3}	1.173
b, Å	10.322 (3)	μ, mm^{-1}	0.243
c, Å	13.425 (7)	R^a	0.0972
β, deg	102.75 (4)	$R_w{}^b$	0.1054
V, Å^3	1327.8		

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w\Delta^2/\sum wF_o{}^2]^{1/2}$.

phorus-containing compound (40 mg) [$\delta(^{31}P)$ +14.0 in CH_2Cl_2], which were separated manually. The former product was identified by comparison of IR and NMR data with the literature values [$\delta(^{31}P)$ +7.8; lit. value +7.6[9]].

Reaction between $Ph_2PN_2(SiMe_3)_3$ with S_2Cl_2. A solution of S_2Cl_2 (1.58 g, 11.7 mmol) in CH_2Cl_2 (40 mL) was added dropwise (1 h) to a stirred solution of $Ph_2PN_2(SiMe_3)_3$ (2.53 g, 5.86 mmol) at −78 °C. After 8 h the solution was allowed to reach 25 °C and then filtered to remove a sticky yellow precipitate, which was mostly sulfur. The filtrate was reduced in volume to ca. 20 mL and cooled to −20 °C for 4 days to give white crystals of 1,5-$Ph_4P_2N_4S_2Cl_2$ (0.25 g) (IR spectrum).[8] Solvent was removed from the filtrate under vacuum and the residue was extracted with CH_3CN (25 mL). When the CH_3CN extract was cooled to −20 °C, white crystals of $Ph_4P_2N_3SCl$ (0.25 g) (IR spectrum)[9] were obtained. The CH_3CN-insoluble solid (0.30 g) had $\delta(^{31}P)$ +14.0 ppm in CH_2Cl_2; mp 125–130 °C dec (to give a purple melt). In CH_2Cl_2 solution at 25 °C this product decomposes to give 1,5-$Ph_4P_2N_4S_2Cl_2$ [$\delta(^{31}P)$ +2.3], 1,5-$Ph_4P_2N_4S_2$ [$\delta(^{31}P)$ +114.1; cf. lit. value δ +113.8[2]], and $Ph_4P_2N_3SCl$ [$\delta(^{31}P)$ +7.8; cf. lit. value δ +7.6[9]].

X-ray Analysis. Crystals of $Ph_2PN_2(SiMe_3)_2(SPh)$ (**1a**) were obtained by recrystallization from acetonitrile. Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf-Nonius CAD-4 diffractometer by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected by the $\omega/2\theta$ scan method using variable scan speed (1.54–6.67° min^{-1}), scan width of (1.00 + 0.35 tan θ)°, and monochromatized Mo Kα radiation in the range $2 < \theta < 25°$ with h = 0 to 11, k = 0 to 12, and l = −15 to 15. Three reflections were monitored every 2 h of exposure time and showed insignificant variations. The intensities of 2699 reflections were measured, of which 2136 had $I > 3\sigma(I)$, where $\sigma^2 I = S + 2B + [0.04(S - B)]^2$, with S = scan count, and B = time-averaged background count extended 25% on each side. Data were corrected for Lorentz–polarization; an absorption correction was considered unnecessary. Crystal data are given in Table I.

The structure was solved by direction methods. Refinement of the structure was by full-matrix least-squares calculations, 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 most of the H atoms, which were included in the subsequent cycles at geometrically idealized positions (C–H = 0.95 Å) and fixed overall isotropic temperature factors; phenyl rings were refined as regular hexagons. Refinement converged with R = 0.097 and R_w = 0.105. The final values of the refined positional parameters are given in Table II. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann[10] and Stewart, Davidson, and Simpson[11] and allowance was made for anomalous dispersion.[12] A difference map calculated at the conclusion of the refinement showed maxima in the vicinity of the Me_3Si group bonded to N(2) which reflected gross disorder in this part of the molecule. The computer program used in this study was SHELX76[13] and Figure 1 was plotted using ORTEPII.[14]

Table II. Atomc Coordinates (×10^4) for $Ph_2PN_2(SiMe_3)_2(SPh)$ with Esd's in Parentheses

atom	x	y	z
P	1958 (3)	2785^a	2473 (2)
S	3709 (3)	2146 (4)	1079 (2)
Si(1)	4833 (3)	4015 (5)	2817 (2)
Si(2)	1467 (3)	3560 (4)	4545 (2)
N(1)	3481 (9)	3027 (10)	2088 (7)
N(2)	2011 (9)	3605 (12)	3419 (6)
C(1)	1830 (5)	1044 (7)	2631 (5)
C(2)	3034 (5)	308 (7)	2972 (5)
C(3)	2928 (5)	−1009 (7)	3174 (5)
C(4)	1618 (5)	−1592 (7)	3034 (5)
C(5)	414 (5)	−856 (7)	2693 (5)
C(6)	520 (5)	461 (7)	2492 (5)
C(7)	532 (7)	3221 (7)	1411 (5)
C(8)	120 (7)	2454 (7)	541 (5)
C(9)	−981 (7)	2850 (7)	−245 (5)
C(10)	−1671 (7)	4013 (7)	−160 (5)
C(11)	−1259 (7)	4780 (7)	710 (5)
C(12)	−158 (7)	4348 (7)	1496 (5)
C(13)	3523 (9)	3235 (8)	47 (6)
C(14)	3967 (9)	2780 (8)	−807 (6)
C(15)	3907 (9)	3587 (8)	−1649 (6)
C(16)	3401 (9)	4849 (8)	−1673 (6)
C(17)	2957 (9)	5303 (8)	−783 (6)
C(18)	3018 (9)	4496 (8)	59 (6)
C(19)	5495 (11)	3288 (16)	4091 (10)
C(20)	4195 (15)	5711 (16)	2920 (13)
C(21)	6242 (12)	4041 (20)	2067 (10)
C(22)	−477 (12)	3601 (18)	4296 (11)
C(23)	2080 (19)	2073 (22)	5307 (12)
C(24)	2210 (20)	4995 (22)	5317 (12)

^{a} Fixed y coordinate to define the origin.

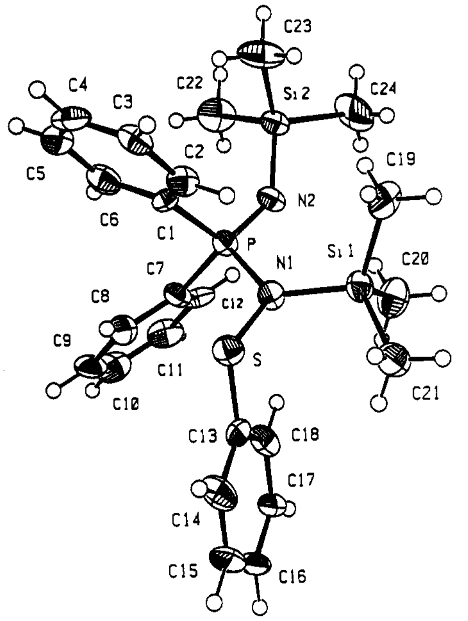


Figure 1. ORTEP plot for $Ph_2PN_2(SiMe_3)_2(SPh)$ (**1a**).

Results and Discussion

Synthesis of Monosubstituted Derivatives $R_2PN_2(SiMe_3)_2(SAr)$. The monosubstituted products $Ph_2PN_2(SiMe_3)_2(SAr)$ [**1a**, Ar = Ph; **1b**, Ar = 2,4-$(NO_2)_2C_6H_3$] are readily obtained in good yields from the reaction of $Ph_2PN_2(SiMe_3)_3$ with ArSCl in a 1:1 molar ratio in methylene dichloride at 0 °C. Compounds **1a** and **1b** are moisture-sensitive, colorless and orange-red crystalline solids, respectively. Two singlets are observed at +0.49 and −0.11 ppm for the Me_3Si groups of **1a** in the ^1H NMR spectrum indicating that substitution of the SAr group has occurred at the amino rather than the imino nitrogen atom. For comparison the related compound $PhCN_2(SiMe_3)_2(SPh)$ exhibits a singlet at 0.25 ppm in the ^1H NMR spectrum at 25 °C, suggesting that both Me_3Si groups are attached to the same (amino) nitrogen atom or that a rapid 1,3-shift of the SPh group occurs at this temperature.[15] The derivative $Me_2PN_2(SiMe_3)_2(SPh)$ (**1c**) was obtained in a similar

---

(9) Chivers, T.; Rao, M. N. S. *Inorg. Chem.* **1984**, *23*, 3605.

(10) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(12) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

(13) Sheldrick, G. M. SHELX76. A program system for crystal structure determination. University of Cambridge, Cambridge, England, 1976.

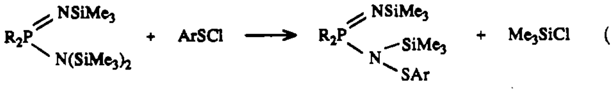
(14) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(15) Chandrasekhar, V.; Chivers, T.; Kumaravel, S. S.; Parvez, M.; Rao, M. N. S. *Inorg. Chem.* **1991**, *30*, 4125.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $Ph_2PN_2(SiMe_3)_2(SPh)$

N(1)–P	1.706 (9)	C(19)–Si(1)	1.849 (13)
N(2)–P	1.518 (10)	C(20)–Si(1)	1.875 (17)
C(1)–P	1.818 (7)	C(21)–Si(1)	1.884 (12)
C(7)–P	1.821 (7)	N(2)–Si(2)	1.711 (9)
N(1)–S	1.687 (9)	C(22)–Si(2)	1.865 (12)
C(13)–S	1.762 (8)	C(23)–Si(2)	1.869 (17)
N(1)–Si(1)	1.786 (9)	C(24)–Si(2)	1.861 (18)
N(2)–P–N(1)	107.5 (5)	C(23)–Si(2)–C(22)	108.1 (8)
C(1)–P–N(1)	105.6 (4)	C(24)–Si(2)–N(2)	108.8 (7)
C(1)–P–N(2)	116.3 (5)	C(24)–Si(2)–C(22)	110.0 (8)
C(7)–P–N(1)	107.6 (4)	C(24)–Si(2)–C(23)	108.0 (9)
C(7)–P–N(2)	113.3 (4)	S–N(1)–P	116.4 (5)
C(7)–P–C(1)	106.0 (3)	Si(1)–N(1)–P	120.9 (5)
C(13)–S–N(1)	106.1 (4)	Si(1)–N(1)–S	122.3 (5)
C(19)–Si(1)–N(1)	110.1 (6)	Si(2)–N(2)–P	139.9 (7)
C(20)–Si(1)–N(1)	110.7 (6)	C(2)–C(1)–P	120.1 (2)
C(20)–Si(1)–C(19)	111.5 (7)	C(6)–C(1)–P	119.7 (2)
C(21)–Si(1)–N(1)	105.1 (6)	C(8)–C(7)–P	123.1 (2)
C(21)–Si(1)–C(19)	110.5 (6)	C(12)–C(7)–P	116.9 (2)
C(21)–Si(1)–C(20)	108.8 (8)	C(14)–C(13)–S	115.8 (2)
C(22)–Si(2)–N(2)	110.4 (5)	C(18)–C(13)–S	124.2 (2)
C(23)–Si(2)–N(2)	112.3 (7)		

manner as a pale green, moisture-sensitive oil, which exhibited two resonances for the methyl groups attached to phosphorus (vide infra) as well as signals for the inequivalent Me_3Si group in the ^1H NMR spectrum.



(1)

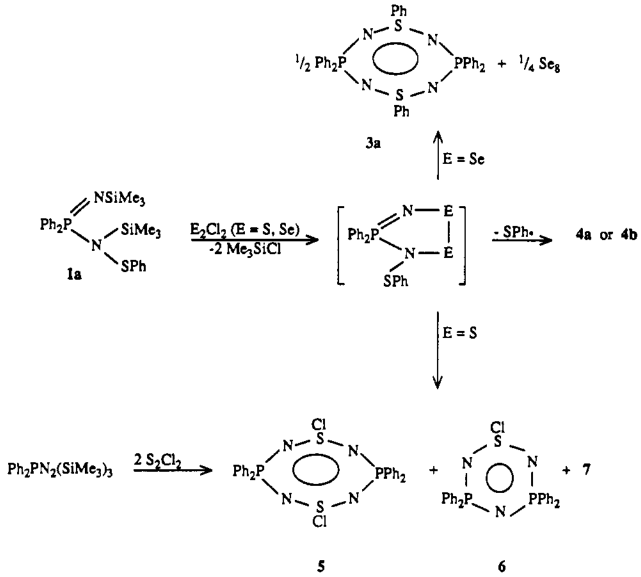
1a, R = Ar = Ph
1b, R = Ph, Ar = 2,4-$(NO_2)_2C_6H_3$
1c, R = Me, Ar = Ph

X-ray Structure of $Ph_2PN_2(SiMe_3)_2(SPh)$ (1a). An ORTEP drawing of **1a** with the atomic numbering scheme is displayed in Figure 1. Selected bond lengths and bond angles are given in Table III. The X-ray structural determination confirms the conclusion, based on ^1H NMR data, that the SPh group is attached to the amino nitrogen atom N(1). The most interesting feature of the structure is the geometry about N(1), which has the unique characteristic of being connected to three consecutive third-row elements, Si, P, and S. These substituents adopt an essentially planar geometry around N(1) ($\sum\hat{N}(1)$ = 359.6°). The N(2)–P–N(1)–S and N(2)–P–N(1)–S(1) units are also almost planar, with torsion angles of 176.6 and 3.9°, respectively. The S–N(1) distance is 1.687 (9) Å [cf. ca. 1.71 Å for S–N single bonds between two-coordinate sulfur and sp^2 (planar) N].[16] The Si(1)–N(1) distance of 1.786 (9) Å is close to the values of 1.765 (2) and 1.774 (2) Å found for the corresponding distances involving the planar amino nitrogen atom in $PhC(NSiMe_3)[N(SiMe_3)_2]$[17] and is substantially longer, as expected, than the Si(2)–N(2) distance of 1.711 (9) Å involving the imino nitrogen atom. The P–N bond lengths of 1.706 (9) Å [P–N(1)] and 1.518 (10) Å [P–N(2)] are indicative of single and double bonds, respectively.[18]

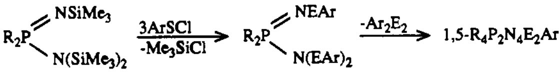
The bond angle at the two-coordinate nitrogen, N(2), is 139.9 (7)°, and the torsion angle N(1)–P–N(2)–Si(2) is –145.54°. Assuming a similar geometry for **1c**, this probably accounts for the inequivalence of the methyl groups attached to phosphorus in **1c**. The N(2)–P–N(1) angle is close to tetrahedral (107.5 (5)°), but the angles N(2)–P–C(1) and N(1)–P–C(7), 116.3 (5) and 107.6 (4)°, differ significantly probably due to the steric interactions between Me_3Si and Ph groups associated with the P–N(2) unit.

Preparation and Decomposition of the Trisubstituted Derivatives $R_2PN_2(EAr)_3$. The reaction of $R_2PN_2(SiMe_3)_3$ with 3 molar equiv of PhECl in CH_2Cl_2 at 0 °C produces the eight-membered rings 1,5-$R_4P_2N_4E_2Ph_2$ (**3a–c**), in ca. 60% yields, presumably by the decomposition of the trisubstituted derivatives $R_2PN_2(EPh)_3$ (**2a–c**) (eq 2). In the absence of a solvent the yield of **3a** was increased to 80%. No other phosphorus-containing product was formed in significant amounts (^{31}P NMR spectrum of the reaction mixture).

Scheme II. Reactions of (i) $Ph_2PN_2(SiMe_3)_2(SPh)$ and E_2Cl_2 (E = S, Se) and (ii) $Ph_2PN_2(SiMe_3)_3$ and S_2Cl_2



The formation of **3a** in CH_2Cl_2 was monitored by ^{31}P NMR spectroscopy and an intermediate, presumably **2a**, was observed at +33.0 ppm, but this intermediate was thermally unstable above 0 °C and could not be isolated. The structure of **3a** was determined by X-ray crystallography to consist of an eight-membered ring in a chair conformation, and structural details have been given in the preliminary communication.[6]



(2)

2a, R = Ar = Ph, E = S
2b, R = Ar = Ph, E = Se
2c, R = Me, Ar = Ph, E = S
2d, R = Ph, Ar = 2,4-$(NO_2)_2C_6H_3$, E = S

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

In contrast to the thermal instability of $Ph_2PN_2(SPh)_3$ (**2a**) [$\delta(^{31}P)$ +33.0] at room temperature, the trisubstituted derivative **2d** is obtained in excellent yields as air stable, orange crystals from the reaction of $Ph_2PN_2(SiMe_3)_3$ with 3 molar equiv of 2,4-$(NO_2)_2C_6H_3SCl$ in CH_2Cl_2 at 23 °C. The compound $Ph_2PN_2(SCCl_3)_3$ was also obtained in a similar manner as a viscous, yellow oil, which is thermally stable at room temperature (^{31}P NMR spectrum), but an analytically pure sample could not be obtained. The derivative **2d** exhibits good thermal stability. It can be recovered unchanged after heating for 3 h at reflux in acetonitrile. After 72 h, **2d** was recovered in ca. 50% yield, and a small amount of the disulfide $(2,4\text{-}(NO_2)_2C_6H_3S)_2$ was isolated.

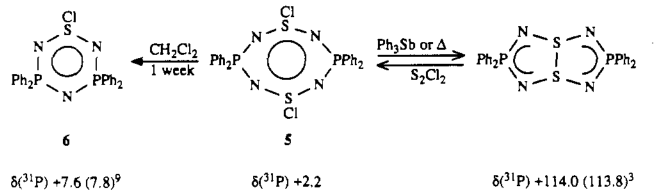
The mechanism of the formation of the eight-membered rings **3a–c** from **2a–c** (eq 2) is of interest. The trisubstituted derivatives $PhCN_2(EPh)_3$ (E = S, Se) have been shown by ESR spectroscopy to decompose with the formation of the intensely colored resonance-stabilized radicals $PhCN_2(EPh)_2^{\bullet}$ to give the diazenes *trans*-PhEN(Ph)CN=NC(Ph)NEPh,[15] which are isomers of the hypothetical eight-membered rings, 1,5-$Ph_2C_2N_4E_2Ph_2$ (cf. **3a** and **3b**). However, there is no evidence for the formation of the corresponding phosphorus-containing radicals $Ph_2PN_2(EPh)_2^{\bullet}$ from the decomposition of **2a** and **2b**; i.e., no intense colors or ESR signals are observed during the formation of **3a** and **3b**.

We note here that the related compound $(PhS)_3N$ readily undergoes homolytic cleavage of the N–S(Ph) bond to give the radical $(PhS)_2N^{\bullet}$,[19] and the selenium analogue $(PhSe)_3N$ also

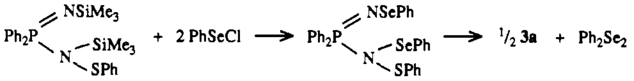
---

[16] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
[17] Ergezinger, C.; Weller, F.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43b*, 1119.
[18] Trinquier, G. *J. Am. Chem. Soc.* **1986**, *108*, 568.

Scheme III

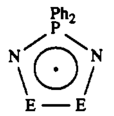


decomposes under mild conditions to give Ph$_2$Se$_2$ quantitatively.[20] The formation of **3a** and **3b** from **2a** and **2b**, respectively, must involve the facile fission of N–E(Ph) bonds. Consequently we have prepared the mixed chalcogen derivative Ph$_2$PN$_2$(SePh)$_2$(SPh) in order to determine which chalcogen-nitrogen bonds are cleaved preferentially. As indicated in eq 3, this decomposition produces 1,5-Ph$_4$P$_2$N$_4$S$_2$Ph$_2$ (**3a**) and Ph$_2$Se$_2$ (in isolated yields of 78 and 65%, respectively). Thus it appears that Se–N bonds are cleaved preferentially in this process.



(3)

Reactions of Ph$_2$PN$_2$(SiMe$_3$)$_2$(SPh) (2a) with E$_2$Cl$_2$ (E = S, Se). In view of the isoelectronic relationship between Ph$_2$P and PhC groups as substituents in an S–N ring, the 7-π-electron molecules Ph$_2$PN$_2$E$_2$$^•$ (**4a**, E = S; **4b**, E = Se), isoelectronic with the well-characterized radicals PhCN$_2$E$_2$$^•$ (E = S,[21] E = Se[22]), are reasonable target molecules.



4a, E = S
4b, E = Se

With this goal in mind we attempted to generate the PN$_2$E$_2$ ring systems by the reaction of **1a** with E$_2$Cl$_2$ in CH$_2$Cl$_2$ at 25 °C (see Scheme II). In the case of Se$_2$Cl$_2$, however, this reaction produced the eight-membered ring **3a** (65%) and elemental selenium (ca. 100%), presumably from the decomposition of $Ph_2\overline{PNSeSeN}(SPh)$. As indicated in Scheme II, the reaction of **1a** with S$_2$Cl$_2$ was more complicated and the eight-membered ring 1,5-Ph$_4$P$_2$N$_4$S$_2$Cl$_2$ (**5**)[8] and the six-membered ring Ph$_4$P$_2$N$_3$SCl (**6**)[9] were isolated as the major products together with a small amount of an unknown PNS heterocycle, **7**, with δ(^{31}P) = +14.1. Moreover, the reaction of Ph$_2$PN$_2$(SiMe$_3$)$_3$ with 2 molar equiv of S$_2$Cl$_2$ also produced **5**, **6**, and a larger amount of **7** (cf. Scheme II). In attempts to obtain a pure sample, it was shown by ^{31}P NMR spectroscopy that **7** decomposes in solution to give **5**, **6**, and 1,5-Ph$_4$P$_2$N$_4$S$_2$. In view of the identity of the decomposition products, it is possible that this thermally unstable product is the five-membered ring Ph$_2$PN$_2$S$_2$Cl.

The *S,S'*-dichloro derivative **5** was previously prepared by the oxidative-addition of Cl$_2$ (as SO$_2$Cl$_2$) to 1,5-Ph$_4$P$_2$N$_4$S$_2$,[8] but the properties of this highly moisture-sensitive compound were not investigated. In this work, the transformations represented in Scheme III were shown to take place by ^{31}P NMR spectroscopy.

Conclusions

The thermal stability of the trithiolato derivatives Ph$_2$PN$_2$(SAr)$_3$ is dependent on the nature of Ar. When Ar = 2,4-(NO$_2$)$_2$C$_6$H$_3$, this derivative is thermally stable whereas the compounds Ph$_2$PN$_2$(EPh)$_3$ (E = S, Se) undergo spontaneous decomposition below room temperature to give the eight-membered rings 1,5-Ph$_4$P$_2$N$_4$E$_2$Ph$_2$. In contrast to the thermal decomposition of the related trisubstituted benzamidines, PhCN$_2$(EAr)$_3$,[15] this conversion does not involve a radical mechanism. The benzenethiolato group in the monosubstituted derivative Ph$_2$PN$_2$(SiMe$_3$)$_2$(SPh) is attached to the amino rather than the imino nitrogen atom. Attempts to generate the unknown five-membered ring systems Ph$_2$PN$_2$E$_2$ (E = S, Se) by reactions of this derivative with E$_2$Cl$_2$ gave rise to known six- and eight-membered PNS rings containing S–Cl bonds as the final products.

Acknowledgment. We thank the NSERC (Canada) for financial support. M.N.S.R. is grateful to IIT Madras (Madras, India) for a sabbatical leave.

Registry No. **1a**, 139426-73-6; **1b**, 139426-74-7; **1c**, 139426-75-8; **2a**, 130010-89-8; **2d**, 139426-76-9; **3a**, 130010-86-5; **3b**, 130010-87-6; **3c**, 130010-88-7; **5**, 90133-21-4; **6**, 84247-67-6; Ph$_2$PN$_2$(SiMe$_3$)$_3$, 61500-31-0; Me$_2$PN$_2$(SiMe$_3$)$_3$, 21385-93-3; 2,4-(NO$_2$)$_2$C$_6$H$_3$SCl, 528-76-7; [2,4-(NO$_2$)$_6$C$_6$H$_3$S]$_2$, 2217-55-2; Ph$_2$PN$_2$(SCCl$_3$)$_3$, 139426-77-0; Cl$_3$CSCl, 594-42-3; PhSeCl, 5707-04-0; benzenesulfenyl chloride, 931-59-9.

Supplementary Material Available: Listings of crystallographic data, anisotropic thermal parameters for non-hydrogen atoms, positional parameters for hydrogen atoms, and torsion angles (6 pages); a table of observed and calculated structure factors for **1a** (13 pages). Ordering information is given on any current masthead page.

---

(19) Barton, D. H. R.; Blair, I. A.; Magnus, P. D.; Norris, R. K. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1031.

(20) Back, T. G.; Kerr, R. G. *J. Chem. Soc., Chem. Commun.* **1987**, 134.

(21) Vegas, A.; Perez-Salazar, A.; Banister, A. J.; Hey, R. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1812.

(22) 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.