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clearly demonstrated. Compared to analogous hypochlorites, these fluoroxy compounds give only low yields of addition products with fluorinated olefins due to the rapid decomposition of the intermediate $^{\bullet}OCF_2CFXSO_2F$ radicals formed in these reactions.

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Registry No. **1**, 677-67-8; **2**, 115784-53-7; **3**, 754-41-6; **4**, 115784-54-8; **5**, 67990-78-7; **6**, 84246-33-3; **7**, 14856-94-1; **8**, 132145-34-7; **9**, 135773-61-4; **10**, 135773-62-5; **11**, 135773-63-6; **12**, 81439-24-9; C_2F_4, 116-14-3; C_3F_6, 116-15-4; $FC(O)OCF_2CF(CF_3)SO_2F$, 135773-64-7; $FSO_2OCF_2CF(CF_3)SO_2F$, 135773-65-8; $FSO_2OOCF_2CF(CF_3)SO_2F$, 135773-66-9; $C_2F_5SO_2F$, 354-87-0.

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

Reactions of *N*,*N*,*N'*-Tris(trimethylsilyl)benzamidine with Organochalcogen Halides: Formation of Diazenes via the Resonance-Stabilized Radicals $PhCN_2(EPh)_2^{\bullet}$ and the X-ray Structure of $PhCN_2(SCCl_3)_3$

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

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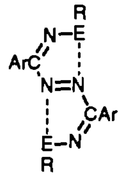
The reactions of *N*,*N*,*N'*-tris(trimethylsilyl)benzamidine (**1**) with organosulfur chlorides in a 1:1 or 1:3 molar ratio in methylene dichloride produce the metathetical products $PhC[N(SiMe_3)_2](NSR)$ [R = Ph, CCl_3, 2,4-$C_6H_3(NO_2)_2$] or $PhCN_2(SR)_3$ [R = CCl_3, 2,4-$C_6H_3(NO_2)_2$], respectively. The structure of $PhCN_2(SCCl_3)_3$ (**4b**) was determined by X-ray crystallography. The crystals of **4b** are triclinic, space group $P\bar{1}$, with $a = 9.972$ (2) Å, $b = 10.517$ (3) Å, $c = 10.968$ (3) Å, $\alpha = 109.75$ (2)°, $\beta = 93.31$ (2)°, $\gamma = 102.76$ (2)°, $V = 1044.8$ Å^3, and $Z = 2$. By contrast, the compound $PhCN_2(SPh)_3$ is thermally unstable and the reactions of **1** with PhECl (E = S, Se) in a 1:3 molar ratio in methylene dichloride produce the intensely colored diazenes *trans*-PhEN(Ph)CN=NC(Ph)NEPh. The ESR spectra of these reaction mixtures consist of a five-line (1:2:3:2:1) signal consistent with a radical mechanism involving the intermediate formation of the resonance-stabilized radicals $PhC(NEPh)_2^{\bullet}$ (E = S, $g = 2.0071$, $a_N = 0.575$ mT; E = Se, $g = 2.0201$, $a_N = 0.59$ mT). The reactions of **1** with $RSeCl_3$ (R = Me, Ph) also yield the diazenes *trans*-RSeN(Ph)CN=NC(Ph)SeR (**2a**, R = Me; **2b**, R = Ph). The reaction of $4\text{-}CF_3C_6H_4CN_2(SiMe_3)_3$ with PhSCl in a 1:3 molar ratio produces the eight-membered ring $(4\text{-}CF_3C_6H_4)_2C_2N_4S_2Ph_2$, as a minor product, in addition to the isomeric diazene. The eight-membered rings $Ph_2C_2N_4S_2R_2$ [R = CCl_3, 2,4-$(NO_2)_2C_6H_3$] are obtained from the reaction of $PhC(NSR)[N(SiMe_3)_2]$ with 2 molar equiv of PhSeCl.

Introduction

Organic sulfur–nitrogen (S–N) compounds have attracted widespread attention in recent years.[1,2] This activity is due to an intrinsic curiosity in the unusual molecular and electronic structures of these π-electron-rich compounds and to their possible role as low-dimensional conducting materials.[3,4] This interest has been extended to organic selenium–nitrogen (Se–N) compounds, e.g. the cyclic 7-π-electron radicals 1,2,4,6-selenatriazinyl, $Ph_2C_2N_3Se^{\bullet}$,[5] and 1,2,3,5-diselenadiazolyl, $PhCN_2Se_2^{\bullet}$.[6] In a seminal paper Woodward et al. reported the first dithiatetrazocines 1,5-$R_2C_2N_4S_2$ (R = Me_2N, Ph) and showed that the structures of these ring systems are remarkably dependent on the nature of the exocyclic substituent.[7] In an attempt to prepare the unknown $C_2N_4Se_2$ ring, we found that the reaction of $PhCN_2(SiMe_3)_3$ (**1**) with $RSeCl_3$ (R = Me, Ph) produces intensely colored materials identified by an X-ray structure determination of **2a** as diazenes.[8] We also mentioned briefly that the diazene **2b** and its sulfur analogue, **2c**, can be prepared in good yields by the reaction of **1** with PhECl (E = S, Se) in a 1:3 molar ratio.



2a (E = Se, R = Me, Ar = Ph)
2b (E = Se, R = Ph, Ar = Ph)
2c (E = S, R = Ph, Ar = Ph)
2d (E = S, R = Ph, Ar = 4–$CH_3C_6H_4$)
2e (E = S, R = Ph, Ar = 4–$CF_3C_6H_4$)

We describe here the full details of an investigation of the reactions of **1** with organochalcogen chlorides, which includes (a) the preparation and characterization of the monosubstituted products $PhCN_2(SiMe_3)_2(SR)$ [**3a**, R = Ph; **3b**, R = CCl_3; **3c**, R = 2,4-$C_6H_3(NO_2)_2$(DNP)], (b) the preparation of the trisubstituted derivatives $PhCN_2(SR)_3$ [**4b**, R = CCl_3; **4c**, R = 2,4-DNP] and the X-ray structure of **4b**, (c) the identification by ESR spectroscopy of the resonance-stabilized radicals $PhC(NEPh)_2^{\bullet}$ [**5a**, E = S; **5b**, E = Se] as intermediates in the formation of the diazenes **2b** and **2c**, and (d) the characterization of the eight-membered rings $Ar_2C_2N_4S_2R_2$ [**6a**, Ar = 4-$CF_3C_6H_4$, R = Ph; **6b**, Ar = Ph, R = CCl_3; **6c**, Ar = Ph, R = 2,4-$(NO_2)_2C_6H_3$].

Experimental Section

Reagents and General Procedures. All reactions and the manipulation of moisture-sensitive compounds were carried out under an atmosphere

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of dry $\mathrm{N_2}$ by using Schlenk techniques or a Vacuum Atmospheres drybox.

The following reagents were prepared by literature procedures: $\mathrm{PhCN_2(SiMe_3)_3}$,[9] $\mathrm{4\text{-}XC_6H_4CN_2(SiMe_3)_3}$ ($\mathrm{X = CH_3, CF_3}$),[9] $\mathrm{Me_2Se_2}$,[10] and PhSCl.[11] The commercially available compounds $\mathrm{Ph_2S_2}$, $\mathrm{Ph_2Se_2}$, $\mathrm{2,4\text{-}(NO_2)_2C_6H_3SCl}$, and PhSeCl (all from Aldrich) were used as received. The reagents $\mathrm{CCl_3SCl}$ (Aldrich) and $\mathrm{SO_2Cl_2}$ (Aldrich) were distilled before use. All solvents were dried and distilled before use: $\mathrm{CH_3CN}$ ($\mathrm{P_4O_{10}}$ and $\mathrm{CaH_2}$), $\mathrm{CH_2Cl_2}$ ($\mathrm{P_4O_{10}}$), and pentane and hexanes ($\mathrm{CaH_2}$).

Preparation of $\mathbf{RSeCl_3}$ (R = Me, Ph). In the typical procedure a solution of $\mathrm{R_2Se_2}$ (ca. 2.5 g) in chloroform (85 mL) was treated with 3 molar equiv of $\mathrm{SO_2Cl_2}$ dissolved in chloroform (20 mL) at 23 °C. Precipitation of the product began to occur toward the end of the addition (ca. 10 min). The precipitate was removed by filtration and washed with chloroform (2 × 15 mL) to give $\mathrm{RSeCl_3}$ in ca. 70% yield. The organoselenium trichlorides were stored in the freezer at −20 °C in order to minimize decomposition by the loss of $\mathrm{Cl_2}$.

Instrumentation. Infrared spectra (4000–400 $\mathrm{cm^{-1}}$) were recorded as Nujol mulls (KBr windows) on a Nicolet 5DX FT-IR spectrophotometer. UV–visible spectra were obtained by using a Cary 219 spectrophotometer and cells that were sealed with rubber septa. Mass spectra were measured on a Kratos MS80RFA instrument (EI/70 eV). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ACE 200 spectrometer, and chemical shifts are reported in ppm relative to $\mathrm{Me_4Si}$ in $\mathrm{CDCl_3}$. ESR spectra were recorded 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.

Chemical analyses were performed by the Analytical Services Division, Department of Chemistry, The University of Calgary, and the Canadian Microanalytical Service, New Westminster, BC, Canada. Molecular weight determinations by vapor-phase osmometry were carried out by Galbraith Laboratories, Knoxville, TN.

Preparation of $\mathbf{PhC(NSPh)[N(SiMe_3)_2]}$ (3a). A solution of $\mathrm{C_6H_5SCl}$ (0.72 g, 5.16 mmol) in methylene dichloride (40 mL) was added dropwise (20 min) to a solution of $\mathrm{PhCN_2(SiMe_3)_3}$ (1.74 g, 5.17 mmol) in methylene dichloride (100 mL) at 23 °C. The formation of $\mathrm{Me_3SiCl}$ was monitored by ^{1}H NMR spectroscopy, and the reaction was complete after 2 h. Removal of the solvent under vacuum produced a colorless oil, which was recrystallized from *n*-pentane at 0 °C to give white crystals of $\mathrm{PhC(NSPh)[N(SiMe_3)_2]}$ (1.42 g, 3.80 mmol). Mp: 60–62 °C. Anal. Calcd for $\mathrm{C_{19}H_{28}N_2SSi_2}$: C, 61.24; H, 7.57; N, 7.52. Found: C, 61.36; H, 7.44; N, 7.97. ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 7.90 (m), 7.65 (m), 7.40 (m), 7.20 (m) ($\mathrm{C_6}H_5$, 10 H), and 0.24 (s, $\mathrm{Me_3Si}$, 18 H). IR ($\mathrm{cm^{-1}}$, Nujol): 1586 m, 1534 m, 1268 s, 1255 vs, 1083 s, 1071 s, 1026 m, 937 s, 919 s, 899 s, 842 vs, 826 s, 765 m, 736 s, 690 m.

Preparation of $\mathbf{PhC(NSCCl_3)[N(SiMe_3)_2]}$ (3b). A solution of $\mathrm{Cl_3CSCl}$ (0.80 g, 4.3 mmol) in $\mathrm{CH_2Cl_2}$ (25 mL) was added slowly (2 h) to a solution of $\mathrm{PhCN_2(SiMe_3)_3}$ (1.45 g, 4.3 mmol) at 23 °C in $\mathrm{CH_2Cl_2}$ (25 mL). After 14 h removal of solvent under vacuum produced **3b** (1.60 g, 3.9 mmol) as a yellow oil, which could not be crystallized. ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 7.83–7.9 and 7.35–7.5 (m, $\mathrm{C_6}H_5$, 5 H) and 0.23 (s, $\mathrm{Me_3Si}$, 18 H). The ^{1}H NMR spectrum indicated that the product was sufficiently pure for subsequent reactions. IR ($\mathrm{cm^{-1}}$, Nujol): 1587 m, 1558 m, 1444 m, 1272 vs, 1256 vs, 1087 s, 1073 s, 1027 m, 935 s, 919 vs, 900 vs, 844 vs, 826 vs, 809 s, 760 vs, 732 s, 693 s, 644 m, 462 m, 451 m.

Preparation of $\mathbf{PhC[NSC_6H_3(NO_2)_2][N(SiMe_3)_2]}$ (3c). A solution of $\mathrm{2,4\text{-}(NO_2)_2C_6H_3SCl}$ (1.30 g, 5.54 mmol) in methylene dichloride (30 mL) was added slowly (1 h) to a solution of $\mathrm{PhCN_2(SiMe_3)_3}$ (1.90 g, 5.65 mmol) at 23 °C in methylene dichloride (25 mL). After 18 h removal of solvent under vacuum gave an orange yellow solid (2.5 g), which was treated with acetonitrile (40 mL). Bright yellow crystals of **3c** (1.81 g, 3.90 mmol) were separated by filtration. Mp: 166–168 °C dec. Anal. Calcd for $\mathrm{C_{19}H_{26}N_4O_4SSi_2}$: C, 49.31; H, 5.68; N, 12.11. Found: C, 49.06; H, 5.44; N, 12.12. ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 8.5–9.2 (m, $\mathrm{C_6}H_3\mathrm{(NO_2)_2}$, 3 H), 7.5–7.9 (m, $\mathrm{C_6}H_5$, 5 H), 0.29 (s, $\mathrm{Me_3Si}$, 18 H). IR ($\mathrm{cm^{-1}}$, Nujol): 1585 vs, 1550 m, 1531 s, 1513 vs, 1446 m, 1341 vs, 1305 s, 1273 vs, 1260 m, 1249 s, 1131 m, 1093 s, 1085 s, 1073 m, 1052 s, 1026 m, 934 m, 921 s, 897 s, 844 vs, 830 s, 824 s, 784 m, 764 s, 734 m, 690 m.

The acetonitrile filtrate yielded yellow-brown crystals of $\mathrm{PhC[NSC_6H_3(NO_2)_2](NH_2)}$ (100 mg). Mp: 184–185 °C. Anal. Calcd for $\mathrm{C_{13}H_{10}N_4O_4S}$: C, 49.05; H, 3.17; N, 17.60. Found: C, 49.13; H, 2.88; N, 17.30. ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 8.4–9.2 (m, $\mathrm{C_6}H_3\mathrm{(NO_2)_2}$, 3 H), 7.5–7.9 (m, $\mathrm{C_6}H_5$, 5 H), 5.5 (s, NH_2, 2 H). IR ($\mathrm{cm^{-1}}$, Nujol): 3485 m, 3370 m, 1637 vs, 1592 s, 1587 s, 1562 s, 1513 s, 1496 m, 1446 m, 1337 vs, 1299 vs, 1137 m, 1084 m, 1054 m, 906 m, 784 m, 754 m, 730 m, 693 m.

Preparation of $\mathbf{PhCN_2(SCCl_3)_3}$ (4b). A solution of $\mathrm{PhCN_2(SiMe_3)_3}$ (1.0 g, 3.0 mmol) in methylene dichloride (15 mL) was added dropwise (1 h) to a solution of $\mathrm{CCl_3SCl}$ (1.7 g, 9.1 mmol) in methylene dichloride (20 mL) at 23 °C. After 20 h the solvent was removed under vacuum and the oily residue was stirred with acetonitrile (15 mL) for 30 min to give white microcrystals of $\mathrm{PhCN_2(SCCl_3)_3}$ (0.24 g, 0.42 mmol). Mp: 168–169 °C. Anal. Calcd for $\mathrm{C_{10}H_5N_2S_3Cl_9}$: C, 21.13; H, 0.89; N, 4.93; Cl, 56.13. Found: C, 21.38; H, 0.83; N, 5.44; Cl, 57.06. ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 7.90–7.47 (m, $\mathrm{C_6H_5}$). IR ($\mathrm{cm^{-1}}$, Nujol): 1618 s, 1447 s, 1259 s, 1242 m, 1048 s, 1021 s, 931 m, 918 m, 848 m, 800 s, 787 s, 753 s, 735 vs, 691 m, 661 m, 564 m, 489 m, 458 m.

Preparation of $\mathbf{PhCN_2[SC_6H_3(NO_2)_2]_3}$ (4c). A solution of $\mathrm{PhCN_2(SiMe_3)_3}$ (1.2 g, 3.6 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added slowly (1 h) to a stirred solution of $\mathrm{2,4\text{-}(NO_2)_2C_6H_3SCl}$ (2.5 g, 10.7 mmol) in $\mathrm{CH_2Cl_2}$ (30 mL) at 23 °C. After 18 h a bright yellow precipitate was isolated by filtration, washed with $\mathrm{CH_2Cl_2}$ (2 × 5 mL) and $\mathrm{CH_3CN}$ (2 × 5 mL), dried, and characterized as **4c** (2.4 g, 3.4 mmol). *Caution*! During the melting point determination crystals of **4c** darkened at 155 °C and exploded at 168 °C. Anal. Calcd for $\mathrm{C_{25}H_{14}N_8S_3O_{12}}$: C, 42.01; H, 1.98; N, 15.68. Found: C, 41.79; H, 2.01; N, 15.35. ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 7.6–9.2 (m, $\mathrm{C_6}H_3\mathrm{(NO_2)_2}$, 9 H) and 7.3–7.6 (m, $\mathrm{C_6}H_5$, 5 H). IR ($\mathrm{cm^{-1}}$, Nujol): 1595 s, 1521 s, 1341 vs, 1305 m, 1260 m, 1092 m, 1048 m, 832 m, 745 m, 735 m, 718 m.

Preparation of *trans*-MeSeN(Ph)CN=NC(Ph)NSeMe (2a). A solution of $\mathrm{PhCN_2(SiMe_3)_3}$ (2.08 g, 6.18 mmol) in acetonitrile (80 mL) was added dropwise to a solution of methylselenium trichloride (1.24 g, 6.18 mmol) in acetonitrile at 23 °C over a period of 40 min. The color of the solution changed from pale yellow to dark purple during the course of the addition. The reaction mixture was stirred for 2^1/$_2$ h at 23 °C, and then a gray precipitate (0.85 g) was removed by filtration. Removal of solvent under vacuum afforded a solid residue (0.20 g). The solid products were combined and dissolved in the minimum amount of a 4:1 $\mathrm{CH_2Cl_2}$–pentane mixture. The resulting solution produced dark maroon rectangular crystals of *trans*-MeSeN(Ph)CN=NC(Ph)NSeMe (0.30 g, 0.70 mmol) at 0 °C. Mp: 123–125 °C. Anal. Calcd for $\mathrm{C_{16}H_{16}N_4Se_2}$: C, 45.51; H, 3.82; N, 13.27. Found: C, 44.75; H, 3.95; N, 12.91. ^{1}H NMR (in $\mathrm{CDCl_3}$): δ 8.25 (m) and 7.51 (m) ($\mathrm{C_6H_5}$, 10 H), 2.31 (s, $\mathrm{CH_3}$, 6 H); ^2J (^{77}Se–^{1}H) = 14.1 Hz. IR ($\mathrm{cm^{-1}}$, Nujol): 1581 m, 1313 s, 1272 s, 1256 s, 1172 m, 1156 m, 1081 m, 1069 sh, 1023 m, 970 w, 922 w, 890 w, 874 w, 778 w, 769 w, 721 s, 695 vs, 683 s, 670 m, 653 m, 628 w, 577 w.

Preparation of *trans*-PhSeN(Ph)CN=NC(Ph)NSePh (2b). (a) From $\mathbf{PhCN_2(SiMe_3)_3}$ and PhSeCl (1:3 Molar Ratio). A solution of PhSeCl (2.17 g, 11.3 mmol) in methylene dichloride (15 mL) was added dropwise to a solution of $\mathrm{PhCN_2(SiMe_3)_3}$ (1.27 g, 3.8 mmol) in methylene dichloride (20 mL) at −78 °C. After the addition the solution was yellow. The reaction mixture was allowed to attain ambient temperature, and at 0 °C it became dark purple. The formation of $\mathrm{Me_3SiCl}$ was monitored by ^{1}H NMR spectroscopy, and the reaction was found to be complete after 3 h. Solvent was removed under vacuum to give a purple-gray solid (ca. 2.3 g), which was treated with hexanes (2 × 30 mL). Removal of hexanes under vacuum gave PhSeSePh (1.19 g, 3.8 mmol) contaminated with a small amount of the purple product. The hexane-insoluble solid (0.96 g) was recrystallized from hexanes to give purple microcrystals of *trans*-PhSeN(Ph)CN=NC(Ph)NSePh (0.65 g, 1.2 mmol). Mp: 110 °C. Anal. Calcd for $\mathrm{C_{26}H_{20}N_4Se_2}$: C, 57.16; H, 3.69; N, 10.25. Found: C, 57.08; H, 3.76; N, 10.14. IR ($\mathrm{cm^{-1}}$, Nujol): 1578 m, 1309 w, 1259 m, 1178 w, 1156 w, 1075 w, 1059 w, 1030 m, 1019 m, 998 w, 929 w, 903 w, 852 w, 824 w, 777 m, 733 vs, 689 vs, 665 m, 657 m, 560 w, 459 m.

(b) From $\mathbf{PhCN_2(SiMe_3)_3}$ and $\mathbf{PhSeCl_3}$. A solution of $\mathrm{PhCN_2(SiMe_3)_3}$ (0.77 g, 2.3 mmol) in acetonitrile (80 mL) was added dropwise to a solution of phenylselenium trichloride (0.60 g, 2.3 mmol) in acetontrile (75 mL) at 23 °C. The pale yellow solution became purple during the last stages of the addition. The reaction mixture was stirred at 23 °C for 18 h, and then solvent was removed under vacuum to give *trans*-PhSeN(Ph)CN=NC(Ph)NSePh (0.30 g, 0.55 mmol) as a purple powder identified by comparison of the IR spectrum with that of an authentic sample (vide supra).

Preparation of *trans*-PhSN(Ph)CN=NC(Ph)NSPh (2c). A solution of $\mathrm{C_6H_5SCl}$ (1.51 g, 10.9 mmol) in methylene dichloride (20 mL) was added dropwise to a solution of $\mathrm{PhCN_2(SiMe_3)_3}$ (1.21 g, 3.6 mmol) in methylene dichloride (100 mL) at 23 °C. The color of the reaction mixture changed quickly from yellow to reddish purple during the addition. The formation of $\mathrm{Me_3SiCl}$ was monitored by ^{1}H NMR spectroscopy, and the reaction was complete after 2 h. Solvent was removed under vacuum to give a brown-purple solid, which was extracted with

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hexanes (4 × 50 mL) to give PhSSPh (0.80 g, 3.7 mmol). The hexane-insoluble residue (0.90 g) was recrystallized from a 3:1 $CHCl_3$–pentane mixture to give *trans*-PhSN(Ph)CN=NC(Ph)NSPh (0.60 g, 1.3 mmol) as purple microcrystals. Mp: 165 °C. Anal. Calcd for $C_{26}H_{20}N_4S_2$: C, 69.00; H, 4.45; N, 12.38. Found: C, 69.04; H, 4.46; N, 12.27. IR (cm^{-1}, Nujol): 1581 m, 1316 m, 1300 m, 1272 s, 1175, 1153, 1084 m, 1069 m, 1032 w, 1018 m, 996 w, 937 w, 923 w, 875 w, 847 w, 777 m, 738 vs, 688 vs, 668 m, 621 w, 472 m, 443 m.

Preparation of *trans*-PhSN(4-$CH_3C_6H_4$)CN=NC(4-$CH_3C_6H_4$)NSPh (2d). A solution of PhSCl (2.14 g, 14.8 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of 4-$CH_3C_6H_4CN_2(SiMe_3)_3$ (1.73 g, 4.90 mmol) in CH_2Cl_2 (20 mL) at −78 °C. The reaction mixture was allowed to reach 23 °C (16 h), and solvent was removed under vacuum. The dark solid residue was extracted with hexanes (4 × 20 mL) to give PhSSPh (1.05 g, 4.8 mmol). The insoluble residue was extracted with CH_2Cl_2 to give **2d** (0.85 g, 1.77 mmol) as a dark purple solid, which was purified by recrystallization from CH_2Cl_2–hexane. Mp: 176–177 °C. Anal. Calcd for $C_{28}H_{24}N_4S_2$: C, 69.97; H, 5.03; N, 11.66. Found: C, 69.57; H, 5.42; N, 11.22. ^1H NMR (in $CDCl_3$): δ 7.76–8.34 (m, C_6H_4, 8 H), 7.27–7.47 (m, C_6H_5, 10 H), and 2.49 (s, CH_3, 6 H). IR (cm^{-1}, Nujol): 1475 s, 1440 s, 1310 m, 1283 m, 1273 m, 827 m, 739 vs, 724 s, 686 m.

Reaction of 4-$CF_3C_6H_4CN_2(SiMe_3)_3$ with PhSCl (1:3 Molar Ratio). A solution of PhSCl (0.52 g, 3.6 mmol) in CH_2Cl_2 (10 mL) was added dropwise (30 min) to a solution of 4-$CF_3C_6H_4CN_2(SiMe_3)_3$ (0.5, 1.2 mmol) in CH_2Cl_2 (10 mL) at 23 °C. The colorless solution became green, then red, and finally purple. After 20 h solvent was removed under vacuum and the solid residue was treated with CH_3CN (25 mL). An insoluble dark purple solid was removed by filtration and identified as PhSNC($C_6H_4CF_3$-4)N=NC($C_6H_4CF_3$-4)NSPh (**2e**) (0.12 g, 0.3 mmol). Mp: 215–216 °C. Anal. Calcd for $C_{28}H_{18}F_6N_4S_2$: C, 57.14; H, 3.08; N, 9.52. Found: C, 56.45; H, 3.02; N, 9.58. IR (cm^{-1}, Nujol): 1440 s, 1406 m, 1331 s, 1122 s, 1111 s, 1068 m, 849 m, 741 s, 684 m.

The CH_3CN filtrate yielded a further 30 mg of **2e** as dark purple needles with a golden luster upon cooling to 0 °C for 1 day. The CH_3CN solution was reduced in volume to ca. 10 mL and cooled to −20 ° for 3 days to give a white solid, which was treated with diethyl ether (5 × 3 mL) to give Ph_2S_2 (0.16 g, 0.7 mmol) as the soluble component and colorless crystals of (4-$CF_3C_6H_4)_2C_2N_4S_2Ph_2$ (35 mg, 0.09 mmol). Mp: 238–240 °C dec. Anal. Calcd for $C_{28}H_{18}F_6N_4S_2$: C, 57.14; H, 3.08; N, 9.52. Found: C, 57.41; H, 3.18; N, 9.53. IR (cm^{-1}, Nujol): 1437 vs, 1402 s, 1322 vs, 1182 m, 1168 s, 1148 m, 1131 s, 1110 m, 1065 s, 1019 m, 934m, 851 s, 788 m, 750 m, 717 m, 639 m. MS: *m/e* 588 (29%, M^+).

Reaction of PhC[$NSC_6H_3(NO_2)_2$][$N(SiMe_3)_2$] (3c) with PhSeCl (1:2 Molar Ratio). A solution of PhSeCl (1.5 g, 7.8 mmol) in CH_2Cl_2 (30 mL) was added slowly (3 h) to a solution of **3c** (1.8 g, 3.9 mmol) in CH_2Cl_2 (30 mL) at 23 °C. After 20 h a dark brown precipitate of 2,4-$(NO_2)_2C_6H_3$SNC(Ph)N=NC(Ph)$NSC_6H_3(NO_2)_2$-2,4 (0.62 g, 1.0 mmol) was isolated by filtration. Mp: 250 °C dec. Anal. Calcd for $C_{26}H_{16}N_8O_8S_2$: C, 49.36; H, 2.55; N, 17.72; S, 10.14. Found: C, 48.21; H, 2.26; N, 16.15; S, 9.90. This precipitate was insoluble in organic solvents and could not be purified by recrystallization. IR (cm^{-1}, Nujol): 1596 s, 1539 s, 1521 s, 1446 s, 1378 m, 1336 vs, 1309 m, 1272 m, 1044 m, 834 m, 747 m, 733 m, 712 m, 703 s.

Solvent was removed from the filtrate under vacuum, and the solid residue was extracted with *n*-hexane (3 × 15 mL). The hexane solution yielded Ph_2Se_2 (0.48 g, 1.5 mmol) upon cooling to 0 °C for 1 day. The hexane-insoluble residue was treated with CH_3CN (25 mL). The CH_3CN solution was cooled to −20 °C for 2 days to give a yellow-brown precipitate, which was washed with diethyl ether (5 × 5 mL) to remove Ph_2Se_2. The yellow-brown powder was identified as $Ph_2C_2N_4S_2[C_6H_3(NO_2)_2]_2$ (200 mg, 0.33 mmol). Mp: 149–151 °C dec. Anal. Calcd for $C_{26}H_{16}N_8O_8S_2$: C, 49.36; H, 2.55; N, 17.72; S, 10.14. Found: C, 49.02; H, 2.37; N, 17.15; S, 10.01. IR (cm^{-1}, Nujol): 1589 s, 1575 m, 1519 m, 1509 m, 1448 m, 1377 m, 1339 vs, 1307 m, 1050 m. MS: *m/e* 632 (33%, M^+).

Reaction of PhC($NSCCl_3$)[$N(SiMe_3)_2$] with PhSeCl (1:2 Molar Ratio). A solution of PhSeCl (1.5 g, 7.8 mmol) in CH_2Cl_2 (25 mL) was added slowly (1 h) to a solution of PhC($NSCCl_3$)[$N(SiMe_3)_2$] (1.6 g, 3.9 mmol) in CH_2Cl_2 (25 mL) at 23 °C. The reaction mixture developed a dark purple color. After 20 h a yellow-brown precipitate was removed by filtration, washed with CH_3CN (2 × 5 mL), dried, and identified as $Ph_2C_2N_4S_2(CCl_3)_2$ (0.32 g, 0.60 mmol). Mp: 146–147 °C. Anal. Calcd for $C_{16}H_{10}Cl_6N_4S_2$: C, 35.91; H, 1.89; N, 10.47; S, 11.98. Found: C, 35.74; H, 1.62; N, 10.17; S, 12.98. IR (cm^{-1} Nujol): 1488 m, 1446 vs, 1277 s, 1066 m, 1026 m, 782 s, 764 s, 702 m, 687 s, 668 m, 442 m. Molecular weight determination (in CH_2Cl_2, by vapor-phase osmometry): calcd for $C_{16}H_{10}Cl_6N_4S_2$, 535.1; found, 535.

Solvent was removed from the purple filtrate (λ_{max} 524 nm) under vacuum, and the residue was extracted with CH_3CN (3 × 10 mL) to give another crop of $Ph_2C_2N_4S_2(CCl_3)_2$ (0.40 g, 0.75 mmol). The dark purple CH_3CN solution yield Ph_2Se_2 (0.50 g, 1.6 mmol), but no other pure product could be isolated.

Table I. Crystallographic Data for $PhCN_2(SCCl_3)_3$ (**4b**)

formula	$C_{10}H_5Cl_9N_2S_3$
fw	568.43
space group	$P\bar{1}$
a, Å	9.972 (2)
b, Å	10.517 (3)
c, Å	10.968 (3)
α, deg	109.75 (2)
β, deg	93.31 (2)
γ, deg	102.76 (2)
V, $Å^3$	1044.8
Z	2
T, °C	22
λ, Å	0.71069
ρ_{calcd}, g cm^{-3}	1.807
μ, mm^{-1}	1.50
R^a	0.056
R_w^b	0.049

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

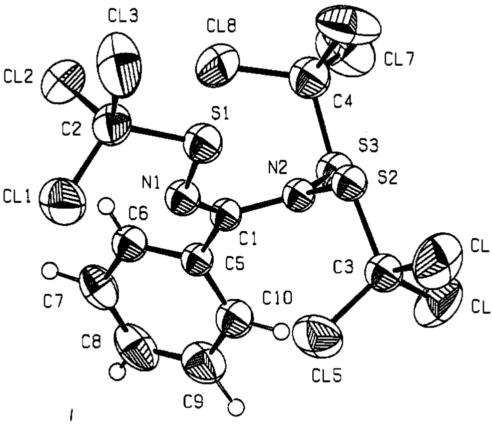

Figure 1. ORTEP plot for $PhCN_2(SCCl_3)_3$ (**4b**).

X-ray Analyses. A suitable colorless crystal of $PhCN_2(SCCl_3)_3$ (**4b**) was obtained by recrystallization from CH_3CN at −20 °C. 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 ω/2θ scan method using variable scan speed (1.27–5.50° min^{-1}), scan width (0.80 + 0.35 tan θ)°, and monochromatized Mo Kα radiation in the range $2 < \theta < 30°$ with h = 0 to 14, k = −14 to 14, and l = −15 to 15. Three reflections were monitored every 2 h of exposure time and showed insignificant variations. The intensities of 6535 reflections were measured, of which 3420 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, and absorption effects,[12] the correction range being 0.584–1.175. Crystal data are given in Table I.

The structure was solved by direct 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 all H atoms, which were included in the subsequent cycles with isotropic temperature factors. Refinement converged with R = 0.056 and R_w = 0.049. In the refinement cycles, weights were derived from the counting statistics. Scattering factors were those of Cromer and Mann[13] and Stewart, Davidson, and Simpson,[14] and allowance was made for anomalous dispersion.[15] A difference map calculated at the conclusion of the refinement had no chemically significant features. All computer programs used in this study were part of XTAL 2.6,[16] and Figure 1 was plotted by using ORTEP II.[17]

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Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $PhCN_2(SCCl_3)_3$

Bond Lengths			
S(1)-N(1)	1.673 (5)	Cl(1)-C(2)	1.768 (5)
S(1)-C(2)	1.785 (6)	Cl(2)-C(2)	1.758 (6)
S(2)-N(2)	1.694 (4)	Cl(3)-C(2)	1.764 (7)
S(2)-C(3)	1.801 (6)	Cl(4)-C(3)	1.745 (6)
S(3)-N(2)	1.700 (3)	Cl(5)-C(3)	1.739 (5)
S(3)-C(4)	1.801 (6)	Cl(6)-C(3)	1.785 (5)
N(1)-C(1)	1.272 (6)	Cl(7)-C(4)	1.740 (5)
N(2)-C(1)	1.423 (6)	Cl(8)-C(4)	1.740 (6)
		Cl(9)-C(4)	1.777 (6)

Bond Angles			
N(1)-S(1)-C(2)	95.2 (3)	Cl(3)-C(2)-S(1)	103.9 (3)
N(2)-S(2)-C(3)	101.0 (2)	Cl(1)-C(2)-S(1)	113.8 (4)
N(2)-S(3)-C(4)	102.1 (2)	Cl(5)-C(3)-Cl(4)	109.5 (3)
C(1)-N(1)-S(1)	124.1 (3)	Cl(5)-C(3)-Cl(6)	109.8 (2)
C(1)-N(2)-S(2)	121.5 (3)	Cl(5)-C(3)-S(2)	113.7 (3)
C(1)-N(2)-S(3)	120.0 (3)	Cl(4)-C(3)-Cl(6)	109.6 (3)
S(2)-N(2)-S(3)	117.8 (2)	Cl(4)-C(3)-S(2)	112.4 (2)
N(1)-C(1)-N(2)	126.4 (4)	Cl(6)-C(3)-S(2)	101.6 (3)
N(1)-C(1)-C(5)	116.6 (4)	Cl(7)-C(4)-Cl(8)	111.0 (3)
N(2)-C(1)-C(5)	117.0 (4)	Cl(7)-C(4)-Cl(9)	108.7 (3)
Cl(2)-C(2)-Cl(3)	108.8 (4)	Cl(7)-C(4)-S(3)	104.2 (4)
Cl(2)-C(2)-Cl(1)	107.3 (3)	Cl(8)-C(4)-Cl(9)	108.2 (4)
Cl(2)-C(2)-S(1)	113.0 (3)	Cl(8)-C(4)-S(3)	112.3 (3)
Cl(3)-C(2)-Ci(1)	109.8 (3)	Cl(9)-C(4)-S(3)	112.3 (3)

Results and Discussion

Synthesis of $PhCN_2(SiMe_3)_2(SR)$ and $PhCN_2(SR)_3$. The readily prepared reagent *N,N,N′*-tris(trimethylsilyl)benzamidine (**1**)[9] has been shown to be a fruitful source of C–N heterocycles containing chalcogens. For example, the reaction of **1** with sulfur or selenium chlorides produces the five-membered rings $PhCN_2E_2^+$ (E = S, Se)[6] or the eight-membered ring $Ph_2C_2N_4S_2$ depending on the reaction conditions.[18,19] By contrast, the treatment of **1** with tellurium tetrachloride yields the four-membered ring $PhC(NSiMe_3)_2TeCl_3$.[20] These cyclocondensation reactions with polyfunctional reagents must involve a complex sequence of events. In an attempt to gain a better understanding of these systems, we have investigated the reactions of **1** (and related derivatives) with the *mono*functional reagents REC1 [R = Ph, CCl_3, 2,4-$(NO_2)_2C_6H_3$ (DNP), E = S; R = Ph, E = Se] in various molar ratios.

The monosubstituted products $PhCN_2(SiMe_3)_2(SR)$ (**3a**, R = Ph; **3b**, R = CCl_3; **3c**, R = 2,4-DNP) are readily obtained in good yields from the reaction of **1** with RSCl in a 1:1 molar ratio in methylene dichloride at 23 °C. Compounds **3a** and **3c** are moisture-sensitive, colorless and orange crystalline solids, respectively, while **3b** was isolated as an oil that is difficult to purify. A small amount of $PhC[NSC_6H_3(NO_2)_2](NH_2)$, formed by hydrolysis, was also isolated in the preparation of **3c**. The singlet observed at ca. 0.25 ppm in the ^1H NMR spectra of **3a–c** suggests that both trimethylsilyl groups are attached to the same (amino) nitrogen atom or that a rapid 1,3-nitrogen shift of the SR group occurs at room temperature. The monosubstituted derivative $PhCN_2(SiMe_3)_2(SePh)$ could not be isolated as a pure compound by the reaction **1** with PhSeCl in a 1:1 molar ratio. The oily purple product so obtained was contaminated with the diazene **2b**.

The trisubstituted derivatives $PhCN_2(SR)_3$ (**4b**, R = CCl_3; **4c**, R = 2,4-DNP) are produced in excellent yields as air-stable, colorless (**4b**) or orange (**4c**) crystals from the reaction of **1** with RSCl in a 1:3 molar ratio in methylene dichloride at 23 °C. By contrast to the thermal instability of $PhCN_2(SPh)_3$ under ambient conditions (vide infra), the compounds **4b** and **4c** do not decompose below 150 °C. The structure of **4b** was determined by X-ray crystallography.

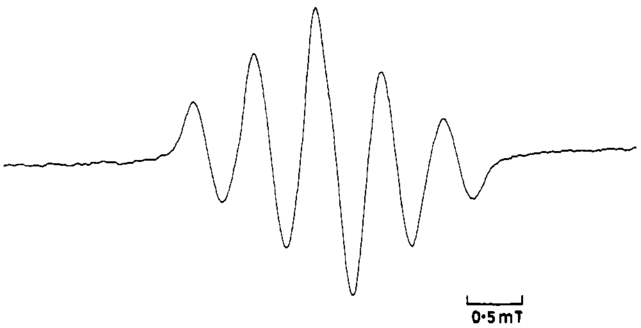
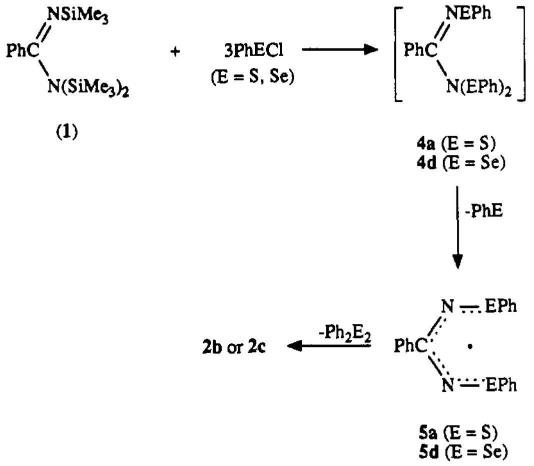


Figure 2. ESR spectrum of a mixture of $PhCN_2(SiMe_3)_3$ and PhSCl (1:3 molar ratio) after ca. 15 min at 23 °C in CH_2Cl_2.

Scheme I. Proposed Mechanism for the Formation of the Diazenes **2b** and **2c** from the Reaction of $PhCN_2(SiMe_3)_3$ with 3 molar equiv of PhECl (E = S, Se)



X-ray Structure of $PhCN_2(SCCl_3)_3$ (4b). An ORTEP drawing of **4b** with the atomic numbering scheme is displayed in Figure 1. Selected bond lengths and bond angles are given in Table II. Both the three-coordinate carbon atom ($\sum\hat{C}(1)$ = 360.0°) and the N(2) atom ($\sum\hat{N}(2)$ = 359.2°) adopt planar geometries. However, the C(1)–N(2) bond distance of 1.423 (6) Å (cf. single-bond value of ca. 1.46 Å[21]) and the dihedral angle of 35.9 (4)° between the S(3)–N(2)–S(2) and N(1)–C(1)–N(2) planes indicate very limited π contributions to the C(1)–N(2) bond. The C(1)–N(1) distance of 1.272 (6) Å is close to that of a C═N double bond (ca. 1.28 Å).[21] The S(1)–N(1) bond length of 1.673 (5) Å is only slightly shorter than the S–N distances involving the three-coordinate nitrogen [d(S(2)–N(2)) = 1.694 (4) and d(S(3)–N(2)) = 1.700 (3) Å] (cf. a mean value of 1.710 Å for an S–N single bond involving a planar (sp^2) N atom).[22] The phenyl ring makes a dihedral angle of 43.6 (2)° with the N(1)–C(1)–N(2) plane. In all these respects the structure of **4b** closely resembles that of $PhCN_2(SiMe_3)_3$ (**1**).[23] A significant difference between the two structures is found for the bond angle at N(1), which has a value 124.1 (3)° in **4b** (cf. ∠Si(1)–N(1)–C(1) = 136.6 (2)° in **1**).[23] The large angle in the latter case was attributed to steric effects.[23]

Formation of the Diazenes *trans*-PhEN(Ph)CN═NC(Ph)NEPh (E = S, Se). In contrast to the thermal stability of **4b** and **4c**, the attempted synthesis of $PhCN_2(SPh)_3$ (**4a**) by the reaction of **1** with PhSCl in a 1:3 molar ratio in methylene dichloride at 23 °C immediately produced a dark purple solution, and the diazene

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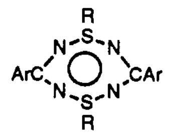
2c was isolated as the final product in 55% yield. Similarly, the selenium analogue, **2b**, was obtained in 56% yield from the reaction of **1** with 3 molar equiv of PhECl. Compound **2b** was also obtained as the major product of the reaction of **1** with PhSeCl$_3$ in the attempted preparation of the eight-membered ring Ph$_2$C$_2$N$_4$Se$_2$Ph$_2$, and the diazene **2a** was obtained in a similar manner from the reaction of **1** with MeSeCl$_3$. The dichalcogenides Ph$_2$E$_2$ (E = S, Se) were isolated in quantitative yields from the reactions of **1** with PhECl in a 1:3 molar ratio.

ESR spectroscopic investigations of the reaction mixtures for the 1:3 reactions of **1** with PhECl have provided evidence for a radical mechanism, as illustrated in Figure 2 for E = S. The observation of a five-line (1:2:3:2:1) ESR signal (g = 2.0071, a_N = 0.575 mT) is consistent with the formation of a radical with two equivalent nitrogen atoms, e.g. PhCN$_2$(SPh)$_2^\bullet$ (**5a**) (Scheme I). The large g value is approximately the same as those found for the closely related thioaminyl radicals R$\dot{N}$SR′[24,25] and indicates delocalization of spin onto the adjacent sulfur atoms, which have a large spin–orbit coupling parameter. The ESR spectrum of a reaction mixture of **1** and PhSeCl (1:3 molar ratio) in CH$_2$Cl$_2$ also revealed a 1:2:3:2:1 quintet (g = 2.0201, a_N = 0.59 mT). The larger g value is consistent with the expected larger spin–orbit coupling contribution of selenium.[5,26] However, the selenium-containing radical, **5d**, decayed quite rapidly (within a few minutes) at room temperature whereas **5a** was stable for at least several hours without stringent precautions to remove oxygen from the solution. Radicals of the type Ar$\dot{N}$SAr′ are known to be exceptionally persistent and oxygen-insensitive in solution. Indeed crystals of such radicals can be isolated if the aryl groups Ar and Ar′ provide the necessary steric and electronic stabilization.[27,28]

The ready formation of the resonance-stabilized radical **5a** from **4a** is likely related to the facile thermal decomposition of (PhS)$_3$N by homolytic cleavage of an S–N bond to give the purple radical (PhS)$_2$N$^\bullet$.[29] The selenium analogue (PhSe)$_3$N also decomposes under mild conditions to produce Ph$_2$Se$_2$ quantitatively.[30] The radicals Ar$\dot{N}$SAr′ have been shown to undergo N–N dimerization, hydrogen abstraction, and C–N dimerization.[24e,31] In the present example nitrogen-centered dimerization of **5a** and **5d** followed by elimination of Ph$_2$E$_2$ would account for the formation of the diazenes **2c** and **2b**, respectively (Scheme I).

We have investigated briefly the effect of introducing substituents in the para position of trisilylated benzamidines on the outcome of the reaction of these reagents with PhSCl in a 1:3 molar ratio. In the case of 4-CH$_3$C$_6$H$_4$CN$_2$(SiMe$_3$)$_3$, the diazene **2d** was obtained in 71% yield. With the reagent 4-CF$_3$C$_6$H$_4$CN$_2$(SiMe$_3$)$_3$, however, white crystals of the eight-membered ring **6a** were isolated in addition to the diazene **2e**.[32]



6a (Ar = 4–CF$_3$C$_6$H$_4$, R = Ph)
6b (Ar = Ph, R = CCl$_3$)
6c (Ar= Ph, R = 2,4–DNP)

Table III. UV–visible Spectroscopic Data for *trans*-REN(Ph)CN=NC(Ph)NER and Related Diazenes

	λ_{max}, nm	ϵ, L mol^{-1} cm^{-1}
2a^a	532	
	502	1×10^4
	472	
2b^a	580 (sh)	
	553	1.3×10^4
2c^a	537	1.7×10^4
2d^a	538	1.65×10^4
2e^a	541	2.9×10^4
4-O$_2$NC$_6$H$_4$N=NC$_6$H$_4$NMe$_2$-4^b	480	3.3×10^4
trans-azobenzene^b	443	5×10^2

^{a} In CH$_2$Cl$_2$. ^{b} Data taken from ref 33; in EtOH.

The reactions of **3b** and **3c** with PhSeCl in a 1:2 molar ratio also produced the eight-membered rings **6b** and **6c**, respectively, in addition to diazenes. The heterocycles **6a–c** were identified on the basis of analytical data and molecular weight determinations by vapor-phase osmometry (**6b**) and by mass spectroscopy (**6a,c**), but attempts to grow crystals suitable for an X-ray structural determination have been unsuccessful.

The formation of eight-membered rings from the decomposition of PhCN$_2$(SR)(SePh)$_2$ (R = CCl$_3$, 2,4-(NO$_2$)$_2$C$_6$H$_3$) or 4-CF$_3$C$_6$H$_4$CN$_2$(SPh)$_3$ suggests that an alternative to the radical pathway (Scheme I) is accessible when an electronegative substituent is attached to either the chalcogen or the carbon atom.

Electronic Spectra of *trans*-REN(Ph)CN=NC(Ph)ER. The UV–visible spectra of **2a–e** are compared in Table III with those for *trans*-azobenzene. The diazenes **2a–e** are dark red or purple and exhibit intense (ϵ = 1–3 × 10^4 L mol^{-1} cm^{-1}) absorption bands in the region 500–550 nm.[34] Preliminary ab initio MO calculations on the model compound *trans*-HSeN(H)CN=NC(H)-NSeH at the STO-3G level indicate that these intense visible absorption bands can probably be assigned the HOMO (π) → LUMO (π^*) transition and that the HOMO involves Se-(4pπ)–N(2pπ) interactions.[35] The orange color of aryl substituted diazenes ($\epsilon \sim 5 \times 10^2$ L mol^{-1} cm^{-1}) is attributed to the n → π^* transition. In azo dyes such as 4-O$_2$NC$_6$H$_4$N=NC$_6$H$_4$NMe$_2$-4 this transition is partially or totally obscured by the batho- and hyperchromically displaced $\pi \rightarrow \pi^*$ band, which is responsible for the intense color of these compounds.[33]

Conclusions

The thermal stability of the trithiolato benzamidines PhCN$_2$(SR)$_3$ shows a remarkable dependence on the nature of the substituent R. When R = CCl$_3$ or 2,4-DNP, these compounds exhibit high thermal stability whereas PhCN$_2$(SPh)$_3$ and its selenium analogue undergo spontaneous decomposition below room temperature to the diazenes *trans*-PhEN(Ph)CN=NC(Ph)NEPh (E = S, Se). ESR evidence indicates that the initial step in this facile transformation involves homolytic E–N bond cleavage to give the resonance-stabilized radicals PhCN$_2$(EPh)$_2^\bullet$. The introduction of a p-CF$_3$ substituent has a significant effect on the outcome of the reaction of trisilylated benzamidines with PhSCl in a 1:3 molar ratio. In this case the eight-membered ring (4-CF$_3$C$_6$H$_4$C)$_2$N$_4$S$_2$Ph$_2$ is produced, as a minor product, in addition to the isomeric diazene. Eight-membered rings of the type Ph$_2$C$_2$N$_4$S$_2$R$_2$ (R = CCl$_3$, 2,4-DNP) are also formed in the reactions of PhC(NSR)[N(SiMe$_3$)$_2$] with 2 equiv of PhSeCl.

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(32) We note that the reaction of Ph$_2$PN$_2$(SiMe$_3$)$_3$ with PhSCl in a 1:3 molar ratio produces the eight-membered ring Ph$_4$P$_2$N$_4$S$_2$Ph$_2$ in 65% yield: Chivers, T.; Kumaravel, S. S.; Meetsma, A.; van de Grampel, J. C.; van der Lee, A. *Inorg. Chem.* **1990**, *29*, 4591.

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(34) Although we have been unable to obtain a crystal of **2c**, **2d**, or **2e** suitable for an X-ray structural determination, the properties of these sulfur-containing diazenes indicate that their solid-state structures resemble that of **2a**; i.e., they incorporate intramolecular S- -N interactions.

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Note Added in Proof. When the reaction of **1** with PhSCl in a 1:3 molar ratio is carried out *in the absence of a solvent*, the yield of the diazene **2e** is ≥90%.

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Registry No. **1**, 24261-90-3; **2a**, 136276-65-8; **2b**, 136276-66-9; **2c**, 136276-67-0; **2d**, 136276-68-1; **2e**, 136276-69-2; **3a**, 136276-70-5; **3b**, 136276-71-6; **3c**, 136276-72-7; **4b**, 136276-73-8; **4c**, 136276-74-9; **5a**, 86602-13-3; **5b**, 136396-53-7; **6a**, 136276-75-0; **6b**, 136276-76-1; **6c**, 136276-77-2; PhSCl, 931-59-9; Cl_3CSCl, 594-42-3; 2,4-$(NO_2)_2C_6H_3SCl$, 528-76-7; Cl_3SeMe, 37826-07-6; TMS-N=C[N(TMS)$_2$]C_6H_4-*p*-Me, 117357-77-4; 2,4-$(NO_2)_2C_6H_3SN$=C(Ph)NH_2, 136276-78-3; TMS-N=C[N(TMS)$_2$]C_6H_4-*p*-CF_3, 117357-81-0; 2,4-$(NO_2)_2C_6H_3SN$=C-(Ph)N=NC(Ph)=NS-2,4-$(NO_2)_2C_6H_3$, 136276-79-4; PhSeCl, 5707-04-0; $PhSeCl_3$, 42572-42-9.

Supplementary Material Available: For **4b**, listings of non-hydrogen and hydrogen coordinates, anisotropic thermal parameters, bond distances, bond angles, torsion angles, and experimental details for the X-ray analyses (7 pages); listings of structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

Contribution from the Institut für Anorganische Chemie,
Universität des Saarlandes, WD-6600 Saarbrücken, Germany

Halide-Complexing Characteristics of Germa- and Stannaimine Cages

Michael Veith,* Joachim Fischer, Timothy R. Prout, Martin Nötzel, Peter Hobein, and Volker Huch

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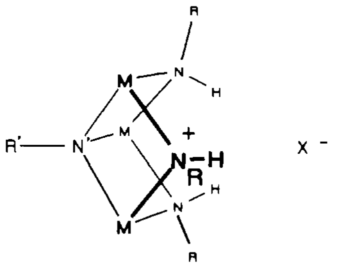
The cations $M_3(N\text{-}t\text{-}Bu)_4H_3^+$ (M = Ge, Sn) coordinate very efficiently via hydrogen bridges to chloride, bromide, and iodide anions. These molecular complexes have the general formula $M_3(N\text{-}t\text{-}Bu)_4H_3X$ (M = Ge, X = Cl (**1**), Br (**2**), I (**3**); M = Sn, X = Cl (**4**), Br (**5**), I (**6**)) and are obtained by three different methods. The newly synthesized compounds have been thoroughly characterized by IR, NMR, and mass spectroscopy. X-ray crystal structure determinations of **1**, **3**, **4**, and **5** reveal the molecules to be built of a M_3N_4-norcubane-type skeleton, which is attached by nitrogen–hydrogen bonds to a H_3X trigonal pyramid. The overall closed cage "$M_3N_4H_3X$" has an approximate $3m$ (C_{3v}) symmetry with one nitrogen and the halogen atom situated on the 3-fold axis. The compounds **3** and **4** crystallize isotypically with 0.5 benzene/molecule in the space group $R\bar{3}$ with $a = b = 11.990$ (7) Å, $c = 34.40$ (1) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $Z = 6$, and $V = 4283$ (2) Å^3 and $a = b = 11.720$ (8) Å, $c = 35.109$ (15) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $Z = 6$, and $V = 4176$ (2) Å^3, respectively, with the final R factors being 0.057 (1369 reflections) and 0.032 (1152 reflections). Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.188$ (6) Å, $b = 19.923$ (8) Å, $c = 12.099$ (7) Å, $\beta = 91.54$ (5)°, $Z = 4$, and $V = 2455$ (1) Å^3. A total of 2859 independent data were collected, giving a final R factor of 0.035. Compound **5** is orthorhombic (space group *Pnma*) with $a = 21.471$ (9) Å, $b = 11.753$ (6) Å, $c = 10.476$ (5) Å, $Z = 4$, and $V = 2644$ (1) Å^3. Refinement of this structure, using 1921 independent reflections, gave an R factor of 0.033. The compounds can be described as being composed of a spherical lipophilic part ($M_3(N\text{-}t\text{-}Bu)_4$) and a somewhat protruding lipophobic part (H_3X pyramid). These properties seem to account for the ease with which these cages exchange the halogen anions in metathesis reactions with simple salts like NaBr, NaI, and TlCl.

Introduction

Of the molecular amino and imino cages of Ge(II), Sn(II) and Pb(II),[1] obtained by aminolysis of bis(amino)germylenes, -stannylenes, and -plumbylenes,[2] the compounds $Ge_3(N\text{-}t\text{-}Bu)_4H_2$ and $Sn_3(N\text{-}t\text{-}Bu)_4H_2$ are peculiar in several respects. They form "open" polycycles (i.e. the skeleton of the molecules may be visualized as a cube with a missing corner, the seven remaining corners being alternately occupied by Ge/Sn and N atoms; for other compounds of this type see also ref 3) and show bond fluctuation behavior as established by variable-temperature NMR studies.[4] One of these movements is a mutual intramolecular displacement of the two hydrogen atoms with respect to the three nitrogen atoms in the "open" corner of the cube. Taking the crystallographic dimensions of $Sn_3(N\text{-}t\text{-}Bu)_4H_2$ into account,[5] it seemed clear to us that by introduction of a simple proton this intramolecular displacement should be arrested, forming a cation $Sn_3(N\text{-}t\text{-}Bu)_4H_3^+$. The whole charged entity should behave as an excellent counterion to simple anions, as the three hydrogen atoms are pointing rigidly in one direction (see formula A). Since macrocyclic counterions or cryptands for simple anions like chloride, bromide, and iodide are less commonly available than for cationic species,[6-10] it seemed interesting to us to study the potential tridentate function of $Ge_3(N\text{-}t\text{-}Bu)_4H_3^+$ or $Sn_3(N\text{-}t\text{-}Bu)_4H_3^+$ toward these halogen anions. At the same time we intended to study the properties of the neutral complexes from a structural and chemical point of view.



A

Experimental Section

Apparatus and Materials. All operations were carried out under an inert atmosphere of nitrogen by using a modified Stock vacuum apparatus and Schlenk techniques. Infrared, ^1H NMR, and mass spectra were obtained by using Perkin-Elmer IR 883, Bruker WP 80 (80 MHz), and Finnigan MAT 90 (DCI$^+$ using isobutane) spectrometers, respectively. ^1H NMR chemical shifts as δ values were measured relative to internal Me_4Si. Elemental analyses were performed by Beller, Mi-

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