Selenium Imides: ^{77}Se NMR Investigations of the $SeCl_2$−$^tBuNH_2$ Reaction and X-ray Structures of $Se_3(N^tBu)_3$, $^tBuNSe(\mu\text{-}N^tBu)_2SO_2$, and $^tBuNSe(\mu\text{-}N^tBu)_2SeO$

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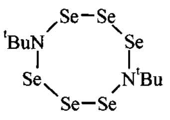
The reaction of $SeCl_2$ with *tert*-butylamine in various molar ratios in THF at −78 °C has been investigated by ^{77}Se NMR spectroscopy. In addition to the known Se−N heterocycles $Se_6(N^tBu)_2$ (**1**) and $Se_9(N^tBu)_6$ (**2**), the acyclic imidoselenium(II) dichlorides $ClSe[N(^tBu)Se]_nCl$ (**4**, $n = 1$; **5**, $n = 2$) and two new cyclic selenium imides $[Se_3(N^tBu)_2]_n$ (**3**, $n = 1$ or 2) and $Se_3(N^tBu)_3$ (**6**) have been isolated and identified. An X-ray analysis shows that **6** is a six-membered ring in a chair conformation with $|d(\text{Se−N})| = 1.833$ Å. Crystal data: **6**, trigonal, $P3c1$, $a = 9.8660(3)$ Å, $c = 20.8427(7)$ Å, $V = 1757.0(1)$ Å^3, $Z = 6$. The ^{1}H, ^{13}C, and ^{77}Se NMR data for **1**−**6** are reported, and some reassignments of earlier literature data for **1**−**3** ($n = 1$) are made. The decomposition of $^tBuN{=}Se{=}N^tBu$ at 20 °C in toluene was monitored by ^{77}Se NMR. The major products are **6** and **3**. The Se(IV)−N systems $^tBuNSe(\mu\text{-}N^tBu)_2E$ (**7**, E = SO_2; **8**, E = SeO) were prepared by the reaction of a mixture of $SeCl_4$ and excess $^tBuNH_2$ with SO_2Cl_2 or $SeOCl_2$, respectively. Compound **8** is also generated by the cycloaddition reaction of $^tBuNSeN^tBu$ with ^tBuNSeO. Both **7** and **8** consist of slightly puckered four-membered rings. The mean terminal and bridging Se−N distances in **7** are 1.665(2) and 1.948(2) Å, respectively. The corresponding values for **8** are 1.687(4) and 1.900(4) Å, and $d(\text{Se=O}) = 1.628(4)$ Å. Crystal data: **7**, monoclinic, $P2_1/c$, $a = 18.669(4)$ Å, $b = 12.329(2)$ Å, $c = 16.463(3)$ Å, $\beta = 115.56(3)°$, $V = 3418.4(11)$ Å^3, $Z = 4$; **8**, triclinic, $P\bar{1}$, $a = 6.372(1)$ Å, $b = 9.926(2)$ Å, $c = 14.034(3)$ Å, $\alpha = 99.320(3)$ Å, $\beta = 95.764(3)$ Å, $\gamma = 103.876(3)$ Å, $V = 841.3(3)$ Å^3, $Z = 2$.

Introduction

Cyclic sulfur imides represent a well characterized class of sulfur−nitrogen (S−N) compounds.[1,2] The most common examples are eight-membered rings of the type $S_{8-n}(NH)_n$ ($n = 1$−4). Although the corresponding selenium−nitrogen (Se−N) heterocycles are unknown, there are two examples of cyclic selenium imides that have been structurally characterized.[3] The eight-membered ring $Se_6(N^tBu)_2$ (**1**) and the fifteen-membered ring $Se_9(N^tBu)_6$ (**2**) were prepared by the reaction of $LiN(^tBu)SiMe_3$ with Se_2Cl_2 (or $SeOCl_2$).[3] Both of these heterocycles contain Se−Se bonds. The formation of the five-membered ring $Se_3(N^tBu)_2$ (**3**) from $SeCl_4$ and $^tBuNH_2$ has also been claimed, but structural confirmation is lacking.[4] Selenium(IV) diimides $RN{=}Se{=}NR$ have been known for nearly 25 years, but they are thermally unstable.[5,6]

The recent discovery of a simple method of generating pure $SeCl_2$[7] has provided an alternative reagent for the preparation of Se(II) imides. In a preliminary investigation we showed that the reaction of $SeCl_2$ with *tert*-butylamine in THF yields, inter alia, the novel acyclic imidoselenium(II) dichlorides $ClSe(N^tBu)NSeCl$ (**4**) and $ClSeN(^tBu)SeN(^tBu)SeCl$ (**5**) in addition to the six-membered ring $Se_3(N^tBu)_3$ (**6**).[8] In this paper, we describe



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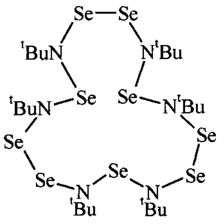

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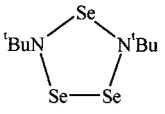

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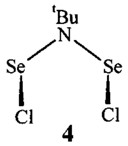

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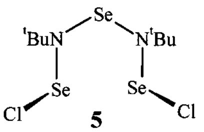

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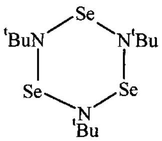

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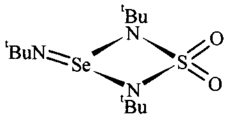

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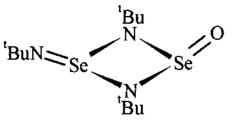

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Table 1. NMR Chemical Shifts and Assignments for **1**−**6**[a]

Se imide	δ ^{1}H[b]	δ ^{13}C[c−e]	δ ^{77}Se[c,f]
$Se_2(N^tBu)Cl_2$ (**4**)	1.10	31.4	1786[g] (N**Se**Cl)
		74.1	
$Se_3(N^tBu)_2Cl_2$ (**5**)	1.16	26.8	1620 (N**Se**Cl) (2)
			1613 (N**Se**N) (1)
$Se_3(N^tBu)_2$ (**3**)	1.19	29.8	1626 (N**Se**N) (1)
		67.4	1183 (Se**Se**N) (2)
$Se_3(N^tBu)_3$ (**6**)	1.23	30.7	1396 (N**Se**N)
		64.8	
$Se_6(N^tBu)_2$ (**1**)	1.15	30.4	1109 (Se**Se**N) (2)
	1.32[h]	70.0	518 (Se**Se**Se) (1)
$Se_9(N^tBu)_6$ (**2**)	1.55	31.5	1425 (N**Se**N) (1)
	1.47[h]	68.2	1203 (Se**Se**N) (2)
	1.43[i]		

[a] NMR data were obtained for analytically pure compounds after separation from reaction mixtures. [b] In toluene-d_8 unless otherwise indicated. [c] In toluene/toluene-d_8 (4:1). [d] The resonances in the regions 27−32 ppm and 65−74 ppm are assigned to $C(CH_3)_3$ and $C(CH_3)_3$, respectively. [e] The resonance for $C(CH_3)_3$ was not observed for **5**. [f] Relative intensities are given in parentheses. [g] δ ^{77}Se for **4** was given incorrectly as 1857 ppm in ref 8. [h] In CD_2Cl_2. [i] In $CDCl_3$.

(a) ^{77}Se NMR investigations of the effect of stoichiometry on the distribution of the products of the $SeCl_2$-$^tBuNH_2$ reaction, (b) an improved synthesis of **2** and the reassignment of the NMR data for **1** and **2**, (c) the X-ray structure of **6** and the formation of **6** by the decomposition of $^tBuN{=}Se{=}N^tBu$, and (d) the formation and X-ray structures of $^tBuNSe(\mu\text{-}N^tBu)_2SO_2$ (**7**) and $^tBuNSe(\mu\text{-}N^tBu)_2SeO$ (**8**).

Experimental Section

General Considerations. All manipulations involving air-sensitive materials were conducted under an argon atmosphere by using Schlenk techniques or in a drybox. Solvents were dried and distilled under an argon atmosphere prior to use: tetrahydrofuran ($LiAlH_4$) and hexane (Na/benzophenone). $^tBuNH_2$ (Aldrich) was distilled over KOH and stored over molecular sieves. Selenium powder, $SeCl_4$, and SO_2Cl_2 (Aldrich) were used without further purification. $SeCl_2$ was prepared from Se and SO_2Cl_2 in THF by the literature procedure.[7] $^tBuNSeN^tBu$ was prepared from $SeCl_4$ and $^tBuNH_2$.[4]

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AC-200 or a Bruker AM-200 spectrometer. The ^{13}C, ^{14}N, and ^{77}Se NMR spectra were recorded on a Bruker AM 400 or a Bruker DPX-400 spectrometer operating at 100.614, 28.915, and 76.312 MHz, respectively. The spectral widths were 23.81, 29.41, and 100.00 kHz, yielding the respective resolutions of 1.45, 3.59, and 6.10 Hz/data point. The ^{13}C pulse width was 3.50 μs, for ^{14}N 20.0 μs, and for ^{77}Se 9.00 μs. The ^{13}C accumulations contained 1000−20000 transients, and for ^{14}N, 20000−200000, and for selenium, 15000−30000 transients. Relaxation delays used were ^{13}C 3.0 s, ^{14}N 1 ms, and ^{77}Se 2 s. The ^{14}N NMR spectra are reported relative to neat CH_3NO_2. All ^{77}Se NMR spectra were referenced externally to a saturated solution of SeO_2 at room temperature. The chemical shifts are reported relative to neat Me_2Se at room temperature [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$]. NMR data are summarized in Table 1.

Preparation of $ClSe[N(^tBu)Se]_nCl$ (4, $n = 1$; 5, $n = 2$). A solution of $SeCl_2$ (15 mmol) in THF (10 mL) was added dropwise to a solution of $^tBuNH_2$ (2.2 mL, 22.5 mmol) in THF (40 mL) at −80 °C. The reaction mixture was stirred for 1 h at −80 °C and then for an additional 1 h at 23 °C. The precipitate of $[^tBuNH_3]Cl$ was separated by filtration, and solvent was removed under vacuum to give a dark red oil. Dark red crystals of **4** and red crystals of **5**, which were separated manually, were obtained from a hexane solution of this oil at −22 °C. Compound **5** can be isolated in 34% yield when the reaction of $SeCl_2$ with $^tBuNH_2$ is carried out in a 1:2 molar ratio. ^{1}H, ^{13}C, and ^{77}Se NMR data for **4** and **5** are given in Table 1. Crystals of **4** are extremely moisture-sensitive and melt to give a red oil at room temperature. Satisfactory CHN analyses could not be obtained. Anal. Calcd for $C_8H_{18}Cl_2N_2Se_3$ (**5**): C, 21.35; H, 4.03; N, 6.22. Found: C, 21.77; H, 4.07; N, 6.18.

Preparation of $[Se_3(N^tBu)_2]_n$ (3). A solution of $SeCl_2$ (18 mmol) in THF (10 mL) was added dropwise to a solution of $^tBuNH_2$ (5.3 mL, 3.94 g, 54 mmol). The reaction mixture was stirred for 1 h at −80 °C and then for 1.5 h at 23 °C. The precipitate of $[^tBuNH_3]Cl$ was separated by filtration, and solvent was removed from the filtrate to give an orange solid which was extracted with hexane (2 × 10 mL). The hexane solution deposited orange crystals of **3** (0.228 g, 0.6 mmol, 10%). Anal. Calcd for $C_8H_{18}N_2Se_3$: C, 25.34; H, 4.79; N, 7.39. Found: C, 25.30; H, 4.48; N, 7.29. ^{1}H, ^{13}C, and ^{77}Se NMR data are given in Table 1.

Preparation of $Se_3(N^tBu)_3$ (6). A solution of $^tBuNSeN^tBu$ (1.99 g, 9.0 mmol) in THF (40 mL) was kept at 20 °C, and the ^{77}Se NMR spectrum was recorded at regular intervals (see Results and Discussion). After 2 d solvent was removed under vacuum, and yellow crystals of **6** (0.248 g, 0.55 mmol, 18%) were isolated by fractional crystallization from *n*-hexane. Anal. Calcd for $C_{12}H_{27}N_3Se_3$: C, 32.01; H, 6.04; N, 9.33. Found: C, 31.81; H, 5.87; N, 9.06. ^{1}H, ^{13}C, and ^{77}Se NMR data are summarized in Table 1.

Preparation of $^tBuNSe(\mu\text{-}N^tBu)_2SO_2$ (7). Neat $^tBuNH_2$ (5.3 mL, 54 mmol) was added dropwise to a mixture of $SeCl_4$ (1.325 g, 6.0 mmol) and SO_2Cl_2 (0.10 g, 6.0 mmol) in THF (40 mL) at −80 °C. The reaction mixture was stirred for 1.5 h at −80 °C and then for 1 h at 23 °C. The precipitate of $[^tBuNH_3]Cl$ was separated by filtration, and solvent was removed from the yellow filtrate under vacuum. The solid residue was extracted with *n*-hexane (20 mL), and the hexane solution was cooled to −18 °C to give **7** (0.117 g, 0.33 mmol, 8%). Anal. Calcd for $C_{12}H_{27}N_3O_2SSe$: C, 40.44; H, 7.64; N, 11.79. Found: C, 39.61; H, 7.66; N, 11.75. NMR: δ ^{1}H (C_7D_8, 25 °C) 1.44 (s, NC_4H_9, 9 H), 1.32 (s, $\mu\text{-}NC_4H_9$, 18 H); δ ^{13}C (C_7H_8, 25 °C) 63.2 [$C(CH_3)_3$], 59.2 [$C(CH_3)_3$], 32.1 [$C(CH_3)_3$], 30.0 [$C(CH_3)_3$]; δ ^{14}N (C_7H_8, 25 °C) −167 and −206; δ ^{77}Se (C_7H_8, 25 °C) 824.

Preparation of $^tBuNSe(\mu\text{-}N^tBu)_2SeO$ (8). Neat $^tBuNH_2$ (5.3 mL, 54 mmol) was added to a mixture of $SeCl_4$ (1.325 g, 6.0 mmol) and $SeOCl_2$ (0.995 g, 6.0 mmol) in THF (40 mL) at −80 °C. The reaction mixture was stirred for 1.5 h at −80 °C and then for 1 h at 23 °C. The precipitate of $[^tBuNH_3]Cl$ was separated by filtration, and solvent was removed from the yellow filtrate under vacuum. The solid residue was extracted with *n*-hexane (20 mL), and the hexane solution was cooled to give yellow crystals of **8** (0.275 g, 0.71 mmol, 12%). Anal. Calcd for $C_{12}H_{27}N_3OSe_2$: C, 37.22; H, 7.03; N, 10.85. Found: C, 36.82; H, 6.98; N, 10.60. NMR: δ ^{77}Se (*n*-hexane, 25 °C) 882, 1157.

Preparation of $Se_9(N^tBu)_6$ (2) and $Se_6(N^tBu)_2$ (1). An equimolar mixture of selenium powder (0.711 g, 9.0 mmol) and $SeCl_4$ (1.987 g, 9.0 mmol) dissolved in THF (20 mL) was added dropwise to a solution of $^tBuNH_2$ (5.3 mL, 3.94 g, 54 mmol) in THF (100 mL) at −80 °C. The reaction mixture was stirred at −80 °C for 2 h. The precipitate of $[^tBuNH_3]Cl$ was separated by filtration. Solvent was removed from the orange filtrate under vacuum, and the solid residue was extracted with *n*-hexane (40 mL). The hexane-insoluble yellow powder was identified by ^{1}H, ^{13}C, and ^{77}Se NMR spectra as **2** (1.465 g, 2.38 mmol, 64%). The hexane solution deposited orange crystals of **1** (0.203 g, 0.33 mmol, 11%). Anal. Calcd for $C_8H_{18}N_2Se_6$: C, 15.60; H, 2.95; N, 4.55. Found: C, 15.80; H, 2.86; N, 4.53. ^{1}H, ^{13}C, and ^{77}Se NMR data for **1** and **2** are summarized in Table 1.

X-ray Analysis. Diffraction data for **6**−**8** were collected on a Nonius Kappa CCD diffractometer at 173 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by recording 180 frames via φ-rotation ($\Delta\varphi = 2°$; two times 40−60 s per frame). Crystallographic data are given in Table 2. The intensity data were corrected for Lorentz and polarization effects. Empirical absorption correction from φ-scan data was applied for the net intensities.

All structures were solved by direct methods using SHELXS-97[9a] and refined using SHELXL-97.[9b] After the full-matrix least-squares refinement on F^2 of the non-hydrogen atoms with anisotropic thermal

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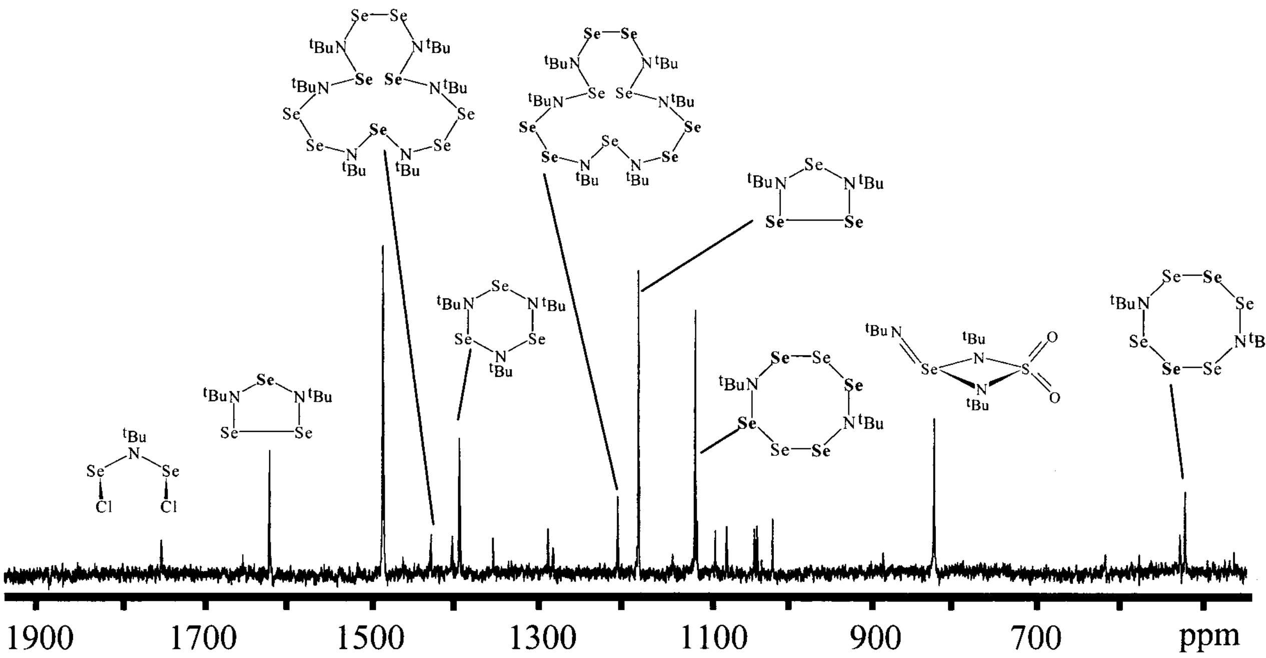

Figure 1. ^{77}Se NMR spectrum of the mixture of products obtained from the reaction of $SeCl_2$ with $^tBuNH_2$ in THF (1:3 molar ratio). Assignments of major resonances are indicated by bold-faced **Se** atoms in the structural formulae.

Table 2. Crystallographic Data for $Se_3(N^tBu)_3$ (**6**), $^tBuNSe(\mu\text{-}N^tBu)_2SO_2$ (**7**), and $^tBuNSe(\mu\text{-}N^tBu)_2SeO$ (**8**)

	6	**7**	**8**
formula	$C_8H_{18}N_2Se_2$	$C_{24}H_{54}N_6O_4S_2Se_2$	$C_{12}H_{27}N_3OSe_2$
fw	300.16	712.77	387.29
cryst syst	trigonal	monoclinic	triclinic
space group	$P3c1$	$P2_1/c$	$P\bar{1}$
a, Å	9.8660(3)	18.669(4)	6.372(1)
b, Å	9.8660(3)	12.329(2)	9.926(2)
c, Å	20.8427(7)	16.463(3)	14.034(3)
α, deg	90	90	99.320(3)
β, deg	90	115.56(3)	95.764(3)
γ, deg	120	90	103.876(3)
V, Å^3	1757.0(1)	3418.4(11)	841.3(3)
Z	6	4	2
T, K	173	173	173
l_{calcd}, g cm^{-3}	1.702	1.385	1.529
μ (Mo Kα), cm^{-1}	62.71	23.22	43.90
radiation, λ, Å	0.71073	0.71073	0.71073
$R_1{}^a$	0.0381	0.0416	0.0447
$wR_2{}^b$	0.1030	0.0902	0.1228

^{a} $R_1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ $[I > 2\sigma(I)]$. ^{b} $wR_2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$ [all data].

parameters, the hydrogen atoms were placed in the calculated positions (C−H = 0.95 Å). In the final refinement the hydrogen atoms were riding with the carbon atom to which they were bonded. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.5 times that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated with the programs.

Results and Discussion

Formation and Characterization of the Acyclic Imidoselenium(II) Dichlorides $ClSe[N(^tBu)Se]_nCl$ (4, *n* = 1; 5, *n* = 2) and the Cyclic Selenium(II) Imides $[Se_3(N^tBu)_2]_n$ (3) and $Se_3(N^tBu)_3$ (6).

The reaction of $SeCl_2$ with *tert*-butylamine in THF at −80 °C gives rise to a complex mixture of new and known imidoselenium compounds **1**−**7**. A ^{77}Se NMR spectrum of a typical reaction mixture is shown in Figure 1. The identification of the resonances in this spectrum is based on the isolation of the individual components and their characterization by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy (Table 1) and, in several cases, by X-ray crystallography.

The composition of the mixture of Se−N compounds obtained from the reaction of $SeCl_2$ with $^tBuNH_2$ is markedly dependent on the stoichiometry. The yields of the imidoselenium(II) dichlorides **4** and **5** are highest when the reaction is carried out in a 2:3 molar ratio, and their lower solubility enables them to be isolated as red crystals by fractional crystallization from *n*-hexane at −20 °C. Both **4** and **5** are extremely moisture-sensitive, but the crystals can be separated manually provided that they are kept cold. Crystals of **4** melt to give a red oil at room temperature. The X-ray structures of **4** and **5** were described in the preliminary communication.[8] The imidoselenium(II) dichloride **5** can be isolated in 34% yield when the reaction is carried out in a 1:2 molar ratio. At 23 °C in THF or toluene solution **5** slowly decomposes to give **4** (^{77}Se NMR) and black selenium. Solutions of **4** also deposit selenium at 23 °C. The imidoselenium(II) dichlorides **4** and **5** represent a new class of chalcogen−nitrogen compound for which there are no S or Te analogues. However, a number of cyclic and acyclic selenium nitride chlorides, e.g., $S_3N_2Cl^+$,[10] $N(SeCl_x)_2{}^+$ (x = 1, 2),[11] and $N(SeCl_3)_2{}^-$,[12] have been reported. The amidoselenium(II) chloride $(Me_3Si)_2NSeCl$ has been obtained as an orange oil.[4]

When the $SeCl_2/^tBuNH_2$ reaction is carried out in a 1:3 molar ratio two new cyclic selenium imides **3** and **6** are formed in significant yields, in addition to the known eight- and fifteen-membered rings, **1** and **2**, respectively (Figure 1). Extraction

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of the products with *n*-hexane, followed by fractional crystallization, produces **3** in ca. 10% yield. CHN analyses for **3** are consistent with the empirical formula $Se_3(N^tBu)_2$, but the NMR data are quite different from those of the fifteen-membered ring **2** (see Table 1). The ^{77}Se NMR spectrum of **3** exhibits two resonances with relative intensities of 1:2 consistent with a cyclic arrangement $[-SeSeN(^tBu)SeN(^tBu)^-]_n$, possibly a five-membered ring. Numerous attempts to obtain X-ray quality crystals of **3** were unsuccessful.

The six-membered ring $Se_3(N^tBu)_3$ (**6**) was also isolated from the products of the 1:3 reaction by fractional crystallization from *n*-hexane. It was identified by CHN analyses, multinuclear NMR spectra (Table 1), and an X-ray structural determination. A better preparation of **6** from the decomposition of the selenium(IV) diimide $^tBuN{=}Se{=}N^tBu$ is described below.

Improved Synthesis of the Cyclic Selenium Imides $Se_6(N^tBu)_2$ (1) and $Se_9(N^tBu)_6$ (2). In the previously reported synthesis of the eight- and fifteen-membered Se−N heterocycles, **1** and **2**, from the reaction of $LiN(^tBu)SiMe_3$ with Se_2Cl_2 the isolated yields were ca. 12 and 19%, respectively.[3] In this study samples of the known Se−N heterocycles **1** and **2** for NMR analyses were obtained from the reaction of $^tBuNH_2$ with an equimolar mixture of elemental selenium and $SeCl_4$. In acetonitrile solution this mixture has been used as a “$SeCl_2$” synthon.[13,14] However, the ^{77}Se NMR spectrum of a THF solution containing equimolar amounts of Se and $SeCl_4$ reveals the presence of Se_2Cl_2 (∼30%) in addition to $SeCl_2$ (70%). The use of this reagent in a reaction with $^tBuNH_2$ in THF produces **1** and **2** in isolated yields of 11 and 64%, respectively. In addition to the substantial improvement in the yield of **2**, the ready availability of the reagents Se, $SeCl_4$, and $^tBuNH_2$ is an attractive feature of this alternative synthesis of **1** and **2**.

X-ray Structure of $Se_3(N^tBu)_3$ (6). An X-ray structural determination of **6** revealed a six-membered ring in the chair conformation (Figure 2) analogous to the structure previously reported for the tellurium analogue $Te_3(N^tBu)_3$.[15] Metrical parameters for **6** are summarized in Table 3. The mean Se−N bond distance of 1.831(8) Å is close to a typical Se(II)−N bond value (cf. $d(Se{-}N) = 1.869(2)$ Å in $Se[N(SiMe_3)_2]_2$ [16] and 1.830(4) Å in $Se_6(N^tBu)_2$ [3]). The geometry at the nitrogen atoms is almost planar ($\Sigma < N(1) = 358.9°$). The endocyclic bond angles at Se and N in **6** are 106.6(2)° and 113.3(2)°, respectively [cf. 104.6(2)° at Te and 112.6(3)° at N in $Te_3(N^tBu)_3$].[15]

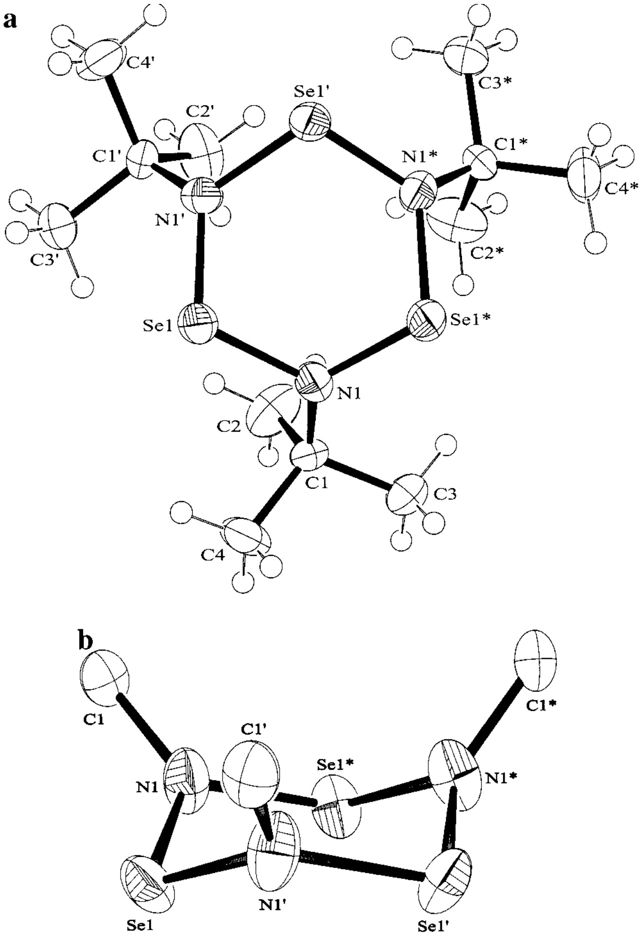

Figure 2. Molecular structure of $Se_3(N^tBu)_3$ (**6**) showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Lengths and Bond Angles for $Se_3(N^tBu)_3$ (**6**)[a]

bond lengths (Å)		bond angles (deg)	
Se(1)−N(1)′	1.825(4)	N(1)′−Se(1)−N(1)	106.6(2)
Se(1)−N(1)	1.842(4)	C(1)−N(1)−Se(1)*	125.7(3)
N(1)−C(1)	1.496(6)	C(1)−N(1)−Se(1)	119.9(3)
N(1)−Se(1)*	1.825(4)	Se(1)′−N(1)−Se(1)	113.3(2)

[a] Symmetry transformations used to generate equivalent atoms: ′ $-x+y, -x+1, z$; * $-y+1, x-y+1, z$.

NMR Data for Acyclic and Cyclic Selenium Imides. The ^1H, ^{13}C, and ^{77}Se NMR data for the new selenium imides **3**−**6** together with those for the known Se−N systems **1** and **2** obtained in this investigation are reported in Table 1. There are some major discrepancies in the NMR data found in earlier studies of cyclic selenium imides.[3,4,6] Roesky et al. have reported a chemical shift of 1.48 ppm (in CH_2Cl_2) for $Se_9(N^tBu)_6$ (**2**),[3] which is in close agreement with our value 1.47 ppm for **2** in the same solvent. Herberhold and Jellen reported chemical shift values of δ ^1H 1.43 and δ ^{13}C 31.5 $[C(CH_3)_3]$, 68.5 $[C(CH_3)_3]$ for “$Se_3(N^tBu)_2$” in $CDCl_3$,[4] which are essentially the same as those found in this work for **2** in $CDCl_3$ (see Table 1). Herberhold and Jellen describe “$Se_3(N^tBu)_2$” as yellow needles.[4] However, in this investigation **2** was obtained as yellow needles whereas **3** was obtained as orange plates. We conclude that the product previously described as “$Se_3(N^tBu)_2$” [4] is, in fact, the known fifteen-membered ring **2** and that the new selenium imide obtained in this work is a smaller cyclic oligomer, i.e., $Se_3(N^tBu)_2$ (**3**) or $Se_6(N^tBu)_4$. The higher solubility of the orange plates in *n*-hexane compared to that of **2** is also consistent with this conclusion.

The previously reported NMR data for $Se_6(N^tBu)_2$ (**1**) are also at variance. Roesky et al. reported a ^1H chemical shift of 1.50 (in CH_2Cl_2)[3] whereas Wrackmeyer et al. published the following values for **1** (solvent unspecified): δ ^1H 1.23, δ ^{13}C 30.7, 64.8. The latter values are *identical* to those we have found for the new six-membered $Se_3(N^tBu)_3$ (**6**) (see Table 1). Our values for **1** are δ ^1H 1.15 (in toluene) and 1.32 (in $CDCl_3$). The ^{77}Se NMR spectrum of **1** in toluene shows the expected two resonances at δ 1109 and 518 with approximate relative intensities of 2:1. A sample of **1**, prepared by the literature procedure,[3] exhibited similar chemical shifts. The assignment

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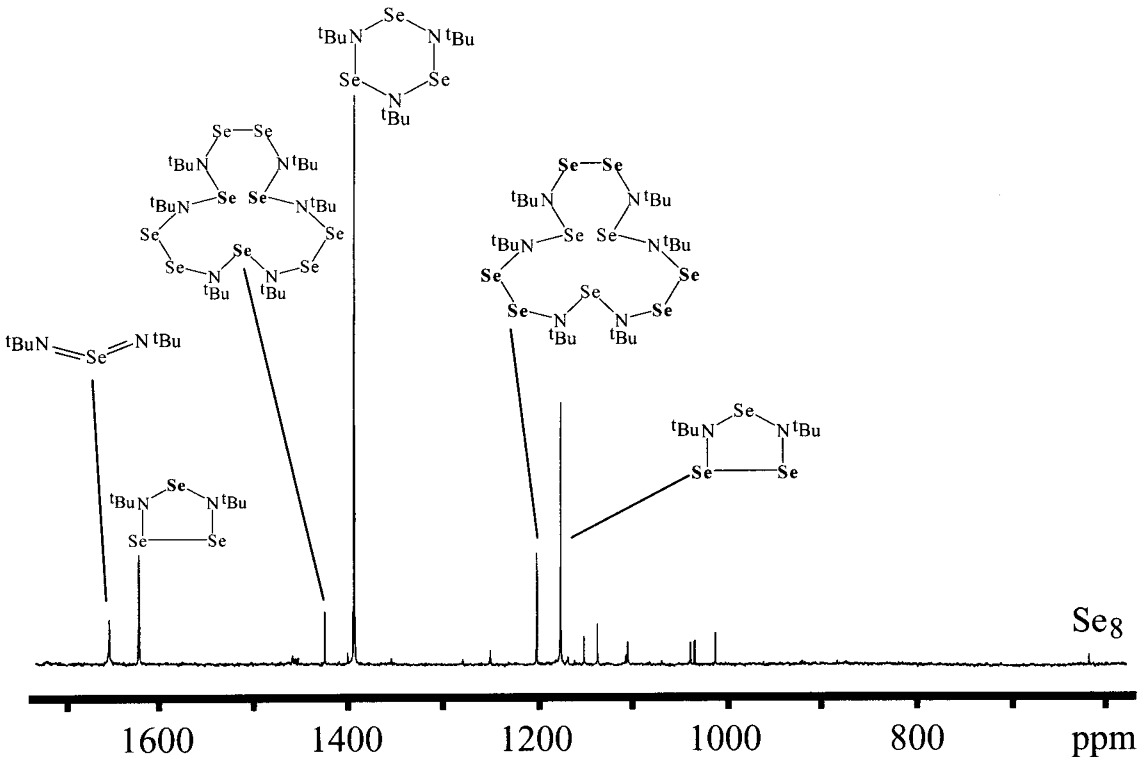

Figure 3. ^{77}Se NMR spectrum of the mixture of products obtained from the decomposition of ^{t}BuN=Se=N^{t}Bu in toluene at 20 °C after 2 days. Assignments of major resonances are indicated by bold-faced **Se** atoms in the structural formulae.

of these resonances to Se**Se**N and Se**Se**Se environments, respectively, is consistent with the observed intensities. Furthermore, the value of δ 518 is in the range expected for a selenium atom attached to two selenium neighbors by analogy with the known ^{77}Se NMR chemical shifts for cyclic selenium sulfides.[7,17] By contrast, Wrackmeyer et al. reported ^{77}Se NMR chemical shifts of 1391.0 and 1163.6 ppm for **1** for CH_2Cl_2.[6] The former resonance is close to the value of 1396 ppm found in this work for the six-membered ring **6** in toluene.

The ^{77}Se NMR data compiled in Table 1 for new and known acyclic and cyclic imidoselenium compounds indicate that the characteristic chemical shifts for the selenium environments N**Se**Cl, N**Se**N and N**Se**Se fall in the regions δ 1620−1785, 1400−1625, and 1100−1200 ppm, respectively.

Formation of $Se_3(N^tBu)_3$ (4) by Decomposition of ^{t}BuN=Se=N^{t}Bu. *N*,*N*′-Dialkyl selenium diimides[4−6] and Me_3SiN=Se=$NSiMe_3$ [18] are thermally unstable. Consequently, investigations of the reactions of these imido transfer reagents have been limited.[19−24] Wrackmeyer et al.[6] have investigated the decomposition of ^{t}BuN=Se=N^{t}Bu by ^{77}Se and ^{15}N NMR and claimed the formation and isolation of $Se_6(N^tBu)_2$ (**1**) as the major product. They report the following ^{15}N NMR data: δ ^{15}N −279.7, $^1J(^{77}Se-^{15}N) = 96.9$ Hz, $^2J(^{77}Se-^{15}N) = 9.7$ Hz. The intensities of the ^{77}Se satellite resonances were in the ratio 2:1. As indicated above, our ^{1}H, ^{13}C, and ^{77}Se NMR data indicate that this product is, in fact, $Se_3(N^tBu)_3$ (**6**). Furthermore, we observe a resonance at δ −278 in the ^{14}N NMR spectrum of **6** (in toluene). Consequently, we suggest that the ^{77}Se satellite resonances observed by Wrackmeyer et al. in the ^{15}N NMR spectrum of the major product of the decomposition of ^{t}BuN=Se=N^{t}Bu should be assigned to $^1J(^{77}Se-^{15}N)$ and $^3J(^{77}Se-^{15}N)$ for **6**. The relative intensities of these resonances are consistent with this suggestion.

We have monitored the decomposition of ^{t}BuN=Se=N^{t}Bu in toluene at ca. 25 °C over a period of 6 days by ^{77}Se NMR. The major products of this decomposition are $Se_3(N^tBu)_3$ (**6**) and $[Se_3(N^tBu)_2]_n$ (**3**). After 4 h a small resonance for **6** is apparent, in addition to the resonance at δ 1655 for ^{t}BuN=Se=N^{t}Bu. After 2 days the ^{77}Se NMR spectrum (see Figure 3) revealed the following approximate composition: **6** (43%), **3** (33%), **1** (3%), $Se(N^tBu)_2$ (20%). The six-membered ring **6** can be isolated in ca. 20% yield by fractional crystallization from *n*-hexane. Thus this route represents a better synthesis of **6** than the reaction of $SeCl_2$ and ^{t}BuNH$_2$ (vide supra). After 6 days the amount of **3** relative to **6** has increased and there are additional small resonances attributable to **1**, **2**, and Se_8.

The formation of **6** as the major product of the decomposition of ^{t}BuN=Se=N^{t}Bu is easier to envisage than the generation of the selenium-rich system **1**. It involves the spontaneous reduction of Se(IV) to Se(II) via elimination of ^{t}BuN=N^{t}Bu, which is observed as a byproduct of the decomposition.[6] We note also that $Te_3(N^tBu)_3$, the tellurium analogue of **6**, is formed in the synthesis of the tellurium(IV) diimide $[Te(N^tBu)_2]_2$, but this dimer is thermally stable up to ca. 100 °C.[15]

Preparation and X-ray Structures of ^{t}BuNSe(μ-N^{t}Bu)$_2$E (7, E = SO_2; 8, E = SeO). A seventh product that was isolated from some reactions of $SeCl_2$ (generated from selenium and

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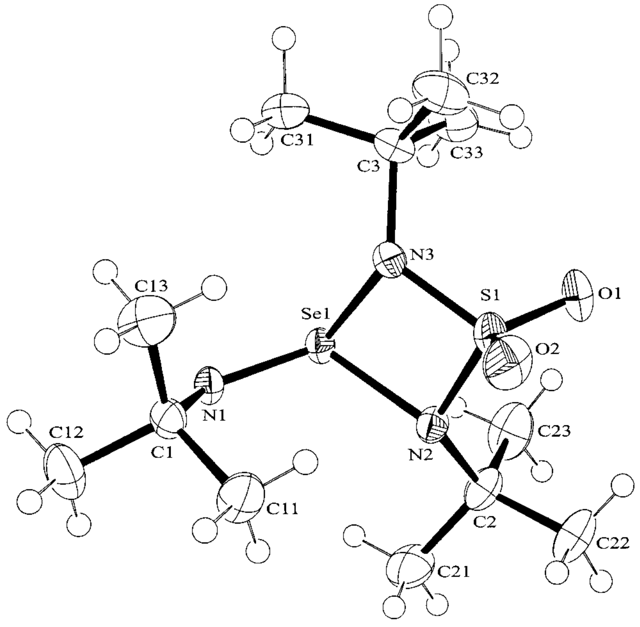

Figure 4. Molecular structure of ^{t}BuNSe(μ-N^{t}Bu)$_2$SO$_2$ (**7**) showing the atomic numbering scheme. Only molecule A is shown. Thermal ellipsoids are drawn at the 50% probability level.

SO_2Cl_2) and ^{t}BuNH$_2$ was identified by ^{1}H, ^{13}C, and ^{77}Se NMR spectra and by X-ray crystallography as ^{t}BuNSe(μ-N^{t}Bu)$_2$SO$_2$ (**7**). The ^{1}H NMR spectrum of **7** in C_7D_8 shows two resonances at δ 1.32 and 1.44 with relative intensities 2:1 corresponding to bridging and terminal N^{t}Bu groups, respectively. Resonances for two N^{t}Bu environments are also observed in the ^{13}C NMR spectrum. The ^{77}Se NMR spectrum of **7** exhibits a singlet at δ 824. Inspection of Figure 1 reveals a resonance at ca. δ 825 indicating that **7** is present in the complex mixture of products generated from the reaction of $SeCl_2$ and ^{t}BuNH$_2$ in a 1:3 molar ratio. An X-ray structural investigation of **7** revealed a four-membered $\overline{\text{Se(IV)NSN}}$ ring (see Figure 4) which, in the context of its generation from Se, SO_2Cl_2, and ^{t}BuNH$_2$, may be formed from the reaction of (^{t}BuNH)$_2$SO$_2$ formed in situ (from the reaction of SO_2Cl_2 and ^{t}BuNH$_2$)[25] and the putative ^{t}BuNSeCl$_2$. The tellurium analogue (^{t}BuNTeCl$_2$)$_6$ has recently been obtained as a thermally stable crystalline solid with a hexameric structure,[26] but the only known imidoselenium(IV) dihalides $R_FN{=}SeCl_2$ ($R_F = CF_3$, C_2F_5) are thermally unstable.[27] Two different molecules of **7**, with essentially the same metrical parameters, were present in the unit cell. Selected bond lengths and bond angles are given in Table 4. The four-membered rings are slightly puckered with SeNSN torsion angles of ca. 9°. There is a marked difference in the mean terminal and bridging selenium−nitrogen distances, 1.665(2) and 1.948(2) Å, consistent with double and single SeN bonds, for which the predicted values are ca. 1.65 and ca. 1.85 Å, respectively.[23] The bridging SeN bond lengths are significantly longer in **7** compared to those in the cyclic Se(II) imide **6** (vide supra). However, the geometry at the bridging nitrogen atoms is distinctly nonplanar in **7** ($\Sigma <$ N (bridging) $= 338.3{-}347.0°$).

In light of the structure of **7** an alternative synthesis via the in situ generation of (^{t}BuNH)$_2$SO$_2$ was investigated (eq 1). This method generated **7** in 8% isolated yield. A similar approach using $SeOCl_2$ instead of SO_2Cl_2 was employed to generate the related four-membered Se_2N_2 ring **8**, which was isolated in 12% yield (eq 2).

$$SeCl_4 + SO_2Cl_2 + 9\,^tBuNH_2 \rightarrow \mathbf{7} + 6\,^tBuNH_2{\cdot}HCl \quad (1)$$

$$SeCl_4 + SeOCl_2 + 9\,^tBuNH_2 \rightarrow \mathbf{8} + 6\,^tBuNH_2{\cdot}HCl \quad (2)$$

The structure of **8** was shown by X-ray crystallography (Figure 5) to involve a puckered four-membered $\overline{\text{Se(IV)NSe(IV)N}}$ ring [torsion angle −16.0(2)°] with the two exocyclic substituents in a cis configuration. The terminal Se=N(^{t}Bu) and

Table 4. Selected Bond Lengths and Bond Angles for ^{t}BuNSe(μ-N^{t}Bu)$_2$SO$_2$ (**7**)

	molecule A	molecule B
	Bond Lengths (Å)	
Se(1)−N(1)	1.665(2)	1.666(2)
Se(1)−N(3)	1.941(2)	1.933(2)
Se(1)−N(2)	1.958(2)	1.961(2)
S(1)−O(1)	1.437(2)	1.437(2)
S(1)−O(2)	1.432(2)	1.433(2)
S(1)−N(2)	1.644(2)	1.635(2)
S(1)−N(3)	1.651(2)	1.651(2)
	Bond Angles (deg)	
N(1)−Se(1)−N(3)	112.69(11)	112.76(10)
N(1)−Se(1)−N(2)	113.92(10)	113.84(10)
N(3)−Se(1)−N(2)	73.41(9)	73.18(9)
O(2)−S(1)−O(1)	114.98(14)	115.19(14)
O(2)−S(1)−N(2)	110.65(13)	111.13(13)
O(1)−S(1)−N(2)	114.17(13)	113.52(13)
O(2)−S(1)−N(3)	110.74(13)	110.45(13)
O(1)−S(1)−N(3)	113.68(13)	114.01(13)
N(2)−S(1)−N(3)	90.05(11)	89.89(12)
C(1)−N(1)−Se(1)	130.99(19)	131.59(18)
C(2)−N(2)−S(1)	123.4(2)	122.48(19)
C(2)−N(2)−Se(1)	119.01(17)	118.83(17)
S(1)−N(2)−Se(1)	97.34(11)	96.95(11)
C(3)−N(3)−S(1)	124.15(19)	125.57(19)
C(3)−N(3)−Se(1)	121.58(17)	122.78(18)
S(1)−N(3)−Se(1)	97.76(11)	98.62(12)

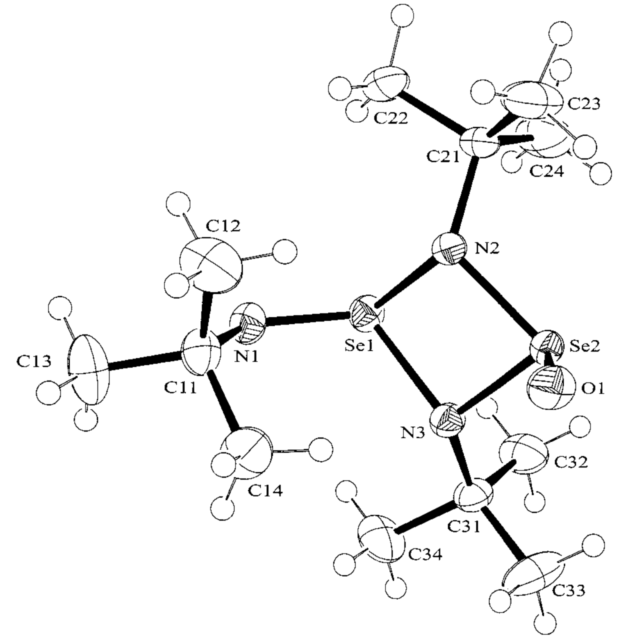

Figure 5. Molecular structure of ^{t}BuNSe(μ-N^{t}Bu)$_2$SeO (**8**) showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

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Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for ^{t}BuNSe(μ-N^{t}Bu)$_2$SeO (**8**)

Bond Lengths (Å)		Bond Angles (deg)	
N(1)−Se(1)	1.687(4)	C(11)−N(1)−Se(1)	128.6(3)
N(2)−Se(1)	1.943(4)	C(21)−N(2)−Se(2)	118.9(3)
N(3)−Se(1)	1.930(4)	C(21)−N(2)−Se(1)	118.9(3)
N(2)−Se(2)	1.866(4)	Se(2)−N(2)−Se(1)	98.60(17)
N(3)−Se(2)	1.862(4)	C(31)−N(3)−Se(2)	119.7(3)
O(1)−Se(2)	1.628(4)	C(31)−N(3)−Se(1)	119.2(3)
		Se(2)−N(3)−Se(1)	99.18(18)
		N(1)−Se(1)−N(3)	113.62(19)
		N(1)−Se(1)−N(2)	113.03(19)
		N(3)−Se(1)−N(2)	77.02(16)
		O(1)−Se(2)−N(3)	105.08(18)
		O(1)−Se(2)−N(2)	105.50(18)
		N(3)−Se(2)−N(2)	80.62(17)

Se═O bond lengths are 1.687(4) and 1.628(4) Å, respectively, consistent with double bonds (see Table 5 for selected bond angles and lengths). Related Se═O bond distances are 1.617(4) Å in OSe(NPPh$_3$)$_2$[28] and 1.612(5) Å in OSeCl$_2$.[29] There is a distinct asymmetry in the bridging Se−N bond lengths. The mean value for the selenium atom attached to oxygen is 1.864(2) Å compared to 1.936(6) Å for the selenium bonded to a terminal N^{t}Bu group (cf. 1.86 Å for a Se−N single bond).[30] The bridging nitrogen atoms are pyramidal ($\Sigma < N(2) = 336.4°$, $\Sigma < N(3) = 338.1°$). The ^{77}Se NMR spectrum of **8** in *n*-hexane at 25 °C shows two resonances at δ 882 and 1157. The former is tentatively assigned to Se═N^{t}Bu, by comparison with the chemical shift of the Se atom in a similar environment in **7**, while the latter is attributed to the Se═O group. A strong resonance is also observed at δ 1643 which is attributed to ^{t}BuN═Se═N^{t}Bu (δ 1655 in toluene). The decomposition of **8** in toluene at 25 °C is extensive and gives rise to ^{t}BuNSeO (δ 1252) and ^{t}BuNSeN^{t}Bu, together with **3** and **6** as the major decomposition products identified by ^{77}Se NMR. The facile decomposition of **8** in solution presumably reflects the weakness of the bridging Se−N bonds in the Se$_2$N$_2$ ring as implied by the bond lengths (vide infra). The novel Se$_2$N$_2$ heterocycle **8** can be formally viewed as a cyclic adduct of ^{t}BuN═Se═N^{t}Bu and ^{t}BuN═Se═O, both of which are thermally unstable.[4] Indeed we showed in a separate experiment that **8** can be generated from these reagents. After 2 days at 25 °C the ^{77}Se NMR spectrum of an equimolar mixture of ^{t}BuNSeN^{t}Bu and ^{t}BuNSeO in *n*-hexane showed resonances at δ 1156 and 881 for **8** together with a strong resonance at δ 1643 (^{t}BuNSeN^{t}Bu). No other resonances were observed in the δ (800−1800) region.

Conclusions

^{77}Se NMR spectroscopy is an excellent technique for the analysis of the complex mixture of imidoselenium compounds formed in the reaction of SeCl$_2$ with *tert*-butylamine. When the molar ratio is 2:3 the major products of this reaction are acyclic imidoselenium(II) dichlorides of the type ClSe[N(^{t}Bu)Se]$_n$Cl ($n = 1, 2$), which are potentially useful reagents for the synthesis of novel Se(II)−N ring systems. An increase in the amount of *tert*-butylamine leads to the formation of the new Se−N heterocycles [Se$_3$(N^{t}Bu)$_2$]$_n$ ($n = 1$ or 2) and Se$_3$(N^{t}Bu)$_3$, in addition to the known compounds Se$_6$(N^{t}Bu)$_2$ and Se$_9$(N^{t}Bu)$_6$. The six-membered ring Se$_3$(N^{t}Bu)$_3$, the first example of a cyclic selenium imide that does not contain Se−Se bonds, is the major product of the decomposition of the selenium(IV) diimide Se(N^{t}Bu)$_2$. The reactions of SeCl$_2$ with other primary amines are being investigated to determine the influence of the size of the R group on the nature of the products formed in cyclocondensation reactions. The novel heterocycle ^{t}BuNSe(μ-N^{t}Bu)$_2$SeO is a unique example of a structurally characterized compound containing both Se═N^{t}Bu and Se═O double bonds.

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Supporting Information Available: Three X-ray crystallographic files in CIF format are available on the Internet only. This material is available free of charge via the Internet at http://pubs.acs.org.

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