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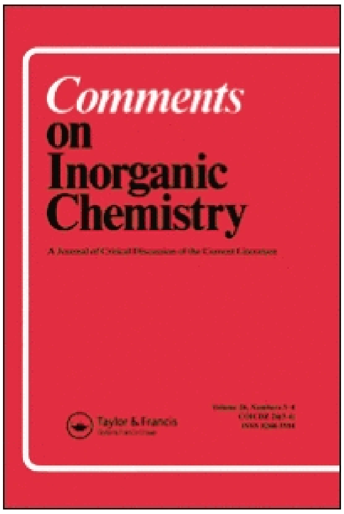

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Heterocyclic Selenium- and Tellurium-Nitrogen Compounds

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Heterocyclic Selenium– and Tellurium–Nitrogen Compounds

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The methods available for the synthesis of selenium–nitrogen (Se–N) heterocycles are discussed. The chemistry of phosphorus-containing Se–N and Te–N ring systems is described and compared with that of the corresponding S–N heterocycles. The $P_2N_4Se_2$ ring is a versatile ligand in transition-metal complexes. The use of ^{77}Se NMR and ESR spectroscopy in the characterization of cyclic Se–N systems is also presented.

Key Words: *synthesis, selenium–nitrogen heterocycles, tellurium–nitrogen heterocycles, phosphorus–nitrogen–chalcogen rings, coordination complexes, ESR spectra, ^{77}Se and ^{125}Te NMR spectra*

INTRODUCTION

Investigations of selenium–nitrogen (Se–N) and tellurium–nitrogen (Te–N) compounds have lagged behind the remarkable developments in sulfur–nitrogen (S–N) chemistry that have occurred in the past 20 years.[1,2] To some extent this is the result of the

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intrinsic instability of the Se(4p)–N(2p) π-bond compared to the relatively strong S(3p)–N(2p) π-bond.[3] For example, whereas sulfur diimides, RN═S═NR, constitute an extensively studied class of S–N compounds, the selenium analogues, RN═Se═NR (with the exceptions of R = CF_3CO, CF_3SO_2) are thermally unstable at room temperature with respect to the formation of elemental selenium.[4–6] Iminoselenyl chlorides RN═$SeCl_2$[7] exhibit a similar instability, but the seleninylamine ^{t}BuN═Se═O has been spectroscopically characterized.[6]

The possibility that the polymer $(SeN)_x$ may exhibit even more unusual properties than those of the metallic superconductor $(SN)_x$[8] has provided some of the impetus for current studies of Se–N compounds. The chemistry of *binary* Se–N species, which are potential precursors of this polymer, has been reviewed by Klapötke.[9] There have also been significant advances in our knowledge of Se–N compounds containing other heteroatoms, e.g., C, P, S and transition metals, in the last 5–6 years. The primary focus of investigations of Se–N–C systems has been the design of low-dimensional molecular conductors, and recent developments have been reviewed by Oakley *et al.*[10] Metal complexes of Se–N ligands are included in the account of metal-stabilized chalcogen nitrides by Woollins *et al.*,[11] and the structural aspects of Se–N and Te–N compounds have been documented by Bjorgvinsson and Roesky.[12] This Comment will attempt to complement these existing reviews on various aspects of Se–N chemistry. In particular an overview of synthetic approaches to Se–N heterocycles will be given and this will be followed by a discussion of the chemistry of Se–N–P systems. A final section will be devoted to NMR and ESR spectroscopic studies. Comparisons with analogous S–N systems will be made and, where appropriate, related developments in Te–N chemistry will be discussed.

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PREPARATIVE METHODS

One of the major impediments to the development of Se–N (and Te–N) chemistry has been the lack of suitable starting materials. There are a variety of reagents that can be used for the synthesis of S–N heterocycles.[1,2,13] These include S_4N_4, $(NSCl)_3$, NS^+,

NS_2^+, SN_2^{2-}, the sulfur imides S_7NH and $S_4N_4H_4$ (and anions derived therefrom), and silylated reagents such as $Me_3SiNSNSiMe_3$ and Me_3SiNSO. The only known selenium analogues of these reagents are Se_4N_4 and the thermally unstable $Me_3SiNSeNSiMe_3$.[5]

1. Tetraselenium Tetranitride

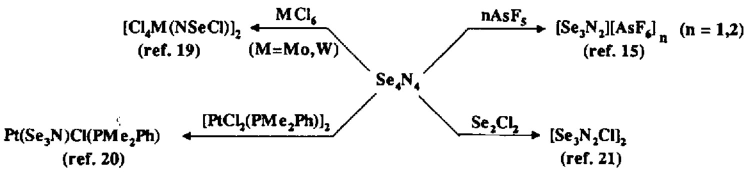
There are two well-established methods for the preparation of Se_4N_4. The first involves the reaction of $(CH_3CH_2O)_2SeO$ with gaseous ammonia in benzene. This procedure has recently been adapted for the preparation of $Se_4{}^{15}N_4$ using stoichiometric amounts of $^{15}NH_3$.[14] The second method uses the reaction of SeX_4 (X = Br, Cl) with ammonia at 70–80°C and modifications to this synthesis have also been described recently.[15] An alternative preparation, which is both quick and efficient, involves the reaction of $(Me_3Si)_2NLi$ with a mixture of selenium chlorides.[16]

$$12(Me_3Si)_2NLi + 2Se_2Cl_2 + 8SeCl_4 \rightarrow 3Se_4N_4 + 24Me_3SiCl + 12LiCl$$

Dry Se_4N_4 is an extremely dangerous material, which can explode at the slightest provocation, e.g., when touched with a metal spatula. It is essential, therefore, to store and handle this compound under an inert solvent (e.g., a hydrocarbon), to limit reactions to small amounts (<500 mg) of Se_4N_4, and to wear appropriate protective clothing.[15,16]

The cage molecule S_4N_4 is a versatile source of other S–N compounds, e.g., S–N halides, S–N cations and anions, P–S–N rings, and transition metal complexes of S–N anions,[11,17,18] By comparison Se_4N_4 has found only limited applications for the preparation of other Se–N compounds (see Scheme 1).

The cation $Se_3N_2^{2+}$, prepared by the oxidation of Se_4N_4 with



SCHEME 1 Preparation of Se–N compounds from Se_4N_4.

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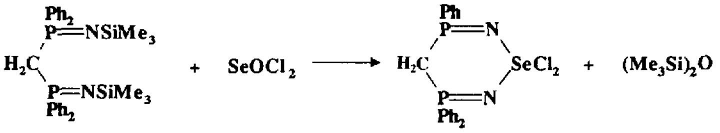
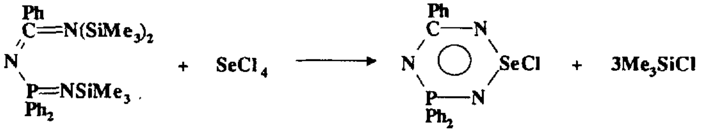
AsF_5, is a potentially useful reagent for the synthesis of other Se–N heterocycles, but no examples of its use have been reported.

2. Cyclocondensation Reactions with Selenium or Tellurium Halides

The most versatile method for the synthesis of Se–N heterocycles is cyclocondensation. This method usually makes use of Si–N reagents which react with selenium halides with the elimination of chlorotrimethylsilane. The selenium halides Se_2Cl_2, $SeCl_4$ and $SeOCl_2$ are all readily available and examples of cyclocondensation reactions using selenium(IV) halides are given in Eqs. (1) and (2).


(1)

(Ref. 22)

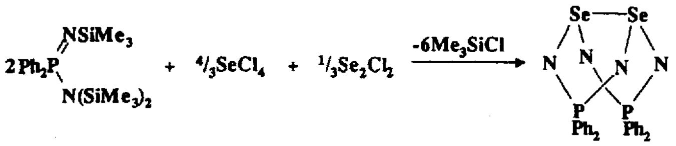

(2)

(Ref. 23, 24)

Selenium in a lower formal oxidation state can be generated in situ by using a mixture of Se_2Cl_2 and $SeCl_4$ in the appropriate amounts to give the desired Se:Cl ratio. The first example of this approach involved the synthesis of the dimers $S_2Se_4N_4^{2+}$ from $[(Me_3Si)_2N]_2S$.[25]

$$2[(Me_3Si)_2N]_2S + \underset{(X = Cl, Br)}{2SeX_4 + Se_2X_2} \xrightarrow{-8Me_3SiX} [S_2Se_4N_4]X_2 \qquad (3)$$

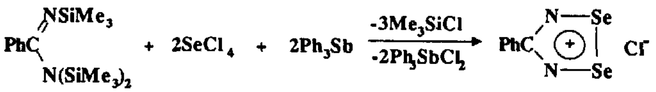
More recently this method has been used to prepare the eight-membered ring 1,5-$Ph_4P_2N_4Se_2$ in 85% yield from $Ph_2PN_2(SiMe_3)_3$.[26]



(4)

Surprisingly, this reaction produces substantial amounts of 1,3-$R_4P_2N_4Se_2$, in addition to 1,5-$R_4P_2N_4Se_2$, when R = Me, Et.[27]

An alternative source of selenium in a lower oxidation state is the in situ reduction of $SeCl_4$ with triphenylantimony. For example, the cyclocondensation of N,N,N′-tris(trimethylsilyl)benzamidine with "$SeCl_2$" in a 1:2 molar ratio provides an excellent route to the cyclic five-membered cation $PhCN_2Se_2^+$.[28]



(5)

This procedure has been extended to the synthesis of the parent ring system $HCN_2Se_2^+$[29] as well as derivatives in which two $CN_2Se_2^+$ rings are attached to an aromatic ring in 1,3- or 1,4-positions.[30] The eight-membered ring system $Ph_2C_2N_4S_2$ is a classic example of a planar, delocalized 10 π-electron system.[31] However, attempts to make the Se analogue by the cyclocondensation of $PhCN_2(SiMe_3)_3$ with "$SeCl_3$" have produced only the cation $PhCN_2Se_2^+$.[32]

Organoselenium trihalides, $RSeCl_3$, are readily prepared by chlorination of organic diselenides. These reagents are thermally more stable than their sulfur counterparts and are well suited for the synthesis of Se–N heterocycles via cyclocondensation with trifunctional Si–N reagents. For example, the reaction of the phosphorus(V) reagent $Ph_2PN_2(SiMe_3)_3$ with $RSeCl_3$ produces the white eight-membered 1,5-$Ph_4P_2N_4Se_2R_2$ in excellent yields.[33] When R = alkyl, however, the formation of 1,5-$Ph_4P_2N_4Se_2R_2$ is accompanied by smaller amounts of the Se-dealkylated product 1,5-$Ph_4P_2N_4Se_2$. An alternative route to 1,5-$Ph_4P_2N_4Se_2Ph_2$ (55% yield) involves the reaction of $Ph_2PN_2(SiMe_3)_3$ with three molar equivalents of PhSeCl.[34]

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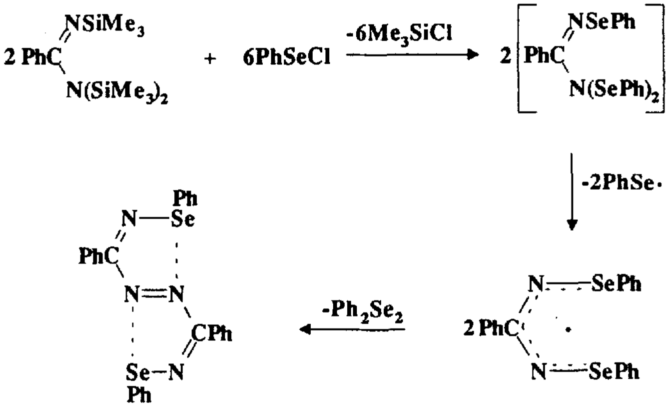

SCHEME 2 Reaction pathway for the formation of a diazene from $PhCN_2(SiMe_3)_3$ and PhSeCl in a 1:3 molar ratio.

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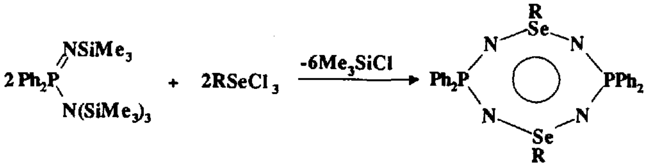
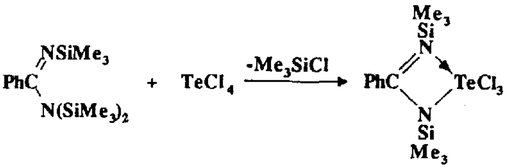
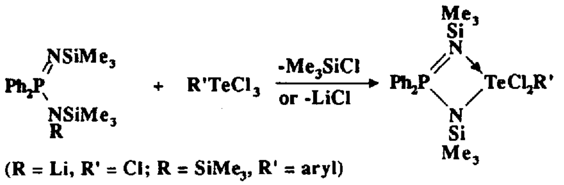
 (6)

By contrast, the reaction of $RSeCl_3$ (R = Me, Ph) with $PhCN_2(SiMe_3)_3$ produces deeply colored (red or purple) diazenes which are isomers of the anticipated eight-membered rings.[35] The same product is obtained from the reaction of $PhCN_2(SiMe_3)_3$ with three molar equivalents of PhSeCl, which has been shown by ESR spectroscopy to occur via the formation of the resonance-stabilized radicals $PhCN_2(SePh)_2\cdot$.[36] (See Scheme 2.)

The only useful binary tellurium chloride for cyclocondensation reactions is $TeCl_4$ which produces a four-membered CN_2Te ring upon reaction with $PhCN_2(SiMe_3)_3$.[37]

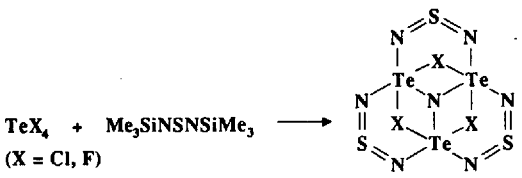
 (7)

In a similar manner the reaction of $Ph_2PN_2(SiMe_3)_3$ with $ArTeCl_3$[38] or $[Ph_2P(NSiMe_3)_2]Li$ with $TeCl_4$[39] produces the four-membered PN_2Te ring in excellent yields.



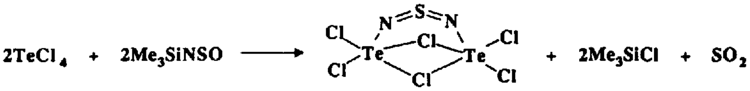
(8)

In these reactions of $TeCl_4$ with trifunctional Si–N reagents only one Te–Cl bond is reactive towards Me_3SiCl elimination. By contrast, the treatment of tellurium(IV) halides with the bifunctional reagent $Me_3SiNSNSiMe_3$ results in the conversion of three Te–X bonds into Te–N bonds to give a twelve-membered $Te_3N_6S_3$ ring in which pairs of tellurium atoms are bridged by an NSN group and a halogen, and a central nitrido atom bridges all three telluriums.[40,41]



(9)

The reaction of $TeCl_4$ with Me_3SiNSO gives the dinuclear complex $Te_2N_2SCl_6$,[42a] which may be an intermediate in the formation of the aforementioned μ^3-nitrido complex.



(10)

The reduction of $Te_2N_2SCl_6$ with Ph_3Sb or the reaction of $TeCl_4$ with $S[N(SiMe_3)_2]_2$ in CH_2Cl_2 in a 1:1 molar ratio produces the five-membered ring $Cl_2TeNSNTe$, which reacts with AsF_5 in SO_2 to give $[ClTeNSNTe][AsF_6]$.[42b]

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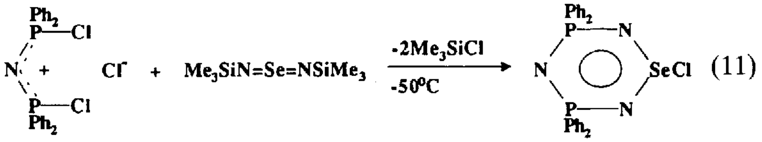
3. Selenium and Tellurium Reagents Containing Silicon–Nitrogen Bonds

Silicon–nitrogen compounds that also contain selenium–nitrogen bonds are potentially useful reagents for the preparation of Se–N heterocycles by cyclocondensation reactions. However, the only example of the application of the thermally unstable derivative $Me_3SiNSeNSiMe_3$[5] for this purpose is the synthesis of $Ph_4P_2N_3SeCl$ which must be conducted at low temperatures.[43]



(11)

The singly bonded Se–N reagents $[(Me_3Si)_2N]_2Se_x$ ($x = 1, 2$), which are readily obtained from the reaction of $(Me_3Si)_2NLi$ with Se_2Cl_2,[44,45] are thermally stable and potentially more useful than the unsaturated compound $(Me_3SiN)_2Se$. Some applications of these reagents in the preparation of Se–N heterocycles are given in Scheme 3.

The tellurium reagent $[(Me_3Si)_2N]_2Te$ is obtained from the reaction of $TeCl_4$ with four molar equivalents of $LiN(SiMe_3)_2$.[44] Applications of this reagent for the synthesis of Te–N heterocycles seem likely. Interestingly, the oxidation of $[(Me_3Si)_2N]_2Te$ by $AgAsF_6$ produces the radical cation $Te[N(SiMe_3)_2]_2^{+\cdot}$ as the black AsF_6^- salt.[48]

$$\begin{tikzcd}
 & Se_4N_4 \text{ (ref. 16, 46)} & \\
(SeS_2N_2Cl)_2 \text{ (ref. 46)} & {[(Me_3Si)_2N]_2Se} \arrow[l, "SCl_2"'] \arrow[u, "SeCl_4"'] \arrow[r, "'Se_2Cl_5'"] \arrow[d, "'SeCl_3'"] & (Se_3N_2Cl)_2 \text{ (ref. 21)} \\
 & Se_3N_2Cl_2 \text{ (ref. 47)} &
\end{tikzcd}$$

SCHEME 3 Preparation of Se–N compounds from $[Me_3Si)_2N]_2Se$.

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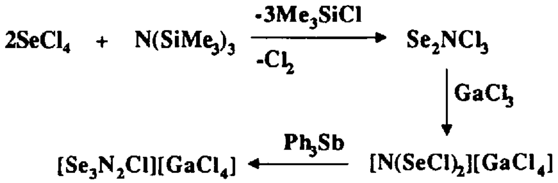
4. Selenium–Nitrogen Halides

The most useful sulfur–nitrogen halide for the synthesis of other S–N heterocycles is the six-membered ring $(NSCl)_3$, which is prepared by chlorination of $S_3N_2Cl_2$. The selenium analogue $(NSeCl)_3$ is unknown and the chlorination of $Se_3N_2Cl_2$ produces a thermally unstable Se–N chloride which decomposes to give N_2 and selenium halides.[21] The explosive black solid $Se_3N_2Cl_2$ is obtained in several ways: (a) from $[(Me_3Si)_2N]_2Se$ and a mixture of $SeCl_4$ and Se_2Cl_2 designed to give a Se:Cl of 1:3 (see Scheme 3), (b) from $[(Me_3Si)_2N]_2Se$ and $SeOCl_2$ in a 1:2 molar ratio, and (c) from Me_3SiN_3 and Se_2Cl_2 in a 2:3 molar ratio.[21,47] The insolubility and thermal instability of this compound inhibit its use as a synthetic reagent. However, a number of Se–N chlorides, which represent potential building blocks for Se–N heterocycles, have been prepared recently.

The attempted synthesis of the SeN^+ cation by the reaction of $N(SiMe_3)_3$ with $SCl_3^+AsF_6^-$ in $CFCl_3$ at 0°C produced instead the $N(SeCl_2)_2^+$ cation.[49]

$$6[SeCl_3][AsF_6] + 5N(SiMe_3)_3 \rightarrow 3[N(SeCl_2)_2][AsF_6] + 9Me_3SiF + 3AsF_3 + N_2 + 6Me_3SiCl \tag{12}$$

The related reaction of $N(SiMe_3)_3$ with $SeCl_4$ in boiling CH_2Cl_2 yields red crystals of Se_2NCl_3.[50] This product reacts with $GaCl_3$ to give $[N(SeCl)_2][GaCl_4]$ in which the cation adopts the horseshoe-shape (*cis,cis*-isomer) that is well established for the corresponding sulfur cation with various anions. The reduction of $[N(SeCl)_2][GaCl_4]$ with Ph_3Sb generates the red five-membered ring $Se_3N_2Cl^+$ (see Scheme 4).[51]



SCHEME 4 Formation of the $Se_3N_2Cl^+$ cation.

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5. Selenium–Nitrogen Anions

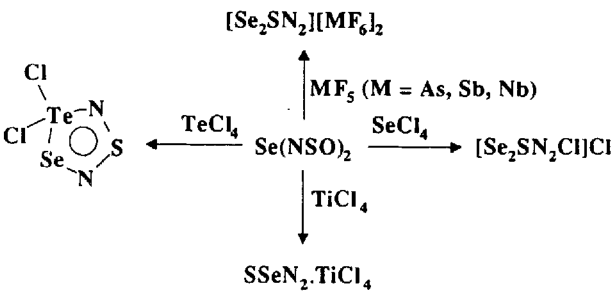
Compared to the rich chemistry of sulfur–nitrogen anions,[52,53] our knowledge of Se–N anions is undeveloped. Solutions of $SeCl_4$ or $SeOCl_2$ in liquid ammonia apparently contain the anions $Se_2N_2^{2-}$ and $Se_2N_2H^-$, which can be trapped by complexation to a metal.[11,54,55]

$$PtCl_2(PR_3)_2 + 2SeCl_4 + 8NH_3 \rightarrow Pt(Se_2N_2)(PR_3)_2 + 6NH_4Cl + 2Cl_2 \qquad (13)$$

A solution of Se_4N_4 in liquid ammonia at high pressure (ca. 50 atm) may also be used for the transformation shown in Eq. (13), leading to the intriguing possibility that such solutions contain the $Se_3N_3^-$ ion (since $S_3N_3^-$ is formed in liquid NH_3 solutions of S_4N_4).[56] Although further applications of these anions in the synthesis of Se–N heterocycles and their spectroscopic characterization in solution can be anticipated, the potential hazards associated with handling such explosive materials, particularly in the isolation of crystalline salts, should not be underestimated.

6. Selenium and Tellurium Thionylimides

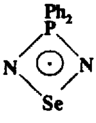
The reaction of Se_2Cl_2 with Me_3SiNSO produces yellow crystals of $Se(NSO)_2$ in excellent yields.[57] The corresponding tellurium compound $Te(NSO)_2$ is prepared from $({}^tBuMe_2Si)_2Te$ and ClNSO in a 1:2 molar ratio.[58] As a result of the propensity of thionylimides to eliminate SO_2, $Se(NSO)_2$ is a fertile source of the unstable molecule $SeSN_2$, which can be trapped as an adduct with $TiCl_4$. Some examples of the use of $Se(NSO)_2$ in the synthesis of Se–N heterocycles are summarized in Scheme 5.[46,59,60]



SCHEME 5 Preparation of Se–N heterocycles from $Se(NSO)_2$.

SELENIUM-NITROGEN-PHOSPHORUS RINGS

Unsaturated Se–N–P rings of the type $(Ph_2PN)_x(SeN)_y$ are hybrids of the well-known cyclophosphazenes and a binary Se–N ring such as Se_4N_4. Some known and potential members of this series of inorganic heterocycles are shown below.



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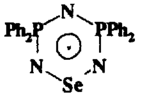

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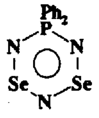

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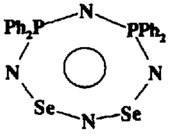

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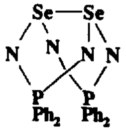

5

The introduction of Ph_2PN units into an Se–N ring improves the thermal stability significantly. For example, both 1,3- and 1,5-$Ph_4P_2N_4Se_2$, **4** and **5**, can be handled without fear of explosions whereas Se_4N_4 is an extremely dangerous material. In addition, ^{31}P NMR spectroscopy provides an informative structural probe for the products of various reactions of these hybrid ring systems, especially for coordination complexes.

1. Radical Formation

Although the Se–N–P rings exhibit many similarities in structure and properties to those of their sulfur analogues, there are also significant differences. For example, a solution of 1,5-$Ph_4P_2N_4Se_2$ (**5**) in dichloromethane is thermochromic, being pale yellow at −20°C and green at 23°C.[27] This green solution exhibits visible absorption bands at 634 and 653 nm and a five line (1:2:3:2:1) ESR spectrum, which has been attributed to the cyclic radical $Ph_2PN_2Se\cdot$. The corresponding sulfur system 1,5-$Ph_4P_2N_4S_2$ shows no tendency to dissociate to $Ph_2PN_2S\cdot$ radicals in solution, and this difference in behavior presumably reflects, in part, the relative weakness of Se–N compared to S–N bonds. A solution of 1,5-$Ph_4P_2N_4Se_2$ (**5**) in CH_2Cl_2 slowly deposits red selenium, and this decomposition has thwarted attempts to obtain crystals for the structural determination of this eight-membered ring.[27] A similar disintegration to elemental selenium has been observed for the homologous radical $Ph_4P_2N_3Se\cdot$ (**2**), which is prepared by the re-

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duction of $Ph_4P_2N_3SeCl$ with Ph_3Sb.[43] The sulfur analogue of this radical, $Ph_4P_2N_3S\cdot$, is known to dimerize to give a twelve-membered ring which contains a transannular S--S contact [d(S–S) = 238.5 pm].[61] It is possible that $Ph_4P_2N_3Se\cdot$ (**2**) dimerizes in a similar manner, but the formation of a cross-ring Se--Se bond promotes the elimination of red selenium, cf. 1,5-$Ph_4P_2N_4Se_2$.

2. Coordination Complexes

Selenium–nitrogen heterocycles are potentially versatile ligands comprised of both soft (Se) and hard (N) donor centers. The insolubility and hazardous nature of Se_4N_4 have impeded investigations of the coordination chemistry of this binary chalcogen nitride. By contrast, the formation of metal complexes from S_4N_4 has received extensive scrutiny.[11,17,18] The higher thermal stability and greater solubility in organic solvents of 1,5-$Ph_4P_2N_4Se_2$ compared to Se_4N_4 facilitate studies of its coordination behavior and the following bonding modes have been established for this ligand: η^1-N, η^2-Se,Se′, and η^2-Se,N-μ,η^1-Se′.[26,62]

The reaction of 1,5-$Ph_4P_2N_4Se_2$ with the chloro-bridged dimer $[PtCl_2(PEt_3)]_2$ in CH_2Cl_2 produces the N-bonded adducts $[PtCl_2(PEt_3)]_n$ (1,5-$Ph_4P_2N_4Se_2$) (n = 1, 2). The two $PtCl_2(PEt_3)$ groups in the di-adduct (**6**) are attached to distal nitrogen atoms of the $P_2N_4Se_2$ ring, which has a folded structure with d(Se–Se) = 2.594 Å.[27] This information has been used to estimate a value of 2.65–2.70 Å for the Se–Se distance in **5**, cf 2.748(9) Å for Se_4N_4.[63]

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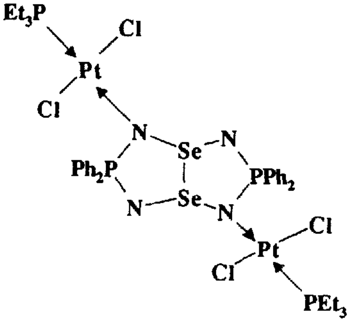


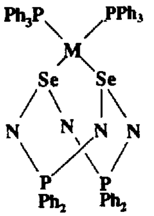
6

Similar N-bonded adducts of platinum(II) with the sulfur-containing ligand 1,5-$Ph_4P_2N_4S_2$ have been spectroscopically characterized.[64]

The reaction of **5** with the zero valent metal complexes $Pt(PPh_3)_2(CH_2{=}CH_2)$ or $Pd(PPh_3)_4$ results in oxidative-addition to give the η^2-Se,Se′-bonded complexes $M(PPh_3)_2(Ph_4P_2N_4Se_2)$ (M = Pt, Pd).[27,62] The structures of these products were established by ^{31}P and, in particular, ^{77}Se NMR spectroscopy.

$$1{,}5\text{-}Ph_4P_2N_4Se_2 + M(PPh_3)_2L \xrightarrow[-C_2H_4 \text{ or } 2PPh_3]{\text{toluene, } 0^\circ C} M(PPh_3)_2(Ph_4P_2N_4Se_2) \quad (14)$$

$$\left[\begin{array}{l} M = Pt,\ L = C_2H_4 \\ M = Pd,\ L = 2PPh_3 \end{array}\right] \qquad (\mathbf{7a},\ M = Pt;\ \mathbf{7b},\ M = Pd)$$



7a, M = Pt
7b, M = Pd

When the monometallic complexes **7a** or **7b** are heated in boiling toluene the loss of one triphenylphosphine ligand occurs to give dimers (Eq. (15)). This process may be reversed upon addition of PPh_3 to the dimers.

$$\begin{array}{l} 2M(PPh_3)_2(1{,}5\text{-}Ph_4P_2N_4Se_2) \\ (M = Pt, Pd) \end{array} \underset{+2PPh_3}{\overset{-2PPh_3}{\rightleftharpoons}} \begin{array}{l} [M(PPh_3)(1{,}5\text{-}Ph_4P_2N_4Se_2)]_2 \\ (\mathbf{8a},\ M = Pt;\ \mathbf{8b},\ M = Pd) \end{array} \quad (15)$$

The dimers **8a** and **8b** have structures similar to those of the sulfur analogues[65] on the basis of ^{31}P NMR spectroscopic data, i.e., each $P_2N_4Se_2$ ring acts as a chelating (N, Se) ligand towards one metal and as a bridging ligand through the other selenium to the other metal.

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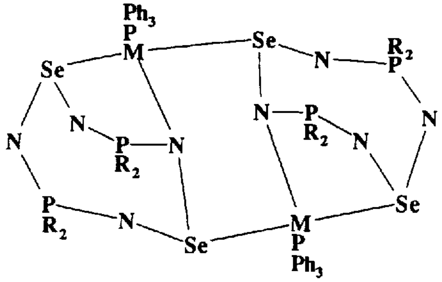


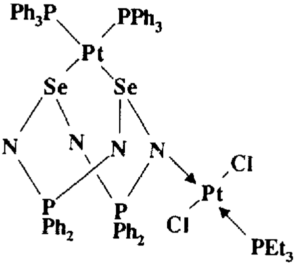
8a, M = Pt; **8b**, M = Pd

The variable temperature ^{31}P NMR spectra of **8a** and **8b** reveal a fluxional process in which the two heterocyclic phosphorus environments are equivalent on the NMR time scale at room temperature. An interconversion barrier of 9.5 ± 0.2 kcal mol^{-1} has been estimated from the NMR data for the Pt complex, cf. 10.2 ± 0.2 kcal mol^{-1} for the sulfur analogue. A [1,3]-metallotropic rearrangement involving oscillation of the Pt atoms between vicinal nitrogen atoms and across a selenium atom of each $P_2N_4Se_2$ ring has been proposed to account for the fluxional behavior.

A complex **9** which combines the η^1-N and η^2-Se,Se′ bonding modes has been prepared by the reaction of the monoadduct $[PtCl_2(PEt_3)][1,5\text{-}Ph_4P_2N_4Se_2]$ with $Pt(CH_2{=}CH_2)(PPh_3)_2$ in CH_2Cl_2 at −78°C and characterized by ^{31}P NMR spectroscopy.[26,62]

3. Reactions of 1,3- and 1,5-$Ph_4P_2N_4Se_2$

The eight-membered rings 1,3- and 1,5-$Ph_4P_2N_4Se_2$, **4** and **5**, are more sensitive to moisture and less thermally stable than their



9

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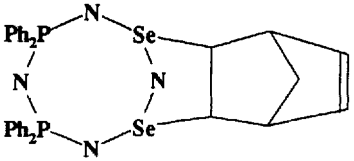
sulfur analogues. For example, a solution of 1,3-$Ph_4P_2N_4Se_2$ in CH_2Cl_2 decomposes slowly to give $[N(PMe_2NH_2)_2]_2Se$ in which the selenide ion is involved in strong Se--HN hydrogen-bonding to four NH_2 groups of the surrounding cations. The 1,3-isomer, like its sulfur analogue,[67] undergoes cycloaddition with norbornadiene, to give an Se,Se′-bonded adduct (**10**), which was characterized by ^1H and ^{31}P NMR spectroscopy.[68]



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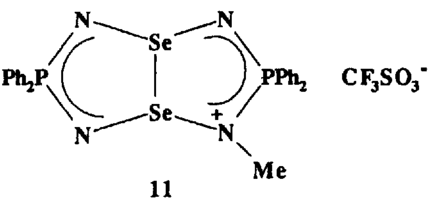
The lower homologue $Ph_2PN_3Se_2$ (**3**) is not known, although the sulfur analogue is a well established example of an eight π-electron six-membered ring.[69] In view of the thermal stability of 1,3-$R_4P_2N_4Se_2$ ring systems, this is probably due to the lack of a suitable synthetic procedure for **3** rather than the inherent instability of the six-membered ring.

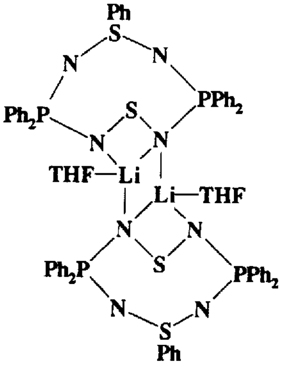
The addition of $MeCF_3SO_3$ to a solution of 1,5-$Ph_4P_2N_4Se_2$ in CH_2Cl_2 at −78°C produces the N-methylated cation $Ph_4P_2N_4 \cdot Se_2Me^+CF_3SO_3^-$ (**11**).[33] The low field ^{31}P NMR chemical shifts of the inequivalent phosphorus atoms in **11** strongly suggest that the cross-ring Se–Se interaction is retained in this cation as has been demonstrated by X-ray crystallography for the S–S bond in the sulfur analogue of **11**.[70]



11

The oxidative-addition of Br_2 or Cl_2 (as SO_2Cl_2) to 1,5-$Ph_4P_2N_4S_2$ occurs smoothly, with retention of the eight-membered ring, to give the S,S′-dihalogeno derivatives 1,5-$Ph_4P_2N_4S_2X_2$ (X = Cl, Br).[67] By contrast the reactions of 1,5-$Ph_4P_2N_4Se_2$ with Br_2 or SO_2Cl_2, even at −78°C, result in disintegration of the $P_2N_4Se_2$ ring.[68] However, the reaction of 1,5-$Ph_4P_2N_4Se_2$ with I_2, which does not react with 1,5-$Ph_4P_2N_4S_2$, produces the diiodo derivative $Ph_4P_2N_4Se_2I_2$ of unknown structure.

The reaction of 1,5-$Ph_4P_2N_4Se_2$ with phenyl-lithium occurs readily and cleanly in THF at −78° to give Li[$Ph_4P_2N_4Se_2Ph$].[62] Although the state of aggregation of this lithium derivative is unknown, the corresponding sulfur compound (**12**) is a centrosymmetric dimer with a step-shaped (ladder structure) and a phenyl group attached to sulfur.[71]



12

The reaction of Li[$Ph_4P_2N_4Se_2Ph$] with *cis*-$MCl_2(PPh_3)_2$ (M = Pt, Pd) at −78°C in THF produces the complexes [$MCl(PEt_3)_2$(1,5-$Ph_4P_2N_4Se_2Ph$)] (**13**) as yellow-orange, air- and moisture-sensitive solids.[62] The ^{31}P and ^{77}Se NMR spectra of these complexes are consistent with a structure similar to that established by X-ray crystallography for a related sulfur complex,[72] viz. the $P_2N_4E_2$ ring (E = S, Se) adopts a chair conformation with symmetry-related PPh_2 groups, but inequivalent PEt_3 ligands. Variable temperature ^{31}P NMR data of the Pt derivative **13a** reveal a two-site exchange process involving the two PEt_3 ligands with an activation energy of 9.3 kcal mol^{-1} (cf. 11.0 kcal mol^{-1} for the corresponding sulfur compound),[72] which is proposed to occur by rotation of the $PtCl(PEt_3)_2$ group around the Pt–Se bond.

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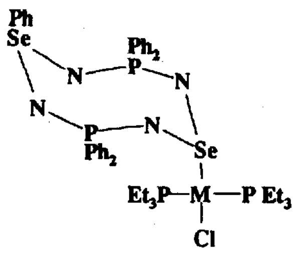
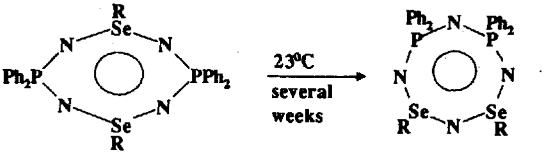


13a, M = Pt
13b, M = Pd

These η^1-Se bonded derivatives of the $Ph_4P_2N_4Se_2Ph^-$ anion represent the first metal complexes of this potentially multidentate ligand for which a versatile coordination chemistry seems likely.

4. Se,Se′-Diorgano Derivatives of the $P_2N_4Se_2$ Ring

The heterocycles 1,5-$Ph_4P_2N_4Se_2R_2$ (**14a**, R = Me, **14b**, R = Et; **14c**, R = Ph) are white solids stable towards exposure to air for several minutes. The Se,Se′-dialkyl derivatives undergo a remarkable *solid state* transformation at room temperature under a nitrogen atmosphere to give the corresponding 1,3-isomers **15a** and **15b** in essentially quantitative yields and, subsequently, small amounts of the Se-dealkylated product 1,3-$Ph_4P_2N_4Se_2$ (**4**).[66]



(16)

14a, R = Me; 14b, R = Et **15a, R = Me; 15b, R = Et**

The eight-membered heterocyclic ring in **14a** adopts a chair conformation in which the two NPN units are essentially planar and the two Se atoms are displaced on either side of the centrosymmetric ring by 1.07 Å.[33,66] An intermolecular process can be envisaged for the isomerization (Eq. (16)),[66] but there are no significant intermolecular Se–N contacts and the mechanism of this process has not been elucidated.

The Se,Se′-diphenyl derivative **14c** does not undergo this isomerization, but thermal decomposition occurs at 140°C to give

PhSeSePh and cyclophosphazenes.[66] Solutions of **14a–c** in boiling toluene (ca. 15 min) or CH_2Cl_2 at room temperature (3–4 days) produce $Ph_2P(NH)(NH_2)$ and dialkyl/aryl diselenides. After several weeks these solutions yield pale yellow crystals of $[Ph_2P(NH_2)_2]_2Se$ in which the Se^{2-} anion is strongly hydrogen-bonded to four different $Ph_2P(NH_2)_2^+$ cations.[66] The reaction of **14a–c** with $[PtCl_2(PEt_3)]_2$ in dichloromethane produces the 2:1 adducts $[PtCl_2(PEt_3)]_2[Ph_4P_2N_4Se_2R_2]$ in which the two platinum(II) atoms are attached to distal nitrogen atoms of the disordered $P_2N_4Se_2$ ring.[73]

5. Hybrid Ring Systems

The hybrid six-membered cyclic radicals $Ph_3PCN_3E\cdot$ (E = S, Se) are readily generated by reduction of the corresponding E–Cl derivative with Ph_3Sb.[43] These radicals are dimers in the solid state with significantly different modes of association. For the sulfur-based radical the dimer is formed through a long S–S bond (ca. 2.49 Å), while the selenium dimer (**16**) is associated through an Se–N interaction (1.99 Å). The structural parameters within the two rings of **16** are indicative of a cation/anion dimer (i.e., charge transfer) rather than a radical dimer.

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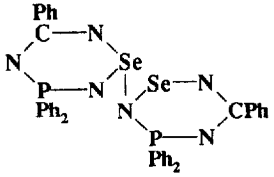


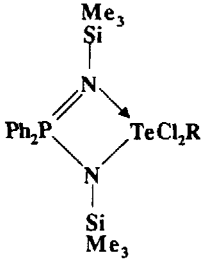
16

TELLURIUM-NITROGEN-PHOSPHORUS RING SYSTEMS

Tellurium chemistry is often significantly different from selenium chemistry owing to the larger size and greater metallic character of tellurium. It is not surprising, therefore, that the chemistry of P–N heterocycles containing tellurium does not resemble that of the Se analogues.

The only known Te–N–P heterocycle is the planar four-membered PN_2Te ring system **17**.[38,39] The Te–N bond distances are

2.056(3) and 2.185(3) Å, and the endocyclic bond angle at Te is 70.3(1)° in **17a**[39] (cf. 2.10 and 2.19 Å in $PhC(NSiMe_3)_2TeCl_3$).[37] The Te–N bonds in these heterocycles are very susceptible to cleavage by a variety of reagents, and attempts to generate P–N–Te rings with tellurium in a lower formal oxidation state, e.g., $P_2N_4Te_2$, have been unsuccessful. For example, the reaction of **17a** with Ph_3Sb produces Te metal, while treatment with ionic fluorides results in cleavage of Te–N bonds.[74]



(17a, R = Cl[39]; 17b, R = aryl[38])

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NMR STUDIES

The availability of convenient NMR nuclei (^{77}Se, I = ½, 7.6%; ^{125}Te, I = ½, 7.0%) provides a useful structural probe for Se–N and Te–N heterocycles that is not accessible for the corresponding S–N compounds. For example, the derivatives **17b** could be unambiguously assigned as four-membered PN_2Te rather than eight-membered $P_2N_4Te_2$ ring systems on the basis of the observation of a doublet (rather than a 1:2:1 triplet) in the ^{125}Te NMR spectrum[38] before the structure of **17a** was determined by X-ray crystallography.[39] The values of $^2J(^{31}P-^{125}Te)$ for **17a** or **17b** are in the range 84.5–144 Hz.[38,39] ^{77}Se NMR has been particularly useful in establishing the structures of metal complexes of Se–N–P ligands prior to, or in the absence of, X-ray structural determinations. The ^{77}Se NMR spectra of **7a** and **7b** display a multiplet characteristic of an $A_2BB'M$ spin system [where M is a ^{77}Se atom in the most abundant isotopomer for which the two PPh_3 phosphorus atoms are magnetically *inequivalent*, but the two ring (Ph_2P) phosphorus atoms are magnetically *equivalent*]. This information established the η^2-Se,Se′ bonding mode, and the simulation of the ^{77}Se NMR spectra provided detailed coupling information.[62] It is interesting to note that the structure of the corresponding η^2-S,S′ complex of Pt was not established (by X-ray crystallography)[65b] until 3 years after its discovery.[75]

In another example the ^{77}Se NMR spectra of platinum(II) diadducts of **14** provided decisive information in favor of the distal isomer (a) prior to the X-ray structural determination (see Scheme 6).[73] The spectra consist of a virtual triplet characteristic of an AA′X system (where X is ^{77}Se for the most abundant isotopomer and the ring phosphorus atoms are magnetically equivalent). The "vicinal" isomer (b) has inequivalent Se atoms that should give rise to two resonances while the Se-coordinated structure (c) (an A_2X system) should generate a 1:2:1 triplet.

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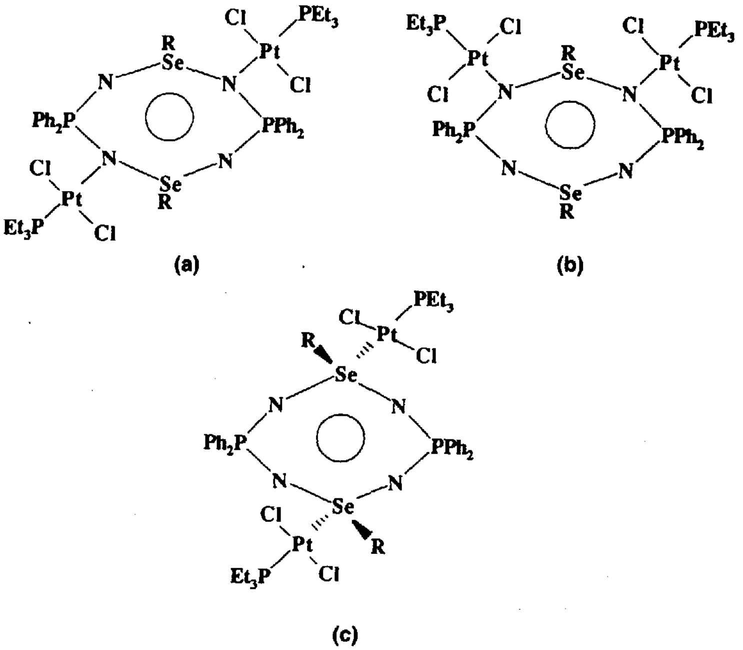

SCHEME 6 Isomers of $[PtCl_2(PEt_3)]_2[Ph_4P_2N_4Se_2R_2]$: (a) N-bonded distal, (b) N-bonded vicinal and (c) Se-bonded.

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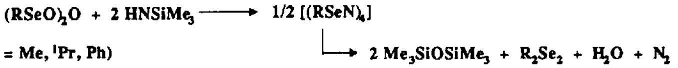
The ^{77}Se chemical shifts (rel. to Me_2Se) of 1,5-$R_4P_2N_4Se_2$ (R = Me, Et, Ph) fall within the narrow range 1066–1076 ppm with $^2J(^{31}P–^{77}Se)$ = 78–82 Hz, while $\delta(^{77}Se)$ values for the corresponding 1,3-isomers are 1193–1356 ppm.[27] η^2-Se,Se′ coordination to Pt of Pd results in a downfield to 830–850 ppm, while η^1-N coordination to platinum(II) produces an upfield shift of ca. 200 Hz.[62] The average values of $^2J(^{31}P–^{77}Se)$ (ca. 80 Hz) for these metal complexes are changed little from those of the ligands themselves. The ^{77}Se NMR chemical shifts of 1,3- and 1,5-$Ph_4P_2N_4Se_2R_2$ (R = Me, Et) are in the range 845–895 ppm[66] and N-coordination to platinum(II) moves this value to 945 ppm for the 1,5-isomer **14a**.[73]

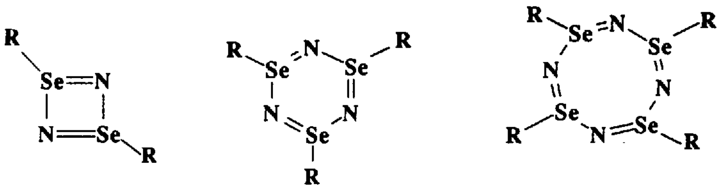
A recent elegant application of ^{77}Se NMR spectroscopy, in conjunction with ^{15}N NMR, involves the identification of the thermally unstable eight-membered rings $(RSeN)_4$ from the reaction of seleninic anhydrides with (^{15}N-enriched) hexamethyldisilazane.[76]



$$\begin{array}{l} (RSeO)_2O + 2\,HNSiMe_3 \longrightarrow 1/2\,[(RSeN)_4] \\ (R = Me, {}^iPr, Ph) \qquad\qquad \longrightarrow 2\,Me_3SiOSiMe_3 + R_2Se_2 + H_2O + N_2 \end{array} \qquad (17)$$

The tetrameric structure was established by carrying out the above reaction with two different seleninic anhydrides, $(PhSeO)_2O$ and $(^iPrSeO)_2O$. Random oligomerization of the two monomeric units PhSeN and ^{i}PrSeN would lead to the cyclic oligomers **18**, **19** and **20** (see Scheme 7) which should exhibit 4, 6 and 12 signals, respectively, in their ^{77}Se NMR spectra.[76]

The ^{77}Se NMR spectrum of the reaction mixture showed 12 distinct resonances in the 900–1000 ppm region consistent with the

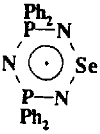
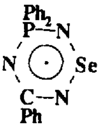
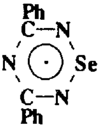
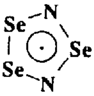
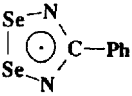


18 **19** **20**

SCHEME 7 Cyclic oligomers formed by random association of RSeN units (where R = Ph or ^{i}Pr or any combination of Ph and ^{i}Pr) (see Ref. 76).

TABLE I

ESR data for cyclic Se–N radicals.

Radical	g	a_N(mT)	Ref.
	2.011	0.67	27
	2.016	0.48	43
	2.017	0.14–0.63	43
	2.017	0.38–0.43	80
	2.043		81
	2.046		81
	2.039		28

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formation of the cyclic tetramer. In contrast to the structure of **14a**,[33] this interpretation assumes the existence of alternating single and double selenium–nitrogen bonds in these ring systems. This assumption is supported by the observation of two different one-bond ^{77}Se–^{15}N couplings in the ^{77}Se NMR spectrum of $(PhSe^{15}N)_4$.[76]

The identification of the eight-membered rings is particularly significant since the corresponding sulfur systems are unknown with the exception of $(FSN)_4$, for which the S–N bond distances in $(FSN)_4$ alternate between approximately single and double bond values of 1.655(2) and 1.544(2) Å,[77] respectively, as a result of Jahn–Teller distortion.[78] *Ab initio* calculations for the model system $(HSeN)_4$ show that the "tub" conformer, with (slightly) alternating Se–N bond lengths, is more stable than other ring geometrics as a result of π-stabilization and the electrostatic effects of relatively ionic Se–N bonds.[79] The steric interactions of Se lone pairs is also important in determining the relative stability of various ring conformations for $(HSeN)_4$.

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ESR STUDIES

A number of cyclic Se–N radicals have been characterized by ESR spectroscopy and two general trends have emerged (see Table I). First, radicals in which the odd electron is coupled to two selenium atoms tend to have *g* values of 2.04–2.05 while coupling to only one selenium produces *g* values of 2.01–2.02. Secondly, the *g* values of Se–N radicals are generally larger than those of the corresponding S–N radicals as a result of the larger spin-orbit coupling contribution of selenium.[24,80] Finally, whereas Se–N radicals have lower stabilities than their S–N analogues in solution, intermolecular interactions between Se–N radicals are stronger than those of S–N systems in the solid state. Consequently the odd electron Se–N compounds are good candidates for the design of molecular conductors.[10]

CONCLUSIONS

The recent discoveries of silicon–nitrogen–selenium reagents and selenium–nitrogen chlorides that are easily prepared and handled will facilitate the development of the chemistry of Se–N ring systems containing other heteroatoms. The synthetic approaches available for Te–N heterocycles are more limited and, at the moment, restricted to the use of $TeCl_4$ or $[(Me_3Si)_2N]_2Te$. Subtle, but significant, differences between the structures of Se–N heterocycles and those of their sulfur analogues may be anticipated. The development of molecular conductors based on cyclic Se–N radicals with strong intermolecular interactions in the solid state is a distinct possibility. The synthesis of hybrid Se–N polymers from cyclic precursors is also an interesting challenge. The differences in the structures and reactivity of Te–N heterocycles compared to their selenium (or sulfur) counterparts are likely to be substantial in view of the larger size and greater metallic character of tellurium. The availability of an informative NMR probe affords a distinct advantage in the study of Se–N and Te–N (as opposed to S–N) compounds.

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