

Chapter 4. Selenium- and Tellurium-Nitrogen Reagents

Tristram Chivers ^a and Risto S. Laitinen ^b

^a Department of Chemistry, University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4

^b Laboratory of Inorganic Chemistry, Environmental and Chemical Engineering, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland

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Abstract

The reactivity of the chalcogen-nitrogen bond towards main-group element or transition-metal halides, as well as electrophilic and nucleophilic reagents, is the source of a variety of applications of Se-N and Te-N compounds in both inorganic or organic chemistry. The thermal lability of Se-N compounds also engenders useful transformations including the formation of radicals via homolytic Se-N bond cleavage. These aspects of Se-N and Te-N chemistry will be illustrated with examples from the reactions of the binary selenium nitride Se_4N_4 , selenium nitrogen halides $[\text{N}(\text{SeCl}_n)_2]^+$ ($n = 1, 2$), the synthons $\text{E}(\text{NSO})_2$ ($\text{E} = \text{Se}, \text{Te}$), chalcogen-nitrogen-silicon reagents, chalcogen(IV) diimides $\text{RN}=\text{E}=\text{NR}$, the triimidotellurite dianion $[\text{Te}(\text{N}^t\text{Bu})_3]^{2-}$, chalcogen(II) amides and diamides $\text{E}(\text{NR}_2)_2$ ($\text{E} = \text{Se}, \text{Te}$; $\text{R} = \text{alkyl}, \text{SiMe}_3$), and heterocyclic systems.

4.1 Scope and Introduction

The development of the chemistry of selenium-nitrogen (Se-N) and tellurium-nitrogen (Te-N) chemistry has lagged behind the remarkable advances in sulfur-nitrogen (S-N) chemistry that have occurred in the past 40 years [1]. In part, this slow progress can be attributed to the lack of simple, easily handled Se-N and Te-N reagents. Nevertheless, a number of such reagents are now available and the goal of this chapter is to provide an overview of their applications in inorganic and organic chemistry.

The chemistry of Se-N and Te-N compounds has been discussed in various reviews and book chapters over the past 30 years [2-11]. While several of these expositions cover the topic in general [2, 3, 6a, 7, 8, 10], other contributions address specific aspects, e.g. metal-Se-N compounds [4], binary Se-N species [5], heterocyclic Se-N and Te-N compounds [6b, 11], and imido-selenium- and – tellurium compounds [9]. A book [1] and three recent book chapters include a discussion of S-N as well as Se-N and Te-N chemistry [8a, 8b, 11].

In keeping with the focus of this treatise on synthetic chemistry, the emphasis of this chapter will be on the preparative methods for the most important reagents containing Se-N and Te-N bonds, as well as their reactions. Comparison will be made with related S-N reagents wherever appropriate. The structural chemistry of Se-N and Te-N compounds will not be discussed, since this aspect is covered well in many of the aforementioned book chapters and reviews.

This overview will start with a discussion of the applications of inorganic selenium-nitrogen reagents commencing with binary selenium nitrides, notably Se_4N_4 , followed by sections on selenium- and tellurium-nitrogen halides, $\text{E}(\text{NSO})_2$ synthons ($\text{E} = \text{Se}, \text{Te}$), and chalcogen-nitrogen-silicon (Se-N-Si and Te-N-Si) reagents. The second half of the chapter will deal with organic Se-N

and Te-N reagents, including the ephemeral selenonitrosyls ArN=Se (Ar = aryl), chalcogen diimides RN=E=NR (E = Se, Te; R = alkyl, aryl), triimidochalcogenite dianions $[\text{E}(\text{NR})_3]^{2-}$ (E = Se, Te), and chalcogen diamides $\text{E}(\text{NR}_2)_2$ (E = Se, Te; R = alkyl, SiMe_3).

4.2 Binary Selenium-Nitrogen and Tellurium-Nitrogen Reagents

4.2.1 Neutral species

The quintessential sulfur-nitrogen cage molecule S_4N_4 is a rich source of novel sulfur-nitrogen chemistry [1, 8]. The selenium analogue Se_4N_4 may be prepared in several ways. One of these involves the reaction of $(\text{CH}_3\text{CH}_2\text{O})_2\text{SeO}$ with gaseous ammonia in benzene; this procedure has been adapted for the preparation of ^{15}N -enriched $\text{Se}_4^{15}\text{N}_4$ by using stoichiometric amounts of $^{15}\text{NH}_3$ [12]. A second method employs the treatment of selenium tetrahalides SeX_4 (X = Cl or Br) with ammonia at elevated temperatures [13, 14]. A more convenient procedure involves the reaction of $(\text{Me}_3\text{Si})_2\text{NLi}$ with a mixture of selenium chlorides (eq. 1). Pure Se_4N_4 is isolated in 66 % yield after washing with 10 % aqueous KCN solution to remove red selenium, selenium halides and selenium oxides and with water to remove LiCl [15].

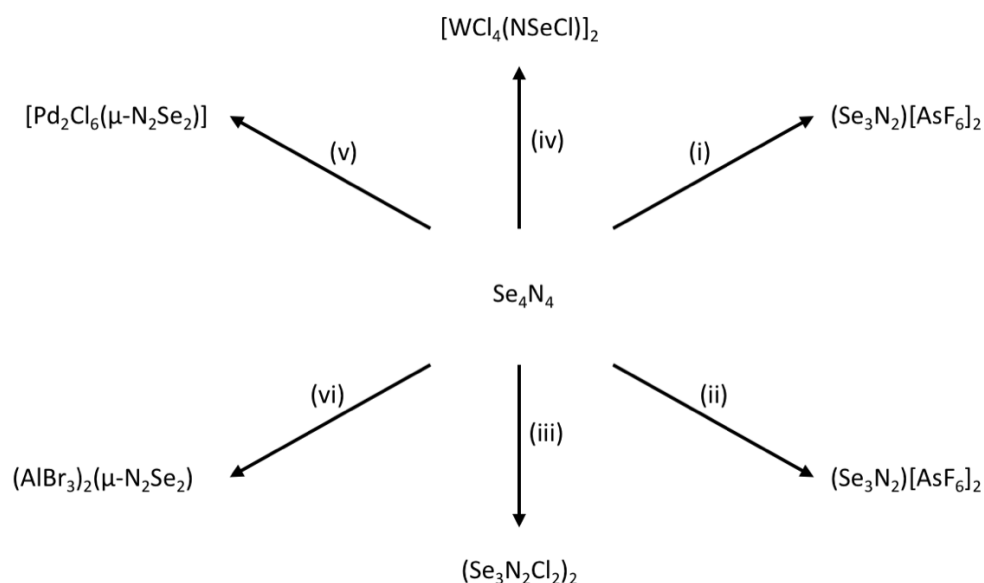


Caution: Dry Se_4N_4 is an extremely dangerous material, which can explode at the slightest provocation, *e.g.* when touched with a metal spatula. It is essential, therefore, to store and handle this

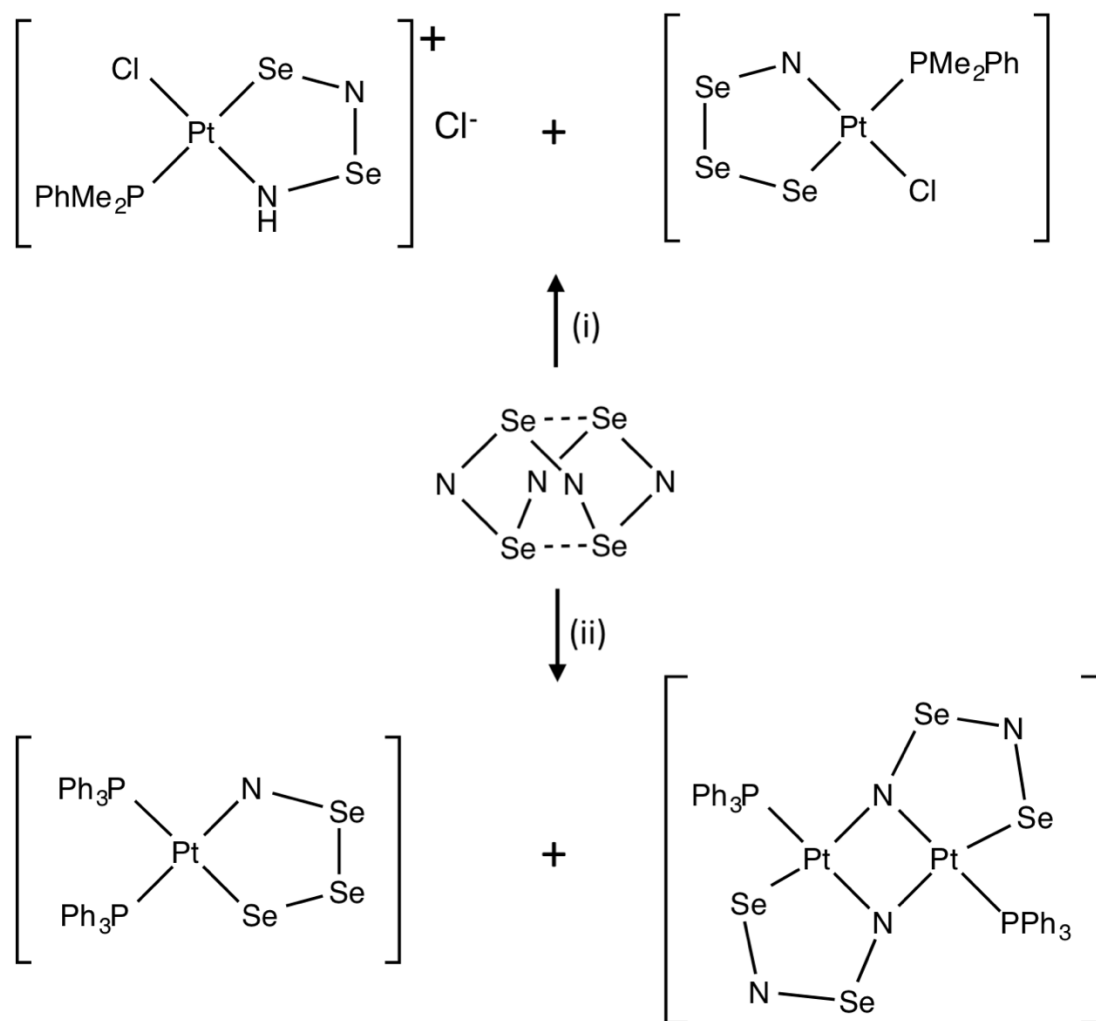
reagent under an inert solvent, *e.g.* a hydrocarbon, to limit reactions to small amounts (<500 mg) of Se_4N_4 , and to wear appropriate protective clothing [14, 15].

Despite its hazardous nature Se_4N_4 has been used as the source of a number of important selenium-nitrogen compounds either via oxidation or adduct formation (Figure 4.1). The first example involved reaction of Se_4N_4 with WCl_6 in boiling dichloromethane, which generates a complex of the monomeric chloroselenonitrene (NSeCl) ligand, *viz.* dimeric $[\text{Cl}_4\text{W}(\text{NSeCl})]_2$ [16]; the analogous molybdenum complex is obtained from treatment of Se_4N_4 with MoCl_5 [17]. The oxidation of Se_4N_4 with $[\text{Se}_4][\text{AsF}_6]_2$ produces $[\text{Se}_3\text{N}_2]_2[\text{AsF}_6]_2$ in high yield as an orange solid that can be manipulated with a metal spatula and is stable to heat [18]; the binary Se-N cation in this salt is a dimer of the radical cation $[\text{Se}_3\text{N}_2]^{\cdot+}$. The corresponding dication $[\text{Se}_3\text{N}_2]^{2+}$ is produced upon treatment of Se_4N_4 with AsF_5 . The chlorinated dimer $[\text{Se}_3\text{N}_2\text{Cl}]_2$ is formed as an explosive, insoluble dark brown powder from the reaction of Se_2Cl_2 with Se_4N_4 in dichloromethane [19].

A major goal in investigations of selenium-nitrogen compounds has been the generation of polymeric $(\text{SeN})_x$ [20], the selenium analogue of the well-known polysulfur nitride $(\text{SN})_x$. The latter is a conducting polymer with metallic properties, which is generated by the polymerization of S_2N_2 formed by heating S_4N_4 [1]. By contrast, the pyrolysis of Se_4N_4 under vacuum at temperatures up to 220 °C results in decomposition to elemental selenium and N_2 gas [20]. Although the binary selenium nitride Se_2N_2 has not been isolated, the reaction of Se_4N_4 with AlBr_3 in dibromomethane at room temperature generates the adduct $[(\text{AlBr}_3)_2(\mu\text{-Se}_2\text{N}_2)]$, incorporating a bridging Se_2N_2 ligand, as an air-sensitive yellow solid [21] (Figure 4.1). Transition-metal complexes of Se_2N_2 are found in the dianion $[\text{Pd}_2\text{Cl}_6(\mu\text{-Se}_2\text{N}_2)]^{2-}$ formed in the high-temperature reaction of Se_4N_4 with $[\text{Pd}_2\text{Cl}_6]^{2-}$ salts in dichloromethane [22].



The reactions of Se_4N_4 with transition-metal reagents have also been employed to generate complexes of the chelating binary selenium-nitrogen anions, *e.g.* Se_3N^- , $\text{Se}_2\text{N}_2^{2-}$ and its protonated derivative $\text{Se}_2\text{N}_2\text{H}^-$, via oxidative addition reactions (Figure 4.2) [4]. For example, the combination of Se_4N_4 with $[\text{PtCl}_2(\text{PMe}_2\text{Ph})]_2$ in boiling chloroform produces a mixture of $[\text{PtCl}(\text{Se}_3\text{N})(\text{PMe}_2\text{Ph})]$ and $[\text{PtCl}(\text{Se}_2\text{N}_2\text{H})(\text{PMe}_2\text{Ph})]\text{Cl}$, which were separated (in low yields) by chromatography [23, 24] (Figure 4.2). Complexes of the *N,Se* chelating $\text{Se}_2\text{N}_2^{2-}$ dianion are also formed via the oxidative addition of Se_4N_4 to the zerovalent platinum complex $\text{Pt}(\text{PPh}_3)_3$ in dichloromethane. The monomeric complex $[\text{Pt}(\text{Se}_2\text{N}_2)(\text{PPh}_3)_2]$ was characterized in solution by ^{31}P NMR spectroscopy while the solid-state structure of the dimer $[\text{Pt}(\text{Se}_2\text{N}_2)(\text{PPh}_3)]_2 \cdot \text{CH}_2\text{Cl}_2$, which was isolated in 30 % yield, was determined by X-ray crystallography [25].



The

binary sulfur nitride S_4N_2 is a six-membered ring with a sulfur diimide --N=S=N-- functionality. It is a low melting red solid (Mp 23 °C), which must be stored below -20 °C to avoid decomposition [26]. The preparation of the selenium analogue Se_4N_2 as a black powder stable at room temperature “in almost quantitative yield” from the reaction of Se_2Cl_2 and trimethylsilyl azide has been claimed [27]. However, a reinvestigation of this reaction showed that the black powder is the selenium-nitrogen chloride $\text{Se}_3\text{N}_2\text{Cl}_2$ [28]. The facile thermal decomposition of acyclic selenium(IV) diimides RN=Se=NR (R = alkyl, SiMe_3) (Section 7) above 0 °C implies that cyclic Se_4N_2 is likely to have low thermal stability due to the presence of the --N=Se=N-- functionality in the ring.

Unlike Se_4N_4 (and S_4N_4) the only known tellurium nitride has the composition Te_3N_4 , as expected for a tellurium(IV) nitride. A highly explosive yellow powder identified as “ Te_3N_4 ” is obtained from the treatment of potassium triimidotellurite $\text{K}_2[\text{Te}(\text{NH})_3]$ with an excess of ammonium nitrate in liquid ammonia [29]. The structure of “ Te_3N_4 ” may involve a μ_3 -nitrido bridging three tellurium(IV) centres of a Te_3N_3 ring [30]. Support for this suggestion comes from the identification of this structural motif in the tetra-adduct $\text{Te}_6\text{N}_8(\text{TeCl}_4)_4$ in which the central feature is a dimer of Te_3N_4 [31]. The highly explosive nature of “ Te_3N_4 ” precludes synthetic applications.

4.2.2 Cations

The simple binary cations NS^+ and NS_2^+ are important reagents in sulfur-nitrogen chemistry [1]. The selenium analogues NSe^+ and NSe_2^+ are unknown as isolated species. However, the latter may be generated *in situ* from the acyclic cation $\text{N}(\text{SeCl})_2^+$ upon reduction with SnCl_2 (see Section 3).

4.2.3 Anions

The acyclic sulfur-nitrogen anions SSNS^- and SNSNH^- may be used as isolated or *in situ* reagents, respectively, for the generation of metal complexes [32]. Although the selenium analogues have not been characterized in solution or in the solid state, solutions of Se_4N_4 in liquid ammonia behave as an *in situ* source of such anions. Thus, Se_4N_4 dissolves in liquid ammonia at high pressure (*ca.* 50 atm.) and reacts with $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$ to give $\text{Pt}(\text{Se}_2\text{N}_2)(\text{PMe}_2\text{Ph})_2$ [33]. It was observed, however, that the ^{15}N -labelled material $\text{Se}_4^{15}\text{N}_4$ can be recovered unchanged from such solutions implying that Se_4N_4 does not react with liquid ammonia. By contrast, liquid ammonia solutions of S_4N_4 have been shown to contain binary S-N anions such as cyclic S_3N_3^- and S_4N_5^- by ^{14}N NMR spectroscopy [34]

Solutions of SeCl_4 in liquid ammonia provide a safer route to metal complexes of the $\text{Se}_2\text{N}_2^{2-}$ dianion than the reactions of Se_4N_4 described in Section 1, as illustrated by the example shown in eq. 2; the orange platinum complex $[\text{Pt}(\text{Se}_2\text{N}_2)(\text{DPPE})]$ ($\text{DPPE} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) is isolated in 74 % yield [35]. Presumably the Cl_2 by-product formed in this reaction is purged under the stream of nitrogen that is used to remove the excess of ammonia, since it is known that complexes of the type $[\text{Pt}(\text{Se}_2\text{N}_2)(\text{PR}_3)_2]$ react with halogens to regenerate Se_4N_4 [36].



4.3 Chalcogen-Nitrogen Halides

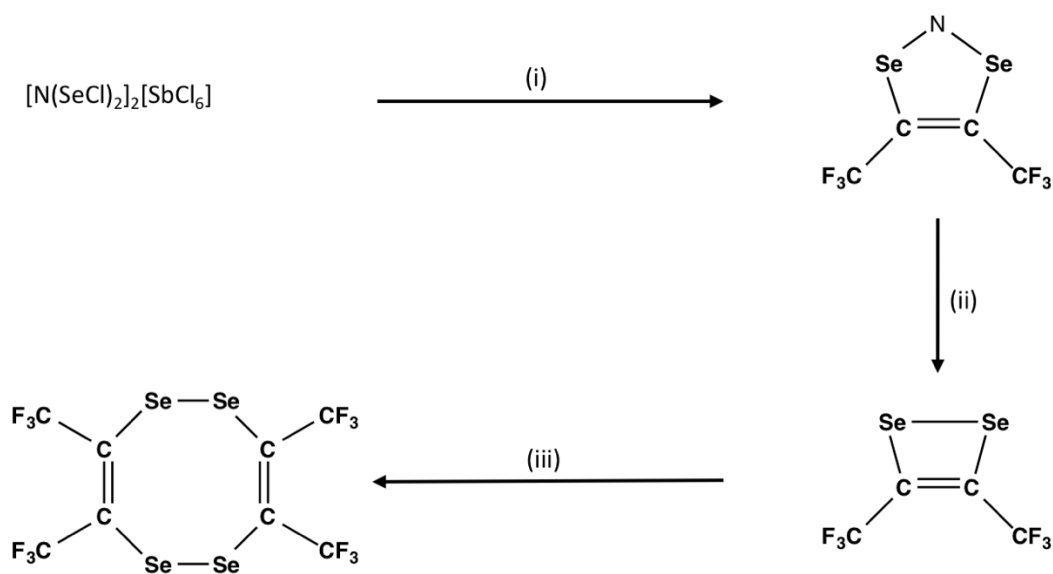
4.3.1 Ternary Selenium-Nitrogen Halides

As a source of the $-\text{SeNSe}-$ unit the cationic selenium-nitrogen halides $[\text{Cl}_2\text{SeNSeCl}_2]^+$ and $[\text{ClSeNSeCl}]^+$ are potential building blocks in Se-N chemistry; they can be prepared in gram-scale quantities from readily available reagents. The former species was obtained in an attempt to generate the binary cation NSe^+ from the reaction of $[\text{SeCl}_3][\text{AsF}_6]$ with $\text{N}(\text{SiMe}_3)_3$. When this reaction is carried out in CFCl_3 solution at 0 °C the orange solid $[(\text{SeCl}_2)_2\text{N}][\text{AsF}_6]$ is produced in 83 % yield (eq. 3) [37]. The use of the hexachloroantimonate $[\text{SeCl}_3][\text{SbCl}_6]$ rather than the hexafluoroarsenate salt results in loss of Cl_2 from the initial product to generate the $[\text{ClSeNSeCl}]^+$ cation as the orange SbCl_6^- salt in 89 % yield [38] (eq. 4).





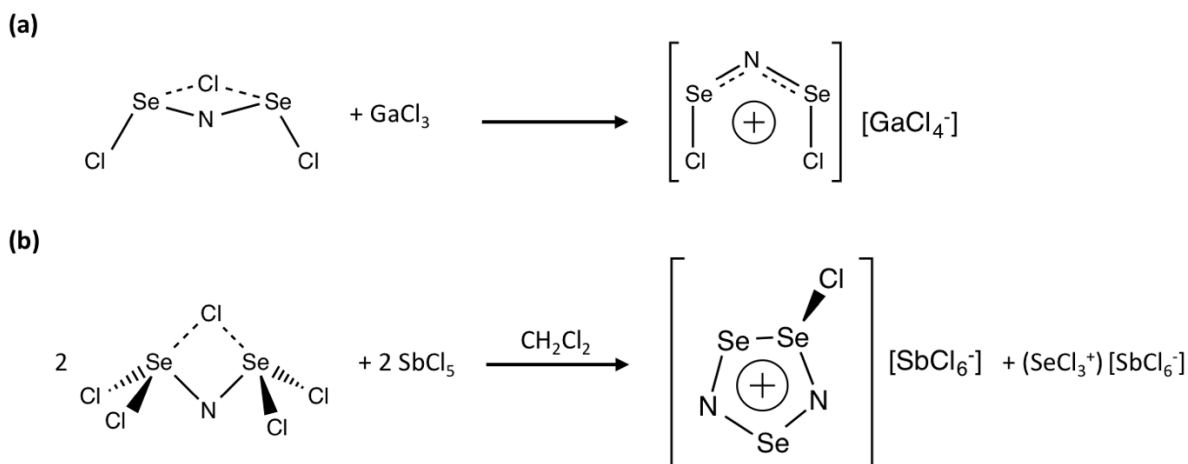
The reaction of $[(\text{SeCl})_2\text{N}][\text{SbCl}_6]$ with $\text{CF}_3\text{C}\equiv\text{CCF}_3$ and SnCl_2 in liquid SO_2 produces the five-membered cationic ring $\text{CF}_3\text{CSeNSeCCF}_3^+$ as the colorless SbCl_6^- salt [39, 40] (Figure 4.3) This transformation probably occurs via the intermediate formation of NSe_2^+ (Section 2.2), which undergoes cycloaddition with the alkyne. The reduction of the cyclic $\text{CF}_3\text{CSeNSeCCF}_3^+$ cation with sodium dithionite in liquid SO_2 occurs with the loss of nitrogen to produce the cyclic diselenide $\text{CF}_3\text{CSeSeCCF}_3$ as a red liquid in 40 % yield, which slowly dimerizes to an eight-membered ring (Figure 4.3). For comparison, the corresponding reaction with the sulfur analogue generates the neutral 7π -electron radical $\text{CF}_3\text{CSNSCCF}_3$ as a black-green liquid via a one-electron reduction [41].



Red crystals of the selenium-nitrogen chloride Se_2NCl_3 are isolated in 57 % yield from the reaction of tris(trimethylsilyl)amine with selenium tetrachloride in a 1:2 molar ratio in *boiling* dichloromethane [42]. If the same reaction is carried out *at 0-20 °C* in CH_2Cl_2 the chlorine-rich

product Se_2NCl_5 is obtained as a pale pink powder in 94 % yield [43]. Under similar conditions the reaction of SeBr_4 with $\text{N}(\text{SiMe}_3)_3$ generates the explosive bromo derivative Se_2NBr_3 [43].

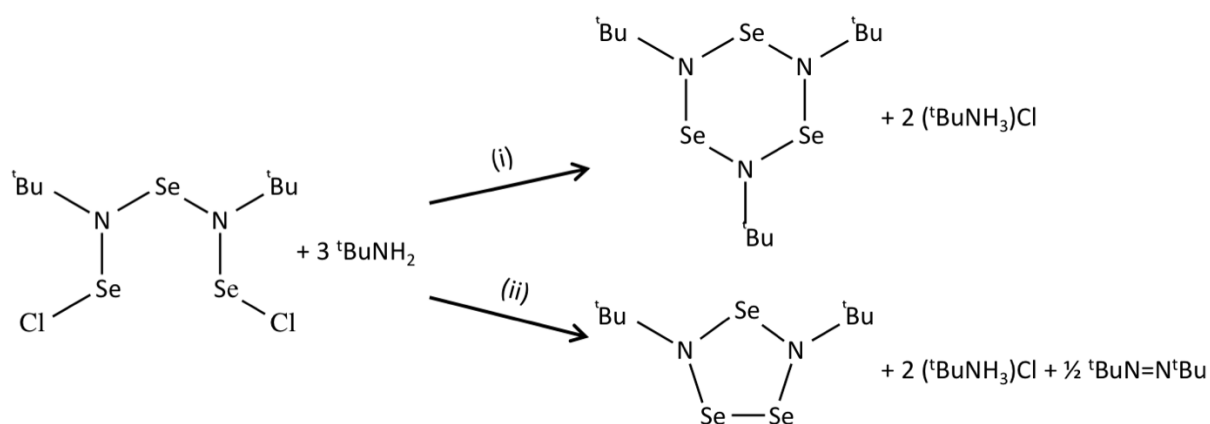
Reaction of Se_2NCl_3 with the chloride-ion acceptor GaCl_3 produces the acyclic $[\text{ClSeNSeCl}]^+$ cation (Figure 4.4a). The cyclic cation $[\text{Se}_3\text{N}_2\text{Cl}]^+$ is formed as the SbCl_6^- salt upon treatment of Se_2NCl_5 with antimony(III) chloride in CH_2Cl_2 (Figure 4.4b); this cation is also obtained, as the GaCl_4^- salt in 50 % yield, upon reduction of $[\text{ClSeNSeCl}]^+$ with triphenylantimony in dichloromethane [45]



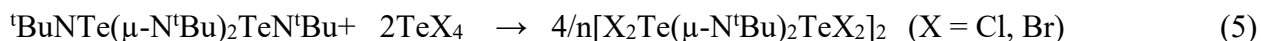
There are no tellurium analogues of the selenium-nitrogen halides Se_2NCl_x ($x = 3, 5$). Instead the reaction of $\text{N}(\text{SiMe}_3)_3$ with tellurium tetrachloride in a 1:2 molar ratio in CH_2Cl_2 followed by treatment of the white precipitate with AsF_5 produces the $\text{Te}_4\text{N}_2\text{Cl}_8^{2+}$ dication as the AsF_6^- salt [46]. This dication is formally a dimer of the hypothetical tellurium(IV) imide $[\text{Cl}_3\text{Te-N=TeCl}]^+$, however no reactions of this species have been reported.

4.3.2 Imido Chalcogen Halides

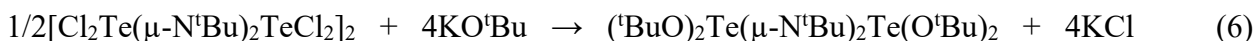
A homologous series of moisture-sensitive, acyclic *tert*-butylimido selenium(II) chlorides $\text{ClSe}[\text{N}(\text{tBu})\text{Se}]_n\text{Cl}$ ($n = 1-3$) have been isolated from the cyclocondensation reactions of *tert*-butylamine with SeCl_2 in various stoichiometries [47]. These intermediates react with *tert*-butylamine to form cyclic selenium imides via either nucleophilic substitution or reduction; the latter process produces rings with an Se-Se linkage (Figure 4.5). The bifunctional reagents $\text{ClSe}[\text{N}(\text{tBu})\text{Se}]_n\text{Cl}$ ($n = 1-3$) are potential synthons for the incorporation of other main group elements into Se-N rings.



Imidoselenium(IV) dihalides of the type RNSeCl_2 are either unknown ($\text{R} = \text{alkyl, aryl}$) or thermally unstable yellow liquids $\text{R}_\text{F}\text{NSeCl}_2$ ($\text{R}_\text{F} = \text{CF}_3$ or C_2F_5); the latter decompose at ambient temperature with the formation of the diazene $\text{R}_\text{F}\text{N}=\text{NR}_\text{F}$ and a mixture of selenium chlorides [48]. By contrast, the tellurium analogues tBuNTeX_2 ($\text{X} = \text{Cl, Br}$) can be isolated as thermally stable yellow-gold ($\text{X} = \text{Cl}$) or red ($\text{X} = \text{Br}$) solids from the redistribution reactions between tellurium tetrahalides and $\text{tBuNTe}(\mu\text{-N}^\text{tBu})_2\text{TeN}^\text{tBu}$ in THF at 23 °C (eq 5) [49]. The halide exchange between $[\text{Cl}_2\text{Te}(\mu\text{-N}^\text{tBu})_2\text{TeCl}_2]_2$ and trimethylsilyl bromide provides a cleaner route to the corresponding bromide.



The potential of the imidotellurium(IV) dichloride as a reagent in Te-N chemistry is indicated by the reaction with potassium *tert*-butoxide in THF, which proceeds at 23 °C to give the metathetical product in 71 % yield (eq 6) [b].



4.4 E(NSO)₂ Reagents (E = Se, Te)

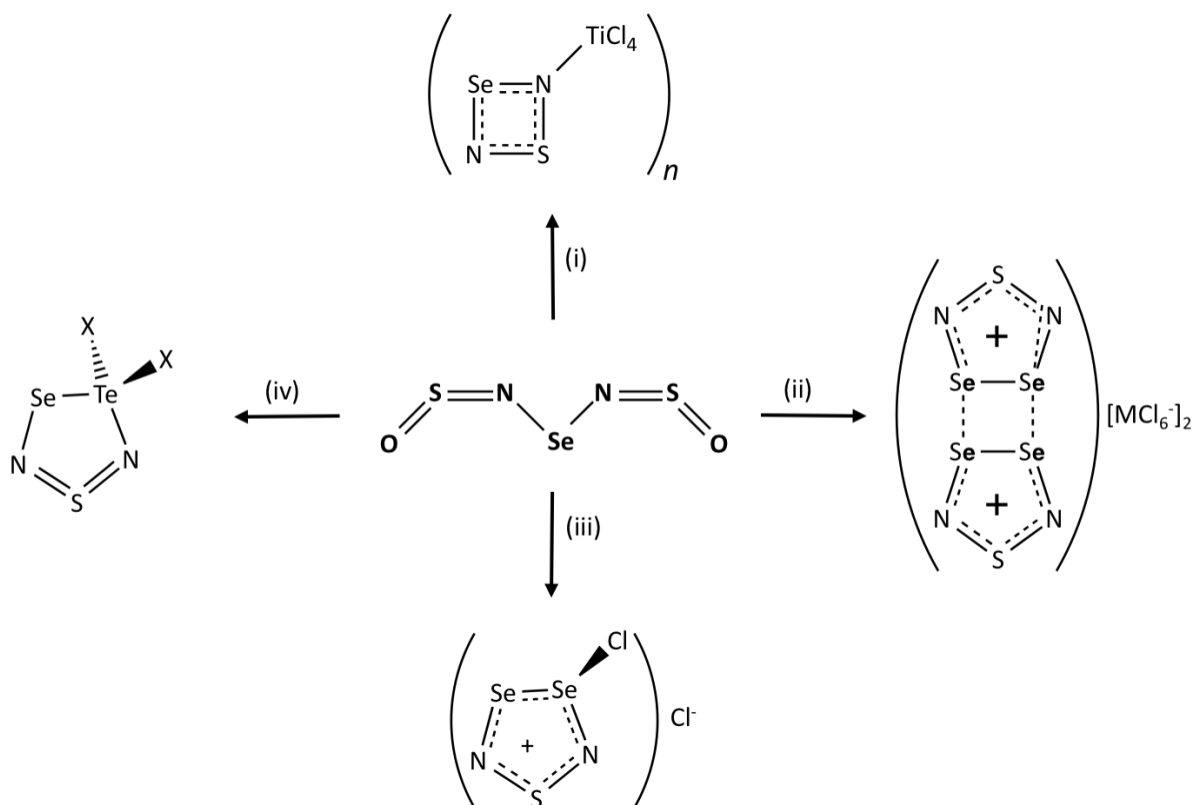
Bis(sulfinylamino)chalcogenanes E(NSO)₂ (E = Se Te) reagents are readily prepared by the methods shown in eq 7 and 8. The yield of yellow crystals of Se(NSO)₂ is 69 % when the reaction is conducted in CH₂Cl₂ [50, 51]. Although SeCl₂ is thermally unstable, it is possible that this reagent could be used (to avoid loss of selenium) if the reaction is carried out in THF at 0 °C [52].



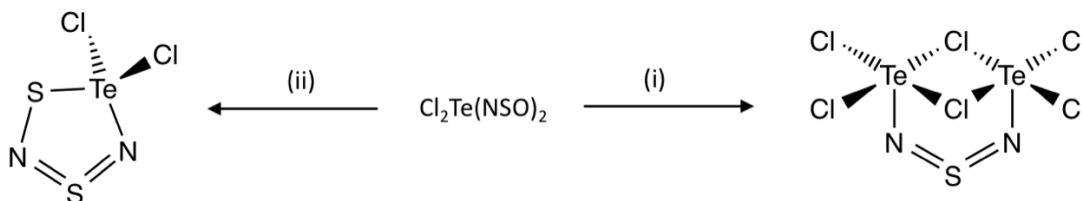
There are a number of synthetic routes to the tellurium analogue Te(NSO)₂. The recommended procedure involves the reaction of Te(SCF₃)₂ with Hg(NSO)₂ in CS₂ at 50 °C for 5 days in the absence of light (eq 8) [53]. The sparingly soluble solid is isolated in 60 % yield after sublimation. The unusual use of photolytically sensitive Te(SCF₃)₂ as a source of tellurium(II) in this synthesis probably reflects the instability of tellurium(II) dihalides TeX₂ (X = Cl, Br).



Bis(sulfinylamino)chalcogenanes $\text{E}(\text{NSO})_2$ ($\text{E} = \text{Se}, \text{Te}$) are versatile reagents in chalcogen-nitrogen chemistry [54, 55]. A common reaction of thionylimines RNSO is the thermal or base-promoted elimination of SO_2 to give the corresponding acyclic sulfur(IV) diimide $\text{RN}=\text{S}=\text{NR}$ [1]. In the case of $\text{Se}(\text{NSO})_2$ this process gives rise to heterocyclic compounds containing different chalcogens. For example, the reaction of $\text{Se}(\text{NSO})_2$ with TiCl_4 produces the highly insoluble yellow adduct $\text{SeSN}_2 \cdot \text{TiCl}_4$ (Figure 4.6), which is assumed to have a polymeric structure with bridging four-membered SeSN_2 rings [51]. By contrast, reactions with the oxidizing Lewis acids MF_5 ($\text{M} = \text{As}, \text{Sb}$) produce the dimeric cation $[\text{Se}_2\text{SN}_2]_2^{2+}$ as $[\text{MF}_6]^-$ salts [51]. A different type of behavior is observed with SeCl_4 , which yields the cations $[\text{ClSe}_2\text{SN}_2]^+$ as the chloride salt [51]. The corresponding reactions with tellurium tetrahalides TeX_4 ($\text{X} = \text{Cl}, \text{Br}$) generate X_2SeSN_2 , a five-membered ring that contains all three heavy chalcogens (Figure 4.6) [56].

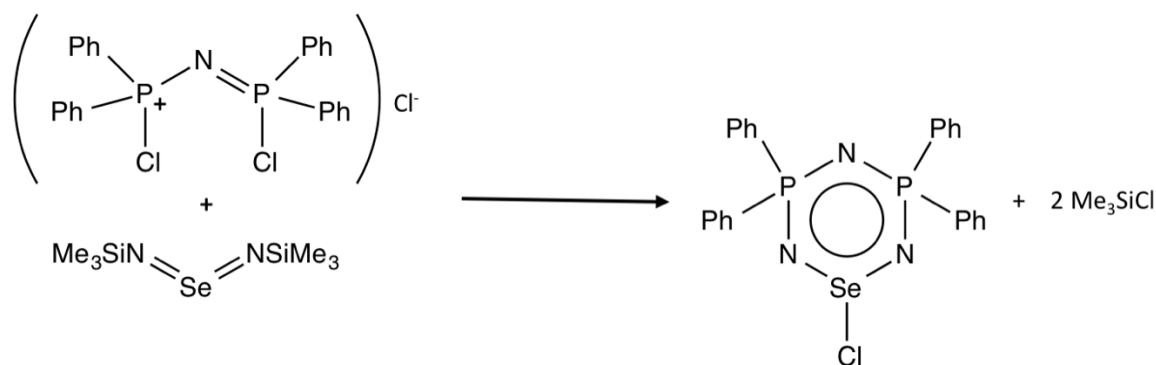


In contrast to the behavior of Se(NSO)_2 , the oxidation of the tellurium analogue Te(NSO)_2 with Cl_2 in CS_2 produces high yields of the tellurium(IV) derivative $\text{Cl}_2\text{Te(NSO)}_2$, which can also be obtained quantitatively by treatment of elemental tellurium with ClNSO in CS_2 at 0°C for 48 h [53]. $\text{Cl}_2\text{Te(NSO)}_2$ undergoes SO_2 elimination upon reaction with Cl_2 to form the dinuclear complex $\text{Cl}_2\text{Te}(\mu\text{-Cl})(\mu\text{-Cl})(\mu\text{-NSN})\text{TeCl}_2$ or when heated at 95°C (Figure 4.7) [53]



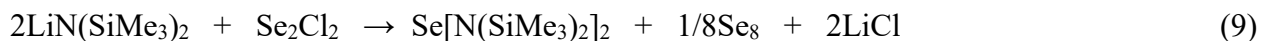
4.5 Selenium/Tellurium-Nitrogen-Silicon Reagents

The susceptibility of Si-N bonds to cleavage by main-group element halides accompanied by facile elimination of volatile trimethylsilyl halides render selenium-nitrogen-silicon reagents versatile sources of other selenium-nitrogen compounds. However, the thermal instability of the selenium(IV) diimide $\text{Me}_3\text{SiNSeNSiMe}_3$ (Section 7) has limited the application of this reagent. It can be prepared by the reaction of $(\text{Me}_3\text{Si})_2\text{NLi}$ with SeOCl_2 in pentane [57] or diethyl ether [58]. Reaction of *in situ*-generated $\text{Me}_3\text{SiNSeNSiMe}_3$ with acyclic $[(\text{NPPh}_2\text{Cl})_2]\text{Cl}$ produces the six-membered ring $(\text{Ph}_2\text{PN})_2(\text{NSeCl})$, which can be isolated as pale yellow crystals in 40 % yield, suggesting that wider use of this reagent should be possible (Figure 4.7) [58].



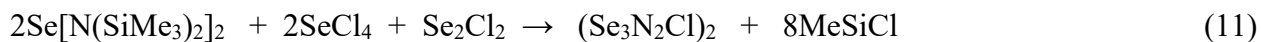
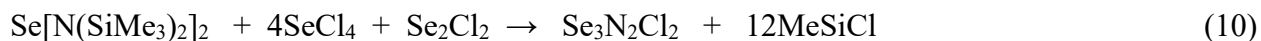
By contrast to the selenium(IV) analogue (*vide supra*), the selenium(II) derivative $(\text{Me}_3\text{Si})_2\text{NSeN}(\text{SiMe}_3)_2$ is thermally more stable and, hence, represents a more useful reagent in Se-N chemistry. The reaction of $\text{LiN}(\text{SiMe}_3)_2$ with Se_2Cl_2 in a 2:1 molar ratio in *n*-hexane at -78°C produces this monoselenide as yellow crystals in 75 % yield (eq 9) [59]. In a subsequent investigation of the same reaction, the diselenide $(\text{Me}_3\text{Si})_2\text{NSeSeN}(\text{SiMe}_3)_2$ was isolated as a yellow oil in 19 % yield, in addition to the monoselenide $(\text{Me}_3\text{Si})_2\text{NSeN}(\text{SiMe}_3)_2$ (64 %) [60]. The triselenide $(\text{Me}_3\text{Si})_2\text{NSeSeSeN}(\text{SiMe}_3)_2$ is the major product of the reaction of $(\text{Me}_3\text{Si})_2\text{NH}$ with Se_2Cl_2 in a 2:1

molar ratio in CH₂Cl₂ at 0 °C; however, the triselenide could not be separated in pure form from the co-formed di- and tetra-selenides [60]

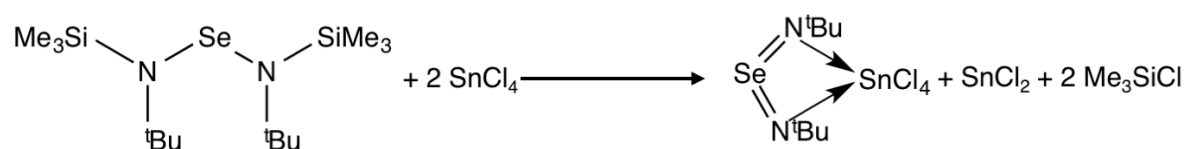


The easily handled reagent (Me₃Si)₂NSeN(SiMe₃)₂ reacts with SeCl₄ to produce pure Se₄N₄ in 71% yield [15], but the method depicted in eq 1 is the preferred route to this explosive material. An extension of this methodology to the reaction of (Me₃Si)₂NSeN(SiMe₃)₂ with a mixture of SCl₂ and SO₂Cl₂ in a 1:1:1 molar ratio produced good yields of the mixed-chalcogen cage 1,5-Se₂S₂N₄ as an insoluble red-brown powder accompanied by small amounts of red selenium [61]. By contrast, a mixture of six-membered rings, predominantly SeS₃N₂, is produced in the reaction of (Me₃Si)₂NSN(SiMe₃)₂ with a 3:1:1 mixture of S₂Cl₂, Se₂Cl₂ and SeCl₄ [62].

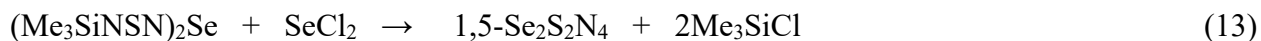
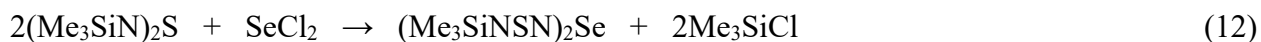
The explosive black selenium-nitrogen chloride Se₃N₂Cl₂ is obtained in 95 % or 89 % yields, respectively, by reaction of (Me₃Si)₂NSeN(SiMe₃)₂ with (a) a mixture of SeCl₄ and Se₂Cl₂ in a 4:1 molar ratio (eq 10) or (b) SeOCl₂ [19]; these reactions are carried out in CH₂Cl₂ at –78 °C The related dimeric selenium-nitrogen chloride (Se₃N₂Cl)₂ is isolated as an insoluble dark brown powder in essentially quantitative yield by adjusting the stoichiometry of the reactants (eq 11) [19].



The unsymmetrically substituted monoselenide $(\text{Me}_3\text{Si})^t\text{BuNSeN}^t\text{Bu}(\text{SiMe}_3)$ with only one Si-N bond per amido group is obtained in 75 % yield as a yellow solid from the reaction of the corresponding lithium amide with Se_2Cl_2 in *n*-hexane [63]. Treatment of this monoselenide with SnCl_4 in a 1:2 molar ratio in dichloromethane produces the *N,N'*-chelated SnCl_4 complex of the selenium(IV) diimide $^t\text{BuN}=\text{Se}=\text{N}^t\text{Bu}$ in a redox process that involves elimination of Me_3SiCl (Figure 4.9) [64].



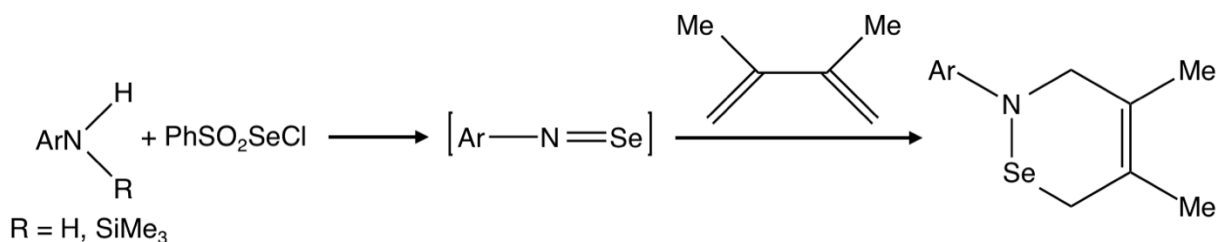
The formation of long chains typified by the polymer $(\text{SN})_x$ is a prominent feature of sulfur-nitrogen chemistry [1]. In that context the preparation of the yellow monoselenide $(\text{Me}_3\text{SiNSN})_2\text{Se}$ in 65 % yield by the route shown in eq 12 is significant [65]. The treatment of this monoselenide with SeCl_2 in $\text{CH}_2\text{Cl}_2/\text{THF}$ at -78°C , however, results in cyclization to give the cage molecule 1,5- $\text{Se}_2\text{S}_2\text{N}_4$ as a dark red precipitate in 73 % yield (eq 13) [65].



4.6 Chalcogenylnitrosyls $\text{ArN}=\text{Se}$

Chalcogenylnitrosyls $\text{RN}=\text{Se}$ are formed as transient species when $\text{R} = \text{aryl}$. The selenium(II) synthon PhSO_2SeCl has been used as a source of selenium in reactions with arylamines ArNH_2 in the

presence of trimethylamine. The selenonitrosoarene $\text{ArN}=\text{Se}$ can be trapped as a Diels-Alder adduct with dimethylbutadiene (Figure 4.10) [66]. The 1,2-selenazines formed in this way have limited stability (2-3 h) at room temperature when $\text{Ar} = 4\text{-XC}_6\text{H}_4$ ($\text{X} = \text{Br}, \text{Me}$), but this is improved to 3 days when $\text{Ar} = 2\text{-MeSC}_6\text{H}_4$. Dimers of RNSe have not been observed, however larger cyclic oligomers $(\text{RNSe})_n$ ($\text{R} = \text{alkyl}, n = 3, 4$) have been isolated as stable crystalline solids from cyclocondensation reactions of SeCl_2 with primary amines [47] or the thermal decomposition of selenium(IV) diimides (Section 7).

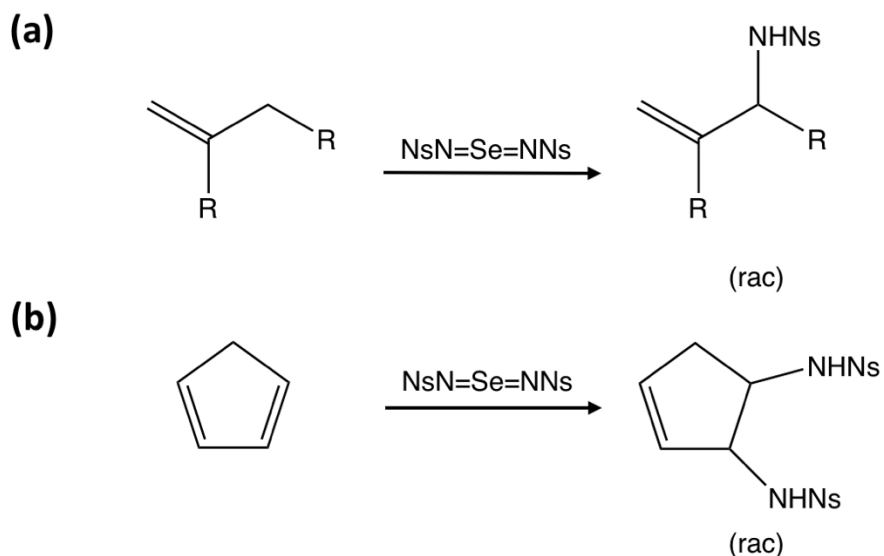


4.7 Chalcogen(IV) Diimides

4.7.1 Synthesis, structures and applications in organic synthesis

The selenium(IV) diimides $\text{RN}=\text{Se}=\text{NR}$ ($\text{R} = \text{'Bu}, \text{Ts}$) ($\text{Ts} = p\text{-toluenesulfonyl}$) were first reported and used as *in situ* reagents for the allylic amination of olefins or 1,3-dienes more than 40 years ago [67,68]. In early experiments these imidoselenium reagents were prepared by the reaction of SeCl_4 with 2 equivalents of the corresponding amine (*tert*-butylamine or *p*-toluenesulfonamide) in CH_2Cl_2 in the presence of 4 equivalents of an amine base. A more reactive aminating reagent is formed when anhydrous chloramine-T (TsNClNa) is stirred with elemental selenium in CH_2Cl_2 [67,68]. Owing to the insolubility of the reactants in this synthesis, a subsequent modification involved the use of the more soluble 2-nitrobenzenesulfonamide (NsNClNa) for the generation of $\text{NsN}=\text{Se}=\text{NNs}$ [69]. This

in situ reagent reacts in a manner similar to selenium dioxide in the allylic amination of olefins and 1,2-diamination of 1,3-dienes (Figure 4.11) [69]

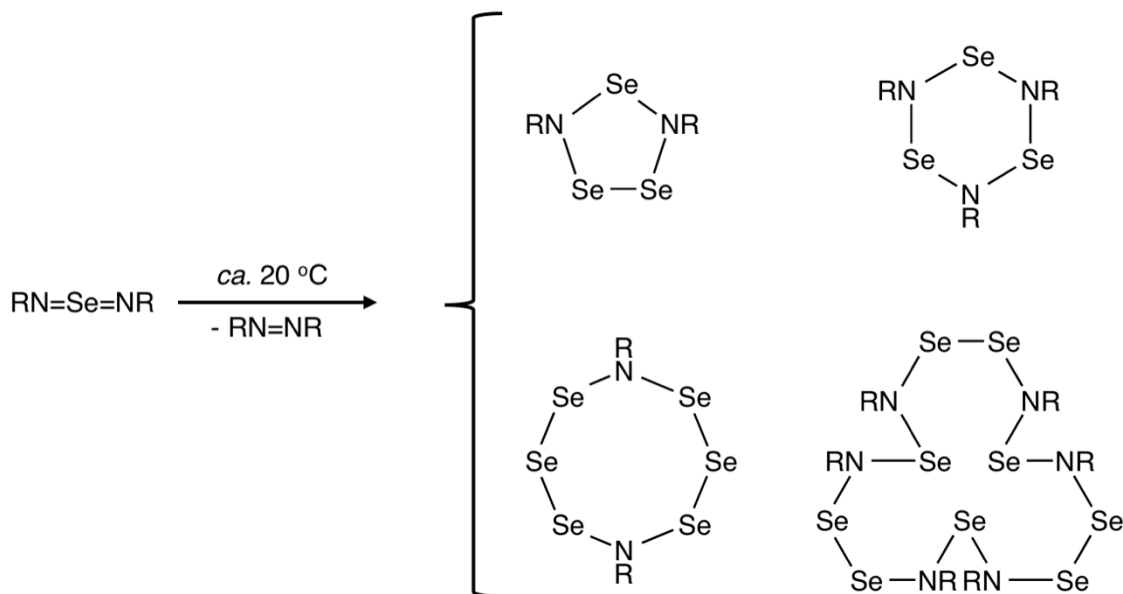


The thermally unstable dialkyl selenium(IV) diimides $\text{RN}=\text{Se}=\text{NR}$ ($\text{R} = \text{'Bu}, \text{Ad}$) ($\text{Ad} = \text{adamantyl}$) have been isolated as an oil or yellow crystals, respectively, from the reaction of the appropriate primary alkylamine with SeCl_4 [70, 71]; the introduction of supermesityl substituents ($\text{R} = \text{Mes}^* = 2,4,6\text{'Bu}_3\text{C}_6\text{H}_2$) enhances the thermal stability of the selenium(IV) diimide [72]. The X-ray analyses of $\text{RN}=\text{Se}=\text{NR}$ ($\text{R} = \text{Ad}, \text{Mes}^*$) reveal monomeric structures in the solid state [71, 72]. By contrast, the tellurium(IV) diimide $\text{'BuNTe}(\mu\text{-N'Bu})_2\text{TeN'Bu}$, which is obtained in good yields as a thermally stable orange solid from the reaction of LiNH'Bu with TeCl_4 in THF, is dimeric [73]. The formation of the tellurium(IV) diimide is accompanied by smaller amounts of the cyclic tellurium(II) imide $(\text{TeN'Bu})_3$ when this reaction is conducted in toluene [74]. The calculated dimerization energy for the $[2 + 2]$ cycloaddition of two $\text{E}(\text{NR})_2$ ($\text{E} = \text{Se}, \text{Te}$; $\text{R} = \text{'Bu}, \text{SiMe}_3$) molecules is strongly exothermic for tellurium(IV) diimides, but approximately thermoneutral for selenium(IV) diimides, consistent with the experimental observations [75, 76]. However, the dimerization of selenium(IV) diimides is

promoted by group 12 metal dihalides MCl_2 ($M = Cd, Hg$) to give N,N' -chelated complexes of ${}^tBuNSe(\mu-N^tBu)_2SeN^tBu$ [77], which are structurally analogous to the $HgCl_2$ complex of the tellurium(IV) diimide dimer ${}^tBuNTe(\mu-N^tBu)_2TeN^tBu$ [78].

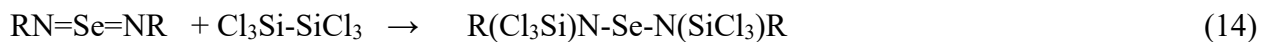
4.7.2 Thermal Decomposition

The thermal decomposition of $RN=Se=NR$ ($R = {}^tBu, Ad$) provides a source of several cyclic selenium imides (Figure 4.12) [76, 79]. Thus, a solution of ${}^tBuN=Se=N^tBu$ in toluene at 20 °C produces the six-membered ring $Se_3(N^tBu)_3$, the five-membered ring $Se_3(N^tBu)_2$ and its higher homologue the fifteen-membered ring $Se_9(N^tBu)_6$ [79]. Similarly, the thermal decomposition of $AdN=Se=NAd$ in THF gives rise to $Se_3(NAd)_3$ and $Se_3(NAd)_2$; the five-membered ring structure of the latter was confirmed by X-ray analysis [76]. Cyclodimerization of acyclic $RN=Se=NR$ to give a four-membered ring (Section 7.1) may be the first step in the formation of these cyclic selenium imides. However, the generation of selenium-rich systems must involve elemental selenium, which is formed during the thermal decomposition as evinced by the detection of ${}^tBuN=N^tBu$ as a by-product [79]. A more versatile route to the generation of cyclic selenium imides is provided by cyclocondensation reactions of $SeCl_2$ with tBuNH_2 , since the stoichiometry can be controlled (Section 3) [47].

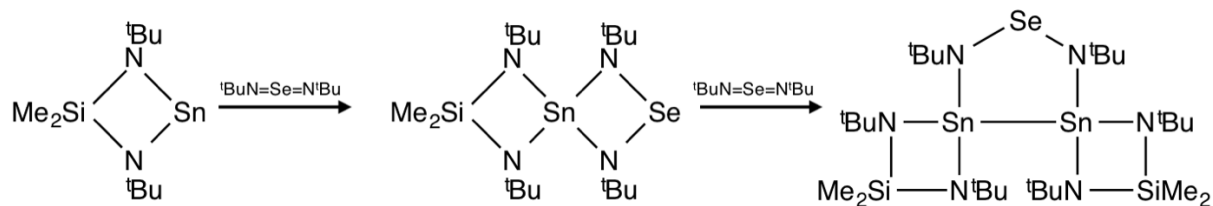


4.7.3 Insertion and Cycloaddition Reactions

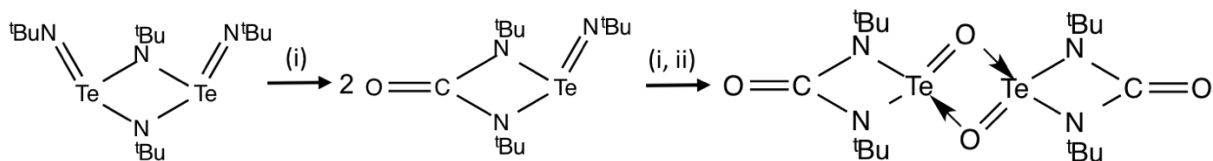
Selenium(IV) diimides readily undergo insertion reactions into the Si-Si bond of hexachlorodisilane (eq 14) [80]. Insertion into the C-B bond of triethylborane occurs at low temperatures, but the initially formed cyclic product $^t\text{BuN}(\mu\text{-SeEt})(\mu\text{-BEt}_2)\text{N}^t\text{Bu}$ decomposes at $-50\text{ }^{\circ}\text{C}$ [81].



A different type of behavior is observed between selenium diimides and bis(amino)stannylenes [82]. In a 1:1 molar ratio these reactants produce a red spirocyclic compound, which formally results from the oxidative addition of the selenium diimide to the Sn(II) center. However, the use of an excess of the stannylene results in the insertion of a Sn(II) centre into an Sn-N bond of the initially formed spirocyclic compound to give a yellow tricyclic compound with a Sn-Sn bond (Figure 4.13) [82].



A double cycloaddition occurs in the reaction of the tellurium(IV) diimide dimer $t\text{BuNTe}(\mu\text{-N}^t\text{Bu})_2\text{TeN}^t\text{Bu}$ with an excess of *tert*-butyl isocyanate (Figure 4.14) [83]. The initial step generates an *N,N'*-ureato tellurium imide, which can be viewed as the cycloaddition product of $t\text{BuNCO}$ and monomeric tellurium(IV) imide. With additional $t\text{BuNCO}$ this intermediate is converted to the corresponding telluroxide, which is isolated as a dimer.



4.7.4 Reactions with Nucleophiles and Electrophiles

The sensitivity of the polar chalcogen-nitrogen bonds in chalcogen(IV) diimides to nucleophilic attack at the chalcogen centre is signified by the ready conversion of the $>\text{E}=\text{NR}$ (Se, Te) functionality to the corresponding $>\text{E}=\text{O}$ group upon exposure to moisture. The formation of the partial hydrolysis products $\text{AdNSe}(\mu\text{-NAd})_2\text{SeO}$ and $\text{OSe}(\mu\text{-NAd})_2\text{SeO}$ during the decomposition of $\text{AdN}=\text{Se}=\text{NAd}$ in THF is a cogent example of this tendency [76]. In the case the tellurium(IV) diimide $t\text{BuNTe}(\mu\text{-N}^t\text{Bu})_2\text{TeN}^t\text{Bu}$ deliberate hydrolysis using stoichiometric amounts of $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{H}_2\text{O}$ results in the successive replacement of the terminal imido groups by oxido ligands [84].

Both monomeric selenium(IV) diimides and dimeric tellurium(IV) diimides are susceptible to nucleophilic attack at the chalcogen centre by reagents such as LiNH^tBu or KO^tBu to give the tripodal

dianions $[E(N^tBu)_3]^{2-}$ [85, 86] and $[Te(O^tBu)(N^tBu)_2]^-$ [87], respectively. Reactions of the tris(*tert*-butylimido)tellurite dianion $Te(N^tBu)_3]^{2-}$ are discussed in Section 9 [88].

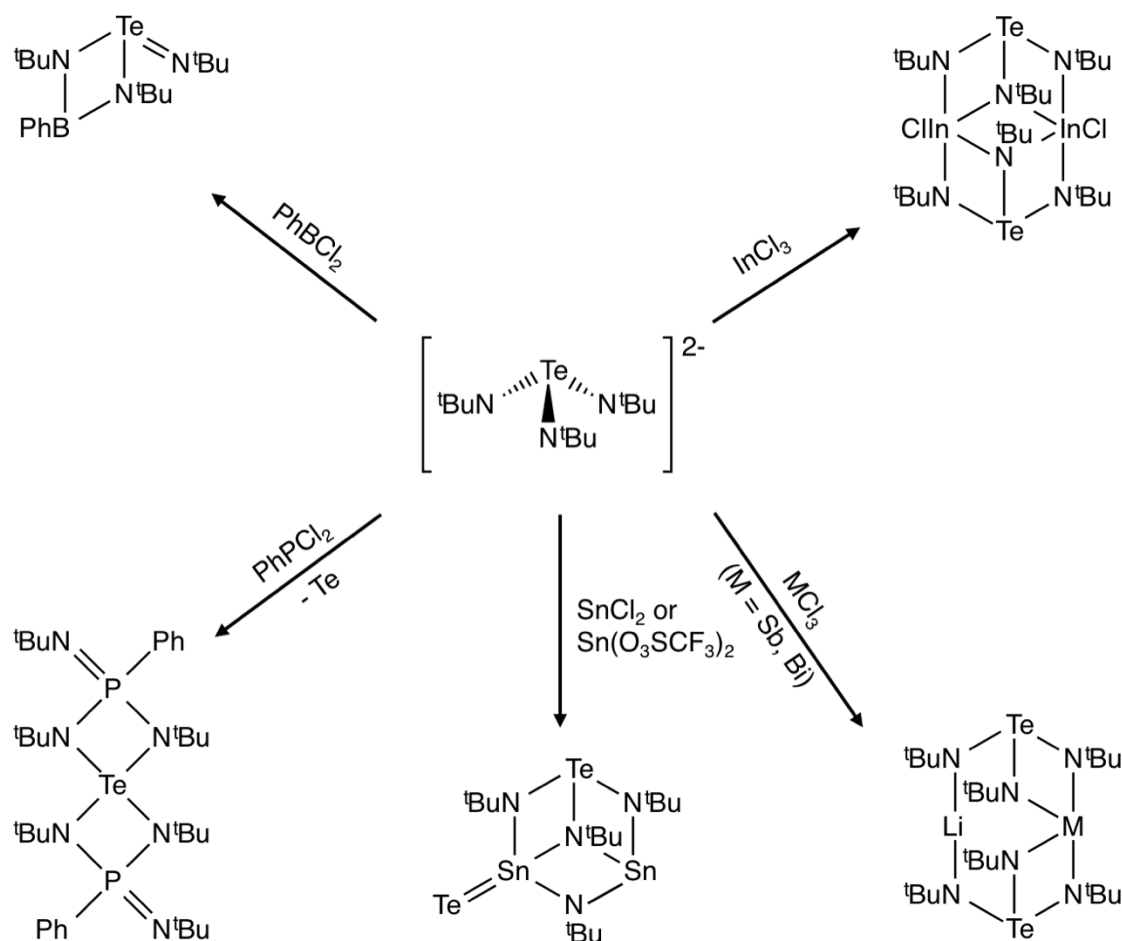
The terminal N^tBu groups in the dimer $^tBuNTe(\mu-N^tBu)_2TeN^tBu$ are readily protonated by Brønsted acids. For example, reaction with HCF_3SO_3 produces the monoprotinated derivative $[(^tBuNH)Te(\mu-N^tBu)_2TeN^tBu][CF_3SO_3]$ in quantitative yields [89]. Similarly, $^tBuNTe(\mu-N^tBu)_2TeN^tBu$ forms a 1:1 adduct with the strong Lewis acid $B(C_6F_5)_3$ [90]. By using the appropriate amount of the electrophile CF_3SO_3Me either mono- or di-methylation of the exocyclic N^tBu groups in the dimer can be achieved [91].

4.8 Tris(*tert*-butylimido)tellurite dianion

Tris(*tert*-butylimido)chalcogenite dianions $[E(N^tBu)_3]^{2-}$ ($E = Se, Te$) are potentially versatile reagents in chalcogen-nitrogen chemistry. In the case of the selenium derivative ($E = Se$) applications are limited due to facile air oxidation to give radical species [92]. However, detailed investigations of the reaction chemistry of the tellurium derivative have revealed a rich coordination chemistry that, in some cases, is accompanied by redox behavior (Figure 4.15) [88]. For example, in group 13 chemistry the reaction with $PhBCl_2$ produces an N,N' -chelated complex with a terminal N^tBu group, which is a unique representative of a monomeric tellurium(IV) imide [85]. By contrast, the reaction with $InCl_3$ involves a second chelation of the $Te(N^tBu)_3]^{2-}$ dianion to give a dimer with two five-coordinate indium centers (Figure 4.15) [93].

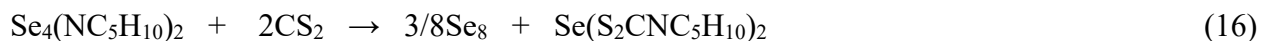
In group 14 chemistry, the reaction with tin(II) chloride provides an intriguing case of redox behavior [94]. The product incorporates the pyramidal $Te(N^tBu)_3]^{2-}$ ligand bridging two tin atoms in different oxidation states, one of which is attached to a terminal telluride. The structure is completed

by an N^tBu bridge between the two tin centres resulting from Te-N^tBu bond cleavage in the redox process. Redox behavior is also observed in the reaction of $\text{Te}(\text{N}^t\text{Bu})_3]^{2-}$ with PhPCl_2 [88]. In this transformation half of the tellurium in the dianion is reduced to tellurium metal while the two phosphorus centers are oxidized from the +3 to +5 oxidation states to give a spirocyclic complex of tellurium (IV) (Figure 4.15). By contrast, the reaction of $\text{Li}_2[\text{Te}(\text{N}^t\text{Bu})_3]$ with the heavier group 15 trihalides ECl_3 ($\text{E} = \text{Sb}, \text{Bi}$) generates the homoleptic monoanionic complexes $\text{E}[\text{Te}(\text{N}^t\text{Bu})_3]^-$ as their monolithium derivatives [95].



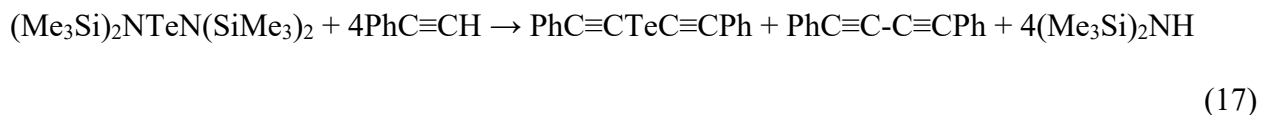
4.9 Chalcogen(II) Amides and Diamides

The selenium(II) derivative ($i\text{-Pr}_2\text{N}$)₂Se has been isolated as a white solid in 61 % yield from the reaction of diisopropylamine with SeOCl₂ in diethyl ether at 0 °C; (Me₂N)₂Se was obtained as an oil in 30 % yield from the decomposition of (Me₂N)₂SeO, which was prepared by reaction an excess of dimethylamine with SeOCl₂ in hexane [96]. In contrast to the poorly characterized Se(NR₂)₂ (R = Me, Et) derivatives [96], polyselanes with terminal piperidino or morpholino groups can be prepared by heating black selenium powder with morpholine or piperidine in the presence of red lead. In the case of piperidine, this procedure provides the tetraselane as red crystals in an optimum yield of 26 % based on selenium (eq 15), whereas morpholine gives a mixture of di-, tri- and tetra-selanes [97]. An intriguing property of piperidinotetraselane is its decomposition in CS₂ at room temperature to produce a new monoclinic form of red *cyclo*-Se₈ (eq 16) [98].



The applications of the silylated chalcogen(II) diamides E[N(SiMe₃)₂]₂ resulting from the facile cleavage of the Si-N bond by main-group element halides are discussed in Section 5. A fascinating feature of the tellurium derivative is the formation of the monomeric radical cation [Te[N(SiMe₃)₂]₂]^{•+} upon one-electron oxidation with AsF₅ [99]. Tellurium(II) diamides are useful reagents in organotellurium chemistry owing to the susceptibility of the Te-N bonds to protolysis by weakly acidic substrates. For example, the reaction of Te[N(SiMe₃)₂]₂ with phenylacetylene in boiling THF

produces a mixture of bis(phenylethynyl)telluride and 1,4-diphenylbutadiene in 38 and 12 % yields, respectively (eq 17) [100, 101].



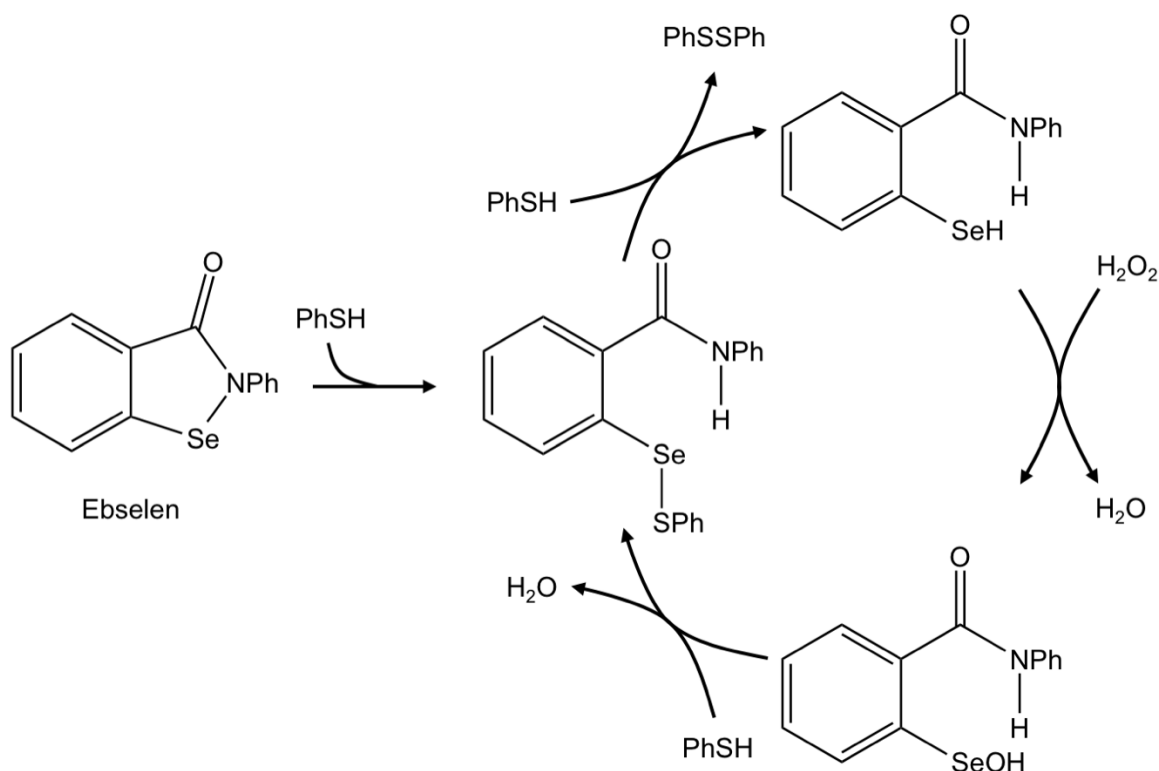
In a similar manner alkynyl tellurides $\text{RC}\equiv\text{CPh}$ may be obtained in good yields ($\text{R} = \text{Ph}$, 72 %; $\text{R} = n\text{Bu}$, 85 %) by treatment of arenetellurenamides with terminal acetylenes in THF at 20 °C (eq 18); the reagent $\text{PhTeN}^i\text{Pr}_2$ is prepared generated *in situ* by treatment of benzenetellurenyl iodide with LiN^iPr_2 in THF [102]. The transformation shown in eq 18 is specific for tellurium, since it does not occur when pure $\text{PhSeN}^i\text{Pr}_2$ is used [102].



Although the dimethylamido derivative $\text{Te}(\text{NMe}_2)_2$ reacts readily with a range of amines, phosphines and thiols, the only stable products that have been isolated from such reactions are those containing bulky thiolate ligands, *e.g.* $\text{Te}(\text{SCPh}_3)_2$, which is obtained as air- and moisture-stable orange crystals from the reaction in toluene at -78 °C (eq 19) [103]. Polymeric $[\text{Te}(\text{NMe}_2)_2]_\infty$ is isolated in 74 % yield as yellow needles from the reduction of TeCl_4 with an excess of LiNMe_2 in THF-diethyl ether; this moisture-sensitive reagent deposits black metallic tellurium on exposure to air [103].

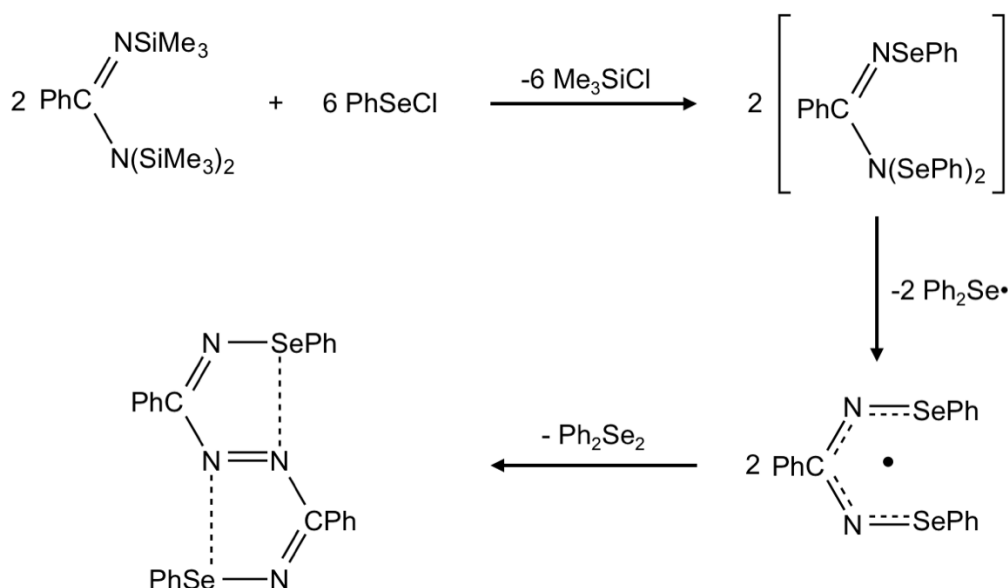


The susceptibility of the selenium-nitrogen bond to protonolysis is the key to the function of the cyclic selenenamide Ebselen, an anti-inflammatory drug that acts as a glutathione peroxidase mimic. Mechanistic studies show that the Se-N bond in Ebselen reacts readily with PhSH to form a selenenyl sulfide, which is subsequently converted to the corresponding selenol and selenenic acid [104,105] (Figure 4.16). The potentially broad range of pharmacological applications of Ebselen are under active investigation [106].

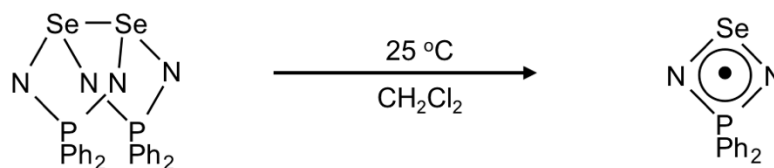


4.10 Radical Chemistry

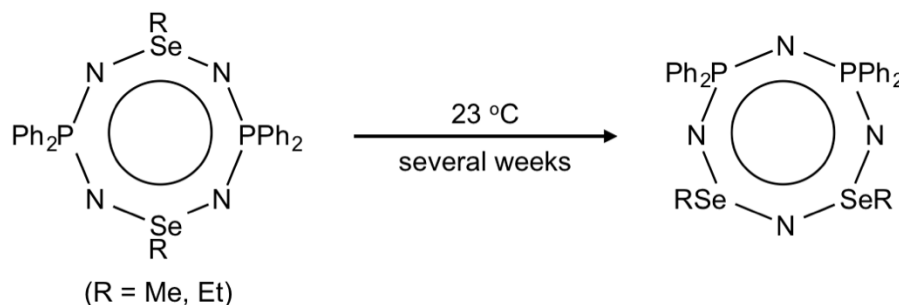
The thermal lability of the Se-N linkage may engender unusual transformations resulting from homolytic cleavage and the concomitant formation of radicals. As a cogent example, the metathesis of $\text{PhC}(\text{NSiMe}_3)[\text{N}(\text{SiMe}_3)_2]$ with three molar equivalents of PhSeCl gives rise to the resonance-stabilized radical $[\text{PhC}(\text{NSePh})_2]^{\bullet}$ (detected by in situ EPR spectroscopy) via Se-N bond scission. This radical undergoes a rapid transformation to an intramolecularly Se---N stabilized diazene [107] (Figure 4.17).



Radical formation is also observed for P,N,Se heterocycles. A pertinent example is the dissociation of the eight-membered ring $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{Se}_2$ into the four-membered cyclic radical $[\text{Ph}_2\text{PN Se}]^{\bullet}$ in CH_2Cl_2 solution at 25°C [108] (Figure 4.18). In marked contrast, the sulfur analogue $1,5\text{-Ph}_4\text{P}_2\text{N}_4\text{S}_2$ is thermally stable up to 150°C [109].



Ring contraction (dissociation) or ring expansion is a common feature of inorganic heterocycles, but isomerization is rare. In this context the slow *solid-state isomerization* of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{Se}_2\text{R}_2$ ($\text{R} =$ alkyl) into the 1,3-isomer in essentially quantitative yields *at room temperature* is remarkable [110] [Figure 4.19]. The mechanism of this transformation is not known, but it represents another manifestation of novel chemistry generated by the lability of Se-N linkages.



4.11 Conclusions

Synthetic applications of selenium-nitrogen or tellurium-nitrogen reagents in inorganic or organic chemistry are less widespread than those of their sulfur-nitrogen analogues, in part, owing to the difficulty in handling highly reactive, unstable compounds. For example, although reactions of Se_4N_4 may generate cyclic Se-N cations or metal complexes of Se-N anions, via oxidation or reduction, respectively, the explosive nature of this binary selenium nitride has limited its applications (Section 2.1). Thus, all attempts to generate the selenium analogue of the conducting polymer $(\text{SN})_x$, which is produced via S_2N_2 generated by the thermolysis of S_4N_4 , have failed. Similarly, although the binary sulfur-nitrogen cations NS_x^+ ($x = 1, 2$) are readily prepared and exhibit a variety of insertion or

cycloaddition reactions [1], the application of the selenium analogue NSe_2^+ is limited to a single example of its use as *situ* reagent (Section 3.1).

The use of selenium diimides $\text{RN}=\text{Se}=\text{NR}$ in organic synthesis is well-established and aminations of unsaturated substrates by these reagents follow a similar pathway to reactions of the isoelectronic reagent selenium dioxide SeO_2 (Section 7.1). Selenium(IV) diimides are, however, thermally unstable and this lability has limited the applications of the silicon-nitrogen-selenium reagent $\text{Me}_3\text{SiN}=\text{Se}=\text{NSiMe}_3$ in reactions with non-metal or metal halides to a single example (Section 5); nonetheless, further examples of the use of this *in situ* reagent can be readily envisaged. On the other hand, the thermal decomposition of selenium(IV) diimides results in chemistry that is not observed for the sulfur analogues, notably the formation of a wide variety of thermally stable, cyclic selenium imides (Section 7.2). Tellurium(IV) diimides exhibit much higher thermal stability than their selenium analogues as a consequence of dimerization without further ring transformations. Consequently, the reactions of these tellurium-nitrogen compounds with electrophiles and nucleophiles have been studied in some detail (Sections 7.3 and 7.4). For example, the dianion $[\text{Te}(\text{N}^t\text{Bu})_3]^2$, isoelectronic with tellurite $[\text{TeO}_3]^{2-}$, is readily obtained and has been shown to have an extensive coordination chemistry with p-block elements (Section 8).

The susceptibility of the tellurium-nitrogen bond in tellurium(II) amides to protonolysis has been exploited in the preparation tellurium acetylides. However, the expansion of this application of tellurium diamides to the formation of other Te-E bonds (e.g., $\text{E} = \text{P}, \text{S}$) is so far limited to a single example (Section 9). This approach to the synthesis of tellurium compounds, as well as further applications of *in situ* reagents such as NSe_2^+ and $\text{Me}_3\text{SiN}=\text{Se}=\text{NSiMe}_3$, certainly merit further investigations.

4.12 References

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Captions to Figures

Figure 4.1. Preparation of Se-N compounds from Se_4N_4 : (i) $[\text{Se}_4][\text{AsF}_6]_2$ (ii) AsF_5 (iii) Se_2Cl_2 (iv) AlBr_3 (v) $[\text{PPh}_4]_2[\text{Pd}_2\text{Cl}_6]$ (vi) WCl_6 .

Figure 4.2. Oxidative-addition reactions of Se_4N_4 with (i) $[\text{PtCl}_2(\text{PMe}_2\text{Ph})]_2$ in boiling CH_2Cl_2 (ii) $\text{Pt}(\text{PPh}_3)_3$ in CH_2Cl_2 at 23 °C.

Figure 4.3. Oxidative-addition of *in situ*-generated “ NSe_2^+ ” to an alkyne: (i) excess SnCl_2 , $\text{CF}_3\text{C}\equiv\text{CCF}_3$ (ii) $\text{Na}_2\text{S}_2\text{O}_4$ (iii) 0 °C, 7d.

Figure 4.4. Formation of (a) acyclic $[\text{ClSeNSeCl}]^+$ and (b) cyclic $[\text{Se}_3\text{N}_2\text{Cl}]^+$ cations from selenium-nitrogen chlorides and Lewis acids.

Figure 4.5. Formation of cyclic selenium imides from reactions of $\text{ClSe}[\text{N}(\text{tBu})\text{Se}]_2\text{Cl}$ with tBuNH_2 via (i) nucleophilic substitution or (ii) reduction.

Figure 4.6. Formation of mixed-chalcogen heterocycles from $\text{Se}(\text{NSO})_2$ and Lewis acids: (i) TiCl_4 , (ii) MF_5 (M = As, Sb), (iii) SeCl_4 , (iv) TeX_4 (X = Cl, Br).

Figure 4.7. SO_2 elimination reactions of $\text{Cl}_2\text{Te}(\text{NSO})_2$: (i) Excess Cl_2 , CS_2 (ii) 95 °C, 12 h.

Figure 4.8. Generation of a $\text{P}_2\text{N}_3\text{Se}$ heterocycle from $\text{Me}_3\text{SiNSeNSiMe}_3$.

Figure 4.9. Formation of a selenium(IV) diimide complex from a bis(amido)selenium(II) reagent.

Figure 4.10. Generation and trapping of $\text{ArN}=\text{Se}$ with dimethylbutadiene.

Figure 4.11. (a) Allylic amination and (b) 1,2-diamination with a diimidoselenium(IV) reagent (Ns = 2-nitrobenzenesulfonyl).

Figure 4.12. Formation of cyclic selenium imides from thermal decomposition of $\text{RN}=\text{Se}=\text{NR}$ ($\text{R} = \text{}^t\text{Bu}, \text{Ad}$).

Figure 4.13. Reactions of selenium diimides with a bis(amino)stannylene.

Figure 4.14. Cycloaddition reactions of a tellurium diimide dimer with *tert*-butyl isocyanate:

(i) $+ 2\text{}^t\text{BuNCO}$ (ii) $- 2\text{}^t\text{BuN}=\text{C}=\text{N}^t\text{Bu}$.

Figure 4.15. Reactions of the tris(*tert*-butylimido)tellurite dianion $\text{Te}(\text{N}^t\text{Bu})_3]^{2-}$ with main-group element halides

Figure 4.16. Catalytic mechanism of action of Ebselen

Figure 4.17. Formation of a diazene via the selenium-nitrogen radical $[\text{PhC}(\text{NSePh})_2]^{\bullet}$

Figure 4.18. Dissociation of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{Se}_2$ into a cyclic radical $[\text{Ph}_2\text{PN Se}]^{\bullet}$

Figure 4.19. Solid-state transformation of 1,5- $\text{Ph}_4\text{P}_2\text{N}_4\text{Se}_2\text{R}_2$ into the 1,3- isomer

