

Chapter 1. Introduction of selenium and tellurium into reaction systems

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Abstract

There are several commercial selenium and tellurium compounds that are useful in synthetic chemistry. The introduction of selenium and tellurium into both organic and inorganic compounds frequently begins with the elements. This chapter provides an overview of the main reactivity of the hexagonal allotropes of selenium and tellurium, which are the most stable form of the elements under ambient conditions. While the two elements have very similar chemical properties, there are also notable differences. Upon reduction, both elements form mono- and poly-chalcogenides, which are useful nucleophilic reagents in several reactions. The elements also react with many main group compounds as well as with transition metal complexes. They also form homopolyatomic cations upon oxidation. Both selenium and tellurium react with Grignard reagents and organyllithium compounds affording organylchalcogenolates, which upon oxidation form dichalcogenides that are themselves useful reagents in organic synthetic chemistry as well as in materials applications. This chapter provides a short introduction to the various topics that will be developed further in the subsequent chapters of this book.

Keywords: Elemental selenium, elemental tellurium, selenides, tellurides, polyselenides, polytellurides, organyl selenolates, organyl tellurolates, homopolyselenium cations, homopolytellurium cations

1. Introduction

The use of selenium and tellurium compounds in diverse applications has grown significantly during the past decades. Consequently, chalcogen chemistry has been reviewed several times during the last twenty years, as exemplified by a selection of review articles [1-6] and books [7-16], which describe recent advances in synthetic inorganic and organic chalcogen chemistry, as well as in more applied areas such as medicinal chemistry and materials science. The current monograph is an overview of this progress and discusses the use of different classes of selenium and tellurium compounds as reagents.

The preparation of selenium and tellurium compounds generally involves simple molecular species such as the elements, inorganic or organic chalcogenides and polychalcogenides, selenium and tellurium halogenides, selenium and tellurium oxides, as well as organyl phosphine selenides and tellurides. These classes are treated in detail in the subsequent chapters of this monograph. In this chapter, the introduction of commercially available selenium and tellurium into the reaction system is considered. The first step in many reactions of selenium and tellurium is the reduction of the elements to form anionic selenides and tellurides, which are the actual reagents.

Alkyl or aryl selenides, tellurides, diselenides, and ditellurides are also common starting materials in many organic syntheses. While many of them are commercially available, they can also be conveniently prepared from the elements. The dimer $\text{PhPSe}(\mu\text{-Se})_2\text{P(Ph)Se}$, which is known as Woollins' reagent, is also commercially available. This P-Se compound is proving to be an important

source of selenium in a wide range of synthetic applications. Its chemistry is discussed in detail in Chapter 5.

2. Elemental selenium

2.1. General

Some reactions of elemental selenium are summarized in Figure 1. Many of the products are themselves useful reagents in further syntheses. Special examples have been discussed in the appropriate chapters of this monograph.

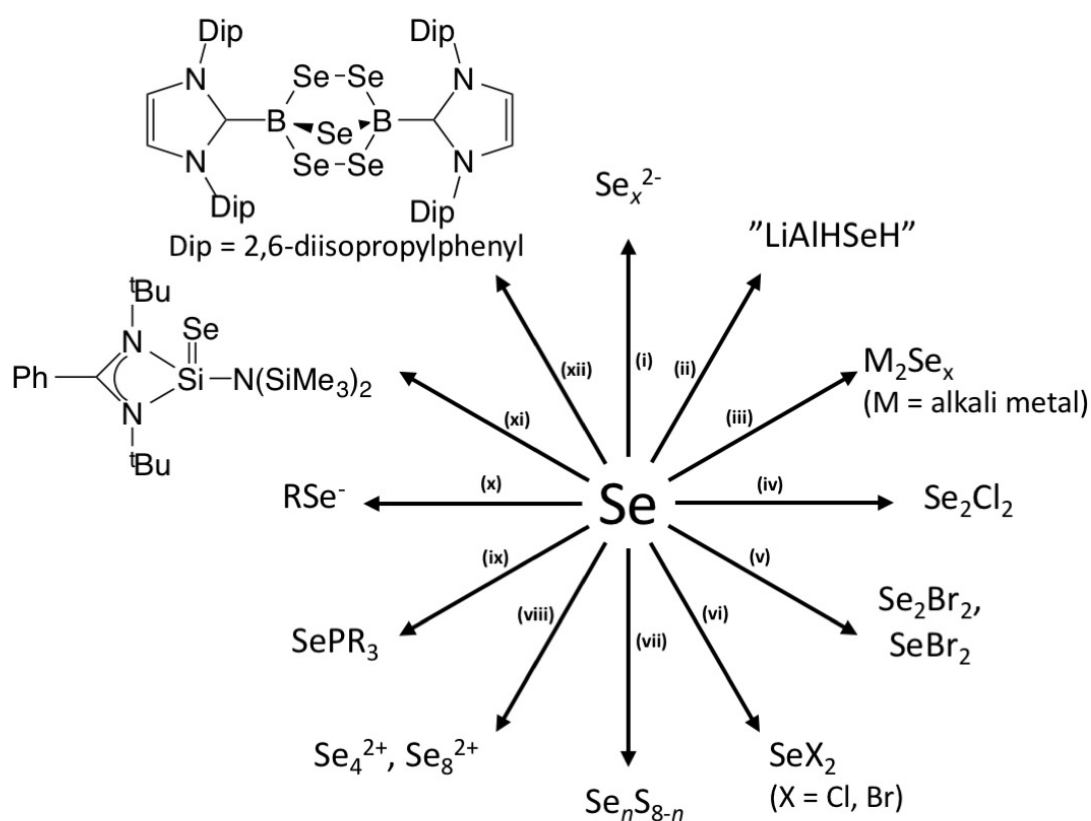


Figure 1. Some reactions of elemental selenium. (i) $\text{M}/\text{NH}_3(\text{l})$ (M = Li, Na, K), $\text{Na}[\text{BH}_4]$, or $\text{Li}[\text{AlEt}_3\text{H}]$, (ii) $\text{Li}[\text{AlH}_4]$, (iii) M_2Se (M = alkali metal), (iv) SeCl_4 , (v) Br_2 , (vi) $\text{SO}_2\text{X}_2/\text{THF}$ (X = Cl, Br), (vii) S_8 , (viii) $\text{AsF}_5/\text{SO}_2(\text{l})$ or $\text{SbCl}_5/\text{SO}_2(\text{l})$, (ix) PR_3 (R = alkyl or aryl), (x) RMgBr/THF or RLi/THF (R = alkyl or aryl), (xi) $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}[\text{N}(\text{SiMe}_3)_2]/\text{THF}$, (xii) $\{[\text{N}(\text{Dip})_2]_2(\text{CH}_2)_2\text{CB}\}_2/\text{C}_6\text{H}_6$.

2.2. Anionic selenides and their derivatives

Selenides and polyselenide anions are useful nucleophiles in synthetic applications. Alkali metal and alkaline earth metal chalcogenides are commonly prepared by mixing the elements at high temperatures, by the reaction of chalcogen elements and alkali-metal carbonates in solution, by solvothermal reactions, and by oxidation–reduction reactions involving Lewis acids [17,18]. The alkali metal or alkaline earth metal selenides and tellurides thus formed can serve as reagents for the preparation of transition-metal or main-group element chalcogenides. A large organic cation or an encapsulating agent such as the crown-ether complex of an alkali-metal cation may stabilize the otherwise unstable anions.

Lithium, sodium and potassium selenides and diselenides have traditionally been prepared by dissolving the chalcogen elements and the alkali metals in appropriate molar ratios in liquid ammonia. The early work by Bergström [19] and Klemm *et al.* [20], as well as that by Brandsma and Wijers [21] has been followed and developed by numerous studies, as exemplified by Müller *et al.* [22], Björgvinsson and Schrobilgen [23], and Colombara *et al.* [24]. Thiele *et al.* [25] have recently reviewed the preparation, structures, and properties of different classes of polyselenides, which have been stabilized by use of bulky cations.

In addition to alkali metals, polyselenides can be produced in liquid ammonia or in methylamine by other less-noble metals such as Mn and Fe to afford $[\text{Mn}(\text{NH}_3)_6]\text{Se}_3$, $[\text{Mn}(\text{NH}_3)_6]\text{Se}_4$, $[\text{M}(\text{NH}_3)_6]\text{Se}_6$ ($\text{M} = \text{Mn}, \text{Fe}$), and disordered phases $[\text{Mn}(\text{NH}_2\text{Me})_6](\text{S}_5)_{0.15}(\text{Se}_{2.43}\text{S}_{1.57})_{0.85}$ and $[\text{Mn}(\text{NH}_3)_6](\text{Se}_{2.29}\text{S}_{2.71})$ [26].

Sandman *et al.* [27] have shown that alkali-metal selenides can also be produced upon reduction of selenium by elemental alkali metals in high-boiling polar aprotic solvents. This concept has been

developed by Thompson and Boudjouk [28], who have demonstrated that lithium, sodium, and potassium selenides and diselenides can conveniently be also prepared in THF by use of ultrasound and in the presence of small amounts of a charge-transfer agent such as naphthalene. The electrochemical reduction of selenium powder in aprotic media such as acetonitrile or THF also provides an effective method to synthesize Se^{2-} and Se_2^{2-} selectively [29,30].

Elemental selenium can also conveniently be reduced by using lithium tetrahydridoaluminate [31], sodium tetrahydridoborate [32], or lithium triethylhydridoborate [33]. The reaction with lithium tetrahydridoaluminate (“lithium aluminium hydride”) has been reported to produce an intermediate product “ LiAlHSeH ”, which can be used *in situ* to produce a wide variety of organic selenoethers and selenones [31]. This reagent is described in more detail in Chapter 8.

Since the distribution of the products in the reduction of elemental selenium with sodium tetrahydridoborate seemed to be sensitive to experimental conditions, Cusic and Dance [34] and Marques de Oliveira *et al.* [35] have studied the reaction in detail using ^{77}Se NMR spectroscopy. Since HSe^- and Se^{2-} co-exist in fast equilibrium, there is no NMR evidence for the presence of Se^{2-} . Similarly, no resonance attributable to Se_2^{2-} has been observed. By contrast, the presence of polyselenide anions Se_x^{2-} ($x = 3-6$) is clearly evident in solution, as indicated in Figure 2 by the ^{77}Se NMR spectrum of a reaction mixture recorded in DMF [34]. These observations are consistent with the detailed ^{77}Se NMR study of Björgvinsson and Schrobiligen in liquid ammonia and ethylenediamine [23] and with the ESI mass spectrometric study of the polyselenide speciation by Raymond *et al.* [36].

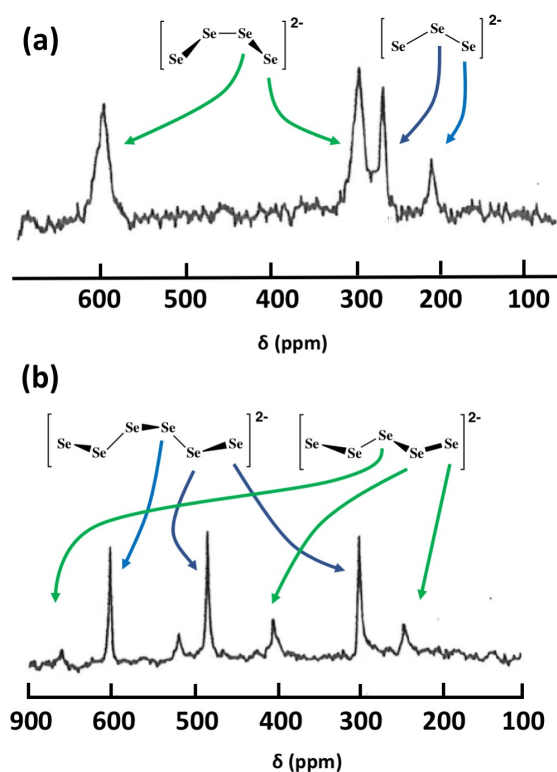
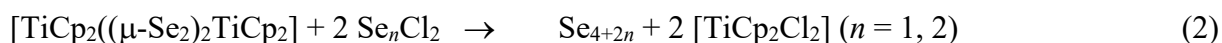
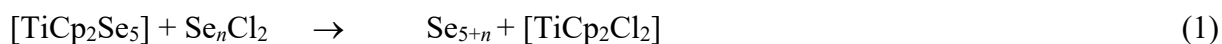


Figure 2. ^{77}Se NMR resonances of (a) Se_3^{2-} and Se_4^{2-} , and (b) Se_5^{2-} and Se_6^{2-} . All spectra have been recorded in DMF [34] (adapted from Cusick J, Dance I. The characterization of $[\text{HSe}]^-$ and $[\text{Se}_x]^{2-}$ ions by ^{77}Se NMR. Polyhedron 1991, 10, 2629-2640. Copyright 1991 Elsevier SA).

Klayman and Griffin [32] and Marques de Oliveira *et al.* [35] have shown that the treatment of Se_x^{2-} solutions with organyl halogenides with careful control of the reaction stoichiometry produces organyl selenides and diselenides in high purity. The solvothermal synthesis of CuInSe_2 also involves Se_x^{2-} , which has been produced by the reduction of selenium with NaBH_4 [37].

The reduction of selenium by lithium triethylhydridoborate (“superhydride”) also results in the formation of a mixture of polyselenides Se_x^{2-} [33]. The distribution of polyselenide anions is dependent on the molar ratio of selenium and the reducing agent. The treatment of the anions with $[\text{TiCp}_2\text{Cl}_2]$ affords $[\text{TiCp}_2\text{Se}_5]$ [38-40] or dinuclear $[\text{TiCp}_2(\mu\text{-Se}_2)_2\text{TiCp}_2]$ [Cp = cyclopentadienyl ligand C_5H_5^- , or its alkyl-substituted derivatives) [41].

Both $[\text{TiCp}_2\text{Se}_5]$ and $[\text{TiCp}_2(\mu\text{-Se}_2)_2\text{TiCp}_2]$ are useful reagents for the preparation of homo- and heterocyclic chalcogen rings by the reaction with Se_2Cl_2 or SeCl_2 [42,43] (see Eqs. 1 and 2). These reactions are similar to those of $[\text{TiCp}_2\text{S}_5]$ and S_nCl_2 , which afford a large number of homocyclic sulfur ring molecules S_{n+5} (for reviews, see refs. [44-46]). The hybrid reactions of $[\text{TiCp}_2\text{S}_5]$ or $[\text{TiCp}_2(\mu\text{-S}_2)_n\text{TiCp}_2]$ ($n = 2, 3$) with Se_2Cl_2 [41] and those of $[\text{TiCp}_2\text{Se}_5]$ or $[\text{TiCp}_2(\mu\text{-Se}_2)_2\text{TiCp}_2]$ with S_nCl_2 ($n = 1, 2$) [41,47,48] afford heterocyclic selenium sulfides, as do the reactions of $[\text{TiCp}_2\text{Se}_n\text{S}_{5-n}]$ mixtures with sulfur or selenium chlorides [48,49].



An intriguing application of the reduction of elemental selenium by lithium triethylhydridoborate involves the reaction of the reduction product with acyl chlorides or carboxylic acids followed by treatment with sugar azides [50] (see Figure 3). A new amide bond is formed and elemental selenium is recovered for further use.

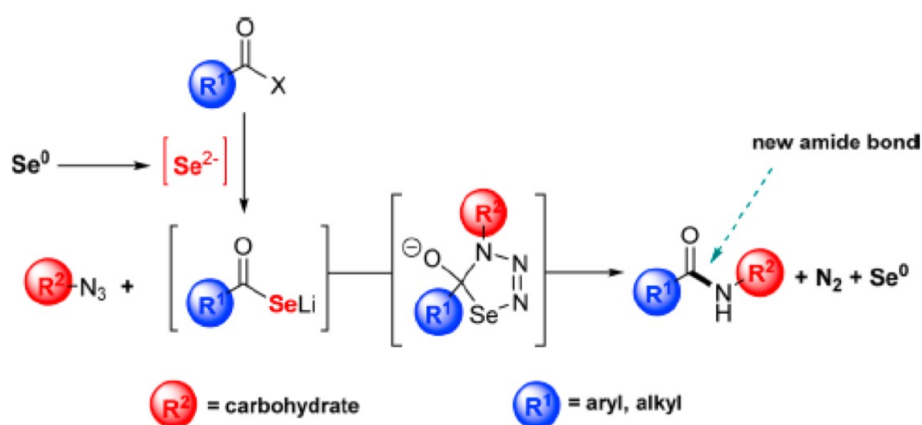
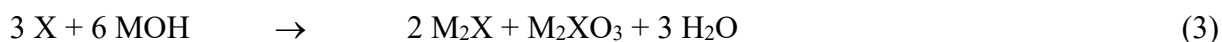


Figure 3. The preparation of sugar-derived amides by reduction of elemental selenium with lithium triethylhydridoaluminum followed by a reaction with an acyl chloride [50] (reproduced with permission from Silva L, Affeldt RF, Lüdtkke DS. Synthesis of glycosyl amides using selenocarboxylates as traceless reagents for amide bond formation. *J Org Chem* 2016, 81, 5464-5473. Copyright 2016 American Chemical Society).

Elemental selenium can also be reduced to Se^{2-} in aqueous alkaline solution [51], though it was reported that the yield of the Se^{2-} ion is only moderate owing to disproportionation (see eq. 3). When tin(II) chloride was added to the basic media, the yield was significantly improved. It has been deduced that tin(II) oxide was *de facto* the reducing agent. However, when selenium powder was irradiated in the microwave oven in a NaOH solution and subsequently treated with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, bulk Cu_5Se_4 could be precipitated from the solution [52].



A direct *in situ* reduction of selenium using aqueous DMF or sodium formaldehydesulfoxylate followed by the reaction with lead acetate afforded PbSe powder [53]. NiSe₂ has been prepared by mixing metallic nickel and elemental selenium in mercaptoethanol at room temperature for a prolonged period resulting in a rust-coloured solution, which upon annealing at 350 °C under a nitrogen atmosphere produced the phase-pure product [54]. The material is an efficient hydrogen evolution reaction catalyst. The reaction of selenium or tellurium and iron(II) bromide in octane-9-enylamine (“oleylamine”) at 170 °C resulted in the formation of FeE_2 (E = Se, Te) nanocrystals [55]. The amine acted as a solvent and as a reducing agent for the chalcogen. The iron dichalcogenides have attractive electronic properties and can have utility in different device applications.

Hydrazine can also be utilized in the reduction of selenium and tellurium [51,56]. The concurrent treatment of the solution with silver nitrate yielded Ag_2Se nanowires [56].

2.3. Selenium halogenides

Elemental selenium can conveniently be converted to Se_2Cl_2 or Se_2Br_2 by mixing the element with SeCl_4 or Br_2 , respectively, in a suitable stoichiometric ratio [57,58]. The reaction with SO_2X_2 (X = Cl, Br) in THF affords SeX_2 [59]. A more detailed description of selenium halogenides in synthetic applications is presented in Chapter 2.

2.4. Heterocyclic selenium sulfides

Crystalline solid solutions of selenium sulfides $\text{Se}_n\text{S}_{8-n}$ can be produced by melting the elements in *vacuo*, quenching the molten mixtures, and extracting the quenched melt with CS_2 followed by crystallization [45]. The composition of the products has been established by ^{77}Se NMR spectroscopy [60] (see Figure 4).

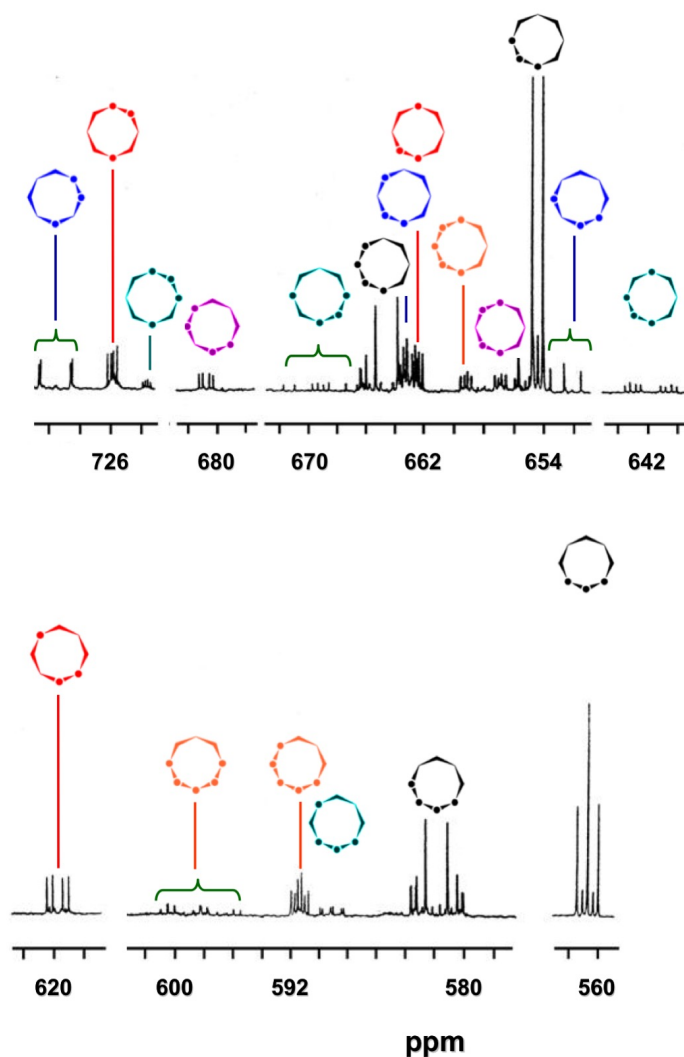


Figure 4. ^{77}Se NMR spectrum of the CS_2 solution of quenched sulfur–selenium melt involving ^{77}Se -enriched selenium (enrichment 92 %) [60,61]. The selenium content in the molten mixture of sulfur and selenium is 30 mol% of selenium. The resonances from different individual $\text{Se}_n\text{S}_{8-n}$ species have been shown in different colours. The closed circles indicate selenium atoms and the empty corners sulfur atoms. (Reproduced with permission from Laitinen RS, Oilunkaniemi R. Catenated Compounds: Group 16 (Se, Te). Laitinen RS, Oilunkaniemi R. Catenated compounds group 16 (Se, Te). In Poeppelmeier, K, Reedijk J. Eds. Comprehensive Inorganic Chemistry II, 2nd Ed., Elsevier, Amsterdam 2013, pp 197-231. Copyright 2013 Elsevier SA).

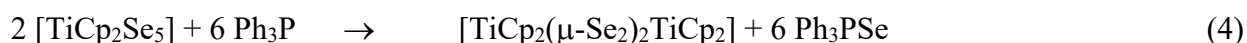
It was deduced that the main components in the CS_2 solutions of the crystalline phases extracted from quenched molten mixtures of sulfur and selenium are sulfur-rich SeS_7 and $1,2\text{-Se}_2\text{S}_6$ ring molecules even in mixtures of high initial selenium content [60]. Other identified main species are $1,2,3\text{-Se}_3\text{S}_5$, $1,2,3,4\text{-Se}_4\text{S}_4$, $1,2,3,4,5\text{-Se}_5\text{S}_3$, $1,2,3,4,5,6\text{-Se}_6\text{S}_2$, and Se_8 , in which the number of homonuclear bonds is maximized.

2.5. Homopolyatomic selenium cations

Elemental selenium can be oxidized to homopolyatomic cations in super acidic media, in acidic melts, and in liquid SO₂ [1,62]. Suitable oxidizing agents are AlCl₃, AsF₅, SbCl₅, BiCl₅, and transition metal halogenides OsF₆, IrF₆, PtF₆, VCl₆, ZrCl₆, HfCl₆, NbCl₆, TaCl₆, and WX₆, ReX₆ (X = F, Cl). In addition, VOCl₃, NbOCl₃, and WOCl₄ can also be used as oxidizing agents. Recently, the selenium cations have also been prepared using chemical vapour transport techniques [63] and ionic liquids [62]. The known homopolyselenium cations include Se₄²⁺, Se₈²⁺, and Se₁₀²⁺, but no applications of these species in synthesis have been reported.

2.6. Triorganylphosphine selenides

Selenium and organic polyselenides react with phosphines yielding phosphine selenides R₃PSe. The reaction with phosphines is often used for abstracting selenium atoms from a polyselenium chain, as exemplified by the formation of [TiCp₂(μ-Se₂)₂TiCp₂] from [TiCp₂Se₅] [41] (eq. 4).

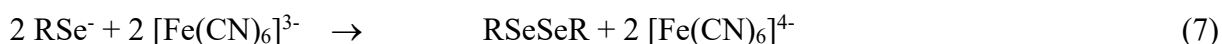
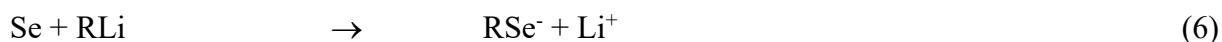
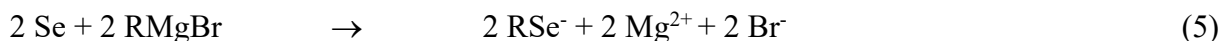


The interaction of elemental selenium with phosphines [64] is exemplified by the one-pot synthesis of diselenophosphinic selenoesters [65]. A more detailed discussion of the preparation and application of phosphorus-selenium reagents is presented in Chapter 5.

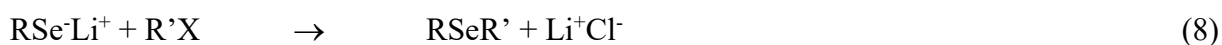
2.7. Grignard and organyllithium reagents

Elemental selenium reacts with Grignard reagents [66] or with organyllithium reagents [67] in dry THF to afford selenolates RSe⁻ (R = organyl group) (eqs. 5 and 6). The nature of the organic substituent is dependent on the substituent in the Grignard reagent. Upon oxidation, the selenolates

can be converted to organyl diselenides, which are themselves convenient reagents in synthetic chemistry (see Chapters 5-11) [66-68]. There are several methods to carry out the oxidation. The best yields have been observed by use of potassium hexacyanidoferrate(III) [67,68] (eq. 7).



Organyl monoselenides can be prepared from lithium selenolate by treatment with an organyl halogenide (eq. 8). By suitable selection of the organic substituent, a number of different selenides can be produced, as exemplified in refs. 69,70.



The cyclopentadienyl rings in $[\text{V}(\text{C}_5\text{H}_5)(\text{C}_7\text{H}_7)]$ [71] or $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ [72] can be lithiated followed by the insertion of selenium or tellurium [71,72]. The treatment of the former complex affords dichalcogenides. In the case of the latter, a chain of three chalcogen atoms links the two cyclopentadienyl rings in the same complex (see Figure 5).

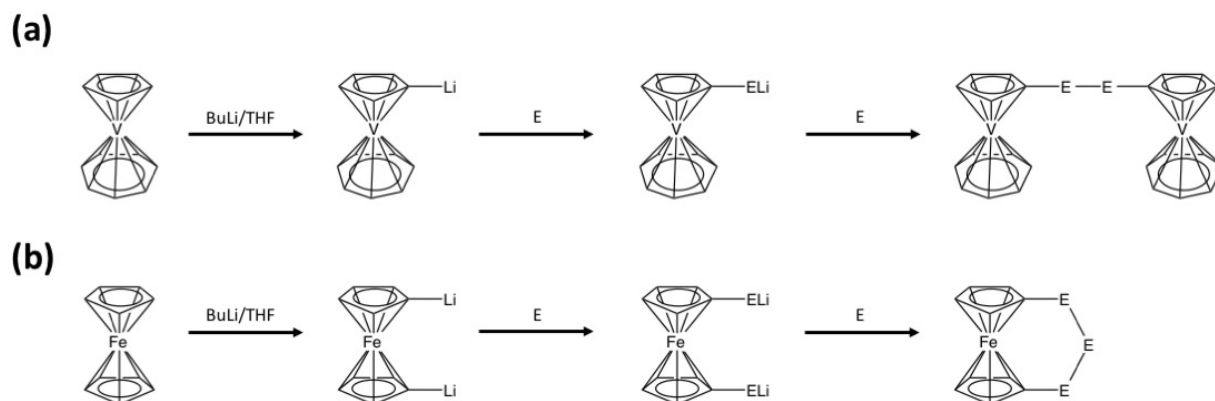


Figure 5. Elemental chalcogens as soft oxidants (E = S, Se, Te). Preparation of (a) [$\{V(C_7H_7)(C_5H_4E)\}_2$] [71] and (b) $[Fe(C_5H_4E)_2E]$ [72].

2.8. Selenium and heavy group 14 reagents

Stable silanechalcogenones containing a terminal $Si=E$ (E = Se, Te) functionality can be formed by the reaction of the amidinate-stabilized silicon(II)bis(trimethylsilyl)amide and selenium or tellurium [73] [see Figure 6(a)] and germaneselonones by the abstraction of selenium from $RR'GeSe_4$ with triphenylphosphine [74]. 1,2,3,4,5-tetraselenagermolane can be prepared by lithiation of $RR'GeH_2$ followed by the treatment with elemental selenium [see Figure 6(b)]. The formation of $RR'GeSe$ in reasonable yields requires very bulky organic substituents.

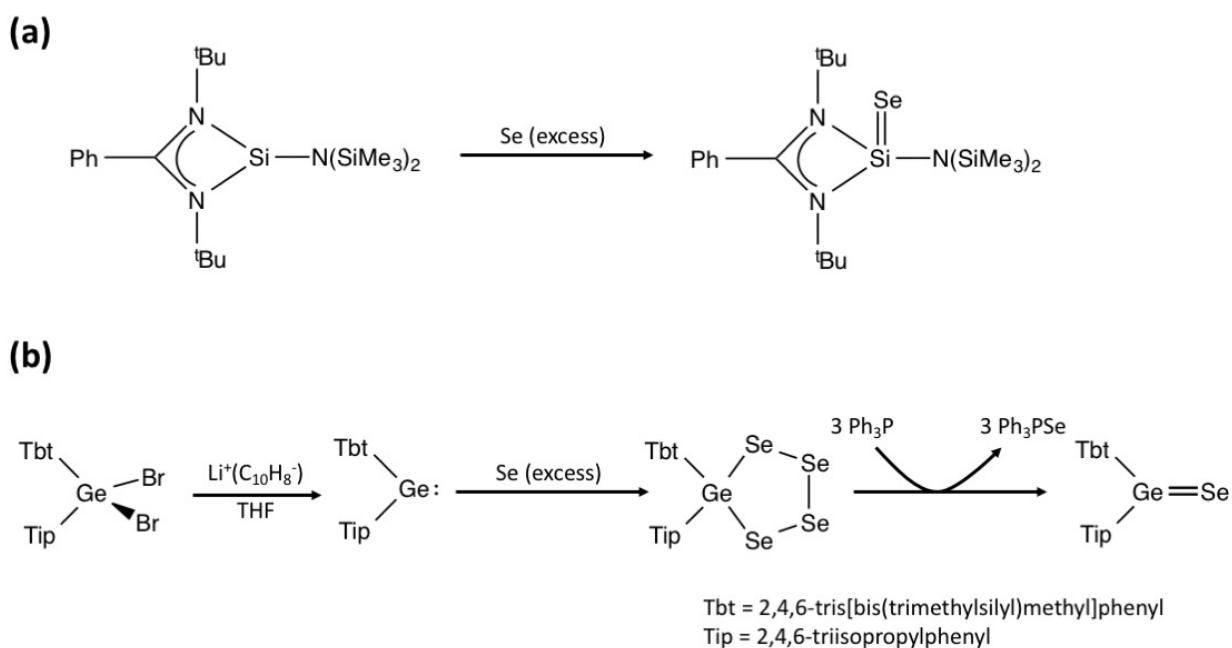


Figure 6. Synthesis of (a) $\text{PhC}(\text{N}^t\text{Bu})_2\text{Si}(\text{Se})\text{N}(\text{SiMe}_3)_2$ [72] and (b) $(\text{Tbt})(\text{Tip})\text{GeSe}$ [73].

Another application of germylenes in the formation of a $\text{Ge}=\text{Se}$ double bond involves the oxidative addition of elemental selenium to a $\text{Ge}(\text{II})$ center [75,76] (see Figure 7). The actual reactant, aminotroponiminato(trimethylsilathio)germylene was obtained by the reaction of the germylene monochloride with $\text{Li}^+(\text{SSiMe}_3^-)$ [75]. When treated with selenium, the oxidative addition was followed by a virtually quantitative condensation step (see Figure 8). By contrast, when $\text{Li}^+(\text{SSiMe}_3^-)$ was substituted by $\text{Li}^+(\text{OSiR}_3^-)$ ($\text{R} = \text{Me}, \text{Ph}$), only a clean single-stage oxidative addition took place [76].

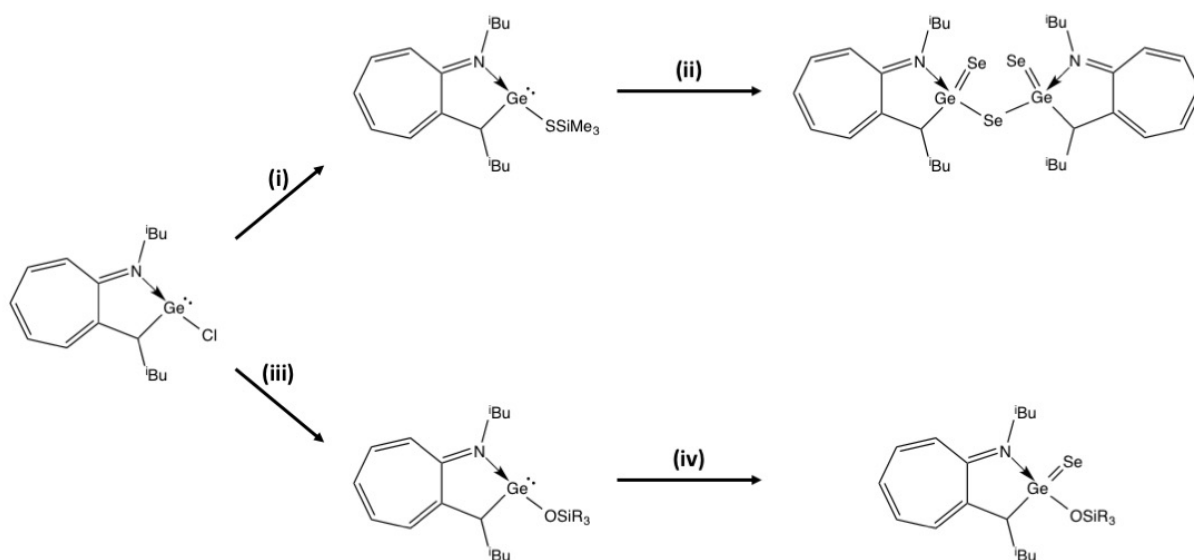


Figure 7. Oxidative addition of selenium to the Ge(II) center [75,76]. (i) $2 \text{ Li}^+(\text{SSiMe}_3)^-\text{THF/hexane}$ 0°C , (ii) Se/THF r.t., (iii) $\text{Li}^+(\text{OSiR}_3)^-\text{toluene}$ r.t. ($\text{R} = \text{Me, Ph}$), (iv) Se/THF r.t.

2.9. Selenium-boron chemistry

Organic diborylenes $\text{RB}=\text{BR}$ can be stabilized by bulky substituents such as Tbt {2,3,6-tris[bis(trimethylsilyl)methyl]phenyl} [77]. Selenium can be inserted into the boron-boron double bond under the influence of uv-radiation. The formal reactant is $\text{TbtB}(\text{SeMe})_2$, but it has been postulated that upon irradiation the reactive component is the borylene Tbt-B: , which is formed upon elimination of Me_2Se_2 from $\text{TbtB}(\text{SeMe})_2$. The monomer Tbt-B: dimerizes forming $\text{Tbt-B}=\text{B-Tbt}$, which then reacts with elemental selenium [77]. It has very recently been shown that the diboryne $\text{RB}\equiv\text{BR}$ ($\text{R} = 1,2\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylene}$) reacts with an excess of elemental selenium to form $\text{RB}(\mu\text{-Se}_2)_2(\mu\text{-Se})\text{BR}$ [78]. By choice of suitable organic groups, it was shown that the diborylene $\text{RR}'\text{B}=\text{BRR}'$ ($\text{R} = 1,3\text{-dimethylimidazol-2-ylidene}$, $\text{R}' = 5\text{-trimethylsilyl-thien-2-yl}$), reacts with elemental selenium yielding diboraselenirane [79]. All three reactions are compared in Figure 8.

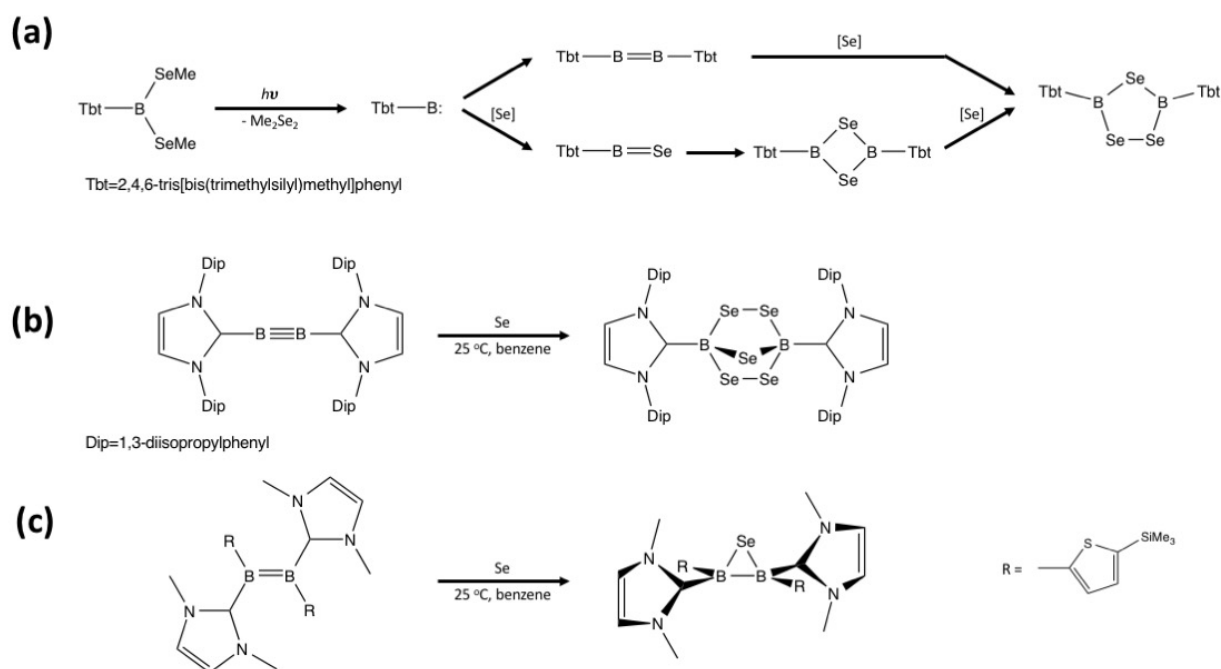


Figure 8. Reactions of boron-boron multiple bonds with elemental selenium. (a) Ref. 77. (b) Ref. 78. (c) Ref. 79.

2.10. Transition metal selenides

Transition metal and main group polyselenides can conveniently be prepared and crystallized by utilizing the molten salt technique [80-82], in which alkali metal polychalcogenides are used as molten fluxes. The reactions are conducted in the temperature range 200-450 °C to ensure the stability of the produced materials. Transition metal polyselenides generally have extended 1D or 2D structures. There is a recent review on the synthesis of lanthanoid-containing heterometallic chalcogenides, which have been prepared by utilizing alkali metal polychalcogenide flux [83]. Polynuclear selenium- and tellurium-containing complexes are discussed in more detail in Chapter 10.

3. Elemental tellurium

3.1. General

Though the chemistry of tellurium and its compounds is mainly similar to that of selenium, there are also notable differences [3]. The general bonding features are significantly different compared to those of the lighter chalcogen congeners. The homonuclear Te-Te bond energies are lower (149 kJ mol⁻¹) than those involving selenium (192 kJ mol⁻¹) or sulfur (266 kJ mol⁻¹). The heteronuclear E-X bonds (E = Te, Se, S) follow the same trend (see ref. 84 for the compilation of bond energies). Consequently, tellurium compounds are generally more labile and more air- and moisture-sensitive. Tellurium also has a weaker tendency for multiple bonding than selenium and sulfur.

By contrast, tellurium shows higher propensity to hypervalency [85] and secondary bonding interactions (SBI) [86]. This is due to the decreased energy difference between $\sigma(\text{Te-X})$ and $\sigma^*(\text{Te-X})$ orbitals and stronger $n(\text{X}) \rightarrow \sigma^*(\text{Te-X})$ interactions. This accounts for stronger intermolecular interactions in tellurium compounds compared to those in related selenium and sulfur species. Electrostatic effects further enhance the strength of the secondary bonding interactions due to the existence of σ -holes in tellurium (see ref. 3 and references cited therein).

An overview of the use of elemental tellurium as a reagent is presented in Figure 9 with some illustrative examples.

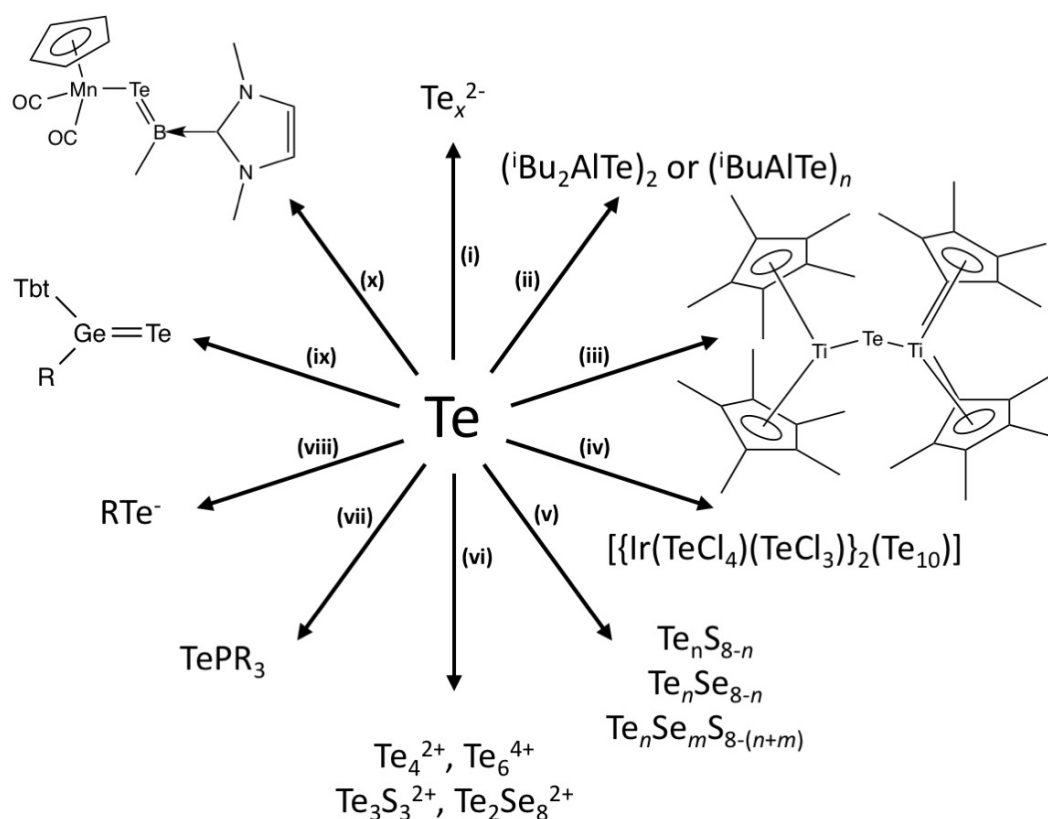


Figure 9. Illustrative examples on the reactivity of elemental tellurium. (i) $M/NH_3(l)$ ($M = Li, Na, K$), $NaBH_4/THF$ or $Li[AlEt_3H]$, (ii) $iBu_2AlH/toluene$, (iii) $[Ti(C_5Me_5)_2TiH]/toluene$, (iv) Te, Ir , and $TeCl_4/250\text{ }^\circ C$, (v) molten mixtures of tellurium, selenium, and sulfur, (vi) $SbF_5/SO_2(l)$, (vii) PR_3 ($R = alkyl$), (viii) $RMgX/THF$ ($X = Cl, Br$) or RLi/THF , (ix) $Ge(Tbt)RGe(Ph_2C_2)/benzene$, (x) $[MnCp(CO)_2\{EB(^tBu)(C[NMe]_2C_2H_2)\}]$.

3.2. Anionic tellurides

As in the case of selenium, the reduction of tellurium to telluride anions is the most convenient method for initial introduction of tellurium into reaction systems. The reduction has been carried out in a similar fashion to selenium, *i.e.* with alkali metals in liquid ammonia [20,21,23] or in dipolar aprotic solutions [27], sodium tetrahydridoborate [87-91], and lithium triethylhydridoaluminate [92,93]. As the effects due to hypervalence and secondary bonding interactions are more significant in the case of tellurium than with the lighter chalcogen congeners [85,86], tellurium shows more

diverse polyanion chemistry than sulfur and selenium. Polytellurides can therefore exhibit charges that deviate from -2.

In addition to selenide and polyselenide anions, Björgvinsson and Schrobilgen [23] have also explored the product distribution of tellurium-containing chalcogenide and polychalcogenide anions in the liquid ammonia or in the ethylene diamine solution using ^{125}Te and ^{77}Se NMR spectroscopy. 2,2,2-crypt was added into the solutions to complex with the alkali metal cation and ensure narrow NMR resonances. As the stoichiometry of the starting materials was varied (see eq. 9), the presence of Te_n^{2-} ($n = 1-4$) and HTe^- was inferred. The synthesis of stable salts of HE^- ($\text{E} = \text{Se}, \text{Te}$) in ionic liquids using large counter-cations has also recently been reported [94]. Their use in syntheses has been discussed in Chapter 8.



Polytelluride and polyselenide anions could also be prepared from the stoichiometric amounts of K_2E and E ($\text{E} = \text{Te}, \text{Se}$) (eq. 10). In the case of mixtures of selenium and tellurium, the reaction affords also a series of tellurium selenide anions. The formation of open-chain potassium-cryptated salts of TeSe_2^{2-} and $\text{Te}_x\text{Se}_{4-x}^{2-}$, as well as pyramidal TeSe_3^{2-} has been reported [95].

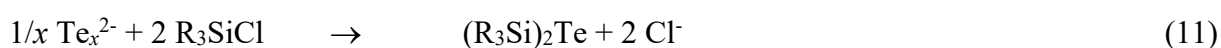


The mixing of Te_n^{2-} and Se_n^{2-} , which have been prepared upon reduction by metallic lithium in liquid ammonia, yielded in addition to open-chain $\text{Te}_2\text{Se}_2^{2-}$ and pyramidal TeSe_3^{2-} anions also the spirocyclic anion TeSe_{10}^{2-} , and extended anionic networks $(\text{Te}_3\text{Se}_6)_n^{2n-}$ and $(\text{Te}_3\text{Se}_7)^{2n-}$ [96].

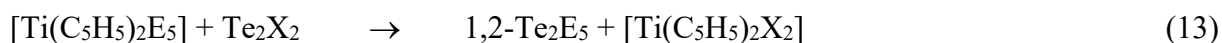
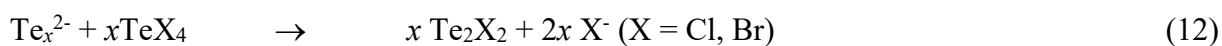
Basmadijan *et al.* [87] have shown that the distribution of the reduction products HTe^- , Te^{2-} , and Te_2^{2-} upon treating elemental tellurium with sodium tetrahydridoborate NaBH_4 in aqueous solution depends on the molar ratio of the reactants as well as on the pH of the solution. The reduction by sodium tetrahydridoborate is generally applied in the production of various binary tellurides [88-90] such as cadmium telluride quantum dots [90] and lead telluride nanocrystals [88].

3.3. Derivatives of anionic tellurides

Lithium ethylhydridoaluminate is an equally useful reducing agent for elemental tellurium as for elemental selenium and sulfur [92,93]. The reaction of thus formed Te_x^{2-} with trialkylsilyl chloride affords bis(trialkylsilyl)tellurides $(\text{R}_3\text{Si})_2\text{Te}$ [92] (see eq. 11), which are convenient reagents in synthetic inorganic chemistry (for examples, see refs. 97, 98), in organic chemistry, as exemplified in refs. 92, 99, in coordination chemistry [100,101], and as a precursor for producing thin films by the ALD technique [102]. The reaction of tellurides with Me_3SiCl is slow and the yield is only moderate. However, a better result can be obtained if $t\text{BuMe}_2\text{SiCl}$ is utilized instead of Me_3SiCl [92].



The reduction of tellurium by lithium triethylhydridoaluminate in THF followed by treatment with TeX_4 ($\text{X} = \text{Cl}, \text{Br}$) (eq. 12) affords Te_2X_2 [103]. Ditellurium dichloride is a yellow liquid, which, though unstable, can be stored for hours in an inert atmosphere. Ditellurium dibromide is orange-red liquid, which is more stable than the corresponding chloride. These tellurium(I) reagents have been used to prepare the heteroatomic rings 1,2- Te_2S_5 and 1,2- Te_2Se_5 by reactions with $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{E}_5]$ ($\text{E} = \text{S}, \text{Se}$) (eq. 13).



Na_2Te or NaTeH can also be utilized in the syntheses of tellurium macrocycles, as reported by Panda [104].

3.4. Tellurium-containing chalcogen rings

Tellurium forms both binary and tertiary heterocyclic molecules with selenium and sulfur, though the systems involving tellurium are much simpler than the binary system of selenium and sulfur (see Section 2.4) [45,61]. As in the case of the $\text{Se}_n\text{S}_{8-n}$ molecules, the eight-membered rings TeS_7 and 1,2-, 1,3-, and 1,4- Te_2S_6 are formed in the binary melt [105], while the ternary species 1,2-, 1,3-, 1,4-, and 1,5- TeSeS_6 are observed in sulfur-rich, sulfur-selenium-tellurium melts, as indicated by the ^{125}Te NMR spectrum of a molten mixture of sulfur (97 mol %), selenium (1,5 mol %), and tellurium (1.5 mol %) shown in Figure 10.

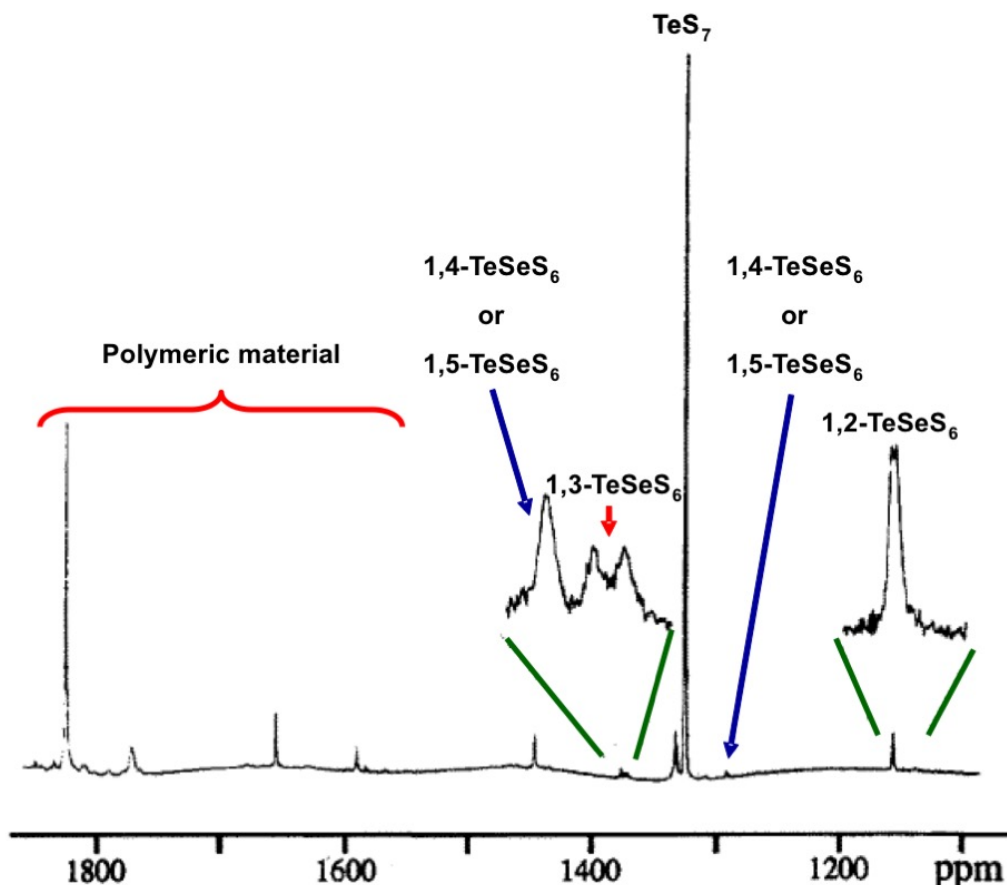


Figure 10. ^{125}Te NMR spectrum of ternary sulfur–selenium–tellurium melt containing ^{77}Se -enriched selenium (1.5 mol%) and ^{125}Te -enriched tellurium (1.5 mol%) (enrichment in both cases 92%). The spectrum has been recorded at 145 °C [105] (Adapted with permission from Chivers T, Laitinen RS, Schmidt KJ, Taavitsainen, J. *Inorg Chem* 1993, 32, 337–340. Copyright 1993 American Chemical Society).

3.5. Homopolyatomic tellurium cations

Tellurium can be oxidized to several different homopolyatomic cations in the same fashion as selenium [1,62,63], e.g. Te_4^{2+} , Te_6^{2+} , Te_6^{4+} , Te_8^{2+} , Te_8^{4+} , etc. However, applications of these cations for the synthesis of other tellurium compounds have not been reported.

3.6. Triorganylphosphine tellurides

Triorganylphosphine tellurides can be prepared from the corresponding phosphine and elemental tellurium [106,107]. Trialkylphosphine tellurides are sufficiently stable for subsequent synthetic

work and have been widely used in the synthesis of semi-conducting metal tellurides [108-113]. More detailed discussion on the phosphorus-tellurium chemistry is presented in Chapter 5.

3.7. Grignard and organyllithium reagents

As in the case of selenium, both Grignard reagents and organyllithium reagents are efficient in producing organylltellurolates [114], which can easily be oxidized to the corresponding ditellurides that are themselves useful reagents in synthetic inorganic and organic chemistry (for some examples in different areas of chemistry, see refs. 115-118). The reactions of ditellurides are discussed in Chapters 5-11 and the ligand chemistry of tellurolates in Chapter 11.

3.8. Silane- and germanetellones

Recent years have seen progress in developing synthetic strategies to prepare silicon-tellurium and germanium tellurium double bonds. A stable dialkylsilylene reacts with elemental tellurium or selenium to form a silanetellone and silaneselone, respectively [119], as shown in Figure 11.

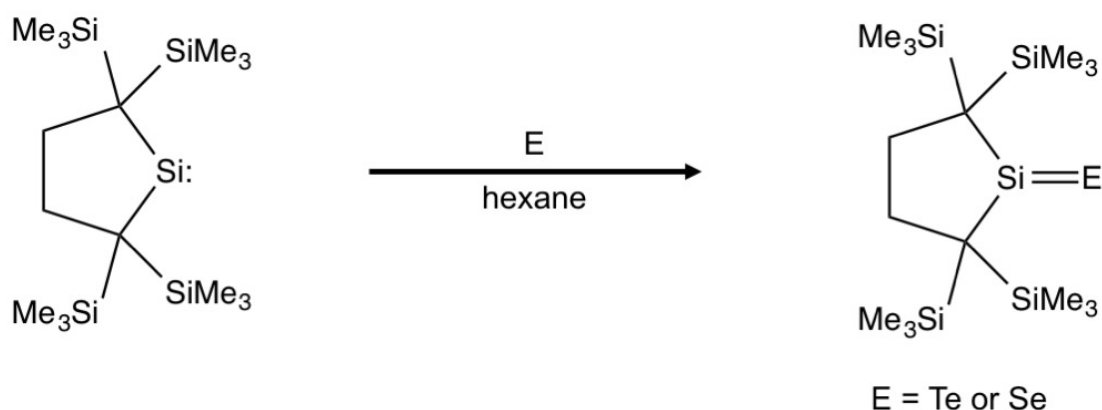


Figure 11. Preparation of silanechalcogenones [119].

Tokito *et al.* [120] carried out a direct telluration of germylene Tbt(R)Ge: containing very bulky substituents on germanium ($\text{Tbt} = 2,4,6\text{-tri[tris(trimethylsilyl)methyl]phenyl}$; $\text{R} = 2,4,6\text{-triisopropylphenyl}$ or $\text{bis(trimethylsilyl)methyl}$) and obtained thermally stable germanetellones (see

Figure 12), which were moisture-sensitive. The presence of a Ge=Te double bond was verified by the X-ray structure determination. The treatment of the germanetellone with mesitonitrile oxide or 2,3-dimethyl-1,3-butadiene resulted in [3+2] or [4+2] cycloaddition products, respectively.

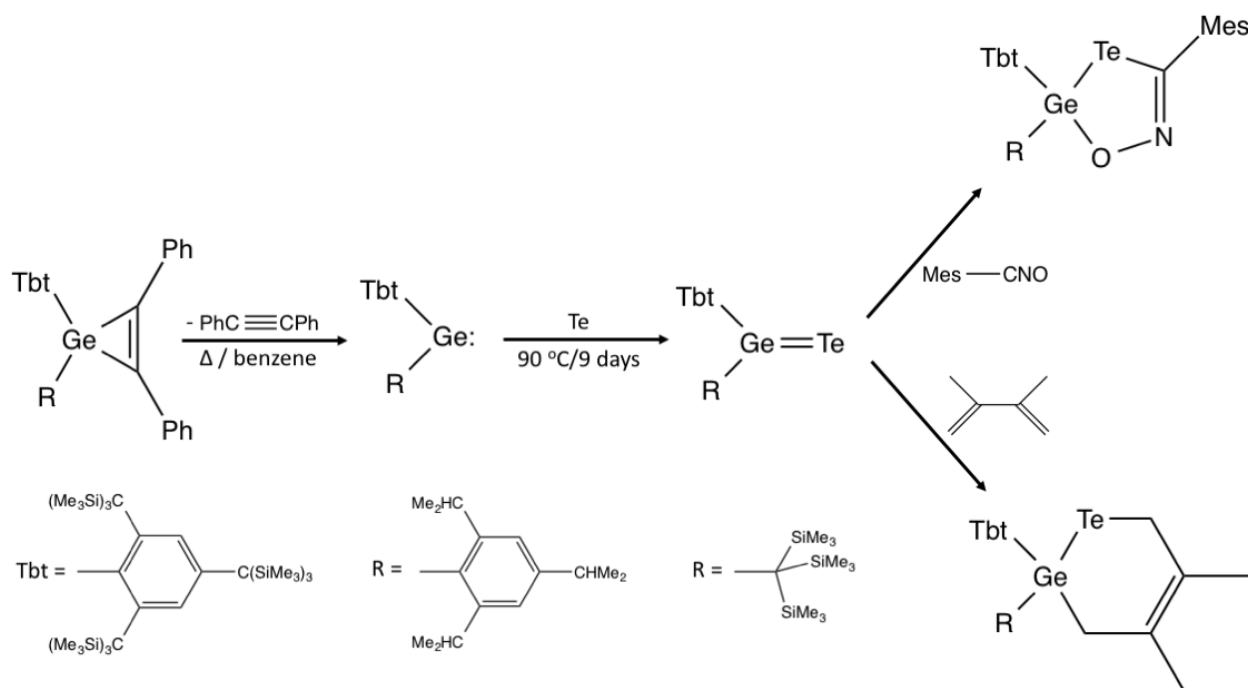


Figure 12. Formation of germanetellone and its cycloaddition reactions [120].

3.9. Group 13 chemistry with tellurium

Tellurium is the heaviest element known to form a double bond with boron [121]. The reaction involves the insertion of tellurium into the $\text{Mn}=\text{B}$ bond in the base-stabilized complex $[\text{Mn}\{\text{B}(\text{tBu})\text{C}[(\text{MeN})_2(\text{CH}_2)]_2\}(\text{C}_5\text{H}_5)(\text{CO})_2]$, as shown in Figure 13. Lighter chalcogens react in a similar fashion.

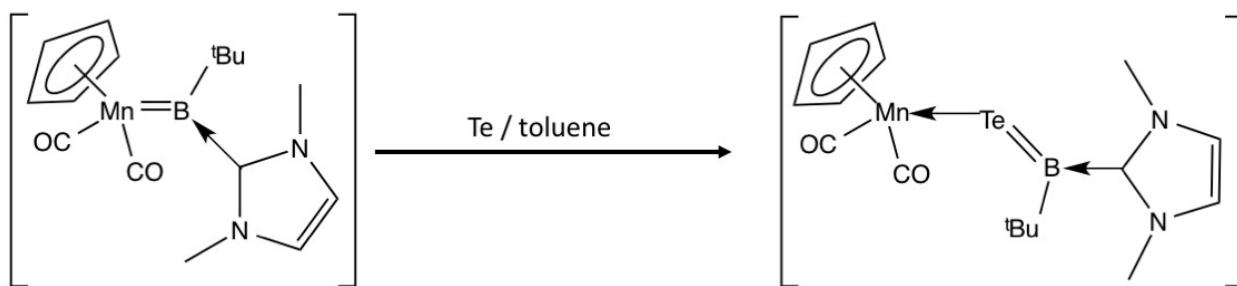


Figure 13. The formation of a B=Te double bond [121].

An excess of elemental tellurium in refluxing toluene reacts with $M(^t\text{Bu})_3$ ($M = \text{Al}, \text{Ga}$) to form the cubane $[M(^t\text{Bu})(\mu_3\text{-Te})]_4$ and $^t\text{BuTeTe}^t\text{Bu}$ [122,123] (see Figure 14). The structure of the tetrameric cage molecule was deduced by comparison of the spectroscopic properties with those of $[M(^t\text{Bu})(\mu_3\text{-Se})]_4$ and $[M(^t\text{Bu})(\mu_3\text{-S})]_4$. The crystal structure of $[\text{Ga}(^t\text{Bu})(\mu_3\text{-S})]_4$ is known [124].

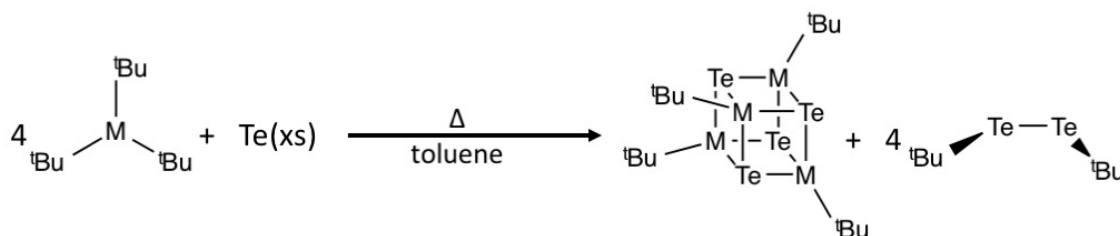


Figure 14. The reaction of $M(^t\text{Bu})_3$ ($M = \text{Al}, \text{Ga}$) with an excess of tellurium [122].

Elemental tellurium and selenium also react with diisobutylaluminium hydride $^i\text{Bu}_2\text{AlH}$ in toluene at 120-130 °C [125]. Mass spectrometric and NMR spectroscopic information indicated the formation a mixture of the dimer $(^i\text{Bu}_2\text{AlE})_2$ and the oligomer $(^i\text{Bu}_2\text{AlE})_n$ together with an unspecified product containing carbon, chalcogen, and aluminium. These *in situ* reagents react with amides to give

chalcogenamides (see Figure 15). While selenoamides are relatively stable, telluroamides easily decompose.

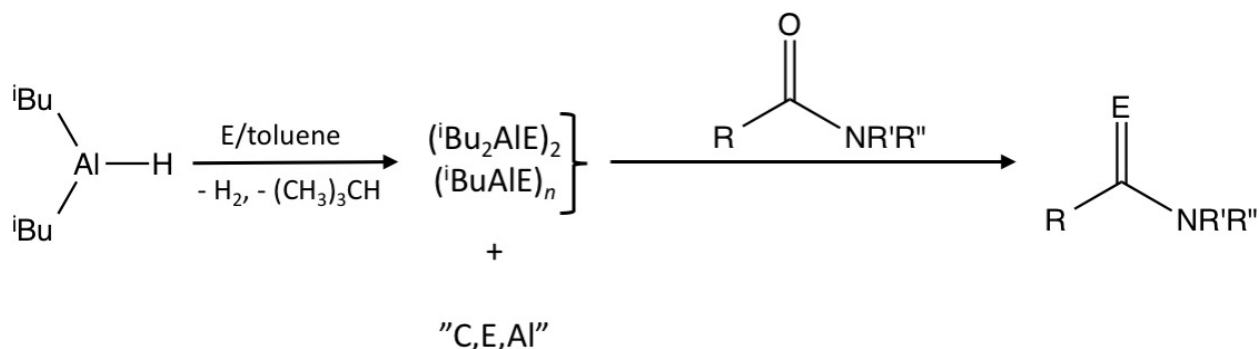


Figure 15. The reaction of tellurium and selenium with diisobutylaluminium hydride and amides (E = Te, Se; R, R', R'' = organyl groups) [125].

3.10. Titanocene chemistry

Bis(pentamethylpentadienyl)hydridotitanium reacts with tellurium or selenium powder to afford titanium complexes that contain monochalcogenido(2-) or dichalcogenido(2-) ligands (see Figure 16) [126,127].

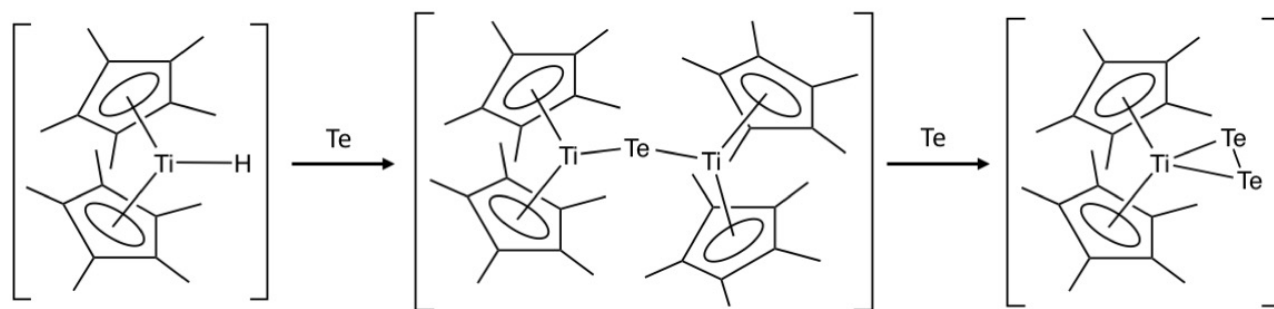


Figure 16. The reaction of $[\text{Ti}(\text{C}_5\text{Me}_5)_2\text{H}]$ with tellurium [127].

While both tellurium and selenium react with $[\text{Ti}(\text{C}_5\text{Me}_5)_2\text{H}]$, the reaction proceeds more smoothly in the case of tellurium, if tributylphosphine telluride is used as a tellurium source [126,127]. Interestingly, $[\text{Ti}(\text{C}_5\text{Me}_5)_2\text{Te}_2]$ is mononuclear, while the related complex, which involves the

methylcyclopentadienyl ligand coordinated to titanium, is dinuclear $[\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2(\mu\text{-Te}_2)_2\text{Ti}(\text{C}_5\text{H}_4\text{Me})_2]$ [96]. This appears to be due to steric effects.

3.11. Solid-state and hydrothermal reactions

Intriguingly, solid-state (hydrothermal) reactions of tellurium with transition metals and tellurium(IV) tetrahalides can produce materials that incorporate unusual homoatomic tellurium rings. For example, prolonged heating of a mixture of elemental tellurium with a late transition metal and tellurium tetrachloride in an evacuated ampoule at 250-300 °C produces $[\{\text{M}(\text{TeX}_4)(\text{TeX}_3)\}_2(\text{Te}_{10})]$ and, $[\{\text{M}(\text{TeI}_4)(\text{TeI}_2)\}_2(\text{TeI}_4)(\text{Te}_2\text{I}_2)(\text{Te}_{10})]$ ($\text{M} = \text{Rh}, \text{Ir}; \text{X} = \text{Cl}, \text{Br}$), as well as $[\{\text{Ru}(\text{TeI}_4)(\text{TeI}_2)\}_2(\text{Te}_{10})]$, which all contain a neutral tellurium cage molecule Te_{10} [128,129]. The same methodology involving tellurium, suitable metals, and tellurium tetrahalogenides yields $[\text{Ru}(\text{Te}_9)][\text{InCl}_4]_2$ and $[\text{Ru}(\text{Te}_8)]\text{Cl}_2$ [130], $[\text{M}(\text{Te}_6)]\text{X}_3$ ($\text{M} = \text{Rh}, \text{Ir}; \text{X} = \text{Cl}, \text{Br}, \text{I}$) and $[\text{Ru}_2(\text{Te}_6)(\text{TeBr}_3)_4(\text{TeBr}_2)_2]$ [131], all of which are one-dimensional coordination polymers containing an uncharged homonuclear tellurium ring.

The hydrothermal reaction of tellurium or selenium with silver and hydrogen iodide at 220 °C afforded $[(\text{AgI})_2(\text{Te}_6)]$ or the isomorphous selenium analogue $[(\text{AgI})_2(\text{Se}_6)]$ [132].

4. Summary

Progress in the synthetic chemistry of selenium and tellurium is largely due to the development of a variety of reagents that can be applied both in inorganic and organic chemistry, as well as in materials science. Many of these useful reagents are available commercially, for instance elemental selenium and tellurium, selenium and tellurium dioxide, selenium and tellurium tetrahalogenides, some

inorganic and organic selenides and tellurides, as well as diselenides and ditellurides. They can be used to synthesize more complex species, which can themselves act as precursors for further applications.

This chapter is an overview of the different reactions involving elemental selenium and tellurium. The synthetic details and reactions of their derivatives will be discussed in greater detail in Chapters 2-11. The first step in synthetic strategies often involves the reduction of the elements to chalcogenide or polychalcogenide ions, since they are stronger nucleophiles than the elements themselves. The most convenient reducing agents are alkali metals in liquid ammonia, sodium tetrahydridoborate, and lithium triethylhydridoaluminate (“superhydride”). Alkali metal and alkaline earth metal chalcogenides can also be prepared by direct mixing of the elements at high temperatures, by the reaction of chalcogen elements and alkali metal carbonates in solution, by solvothermal reactions, or by oxidation–reduction reactions involving Lewis acids.

Unlike commercially available SeX_4 and TeX_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), the less-stable reagents, such as SeCl_2 or SeBr_2 need to be prepared and used *in situ*. This can conveniently be accomplished by the treatment of elemental selenium with sulfuryl chloride or bromide in THF. Both dihalides are stabilized in coordinating solvents. Tellurium dihalogenides cannot be prepared by the same route. Elemental selenium and tellurium also react with the Grignard reagents or organyllithium compounds affording organyl chalcogenolates that can easily be oxidized into organyl dichalcogenides. They play a role among the key reagents in organic and organometallic syntheses.

There are several methods to oxidize elemental selenium and tellurium to homo- and heteropolychalcogen cations. Their most significant feature is that they have been a source of new

understanding of chemical bonding in main group compounds and have provided information of the relationships between the electronic structures and molecular structures.

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