Chapter 2. Selenium- and Tellurium-Halogen Reagents

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Abstract

Selenium and tellurium form binary halides in which the chalcogen can be in formal oxidation states (IV), (II) or (I). They are versatile reagents for the preparation of a wide range of inorganic and organic selenium and tellurium compounds taking advantage of the reactivity of the chalcogen-halogen bond. With the exception of the tetrafluorides, the tetrahalides are either commercially available or readily prepared. On the other hand, the low-valent species, EX_2 ($E = \text{Se, Te}$; $X = \text{Cl, Br}$) and E_2X_2 ($E = \text{Se, Te}$; $X = \text{Cl, Br}$) are unstable with respect to disproportionation and must be used as *in situ* reagents. Organoselenium and tellurium halides are well-known in oxidation states (IV) and (II), as exemplified by REX_3 , R_2EX_2 , and REX ($R = \text{alkyl, aryl}$; $E = \text{Se, Te}$; $X = \text{F, Cl, Br, I}$), as well as mixed-valent (IV/II) compounds of the type $R\text{Te}X_2\text{Te}R$ are also known. This chapter surveys the availability and/or preparative methods for these widely used reagents followed by examples of their applications in synthetic inorganic and organic selenium and tellurium chemistry. For both the binary halides and their organic derivatives the discussion is sub-divided according to the formal oxidation state of the chalcogen.

2.1 Scope and Introduction

The diverse applications of halides of selenium and tellurium as reagents for the synthesis of organic and inorganic compounds stems from a combination of the reactivity of the E-X bond (E = Se, Te; X = halogen) and the availability of these reagents in a variety of oxidation states, namely EX_4 , OEX_2 , EX_2 and E_2X_2 . This chapter will begin with a survey of the reactions of tetrahalides E(IV)X_4 . The latter are generally more easily handled than the halides in which the chalcogen is in a lower oxidation state, E(II)X_2 and $\text{E(I)}_2\text{X}_2$, which are discussed subsequently. In keeping with this sequence the reactions of organochalcogen halides will be treated in the order, RE(IV)X_3 , $\text{R}_2\text{E(IV)X}_2$, mixed-valent $\text{RTe(IV)X}_2\text{Te(II)R}$ compounds, and, finally, RTe(II)X (R = alkyl, aryl) reagents. Triorganochalcogen monohalides, which exist as chalcogenonium salts $[\text{R}_3\text{E(IV)}]\text{X}$ in the solid state and in solution, are not discussed because they do not incorporate covalent E-X bonds [1]. In each section the discussion will commence with a review of the available procedures for the preparation of each of the chalcogen halides together with some comments on their stability. Where appropriate, cross-references will be made to accompanying chapters in this book in which selenium or tellurium halides are used to generate other functional groups, *e.g.* E-O (Chapter 3) and E-N (Chapter 4). For information on the structural chemistry and spectroscopic data of heavy chalcogen halides, the reader is referred to a recent book chapter [2].

2.2 Binary Chalcogen-Halogen Reagents

2.2.1 Selenium tetrahalides

Selenium tetrachloride and tetrabromide are commercially available white solids, which have been used widely in the preparation of inorganic and organic selenium compounds. Although mildly moisture-sensitive, they are thermally stable and easily manipulated under a dry atmosphere. By

contrast, the use of teflon vessels is recommended for the use of highly reactive SeF₄, which is sometimes preferred over the heavier tetrahalides SeX₄ (X = Cl, Br), *e.g.* in the low- temperature (-50 °C) synthesis of the binary selenium azide Se(N₃)₄ in liquid SO₂ (eq. 1) [3]. The formation of the very strong Si-F bond in volatile Me₃SiF provides a powerful driving force in reactions of binary and organochalcogen fluorides with trimethylsilyl reagents (*vide infra*).

The reactions of organolithium reagents with selenium tetrahalides are not a fruitful source of selenenuranes R₄Se. Consequently, recent investigations of the preparation and stability of (C₆H₅)₄Se have used (C₆H₅)₂SeF₂ as the starting material (Section 3.2) [4]. Selenium tetrachloride is, however, a convenient source of selenium(IV) for the preparation of selenium(IV) diimides RN=Se=NR by reaction with the appropriate primary amine RNH₂ (R = ^tBu [5] Ad [6a]) or the monolithiated primary amine Mes*N(H)Li [6b]; the applications of RN=Se=NR reagents are discussed in Chapter 4, Section 7.1. However, the analogous reaction of SeCl₄ with MesNHLi does effect reduction to afford the selenium(II) diamide Se[N(H)Mes]₂ [6b]. A series of tetraalkoxyselenenuranes Se(OR)₄ (R = Me, Et, ⁱPr, neo-pentyl, CF₃CH₂) has been prepared by the reaction of the appropriate alcohol with SeCl₄ in the presence of trimethylamine; however, the R = Me or Et derivatives are thermally unstable [7]. By contrast, ethylene glycol, pinacol and neopentyl glycol give selenuranes that can be isolated as white crystalline solids [7]. Solutions of SeCl₄ in liquid ammonia act as an *in situ* source of binary selenium-nitrogen anions, *e.g.* [Se₂N₂]²⁻, for the preparation of metal complexes [8] (See Chapter 4, Section 2.3).

Selenium tetrahalides also exhibit a propensity for reduction in reactions with Lewis bases (two-electron ligands) as illustrated by the examples depicted in Figure 2.1 [9]. An early example of this behaviour is the formation of base-stabilised $\text{SeCl}_2 \cdot \text{tmtu}$ from treatment of SeCl_4 with tetramethylthiourea (tmtu) [10]. More, recently, it has been shown that thioether ligands also engender the formation of adducts of Se(II)X_2 either as the monomer *trans*- $[\text{SeX}_2(\text{tht})_2]$ ($\text{X} = \text{Cl}, \text{Br}$; tht = tetrahydrothiophene) or as halo-bridged polymers $[\text{SeX}_2(\text{SMe}_2)]$ ($\text{X} = \text{Cl}, \text{Br}$), whereas bidentate sulfur-centred ligands form *cis*- $[\text{SeBr}_2(\text{MeS}(\text{CH}_2)_2\text{SMe})]$ [11]. A 1:1 adduct of SeCl_2 is also produced from the reaction of SeCl_4 with the carbene 2,5-diisopropylimidazole-2-ylidene in THF [12a]. Treatment of SeX_4 ($\text{X} = \text{Cl}, \text{Br}$) with the bidentate nitrogen-centred ligand 1,4-di-*tert*-butyl-1,3-diazabutadiene also results in a two-electron-redox process accompanied, in this case, by reductive elimination of X_2 to give 1,2,5-selenadiazolium cations as $[\text{SeX}_6]^{2-}$ salts [12b]. Triphenylphosphine reacts with SeX_4 ($\text{X} = \text{Cl}, \text{Br}$) to form the $[\text{Ph}_3\text{PX}]^+$ cation accompanied by the Se(II) -centred anion $[\text{SeX}_3]^-$ [12a].

Although reactions of selenium tetrahalides with alkenes and alkynes have been studied extensively in early work, recent attention has been focused on the applications of selenium dihalides for the synthesis of organoselenium compounds (see Section 2.3) [13].

2.2.2 Selenium Oxychloride

Selenium oxychloride SeOCl_2 is an alternative to selenium tetrahalides for applications in both inorganic and organic chemistry. This selenium(IV) reagent is readily obtained as a moisture-sensitive orange liquid in 84 % yield from the reaction of selenium dioxide and chlorotrimethylsilane (eq. 2) [14].

Reactions of SeOCl_2 with secondary amines, *e.g.* $^i\text{Pr}_2\text{NH}$, in a non-polar solvent (pentane) can be stopped at the mono-substituted stage to give $^i\text{Pr}_2\text{NSe(O)Cl}$ as a white solid in 65 % yield. The use of an excess of $^i\text{Pr}_2\text{NH}$ in diethyl ether results in reduction of Se(IV) to Se(II) to give $(^i\text{Pr}_2\text{N})_2\text{Se}$ [14]. In order to avoid the difficult separation of dialkylammonium salts from sensitive selenium-containing products, trimethylsilyl derivatives are often preferable to the amines. Thus, reaction of SeOCl_2 with $^i\text{Pr}_2\text{NSiMe}_3$ in a 1:1 molar ratio is an alternative route to $^i\text{Pr}_2\text{NSe(O)Cl}$ (68 % yield) and the volatile by-product Me_3SiCl is easily removed (eq. 3) [14]. However, the reactions of SeOCl_2 with $\text{Me}_3\text{Si-N}$ reagents may involve formation of $(\text{Me}_3\text{Si})_2\text{O}$ rather than Me_3SiCl , as shown by the synthesis of $(\text{Ph}_3\text{P}=\text{N})_2\text{SeCl}_2$ (eq. 4), which is also obtained from treatment of SeCl_4 with two equivalents of $\text{Ph}_3\text{P}=\text{NSiMe}_3$ [15].

The reaction of the primary amine ${}^t\text{BuNH}_2$ with SeOCl_2 in a 3:1 molar ratio in diethyl ether at -10°C produced the first selenenylamine ${}^t\text{BuNSeO}$ as a brown-orange oil (90 % yield) [5], which can be recrystallised from THF at -20°C to reveal a dimeric structure [6]. In the case of diamines, *e.g.* 4,5-dimethyl-1,2-phenyldiamine, the reaction with SeOCl_2 in boiling toluene results in cyclocondensation to give the corresponding 2,1,3-benzoselenadiazole (61 % yield) (Fig. 2.2) [15]. Selenium oxychloride has also been used as a “selenium transfer reagent” for the synthesis of cyano-substituted selenophenes [16].

The potentially useful reagent $\text{Me}_3\text{SiNSeNSiMe}_3$ is generated by the reaction of SeOCl_2 with $\text{LiN}(\text{SiMe}_3)_2$ in a 1:2 molar ratio in diethyl ether. However, this thermally unstable selenium(IV) diimide must be used *in situ* and applications have been limited to the preparation of the six-membered $\text{P}_2\text{N}_3\text{Se}$ heterocycle (Chapter 5, Section 5) [17].

2.2.3 Selenium Dihalides

The strong tendency of selenium dihalides SeX_2 ($\text{X} = \text{Cl}, \text{Br}$) to disproportionate in solution according to eq. 5 and 6 necessitates the use of these important selenium sources as *in situ* reagents [18].

The reduction of SeCl_4 with an equimolar amount SbPh_3 has been employed successfully to generate SeCl_2 *in situ* for the synthesis of Se-N heterocycles [19], but the separation of $\text{Ph}_3\text{Sb Cl}_2$ from the desired product can be difficult. The use of PhSO_2SeCl as a synthetic equivalent of SeCl_2 was demonstrated in reactions with arylaminines to give ephemeral selenonitrosoarenes ArN=Se [20] (see Chapter 5, Section 6). Subsequently, however, it was shown that pure SeCl_2 is readily obtained by treatment of elemental selenium with an equimolar amount of SO_2Cl_2 (eq. 7) in THF; such solutions are stable towards disproportionation for 1 day at 23 °C as determined by ^{77}Se NMR spectroscopy [21]. Similarly, the facile preparation of solutions of pure selenium dibromide is achieved by treatment of grey selenium with bromine (Br_2) in a chlorocarbon solvent such as CHCl_3 or CCl_4 (eq. 8) [22,23]

THF solutions of SeCl_2 prepared according to eq. 7 have been widely used for the preparation of inorganic selenium-nitrogen heterocycles. The reactions of SeCl_2 with primary amines in various molar ratios in THF have been investigated in particular detail [24]. In the case of *tert*-butylamine, these studies have revealed the successive formation of a series of acyclic imidoselenium dichlorides $\text{ClSe}[\text{N}(\text{tBu})\text{Se}]_n\text{Cl}$ ($n = 1\text{-}3$) via the initial intermediate tBuN(H)SeCl , which serves as a source of

^tBuNSe units in the build-up of longer chains (Figure 2.3) [25-27]. Cyclocondensation reactions or reduction of the bifunctional dichlorides ClSe[N(^tBu)Se]_nCl with an excess of ^tBuNH₂ account for the formation of the variety of cyclic selenium imides that are the ultimate products of this reaction [24].

The cyclocondensation reaction with primary amines is a lot cleaner if a bis-silylated derivative is employed. Thus, the treatment of SeCl_2 with an equimolar amount of $(\text{Me}_3\text{Si})_2\text{NMe}$ at $-10\text{ }^\circ\text{C}$ affords the eight-membered ring 1,3,5,7- $\text{Se}_4(\text{NMe})_4$ exclusively in 90 % yield (eq. 9) [28]. The reagent SeCl_2 also plays a key role in the stepwise generation of the cage molecule 1,5- $\text{Se}_2\text{S}_2\text{N}_4$. In the first step the reaction of SeCl_2 with 2 molar equivalents of the sulfur(IV) diimide $\text{Me}_3\text{SiNSNSiMe}_3$ produces yellow crystals of $(\text{Me}_3\text{SiNSN})_2\text{Se}$ (65 % yield), which undergoes cyclocondensation with SeCl_2 to dark red 1,5- $\text{Se}_2\text{S}_2\text{N}_4$ (73 %) (eq. 10) [29].

In the area of organometallic chemistry the SeCl_2 electrophile has been employed to introduce a μ_4 -Se bridge in double butterfly cluster complexes (Figure 2.4) [30].

In the past 15 years solutions of SeCl_2 or SeBr_2 (eq. 7 and 8, respectively) have been shown to have wide applications for the synthesis of organoselenium compounds, especially selenium-containing heterocycles [31]. Some representative examples are illustrated in Figure 2.5. An early report revealed the formation of selenasilafulvenes from the reactions of SeX_2 ($\text{X} = \text{Cl}, \text{Br}$) with diorganyl diethynylsilanes [32] and this methodology has been extended to germanium-containing systems [22]. These reactions proceed with chemo-, regio- and stereoselectivity in chloroform at room temperature [22, 33]. The transannular addition of SeX_2 to *cis,cis*-1,5-cyclooctadiene takes place chemo- and regio-selectively to give 2,6-dihalo-9-selenobicyclo[3.3.1]nonanes in high yields [23]. The reactions of SeX_2 with divinyl sulfide or selenide initially produces the six-membered 2,6-dihalo-1,4-chalcogenaselenanes, which readily undergo isomerization to the thermodynamically preferred five-membered rings, 1,3-chalcogenaselenolanes [34,35]. The involvement of a seleniranium cation in this ring-contraction process is supported by quantum chemical calculations [34]. In the case of divinyl sulfone $\text{O}_2\text{S}(\text{CH}=\text{CH}_2)_2$, the presence of the strongly electron-withdrawing group results in

the predominant formation of a four-membered ring in 85 % yield [36]. The use of SeCl_2 to generate selenophene monomers that undergo polymerization to give materials with potentially useful electrochromic and photothermal properties is a promising development [37-39]. For example, the reaction of SeCl_2 with 2,3-dimethoxy-1,3-butadiene gives 3,4-dimethoxyselenophene in 41 % yield [37].

Annulation reactions are observed in the reactions of SeX_2 (X = Cl, Br) with substrates that incorporate phenyl substituents. A simple example is the formation of 3-bromo-2-phenylbenzo[*b*]selenophene in 92 % yield from the reaction of SeBr_2 with diphenylacetylene in diethyl ether at room temperature (Figure 2.5) [40]. Annulation is also observed in the reactions of SeX_2 with thiophenyl-substituted alkynes [41] and with unsaturated ethers [42, 43]. The electrophilic addition of SeX_2 to the triple bond of a large range of propargyl alcohols has also been investigated, including the formation of selenium-containing spiroketals with potential biological

activity [44a, 44b]. Selenium dihalides have also been shown to undergo a stereoselective (*anti*-addition) pathway with hex-2-yne [45a] and to exhibit high regioselectivity in reactions with methyl vinyl ketone [45b].

The *in situ* reagent SeCl_2 is also a versatile source of diaryl selenides Ar_2E via salt elimination involving aryl-lithium or Grignard reagents [46-48]. Derivatives that are available from this methodology include $\text{Ar} = \text{Ph}$, *o*-tolyl, 2-methylnaphthyl [46], $\text{Ar} = \text{bromo-}$ or dibromo- substituted pyridyl [47], and $\text{Ar} = \text{intramolecularly coordinated azobenzene derivatives}$ [48]. Diaryl selenides are also accessible via electrophilic aromatic substitution. Thus, $(4\text{-MeOC}_6\text{H}_4)_2\text{Se}$ is obtained in 91 % yield from the reaction of SeCl_2 with 4-methoxybenzene in chloroform [49]. Interestingly, this route is tolerant to the presence of OH substituents on the aromatic ring [50]. For example, the reaction of SeCl_2 in diethyl ether with 2-naphthol in a 1:2 molar ratio, in the presence of a catalytic amount of AlCl_3 , yields the selenide $(2\text{-HOC}_{10}\text{H}_6)_2\text{Se}$ in 56 % yield [50]. A promising application of SeCl_2 in electrophilic aromatic substitution involves the formation of tetrameric macrocycles in good yields from 3,5-dialkoxythiophenes in diethyl ether at room temperature as illustrated in Figure 2.6 [50].

2.2.4 Diselenium Dihalides

Diselenium dihalides Se_2X_2 are yellow-brown ($\text{X} = \text{Cl}$) or blood-red ($\text{X} = \text{Br}$) moisture-sensitive liquids. With careful control of the stoichiometry these selenium(I) reagents can be prepared by the reactions shown in eq. 11 and 12, respectively, carried below 0°C in the case of $\text{X} = \text{Br}$ [51]. On the basis of Raman and ^{77}Se NMR spectra, diselenium dihalides Se_2X_2 exist in equilibrium with small amounts selenium(II) dihalides SeX_2 and Se_nX_2 ($n = 3, 4$) [52]. This observation is significant when considering the outcome of reactions of these selenium(I) halides. For example the reactions of $\text{C}_6\text{F}_5\text{Li}$ with Se_2Cl_2 affords the monoselenide $(\text{C}_6\text{F}_5)_2\text{Se}$ in 60 % yield [53]. For comparison, SeCl_4 is reduced by $\text{C}_6\text{F}_5\text{Li}$ to give $(\text{C}_6\text{F}_5)_2\text{Se}$ in only 20 % yield [53].

Diselenium dichloride also reacts effectively as SeCl_2 for the synthesis of the monoselenides $\text{Se}[\text{N}(\text{SiMe}_3)\text{R}]_2$ ($\text{R} = \text{SiMe}_3$ [54], ^tBu [55]) in 75 and 65 % yields, respectively, in hexane with concomitant formation of red selenium (eq. 13). By contrast, the reaction of the amine $(\text{Me}_3\text{Si})_2\text{NH}$ with Se_2Cl_2 in dichloromethane at 0°C produces a mixture of polyselenides $\text{Se}_n[\text{N}(\text{SiMe}_3)_2]_2$ ($n = 2, 3, 4$) from which the predominant triselenide ($n = 3$) cannot be separated in pure form [56].

The outcome of the reaction with Me₃SiNPPPh₃ is another example of Se₂Cl₂ behaving as SeCl₂. In acetonitrile solution the ion-separated salt [SeCl(NPPPh₃)₂]⁺SeCl₃⁻, in which selenium(II) is present in both the cation and anion, is formed together with elemental selenium (eq. 14) [57].

The reaction of Se₂Cl₂ with trimethylsilyl azide in dichloromethane produces an insoluble black powder with the composition Se₃N₂Cl₂, which incorporates the five-membered Se₃N₂Cl⁺ cation with one Se(IV) and two Se(II) centres (a better synthesis of Se₃N₂Cl₂ is described in Section 2.5) [58, 59]. The dimeric selenium-nitrogen chloride (Se₃N₂Cl)₂ is isolated as an explosive dark brown powder in 75 % yield from the reaction of equimolar amounts Se₂Cl₂ with the cage molecule Se₄N₄ [59].

Diselenium dichloride has also been utilised to generate cyclic selenium allotropes. Thus, the reaction of titanocene pentaselenide with Se₂Cl₂ in CS₂ at 20 °C produces dark red *cyclo*-Se₇ in 75 % yield (eq. 15) [60]. Unpredictably, heating RhCl₃•4H₂O with an excess of Se₂Cl₂ yields the complex Rh₂Se₉Cl₆ in which the nine-membered *cyclo*-Se₉ is sandwiched between two Rh(III) centres [61].

The reactions of gallium metal with Se₂X₂ (X = Cl, Br) are the most convenient preparation of ternary gallium(III) selenide halides GaSeX, which are soluble in pyridine to give the six-membered rings [GaSeX•Py]₃ [62].

Se₂Cl₂ has been utilised to generate compounds with discrete Se=N bonds by reaction with dichloramines according to eq. 16 [63,64].

The passage of acetylene gas through a solution of Se_2Cl_2 in CCl_4 under pressure (10-12 atm., 30-40 °C) produces *E,E*-bis(2-chlorovinyl)selenide in 98 % yield together with elemental selenium (eq.17) [65].

2.2.5 Mixtures of Selenium Halides

The use of a mixtures of selenium halides has been used effectively for the synthesis of selenium compounds with (a) different functional groups on selenium, (b) selenium centres in formal oxidation states II and IV, or (c) selenium in formal oxidation state III as illustrated by the examples in Figure 2.7. In reactions with *tert*-butylamine a mixture of SeOCl_2 with SeCl_4 produces the four-membered ring ${}^t\text{BuN}=\text{Se}(\mu\text{-N}^t\text{Bu})_2\text{Se}=\text{O}$ with terminal $\text{Se}=\text{NR}$ and $\text{Se}=\text{O}$ functionalities [26], whereas the use of SeCl_2 in combination with SeOCl_2 generates the acyclic compound $\text{ClSeN}({}^t\text{Bu})\text{Se}(\text{O})\text{Cl}$ with Se(II) and Se(IV) centres [66]. The reaction of $\text{LiN}(\text{SiMe}_3)_2$ with a mixture of Se_2Cl_2 and SeCl_4 in a 1:4 molar ratio (designed to mimic “ SeCl_3 ”) produces pure Se_4N_4 in 66 % yield [67], whereas the “ SeCl_3 ”

reagent reacts with the monoselenide $\text{Se}[\text{N}(\text{SiMe}_3)_2]_2$ to give the five-membered ring $[\text{Se}_3\text{N}_2\text{Cl}]\text{Cl}$ (95 % yield) [58,59].

2.2.6 Tellurium Tetrahalides

Tetrahalides of tellurium TeX_4 are white ($\text{X} = \text{Cl}, \text{Br}$) or yellow ($\text{X} = \text{I}$) solids that are available from commercial sources and have been used for the preparation of a wide range of inorganic and organic tellurium compounds. Tellurium tetrafluoride is a very moisture-sensitive, colourless solid that can be obtained in 78 % yield by heating a mixture of TeO_2 with sulfur tetrafluoride at 130 °C for 48h in a stainless steel or Monel (a nickel-copper alloy) autoclave [68,69]. As in the case of selenium tetrahalides, TeF_4 is preferred over TeCl_4 for the preparation of the extremely explosive binary azide, $\text{Te}(\text{N}_3)_4$, by reaction with trimethylsilyl azide in CFCl_3 at 0 °C (*cf.* eq. 1); the use of TeCl_4 results in only partial metathesis to give $\text{TeCl}_{4-n}(\text{N}_3)_n$ ($n = 1,2$) [70a]. The reaction of the hexafluoride TeF_6 with trimethylsilyl azide in MeCN also produces $\text{Te}(\text{N}_3)_4$ [70b]. Tellurium

tetrafluoride has also been used to prepare $\text{Te}(\text{CN})_4$ as solvates with THF or MeCN by reactions with trimethylsilyl cyanide in those solvents [71].

Tetraaryl-tellurium(IV) compounds can be prepared from aryl-lithium or Grignard reagents, however yields may be low owing to concomitant reductive elimination to give diaryl-tellurium(II) compounds and biphenyls. Tetraphenyl-tellurium(IV) and tetra(*p*-tolyl)-tellurium(IV) have been prepared from ArLi and TeCl_4 by salt metathesis in 70 % and 52 % yields, respectively, and it was shown that phenyl radicals are not involved in the formation of biphenyls [72]. The perfluoro derivative $(\text{C}_6\text{F}_5)_4\text{Te}$ is obtained in 75 % yield from the reaction of the Grignard reagent $\text{C}_6\text{F}_5\text{MgBr}$ and TeCl_4 at 30 °C in diethyl ether or in “good yields” from AgC_6F_5 and TeCl_4 in EtCN at -78 °C [73]. Tetraalkyl-tellurium(IV) derivatives R_4Te (R = Me, ⁿBu, Me_3SiCH_2 , $\text{CH}_2=\text{CH}$) are available from the reactions of the appropriate lithium or Grignard reagent in ether solvents at low temperature, however they exhibit a strong tendency to decompose to the corresponding dialkyl-tellurium(II) species [74,75].

The reactions of aryl-lithium reagents with TeCl_4 have also been used to generate hypervalent tellurium compounds. Thus, the one-pot reaction of TeCl_4 with LiAr (Ar = 4- $\text{CF}_3\text{C}_6\text{H}_4$) in a 1:4 molar ratio in diethyl ether at room temperature produces the hexaaryl compound TeAr_6 in 17 % yield, accompanied by Te(IV) and Te(II) derivatives (eq. 18) [76,77]. Changing the molar ratio to 1:6 did not improve the yield of TeAr_6 , however the reaction of 5 equivalents of PhLi with TeX_4 (X = Cl, Br) generates Ph_5TeLi , which is converted to pentaphenyltellurium halides Ph_5TeX (X = Cl, Br) by treatment with SO_2Cl_2 or Br_2 in a one-pot reaction [78].

In an early report several tetraalkoxytelluranes $\text{Te}(\text{OR})_4$ were prepared in unspecified yields by reactions of TeCl_4 with the corresponding alcohol ($\text{R} = \text{Me}, \text{Et}, ^i\text{Pr}, \text{neopentyl}$) or sodium alkoxide ($\text{R} = \text{CF}_3\text{CH}_2, (\text{CF}_3)_2\text{CH}$) in a 1:4 molar ratio [7]. A subsequent investigation of the sodium alkoxide- TeCl_4 system achieved isolated yields of 58 % ($\text{R} = \text{Me}$) or 64 % ($\text{R} = \text{CF}_3\text{CH}_2$) [79]. An unexpected transformation is observed in the reaction of TeCl_4 with ethane-1,2-diol in a 1:1 molar ratio *in acetonitrile* at reflux. The ammonium salt $[\text{NH}_4]^+[(\text{OCH}_2\text{CH}_2\text{O})\text{TeCl}_3]^-$, which exhibits immunomodulatory activity, is obtained in 79 % yield; the solvent CH_3CN is the apparent source of nitrogen in the NH_4^+ cation of this salt [80].

As depicted in Figure 2.8 the reactions of tellurium tetrahalides with nitrogen-centered nucleophiles may result in reduction to tellurium(II), as exemplified by the formation of the tellurides $\text{Te}[\text{N}(\text{SiMe}_3)\text{R}]_2$ (50 %, $\text{R} = \text{SiMe}_3$ [54]; 35 %, ^tBu [55]) from salt metathesis of TeCl_4 with the corresponding lithium reagents. Similarly, the polymeric tellurium(II) complex $[\text{Te}(\text{NMe}_2)_2]_\infty$ is isolated as a yellow, moisture-sensitive solid (74 % yield) from the reaction of LiNMe_2 with TeCl_4 in a 4:1 molar ratio in THF- Et_2O solutions [81]. This propensity for reduction has been used in the synthesis of a wide range of dialkynyl tellurides in moderate-to-high yields from the reactions of TeCl_4 with lithium amides, *e.g.* LiN^iPr_2 , followed by treatment with terminal alkynes [82]. However, dialkynyl tellurides $\text{Te}(\text{C}\equiv\text{CR})_2$ ($\text{R} = \text{Me}, \text{Et}, ^n\text{Pr}, ^t\text{Bu}, \text{Me}_3\text{Si}, \text{Ph}$) can also be prepared in 42-69 % yields by the reactions of TeCl_4 with four equivalents of the corresponding alkynyl-lithium reagent [83].

The use of $\text{Me}_3\text{Si-N}$ derivatives and/or a chelating ligand reduces the tendency towards reduction as exemplified by the syntheses of the tellurium(IV) derivatives $[\text{TeCl}_2(\text{NPMe}_3)_2]_2$ ($\text{R} = \text{Ph}$ [84]; $\text{R} = \text{Me}$ [85], $[\text{TeCl}_2(\text{NEPh}_2)_2]$ ($\text{E} = \text{C}, \text{S}$) [86], $\text{PhC}(\text{NSiMe}_3)_2\text{TeCl}_3$ [87], and $\text{PhB}(\mu\text{-N}^t\text{Bu})_2\text{TeCl}_2$ [88] (Figure 2.8). Moreover, the reaction of TeCl_4 with one equivalent of dilithium *meso*-tetra-*p*-

tolylporphyrin, $\text{Li}_2(\text{ttp})$, in hexane at reflux yields the dark green tellurium(IV) porphyrin complex $[\text{Te}(\text{ttp})\text{Cl}_2]$ in which only three nitrogen atom of the porphyrin ligand are coordinated to tellurium [89]. However, the reaction of TeCl_4 with the multifunctional reagent $\text{N}(\text{SiMe}_3)_3$ in a 2:1 molar ratio produces a dimer of the hypothetical tellurium(IV) imide $[\text{Cl}_3\text{Te}-\text{N}=\text{TeCl}]^+$ [90] (Figure 2.8). The tellurium(IV) imide $^t\text{BuN}=\text{TeCl}_2$ is obtained as a trimer from the redistribution reaction of TeCl_4 with the tellurium(IV) dimide dimer $[^t\text{BuNTe}(\mu\text{-N}^t\text{Bu})_2\text{TeN}^t\text{Bu}]_2$ [91].

Tellurium tetrahalides are key reagents for the synthesis of 1,2,5-telluradiazoles and benzo-2,1,3-telluradiazoles, which exhibit supramolecular chromotropism. The latter are generally prepared by cyclocondensation of TeCl_4 with the appropriate phenylenediamine in pyridine followed by the addition of triethylamine. Yields of pure benzo-2,1,3-telluradiazoles, after removal $[\text{Et}_3\text{NH}]\text{Cl}$, range from 43 % for the 3,6-dibromo derivative [92] to 84% for the 4,5,6,7-tetrafluoro derivative [93]. The reaction of 2,3-diaminomaleonitrile with TeX_4 ($\text{X} = \text{Cl}, \text{Br}$) in the presence of pyridine and

triethylamine gives a product that is contaminated with $[\text{Et}_3\text{NH}]\text{Cl}$ and pyridine. Pure dicyano-1,2,5-telluradiazole is obtained in 57 % yield after treatment of this product with iced water [94].

The reactions of tellurium tetrahalides with a wide range of N, P, O, S and Se-centered Lewis bases have been investigated and reduction is sometimes observed, especially for the heavier halogens (Figure 2.9) [9]. For example, tellurium(II) diiodide is trapped by the chelating nitrogen ligand in the reaction of TeI_4 with a 1,2-bis(arylimino)acenaphthene [95a]; however, similar reactions with TeX_4 ($\text{X} = \text{Cl}, \text{Br}$) result in C-H activation of an isopropyl group in the ligand to give a *N,N,C*-bound TeX_3 complex [95a,b]. The reaction of TeI_4 with a carbene ligand, 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, in THF at reflux also produces a 1:1 adduct with TeI_2 (66 % yield) via reductive elimination of I_2 from the initially formed TeI_4 adduct [96]. The 1:1 adduct of TeI_2 with the *Se,Se'*-chelating ligand $\text{SePPh}_2\text{CH}_2\text{Ph}_2\text{PSe}$ has been prepared in 85 % yield from a combination of elemental tellurium and I_2 with an equimolar amount of the ligand in CH_2Cl_2 for 4 days at room temperature [97].

In contrast to the behavior of SeX_4 (Figure 2.1), the tellurium tetrahalides TeX_4 ($\text{X} = \text{Cl}, \text{Br}$) form 1:1 adducts with 1,4-di-*tert*-butyl-1,3-diazabutadiene (Figure 2.9) and TeI_4 does not react at room temperature with this *N,N'*-chelating ligand [11]. The reactions of TeX_4 ($\text{X} = \text{Cl}, \text{Br}$) with 2,2'-bipyridine (bipy) also produce 1:1 adducts in the ionic form $[\text{Te}(\text{bipy})\text{X}_3]\text{X}$, which for $\text{X} = \text{Cl}$ can be reduced by SbPh_3 in dichloromethane to give the tellurium(II) complex $[\text{Te}(\text{bipy})\text{Cl}_2]$ (Section 2.7) [98].

In early work a 2:1 *trans*-octahedral complex was isolated in 34 % yield from the reaction of tetramethylthiourea (tmtu) with TeCl_4 [99]. Recently, the reactions of TeX_4 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) with chalcogen-centered ligands, including phosphine chalcogenides and thio- or seleno-ethers, have been investigated extensively [100, 101]. In the case of phosphine oxides OPR_3 ($\text{R} = \text{Me}, \text{Ph}$), the adduct

obtained is dependent upon the nature of the halogen. Thus, TeF_4 forms the square-pyramidal 1:1 complexes $[\text{TeF}_4(\text{OPR}_3)]$ [100], whereas the heavier tetrahalides give distorted *cis*-octahedral 1:2 complexes $[\text{TeX}_4(\text{OPR}_3)_2]$ ($\text{X} = \text{Cl}, \text{Br}; \text{R} = \text{Me}, \text{Ph}$) (Figure 2.9) [101a]. Chelating thioether ligands also give *cis*-octahedral 1:2 complexes $[\text{TeX}_4(\text{RS}(\text{CH}_2)_2\text{SR})]$ ($\text{X} = \text{Cl}, \text{Br}; \text{R} = \text{Me}, \text{}^i\text{Pr}$), whereas the monodentate thioether dimethyl sulfide generates 1:1 complexes, which exist as halo-bridged dimers $[\text{X}_3(\text{Me}_2\text{S})\text{Te}]_2(\mu\text{-X})_2$ [101b]. Soft selenoether ligands form 2:1 *trans*-octahedral complexes of the type $[\text{TeX}_4(\text{SeMe}_2)]$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) and chelating selenium ligands, *e.g.* $\text{o-C}_6\text{H}_4(\text{SeMe})_2$, produce *cis*-octahedral 1:1 complexes [101a]. However, reduction of the tellurium center does occur in the reaction of TeBr_4 with a chelating phosphine selenide to give $[\text{TeBr}_2(\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{P}(\text{Se})\text{Ph}_2)]$ (Figure 2.9) [100].

In contrast to the reactions of selenium tetrahalides with triphenylphosphine Ph_3P , which involve oxidative addition to the phosphorus(III) centre (Figure 2.1), the corresponding reaction with TeCl_4 results in reduction of one-half of the tellurium to tellurium metal (eq. 19) [12].

Surprisingly, tellurium tetrachloride also acts as a Lewis acid upon treatment with the nucleophile $[\text{Mn}(\text{CO})_5]^-$ in THF at $-15\text{ }^\circ\text{C}$ to give the six-coordinate adduct $[\text{Mn}(\text{CO})_5(\text{TeCl}_4)]^-$ as a PPN^+ salt [102]. Alternatively, tellurium tetrahalides may act as sources of the TeX_3 ligand in oxidative-addition reactions with Rh(I), Ru(I) or Ir(I) complexes as exemplified by formation of the ion-separated rhodium(III) complex $[\text{RhCl}(\text{TeF}_3)(\text{CO})(\text{PEt}_3)_2][\text{TeF}_5]$ [103] and the octahedral iridium(III) complex $[\text{IrCl}_2(\text{CO})(\text{PPh}_3)_2(\text{TeCl}_3)]$ [104]. However, TeCl_4 may also behave as a mild chlorinating agent rather than an electrophile with other metal carbonyl complexes, *e.g.* the formation of $[\text{FeCl}_2(\text{CO})_3\text{L}_2]$ from reactions with $[\text{Fe}(\text{CO})_3\text{L}_2]$ ($\text{L} = \text{CO}, \text{PPh}_3$) [104].

There have been extensive investigations of the addition of TeCl_4 to unsaturated organic compounds, which is covered in the earlier review literature. A recent example of involves reactions of TeX_4 ($\text{X} = \text{Cl}, \text{Br}$) with 3-hexyne and 4-octyne which give either monoaddition products with *E*-stereochemistry (Figure 2.10a) or bis-addition products (Figure 2.10b) [105]. These addition products can be considered as examples of RTeCl_3 (Section 3.1) and R_2TeCl_2 derivatives, respectively, and they are readily reduced to either ditellurides (Figure 2.10a) or monotellurides (Figure 2.10b) in high yields using either aqueous sodium metabisulfite in CCl_4 or aqueous NaBH_4 sodium borohydride in THF [105].

2.2.7 Tellurium Dihalides and Ditellurium Dihalides

In early work tellurium dihalides TeX_2 ($\text{X} = \text{Cl}, \text{Br}$) were prepared by the reaction of molten tellurium with CF_2Cl_2 or CF_3Br , respectively [106a, 106b]. These dihalides disproportionate readily in ether solvents to give TeX_4 and elemental tellurium. However, the reaction of TeCl_2 with liquid bromine was reported to give TeCl_2Br_2 as a yellow solid [106a]. The isolation of TeCl_2 in 60 % yield from the reaction of TeCl_4 with an equimolar quantity of hexamethyl disilane at reflux has been claimed and Me_3SiCl was identified as a by-product [107]. This source of *in situ* TeCl_2 has been used to prepare the silane or germane tellones $[(\text{Tbt})(\text{Dip})\text{M}=\text{Te}]$ ($\text{M} = \text{Si}, \text{Ge}$) by reaction with $[(\text{Tbt})(\text{Dip})\text{MLi}_2]$ ($\text{Tbt} = 2,4,6\text{-tris}[\text{bis}(\text{trimethylsilyl})\text{methyl}]\text{phenyl}$, $\text{Dip} = 2,6\text{-diisopropylphenyl}$) [108]. The same reagent has also been used in a ring-closure reaction with 2,3-dimethoxy-1,3-butadiene for the efficient synthesis of 3,4-dimethoxytellurophene (Figure 2.11a) [109]. Alternatively, a Lewis base adduct of TeCl_2 (*vide infra*) may be used to generate a tellurophene ring via Zr/Te transmetallation (Figure 2.11b) [110].

(a)

(b)

In fact, Lewis base adducts of TeX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are used more frequently than the *in situ* reagent for the synthesis of inorganic or organic tellurium compounds [9]. Examples of these sources of TeX_2 include the 1:1 adduct with tmtu, which has been known for many years [111] and the more recent discoveries of $[\text{Te}(\text{bipy})\text{Cl}_2]$ (Section 2.6) [97] and $[\text{Te}(\text{PET}_3)\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [112]. In addition to the example shown in Figure 2.10b, some other illustrations of the applications of these adducts in

the synthesis of tellurium compounds are depicted in Figure 2.11. The $\text{Te}(\text{bipy})\text{Cl}_2$ complex provides a source of diaryl tellurides via reactions with Grignard reagents [9]. The bidentate bipy ligand in this complex can be replaced by two N-heterocyclic carbenes to give the 2:1 adduct $\text{Te}(\text{iPr}_2\text{IM})_2\text{Cl}_2$ [9]. Treatment of $[(\text{Dipp}_2\text{BIAN})\text{TeI}_2]$ with 2.5 equivalents of silver triflate in CH_2Cl_2 rapidly generates the corresponding bis-triflate, which acts as a source of a tellurium-centered dication upon reaction with two equivalents of iPr_2IM [113]. The metathetical reaction of $(\text{tmtu})\text{TeCl}_2$ with 2.5 equivalents of $\text{Li}[\text{HC}(\text{PPh}_2\text{Se})_2]$ results in disproportionation to give elemental tellurium and an unusual tellurium(IV) complex (Figure 2.12) [114].

Ditellurium dihalides Te_2X_2 ($\text{X} = \text{Cl}, \text{Br}$) are prepared by reducing elemental tellurium with the superhydride $\text{Li}[\text{BHEt}_3]$ and treating the resulting telluride with the appropriate tellurium tetrahalide

TeX₄ [115]. These tellurium(I) halide reagents are obtained as yellow and orange liquids, respectively, but they have limited stability. However, they have been used to generate the seven-membered, heteroatomic chalcogen rings 1,2-Te₂E₅ (E = S, Se) via metathesis with titanocene pentachalcogenides (eq. 20) [115].

2.3 Organochalcogen-Halogen Reagents

A wide variety of organochalcogen(IV)-halogen reagents of the type REX₃ and R₂EX₂ (E = Se, Te; X = F, Cl, Br, I) are known and their applications in organic chemistry have been surveyed [116]. Organochalcogen(II) compounds, especially PhSe(II) halides and their derivatives, are widely used as electrophilic reagents in the functionalization of carbon-carbon multiple bonds [117]. In addition, understanding the structural features of organochalcogen halides, especially the tellurium derivatives, has been a major goal of recent investigations and this aspect is addressed in several surveys [118]. After a brief introduction to the most common representatives of each compound class, the following sections will focus on the synthesis and reactions of derivatives that incorporate bulky R groups on the chalcogen or intramolecular heteroatom-chalcogen interactions, since these strategies enable access to derivatives with functionalities that are not stable with simple alkyl or aryl groups attached to the chalcogen.

2.3.1 Organoselenium and -tellurium Trihalides

Arylselenium trihalides have been known since the 1930s. They are usually prepared by halogenation of the corresponding arylselenocyanate or diaryldiselenide [119]. For example, the series 4-XC₆H₄SeBr₃ (X = H, Br, Cl, CH₃) was obtained by treating the appropriate diaryldiselenide with three equivalents of a solution of bromine in chloroform [119]. These solid tribromides are moisture-sensitive and decompose upon prolonged storage or when exposed to a laser beam or heat with loss of Br₂. Aryl or alkyl-selenium trichlorides are prepared similarly, *e.g.* by chlorination of PhSeSePh or MeSeSeMe with Cl₂ gas in methylene dichloride [120a,b]; PhSeCl₃ is isolated as hygroscopic, pale yellow crystals [120a]. These organoselenium(IV) trichlorides form 1:1 adducts with SbCl₅, which are formulated as ionic salts [RECl₂⁺][SbCl₆⁻] [120a].

In early work a series of arylselenium trifluorides ArSeF₃ (Ar = C₆H₅, 4-CH₃C₆H₄, 4-FC₆H₄, 2-C₂H₅C₆H₄, 2-NO₂C₆H₄) was prepared by oxidative fluorination of the corresponding diaryl diselenide with silver difluoride; yields were in the range 24-77% [121a]. As a representative example, PhSeF₃ was obtained from the reaction of PhSeSePh with an excess of AgF₂ in boiling CF₂ClCCl₂F (bp. is 47 °C) in a *polypropylene* vessel (to avoid etching of glass). The very moisture-sensitive arylselenium trifluorides are readily hydrolysed to seleninic acids ArSeO₂H upon exposure to moisture [121a]. More recently, the use of XeF₂ in CH₂Cl₂ at 0 °C as fluorinating agent in perfluoroalkoxy-copolymer vessels has extended the range of known RSeF₃ derivatives to alkyl (R = Me, ⁱPr) or bulky aryl derivatives [R = 2,4,6-R'₃C₆H₄ (R' = Me, ⁱPr, ^tBu)], as well as the R = 2-Me₂NCH₂C₆H₄ compound (eq. 21) [121b]. Although of limited thermal stability above 0 °C, reactions of these selenium trifluorides with trimethylsilyl azide occur rapidly in CH₂Cl₂ at – 50 °C to give the corresponding triazides, which have even lower thermal stability [121b].

In contrast to the formation of TeCl_2 from the reaction of TeCl_4 with hot $\text{Me}_3\text{SiSiMe}_3$ (Section 2.7), when combined in CS_2 these reagents generate a polymeric methyltellurium trichloride $(\text{MeTeCl}_3)_\infty$ as very moisture-sensitive, brownish crystals in 43 % yield [122]. The ethyl derivative EtTeCl_3 is obtained in 75 % yield by chlorination of EtTeTeEt with Cl_2 gas in cold (-20°C) methylene dichloride [120]. The bis-substituted derivative, $\text{CH}_2(\text{TeCl}_3)_2$, is an interesting example of an organotellurium trichloride, which is obtained as a white crystalline solid from the reaction of acetic anhydride with TeCl_4 in a 1:3 molar ratio at reflux for ca. 1 day [123]. Reduction of $\text{CH}_2(\text{TeCl}_3)_2$ with aqueous sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) produces an almost quantitative yield of the grey polymer $(\text{CH}_2\text{TeTe})_n$ [123].

Halogenation of ditellurides with an excess of Cl_2 (or SO_2Cl_2), Br_2 or I_2 is a common route to aryl derivatives ArTeX_3 , which are also accessible from reactions of TeX_4 with arylmercury halides or via Friedel-Crafts reactions of TeCl_4 with arenes [124]. Supermesityltellurium trichloride $\text{Mes}^*\text{TeCl}_3$ ($\text{Mes}^* = 2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2$) is obtained as bright yellow crystals in 96 % yield by chlorination of $\text{Mes}^*\text{TeTeMes}^*$ with SO_2Cl_2 in a molar ratio of ca. 1:2.8 in diethyl ether [125]. However, the installation of the very bulky aryl group on tellurium engenders some unusual reactivity. As depicted in Figure 2.13, intramolecular HCl elimination involving an ortho *tert*-butyl group with the formation of a Te-C bond occurs in the solid state at room temperature. On the other hand, an equilibrium exists between $\text{Mes}^*\text{TeCl}_3$ and the tellurium (II) species Mes^*TeCl and chlorine gas in solution (Section 3.4) [125]. On exposure to moist air partial hydrolysis occurs to give $\text{Mes}^*\text{Te}(\text{OH})\text{Cl}_2$ [125].

The stabilizing influence of intramolecular heteroatom interactions on organo-tellurium(IV) is exemplified by 2-dimethylaminomethylphenyl derivatives ArTeX_3 ($\text{Ar} = 2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4$), which are prepared by halogenation of the corresponding ditelluride ArTeTeAr by SO_2Cl_2 ($\text{X} = \text{Cl}$) or Br_2 ($\text{X} = \text{Br}$) [118a, 126]. More recently, fluorination of this ditelluride with XeF_2 in dichloromethane at room temperature was shown to produce almost quantitative yields of the colourless trifluoride $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{TeF}_3$, which reacts with trimethylsilyl azide to give the thermally unstable triazide $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)\text{Te}(\text{N}_3)_3$ [127].

Similar to the behaviour of TeCl_4 (Section 2.6), reactions of aryltellurium trichlorides with $\text{Me}_3\text{Si-N}$ derivatives take place without reduction of the tellurium centre. Examples of aryltellurium(IV)

compounds prepared in this manner include $\text{Ph}_3\text{P}=\text{N}(\text{Ar})\text{TeCl}_2$, $\text{Me}_2\text{S}(\text{O})\text{N}(\text{Ar})\text{TeCl}_2$, $\text{Me}_3\text{SiN}=\text{S}=\text{N}(\text{Ar})\text{TeCl}_2$ ($\text{Ar} = 4\text{-MeOC}_6\text{H}_4$) [84], and $\text{Ar}(\text{R}'_2\text{N})\text{TeCl}_2$ ($\text{Ar} = \text{C}_6\text{H}_5$, $4\text{-MeOC}_6\text{H}_4$, $4\text{-C}_6\text{H}_5\text{OC}_6\text{H}_4$; $\text{R}'_2 = \text{Et}_2$, C_4H_8) [128].

The base hydrolysis of aryltellurium trichlorides provides a general route to aryltellurinic acids $[\text{ArTe}(\text{O})\text{OH}]_n$, which are usually polymeric, high-melting solids with low solubility in organic solvents [129]. However, the installation of a highly bulky group on tellurium enables the isolation of a partial hydrolysis product, *e.g.* $\text{Mes}^*\text{Te}(\text{OH})\text{Cl}_2$ (Figure 2.12) [125]. In the case of ArTeCl_3 ($\text{Ar} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$), the controlled base hydrolysis proceeds in two steps to give the aryltellurinic chloride $[\text{ArTe}(\text{O})\text{Cl}]_2$ and, subsequently, the aryltellurinic acid $[\text{ArTe}(\text{O})\text{OH}]_2$, both of which are dimeric (Figure 2.14) [130]. The hydrolysis of the intramolecularly coordinated ArTeCl_3 ($\text{Ar} = 8\text{-Me}_2\text{NC}_{10}\text{H}_6$) with an excess of aqueous NaOH generates a series of polynuclear telluroxanes as crystalline materials [131].

2.3.2 Diorgano-selenium and -tellurium Dihalides

Simple dialkyl and diaryl-selenium dihalides R_2SeX_2 ($\text{R} = \text{Me}$, Ph ; $\text{X} = \text{Cl}$, Br) are obtained as monomeric solids from halogenation of the corresponding selenide R_2Se with an equivalent amount of Cl_2 or Br_2 [132]. By contrast, the difluorides are liquids ($\text{R} = \text{Me}$, Et , ^nPr , ^iPr) or low-melting solids ($\text{R} = (\text{CH}_2)_4$, Ph) that are generated by treatment of R_2Se with AgF_2 [133]. Alternatively, XeF_2 in CH_2Cl_2 can be used as the fluorinating agent to prepare R_2SeF_2 ($\text{R} = \text{Me}$, Et , ^iPr , Ph , Mes , Mes^* , $2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2$, $2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4$) [127]. Ph_2SeF_2 is obtained as a dark purple crystalline solid, which

reacts with two equivalents of PhLi in diethyl ether to produce the explosive tetraphenylselenurane Ph₄Se (Section 2.1) [4].

Diorganotellurium dihalides are accessible in a number of ways: (a) condensation reactions with aromatic compounds such as ROC₆H₅ or R₂NC₆H₅, (b) arylation of TeCl₄ with ArHgCl, (c) halogenation of tellurides R₂Te with Cl₂ (or SO₂Cl), Br₂, I₂, and (d) reactions of elemental tellurium with alkyl halides [124]. As a recent example of method (c), the diorganotellurium diiodides TeI₂(CH₂SiMe₃)₂, TeI₂Th(CH₂SiMe₃), TeI₂Ph(CH₂SiMe₃), and TeI₂Th₂ (Th = 2-thienyl) are obtained as air-stable orange or red crystals in >90 % yields by treatment of the appropriate telluride with I₂ in THF [134]. The oxidative-addition of alkyl bromides or iodides to elemental tellurium [method (d)] is a well-established procedure that has been applied to the preparation of (PhCOCH₂)₂TeX₂ as colourless (X = Br) or red (X = I) crystals, in 50 % or 65 % yields, respectively [135].

In the case of 1,5-ditelluracyclooctane, reaction with Cl₂ or I₂ [method (c)] generates dihalogenoditelluranes with a transannular Te-Te bond in almost quantitative yields (Figure 2.15) [136a]. The thermolysis of the dichloroditellurane in boiling DMF (160 °C) for 5 min. engenders the ring-expansion product Cl₆[12]aneTe₃, which exhibits redox behaviour upon treatment with six equivalents of PhSH in DMSO at 50 °C to give a cyclic tritelluride in 90 % yield (Figure 2.15) [136b].

Diaryltellurium difluorides 4-(ROC₆H₄)₂TeF₂ (R = Me, Et) are obtained as colourless crystals in low yields by fluorination of the corresponding dichlorides with AgF₂ in boiling toluene [124b]. Similar to the preparation of aryltellurium trifluorides (*vide supra*), the reaction of XeF₂ in dichloromethane at room temperature with the monotelluride (2-Me₂NCH₂C₆H₄)₂Te produces the colorless difluoride (2-Me₂NCH₂C₆H₄)₂TeF₂, which reacts with trimethylsilyl azide to give the thermally unstable diazide (2-Me₂NCH₂C₆H₄)₂Te(N₃)₂ [127].

The hydrolysis of diaryltellurium dihalides with an excess of base in aqueous ethanol is an important route for the preparation of the ditellurium oxides (telluroxanes), (R₂TeO)_n, as crystalline solids [129]. Incomplete hydrolysis using water gives rise to either diaryltellurium hydroxyhalides R₂Te(OH)X or their condensation products XR₂TeOTeR₂X. A better route to the latter class of ditelluroxane is the redistribution reaction between R₂TeO and R₂TeX₂, *e.g.* R = 4-MeOC₆H₄, X = I) [137].

The bifunctionality of diaryltellurium dihalides provides an opportunity to generate tellurium-containing macrocycles through cyclocondensation reactions with carboxylic or phosphinic acids. Thus, the reactions of Ar₂TeCl₂ (Ar = 4-MeOC₆H₄) with 1,1'-ferrocenedicarboxylic acid in the presence of NEt₃ in benzene generates an almost quantitative yield of a 16-membered macrocycle [138], while a similar reaction with 1,1,2,3,3-pentamethyltrimethylenephosphinic acid produces a 12-membered Te₄P₂O₆ ring [139].

2.3.3 Mixed-valent State Compounds RTeX₂TeR

Tellurium can form an unusual class of mixed-valent (Te(IV)/Te(II)) compounds if a deficiency of the halogen reagent is used in the halogenation of ditellurides. Thus, the reaction of PhTeTePh with only one molar equivalent of Br₂ produces red-brown PhTeBr₂TePh in almost quantitative yield

[140]. Derivatives with a bulky aryl group $\text{ArTeX}_2\text{TeAr}$ ($\text{Ar} = 2,6\text{-MesC}_6\text{H}_3$; $\text{X} = \text{Cl}, \text{Br}$) are obtained in a similar manner from ArTeTeAr and SO_2Cl_2 or Br_2 [140] and a mixed-valent difluoride $\text{BbtTeF}_2\text{TeBbt}$ is prepared as air-stable, red-brown crystals in 64 % yield by treatment of the ditelluride with XeF_2 in dichloromethane at -78°C (Figure 2.16) [141]

The applications of ditelluride dihalides RTeX_2TeR for the generation of aryltellurenyl cations are discussed at the end of the next section.

2.3.4 Organo-selenium and -tellurium Monohalides

In marked contrast to the thermal instability of selenium(II) dihalides (Section 2.3), phenyl selenium(II) halides PhSeX ($\text{X} = \text{Cl}, \text{Br}$) are commercially available solids that can be readily prepared by treatment of PhSeSePh with one equivalent of SO_2Cl_2 or Cl_2 in hexane or Br_2 in THF. By contrast, the treatment of PhSeSePh with I_2 produces the 1:1 complex $\text{Ph}_2\text{Se}\cdot\text{I}_2$ [142]. However,

the presence of a bulky aryl group causes Se-Se bond cleavage to give the black selenenyl iodide ArSeI (Ar = Mes*) in almost quantitative yield [143]. A bulky alkyl group also stabilizes the Se-I functionality in (Me₃Si)₃CSeI [144]. The complex Ph₂Se•I₂ is commercially available and behaves as the reagent “PhSeI” in the iodoselection of 2-hexyne [142]. Arylselenenyl fluorides ArSeF in which a substituent in the *ortho* position provides steric or electronic protection are obtained by treatment of diselenides ArSeSeAr or aryl selenotrimethylsilanes AeSeSiMe₃ with XeF₂ in dichloromethane at low temperatures in perfluoroethylene-perfluorovinyl ether copolymer (PFA) vessels [145]. They were identified by low-temperature ¹⁹F and ⁷⁷Se NMR spectroscopy but, at ambient temperature, they readily undergo disproportionation.

The applications of phenylselenenyl reagents in organic chemistry, primarily for the functionalization of carbon-carbon multiple bonds, are discussed in Chapter 6. The halide ion in PhSeX often replaced *in situ* in order to avoid the incorporation of halide nucleophiles during selenenylation reactions [117]. For example, the following PhSe⁺X⁻ equivalents have been used for addition to alkynes: Ph₂Se₂/XeF₂/2SbF₅, Ph₂Se₂/Br₂/AgSbF₆, Ph₂Se₂/2NOSbF₆, and PhSeCl/SbCl₅ [146]. The latter reagent reacts with alkynes RC≡CR in dichloromethane at -40 °C to give selenirenium cations as SbCl₆⁻ salts which, in the case of R = ^tBu, Ad, can be isolated as stable crystalline solids (Figure 2.17) [146].

The reactions of arylselenium chlorides ArSeCl with trimethylsilyl azide produces the corresponding azides ArSeN₃, which decompose with loss of N₂ to give diselenides ArSeSeAr even

for very bulky aryl derivatives. However, the strategy of intramolecular heteroatom-stabilization produces 2-Me₂NCH₂C₆H₄SeN₃ as pale yellow crystals in 88 % yields from the reaction of 2-Me₂NCH₂C₆H₄SeCl with sodium azide in acetone; for prolonged storage this azide must be stored at 0 °C [147].

Similar to binary tellurium(II) halides, TeX₂ (X = Cl, Br) (Section 2.7), simple organic derivatives RTeX (R = Me, Ph; X = Cl, Br) are unstable with respect to disproportionation. However, the bulky alkyl derivatives (Me₃Si)₃CTeX (X = Cl, Br, I) are obtained quantitatively as blue-black crystals by halogenation of the ditelluride (Me₃Si)₃CTeTeC(SiMe₃)₃ with one molar equivalent of SO₂Cl₂, Br₂ or I₂ in THF at room temperature [148a]. Reactions of the iodide with organolithium reagents give the corresponding methyl and phenyl derivatives (Me₃Si)₃CTeR as yellow needles in 85 % (R = Me) and 80 % (R = Ph) yields [148b]. The iodide has also been used in metathetical reactions with silver or potassium salts of pseudo- halides or pseudo-chalcogenides to generate (Me₃Si)₃CTeX (X = CN, SCN, SeCN, NCO, N₃) and (Me₃Si)₃CTeYTeC(SiMe₃)₃ (Y = NCN, NSN), respectively, in yields ranging from 72 to 92 % [148b].

Bulky substituents or intramolecular heteroatom-tellurium coordination can also serve to stabilize aryltellurenyl halides, as illustrated by the monomeric species 2,4,6-R₃C₆H₂TeX (R = ⁱPr, ^tBu; X = Br, I), which are prepared by reactions of the corresponding ditellurides with equimolar amounts of Br₂ or I₂; the iodides are thermally more stable than the bromides [149]. Stabilization can also be achieved by intramolecular heteroatom-tellurium interaction as in 2-Me₂NCH₂C₆H₄TeI [150]. The kinetic or donor stabilization afforded by bulky aryl groups or the presence of coordinating heteroatoms extends to the corresponding azides, *e.g.* 2,4,6-R₃C₆H₂TeN₃, Mes*TeN₃ and 2-Me₂NCH₂C₆H₄TeN₃, which are prepared by reactions of the iodides with silver azide in acetonitrile [150].

Aryltellurenyl iodides behave as iodine-like acceptors in reactions with iodide ion, phosphine selenides or TeMes_2 (Figure 2.18). For example, the green iodide $2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2\text{TeI}$ forms the stable, red adduct $[\text{Et}_4\text{N}][2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2\text{TeI}_2]$ upon treatment with $[\text{Et}_4\text{N}]\text{I}$ [149]. The bifunctional phosphine selenides $\text{SePPh}_2(\text{CH}_2)_n\text{Ph}_2\text{PSe}$ ($n = 1,2$) react with MesTeI in dichloromethane to give 1:2 complexes in *ca.* 75 % yields [97]. In related behaviour, attempts to recrystallize MesTeI always produced the 1:1 adduct $\text{Mes(I)Te(TeMes}_2)$ [151]

Halogenation reactions of a ditelluride with bulky aryl substituents RTeTeR ($\text{R} = \text{Bbt} = 2,4,6\text{-(Me}_3\text{Si)}_2\text{CH-C}_6\text{H}_2$) have also been investigated using different molar ratios of the reagents [152]. With one molar equivalent of SO_2Cl_2 , Br_2 or I_2 in CH_2Cl_2 , the thermally stable monohalides BbtTeX were isolated in 82-95 % yields as red-purple, blue and green crystals, respectively. Changing the molar ratio to 3:1 produced the trihalides BbtTeX_3 ($\text{X} = \text{Cl}$, yellow crystals, 93 %; $\text{X} = \text{Br}$, red crystals, 99 %), but only the monoiodide BbtTeI when 3 equivalents of I_2 were used [152].

The heteroatom (*ortho*-methoxy) substituents in the ditelluride RTeTeR ($\text{R} = 2,6\text{-dimethoxyphenyl}$) have a notable influence on the outcome of the reaction with I_2 [153]. When this reaction is carried out in a 1:1 molar ratio in dichloromethane at -10°C the mixed-valent compound RTeTeI_2R is isolated in very high yields. At room temperature the tellurenyl iodide is formed, but it reacts further with an additional molar equivalent of I_2 to give the adduct RTe(I)I_2 [153].

The reaction of PhTeTePh with one equivalent of I_2 in diethyl ether produces black crystals of stoichiometry “ PhTeI ” which, in contrast to the other monohalides PhTeX ($\text{X} = \text{Cl}, \text{Br}$) (*vide supra*), is stable in the solid state. In the absence of bulky substituents on the aryl group, this species exists

as the tetramer $\text{Ph}_4\text{Te}_4\text{I}_4$ with a four-membered Te_4 ring [154]. However, the tetrameric structure is easily disrupted upon addition of PPh_3 to give the 1:1 adduct $\text{Ph}_3\text{PTe(Ph)I}$ [154]. Although this monomeric complex does not act as a source of PhTe^+ , aryltellurenyl cations stabilized by two-electron donors, *e.g.* PPh_3 or NHC, can be generated from mixed-valent ditellurium dihalides ArX_2TeAr (Section 3.3) as illustrated in Figure 2.19 [155, 156].

2.4 Conclusions

The reactivity, variety and, in some cases, ready access to Se/Te-halides facilitates the wide use of these reagents in the preparation of both inorganic and organic compounds. In particular, the commercial availability of the easily-manipulated tetrahalides E(IV)X_4 ($\text{E} = \text{Se}, \text{Te}$; $\text{X} = \text{Cl}, \text{Br}$) enables their applications in inorganic and organic synthesis. Although lower-valent dihalides E(IV)X_2 ($\text{E} = \text{Se}, \text{Te}$; $\text{X} = \text{Cl}, \text{Br}$) have a propensity for disproportionation, methods have been developed to allow their use as *in situ* reagents. Specifically, an extensive chemistry of selenium dihalides especially in organic synthesis, but also for the preparation of inorganic compounds, has emerged. To a lesser extent tellurium dihalides are also effective reagents in the form of adducts with Lewis bases, provided that the electron donors released in these reactions do not interfere with the desired transformation. In the case of selenium, the existence of a halides in a variety of formal

oxidation states, *e.g.*, SeCl_4 , SeOCl_2 , SeCl_2 and Se_2Cl_2 , has permitted the creative use of mixtures of these reagents for the synthesis of unusual selenium compounds.

In contrast to the binary systems, organoselenium(II) halides PhSe(II)X ($\text{X} = \text{Cl}, \text{Br}$) are commercially available, thermally and reasonably air-stable reagents that have wide applications in organic synthesis, notably for additions to carbon-carbon multiple bonds. On the other hand, the tellurium analogues PhTe(II)X , like their inorganic counterparts, are unstable towards disproportionation. However, this tendency can be suppressed by invoking the strategies of kinetic stabilization using either very bulky substituents on the tellurium atom or groups that provide intramolecular heteroatom-tellurium coordination. These strategies have also been applied to the preparation of reasonably stable organotellurium(IV) fluorides. The heavier organotellurium(IV) halides, as exemplified by REX_3 and R_2TeX_2 ($\text{R} = \text{alkyl, aryl}$; $\text{X} = \text{Cl, Br}$), are readily prepared and easily handled in the case of aryl derivatives. The multifunctionality of these reagents presages wide applications in synthesis, which have only been partially realized. A unique feature of organotellurium halides is the existence of mixed-valent species of the type $\text{RTe(IV)X}_2\text{Te(II)R}$. The synthetic potential of these reagents has only recently been exploited, *e.g.* in the generation of RTe^+ cations.

2.5 References

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Captions for Figures

Figure 2.1. Reactions of SeX_4 ($\text{X} = \text{Cl}, \text{Br}$) with Lewis bases: (i) tetrahydrothiophene; (ii) $\text{MeS}(\text{CH}_2)_2\text{SMe}$; $\text{X} = \text{Br}$ (iii) 2,5-diisopropylimidazole-2-ylidene; $\text{X} = \text{Cl}$ (iv) 1,4-di-*tert*-butyl-1,3-diazabutadiene; $\text{X} = \text{Cl}, \text{Br}$; (v) PPh_3 ; $\text{X} = \text{Cl}, \text{Br}$

Figure 2.2. Synthesis of a selenophene using SeOCl_2

Figure 2.3. Formation of imidoselenium(II) dichlorides $^t\text{ClSe}[\text{N}(^t\text{Bu})\text{Se}]_n\text{Cl}$ ($n = 1-3$) from reactions of SeCl_2 with $^t\text{BuNH}_2$

Figure 2.4. Insertion of selenium into a metal cluster using SeCl_2

Figure 2.5. Preparation of selenium-containing heterocycles using SeX_2 reagents ($\text{X} = \text{Cl}, \text{Br}$): (i) $(\text{HC}\equiv\text{C})_2\text{SiMe}_2$ (ii) *cis,cis*-1,5-cyclooctadiene (iii) $\text{E}(\text{CH}=\text{CH}_2)_2$ ($\text{E} = \text{S}, \text{Se}$) (iv) $\text{O}_2\text{S}(\text{CH}=\text{CH}_2)_2$ ($\text{X} = \text{Cl}$) (v) $\text{Ph}\equiv\text{CPh}$ ($\text{X} = \text{Br}$) (vi) 2,3-dimethoxy-1,3-butadiene

Figure 2.6. Synthesis of selenacalix[4]thiophenes from SeCl_2 with 3,4-dialkoxythiophenes ($\text{R} = \text{methyl}, \text{hexyl}$)

Figure 2.7. Preparation of selenium-nitrogen compounds from mixtures of selenium halides: (i) $^t\text{BuNH}_2$ (ii) $\text{LiN}(\text{SiMe}_3)_2$ (iii) $\text{Se}[\text{N}(\text{SiMe}_3)_2]_2$

Figure 2.8. Reactions of TeCl_4 with N-centred nucleophiles: (i) $\text{Li}[\text{N}(\text{SiMe}_3)\text{R}]$ (ii) LiNMe_2 (iii) $\text{Me}_3\text{SiNPR}_3$ ($\text{R} = \text{Me}, \text{Ph}$) (iv) $\text{Me}_3\text{SiNEPh}_2$ ($\text{E} = \text{C}, \text{S}$) (v) $\text{Li}_2[\text{PhB}(\text{N}^t\text{Bu})_2]$ (vi) $(\text{Me}_3\text{Si})_3\text{N}$

Figure 2.9. Reactions of TeX_4 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) with Lewis bases: (i) bis(arylimino)acenaphthene; $\text{R} = 2,6$ -diisopropylphenyl, mesityl (ii) 1,4-di-*tert*-butyl-1,3-diazabutadiene, $\text{X} = \text{Cl}, \text{Br}$ (iii) OPR_3 ($\text{R} = \text{Me}, \text{Ph}$), $\text{X} = \text{F}$ (iv) $\text{L} = \text{OPR}_3$ ($\text{R} = \text{Me}, \text{Ph}$), $\text{X} = \text{Cl}, \text{Br}$ (v) $\text{Ph}_2\text{P}(\text{Se})\text{CH}_2\text{P}(\text{Se})\text{PPh}_2$ (vi) $\text{RSCH}_2\text{CH}_2\text{SR}$ ($\text{R} = \text{Me}, ^i\text{Pr}$), $\text{X} = \text{Cl}, \text{Br}$

Figure 2.10. Addition of TeCl_4 to alkynes $\text{RC}\equiv\text{CR}$ ($\text{R} = \text{Et}, \text{Pr}$).

Figure 2.11. Synthesis of tellurophenes using (a) *in situ* TeCl_2 (b) the Lewis base adduct $(\text{bipy})\text{TeCl}_2$

Figure 2.12. Synthesis of tellurium compounds from Lewis base adducts of TeX_2 : (a) RMgCl ($\text{R} = \text{Ph}, \text{CH}_2\text{Ph}$), $\text{L} = \text{bipy}$, $\text{X} = \text{Cl}$ (ii) $^i\text{Pr}_2\text{IM}$, $\text{L} = \text{bipy}$, $\text{X} = \text{Cl}$ (iii) $\text{Li}[\text{HC}(\text{PPh}_2\text{Se})_2]$, $\text{L} = \text{tmtu}$, $\text{X} = \text{Cl}$ (iv) 2.5AgOTf , $\text{L} = \text{Dipp}_2\text{BIAN}$, $\text{X} = \text{I}$.

Figure 2.13. Decomposition pathways of ArTeCl_3 ($\text{Ar} = 2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2$)

Figure 2.14 Hydrolysis of ArTeCl_3 ($\text{Ar} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$)

Figure 2.15. Halogenation of 1,5-ditelluracyclooctane and subsequent ring-expansion upon thermolysis; (i) Cl_2 or I_2 in benzene at RT (ii) DMF, $160\text{ }^\circ\text{C}$, $\text{X} = \text{Cl}$ (iii) 6PhSH , NEt_3 , DMSO, $50\text{ }^\circ\text{C}$

Figure 2.16. Synthesis of a mixed-valent aryltellurenyl halides $\text{ArX}_2\text{TeTeAr}$

Figure 2.17. Preparation of selenirenium ions from $\text{PhSeCl}/\text{SbCl}_5$ and alkynes

Figure 2.18. Adducts of ArTeI with (a) iodide ion ($\text{Ar} = 2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2$) (b) $\text{SePPh}_2(\text{CH}_2)_n\text{Ph}_2\text{PSe}$ ($n = 1,2$) ($\text{Ar} = \text{Mes}$) and (c) TeMes_2 ($\text{Ar} = \text{Mes}$)

Figure 2.19. Synthesis of phosphine and carbene adducts of PhTe^+ : $\text{Ar} = \text{Bbt}$ (upper reaction); $2,6\text{-Mes}_2\text{C}_6\text{H}_3$ (lower reaction)