Selenium-containing π-Bond Compounds of Heavier Main-Group Elements

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Abstract

This review highlights the unique chemistry of π-bond compounds consisting of both selenium and other heavier main-group element, which exhibit intriguing reactivity and potential applications in catalysis, materials science, and bioinorganic chemistry. While selenium shares similarities with sulfur, its larger atomic size and greater polarizability give Se-containing double bonds distinctive characteristics that often result in higher reactivity. This review will focus on recent advancements of compounds that contain a π-bond containing selenium and other heavier main-group elements as well as unique π-conjugated systems, rather than on well-established compounds such selenoketones and selenoamides.

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1. Introduction

1.1 General introduction

Selenium, a member of the chalcogen family (group-16 elements), exhibits a rich and versatile chemistry that has garnered significant attention in recent decades[1]. Among its various bonding modes, the formation of double bonds involving selenium is of particular interest due to its implications in a wide array of chemical and biological processes. Indeed, compounds featuring selenium double bonds offer intriguing properties, including unique reactivity patterns and potential applications in catalysis, materials science, and bioinorganic chemistry[1,2]. Despite the structural similarities between selenium and sulfur, the chemistry of selenium double bonds reveals distinct characteristics arising from the larger atomic size, lower electronegativity, and greater polarizability of selenium. These factors influence the stability, electronic properties, and reactivity of selenium-containing double-

bond systems. As a result, selenium double bonds often exhibit reactivity higher than their sulfur counterparts, unlocking avenues for the development of new synthetic methodologies.

This review aims to provide a comprehensive overview of recent advancements in the study of selenium double-bond compounds, focusing on their synthesis, structural features, and fundamental reactivity. By comparing the behavior of selenium-based double-bond systems with systems that contain other group-16 elements, we seek to highlight the unique features of selenium chemistry and its potential for further exploration in both fundamental and applied research. It should be noted here that simple double-bond systems that contain selenium and second-row-elements such as selenoketones and selenoamides have already been introduced and discussed in several reviews/books[2,3], and will thus not be considered in this review. This mini-review focuses on recent examples of compounds with double bonds that contain selenium and other heavier main-group elements as well as unique π-conjugated systems that include selenium. These reactive Se-containing double-bond systems are often stabilized by intermolecular coordination from an electron-donor, which electronically perturbs the intrinsic nature of the Se-π bonds.

1.2. Theoretical aspects

For many years, it had been commonly accepted that compounds that contain double bonds between heavier main-group elements are most likely unstable species due to their substantially higher reactivity compared to that of their second-row-element analogues ("double-bond rule")[4]. Although several examples of C=S and C=Se double-bond compounds had been isolated and characterized, examples of selenium-containing double-bond compounds with a heavier main-group element remained elusive. However, following the pioneering reports on the synthesis and isolation of the first stable disilene[5] and diphosphene[6] in 1981 by the groups of West and Yoshifuji, respectively, it was demonstrated that compounds with double bonds between heavier main-group elements can be isolated as stable compounds when sufficiently stabilized by sterically demanding substituents (kinetic stabilization)[7]. After this breakthrough, the so-called heavy ketones (E=Ch double-bond compounds; E = Si, Ge, Sn, Ch = S, Se, Te), i.e., the heavier-element analogues of ketones, were successfully synthesized, isolated, and fully characterized[8].

The predominant reason for the difficulties associated with the isolation of compounds that contain a double bond between heavier main-group elements is that the bonding energy of a π-bond between heavier main-group elements is very small relative to the corresponding σ-bond energy, which causes facile oligomerization even under inert atmospheres. As shown in **Table 1-1**[9], the energy of the Se=E (E = C, Si, Ge, Sn, Pb) π-bonds is significantly lower than the energy of the corresponding σ-bonds and of the (S=E) π-bond energy of the corresponding sulfur analogues.

Table 1-1. Energy values (kcal/mol) and lengths (Å) of the σ-bond energy and π-bond energy of $Ch=EH_2$ (E = C, Si, Ge, Sn, Pb) compounds.

Ch=EH2		Ch = O	Ch = S	Ch = Se	Ch = Te
E = C	σ-BE[a]	93.6	73.0	65.1	57.5
	π-BE[b]	95.3	54.6	43.2	32.0
	distance[c]	1.200	1.617	1.758	1.949
E = Si	σ-BE[a]	119.7	81.6	73.7	63.2
	π-BE[b]	58.5	47.0	40.7	32.9
	distance[c]	1.514	1.945	2.082	2.288
E = Ge	σ-BE[a]	101.5	74.1	67.8	59.1
	π-BE[b]	45.9	41.1	36.3	30.3
	distance[c]	1.634	2.042	2.174	2.373
E = Sn	σ-BE[a]	94.8	69.3	64.3	56.4
	π-BE[b]	32.8	33.5	30.6	26.3
	distance[c]	1.802	2.222	2.346	2.543
E = Pb	σ-BE[a]	80.9	60.9	57.0	50.3
	π-BE[b]	29.0	30.0	27.8	24.4
	distance[c]	1.853	2.273	2.394	2.590

[a] Ch=E s-bond energy (kcal/mol); [b] Ch=E p-bond energy (kcal/mol); [c] Ch=E distance (Å).

Natural-bond-orbital (NBO) calculations on the bonding character of Se=E double bonds (E = group 13-15 elements)[10], suggested that the Se=E σ-bonds should be composed of a –60% contribution from the Se atom with its sp^n hybridized orbital (n > 4.7), reflecting the intrinsic nature of unfavorable formation of hybridized orbitals in heavier main-group elements. The π-bonds of Se=E should consist predominantly of contributions from the p-orbital of the Se atom (>60%) probably due to the larger effective nuclear charge for the valence orbitals of the Se atom. Accordingly, the Se atoms should be negatively charged relative to the bonding E atoms. It should also be noted here that a nucleophile, such as a phosphine or alkyl lithium, sometimes attacks the Se atom of Se=E compounds despite the negative charge of the Se atom, which is probably due to the low-lying π* orbitals of the Se=E bonds that spreading largely around the Se atom. This bonding behavior should result in amphiphilic character of the Se atoms in Se=E compounds.

Table 1-2. Bonding characters, bond lengths (Å), and natural charges for Ch=EH₂ (E = C, Si, Ge, Sn, Pb) compounds calculated at the B3PW91-D3(BJ)/def2TZVPP level using Gaussian 16 (rev. C) and NBO 7.0.

E=Se (Å) σ: E + Se π: E + Se NPA: E, Se	group-13 HE=Se (E = B, Al, Ga, In, Tl)	group-14 H2E=Se (E = C, Si, Ge, Sn, Pb)
2nd row	**E = B**: HB=Se: 1.7279 σ: B(sp$^{1.04}$, 43.5%)+Se(sp$^{2.88}$, 56.5%) π: B(p, 25.3%)+Se(p, 74.7%) π: B(p, 25.3%)+Se(p, 74.7%) NPA: B(+0.15), Se(–0.10)	**E = C**: H₂C=Se: 1.7441 σ: C(sp$^{1.80}$, 58.1%)+Se(sp$^{4.67}$, 41.8%) π: C(p, 46.3%)+Se(p, 53.7%) NPA: C(–0.54), Se(+0.16)
3rd row	**E = Al**: HAl=Se: 2.1238 σ: Al(sp$^{0.89}$, 31.5%)+Se(sp$^{4.88}$, 68.5%) π: Al(p, 14.0%)+Se(p, 86.0%) π: Al(p, 14.0%)+Se(p, 86.0%) NPA: Al(+1.13), Se(–0.78)	**E = Si**: H₂Si=Se: 2.0743 σ: Si(sp$^{1.67}$, 41.2%)+Se(sp$^{4.72}$, 58.8%) π: Si(p, 28.3%)+Se(p, 71.7%) NPA: Si(+0.79), Se(–0.45)
4th row	**E = Ga**: HGa=Se: 2.1252 σ: Ga(sp$^{0.91}$, 36.1%)+Se(sp$^{5.19}$, 63.8%) π: Ga(p, 14.3%)+Se(p, 85.7%) π: Ga(p, 14.3%)+Se(p, 85.7%) NPA: Ga(+0.93), Se(–0.69)	**E = Ge**: H₂Ge=Se: 2.1529 σ: Ge(sp$^{1.69}$, 43.0%)+Se(sp$^{5.84}$, 57.0%) π: Ge(p, 28.1%)+Se(p, 71.9%) NPA: Ge(+0.74), Se(–0.45)
5th row	**E = In**: HIn=Se: 2.2979 σ: In(sp$^{0.85}$, 36.9%)+Se(sp$^{8.20}$, 63.2%) π: In(p, 12.1%)+Se(p, 87.9%) π: In(p, 12.1%)+Se(p, 87.9%) NPA: In(+1.03), Se(–0.74)	**E = Sn**: H₂Sn=Se: 2.3290 σ: Sn(sp$^{1.57}$, 42.3%)+Se(sp$^{7.70}$, 57.7%) π: Sn(p, 23.7%)+Se(p, 76.3%) NPA: Sn(+0.95), Se(–0.57)
6th row	**E = Tl**: HTl=Se: 2.3322 σ: Se(sp$^{10.5}$)→Tl(p) (coordination) π: Tl(p, 11.4%)+Se(p, 88.6%) π: Tl(p, 11.4%)+Se(p, 88.6%) NPA: Tl(+0.90), Se(–0.68)	**E = Pb**: H₂Pb=Se: 2.4040 σ: Pb(sp$^{1.47}$, 46.9%)+Se(sp$^{11.28}$, 53.1%) π: Pb(p, 21.2%)+Se(p, 78.8%) NPA: Pb(+0.87), Se(–0.54)

E=Se (Å) σ: E + Se π: E + Se NPA: E, Se	group-15 HE=Se (E = N, P, As, Sb, Bi)	group-16 E=Se (E = O, S, Se, Te, Po)
2nd row	**E = N**: HN=Se: 1.7110 σ: N(sp$^{3.42}$, 64.1%)+Se(sp$^{5.96}$, 35.9%) π: N(p, 56.2%)+Se(p, 43.8%) NPA: N(–0.74), Se(+0.42)	**E = O**: O=Se: 1.6401 σ: O(sp$^{4.41}$, 69.3%)+Se(sp$^{6.81}$, 30.7%) π: O(p, 65.7%)+Se(p, 34.3%) NPA: O(–0.68), Se(+0.68)
3rd row	**E = P**: HP=Se: 2.0718 σ: P(sp$^{5.37}$, 45.8%)+Se(sp$^{5.95}$, 54.2%) π: P(p, 41.5%)+Se(p, 58.5%) NPA: P(+0.25), Se(–0.18)	**E = S**: S=Se: 2.0380 σ: S(sp$^{6.85}$, 53.1%)+Se(sp$^{7.71}$, 46.9%) π: S(p, 53.2%)+Se(p, 46.8%) NPA: S(–0.12), Se(+0.12)

4th row	**E = As**: HAs=Se: 2.1823	**E = Se**: Se=Se: 2.1737
	σ: As(sp$^{7.07}$, 44.0%)+Se(sp$^{6.71}$, 56.0%)	σ: Se(sp$^{8.88}$, 50.0%)+Se(sp$^{8.88}$, 50.0%)
	π: As(p, 39.9%)+Se(p, 60.1%)	π: Se(p, 50.0%)+Se(p, 50.0%)
	NPA: As(+0.35), Se(−0.26)	NPA: Se(0.0), Se(0.0)
5th row	**E = Sb**: HSb=Se: 2.3594	**E = Te**: Te=Se: 2.3628
	σ: Sb(sp$^{7.98}$, 40.1%)+Se(sp$^{7.64}$, 59.9%)	σ: Te(sp$^{10.20}$, 45.4%)+Se(sp$^{9.95}$, 54.6%)
	π: Sb(p, 35.2%)+Se(p, 64.8%)	π: Te(p, 44.8%)+Se(p, 55.2%)
	NPA: Sb(+0.61), Se(−0.43)	NPA: Te(+0.19), Se(−0.19)
6th row	**E = Bi**: HBi=Se: 2.4427	**E = Po**: Po=Se: 2.4529
	σ: Bi(sp$^{11.7}$, 39.4%)+Se(sp$^{8.81}$, 60.6%)	σ: Po(sp$^{14.81}$, 44.2%)+Se(sp$^{11.24}$, 55.8%)
	π: Bi(p, 34.2%)+Se(p, 65.8%)	π: Po(p, 43.4%)+Se(p, 56.6%)
	NPA: Bi(+0.66), Se(−0.47)	NPA: Po(+0.25), Se(−0.25)

Given that there have recently been reported several examples of Se-containing π-bond compounds with heavier main-group elements, which have been isolated by using kinetic and/or thermodynamic stabilization, we will introduce in the next section the synthesis and structural features of these examples.

2. Group-13 – Selenium π-bond compounds

Figure 2-1. Isolobal relationship between the carbonyl group and its heavier main-group analogues.

E^{14} = group-14 elements; E^{13} = group-13 elements; Ch = group-16 elements

a) The first transient oxoborane **A** (West)
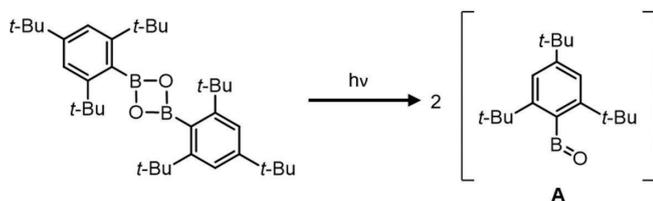
b) The first transient thioxoborane **B** (Okazaki)
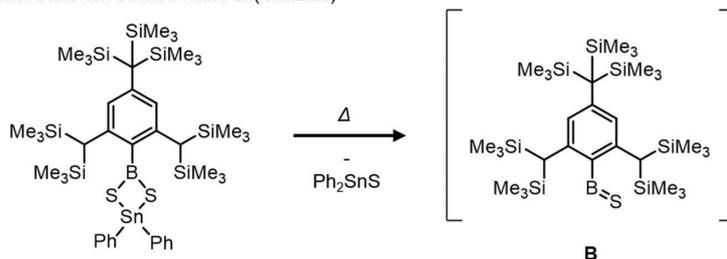
c) The first stable oxoborane complex **C** (Cowley)
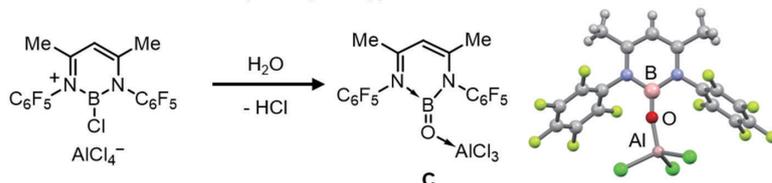
Figure 2-2. Pioneering studies on a) oxoborane **A**, b) thioxoborane **B**, and c) oxoborane complex **C**.

Due to the synthetic importance of the carbonyl group, the synthesis of their main-group analogues containing a multiple bond to a group-16 element (Ch = O, S, Se, Te) has been investigated extensively. As group-13 elements (E^{13} = B, Al, Ga, In, Th) are more electropositive than carbon, the resulting E^{13}=Ch bonds are highly polarized compared to the carbonyl C=O bond (**Figure 2-1**). Unfortunately, the isolation of compounds with E^{13}=Ch bonds is usually difficult due to self-oligomerization. A pioneering study on transient oxoborane **A** was reported by West and co-workers, who generated it via the irradiation of 1,3-dioxa-2,4-boretane[11]. The elusive nature of **A**

indicates that the bulky aryl group, Mes*, is insufficient to kinetically stabilize this highly reactive oxoborane species at ambient temperature (**Figure 2-2a**). The first example of compounds with an E^{13}=S bond, i.e., thioxoborane **B** with a bulky aryl substituent, was reported by Okazaki and co-workers in 1996 (**Figure 2-2b**)[12]. In 2005, Cowley and co-workers reported that the isolation of the first example of a monomeric stable oxoborane bearing a B=O moiety (**C**)[13]. The compound was synthesized using a β-diketiminate as a supporting ligand for boron, and it was stabilized by the addition of the Lewis acid $AlCl_3$. Further investigations led to the synthesis of several compounds that contain E^{13}=Ch multiple bonds[14,15]. However, examples of E^{13}=Se compounds are more scarce compared to other chalcogenides due to the high propensity for dimerization of the E^{13}=Se bond. In this chapter, the synthesis and properties of compounds with an E^{13}=Se bond are described.

2.1. B=Se compounds
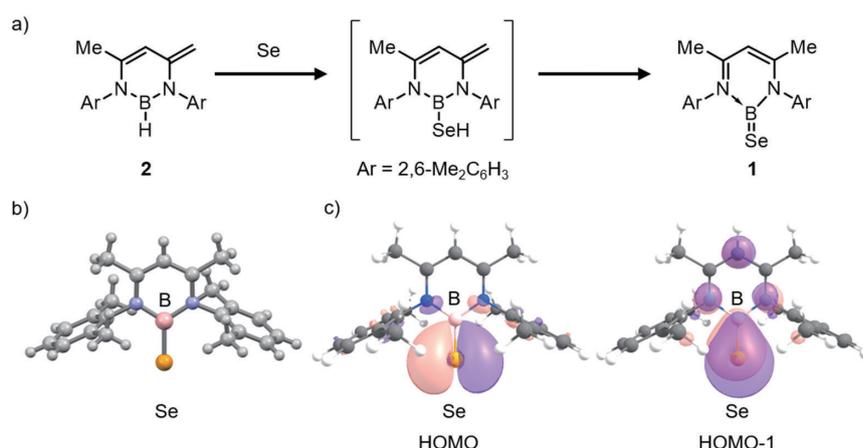
Figure 2-3. a) Synthesis of stable selenoxoborane **1**. b) Molecular structure of **1** in the crystalline state. c) Representations of the frontier orbitals of **1**.

In 2010, Cui and co-workers reported the synthesis of stable selenoxoborane **1** as orange crystals from the reaction of hydroborane **2**, which bears a β-diketiminate ligand, with **1** equivalent of elemental selenium at 70 °C in toluene[16]. The formation mechanism was interpreted in terms of a B-H bond insertion of selenium, followed by an H-migration to the exocyclic methylene group (**Figure 2-3a**). Selenoxoborane **1** is extremely air- and moisture-sensitive. The ^{11}B NMR spectrum of **1** exhibits a broad resonance at 40.88 ppm, which is downfield-shifted relative to that of **2** (29.3 ppm). The ^{77}Se NMR resonance for **1** is observed at -196 ppm. The molecular structure of **1** in the crystalline state revealed that the length of the B-Se bond (1.896(4) Å) is comparable to Pyykkö's standard value for a B-Se double bond (1.85 Å), and significantly shorter than those of reported B-Se single bonds (1.960-2.13 Å) (**Figure 3b**)[17-22]. The central boron atom adopts an approximately trigonal-planar coordination geometry. These structural features are consistent with a B-Se multiple bond. The bonding situation was furthermore analyzed by theoretical calculations on the Kohn-Sham orbitals of **1**, which revealed that the HOMO corresponds predominantly to the selenium lone pair and that the HOMO-1 refers to the B-Se π-bond.
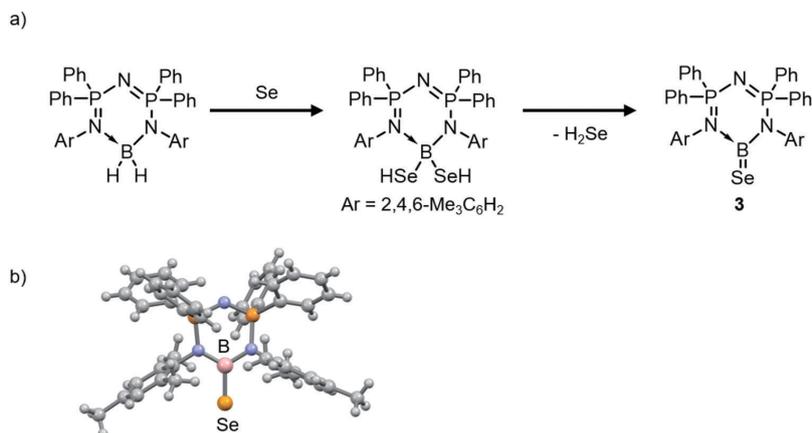
Figure 2-4. Synthesis of stable selenoxoborane **3**. b) Molecular structure of **3** in the crystalline state.

Singh and co-workers have obtained bis(phosphinimino)amide-substituted selenoxoborane **3** from the reaction of a hydroborane with elemental selenium (**Figure 2-4a**)[23]. Compound **3** exhibits structural features and properties similar to those of **1**. The ^{11}B NMR spectrum of **3** shows a broad singlet resonance at 45.2 ppm, similar to the shift for **1** (40.88). The length of the B-Se bond (1.871(5) Å) is almost identical to that of **1** (1.896(4) Å).
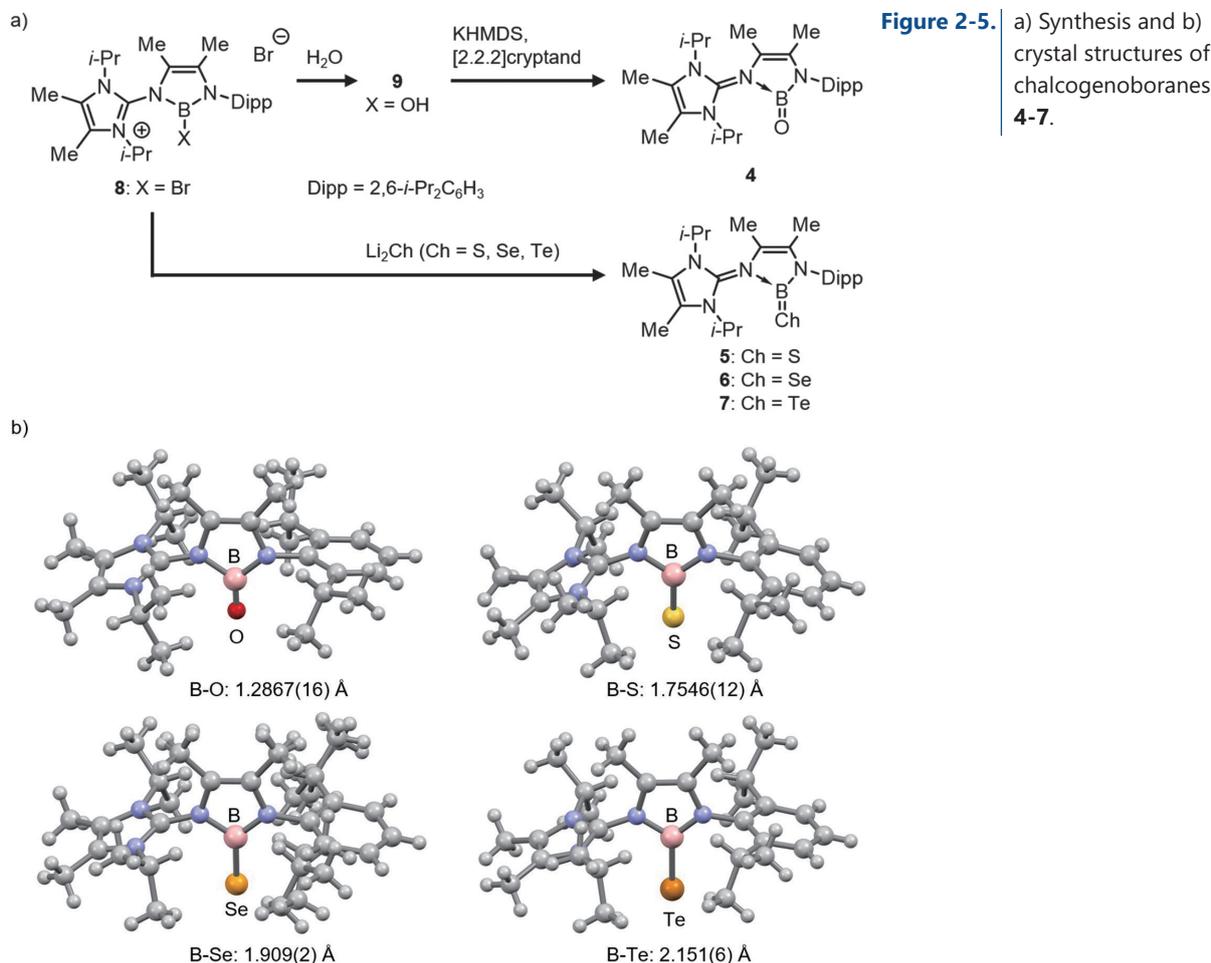
Figure 2-5. a) Synthesis and b) crystal structures of chalcogenoboranes **4-7**.

Trzaskowski and Frank have reported the synthesis of a series of chalcogenoxoboranes (**4-7**) using the same NacNac-type ligand, i.e., HAmIm (**Figure 2-5**)[24]. Oxoborane **4** was obtained from the reaction of bromoborane **8** with H_2O to give the hydroxyborane **9**, followed by a deprotonation reaction with KHMDS in the presence of [2.2.2] cryptand. Heavier B=Ch compounds **5-7** were synthesized by the reaction of bromoborane **8** with the corresponding lithium chalcogenides (Li_2Ch; Ch = S, Se, Te). The ^{11}B NMR spectra of **4-7** show similar values (21.4 ppm for **4**, 35.2 ppm for **5**, 35.8 ppm for **6**, and 30.2 ppm for **7**). The crystal structures of **4-7** revealed that all compounds contain a boron center with a trigonal-planar coordination geometry and B-Ch double-bond character. The length of the B=Se bond in **7** (1.909(2) Å) is the longest B=Se distance reported so far. The Wiberg bond indices (WBIs) decrease continuously with increasing atomic number of the chalcogen element from 1.86 in **4** to 1.69 in **7**, which indicates diminished π-π interactions between the boron atom and the heavier chalcogen atoms. Meanwhile, the values for **4-7** (>1.60) justify the formulation of the B=Ch bonds as true double bonds.
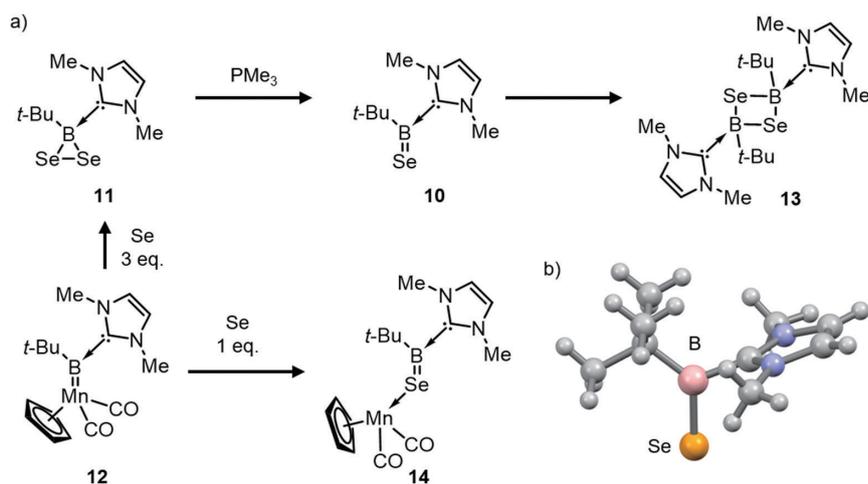
Figure 2-6. a) Synthesis of selenoxoborane **10**, its dimer **13**, and Mn complex **14**. b) Crystal structure of **13**.

Braunschweig and co-workers have reported the synthesis of *N-heterocycliccarbene* (NHC)-stabilized selenoxoborane **10** via the deselenization of boradiselenirane **11**, which was obtained from the reaction of borylene complex **12** with elemental selenium (**Figure 2-6**)[25]. At 60 °C, **10** slowly dimerizes (48 h) to give four-membered cycle **13**. The ^{11}B NMR spectrum of **10** exhibits a broad resonance at -2.9 ppm, which is upfield-shifted relative to that of **1** (40.88 ppm). The ^{77}Se NMR resonance of **10** is observed at 250 ppm, which is significantly downfield-shifted compared to that of **1** (-196 ppm) and upfield-shifted relative to that of previous reported selenoxoborane Mn complex **14** (370 ppm)[26]. The crystal structure of **10** revealed a length of the B-Se bond (1.876(4) Å) and a coordination geometry (trigonal planar) of the boron atom that are typical for selenoxoboranes.

2.2. Al=Se compounds
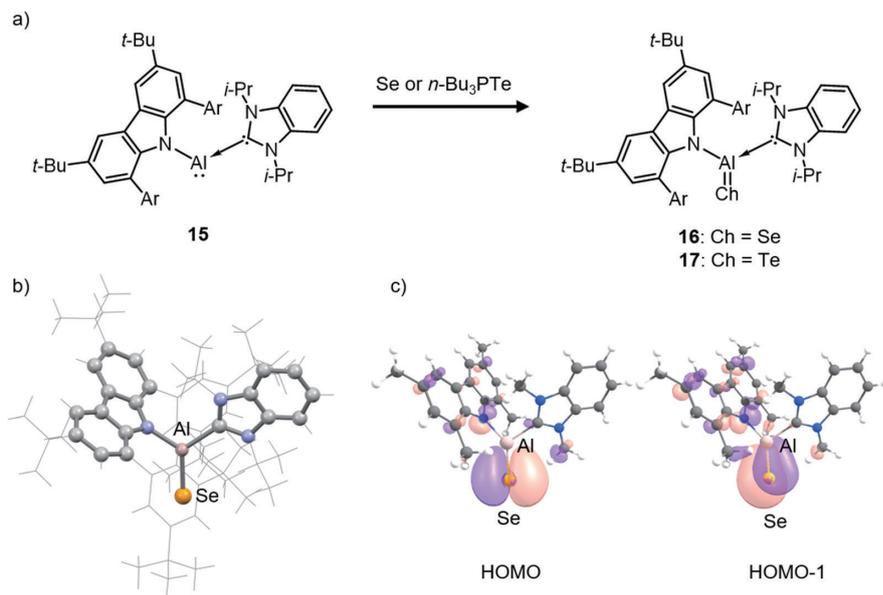
Figure 2-7. Synthesis of stable selenoxoalumane **16** and telluroxoalumane **17**. b) Crystal structure of **16**. c) Kohn-Sham frontier orbitals of **16**.

In 2023, Braunschweig and co-workers reported the synthesis of neutral aluminum selenide **16** by reacting NHC-stabilized alumylene **15** with elemental selenium in almost quantitative yield (**Figure 2-7**)[27]. Inoue and co-workers had previously attempted the synthesis of a neutral aluminum selenide, but obtained only the corresponding dimer[28]. The ^{77}Se NMR spectrum of **16** exhibits a characteristic resonance signal at -264 ppm, which is up-field shifted compared to those of the compounds with B=Se bonds (**Table 1**). The crystal structure of **16** revealed that the central Al atom adopts a tricoordinate distorted trigonal-planar coordination geometry with an angle sum

around Al of 359.8°. The Al-Se bond (2.1935(8) Å) is currently the shortest reported Al-Se bond, and comparable to Pyykkö's standard value for an Al-Se double bond (2.20 Å). The WBI for the Al-Se bond in **16** (1.31) is smaller than that for tellurium derivative **17** (1.47). The Kohn-Sham orbitals of **16** show that the HOMO corresponds mainly to the selenium lone pair and the HOMO-1 to the Al-Se π-bond (**Figure 2-7c**). The NBO charges of Al (+1.56 for **16**, +1.40 for **17**) and Ch (−1.05 for **16**, −0.89 for **17**) suggest a considerable amount of charge separation. The NBO results suggest that the Al-Se bond is more polar than the Al-Te bond, which is consistent with the fact that the electronegativity of Se (2.55) is higher than that of Te (2.12). Furthermore, an intrinsic-bond-orbital (IBO) analysis indicated the presence of a single Al-Ch σ-bond, strengthened by the electrostatic attraction between the Al^+ and Se^- centers as well as a slight donation from the lone pairs of Se to the vacant orbitals at Al. These results suggest multiple-bond character for the Al-Se bond, albeit with an ambiphilic nature.
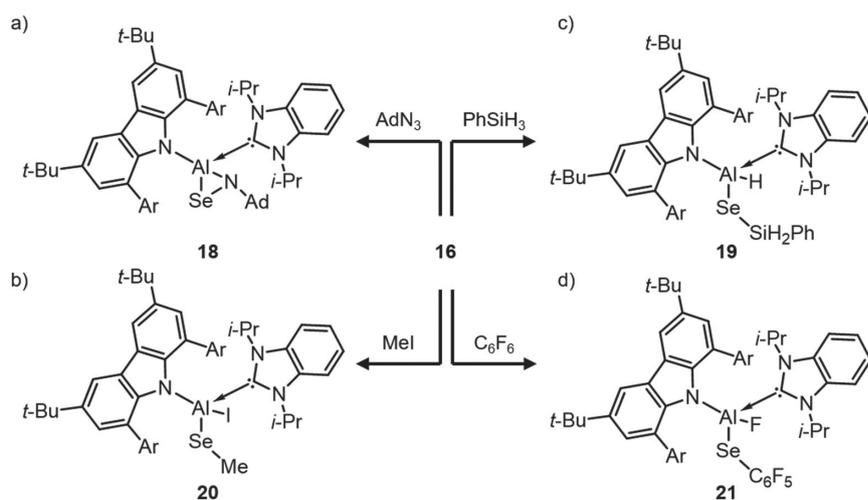
Figure 2-8. Reactivity of selenoxoborane **16**.

The reactivity of **16** corroborates its proposed ambiphilic multiple-bond character (**Figure 2-8**). The reaction of **16** with adamantylazide (AdN_3) in toluene at room temperature rapidly afforded **18** with a three-membered Al-N-Se cycle, which is the first example of an aluminum and selenium containing analog of aziridine (**Figure 2-8a**). Compound **18** is likely formed via a [3 + 2] cycloaddition of AdN_3 with **16** followed by N_2 elimination. Furthermore, **16** can activate small molecules such as methyl iodide (MeI), phenylsilane ($PhSiH_3$), and perfluorobenzene (C_6F_6), whereby the corresponding C–I, Si–H, and C–F bonds are cleaved to furnish addition products **19**, **20**, and **21**, respectively.
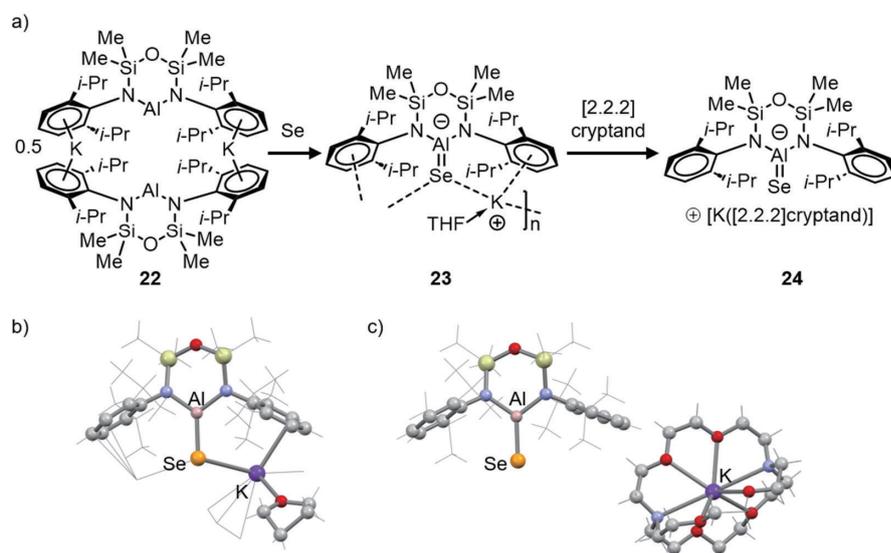
Figure 2-9. a) Synthesis and b,c) crystal structures of anionic selenoxoalumanes **23** and **24**.

In 2019, Coles and co-workers reported the synthesis of anionic selenoxoalumane [K(THF)][Al(NON^{Ar})(Se)] (NON^{Ar} = [O(SiMe$_2$NAr)$_2$]$^{2-}$, Ar = 2,6-i-Pr$_2$C$_6$H$_3$) (**23**) by reacting aluminyl anion Al(NON^{Ar})$^-$ (**22**) with elemental selenium (**Figure 2-9a**)[29]. The crystal structure of **23** revealed the formation of an infinite chain structure by linking K$^+$ cations through Se···K and π-arene interactions. In the crystal, the aluminum center adopts a three-coordinate distorted trigonal-planar coordination environment with a short Al-Se bond (2.225(1) Å). The selenium atom interacts with two solvated potassium cations (Se···K: 3.2965(10) Å/3.3730(10) Å) to form a one-dimensional chain. To isolate the aluminum-selenium bond from Se···K interactions, the reaction was performed in the presence of [2.2.2]cryptand, which provided selenoxoalumane **24**, wherein the potassium cation is fully solvated by the [2.2.2] cryptand. The Al–Se bond in **24** (2.2032(6) Å) is shorter than that of **23**, confirming that the Se···K interactions in **24** cause a slight elongation of the bond. The WBI for the Al-Se bond in **24** (1.39) is slightly higher than that of **16** (1.31), which indicates the presence of significant multiple-bond character in **24**. The NBO charges in **24** for Al (+1.61) and Se (–1.06) are indicative of a slightly higher polarization of the Al–Se bond in **24** compared to that in **16**. The spectroscopic analysis of **23** was limited by its low solubility and/or instability in common solvents, whereas **24** allowed for a successful analysis due to its improved solubility. The ^{77}Se NMR spectrum of **24** displays a singlet at -563 ppm, which is upfield-shifted compared to those of reported E^{13}=Se compounds.
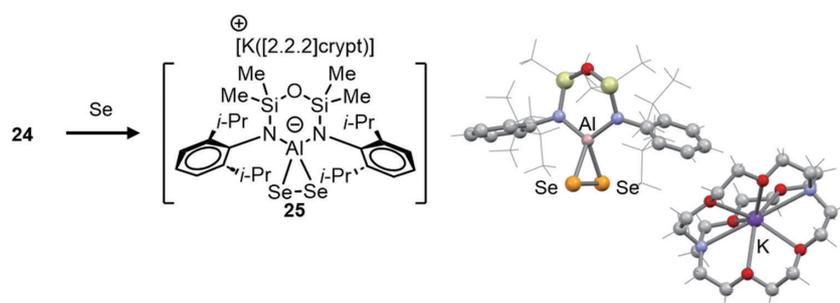
Figure 2-10. Reactivity of selenoxoalumane **24**.

Treatment of selenoxoalumane **24** with an equimolar amount of elemental selenium in THF afforded diselenirane **25** as bright purple crystals (**Figure 2-10**).

3. Group-14 – Selenium π-bond compounds

Arguably the most common molecules containing a π-bond between group-14 elements (E^{14} = C, Si, Ge, Sn, Pb) and group-16 elements (Ch = O, S, Se, Te) are ketones. Heavy ketones (R$_2$E^{14}=Ch), which feature a double bond between heavier group-14 and -16 elements, are attractive synthetic targets due to their unique properties and high reactivity. Among these, selenium analogues are particularly valuable because their electronic state in solution can be analyzed using ^{77}Se NMR spectroscopy. Unfortunately, their isolation is usually difficult due to self-oligomerization (as in the case of E^{13}=Ch species; *vide supra*). The study of selenium-containing heavy ketones has a long history, beginning with Burton and co-workers, who reported in 1975 the synthesis of di-t-butylselenoketone (**D**) as the first monomeric compound of this class (**Figure 3-1**)[30]. Subsequently, in 1989, Corriu and co-workers reported the first silaneselone derivatives (**E**) stabilized by an intramolecular N→Si donor-acceptor interaction (thermodynamic stabilization)[31]. This method, remains widely used today and has become one of the strongest tools for stabilizing highly reactive species of main-group elements. Another primary method for stabilizing reactive main-group elements species is the previously mentioned kinetic stabilization by taking advantage of steric protection groups. Pioneering work on stable heavy ketones with a terminal group-16 element has been reported mainly by Okazaki and Tokitoh through the introduction of bulky 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl and 2,6-bis(bis(trimethylsilyl)methyl)-4-(tris(trimethylsilyl)methyl)phenyl groups to group-14 elements[8]. The Ge-Se bond in germaneselone **F** (2.180(2) Å) is comparable to Pyykkö's standard value for a Ge-Se double bond (2.18 Å) [17,32], while, those of thermodynamically stabilized germaneselones show slightly longer (2.194(1) Å-2.237(2) Å) due to the effect of zwitterionic canonical structures (**Figure 3-1b**)[33-54]. However, such base-stabilization

(thermodynamic stabilization) provides access only to a relatively limited range of heavier analogues of common, small organic molecules such as ketones. In this chapter, notable achievements of new types of E^{14}=Se species, such as heavier analogues of carboxylic acids, acylium ions, carbon dioxide, and carbonyl ylides, are described.

a) The first monomeric selenoketone **D** (Barton)
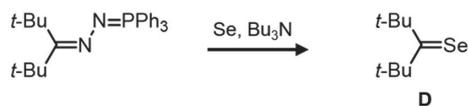
b) The first silaneselenone **E** (Corriu)
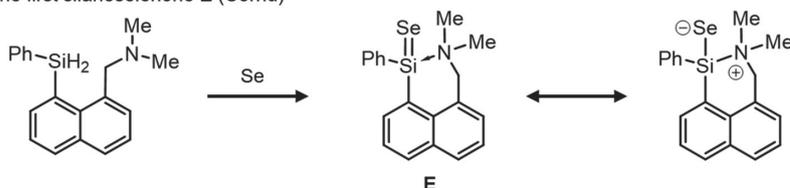
c) The first germaneselone **F** (Okazaki and Tokitoh)
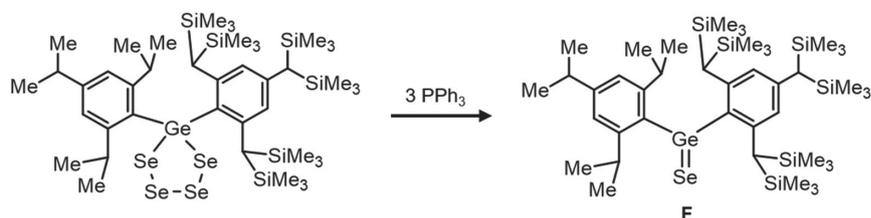
Figure 3-1. Pioneering studies on a) selenoketone **D**, b) silaneselone **E**, and c) germaneselone **F**.

3.1. Heavier analogues of carboxylic acids

a)

27   Ar = 2,6-i-PrC$_6$H$_3$

28: Ch = S
29: Ch = Se

b)

c)
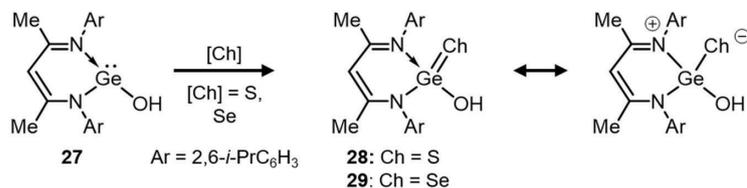
Figure 3-2. a) Synthesis of chalcogenogermanoic acids **28** and **29** as well as packing structures for b) **28** and c) **29**.
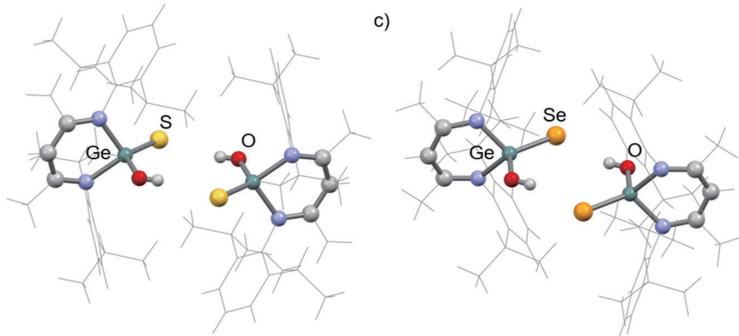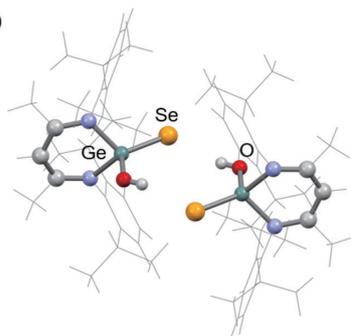
In 2004, Roesky and co-workers reported the synthesis of thiogermanoic acid **28** as the first heavier carboxylic acid, by reacting hydroxygermylene **27** with elemental sulfur (**Figure 3-2**)[55]. In 2006, selenogermanoic acid **29** was obtained by the same manner using elemental selenium instead of elemental sulfur[37]. The OH stretching frequency of **29** shows a broad absorption at 3299 cm^{-1}, which is at slightly higher wavenumber than that of **28** (3238 cm^{-1}). These values are significantly shifted to lower wavenumbers compared to that of **27** (3571 cm^{-1}), indicating the formation of hydrogen bonds in **28** and **29**. In the ^{1}H NMR spectra of **28** and **29**, their OH protons were observed at 2.30 ppm and 2.19 ppm, respectively, which are significantly upfield-shifted compared to carboxylic acids, indicating the weaker acidity for **28** and **29** than for common carboxylic acids. The ^{77}Se NMR

resonance of **29** is observed at –439 ppm, which falls within the range of compounds exhibiting ylide-type and multiple-bond character at the germanium-selenium moiety[56]. In the crystal, **29** exists as a selenoxo tautomeric form of hydrogen-bonded dimers with weak intermolecular hydrogen interactions. The length of the Ge-Se bond in **29** (2.206(1) Å) is comparable to Pyykkö's standard value for a Ge-Se double bond (2.18 Å), and very much consistent with resonance-structure contributions from both a Ge-Se ylide-type bond and a multiple bond rather than a pure germanium-selenium single bond (2.37 Å)[17]. The pKa values of **28** (37.2) and **29** (38.3) fall in the range expected for aromatic (–33) and aliphatic (–48) compounds. Importantly, these values are significantly lower than those observed for representative oxygen-containing Brønsted acids (–15) [57].
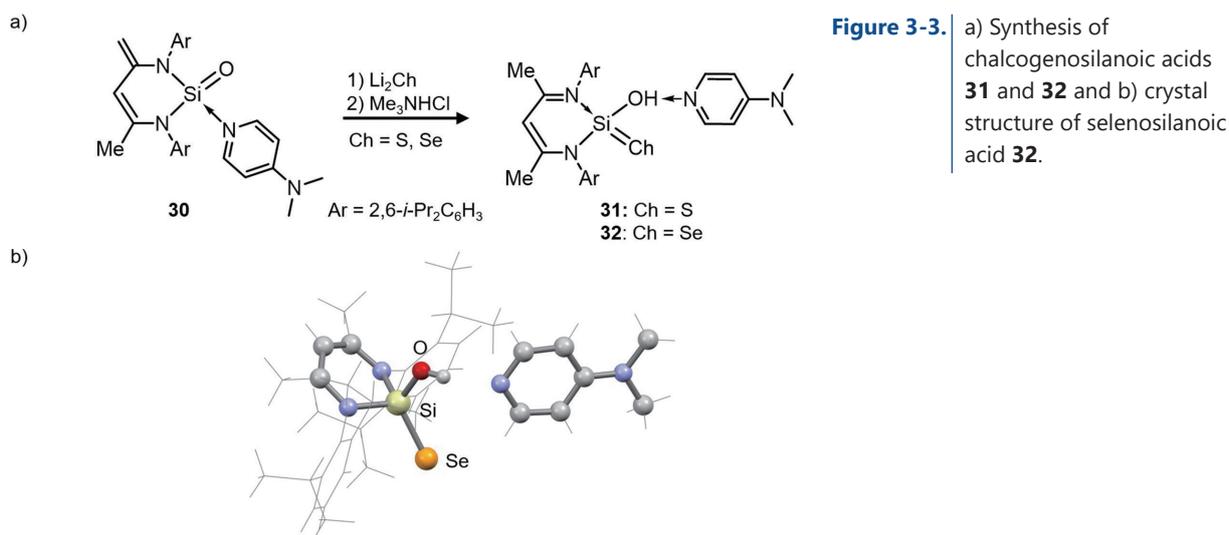
Figure 3-3. a) Synthesis of chalcogenosilanoic acids **31** and **32** and b) crystal structure of selenosilanoic acid **32**.

Subsequently, in 2013, Driess and co-workers reported the synthesis of the stable selenosilanoic acid-base adduct of the type [LSi(Se)=OH(dmap)] (**32**) by reacting silanone complex **30** with H_2Se (**Figure 3-3**)[58]. Compound **32** is the heavier analogue of a carboxylic acid and its sulfur analogue of the type [LSi(S)=OH(dmap)] (**31**), which had been reported by the same group in 2010[59]. In the ^{1}H NMR spectra of **31** and **32** their OH protons are observed at 6.35 and 6.42 ppm, respectively, which are significantly downfield-shifted compared to those of germanium derivatives **28** and **29**. The ^{77}Se NMR resonance of **32** is observed at –545 ppm, which is similar to that of germanium derivative **29**. The crystal structures of **31** and **32** show that they are acid-base complexes, wherein one dmap ligand is connected to the chalcogenosilanoic-acid moiety through an O-H···N hydrogen bond. The length of the Si-Se bond in **32** (2.1348(7) Å) is close to Pyykkö's standard value for a Si-Se double bond (2.14 Å)[17].

3.2. Heavier analogues of acylium ions

Koley and Inoue have reported the synthesis of NHC-stabilized germa-acylium ion **34** by reacting germyliumylidene ion **33** with N_2O[60]. Subsequently, the reaction of **34** with Lawesson's reagent (LR) and Woollins' reagent (WR) afforded the corresponding sulfur (**35**) and selenium analogues (**36**). The driving force of these reactions is the formation of a stable P=O bond in a cycloreversion step that resembles the mechanism of Wittig reactions, indicating that the reactivity of germa-acylium ion **34** is akin to classical acylium-like behavior. The Ge-Se bond in **36** (2.2372(5) Å) is slightly longer than Pyykkö's standard value for a Ge-Se double bond (2.18 Å), and comparable to those of thermodynamically stabilized germaneselones (2.194(1) Å-2.237(2) Å)[17, 33-54]. NBO analyses of **34-36** suggested that the Ge–Ch bond becomes less polarized upon descending group-16 (O: 78.9%; S: 60.5%; Se: 55.3%). Furthermore, unlike the Ge–O bond in **33**, the Ge–S and Ge–Se bonds of **35** and **36** exhibit partial double-bond character, as indicated by the calculated WBI values of 1.279 and 1.302, respectively.
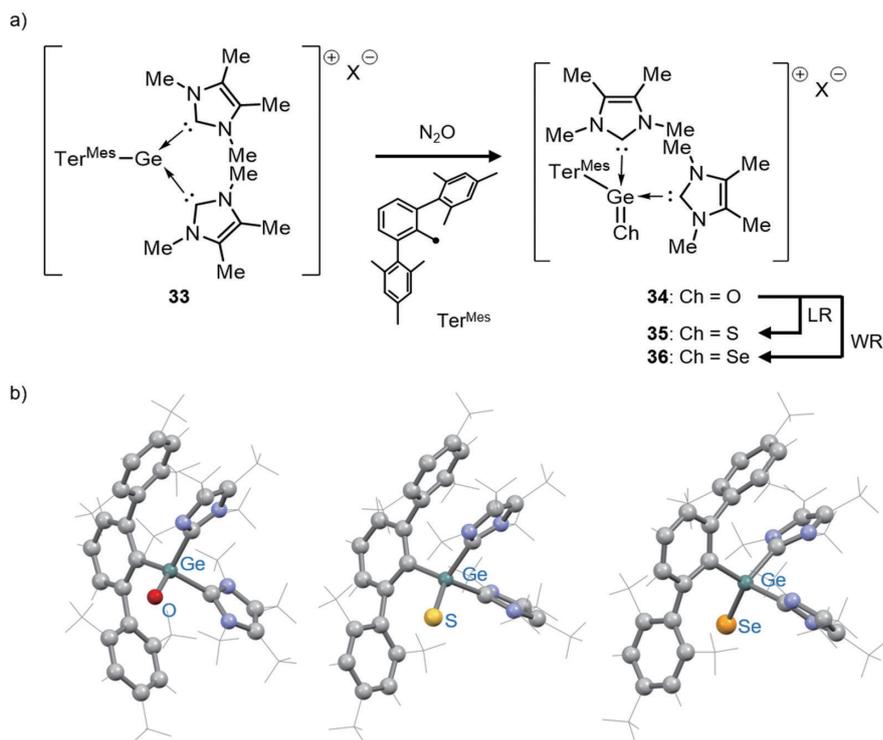
a)

b)

34: Ch = O
35: Ch = S
36: Ch = Se

3.3. Heavier analogues of CO and CO_2

a)

Dipp = 2,6-i-Pr$_2$C$_6$H$_3$

37   **38**   **39**

b)
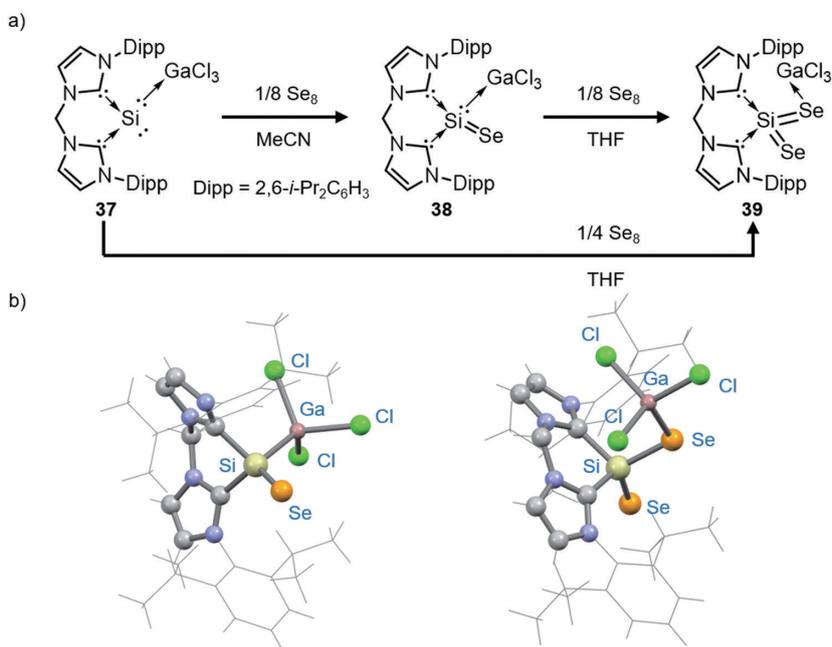
Figure 3-5. a) Synthesis of silicon and selenium analogues of CO (**38**) and CO_2 (**39**) together with b) their crystal structures.

Kaupp and Driess have reported the synthesis of bis-NHC-stabilized monomeric silicon chalcogenides. Silicon selenide **38** and diselenide **39** were obtained from the reaction of silylone **37** with elemental selenium[61]. Compounds **38** and **39** serve as base-stabilized heavier analogues of CO and CO_2, respectively. Interestingly, the formation of **38** and **39** is solvent-dependent, i.e., **38** forms in acetonitrile, while **39** forms in THF. Notably, **38** does not react further in acetonitrile with additional Se, while solvent exchange to THF smoothly converts **38** into **39**. The ^{77}Se NMR resonances of **38** and **39** appear at –655 ppm and –391 ppm, respectively. The length of the Si–Se bonds in **38** (2.135(1) Å/2.1439(9) Å in the two independent molecules) are consistent with Pyykkö's standard value

for a Si=Se double bond (2.14 Å)[17]. In **39**, the longer Si1–Se2 bond (2.241(6) Å) approaches Pyykkö's standard value for a Si–Se single bond (2.32 Å), while the shorter Si1–Se1 bond (2.129(2) Å) resembles that of **38**[17].

3.4. Heavier analogues of allenes

Figure 3-6. a) Synthesis of bis(methylene)-λ^4-selane **40**, and its b) crystal structure.
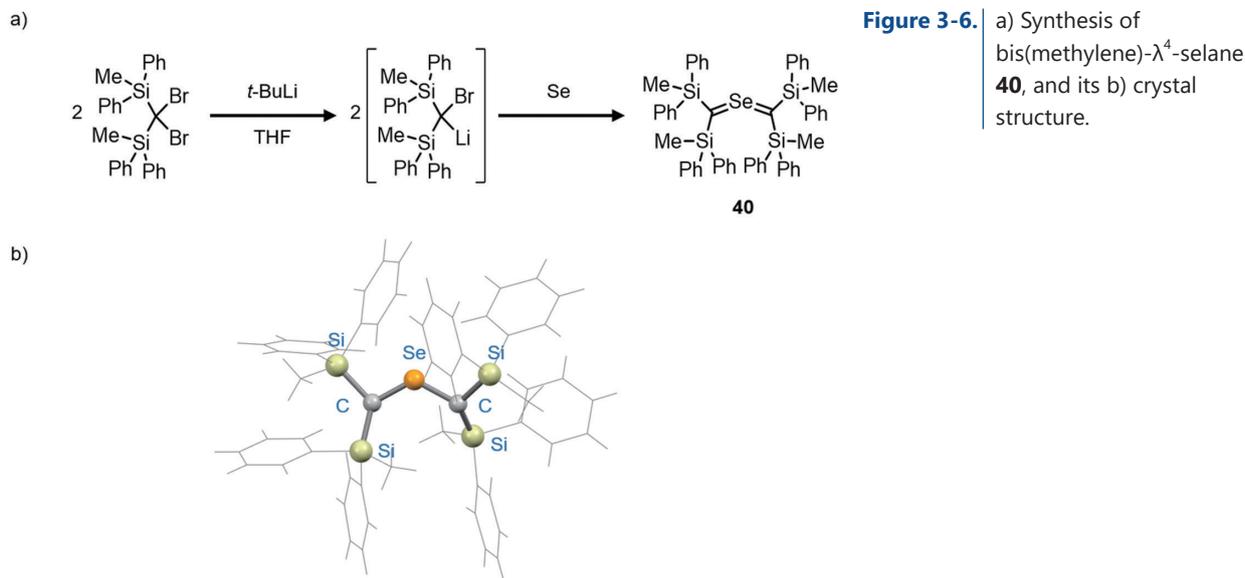
Sugamata and co-workers have reported on the synthesis of a series of bis(methylene)-λ^4-chalcogenanes, i.e., 2-chalcogenaallene-type molecules, using bulky silyl substituents[62-65]. The selenium analogue, i.e., bis(methylene)-λ^4-selane **40**, was obtained from the reaction of a transient bis(silyl)carbenoid with elemental selenium. While **40** represents a heavier analogue of a carbonyl ylide, it is also a significant example of a bent-allene–type structure rather than an ylide, being characterized as a symmetric molecule. The ^{77}Se NMR resonance of **40** appears at 1501 ppm, which is characteristic for unsaturated oraganoselenium compounds[66,67]. The crystal structure of **40** exhibits pseudo-C_2 symmetry with a bent C–Se–C configuration. The nearly identical, short C–Se bond lengths (1.801(4) Å/1.808(3) Å) in **40** falls between Pyykkö's standard values for a C=Se double bond (1.74 Å) and a C–Se single bond (1.91 Å), indicating significant multiple-bond character[17]. An NBO analysis of **40** revealed two C-Se bonds and a 3-center-4-electron π-bond on the C–Se–C moiety.

Figure 3-7. Reactions of **40**.
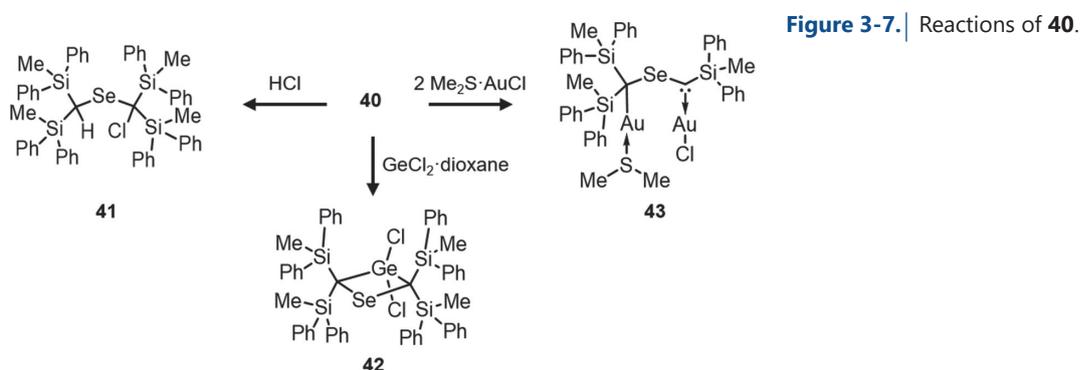
Bis(methylene)-λ^4-selane **40** is inert toward a variety of alkynes and alkenes, despite being an analogue of carbonyl ylides, which are known as 1,3-dipole reagents. However, the reaction with hydrogen chloride yielded the corresponding 1,3-adduct (**41**) in a quantitative yield. Furthermore, treatment of **40** with GeCl$_2$·dioxane produced unique four-membered ring compound **42**, suggesting that the formal [3 + 1] cycloaddition represents

a specific reactivity pattern of bis(methylene)-λ^4-chalcogenanes. The reaction with AuCl·Me$_2$S selectively afforded the unexpected dinuclear carbene gold(I) complex 43 *via* the elimination of Ph$_2$MeSiCl[68].

4. Group-15 – Selenium π-bond compounds
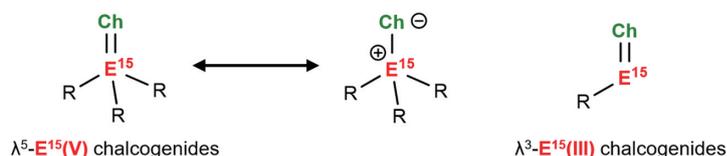
Figure 4-1. Compounds with terminal E^{15}=Ch bonds.

The synthesis of compounds with multiple bonds between heavier group-15 elements (E^{15} = P, As, Sb, Bi) and chalcogens (Ch = S, Se, Te) has received increased attention over the last few decades. Phosphine oxides and their heavier analogues, which are P(V) species, are well known as useful reagents in organic synthesis (**Figure 4-1**). Their heavier analogues should be described as polar single-bonded structures[69]. In contrast, E^{15}(III) chalcogenides are extremely rare species due to their low stability. The stabilization of such compounds typically requires sterically overcrowded ligands to prevent self-oligomerization. Tokitoh and co-workers have reported the selenization of kinetically stabilized diphosphene (**G** and **J**; ArP=PAr), distibenes (**H** and **K**; ArSb=SbAr) and dibismuthenes (**I** and **L**; ArBi=BiAr) to afford the corresponding E^{15}(III) selenides (**M-P**)[70-72], (**Figure 4-2**). Nevertheless, evidence for monomeric compounds that bear an unsupported terminal E^{15}(III) chalcogen double bond is still missing. Breunig and co-workers have suggested the presence of a terminal antimony-selenium double bond for tungsten complex **Q** in benzene solution, albeit that **Q** forms a dimer in the solid state. In this chapter, notable achievements of E^{15}(III) selenides are described.
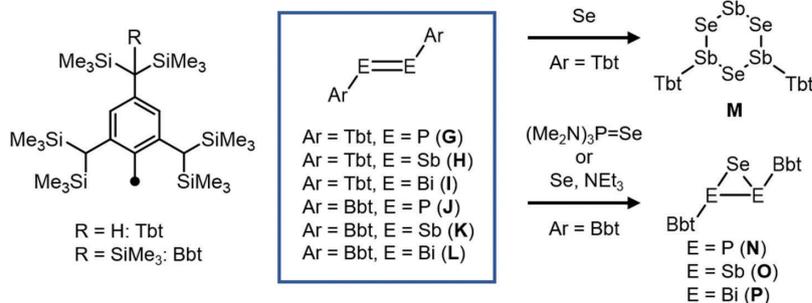
Figure 4-2. Pioneering studies on E^{15}(III) selenides.
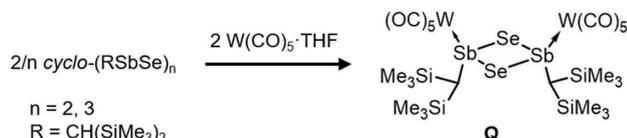
4.1. Antimony(III) selenides

Dostál and co-workers have reported the synthesis of the first stable antimony(III) selenide using an NCN-pincer ligand[73]. The reaction of the cyclic organoantimony compound of the type Ar$_4$Sb$_4$ (**44**) with an excess of elemental selenium in THF afforded the corresponding antimony(III) selenide (**45**) as a highly air-sensitive yellow crystalline solid[74]. The ^{1}H and ^{13}C NMR spectra of **45** displayed only one set of signals, indicating a highly symmetric structure in solution. A single signal at –197 ppm was observed in the ^{77}Se spectrum, and the ^{77}Se CP/MAS NMR spectrum at –153 ppm confirmed that the monomeric structure of **45** in the solid state is retained in solution. In the solid state, **45** is monomeric, with a Sb-Se bond length of 2.4396(7) Å, which is approximately 9% shorter than Pyykkö's standard value for a Sb–Se single bond (2.56 Å), approaching the length of a Sb=Se double bond (2.40

Å)[17]. The Kohn-Sham orbitals of **45** show that the HOMO corresponds mainly to the selenium lone pair and the HOMO-1 to the Sb-Se π-bond (**Figure 4-3**). The WBI for Sb-Se in **45** is 1.41. An NBO analysis showed notable charge separation, with NBO charges of +0.999 on Sb and –0.788 on Se. Moreover, the NBO analysis revealed a large back-donation from the lone pair on Se into an empty orbital on Sb, suggesting that the terminal Sb–Se bond in **45** exhibits appreciable double-bond character, albeit that the electron density is strongly polarized toward selenium.
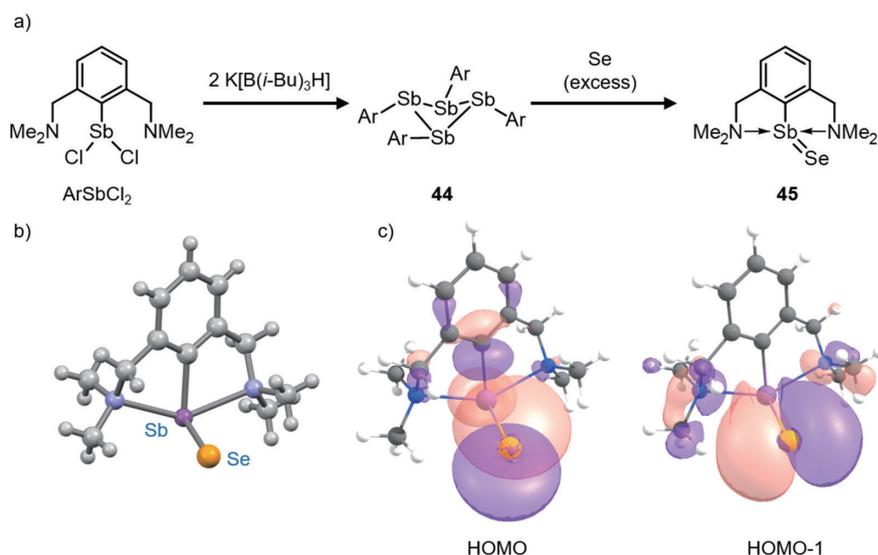
Figure 4-3. a) Synthesis of antimony(III) selenide **45** together with b) its crystal structure. c) Kohn-Sham frontier orbitals of **45**.
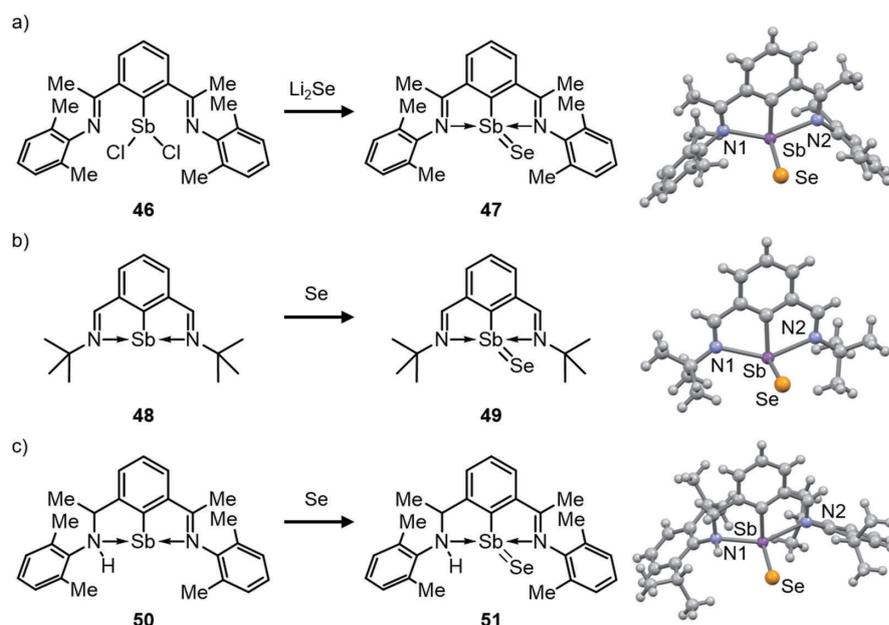
Figure 4-4. a) Synthesis and molecular structures of antimony(III) selenides **47**, **49**, **51**.

Table 4-1. | Comparisons among the antimony(III) selenides **45**, **47**, **49**, **51**.

	Sb-Se (Å)	C-Sb (Å)	N1-Sb (Å)	Sb-N2 (Å)	WBI[a]	NBO charge[a]		δ^{77}Se	Ref.
						Sb	Se		
45	2.4396(6)	2.135(4)	2.461(3)	2.518(3)	1.376	1.023	–0.807	–197	[74]
47	2.4329(5)	2.124(3)	2.395(2)	2.393(2)	1.288	1.105	–0.779	–140	[75]
49	2.4498(6)	2.129(1)	2.549(1)	2.391(1)	1.242	1.099	–0.807	—	[76]
51	2.4371(5)	2.147(4)	2.536(3)	2.458(3)	1.271	1.096	–0.811	–17.3	[77]

a) Calculated at the B3PW91-D3(BJ)/SDD level for Sb, and the corresponding 6-31G(d) level for all other atoms.

To investigate the impact of donating N atoms on the character of the Sb–Se bond, the same research group synthesized antimony(III) selenides **47**[75], **49**[76], and **51**[77] with different NCN-pincer ligands (**Figure 4-4**). The reaction of antimony chloride **46** with Li_2Se yielded monomeric antimony(III) selenide **47**, while **49** and **51** were obtained from the reactions of elemental selenium with stibinidenes **48** and **50**, respectively. The ^{77}Se NMR spectra of the antimony(III) selenides showed a single peak at –139.6 ppm (**47**) and –17.3 ppm (**51**), which are slightly downfield shifted from that of **45**; for **49**, no apparent signal was observed. The length of the Sb–Se bonds in **47** (2.4329(5) Å), **49** (2.4497(4) Å), and **51** (2.4371(5) Å) suggest double-bond character similar to that in **45**. NBO calculations were performed to analyze the bonding nature of the Sb–Se bond in these antimony(III) selenides, using a consistent level of calculations (**Table 4-1**). The results indicate that the terminal Sb–Se bonds in these antimony(III) selenides exhibit lower polarity and stronger double-bond character, influenced by the electron-donating strength of the pincer ligands.

4.2. As(III) selenides
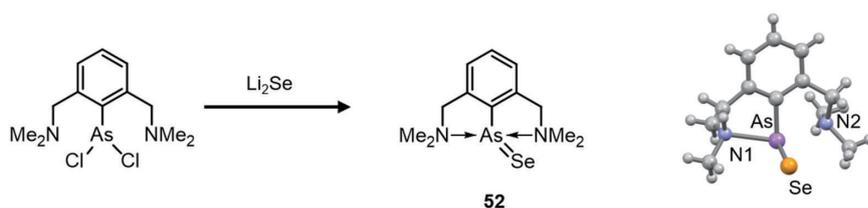
Figure 4-5. a) Synthesis and molecular structures of arsenic(III) selenide **52**.

Dostál and co-workers have also reported the synthesis of arsenic(III) selenide **52** using the same NCN-pincer ligand as for the synthesis of **45** (**Figure 4-5**)[78]. The reaction of a dichloroarsine with Li_2Se afforded arsenic(III) selenide **52** as a yellow solid. Its ^{77}Se NMR spectrum showed a resonance at 0 ppm, which is downfield shifted compared to those of other antimony(III) selenides. The terminal As-Se bond (2.2736(5) Å) is significantly shorter than Pyykkö's standard value for an As–Se single bond (2.37 Å), approaching the length of a typical As=Se double bond (2.21 Å). The NBO charges on As and Se amount to +0.740 and –0.645, respectively. The WBI of **52** (1.48) is higher than those of antimony analogue **45** (1.41).

5. Summary

In this mini-review, we have presented recent examples of isolated compounds that feature both selenium and heavier main-group elements in a π-bond, which are stabilized through kinetic and thermodynamic means using judiciously designed substituents. A notable characteristic of these species is the highly electrophilic nature of the selenium atom in the π-bond, due to the presence of a low-lying π* orbital. This represents a captivating area of study within main-group element chemistry. Despite their remarkable properties, these intriguing compounds remain relatively unexplored, offering significant opportunities for further advancements across various research domains.

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