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Selenium Heterocycles: Reactions of SeX_4 (X = Cl, Br) with the Enamine Form of β-Diketiminato Ligands

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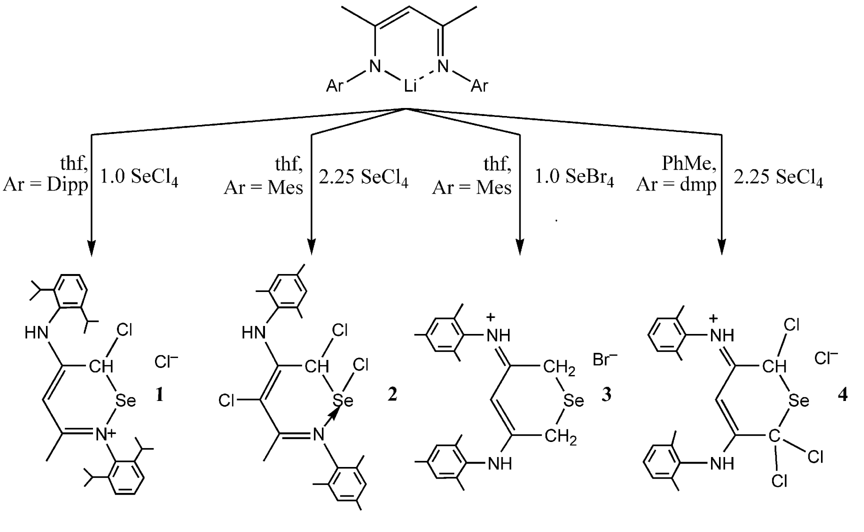
Treatment of SeX_4 (X = Cl, Br) with either MesnacnacLi (nacnac = $[\{N(Ar)C(Me)\}_2CH]^-$, Ar = Mes = $C_6H_2Me_3$-2,4,6) or DmpnacnacLi (Ar = Dmp = $C_6H_3Me_2$-2,6) affords four new Se^{II} six-membered heterocycles, [$MesnacnacHCl_2SeCl$] (**2**), $[MesnacnacH_2Se]^+Br^-$ (**3**), $[DmpnacnacH_2Cl_3Se]^+Cl^-$ (**4**), and [$MesnacnacH_2(O)Br_2Se$] (**5**). All have been characterized in the solid state by X-ray crystallography. Each of the four complexes is proposed to have formed from the initial reaction of SeX_4 with the C–C double bond that results from the enamine form of the ligand, giving rise to an Se–C single bond. Subsequent nucleophilic attack by either the more distant nitrogen atom or the remaining C–C double bond of the enamine form results in the Se heterocycle. In complexes **2**, **4**, and **5** varying degrees of halogenation of the newly formed heterocycles was observed.

Introduction

β-Diketiminato ligands, $[\{N(Ar)C(Me)\}_2CH]^-$, commonly referred to as nacnac, have played an important role in many different areas of inorganic and organic chemistry.[1] They can afford a variety of coordination modes for many different elements and stabilize a wide range of oxidation states.[1] Recently, we reported the first examples of (β-diketiminato)tellurium and -selenium complexes (**1**; Scheme 1)[2] prepared by the direct 1:1 reaction of the lithium salt of Dippnacnac (Dipp = 2,6-diisopropylphenyl) and the chalcogen tetrahalide. Like many of the electron-rich p-block β-diketiminato complexes, these avoided the usual N,N′-chelation[3] and instead favored reaction at the former backbone methyl carbon atom. Perhaps more intriguingly, **1** featured chloride atom rearrangement to the ligand. Encouraged by the recent success of Ragogna and co-workers in the isolation of N,N′-chelated Se complexes using the 1,4-R_2-1,4-diaza-1,3-butadiene (DAB) ligand,[4] and Cowley et al. of N,N′-chelated phosphenium ions supported by a β-diketiminato ligand[5] and N,N′-chelated Te complexes with 2,6-diisopropylphenyl-substituted 1,2-bis-



Scheme 1. Synthesis of compounds **1**–**4**.

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(arylimimo)acenaphthene ligand,[6] we revisited the reactivity of selenium tetrahalides with nacnac ligands with the goal of isolating an N,N′-chelated selenium complex. Herein, we report the synthesis of the neutral complex, [MesnacnacHCl$_2$SeCl] (**2**), two ionic (β-diketiminato)Se^{II} complexes, [MesnacnacH$_2$Se]$^+$Br$^-$ (**3**), [DmpnacnacH$_2$Cl$_3$Se]$^+$Cl$^-$ (**4**) and [MesnacnacH$_2$(O)Br$_2$Se] (**5**). Structural characterization has allowed the elucidation of a potential mechanism for the formation of **1**–**4**.

Results and Discussion

Following the isolation of **1**, the N′SeC species, that bears only one chlorine atom on the ligand backbone (Scheme 1), we postulated that the neutral species, NN′SeCl$_3$, could be isolated through careful manipulation of the reaction conditions, stoichiometry and tuning of the nacnac substituents to promote crystallinity. To this end the reactions of MesnacnacLi and DmpnacnacLi with SeX$_4$ were performed.

Synthesis of 2

It was observed that the formation of **1** was coincident with the reduction of SeCl$_4$ to elemental selenium.[2] This occurrence, along with chlorination of the ligand, suggested that Cl$_2$, formed in situ from SeCl$_4$, was halogenating the ligand backbone.

The addition of 1 equiv. of MesnacnacLi to 2.25 equiv. of SeCl$_4$ at –78 °C generated a yellow solution that slowly turned dark red on warming to ambient temperature. Filtration, concentration, and storage of the reaction mixture at room temperature for 1 d afforded yellow crystalline needles of **2** (Figure 1) in 29% yield, (crystal data[7] shown in Table 2). Optimal reaction conditions were determined experimentally and led to employing a 1:2.25 ratio of ligand/chalcogen halide, as it allows generation of X$_2$ (along with elemental Se) which appears to be a reaction intermediate even when an excess of ligand is present.

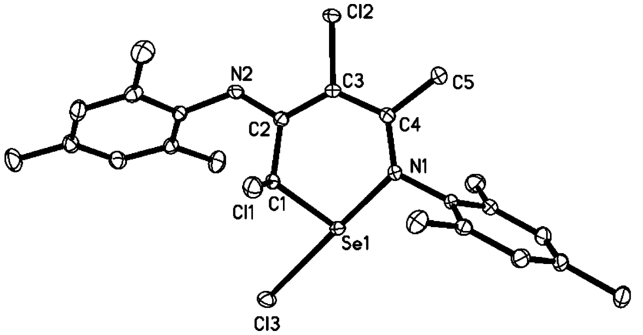


Figure 1. Solid-state structure of **2**. Hydrogen atoms and THF solvent molecule are omitted for clarity. Ellipsoids are drawn at 30% probability.

The solid-state analysis shows a structural arrangement similar to **1**. N,N′-Chelation was avoided, instead forming a C–Se^{II}–N six-membered heterocycle. This neutral compound exhibits typical T-shaped geometry at the Se center, indicative of a selenium atom with two “formal lone pairs” that is coordinated to nitrogen, carbon and chlorine atoms.[8]

The presence of excess SeCl$_4$ in the reaction mixture is likely responsible as the source for the increase in the degree of halogenation in **2**, which features an additional chlorine atom at the γ-position of the ligand backbone. Indeed, it is documented that the chalcogen halides readily undergo reduction to EX$_2$ (E = Se, Te) concomitant with formation of X$_2$, which is also documented for group 15 halides;[9,10] however, these spontaneous redox reactions are usually in the presence of neutral Lewis bases, for example the reaction of N-heterocyclic carbenes with SeCl$_4$.[10] Attempts were made to isolate a product from the yellow solution before the reaction mixture turned red, by maintaining low temperature reaction conditions and workup, presence of excess ligand to prevent Se^0 generation and using different reaction solvents. In all cases a red solution prevailed upon standing, and complex **2** could always be isolated, but the yield varied, leading us to believe that **2** is the preferential and most stable product. Complex **2** is thermally stable, with decomposition to a metallic looking solid at 128–130 °C but not melting at <250 °C. Protonation of the nitrogen atom N(2) was confirmed by infrared spectroscopy with a distinct N–H stretch observed at 3174 cm^{-1}. Solution ^{1}H NMR spectroscopy confirmed the solid-state analysis and the positive-mode LRMS spectrum of **2** exhibits a peak at *m/z* = 481.1 corresponding to [M – Cl], followed by sequential loss of the second chloride ion and mesityl groups.

X-ray Crystal Structure of 2

The crystal structure of **2** reveals an Se–N bond length of 1.980(2) Å which is longer than in previously reported **1** [1.931(3) Å] and longer than a nominal Se–N single bond which usually lies in the range 1.8245–1.846 Å (covalent radii 1.865 Å)[4a,11] but comparable with values for complexes that show Se–N intramolecular interactions.[12] The C–Se–N bond angle of 91.65(10)° is slightly more acute than that of **1** (Table 1) and of other previously reported two-coordinate Se–N systems,[13] but larger than those in the Se–N heterocycles reported by Ragogna et al.[4] The Se(1)–Cl(1) bond in **2** [2.5799(7) Å] is fairly long,[14] but can be attributed to an effective overlap between the nitrogen lone pair with the σ*-orbital of the Se–Cl bond, which is favorable because of the N–Se–Cl angle that is close to linear (177.84°).

The solid-state analysis further reveals that **2** packs (Figure 2) so as to maximize the interactions between the γ-chlorine atom and the selenium center of an adjacent molecule of **2** [Cl(2)···Se(1) 3.3861 Å; sum of van der Waals radii for Se–Cl 3.65 Å],[14e] and the hydrogen-bonding interactions between Cl(3) and the protonated nitrogen atom of the same adjacent molecule of **2** [Cl(3)···H(2) 2.53 Å]. A system of alternating rows is thus formed in which all molecules within a row are oriented in the same direction, and

Table 1. Comparison of selected bond lengths [Å] and bond angles [°] for **1**–**4**.

	1	**2**	**3**	**4**
Se(1)–C(1)	1.925(3)	1.933(3)	1.942(5)	1.959(5)
Se(1)–C(5)	–	–	1.943(5)	1.919(5)
Se(1)–N(1)	1.931(3)	1.980(2)	–	–
Se(1)–X (X = Cl, Br)[a]	2.747	2.5799(7)	4.685	3.224
C(1)–C(2)	1.498(5)	1.498(4)	1.493(6)	1.531(7)
C(2)–C(3)	1.380(5)	1.379(4)	1.393(6)	1.361(7)
C(3)–C(4)	1.395(5)	1.418(4)	1.380(6)	1.410(7)
C(4)–C(5)	–	–	1.501(7)	1.511(7)
C–Cl[b]	1.800(4)	1.745(3)–1.813(3)	–	1.773(6)–1.792(6)
C(4)–N(1)	1.317(5)	1.313(3)	–	–
C(2)–N(2)	1.317(5)	1.341(3)	–	–
N(1)–C(2)	–	–	1.334(6)	1.329(6)
N(2)–C(4)	–	–	1.335(6)	1.302(7)
C(1)–Se(1)–N(1)	93.33(14)	91.65(10)	–	–
C(1)–Se(1)–C(5)	–	–	89.3(2)	96.9(2)
Se(1)–C(1)–C(2)	111.1(2)	112.44(18)	113.1(3)	115.6(3)
Se(1)–C(5)–C(4)	–	–	112.0(3)	109.9(4)
Se(1)–N(1)–C(4)[c]	124.7(2)	125.36(18)	–	–
N(1)–Se(1)–Cl(3)	–	177.84(7)	–	–

[a] For complexes **1**, **3** and **4**, this is an ionic interaction. [b] A range is given for structures with multiple C–Cl bonds. [c] Se(1)–N(1)–C(14) in **1**.

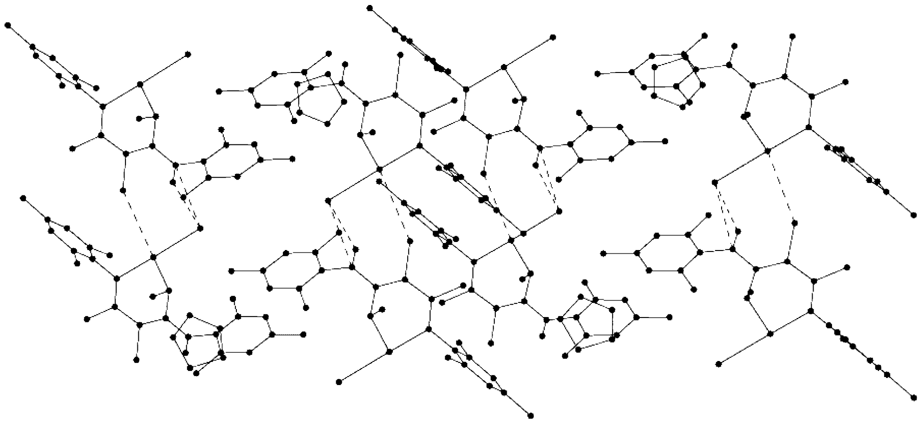


Figure 2. Packing diagram of **2**. All hydrogen atoms are omitted for clarity, except the N–H proton that participates in hydrogen bonding.

all the molecules in the neighboring row are oriented in the opposite direction.

Synthesis of 3, 4 and 5

To compare the reaction outcome with various selenium halide precursors, $SeBr_4$ was treated with MesnacnacLi. The overnight reaction between stoichiometric quantities of $SeBr_4$ and MesnacnacLi in THF afforded a dark red-brown solution and, following reaction workup, a very small number of red rectangular blocks of **3** (Scheme 1), which co-crystallized with a large quantity of red monoclinic elemental selenium.[15]

The extremely low yield and the co-crystallization of two similar crystal types made separation and further characterization of this highly air- and moisture-sensitive complex exceedingly difficult. Subsequent attempts were made at improving the yield and crystal separation but were unsuccessful in permitting an isolable amount of **3** (Figure 3). This

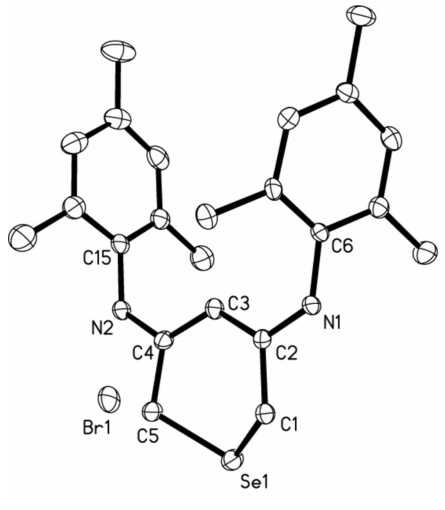
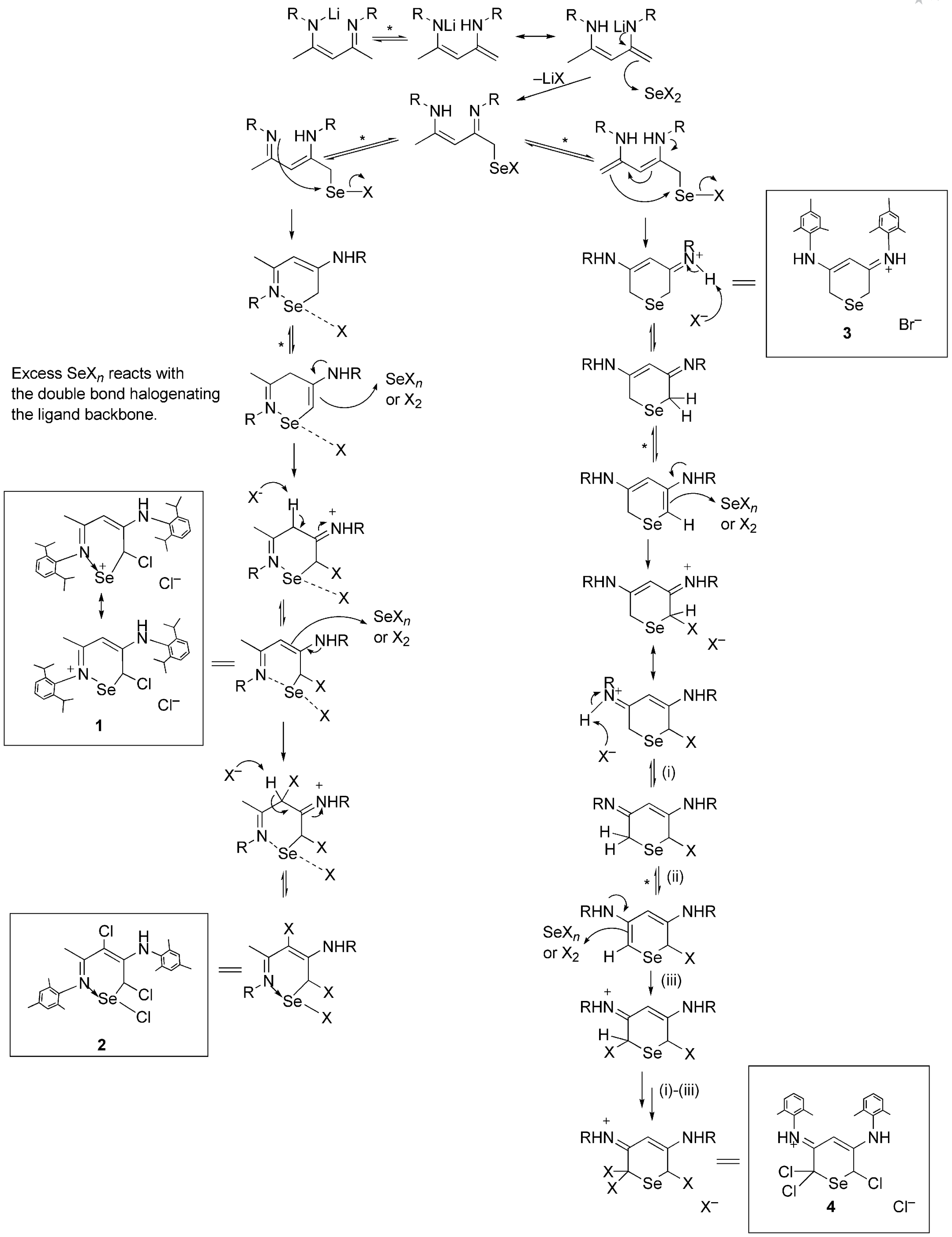


Figure 3. Solid-state structure of **3**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability.



Scheme 2. Possible mechanism for the formation of **1**–**4**. Asterisks (*) indicate a tautomerization of the ligand backbone. For SeX$_n$, n = 2 or 4.

irreproducibility is presumably due to **3** representing an intermediate in the overall halogenation process (Scheme 2). In an attempt to increase the yield of **3** and determine the side product composition, the aryl substituents of nacnac were exchanged for dimethylphenyl groups (Dmp). The 1:1 reaction of DmpnacnacLi and SeBr$_4$ yielded a red oil and no crystalline product; in parallel to this the reaction of DmpnacnacLi and SeCl$_4$ in toluene was performed. Reaction workup yielded **4** (Scheme 1, Figure 4) as dark red crystalline chunks alongside an unidentified side product of small orange crystalline needles, which were not of single-crystal X-ray quality, insoluble in a range of deuterated solvents and decomposed to a gray powder on heating. FT-IR Raman spectroscopy confirmed this as elemental selenium.

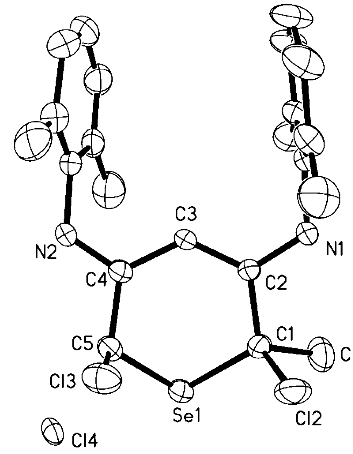


Figure 4. Solid-state structure of **4**. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at 30% probability.

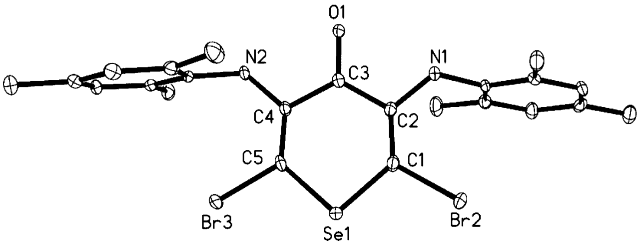


Figure 5. X-ray structure of **5**, thermal ellipsoids at 30% probability. Selected bond lengths [Å] and angles [°]: Br(2)–C(1) 1.901(4), Br(3)–C(5) 1.894(4), Se(1)–C(1) 1.855(4), Se(1)–C(5) 1.858(4), O(1)–C(3) 1.236(5); C(1)–Se(1)–C(5) 97.74(18), C(2)–N(1)–C(6) 124.0(4), C(2)–C(3)–C(4) 123.3(4) 1.858(4).

Discussion of the Crystal Structures of 3, 4 and 5

The solid-state structural analysis of both **3** and **4** revealed that N,N′-chelation was again disfavored, but in each case, unlike **1** and **2**, a C–Se–C heterocycle with a bent Se^{II} center was produced. The stoichiometry of SeX_4 used in the formation of both **3** and **4**, 1:1 for the former and 1:2.25 for the latter, further suggests that this is the primary factor in determining the degree of halogenation in the resultant complex. This is confirmed by the serendipitous formation of **5**, (Figure 5) from the reaction of MesnacnacLi with 2.25 equiv. of $SeBr_4$. The presence of excess $SeBr_4$ in the reaction mixture causes halogenation of the newly formed heterocycle at C(1) and C(5). Complex **5** is unusual as it features an oxygen atom in the γ-position of the ligand, C(3). Examination of bond lengths from the single-crystal analysis suggest a C=O bond,[16] which is confirmed by the absence of electron density in the difference map, a strong C=O stretch in the infrared spectrum at 1590.8 cm^{-1} which is lower than expected but corresponds well to the limited literature data for related species.[17] Mass spectral analysis of crystalline **5** exhibits peaks associated with [M – Br], followed by loss of a second bromine atom. The cause of oxygen contamination is not confirmed, but could have arisen from the selenium halide precursor, or from atmospheric oxygen/water contamination during the reaction. Nevertheless, **5** was isolated in moderate yield (46%) and was the only isolated crystalline product from the reaction. A survey of the Cambridge Crystallographic database reveals that **5** is structurally unusual because of the C=O bond present, with only a handful of similar structures reported and structurally characterized.[17] The C(1)–C(2) and C(4)–C(5) bonds have distances of 1.340(6) Å and 1.356(6) Å, respectively, indicative of C=C bonds. Both nitrogen atoms are protonated. The substituted γ-carbon atom results in a more "symmetrical" structure as reflected in the similar bond lengths and angles on either side of the selenium atom, although they are not symmetry-related.

The C–Se–X (X = C or N) angle of **4** [96.9(2)°] is larger than that of **1**, **2**, and **3** [89.3(2)–93.33(14)°] due to the repulsion of the three chlorine atoms adjacent to the Se center of **4**, relative to **1** and **2** (with one adjacent chlorine atom each) and **3** (with no adjacent halogen atoms). This trend is further illustrated by the increased bond length of Se(1)–C(1) [1.959(5) Å] relative to that of Se(1)–C(5) [1.919(5) Å] of **4**, caused by repulsion of the two chlorine atoms at C(1) compared with only one chlorine atom at C(5). Conversely, the absence of halogenation in **3** causes both Se–C bonds to be almost completely identical in length [1.942(5) and 1.942(3) Å]. Surprisingly, the C–Se–C angle of the non-halogenated **3** [89.3(2)°] is significantly more acute than those of previously published C_5Se heterocycles [95.0(9)–96.63°],[18] none of which were substituted at the α-carbon atoms. The N–C(2)–C(3)–C(4)–N bonds of **2**, **3**, and **4** are all short, indicating delocalization across these bonds.[19]

Packing Arrangement of 3, 4 and 5

Compounds **3** and **5** are arranged in the crystalline lattice into alternating rows of complexes in which the selenium atom protrudes upward in one row and is inverted to point downward in the next (Figure 6). In **3**, a distance of 10.06 Å separates selenium atoms in adjacent rows, indicating no Se–Se interactions. Hydrogen bonding is a common feature of these structures and in **3** exists between protonated nitrogen atoms of two neighboring cationic Se heterocycles within a row [Br(1)–H(1A) 2.327 Å, Br(1)–H(2A) 2.490 Å]. In **5**, hydrogen bonding between the C=O and the protonated nitrogen atoms is also present.

The solid-state packing arrangement of **4** is complicated by the presence of the three chlorine atoms adjacent to the selenium center and is depicted in Figure 7. Each selenium atom interacts with one of the ligand α-chlorine atoms of the molecule it points toward, and with a lattice chloride anion (3.224 Å). In addition to this Cl···Se interaction, and analogous to the packing of **3**, each chloride anion also forms hydrogen bonds with the protonated nitrogen atoms of the two ionic Se heterocycles of **4** between which it lies [Cl(4)–H(1A) 2.291 Å, Cl(4)–H(2A) 2.222 Å]. Complex **4** has low thermal stability, decomposing at 48–54 °C and melting at 73–75 °C. ^1H NMR spectroscopy shows no un-

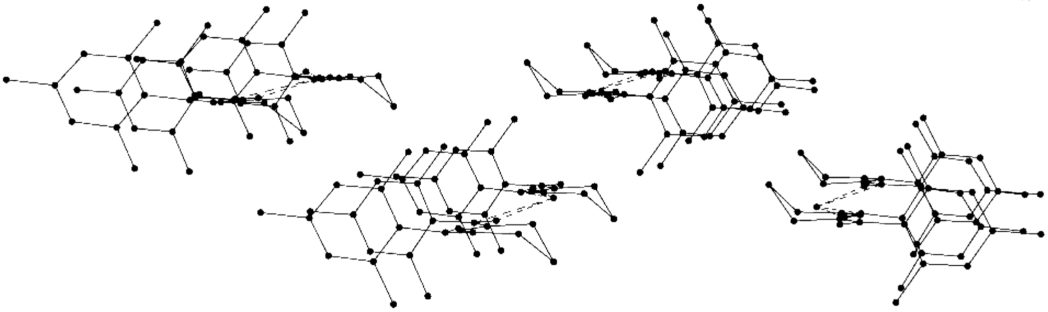


Figure 6. Packing diagram of **3**. Only N–H hydrogen atoms are shown for clarity.

usual features, while the ^{13}C NMR spectrum exhibits distinctive downfield chemical shifts for the halogenated carbon atoms [δ = 162.9 (ClCH*C*NH) and 174.9 (Cl_2C*C*NH) ppm]. The N–H stretches at 3369 and 3170 cm^{-1} in the infrared spectrum confirm the X-ray analysis.

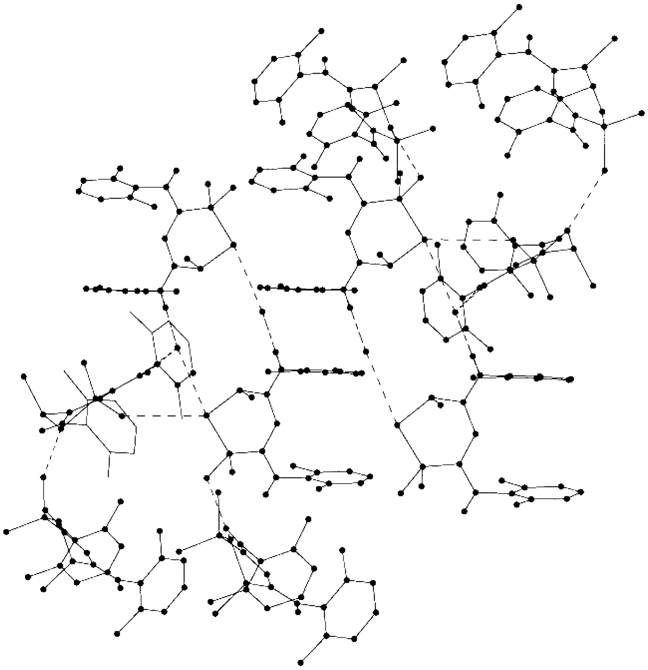


Figure 7. Packing diagram of **4**. Only N–H hydrogen atoms are shown for clarity.

Discussion of the Mechanism

The reactions of enol and enamine tautomers of ketones and imines are well documented,[20] and the current investigation strongly suggests that the formation of **1**–**4** occurs by reaction of SeX_2 with the anionic enamine form of the ligand, rather than with the imine (Scheme 2).

Following addition of the lithiated ligand to SeX_4 (X = Cl, Br), the initial step of the mechanism for complexes **1**–**4** is ostensibly the reduction to SeX_2 with the elimination of X_2 as the oxidation byproduct, which has been previously shown to occur in the presence of neutral Lewis bases.[9,10] The isolation of **1**–**4** suggests that reductive elimination of X_2 can also occur in the presence of an anionic base. The following step is envisaged to involve the reaction of the C–C π-electron density (from a former backbone methyl group) of the enamine tautomer with either SeX_2. Similar mechanisms have been previously proposed to explain both the γ-addition to the nacnac ligand by PPh_2Cl and the further reaction of ECl_3 (E = As, Sb) at the backbone methyl group of the resulting nacnacPPh_2 ligand.[3c] Once the Se–C single bond has formed, the Se atom can undergo nucleophilic attack by either the more distant nitrogen atom or by the C–C π-electron density (from the other former backbone methyl group) of the enamine tautomer of the selenium complex. In either case, a six-membered Se heterocycle is formed, which can be isolated as a non-halogenated intermediate, as in complex **3**, or can undergo further reaction, presumably with excess SeX_n (n = 2 or 4), to form the halogenated products **1**, **2**, and **4**. This likely involves the halogenation of the C–C double bonds with concurrent elimination of HX, supported by the low pH of the reaction mixtures, measured over the reaction period.

Conclusions

We have studied the reaction of selenium tetrahalides with variously substituted β-diketiminato ligands. This investigation has yielded four new selenium heterocycles, which have all undergone reduction of Se^{IV} to Se^{II} and all preferentially reacted initially at the enamine form of the former backbone methyl carbon atom, rather than at the sterically hindered nitrogen atom. In light of the subsequent nucleophilic attack by the nitrogen atom to form an Se–N bond in both **1** and **2** and of the varying degrees of halogenation, current work is investigating whether **4** can be isolated from complexes similar to **3** through the in situ addition of the halogen and if tuning of the reaction conditions and ligand substituents will lead to the desired N,N′-chelated Se complex. Investigations are also underway to repeat the formation of **5** through addition of water or oxygen and whether this could be extended to reactions with NH_3, ROH to enable direct derivatization of the ligand backbone.

Experimental Section

General: All manipulations were performed under anaerobic conditions using standard Schlenk techniques. Toluene was dried using an MBraun-SPS solvent purification system, and THF was dried with potassium before use. MesnacnacH {nacnacH = H[N(Ar)-C(Me)]$_2$CH; Ar = Mes = 2,4,6-trimethylphenyl} and DmpnacnacH (Dmp = 2,6-dimethylphenyl) and the corresponding lithium salts were prepared according to literature procedures.[21] $SeBr_4$ was purchased from Strem Chemicals. All other chemicals were purchased from Aldrich and used as received. Crystal data were collected with a Bruker SMART 1000 diffractometer, molybdenum radiation (λ = 0.7107 Å). The data were corrected for absorption. Structures were solved by direct methods[7] and refined[7] by full-matrix least squares. The NMR spectroscopic data were recorded with a Varian XL-300 instrument, IR analysis was conducted with an MIDAC M4000 Fourier transform infrared (FT IR) spectrometer, UV/Vis absorption spectra were recorded with an Agilent 8453 UV/Vis spectrometer, and mass spectrometry analysis was carried out using a Bruker Esquire 6000 mass spectrometer. Melting points were determined in capillaries under nitrogen and are uncorrected.

Synthesis of [MesnacnacHCl$_2$SeCl] (2): A THF solution of MesnacnacLi (0.35 g, 1.0 mmol) was added rapidly through a cannula to a stirred THF solution of $SeCl_4$ (0.51 g, 2.3 mmol) that had been cooled to –78 °C. The initial yellow reaction mixture gradually turned dark red and was slowly allowed to reach ambient temperature. Stirring was maintained overnight, and the resultant clear dark red solution was filtered and concentrated. Overnight storage of the THF solution at room temperature afforded yellow crystalline needles of **2** in 29% yield (170 mg, yield based on ligand). Decomposition point: 128–130 °C turned shiny black, 140–141 °C turned dull black, did not melt below 250 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.78 (m, $^1J_{H-H}$ = 6.5 Hz, 2 H,THF CH_2), 2.06 (s, 3 H, *para* Mes CH_3), 2.16 (s, 3 H, *para* Mes CH_3), 2.19 (s, 3 H, *ortho* Mes CH_3), 2.23, 2.25 (2 overlapping s, height ratio ca. 2:1, respectively, 9 H, *ortho* Mes CH_3), 2.37 (s, 3 H, backbone CH_3), 3.52 (m, $^1J_{H-H}$ = 6.5 Hz, ClC*H*Se), 3.68 (m, $^1J_{H-H}$ = 6.7 Hz, 2 H, THF CH_2O), 4.31 (m, $^1J_{H-H}$ = 5.9 Hz, NH), 6.84 (s, 1 H, *meta* Mes CH), 6.88, 6.90 (2 overlapping s, equal height, 2 H, *meta* Mes CH), 7.00 (s, 1 H, *meta* Mes CH) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 18.5, 18.7, 18.9, 21.2, 21.3, 21.4 (Mes CH_3), 25.8 (backbone CH_3), 59.2 (Se*C*HCl), 68.2 [C(CH_3)*C*ClCNH], 128.7, 129.2, 129.7, 129.7 (*meta* Mes CH), 130.3, 130.4 (*para* Mes *C*CH_3), 134.9, 135.9, 136.3, 137.2 (*ortho* Mes *C*CH_3), 139.3, 140.0 (*ipso* Mes CN), 146.7 (SeN*C*CH_3), 150.5 (ClCH*C*NH) ppm. IR (Nujol mull): $\tilde{\nu}$ = 3174 (shoulder, N–H stretch), 1722 (w), 1154 (m) cm^{-1}. UV/Vis (THF, 25 °C): λ = 283, 369 nm. MS: m/z = 516.8, 481.1 [M – Cl], 366.2 [M – Cl – Mes], 331.2 [M – 2 Cl – Mes], 315.3 [M – 2 Cl – Mes – CH_3], 196.1 [M – 2 Cl – Mes$_2$ – CH_3].

Synthesis of [MesnacnacH$_2$Se]$^+$Br$^-$ (3): A THF solution of MesnacnacLi (0.35 g, 1.0 mmol) was added to a stirred THF suspension of $SeBr_4$ (0.41 g, 1.0 mmol) at –78 °C through a cannula, at which time no visible change occurred. The reaction mixture was allowed to gradually warm to room temperature and stirred overnight, resulting in a dark red-brown solution. After concentrating, filtering, and storage at room temperature for several weeks, a very small quantity of **3** was obtained as red rectangular blocks alongside a large quantity of red monoclinic elemental selenium.[6] Due to the extremely low yield and the difficulty in separating these crystals, the crystals could not be successfully isolated for further characterization.

Synthesis of [DmpnacnacH$_2$Cl$_3$Se]$^+$Cl$^-$ (4): A toluene solution of DmpnacnacLi (0.25 g, 0.80 mmol) was added rapidly through a cannula to a stirred toluene suspension of $SeCl_4$ (0.40 g, 1.8 mmol) at –78 °C. The resultant yellow reaction mixture was removed from the dry ice bath after 45 min with slow warming to ambient temperature and was then stirred overnight. The resulting dark red-

Table 2. Crystal data for compounds **2**–**4**.

	2	**3**	**4**
Chemical formula	$C_{27}H_{35}Cl_3N_2OSe$	$C_{23}H_{29}BrN_2Se$	$C_{21}H_{22}Cl_4N_2Se$
Formula mass	588.88	492.35	523.17
Crystal system	monoclinic	triclinic	trigonal
Space group	$P2_1/c$	$P\bar{1}$	$R\bar{3}$
T [K]	213(2)	213(2)	213(2)
a [Å]	7.9882(5)	9.1578(11)	38.8331(13)
b [Å]	16.4354(1)	10.0656(12)	38.8331(13)
c [Å]	21.5882(13)	12.9607(16)	10.3843(7)
α [°]	90	72.417(2)	90
β [°]	100.0170(1)	89.400(2)	90
γ [°]	90	88.570(2)	120
V [Å^3]	2791.1(3)	1138.5(2)	13561.6(11)
Z	4	2	18
Reflections collected	17271	5967	26538
Independent reflections	5045	4026	5419
Data/restraints/parameters	5045/1/318	4026/2/258	5419/2/265
Unique data (R_{int})	0.0392	0.0357	0.0728
$D_{calcd.}$ [Mg/m^3]	1.401	1.436	1.153
Absorption coefficient [mm^{-1}]	1.655	3.414	1.608
F(000)	1216	500	4752
Crystal size [mm]	0.42 × 0.16 × 0.11	0.20 × 0.15 × 0.13	0.29 × 0.26 × 0.20
Θ range for collection [°]	1.92–25.25	1.65–25.25	2.05–25.24
R indices (all data)	R_1 = 0.0504, wR_2 = 0.0861	R_1 = 0.0737, wR_2 = 0.1218	R_1 = 0.1118, wR_2 = 0.1854
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0320, wR_2 = 0.0762	R_1 = 0.0464, wR_2 = 0.1111	R_1 = 0.0565, wR_2 = 0.1498
Largest difference in peak/hole [e Å^{-3}]	0.632/–0.298	1.136/–0.535	0.865/–0.451

brown solution and precipitate were filtered and stored at room temperature overnight, affording large dark red crystalline chunks of **4** that crystallized alongside a large quantity of small, bright orange crystalline needles. These were not of X-ray quality, despite numerous attempts at recrystallization of this side product. The red crystals were separated from the side product by hand in the dry box and used for further characterization. Yield (based on ligand): 170 mg, 41%. Decomposition point: 49–54 °C turned black, 73–75 °C melted. ^{1}H NMR (CDCl$_3$, 25 °C): δ = 1.54 (br. s, 1 H, SeC*H*Cl), 1.97 (d, $^1J_{\text{H–H}}$ = 7.3 Hz, 6 H, Dmp CH$_3$), 2.08 (d, $^1J_{\text{H–H}}$ = 7.7 Hz, 6 H, Dmp CH$_3$), 4.15 (s, 1 H, backbone CH), 6.87 (d, $^1J_{\text{H–H}}$ = 7.0 Hz, 2 H, *meta* Dmp CH), 6.96 (d, $^1J_{\text{H–H}}$ = 7.9 Hz, 1 H, *meta* Dmp CH) 7.02 (t, $^1J_{\text{H–H}}$ = 7.3 Hz, 1 H, *para* Dmp CH), 7.10 (t, $^1J_{\text{H–H}}$ = 7.3 Hz, 1 H, *para* Dmp CH), 7.77 (s, 1 H, NH), 7.93 (br. s, 1 H, NH) ppm. ^{13}C NMR (CDCl$_3$, 25 °C): δ = 16.7, 16.8, 17.4, 17.7 (Dmp CH$_3$), 28.6 (SeCHCl), 59.6 (SeCCl$_2$), 96.3 (backbone CH), 126.8, 127.0 (*para* dmp C-H), 127.1, 127.2, 127.5 (*meta* dmp C-H), 127.6, 127.6, 128.0, 128.1 (*ortho* dmp *C*-CH$_3$), 129.0, 130.0 (*ipso* CN), 162.9 (ClCH*C*NH), 174.9 (Cl$_2$C*C*NH) ppm. IR (Nujol mull): $\tilde{\nu}$ = 3369 (N–H stretch), 3170 (shoulder, N–H stretch), 2361 (w), 1722 (m), 1674 (w), 1594 (w), 769 (s) cm^{-1}. UV/Vis (CH$_2$Cl$_2$, 25 °C): λ = 277 nm.

Synthesis of [MesnacnacH$_2$(O)Br$_2$Se] (5): A THF solution of MesnacnacLi (0.17 g, 0.48 mmol) was added rapidly to a stirred THF suspension of SeBr$_4$ (0.43 g, 1.1 mmol) at –78 °C through a cannula, resulting in a red-orange solution that turned red-brown upon stirring for ca. 5 min. Following removal from the dry ice bath after 10 min of stirring, the reaction mixture was allowed to slowly reach ambient temperature and stirred for a total of 90 min. At this time the deep red-brown solution was filtered, concentrated, and stored at room temperature overnight, to afford yellow rectangular blocks of **5** in 46% yield based on the ligand (130 mg). Decomposition point: 136–142 °C became waxy dark red, did not melt below 250 °C. ^{1}H NMR (CDCl$_3$, 25 °C): δ = 3.39 (t, $^1J_{\text{H-H}}$ = 6.7 Hz, 1 H, NH), 3.65 (m, $^1J_{\text{H–H}}$ = 6.5 Hz, NH), 2.07 (s, 12 H, *ortho* Mes CH$_3$), 2.21 (s, 6 H, *para* Mes CH$_3$), 6.78 (s, 4 H, *meta* Mes CH) ppm. ^{13}C NMR (CDCl$_3$, 25 °C): δ = 19.2 (*ortho* Mes CH$_3$), 21.1 (*para* Mes CH$_3$), 100.1 [C(Br)Se], 128.8 (*meta* Mes CH), 135.6 (*para* Mes *C*CH$_3$), 135.8 (*ortho* Mes *C*CH$_3$), 136.2 (*ipso* Mes *C*N), 139.1 [C(O)*C*N], 194.6 (C=O) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3432.1 (br., m), 3302.3 (m), 2968.1 (w), 2911.7 (w), 1647.1 (w), 1590.8 (s), 1550.5 (m), 1482.0 (s), 1449.8 (s), 1381.3 (w), 1280.7 (w), 1260.5 (w), 1232.3 (w) 1184.0 (w), 1099.4 (br., m), 1026.9 (br., m), 865.9 (m), 801.42 (m), 684.6 (w) cm^{-1}. MS: *m*/*z* = 583.2, 504.2 [M – Br], 421.3 [M – 2 Br], 303.2 (M – 2 Br – Mes), 288.3 (M – 2 Br – MesN).

Single-Crystal X-ray Crystallography: Crystal data for compounds **2**–**4** are shown in Table 2. CCDC-664826, -664827, -664828 (for **2**–**4**) and -665192 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): NMR spectra compounds **2** and **5**.

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[16] Crystal data for **5**: Monoclinic, *P*2$_1$/*c*, *a* = 8.2284(8) Å, *b* = 13.5585(14) Å, *c* = 19.957(2) Å, β = 100.094(2)°, *V* =

2192.0(4) Å^3, $Z = 4$, reflections collected 17982, independent reflections 3956 [R(int)= 0.0468], GOF = 1.038, Final R indices [$I > 2\sigma(I)$] $R1 = 0.0343$, $wR2 = 0.0783$, R indices (all data): $R1 = 0.0574$, $wR2 = 0.0902$, Largest difference peak/hole 0.650/–0.523 e Å^{-3}.

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