Dalton Transactions

PAPER



Cite this: DOI: 10.1039/c5dt04236d

The role of imidoselenium(II) chlorides in the formation of cyclic selenium imides *via* cyclocondensation[†]

Aino J. Karhu,^a Olli J. Pakkanen,^a J. Mikko Rautiainen,^a Raija Oilunkaniemi,^a Tristram Chivers^b and Risto S. Laitinen*^a

The third member of the series of imidoselenium(II) chlorides $ClSe[N({}^{t}Bu)Se]_{n}Cl (n = 3)$ (9) has been isolated from the cyclocondensation reaction of ${}^{t}BuNH_{2}$ and $SeCl_{2}$ in THF in a molar ratio of *ca*. 3 : 1 and characterized in the form of two polymorphs **9a** and **9b** by single crystal X-ray analysis. The unusual structural features of this nine-atom chain are explained satisfactorily in terms of a bonding model that invokes intra-molecular secondary bonding interactions and hyperconjugation. The reaction of the bifunctional reagent $ClSe[N({}^{t}Bu)Se]_{2}Cl$ (**8**) with ${}^{t}BuNH_{2}$ in THF occurs *via* concurrent pathways to give 1,3,5-Se₃(N{}^{t}Bu)_{3} (**1**) and 1,3-Se₃(N{}^{t}Bu)_{2} (**3**a). The energetics of the reactions of ${}^{t}BuNH_{2}$ and SeCl₂ in THF have been calculated at the PBE0/def2-TZVPP level of theory in order to assess the feasibility of ClSe-[N({}^{t}Bu)Se]_{n}Cl (**7**–**9**, n = 1-3) as intermediates in the formation of known cyclic selenium imides. DFT calculations were also employed to explore the energy profile of the pathway of the formation of the first member of the series $ClSeN({}^{t}Bu)SeCl$ (**7**) from ${}^{t}BuNH_{2}$ and $SeCl_{2}$ in THF at 298 K. The neutral ligand $ClSeN({}^{t}Bu)SeCl$ (**7**) is *Se*,*Se*'-coordinated to the metal centre in the unusual adduct $[PdCl_{2}{Se},Se'-(SeCl)_{2}N-({}^{t}Bu)]\cdot[PdCl_{2}{Se},Se'-Se_{4}(N{}^{t}Bu)_{3}]\cdotMeCN$ (**10**-MeCN), which is the first metal complex of an imidoselenium(III) chloride.

Received 28th October 2015, Accepted 20th November 2015 DOI: 10.1039/c5dt04236d

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Introduction

Cyclocondensation reactions represent a common transformation for the synthesis of main group heterocycles, especially those containing nitrogen.¹ Although this preparative route is often a multi-step process, in the case of cyclophosphazenes (NPCl₂)_n it has been established with ³¹P NMR spectroscopy that the formation of different ring sizes, *e.g.* n = 3-8, occurs *via* the following three steps: (i) generation of an acyclic building block, (ii) chain growth and (iii) cyclisation.² The creation of chalcogen-nitrogen rings *via* cyclocondensation reactions may be more complex, as exemplified by the convenient synthesis of the S₄N₄ cage by the treatment of S[N(SiMe₃)₂]₂ with equimolar amounts of SCl₂ and SO₂Cl₂.³ In a recent book Ghosh and Berg speculated that the production of an eightmembered ring from these reagents involves more than ten steps.⁴

Investigations of the preparation of cyclic selenium imides *via* a variety of cyclocondensation routes over the past 32 years⁵⁻⁹ have revealed three classes of these inorganic heterocycles (see Chart 1): (a) $\text{Se}_m(\text{NR})_m$ (1, m = 3, $\text{R} = {}^t\text{Bu}$;⁷ 2a, m = 4, $\text{R} = {}^t\text{Bu}$;⁹ 2b, m = 4, $\text{R} = \text{Me}^9$), (b) the selenium-rich systems that incorporate an Se–Se bond [$\text{Se}_m(\text{NR})_{m-1}$]_n [m = 3, n = 1, 3a, $\text{R} = {}^t\text{Bu}$;^{7b} 3b, R = adamantyl;⁸ 4, m = 3, n = 3, $\text{R} = {}^t\text{Bu}$;⁶ 5, m = 4, n = 1, $\text{R} = {}^t\text{Bu}^{10}$] and (c) heterocycles with an Se–Se–Se functionality as represented by the unique examples 6a,b.^{6,9} The seven-membered ring 5 has only been characterised as a palladium complex.¹⁰

In previous investigations we have shown that the cyclocondensation reaction of ^{*t*}BuNH₂ with *in situ*-generated SeCl₂¹¹ in THF is a rich source of imido-selenium derivatives and the outcome of this reaction was found to be markedly dependent on the stoichiometry.^{7,9} In connection with the pathway to the formation of cyclic selenium imides, the main products are imidoselenium(II) chlorides $ClSe[N(^{t}Bu)Se]_{n}Cl$ (7, n = 1; 8, n =2; see Chart 2) when the molar ratio of ^{*t*}BuNH₂: SeCl₂ is <2 : 1.⁷ An increase in the molar ratio to >2 : 1 results in the formation of cyclic selenium imides.^{7b} For molar ratios in the



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 ^aLaboratory of Inorganic Chemistry, Center for Molecular Materials, University of Oulu, P.O. Box 3000, Oulu FI-90014, Finland. E-mail: risto.laitinen@oulu.fi
 ^bDepartment of Chemistry, University of Calgary, 2500 University Drive, N.W., Calgary, Alberta T2N 1N4, Canada

[†] Electronic supplementary information (ESI) available: QTAIM analyses of ClSe $[N(^tBu)Se]_nCl (n = 1-3)$, thermochemical cycles, selected bond parameters of **10**-MeCN PBE0/def2-TZVPP optimized Cartesian coordinates of ClSe $[N(^tBu)Se]_nCl (n = 1-3)$ and $Se_m(N^tBu)_m$ and $Se_m(N^tBu)_{m-1} (m = 3, 4)$ in the gas phase. CCDC 1433614–1433616. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt04236d



Chart 2 Imidoselenium(1) chlorides. range from 2:1 to 3:1, the heterocycles $1,5-\text{Se}_6(\text{N}^t\text{Bu})_2$ (6a), $1,3-\text{Se}_3(\text{N}^t\text{Bu})_2$ (3a), $1,3,5-\text{Se}_3(\text{N}^t\text{Bu})_3$ (1) and $1,3,5,7-\text{Se}_4(\text{N}^t\text{Bu})_4$ (2a)⁹ are the main products; the fifteen-membered ring $1,3,6,8,11,13-\text{Se}_9(\text{N}^t\text{Bu})_6$ (4)^{7b} is also observed when the molar ratio exceeds 3:1. Very recently, we reported a high-yield symptotic and the structure of the singlet

C

8

CI

N

9

^tBu

CI

7

ratio exceeds 3:1. Very recently, we reported a high-yield synthesis and the structural characterisation of the eightmembered ring 1,3,5,7-Se₄(NMe)₄ (**2b**) from cyclocondensation of (Me₃Si)₂NMe, with SeCl₂.⁹

In the light of the foregoing results we were interested in determining whether longer chain imidoselenium(π) chlorides, *e.g.* ClSe[N(^tBu)Se]₃Cl (9; see Chart 2), could be characterised and in assessing the role of such derivatives as intermediates in the formation of cyclic selenium imides.^{5*a*} In the present contribution we report (a) the isolation, structural characterization and bonding characteristics of $CISe[N(^{t}Bu)Se]_{3}CI$ (9), (b) the concurrent formation of 1 and 3a from the reaction of isolated $CISe[N(^{t}Bu)Se]_{2}CI$ (8) with ^{*t*}BuNH₂, (c) DFT calculations of the Gibbs energies at the PBE0/def2-TZVPP level of theory for the formation of imidoselenium(II) chlorides, $CISe[N(^{t}Bu)Se]_{n}CI$ (n = 1-3, 7-9) from $SeCl_{2}$ and ^{*t*}BuNH₂ and the subsequent generation of cyclic selenium imides from reactions of these intermediates with ^{*t*}BuNH₂, (d) DFT calculations of the energy profile of the pathway for the creation of the first member of the series $CISeN(^{t}Bu)SeCI$ (7) and (e) the X-ray structure of the unusual adduct $[PdCl_{2}{Se,Se'-(SeCI)_{2}N(^{t}Bu)}]$. $[PdCl_{2}{Se,Se'-Se_{4}(N^{t}Bu)_{3}}]$ (10), which incorporates the first metal complex of an imidoselenium(II) chloride.

Experimental section

General procedures

All reactions and manipulations of air- and moisture-sensitive compounds were carried out under an inert atmosphere by using a standard drybox or Schlenk techniques. Tetrahydrofuran and *n*-hexane were dried by distillation over Na/benzophenone and acetonitrile over CaH₂ under an argon atmosphere prior to use. Selenium granules (Merck) and SO₂Cl₂ (Aldrich) were used as purchased. ^tBuNH₂ (Aldrich) was distilled over KOH and stored over molecular sieves. SeCl₂ was prepared from freshly ground selenium and SO₂Cl₂ in THF by the literature procedure.¹¹ The reagents ClSe[N(^tBu)Se]₂Cl (8)^{7a} and [PdCl₂(NCPh)₂]¹² were also synthesized by published methods.

NMR spectroscopy

The ⁷⁷Se and the ¹⁴N NMR spectra were recorded unlocked on a Bruker Avance III 400 and Bruker DPX400 spectrometers operating at 76.31 and 28.91 MHz, respectively. The respective spectral widths were 113.64 and 20.00 kHz and the pulse widths were 16.75 and 12.0 μ s. The pulse delay for selenium was 1.0 s and for nitrogen 0.01 s. The ⁷⁷Se NMR spectra were referenced externally to a saturated aqueous solution of selenium dioxide and the chemical shifts are reported relative to neat Me₂Se [δ (Me₂Se) = δ (SeO₂) + 1302.6].¹³ The ¹⁴N NMR chemical shifts are referenced and reported relative to neat CH₃NO₂.

Formation and isolation of (a) $ClSe[N(^{t}Bu)Se]_{3}Cl (9)$ and (b) [PdCl₂{Se,Se'-(SeCl)₂N(^{t}Bu)}]·[PdCl₂{Se,Se'-Se₄(N ^{t}Bu)₃}]· MeCN (10·MeCN)

(a) A solution of SeCl₂ (6.6 mmol) in THF (5 cm³) was added to a solution of ^{*t*}BuNH₂ (2.2 cm³, 20.9 mmol) in THF (35 cm³) at -80 °C. The total initial concentration of selenium was [Se]_{Tot} = 0.16 mol dm⁻³. The reaction mixture was stirred for 30 min at -80 °C and for a further 1.5 h at room temperature. The precipitate of ^{*t*}BuNH₃Cl was removed by filtration. The ⁷⁷Se NMR spectrum of the reaction solution is shown in Fig. 1(a). The solvent was evaporated under dynamic vacuum to give a



Fig. 1 ⁷⁷Se NMR spectra of the product distribution from the reaction of ^tBuNH₂ and SeCl₂ (molar ratio *ca.* 3 : 1) in THF (a) initial total selenium concentration [Se]_{Tot} = 0.16 mol dm⁻³; (b) initial total selenium concentration [Se]_{Tot} = 0.07 mol dm⁻³. The spectra were recorded *ca.* 3 h after the commencement of the reaction.

dark red oil. An *n*-hexane solution of this oil at -20 °C deposited a small amount of red-brown crystals of $ClSe[N(^tBu)-Se]_3Cl$ (9), red-orange crystals of $ClSe[N(^tBu)Se]_2Cl$ (8), orange crystals of 1,5-Se₆(N^tBu)₂ (6a) and colourless crystals of (^tBuNH)₂SO₂, as well as pale yellow needle-shaped crystals. The products were separated manually under a microscope. Two polymorphs 9a and 9b were isolated from different batches of crystals. Anal. Calcd for $C_{12}H_{27}Cl_2N_3Se_4$ (9): C, 24.02; H, 4.54; N, 7.00%. Found: C, 24.12; H, 4.61; N, 7.11%.

(b) A solution of SeCl₂ (1.4 mmol) in THF (5 cm³) was added to a solution of ^{*t*}BuNH₂ (0.44 cm³, 4.2 mmol) in THF (15 cm³) (total initial concentration of selenium [Se]_{Tot} = 0.07 mol dm⁻³) and the reaction mixture was treated in the manner described in (a) above. The ⁷⁷Se NMR spectrum of the reaction solution is shown in Fig. 1(b). After filtration and reduction of the solution volume to *ca*. 5 cm³ under dynamic vacuum, the filtrate was added into a solution of [PdCl₂(NCPh)₂] (0.067 g, 0.17 mmol) in THF (15 cm³) at -80 °C. The reaction mixture was stirred for 30 min at -80 °C and then for 19 h at room temperature. A small amount of red precipitate was allowed to settle and a red solution was

decanted *via* cannula. Solvent was evaporated under dynamic vacuum to give a red-brown oil, which was extracted with acetonitrile (5 cm³). The extract was cooled to -20 °C to give a few red crystals of $[PdCl_2{Se,Se'-(SeCl)_2N(^tBu)}]\cdot[PdCl_2{Se,Se'-Se_4(N^tBu)_3}]\cdotMeCN$ (**10**·MeCN).

Reaction of ClSe[N(^tBu)Se]₂Cl (8) with ^tBuNH₂

^tBuNH₂ (0.08 cm³, 0.76 mmol) was added to a solution of ClSe $[N(^{t}Bu)Se]_{2}Cl$ (0.225 g, 0.50 mmol) in THF (10 cm³) at -80 °C. The reaction mixture was stirred for 15 min at -80 °C and for further 2 h at room temperature. The ^tBuNH₃Cl precipitate was removed by filtration. The ⁷⁷Se NMR identification of the components in the THF solution of ClSe[N(^tBu)Se]_{2}Cl before the addition of ^tBuNH₂ and that of the products in the yellow filtrate is discussed in the Results and discussion section.

X-ray crystallography

Diffraction data for compounds 9a, 9b and 10 were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K_{α} radiation (λ = 0.71073 Å). Crystal data and the details of structure determinations are given in Table 1. All structures were solved by direct methods using SHELXS-2013 and refined using SHELXL-2013.¹⁴ 9b is chiral but was found to be a racemic twin. The refinement of the structure was therefore carried out by utilising the TWIN command, which is incorporated in SHELXL-2013. After the full-matrix leastsquares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions in the methyl groups (C-H = 0.98 Å). In the final refinement the hydrogen atoms were riding with the carbon atom to which they were bonded. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.5 times to that of the corresponding carbon. The scattering factors for the neutral atoms were those incorporated with the program.

Computational details

All calculations were performed on Gaussian 09 program¹⁵ by employing the PBE0 hybrid functional¹⁶ together with the def2-TZVPP basis sets¹⁷ taken from EMSL basis set exchange.¹⁸ Dispersion forces were treated by using the D3BJ version of Grimme's empirical correction with Becke-Johnson damping parameterized for PBE0 functional.¹⁹ Full structure optimisation was carried out for each species considered in this work and the frequencies were calculated for the optimum geometries to ascertain that the nature of the stationary points. Energies in THF were calculated using CPCM method implemented in Gaussian 09.20 The quantum theory of atoms in molecules (QTAIM) was used to study intramolecular interactions in ClSe[N(^tBu)Se]_nCl (n = 1, 2, 3) structures.²¹ In the gas phase structures, four different parameters were used to characterize interactions, namely charge density, Laplacian of charge density, electronic electron density and kinetic energy per electron. In addition, delocalisation index was used as a measure of bond strength. AIMAll software was used to QTAIM calculations.22

Table 1	Details of the structure determinations of	ClSe[N(^t Bu)Se] ₃ Cl (9a and 9b)) and [PdCl ₂ {Se,Se'-(SeCl) ₂ N	J(^t Bu)}]·[PdCl ₂ {Se,Se'-Se ₄ (N ^t Bu) ₃ }]·MeCN
(10·MeC)	1)			

	9a	9b	10·MeCN
Empirical formula	C12H27Cl2N3Se4	C12H27Cl2N3Se4	C ₁₈ H ₃₉ Cl ₆ N ₅ Pd ₂ Se ₆
Formula weight	600.10	600.10	1224.80
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_{1}2_{1}2_{1}$	$P2_1/n$
a (Å)	12.390(3)	10.972(2)	13.627(3)
$b(\mathbf{A})$	10.575(2)	12.070(2)	14.720(3)
$c(\mathbf{A})$	16.502(3)	15.887(3)	18.670(4)
$\beta(\circ)$	106.96(3)	90.00	101.52(3)
$V(A^3)$	2068.0(8)	2104.0(7)	3669.4(13)
$T(\mathbf{K})$	150(2)	120(2)	150(2)
Z	4	4	4
F(000)	1160	1160	2320
$D_{\rm c} ({\rm g \ cm^{-1}})$	1.927	1.894	2.217
$\mu(Mo-K_{\star})$ (mm ⁻¹)	7.352	7.226	7.388
Crystal size (mm)	0.40 imes 0.20 imes 0.20	$0.40 \times 0.20 \times 0.20$	$0.30 \times 0.30 \times 0.05$
θ range (°)	3.28-26.00	3.59-26.00	3.05-26.00
Number of reflections collected	8089	8154	26214
Number of unique reflections	3891	4026	7124
Number of observed reflections ^{<i>a</i>}	3304	3867	5607
Number of parameters	200	200	348
RINT	0.0515	0.0375	0.1634
R_1^{hb}	0.0400	0.0261	0.0515
wR ₂ ^b	0.0880	0.0576	0.1075
R_1 (all data)	0.0524	0.0286	0.0789
wR_2 (all data)	0.0940	0.0590	0.1231
GOF	1.061	1.034	1.035
Max. and min. heights in final difference Fourier synthesis (e \AA^{-3})	0.558-(-0.485)	0.491-(-0.379)	1.334-(-1.887)
${}^{a}I \geq 2\sigma(I). {}^{b}R_{I} = \Sigma F_{o} - F_{c} / \sum F_{o} , wR_{2} = [\sum w(F_{o}{}^{2} - F_{c}{}^{2})^{2} / \sum wF_{o}{}^{4}]^{1/2}.$			

Natural bond orbital (NBO) method²³ was used to study donor-acceptor interactions in gas-phase optimized geometries. NBO analyses were done using the NBO 5.9 software.²⁴

The energetics of the formation of imidoselenium(π) chlorides of different chain lengths has also been computed at PBE0/def2-TZVPP level of theory. The contribution of the formation of solid 'BuNH₃Cl in the energetics of the reactions was estimated by computing the energy of formation of the ion-pair 'BuNH₃⁺ and Cl⁻ and correcting the energy for lattice effects by involving solid-state DFT calculations, which utilize periodic boundary conditions.

Optimisations and frequency calculations for the ^tBuNH₃Cl sublimation energy estimations were performed with Crystal14 program²⁵ using the PBE0 functional¹⁶ and pob-TZVP basis set.²⁶ For the crystal calculations, the Hamiltonian matrix has been diagonalised in a set of k-points in a reciprocal space generated according to the Pack-Monkhorst method for sampling the first Brillouin zone with shrinking factor (8, 8). The five truncation factors controlling the infinite coulomb and exchange sums were set to [8 8 8 8 16] for all calculations.²⁷ Default SCF convergence threshold on total energy $(10^{-7} \text{ hartree})$ was used for optimizations while for frequency calculations the threshold was increased to 10⁻¹¹ hartree. Vibrational corrections to energies for crystal structure were determined using harmonic phonon frequencies calculated at Γ -point of the Brillouin zone without considering phonon dispersion.27

Results and discussion

Effect of concentration on the formation of cyclic selenium imides

As discussed in the Introduction, the outcome of the cyclocondensation reaction of ^tBuNH₂ and SeCl₂ is markedly dependent on the molar ratio of the reagents.^{5,7,9} For a molar ratio of $2\frac{1}{2}$: 1, the initial reaction mixture gives rise to a complex mixture of Se-N products. After a period of several days, the solution contains predominantly 1,3,5,7-Se₄(N^tBu)₄ (2a) with the concomitant formation of a red precipitate.9 In this study we report, for the first time, that the concentration of the reagents is influential on the product distribution in the solution. For a molar ratio of *ca.* 3 : 1, the ⁷⁷Se NMR spectrum of the reaction solution with a selenium concentration of 0.16 mol dm⁻³ in THF shows a mixture of products similar to that observed previously for the $2\frac{1}{2}$: 1 reaction⁹ [Fig. 1(a)]. However, dilution of the initial selenium concentration by a factor of ca. 2.3 results in the almost exclusive detection of the eightmembered ring 2a in the solution [Fig. 1(b)]. It should be noted, however, that at both concentrations shown in Fig. 1, the reactions also afforded insoluble products, which were filtered from the solution prior to the recording of the ⁷⁷Se NMR spectrum.

X-ray structure and bonding of ClSe[N(^tBu)Se]₃Cl (9)

Upon evaporation of the solvent from the THF solution shown in Fig. 1(a) and subsequent extraction with *n*-hexane, five

kinds of crystals were isolated: (a) a small amount of red crystals of the new imidoselenium(II) chloride ClSe[N(^tBu)Se]₃Cl (9), (b) red-orange crystals of 8, (c) orange crystals of 6a, (d) colourless crystals of (^tBuNH)₂SO₂ and (e) pale yellow needles. The crystals were separated manually and the new imidoselenium(II) chloride $ClSe[N(^{t}Bu)Se]_{3}Cl$ (9) was characterised by elemental (CHN) analysis and single-crystal X-ray crystallography (the crystal structures of two polymorphs 9a and 9b are described below). Compounds $8^{7a}_{,7a}$ $6a^{6}_{,a}$ and $({}^{t}BuNH)_{2}SO_{2}^{,28}$ were identified by comparison of the unit cell parameters with the literature values. The small amount of the pale yellow needles and the poor quality of the crystals precluded their identification.

The acyclic derivative $ClSe[N(^{t}Bu)Se]_{3}Cl$ (9) crystallises mainly as a monoclinic polymorph, 9a, but from one reaction under identical conditions, an orthorhombic polymorph 9b was obtained. The molecular structures of 9a and 9b are virtually identical, but their packing and intermolecular contacts are different. The molecular structure of 9a together with the atomic numbering scheme is shown in Fig. 2 and the selected bond lengths and bond angles in both 9a and 9b are shown in Table 2 with comparison to the corresponding parameters in the lower homologue $ClSe[N(^{t}Bu)Se]_{2}Cl$ (8).

The molecular structures of both polymorphs of 9 show features similar to those determined earlier for ClSe[N(^tBu)Se]₂Cl (8).^{7*a*} There is a characteristic short secondary bonding Se…Se contact of 3.3445(9) Å in 9a [3.3677(6) Å in 9b], cf. sum of van der Waals radii for Se is 3.8 Å (ref. 29a) or 4.0 Å.^{29b} The corresponding Se...Se contact of 2.891(10) Å in 8^{7a} is markedly shorter. This secondary intramolecular interaction leads to significant variations in the bond lengths within the molecules (see Table 2). These differences may be explained qualitatively by a simple model involving hyperconjugation, as shown in Fig. 3.^{5a} This model is similar to that used to rationalise the bond length alternations in the homocyclic S₇ molecule³⁰ or the

Fig. 2 Molecular structure of the monoclinic polymorph of CISe[N(^tBu) Se]₃Cl (9a) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

CI11

N2

Table 2 Selected bond lengths (Å) and angles (°) in 9a, 9b and 8

	9a exptl	9b exptl	9 DFT ^{<i>a</i>}	$8 \operatorname{exptl}^{b,c}$	8 DFT ^a
Se1–N1	1.754(4)	1.764(5)	1.768	1.758(3)	1.764
Se2-N1	1.933(4)	1.932(5)	1.916	1.948(3)	1.920
Se2-N2	1.806(4)	1.814(5)	1.799	1.803(3)	1.798
Se3-N2	1.839(4)	1.857(5)	1.856	1.822(3)	1.830
Se3-N3	1.907(4)	1.903(5)	1.884		
Se4-N3	1.791(4)	1.784(5)	1.789		
Se1–Cl11	2.2761(16)	2.2618(17)	2.224	2.269(1)	2.224
Se4-Cl41	2.2536(17)	2.2541(17)	2.218	$2.312(1)^d$	2.224^{d}
Cl11-Se1-N1	107.17(15)	106.78(17)	106.5	109.24(10)	107.4
Cl41-Se4-N3	105.08(14)	105.36(16)	105.7	98.93(3)	99.5
N1-Se2-N2	97.85(19)	101.9(2)	100.8	96.54(12)	98.0
N2-Se3-N3	102.55(18)	101.6(2)	101.5		
Se1-N1-Se2	116.7(2)	117.4(3)	116.8	118.03(14)	116.9
Se2-N2-Se3	115.5(2)	113.6(2)	114.2	112.97(16)	113.2
Se3-N3-Se4	111.5(2)	111.7(2)	114.0		
Se1…Se3	3.3445(9)	3.3677(6)	3.272	2.891(10)	3.075
Se3…Cl41	3.6297(17)	3.6897(16)	3.848		

^a PBE0/def2-TZVPP optimisation in the gas phase. ^b From the crystal structure determination in ref. 7a. ^c The numbering of the corresponding atoms in **8** follow a different scheme, 7^a which has been transformed in this table to facilitate comparison. ^{*d*} According to this scheme, this Se–Cl bond in 8 should be numbered Se3-Cl31.



Fig. 3 A simple hyperconjugation model describing the observed short Se...Se contact and the bond length alternation in 8 and 9 (see Table 3). $Q = Cl(8) \text{ or } N(^{t}Bu)SeCl(9).$

charge delocalization in the $Se_6I_2^{2+}$ cation.³¹ The p electron lone pair at Se1 (see Fig. 2 for the numbering scheme) can interact with the σ^* orbital of the Se3–Cl31 bond in 8 or Se3–N3 bond in 9, respectively, leading to lengthening of the corresponding bonds from their respective single-bond values of 2.16 or 1.87 Å.³² The hyperconjugation of the same lone pair of electrons along the chain with the σ^* orbital involving atoms Se2 and N1 leads to the shortening of the Se1-N1 bond and lengthening of Se2-N1 from their single-bond values (Fig. 3).³² This model also accounts for the observation that the Se2-N2 and Se3-N2 bonds in 9a,b and 8 are close to single-bond lengths. This simple model, however, fails to explain why the Se4-N3 bond in 9 is short.

In order to gain a more quantitative insight into the nature of the hyperconjugative interactions we have carried out both QTAIM and NBO calculations of 8 and 9 at PBE0/def2-TZVPP level of theory. The optimised bond parameters are presented

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Fig. 4 QTAIM electron densities at the bond critical points in (a) 8 and (b) 9. The most important $n^2 \rightarrow \sigma^*$ interaction energies based on NBO analysis in (c) 8 and (d) 9. The calculations were carried out at PBE0/def2-TZVPP level of theory.

in Table 2 and show a good agreement with the experimental values. The summaries of QTAIM analyses in 8 and 9 are included in Fig. 4(a) and (b), respectively. Further details of the QTAIM results are presented in ESI.[†]

QTAIM calculations show that there is a bond critical point between atoms Se1 and Se3 in both 8 [Fig. 4(a)] and 9 [Fig. 4(b)]. It can be seen from the electron density values at bond critical points illustrated in Fig. 4(a) and (b) that the Se1...Se3 interaction is stronger in 8 than the corresponding interaction in 9. This is also manifested by the relative Se...Se distances (see Table 2). The relative magnitudes of the electron densities in Se–N and Se–Cl bonds are consistent with the observed bond length alternations. We note that though there is a relatively short Se3...Cl41 close contact in 9 (see Table 2), QTAIM indicates no bond critical point.

The most important interaction energies in 8 and 9 based on the NBO analyses at the PBE0/def2-TZVPP level of theory are shown in Fig. 4(c) and (d). These findings are expectedly consistent with the QTAIM results and also indicate that the Se…Se interaction is weaker in $ClSe[N(^{t}Bu)Se]_{3}Cl$ (9) than in $ClSe[N(^{t}Bu)Se]_{2}Cl$ (8). Various $n^{2} \rightarrow \sigma^{*}$ donor-acceptor interactions explain the alternating bond lengths in $ClSe[N(^{t}Bu) Se]_{n}Cl$ (n = 2, 3). In addition to the $n^{2}(Se) \rightarrow \sigma^{*}(Se-Cl)$ and $n^{2}(Se) \rightarrow \sigma^{*}(Se-N)$ hyperconjugation, the NBO interactions indicate that $n^2(N) \rightarrow \sigma^*(\text{Se-Cl})$ and $n^2(N) \rightarrow \sigma^*(\text{Se-N})$ interactions also play a significant role in the bond length alternation and reinforce the simple qualitative model shown in Fig. 3. Analogous $n^2 \rightarrow \sigma^*$ interactions have also been computed for the ClSeNSeCl⁺ cation.³³ Consistent with the QTAIM results, NBO indicates no significant interaction energy $n^2(\text{Cl41}) \rightarrow \sigma^*(\text{Se3-N3})$ [see Fig. 4(d)].

In principle, the molecular packing in the solid state could also have an effect on the observed short Se…Se contacts and bond length alternations. The fortuitous crystallisation of the two polymorphs **9a** and **9b** rules out this possibility. The comparison of their close intermolecular contacts in Fig. 5 clearly shows that, although these interactions differ significantly from each other in **9a** and **9b**, the molecular geometries and structures of the two polymorphs are virtually identical.

Reaction of ClSe[N(^tBu)Se]₂Cl with ^tBuNH₂

In order to assess the proposed role of acyclic imidoselenium (II) chlorides $ClSe[N({}^{t}Bu)Se]_{n}Cl (n = 1-3) (7-9)$ in the formation of cyclic selenium imides,^{5*a*} we carried out the reaction of the bifunctional reagent $ClSe[N({}^{t}Bu)Se]_{2}Cl (8)$ with ${}^{t}BuNH_{2}$ in THF (the homologue 8 was chosen because it is available in much larger amounts than the smallest homologue 7⁷ and the longest chain 9 isolated in the current work).



Fig. 5 Shortest intermolecular Se-Se and Se-Cl contacts in (a) monoclinic polymorph 9a and (b) orthorhombic polymorph 9b.

A solution of the crystals of **8** in THF exhibited four resonances in the ⁷⁷Se NMR spectrum [Fig. 6(a)]. Two resonances at 1657 and 1629 ppm in the intensity ratio of 2:1 can be assigned to **8**, *cf.* δ (⁷⁷Se) = 1620 and 1613 ppm in toluene.⁷ The resonance at 1807 ppm is attributed to ClSeN(^{*t*}Bu)SeCl (7), *cf.* 1786 ppm in toluene,^{7b} and that at 1486 ppm is due to 1,3,5,7-Se₄(N^{*t*}Bu)₄ (2**a**).⁹ Semi-quantitative integration of the intensities indicates that the mixture presented in Fig. 6(a) contained *ca.* 65% of **8**, 20% of 7 and 15% of **2a.** The composition of the solution varied from batch to batch, but the basic features were quite reproducible.

It can be seen from Fig. 6(b) that the addition of ${}^{t}BuNH_{2}$ into the THF solution of the crystals of $ClSe[N({}^{t}Bu)Se]_{2}Cl$ (8)

afforded a mixture of 1,3-Se₃(N^{*t*}Bu)₂ (**3a**), 1,3,5-Se₃(N^{*t*}Bu)₃ (**1**) and 1,3,5,7-Se₄(N^{*t*}Bu)₄ (**2a**) with a relative composition of *ca*. 50, 30 and 20% as judged by intensities of the resonances in the ⁷⁷Se NMR spectrum. The concurrent reactions of **8** and ^{*t*}BuNH₂ leading to the formation of **3a** and **1** can be formulated according to eqn (1) and (2). The comparison of the composition of the product mixture shown in Fig. 6(b) to that of the THF solution of dissolved crystals of **8** prior to the addition of ^{*t*}BuNH₂ indicates that *ca*. 60% of **8** has reacted according to eqn (1) and *ca*. 40% according to eqn (2). ClSeN(^{*t*}Bu)SeCl (7) is also expected to react with ^{*t*}BuNH₂ and its resonance in the spectrum shown in Fig. 6(b) is indeed very weak. One possibility is that it has formed **8** upon the reaction with ^{*t*}BuNH₂

$$ClSe[N({}^{t}Bu)Se]_{2}Cl + 3{}^{t}BuNH_{2} \rightarrow 1, 3-Se_{3}(N{}^{t}Bu)_{2} + 1/2{}^{t}BuN = N{}^{t}Bu + 2{}^{t}BuNH_{3}Cl$$

(1)

$$ClSe[N(^{t}Bu)Se]_{2}Cl + 3^{t}BuNH_{2} \rightarrow 1, 3, 5 \cdot Se_{3}(N^{t}Bu)_{3} + 2^{t}BuNH_{3}Cl$$
(2)

Paper

and has therefore also contributed to the formation of **1** and **3a**. The eight-membered 1,3,5,7-Se₄(N^{*t*}Bu)₄ (**2a**) ring seems to have been formed only during the dissolution of crystals of **8** in THF. The ¹⁴N NMR spectrum of the same solution exhibited a resonance at 150 ppm, which is attributed to the diazene ^{*t*}BuN=N^{*t*}Bu^{7*b*} *cf*. δ (¹⁴N) = 154.0 ppm for EtN=NEt.³⁴ This identification indicates that a redox process has taken place during the reaction.

This experiment demonstrates that the two main classes of cyclic selenium imides (*vide supra*) are generated from the same bifunctional intermediate **8** *via* either reduction to give **3a** or nucleophilic substitution to give **1**. Since *ca*. 50% of **8**



Fig. 6 77 Se NMR spectra of (a) the crystals of ClSe[N(^tBu)Se]₂Cl (8) dissolved in THF and (b) the cyclic selenium imides formed upon addition of ^tBuNH₂ into the THF solution.

has dissociated upon dissolution in THF, the reaction of ${}^{t}BuNH_{2}$ with 8 was carried out in a 3 : 2 molar ratio rather than the 3 : 1 ratio required for eqn (1) and (2).

Reaction pathways to cyclic selenium imides

The final products from the cyclocondensation reaction of ^{*t*}BuNH₂ and SeCl₂ are mainly cyclic selenium imides of varying ring sizes.^{5,7,9} It has been suggested that imidoselenium(π) chlorides are key intermediates in the formation of these heterocycles.^{5*a*} Reaction pathways that invoke the involvement of all three known bifunctional reagents of the type ClSe[N(^{*t*}Bu) Se]_{*n*}Cl (*n* = 1–3) (7–9) and account for the formation of the known cyclic selenium imides **1**, **2a**, **3a** and **5** are depicted in Scheme **1**.

The PBE0/def2-TZVPP Gibbs energies of successive formation of the imidoselenium(π) chlorides of different chain length $ClSe[N(^{t}Bu)Se]_{n}Cl$ (*n* = 1-3) (7-9) are presented in Table 3 and indicate very favourable reactions in THF. The calculated Gibbs energies of formation of the cyclic selenium imides $\operatorname{Se}_m(N^t \operatorname{Bu})_m$ and $\operatorname{Se}_m(N^t \operatorname{Bu})_{m-1}$ (m = 3, 4) from ClSe-[N(^tBu)Se]₂Cl (8) and ClSe[N(^tBu)Se]₃Cl (9) are also summarised in Table 3 for reactions at room temperature. It can be seen that the redox processes leading from $ClSe[N(^{t}Bu)Se]_{2}Cl$ (8) to $1,3-Se_3(N^tBu)_2$ (3a) or from $ClSe[N(^tBu)Se]_3Cl$ (9) to 1,3,5- $Se_4(N^tBu)_3$ (5) are clearly more favourable than the formation of $1,3,5-Se_3(N^tBu)_3$ (1) from 8 or that of $1,3,5,7-Se_4(N^tBu)_4$ (2a) from 9 which, however, are also spontaneous. The driving force in all reactions shown in Table 3 is the formation of ^tBuNH₃Cl(s), but the additional elimination of the diazene ^tBuN=N^tBu accounts for the larger negative ΔG values for the redox processes. The thermochemical cycles leading to the Gibbs values reported in Table 3 are given in the ESI.†

The energy profile of the first steps in the formation of the shortest imidoselenium(II) chloride ClSeN(^tBu)SeCl (7) is shown in Fig. 7. There are intermediate products lying in local minima and two transition states, TS1 and TS2, with a single imaginary frequency corresponding to the reaction coordinate. After an initial adduct formation between the nitrogen atom of ^tBuNH₂ and the selenium atom of SeCl₂, the intermediate interacts with another molecule of the amine leading to rearrangement, proton transfer and the precipitation of solid ^tBuNH₃Cl. The key building block ^tBuN(H)SeCl then interacts with yet another amine molecule and SeCl₂ to give $ClSeN(^{t}Bu)SeCl$ (7) and $^{t}BuNH_{3}Cl(s)$ via TS2. The activation energies for the transition states TS1 and TS2 are reasonably low (Fig. 7) and the driving force for the reaction is indeed the formation of ^tBuNH₃Cl(s). It is conceivable that subsequent transformations $7 \rightarrow 8 \rightarrow 9$ follow similar routes with moderate activation barriers. However, they may also involve alternative pathways, which are not considered here.

X-ray structure of $[PdCl_2{Se,Se'-(SeCl)_2N(^tBu)}]\cdot [PdCl_2{Se,Se'-Se_4(N^tBu)_3}]\cdot MeCN (10 \cdot MeCN)$

We have reported previously that the reaction of the selenium(v) diimide Se(N^tBu)₂ with [PdCl₂(NCPh)₂] in a 2:1 molar ratio



Scheme 1 Proposed reaction pathways for the production of imidoselenium(μ) chlorides and cyclic selenium imides from the cyclocondensation reaction of ${}^{t}BuNH_{2}$ and SeCl₂.

Table 3 PBE0/def2-TZVPP Gibbs energies of the formation of (a) $ClSe[N({}^{t}Bu)Se]_{n}Cl (n = 1-3) (7-9)$ from $SeCl_{2}$ and ${}^{t}BuNH_{2}$ in THF and (b) cyclic selenium imides from $ClSe[N({}^{t}Bu)Se]_{n}Cl [n = 2 (8) \text{ or } 3 (9)]$ in THF (see ESI for the thermochemical cycles leading to the Gibbs energies of these reactions)

Reaction	ΔG (298 K) (kJ mol ⁻¹)
(a) $CISe[N(^{t}Bu)Se]_{u}CI(n = 1-3)$	
$2SeCl_{2}(solv) + 3^{t}BuNH_{2}(solv) \rightarrow ClSeN(^{t}Bu)SeCl(solv) + 2^{t}BuNH_{3}Cl(s)$	-169
$ClSeN(^{t}Bu)SeCl(solv) + SeCl_{2}(solv) + 3^{t}BuNH_{2}(solv) \rightarrow ClSe[N(^{t}Bu)Se_{2}(solv) + 2^{t}BuNH_{3}Cl(s)$	-153
$ClSe[N(^{t}Bu)Se]_{2}Cl(solv) + SeCl_{2}(solv) + 3^{t}BuNH_{2}(solv) \rightarrow ClSe[N(^{t}Bu)Se]_{3}Cl(solv) + 2^{t}BuNH_{3}Cl(s)$	-134
(b) Cyclic $\operatorname{Se}_m(N^t \operatorname{Bu})_m$ and $\operatorname{Se}_m(N^t \operatorname{Bu})_{m-1}$ $(m = 3, 4)$	
$ClSe[N(^{t}Bu)Se]_{2}Cl(solv) + 3^{t}BuNH_{2}(solv) \rightarrow 1,3-Se_{3}(N^{t}Bu)_{2}(solv) + 1/2^{t}BuN=N^{t}Bu(solv) + 2^{t}BuNH_{3}Cl(s)$	-162
$ClSe[N('Bu)Se_2Cl(solv) + 3'BuNH_2(solv) \rightarrow 1,3,5-Se_3(N'Bu)_3(solv) + 2'BuNH_3Cl(s)$	-76
$ClSe[N('Bu)Se]_{3}Cl(solv) + 3'BuNH_{2}(solv) \rightarrow 1,3,5-Se_{4}(N'Bu)_{3}(solv) + 1/2'BuN=N'Bu(solv) + 2'BuNH_{3}Cl(s)$	-163
$ClSe[N('Bu)Se]_{3}Cl(solv) + 3'BuNH_{2}(solv) \rightarrow 1,3,5,7-Se_{4}(N'Bu)_{4}(solv) + 2'BuNH_{3}Cl(s)$	-51

unexpectedly produces the palladium complex $[PdCl_2{Se,Se'-Se_4(N^tBu)_4}]$, which contains the elusive cyclic selenium imide 1,3,5,7-Se_4(N^tBu)_4 (2a).¹⁰ In this work we showed that 2a is detected almost exclusively in the filtered dilute THF solution from the reaction of tBuNH_2 and SeCl₂ in a 3 : 1 molar ratio [Fig. 1(b)]. In the light of this new finding, we attempted to prepare a palladium complex of 2a by the direct reaction of PdCl₂(NCPh)₂] with a THF solution of 2a prepared in this manner. Interestingly, the work-up of the reaction mixture *via*

acetonitrile extraction produced a small amount of red crystals of the unusual adduct $[PdCl_2{Se,Se'-(SeCl)_2N(^tBu)}]\cdot[PdCl_2{Se, Se'-Se_4(N^tBu)_3}]\cdotMeCN (10 \cdot MeCN), which was identified by single crystal X-ray analysis.$

The molecular structure and atomic numbering scheme of **10**·MeCN are shown in Fig. 8, together with selected bond lengths and angles. This adduct consists of two different palladium complexes $[PdCl_2{Se,Se'-(SeCl)_2N(^tBu)}]$ and $[PdCl_2{Se, Se'-Se_4(N^tBu)_3}]$ in the same crystalline lattice. The former is



Fig. 7 PBE0/def2-TZVPP energy profile in the creation of ClSeN(t Bu)SeCl (7) from the reaction of t BuNH₂ and SeCl₂ in a 3 : 2 molar ratio in THF at 298 K. Energies are given in kJ mol⁻¹. The species that are not involved in the actual interactions are indicated as molecular formulae in black for each step. Their contributions to total energetics have, however, been taken into account in order to keep the composition of the reaction system constant throughout the reaction.

the first representative of a coordination complex of an imidoselenium(π) chloride, specifically ClSeN(^{*t*}Bu)SeCl (7), while the latter is the second example of a palladium complex of the seven-membered ring 5.¹⁰ These two complexes are linked together by Se…Cl contacts in the range 2.8186(24)–3.4342(28) Å, *cf.* sum of van der Waals' radii of Cl and Se is 3.81 Å.²⁹ Such interactions are relatively common in chalcogenolato and chalcogenoether complexes of palladium(π) and platinum(π).³⁵

The neutral ligand ClSeN(^{*t*}Bu)SeCl (7) in the [PdCl₂{*Se*,*Se'*-(SeCl)₂N(^{*t*}Bu)}] component of **10** is *Se*,*Se'*-chelated to the palladium centre. The cyclic **1**,3,5-Se₄(N^{*t*}Bu)₃ (5) ligand in the other half of the adduct is also *Se*,*Se'*-chelated, as found previously for the individual complex [PdCl₂{*Se*,*Se'*-Se₄(N^{*t*}Bu)₃}].¹⁰ In both components of **10**, palladium has an essentially square-planar coordination [$\Sigma \angle$ (Pd) = 359.9° in both cases].

Coordination of 7 to the metal centre in $[PdCl_2{Se,Se'-(SeCl)_2N-({}^{t}Bu)}]$ has little effect on the Se–N bond distances compared to those in the free ligand 7 [1.811(6) and 1.825(6) Å in **10**, and 1.804 (6) and 1.816(7) Å in 7^{7a}], whereas the Se–N–Se bond angle of 107.8(3)° in the complex is constrained by *ca.* 9° from the value of 116.7(4)° in the free ligand^{7a} as a result of the *Se,Se'*-chelation (see ESI† for a complete comparison of bond parameters). The Se–Cl distances of 2.233(2) and 2.223(2) Å are slightly longer than those of 2.215(2) and 2.223(2) Å in 7. The Cl–Se–N bond angles of 100.8(2) and 101.0(2)° are smaller than the corresponding angles of 103.8(2) and 103.9(2)° in the free molecule.

The structural parameters for the $[PdCl_2{Se,Se'-Se_4(N'Bu)_3}]$ component of the adduct **10** (see ESI[†]) are similar to those reported for the individual complex¹⁰ and do not warrant further comment.



Fig. 8 Molecular structure of $[PdCl_2\{Se,Se'-(SeCl)_2N(^tBu)\}] \cdot [PdCl_2\{Se,Se'-Se_4(N^tBu)_3]] \cdot MeCN (10 \cdot MeCN) indicating the numbering of the atoms. The thermal ellipsoids have been drawn at the 50% probability level. The MeCN molecule and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd2–Se5 2.3647(10), Pd2–Se6 2.3520(10), Pd2–Cl3 2.3138(19), Pd2–Cl4 2.315(2), Se5–Cl5 2.233(2), Se6–Cl6 2.250(2), Se5–N4 1.811(6), Se6–N4 1.825(6), Se5–Pd2–Se6 77.07(3), Se5–Pd2–Cl3 94.69(6), Se5–Pd2–Cl4 170.66(5), Se6–Pd2–Cl3 171.27(6), Se6–Pd2–Cl4 93.70(5), Cl3–Pd2–Cl4 94.45(7), Cl5–Se5–N4 100.8(2), Cl6–Se6–N4 101.0(2), Se5–N4–Se6 107.8(3). The bond parameters of [PdCl_2{Se,Se'-Se_4(N^tBu)_3}] have been given in ESI.†$

Conclusions

The product distribution in the cyclocondensation reaction of ^{*i*}BuNH₂ and SeCl₂ depends, not only on the molar ratio, but also on the concentration of the reagents. Dilute solutions contain only 1,3,5,7-Se₄(N^{*t*}Bu)₄ (2a), whereas the doubling of the concentration produces a complicated mixture of soluble products from which the third member of the series of imidose-lenium(II) chlorides $ClSe[N(^tBu)Se]_nCl$ (n = 3) has been isolated as two polymorphs **9a** and **9b**. The structural features of this nine-atom chain can be explained by a bonding model that invokes hyperconjugation and secondary bonding. The concurrent formation of 1,3-Se₃(N^{*t*}Bu)₂ (**3a**) and 1,3,5-Se₃(N^{*t*}Bu)₃ (**1**) from the reaction of the bifunctional reagent $ClSe[N(^tBu)Se]_2Cl$ (**8**) with ^{*t*}BuNH₂ in THF suggests that the two main classes of cyclic selenium imides are generated from the acyclic precursor *via* either reduction or nucleophilic substitution.

The cyclocondensation reaction of ^{*t*}BuNH₂ and SeCl₂ in THF was also explored computationally *via* DFT calculations at the PBE0/def2-TZVPP level of theory. The calculated Gibbs energies confirmed that the formation of the imidoselenium(II) chlorides ClSe[N(^{*t*}Bu)Se]_nCl (7–9, n = 1-3) is energetically favourable. Furthermore, the reactions of these bifunctional intermediates (n = 2 or 3) with ^{*t*}BuNH₂ to generate ring systems of the type Se_m(N^{*t*}Bu)_m or Se_m(N^{*t*}Bu)_{m-1} (m = 3, 4) are also favoured energetically. Both step are assisted by the formation of solid ^{*t*}BuNH₃Cl but, significantly, the cyclization processes that involves formation of an Se–Se bond is preferred on energetic grounds owing to the additional formation of the diazene ^{*t*}BuN=N^{*t*}Bu *via* a redox process. The individual steps in the reaction pathway leading to the shortest imidoselenium(II) chloride ClSeN(^tBu)SeCl (7) exhibit reasonably low activation energies lending credibility to key role of this intermediate. The X-ray structure of the unusual adduct [PdCl₂{*Se*, *Se'*-(SeCl)₂N(^tBu)}]·[PdCl₂{*Se*,*Se'*-Se₄(N^tBu)₃]·MeCN (**10**·MeCN), which incorporates the first coordination complex of an imidoselenium(II) chloride is also reported.

In summary, a combination of experimental and computational approaches has demonstrated that the formation of cyclic selenium imides via the cyclocondensation reaction of ^tBuNH₂ and SeCl₂ in THF shows some parallels to the established pathway for the generation of cyclophosphazenes of different ring sizes.² Specifically, the first step involves the production of ^tBuN(H)SeCl (an acyclic building block), which is followed by generation of the homologous series ClSe[N(^tBu)- Se_nCl (n = 1-3) (chain growth). However, the final step (cyclization) differs from that in the formation cyclophosphazenes, which involves an intramolecular process,² because the intermediates $ClSe[N(^{t}Bu)Se]_{n}Cl$ (*n* = 2 or 3) are bifunctional. They may react with ^tBuNH₂ via either (a) nucleophilic substitution to give heterocycles of the type $\text{Se}_m(N^t\text{Bu})_m$ (m = 3, 4) or (b) reduction to form ring systems with Se-Se bonds, $\operatorname{Se}_{m}(\operatorname{N}^{t}\operatorname{Bu})_{m-1}$ (m = 3, 4). As in the case of cyclophosphazenes, the formation of acyclic intermediates, *i.e.* $ClSe[N(^{t}Bu)Se]_{n}Cl$, with different chain lengths (n = 2 or 3) accounts for the generation of cyclic selenium imides of varying ring sizes.

Acknowledgements

We thank Ms. Elisa Männistö for help in the synthetic work. Financial support from Academy of Finland [grant numbers 134548 (R. S. L.) and 253400 (J. M. R)], Finnish Cultural Foundation (A. J. K.), Magnus Ehrnrooth Foundation (A. J. K.), Oulu University Scholarship Foundation (A. J. K.) and the Natural Sciences and Engineering Research Council (NSERC, Canada) (T. C.) is gratefully acknowledged. We are also grateful to Finnish CSC-IT Center for Science Ltd for their generous provision of computational resources.

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