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Experimental and computational investigations of platinum complexes of selenium diimide and some novel selenium-nitrogen ligands

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Draft

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Abstract: The reaction of selenium diimide $\text{Se}[\text{N}(\text{t-Bu})]_2$ and PtCl_2 afforded an N,N' -chelated complex $[\text{PtCl}_2\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ (**1**) in good yield and $[\text{PtCl}_2\{N,N'\text{-SeO}[\text{NH}(\text{t-Bu})]_2\}]$ (**2**) as a minor product. Attempts to prepare **2** by direct reaction of SeOCl_2 with $\text{Li}[\text{NH}(\text{t-Bu})]$ in toluene followed by addition of PtCl_2 produced cyclic $\text{Se}_4[\text{N}(\text{t-Bu})]_4$ in solution (^{77}Se NMR spectrum) and a small amount of the complex $[\text{PtCl}_3\{Se,Se',Se''\text{-Se}_4[\text{N}(\text{t-Bu})]_4\}][\text{Pt}_2\text{Cl}_5\{Se,Se',Se''\text{-Se}_3[\text{N}(\text{t-Bu})]_2\}]\cdot 3\text{MeCN}$ (**3**·3MeCN), which contains tridentate $\text{Se}_4[\text{N}(\text{t-Bu})]_4$ in the cation and the novel, acyclic bridging ligand $[\text{SeN}(\text{t-Bu})\text{SeN}(\text{t-Bu})\text{Se}]^{2-}$ in the anion. The reaction of $\text{Se}[\text{N}(\text{t-Bu})]_2$ with $[\text{PtCl}_2(\text{NCPh})_2]$ in THF produced the dinuclear complex $[\text{Pt}_2\text{Cl}_6\{\text{SeN}(\text{t-Bu})\text{C}(\text{Ph})\text{NH}\}_2]\cdot 2\text{C}_4\text{H}_8\text{O}$ (**4**·2THF) as the major product and only a few crystals of **1**. The possible formation of $\text{SeO}[\text{NH}(\text{t-Bu})]_2$ or **2** by the reaction of $\text{Se}[\text{N}(\text{t-Bu})]_2$ or **1**, respectively, with adventitious water and the pathway for the production of **4** were investigated through density functional theory calculations. The X-ray structures of **1**, **2**, **3**·3MeCN, and **4**·2THF have been determined.

Key words: platinum, selenium diimide, ^{77}Se NMR spectroscopy, X-ray structures, DFT calculations

Introduction

Chalcogen diimides show versatile coordination chemistry due to the availability of three potential donor sites and two formal π -bonds.¹⁻⁶ The possible coordination modes are shown in Chart 1 and are dependent on the metal centre as well as the steric and electronic properties of the diimide ligands.

(Chart 1 here)

While N,N' -chelation of sulfur diimides to both transition and main group metal centers is the most common mode of coordination,⁷⁻¹⁰ several complexes exhibit monodentate N -coordinated ligands;¹¹⁻¹³ in addition, Resonance Raman spectra have indicated that the $M(CO)_5$ fragment in the $\sigma(N)$ -trigonal complex $[W(CO)_5\{S(NMe)_2\}]$ undergoes a 1,3-shift.^{14,15} The unusual $\pi(N,N',S)$ coordination is found in $[Mn_2(CO)_6\{S([N(t-Bu)]_2)\}]$.⁹

Most structurally characterized selenium diimide ligands are also monomeric and, like sulfur diimides, form N,N' -chelated complexes.¹⁶⁻¹⁸ However, the bridging N,N' -mode between two metal centres has also been observed.^{19,20} In addition to $[PdCl_2\{N,N'-Se[N(t-Bu)]_2\}]$, which has been prepared by the reaction of $[PdCl_2(NCPh)_2]$ with one equivalent of $Se[N(t-Bu)]_2$,¹⁸ the reaction with two equivalents of $Se[N(t-Bu)]_2$ affords $[PdCl_2\{Se,Se'-Se_4[N(t-Bu)]_3\}]$ and $[PdCl_2\{Se,Se'-Se_4[N(t-Bu)]_4\}]$, which contain novel cyclic selenium imides.

The $[2 + 2]$ cyclodimerization of chalcogen diimides becomes more favorable for the heavier chalcogens. This process is strongly endothermic for sulfur diimides, approximately thermoneutral for selenium diimides, and strongly exothermic for tellurium diimides.²¹⁻²³

Consistently, tellurium diimides occur only as thermally stable dimers $\text{RNTe}(\mu\text{-NR})_2\text{TeNR}$,²⁴⁻²⁶ which may act as *N,N'*-chelating or bridging ligands coordinating to the metal centers through exocyclic nitrogen atoms, e.g. in complexes with $\text{LiI}/[\text{Li}(\text{THF})_2]^+$,²⁷ HgCl_2 ,²⁸ CoCl_2 ,¹⁷ and $\text{M}(\text{CF}_3\text{SO}_3)$ ($\text{M} = \text{Ag}, \text{Cu}$).^{29,30}

We have recently observed that the complexation of $\text{Se}[\text{N}(\text{t-Bu})]_2$ with cadmium or mercury dichlorides results in cyclodimerization and formation of $[\text{MCl}_2\{N,N'-(\text{t-Bu})\text{NSe}[\mu\text{-N}(\text{t-Bu})]_2\text{SeN}(\text{t-Bu})\}]$ ($\text{M} = \text{Cd}, \text{Hg}$),³¹ which are isostructural with the mercury²⁸ and cobalt¹⁷ complexes of tellurium diimide dimer. These complexes provided the first examples of the existence of dimeric selenium diimide. Furthermore, DFT calculations³¹ indicated that complexation of monomeric selenium diimides is favoured for group 10 metal dichlorides, as observed for PdCl_2 ,¹⁸ whereas coordination of dimeric selenium diimide ligands is preferred with group 12 metal dichlorides.³¹

In the light of our previous findings,^{18,31} we have now explored the reactions of $\text{Se}[\text{N}(\text{t-Bu})]_2$ with PtCl_2 and $[\text{PtCl}_2(\text{NCPh})_2]$. The former produced the expected 1:1 adduct $[\text{PtCl}_2\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ (**1**) and a small amount of $[\text{PtCl}_2\{N,N'\text{-SeO}[\text{NH}(\text{t-Bu})]_2\}]$ (**2**) containing the hitherto unknown selenoxide ligand $\text{SeO}[\text{NH}(\text{t-Bu})]_2$. Attempts to prepare **2** by reaction of SeOCl_2 with $\text{Li}[\text{NH}(\text{t-Bu})]$ in toluene yielded cyclic selenium imides. The treatment of the resulting solution with PtCl_2 afforded a few crystals of the ion pair $[\text{PtCl}_3\{Se,Se',Se''\text{-Se}_4[\text{N}(\text{t-Bu})]_4\}][\text{Pt}_2\text{Cl}_5\{Se,Se',Se''\text{-Se}_3[\text{N}[(\text{t-Bu})]_2]\}]\cdot 3\text{MeCN}$ (**3**·3MeCN). By contrast to the behaviour of $[\text{PdCl}_2(\text{NCPh})_2]$,¹⁸ the treatment of $\text{Se}[\text{N}(\text{t-Bu})]_2$ with an equimolar amount of $[\text{PtCl}_2(\text{NCPh})_2]$ produced the complex $[\text{Pt}_2\text{Cl}_6\{\text{SeN}(\text{t-Bu})\text{C}(\text{Ph})\text{NH}\}_2]\cdot 2\text{C}_4\text{H}_8\text{O}$ (**4**·2THF).

We describe here the structural characterization of the complexes **1-4** (Chart 2). Reaction pathways for the unexpected formations of **2-4** are also proposed on the basis of DFT calculations (in the cases of **2** and **4**).

(Chart 2 here)

Experimental section

General procedures

All reactions and manipulations of air- and moisture-sensitive products were carried out under an inert atmosphere by using a standard drybox and Schlenk techniques. Tetrahydrofuran, diethylether, and toluene were dried by distillation over Na/benzophenone and acetonitrile was dried over CaH_2 under an argon atmosphere prior to use. SeCl_4 (Aldrich), SeOCl_2 (Aldrich), PtCl_2 (Johnson Matthey), n-BuLi (2.5 M in hexane, Aldrich) and benzonitrile (Fluka) were used as purchased. t-BuNH₂ (Aldrich) was distilled over KOH and stored over molecular sieves. $\text{Se}[\text{N}(\text{t-Bu})]_2$,³² $[\text{PtCl}_2(\text{NCPH})_2]$ ³³ and $\text{Li}[\text{NH}(\text{t-Bu})]$ ³⁴ were synthesized by the literature procedure.

NMR spectroscopy

The $^{13}\text{C}\{^1\text{H}\}$, ^{14}N , ^{77}Se , and ^{195}Pt NMR spectra were recorded unlocked on a Bruker Avance III 400 spectrometer operating at 100.61, 28.91, 76.31, and 86.02 MHz, respectively. The typical respective spectral widths were 24.04, 28.99, 113.64, and 100.00 kHz, and the pulse widths were 14.30, 12.00, 16.75, and 24.50 μs . The pulse delays for carbon, nitrogen, selenium, and platinum were 2.0, 0.01, 1.0, and 0.5 s, respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to the solvent resonances and are reported relative to Me_4Si . Neat CH_3NO_2 , a saturated D_2O solution of selenium dioxide, and a D_2O solution of $\text{K}_2[\text{PtCl}_6]$ were used as external standards for ^{14}N , ^{77}Se , and ^{195}Pt chemical shifts, respectively. The ^{14}N and ^{195}Pt chemical shifts are reported relative to

the external standards, and the ^{77}Se chemical shifts relative to neat Me_2Se [$\delta(\text{Me}_2\text{Se}) = \delta(\text{SeO}_2) + 1302.6$].³⁵

Preparation of $[\text{PtCl}_2\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ (**1**)

A slight excess of $\text{Se}[\text{N}(\text{t-Bu})]_2$ (0.279 g, 1.26 mmol), which was dissolved in toluene (5 mL), was added dropwise to a stirred brown slurry of PtCl_2 (0.285 g, 1.07 mmol) in toluene (15 mL) at $-80\text{ }^\circ\text{C}$. After 30 min at $-80\text{ }^\circ\text{C}$, the reaction mixture was warmed slowly to room temperature and stirred overnight to give a reddish-brown solution and a reddish-brown precipitate. The solvent was removed under dynamic vacuum, and the solid residue was extracted with acetonitrile (8 x 10 mL). The solvent was removed from the combined extracts under vacuum to give **1** as a reddish-brown solid (0.380 g, 0.78 mmol; yield 73 % based on PtCl_2). Anal. Calcd. for $\text{C}_8\text{H}_{18}\text{Cl}_2\text{N}_2\text{PtSe}$ (**1**): C, 19.72; H, 3.72; N, 5.75 %. Found: C, 19.81; H, 3.60; N, 5.68 %. NMR: δ $^{13}\text{C}\{^1\text{H}\}$ (MeCN, $25\text{ }^\circ\text{C}$): 56.63 [$-\text{C}(\text{CH}_3)_3$] and 30.74 ppm [$-\text{C}(\text{CH}_3)_3$]; δ ^{77}Se (MeCN, $25\text{ }^\circ\text{C}$): 1761, δ ^{195}Pt (MeCN, $25\text{ }^\circ\text{C}$): -1920. Reddish-brown crystals of **1** were obtained by recrystallization from the acetonitrile solution at $-20\text{ }^\circ\text{C}$ and were used for the determination of the crystal structure. Anal. Calcd. for $\text{C}_8\text{H}_{18}\text{Cl}_2\text{N}_2\text{PtSe}$ (**1**): C, 19.72; H, 3.72; N, 5.75 %. Found: C, 19.88; H, 3.78; N, 5.52 %. A few yellow crystals of $[\text{PtCl}_2\{N,N'\text{-SeO}[\text{NH}(\text{t-Bu})]_2\}]$ (**2**) were obtained in some batches during the crystallization of **1**. Attempts to prepare complex **2** or the ligand $\text{SeO}[\text{NH}(\text{t-Bu})]_2$ are described in the Results and Discussion.

Formation of $[\text{Pt}_2\text{Cl}_6\{\text{SeN}(\text{t-Bu})\text{C}(\text{Ph})\text{NH}\}_2]\cdot 2\text{C}_4\text{H}_8\text{O}$ (**4**·2THF)

A solution of $\text{Se}[\text{N}(\text{t-Bu})]_2$ (0.313 g, 1.42 mmol) in THF (10 mL) was added to a slurry of $[\text{PtCl}_2(\text{NCPH})_2]$ (0.668 g, 1.42 mmol) in THF (20 mL) at $-80\text{ }^\circ\text{C}$. The reaction mixture was

stirred for 15 min at -80 °C and then allowed to warm overnight to room temperature. Unreacted $[\text{PtCl}_2(\text{NCPh})_2]$ was allowed to settle down and a dark red solution was decanted through a cannula. The solution was concentrated to a volume of *ca.* 15 mL under dynamic vacuum and cooled to -20 °C to give yellow crystals of **4**·2THF and a few dark red crystals of **1**. Although the yellow crystals of **4**·2THF were predominant, it was not possible to separate the bulk product as a pure compound for overall yield or elemental analysis. However, a single crystal X-ray determination established the identity of this product.

X-Ray crystallography

Single-crystal X-ray diffraction data of **1**, **2**, **3**·3MeCN, and **4**·2THF were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ 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-2013.³⁶

(Table 1 here)

The complex $[\text{PtCl}_2\{N,N'\text{-SeO}[\text{NH}(\text{t-Bu})_2]\}]$ (**2**) contained a minor twin component in the crystal resulting in apparent crystallographic disorder. This disorder was resolved in terms of two alternative orientations of the complex. The site occupation factors were refined by constraining the anisotropic displacement parameters of the disordered pairs of atoms to be equal. The refined values of the s.o.f. were 0.9738(15) and 0.0262(15).

All methyl groups in the *tert*-butyl substituents of **3**·3MeCN can assume two different orientations. The consequent disorder was treated in the same way as above by constraining the anisotropic displacement parameters of all carbon atoms in the pairs of the disordered *tert*-butyl

groups to be equal. The refined s.o.f. values of the two orientations of the three t-Bu groups are 0.77(2)/0.23(2), 0.52(2)/0.48(2), and 0.51(2)/0.49(2). The three solvent MeCN molecules lie on the symmetry element and also assume two different orientations. Because of symmetry, the s.o.f. values of each disordered pair is exactly 0.5.

After the full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions in the CH₃ groups (C-H = 0.98 Å), in the CH₂ groups (C-H = 0.99 Å), and in the phenyl groups (C-H = 0.95 Å). Upon the final refinement, they were riding with the carbon atom they were bonded to. For the complex **4** and for the more abundant orientation of the disordered pair in **2**, the NH hydrogens were found in the respective difference Fourier maps and refined isotropically. In case of the less-abundant orientation of **2**, the NH hydrogen was placed in the calculated position (N-H = 0.93 Å). The isotropic displacement parameters of the calculated hydrogen atoms were fixed at 1.2 (CH₂, NH, phenyl groups) or 1.5 (CH₃) times to that of the corresponding carbon or nitrogen atom. The scattering factors for the neutral atoms were those incorporated with the program.

Computational details

All structures considered in this work were optimized using the ORCA program involving gradient techniques³⁷ and employing a revPBE GGA functional³⁸⁻⁴⁰ and def2-TZVP⁴¹⁻⁴⁴ basis sets together with the RI approximation⁴⁵ and Grimme's dispersion corrections.^{46,47} The fundamental frequencies were calculated to assess the nature of stationary points and to estimate the zero-point energy (ZPE) corrections and Gibbs reaction energies.

Results and discussion

Preparation and crystal structure of [PtCl₂{*N,N'*-Se[N(t-Bu)]₂}] (**1**)

The reaction of a slight excess of $\text{Se}[\text{N}(\text{t-Bu})]_2$ and PtCl_2 in toluene or THF afforded $[\text{PtCl}_2\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ (**1**). The crude product could be purified by extraction into acetonitrile followed by recrystallization and was isolated in 73 % yield as reddish-brown crystals. The complex was characterized as a 1:1 adduct by elemental analysis, multinuclear NMR spectroscopy in acetonitrile solution, and X-ray crystallography. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** showed the presence of equivalent *tert*-butyl groups [the chemical shifts are 56.63 ppm for $-\text{C}(\text{CH}_3)_3$ and 30.74 ppm for $-\text{C}(\text{CH}_3)_3$] (intensity ratio 1:4), the ^{77}Se NMR spectrum displayed one resonance at 1761 ppm, and the ^{195}Pt NMR spectrum exhibited one resonance at -1920 ppm. The ^{77}Se NMR chemical shift for the palladium analogue is 1717 ppm.¹⁸

The molecular structure of **1** indicating the numbering of the atoms and selected bond parameters is shown in Fig. 1. Complex **1** is isostructural with the palladium analogue $[\text{PdCl}_2\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$.¹⁸ The platinum centre is coordinated by two chlorido ligands and two nitrogen atoms from the chelating selenium diimide ligand and exhibits an almost square-planar coordination [$\Sigma\angle_{\text{Pt}} = 365.0^\circ$]. Upon complexation, the *tert*-butyl selenium diimide expectedly assumes the energetically least-favourable *anti,anti*-configuration,⁴⁸ which is also observed in all other complexes containing the monomeric selenium diimide ligand.¹⁶⁻²⁰

(Fig. 1 here)

The Se-N bond distances [1.743(6)-1.751(6) Å] in **1** are similar to those reported earlier for the related complexes $[\text{SnCl}_4\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ [1.710(3) Å],¹⁶ $[\text{PdCl}_2\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ [1.731(4)-1.736(4) Å],¹⁸ $[\text{Co}_2(\mu\text{-Cl})_3\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}_2(\text{THF})_2]$ - $[\text{CoCl}_3\{\text{NH}_2(\text{t-Bu})\}] \cdot 1\frac{1}{2}\text{THF}$ [1.716(5)-1.723(5) Å],¹⁷ $[\text{Ag}_2\{\mu\text{-}N,N'\text{-Se}(\text{NR})_2\}_2](\text{CF}_3\text{SO}_3)_2$ (R = t-Bu, adamantyl) [1.712(4)-

1.749(7) Å,²⁰ and $[\text{Cu}_2\{\mu\text{-}N,N'\text{-Se}(\text{NR})_2\}_2](\text{CF}_3\text{SO}_3)_2$ (R = t-Bu, adamantyl) [1.708(4)-1.729(6) Å].²⁰ The Pt-N bond lengths of 2.022(7) and 2.030(6) Å in **1** are close to the single bond lengths (the sum of covalent radii of platinum and nitrogen is 1.99 Å⁴⁹) and similar to those in related platinum(II) complexes {cf. 1.997(12)-2.025(9) Å in $[\text{PtCl}_2\{E\text{-N}(\text{H})=\text{C}(\text{SEt})\text{R}\}_2]$, R = Me, Et, CH₂Ph⁵⁰}. The Pt-Cl bond lengths of **1** also show typical single bond values [2.284(2)-2.297(2) Å] (the sum of the covalent radii of platinum and chlorine is 2.28 Å⁴⁹). The corresponding bond lengths in $[\text{PtCl}_2\{E\text{-N}(\text{H})=\text{C}(\text{SEt})\text{R}\}_2]$ are in the range 2.301(3)-2.314(4) Å.⁵⁰

The crystal lattice of **1** is composed of discrete molecules that are linked together into a continuous three-dimensional network by Se...Cl intermolecular contacts [Se1...Cl1 = 3.5637(4) Å, Se1...Cl2 = 3.3943(5) Å] (the sum of van der Waals radii of selenium and chlorine is 3.81 Å⁴⁹) as also observed for $[\text{PdCl}_2\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ [Se...Cl = 3.270(14)-3.5058(14) Å].¹⁸ This continuous polymeric network (see Figure 1S in Supporting Information) may explain the low solubility of **1** in common organic solvents. Similar intermolecular contacts have been observed for the mercury and cobalt complexes of tellurium diimide dimer $[\text{HgCl}_2\{(t\text{-Bu})\text{NTe}[\mu\text{-N}(t\text{-Bu})]_2\text{TeN}(t\text{-Bu})\}]$ ²⁸ and $[\text{CoCl}_2\{(t\text{-Bu})\text{NTe}[\mu\text{-N}(t\text{-Bu})]_2\text{TeN}(t\text{-Bu})\}]$.¹⁷

Crystal structure of $[\text{PtCl}_2\{N,N'\text{-SeO}[\text{NH}(t\text{-Bu})]_2\}]$ (**2**)

In some reaction batches, reddish-brown crystals of **1** were obtained together with a small amount of yellow crystals of $[\text{PtCl}_2\{N,N'\text{-SeO}[\text{NH}(t\text{-Bu})]_2\}]$ (**2**). The molecular structure of **2** together with the numbering of the atoms and the selected bond parameters is shown in Fig. 2. The novel ligand $\text{SeO}[\text{NH}(t\text{-Bu})]_2$ is *N,N'*-coordinated to the platinum centre, which has a square-planar coordination environment [$\Sigma\angle_{\text{Pt}} = 359.9^\circ$] similar to that in **1**. The molecular framework adopts two orientations because of the apparent disorder, which is probably due to

twinning, with the major and minor components (**A** and **B**, respectively) showing site occupancy factors of 0.9738(15) and 0.0262(15), respectively. The square-planar coordination environments of platinum in these two disordered components form an angle of 85(1) °. Since the metrical values in the two disordered molecules are similar, the molecular and crystal structures are only discussed in terms of the major component.

(Fig. 2 here)

The Pt-Cl bond lengths of 2.318(4) and 2.320(4) Å and Pt-N bond lengths of 2.072(12) Å are quite normal. The Se-N bond lengths of 1.907(12) and 1.937(13) Å are consistent with the lengths of the endocyclic Se-N bonds in (t-Bu)NSe[μ-N(t-Bu)]₂SeO and (t-Bu)NSe[μ-N(t-Bu)]₂SO₂, which show a range of 1.930(4)-1.943(4) Å and 1.941(2)-1.958(2) Å, respectively.⁵¹ The Se=O bond length is 1.633(11) Å and can be compared to the values of 1.621(2) Å and 1.628(4) Å in OSe[μ-N(t-Bu)]₂SeO⁵² and (t-Bu)NSe[μ-N(t-Bu)]₂SeO, respectively.⁵¹ In contrast to **1**, which shows a planar PtNSeN ring [$\Sigma\angle_N = 359.8-360.0^\circ$], that in **2** deviates significantly from planarity [$\Sigma\angle_N = 334.8-336.7^\circ$].

The discrete complexes of **2** form dimeric units *via* weak N-H...Cl hydrogen bonds of 2.285(5) and 2.306(5) Å (see Figure 2S in Supporting Information). These dimeric units are further linked into a continuous polymeric network by the Se...O intermolecular contacts of 3.325(12) Å.

Attempted preparation of SeO[NH(t-Bu)]₂

Since the ^{77}Se NMR spectrum of the commercial SeCl_4 that was used for the synthesis of $\text{Se}[\text{N}(\text{t-Bu})]_2$ indicated that it contained *ca.* 5 % of SeOCl_2 (the ^{77}Se NMR chemical shift is 1500 ppm⁵³), we considered that the reaction of SeOCl_2 with t-BuNH_2 is the source of $\text{SeO}[\text{NH}(\text{t-Bu})]_2$ (Eq. 1) for the formation of **2**.

The ^{77}Se NMR spectrum of the THF solution of the reaction mixture, after filtration, is shown in Fig. 3. The major resonance at 1245 ppm can be assigned to $\text{OSe}[\mu\text{-N}(\text{t-Bu})]_2\text{SeO}$ (cf. lit. value 1242 ppm in THF²²), which has previously been prepared by the reaction of SeOCl_2 and t-BuNH_2 in diethyl ether.³² The resonance at 1656 ppm is attributed to $\text{Se}[\text{N}(\text{t-Bu})]_2$.⁵⁴ There are two resonances at 1179 and 1155 ppm, either of which may be due to $\text{SeO}[\text{NH}(\text{t-Bu})]_2$. The ^{77}Se NMR chemical shift of 1136 ppm calculated at PBE0/def2-TZVPP level for $\text{SeO}[\text{NH}(\text{t-Bu})]_2$ following a recently described theoretical approach⁵⁵ suggests that the latter is more likely. The resonance at 1459 ppm is at too low field to be due to $\text{SeO}[\text{NH}(\text{t-Bu})]_2$. Yellow crystals found in the precipitate after filtration were identified by unit cell determinations as $\text{OSe}[\mu\text{-N}(\text{t-Bu})]_2\text{SeO}$.⁵²

(Fig. 3 here)

We have also considered the possibility that $\text{SeO}[\text{NH}(\text{t-Bu})]_2$ is formed from $\text{Se}[\text{N}(\text{t-Bu})]_2$ by interaction with adventitious water during the preparation of **1** (Eq. 2):

The reaction pathway based on DFT calculations at the revPBE/def2-TZVP level of theory is depicted in Fig. 4. The reaction begins with the interaction of one of the hydrogen atoms of water with a nitrogen atom of $\text{Se}[\text{N}(\text{t-Bu})]_2$ (transition state **TS1**, $\Delta G_f^\circ = 99 \text{ kJ mol}^{-1}$;) leading to the cleavage of one O-H bond in H_2O , followed by the immediate formation of a Se-O bond represented in the local minimum structure **B** ($\Delta G_f^\circ = 9 \text{ kJ mol}^{-1}$). The second hydrogen transfer from the oxygen atom to a nitrogen atom proceeds *via* transition state **TS2** ($\Delta G_f^\circ = 66 \text{ kJ mol}^{-1}$) resulting in the product $\text{SeO}[\text{NH}(\text{t-Bu})]_2$ (**C**). The overall Gibbs energy of the reaction is calculated to be -41 kJ mol^{-1} .

Alternatively, **2** may be generated by the reaction of adventitious water with $[\text{PtCl}_2\{\text{N},\text{N}'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ (**1**). However, this route is less likely than the direct reaction between $\text{Se}[\text{N}(\text{t-Bu})]_2$ and H_2O , because the activation energies are significantly higher, and the total gain in Gibbs energy for the overall reaction is relatively small ($\Delta G_f^\circ = -4 \text{ kJ mol}^{-1}$) (see Fig. 5S in Supporting Information).

(Fig. 4 here)

Formation and crystal structure of $[\text{PtCl}_3\{\text{Se},\text{Se}',\text{Se}''\text{-Se}_4[\text{N}(\text{t-Bu})]_4\}][\text{Pt}_2\text{Cl}_5\{\text{Se},\text{Se}',\text{Se}''\text{-Se}_3[\text{N}(\text{t-Bu})]_2\}]\cdot 3\text{MeCN}$ (**3·3MeCN**)

An attempt was also made to prepare $[\text{PtCl}_2(\text{N},\text{N}'\text{-SeO}[\text{NH}(\text{t-Bu})]_2)]$ (**2**) by a two-stage reaction. The first stage involved the reaction of SeOCl_2 and $\text{Li}[\text{NH}(\text{t-Bu})]$ in a molar ratio of 1:2 in toluene. The ^{77}Se NMR spectrum recorded from the filtrate of the reaction mixture showed the

presence of $\text{Se}[\text{N}(\text{t-Bu})]_2$ (δ 1654),⁵⁴ $\text{Se}_3[\text{N}(\text{t-Bu})]_2$ (δ 1626 and 1183),⁵¹ and $\text{Se}_3[\text{N}(\text{t-Bu})]_3$ (δ 1396)⁵¹ in addition to a strong resonance at 1451 ppm, which has been attributed to $\text{Se}_4[\text{N}(\text{t-Bu})]_4$.⁵⁵ In THF, this eight-membered ring shows a resonance at 1486 ppm.⁵⁵

In the second stage, the resulting solution was treated with PtCl_2 . An acetonitrile extract of the crude product deposited a small amount of reddish-brown crystals of $[\text{PtCl}_3\{\text{Se}, \text{Se}', \text{Se}''\text{-Se}_4[\text{N}(\text{t-Bu})]_4\}][\text{Pt}_2\text{Cl}_5\{\text{Se}, \text{Se}', \text{Se}''\text{-Se}_3[\text{N}(\text{t-Bu})]_2\}]\cdot 3\text{MeCN}$ (**3** $\cdot 3\text{MeCN}$) together with pale yellow crystals of $\text{t-BuNH}_3\text{Cl}$, identified by determination of the unit cell parameters.⁵⁶

The molecular structure of **3** $\cdot 3\text{MeCN}$ together with the numbering of the atoms and the selected bond parameters is shown in Fig. 5. The structure is composed of discrete mononuclear $[\text{PtCl}_3\{\text{Se}, \text{Se}', \text{Se}''\text{-Se}_4[\text{N}(\text{t-Bu})]_4\}]^+$ cations and dinuclear $[\text{Pt}_2\text{Cl}_5\{\text{Se}, \text{Se}', \text{Se}''\text{-Se}_3[\text{N}(\text{t-Bu})]_2\}]^-$ anions. The asymmetric unit contains one half of atoms in both the cation and anion and the structure is completed by symmetry. In the solid state, the ions are paired together by $\text{H}\cdots\text{Cl}$ hydrogen bonds of 2.515(5) and 2.813(5) Å; only the latter distance involving the more abundant orientation of the *t*-Bu-group in question is shown in Fig. 5. There is also a weak secondary bonding interaction of 3.220(6) Å between the atoms Se3 and Cl31.

(Fig. 5 here)

The $[\text{PtCl}_3\{\text{Se}, \text{Se}', \text{Se}''\text{-Se}_4[\text{N}(\text{t-Bu})]_4\}]^+$ cation consists of a puckered eight-membered cyclic selenium imide $\text{Se}_4[\text{N}(\text{t-Bu})]_4$ ligand coordinating to platinum *via* three Se donors [Pt-Se = 2.381(3)-2.4383(17) Å]. The conformation of the ring is similar to that observed in $[\text{PdCl}_2\{\text{Se}, \text{Se}'\text{-Se}_4[\text{N}(\text{t-Bu})]_4\}]$,¹⁸ in which this ligand is bidentate 1,5- $\text{Se}, \text{Se}'\text{-Se}_4[\text{N}(\text{t-Bu})]_4$ ligand; we note, however, that there is a weak contact of 3.1475(11) Å between the palladium centre and the Se atom in the 3 position in this Pd complex.¹⁸ The free eight-membered ring

$\text{Se}_4(\text{NMe})_4$ adopts a crown conformation.⁵⁵ The platinum centre Pt1 shows a slightly distorted octahedral geometry. The Pt-Cl bond involving axial chlorine atom [Pt1-Cl11 = 2.318(6) Å] is slightly shorter than those involving equatorial chlorine atoms [Pt1-Cl12 = 2.366(4) Å]. The axial Pt1-Se1 bond of 2.381(3) Å is also shorter than the equatorial Pt1-Se2 bond of 2.4383(17) Å.

The Se-N bond lengths of 1.811(12)-1.858(14) Å in the cation of **3** correspond to the typical single bond length of 1.87 Å⁴⁹ and are similar to those reported for [PdCl₂{Se,Se'-Se₄[N(t-Bu)]₄}] [1.842(5)-1.886(4) Å].¹⁸ They are also consistent with the values found for the cyclic selenium imides Se₄(NMe)₄ [1.823(10)-1.883(10) Å],⁵⁵ Se₃(NAd)₂ [1.846(4)-1.892(4) Å],²² Se₃[N(t-Bu)]₃ [1.825(4)-1.842(4) Å],⁵¹ Se₆[N(t-Bu)]₂ [1.830(4) Å],⁵⁷ and Se₉[N(t-Bu)]₆ [1.80(2)-1.90(1) Å].⁵⁷ The nitrogen atoms show a nearly planar bonding environment [$\Sigma\angle\text{N} = 351.7\text{--}359.6^\circ$], which, with the exception of Se₃(NAd)₂,²² is consistent with values reported for structurally characterized cyclic selenium imides.^{51,55,57}

The most interesting feature of the structure of **3** is the presence of the bridging, acyclic [Se₃{N(t-Bu)}₂]²⁻ ligand in the anion. This is the first example of this class of anionic chalcogen-nitrogen ligand, although the bridging acyclic nitrido ligands S₃N₂²⁻⁵⁸⁻⁶⁰ and SeS₂N₂²⁻⁶¹ bear a close relationship to this *imido*-selenium dianion. The platinum centres in the [Pt₂Cl₅{Se,Se',Se''-Se₃[N(t-Bu)]₂}]⁻ anion are in different oxidation states Pt^{IV} and Pt^{II}. Similar dinuclear complexes involving mixed oxidation states are also exemplified by (Et₄N)[Cl₂Pt{μ-Cl(NO)}PtCl₃(NO)],⁶² [(Et₃P)₂Pt(μ-SiH-Ph)₂Pt(SiH₂)₂(PEt₃)₂],⁶³ [Pt{PtMe₃(SCH₂CH₂NMe₂)₂}₂],⁶⁴ and [{(Me₃P)₂Pt}₃Pt(OH)₆](NO₃)₄.⁶⁵

The platinum center Pt2^{IV} in the [Pt₂Cl₅{Se,Se',Se''-Se₃[N(t-Bu)]₂}]⁻ anion exhibits a distorted octahedral coordination sphere, whereas the coordination geometry at the platinum center Pt3^{II} is

square-planar. The axial Pt2-Se5 bond of 2.399(2) Å is shorter than the equatorial Pt2-Se4 bond of 2.4240(17) Å, as also found for Pt1 in the cation. The corresponding Pt-Cl bonds, however, show almost equal lengths [2.365(6) and 2.362(5) Å]. The Pt3-Se4 bond of 2.3617(17) Å and the Pt3-Cl31 bonds of 2.342(4) Å involving the square-planar centre Pt3^{II} are shorter than those of octahedral Pt(IV) centres Pt1 and Pt2. As in the cation, the Se-N bond distances of 1.840(14)-1.880(13) Å in the Se₃[N(t-Bu)]₂²⁻ ligand of the anion are close to the predicted Se-N single bond length. The bonding environment at the nitrogen atoms is close to planar [$\Sigma\angle N = 356.5^\circ$]. In the solid state, the ion pairs are linked together by a complicated three-dimensional H...Cl hydrogen bonding network, as shown in Fig. 3S in Supporting Information.

Since the ⁷⁷Se NMR spectrum shows that the toluene solution from the reaction of Li[NH(t-Bu)] and SeOCl₂ contains Se₄[N(t-Bu)]₄, Se₃[N(t-Bu)]₃, and Se₃[N(t-Bu)]₂, in addition to Se[N(t-Bu)]₂, it is likely that imidoselenium chlorides ClSe[N(t-Bu)Se]_nCl (*n* = 1,2) are also present in the solution.^{51,66} Consequently, the formation of **3** can be envisaged to involve a redox process between PtCl₂ and ClSe[N(t-Bu)Se]₂Cl concomitant with the formation of a complex of Se₄[N(t-Bu)]₄ with PtCl₂ in the presence of Cl⁻ ions (see Scheme 1).

(Scheme 1 here)

Formation of $[\text{Pt}_2\text{Cl}_6\{\text{SeN}(\text{t-Bu})\text{C}(\text{Ph})\text{NH}\}_2]$ (**4**)

By contrast to the reaction of $\text{Se}[\text{N}(\text{t-Bu})]_2$ with $[\text{PdCl}_2(\text{NPh})_2]$,¹⁸ the corresponding reaction with $[\text{PtCl}_2(\text{NPh})_2]$ in THF produced a complex mixture of selenium-nitrogen compounds, including $\text{Se}_3[\text{N}(\text{t-Bu})]_3$, $\text{Se}_4[\text{N}(\text{t-Bu})]_4$, and $\text{OSe}[\mu\text{-(t-Bu)}]_2\text{SeO}$, as indicated by the ^{77}Se NMR spectra in Fig. 6. Only a small amount of **1** in the form of dark red crystals was obtained (see Experimental Section). It can also be seen from Fig. 6(b) that a large amount of $\text{Se}[\text{N}(\text{t-Bu})]_2$ remained unreacted when the molar ratio was changed from 1:1 to 2:1.

(Fig. 6 here)

Upon standing of the reaction solution overnight at $-20\text{ }^\circ\text{C}$, yellow crystals of the dinuclear $[\text{Pt}_2\text{Cl}_6\{\text{SeN}(\text{t-Bu})\text{C}(\text{Ph})\text{NH}\}_2]$ **4**·2THF and a small amount of dark red crystals of mononuclear **1** could be obtained. The molecular structure of **4**·2THF together with the numbering of atoms and selected bond parameters is shown in Fig. 7. The asymmetric unit contains one half of the atoms in the complex and the full molecular structure is completed by symmetry. The structure consists of two chelating and bridging $\text{N}(\text{H})\text{C}(\text{Ph})\text{N}(\text{t-Bu})\text{Se}$ ligands, which link two PtCl_3 fragments into a dinuclear complex. Both platinum(IV) centers exhibit an octahedral coordination sphere. The Pt-Se bond distances are $2.3790(7)\text{ \AA}$ and $2.4482(8)\text{ \AA}$ {cf. $2.384(2)$ – $2.423(2)\text{ \AA}$ } in the dimeric $[\text{PtCl}_2(\text{Se}_2\text{C}_7\text{H}_5)(\text{C}_7\text{H}_5)]_2$.⁶⁷ The Pt-Cl bonds *trans* to selenium [$2.3518(15)$ and $2.3598(16)\text{ \AA}$] are slightly longer than those *trans* to the nitrogen atom [$2.3293(15)\text{ \AA}$]. Both C-N bonds [$1.315(8)$ and $1.359(8)\text{ \AA}$] exhibit significant double bond character [$\text{C-N} = 1.47\text{ \AA}$, $\text{C=N} = 1.30\text{ \AA}$ ⁴⁹] indicating delocalization of the π -electron density. Consistently, the bonding arrangements around the C1, N1 and N2 atoms are all nearly planar

$[\Sigma\angle C = 359.9^\circ$ and $\Sigma\angle N = 358.9\text{--}360.0^\circ]$. The Se1-N2 bond length of 1.865(5) Å indicates a single bond.⁴⁹ The combined structural data suggest that the bridging ligand can be formulated as $\text{N(H)}\text{:}\text{C(Ph)}\text{:}\text{N(t-Bu)-Se}^-$. The packing arrangement is shown in Fig. 4S in Supporting Information.

The reaction pathway to this ligand merits further consideration in the light of the findings of Belluco *et al.*,⁶⁸ who have demonstrated that the benzonitrile ligands in $[\text{PtCl}_2(\text{NCPh})_2]$ react with primary or secondary amines. The ^{195}Pt NMR spectrum of $[\text{PtCl}_2(\text{NCPh})_2]$ shows two resonances at -2295 and -2387 ppm of approximately equal intensities attributable to *cis*- and *trans*-isomers, respectively. Consistently, the revPBE/def2-TZVP calculations also show that the difference in Gibbs energies of *cis*- and *trans*- $[\text{PtCl}_2(\text{NCPh})_2]$ is only 11 kJ mol⁻¹ with the *trans*-isomer being more stable. As proposed in Scheme 2 the first step in the formation of **4** is the reaction of t-BuNH₂ with a C≡N triple bond in *cis*- $[\text{PtCl}_2(\text{NCPh})_2]$, which gives *cis*- $[\text{PtCl}_2(\text{NCPh})\{\text{N(H)=C(Ph)-N(t-Bu)(H)}\}]$. The reaction with *trans*- $[\text{PtCl}_2(\text{NCPh})_2]$ results in the formation of the *trans*-isomer. The ^{77}Se NMR spectra of some reaction mixtures showed the presence of SeCl₂ at 1828 ppm,⁶⁹ presumably formed from SeCl₄ via the redox transformation depicted in eq (3). In support of this suggestion, the ^{14}N NMR spectra of the solutions demonstrated the formation of (t-Bu)N=N(t-Bu) (151 ppm).⁵¹

The reaction of SeCl₂ with the NH group of $[\text{PtCl}_2(\text{NCPh})\{\text{N(H)=C(Ph)-N(t-Bu)(H)}\}]$ will produce the Se-N bond in the intermediate $[\text{PtCl}_2(\text{NCPh})\{\text{N(H)=C(Ph)-N(t-Bu)(SeCl)}\}]$ and a precipitate of t-BuNH₃Cl(s), which is the driving force of the reaction (see Scheme 2). The

subsequent oxidative addition of the Se-Cl bond of the ligand to the platinum center, and the dimerization of the monomer so formed subsequently generates the observed dinuclear complex **4**.

(Scheme 2 here)

We have investigated the oxidative-addition step and the subsequent dimerization by using DFT techniques at revPBE/def2-TZVP level of theory. The reactions of both *cis*- and *trans*-[PtCl₂(NCPh){N(H)=C(Ph)-N(t-Bu)(SeCl)}] (**A**) were considered separately. The energy profile of the reaction involving the *cis*-isomer of **A** is shown in Fig. 8. The selenium atom in **A** is first attached to the platinum atom *via* the transition state **TS1** forming an intermediate **B**, after which the chlorine atom is transferred from selenium to platinum *via* the transition state **TS2** with the formation of the *fac* isomer of the six coordinate platinum(IV) complex **C**. The activation energies for the two transition states **TS1** and **TS2** are 59 and 16 kJ mol⁻¹, respectively. The relatively low activation energy of **TS3** (24 kJ mol⁻¹) indicates the ease with which the remaining PhCN ligand can leave the six-coordinate platinum centre. The virtually simultaneous dimerization of the [PtCl₃{N(H)C(Ph)N(t-Bu)Se}] monomer structure shows no activation barrier and leads to the final dinuclear complex **4**. The total Gibbs energy change in the oxidation and dimerization process is very exothermic ($\Delta G = -151$ kJ mol⁻¹).

(Fig. 8 here)

The oxidative addition starting from *trans*-[PtCl₂(NCPh){N(H)=C(Ph)-N(t-Bu)(SeCl)}] yields the *mer*-arrangement of chlorido ligands in the intermediate **C**. The *mer*-isomer must undergo isomerization to the *fac*-isomer for the dimerization to lead to the observed product **4**. However, the energy barrier to isomerize the *mer*-isomer into the *fac*-isomer is very high rendering this route unlikely. It can therefore be inferred that only *cis*-[PtCl₂(NCPh)₂] will result in the formation of the dinuclear complex **4**. This conclusion finds qualitative experimental support from ¹⁹⁵Pt spectroscopy. The isomeric composition of the unreacted [PtCl₂(NCPh)₂] in the final reaction solution is *ca.* 10 mol-% *cis*-isomer and 90 mol-% *trans*-isomer (cf. the initial approximately equal isomeric composition) indicating that during the reaction the *cis*-isomer has been consumed in preference to the *trans*-isomer.

A similar difference in the behaviour between palladium and platinum has been reported by Bates *et al.*⁶⁷ Whereas the reaction of cyclohepteno-1,4-diselenin with [PdCl₂(NCPh)₂] leads to exchange of two benzonitrile ligands by two diselenin ligands to give a mononuclear *trans* complex coordinating *via* selenium, the corresponding reaction with [PtCl₂(NCPh)₂] results in the oxidation of platinum(II) to six-coordinate platinum(IV) with the formation of a dinuclear complex, which shows structural features similar to those in **4** (see Scheme 3).

(Scheme 3 here)

Conclusions

The reaction of Se[N(t-Bu)]₂ and PtCl₂ affords a complex of the monomeric selenium diimide [PtCl₂{*N,N'*-Se[N(t-Bu)]₂}] (**1**), as predicted by theoretical calculations.³¹ The structure of the

minor product $[\text{PtCl}_2\{N,N'\text{-SeO}[\text{NH}(\text{t-Bu})]_2\}]$ (**2**), which contains the hitherto unknown $\text{SeO}[\text{NH}(\text{t-Bu})]_2$ ligand, was also determined. DFT calculations showed that the reaction of $\text{Se}[\text{N}(\text{t-Bu})]_2$ with adventitious water is a plausible source of this ligand. The structurally intriguing ion pair $[\text{PtCl}_3\{Se,Se',Se''\text{-Se}_4[\text{N}(\text{t-Bu})]_4\}][\text{Pt}_2\text{Cl}_5\{Se,Se',Se''\text{-Se}_3[\text{N}(\text{t-Bu})]_2\}]\cdot 3\text{MeCN}$ (**3** $\cdot 3\text{MeCN}$) was also characterized as a minor product in attempts to generate **2**. The anion in **3** embodies the acyclic $[\text{Se}_3[\text{N}(\text{t-Bu})]_2]^{2-}$ dianion as a bridging ligand, which is likely formed by a redox process involving $\text{ClSe}[\text{N}(\text{t-Bu})\text{Se}]_2\text{Cl}$, $\text{Se}_4[\text{N}(\text{t-Bu})]_4$, and PtCl_2 . This finding suggests a rich coordination chemistry for complexes of new Se-N ligands generated from imidoselenium chlorides^{51,66} and metal halides.

The reaction of $[\text{PtCl}_2(\text{NCPh})_2]$ and $\text{Se}[\text{N}(\text{t-Bu})]_2$ produced the dinuclear complex $[\text{Pt}_2\text{Cl}_6\{\text{SeN}(\text{t-Bu})\text{C}(\text{Ph})\text{NH}\}_2]\cdot 2\text{C}_4\text{H}_8\text{O}$ (**4** $\cdot 2\text{THF}$) as the main product and only a small amount of **1**. The formation of **4** via the initial addition of t-BuNH_2 to the $\text{C}\equiv\text{N}$ triple bond of a platinum-activated PhCN ligand in *cis*- $[\text{PtCl}_2(\text{NCPh})_2]$, and subsequent reaction with SeCl_2 , is suggested. DFT calculations of the energy profile for the proposed reaction pathway indicated that only the *cis*-isomer of $[\text{PtCl}_2(\text{NCPh})_2]$ leads to the dinuclear complex **4**.

Supplementary Material

Supplementary material (packing of complexes in **1**, **2**, **3** $\cdot 3\text{MeCN}$, and **4** $\cdot 2\text{THF}$, the Gibbs energy profile of the reaction of $[\text{PtCl}_2\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ (**1**) with water is available with the article through the journal Web site at <http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2015-xxxx>. CCDC 1418459-1418462 contain the X-ray data for **1**, **2**, **3** $\cdot 3\text{MeCN}$, and **4** $\cdot 2\text{THF}$ in CIF format. These data can be obtained, free of charge, via <http://www.ccdc.cam.ac.uk/products/csd/request> (or from the Cambridge Crystallographic Data

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Table 1. Details of the structure determinations of **1**, **2**, **3**·3MeCN, and **4**·2THF.

	1	2	3 ·3MeCN	4 ·2THF
Empirical Formula	C ₈ H ₁₈ Cl ₂ N ₂ PtSe	C ₈ H ₂₀ Cl ₂ N ₂ OPtSe	C ₃₀ H ₆₃ Cl ₈ N ₉ Pt ₃ Se ₇	C ₁₅ H ₂₃ Cl ₃ N ₂ OPtSe
Formula weight	487.19	505.21	1971.48	837.01
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>Cm</i>	<i>P2₁/n</i>
<i>a</i> (Å)	13.479(3)	10.318(2)	17.434(5)	11.648(2)
<i>b</i> (Å)	11.032(2)	16.462(3)	10.913(5)	10.293(2)
<i>c</i> (Å)	18.358(4)	9.0157(18)	15.833(5)	17.338(4)
β (°)		113.72(3)	113.525(5)	105.55(3)
<i>V</i> (Å ³)	2729.7(9)	1402.0(6)	2762.0(17)	2002.7(7)
<i>T</i> (K)	100(2)	120(2)	150(2)	100(2)
<i>Z</i>	8	4	2	4
<i>F</i> (000)	1808	944	1828	1192
<i>D_c</i> (g cm ⁻³)	2.371	2.394	2.371	2.082
μ(Mo-Kα) (mm ⁻¹)	13.308	12.965	12.611	9.228
Crystal size (mm)	0.5 x 0.15 x 0.02	0.1 x 0.05 x 0.05	0.2 x 0.1 x 0.1	0.2 x 0.1 x 0.03
θ range (deg.)	2.63-26.00	3.50-25.00	3.18-26.00	2.69-26.00
Number of reflections collected	10975	7474	9586	20825
Number of unique reflections	2647	2439	5143	3930
Number of observed reflections ^a	2355	2010	4963	3613
Number of parameters	128	107	260/20	211
R _{INT}	0.1143	0.1096	0.0488	0.0696
R _I ^b	0.0470	0.0641	0.0369	0.0368
wR ₂ ^b	0.1219	0.1412	0.0929	0.0858
R _I (all data)	0.0550	0.0822	0.0394	0.0424
wR ₂ (all data)	0.1281	0.1515	0.0955	0.0880
GOOF	1.127	1.109	1.050	1.108
Max. and min. heights in final difference Fourier synthesis (e Å ⁻³)	2.254, -2.219	1.856, -2.000	2.039, -0.790	1.149, -2.348

^a $I \geq 2\sigma(I)$. ^b $R_I = \sum | |F_o| - |F_c| | / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

Figure Captions

Fig. 1. The molecular structure of $[\text{PtCl}_2\{N,N'\text{-Se}[\text{N}(\text{t-Bu})]_2\}]$ (**1**) indicating the numbering of the atoms. Thermal ellipsoids are drawn at 50 % probability level. Selected bond lengths (Å) and angles (°): Pt1-N1 2.030(6), Pt1-N2 2.022(7), Pt1-Cl1 2.297(2), Pt1-Cl2 2.284(2), Se1-N1 1.751(6), Se1-N2 1.743(6), N1-Pt1-N2 73.0(3), N1-Pt1-Cl1 100.5(2), N1-Pt1-Cl2 171.8(2), Cl1-Pt1-Cl2 87.55(8), Cl1-Pt1-N2 173.5(2), Cl2-Pt1-N2 98.9(2), N1-Se1-N2 87.3(3).

Fig. 2. The molecular structure of $[\text{PtCl}_2\{N,N'\text{-SeO}[\text{NH}(\text{t-Bu})]_2\}]$ (**2**) indicating the numbering of the atoms. Thermal ellipsoids are drawn at 50 % probability level. The s.o.f. of the two disordered molecules are 0.9738(15) and 0.0262(15). Selected bond lengths (Å) and angles (°) in the more abundant orientation (complex A): Pt1A-N1A 2.072(12), Pt1A-N2A 2.072(12), Pt1A-Cl1 2.318(4), Pt1A-Cl2 2.320(4), Se1A-N1A 1.907(12), Se1A-N2A 1.937(13), Se1A-O1A 1.633(11), N1A-C10 1.55(2), N2A-C20 1.52(2), N1A-Pt1A-N2A 76.4(5), N1A-Pt1A-Cl1 98.5(3), N1A-Pt1A-Cl2 174.1(3), Cl1-Pt1A-Cl2 87.16(15), Cl1-Pt1A-N2A 174.3(3), Cl2-Pt1A-N2A 97.8(4), N1A-Se1A-N2A 83.7(5), N1A-Se1A-O1A 103.6(5), O1A-Se1A-N2A 104.9(5), Se1A-N1A-C10 112.9(10), Se1A-N1A-Pt1A 98.2(6), C10-N1A-Pt1A 125.6(10), Se1A-N2A-C20 110.9(10), Se1A-N2A-Pt1A 97.3(5), C20-N2A-Pt1A 126.6(10).

Fig. 3. The ^{77}Se NMR spectrum of the soluble portion of the reaction mixture of SeOCl_2 and t-BuNH_2 in THF.

Fig. 4. Gibbs energy profile [$\Delta G(298\text{ K})$; kJ mol^{-1}] of the reaction of $\text{Se}[\text{N}(\text{t-Bu})]_2$ and H_2O calculated at the revPBE/def2-TZVP level.

Fig. 5. Molecular structure of $[\text{PtCl}_3\{\text{Se}, \text{Se}', \text{Se}''\text{-Se}_4[\text{N}(\text{t-Bu})]_4\}][\text{Pt}_2\text{Cl}_5\{\text{Se}, \text{Se}', \text{Se}''\text{-Se}_3[\text{N}(\text{t-Bu})]_2\}]\cdot 3\text{MeCN}$ (**3·3MeCN**) indicating the numbering of selected atoms. Thermal ellipsoids are drawn at 50 % probability level. For clarity, only the more abundant orientations of the *tert*-butyl groups are shown in the figure. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Pt1-Se1 2.381(3), Pt1-Se2 2.4383(17), Pt1-Cl11 2.318(6), Pt1-Cl12 2.366(4), Pt2-Se4 2.4240(17), Pt2-Se5 2.399(2), Pt2-Cl21 2.362(5), Pt2-Cl22 2.365(6), Pt3-Se4 2.3617(17), Pt3-Cl31 2.342(4), Se1-N1 1.858(14), Se2-N1 1.836(14), Se2-N2 1.811(12), Se3-N2 1.853(12), Se4-N3 1.880(13), Se5-N3 1.840(14), Se1-Pt1-Se2 77.06(5), Se1-Pt1-Cl11 170.65(18), Se2-Pt1-Se2ⁱ 100.82(8), Cl11-Pt1-Cl12 91.43(17), Cl12-Pt1-Cl12ⁱ 97.5(2), Se4-Pt3-Se4ⁱ 85.03(8), Cl31-Pt3-Se4 91.23(12), Cl31-Pt3-Se4ⁱ 176.15(12), Cl31-Pt3-Cl31ⁱ 92.5(2), Se4-Pt2-Se5 77.07(6), Se4-Pt2-Se4ⁱ 82.36(8), Se5-Pt2-Cl21 95.13(13), Se5-Pt2-Cl22 167.90(17), Cl21-Pt2-Cl22 93.23(17), Cl21-Pt2-Cl21ⁱ 92.4(3), N1-Se1-N1ⁱ 100.9(10), Se1-N1-Se2 108.7(7), Se2-N2-Se3 119.9(7), N2-Se3-N2ⁱ 103.7(8), Se4-N3-Se5 107.7(6), N3-Se5-N3ⁱ 112.0(9). The symmetry operation (*i*): *x*, -*y*, *z*.

Fig. 6. The ^{77}Se NMR spectra of the reaction solution from the reaction of $\text{Se}[\text{N}(\text{t-Bu})]_2$ and $[\text{PtCl}_2(\text{NPh})_2]$. (a) Molar ratio 1:1, (b) molar ratio 2:1.

Fig. 7. The molecular structure of $[\text{Pt}_2\text{Cl}_6\{\text{SeN}(\text{t-Bu})\text{C}(\text{Ph})\text{NH}\}_2]\cdot 2\text{C}_4\text{H}_8\text{O}$ (**4·2THF**) indicating the numbering of the atoms. Thermal ellipsoids are drawn at 50 % probability level. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$): Pt1-Se1 2.3790(7), Pt1-Se1ⁱ 2.4482(8), Pt1-N1 2.024(5), Pt1-

Cl1 2.3518(15), Pt1-Cl2 2.3293(15), Pt1-Cl3 2.3598(16), Se1-N2 1.865(5), N1-C1 1.315(8), N2-C1 1.359(8), N1-Pt1-Cl1 94.61(16), N1-Pt1-Cl2 172.61(16), N1-Pt1-Cl3 85.45(16), N1-Pt1-Se1 82.10(15), N1-Pt1-Se1ⁱ 86.99(16), Se1-Pt1-Se1ⁱ 86.00(3), Se1-Pt1-Cl1 173.78(4), Se1-Pt1-Cl2 91.80(4), Se1-Pt1-Cl3 91.71(5), Se1ⁱ-Pt1-Cl1 88.57(5), Se1ⁱ-Pt1-Cl2 96.77(4), Se1ⁱ-Pt1-Cl3 172.33(4), Cl1-Pt1-Cl2 91.85(6), Cl1-Pt1-Cl3 93.29(6), Cl2-Pt1-Cl3 90.61(6), Pt1-Se1-Pt1ⁱ 94.00(3), Pt1-Se1-N2 94.03(15), Pt1ⁱ-Se1-N2 106.62(16), Se1-N2-C1 115.3(4), Se1-N2-C20 116.6(4), C1-N2-C20 128.0(5), Pt1-N1-C1 120.8(4). Symmetry operation (*i*): 2-x, 1-y, -z.

Fig. 8. The revPBE/def2-TZVP Gibbs energy profile of the oxidative addition leading to the formation of the dinuclear platinum(IV) complex **4**.

Scheme 1. A possible formation of **3** via a redox process.

Scheme 2. A possible pathway for the formation of **4** from [PtCl₂(NCPh)₂]

Scheme 3. The reaction of cyclohepteno-1,4-diselenin with [MCl₂(NCPh)₂] (M = Pd, Pt).⁶⁷

Chart 1. Coordination modes in chalcogen diimide complexes.

Chart 2. Complexes **1-4**.

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Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Scheme 1.

Scheme 3.

Chart 1

Chart 2.

(Graphical abstract entry)

**Experimental and computational investigations of platinum complexes of
selenium diimide and some novel selenium-nitrogen ligands**

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Chivers, and Risto S. Laitinen