Polyazides

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The Binary Selenium(IV) Azides $Se(N_3)_4$, $[Se(N_3)_5]^-$, and $[Se(N_3)_6]^{2-}$**

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Dedicated to Professor Wolfgang Beck on the occasion of his 75th birthday

As a part of main-group azide chemistry, the area of binary chalcogen azides has sparked significant interest during the last years. Thus, a theoretical study of the nitrogen-rich sulfur compounds $S(N_3)_n$ ($n = 1$–4) was carried out, which included the neutral sulfur(IV) azide $S(N_3)_4$.[1] Furthermore, the binary tellurium azides $[Te(N_3)_3]^+$, $Te(N_3)_4$, $[Te(N_3)_5]^-$, and $[Te(N_3)_6]^{2-}$ have been synthesized and characterized.[2] The calculated structures of $Te(N_3)_4$ and $Te(N_3)_6$ were also reported.[2c,3] Contrary to the vast body of known binary tellurium–nitrogen chemistry,[2–4] the only previously reported examples of binary selenium–nitrogen compounds were selenium nitrides.[5] Herein, we present a study of the first binary selenium azide compounds, $Se(N_3)_4$, $[Se(N_3)_5]^-$, and $[Se(N_3)_6]^{2-}$.

By analogy with our previous syntheses of $Te(N_3)_4$,[2b,c] SeF_4 was treated with Me_3SiN_3 in either [D$_2$]dichloromethane at −50 °C or SO_2 at −64 °C. Yellow solutions of $Se(N_3)_4$ (**1**) together with pale yellow precipitates were obtained [Eq. (1)].

$$SeF_4 + 4\,Me_3SiN_3 \xrightarrow[SO_2,\,-64\,^\circ C]{CD_2Cl_2,\,-50\,^\circ C} Se(N_3)_4\ (\mathbf{1}) + 4\,Me_3SiF \qquad (1)$$

The pure tetraazide **1** is a lemon-yellow solid that readily precipitates, owing to its relatively low solubility in CD_2Cl_2 or SO_2. At −50 °C, the compound is stable only for a few hours, and the precipitate has detonated violently without provocation at −64 °C, even before removal of the supernatant SO_2 solvent. Therefore, further handling and characterization of the compound were restricted to the solutions.

Selenium tetraazide **1** was characterized by Raman and NMR spectroscopy. Its structure was of significant interest, because our B3LYP calculations predicted two minimum-energy structures of equal energy (see Figure 1 and the Supporting Information). One is based on a trigonal-bipyramidal C_2 arrangement, analogous to the experimentally known structures of the pnicogen tetrahalides and the isoelectronic tetrafluorohalogen cations[6–9] and the predicted structure of $Te(N_3)_4$.[2c,3] It is derived from a pseudo-trigonal bipyramid in which the free valence electron pair on Se is sterically active and occupies an equatorial position. Although three different C_2 structures were predicted for $Te(N_3)_4$,[2c,3] they differ only in the orientation of the azido ligands, and one of them is analogous to that predicted for **1**.

The second predicted minimum-energy structure is a tetragonal pyramid with C_4 symmetry. This structure is highly unusual and has no precedence in main-group chemistry. It possesses four equivalent Se−N bonds and N-Se-N angles. The four N_α atoms form a tetragonal plane; the selenium atom is positioned above this plane, and the four azido ligands point away from it. The significant displacement of the Se atom from the N_4 plane implies the presence of a sterically active free electron pair on Se located along the C_4 axis. This C_4 structure closely resembles the transition state expected for a turnstile Berry mechanism for equatorial–axial ligand exchange in trigonal-bipyramidal molecules.[10] In **1**, this transition state may have become a local minimum by a minimization of the mutual repulsion energy between the

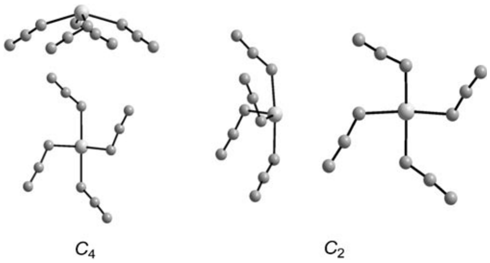

Figure 1. Calculated structures of the C_4 (side view and top view along the C_4 axis) and C_2 (side views emphasizing the pseudo-trigonal-bipyramidal structure and the close relationship to the C_4 structure) isomers of **1**. Selected bond lengths [Å] and angles [°] (Se large spheres; N small spheres; ax and eq are explained in the text): C_4 isomer: Se-N 2.050, N_α-N_β 1.260, N_β-N_γ 1.172; N-Se-N 149.0, Se-N-N 122.1, N-N-N 175.1. C_2 isomer: Se-N_{ax} 2.008, Se-N_{eq} 1.951, $(N_\alpha\text{-}N_\beta)_{ax}$ 1.259, $(N_\alpha\text{-}N_\beta)_{eq}$ 1.273, $(N_\beta\text{-}N_\gamma)_{ax}$ 1.172, $(N_\beta\text{-}N_\gamma)_{eq}$ 1.165; $(\text{N-Se-N})_{ax}$ 174.1, $(\text{N-Se-N})_{eq}$ 114.0, $(\text{Se-N-N})_{ax}$ 126.2, $(\text{Se-N-N})_{eq}$ 118.3, $(\text{N-N-N})_{ax}$ 175.0, $(\text{N-N-N})_{eq}$ 174.4.

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azido ligands. The fact that its energy is essentially the same as that of the C_2 structure implies little or no energy barrier to ligand inversion in **1**. Because of the slow time scale of NMR spectroscopy, this method was not suitable for distinction between the two isomers. However, the time scale of vibrational spectroscopy is much faster than that of the ligand exchange and allowed a distinction between the C_2 and the C_4 isomers.

In the ^{77}Se NMR spectrum (Table 1), a resonance at $\delta = 1323$ ppm was observed, which is deshielded compared to that of SeF_4 (in CD_2Cl_2 at 0 °C, $\delta = 1120$ ppm). In the ^{14}N NMR spectrum, the resonances for N_β ($\delta = -136$ ppm) and N_γ ($\delta = -173$ ppm) are readily detected, but the resonance for N_α ($\delta \approx -315$ ppm) is extremely broad and, therefore, poorly defined. Allowing a solution of **1** to warm up slowly to ambient temperature resulted in vigorous formation of gaseous dinitrogen and elemental selenium. Even after only 30 min at −50 °C, the formation of some red selenium was observed.

The Raman spectrum of **1** in SO_2 was recorded at −70 °C. It is complicated by bands associated with the SO_2 solvent, the Me_3SiF byproduct, and the teflon–FEP sample container (see the Supporting Information). However, there is no interference in the region of the antisymmetric azido ligand stretching vibrations (2200–2000 cm^{-1}). An analysis of the bands in this region (Figure 2) provides convincing evidence that **1** has the C_2 structure. The region of the SeN_4 skeletal modes does not permit a distinction between the two isomers, because our theoretical calculations predict only one Raman band of high intensity for each isomer, at 384 cm^{-1} for the C_4 and at 388 cm^{-1} for the C_2 isomer. The observed spectrum exhibits only one intense band at 362 cm^{-1}, compatible with either isomer. It is interesting to note that the structure previously predicted for the sulfur analogue $S(N_3)_4$[1] has C_1 symmetry and four different S–N bond lengths, one of which is very long (2.115 Å), thus implying an ionic complex, $[S(N_3)_3]^+N_3^-$, which easily dissociates.

As found for numerous other neutral polyazido compounds,[2,11–15] $Se(N_3)_4$ (**1**) can also be stabilized by anion formation. Thus, the pentaazidoselenite $[Se(N_3)_5]^-$ and hexaazidoselenite $[Se(N_3)_6]^{2-}$ anions were prepared as their bis(triphenylphosphoranylidene)ammonium (PNP^+) (**2** and **4**) or Ph_4P^+ (**3** and **5**) salts [Eqs. (2)–(5)].

Table 1: ^{77}Se, ^{125}Te, and ^{14}N NMR data of the binary selenium and tellurium azides.[a]

	δ ^{77}Se	δ ^{125}Te	δ ^{14}N (Se)			δ ^{14}N (Te)		
			β	γ	α	β	γ	α
$M(N_3)_4$	1323[b]	1380[c] 1376[d] 1427[e]	−136	−173	−315 (br)[b]	−141 −140	−234 −238[d]	−270 (br)[c]
$[M(N_3)_5]^-$	1252[f]	1258[g] 1256[h]	−138	−221	−309 (br)[f]	−139 −138	−236 −233[h]	−250 (br)[g]
$[M(N_3)_6]^{2-}$	1246[f]	1250[h]	−139	−248	−292 (br)[f]	−139	−239[h]	

[a] δ values in ppm; M = Se, Te. [b] CD_2Cl_2, −50 °C. [c] DMSO, 25 °C.[2b] [d] DMSO, 25 °C.[2c] [e] CH_3CN, 25 °C.[2c] [f] $[PNP]^+$ salt, CD_2Cl_2, −50 °C. [g] $[Me_4N]^+$ salt, CD_2Cl_2, 25 °C.[2b] [h] $[Ph_4P]^+$ salt, CH_3CN, 25 °C.[2c]

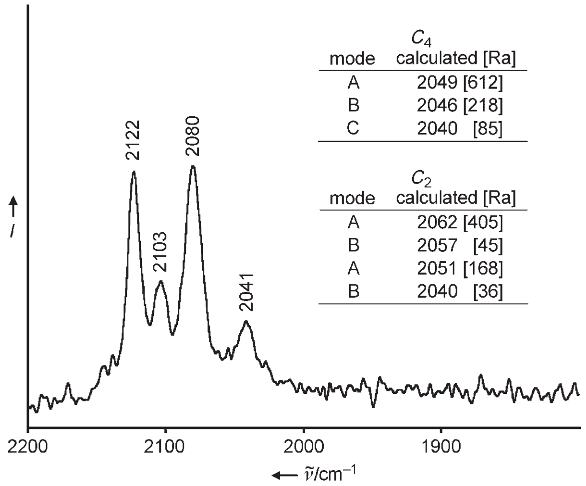

Figure 2. Low-temperature Raman spectrum of $Se(N_3)_4$ (**1**) in SO_2 solution, showing a comparison between the observed antisymmetric N_3 stretching vibrations and the frequency and Raman intensity predictions for the C_4 and the C_2 isomers.

$$[PNP][SeF_5] + 5\,Me_3SiN_3 \xrightarrow[-5\,Me_3SiF]{CD_2Cl_2,\,-50\,^\circ C} [PNP][Se(N_3)_5]\ (\mathbf{2}) \qquad (2)$$

$$SeF_5 + [Ph_4P]N_3 + 4\,Me_3SiN_3 \xrightarrow[-4\,Me_3SiF]{CH_3CN,\,-35\,^\circ C} [Ph_4P][Se(N_3)_5]\ (\mathbf{3}) \qquad (3)$$

$$[PNP]_2[SeF_6] + 6\,Me_3SiN_3 \xrightarrow[-6\,Me_3SiF]{CD_2Cl_2,\,-50\,^\circ C} [PNP]_2[Se(N_3)_6]\ (\mathbf{4}) \qquad (4)$$

$$SeF_4 + 2\,[Ph_4P]N_3 + 4\,Me_3SiN_3 \xrightarrow[-4\,Me_3SiF]{CH_3CN,\,-35\,^\circ C} [Ph_4P]_2[Se(N_3)_6]\ (\mathbf{5}) \qquad (5)$$

The compounds **2** and **4** were characterized by NMR spectroscopy in CD_2Cl_2 solutions (Table 1). Compared to $Se(N_3)_4$ (**1**), the ^{77}Se NMR resonances of the anions are, as expected from the increased negative charges, more shielded (**2**: $\delta = 1252$ ppm; **4**: $\delta = 1246$ ppm) and for both anionic species are in a narrow range. The same trend was previously observed for the corresponding tellurium azides in their ^{125}Te NMR spectra (Table 1).[2b,c]

Compounds **3** and **5** were isolated at −35 °C as temperature-sensitive orange and red solids and were characterized by low-temperature Raman spectroscopy. As can be seen from Figures 3 and 4, which highlight the bands arising from the anions, the spectra of the $[Se(N_3)_5]^-$ and $[Se(N_3)_6]^{2-}$ ions differ significantly and allow clear distinction between the two anions. Vibrational bands were assigned to individual modes by comparison with the spectra calculated at the B3LYP level of theory, and the agreement between observed and calculated spectra is satisfactory. The discrepancy in the observed and calculated spectra of **5** is due to distortion in the solid state by packing effects (see the Supporting Information). The thermal decomposition of **5** could be controlled by warming its CH_3CN solution very slowly from −40 °C to ambient temper-

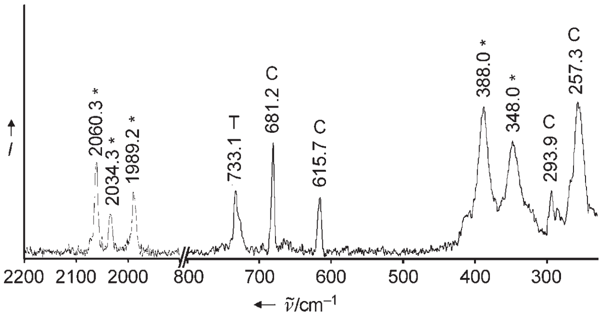

Figure 3. Raman spectrum of **3**. The bands belonging to the $[Se(N_3)_5]^-$ anion are marked with asterisks. Bands marked with C belong to the cation, and the band marked with T belongs to the teflon–FEP sample container.

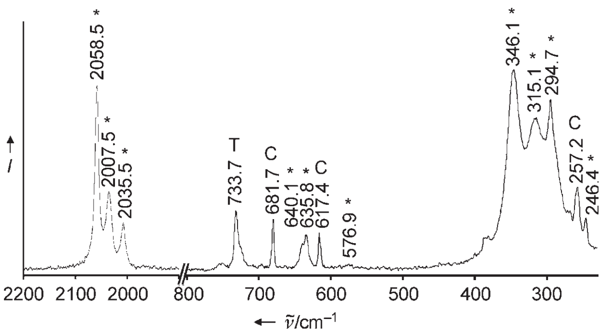

Figure 4. Raman spectrum of **5**. The bands belonging to the $[Se(N_3)_6]^{2-}$ anion are marked with asterisks. Bands marked with C belong to the cation, and the band marked with T belongs to the teflon–FEP sample container.

ature. This treatment resulted in the formation of $[Ph_4P]N_3$, amorphous selenium, and dinitrogen [Eq. (6)].

$$[Ph_4P]_2[Se(N_3)_6]\ (\mathbf{5}) \rightarrow 2[Ph_4P]N_3 + Se + 6\,N_2 \qquad (6)$$

The structure of **5** was verified by single crystal X-ray diffraction and is shown in Figure 5. The $[Se(N_3)_6]^{2-}$ anion has perfect S_6 symmetry, with Se–N bond lengths of 2.11–2.16 Å, N_α–N_β 1.20 Å, and N_β–N_γ 1.13–1.14 Å. These values are similar to those found in the crystal structure of the organoselenium(II) azide $2\text{-}Me_2NCH_2C_6H_4SeN_3$.[16] The symmetry is as predicted by the theoretical calculations and previously found for the similar hexaazides $[As(N_3)_6]^-$,[17] $[Sb(N_3)_6]^-$,[11] $[Si(N_3)_6]^{2-}$,[18] $[Ge(N_3)_6]^{2-}$,[19] $[Nb(N_3)_6]^-$,[12] $[Ta(N_3)_6]^-$,[12] $W(N_3)_6$,[13] and $[Ti(N_3)_6]^{2-}$.[14] In the structure of $[Te(N_3)_6]^{2-}$,[2c] on the other hand, the free valence electron pair on the central atom becomes sterically active. The steric activity of the free valence electron pair E in AX_6E-type compounds is a fascinating problem.[20] The energy differences between O_h and C_{3v} structures are very small, and the free pairs can range from inactive to strongly active. In the case of weakly active pairs, the structures can be influenced by very subtle effects, such as cation–anion interactions and crystal packing. Similarly, the results from theoretical calculations are strongly method-dependent.

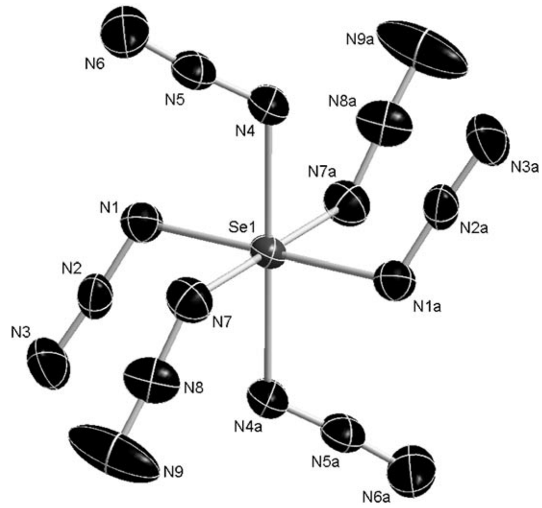

Figure 5. ORTEP drawing of the dianion $[Se(N_3)_6]^{2-}$ in the crystal structure of **5**. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Se-N1 2.132(2), Se-N4 2.113(2), Se-N7 2.155(2), N1-N2 1.204(3), N2-N3 1.140(3), N4-N5 1.199(3), N5-N6 1.140(3), N7-N8 1.205(3), N8-N9 1.125(3), N1-N2-N3 177.1(3), N4-N5-N6 175.9(3), N7-N8-N9 175.5(3), N1-Se-N4 90.89(9), N1-Se-N7 90.49(9), N4-Se-N7 89.16(9), Se-N1-N2 113.46(17), Se-N4-N5 116.21(17), Se-N7-N8 115.76(18).

The calculated structure of the $[Se(N_3)_5]^-$ anion is derived from a pseudo-octahedral arrangement with one "axial" position occupied by a stereochemically active lone pair of electrons (Figure 6). The four "equatorial" N_α atoms lie in one plane, with three azido ligands pointing away from the lone pair and one pointing towards it. The fifth azido group occupies the second axial position. It has a significantly shorter Se–N bond and lower negative partial charges than the four equatorial ligands, implying that the bond to the axial ligand is more covalent. This finding is in accord with the three-center-four-electron bonding schemes generally used for explaining the bonding in hypervalent AX_5E-type main-group compounds.[21] An analogous bonding situation is predicted for the pseudo-trigonal-bipyramidal C_2 isomer of **1**, in which the sterically active equatorial free valence electron pair of Se causes bonds to the equatorial azido

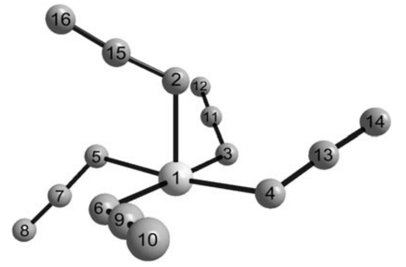

Figure 6. Calculated structure of the $[Se(N_3)_5]^-$ anion. Selected bond lengths [Å] and angles [°]: 1-2 1.979, 1-3 2.071, 1-4 2.063, 1-5 2.138, 1-6 2.114, 2-15 1.264, 3-11 1.251, 4-13 1.251, 5-7 1.248, 6-9 1.250, 7-8 1.184, 9-10 1.182, 11-12 1.180, 13-14 1.179, 15-16 1.171; 2-1-3 86.6, 2-1-4 88.5, 2-1-5 84.7, 2-1-6 91.4, 3-1-4 89.7, 3-1-5 92.0, 4-1-5 172.8, 4-1-6 89.5, 5-1-6 88.6.

ligands to become more covalent, with significantly shorter Se–N bonds and smaller negative charges.

In all three selenium azide species, the azido groups have strong covalent character, which is exemplified by typical N-N-N bond angles of 175–177°, the longer N_α–N_β bonds (1.20 Å in **5**) and the shorter terminal N_β–N_γ bonds (1.125–1.140 Å in **5**). The calculated Mulliken partial charges (see the Supporting Information) on the selenium atoms are all close to unity; the additional negative charges in the anions are spread over the azido ligands.

In summary, we were able to show that the binary selenium azide $Se(N_3)_4$ and its anions $[Se(N_3)_5]^-$ and $[Se(N_3)_6]^{2-}$ exist. The neutral azide is thermally unstable and explosive, but the anions, particularly when combined with large inert counterions, are more manageable.

Experimental Section

CAUTION! *Binary selenium azides are unstable, hazardous, and moisture-sensitive materials. $Se(N_3)_4$ is extremely sensitive and, even as a suspension in SO_2 solution, has exploded violently at low temperatures without any provocation. All compounds should be handled only on a scale of less than 2 mmol with appropriate safety precautions (safety shields, safety glasses, face shields, leather suits, gloves, and ear plugs). Teflon containers and stainless steel Dewar flasks should be used whenever possible to avoid hazardous shrapnel formation and to contain explosions, respectively. The use of chlorinated solvents is not recommended when working with azides, owing to facile chloride–azide exchange reactions, which can result in the formation of explosive alkylazides.[22] However, during our studies at LMU, such hazardous byproducts were never observed.* ***Ignoring these safety precautions can result in serious injury.***

At LMU, all manipulations of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using flame-dried glass vessels or oven-dried plastic equipment and Schlenk techniques.[23] The selenium fluorides were handled in perfluoroalkoxy copolymer (PFA) vessels owing to their moisture-sensitivity. For the NMR spectroscopic measurements, 4-mm PFA tubes were used, which were placed into standard 5-mm NMR glass tubes. Selenium tetrafluoride (Galaxy Chemicals), silver fluoride (ABCR), bis(triphenylphosphoranylidene)ammonium chloride ([PNP]Cl, Aldrich), and trimethylsilyl azide (Aldrich) were used as received. The solvents dichloromethane and acetonitrile were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded on a JEOL Eclipse 400 instrument, and chemical shifts are reported with respect to $MeNO_2$ (^{14}N, 28.9 MHz) and Me_2Se (^{77}Se, 76.3 MHz).

At USC, all reactions were carried out in teflon–FEP ampules that were closed by stainless steel valves. Volatile materials were handled in a pyrex glass vacuum line. Nonvolatile materials were handled in the dry argon atmosphere of a glove box. Raman spectra were recorded at −80 °C in the range 4000–80 cm^{-1} on a Bruker Equinox 55 FT-RA spectrometer using a Nd-YAG laser at 1064 nm with power levels of less than 100 mW. Teflon–FEP tubes with stainless steel valves were used as sample containers. The starting materials $SeCl_4$, SeO_2, and $[Ph_4P]Cl$ (all from Aldrich) were used without further purification. Me_3SiN_3 (Aldrich) was purified by fractional condensation prior to use. Solvents were dried by standard methods and freshly distilled prior to use. $[Ph_4P]N_3$ was prepared from $[Ph_4P]Cl$ and NaN_3 by ion exchange.[24] SeF_4 was prepared from $SeCl_4$ or SeO_2 and ClF_3 in HF solution.

1: A solution of SeF_4 (0.18 mmol) in CD_2Cl_2 (1 mL) was treated with Me_3SiN_3 (0.79 mmol) at −50 °C. After 30 min stirring, a pale yellow precipitate was obtained and dissolved in additional CD_2Cl_2 (1 mL), yielding a yellow solution. After 30 min at −50 °C, the significant formation of red selenium indicated decomposition.

In another experiment, a sample of SeF_4 (0.80 mmol) was condensed into a teflon–FEP ampule with subsequent addition of SO_2 (2 mL) and Me_3SiN_3 (4.00 mmol) by condensation in vacuo at −196 °C. The mixture was warmed to −64 °C. Within minutes, the mixture turned yellow, the color intensified, and a lemon-yellow solid precipitated while the reaction proceeded. Keeping the reaction mixture for about 15 min at −64 °C resulted in a violent explosion that destroyed the sample container and the surrounding stainless-steel Dewar flask.

$[PNP][SeF_5]$: Silver fluoride (1.77 mmol) was added at ambient temperature to a solution of SeF_4 (1.77 mmol) in CH_3CN (4 mL). The resulting solution was stirred for 2 h, and then [PNP]Cl (1.77 mmol) was added. After additional stirring for 30 min, the pale yellow solution was decanted from a gray precipitate, and all volatile material was removed from the filtrate in vacuo, yielding a colorless solid.[25]

2: A solution of $[PNP][SeF_5]$ (0.26 mmol) in CD_2Cl_2 (0.6 mL) was treated with Me_3SiN_3 (1.4 mmol) at −50 °C. After a few minutes, a yellow solution had formed, which was analyzed by NMR spectroscopy. After 1 h at −50 °C, the significant formation of red selenium indicated decomposition.

$[PNP]_2[SeF_6]$: Silver fluoride (3.55 mmol) was added at ambient temperature to a solution of SeF_4 (1.77 mmol) in CH_3CN (6 mL). The resulting solution was stirred for 2 h, and then [PNP]Cl (3.55 mmol) was added. After additional stirring for 30 min, the pale yellow solution was decanted from a gray precipitate, and all volatile material was removed from the filtrate in vacuo, yielding a colorless solid.[25]

4: A solution of $[PNP]_2[SeF_6]$ (0.17 mmol) in CD_2Cl_2 (0.6 mL) was treated with Me_3SiN_3 (1.1 mmol) at −50 °C. After a few minutes, a pale yellow solution was formed and analyzed by NMR spectroscopy. After 1 h at −50 °C, decomposition was evident from the observation of significant amounts of red selenium.

3 and **5**: Under a stream of dry dinitrogen gas, a stochiometric amount of $[Ph_4P]N_3$ was added to a frozen solution of SeF_4 (0.43 mmol) in CH_3CN (1.5 mL) at −196 °C. The reactor was evacuated, and CH_3CN (0.3 mL) and Me_3SiN_3 (3.16 mmol) were condensed in. The reaction mixture was warmed to −40 °C, and the reactor was gently agitated. After 30 minutes, an orange-red solution with either an orange or a red precipitate was obtained. All volatile material was removed in vacuo at −35 °C. The solids **3** and **5** were characterized by low-temperature Raman spectroscopy, and **5** was also characterized by its crystal structure. **3**: orange, temperature-sensitive solid (0.30 g, weight calculated for 0.43 mmol: 0.27 g). **5**: red, temperature-sensitive solid (0.45 g, weight calculated for 0.43 mmol: 0.43 g). Single crystals were grown from a solution in CH_3CN by slow evaporation of the solvent in a dynamic vacuum at −35 °C.[26]

Thermal decomposition of **5**: A solution of **5** (0.4 mmol) in CH_3CN (4 mL) at −40 °C was warmed to ambient temperature over a period of 6 h. A light yellow solution and a maroon precipitate formed. The reaction mixture was cooled to −196 °C and inspected for dinitrogen (noncondensible compounds). P,V,T measurements indicated that 2.1 mmol dinitrogen had formed. The reaction mixture was then warmed to ambient temperature and the precipitate filtered off. The precipitate was identified as amorphous selenium by its Raman spectrum, which showed a single, very intense line at 252 cm^{-1}.[27] Volatile components were removed from the light yellow solution in vacuo, leaving behind a pale yellow solid that was identified by Raman spectroscopy as $[Ph_4P]N_3$.[24]

The structure and frequency calculations were performed at the B3LYP level of theory using a D95 V basis set for N, while the core electrons of Se were treated with an ECP28MWB pseudopotential;

for the valence electrons the following contraction was used (4s5p1d)/[2s3p1d] (for details see the Supporting Information).[28]

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[26] Crystal data for **5**, $C_{48}H_{40}N_{18}P_2Se$: $M_r = 1009.88$, triclinic, space group $P\bar{1}$, $a = 10.221(2)$, $b = 10.563(2)$, $c = 12.438(3)$ Å, $\alpha = 87.569(3)$, $\beta = 72.990(3)$, $\gamma = 67.704(3)°$, $V = 1184.4(4)$ Å^3, $F(000) = 518$, $\rho_{calcd}(Z{=}1) = 1.416\ g\,cm^{-3}$, $\mu = 0.917\ mm^{-1}$, approximate crystal dimensions $0.22 \times 0.17 \times 0.09\ mm^3$, $\theta = 1.72$–$27.55°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 123$ K, 7384 measured data (Bruker three-circle, SMART APEX CCD with χ-axis fixed at 54.74°, using the SMART V 5.625 program, Bruker AXS: Madison, WI, 2001), of which 5142 ($R_{int} = 0.0205$) unique. Lorentz and polarization correction (SAINT V 6.22 program, Bruker AXS, Madison, WI, 2001), absorption correction (SADABS program, Bruker AXS, Madison, WI, 2001). Structure solution by direct methods (SHELXTL 5.10, Bruker AXS, Madison, WI, 2000), full-matrix least-squares refinement on F^2, data to parameters ratio: 16.4:1, final R indices $[I > 2\sigma(I)]$: $R1 = 0.0403$, $wR2 = 0.0920$, $R1 = 0.0556$ (all data), $wR2 = 0.1003$ (all data), GOF on $F^2 = 1.039$. CCDC-645973 contains 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.

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