

Isolation of a Stable Covalent Selenium Azide RSeN₃

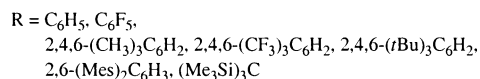
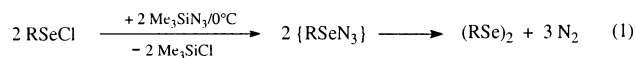
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The chemistry of main-group element azides has been thoroughly investigated over the past decades.¹ A considerable part of our own research in the last years has focused on the synthesis of, in some cases, rather labile azide compounds of the heavier chalcogens. We and others, aside from some older scattered reports cited therein, have performed systematic studies on the preparation and properties of tellurium azides.² However, until now, covalent azide compounds of the lighter homologue, selenium, are unknown. Recently, we have been successful in the structural characterization of the first examples of ionic selenonium azides of the type [R₃Se]N₃.³ There are several reports in the literature on the in situ generation of a proposed, but never characterized or isolated, selenium azide reagent, "PhSeN₃", which proved to be a useful tool for the azidoselenenylation of alkenes and subsequently to construct enantiomerically enriched nitrogen-containing compounds.⁴

A possible approach to check the stability of RSeN₃ would be a variation of the substituent R. Suitable precursors for a conversion into the corresponding azides are benzeneselenenyl chlorides RSeCl,⁵ which were treated with trimethylsilyl azide, a common azide transfer reagent (eq 1).



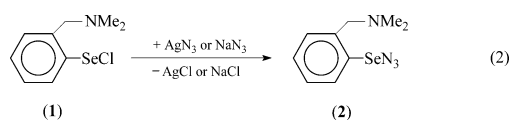
The selenenyl azides were formed as intermediates, which under elimination of dinitrogen form the corresponding stable diselanes. Nevertheless, the initial conversion into RSeN₃ could be monitored by ⁷⁷Se NMR spectroscopy. The ⁷⁷Se resonances of RSeN₃ are slightly shifted downfield compared to those of RSeCl (Table 1). Independent of the temperature, reaction mixtures of RSeCl/RSeN₃ (or alternatively RSeBr/RSeN₃) are always accompanied by significant amounts of (RSe)₂ observed at higher field, which increase with the reaction time.

The use of sterically demanding substituents (eq 1) does not prevent the decomposition of RSeN₃ into (RSe)₂. Another approach is the application of donor-stabilized selenium centers in RSeCl (known for the stabilization of low-valent group 14 azides⁷). Such compounds contain amino moieties at the ortho position of a benzeneselenenyl chloride, i.e. in this study 2-Me₂NCH₂C₆H₄SeCl (**1**).⁸ However, a reaction of **1** with trimethylsilyl azide did not occur but, with silver azide, a conversion into the corresponding azide 2-Me₂NCH₂C₆H₄SeN₃ (**2**) is possible. Due to the hazard of AgN₃, only small amounts of **2** can be prepared. In general, compounds of the type RSeCl or RSeBr display moisture-sensitive materials, which in the case of **1** is reduced by the donor-stabilized selenium atom. Therefore, also a reaction of **1** with ionic sodium azide in

Table 1. ⁷⁷Se NMR Resonances of RSeCl/Me₃SiN₃ Reaction Mixtures (0 °C, CDCl₃, Relative to Me₂Se, ppm)

R	RSeCl	RSeN ₃	(RSe) ₂
C ₆ H ₅	1044	1128	459
C ₆ F ₅	798	911	371
2,4,6-(CH ₃) ₃ C ₆ H ₂ (=Mes)	949	1009	367
2,4,6-(CF ₃) ₃ C ₆ H ₂	907	1011	508
2,4,6-(<i>t</i> Bu) ₃ C ₆ H ₂	998	1001	514
2,6-(Mes) ₂ C ₆ H ₃	1023	1084	420
(Me ₃ Si) ₃ C	1152	not detected	395

dry acetone was found to occur quantitatively, which makes **2** available on larger scale (eq 2).⁹



The selenenyl azide **2** is stable at 25 °C, but for prolonged periods dinitrogen elimination takes place under formation of the corresponding diselane. Storage is recommended at least at 0 °C under light exclusion. Alternatively, azide **2** can also be synthesized by treating the corresponding bromide 2-Me₂NCH₂C₆H₄SeBr or iodide 2-Me₂NCH₂C₆H₄SeI (**3**), respectively, with AgN₃. The latter react only slowly and incompletely with NaN₃, and separation of **2** from 2-Me₂NCH₂C₆H₄SeBr or **3** is not practicable. The structure of the selenenyl azide **2** (Figure 1), and as well those of **1** and **3** (not depicted, crystallized isotypically),¹⁰ were confirmed by an X-ray crystallographic analysis.

The structures show the expected coordination of the amino-methyl nitrogen atom to selenium, leading to five-membered heterocyclic zwitterions with a 3-coordinated selenium anion and a 4-coordinated ammonium cation (3c-4e bond system), resulting in rather short Se–N distances of 2.135(4) **1**, 2.204(6) **2**, and 2.172(3) Å **3**. A similar short distance was found for the corresponding bromide RSeBr, Se–N 2.143(6) Å.^{11b} In reverse, this effect causes elongated Se–Hal and Se–N₃ distances (2.471(2) **1**, 2.107(8) **2**, 2.634(1) in RSeBr,^{11b} and 2.8079(7) Å **3**), compared to undisturbed "regular" (2c-2e bond systems) Se–Hal bond lengths in e.g. 2,4,6-(CH₃)₃C₆H₂SeHal derivatives, 2.186(1) Se–Cl, 2.3331(8) Se–Br, 2.529(1) Se–I.^{5c,12} The difference of only 0.1 Å in the Se1–N1/N2 bond lengths in the structure of **2** allows regarding both Se–N bonds as parts of a slightly unsymmetric 3c case with formal bond orders close to 0.5 for both Se–N bonds. A comparison to another structurally characterized SeN selenenyl pseudohalide bond is possible only for the selenenyl sulfinylimine 2,4,6-(CF₃)₃C₆H₂SeNSO with a Se–N bond length of 1.850(7) Å,¹³ in good agreement with the trend observed of approximately 0.3 Å longer Se–Hal and Se–N₃ bond lengths found in 2-Me₂NCH₂C₆H₄SeHal (Hal = Cl, Br, I and N₃). Consequently, as a function of the coordinating dimethylamino group, the N–N distances in **2** are almost identical (N_α–N_β 1.17(1), N_β–N_γ 1.15(1) Å), compared to

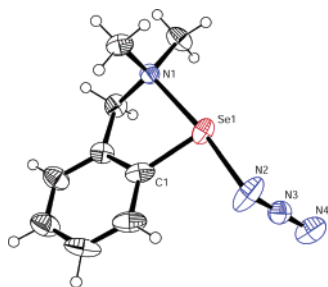


Figure 1. Molecule of **2** in the crystal. Ellipsoids are drawn at 40% probability. Selected bond lengths (Å) and angles (deg): Se(1)–C(1) 1.909(9), Se(1)–N(1) 2.204(6), Se(1)–N(2) 2.107(8), N(2)–N(3) 1.17(1), N(3)–N(4) 1.15(1); C(1)–Se(1)–N(1) 80.7(3), C(1)–Se(1)–N(2) 92.7(4), N(1)–Se(1)–N(2) 172.5(3), Se(1)–N(2)–N(3) 114.0(7), N(2)–N(3)–N(4) 177(1).

usually elongated N_{α} – N_{β} and shortened N_{β} – N_{γ} bond lengths in covalent azides.^{1,2} There are no significant intermolecular $\text{Se}\cdots\text{N}$ distances found, with the closest contact $\text{Se}\cdots\text{N}_{\gamma}$ being 3.745 Å (cf. 3.45 Å for $\Sigma\text{vdWr SeN}^{14}$). The calculated structures of **2**, as well as of **1**, are in good accord with the experimentally observed (X-ray) structural parameters (calcd SeCl 2.456 Å **1**; SeN1 2.370, SeN2 2.040 Å **2**).^{15,16}

The spectroscopic data⁹ indicate the presence of a covalently bound azide unit in **2** (and support the crystallographic results). Three distinct resonances for the azide moiety are observed in the ¹⁵N NMR spectrum. The antisymmetric azide stretching vibration $\nu_{\text{as}}\text{N}_3$ is found as a very strong peak at 2036/2028 cm^{-1} in the IR spectrum, and as a peak of medium intensity at 2019 cm^{-1} in the Raman spectrum, respectively, in the typical region of both covalent and ionic azides. However, the νSeN (azide) in **2**, as well as the νSeCl stretching frequencies in **1**, cannot be unambiguously identified and assigned, as generally is the case for RSeCl derivatives^{5b,c} without additional coordinating substituents.

The relative ease of preparation and stability of the first isolable selenenyl azide, makes **2** an attractive potential candidate for further applications in organic chemistry, which are part of our future projects.

Acknowledgment. The University of Munich and the Fonds der Chemischen Industrie are gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files for compounds **1**, **2**, and **3** (CIF); calculations and tables of computed vibrational frequencies of **1** and **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- The claimed preparation, isolation, and data of 2,4,6-(CH₃)₃C₆H₂SeN₃, reported by Back and Kerr (Back, T. G.; Kerr, R. G. *J. Chem. Soc., Chem. Commun.* **1987**, 134) could not be reproduced and therefore remain doubtful. In an additional experiment to Table 1, we used THF as the solvent (⁷⁷Se NMR, ppm, THF, 0 °C: 957 (MesSeCl), 1016 (MesSeN₃), 363 (MesSeSeMes)), and found, that the reported shifts by Back and Kerr (recalculated to Me₂Se as reference) do not agree with our obtained values both in CDCl₃ or THF.
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- All manipulations were carried out under dry nitrogen atmosphere with dried solvents. 2-Me₂NCH₂C₆H₄SeCl (**1**): Into a solution of (2-Me₂NCH₂C₆H₄Se)₂¹¹ (10.7 g, 25 mmol) in dichloromethane (40 mL) was added a solution of freshly distilled SO₂Cl₂ (3.4 g, 25 mmol) in dichloromethane (10 mL) at 0 °C and stirred for 30 min. The resulting mixture was separated from all insoluble material and then removed from all volatile materials to give a yellowish oil, which crystallizes after some minutes. The raw product was washed with methanol and afforded **1** as pale yellow crystals (9.8 g, 79% yield; mp 118–121 °C, dec). ¹H NMR (CDCl₃): δ 8.08–8.06 (m, 1H, ar-H), 7.31–7.08 (m, 3H, ar-H), 3.99 (s, 2H, CH₂), 2.76 (s, 6H, Me₂N). ¹³C NMR (CDCl₃): δ 138.0 (C-1, ¹J_{C–Se} = 133.8 Hz), 134.3/129.1/129.0/126.2/125.1 (C-2/C-3/C-4/C-5/C-6), 66.2 (CH₂, ³J_{C–Se} = 7.7 Hz), 47.3 (Me₂N). ¹⁵N NMR (CDCl₃): δ –325.5. ⁷⁷Se NMR (CDCl₃): δ 1030. IR (KBr): 3063 w (νCH), 2920 w (νCH₂), 1589/1572 w (νC=C), 1461 s, 1441 m, 999 m, 836 s, 752 s, 472 s, 304 m cm^{-1} . Raman (100 mW): 3056 (16) (νCH), 2935 (27) (νCH₂), 1589/1574 (9) (νC=C), 835 (16), 473 (80), 379 (17), 261 (24), 241 (33), 199 (100), 186 (42), 149 (26) cm^{-1} (selected vibrational data). MS (D-EI), *m/e* (%): 249 (23) [M⁺], 214 (100) [M⁺ – Cl], 169 (22) [M⁺ – HCl – Me₂N], 134 (44) [M⁺ – Cl – Se], 91 (34) [C₇H₇⁺], 58 (19) [Me₂NCH₂⁺], 44 (24) [Me₂N⁺]. Anal. Calcd for C₉H₉ClN₂Se: C, 43.5; H, 4.9; Cl, 14.3; N, 5.6. Found: C, 42.8; H, 5.0; Cl, 13.6; N, 5.5.
- 2-Me₂NCH₂C₆H₄SeN₃ (**2**): Into a solution of **1** (1.0 g, 4 mmol) in acetone (25 mL) was added an excess of sodium azide (1.3 g, 20 mmol) at ambient temperature and stirred for 1 h. A slight lightening of the yellowish suspension occurred. The resulting mixture was separated from the insoluble sodium salts and the solvent removed in vacuo to give a yellowish oil. It crystallized after some minutes to afford **2** as pale yellow crystals, pale yellow-green in thin layers (0.9 g, 88% yield; dec >65 °C, gas evolution). Alternative procedure (**Caution: recommended only for small scale!**): Into solutions of 2-Me₂NCH₂C₆H₄SeHal (0.5 mmol; Hal = Cl, Br, I) in dichloromethane (5 mL) was added AgN₃ (150 mg, 1.0 mmol) at ambient temperature and the mixture stirred for 3 h. After approximately 30 min a clear lightening of the colored solutions occurred. Filtration from the silver salts and removal of the solvent afforded **2** in yields of 90–95%. ¹H NMR (CDCl₃): δ 7.72–7.70 (m, 1H, ar-H), 7.30–7.09 (m, 3H, ar-H), 3.78 (s, 2H, CH₂), 2.53 (s, 6H, Me₂N). ¹³C NMR (CDCl₃): δ 137.5 (C-1, ¹J_{C–Se} = 130.7 Hz), 134.5/128.8/127.3/126.1/125.9 (C-2/C-3/C-4/C-5/C-6), 64.3 (CH₂, ³J_{C–Se} = 8.5 Hz), 45.4 (Me₂N). ¹⁵N NMR (CDCl₃): δ –130.2 (N_β, ²J_{N–Se} = 18.9 Hz), –197.7 (N_γ), –304.3 (N_α), –334.5 (Me₂N). ⁷⁷Se NMR (CDCl₃): δ 1048. IR (KBr): 3063 m (νCH), 2931 m (νCH₂), 2036/2028 (vs) (ν_{as}N₃), 1589/1572 w (νC=C), 1462 s, 1440 s, 1265 s, 839 s, 748 s, 467 m, 310 s, 282 m cm^{-1} . Raman (100 mW): 3054 (24) (νCH), 2933 (48) (νCH₂), 2019 (44) (ν_{as}N₃), 1589/1572 (14) (νC=C), 837 (27), 467 (100), 376 (24), 299 (55), 277 (97), 191 (60), 178 (50), 159 (61) cm^{-1} (selected vibrational data). MS (D-EI), *m/e* (%): 256 (0.4) [M⁺], 228 (0.7) [M⁺ – N₂], 214 (100) [M⁺ – N₃], 169 (28) [M⁺ – HN₃ – Me₂N], 134 (50) [M⁺ – N₃ – Se], 91 (39) [C₇H₇⁺], 58 (12) [Me₂NCH₂⁺], 44 (32) [Me₂N⁺]. Anal. Calcd for C₉H₁₂N₄Se: C, 42.4; H, 4.8; N, 22.0. Found: C, 42.8; H, 4.9; N, 20.5.
- A semiempirical absorption correction by ψ -scans was performed for all three data sets resulting in a nonperfect absorption correction. A partial decay of the crystal was observed in the case of the selenenyl azide **2** during the data collection.
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- The structures and vibrational frequencies of **1** and **2** were calculated at the RMPWPW91/SDD level of theory (see Supporting Information).
- The structure of **1** has previously been the subject of theoretical studies, see: Iwaoka, M.; Tomoda, S. *J. Org. Chem.* **1995**, *60*, 5299 and *J. Am. Chem. Soc.* **1996**, *118*, 8077.

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