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3,1,2,4-Benzothiaselenadiazine and related heterocycles: synthesis and transformation into Herz-type radicals

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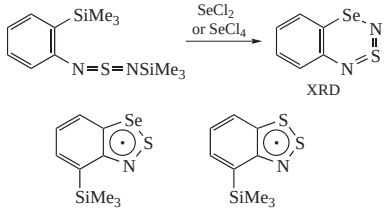
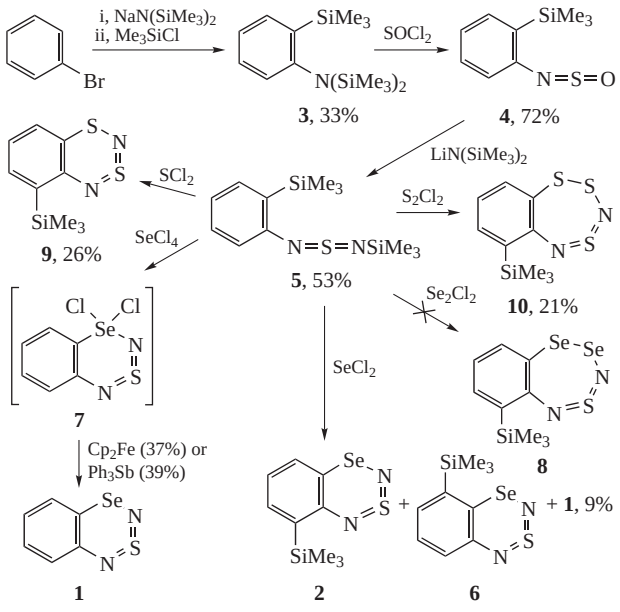
The archetypal 3,1,2,4-benzothiaselenadiazine, its 5- and 8-Me_3Si derivatives and related dithiadiazine and trithiadiazepine were synthesized from 2-$Me_3SiC_6H_4N{=}S{=}NSiMe_3$ by the action of $SeCl_2$, $SeCl_4$, SCl_2, and S_2Cl_2 and converted into persistent 2,1,3-benzothiaselenazolyl and 1,2,3-benzodithiazolyl radicals characterized by EPR spectroscopy and DFT calculations.



Chemistry of chalcogen-nitrogen rings and cages, revealing wide diversity of molecular and electronic structures and reactivities, belongs to the hot topics of contemporary main group chemistry.[1] Amongst chalcogen-nitrogen rings, 1,3,2,4-benzodithiadiazines are rare examples of 12π-electron antiaromatics according to the NICS values and some other criteria.[2] These compounds were synthesized in both the hydrocarbon and fluorocarbon series and demonstrated high and varied heteroatom reactivity covering transformation into persistent 1,2,3-benzodithiazolyls, *i.e.* Herz radicals,[3] including species inaccessible by other approaches.[2(a),4] The Herz radicals are of interest not only for fundamental chemistry but also for materials science as building blocks of real or potential molecule-based conductive or/and magnetic functional materials.[3] Recently, negatively charged congeners of Herz radicals, *i.e.* 1,2,3-dithiazolidyl radical anions, were synthesized to expand this promising field further.[5] Importantly, replacement of S with Se in Herz radicals frequently leads to enhanced conductivity or/and ferromagnetism thus stimulating synthesis of novel Se derivatives.[6]

Selenium congeners of 1,3,2,4-benzodithiadiazines, *i.e.* rare heterocycles containing two different chalcogens, are poorly studied. In the fluorocarbon series, 5,6,7,8-tetra- and 5,6,8-trifluoro derivatives were obtained by the nucleophilic ring-closure of the corresponding ArSeN=S=$NSiMe_3$ under the action of CsF.[7] In the hydrocarbon series, attempts of electrophilic cyclization of ArN=S=$NSiMe_3$ under the action of $SeCl_2$ failed (see Online Supplementary Materials) in contrast to successful cyclizations with SCl_2.[2] It was assumed that under electrophilic conditions Me_3Si should be a better leaving group than H. In this work we report on successful preparation of the archetypal 3,1,2,4-benzothiaselenadiazine **1** by electrophilic cyclization of 2-$Me_3SiC_6H_4N{=}S{=}NSiMe_3$ **5** under the action of $SeCl_2$ or $SeCl_4$.

Compound **5** was synthesized from bromobenzene *via* compounds **3** and **4** (Scheme 1)[†] using previously elaborated approaches.[2(c)–(e),8] With **5** and $SeCl_2$, a mixture of **1** with its 5- and 8-Me_3Si derivatives (**2** and **6**, respectively) was obtained as a result of competitive substitution of Me_3Si and H, the **1**:**2**:**6** ratio was 1.0:1.1:0.4 (^{1}H NMR; structures of **2** and **6** were assigned with COSY, NOESY and HMBC ^{1}H-^{1}H and ^{1}H-^{13}C correlations; see Online Supplementary Materials). In reactions



Scheme 1

[†] NMR spectra were measured with Bruker AV-400 (^{1}H, 400.1 MHz) and Bruker AV-600 (^{1}H, 600.3 MHz; ^{13}C, 151.0 MHz; ^{14}N, 43.4 MHz; ^{15}N, 60.8 MHz; ^{29}Si, 119.3 MHz; ^{77}Se, 114.5 MHz) spectrometers for solutions in $CDCl_3$ with TMS, NH_3 (liq.) and Me_2Se as standards. HRMS (EI, 70 eV) were performed using a Thermo DFS mass spectrometer. UV-VIS spectra were collected with a Varian Cary 5000 spectrophotometer for heptane solutions.

of 2-$RC_6H_4N{=}S{=}NSiMe_3$ with SCl_2, the formation of 8-R substituted 1,3,2,4-benzodithiadiazines has never been observed.[2] According to the DFT calculations, formation of isomeric **2** and **6** could be explained by the low-barrier Me_3Si-migration (see Online Supplementary Materials).

Reaction of **5** with $SeCl_4$ followed by the action of $FeCp_2$ or $SbPh_3$ on the intermediate **7** detected by NMR resulted in **1**, formation of **2** and **6** was not observed (see Scheme 1),† *i.e.* only substitution of the Me_3Si group effectively occurred.

Attempt to prepare thiadiselenadiazepine **8** by reaction of **5** with Se_2Cl_2 failed and only compounds **2** and **9** were identified by ^1H NMR in the reaction mixtures (Scheme 1).

With sulfur chlorides instead of selenium ones, synthetic situation was different. For interaction of **5** with SCl_2 or S_2Cl_2 only substitution of H atoms was observed to give dithiadiazine **9** and trithiadiazepine **10**,[9] respectively (see Scheme 1). Two singlets in ^{15}N NMR spectrum of **9** confirm its 5-Me_3Si structure and reject 8-Me_3Si alternative.[2(*c*)–(*e*)]

Structure of **1** was confirmed by X-ray diffraction (XRD; Figure 1).‡ Similar to its S congener,[2(*b*)] the compound is planar in the crystal (for discussion of magnetic shielding and NICS values, see Online Supplementary Materials).

N,N,*2-Tris(trimethylsilyl)aniline* **3** *(modified procedure)*.[8] At ambient temperature and under argon, 35.63 g (0.23 mol) of C_6H_5Br was added dropwise over 0.5 h to a stirred solution of 75.51 g (0.41 mol) of $NaN(SiMe_3)_2$ in 250 ml of THF. The reaction mixture was refluxed for 4 h, cooled to 20 °C, and 58 ml (0.41 mol) of Me_3SiCl in 15 ml of THF was added over 0.5 h. The reaction solution was filtered, the solvent was distilled off, and the residue was redistilled twice under reduced pressure to afford compound **3** as a colourless oil solidifying upon standing, yield 23.12 g (33%), bp 86–88 °C (0.6 Torr), mp 35–36 °C. ^1H NMR ($CDCl_3$) δ: 7.46 (dd, 1H), 7.18 (t, 1H), 7.09 (t, 1H), 6.89 (d, 1H), 0.33 (s, 18H), 0.09 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 152.3, 139.3, 135.6, 130.4, 128.6, 123.1, 1.80, 1.40. ^{14}N NMR ($CDCl_3$) δ: 59. ^{29}Si NMR ($CDCl_3$) δ: 4.6 (m), –5.2 (m). MS (EI), *m*/*z*: 309.1728 $[C_{15}H_{31}NSi_3]^+$ (calc. for $C_{15}H_{31}NSi_3$, *m*/*z*: 309.1800). Found (%): C, 58.22; H, 9.97; N, 4.68. Calc. for $C_{15}H_{31}NSi_3$ (%): C, 58.18; H, 10.09; N, 4.52.

N-*Sulfinyl-2-trimethylsilylaniline* **4**. Under $CaCl_2$-tube, a solution of 5.5 ml (75 mmol) of $SOCl_2$ in 30 ml of CH_2Cl_2 was added dropwise over 0.5 h to a stirred solution of 23.12 g (75 mmol) of compound **3** in 100 ml of CH_2Cl_2. The reaction mixture was refluxed for 1 h, the solvent distilled off, and the residue redistilled under reduced pressure to afford compound **4** as a yellow oil, yield 15.81 g (72%); bp 60–62 °C (1 Torr). ^1H NMR ($CDCl_3$) δ: 8.53 (dd, 1H), 7.63 (dd, 1H), 7.47 (td, 1H), 7.41 (td, 1H), 0.40 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 147.3, 138.5, 134.4, 129.7, 129.4, 127.9, –0.9. ^{14}N NMR ($CDCl_3$) δ: 322. ^{29}Si NMR ($CDCl_3$) δ: –3.7 (m). Found (%): C, 51.12; H, 6.20; N, 6.51; S, 15.14. Calc. for $C_9H_{13}NOSSi$ (%): C, 51.14; H, 6.20; N, 6.63; S, 15.17.

1-(2-Trimethylsilylphenyl)-3-trimethylsilyl-1,3-diaza-2-thiaallene **5**. At –30 °C and under argon, a solution of 7.84 g (37.1 mmol) of compound **4** in 40 ml of hexane was added dropwise over 1 h to a stirred solution of 6.19 g (37.1 mmol) of $LiN(SiMe_3)_2$ in 80 ml of hexane. The reaction mixture was warmed to 20 °C and 5.2 ml (41 mmol) of Me_3SiCl in 10 ml of hexane was added over 15 min. The mixture was refluxed for 0.5 h and filtered, the solvent was distilled off, and the residue was redistilled under reduced pressure to afford compound **5** as an orange oil, yield 5.53 g (53%); bp 95–97 °C (0.4 Torr). ^1H NMR ($CDCl_3$) δ: 8.17 (br., 1H), 7.49 (dd, 1H), 7.33 (td, 1H), 7.16 (td, 1H), 0.33 (s, 9H), 0.26 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 150.3, 135.0, 134.5, 129.4, 126.1, 123.7, 1.0, –0.7. ^{14}N NMR ($CDCl_3$) δ: 305. ^{29}Si NMR ($CDCl_3$) δ: 2.9 (m), –4.5 (m). UV-VIS [λ/nm (log ε)]: 251 (4.00), 351 (4.20). MS (EI), *m*/*z*: 282.1035 $[C_9HN_5S_3]^+$ (calc. for $C_9HN_5S_3$, *m*/*z*: 282.1037). Found (%): C, 50.99; H, 7.74; S, 11.40; N, 9.93. Calc. for $C_{12}H_{22}N_2SSi_2$ (%): C, 51.01; H, 7.85; S, 11.35; N, 9.91.

3,1,2,4-Benzothiaselenadiazine **1**, *5-trimethylsilyl-3,1,2,4-benzothiaselenadiazine* **2** and *8-trimethylsilyl-3,1,2,4-benzothiaselenadiazine* **6**.

(*a*) At ambient temperature and under argon, solutions of 0.282 g (1 mmol) of compound **5** in 15 ml of CH_2Cl_2 and 0.221 g (1 mmol) of $SeCl_4$ dissolved in 1 ml of THF and diluted with 14 ml of CH_2Cl_2 were simultaneously added dropwise to stirred CH_2Cl_2 (60 ml) over 1 h. Then a solution of 0.262 g (1 mmol) of $SbPh_3$ or 0.186 g (1 mmol) of $FeCp_2$ in CH_2Cl_2 (10 ml) was added dropwise. After additional 1 h, the solvent was distilled off, and the residue was extracted with hexane (4 × 15 ml) under argon. The extract was evaporated and the residue was chromotographed on a Bio-Beads SX-3 column with toluene. The dark-blue zone was collected, evaporated, and the residue was recrystallized from hexane. In a case of $SbPh_3$, extraction and all manipulations before the chromatography were performed under argon to avoid air-moisture hydrolysis of compound **1** known to be catalyzed by triarylpnictogens.[7(*a*),10] Compound **1** was obtained as blue-black needles, yield 0.083 g (39%) (with $SbPh_3$) or 0.080 g (37%) (with $FeCp_2$). Intermediate **7** (see Scheme 1) was detected by ^1H NMR ($CDCl_3$) δ: 7.74 (1H), 7.66 (2 H), 7.50 (1H).

(*b*) Under argon, solutions of 0.282 g (1 mmol) of compound **5** in 15 ml of CH_2Cl_2 and 0.145 g (1 mmol) of $SeCl_2$[11] in 15 ml of THF were simultaneously added dropwise to a stirred CH_2Cl_2 (60 ml) over 1 h. The mixture was refluxed for 1 h, cooled to 20 °C, filtered and the solvent was distilled off under reduced pressure. The residue was worked-up in two ways. (1) Fractional sublimation at 40–50 °C (0.4 Torr) followed by recrystallization from pentane or hexane afforded compound **1** as blue-black needles, yield 0.019 g (9%) together with mixture of compounds **2** and **6** as dark-blue oil, yield 0.037 g (13%). (2) Extraction with hexane (4 × 15 ml) followed by evaporation and chromatography on a Bio-Beads SX-3 column with toluene gave two dark-blue zones. Concentrating the first zone afforded mixture of compounds **2** and **6** as dark-blue oil, yield 0.048 g (17%). Concentrating the second zone followed by recrystallization of the residue from hexane gave compound **1** as blue-black needles, yield 0.015 g (7%).

Compound **1**, mp 61–62 °C. ^1H NMR ($CDCl_3$) δ: 6.96 (td), 6.78 (td), 6.24 (dd), 6.21 (dd). ^{13}C NMR ($CDCl_3$) δ: 138.1, 133.25, 130.5, 126.7, 123.2, 109.4. ^{14}N NMR ($CDCl_3$) δ: 272, 254. ^{77}Se NMR ($CDCl_3$) δ: 772 (s). UV-VIS [λ/nm (log ε)]: 253 (3.68), 283 (4.11), 291 (4.15), 327 (3.20), 593 (2.58). MS (EI), *m*/*z*: 213.9261 $[M]^+$ (calc. for $C_6H_4N_2S^{78}Se$, *m*/*z*: 213.9263). Found (%): C, 33.52; H, 2.04; S, 14.78; N, 13.02; Se, 36.70. Calc. for $C_6H_4N_2SSe$ (%): C, 33.50; H, 1.87; S, 14.90; N, 13.02; Se, 36.70. Single crystals of **1** suitable for XRD were grown by slow evaporating its hexane solution.

Compound **2**. ^1H NMR ($CDCl_3$) δ: 6.92 (m, 2H), 6.21 (dd, 1H), 0.17 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 143.0, 136.0, 135.0, 132.7, 127.7, 109.0 ($^1J_{^{13}C-^{77}Se}$ 107.4 Hz), –0.91. ^{14}N NMR ($CDCl_3$) δ: 277, 255; ^{77}Se NMR ($CDCl_3$) δ: 767. MS (EI), *m*/*z*: 285.9657 $[M]^+$ (calc. for $C_9H_{12}N_2S^{78}SeSi$, *m*/*z*: 285.9658).

Compound **6**. ^1H NMR ($CDCl_3$) δ: 7.18 (dd, 1H), 6.8 (t, 1H), 6.28 (dd, 1H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 139.9, 139.8, 138.7, 129.4, 123.6, 116.7, –0.1. ^{77}Se NMR ($CDCl_3$) δ: 754. MS (EI), *m*/*z*: 285.9657 $[M]^+$ (calc. for $C_9H_{12}N_2S^{78}SeSi$, *m*/*z*: 285.9658).

5-Trimethylsilyl-1,3,2,4-benzodithiadiazine **9**. Under argon, solution of 0.282 g (1 mmol) of compound **5** and 0.103 g (1 mmol) of SCl_2, each in 15 ml of CH_2Cl_2, were added simultaneously by drops to refluxed and stirred CH_2Cl_2 (60 ml) over 1 h. After additional 1 h, the precipitate was filtered off, the filtrate was concentrated, and the residue was repeatedly sublimed *in vacuo* onto liquid nitrogen-cold finger. Compound **9** was obtained as green oil, yield 0.062 g (26%). ^1H NMR ($CDCl_3$) δ: 6.75 (m, 2H), 5.78 (dd, 1H), 0.12 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 143.9, 135.9, 135.0, 132.6, 125.2, 114.8, –1.0. ^{15}N NMR ($CDCl_3$) δ: 270.5 (s), 270.0 (s). ^{29}Si NMR ($CDCl_3$) δ: –3.9 (m). UV-VIS, [λ/nm (log ε)]: 213 (4.41), 247 (3.99), 292 (4.36), 301 (4.36), 365 (3.31), 379 (3.30), 626 (2.83). MS (EI), *m*/*z*: 240.0209 $[M]^+$ (calc. for $C_9H_{12}N_2S_2Si$, *m*/*z:* 240.0206). Found (%): C, 45.00; H, 5.08; S, 26.85; N, 11.40. Calc. for $C_9H_{12}N_2S_2Si$ (%): C, 44.98; H, 5.03; S, 26.67; N, 11.65.

6-Trimethylsilyl-1,2,4,3,5-trithiadiazepine **10**. At ambient temperature and under argon, solutions of 0.282 g (1 mmol) of compound **5** and 0.135 g (1 mmol) of S_2Cl_2, each in 15 ml of CH_2Cl_2, were added simultaneously by drops to stirred CH_2Cl_2 (60 ml) over 1 h. After additional 2 h, the solvent was distilled off and the residue was chromatographed twice on silica column with hexane. Concentrating the second orange zone gave compound **10** as red oil, yield 0.042 g (21%). ^1H NMR ($CDCl_3$) δ: 7.65 (dd, 1H), 7.52 (dd, 1H), 6.98 (t, 1H), 0.29 (s, 9H). ^{13}C NMR ($CDCl_3$) δ: 156.6, 146.2, 143.2, 135.7, 133.3, 123.4, –1.1. ^{14}N NMR ($CDCl_3$) δ: 317, 296. ^{29}Si NMR ($CDCl_3$) δ: –4.0 (m). UV-VIS [λ/nm (log ε)]: 216 (4.38), 272 (3.97), 327 (3.60), 463 (3.48). Found (%): C, 39.81; H, 4.44; N, 10.12; S, 35.59. Calc. for $C_9H_{12}N_2S_3Si$ (%): C, 39.67; H, 4.44; N, 10.28; S, 35.30.

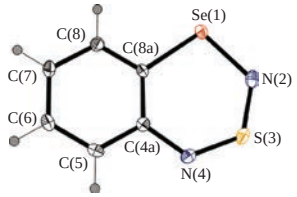


Figure 1 ORTEP plot of **1** (displacement ellipsoids at 30%, H atoms are shown as circles). The compound is planar within 0.049 Å, selected bond distances (Å) and angles (°): Se(1)–N(2) 1.848(2), N(2)–S(3) 1.543(3), S(3)–N(4) 1.537(2), N(4)–C(4a) 1.420(3), C(4a)–C(8a) 1.406(3), C(8a)–Se(1) 1.927(2); C(8a)–Se(1)–N(2) 102.2(1), Se(1)–N(2)–S(3) 121.6(1), N(2)–S(3)–N(4) 121.9(1), S(3)–N(4)–C(4a) 125.1(2), N(4)–C(4a)–C(8a) 125.1(2), C(4a)–C(8a)–Se(1) 124.2(2).

Previously, thermolysis and photolysis of 1,3,2,4-benzodithiadiazines and 1,2,4,3,5-benzotrithiadiazepines were successfully applied for generation of Herz radicals including derivatives inaccessible by other approaches.[2(a),(e),4(a),(d),(e)] Thermolysis of fluorinated 3,1,2,4-benzothiaselenadiazines produced corresponding 2,1,3-benzothiaselenazolyls together with minor 1,2,3-benzodithiazolyls.[7(a)] However, both mild thermolysis (80–100 °C) and ambient-temperature photolysis (at 313 nm) of **1** in squalane[§] gave only EPR-silent products. This was the first found limitation of generating Herz-type radicals from the heterocycles under discussion.[2(a),4(a)] The reasons are not entirely clear, one can think that expected 2,1,3-benzothiaselenazolyl is unstable under the reaction conditions or the thermolysis and photolysis of **1** proceed in another way. In contrast, thermolysis of a sample of **2** containing 22% of **6** gave a mixture of radicals **11**, **12**, and **14**

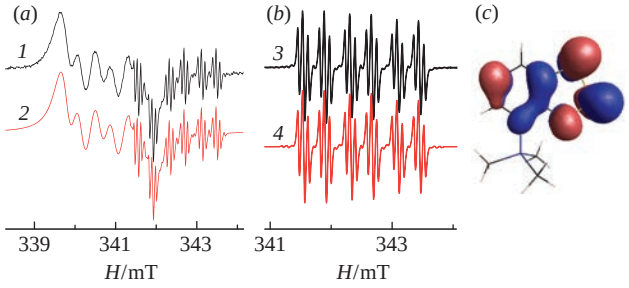
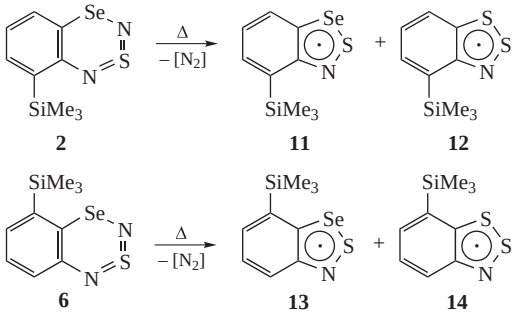
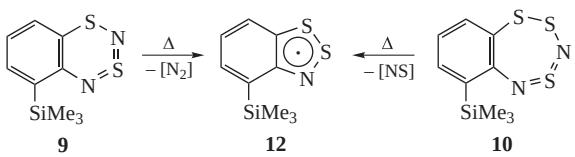


Figure 2 (*a*) (*1*) Experimental and (*2*) simulated EPR spectra from thermolysis of ~ 4 : 1 mixture of **2** and **6** in squalane. The simulated spectrum is superposition of spectra of three radicals: **11** [abundance 98.56%, including it masked minor **13** (see Online Supplementary Materials); *g*-value 2.0186], hfc constants (mT), experimental / UB3LYP/6-31G(dp)-calculated: a_N 0.830 / 0.876, a_{H^6} 0.377 / –0.474; **12** (abundance 1.19%, *g*-value 2.0061), hfc constants, experimental / UB3LYP/TZV//UB3LYP/6-31G(dp)-calculated: a_N 0.812 / 0.692, a_{H^5} 0.077 / 0.171, a_{H^6} 0.372 / –0.463, a_{H^7} 0.095 / 0.182; **14** (abundance 0.25%, *g*-value 2.0061), hfc constants, experimental / UB3LYP/TZV//UB3LYP/6-31G(dp)-calculated: a_N 0.818 / 0.706, a_{H^4} 0.304 / –0.427, a_{H^5} 0.072 / 0.180, a_{H^6} 0.379 / –0.465. (*b*) (*3*) Experimental and (*4*) simulated EPR spectra of radical **12**, experimental hfc constants: a_N 0.812, a_{Si} 0.536 (calc. –0.266, ^{29}Si natural abundance 4.67%), a_{H^5} 0.078, a_{H^6} 0.372, a_{H^7} 0.095; *g*-value 2.0077. (*c*) The SOMO of **12** from DFT calculations.



Scheme 2 Persistent radicals from thermolysis of ~4 : 1 mixture of **2** and **6**.

observed by EPR, most likely with minor **13** whose assignment was problematic in the presence of major **11** (Scheme 2, Figure 2; see Online Supplementary Materials).[§] Thermolysis of both **9** and **10** in squalane at 140 °C afforded radical **12** (Scheme 3, Figure 2; see Online Supplementary Materials).[§] Note that formation of **12** but not **14** independently confirms structures of **9** and **10**. The spectrum of **12** is slightly asymmetric due to known[4(d)] inequality of the line widths in its high- and low-field areas (see Online Supplementary Materials). Interestingly, the DFT-calculated SOMO of **12** is essentially antibonding (see Figure 2). It should be emphasized that **11**–**14** are the first examples of Herz-type radicals bearing Me_3Si substituents. The *g*-values of the studied species are typical of Herz radicals.[3,4,7(a)] For the Se containing ones, the line broadening is well-known to be caused by the anisotropy of their *g*-tensors.[4(b),(c)]



Scheme 3 Persistent radical **12** from thermolysis of **9** or **10**.

Overall, the archetypal 3,1,2,4-benzothiaselenadiazine **1** was synthesized using $SeCl_2$ or $SeCl_4$ as cyclizing agents and Me_3Si instead of H as the leaving group, and was structurally defined by XRD. At the same time, competition between Me_3Si and H substitution was observed for selenium and sulfur chlorides in the studied ring-closure reactions. The chalcogen-nitrogen hetero-

‡ *Crystal data for* **1**. $C_6H_4N_2SSe$, M = 215.13, orthorhombic, space group $P2_12_12_1$, a = 5.7187(2), b = 5.8342(2) and c = 20.3940(9) Å, V = 680.43(4) Å^3, Z = 4, T = 200(2) K, μ(MoK$_\alpha$) = 5.733 mm^{-1}, d_{calc} = 2.100 g cm^{-3}, 10926 reflections collected, 1571 unique (R_{int} = 0.034) which were used in all calculations. The final R_1 was 0.0198 [for 1506 reflections with $I > 2\sigma(I)$] and wR_2 was 0.0610 (all data). The XRD data were collected with a Bruker Kappa Apex II diffractometer, using MoK$_\alpha$ (λ = 0.71073 Å) radiation with a graphite monochromator. Absorption corrections were applied using the empirical multiscan method with the SADABS program. The structures were solved by direct methods using the SHELXS-97 program and refined by the least-squares method in the full-matrix anisotropic approximation using the SHELXL-97 program.[12] The H atom positions were located geometrically and refined using a riding model.

CCDC 1471317 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

§ Thermolysis was performed in a 10^{-3} M squalane solution of **1**, **9**, **10** or mixture of **2** and **6** placed in an EPR tube equipped with a Teflon valve and degassed by three freeze-pump-thaw cycles. The tube was heated at 140 °C for 1 h and cooled to room temperature at which EPR spectra were measured.

Photolysis was performed in a 10^{-2} M solution of **1** in squalane placed in an EPR quartz tube fitted with a Teflon valve and degassed as above. The tube was irradiated at 313±5 nm using an OSRAM XBO 150W/4 xenon short arc lamp equipped with a DMR-4 prism monochromator. After 0.5 h of irradiation paramagnetic products were not detected.

EPR spectra were acquired using a Bruker EMX spectrometer (MW power 2.07 mW, modulation frequency 100 kHz, and modulation amplitude 0.01 mT). The spectra integration and simulation were performed with the WIN-EPR and Winsim[13] programs. The accuracy of a calculation was ±0.001 mT. The *g*-values were measured using a DPPH standard with accuracy of ±0.0001.

DFT calculations with the UB3LYP functional and 6-31G(d,p) and TZV basis sets were performed with the GAMESS program,[14] and those with the PBE functional and L1 relativistic basis set (cc-pVDZ analog) with the PRIRODA program,[15] in all cases (except TZV) with full geometry optimization. For calculations with the PRIRODA program, facilities of the Informational and Computational Center, Novosibirsk State University, were used.

cycles synthesized were thermolyzed into new persistent Herz-type radicals.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.01.005.

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