Germanium(II) azides: synthesis and crystal structure of Tp′GeN$_3$ [Tp′ = hydrotris(3,5-dimethylpyrazol-1-yl)borato]

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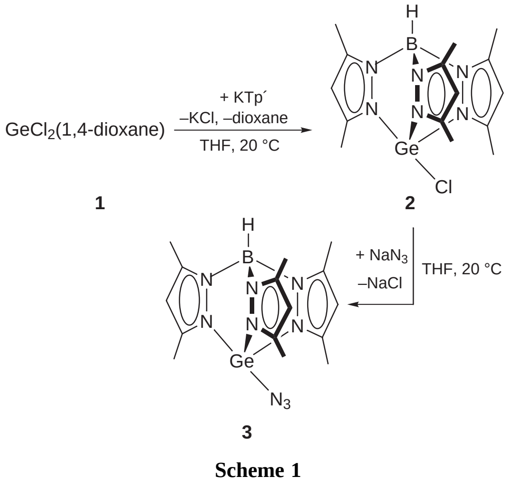
The synthesis of the germanium(II) azide Tp′GeN$_3$ (3) from Tp′GeCl (2) [Tp′ = HB(3,5-Me$_2$pz)$_3$] and NaN$_3$ is reported and the crystal structures of 2 and 3 are compared.

Silicon(IV) and tin(IV) azides have been reported to be versatile reagents in main-group element chemistry[1] and in organic synthesis.[2] In comparison, studies on germanium(IV) azides are still limited[3] and germanium(II) azides are to our knowledge not known, probably due to their propensity to decompose to germanium(IV) nitrides. This has prompted us to carry out the following work describing the synthesis and characterization of the germanium(II) azide Tp′GeN$_3$ (**3**). **3** was obtained from GeCl$_2$(1,4-dioxane) (**1**)[4] in two steps. In the first step **1** was converted with KTp′ to Tp′GeCl (**2**), which then was treated with NaN$_3$ to afford selectively **3** (Scheme 1).

Compounds **2** and **3** were isolated as white, slightly air sensitive solids, which are soluble in CH$_2$Cl$_2$, moderately soluble in THF and insoluble in pentane, and were fully characterized.† Thus, the IR spectra of **2** and **3** in KBr display the expected absorption bands for the Tp′ ligand. In addition, the azide group in **3** gives rise to two absorptions at 2043 cm^{-1} and 1272 cm^{-1}, which are assigned to the N$_3$ asymmetric and symmetric stretching vibrations, respectively. The ν_{asym}(N$_3$) absorption of **3** appears at lower frequency than that of the germanium(IV) azide Me$_3$GeN$_3$ [ν_{asym}(N$_3$) = 2103 cm^{-1}][3b] and higher than that of the azide anion [ν_{asym}(N$_3$) of [N(PPh$_3$)$_2$]N$_3$ in CH$_2$Cl$_2$ = 2005 cm^{-1}]. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **2** and **3** display resonances for three equivalent pyrazolyl rings and indicate, taking into consideration the crystal structures of **2** and **3**, that these compounds are fluxional at room temperature.† The activation barrier to the process which equilibrates the pyrazolyl rings is low, since the static structures of **2** and **3** were not observed in CD$_2$Cl$_2$ solution even at −83 °C (300 MHz spectrometer).

Compounds **2** and **3** were characterized by X-ray diffraction as shown in Figs. 1 and 2.‡ Single crystals of **2** and **3** were obtained upon diffusion of pentane into a CH$_2$Cl$_2$ solution of **2** at ambient temperature and diffusion of an Et$_2$O–pentane mixture into a THF solution of **3** at −30 °C respectively. Both compounds show a distorted pseudo trigonal bipyramidal coordination geometry around the germanium atom, which is similar to that of related tin(II) compounds.[5] The halogen atom (pseudohalogen) occupies one axial site and the tridentate Tp′ ligand spans the other axial and two equatorial sites. The stereochemically active lone pair at germanium presumably is oriented towards the remaining equatorial vertex. Consequently, the N$_{ax}$(pz)–Ge–Cl bond angle in **2** [163.15(9)°] and the N$_{ax}$(pz)–Ge–N$_{azide}$ bond angle in **3** [162.8(2)°] deviate from



Scheme 1

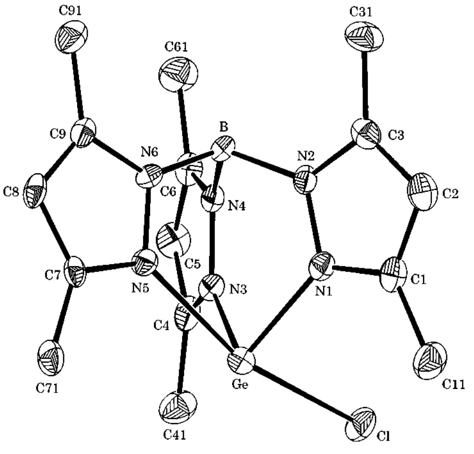


Fig. 1 ZORTEP plot of the molecular structure of **2** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge–N(1) 2.023(3), Ge–N(3) 2.013(4), Ge–N(5) 2.379(3), Ge–Cl 2.536(1), N(1)–Ge–N(3) 88.7(1), N(1)–Ge–N(5) 79.9(1), N(3)–Ge–N(5) 79.9(1), Cl–Ge–N(1) 88.4(1), Cl–Ge–N(3) 87.8(1), Cl–Ge–N(5) 163.15(9).

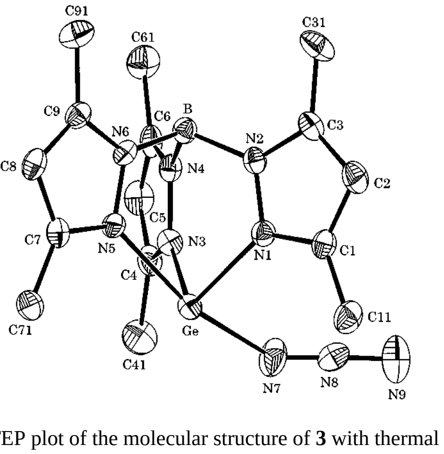


Fig. 2 ZORTEP plot of the molecular structure of **3** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge–N(1) 2.034(3), Ge–N(3) 2.013(3), Ge–N(5) 2.297(3), Ge–N(7) 2.262(4), N(7)–N(8) 1.136(5), N(8)–N(9) 1.179(6), N(1)–Ge–N(3) 88.5(1), N(1)–Ge–N(5) 81.9(1), N(3)–Ge–N(5) 80.2(1), N(1)–Ge–N(7) 89.4(1), N(3)–Ge–N(7) 84.8(1), N(5)–Ge–N(7) 162.8(2), Ge–N(7)–N(8) 136.8(3), N(7)–N(8)–N(9) 176.9(5).

180°, the N_{ax}(pz)–Ge–N_{eq}(pz) bond angles are smaller than 90°, and the Ge–N_{ax}(pz) bond [**2**: 2.379(3) Å; **3**: 2.297(3) Å] is considerably longer than the Ge–N_{eq}(pz) bonds [**2**: 2.013(4) and 2.023(3) Å; **3**: 2.013(3) and 2.034(3) Å].[5,6] Striking features of the structures of **2** and **3** are the bonding parameters of the Ge–X groups (X = Cl, N_3). Thus, the Ge–Cl bond of **2** [2.536(1) Å] is considerably longer than those of other germanium(II) chlorides [*e.g.* (C_5Me_5)GeCl: 2.3841(8) Å; $GeCl_2$(1,4-dioxane): 2.265 Å; $GeCl_2$ (g): 2.186(4) Å],[7] and the Ge–N_{azide} bond of **3** [2.262(4) Å] is considerably longer than that of H_3GeN_3 (g) [1.845(6) Å].[3e] Furthermore, the angle at the germanium-bonded nitrogen atom of the azide group is, at 136.8(3)°, larger than those found in covalent main-group element azides, the azide group is almost linear as shown by the angle N(7)–N(8)–N(9) of 176.9(5)°, and the N(7)–N(8) bond is, at 1.136(5) Å, shorter than the N(8)–N(9) bond [1.179(6) Å]. These bonds have lengths between those of a N–N double [1.24 Å] and a N–N triple bond [1.10 Å].[8] All these data let us suggest in valence bond terms a certain contribution of the ionic resonance form $[Tp'Ge]^+X^-$ to the Ge–X bond in **2** and **3**.

In conclusion, we have shown that germanium(II) azides can be stabilized using a combination of electronic and steric properties as found in the Tp′ ligand.[9] Preliminary studies show that this concept can be extended also to other ligands providing a valuable access to this interesting class of compounds.

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Notes and references

† *Synthesis of* **2**: KTp′ (500 mg, 1.49 mmol) and $GeCl_2$(1,4-dioxane) (344 mg, 1.49 mmol) were weighed into a Schlenk tube and suspended in THF (20 ml). The suspension was stirred for 2 h at room temperature and the solvent was removed *in vacuo*. The residue was treated with CH_2Cl_2 (20 ml) and the solution was filtered through KCl. The filtrate was evaporated to dryness and the residue was washed with pentane (3 × 20 ml) to afford **2** (593 mg, 98%) as a white, microcrystalline solid, 295 °C (decomp. TG–DTA). Anal. Found: C, 44.55; H, 5.59; Cl, 8.79; N, 20.76; $C_{15}H_{22}BClGeN_6$ (405.26) requires: C, 44.46; H, 5.47; Cl, 8.75; N, 20.74%. IR (KBr, cm^{-1}): 2552 [ν(BH)], 1540 [ν(CN)]. ^1H NMR (CD_2Cl_2, 300.1 MHz, 298 K): δ 2.39 (s, 9H, CH_3), 2.54 (s, 9H, CH_3), 5.87 (s, 3H, CH). ^1H NMR (CD_2Cl_2, 300.1 MHz, 190 K): δ 2.32 (s, 9H, CH_3), 2.49 (s, 9H, CH_3), 5.90 (s, 3H, CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 298 K): δ 12.2 (CCH_3), 12.5 (CCH_3), 106.7 (*C*H), 146.2 (*C*CH_3), 150.4 (*C*CH_3). EI-MS (70 eV): *m*/*z* (rel. intensity), 406 (1) $[M]^+$, 405 (2) $[M - H]^+$, 371 (100) $[M - Cl]^+$, 311 (23) $[M - 3,5\text{-}Me_2pz]^+$, 275 (9) $[M - Cl - 3,5\text{-}Me_2pzH]^+$, 169 (35) $[M - Cl - HB(3,5\text{-}Me_2pz)_2]^+$, 128 (14) $[M - Cl - HB(3,5\text{-}Me_2pz)_2 - CH_3CN]^+$.
Synthesis of **3:** A Schlenk tube was charged with **2** (330 mg, 0.81 mmol) and NaN_3 (98 mg, 1.51 mmol) and the mixture was suspended in THF (30 ml). The suspension was stirred for 8 h at room temperature and the solvent was removed *in vacuo*. The residue was treated with CH_2Cl_2 (20 ml) and the solution was filtered. The filtrate was concentrated *in vacuo* to approximately 1 ml and Et_2O (10 ml) was added. The resulting precipitate was washed with Et_2O (10 ml) and dried *in vacuo* to afford **3** (243 mg, 72%) as a white solid, 216 °C (decomp. TG–DTA). Anal. Found: C, 42.87; H, 5.18; N, 31.01; $C_{15}H_{22}BGeN_9$ (411.80) requires: C, 43.75; H, 5.38; N, 30.61%. IR (KBr, cm^{-1}): 2544 [ν(BH)], 2043 [$\nu_{asym}(N_3)$], 1541 [ν(CN)], 1272 [$\nu_{sym}(N_3)$]. ^1H NMR (CD_2Cl_2, 300.1 MHz, 298 K): δ 2.40 (s, 9H, CH_3), 2.46 (s, 9H, CH_3), 5.88 (s, 3H, CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 298 K): δ 12.3 (CCH_3), 12.9 (CCH_3), 106.5 (*C*H), 145.6 (*C*CH_3), 149.7 (*C*CH_3). EI-MS (70 eV): *m*/*z* (rel. intensity), 371 (100) $[M - N_3]^+$, 275 (24) $[M - N_3 - 3,5\text{-}Me_2pzH]^+$, 169 (33) $[M - N_3 - HB(3,5\text{-}Me_2pz)_2]^+$, 128 (24) $[M - N_3 - HB(3,5\text{-}Me_2pz)_2 - CH_3CN]^+$.

‡ *Crystal data*: for **2**: $C_{15}H_{22}BClGeN_6$, M = 405.26, triclinic, space group $P1$ (no. 2), a = 7.9795(14), b = 8.683(2), c = 13.350(2) Å, α = 100.860(16), β = 90.781(12), γ = 99.118(16)°, U = 896.0(3) $Å^3$, Z = 2, D_c = 1.502 g cm^{-3}, μ(Mo-Kα) = 1.803 mm^{-1}, $F(000)$ = 416, λ = 71.073 pm, T = 180 K. A colourless column of dimensions 0.57 × 0.11 × 0.08 mm was used. STOE-STADI4 four circle diffractometer, ω–2θ scan, $3° < 2\theta < 50°$, 4158 total reflections, 3113 unique. Refinement of the 221 parameters by full-matrix least-squares resulted in R_1 = 0.0448, wR_2 = 0.1128 for $I > 2\sigma(I)$, GOF = 1.034. For **3**: $C_{15}H_{22}BGeN_9$, M = 411.80, monoclinic, space group $P2_1/n$ (no. 14), a = 8.913(3), b = 8.0587(18), c = 25.908(8) Å, β = 96.56(4)°, U = 1848.8(9) $Å^3$, Z = 4, D_c = 1.480 g cm^{-3}, μ(Mo-Kα) = 1.614 mm^{-1}, $F(000)$ = 848, λ = 71.073 pm, T = 170 K. A colourless prism of dimensions 0.38 × 0.30 × 0.15 mm was used. STOE-IPDS area detector, ϕ-rotation mode $4.7° < 2\theta < 52.1°$, 12579 total reflections, 3508 unique. Refinement of the 235 parameters by full-matrix least-squares resulted in R_1 = 0.0496, wR_2 = 0.1204 for $I > 2\sigma(I)$, GOF = 1.014. Both structures were solved using the Patterson Method (SHELXS-86) and refined anisotropically *versus* F^2 (SHELXL-97). Hydrogen atoms were placed on calculated positions and refined using a riding model. CCDC 182/1027.

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