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Synthesis and Structural Characterization of Two New Main Group Element Carboranylamidates

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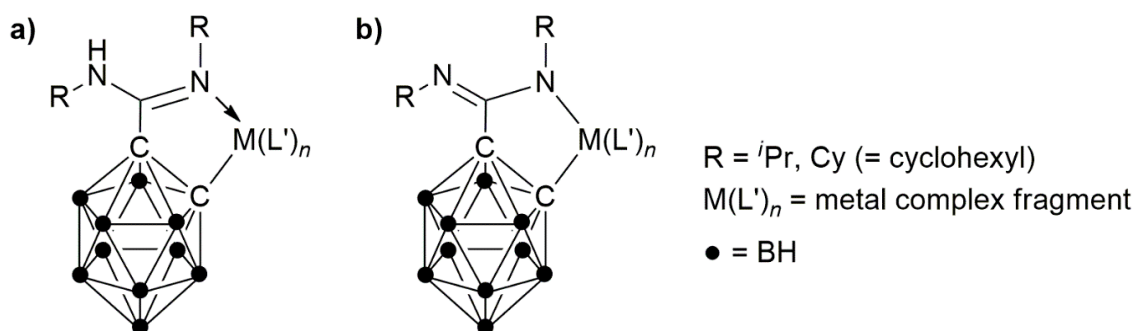
Abstract: Two new main group element carboranylamidates were synthesized using a bottom-up approach starting from *ortho*-carborane, *ortho*-C₂B₁₀H₁₂ (**1**, = 1,2-dicarba-*closo*-dodecaborane). The first divalent germanium carboranylamidate, GeCl[HL^{Cy}] (**3**, [HL^{Cy}][−] = [*o*-C₂B₁₀H₁₀C(NCy)(NHCy)][−], Cy = cyclohexyl), was synthesized by treatment of GeCl₂(dioxane) with 1 equiv. of in situ-prepared Li[HL^{Cy}] (**2a**) in THF and isolated in 47% yield. In a similar manner, the first antimony(III) carboranylamidate, SbCl₂[HL^{*i*Pr}] (**4**, [HL^{*i*Pr}][−] = [*o*-C₂B₁₀H₁₀C(N^{*i*Pr})(NH^{*i*Pr})][−]), was obtained from a reaction of SbCl₃ with 1 equiv. of Li[HL^{*i*Pr}] in THF (56% yield). The title compounds were fully characterized by analytical and spectroscopic methods as well as single-crystal X-ray diffraction. Both compounds **3** and **4** are monomeric species in the solid state, and the molecular geometries are governed by a stereo-active lone pair at the metal centers.

Keywords: boron; carborane; carboranylamidate; germanium; antimony; crystal structure

1. Introduction

Dodecahedral carborane cage compounds of the composition C₂B₁₀H₁₂ [1] are of tremendous scientific and technological interest due to a variety of practical applications, including the synthesis of polymers and ceramics [2], catalysts [3–5], radiopharmaceuticals [6], and non-linear optical materials [7]. The novel chelating ligand type of *ortho*-carboranylamidates was first synthesized in our laboratory in 2010 by *in-situ* metalation of *ortho*-carborane, *ortho*-C₂B₁₀H₁₂ (**1**, = 1,2-dicarba-*closo*-dodecaborane) with *n*-butyllithium, followed by treatment with 1 equiv. of a 1,3-diorganocarbodiimide [8]. They combine the carborane cage with the versatile chelating amidinate anions, [RC(NR')₂][−] [9–12] in one ligand system. In the resulting lithium *ortho*-carboranylamidates Li[(*o*-C₂B₁₀H₁₀)C(NR)(NHR)] (= Li[HL]; **2a**: R = ^{*i*}Pr, **2b**: R = Cy (cyclohexyl)), a proton is formally shifted from a carboranyl carbon atom to the amidinate unit, resulting in an amidine moiety acting as a monodentate *N*-donor functionality (Scheme 1a). The lithium derivatives were further treated with various metal and non-metal chloride precursors to yield carboranylamidates of e.g., Sn(II) and Cr(II) [8], Rh(I) and Ir(I) [13–16], Fe(II) and Fe(III) [17,18], Mo(II), Mn(II), Co(II), Ni(II), Cu(II) [18,19], Ti(IV), Zr(IV), Si(IV), Ge(IV), Sn(IV), Pb(IV), and P [20–22]. In the case of reactions with Cp₂TiCl₂, Cp₂ZrCl₂, PhPCl₂, and various dichlorosilanes R₂SiCl₂, formal dehydrochlorination led to complexes with dianionic [(*o*-C₂B₁₀H₁₀)C(NR)₂]^{2−} (= [L]^{2−}) ligands having a deprotonated amidine group [20,22]. In a recent study, we have shown that the formation of this product class is preferred for highly Lewis-acidic centers, while “soft” metal centers form stable complexes with the original [(*o*-C₂B₁₀H₁₀)C(NR)(NHR)][−] (= [HL][−]) ligand [22]. In all cases (i.e., for both [HL][−] and [L]^{2−}-type ligands, and independent from the choice of the central atom), the ligand adopts a characteristic $\kappa C, \kappa N$ -chelating coordination mode instead of the “normal” $\kappa N, \kappa N'$ -chelating mode of

coordinated amidinate anions [23,24]. In this contribution, we report the synthesis and full characterization of the first germanium(II) carboranylamidinate as well as the first antimony compound of this type.



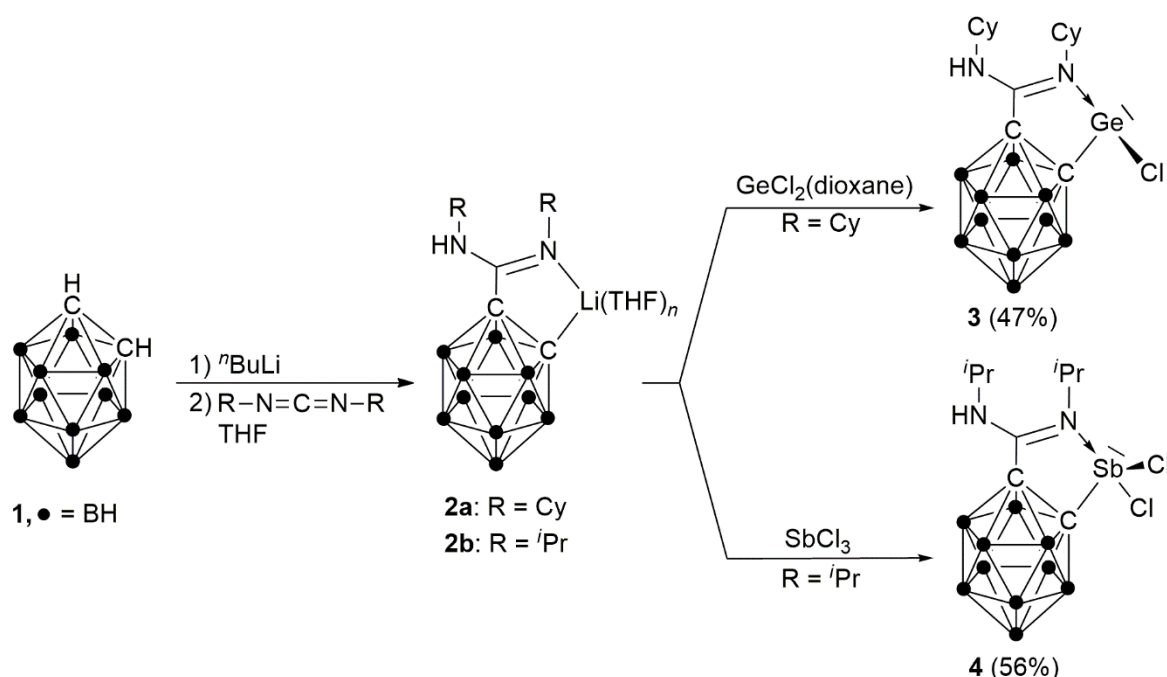
Scheme 1. General schematic representation of carboranylamidinate complexes showing the characteristic $\kappa C, \kappa N$ -chelating coordination mode [23,24], (a) with a monoanionic $[(o-C_2B_{10}H_{10})C(NR)(NHR)]^- (= [HL]^-)$ ligand, and (b) with a dianionic $[(o-C_2B_{10}H_{10})C(NR)_2]^{2-} (= [L]^{2-})$ ligand.

2. Results and Discussion

2.1. Synthesis and Characterization of $GeCl[HL^{Cy}]$ (3) and $SbCl_2[HL^{iPr}]$ (4)

The synthetic protocol leading to the title compounds is outlined in Scheme 2. In the first step, the lithium carboranylamidinates **2a** and **2b** were prepared in a one-pot reaction from *o*-carborane (1) and the corresponding carbodiimide. Subsequent reaction of **2a** with 1 equiv. of the readily accessible germanium(II) precursor $GeCl_2(\text{dioxane})$ [25] led to formation of $GeCl[HL^{Cy}]$ (**3**) as the first carbonylamidinate of divalent germanium. Compound **3** was isolated in 47% yield as colorless, block-like crystals after recrystallization from toluene. In a similar manner, the first antimony(III) carboranylamidinate, $SbCl_2[HL^{iPr}]$ (**4**) was prepared from $SbCl_3$ and 1 equiv. of $Li[HL^{iPr}]$ (**2b**) in THF. After crystallization from toluene, compound **4** could be isolated in 56% yield as colorless, needle-like crystals which, like **3**, are significantly moisture-sensitive. In both cases, the complex having a $[HL]^-$ -type ligand is the only identified product, and no evidence for the formation of products with $[L]^{2-}$ ligands has been observed. Consequently, the divalent germanium precursor turned out to react with $Li[HL]$ in a similar manner as $GeCl_4$ [22], while the reaction of $SbCl_3$ took a different course than that of $PhPCl_2$ [20].

Both title compounds **3** and **4** were fully characterized through the usual set of elemental analyses and spectroscopic methods. The 1H - and ^{13}C -NMR data of **3** were in good agreement with the expected composition. In the 1H -NMR spectrum, a singlet at δ 8.06 ppm could be assigned to the uncoordinated NH functionality of the amidine unit. High molecular mass peaks in the mass spectrum of **3** were detected at m/z 457 (87% rel. int.) $[M - H]^+$ and 422 (13% rel. int.) $[M - Cl]^+$. The absence of peaks at higher molecular masses confirmed the monomeric nature of **3**. In the IR spectrum of **3**, typical bands of the amidine moiety were observed at 3403 cm^{-1} (ν_{N-H}), 1577 cm^{-1} ($\nu_{C=N}$), and 1260 cm^{-1} (ν_{C-N}). A medium strong band at 2584 cm^{-1} can be assigned to the carborane cage (ν_{B-H}) [22]. The antimony derivative **4** was fully characterized in the same manner. The 1H -NMR spectrum of **4** displayed a characteristic signal pattern of the two chemically inequivalent isopropyl groups (two doublets and two septets). In this case, the NH resonance could not be observed. However, the presence of a $[HL^{iPr}]^-$ ligand in **4** was confirmed by a sharp ν_{N-H} band at 3396 cm^{-1} in the IR spectrum. Additional characteristic bands of the amidine group were observed at 1605 cm^{-1} ($\nu_{C=N}$) and 1251 cm^{-1} (ν_{C-N}), and the carborane backbone gave rise to a series of strong bands around 2590 cm^{-1} (ν_{B-H}) [22]. In the mass spectrum of **4**, the highest molecular mass peak at m/z 426 (60% rel. int.) could be assigned to the ion $[M - Cl]^+$.



Scheme 2. Synthetic route to the title compounds **3** and **4**.

2.2. Crystal and Molecular Structures

Both title compounds **3** and **4** crystallize from toluene in solvent-free form with one monomeric molecule in the asymmetric unit. Crystal structure determinations confirmed the presence of one monoanionic carboranylamidinate ligand attached to the metal center in a typical $\kappa C, \kappa N$ -chelating mode. The protonated NHR residue (**3**: R = Cy; **4**: R = *i*Pr) is directed away from the metal center and does not contribute to coordinative saturation thereof. Both **3** and **4** exist as the *antitrotamer* in the crystal (relating to the orientation of the NHR group relative to the carboranyl group). In both compounds, the C–N bond to the metal-attached nitrogen (N1) is shorter than the C–N bond to the protonated nitrogen (N2), which is in agreement with the presence of a formal double bond between C1 and N1. The observed C–N distances resemble those observed in previously described complexes with [HL][−] ligands [21,22].

In the germanium(II) derivative **3**, the stereo-active lone pair leads to a trigonal-pyramidal coordination environment of the Ge center (Figure 1). At 204.0(5) and 229.4(2) pm, respectively, the Ge–C and Ge–Cl bond lengths are expectedly longer than in the previously reported germanium(IV) derivative GeCl₃[HL^{*i*Pr}] (Ge–C 195.6(2) pm, Ge–Cl 226.4(1) pm) [22]. However, the Ge–N distances are very similar in both compounds (**3**: 205.3(5) pm, GeCl₃[HL^{*i*Pr}]: 204.8(2) pm). Rather untypical for carboranylamidinates, the molecules in **3** are assembled through weak N–H···Cl hydrogen bonds to infinite supramolecular chains (Figure 2). In the previously reported complexes with [HL][−]-type ligands, no hydrogen bonding with participation of the amidine NH moiety has been observed [21,22].

In the antimony(III) derivative **4**, the central Sb atom displays a pseudo-trigonal-bipyramidal coordination by the $\kappa C, \kappa N$ -chelating [HL^{*i*Pr}][−] ligand, two chlorido ligands, and a stereo-active lone pair (Figure 3). The axial positions are occupied by the nitrogen donor (N1) and one of the chlorine atoms (Cl2), with the N1–Sb1–Cl2 angle being 163.63(5)°. This assignment is in agreement with the Sb1–Cl2 bond lengths of 249.7(1) pm, which is considerably longer than the equatorial Sb1–Cl1 bond (234.8(1) pm). The Sb1–C3 bond is 218.6(2) pm and therefore slightly longer than the mean value for tetra-coordinated Sb(III) compounds in the Cambridge Structural Database (214 pm for 664 entries with $R_1 \leq 0.075$) [26]. The same is true for the Sb1–N1 bond, which is 237.0(2) pm (mean value for 167 CSD entries with $R_1 \leq 0.075$: 230 pm) [26]. The molecular structure of **4** is closely related to those of the previously reported ECl₃[HL] compounds (E = Ge, Sn) [22], with one of the equatorial chlorido

ligands being formally replaced by a lone pair. Different from **3**, the amidine NH moiety in **4** is not involved in hydrogen bonding.

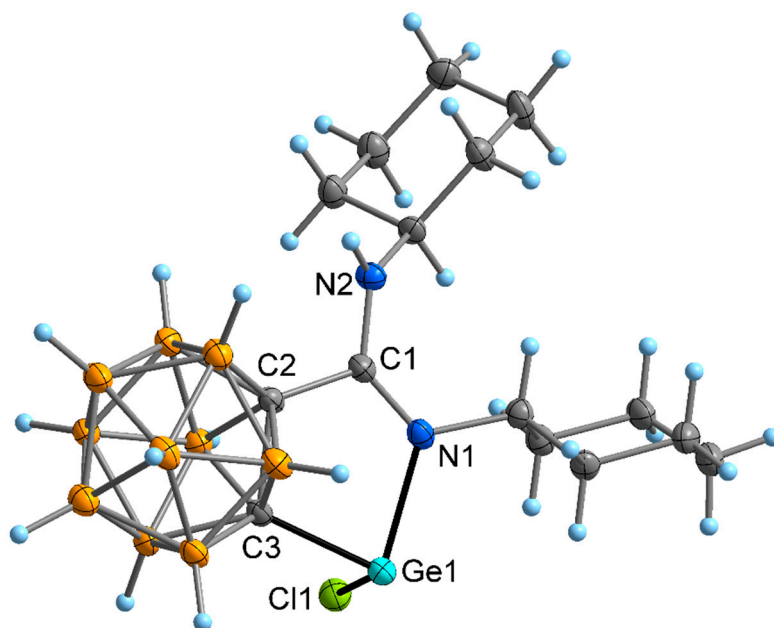


Figure 1. Molecular structure of **3** in the crystal. Displacement ellipsoids of the heavier atoms are drawn with 50% probability. Selected bond lengths (pm) and angles (deg.): Ge1–C3 204.1(5), Ge1–N1 205.3(4), Ge1–Cl1 229.4(2), C3–Ge1–N1 82.5(2), C3–Ge1–Cl1 95.1(2), N1–Ge1–Cl1 97.3(1), C1–N1 130.3(7), C1–N2 133.2(7), C1–C2 150.8(7), N1–C1–N2 128.8(5).

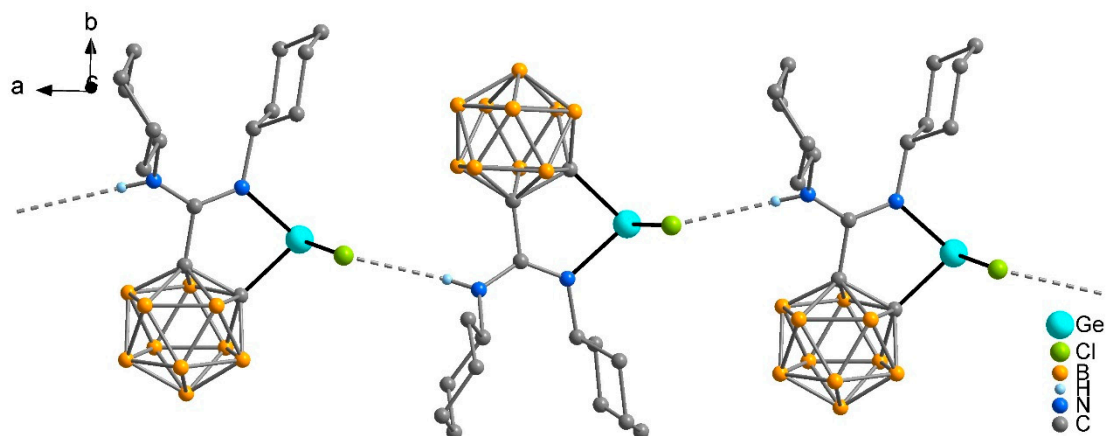


Figure 2. Hydrogen-bonded chain structure of **3** in the crystalline state. Hydrogen atoms attached to B and C atoms omitted for clarity. N2···Cl1 488.7(5) pm, Cl1···H approximately 268 pm.

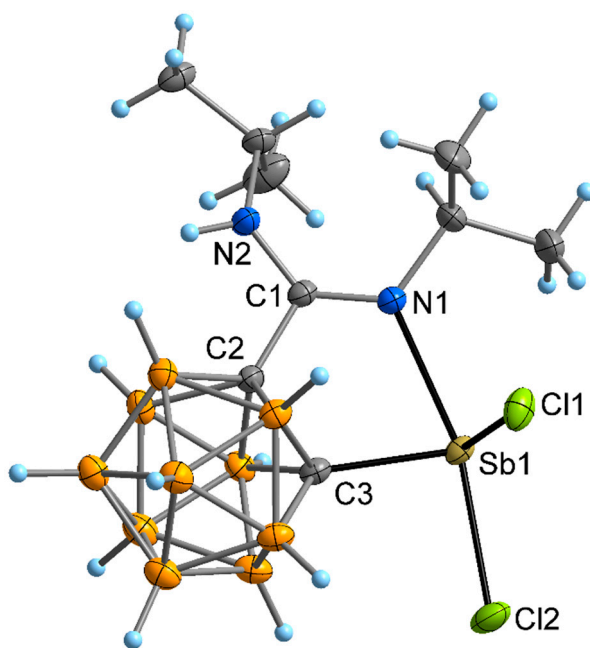


Figure 3. Molecular structure of **4** in the crystal. Displacement ellipsoids of the heavier atoms are drawn with 50% probability. Selected bond lengths (pm) and angles (deg.): Sb1–C3 218.7(3), Sb1–N1 237.0(2), Sb1–Cl1 234.8(1), Sb1–Cl2 249.7(1), C3–Sb1–N1 75.44(8), C3–Sb1–Cl1 97.25(7), C3–Sb1–Cl2 88.75(7), N1–Sb1–Cl1 88.11(5), N1–Sb1–Cl2 163.63(5), Cl1–Sb1–Cl2 89.74(3), C1–N1 128.9(3), C1–N2 134.1(3), C1–C2 151.3(3), N1–C1–N2 130.8(2).

3. Experimental Section

3.1. General Procedures and Instrumentation

All reactions were carried out in oven-dried or flame-dried glassware under an inert atmosphere of dry argon employing standard Schlenk and glovebox techniques. The solvent THF was distilled from sodium/benzophenone under nitrogen atmosphere prior to use. $\text{GeCl}_2(\text{dioxane})$ was prepared according to a published procedure [25]. All other starting materials were purchased from commercial sources and used without further purification. ^1H -NMR (400 MHz) and ^{13}C -NMR (100.6 MHz) spectra were recorded in $\text{THF-}d_8$ solution on a Bruker DPX 400 spectrometer (Bruker BioSpin, Rheinstetten, Germany). IR spectra were measured with a Bruker Vertex 70V spectrometer (Bruker Optics, Rheinstetten, Germany) equipped with a diamond ATR unit between 4000 cm^{-1} and 50 cm^{-1} . Microanalyses (C, H, N) were performed using a VARIO EL cube apparatus (Elementar Analysensysteme, Langenselbold, Germany).

3.2. Synthesis of Compound 3

A solution of $\text{Li}[\text{HL}^{\text{Cy}}]$ was prepared as described previously [8] by treatment of **1** (0.95 g, 6.56 mmol) in THF (50 mL) with a 2.5 M solution of $n\text{BuLi}$ in hexanes (2.7 mL, 6.56 mmol) followed by addition of 1,3-dicyclohexylcarbodiimide (1.35 g, 6.56 mmol). After stirring for 2 h at r.t., $\text{GeCl}_2(\text{dioxane})$ (1.52 g, 6.56 mmol) was added as a solid and stirring was continued for 24 h. The reaction mixture was evaporated to dryness, and the solid residue was extracted with toluene ($2 \times 20\text{ mL}$). The combined extracts were filtered and the clear, yellow filtrate was concentrated to a total volume of ca. 10 mL. Crystallization at r.t. for a few days afforded **3** (1.39 g, 47%) as colorless, block-like, moisture-sensitive crystals. M.p. $177\text{ }^\circ\text{C}$ (dec. ca. $220\text{ }^\circ\text{C}$). Elemental analysis calculated for $\text{C}_{15}\text{H}_{33}\text{B}_{10}\text{ClGeN}_2$ ($457.59\text{ g}\cdot\text{mol}^{-1}$): C, 39.37; H, 7.27; N, 6.12; found C, 38.88; H, 7.20; N, 5.99. ^1H NMR (400.1 MHz, $\text{THF-}d_8$, $23\text{ }^\circ\text{C}$): δ 8.06 (s, NH), 3.30–3.22 (m, CH), 3.15–3.03 (m, CH), 1.85–0.67 (m, Cy/BH) ppm. ^{13}C NMR (100.6 MHz, $\text{THF-}d_8$, $23\text{ }^\circ\text{C}$): δ 157.5 (CN(NH)), 56.0 (CH), 53.8 (CH), 34.3 (Cy),

26.2 (Cy) ppm. IR (ATR): ν 3403 w ($\nu_{\text{N-H}}$), 3305 w, 3066 w, 2929 m, 2854 m ($\nu_{\text{B-H}}$), 2634 w, 2582 s, 2113 w, 1661 w, 1577 s ($\nu_{\text{C=N}}$), 1531 s, 1464 w, 1449 m, 1366 w, 1348 w, 1332 m, 1300 w, 1260 w ($\nu_{\text{C-N}}$), 1243 w, 1229 w, 1192 w, 1146 w, 1078 m, 1059 m, 1042 m, 1022 m, 973 w, 940 w, 921 w, 907 w, 890 m, 868 w, 843 m, 820 m, 799 w, 790 w, 767 w, 729 m, 718 m, 693 m, 656 m, 593 w, 558 w, 541 w, 507 w, 480 w, 446 w, 410 w, 380 w, 361 w, 300 s, 266 s, 227 m, 197 m, 176 m, 158 m, 121 m, 113 m, 98 m, 75 m, 66 m cm^{-1} . MS (EI): m/z (%) 457 (87) $[\text{M} - \text{H}]^+$, 422 (13) $[\text{M} - \text{Cl}]^+$, 367 (47) $[\text{M} - \text{Cy} + \text{H}]^+$, 351 (14) $[\text{M} - \text{GeCl}]^+$, 339 (17) $[\text{M} - \text{Cy} - \text{Cl}]^+$, 295 (60) $[\text{M} - 2\text{Cy}]^+$, 269 (69) $[\text{M} - \text{GeCl} - \text{Cy}]^+$, 255 (100) $[\text{C}_4\text{H}_7]^+$, 83 (83) $[\text{Cy}]^+$, 187 (60) $[\text{M} - \text{GeCl} - 2\text{Cy} + 2\text{H}]^+$, 98 (26) $[\text{NCy} + \text{H}]^+$, 58 (16) $[\text{M} - \text{Cl} - 2\text{Cy} + \text{H}]^+$.

3.3. Synthesis of Compound 4

In a similar manner as for **3**, a solution of $\text{Li}[\text{HL}^i\text{Pr}]$ was prepared from **1** (0.95 g, 6.56 mmol) in THF (50 mL), a 2.5 M solution of $n\text{BuLi}$ in hexanes (2.7 mL, 6.56 mmol) and 1,3-diisopropylcarbodiimide (0.83 g, 1 mL, 6.56 mmol) [8]. The addition of solid SbCl_3 (1.50 g, 6.56 mmol) produced a yellow solution and precipitation of a small amount of black solid (presumably Sb). Work-up as described for **3** afforded compound **4** as colorless, needle-like, moisture-sensitive crystals in 56% isolated yield (1.70 g). M.p. 141 °C. Elemental analysis calculated for $\text{C}_9\text{H}_{25}\text{B}_{10}\text{Cl}_2\text{N}_2\text{Sb}$ (462.07 $\text{g}\cdot\text{mol}^{-1}$): C, 23.39; H, 5.45; N, 6.06; found C, 23.50; H, 5.47; N, 6.10. ^1H NMR (400.1 MHz, $\text{THF-}d_8$, 23 °C): δ 3.26 (sept, 2 H, CH, $J = 6.4$ Hz), 3.15 (sept, 2 H, CH, $J = 6.4$ Hz), 1.48–1.16 (br m, BH), 0.86 (d, 6 H, CH_3 , $J = 6.4$ Hz), 0.55 (d, 6 H, CH_3 , $J = 6.4$ Hz) ppm. ^{13}C NMR (100.6 MHz, $\text{THF-}d_8$, 23 °C): δ 153.2 (CN(NH)), 50.3 (CH), 47.8 (CH), 23.1 (CH_3), 23.0 (CH_3) ppm. IR (ATR): ν 3396 w ($\nu_{\text{N-H}}$), 3375 w, 2970 w, 2930 w, 2873 w, 2599 m, 2590 m ($\nu_{\text{B-H}}$), 2568 w, 2113 w, 1999 w, 1738 w, 1605 m ($\nu_{\text{C=N}}$), 1530 m, 1459 w, 1390 w, 1370 w, 1333 w, 1289 w, 1251 w ($\nu_{\text{C-N}}$), 1159 w, 1122 m, 1067 m, 1038 w, 969 w, 947 w, 930 w, 899 w, 872 w, 856 w, 838 w, 815 w, 760 w, 735 w, 681 w, 665 w, 634 w, 621 w, 597 w, 575 w, 555 w, 539 w, 517 w, 480 w, 455 w, 412 w, 380 w, 341 m, 303 w, 249 s, 213 m, 193 s, 160 s, 141 s, 113 s, 78 s cm^{-1} . MS (EI): m/z (%) 426 (60) $[\text{M} - \text{Cl}]^+$, 368 (31) $[\text{M} - \text{Cl} - i\text{Pr} - \text{CH}_3]^+$, 326 (24) $[\text{Sb}(\text{C}_2\text{H}_{10}\text{B}_{10})\text{CNH} + \text{H}]^+$, 270 (10) $[\text{M} - \text{SbCl}_2]^+$, 256 (20) $[\text{M} - \text{SbCl}_2 - \text{CH}_3 + \text{H}]^+$, 227 (97) $[\text{M} - \text{SbCl}_2 - i\text{Pr}]^+$, 213 (18) $[\text{M} - \text{SbCl}_2 - i\text{Pr} - \text{CH}_3 + \text{H}]^+$, 192 (54) $[\text{SbCl}_2]^+$, 170 (25) $[(\text{C}_2\text{H}_{10}\text{B}_{10})\text{CNH} + \text{H}]^+$, 120 (9) $[\text{Sb}]^+$, 462 (3) $[\text{M}]^+$, 69 (35) $[\text{CN}^i\text{Pr}]^+$, 58 (100) $[\text{HN}^i\text{Pr}]^+$.

3.4. X-ray Crystallography

Single crystal X-ray intensity data of **3** and **4** were collected on a STOE IPDS 2T diffractometer [27] equipped with a 34 cm image plate detector, using graphite-monochromated Mo $\text{K}\alpha$ radiation, at $T = 100(2)$ K. The structure was solved by dual-space methods (*SHELXT*-2014/5) [28] and refined by full matrix least-squares methods on F^2 using *SHELXL*-2017/1 [29]. Crystallographic data for the compounds (see Supplementary Materials) have been deposited at the CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers 1899321 (**3**) and 1899321 (**4**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

4. Conclusions

To summarize the results reported here, two new carboranylamidates of main group elements in low oxidation states were prepared and structurally characterized. Compound **3** represents the first carboranylamidate species containing divalent germanium, while **4** is the first antimony carboranylamidate. Both compounds were formed in a straightforward manner from the corresponding $\text{Li}[\text{HL}]$ derivative, and no products containing dianionic $[\text{L}]^{2-}$ ligands were obtained. This finding meets the expectation in view of the previously discussed influence of the “hardness” of the central atom on the resulting product [22], as Ge(II) and Sb(II) are rather soft. In both products, the molecular geometries are governed by a stereo-active lone pair at the metal centers. Due to their chloro functions, both compounds should be promising starting materials for further derivative chemistry.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2304-6740/7/3/41/s1>: Cif and Checkcif files for 3 and 4.

Author Contributions: N.H. and F.Z. performed the experimental work. P.L. and F.E. carried out the crystal structure determinations. L.H. measured the IR and NMR spectra, and S.B. measured the mass spectra and carried out the elemental analyses. F.T.E. conceived and supervised the experiments. F.T.E. and P.L. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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