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Synthesis and Structure of Base-Stabilized Germanium(II) Diazide $IPrGe(N_3)_2$

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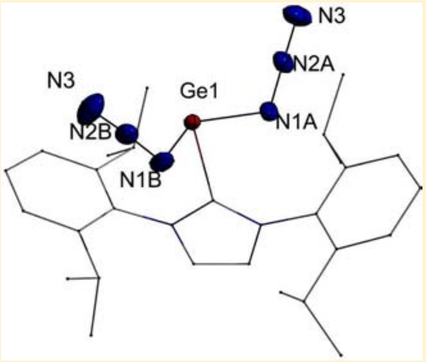
Supporting Information

ABSTRACT: Coordination of a strong σ-base has been shown to be an effective method for the stabilization of low valent main group element complexes. This general method was now used for the synthesis of the divalent germanium diazide. $IPrGe(N_3)_2$ **1** represents the first neutral homoleptic germanium diazide that could be structurally characterized.



INTRODUCTION

The synthesis of neutral p-block element azides is experimentally challenging because of their expressed heat- and shock-sensitivity.[1] Even though some of these complexes have been known for many years,[2] their solid state structures remained almost completely unknown. Aside from TlN_3 and $Pb(N_3)_2$,[3,4] only two group 15-triazides ($As(N_3)_3$,[5] $Sb(N_3)_3$[5,6]) as well as three halogen azides (ClN_3,[7] BrN_3,[8] IN_3[7,9]) have been structurally characterized within the past few years, often by use of a specific in situ crystallization technique. In addition, the solid state structures of several anionic and cationic binary azides[10] as well as of a few base-stabilized neutral azides such as $L^{1/2}Si(N_3)_4$, $L^{1/2}Ge(N_3)_4$ (L^1 = bipy, L^2 = phen) or $(py)_2Bi(N_3)_3$ have been determined by single crystal X-ray diffraction.[6,10b,c,11] Both the ionic complexes and the base-stabilized compounds are less sensitive toward heat and shock than the corresponding neutral base-free complexes.

Binary neutral group 14 azides have only been scarcely reported. Two homoleptic tetraazides $E(N_3)_4$ (E = C,[12] Si[11a,13]), have been clearly synthesized, whereas $Ge(N_3)_4$[14] still awaits its final confirmation, and $Sn(N_3)_4$ and $Pb(N_3)_4$ are completely unknown. Moreover, α-$Pb(N_3)_2$, which is an important initiating explosive, represents the only binary group 14 diazide, to date, and structurally characterized binary group 14 azides are limited to α-$Pb(N_3)_2$[4] as well as the ionic polyazides $[C(N_3)_3]^+$, $[E(N_3)_6]^{2-}$ (E = Si, Ge, Sn, Pb) and $[Ge(N_3)_3]^-$, respectively.[15,10b,c,16]

Aside from their expressed heat- and shock-sensitivity, group 14 diazides also suffer from their lability toward redox reactions. The same is true for group 13 monoazides MN_3 (M = Al, Ga, In), which have been spectroscopically identified in matrix isolation experiments,[17] but to date they could not be isolated in their pure form.[2d] In recent years, base-stabilization was found to be a very powerful tool for the stabilization of binary neutral p-block element polyazides as well as of low valent complexes.[10b,11,18] In particular the use of N-heterocyclic carbenes (NHC) as very strong σ-donors allowed the synthesis and structural characterization of several remarkable neutral diatomic complexes E_2 of group 13,[19] group 14,[20] and group 15 elements.[21]

Herein we report on our studies on the synthesis of binary, base-stabilized group 14 diazides and the structural characterization of $IPrGe(N_3)_2$ **1**, the first Ge(II) diazide.

EXPERIMENTAL SECTION

General Procedures. *Caution! Covalent azides are potentially toxic and can decompose explosively under various conditions. They should be handled only on a scale of less than 2 mmol with appropriate safety precautions (safety shields, safety glasses, face shields, leather gloves, protective clothing, such as leather suits, and ear plugs). Teflon containers should be used, whenever possible, to avoid hazardous fragmentation. Ignoring safety precautions can lead to serious injuries.*

Reactions were carried out in traps constructed from FEP tubes. Volatile materials were handled in a stainless steel-Teflon-FEP or Duran glass vacuum line, nonvolatile materials under Ar in a glovebox. Solvents were carefully dried over Na/K alloy (THF-d_8) and CaH_2 (CH_2Cl_2) and degassed prior to use. $GeCl_2\cdot$dioxane was commercially available and used without further purification. NaN_3 was dried at 110 °C and 10^{-3} mbar for 24 h. IPr was synthesized according to a literature method.[22] NMR spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C at 300.1 MHz (^1H), 75.5 MHz (^{13}C) and 21.7 MHz (^{14}N) and referenced to internal THF-d_8 (^1H: δ = 3.58; ^{13}C: δ = 25.31) and external CH_3NO_2 ($\delta(^{14}N)$ = 0). The Raman spectrum was recorded with a Bruker FT-Raman spectrometer RFS 100/S using the 1064 nm line of a Nd:YAG laser. The backscattered

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(180°) radiation was sampled and analyzed (Stokes range: 0 to 3500 cm^{-1}). The powdered sample was measured in a sealed capillary (1000 scans, resolution of 2 cm^{-1}) using a laserpower of 100 mW. The IR spectrum was recorded on a Alpha-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Elemental analysis was performed at the Elementaranalyse Labor der Universität Duisburg-Essen.

IPrGe(N$_3$)$_2$ (1). A 0.50 g portion of (1.29 mmol) IPr was added to a suspension of 0.30 g of (1.30 mmol) GeCl$_2$·dioxane in CH$_2$Cl$_2$ at ambient temperature, and the solution was stirred for additional 12 h. One gram (15 mmol) NaN$_3$ was added, and the resulting suspension was stirred for 7 days. NaCl and excess of NaN$_3$ were removed by filtration, and the solvent was removed at reduced pressure. **1** was obtained as cream-colored solid in 77% (0.54 g) yield.

Elemental analysis C$_{27}$H$_{36}$N$_8$Ge (545.23 g/mol) found (calc.): H 6.72 (6.65), C 59.23 (59.47), N 20.41 (20.55) %. IR (ATR, 25 °C, 32 Scans): ν = 3152 (w), 3124 (w), 3073 (w), 2962 (m), 2928 (w), 2870 (w), 2075 (s), 1591 (w), 1548 (w), 1534 (w), 1507 (w), 1456 (m), 1413 (w), 1386 (w), 1365 (w), 1325 (m), 1260 (s), 1209 (w), 1183 (w), 1094 (s), 1060 (s), 1017 (s), 935 (w), 865 (w), 800 (s), 754 (s), 700 (w), 681 (w), 660 (w), 583 (w), 545 (w), 455 (w), 397 (s), 382 (s) cm^{-1}. Raman (1000 mW, 25 °C, 1000 Scans): ν = 3152, 3125, 3072, 3036, 2967, 2909, 2868, 2762, 2717, 2091, 2076, 1590, 1548, 1466, 1444, 1372, 1331, 1307, 1237, 1183, 1167, 1106, 1044, 972, 959, 886, 809, 768, 731, 613, 523, 455, 401, 314, 268, 206, 145, 84 cm^{-1}. ^{1}H NMR (300.1 MHz, 25 °C, THF-d$_8$): δ = 1.19 (d, 12H, $^3J_{HH}$ = 6.85 Hz, CH(C*H*$_3$)$_2$), 1.27 (d, 12H, $^3J_{HH}$ = 6.85 Hz, CH(C*H*$_3$)$_2$), 2.49 (sept, 4H, $^3J_{HH}$ = 6.85 Hz, C*H*(CH$_3$)$_2$), 6.53 (s, 2H, NC*H*), 7.39−7.61 (m, 6H, C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, 25 °C, THF-d$_8$): δ = 23.8 (CH(CH$_3$)$_2$), 24.9 (CH(CH$_3$)$_2$), 29.9 (CH(CH$_3$)$_2$), 125.3 (NCH), 127.1 (*m*-C$_6$H$_3$), 131.6 (*ipso*-C$_6$H$_3$), 132.5 (*p*-C$_6$H$_3$), 141.7 (CGe), 146.2 (*o*-C$_6$H$_3$). ^{14}N{^{1}H} NMR (21.7 MHz, 25 °C, THF-d$_8$): δ = −137 (N$_\beta$, $\Delta\nu_{1/2}$ = 30 Hz), −213 (N$_\gamma$, $\Delta\nu_{1/2}$ = 118 Hz), −295 (N$_\alpha$, $\Delta\nu_{1/2}$ = 298 Hz).

Crystal Structure Determination of 1. Figure 2 shows the diagram of the solid state structure of **1**. The crystal was mounted on a nylon loop in inert oil. Data were collected on a AXS D8 Kappa diffractometer with APEX2 detector (MoK$_\alpha$ radiation, λ = 0.71073 Å; T = 143(1) K). The structure was solved by Direct Methods (SHELXS-97) and refined by full-matrix least-squares on F^2.[23] An absorption correction was performed semiempirically from equivalent reflections on the basis of multiscans (Bruker AXS APEX2). All non-hydrogen atoms were refined anisotropically, methyl hydrogen atoms as rigid groups and others by a riding model (SHELXL-97).[24] **1**: C$_{27}$H$_{36}$GeN$_8$, M = 545.23, colorless crystal (0.50 × 0.17 × 0.10 mm); monoclinic, space group $C2/c$; a = 16.5337(3), b = 9.4188(2), c = 17.7940(4) Å; β = 90.6310(10)°, V = 2770.85(10) Å^3; Z = 4 μ = 1.136 mm^{-1}; $\rho_{ber.}$ = 1.307 g cm^{-3}; 20675 reflexes ($2\theta_{max}$ = 66°), 5218 unique (R_{int} = 0.0218); 186 parameters; largest max./min in the final difference Fourier synthesis 0.591 e Å^{-3}/−0.311 e Å^{-3}; max./min transmission 0.75/0.62; $R1$ = 0.0412 ($I > 2\sigma(I)$), $wR2$ (all data) = 0.1168. The Ge atom and the azido groups are disordered over two positions. The crystallographic data (without structure factors) were deposited as "supplementary publication no. CCDC-925704 (**1**)" at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam-ak.uk).

Computational Studies. All geometries were fully optimized (using tightened convergence criteria and improved integration grids) at the density functional theory level, employing the BP86 exchange-correlation functional and including a third-generation dispersion correction as implemented in the Turbomole V6.3 quantum chemistry program package.[25−27] A triple-ζ valence quality Gaussian type function basis set termed def2-TZVP has been used throughout.[28] The resolution-of-the-identity approximation was employed, making use of an appropriate auxiliary basis set.[29] Atom coordinates, energies and atomic partial charges (NPA) of all optimized geometries are given below.[30]

RESULTS AND DISCUSSION

Several attempts to prepare IPrSi(N$_3$)$_2$ by reaction of IPrSiCl$_2$[31] with various azide-transfer reagents such as NaN$_3$, AgN$_3$, and TmsN$_3$ were unsuccessful. The reaction with AgN$_3$ resulted even at low temperatures (−40 °C) with quantitative formation of elemental silver, whereas no reaction occurred with NaN$_3$ and TmsN$_3$, even at elongated reaction times. In contrast, **1** was obtained in good yield by reaction of NaN$_3$ with in situ prepared IPrGeCl$_2$ (Scheme 1).[20b]

Scheme 1. Synthesis of IPrGe·(N$_3$)$_2$ 1

$$\mathrm{GeCl_2(dioxan)} + \mathrm{:IPr} \longrightarrow \mathrm{IPrGeCl_2}$$

$$\mathrm{IPrGeCl_2} + \mathrm{NaN_{3exc.}} \longrightarrow \mathrm{IPrGe(N_3)_2}\ \mathbf{1}$$

The base-stabilized germanium bisazide **1** shows no shock-sensitivity, is soluble in aprotic, polar solvents, and melts at 205 °C with decomposition and subsequent elimination of N$_2$. Pure **1** can be stored without any sign of decomposition under an argon-atmosphere in a glovebox.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** show the expected resonances of the organic substituent (IPr). The ^{14}N NMR spectrum shows three well-resolved resonances of the azido groups for N$_\alpha$ (δ = −295, $\Delta\mu_{1/2}$ = 298 Hz), N$_\beta$ (δ = −137, $\Delta\mu_{1/2}$ = 30 Hz) and N$_\gamma$ (δ = −213, $\Delta\mu_{1/2}$ = 118 Hz) as is typical for covalently bound azido groups. The resonances agree very well with those observed for [(*n*-Pr)$_2$ATI]GeN$_3$ (N$_\alpha$: δ = −250, N$_\beta$: δ = −135, N$_\gamma$: δ = −213) and [(Mes)$_2$DAP]GeN$_3$ (N$_\alpha$: δ = −291, N$_\beta$: δ = −136, N$_\gamma$: δ = −215), respectively.[32,33] The ^{14}N NMR spectrum of the octahedrally coordinated hexaazidogermanate(IV)-anion also shows comparable resonances (N$_\alpha$: δ = −289, N$_\beta$: δ = −136 (overlapped with resonances from the solvent), N$_\gamma$: δ = −208),[10b] whereas no ^{14}N NMR shifts of the base-stabilized germanium tetraazides have been reported.

The IR spectrum of **1** (Figure 1) shows a very strong absorption band due to the asymmetric N$_\alpha$−N$_\beta$−N$_\gamma$ stretching mode (ν = 2075 cm^{-1}), whereas the Raman spectrum shows two absorption bands due to the asymmetric N$_\alpha$−N$_\beta$−N$_\gamma$ stretching mode (ν = 2091, 2076 cm^{-1}). The broadness of the absorption band due to the N$_\alpha$−N$_\beta$−N$_\gamma$ stretching mode in the IR spectrum probably results from an overlap of two absorption bands. The correct assignment of further absorption band is hampered because of overlap with absorption bands of the organic ligand (IPr). Computational determination of the

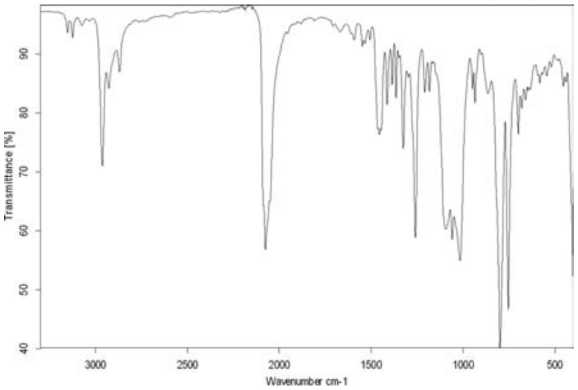

Figure 1. IR spectrum of IPrGe(N$_3$)$_2$ **1**.

harmonic IR-frequencies using density functional theory including a dispersion correction (BP+D3/def2-TZVP) gave values of 2138 and 2123 cm^{-1} for the asymmetric $N_\alpha-N_\beta-N_\gamma$ stretching mode, which correspond reasonably well with the experimental values.[25−29] The asymmetric N_3 stretching absorption band as observed for **1** is slightly shifted to a higher frequency compared to the values reported for Ge^{II} azides such as $[(n\text{-Pr})_2\text{ATI}]\text{GeN}_3$[32] ($\nu_{\text{asym.}}(N_3)$ = 2048 cm^{-1}) and $[(\text{Mes})_2\text{DAP}]\text{GeN}_3$[33] ($\nu_{\text{asym.}}(N_3)$ = 2062 cm^{-1}), but shifted to a lower frequency compared to Ge^{IV} azides such as base-stabilized germanium tetraazides $\text{LGe(N}_3)_4$ (L^1: ν = 2120, 2097, 2091, L^2: ν = 2120, 2093 cm^{-1}) as well as the hexaazidogermanate(IV)-anions in $[\text{PPN}]_2[\text{Ge(N}_3)_6]$ (PPN = $[\text{N(PPh}_3)_2$, ν = 2083 cm^{-1}) and $[\text{Na}]_2[\text{Ge(N}_3)_6]$ (ν = 2123, 2089 cm^{-1}).[10b] These findings indicate that the covalent character of the Ge−N_3 bond in **1** is slightly higher than in other Ge^{II} azides, hence the polarity of Ge−N_3 bond in **1** is slightly lower than in Ge^{II} but still higher than in Ge^{IV} azides.[35d]

Single crystals of **1** suitable for a single crystal X-ray analysis were obtained after storage of a solution of **1** for 24 h in 1,2-difluorobenzene at 0 °C (Figure 2). $\text{IPrGe(N}_3)_2$ **1** crystallizes in the monoclinic space group $C2/c$ with the molecule on a 2-fold axis. As a consequence, the germanium atom and the azido groups are disordered over two sites with a common N_γ atom. The Ge atom of the asymmetric unit as well as the azido component **B** and the symmetry-generated component **A** (via 2-fold-axis) represent one position of the molecule, whereas the symmetry-equivalent Ge atom, component **A** and the symmetry-generated component **B** form the second position. A possible explanation for this disorder is the presence of nonclassical CH···N contacts. The azido groups show asymmetric N−N bond lengths ($N_\alpha-N_\beta$: 1.206(4), 1.211(4) Å, $N_\beta-N_\gamma$: 1.131(4), 1.173(4) Å) and almost linear bond angles (178.4(4), 176.7(4)°) as is typical for covalently bound p-block element azides. The Ge−$N_\alpha-N_\beta$ bond angles of 115.4(2) and 115.7(2)° are somewhat smaller than the expected value for a sp^2-hybridized nitrogen atom. The N_α−Ge−N_α (93.09(12) Å) and the C−Ge−N_α bond angles (90.42(7), 93.4287)°) are close to 90°, pointing to a large p-orbital contribution of the bonding electron pairs and a high s-character of the electron lone pair (Ge bond angular sum 276.9°). The Ge−N_α bond lengths of 1.9648(2) and 1.974(2) Å are slightly elongated compared to the sum of the covalent radii for 4-fold-coordinated Ge atoms (1.92 Å).[34] The NHC ligand shows no unusual bonding parameters.

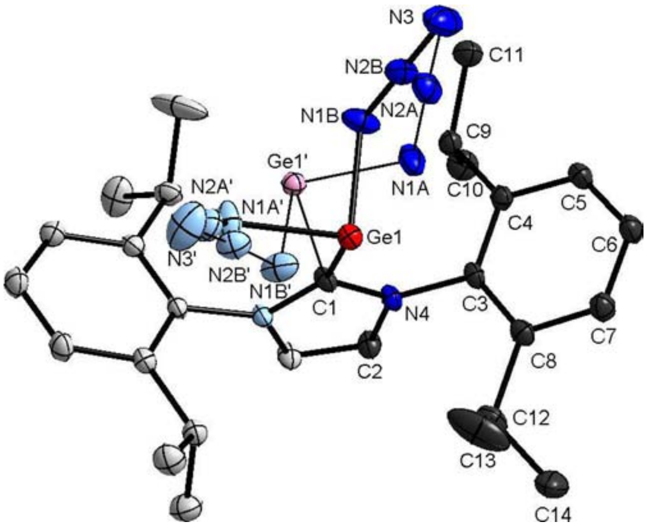

Figure 2. Representation of $\text{IPrGe(N}_3)_2$ **1**. Hydrogen atoms are omitted for clarity, thermal ellipsoids are shown at 50% probability levels, symmetry-generated atoms (′: $-x+1,y,-z+3/2$) in pale colors and the second component of the disorder with thin bonds.

Since **1** represents the first structurally characterized germanium(II) diazide, its structural parameters can only be compared with those of base-stabilized octahedrally coordinated germanium(IV) tetraazides $\text{LGe(N}_3)_4$ (L = bipy, phen).[10b] The tetraazides show almost identical Ge−$N_\alpha-N_\beta$ and $N_\alpha-N_\beta-N_\gamma$ bond angles as well as $N_\alpha-N_\beta$ and $N_\beta-N_\gamma$ bond lengths. In addition, the Ge−N_α bond lengths of the base-stabilized tetraazidogermanate complexes (1.955(2); 1.949(2) Å) are also almost identical. Comparable Ge−N_α bond lengths (1.981(5), 1.974(2) Å) were reported for the hexaazidogermanate(VI) dianions $[\text{Na}_2(\text{thf})_3(\text{Et}_2\text{O})][\text{Ge(N}_3)_6]$ and $(\text{PPN})_2[\text{Ge(N}_3)_6]$.[10b] In addition, a few heteroleptic Ge(II) monoazides of the general type LGeN_3 with a terminal azido group as well as several Ge(IV) complexes of the type $\text{L}_x\text{Ge(N}_3)_{4-x}$ have been structurally characterized.[32,33,35,36] The Ge−N_α, $N_\alpha-N_\beta$, and $N_\beta-N_\gamma$ bond lengths as well as the Ge−$N_\alpha-N_\beta$ and $N_\alpha-N_\beta-N_\gamma$ bond angles in these complexes are very similar to those observed in **1**.[37] In contrast, Filippou et al. reported on the solid state structure of the pyrazolylborate complex $\text{Tp}'\text{GeN}_3$, which show very unusual Ge−N_α (2.262(4) Å), $N_\alpha-N_\beta$ (1.136(5) Å), and $N_\beta-N_\gamma$ bond lengths (1.179(6) Å) as well as a much wider Ge−$N_\alpha-N_\beta$ bond angle (136.8(3)°).[35c]

An analysis of the packing of **1** in the solid state clearly shows that the azido ligand forms contacts to several hydrogen atoms (see Table 1 and Figure 3). Of particular interest are those formed by N_α and N_β. Since the C_2-symmetric environment of the azido groups allows the formation of intermolecular contacts for both components **A** and **B**, two equally favorable arrangements results for the azido ligands and the Ge atom, most likely leading to the disorder as was observed in the solid state structure. Moreover, the structure shows a H···Ge-contact with typical bond lengths and angles of a nonclassical hydrogen bridge (2.76 Å, 150.3°).

Table 1. C−H···N Contacts in 1[a]

	H···A [Å]	D···A [Å]	D−H···A [deg]
C2−H2···N3[#1]	2.83	3.639(2)	143.9
C7−H7···N2A[#2]	2.57	3.462(3)	156.7
C7−H7···N3[#2]	2.70	3.634(2)	169.1
C10−H10B···N1B[#3]	2.72	3.663(3)	163.4
C10−H10B···N2B[#3]	2.74	3.694(3)	163.9
C11−H11B···N3#3	2.81	3.739(2)	158.9
C13−H13B···N3[#4]	2.85	3.788(2)	161.3
C13−H13C···Ge1	2.76	3.646(3)	150.3
C14−H14C···N3[#2]	2.77	3.747(2)	174.4

[a]#1 $x, y+1, z$; #2 $-x+1, -y+1, -z+1$; #3 $-x+3/2, y+1/2, -z+3/2$; #4 $x-1/2, y+1/2$.

To analyze the bonding situation in **1** in more detail and to allow structural comparisons to that of other binary germanium polyazides, quantum chemical calculations using density functional theory were carried out with the TURBOMOLE program using the Becke−Perdew functional and an empirical dispersion correction (BP+D3/def2-TZVP).[25−29] Starting from the crystal structure of **1**, the average Ge−N_α bond length in

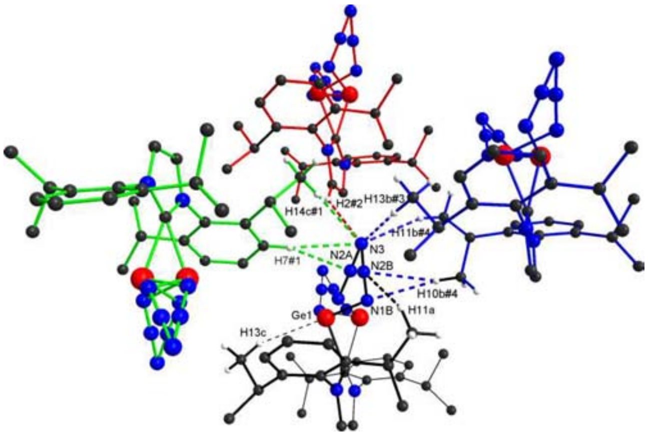

Figure 3. C−H···N contacts of the azido ligands. Hydrogen atoms are omitted for clarity. #1: 1−*x*, 1−*y*, 1−*z*; #2: *x*, −1+*y*, *z*; #3: 1/2+*x*, −1/2+*y*, *z*; #4: 3/2−*x*, −1/2+*y*, 3/2−*z*. The asymmetric unit is accentuated by thick bonds, and the symmetry-generated molecules are colored.

Table 2. Selected Structural Parameters of Germanium(II)azides and Germanium(IV)azides

	Ge−N_α [Å]	N_α−N_β [Å]	N_β−N_γ [Å]	Δ(NN) [pm]	ref
$LGe(N_3)_2$ **1**	1.969	1.209	1.152	5.7	*a*
$LGe(N_3)_2$ **1a**	1.992	1.218	1.154	6.4	*a*
$Ge(N_3)_2$ **2a**	1.909	1.231	1.145	8.6	*a*
$Ge(N_3)_4$ **3a**	1.856	1.236	1.141	9.5	*a*
$L^1Ge(N_3)_4$	1.955	1.216	1.140	7.6	10b
$L^2Ge(N_3)_4$	1.949	1.221	1.136	8.5	10b
$[PPN]_2[Ge(N_3)_6]$	1.974	1.212	1.147	6.5	10b
$[Na]_2[Ge(N_3)_6]$	1.981	1.204	1.132	7.2	10b
$[Ge(N_3)_6]^{2-}$ **4a**	2.017	1.208	1.161	4.7	*a*

[a] This work.

the optimized gas phase structure **1a** (calc. 1.992 Å) is comparable to that observed for **1** in the solid state (exp. 1.969 Å). In contrast, the calculated base-free germanium diazide $Ge(N_3)_2$ **2a**, which is a planar molecule, shows significantly shorter Ge−N_α bond lengths (av. 1.909 Å), most likely because of the lower coordination number of the Ge atom (2 vs 3). The population number of the 4s orbital, which was determined using natural population analysis (NPA),[30] of **1a** is 1.68, whereas that of base-free diazide **2a** is 1.78. The electron lone pair in both complexes adopts the 4s orbital, which corresponds very well with the structural findings, in particular the bond angular sum at the Ge atom in **1a** (274.9°) as well as the N_α−Ge−N_α bond angle in **2a** (94.7°). To verify the influence of the formal oxidation number of the Ge atom on the resulting structure, we expanded our studies on the neutral germanium(IV) tetraazide $Ge(N_3)_4$ **3a**. The N_α atoms in **3a** adopt a slightly distorted tetrahedral environment around Ge in the S_4-symmetric Ge tetraazide, with a Ge−N_α bond length of 1.856 Å. The population number of the 4s-orbital is significantly reduced to 0.83, as was expected. The base-stabilized tetraazides $LGe(N_3)_4$ (L^1 1.955, L^2 1.949 Å) show elongated Ge−N_α bond lengths compared to the base-free tetraazide $Ge(N_3)_4$ **3a**, which results from the increased coordination number due to base-coordination. However, they are only marginally shorter than that observed for base-stabilized diazide **1**. The Ge atom in the germanium(IV) hexaazide dianion $[Ge(N_3)_6]^{2-}$ **4a** adopts an almost octahedral coordination sphere with S_6-symmetry as was already shown by Filippou et al. In contrast, an S_2-symmetric (almost S_6 symmetric) structure was observed in $(PPN)_2[Ge(N_3)_6]$. The Ge−N_α bond length of 2.017 Å at the BP+D3/def2-TZVP level of theory agrees very well with that previously reported by Filippou et al. at the BP86/dzp level of theory (Ge−N_α 2.022 Å).[10b] In contrast, the Ge−N_α bond lengths as observed for $[Na]_2[Ge(N_3)_6]$ (1.981 Å) and $[PPN]_2[Ge(N_3)_6]$ (1.974 Å) in the solid state were slightly shorter. The population number of the 4s-orbital for **4a** was calculated to 0.89.

The difference Δ(NN) (Table 2) between the average N_α−N_β and N_β−N_γ bond lengths in **1** and **1a** (exp. 5.7 pm; calc. 6.4 pm) is slightly smaller than in $Ge(N_3)_2$ **2a** (calc. 8.6 pm) but significantly smaller compared to the tetraazidogermane $Ge(N_3)_4$ **3a** (calc. 9.5 pm). In contrast, the slightly distorted octahedral arrangement of the S_6-symmetric hexaazidogermanate **4a** (calc. 4.7 pm) shows significantly smaller differences, whereas more pronounced differences were observed in the solid state structures of $[Na]_2[Ge(N_3)_6]$ (7.2 pm) and $[PPN]_2[Ge(N_3)_6]$ (6.5). These findings correspond very well to the IR spectra, which also indicated that the covalent character of the Ge−N_3 bond in **1** is lower than in Ge(IV) azides.

Population analyses show an increase of the ionic character of the azido group from **3a** (N_3 charge −0.49) to **4a** (N_3 charge −0.63), as was reported for the analogue silicon(IV) tetraazides.[11a] The azido groups in the germanium(II) diazide **2a** also show a slightly less ionic character compared to the base-stabilized complex **1a** (N_3 charge −0.55 vs −0.62).[38] Analogous tendencies were observed for base-free and base-stabilized binary silicon(IV) tetraazides and explained by an increasing polarity of the Si−N_α bonds ($Si(N_3)_4$ < $[Si(N_3)_4(L_2)]$ < $[Si(N_3)_6]^{2-}$ (L_2 = bipy, phen)).[11a]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF file giving crystallographic data for complex **1** as well as details on the theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Dr. W. A. Herrmann on the occasion of his 65th birthday.

■ ABBREVIATIONS

bipy, bipyridine; py, pyridine; phen, 1,10-phenanthroline; IPr, :C{N(Dipp)C(H)}2; Dipp, 2,6-*i*-$Pr_2-C_6H_3$; (*n*-$Pr)_2$ATI, *N*-(*n*-Propyl)-2-(*n*-propylamino)troponiminate; $(Mes)_2$DAP, 2,4-Dimethyl-*N*,*N*′-bis(2,4,6-trimethylphenyl)-1,5-diazapentadienyl; Tp′, hydrotris(3,5-dimethylpyrazol-1-yl)borato.

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(38) Tables with population analyses are given in the Supporting Information.