Okumoto, T. Tadokoro, A. Nishimura, M. Rashid, *Tetrahedron Lett.* **1993**, *34*, 2139–2142). An alternative route would involve the coupling of iodide **3** with a 1,1-bis(trialkylstannyl)ethylene. Thus far we have been unable to prepare 1,1-bis(trimethylstannyl)ethylene (T. N. Mitchell, A. Amamria, *J. Organomet. Chem.* **1983**, *252*, 47–56).
[12] H. J. Reich, I. L. Reich, K. E. Yelm, J. E. Holladay, D. Gschneidner, *J. Am. Chem. Soc.* **1993**, *115*, 6625–6635.
[13] The Supporting Information contains ^{1}H NMR, ^{13}C NMR, and UV/Vis spectra of the [*n*]dendralenes.
[14] Gas phase electron diffraction measurements indicate that [3]dendralene adopts a conformation consisting of a planar *s-trans*-1,3-butadiene with the 2-vinyl group skewed 40° out of plane: A. Almenningen, A. Gatail, D. S. B. Grace, H. Hopf, P. Klaeboe, F. Lehrich, C. J. Nielsen, D. L. Powell, M. Tratteberg, *Acta Chem. Scand.* **1988**, *A42*, 634–650. [4]Dendralene behaves similarly, adopting an *s-trans, s-trans,* skew conformation.[2]
[15] Potential applications of dendralenes in molecular electronic and ferromagnetic devices: a) M. R. Bryce, M. A. Coffin, P. J. Skabara, A. J. Moore, A. S. Batsanov, J. A. K. Howard, *Chem. Eur. J.* **2000**, *6*, 1955–1962; b) N. Tyutyulkov, *Pure Appl. Chem.* **1996**, *68*, 345–352.
[16] "Expanded dendralenes", in which ethynyl units are inserted between each "etheno"[1] group have been reported: a) A. M. Boldi, J. Anthony, V. Gramlich, C. B. Knobler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 779–796; b) Y. Zhao, R. R. Tykwinski, *J. Am. Chem. Soc.* **1999**, *121*, 458–459; c) Y. Zhao, R. McDonald, R. R. Tykwinski, *Chem. Commun.* **2000**, 77–78.

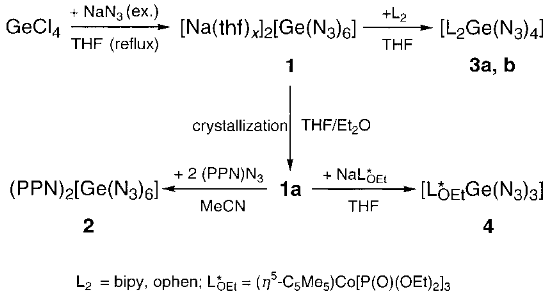
The Hexaazidogermanate(IV) Ion: Syntheses, Structures, and Reactions**

Alexander C. Filippou,* Peter Portius,
Dirk U. Neumann und Klaus-Dieter Wehrstedt

Dedicated to Professor Herbert Schumann
on the occasion of his 65th birthday

The synthesis, isolation, and structural characterization of high-energy compounds is an experimental challenge.[1] Binary azides of the main Group IV elements belong to this class of compounds, however, very little is known about their structure and reactivity.[2] To date only the ions $[C(N_3)_3]^+$[2d] and $[E(N_3)_6]^{2-}$ (E = Sn, Pb),[2g,h] as well as α-$Pb(N_3)_2$[2f] have been structurally characterized; in comparison there is no structural information for the analogous silicium and germanium compounds. We recently reported the syntheses, structures, and oxidation reactions of Ge^{II} azides with HN_3;[3] hypercoordinate triazidogermane compounds of the type $[L_3Ge(N_3)_3]$ ($L_3 = [CpCo\{P(O)(OEt)_2\}_3]$, $HB(pz^*)_3$; $Cp = C_5H_5$; pz* = 3,5-dimethylpyrazol-1-yl) could be prepared and structurally characterized.[4] As an extension to this work on germanium compounds with a high nitrogen content[5] we report herein the formation, structure, and first reactions of the hexaazidogermanate(IV) ion to give derivatives of $Ge(N_3)_4$.

The reaction of $GeCl_4$ with excess NaN_3 in boiling THF leads selectively to disodium hexaazidogermanate(IV) **1**, which, after workup and crystallization, was isolated as colorless, hydrolysis-sensitive, single crystals of composition $[Na_2(thf)_3(Et_2O)][Ge(N_3)_6]$ (**1a**; Scheme 1).[6] The crystal lattice of **1a** is composed of distorted octahedral $[Ge(N_3)_6]^{2-}$ ions of C_1 symmetry and two symmetry independent sodium ions, of which one is solvated by two THF molecules (Na1–O1 2.327(4), Na1–O2 2.287(5) Å) and the other by one THF and one Et_2O molecule (Na2–O3 2.265(5), Na2–O4 2.304(11) Å; Figure 1).[7] The Na–O bond lengths are in the range reported for other Na–THF/Et_2O complexes.[8] Short Na–N contacts exist between the Na^+ ions and the N_α and N_γ atoms of the azide groups of the $[Ge(N_3)_6]^{2-}$ ions. These contacts link each $[Ge(N_3)_6]^{2-}$ ion with two Na1 and Na2 cations and each sodium cation with two $[Ge(N_3)_6]$ anions to give a layer structure. This arrangement results in a strongly distorted octahedral coordination geometry of the Na1 cations and a coordination polyhedron for the pentacoordinate Na2 cations that can be rationalized using the Kepert model for chelate complexes.[9] The Na–N distances (2.410(5)–2.636(6) Å) are in the range found for Na–N coordinate bonds[10] and increase as the coordination number of the Na^+ ions and of the azide nitrogen atoms increases. The short interionic Na–N contacts in **1a** have only a slight influence on the average bonding parameters of the $[Ge(N_3)_6]^{2-}$ ion. This point is shown by a comparison with the crystal structure of the salt $(PPN)_2[Ge(N_3)_6]$ **2** ($(PPN)^+ = [N(PPh_3)_2]^+$), which contains less-polarizing cations (Table 1). Compound **2** is formed in the reaction of **1a** with $(PPN)N_3$ in MeCN (Scheme 1) and was fully characterized. It was isolated in 55% yield as a colorless microcrystalline powder that is very soluble in CH_2Cl_2 but insoluble in THF. In the solid state **2** is air stable for a short time, whereas in solution it is rapidly hydrolyzed releasing HN_3 and $(PPN)N_3$. IR spectroscopy of **2** in MeCN at



Scheme 1. Synthesis of $Ge(N_3)_4$ derivatives starting from $GeCl_4$.

---

[*] Prof. Dr. A. C. Filippou, Dipl.-Chem. P. Portius,
Dipl.-Chem. D. U. Neumann
Institut für Chemie der Humboldt-Universität zu Berlin
Hessische Strasse 1–2, 10115 Berlin (Germany)
Fax: (+49) 30-2093-6939
E-mail: filippou@chemie.hu-berlin.de
Dr. K.-D. Wehrstedt
Bundesanstalt für Materialforschung und -prüfung (BAM)
Unter den Eichen 87, 12205 Berlin (Germany)

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. G. Kociok-Köhn, Dr. B. Ziemer and Ms P. Neubauer for the X-ray crystal structure analyses, Dr. W.-D. Hunnius (Freie Universität Berlin) for the Raman spectra, and Prof. Dr. B. Wrackmeyer (Universität Bayreuth) for the ^{14}N and ^{73}Ge NMR Spectra.

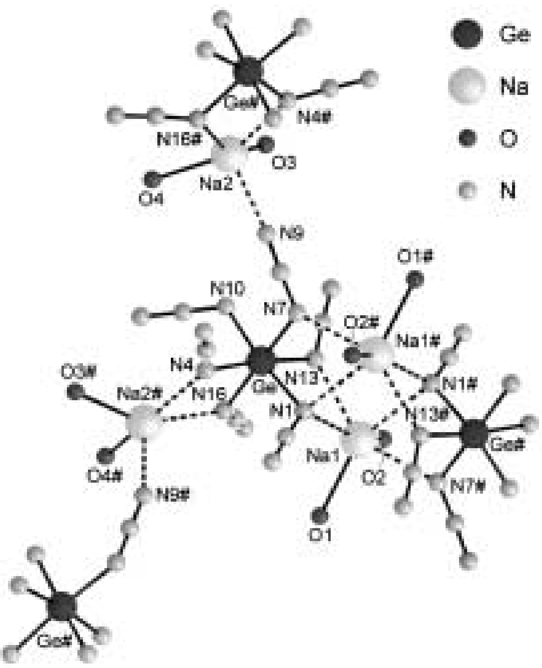


Figure 1. View of the crystal structure of **1a** that shows the interionic interactions between the $[Ge(N_3)_6]^{2-}$ ion and the solvated cations Na1 and Na2. For clarity, only the O atoms of the solvent molecules are shown. Selected distances [Å] and angles [°]: Ge-N1 1.984(5), Ge-N4 1.983(4), Ge-N7 1.990(6), Ge-N10 1.985(5), Ge-N13 1.959(4), Ge-N16 1.985(6), Na1-N1 2.552(5), Na1-N1# 2.636(6), Na1-N7# 2.487(6), Na1-N13 2.523(4), Na2-N4# 2.473(7), Na2-N9 2.410(5), Na2-N16# 2.450(5); N1-Ge-N10 173.3(2), N4-Ge-N13 173.7(2), N7-Ge-N16 176.5(2).

Table 1. Experimentally determined average bond lengths [Å] and angles [°] of the azide groups in compounds **1a**–**4** (standard deviations in parentheses) and calculated values for the S_6-symmetric minimum structure of $[Ge(N_3)_6]^{2-}$ with various DFT methods/basis sets.

Compound	Ge-N_α	N_α-N_β	N_β-N_γ	Ge-N_α-N_β	N_α-N_β-N_γ
1a	1.981(5)	1.204(7)	1.132(8)	119.3(4)	176.9(6)
2	1.974(2)	1.212(3)	1.147(3)	119.8(2)	175.9(2)
3a	1.955(2)	1.216(2)	1.140(3)	117.7(1)	176.8(2)
3b[a]	1.949(2)	1.221(2)	1.136(3)	117.1(1)	176.1(2)
4[a]	1.92(1)	1.20(2)	1.17(2)	117(1)	174(1)
$[Ge(N_3)_6]^{2-}$					
BP86/dzp	2.022	1.213	1.168	123.7	174.5
BP86/svp	2.016	1.211	1.168	124.9	174.8
BLYP/dzp	2.044	1.218	1.172	123.4	174.5
BLYP/svp	2.036	1.216	1.171	124.6	174.8

[a] A. C. Filippou, P. Portius, unpublished results.

different concentrations gave no evidence of a dissociation of **2** into $Ge(N_3)_4$ and $(PPN)N_3$. Compound **2** is not impact sensitive, as demonstrated in experiments with the drop hammer of the Bundesanstalt für Materialforschung und -prüfung (BAM Fallhammer),[11] and is thermally astoundingly stable. Thus it melts in vacuum, without decomposition, at 211 °C. In addition, a thermal analysis of **2** by differential scanning calorimetry (DSC) showed that the melting of **2** (extrapolated onset temperature $T_e = 194\,°C$, peak temperature $T_p = 213\,°C$, $\Delta H_f = +46\,J\,g^{-1}$) follows a strongly exothermic decomposition, which takes place in two steps ($T_e = 256\,°C$, $\Delta H = -503\,J\,g^{-1}$; $T_e = 312\,°C$, $\Delta H = -344\,J\,g^{-1}$). The crystal structure of **2**[7] reveals the presence of separated $[Ge(N_3)_6]^{2-}$ ions of S_2 symmetry (roughly S_6 symmetry; Figure 2) enclosed by the voluminous $(PPN)^+$ ions.[12] This encapsulation makes the $[Ge(N_3)_6]^{2-}$ions "phlegmatic" (inert) and offers an explanation for the thermal and mechanical stability of **2**. Density functional theory (DFT) calculations using various methods predict a S_6-symmetric minimum structure for the $[Ge(N_3)_6]^{2-}$ion and show a very good agreement between the calculated and experimentally determined bond lengths and angles (Table 1).[13] These results suggest a reduction of symmetry of the anion in the crystal through packing effects. The solution IR and Raman spectra (including the polarization measurements) of **2** are also consistent with S_6-symmetric anion, and allow in combination with the calculated IR and Raman spectra an assignment of the individual fundamental vibrations of the $[Ge(N_3)_6]^{2-}$ ion (see Experimental Section). In addition, the ^{73}Ge NMR spectrum of **2** displays a sharp signal at $\delta = -290.6$ ($\Delta\nu_{1/2} = 15\,Hz$), which suggests a highly symmetrical environment for the germanium atom.[14] The bond lengths and angles of the $[Ge(N_3)_6]^{2-}$ ion in **2** are in good agreement with those of other hexa-coordinate Ge^{IV} azide compounds (Table 1) and indicate the presence of polar, covalent Ge–N bonds.[4] Correspondingly two well-resolved singlets at $\delta = -288.9$ and -208.0 are found in the ^{14}N NMR spectrum of **2** in MeCN, which, by comparison with the data of other covalent azide compounds,[15] can be assigned to the N_α and N_γ atoms of the azide groups (the N_β signal of **2** is masked by the solvent signal at $\delta = -136.3$).

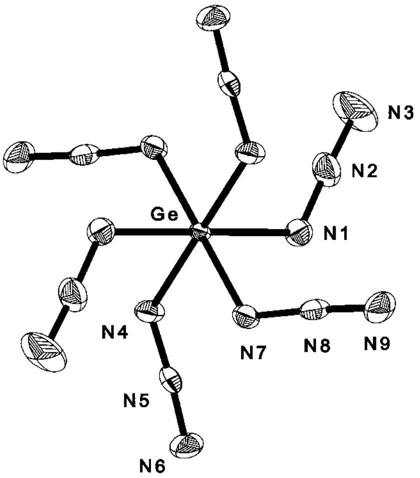


Figure 2. ZORTEP drawing of the molecular structure of the $[Ge(N_3)_6]^{2-}$ ion in the crystal lattice of **2**. The thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°]: Ge-N1 1.980(2), Ge-N4 1.969(2), Ge-N7 1.974(2), N1-N2 1.213(3), N2-N3 1.152(4), N4-N5 1.214(3), N5-N6 1.143(3), N7-N8 1.210(3), N8-N9 1.146(3); N1-Ge-N4 89.2(1), N1-Ge-N7 90.4(1), N4-Ge-N7 90.9(1), Ge-N1-N2 118.4(2), Ge-N4-N5 122.7(2), Ge-N7-N8 118.4(2), N1-N2-N3 176.6(3), N4-N5-N6 175.0(2), N7-N8-N9 176.1(2).

Whereas **2** has proved so far to be relatively unreactive, **1** and **1a** react readily with nucleophiles. Thus the reactions of **1** with 2,2′-bipyridine (bipy) and 1,10-phenanthroline (ophen) leads to the Lewis-base adducts of $Ge(N_3)_4$, **3a** and **3b**, respectively, and the reaction of **1a** with NaL^{*}_{OEt} gives the hexacoordinate triazidogermane **4** (Scheme 1). The compounds were isolated in good yields as surprisingly thermally stable colorless crystals (**3a**, **3b**$\cdot$0.5MeCN) or as a yellow powder (**4**); these compounds were fully characterized and their molecular structures determined by single-crystal X-ray diffraction (Table 1, Figure 3).[7]

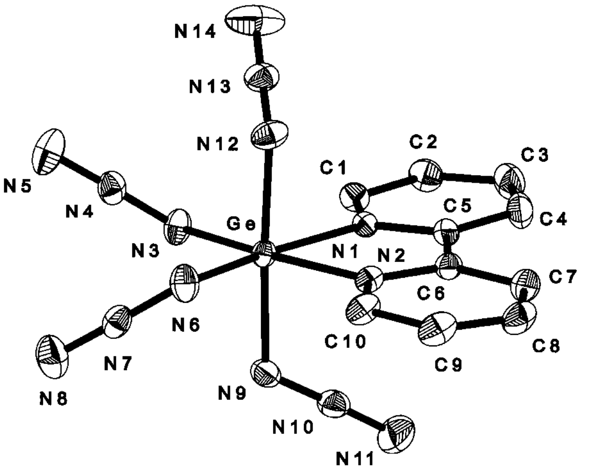


Figure 3. ZORTEP drawing of the molecular structure of **3a**. The thermal ellipsoids are set at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge-N1 2.057(2), Ge-N2 2.046(2), Ge-N3 1.958(2), Ge-N6 1.925(2), Ge-N9 1.972(2), Ge-N12 1.966(2), N3-N4 1.218(2), N4-N5 1.139(3), N9-N10 1.208(2), N10-N11 1.142(3); N1-Ge-N6 170.02(6), N2-Ge-N3 170.22(6), N9-Ge-N12 176.55(6), Ge-N3-N4 116.9(1), Ge-N9-N10 119.2(1), N3-N4-N5 176.7(2), N9-N10-N11 177.6(2).

The complexes **1a**–**3b** are not just examples of a very rare class of hypercoordinate compounds containing a GeN_6 framework,[4] but are also the first structurally characterized derivatives of the long sought after species $Ge(N_3)_4$ and are thus promising starting materials for the preparation of new binary germanium nitride compounds.[16]

Experimental Section

The experiments were performed using appropriate safety procedures (conditions see ref [4]) because of the risk of explosion in handling azides (armored glass, face shield, metal gauntlets, protective clothing). $GeCl_4$[17] and $(PPN)N_3$[18] were prepared by literature methods. The solution IR spectra were recorded in a NaCl cell under rigorous exclusion of moisture. (Bruker-IFS 55 Spectrometer). Raman spectra: Bruker-RFS-100 FT Raman Spectrometer, Nd:YAG Laser, power 500 mW. The NMR spectra were recorded at room temperature; ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR: Bruker-AM-300 Spectrometer; ^{14}N and ^{73}Ge NMR: Bruker-DRX-500 Spectrometer; ^{31}P, ^{14}N and ^{73}Ge NMR signals relative to $\delta(H_3PO_4)_{ext}$, $\delta(CH_3NO_2)_{ext}$, and $\delta(GeMe_4)_{ext} = 0$, respectively; coupling constants [Hz] of the ring protons of **3a**: $^3J(H3,H4) = 8.0$, $^4J(H3,H5) = 1.1$, $^5J(H3,H6) = 0.9$, $^3J(H4,H5) = 7.7$, $^4J(H4,H6) = 1.5$, $^3J(H5,H6) = 5.6$; **3b**: $^3J(H2,H3) = 5.1$, $^4J(H2,H4) = 1.3$, $^3J(H3,H4) = 8.2$. Mass spectrometry: Hewlett-Packard 5995A Spectrometer, *m/z* values relative to the ^{74}Ge isotope. The DSC measurement was carried out in a high-pressure stainless-steel vessel with a gold coated copper sealing disk (7 mg weight of sample, heating rate 5 K min^{-1}) using a Perkin-Elmer differential scanning calorimeter "Pyris 1"; $T_e =$ extrapolated onset temperature, $T_p =$ peak temperature.

1a: Into a reflux apparatus, which had been thoroughly baked-out, was placed NaN_3 (5.30 g, 81.5 mmol) suspended in THF (41 mL). The mixture was treated with $GeCl_4$ (1.16 mL, 2.14 g, 9.98 mmol). The suspension was stirred vigorously and heated under reflux for 140 h. After cooling an IR spectrum of a diluted sample of the supernatant solution was recorded and showed the selective formation of **1** [$\tilde{\nu} = 2123$ (vw), 2089 cm^{-1} (vs), ($\nu_{as}(N_3)$)].[6] The colorless solution was separated from the white precipitate by filtration; the precipitate weighed 4.47 g after drying. The filtrate was used directly in the synthesis of **3a**, **b** or worked up as follows for the isolation of **1a**: the volume of the solution was reduced under vacuum, until a clear oil remained from which, after the addition of Et_2O (10 mL) a solid (**1a**) started to slowly crystallize radially. The supernatant solution was decanted, the residue was dissolved in THF (10 mL) and separated from the white insoluble material by filtration. The filtrate was crystallized again as above. The resulting crystal mass of **1a** was washed with a little Et_2O and dried for a few minutes under fine vacuum. The resulting powder did not contain chlorine;[6] yield 2.93 g (approximately 44% from $GeCl_4$). Single crystals of **1a** were obtained from this powder by crystallization from THF/Et_2O.

2: A solution of $(PPN)N_3$ (1.01 g, 1.74 mmol) in acetonitrile (11 mL) was added dropwise to a stirred solution of **1a** (661 mg, 1.00 mmol) in acetonitrile (20 mL) at room temperature. A suspension was formed immediately and became more cloudy during the course of the reaction. After 0.5 h the IR spectrum of the reaction solution showed that the $\nu_{as}(N_3)$ absorption band of $(PPN)N_3$ at 2005 cm^{-1} had vanished and only the $\nu_{as}(N_3)$ absorption band of **2** could be identified. The white suspension was filtered, the clear, colorless filtrate collected and the solvent removed by vacuum. The resulting crude product (1.06 g) was dissolved in acetonitrile (20 mL), the cloudy solution was filtered to remove insoluble material, and the filtrate concentrated to a few mL and left to stand for 2 d at −30 °C. The colorless crystals thus obtained were washed with pentane (10 mL) and dried for 0.5 h under high vacuum; yield 771 mg (55% from **1a**); elemental analysis calcd (%) for $C_{72}H_{60}GeN_{20}P_4$ (1401.91): C 61.69, H 4.31, N 19.98, P 8.84; found: C 61.84, H 4.60, N 20.04, P 8.39; the substance did not contain chlorine; IR (MeCN): $\tilde{\nu}([Ge(N_3)_6]^{2-}) = 2083$ (vs) ($\nu_{as}(N_3)$, E_u and A_u), 1297 cm^{-1} (w) ($\nu_s(N_3)$, E_u and A_u); Raman (MeCN, RT; p = polarized, dp = depolarized): $\tilde{\nu}([Ge(N_3)_6]^{2-}) = 2113$ (m, p) ($\nu_{as}(N_3)$, A_g), 2082 (w, dp) ($\nu_{as}(N_3)$, E_g), 1307 (m, p) ($\nu_s(N_3)$, A_g), 1085 (m, dp), 414 cm^{-1} (vs, p) (ν(Ge-N), A_g); ^{1}H NMR (CD_3CN): $\delta = 7.44-7.50$ (m, 24 H, *m*-H, Ph), 7.54–7.68 (m, 36 H, *o*- and *p*-H, Ph); ^{13}C{^{1}H} NMR (CD_3CN): $\delta = 128.2$, 130.4, 133.3, 134.6 (each m, Ph); ^{31}P{^{1}H} NMR (CD_3CN): $\delta = 22.3$ (s); ^{73}Ge NMR (CH_3CN): $\delta = -290.6$ (s, $\Delta\nu_{1/2} = 15$ Hz); ^{14}N NMR (CH_3CN): $\delta = -208.0$ (s, N_γ), −288.9 (s, N_α).

3a: Yield 50% (from $GeCl_4$), colorless crystals, m.p. 197 °C; 273 °C (detonation); elemental analysis calcd (%) for $C_{10}H_8GeN_{14}$ (396.88): C 30.26, H 2.03, N 49.41; found: C 30.22, H 2.61, N 49.14; the substance did not contain chlorine; selected spectroscopic data: IR (MeCN): $\tilde{\nu} = 2120$ (s), 2097 (s, sh), 2091 (vs) ($\nu_{as}(N_3)$), 1607 cm^{-1} (w) (ν_{ring}(bipy)); ^{1}H NMR ([D$_8$]THF): $\delta = 8.06$ (ddd, 2 H, H5), 8.52 (ddd, 2 H, H4), 8.81 (ddd, 2 H, H3), 9.35 (ddd, 2 H, H6); ^{13}C{^{1}H} NMR ([D$_8$]THF): $\delta = 124.2$, 128.9, 142.7, 144.4, 146.0 (each s, bipy); EI-MS (70 eV): *m/z* (%): 242 (1) [$M^+ -$ bipy], 200 (22) [$M^+ -$ bipy $- N_3$], 156 (100) [bipy$^+$], 116 (20) [$M^+ -$ bipy $- 3N_3$], 88 (8) [$M^+ -$ bipy $- 3N_3 - N_2$], 74 (11) [Ge$^+$].

3b$\cdot$0.5MeCN: Yield 45% (from $GeCl_4$), colorless needles, 125–130 °C (crepitation), m.p. 205 °C (decomp); elemental analysis calcd (%) for $C_{13}H_{9.5}GeN_{14.5}$ (441.41): C 35.37, H 2.17, N 46.01; found C 35.55, H 2.41, N 45.67; the substance did not contain chlorine; selected spectroscopic data: IR (MeCN): $\tilde{\nu} = 2120$ (vs), 2093 (vs, br) ($\nu_{as}(N_3)$), 1523 cm^{-1} (w) (ν_{ring}(ophen)); ^{1}H NMR ([D$_8$]THF): $\delta = 8.34$ (dd, 2 H, H3/H8), 8.41 (s, 2 H, H5/H6), 9.08 (dd, 2 H, H4/H7), 9.59 (dd, 2 H, H2/H9); ^{13}C{^{1}H} NMR ([D$_8$]THF): $\delta = 126.9$, 128.5, 130.7, 134.3, 142.9, 146.6 (each s, ophen); EI-MS (70 eV): *m/z* (%): 242 (1) [$M^+ -$ ophen], 200 (25) [$M^+ -$ ophen $- N_3$], 180 (100) [ophen$^+$], 116 (21) [$M^+ -$ ophen $- 3N_3$], 88 (9) [$M^+ -$ ophen $- 3N_3 - N_2$], 74 (16) [Ge$^+$].

4: Yield 66% (from **1a**), light yellow powder, m.p. 229 °C (decomp); elemental analysis calcd (%) for $C_{22}H_{45}CoGeN_9O_9P_3$ (804.12): C 32.86, H 5.64, N 15.68; found: C 32.83, H 5.50, N 15.14; IR (CH_2Cl_2): $\tilde{\nu} = 2112$ (m), 2093 cm^{-1} (vs) ($\nu_{as}(N_3)$); ^{1}H NMR (CD_2Cl_2): $\delta = 1.31$ (t, $^3J(H,H) = 7.1$ Hz, 18 H, 6 × CH_3), 1.71 (q, $^4J(P,H) = 2.4$ Hz, 15 H, C_5Me_5), 4.22 (m, 12 H, 6 × CH_2); ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta = 116.7$ (s); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta =$ 10.1 (s, $C_5\mathit{Me}_5$), 16.2 (pseudo-q, $^3J(P,C) = 6.5$ Hz, $CH_2\mathit{C}H_3$), 63.3 (pseudo-q, $^2J(P,C) = 10.6$ Hz, $\mathit{C}H_2CH_3$), 102.5 (q, $^2J(P,C) = 1.5$ Hz, C_5Me_5).

Received July 17, 2000 [Z15460]

[1] a) T. Grewer, *Thermal Hazards of Chemical Reactions*, *Industrial Safety Series 4*, Elsevier, Amsterdam, **1994**; b) *Bretherick's Handbook of Reactive Chemical Hazards*, 5. ed. (Ed.: P. G. Urben), Butterworth–Heinemann, **1995**.

[2] a) E. Wiberg, H. Michaud, *Z. Naturforsch. B* **1954**, *9*, 500–501; b) U. Müller, K. Dehnicke, *Angew. Chem.* **1966**, *78*, 825–826; *Angew. Chem. Int. Ed. Engl.* **1966**, *5,* 841–842; c) W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer, K. Feldl, *Chem. Ber.* **1967**, *100*, 2335–2361; d) U. Müller, H. Bärnighausen, *Acta Crystallogr. Sect. B* **1970**, *26*, 1671–1679; e) J. E. Drake, R. T. Hemmings, *Can. J. Chem.* **1973**, *51*, 302–311; f) C. S. Choi, E. Prince, W. L. Garrett, *Acta Crystallogr. Sect. B* **1977**, *33*, 3536–3537; g) D. Fenske, H.-D. Dörner, K. Dehnicke, *Z. Naturforsch. B* **1983**, *38*, 1301–1303; h) K. Polborn, E. Leidl, W. Beck, *Z. Naturforsch. B* **1988**, *43*, 1206–1208; i) M. A. Petrie, J. A. Sheehy, J. A. Boatz, G. Rasul, G. K. S. Prakash, G. A. Olah, K. O. Christe, *J. Am. Chem. Soc.* **1997**, *119*, 8802–8808.

[3] A. C. Filippou, P. Portius, G. Kociok-Köhn, *Chem. Commun.* **1998**, 2327–2328.

[4] A. C. Filippou, P. Portius, G. Kociok-Köhn, V. Albrecht, *J. Chem. Soc. Dalton Trans.* **2000**, 1759–1768, and references therein.

[5] Selected literature on other main group element compounds with a high nitrogen content: a) E. Wiberg, H. Michaud, *Z. Naturforsch. B* **1954**, *9*, 495–499; b) P. I. Paetzold, M. Gayoso, K. Dehnicke, *Chem. Ber.* **1965**, *98*, 1173–1180; c) N. Wiberg, W.-Ch. Joo, K. H. Schmid, *Z. Anorg. Allg. Chem.* **1972**, *394*, 197–208; d) W. Buder, A. Schmidt, *Z. Anorg. Allg. Chem.* **1975**, *415*, 263–267; e) P. Volgnandt, A. Schmidt, *Z. Anorg. Allg. Chem.* **1976**, *425*, 189–192; f) K. Dehnicke, *Angew. Chem.* **1979**, *91*, 527–534; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 507–514; g) K. B. Dillon, A. W. G. Platt, T. C. Waddington, *J. Chem. Soc. Dalton Trans.* **1980**, 1036–1041; h) T. M. Klapötke, *Chem. Ber.* **1997**, *130*, 443–451; i) K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, *Angew. Chem.* **1999**, *111*, 2112–2118; *Angew. Chem. Int. Ed.* **1999**, *38*, 2004–2009; j) R. T. Paine, W. Koestle, T. T. Borek, G. L. Wood, E. A. Pruss, E. N. Duesler, M. A. Hiskey, *Inorg. Chem.* **1999**, *38*, 3738–3743; k) T. M. Klapötke, H. Nöth, T. Schütt, M. Warchhold, *Angew. Chem.* **2000**, *112*, 2197–2199; *Angew. Chem. Int. Ed.* **2000**, *39*, 2108–2109.

[6] The reaction of $GeCl_4$ with NaN_3 and the workup of the reaction solution was carried out many times following the method described for the preparation of $Ge(N_3)_4$.[2e] In none of the experiments could we detect $Ge(N_3)_4$. The solvate **1a** rapidly looses solvent at room temperature in an argon stream or under fine vacuum and is thereby transformed into an amorphous white powder of varying composition. On one occasion a violent explosion occured upon grinding a sample of **1a**, which had been dried under vacuum at room temperature for several hours, with a stainless-steel spatula. We assume that on prolonged drying under vacuum **1a** decomposes through loss of the solvent to give NaN_3 and inherent $Ge(N_3)_4$, which is probably very sensitive to friction. Therefore it is recommended that the crystal mass of **1a** obtained from the reaction of $GeCl_4$ and NaN_3 should be dried only briefly under vacuum and, that for all syntheses involving **1a** plastic spatulas should be used.

[7] Crystal structure determination of **1a**: $C_{16}H_{34}GeN_{18}Na_2O_4$, $M_r = 661.20$; colorless rectangular parallelepipeds ($1.2 \times 1.1 \times 0.5$ mm), from THF/Et_2O upon diffusion at room temperature; monoclinic, space group $P2_1/c$, $a = 14.356(14)$, $b = 15.686(13)$, $c = 15.542(13)$ Å, $\alpha = \gamma = 90$, $\beta = 116.63(7)^\circ$, $V = 3129(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.404$ g cm^{-3}, $T = 180(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 1.020$ mm^{-1}, $F(000) = 1360$, 3891 reflections, 3891 unique reflections, 370 parameters, $R_1 = 0.0611$ $[I > 2\sigma(I)]$, $wR_2 = 0.1541$, GOF = 1.088, min./max. residual electron density $-0.774/0.879$ e Å^{-3}. Crystal structure determination of **2**: $C_{72}H_{60}GeN_{20}P_4$, $M_r = 1401.89$; colorless prisms ($0.76 \times 0.43 \times 0.23$ mm) from MeCN/Et_2O upon diffusion at -28 °C; triclinic, space group $P-1$, $a = 11.569(4)$, $b = 12.790(4)$, $c = 13.452(5)$ Å, $\alpha = 65.04(4)$, $\beta = 71.33(4)$, $\gamma = 75.59(4)^\circ$, $V = 1694.6(11)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.374$ g cm^{-3}, $T = 160(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 0.589$ mm^{-1}, $F(000) = 724$, 18588 reflections, 6250 unique reflections, 439 parameters, $R_1 = 0.0474$ $[I > 2\sigma(I)]$, $wR_2 = 0.1296$, GOF = 1.070, min./max. residual electron density $-0.964/0.512$ e Å^{-3}. Crystal structure determination of **3a**: $C_{10}H_8GeN_{14}$, $M_r = 396.89$; colorless crystals ($0.64 \times 0.40 \times 0.28$ mm) from MeCN upon cooling from room temperature to -28 °C; triclinic, space group $P-1$, $a = 8.025(2)$, $b = 10.254(5)$, $c = 10.856(4)$ Å, $\alpha = 65.39(4)$, $\beta = 75.24(4)$, $\gamma = 68.70(4)^\circ$, $V = 751.0(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.755$ g cm^{-3}, $T = 180(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 2.070$ mm^{-1}, $F(000) = 396$, 8634 reflections, 3333 unique reflections, 226 parameters, $R_1 = 0.0255$ $[I > 2\sigma(I)]$, $wR_2 = 0.0670$, GOF = 1.059, min./max. residual electron density $-0.508/0.416$ e Å^{-3}. Instruments: STOE-STADI4 four-circle diffractometer with scintillation counter (**1a**) and STOE-IPDS diffractometer with area detector (**2**, **3a**). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147160 (**1a**), -147159 (**2**), and -147161 (**3a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] a) H. Bock, K. Ruppert, D. Fenske, *Angew. Chem.* **1989**, *101*, 1717–1719; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1685–1687; b) J. Knizek, I. Krossing, H. Nöth, H. Schwenk, T. Seifert, *Chem. Ber.* **1997**, *130*, 1053–1062; c) S. Wingerter, M. Pfeiffer, F. Baier, T. Stey, D. Stalke, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1121–1130.

[9] a) D. L. Kepert, *Inorg. Chem.* **1973**, *12*, 1938–1949; b) D. L. Kepert, *Inorganic Stereochemistry*, Springer, Berlin, **1982**.

[10] a) E. Weiss, *Angew. Chem.* **1993**, *105*, 1565–1587; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1501–1523, and references therein; b) J. Ellermann, M. Schütz, F. W. Heinemann, M. Moll, *Z. Anorg. Allg. Chem.* **1998**, *624*, 257–262, and references therein.

[11] The investigation of the impact sensitivity using the drop hammer of the Bundesanstalt für Materialforschung und -prüfung showed a safe decomposition of **2** in each of three experiments involving an impact energy of 40 and 50 J: H. Koenen, K. H. Ide, K.-H. Swart, *Sicherheitstechnische Kenndaten explosionsfähiger Stoffe*, I. Mitteilung Prüfverfahren der Bundesanstalt für Materialprüfung (BAM), Berlin-Dahlem, *Explosivstoffe* **1961**, *9*, p. 4 ff. and 30 ff.

[12] The shortest distances are found between the N_α azide nitrogen atoms of the $[Ge(N_3)_6]^{2-}$ ions and the phenyl protons of the $(PPN)^+$ ions. These distances are 2.50 Å and are shorter than the sum of the van der Waals radii of the two atoms ($r_W(N) = 1.55$ Å, $r_W(H) = 1.20-1.45$ Å): a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451; b) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, F. A. Van-Catledge, *J. Am. Chem. Soc.* **1968**, *90*, 1199–1210.

[13] The gradient corrected functionals BP86 and BLYP (A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824; C. Lee, W. Yang, R. G. Parr, Phys. Rev. B **1988**, *37*, 785–789) were used in conjunction with the dzp basis set (A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577). The calculations were carried out using the Turbomole 4.0 program package (R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169).

[14] As a result of the large nuclear quadrupole moment the ^{73}Ge nucleus can only be detected in a symmetrical environment: a) E. Liepins, I. Zicmane, E. Lukevics, *J. Organomet. Chem.* **1988**, *341*, 315–333; b) E. Kupce, L. M. Ignatovich, E. Lukevics, *J. Organomet. Chem.* **1989**, *372*, 189–191.

[15] a) M. Witanowski, *J. Am. Chem. Soc.* **1968**, *90*, 5683–5689; b) W. Beck, W. Becker, K. F. Chew, W. Derbyshire, N. Logan, D. M. Revitt, D. B. Sowerby, *J. Chem. Soc. Dalton Trans.* **1972**, 245–247.

[16] W. Schnick, *Angew. Chem.* **1999**, *111*, 3511–3512; *Angew. Chem. Int. Ed.* **1999**, *38*, 3309–3310, and references therein.

[17] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie, Vol. II*, F. Enke, Stuttgart, **1978**, p. 721, method I.

[18] A. Martinsen, J. Songstad, *Acta Chem. Scand. A* **1977**, *31*, 645–650.