Electronic Supplementary Information

Synthesis and structure of the azidogermyliumylidene azide complex $[L(N_3)Ge:]^+N_3^-$ with covalently and ionic bonded azide ligands at germanium(II) [L = bis(N-heterocyclic carbene)]

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A. Experimental Section

General Considerations

All experiments except the synthesis of the ligand precursors were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. Compound **1** was synthesized as in our previous work. [1] The NMR spectra were recorded with Bruker spectrometers ARX200 and AV400 referenced to residual solvent signals as internal standards (^{1}H and ^{13}C{H}). Abbreviations: s = singlet; d = doublet; t = triplet; q = quint, sept = septet; m = multiplet; br = broad. Elemental analyses and ESI-MS were performed by the analytical labor and MS-Service in the Institute of Chemistry, Technical University of Berlin, Germany. IR spectra were measured with a FT-IR Spectrometer (PerkinElmer Spectrum 100).

Single-Crystal X-ray Structure Determination

Crystals were each mounted on a glass capillary in per-fluorinated oil and measured in a cold N_2 flow. The data of **2** and **3** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo *Kα*-radiation, λ = 0.71073 Å), and the date of **4** were collected on an Oxford Diffraction Supernova, Single source at offset, Atlas at 150 K (Cu- *Kα*-radiation, λ = 1.5418 Å). The structures were solved by Direct Method and refined on F^2 with the *SHELX-97* [2] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC-935359 (compound **2**), 935360 (compound **3**), 935361 (compound **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk./data_request/cif.

A1. Synthesis and Characterization

Compound 2. To a solution of **1** (0.48 g, 0.78 mmol) in acetonitrile (30 mL) was added NaN_3 (0.10 g, 1.5 mmol) at room temperature. The reaction mixture was stirred for 4h. The product **2** was separated from NaCl by filtration and recrystallized in acetonitrile at -20 °C. It afforded 0.40 g (0.64 mmol, 82%) of compound **2**. M.p. 125 ºC (decomp.); ^{1}H NMR (200.13 MHz, [D$_3$]acetonitrile, 25 ºC): δ = 1.05 (d, ^3J (H,H) = 6.8 Hz, 12 H; CH(C*H*$_3$)$_2$), 1.14 (d, ^3J (H,H) = 6.8 Hz, 12 H; CH(C*H*$_3$)$_2$), 2.44 (sept, ^3J (H,H) = 6.8 Hz, 4 H; C*H*(CH$_3$)$_2$), 6.91 (s, 2 H; C*H*$_2$), 7.34 (d, ^3J (H,H) = 7.4 Hz, 4 H; *Ph*), 7.47 (dd, ^3J (H,H) = 7.2 Hz, 7.4 Hz, 2 H; *Ph*), 7.51 (d, ^3J (H,H) = 1.8 Hz, 2 H; C*H*(imid)), 8.04 ppm (d, ^3J (H,H) = 1.8 Hz, 2 H, C*H*(imid)); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_3$]acetonitrile, 25 ºC): δ = 22.5, 25.1 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 62.8 (*C*H$_2$), 123.5, 124.7, 125.6, 131.6, 132.1, 146.2, 166.9 ppm; ESI-MS: *m*/*z*: 469.33118 (calc. 469.33257 [M-GeN$_6$ +H]$^+$. IR(KBr, cm^{-1}): 2965(s), 2928(w), 2868(w), 2077(vs, N_3^-), 2003(vs, N_3^-), 1470(m), 1384(vs), 1273(m), 1193(s), 1119(m), 1059(m), 903(m), 765(m); elemental analysis calcd. (%) for $C_{31}H_{40}N_{10}Ge$ (molecular weight 625.31 g mol^{-1}): C 59.54, H 6.45, N 22.40; found: C 59.24, H 6.32, N 22.34.

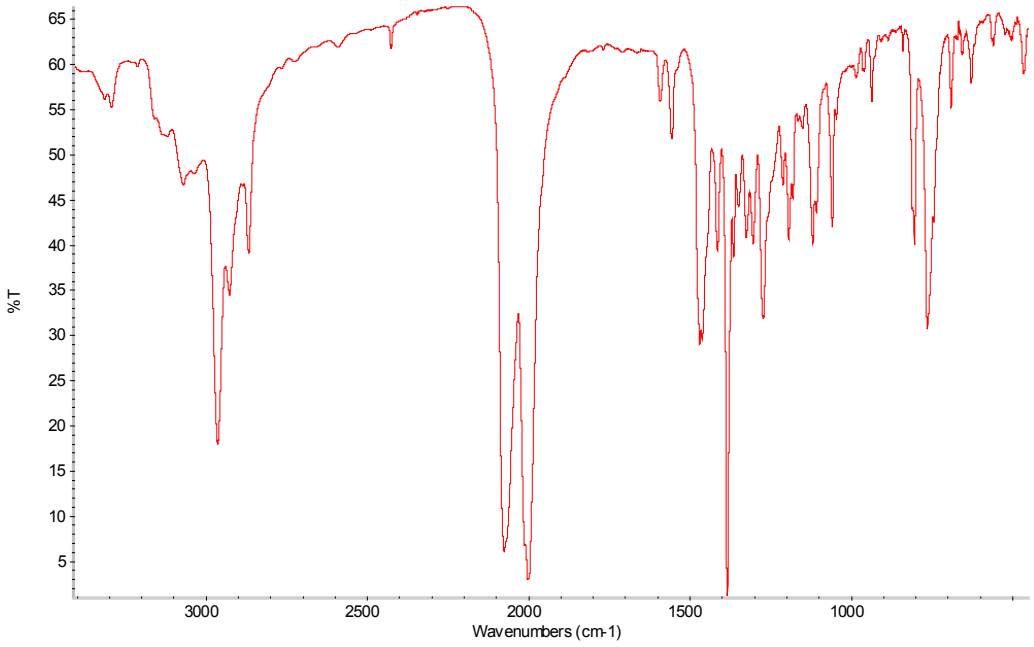
Compound 3. THF (50 mL) was added to a mixture of **1** (0.76 g, 1.2 mmol) and $NaBPh_4$ (0.42 g, 1.2 mmol) at room temperature. The reaction mixture was stirred overnight. Compound **3** was separated from NaCl by filtration and dried under vacuum. Single crystals suitable for X-ray diffraction analysis were grown in acetonitrile at -20 °C. It afforded 0.92 g (1.0 mmol, 83%) of compound **3**. M.p. 236 ºC (decomp.); ^{1}H NMR (200.13 MHz, [D$_3$]acetonitrile, 25 ºC): δ = 1.05 (d, ^3J (H,H) = 6.8 Hz, 12 H; CH(C*H*$_3$)$_2$), 1.08 (d, ^3J (H,H) = 6.8 Hz, 12 H; CH(C*H*$_3$)$_2$), 2.36 (sept, ^3J (H,H) = 6.8 Hz, 4 H; C*H*(CH$_3$)$_2$), 6.43 (s, 2 H; C*H*$_2$), 6.82 (dd, ^3J (H,H) = 7.1, 7.6 Hz, 4 H; B*Ph*$_4$), 6.98 (dd, ^3J (H,H) = 7.1 Hz, 7.2 Hz, 8 H; B*Ph*$_4$), 7.28 (b, 8 H; B*Ph*$_4$), 7.34 (d, ^3J (H,H) = 8.0 Hz, 4 H, *Ph*), 7.48 (d, 2 H; ^3J (H,H) = 1.9 Hz, C*H*(imid), 7.53 (dd, ^3J (H,H) = 7.0, 8.0 Hz, 2 H; *Ph*), 7.70 (d, ^3J (H,H) = 1.9 Hz, 2 H; C*H*(imid)); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_3$]acetonitrile, 25 ºC): δ = 22.8, 24.5 (CH(*C*H$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 61.8 (*C*H$_2$), 121.8 (B*Ph*$_4$), 123.6, 124.4, 125.1, 126.0 (q, ^2J (C, B) = 2.6 Hz, B*Ph*$_4$), 131.5, 131,6, 135.8 (q, ^3J (C, B) = 1.3 Hz, B*Ph*$_4$), 145.9, 163.8 (q, ^1J (C, B) = 49 Hz, B*Ph*$_4$), 165.9 ppm (carbene *C*); ^{11}B NMR (64.21 MHz, [D$_3$]acetonitrile, 25 ºC): δ =-6.54 ppm (q, ^2J (B,C) =2.48 Hz, *B*Ph$_4$); ESI-MS: *m*/*z*: 577.21492 (calc. 577.21478 [M-BPh$_4$]$^+$, ESI-MS: *m*/*z* (negative ion mode): 319.16512 (calc. 319.16526); elemental analysis calcd. (%) for $C_{55}H_{60}N_4GeBCl$ (molecular weight 895.96 g mol^{-1}): C 73.73, H 6.75, N 6.25; found: C 73.34, H 6.66, N 6.30.

Compound 4. To a solution of **3** (0.23 g, 0.26 mmol) in acetonitrile (15 mL) was added NaN_3 (0.024 g, 0.37 mmol) at room temperature. The reaction mixture was stirred for 4 days. Compound **4** was separated from NaCl and the excess of NaN_3 by centrifugation. The clear solution was concentrated to 3 mL and stored at -20 ºC. It afforded 0.21 g (0.23 mmol, 88 %) of compound **4**. M.p. 157 ºC (decomp.); ^{1}H NMR (200.13 MHz, [D$_3$]acetonitrile, 25 ºC): δ = 1.07 (d, ^3J (H,H) = 6.8 Hz, 12 H; CH(C*H*$_3$)$_2$), 1.16 (d, ^3J (H,H) = 6.8 Hz, 12 H; CH(C*H*$_3$)$_2$), 2.38 (sept, ^3J (H,H) = 6.8 Hz, 4 H; C*H*(CH$_3$)$_2$), 6.17 (s, 2 H; C*H*$_2$), 6.82 (dd, ^3J (H,H) = 7.1, 7.2 Hz, 4 H; B*Ph*$_4$), 6.99 (dd, ^3J (H,H) = 7.1 Hz, 7.5 Hz, 8 H; B*Ph*$_4$), 7.30 (b, 8 H; B*Ph*$_4$), 7.36 (d, ^3J (H,H) = 7.3 Hz, 4 H, *Ph*), 7.48 (d, 2 H; ^3J (H,H) = 1.8 Hz, C*H*(imid), 7.53 (dd, ^3J (H,H) = 7.0, 7.3 Hz, 2 H; *Ph*), 7.59 (d, ^3J (H,H) = 1.8 Hz, 2 H; C*H*(imid)); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_3$]acetonitrile, 25 ºC): δ = 22.6, 25.0 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 62.6 (*C*H$_2$), 122.2 (B*Ph*$_4$), 123.5, 124.8, 125.8, 126.0 (q, ^2J (C, B) = 2.6 Hz, B*Ph*$_4$), 131.8, 131.9, 136.0 (q, ^3J (C, B) = 1.3 Hz, B*Ph*$_4$), 146.1, 164,0 (q, ^1J (C, B) = 49 Hz, B*Ph*$_4$), 165.8 ppm (carbene *C*); ^{11}B NMR (64.21 MHz, [D$_3$]acetonitrile, 25 ºC): δ =-6.52 ppm (q, ^2J (B,C) =2.45 Hz, *B*Ph$_4$); ESI-MS: *m*/*z*: 584.25513 (calc. 584.25515 [M-BPh$_4$]$^+$, ESI-MS: *m*/*z* (negative ion mode): 319.16514 (calc. 319.16526). IR(KBr, cm^{-1}): 3123(w), 3054(w),

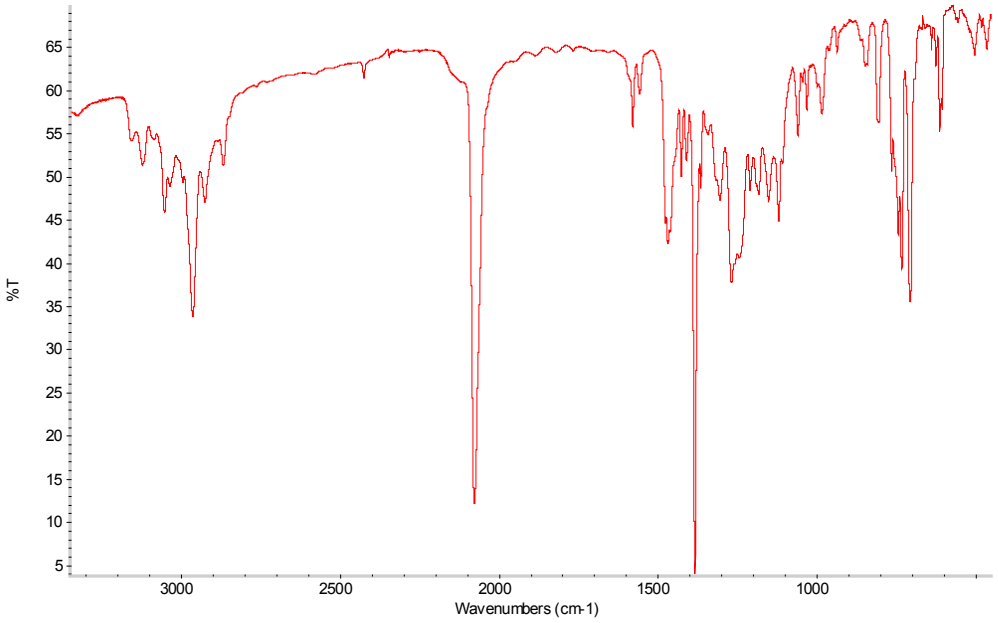
2966(s), 2078(vs, N_3^-), 1580(w), 1469(s), 1427(w), 1384(vs), 1366(w), 1305(m), 1269(s), 1210(w), 1120(m), 1059(w), 984(w), 805(m), 764(m), 732(s), 706(s), 614(m); elemental analysis calcd. (%) for $C_{55}H_{60}N_7GeB$ (molecular weight 902.53 g mol^{-1}): C 73.20, H 6.70, N 10.86; found: C 72.92, H 6.49, N 10.90.

A2. IR Spectra of 2 and 4

IR Spectrum of 2 (KBr)



IR Spectrum of 4 (KBr)



A3. Crystallographic data

For Compound 2:

Figure S 1. Molecular structure of compound **2**. Thermal ellipsoids are drawn at 50% probability level. H atoms, and CH_3CN molecules are omitted for clarity.

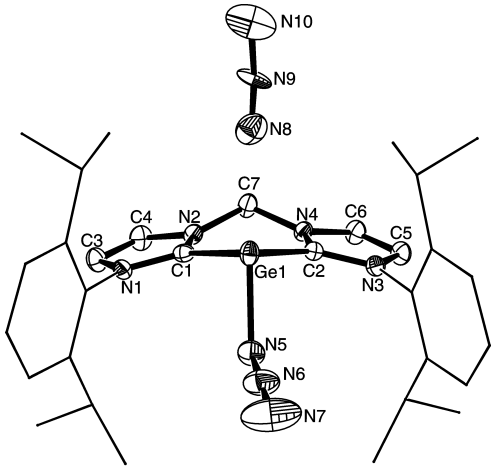


Table S1. Crystal data and structure refinement for **2**.

Empirical formula	C37 H49 Ge N13	
Formula weight	748.48	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 18.2975(12) Å	α= 90°.
	b = 15.6680(6) Å	β= 114.497(9)°.
	c = 15.2402(11) Å	γ = 90°.
Volume	3975.8(4) $Å^3$	
Z	4	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.814 mm^{-1}	
F(000)	1576	
Crystal size	0.52 x 0.28 x 0.21 mm^3	
Theta range for data collection	3.57 to 25.00°.	

Index ranges	-21<=h<=21, -14<=k<=18, -18<=l<=15
Reflections collected	16291
Independent reflections	6881 [R(int) = 0.0360]
Completeness to theta = 25.00°	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.56494
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6881 / 0 / 471
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0761
R indices (all data)	R1 = 0.0520, wR2 = 0.0816
Largest diff. peak and hole	0.359 and -0.503 e.Å^{-3}

Table S2. Interatomic distances [Å] and angles [°] for compound **2**.

Ge(1)-N(5)	2.037(2)
Ge(1)-C(2)	2.046(2)
Ge(1)-C(1)	2.051(2)
N(1)-C(1)	1.341(3)
N(1)-C(3)	1.378(3)
N(1)-C(8)	1.442(3)
C(1)-N(2)	1.347(3)
C(2)-N(4)	1.342(3)
C(2)-N(3)	1.345(3)
N(3)-C(5)	1.380(3)
N(3)-C(20)	1.446(3)
C(3)-C(4)	1.341(3)
N(4)-C(6)	1.377(3)
N(4)-C(7)	1.453(3)
C(4)-N(2)	1.375(3)
N(5)-N(6)	1.199(3)
C(5)-C(6)	1.343(3)
N(6)-N(7)	1.148(3)
C(7)-N(2)	1.455(3)
N(8)-N(9)	1.098(3)
C(8)-C(9)	1.394(3)
C(8)-C(13)	1.397(3)
N(9)-N(10)	1.185(3)
C(9)-C(10)	1.393(3)
C(9)-C(17)	1.516(3)

C(10)-C(11)	1.377(4)
N(11)-C(32)	1.121(4)
C(11)-C(12)	1.373(4)
N(12)-C(34)	1.123(3)
C(12)-C(13)	1.387(3)
N(13)-C(36)	1.126(6)
C(13)-C(14)	1.513(3)
C(14)-C(15)	1.524(3)
C(14)-C(16)	1.530(4)
C(17)-C(19)	1.508(3)
C(17)-C(18)	1.514(3)
C(20)-C(21)	1.390(3)
C(20)-C(25)	1.396(3)
C(21)-C(22)	1.393(3)
C(21)-C(29)	1.513(4)
C(22)-C(23)	1.379(4)
C(23)-C(24)	1.366(4)
C(24)-C(25)	1.388(3)
C(25)-C(26)	1.513(4)
C(26)-C(27)	1.523(4)
C(26)-C(28)	1.523(3)
C(29)-C(30)	1.522(4)
C(29)-C(31)	1.529(4)
C(32)-C(33)	1.427(4)
C(34)-C(35)	1.445(4)
C(36)-C(37)	1.448(6)

N(5)-Ge(1)-C(2)	89.14(8)
N(5)-Ge(1)-C(1)	89.38(8)
C(2)-Ge(1)-C(1)	84.49(9)
C(1)-N(1)-C(3)	110.74(18)
C(1)-N(1)-C(8)	125.20(18)
C(3)-N(1)-C(8)	123.88(18)
N(1)-C(1)-N(2)	104.87(19)
N(1)-C(1)-Ge(1)	127.28(16)
N(2)-C(1)-Ge(1)	127.79(16)
N(4)-C(2)-N(3)	104.88(18)
N(4)-C(2)-Ge(1)	127.97(15)
N(3)-C(2)-Ge(1)	127.01(16)
C(2)-N(3)-C(5)	110.71(18)

C(2)-N(3)-C(20)	125.05(18)
C(5)-N(3)-C(20)	124.23(18)
C(4)-C(3)-N(1)	107.0(2)
C(2)-N(4)-C(6)	111.20(18)
C(2)-N(4)-C(7)	126.18(18)
C(6)-N(4)-C(7)	122.20(18)
C(3)-C(4)-N(2)	106.4(2)
N(6)-N(5)-Ge(1)	114.40(18)
C(6)-C(5)-N(3)	106.8(2)
N(7)-N(6)-N(5)	177.0(3)
C(5)-C(6)-N(4)	106.40(19)
N(4)-C(7)-N(2)	111.87(17)
C(9)-C(8)-C(13)	123.5(2)
C(9)-C(8)-N(1)	117.53(19)
C(13)-C(8)-N(1)	119.0(2)
N(8)-N(9)-N(10)	173.0(3)
C(10)-C(9)-C(8)	116.9(2)
C(10)-C(9)-C(17)	120.1(2)
C(8)-C(9)-C(17)	122.9(2)
C(11)-C(10)-C(9)	120.8(2)
C(12)-C(11)-C(10)	120.7(2)
C(11)-C(12)-C(13)	121.3(2)
C(12)-C(13)-C(8)	116.7(2)
C(12)-C(13)-C(14)	120.5(2)
C(8)-C(13)-C(14)	122.8(2)
C(13)-C(14)-C(15)	111.5(2)
C(13)-C(14)-C(16)	111.3(2)
C(15)-C(14)-C(16)	110.4(2)
C(19)-C(17)-C(18)	110.9(2)
C(19)-C(17)-C(9)	112.8(2)
C(18)-C(17)-C(9)	110.3(2)
C(21)-C(20)-C(25)	124.2(2)
C(21)-C(20)-N(3)	118.0(2)
C(25)-C(20)-N(3)	117.8(2)
C(20)-C(21)-C(22)	116.6(2)
C(20)-C(21)-C(29)	122.6(2)
C(22)-C(21)-C(29)	120.7(2)
C(23)-C(22)-C(21)	120.6(3)
C(24)-C(23)-C(22)	121.1(2)
C(23)-C(24)-C(25)	121.3(3)

C(24)-C(25)-C(20)	116.3(2)
C(24)-C(25)-C(26)	121.1(2)
C(20)-C(25)-C(26)	122.6(2)
C(25)-C(26)-C(27)	111.7(2)
C(25)-C(26)-C(28)	112.7(2)
C(27)-C(26)-C(28)	110.0(2)
C(21)-C(29)-C(30)	113.0(2)
C(21)-C(29)-C(31)	109.9(2)
C(30)-C(29)-C(31)	111.2(2)
N(11)-C(32)-C(33)	179.0(4)
N(12)-C(34)-C(35)	178.5(4)
N(13)-C(36)-C(37)	177.9(5)
C(1)-N(2)-C(4)	111.06(18)
C(1)-N(2)-C(7)	125.86(19)
C(4)-N(2)-C(7)	122.41(18)

For Compound 3:

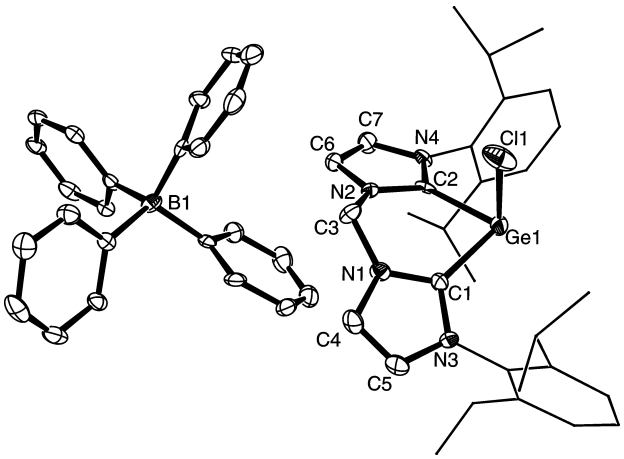


Figure S2. Molecular structure of compound **3**. Thermal ellipsoids are drawn at 50% probability level. H atoms and CH_3CN molecules are omitted for clarity.

Table S3. Crystal data and structure refinement for **3**.

Empirical formula	C58 H64.50 B Cl Ge N5.50
Formula weight	957.50
Temperature	150(2) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	p21/c	
Unit cell dimensions	a = 14.1255(12) Å	α= 90°.
	b = 12.1448(9) Å	β= 91.799(8)°.
	c = 31.202(3) Å	γ = 90°.
Volume	5350.1(7) $Å^3$	
Z	4	
Density (calculated)	1.189 Mg/m^3	
Absorption coefficient	0.664 mm^{-1}	
F(000)	2020	
Crystal size	0.14 x 0.12 x 0.10 mm^3	
Theta range for data collection	3.38 to 25.00°.	
Index ranges	-16<=h<=16, -14<=k<=14, -37<=l<=37	
Reflections collected	22821	
Independent reflections	9398 [R(int) = 0.1160]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.15401	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9398 / 36 / 627	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0793, wR2 = 0.1360	
R indices (all data)	R1 = 0.1337, wR2 = 0.1582	
Largest diff. peak and hole	0.850 and -0.916 $e.Å^{-3}$	

Table S4. Selected interatomic distances [Å] and angles [°] for compound **3**.

Ge(1)-C(1)	2.045(4)
Ge(1)-C(2)	2.048(4)
Ge(1)-Cl(1)	2.3078(14)
N(1)-C(1)	1.357(5)
N(1)-C(4)	1.376(5)
N(1)-C(3)	1.462(5)
C(1)-N(3)	1.344(5)
B(1)-C(32)	1.631(7)
B(1)-C(50)	1.636(6)
B(1)-C(44)	1.642(7)
B(1)-C(38)	1.647(6)
C(18B)-C(17)	1.60(3)
C(19B)-C(17)	1.28(2)

N(2)-C(2)	1.351(5)
N(2)-C(6)	1.374(5)
N(2)-C(3)	1.457(5)
C(2)-N(4)	1.339(5)
N(3)-C(5)	1.370(5)
N(3)-C(8)	1.456(5)
N(4)-C(7)	1.391(5)
N(4)-C(20)	1.443(5)
C(4)-C(5)	1.340(6)
N(5)-C(56)	1.122(7)
N(6)-C(58)	1.116(15)
C(6)-C(7)	1.342(6)
C(8)-C(9)	1.392(6)
C(8)-C(13)	1.395(6)
C(9)-C(10)	1.389(6)
C(9)-C(14)	1.513(7)
C(10)-C(11)	1.367(7)
C(11)-C(12)	1.371(7)
C(12)-C(13)	1.391(6)
C(13)-C(17)	1.504(7)
C(14)-C(15)	1.487(8)
C(14)-C(16)	1.552(8)
C(17)-C(18A)	1.427(12)
C(17)-C(19A)	1.632(10)
C(20)-C(25)	1.396(6)
C(20)-C(21)	1.397(6)
C(21)-C(22)	1.401(7)
C(21)-C(26)	1.509(7)
C(22)-C(23)	1.378(7)
C(23)-C(24)	1.366(7)
C(24)-C(25)	1.380(7)
C(25)-C(29)	1.514(7)
C(26)-C(27)	1.524(7)
C(26)-C(28)	1.536(7)
C(29)-C(31)	1.516(7)
C(29)-C(30)	1.531(7)
C(32)-C(33)	1.405(6)
C(32)-C(37)	1.407(6)
C(33)-C(34)	1.381(6)
C(34)-C(35)	1.373(7)

C(35)-C(36)	1.384(7)
C(36)-C(37)	1.389(6)
C(38)-C(43)	1.388(6)
C(38)-C(39)	1.408(6)
C(39)-C(40)	1.399(6)
C(40)-C(41)	1.370(7)
C(41)-C(42)	1.386(6)
C(42)-C(43)	1.396(6)
C(44)-C(45)	1.397(6)
C(44)-C(49)	1.407(6)
C(45)-C(46)	1.392(6)
C(46)-C(47)	1.383(6)
C(47)-C(48)	1.395(7)
C(48)-C(49)	1.374(6)
C(50)-C(51)	1.397(6)
C(50)-C(55)	1.419(6)
C(51)-C(52)	1.383(6)
C(52)-C(53)	1.399(6)
C(53)-C(54)	1.368(6)
C(54)-C(55)	1.382(6)
C(56)-C(57)	1.460(7)
C(58)-C(59)	1.408(16)

C(1)-Ge(1)-C(2)	84.86(16)
C(1)-Ge(1)-Cl(1)	92.02(13)
C(2)-Ge(1)-Cl(1)	91.71(12)
C(1)-N(1)-C(4)	110.9(4)
C(1)-N(1)-C(3)	123.8(4)
C(4)-N(1)-C(3)	125.1(3)
N(3)-C(1)-N(1)	104.0(4)
N(3)-C(1)-Ge(1)	128.1(3)
N(1)-C(1)-Ge(1)	127.9(3)
C(32)-B(1)-C(50)	111.7(4)
C(32)-B(1)-C(44)	113.0(4)
C(50)-B(1)-C(44)	103.7(3)
C(32)-B(1)-C(38)	102.7(3)
C(50)-B(1)-C(38)	114.9(4)
C(44)-B(1)-C(38)	111.2(4)
C(2)-N(2)-C(6)	110.3(4)
C(2)-N(2)-C(3)	125.4(4)

C(6)-N(2)-C(3)	123.7(3)
N(4)-C(2)-N(2)	106.1(4)
N(4)-C(2)-Ge(1)	127.5(3)
N(2)-C(2)-Ge(1)	126.4(3)
C(1)-N(3)-C(5)	111.7(4)
C(1)-N(3)-C(8)	122.7(4)
C(5)-N(3)-C(8)	125.5(4)
N(2)-C(3)-N(1)	110.5(3)
C(2)-N(4)-C(7)	109.7(4)
C(2)-N(4)-C(20)	124.6(4)
C(7)-N(4)-C(20)	125.7(4)
C(5)-C(4)-N(1)	106.7(4)
C(4)-C(5)-N(3)	106.6(4)
C(7)-C(6)-N(2)	106.9(4)
C(6)-C(7)-N(4)	107.1(4)
C(9)-C(8)-C(13)	124.9(4)
C(9)-C(8)-N(3)	118.0(4)
C(13)-C(8)-N(3)	117.1(4)
C(10)-C(9)-C(8)	116.0(4)
C(10)-C(9)-C(14)	121.5(5)
C(8)-C(9)-C(14)	122.4(4)
C(11)-C(10)-C(9)	121.5(5)
C(10)-C(11)-C(12)	120.4(5)
C(11)-C(12)-C(13)	122.1(5)
C(12)-C(13)-C(8)	115.2(5)
C(12)-C(13)-C(17)	121.3(5)
C(8)-C(13)-C(17)	123.5(4)
C(15)-C(14)-C(9)	113.4(5)
C(15)-C(14)-C(16)	110.8(6)
C(9)-C(14)-C(16)	109.2(5)
C(19B)-C(17)-C(18A)	124.1(13)
C(19B)-C(17)-C(13)	121.9(13)
C(18A)-C(17)-C(13)	113.8(7)
C(19B)-C(17)-C(18B)	116.7(16)
C(18A)-C(17)-C(18B)	29.4(10)
C(13)-C(17)-C(18B)	110.9(11)
C(19B)-C(17)-C(19A)	48.1(13)
C(18A)-C(17)-C(19A)	109.8(7)
C(13)-C(17)-C(19A)	109.4(6)
C(18B)-C(17)-C(19A)	84.6(11)

C(25)-C(20)-C(21)	123.8(4)
C(25)-C(20)-N(4)	118.2(4)
C(21)-C(20)-N(4)	118.0(4)
C(20)-C(21)-C(22)	116.8(5)
C(20)-C(21)-C(26)	122.0(4)
C(22)-C(21)-C(26)	121.2(5)
C(23)-C(22)-C(21)	120.3(5)
C(24)-C(23)-C(22)	120.8(5)
C(23)-C(24)-C(25)	122.1(5)
C(24)-C(25)-C(20)	116.2(5)
C(24)-C(25)-C(29)	121.2(5)
C(20)-C(25)-C(29)	122.6(4)
C(21)-C(26)-C(27)	109.7(4)
C(21)-C(26)-C(28)	114.5(5)
C(27)-C(26)-C(28)	109.7(5)
C(25)-C(29)-C(31)	112.8(5)
C(25)-C(29)-C(30)	110.9(5)
C(31)-C(29)-C(30)	110.4(5)
C(33)-C(32)-C(37)	114.2(4)
C(33)-C(32)-B(1)	120.9(4)
C(37)-C(32)-B(1)	124.3(4)
C(34)-C(33)-C(32)	123.2(5)
C(35)-C(34)-C(33)	120.3(5)
C(34)-C(35)-C(36)	119.4(5)
C(35)-C(36)-C(37)	119.6(5)
C(36)-C(37)-C(32)	123.3(5)
C(43)-C(38)-C(39)	115.2(4)
C(43)-C(38)-B(1)	121.3(4)
C(39)-C(38)-B(1)	122.9(4)
C(40)-C(39)-C(38)	122.2(4)
C(41)-C(40)-C(39)	120.4(5)
C(40)-C(41)-C(42)	119.3(4)
C(41)-C(42)-C(43)	119.5(5)
C(38)-C(43)-C(42)	123.3(4)
C(45)-C(44)-C(49)	114.8(4)
C(45)-C(44)-B(1)	123.3(4)
C(49)-C(44)-B(1)	121.6(4)
C(46)-C(45)-C(44)	122.9(4)
C(47)-C(46)-C(45)	120.4(5)
C(46)-C(47)-C(48)	118.3(5)

C(49)-C(48)-C(47)	120.3(5)
C(48)-C(49)-C(44)	123.2(5)
C(51)-C(50)-C(55)	114.3(4)
C(51)-C(50)-B(1)	126.5(4)
C(55)-C(50)-B(1)	119.0(4)
C(52)-C(51)-C(50)	123.4(4)
C(51)-C(52)-C(53)	120.1(4)
C(54)-C(53)-C(52)	118.4(4)
C(53)-C(54)-C(55)	120.9(4)
C(54)-C(55)-C(50)	122.8(4)
N(5)-C(56)-C(57)	179.1(7)
N(6)-C(58)-C(59)	178.2(17)

For Compound 4:

Figure S 3. Molecular structure of compound **4**. Thermal ellipsoids are drawn at 50% probability level. H atoms, and one CH_3CN molecule are omitted for clarity.

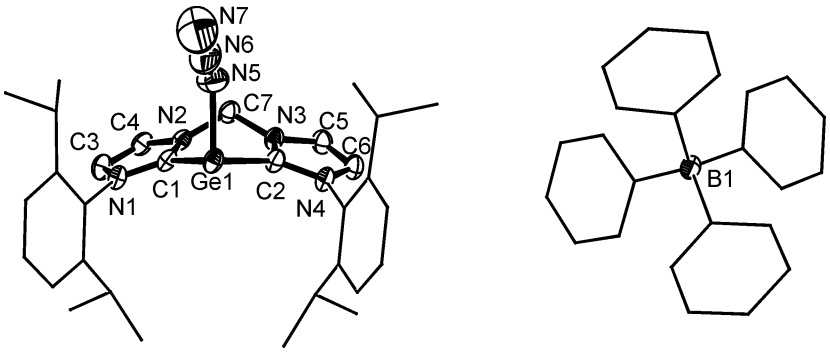


Table S5. Crystal data and structure refinement for **4**.

Empirical formula	C57 H63 B Ge N8	
Formula weight	943.55	
Temperature	150(2) K	
Wavelength	1.5418 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 14.1299(3) Å	a= 90°.
	b = 12.3150(2) Å	b= 91.667(2)°.
	c = 30.9315(7) Å	g = 90°.
Volume	5380.10(19) Å3	
Z	4	

Density (calculated)	1.165 Mg/m3
Absorption coefficient	1.099 mm-1
F(000)	1992
Crystal size	0.59 x 0.40 x 0.09 mm3
Theta range for data collection	2.86 to 67.50°.
Index ranges	-13<=h<=16, -14<=k<=14, -36<=l<=33
Reflections collected	36892
Independent reflections	9652 [R(int) = 0.0381]
Completeness to theta = 67.50°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.52801
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	9652 / 60 / 650
Goodness-of-fit on F2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1469
R indices (all data)	R1 = 0.0616, wR2 = 0.1495
Largest diff. peak and hole	1.521 and -0.540 e.Å-3

Table S6. Interatomic distances [Å] and angles [°] for compound **4**.

N(1)-C(1)	1.341(3)
N(1)-C(3)	1.383(3)
N(1)-C(8)	1.454(3)
C(1)-N(2)	1.348(3)
C(1)-Ge(1B)	2.034(6)
C(1)-Ge(1A)	2.050(3)
B(1)-C(32)	1.640(4)
B(1)-C(50)	1.644(4)
B(1)-C(38)	1.645(4)
B(1)-C(44)	1.647(4)
N(6B)-N(7B)	1.203(9)
N(6B)-N(5B)	1.206(9)
N(2)-C(4)	1.376(3)
N(2)-C(7)	1.457(3)
C(2)-N(3)	1.339(3)
C(2)-N(4)	1.343(3)
C(2)-Ge(1A)	2.054(3)
C(2)-Ge(1B)	2.083(6)
N(3)-C(5)	1.383(3)
N(3)-C(7)	1.465(3)

C(3)-C(4)	1.346(4)
N(4)-C(6)	1.383(3)
N(4)-C(20)	1.445(3)
C(5)-C(6)	1.343(4)
N(8)-C(57)	1.132(5)
C(8)-C(9)	1.387(4)
C(8)-C(13)	1.402(4)
C(9)-C(10)	1.397(4)
C(9)-C(17)	1.521(5)
C(10)-C(11)	1.380(6)
C(11)-C(12)	1.375(6)
C(12)-C(13)	1.399(5)
C(13)-C(14)	1.503(5)
C(14)-C(15)	1.539(5)
C(14)-C(16)	1.544(5)
C(17)-C(18)	1.520(6)
C(17)-C(19)	1.530(5)
C(20)-C(21)	1.393(4)
C(20)-C(25)	1.401(4)
C(21)-C(22)	1.397(4)
C(21)-C(29)	1.513(4)
C(22)-C(23)	1.382(5)
C(23)-C(24)	1.381(5)
C(24)-C(25)	1.384(4)
C(25)-C(26)	1.525(5)
C(26)-C(28)	1.465(6)
C(26)-C(27)	1.580(6)
C(29)-C(31)	1.508(6)
C(29)-C(30)	1.510(6)
C(32)-C(37)	1.403(3)
C(32)-C(33)	1.414(4)
C(33)-C(34)	1.395(4)
C(34)-C(35)	1.383(4)
C(35)-C(36)	1.383(5)
C(36)-C(37)	1.389(4)
C(38)-C(43)	1.403(4)
C(38)-C(39)	1.407(3)
C(39)-C(40)	1.385(4)
C(40)-C(41)	1.391(4)
C(41)-C(42)	1.375(4)

C(42)-C(43)	1.396(4)
C(44)-C(45)	1.400(4)
C(44)-C(49)	1.405(3)
C(45)-C(46)	1.394(4)
C(46)-C(47)	1.375(4)
C(47)-C(48)	1.392(4)
C(48)-C(49)	1.384(4)
C(50)-C(51)	1.398(4)
C(50)-C(55)	1.407(3)
C(51)-C(52)	1.385(4)
C(52)-C(53)	1.386(4)
C(53)-C(54)	1.376(4)
C(54)-C(55)	1.392(4)
C(56)-C(57)	1.459(5)
Ge(1A)-N(5A)	2.003(5)
N(5A)-N(6A)	1.179(6)
N(6A)-N(7A)	1.155(5)
Ge(1B)-N(5B)	1.870(18)

C(1)-N(1)-C(3)	110.1(2)
C(1)-N(1)-C(8)	124.0(2)
C(3)-N(1)-C(8)	125.9(2)
N(1)-C(1)-N(2)	105.5(2)
N(1)-C(1)-Ge(1B)	123.1(2)
N(2)-C(1)-Ge(1B)	130.1(2)
N(1)-C(1)-Ge(1A)	129.09(19)
N(2)-C(1)-Ge(1A)	125.34(19)
Ge(1B)-C(1)-Ge(1A)	13.10(11)
C(32)-B(1)-C(50)	112.2(2)
C(32)-B(1)-C(38)	110.82(19)
C(50)-B(1)-C(38)	104.31(19)
C(32)-B(1)-C(44)	102.42(19)
C(50)-B(1)-C(44)	112.08(19)
C(38)-B(1)-C(44)	115.3(2)
N(7B)-N(6B)-N(5B)	172(3)
C(1)-N(2)-C(4)	110.9(2)
C(1)-N(2)-C(7)	125.0(2)
C(4)-N(2)-C(7)	123.6(2)
N(3)-C(2)-N(4)	105.5(2)
N(3)-C(2)-Ge(1A)	126.16(18)

N(4)-C(2)-Ge(1A)	128.18(19)
N(3)-C(2)-Ge(1B)	130.1(2)
N(4)-C(2)-Ge(1B)	123.3(2)
Ge(1A)-C(2)-Ge(1B)	12.92(11)
C(2)-N(3)-C(5)	110.9(2)
C(2)-N(3)-C(7)	124.3(2)
C(5)-N(3)-C(7)	124.6(2)
C(4)-C(3)-N(1)	107.3(2)
C(2)-N(4)-C(6)	110.3(2)
C(2)-N(4)-C(20)	124.1(2)
C(6)-N(4)-C(20)	125.6(2)
C(3)-C(4)-N(2)	106.2(2)
C(6)-C(5)-N(3)	106.2(2)
C(5)-C(6)-N(4)	107.0(2)
N(2)-C(7)-N(3)	110.83(19)
C(9)-C(8)-C(13)	124.2(3)
C(9)-C(8)-N(1)	117.9(2)
C(13)-C(8)-N(1)	118.0(3)
C(8)-C(9)-C(10)	117.2(3)
C(8)-C(9)-C(17)	122.7(3)
C(10)-C(9)-C(17)	120.1(3)
C(11)-C(10)-C(9)	120.3(4)
C(12)-C(11)-C(10)	121.2(3)
C(11)-C(12)-C(13)	121.2(3)
C(12)-C(13)-C(8)	116.0(3)
C(12)-C(13)-C(14)	121.9(3)
C(8)-C(13)-C(14)	122.0(3)
C(13)-C(14)-C(15)	112.6(4)
C(13)-C(14)-C(16)	109.9(3)
C(15)-C(14)-C(16)	110.7(4)
C(18)-C(17)-C(9)	110.6(3)
C(18)-C(17)-C(19)	109.7(3)
C(9)-C(17)-C(19)	112.7(4)
C(21)-C(20)-C(25)	124.0(2)
C(21)-C(20)-N(4)	118.1(2)
C(25)-C(20)-N(4)	117.9(2)
C(20)-C(21)-C(22)	116.7(3)
C(20)-C(21)-C(29)	122.1(3)
C(22)-C(21)-C(29)	121.2(3)
C(23)-C(22)-C(21)	120.4(3)

C(24)-C(23)-C(22)	121.2(3)
C(23)-C(24)-C(25)	120.9(3)
C(24)-C(25)-C(20)	116.7(3)
C(24)-C(25)-C(26)	120.6(3)
C(20)-C(25)-C(26)	122.6(3)
C(28)-C(26)-C(25)	112.0(3)
C(28)-C(26)-C(27)	105.6(4)
C(25)-C(26)-C(27)	110.7(4)
C(31)-C(29)-C(30)	111.0(5)
C(31)-C(29)-C(21)	112.0(4)
C(30)-C(29)-C(21)	110.4(3)
C(37)-C(32)-C(33)	114.9(2)
C(37)-C(32)-B(1)	121.8(2)
C(33)-C(32)-B(1)	122.7(2)
C(34)-C(33)-C(32)	122.5(3)
C(35)-C(34)-C(33)	120.4(3)
C(34)-C(35)-C(36)	118.8(3)
C(35)-C(36)-C(37)	120.6(3)
C(36)-C(37)-C(32)	122.8(3)
C(43)-C(38)-C(39)	115.1(2)
C(43)-C(38)-B(1)	125.2(2)
C(39)-C(38)-B(1)	119.5(2)
C(40)-C(39)-C(38)	123.2(2)
C(39)-C(40)-C(41)	119.8(2)
C(42)-C(41)-C(40)	118.8(2)
C(41)-C(42)-C(43)	120.9(3)
C(42)-C(43)-C(38)	122.1(2)
C(45)-C(44)-C(49)	115.0(2)
C(45)-C(44)-B(1)	123.8(2)
C(49)-C(44)-B(1)	120.8(2)
C(46)-C(45)-C(44)	122.5(3)
C(47)-C(46)-C(45)	120.7(3)
C(46)-C(47)-C(48)	118.6(3)
C(49)-C(48)-C(47)	120.1(3)
C(48)-C(49)-C(44)	123.1(3)
C(51)-C(50)-C(55)	115.0(2)
C(51)-C(50)-B(1)	122.0(2)
C(55)-C(50)-B(1)	122.8(2)
C(52)-C(51)-C(50)	123.1(2)
C(51)-C(52)-C(53)	120.2(3)

C(54)-C(53)-C(52)	118.7(3)
C(53)-C(54)-C(55)	120.7(2)
C(54)-C(55)-C(50)	122.3(3)
N(8)-C(57)-C(56)	178.6(4)
N(5A)-Ge(1A)-C(1)	90.20(18)
N(5A)-Ge(1A)-C(2)	90.84(17)
C(1)-Ge(1A)-C(2)	84.38(11)
N(6A)-N(5A)-Ge(1A)	117.9(4)
N(7A)-N(6A)-N(5A)	175.7(8)
N(5B)-Ge(1B)-C(1)	94.5(5)
N(5B)-Ge(1B)-C(2)	93.8(6)
C(1)-Ge(1B)-C(2)	84.1(2)
N(6B)-N(5B)-Ge(1B)	122(2)

B. References

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