ESI for:

Diverse Reactivity of a Boraguanidinato Germylene toward Organic Pseudohalides.

*Jiří Böserle, Grigory Zhigulin, Sergey Ketkov,*Roman Jambor, Aleš Růžička and Libor Dostál**

*E-mail: libor.dostal@upce.cz (L.D.), sketkov@iomc.ras.ru (S.K.)

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1) General comments

All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube technique. Solvents were dried using a Pure Solv–Innovative Technology equipment under argon gas atmosphere. C_6D_6 was tried with sodium, degassed and stored over molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Ascend 500 MHz or Bruker 400 MHz Ultrashield spectrometers using 5 mm tuneable broad-band probe. Appropriate chemical shifts in ^1H and $^{13}C\{^1H\}$NMR spectra were related to the residual signals of the solvent (C_6D_6: $\delta(^1H) = 7.16$ ppm and $\delta(^{13}C) = 128.39$ ppm). The assignment of the NMR spectra was achieved using various 2D techniques especially H,C-HSQC and H,C-HMBC experiments. The abbreviations used in the synthesis description and assignment of respective NMR data are as follows: Dmp = $2,6\text{-}Me_2C_6H_3$; Ad = adamantyl. Elemental analyses were performed on an LECO-CHNS-932 analyzer. IR spectra were recorded on a Nicolet 6700 FTIR spectrometer using single-bounce diamond ATR crystal (resolution 2 cm^{-1}) and Raman spectra were run in sealed quartz capillary on Nicolet iS50 equipped with iS50 Raman module (resolution 2 cm^{-1}, excitation laser 1064 nm). Starting germylene $(i\text{-}Pr)_2NB(NDmp)_2Ge$(**1**) was synthesized according to literature[S1] and other compounds were purchased from commercial suppliers and used as delivered.

2) Syntheses

Synthesis of [(*i*-Pr)$_2$NB(NDmp)$_2$Ge]$_2$NAd (2).

A sample of AdN_3 223 mg (1.258 mmol) was added to a solution of **1** 531 mg (1.258 mmol) in benzene (15 mL) the reaction mixture was stirred for 2 h at r.t and the evolution of nitrogen gas was visible, while the color of the solution changed from intensively yellow to colorless and a opalescent precipitate formed. The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to *ca*3 mL and carefully layered with hexane (*ca* 10 mL). This solution was kept for several days at 4°C giving colorless single-crystals of **3** suitable for X-ray diffraction analysis. These were collected by filtration and dried *in vacuo*. Yield (283mg, 45 %). Mp 182-184°C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.86 (s(br), 24H, i-Pr-C*H*$_3$), 1.42 (s(br), 6H, Ad-C*H*$_2$), 1.54 (m, 6H, Ad-C*H*$_2$), 1.85 (s, 3H, Ad-C*H*), 2.27 (s, 12H, Dmp-C*H*$_3$), 2.52 (s, 12H, Dmp-C*H*$_3$), 3.18 (h, 4H, *i*-Pr-C*H*, $^3J_{H,H}$ = 6.8 Hz), 6.90 (t, 4H, Dmp-*H*4, $^3J_{H,H}$ = 7.5 Hz), 7.01 (m, 8H, Dmp-*H*3,5) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ 19.7 (s, Dmp-*C*H$_3$), 20.6 (s, Dmp-*C*H$_3$), 24.0 (s, *i*-Pr-*C*H$_3$), 30.7 (s, Ad-*C*H), 36.6 (s, Ad-*C*H$_2$), 46.8 (s, *i*-Pr-*C*H), 47.9 (s, Ad-*C*H$_2$), 56.2 (s, Ad-*C*), 124.2 (s, Dmp-*C*4), 128.7 (s, Dmp-*C*3,5), 128.8 (s, Dmp-*C*3,5), 135.7 (s, Dmp-*C*2,6), 136.0 (s, Dmp-*C*2,6), 144.3 (s, Dmp-*C*1) ppm. ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6, 298 K): 26.1 ppm. Anal. Calcd for $C_{54}H_{79}B_2Ge_2N_7$ (993.15): C 65.3; H 8.0; N 9.9. Found: C 65.4; H 8.2; N 10.0.

Synthesis of [(*i*-Pr)$_2$NB(NDmp)$_2$Ge]$_3$S (3). A sample of *t*-BuNCS 114 μL (0.891 mmol) was added to a pre-cooled (0°C) solution of **1** 376 mg (0.891 mmol) in benzene (10 mL) and the reaction mixture was stirred for 1 h at r.t. The reaction mixture was evaporated *in vacuo* and extracted with hexane (10 mL). The yellowish solution was concentrated and crystallized at r.t. Thus obtained bright yellow single-crystals of **3** suitable for X-ray diffraction analysis were collected by filtration and dried *in vacuo*. Yield (178mg, 46 %). Mp 202-204°C. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 0.77 (d, 24H, *i*-Pr-C*H*$_3$, $^3J_{H,H}$ = 7.1 Hz), 0.82 (d, 12H, *i*-Pr-C*H*$_3$, $^3J_{H,H}$ = 7.1 Hz), 2.30 (s, 12H, Dmp-C*H*$_3$), 2.36 (s, 12H, Dmp-C*H*$_3$), 2.49 (s, 12H, Dmp-C*H*$_3$), 3.02 (h, 4H, *i*-Pr-C*H*, $^3J_{H,H}$ = 7.1 Hz), 3.09 (h, 2H, *i*-Pr-C*H*, $^3J_{H,H}$ = 7.1 Hz), 6.72-6.82 (m, 18H, Dmp-*H*3,4,5) ppm.^{13}C NMR (125.7 MHz, C_6D_6): δ 20.8 (s, Dmp-*C*H$_3$), 21.3 (s, Dmp-*C*H$_3$), 21.4 (s, Dmp-*C*H$_3$), 23.8 (s, *i*-Pr-*C*H$_3$), 23.9 (s, *i*-Pr-*C*H$_3$), 46.2 (s, *i*-Pr-*C*H), 46.3 (s, *i*-Pr-*C*H), 124.7 (s, Dmp-*C*4), 125.1 (s, Dmp-*C*4), 129.0 (s, Dmp-*C*3,5), 129.2 (s, Dmp-*C*3,5), 135.2 (s, Dmp-*C*2,6), 135.7 (s, Dmp-*C*2,6), 136.7 (s, Dmp-*C*2,6), 143.9 (s, Dmp-*C*1), 144.2 (s, Dmp-*C*1) ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6, 298 K): 23.4 and 27.4 ppm. Anal. Calcd for $C_{66}H_{96}B_3Ge_3N_9S$ (1297.95): C 61.1; H 7.5; N 9.7. Found: C 61.2; H 7.4; N 9.9.

Procedure starting from AdNCS. A sample of AdNCS 98 mg (0.505 mmol) was added to a solution of **1** 213 mg (0.505 mmol) in benzene (10 mL) and the reaction mixture was stirred for 1 h at r.t. The reaction mixture was evaporated *in vacuo* and extracted with hexane (10 mL). The yellowish solution was concentrated and crystallized at r.t. Thus obtained bright yellow single-crystals of **3** suitable for X-ray diffraction analysis were collected by filtration and dried *in vacuo*.

Synthesis of [(*t*-Bu)NC(O)(Dmp)N(*i*-Pr$_2$N)BN(Dmp)Ge] (4).

A sample of *t*-BuNCO 154 µL (1.348 mmol) was added to a pre-cooled (0°C) solution of **1** 569 mg(1.348 mmol) in benzene (15 mL) and the reaction mixture was stirred for 30 min at r.t. The reaction mixture was evaporated *in vacuo* and extracted with a minimum amount of hexane (~ 5 mL). The extract was stored at 4°C to give colorless single-crystals of **4** suitable for X-ray diffraction analysis that were collected by decantation and dried *in vacuo*. Yield (221mg, 31 %). Mp 94°C with decomposition. ^1H NMR (400 MHz, C_6D_6, 298 K): δ 0.65 (d, 12H, i-Pr-C*H*$_3$,$^3J_{H,H}$ = 7.0 Hz), 1.67 (s, 9H, *t*-Bu), 2.25 (s, 6H, Dmp-C*H*$_3$), 2.34 (s, 6H, Dmp-C*H*$_3$), 3.32 (h, 2H, *i*-Pr-C*H*, $^3J_{H,H}$ = 7.0 Hz), 6.97 (m, 1H, Dmp-*H*4) 7.03 (m, 5H, Dmp-*H*3,4,5) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): δ 20.1 (s, Dmp-*C*H$_3$), 21.2 (s, Dmp-*C*H$_3$), 25.8 (s, *i*-Pr-*C*H$_3$), 33.4 (s, *t*-Bu-*C*H$_3$), 49.3 (s, *i*-Pr-*C*H), 59.0 (s, *t*-Bu-*C*), 126.0 (s, Dmp-*C*4), 126.3 (s, Dmp-*C*4), 128.9 (s, Dmp-*C*3,5), 129.4 (s, Dmp-*C*3,5), 136.1 (s, Dmp-*C*2,6), 137.2 (s, Dmp-*C*2,6), 144.5 (s, Dmp-*C*1), 144.6 (s, Dmp-*C*1), 159.1 (s, *C*=O) ppm. $^{11}B\{^1H\}$ NMR (128.4 MHz, C_6D_6, 298 K): 26.8 ppm. IR (cm^{-1}): 1639s ($\nu_{C=O}$). Raman (cm^{-1}): 1641m ($\nu_{C=O}$). Anal. Calcd for $C_{27}H_{41}BGeN_4O$ (521.09): C 62.2; H 7.9; N 10.8. Found: C 62.4; H 7.8; N 11.0.

Synthesis of [(Ad)NC(O)(Dmp)N(*i*-Pr$_2$N)BN(Dmp)Ge] (5).

A sample of AdNCO 360 mg (2.03 mmol) was added to a pre-cooled (0°C) solution of **1** 857 mg (2.03 mmol) in benzene (15 mL) the reaction mixture was stirred for 1 h at r.t. The solution was slightly concentrated resulting in precipitation of a white solid, which was again dissolved by a gentle heating. Storage of this solution at r.t. overnight produced colorless single-crystals of **5** suitable for X-ray diffraction analysis that were collected by decantation and dried *in vacuo*. Yield (925mg, 76 %). Mp 145-147°C. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 0.67 (d, 12H, i-Pr-C*H*$_3$,$^3J_{H,H}$ = 7.1 Hz),1.58 (d, 3H, Ad-C*H*$_2$, $J_{H,H}$ = 12.1 Hz), 1.67 (d, 3H, Ad-C*H*$_2$, $J_{H,H}$ = 12.1 Hz), 2.04 (s, 3H, Ad-C*H*),2.29 (s, 6H, Dmp-C*H*$_3$), 2.35 (s, 6H, Dmp-C*H*$_3$), 2.50 (d, 6H, Ad-C*H*$_2$, $J_{H,H}$ = 2.0 Hz), 3.35 (h, 2H, *i*-Pr-C*H*, $^3J_{H,H}$ = 7.1 Hz), 6.98 (m, 1H, Dmp-*H*4), 7.05 (m, 5H, Dmp-*H*3,4,5) ppm. ^{13}C NMR (125.7 MHz, C_6D_6): δ 20.1 (s, Dmp-*C*H$_3$), 21.2 (s, Dmp-*C*H$_3$), 25.8 (s, *i*-Pr-*C*H$_3$), 31.2 (s, Ad-*C*H), 37.2 (s, Ad-*C*H$_2$), 45.9 (s, Ad-*C*H$_2$), 49.3 (s, *i*-Pr-*C*H), 60.9 (s, Ad-*C*), 125.9 (s, Dmp-*C*4), 126.3 (s, Dmp-*C*4), 128.9 (s, Dmp-*C*3,5), 129.4 (s, Dmp-*C*3,5), 136.1 (s, Dmp-*C*2,6), 137.2 (s, Dmp-*C*2,6), 144.7 (s, Dmp-*C*1), 144.8 (s, Dmp-*C*1), 158.6 (s, *C*=O) ppm. ^{11}B{^{1}H} NMR (128.4 MHz, C_6D_6, 298 K): 26.8 ppm. IR (cm^{-1}): 1635vs ($\nu_{C=O}$). Raman (cm^{-1}): 1636m ($\nu_{C=O}$). Anal. Calcd for $C_{33}H_{47}BGeN_4O$ (599.20): C 66.2; H 7.9; N 9.4. Found: C 66.4; H 7.8; N 9.3.

3) NMR spectra of studied compounds.

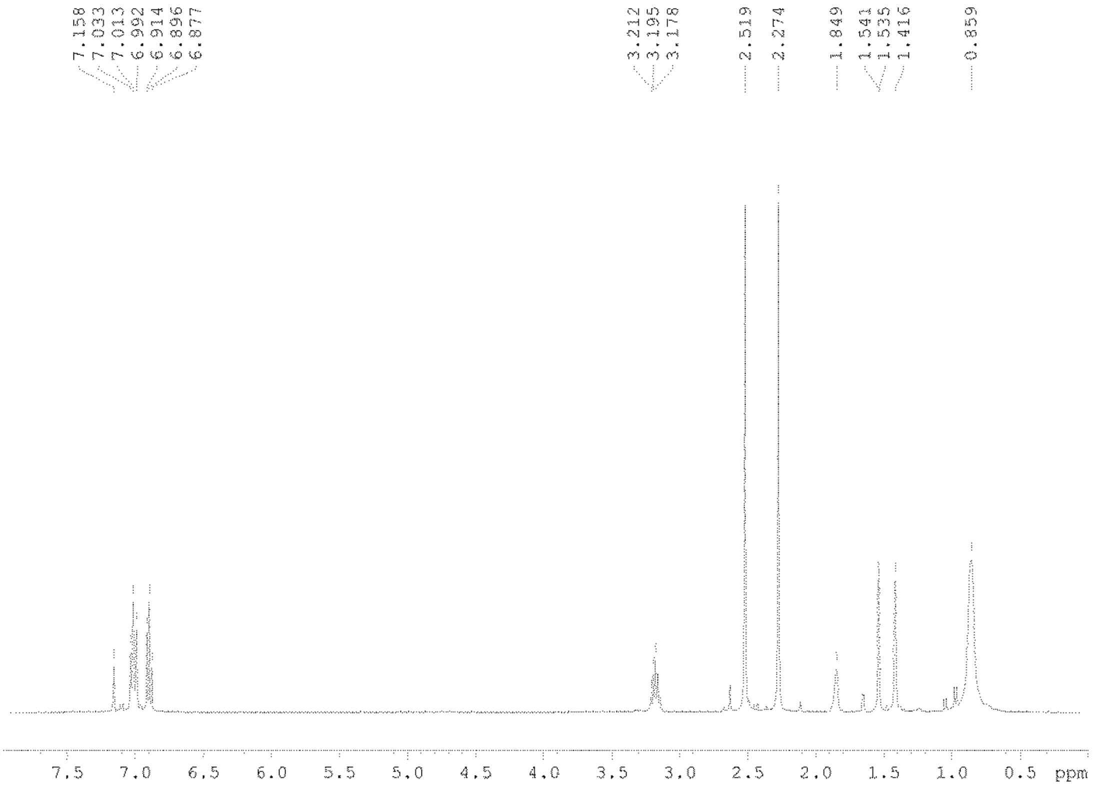


Figure S1: ^{1}H NMR spectrum of compound **2** acquired in C_6D_6.

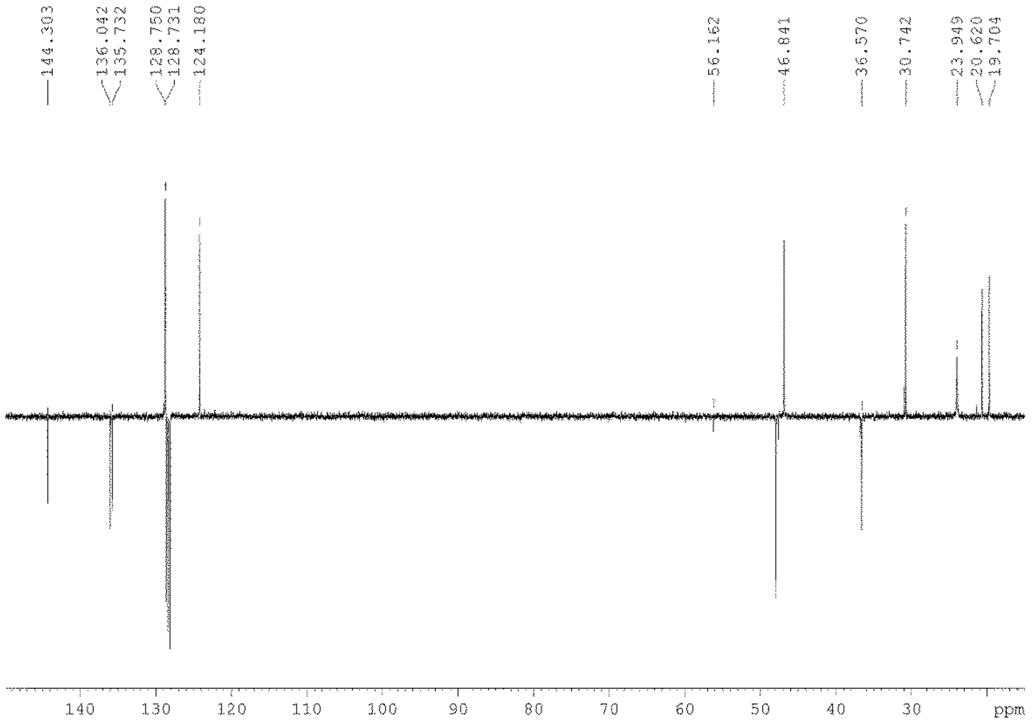


Figure S2: $^{13}C\{^1H\}$ NMR spectrum of compound **2** acquired in C_6D_6.

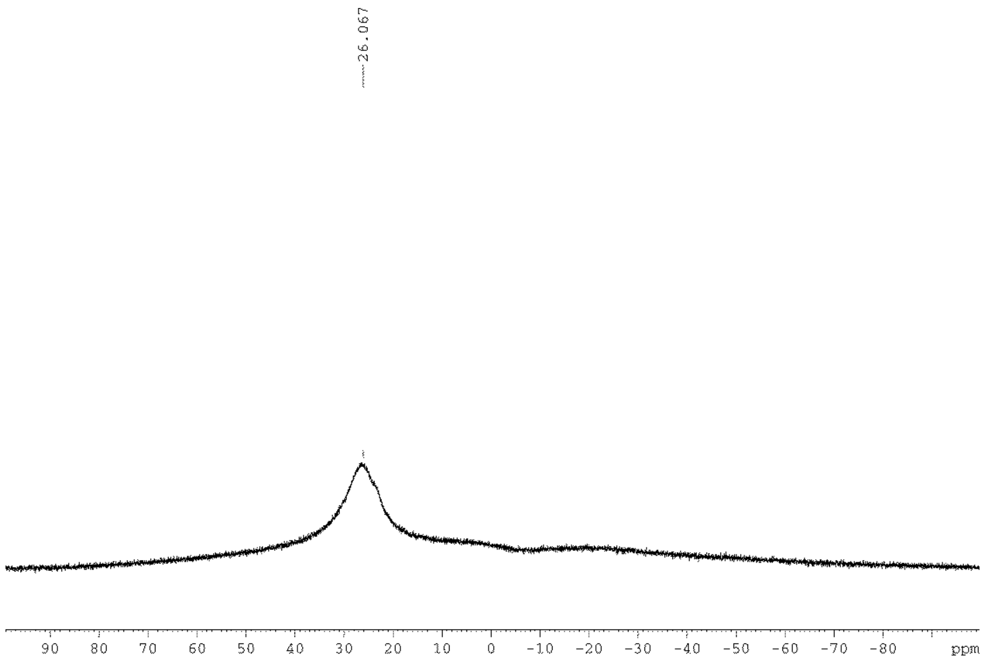


Figure S3: $^{11}B\{^{1}H\}$ NMR spectrum of compound **2** acquired in C_6D_6.

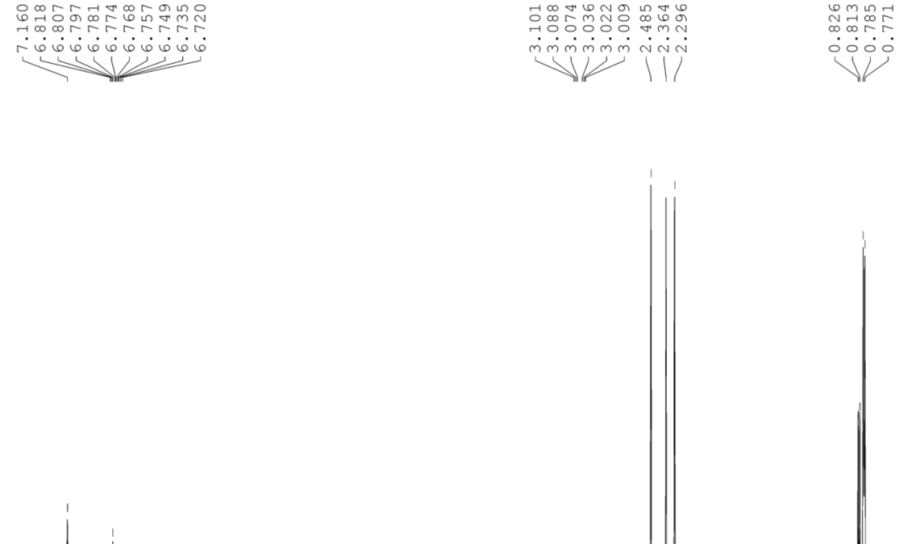


Figure S4: ^{1}H NMR spectrum of compound **3** acquired in C_6D_6.

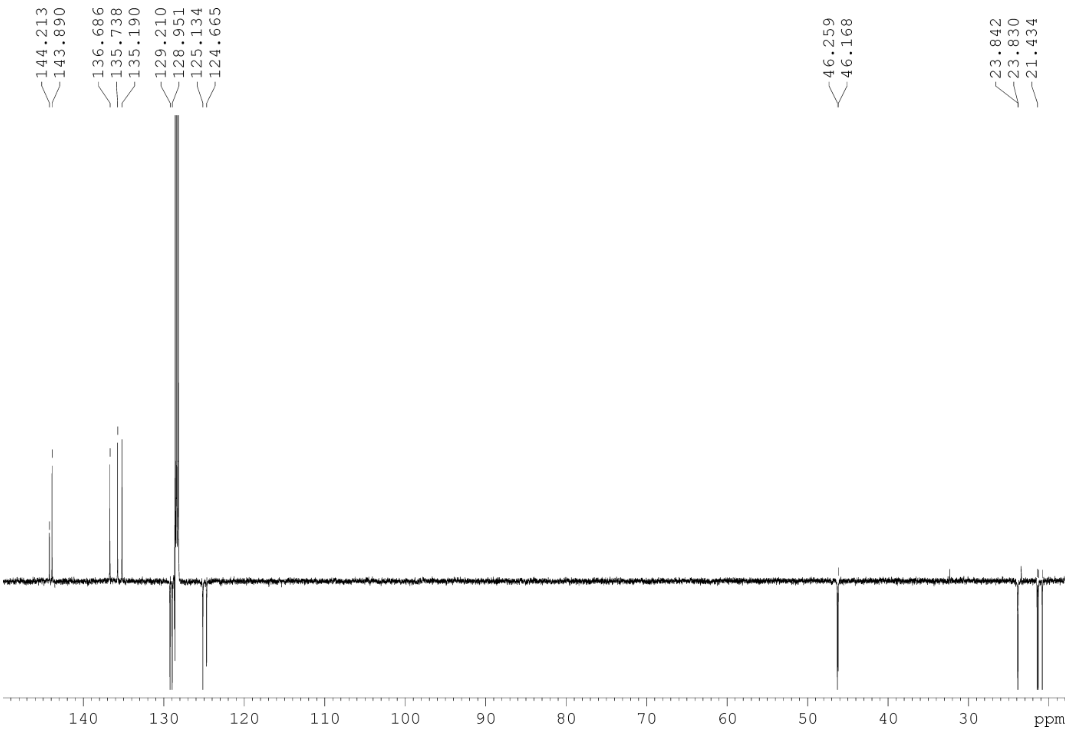


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** acquired in C_6D_6.

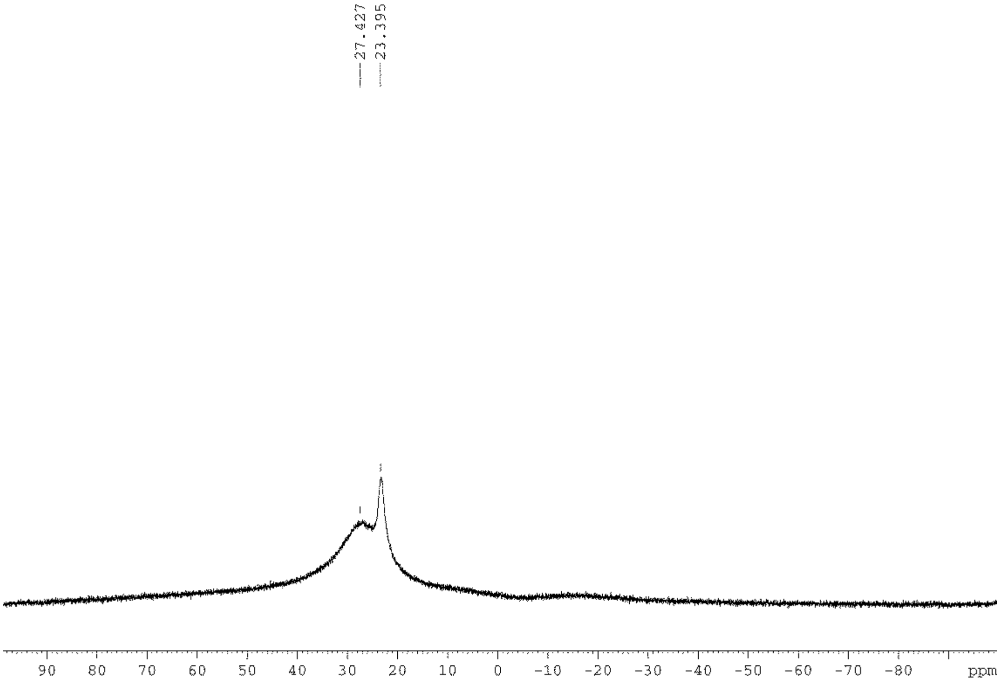


Figure S6: $^{11}B\{^{1}H\}$ NMR spectrum of compound **3** acquired in C_6D_6.

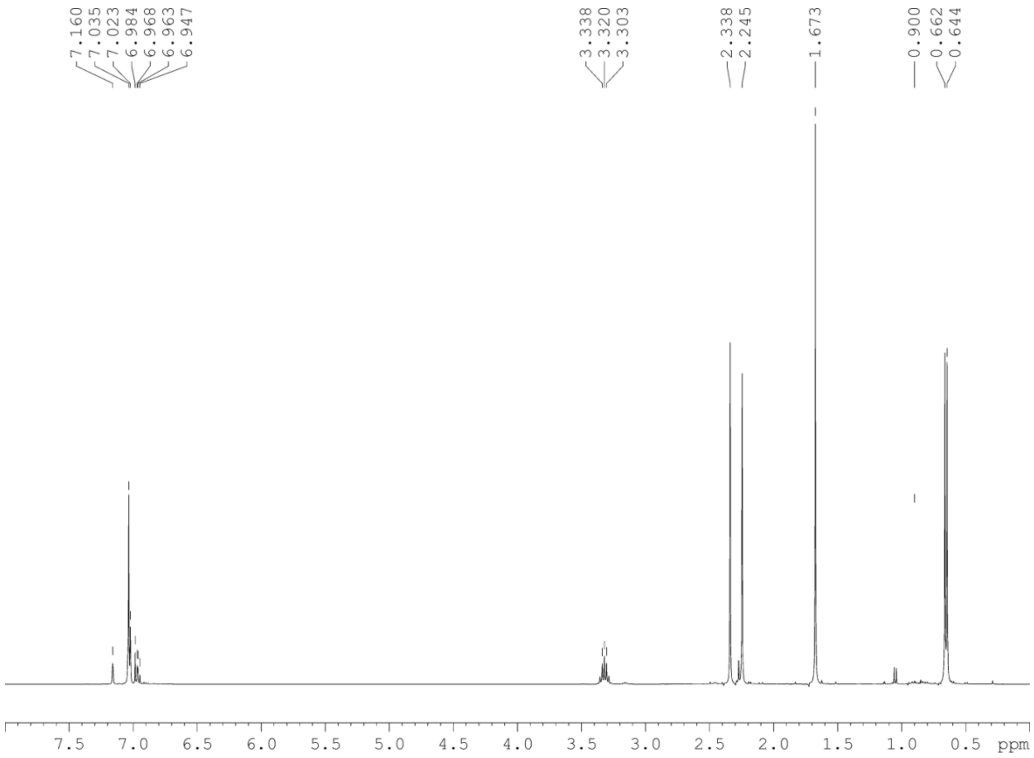


Figure S7: ^{1}H NMR spectrum of compound **4** acquired in C_6D_6.

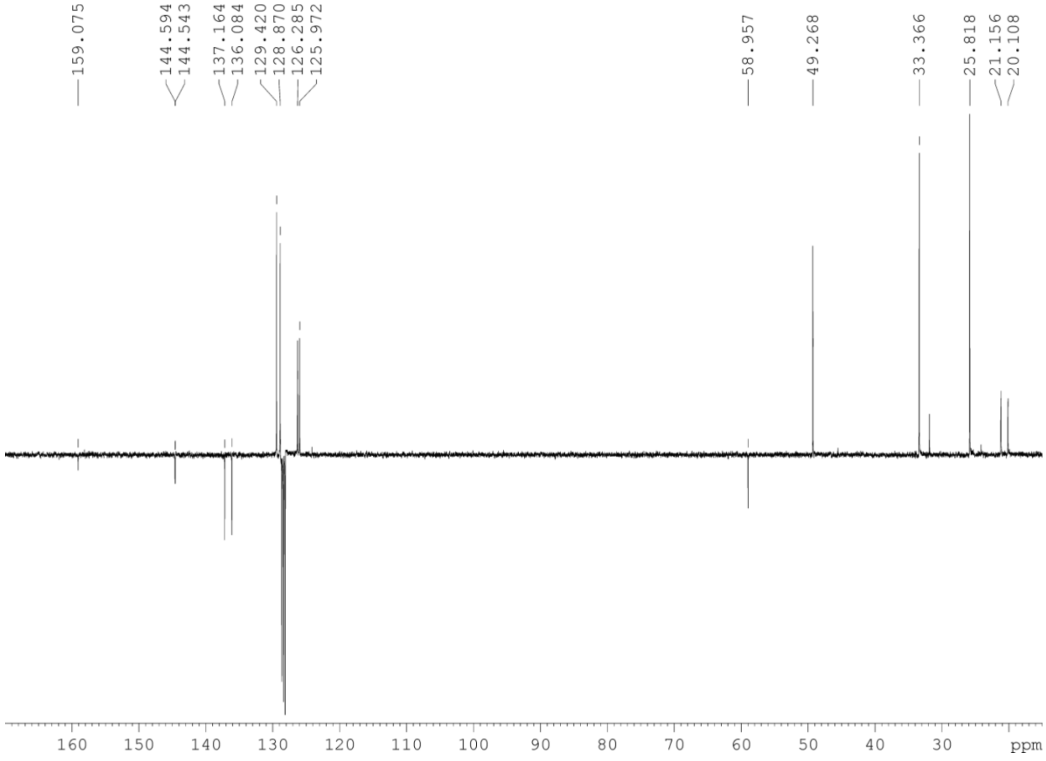


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** acquired in C_6D_6.

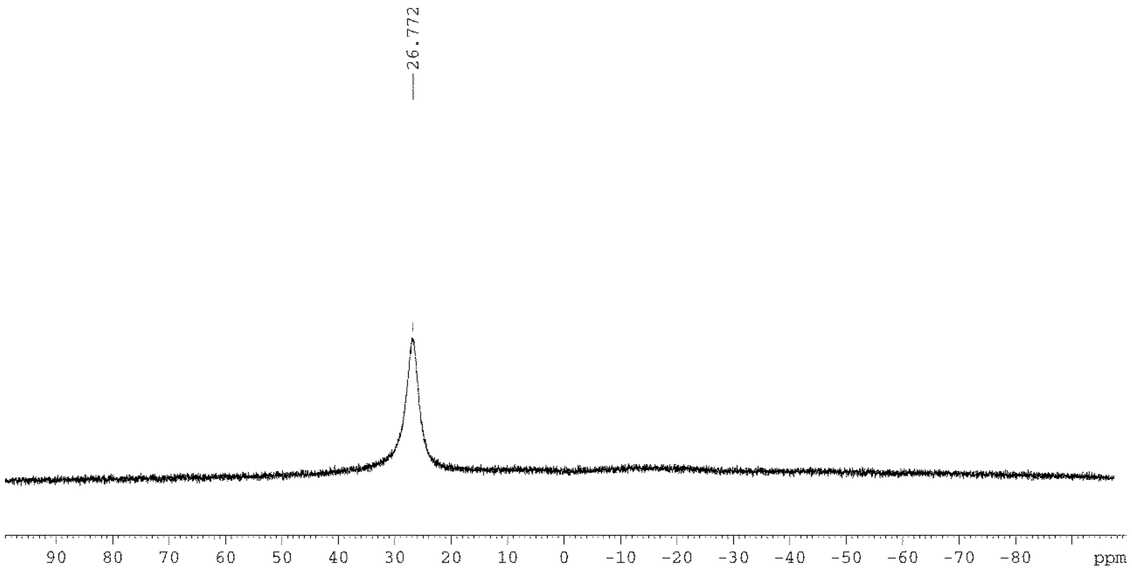


Figure S9: $^{11}B\{^{1}H\}$ NMR spectrum of compound **4** acquired in C_6D_6.

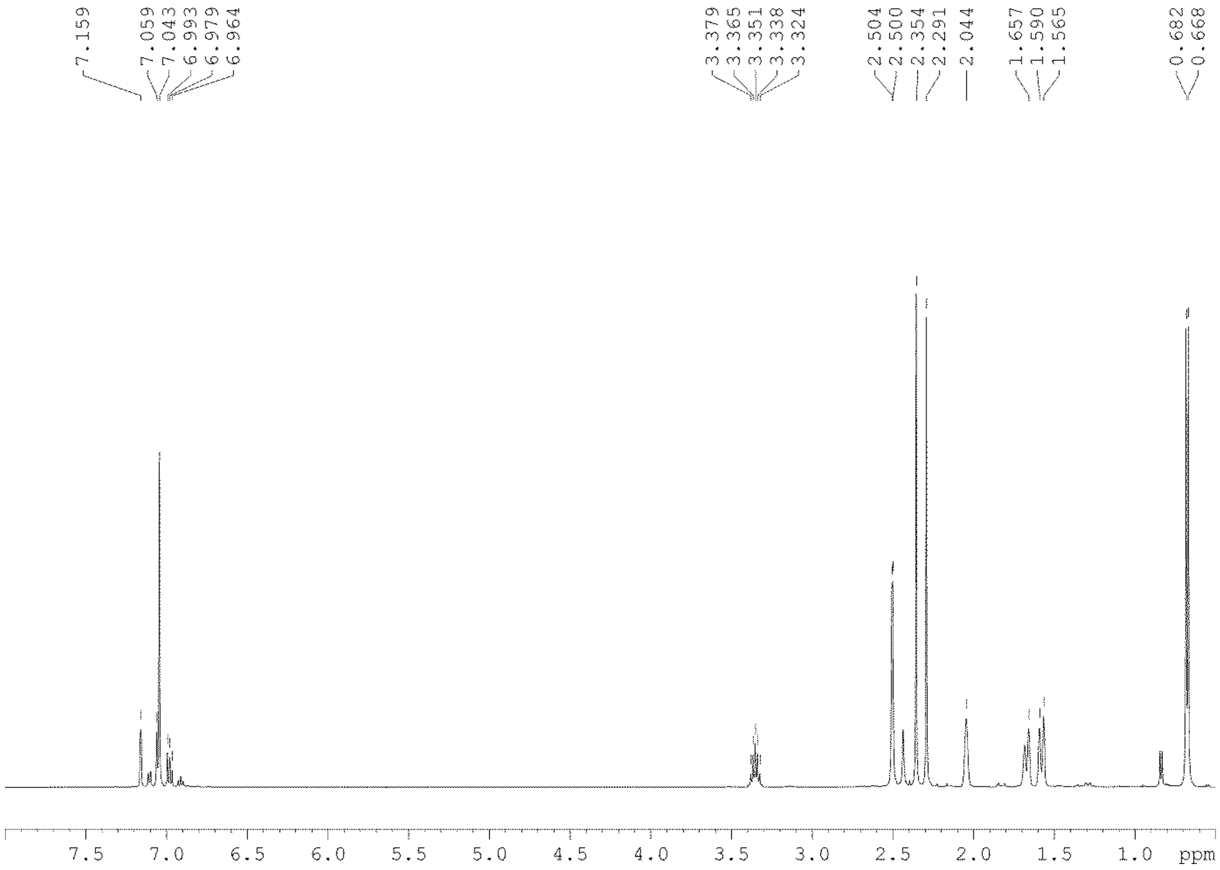


Figure S10: ^{1}H NMR spectrum of compound **5** acquired in C_6D_6.

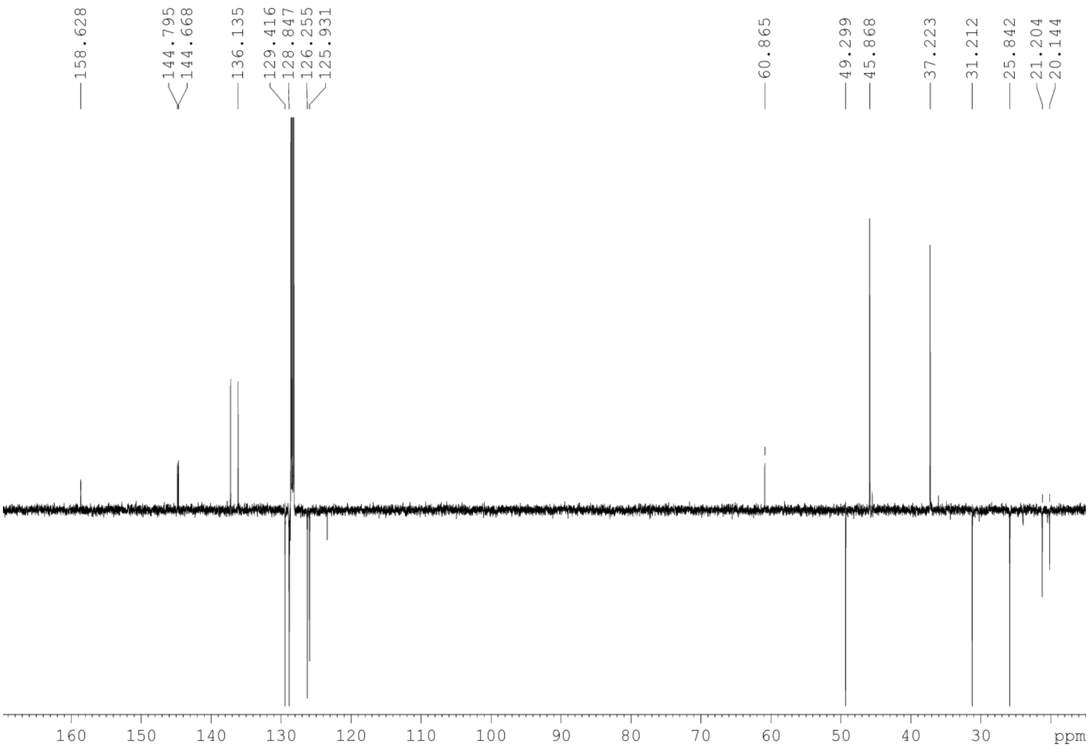


Figure S11: $^{13}C\{^1H\}$ NMR spectrum of compound **5** acquired in C_6D_6.

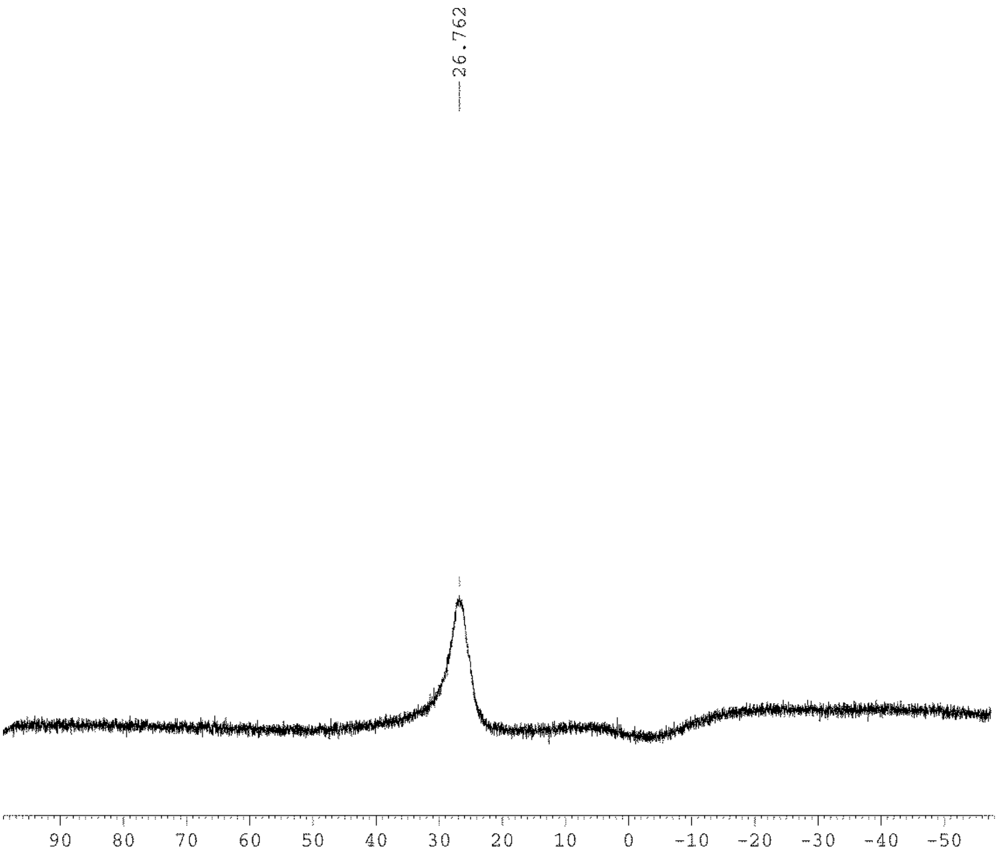


Figure S12: $^{11}B\{^1H\}$ NMR spectrum of compound **5** acquired in C_6D_6.

4) Crystallographic studies.

Full set of diffraction data for studied compounds**2-5** were collected at 150(2)K with a Bruker D8-Venture diffractometer equipped with Mo (Mo/K_α radiation; λ = 0.71073 Å) microfocus X-ray (IµS) source, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption using the Multi-Scan method (SADABS). Obtained data were treated by XT-version 2014/5 and SHELXL-2014/7 software implemented in APEX3 v2016.5-0 (Bruker AXS) system.[S2] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure the uniformity of the treatment of the crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of $1.5U_{eq}$ (methyl). H atoms in methyl, methylene, methine groups and hydrogen atoms in aromatic rings were placed with C-H distances of 0.96, 0.97, 0.98 and 0.93 Å, respectively. Structure of compound **5** was refined as a perfect inversion twin. There are residual electron maxima within the unit cell probably originated from the disordered solvent in the structure of **3**. PLATON/SQUEZZE [S3] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 934 $Å^3$ was found. 158 electrons per unit cell worth of scattering were located in the void. The calculated stoichiometry of solvent was calculated to be two molecules of hexane per unit cell which results in 100 electrons per unit cell.

Crystallographic data for structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 1860359 (**2**), 1860360 (**5**), 1860361 (**3**) and 1860362 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table S1: Comparison of experimental (crystal) and calculated (gas phase) structural parameters for compounds **4** and **5**.

	Compound **4**		Compound **5**	
	Expr.[a]	Calc.	Expr.	Calc.
Ge(1)-N(1)	1.848(4) 1.831(4)	1.866	1.816(10)	1.860
Ge(1)-N(4)	1.860(3) 1.854(3)	1.896	1.866(10)	1.902
N(1)-B(1)	1.447(6) 1.447(6)	1.446	1.487(18)	1.446
N(2)-B(1)	1.479(6) 1.463(6)	1.473	1.518(17)	1.468
N(2)-C(1)	1.407(5) 1.445(6)	1.407	1.397(17)	1.413
C(1)-O(1)	1.220(6) 1.120(7)	1.226	1.225(16)	1.226
C(1)-N(4)	1.381(6) 1.416(6)	1.395	1.421(17)	1.396
N(1)-Ge(1)-N(4)	96.84(15) 97.35(15)	97.09	97.8(5)	97.65

[a] values for two independent molecules in the unit cell are given

5) Computational details

The interactions between germylenes and isocyanates were investigated by DFT with use of the Gaussian09 suite.[S4] Full geometry optimizations of the molecules were performed employing the M062X hybrid meta-GGA exchange-correlation functional[S5] in combination with the double-ζ-plus-polarization DGDZVP basis set[S6] for all atoms. This level of theory provided earlier a correct description of reactions between boraquanidinatogermylenes and alkynes.[S7] All molecular structures were considered in closed-shell singlet electronic states, the X-ray atomic coordinates being used as starting geometries for species **4**, **5**. The optimized structure of **1** was taken from our previous calculations.[S7] The transition state was searched by the QST3 procedure.[S8] Harmonic vibrational analysis was carried out to confirm the energy minimum or the first-order saddle point and to compute enthalpies and Gibbs free energies. Nonspecific solvation in benzene was taken into account by the PCM model.[S9] The optimized molecular structures in the gas phase and in solution are similar. To study donor-acceptor interactions the Natural Bond Orbital analysis[S10] of the gas-phase species was performed using the NBO 3.1 version implemented in Gaussian09. The Deformation Electron Density (DED) was built using the Multiwfn code[S11] by subtraction of atomic EDs from the electron density of a molecule.

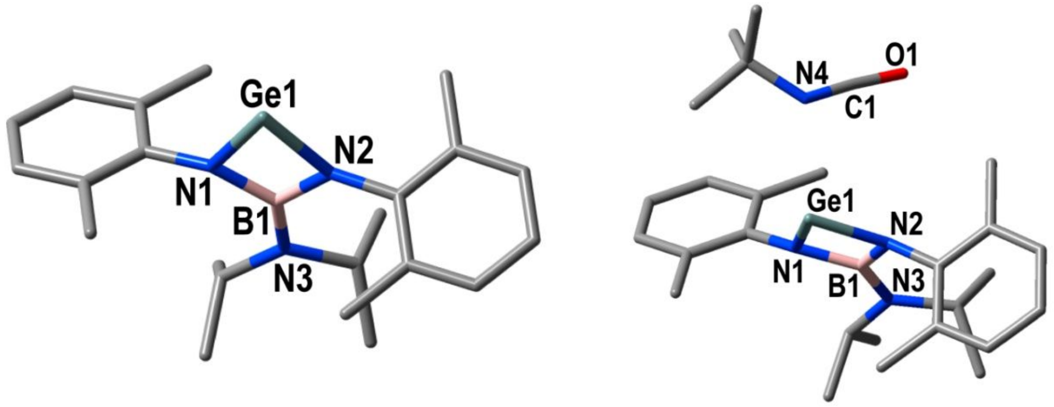


Figure S9. Optimized geometries and atom numbering in germylene **1** (left) and pre-reaction complex **1**·*t*-BuNCO (right) in the gas phase. Hydrogen atoms are omitted for clarity.

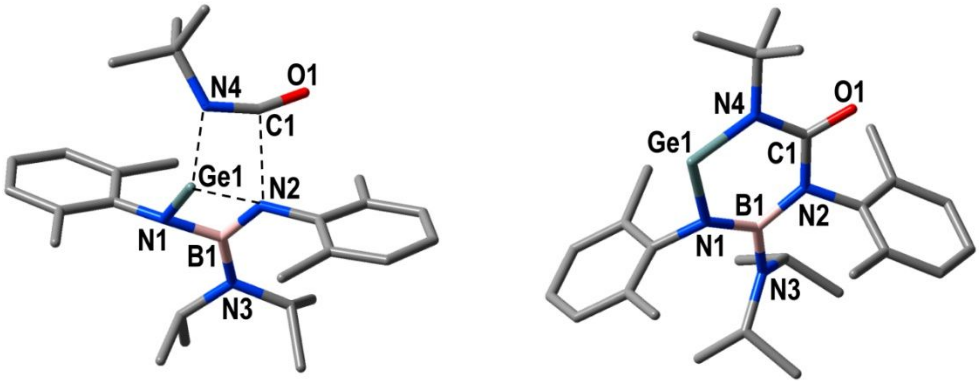
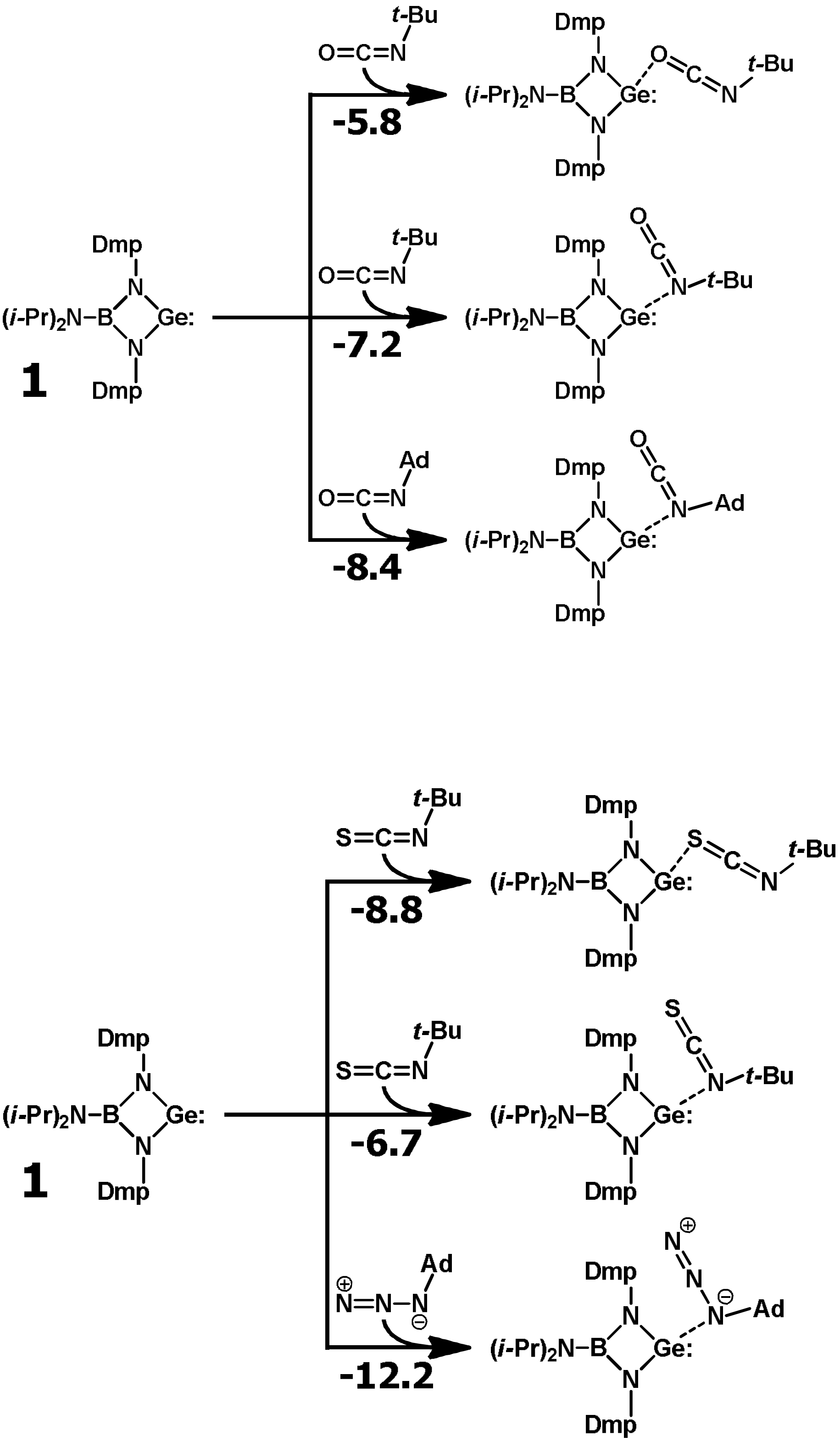


Figure S10. Optimized geometries and atom numbering in transition state TS (left) and final product **4** (right) in the gas phase. Hydrogen atoms are omitted for clarity.



Scheme S1. Formation of possible pre-reaction complexes between germylene **1** and relevant unsaturated substrates. The corresponding enthalpies (kcal mol^{-1}) in benzene solution are presented.

Table S2. Calculated bond lengths and bonding angles in the reactants, transition state and product of the reaction between **1** and *t*-BuNCO in the gas phase.

	1/*t*-BuNCO	**1**·*t*-BuNCO	TS	**4**
Bond lengths (Å)				
Ge1−N1	1.886 / —	1.908	1.906	1.866
Ge1−N2	1.886/ —	1.899	2.047	—
B1−N1	1.476/ —	1.469	1.461	1.446
B1−N2	1.476/ —	1.475	1.492	1.473
Ge1−N4	— / —	2.798	2.123	1.896
C1–N4	— / 1.204	1.217	1.262	1.395
C1–O1	— / 1.179	1.172	1.171	1.226
C1–N2	— / —	3.633	2.231	1.407
Bonding angles (°)				
N1–Ge1–N2	74.97/ —	74.38	72.01	—
N1–Ge1−N4	— / —	—	—	97.09
C1–N4–C(sp^3,*t*-Bu)	— / 137.99	127.36	120.55	115.43
N4–C1–O1	— / 174.17	175.43	157.86	122.25

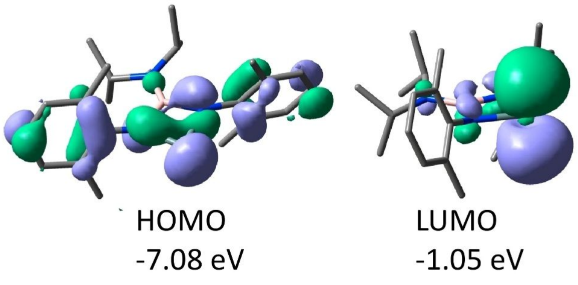


Figure S11. M062X/DGDZVP isosurfaces (isovalue 0.04) and energies of the HOMO (left) and LUMO (right) orbitals of **1**. The isosurfaces agree very well with those obtained earlier at the M06/cc-pVDZ(-PP) level of theory [S1].

6) References.

[S1] J. Böserle, M. Alonso, R. Jambor, A. Růžička and L. Dostál, *RSC Adv.*, 2016, **6**, 19377-19388.

[S2] G.M. Sheldrick, *ActaCryst.*, 2015, **A71**, 3-8.

[S3] A. L. Spek, *ActaCryst.* 2015, **C71**, 9-18.

[S4] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT, 2010.

[S5] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.

[S6] (*a*) N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560-571; (*b*) C. Sosa, J. Andzelm, B. C. Elkin, E. Wimmer, K. D. Dobbs and D. A. Dixon, *J. Phys. Chem.*, 1992, **96**, 6630-6636.

[S7] J. Böserle, G. Zhigulin, P. Štěpnička, F. Horký, M. Erben, R. Jambor, A. Růžička, S.Ketkov and L. Dostál, *Dalton Trans.*, 2017, **46**, 12339-12353.

[S8] (*a*) C. Peng and H. B. Schlegel, *Isr. J. Chem.*, 1993, **33**, 449-454; (*b*) C. Peng, P. Y. Ayala, H. B. Schlegel and M. J. Frisch, *J. Comput. Chem.*, 1996, **17**, 49-56.

[S9] J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999-3093.

[S10] A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899-926.

[S11] (*a*) T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592; (*b*) T. Lu and F. Chen, *J. Mol. Graphics Modell.*, 2012, 38, 314-323.