Electronic Supplementary Information for:

Synthesis and Reactivity of a Germylene Stabilized by a Boraguanidinate Ligand.

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Table S1. Gibbs free energies (ΔG_{298}), enthalpies (ΔH_{298}) and entropies (ΔS_{298}) for the dimerization of germylene **1** both in gas phase and in benzene.[a]

compound	ΔH_{gas}(VDZ)[b]	ΔG_{gas}(VDZ)[b]	ΔH_{gas}(VTZ)[c]	ΔG_{gas}(VTZ)[c]	ΔH_{bz}(VTZ)[c]	ΔG_{bz}(VTZ)[c]	ΔS_{bz}(VTZ)[c]
1→(1)$_2$	-24.7	-6.0	-18.0	0.7	-13.8	4.9	-62.8
1→digermene	-12.3	8.8	-10.9	4.1	-8.3	6.7	-50.2

[a] ΔG_{298} andΔH_{298} are given in kcal mol^{-1} and ΔS_{298} in cal mol^{-1} K^{-1}. [b] M06/cc-pVDZ(-PP) level of theory. [c] M06/cc-pVTZ(-PP) level of theory.

Table S2. Crystallographic Data for Studied Compounds

	1	**2**	**3**	**4**
empirical formula	$C_{44}H_{64}B_2Ge_2N_6$	$C_{34}H_{42}BGeN_3S_2$	$C_{34}H_{42}BGeN_3Se_2$	$C_{34}H_{42}BGeN_3Te_2$
cryst syst	Triclinic	monoclinic	monoclinic	orthorhombic
space group	*P*-1	*P*21/*c*	*P*21/*c*	*Pbca*
a[Å]	8.9930(5)	20.0901(14)	20.4250(16)	8.3340(5)
b[Å]	11.4140(6)	8.4960(4)	8.5540(7)	19.7050(18)
c[Å]	11.9331(6)	19.6849(16)	19.569(2)	42.118(č)
α[deg]	112.083(3)	90	90	90
β[deg]	94.293(4)	91.921(6)	99.855(7)	90
γ[deg]	107.174(4)	90	90	90
Z	1	4	4	8
μ[mm^{-1}]	1.456	1.063	3.052	2.566
D_x [Mg m^{-3}]	1.322	1.266	1.426	1.597
cryst size [mm]	0.37x0.17x0.17	0.42x0.17x0.09	0.25x0.24x0.18	0.40x0.14x0.13
θ range, [deg]	1 – 27.5	1 – 27.5	1 – 27.5	1 – 27.5
T_{min}, T_{max}	0.741, 0.853	0.755, 0.926	0.565, 0.690	0.569, 0.763
no. of reflections measured	17 968	28 460	30 924	35 467
no. of unique reflns, R_{int}[a]	4807, 0.028	7423, 0.042	7728, 0.071	7678, 0.030
no. of observed reflns [$I>2\sigma(I)$]	4318	5797	5729	6386
no. of parameters	244	370	370	370
S[b] all data	1.070	1.104	1.126	1.215
final R[b] indices [$I>2\sigma(I)$]	0.033	0.037	0.096	0.037
wR2[b] indices (all data)	0.073	0.071	0.204	0.062
Δρ, max., min. [e $Å^{-3}$]	1.122, -0.620	0.325, -0.379	2.033, -0.802	0.644, -0.681

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$, [b] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$. [b] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$

Table S2 (continue). Crystallographic Data for Studied Compounds

	5	**6**	**7**	**8**
empirical formula	$C_{22}H_{32}BGeI_2N_3$	$C_{23}H_{35}BGeIN_3$	$C_{22}H_{33}BBrGeN_3$	$C_{22}H_{33}BBr_3GeN_3$
cryst syst	monoclinic	triclinic	triclinic	triclinic
space group	*P*21/*c*	*P*-1	*P*-1	*P*-1
a[Å]	14.7200(9)	8.4040(3)	8.3520(4)	9.480(3)
b[Å]	8.2140(7)	11.0410(9)	10.4790(5)	9.5290(11)
c[Å]	21.3591(15)	13.8139(10)	13.5181(10)	31.902(6)
α[deg]	90	84.933(5)	95.684(5)	86.052(12)
β[deg]	94.762(7)	80.365(4)	100.864(6)	86.293(16)
γ[deg]	90	89.771(4)	90.338(4)	65.709(16)
Z	4	2	2	4
μ[mm^{-1}]	3.602	2.457	3.066	5.762
D_x [Mg m^{-3}]	1.744	1.488	1.445	1.681
cryst size [mm]	0.23x0.16x0.14	0.42x0.35x0.30	0.32x0.19x0.15	0.29x0.18x0.07
θ range, [deg]	1 – 27.5	1 – 27.5	1 – 27.5	1 – 27.5
T_{min}, T_{max}	0.557, 0.684	0.472, 0.623	0.525, 0.751	0.404, 0.713
no. of reflections measured	24 377	25 885	24 163	18 932
no. of unique reflns, R_{int}[a]	5768, 0.028	5735, 0.027	5291, 0.031	9959, 0.068
no. of observed reflns [$I>2\sigma(I)$]	4971	5156	4313	8145
no. of parameters	262	262	253	541
S[b] all data	1.117	1.076	1.085	1.281
final R[b] indices [$I>2\sigma(I)$]	0.031	0.031	0.031	0.086
wR2[b] indices (all data)	0.062	0.077	0.063	0.190
Δρ, max., min. [e $Å^{-3}$]	1.444, -0.897	1.490, -1.073	0.428, -0.668	1.120, -1.019

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$, [b] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$. [b] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$

Table S2 (continue). Crystallographic Data for Studied Compounds

	9	**10**	**11**	**12**	**Ligand-precursor**
empirical formula	$C_{22}H_{33}BClGeN_3$	$C_{28}H_{42}BGeN_3$	$C_{40}H_{50}BGeN_3$	$C_{48}H_{68}BGeN_5$.(C_6H_{14})	$C_{22}H_{34}BN_3$
cryst syst	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	*P*-1	*P*-1	*P*21/*c*	*P*-1	*P*-1
a[Å]	8.4670(3)	8.4040(3)	13.7260(7)	12.4100(12)	8.6562(5)
b[Å]	9.7781(7)	10.2400(7)	19.8081(17)	15.9710(5)	10.2840(4)
c[Å]	14.5579(9)	17.1711(10)	14.7940(8)	26.276(3)	12.9948(8)
α[deg]	79.339(5)	99.375(6)	90	101.779(6)	73.067(4)
β[deg]	76.990(4)	92.648(6)	117.858(6)	95.207(8)	86.430(5)
γ[deg]	79.439(4)	107.632(5)	90	98.138(5)	76.579(3)
Z	2	2	4	4	2
μ[mm^{-1}]	1.471	1.128	0.893	0.652	0.063
D_x [Mg m^{-3}]	1.334	1.211	1.226	1.173	1.084
cryst size [mm]	0.51x0.19x0.19	0.47x0.22x0.15	0.41x0.22x0.20	0.53x0.40x0.19	0.59x0.35x0.33
θ range, [deg]	1 – 27.5	1 – 27.5	1 – 27.5	1 – 27.5	1 – 27.5
T_{min}, T_{max}	0.658, 0.844	0.688, 0.859	0.808, 0.873	0.793, 0.923	0.976, 0.988
no. of reflections measured	23 008	28 009	34 637	90 026	18 373
no. of unique reflns, R_{int}[a]	5205, 0.028	6234, 0.021	7937, 0.031	21719, 0.037	4843, 0.023
no. of observed reflns [$I>2\sigma(I)$]	4578	5653	6527	17098	3991
no. of parameters	253	298	406	991	246
S[b] all data	1.098	1.119	1.127	1.087	1.072
final R[b] indices [$I>2\sigma(I)$]	0.036	0.026	0.034	0.045	0.050
wR2[b] indices (all data)	0.082	0.067	0.066	0.102	0.120

Δρ, max., min. [e Å^{-3}]	1.568, -0.421	0.273, -0.395	0.298, -0.317	1.030, -0.588	0.418, -0.353

^{a} $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$, ^{b} $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$. ^{b} $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$

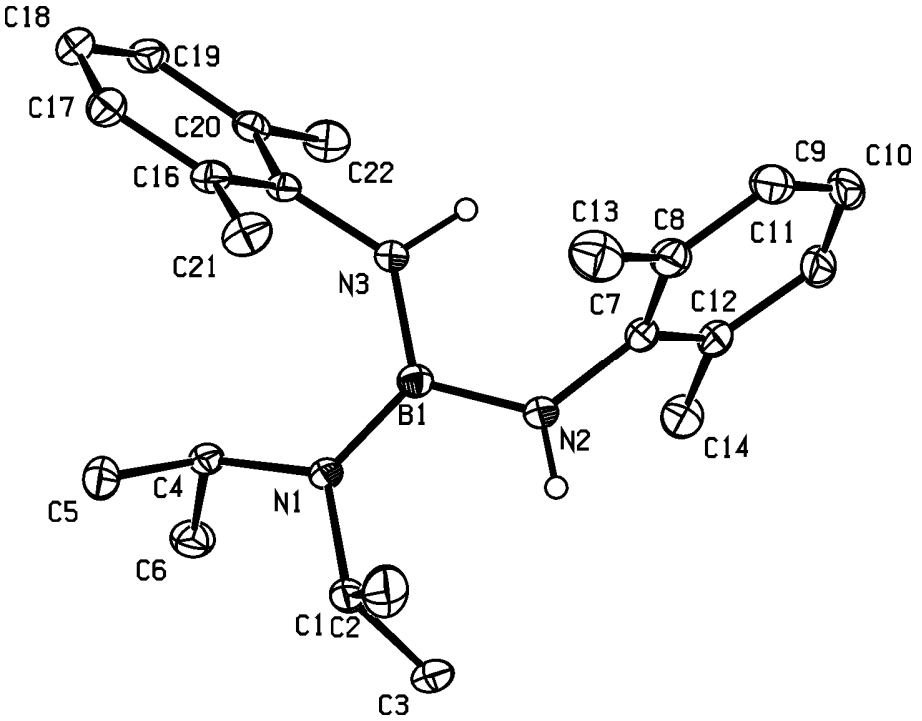

Figure S1: Molecular structure of ligand precursor.

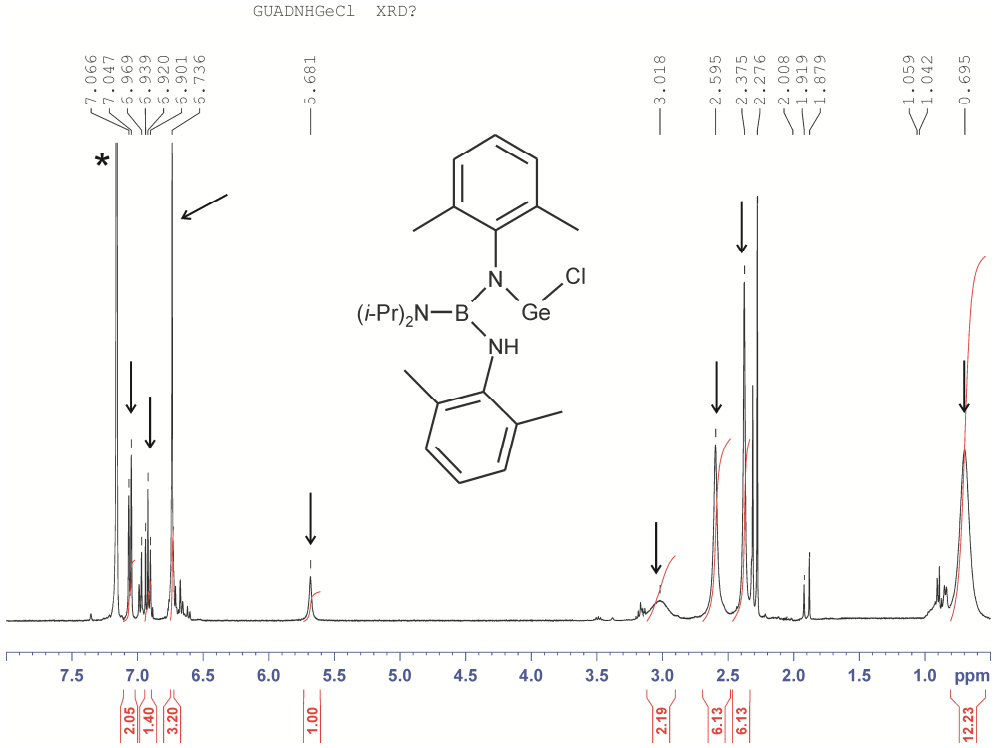

Figure S2: The ^{1}H NMR spectrum of **9** in C_6D_6 **(*).**

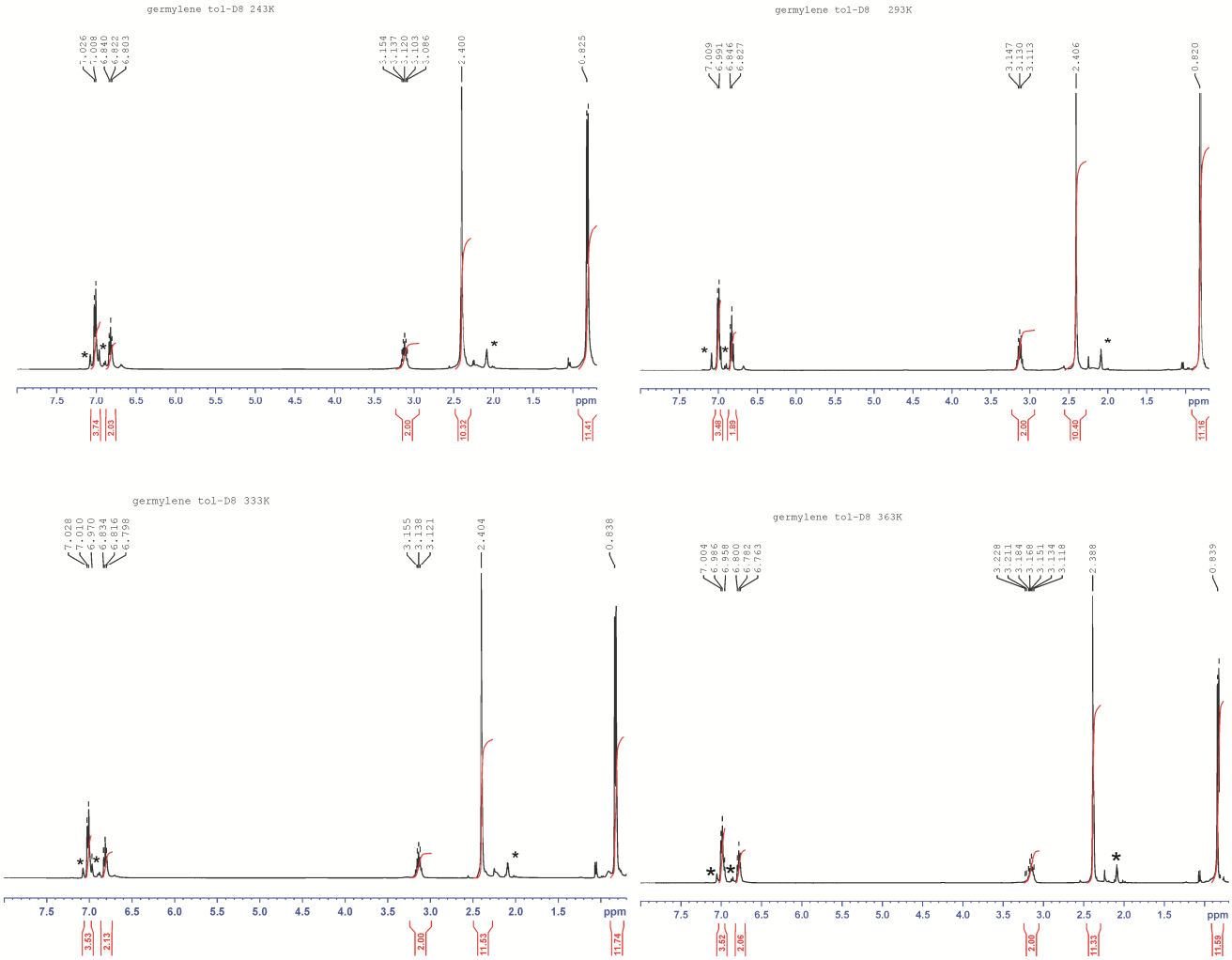

Figure S3: The VT-^{1}H NMR spectrum of **1** in toluene-D8 **(*)**. Top-left 243 K, top-right 293 K, bottom-left 333K and bottom right 363 K.