Electronic Supplementary Information for:

An unsymmetric *N*-donor stabilised digermylene with a Ge(I)-Ge(I) bond and synthesis of a germylene-stannylene with a Ge(I)-Sn(I) bond

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General Considerations

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere glovebox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material potassium cyclogermylidenide **1**[1] L'GeCl **2**[2], L'SnCl **3**[2] (L = $HC[C(Me)NR]_2$, R = 2,6-$^{i}Pr_2C_6H_3$) were prepared according to literature procedure. The NMR spectra were recorded on Bruker Spectrometer AV 400 with residual solvent signals as internal reference (^{1}H and $^{13}C\{^{1}H\}$). Abbreviations: s = singlet; d = doublet; t = triplet; sept = septet; mult = multiplet; br = broad.

Single-Crystal X-ray Structure Determinations: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N2 flow. The data of Compounds **4** and **5** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo- Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods 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.

Experimental selections

Digermylene 4:

To a solution of **2** (138 mg, 0.263 mmol) in THF (10 ml) at -30 °C was added the solution of **1** (93 mg, 0.263 mmol) in THF (10 ml). The colour of the solution changed from yellow to dark red. After stirring for additional 2 h at room temperature, the volatiles were removed under reduced pressure and the residue was extracted with hexane (30 ml). The filtrate was concentrated and stored at -30°C for 5 days yielding **4** as dark red crystals (140 mg, 0.17 mmol, 66%).

M.p. >169 °C (decomp.)

^{1}H NMR (400.13 MHz, C_6D_6, 298K): δ = 1.07 (d, $^3J_{HH}$ = 7 Hz, 12 H, CH*Me*$_2$), 1.11 (d, $^3J_{HH}$ = 7 Hz, 12 H, CH*Me*$_2$), 1.20 (d, $^3J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.24 (d, $^3J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.61 (s, 6 H, NC*Me*), 2.02 (s, 3 H, NC*Me*), 2.62 (s, 3 H, GeC*Me*), 3.01 (sept, $^3J_{HH}$ = 7 Hz, 2 H, C*H*Me$_2$), 3.19 (sept, $^3J_{HH}$ = 7 Hz, 2 H, C*H*Me$_2$), 3.67 (sept, $^3J_{HH}$ = 7 Hz, 2 H, C*H*Me$_2$), 5.18 (s, 1 H, 6-ring-γ-C*H*), 6.82 (s, 1 H, 5-ring-β-C*H*), 7.02- 7.18 (m, 9 H, arom. *H*).

^{13}C{^{1}H} NMR (100.61 MHz, THF-D_8, 298K): δ = 19.1 (5-ring-NC*Me*), 21.0 (GeC*Me*), 24.0 (6-ring-NC*Me*), 24.8 (CH*Me*$_2$), 24.9 (CH*Me*$_2$), 25.0 (CH*Me*$_2$), 25.8 (CH*Me*$_2$), 25.9 (CH*Me*$_2$), 26.1 (CH*Me*$_2$), 27.9 (*C*HMe$_2$), 28.8 (*C*HMe$_2$), 28.9 (*C*HMe$_2$), 102.8 (6-ring-γ-*C*), 123.8 (5-ring-β-*C*), 124.0 – 169.4 (arom. *C*, Ge*C*Me, N*C*Me).

UV-vis λ [nm] = 315 (intense), 358 (intense), 501 (2600).

EI-MS m/z (%): 491 (45, [M – (C_3NGe) ring fragment]$^+$), 316 (15, [M – (C_3N_2Ge) ring fragment]$^+$).

Elemental analysis (%): calcd for $C_{46}H_{65}Ge_2N_3$: C, 68.61; H, 8.14; N, 5.22. Found C, 68.84; H, 8.00; N, 5.16.

Germylene-stannylene 5:

To a suspension of **1** (116 mg, 0.328 mmol) in Et_2O (15 ml) at -70 °C was added the solution of **3** (187 mg, 0.328 mmol) in Et_2O (15 ml). The colour of the solution changed from yellow to dark red. After stirring for further 2 h at room temperature the ^{1}H NMR spectrum of the reaction solution showed that the compound **L'H** was the only side product. The volatiles of the reaction mixture were removed under reduced pressure and the residue extracted with hexane (30 ml). The filtrate was concentrated and stored at -30°C for 10 days yielding **5** as dark red-black solid (96 mg, 0.11 mmol, 34%).

M.p. >143 °C (decomp.)

^{1}H NMR (400.13 MHz, C_6D_6, 298K): δ = 0.85 (d, $^{3}J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.06 (d, $^{3}J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.14 (d, $^{3}J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.21 (d, $^{3}J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.27 (d, $^{3}J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.29 (d, $^{3}J_{HH}$ = 7 Hz, 6 H, CH*Me*$_2$), 1.65 (s, 6 H, SnNC*Me*), 2.27 (s, 3 H, GeNC*Me*), 3.00 (s, 3 H, GeC*Me*), 3.05 (sept, $^{3}J_{HH}$ = 7 Hz, 2 H, C*H*Me$_2$), 3.33 (sept, $^{3}J_{HH}$ = 7 Hz, 2 H, C*H*Me$_2$), 3.78 (sept, $^{3}J_{HH}$ = 7 Hz, 2 H, C*H*Me$_2$), 5.10 (s, 1 H, 6-ring-γ-C*H*), 6.91 (s, 1 H, 5-ring-β-C*H*), 7.05- 7.21 (m, 9 H, arom. *H*).

^{13}C{^{1}H} NMR (100.61 MHz, THF-D_8, 298K): δ = 18.8 (5-ring-NC*Me*), 20.7 (GeC*Me*), 24.2 (6-ring-NC*Me*), 24.6 (CH*Me*$_2$), 24.8 (CH*Me*$_2$), 24.9 (CH*Me*$_2$), 25.9 (CH*Me*$_2$), 26.0 (CH*Me*$_2$), 26.8 (CH*Me*$_2$), 28.0 (*C*HMe$_2$), 28.2 (*C*HMe$_2$), 28.7 (*C*HMe$_2$), 103.5 (6-ring-γ-*C*), 123.7 (5-ring-β-*C*), 124.4 – 170.4 (arom. *C*, Ge*C*Me, N*C*Me).

^{119}Sn NMR (C_6D_6): δ = -197

UV-vis λ [nm] = 314 (15000), 363 (14500), 541 (2800).

EI-MS m/z (%): 537 (8, [M - (C_3NGe) ring fragment]$^+$), 316 (17, [M - (C_3N_2Ge) ring fragment]$^+$).

Elemental analysis (%): calcd for $C_{46}H_{65}GeN_3Sn$: C, 64.89; H, 7.70; N, 4.94. Found C, 64.44; H, 7.64; N, 4.77.

References

1. W. Wang, S. Yao, C. van Wuellen, M. Driess, *J. Am. Chem. Soc.* 2008, **130**, 9640.
2. Y. Ding, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, *Organometallics* 2001, **20**, 1190.

Crystallographic data for compound 4

Empirical formula	C46 H65 Ge2 N3	
Formula weight	805.19	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 44.536(2) Å	α= 90°.
	b = 9.8204(5) Å	β= 116.030(4)°.
	c = 21.8135(10) Å	γ = 90°.
Volume	8572.7(7) $Å^3$	
Z	8	
Density (calculated)	1.248 Mg/m^3	
Absorption coefficient	1.436 mm^{-1}	
F(000)	3408	
Crystal size	0.38 x 0.24 x 0.10 mm^3	
Theta range for data collection	3.05 to 25.00°.	
Index ranges	-49<=h<=52, -10<=k<=11, -24<=l<=25	
Reflections collected	20162	
Independent reflections	7493 [R(int) = 0.0954]	
Completeness to theta = 25.00°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.74676	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7493 / 0 / 476	
Goodness-of-fit on F^2	0.917	
Final R indices [I>2sigma(I)]	R1 = 0.0559, wR2 = 0.0778	
R indices (all data)	R1 = 0.1461, wR2 = 0.0966	
Largest diff. peak and hole	0.590 and -0.578 $e.Å^{-3}$	

Table 1. Bond lengths [Å] and angles [°] for **4**.

Ge(1)-N(1)	2.015(4)	C(24)-C(26)	1.529(7)
Ge(1)-N(2)	2.038(4)	C(27)-C(28)	1.523(6)
Ge(1)-Ge(2)	2.5498(8)	C(27)-C(29)	1.534(6)
N(1)-C(2)	1.333(6)	C(30)-C(31)	1.508(6)
N(1)-C(6)	1.447(6)	C(31)-C(32)	1.377(6)
C(1)-C(2)	1.515(6)	C(32)-C(33)	1.391(7)
Ge(2)-C(31)	1.903(5)	C(33)-C(34)	1.504(6)
Ge(2)-N(3)	1.951(4)	C(35)-C(40)	1.404(6)
N(2)-C(4)	1.322(6)	C(35)-C(36)	1.405(6)
N(2)-C(18)	1.456(6)	C(36)-C(37)	1.404(7)
C(2)-C(3)	1.401(6)	C(36)-C(44)	1.536(7)
N(3)-C(33)	1.348(6)	C(37)-C(38)	1.374(6)
N(3)-C(35)	1.450(6)	C(38)-C(39)	1.374(6)
C(3)-C(4)	1.398(6)	C(39)-C(40)	1.392(7)
C(4)-C(5)	1.510(6)	C(40)-C(41)	1.525(7)
C(6)-C(7)	1.395(6)	C(41)-C(43)	1.513(7)
C(6)-C(11)	1.401(7)	C(41)-C(42)	1.526(6)
C(7)-C(8)	1.396(7)	C(44)-C(45)	1.512(7)
C(7)-C(15)	1.531(7)	C(44)-C(46)	1.541(6)
C(8)-C(9)	1.379(6)		
C(9)-C(10)	1.376(6)	N(1)-Ge(1)-N(2)	88.67(15)
C(10)-C(11)	1.387(6)	N(1)-Ge(1)-Ge(2)	104.30(11)
C(11)-C(12)	1.522(7)	N(2)-Ge(1)-Ge(2)	101.49(12)
C(12)-C(14)	1.512(7)	C(2)-N(1)-C(6)	118.0(4)
C(12)-C(13)	1.520(8)	C(2)-N(1)-Ge(1)	113.3(3)
C(15)-C(17)	1.513(7)	C(6)-N(1)-Ge(1)	127.2(3)
C(15)-C(16)	1.540(7)	C(31)-Ge(2)-N(3)	84.47(19)
C(18)-C(19)	1.400(6)	C(31)-Ge(2)-Ge(1)	118.90(15)
C(18)-C(23)	1.405(6)	N(3)-Ge(2)-Ge(1)	99.62(12)
C(19)-C(20)	1.390(7)	C(4)-N(2)-C(18)	119.1(4)
C(19)-C(24)	1.499(7)	C(4)-N(2)-Ge(1)	114.8(3)
C(20)-C(21)	1.371(7)	C(18)-N(2)-Ge(1)	122.5(3)
C(21)-C(22)	1.373(7)	N(1)-C(2)-C(3)	122.5(5)
C(22)-C(23)	1.390(6)	N(1)-C(2)-C(1)	121.7(4)
C(23)-C(27)	1.520(6)	C(3)-C(2)-C(1)	115.8(5)
C(24)-C(25)	1.527(7)	C(33)-N(3)-C(35)	120.3(4)

C(33)-N(3)-Ge(2)	111.4(3)	C(22)-C(23)-C(27)	118.6(5)
C(35)-N(3)-Ge(2)	126.7(3)	C(18)-C(23)-C(27)	123.0(4)
C(4)-C(3)-C(2)	126.7(5)	C(19)-C(24)-C(25)	113.5(5)
N(2)-C(4)-C(3)	122.4(5)	C(19)-C(24)-C(26)	111.2(5)
N(2)-C(4)-C(5)	120.5(5)	C(25)-C(24)-C(26)	110.2(5)
C(3)-C(4)-C(5)	117.1(4)	C(23)-C(27)-C(28)	110.8(4)
C(7)-C(6)-C(11)	121.4(5)	C(23)-C(27)-C(29)	113.4(4)
C(7)-C(6)-N(1)	119.5(5)	C(28)-C(27)-C(29)	110.4(4)
C(11)-C(6)-N(1)	119.0(5)	C(32)-C(31)-C(30)	119.2(5)
C(6)-C(7)-C(8)	118.5(5)	C(32)-C(31)-Ge(2)	110.5(4)
C(6)-C(7)-C(15)	122.8(5)	C(30)-C(31)-Ge(2)	129.5(4)
C(8)-C(7)-C(15)	118.8(5)	C(31)-C(32)-C(33)	117.5(5)
C(9)-C(8)-C(7)	120.6(5)	N(3)-C(33)-C(32)	114.7(5)
C(10)-C(9)-C(8)	120.1(5)	N(3)-C(33)-C(34)	122.7(5)
C(9)-C(10)-C(11)	121.3(5)	C(32)-C(33)-C(34)	122.4(5)
C(10)-C(11)-C(6)	118.0(5)	C(40)-C(35)-C(36)	121.7(5)
C(10)-C(11)-C(12)	118.9(5)	C(40)-C(35)-N(3)	120.4(4)
C(6)-C(11)-C(12)	123.1(5)	C(36)-C(35)-N(3)	117.8(4)
C(14)-C(12)-C(13)	107.6(5)	C(37)-C(36)-C(35)	117.7(5)
C(14)-C(12)-C(11)	113.8(5)	C(37)-C(36)-C(44)	118.3(5)
C(13)-C(12)-C(11)	112.0(5)	C(35)-C(36)-C(44)	123.8(5)
C(17)-C(15)-C(7)	112.0(5)	C(38)-C(37)-C(36)	121.0(5)
C(17)-C(15)-C(16)	111.0(5)	C(37)-C(38)-C(39)	120.3(5)
C(7)-C(15)-C(16)	110.8(5)	C(38)-C(39)-C(40)	121.7(5)
C(19)-C(18)-C(23)	120.9(5)	C(39)-C(40)-C(35)	117.6(5)
C(19)-C(18)-N(2)	119.4(5)	C(39)-C(40)-C(41)	120.5(5)
C(23)-C(18)-N(2)	119.6(4)	C(35)-C(40)-C(41)	121.9(5)
C(20)-C(19)-C(18)	117.8(5)	C(43)-C(41)-C(40)	111.8(4)
C(20)-C(19)-C(24)	119.8(5)	C(43)-C(41)-C(42)	110.3(5)
C(18)-C(19)-C(24)	122.4(5)	C(40)-C(41)-C(42)	110.5(4)
C(21)-C(20)-C(19)	122.1(5)	C(45)-C(44)-C(36)	110.9(4)
C(20)-C(21)-C(22)	119.4(5)	C(45)-C(44)-C(46)	113.0(5)
C(21)-C(22)-C(23)	121.4(5)	C(36)-C(44)-C(46)	110.5(5)
C(22)-C(23)-C(18)	118.3(5)		

Crystallographic data for compound 5

Empirical formula	C46 H65 Ge N3 Sn	
Formula weight	851.29	
Temperature	150(2) K	
Wavelength	71.073 pm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 867.780(10) pm	α= 96.333(2)°.
	b = 1205.14(4) pm	β= 97.393(2)°.
	c = 2107.97(6) pm	γ = 99.141(2)°.
Volume	2.13908(10) nm^3	
Z	2	
Density (calculated)	1.322 Mg/m^3	
Absorption coefficient	1.320 mm^{-1}	
F(000)	888	
Crystal size	0.16 x 0.14 x 0.12 mm^3	
Theta range for data collection	2.95 to 25.00°.	
Index ranges	-10<=h<=10, -14<=k<=14, -25<=l<=25	
Reflections collected	16936	
Independent reflections	7496 [R(int) = 0.0251]	
Completeness to theta = 25.00°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.99037	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7496 / 0 / 495	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0706	
R indices (all data)	R1 = 0.0437, wR2 = 0.0733	
Largest diff. peak and hole	1.468 and -0.424 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **2**.

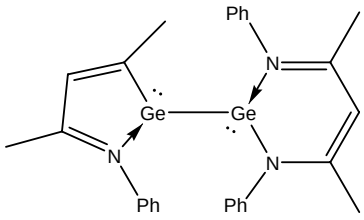
Sn(1)-N(2)	223.1(2)	C(23)-C(24)	153.5(4)
Sn(1)-N(1)	223.3(2)	C(24)-C(25)	152.4(4)
Sn(1)-Ge(1)	272.10(4)	C(24)-C(26)	153.0(4)
Ge(1)-C(31)	191.5(3)	C(27)-C(29)	151.3(5)
Ge(1)-N(3)	196.4(2)	C(27)-C(28)	152.8(4)
N(1)-C(2)	132.4(4)	C(27)-Sn(1A)	266.6(8)
N(1)-C(6)	145.0(3)	C(30)-C(31)	149.6(4)
N(1)-Sn(1A)	234.6(7)	C(31)-C(32)	137.9(4)
C(1)-C(2)	151.2(4)	C(31)-Ge(1A)	212.1(13)
N(2)-C(4)	132.7(4)	C(32)-C(33)	140.3(4)
N(2)-C(18)	144.4(3)	C(33)-C(34)	148.8(4)
N(2)-Sn(1A)	241.7(7)	C(35)-C(36)	140.4(4)
C(2)-C(3)	140.6(4)	C(35)-C(40)	140.9(4)
N(3)-C(33)	134.2(3)	C(36)-C(37)	139.0(4)
N(3)-C(35)	143.9(3)	C(36)-C(44)	152.4(4)
N(3)-Ge(1A)	192.7(13)	C(37)-C(38)	138.0(4)
C(3)-C(4)	141.5(4)	C(38)-C(39)	138.5(5)
C(4)-C(5)	150.3(4)	C(39)-C(40)	139.2(4)
C(6)-C(7)	139.4(4)	C(40)-C(41)	151.3(4)
C(6)-C(11)	141.5(4)	C(41)-C(42)	151.5(5)
C(7)-C(8)	139.4(4)	C(41)-C(43)	152.6(4)
C(7)-C(15)	153.1(4)	C(44)-C(45)	151.2(5)
C(8)-C(9)	138.2(4)	C(44)-C(46)	153.5(5)
C(9)-C(10)	137.2(4)	Sn(1A)-Ge(1A)	275.9(16)
C(10)-C(11)	139.1(4)		
C(11)-C(12)	152.4(4)	N(2)-Sn(1)-N(1)	82.88(8)
C(12)-C(13)	152.9(5)	N(2)-Sn(1)-Ge(1)	95.42(5)
C(12)-C(14)	153.4(5)	N(1)-Sn(1)-Ge(1)	103.68(5)
C(15)-C(16)	152.5(5)	C(31)-Ge(1)-N(3)	84.33(12)
C(15)-C(17)	152.8(4)	C(31)-Ge(1)-Sn(1)	114.95(9)
C(18)-C(23)	139.9(4)	N(3)-Ge(1)-Sn(1)	102.00(6)
C(18)-C(19)	140.7(4)	C(2)-N(1)-C(6)	119.7(2)
C(19)-C(20)	138.6(4)	C(2)-N(1)-Sn(1)	112.43(17)
C(19)-C(27)	152.5(4)	C(6)-N(1)-Sn(1)	124.80(18)
C(20)-C(21)	137.2(4)	C(2)-N(1)-Sn(1A)	126.1(3)
C(21)-C(22)	138.4(4)	C(6)-N(1)-Sn(1A)	100.6(2)
C(22)-C(23)	138.8(4)	Sn(1)-N(1)-Sn(1A)	58.17(19)

C(4)-N(2)-C(18)	120.2(2)	C(19)-C(18)-N(2)	118.5(2)
C(4)-N(2)-Sn(1)	114.44(17)	C(20)-C(19)-C(18)	118.1(3)
C(18)-N(2)-Sn(1)	122.65(17)	C(20)-C(19)-C(27)	120.5(2)
C(4)-N(2)-Sn(1A)	123.7(3)	C(18)-C(19)-C(27)	121.4(2)
C(18)-N(2)-Sn(1A)	102.1(2)	C(21)-C(20)-C(19)	121.7(3)
Sn(1)-N(2)-Sn(1A)	57.12(18)	C(20)-C(21)-C(22)	119.7(3)
N(1)-C(2)-C(3)	124.1(3)	C(21)-C(22)-C(23)	120.9(3)
N(1)-C(2)-C(1)	119.8(2)	C(22)-C(23)-C(18)	118.8(2)
C(3)-C(2)-C(1)	116.1(2)	C(22)-C(23)-C(24)	118.6(3)
C(33)-N(3)-C(35)	120.4(2)	C(18)-C(23)-C(24)	122.6(2)
C(33)-N(3)-Ge(1A)	100.3(4)	C(25)-C(24)-C(26)	109.6(3)
C(35)-N(3)-Ge(1A)	124.3(4)	C(25)-C(24)-C(23)	109.9(2)
C(33)-N(3)-Ge(1)	111.53(18)	C(26)-C(24)-C(23)	112.6(2)
C(35)-N(3)-Ge(1)	126.91(18)	C(29)-C(27)-C(19)	111.0(3)
Ge(1A)-N(3)-Ge(1)	50.1(4)	C(29)-C(27)-C(28)	110.7(3)
C(2)-C(3)-C(4)	128.5(2)	C(19)-C(27)-C(28)	111.7(3)
N(2)-C(4)-C(3)	122.8(2)	C(29)-C(27)-Sn(1A)	127.4(3)
N(2)-C(4)-C(5)	120.5(2)	C(19)-C(27)-Sn(1A)	93.6(2)
C(3)-C(4)-C(5)	116.7(2)	C(28)-C(27)-Sn(1A)	101.0(3)
C(7)-C(6)-C(11)	120.4(3)	C(32)-C(31)-C(30)	120.6(3)
C(7)-C(6)-N(1)	120.0(2)	C(32)-C(31)-Ge(1)	110.0(2)
C(11)-C(6)-N(1)	119.6(2)	C(30)-C(31)-Ge(1)	128.2(3)
C(6)-C(7)-C(8)	119.2(3)	C(32)-C(31)-Ge(1A)	92.5(4)
C(6)-C(7)-C(15)	123.1(2)	C(30)-C(31)-Ge(1A)	133.6(4)
C(8)-C(7)-C(15)	117.7(3)	Ge(1)-C(31)-Ge(1A)	47.8(4)
C(9)-C(8)-C(7)	120.9(3)	C(31)-C(32)-C(33)	117.9(3)
C(10)-C(9)-C(8)	119.5(3)	N(3)-C(33)-C(32)	114.5(3)
C(9)-C(10)-C(11)	121.9(3)	N(3)-C(33)-C(34)	122.5(3)
C(10)-C(11)-C(6)	118.0(3)	C(32)-C(33)-C(34)	122.5(3)
C(10)-C(11)-C(12)	118.5(3)	C(36)-C(35)-C(40)	122.0(3)
C(6)-C(11)-C(12)	123.5(3)	C(36)-C(35)-N(3)	119.3(2)
C(11)-C(12)-C(13)	110.3(3)	C(40)-C(35)-N(3)	118.7(3)
C(11)-C(12)-C(14)	112.2(3)	C(37)-C(36)-C(35)	117.6(3)
C(13)-C(12)-C(14)	109.5(3)	C(37)-C(36)-C(44)	120.1(3)
C(16)-C(15)-C(17)	111.2(3)	C(35)-C(36)-C(44)	122.3(3)
C(16)-C(15)-C(7)	111.7(3)	C(38)-C(37)-C(36)	121.7(3)
C(17)-C(15)-C(7)	110.5(2)	C(37)-C(38)-C(39)	119.7(3)
C(23)-C(18)-C(19)	120.7(3)	C(38)-C(39)-C(40)	121.4(3)
C(23)-C(18)-N(2)	120.7(2)	C(39)-C(40)-C(35)	117.5(3)

C(39)-C(40)-C(41)	120.2(3)	N(1)-Sn(1A)-C(27)	120.9(3)
C(35)-C(40)-C(41)	122.3(3)	N(2)-Sn(1A)-C(27)	69.1(2)
C(40)-C(41)-C(42)	111.6(3)	N(1)-Sn(1A)-Ge(1A)	87.5(3)
C(40)-C(41)-C(43)	112.4(3)	N(2)-Sn(1A)-Ge(1A)	104.2(4)
C(42)-C(41)-C(43)	109.7(3)	C(27)-Sn(1A)-Ge(1A)	146.2(4)
C(45)-C(44)-C(36)	110.8(3)	N(3)-Ge(1A)-C(31)	79.9(5)
C(45)-C(44)-C(46)	110.5(3)	N(3)-Ge(1A)-Sn(1A)	113.5(6)
C(36)-C(44)-C(46)	112.0(3)	C(31)-Ge(1A)-Sn(1A)	77.9(5)
N(1)-Sn(1A)-N(2)	76.7(2)		

Computational Methods

DFT calculations of the model compound of LGeGeL' [L = CH{CMe(NPh)$_2$, L' = CH(CMe)$_2$NPh} (**6**) were performed at the B3LYP/6-31(d) level; that on the model compound LSnGeL' [L = CH{CMe(NPh)$_2$, L' = CH(CMe)$_2$NPh} (**7**) were performed at B3LYP level using the 6-31G(d) basis set for Ge, N, C, and H atoms and the LANL2DZ level for the Sn atom in the GAUSSIAN-03 program package.[3] The NBO approach was applied to calculate NPA charges, orbital populations, Wiberg bond index and other bonding nature. Respective Cartesian coordinates of optimized structures are listed in Table 3 and Table 4.



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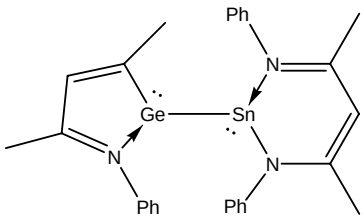

7

References

3. M. J. Frisch, *Gaussian 03*, revision D. 01; Gaussian, Inc.: Wall-ingford, CT 2004..

Table 3. Cartesian coordination (x, y, z) for the optimized structure of **6**.

Ge	−0.35733	−0.32428	−0.75754
N	−1.22824	−2.13832	−0.6528
C	−1.76318	−4.34355	0.291504
Ge	−0.98732	0.5401	1.533157
N	1.364471	−1.17085	−0.10835
C	−0.85724	−3.14029	0.139725
N	−2.27315	1.806152	0.801636
C	0.365387	−3.14346	0.836868
C	1.454605	−2.27702	0.625885
C	2.783829	−2.6492	1.247971
C	−2.40317	−2.20053	−1.46527
C	−2.37654	−2.87967	−2.6891
C	−3.50468	−2.88693	−3.50876
C	−4.65662	−2.19652	−3.12489
C	−4.67152	−1.49318	−1.91905
C	−3.54765	−1.48334	−1.09073
C	2.515244	−0.38446	−0.43205
C	2.797119	0.784393	0.287704
C	3.895935	1.569031	−0.06711
C	4.707764	1.205353	−1.14247
C	4.411255	0.053146	−1.87415
C	3.313889	−0.73421	−1.52788
C	−2.45757	−1.35162	3.422073
C	−2.47742	−0.20113	2.453369
C	−3.60457	0.593872	2.256378
C	−3.49915	1.668015	1.346939
C	−4.62997	2.619308	1.058853
C	−1.92738	2.69339	−0.24365
C	−0.78931	3.502563	−0.10561
C	−0.37871	4.323273	−1.1553
C	−1.09193	4.347122	−2.35486
C	−2.2101	3.52388	−2.50516
C	−2.6183	2.690018	−1.46596
H	−1.79158	−4.93308	−0.63173
H	−2.79111	−4.03229	0.503159
H	−1.41446	−4.9911	1.098953

H	0.544952	−3.99149	1.485748
H	3.521362	−2.89717	0.476776
H	2.675217	−3.51108	1.909683
H	3.193054	−1.81064	1.820984
H	−1.46706	−3.39273	−2.98935
H	−3.47951	−3.42348	−4.45355
H	−5.53397	−2.20096	−3.76588
H	−5.5618	−0.94727	−1.61777
H	−3.54428	−0.93254	−0.15402
H	2.150116	1.069183	1.113007

Table 2. Cartesian coordination (x, y, z) for the optimized structure of **7**.

Sn	−0.55415	0.078537	−1.18549
Ge	0.735062	−0.78871	1.16066
N	−0.90888	2.210373	−0.66435
N	−2.55995	−0.23462	−0.28304
N	2.558777	−0.98673	0.395279
C	−1.71487	4.13797	0.638306
C	−1.76302	2.670593	0.2509
C	−2.73958	1.881958	0.889587
C	−3.17075	0.576569	0.582291
C	−4.42783	0.0934	1.283066
C	−0.04527	3.102875	−1.37614
C	−0.5412	3.888962	−2.4267
C	0.318237	4.709137	−3.15747
C	1.68251	4.744431	−2.85768
C	2.181381	3.95047	−1.82369
C	1.32663	3.12941	−1.08456
C	0.778473	1.719025	2.945251
C	1.485947	0.770187	2.014328
C	2.855728	0.854172	1.784378
C	3.4292	−0.09583	0.912109
C	4.910614	−0.15927	0.642838
C	2.929352	−1.99124	−0.53668
C	2.738953	−3.34421	−0.21875
C	3.052582	−4.33652	−1.14835
C	3.559753	−3.99522	−2.40358
C	3.742004	−2.64888	−2.72821
C	3.423355	−1.65202	−1.80652
C	−3.14858	−1.49324	−0.63498
C	−2.68048	−2.6783	−0.05039
C	−3.21649	−3.90807	−0.43926
C	−4.21503	−3.96806	−1.41278
C	−4.67438	−2.78885	−2.00468
C	−4.14143	−1.55739	−1.62344
H	−2.09178	4.770874	−0.17256
H	−2.32338	4.324051	1.525909
H	−0.68695	4.455994	0.838654

H	−3.32216	2.3929	1.645859
H	−4.26566	−0.88782	1.740738
H	−4.7381	0.7986	2.056824
H	−5.25291	−0.02148	0.571533
H	−1.59924	3.840729	−2.6694
H	−0.07771	5.3145	−3.96866
H	2.351181	5.380783	−3.43076
H	3.241943	3.968094	−1.5864
H	1.711243	2.511154	−0.27745
H	−0.29829	1.525497	2.997314