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Electronic Supplementary Information

From NHC→Germylenes to Stable NHC→Germanone Complexes

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A. Synthesis

General Considerations.

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting material LGe:(**1**)[1] {L = CH[(C=CH_2)CMe][N(Ar)]$_2$], Ar = 2,6-*i*$Pr_2C_6H_3$}, 1,3,4,5-tetramethylimidazol-2-ylidene, and 1,3-dimethyl-4,5-diisopropylimidazol-2-ylidene [2] were prepared according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on Brucker ARX200 and AV 400 Spectrometers.

Compound **2a**: 1,3,4,5-tetramethylimidazol-2-ylidene (0.25 g, 2.0 mmol) in toluene (15ml) was added to a solution of germylene **1** (1.00 g, 2.0 mmol) in toluene (15 ml) at -30ºC. After 30 min the resulting reaction solution was allowed to warm to room temperature and concentrated to about 10 ml. Subsequent cooling of the solution at -20 ºC afforded **2a** as yellow crystals (1.04 g, 1.7 mmol, 85 %). M.p. 181 ºC (decomp.). ^{1}H NMR (400.13 MHz, [D_6]benzene, 25ºC): δ = 0.35 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 0.38 (d, ^3J (H,H) = 7 Hz, 3 H;

CH*Me*$_2$), 1.08 (s, 3 H; C$_2$*Me*$_2$), 1.12 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.41 (s, 3 H, C$_2$*Me*$_2$), 1.46 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.48 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.59 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.63 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.66 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.72 (s, 3 H; NC*Me*), 2.81 (s, 3 H; N*Me*), 3.08 (setp, ^3J (H,H) = 7 Hz, 1 H; C*H*Me$_2$), 3.16 (setp, ^3J (H,H) = 7 Hz, 1 H; C*H*Me$_2$), 3.22 (s, 1 H; NCC*H*$_2$), 3.85 (s, 3 H, N*Me*), 3.94 (s, 1 H; NCC*H*$_2$), 4.07 – 4.21 (m, 2 H; C*H*Me$_2$), 5.48 (s, 1 H; γ-C*H*), 7.03 – 7.40 ppm (m, br, 6 H; 2,6-*i*Pr$_2$C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25ºC): δ = 7.4, 7.8 (C$_2$*Me*$_2$), 23.5 –29.7 (NC*Me*, *C*H*Me*$_2$); 32.5, 34.3 (N*Me*); 79.3 (NC*C*H$_2$), 102.3 (γ-*C*), 123.0 – 152.8 (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$, *C*$_2$Me$_2$); 176.0 (Ge*C*). EI-MS: m/z (%): 614.34 (1 [M$^+$]), 491.12 (41, [(M-NHC)$^+$]), 475.07 (100, [(M-NHC-Me)$^+$]), 124.08 (32, [NHC]$^+$). Elemental analysis calcd (%) for $C_{36}H_{52}N_4Ge$: C 70.47, H 8.54, N 9.13, found: C 69.98, H 8.19, N 9.10. IR (KBr, cm^{-1}): 441 (W), 577 (W), 702 (w), 729 (w), 761 (m), 789 (m), 801 (m), 937 (w), 1022 (w), 1058 (w), 1104 (w), 1140 (w), 1176 (m), 1196 (w), 1238 (w), 1254 (w), 1276 (m), 1322 (m), 1360 (w), 1380 (m), 1440 (m), 1466 (m), 1484 (w), 1554 (s), 1623 (s), 2868 (w), 2926 (m), 2962 (s), 3054 (w), 3103 (w).

Compound **2b**: 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (0.22 g, 1.2 mmol) in toluene (10 ml) was added to a solution of germylene **1** (0.60 g, 1.2 mmol) in toluene (10 ml) at -30ºC. After 30 min the resulting reaction solution was allowed to warm to room temperature and concentrated to about 8 ml. Subsequent cooling of the solution at -20 ºC afforded **2b** as yellow crystals (0.69 g, 1.0 mmol, 86 %). M.p. 167 ºC (decomp.). ^{1}H NMR (200.13 MHz, [D$_6$]benzene, 25ºC): δ = 0.70 -1.66 (m, br. 45 H; CH*Me*$_2$, C$_2$*Me*$_2$, NCH*Me*$_2$, NC*Me*), 3.5 - 5.7 (m, br. 6 H; NC*H*Me$_2$, C*H*Me$_2$), 3.24 (s, 1 H; NCC*H*$_2$), 3.92 (s, 1 H; NCC*H*$_2$), 5.53 (s, 1 H; γ-C*H*), 7.01 – 7.25 ppm (m, br, 6 H; 2,6-*i*Pr$_2$C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25ºC): δ = 9.5 (C$_2$*Me*$_2$), 21.0 - 28.2 (NCH*Me*$_2$, NC*Me*, *C*H*Me*$_2$), 50.0 (N*C*HMe$_2$), 79.7 (NC*C*H$_2$), 105.4 (γ-*C*), 123.1 – 147.8 (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$, *C*$_2$Me$_2$); 151.2 (Ge*C*). EI-MS: m/z (%): 491.13 (59, [(M-NHC)$^+$]), 475.09 (100, [(M-NHC-Me)$^+$]), 180.13 (12, [NHC]$^+$). Elemental analysis calcd (%) for $C_{40}H_{60}N_4Ge$: C 71.76, H 9.03, N 8.37, found: C 72.06, H 8.88, N 7.98. IR (KBr, cm^{-1}): 437 (W), 505 (W), 650 (w), 714 (w), 735 (w), 758 (w), 802 (m), 847 (w), 865 (w), 895 (w), 936 (w), 971 (w), 1020 (w), 1034 (m), 1056 (w), 1104 (w), 1173 (m), 1204 (m), 1248 (m), 1309 (m), 1320 (m), 1355 (m), 1384 (s), 1440 (m), 1462 (m), 1550 (m), 1604 (m), 1618 (s), 1652 (w), 2864 (m), 2924 (m), 2962 (s), 3022 (w), 3054 (w), 3098 (w).

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Compound **3a**: A solution of **2a** (0.48 g, 0.78 mmol) in toluene (15 ml) was allowed to exposed to dried N_2O at room temperature. After 12 h, **3a** precipitated in the form of colorless crystals (0.38 g, 0.60 mmol, 77 %). X-ray diffraction-quality crystals of **3a** were obtained by recrystallization from diethyl ether/dichloromethane (v/v: 3:1) at -20 °C. M.p. 151 °C (decomp.). ^{1}H NMR (200.13 MHz, [D_6] benezene, 25ºC): δ = 0.28 (d, ^3J (H,H) = 7 Hz, 6 H; CH*Me*$_2$), 1.08 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.36 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.46 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.63 (d, ^3J (H,H) = 8 Hz, 3 H; CH*Me*$_2$), 1.81 (d, ^3J (H,H) = 7 Hz, 6 H; CH*Me*$_2$); 1.21 (s, 3 H; C_2*Me*$_2$), 1.38 (s, 3 H; C_2*Me*$_2$), 1.59 (s, 3 H; NC*Me*); 2.90 (sept, ^3J (H,H) = 7 Hz, 2 H; C*H*Me$_2$), 3.31 (s, 1 H; NCC*H*$_2$), 3.63 (s, 3 H; N*Me*), 3.87 (s, 3 H; N*Me*), 3.91 (s, 1 H; NCC*H*$_2$), 4.22 (sept, ^3J (H,H) = 7 Hz, 1 H; CH*Me*$_2$), 4.30 (sept, ^3J (H,H) = 7 Hz, 1 H; CH*Me*$_2$); 5.36 (s, 1 H; γ-C*H*), 6.92 – 7.41 ppm (m, 6 H; 2,6-*i*Pr$_2$C$_6$*H*$_3$). ^{13}C{^{1}H} NMR (100.61 MHz, [D_6] benzene, 25ºC): δ = 7.6 (C_2*Me*$_2$), 20.7 – 29.4 (NC*Me*, *C*H*Me*$_2$); 33.5, 33.9 (N*Me*); 83.0 (NC*C*H$_2$), 101.8 (γ- C); 122.8 – 155.4 (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$, *C*$_2$Me$_2$); 161.5 (Ge*C*). EI-MS: m/z (%): 630.12 (0.9, [M]$^+$), 615.20 (1, [M-Me]$^+$), 491.13 (23, [(M-NHC-O)$^+$]), 403.21 (100, [L-Me]$^+$). Elemental analysis (%): calcd for $C_{36}H_{52}N_4GeO$: C, 68.70; H, 8.33; N, 8.90. Found C, 69.07; H, 7.99, N, 8.74. IR (KBr, cm^{-1}): 440 (W), 554 (w), 703 (w), 727 (w), 760 (w), 790 (w), 802 (w), 869 (w), 936 (w), 1041 (w), 1057 (w), 1104 (w), 1177 (w), 1202 (w), 1254 (w), 1275 (m), 1324 (m), 1360 (m), 1380 (m), 1440 (m), 1465 (m), 1488 (w), 1552 (s), 1624 (s), 2866 (m), 2925 (m), 2966 (s), 3055 (w).

Compound **3b**: A solution of **3a** (0.51 g, 0.76 mmol) in toluene (15 ml) was allowed to exposed to dried N_2O at room temperature. After 12 h, **3b** precipitated in the form of colorless crystals (0.44 g, 0.64 mmol, 84 %), which were suitable for X-ray single crystal diffraction analysis. M.p. 226 °C (decomp.). ^{1}H NMR (400.13 MHz, [D_2] dichloromethane, 25ºC): δ = 0.43 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 0.77 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 0.81 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.09 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.11 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.14 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.22 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.24 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.33 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.35 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.57 (s, 3 H; NC*Me*), 1.66 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 1.72 (d, ^3J (H,H) = 7 Hz, 3 H; CH*Me*$_2$), 2.22 (s, 3 H; C_2*Me*$_2$), 2.38 (s, 3 H; C_2*Me*$_2$), 2.83 (sept, ^3J (H,H) = 7 Hz, 1 H; C*H*Me$_2$), 2.85 (s, 1 H; NCC*H*$_2$), 3.25 (sept, ^3J (H,H) = 7 Hz, 1 H;

C*H*Me$_2$), 3.56 (s, 1 H; NCC*H*$_2$), 3.73 (sept, ^3J (H,H) = 7 Hz, 1 H; C*H*Me$_2$), 3.76 (sept, ^3J (H,H) = 7 Hz, 1 H; C*H*Me$_2$), 5.33 (s, 1 H; γ-C*H*), 5.64 (sept, ^3J (H,H) = 7 Hz, 1 H; NC*H*Me$_2$), 6.98 – 7.22 ppm (m, 6 H; 2,6-*i*Pr$_2$C$_6$*H*$_3$), 7.95 (sept, ^3J (H,H) = 7 Hz, 1 H; NC*H*Me$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, [D$_2$] dichloromethane, 25ºC): δ = 11.0, 11.1 (C$_2$*Me*$_2$); 21.3 - 29.1 (NCH*Me*$_2$, NC*Me*, *C*H*Me*$_2$); 49.8, 52.8 (N*C*HMe$_2$); 83.2 (NC*C*H$_2$), 105.0 (γ-*C*); 123.3 – 151.0 (N*C*Me, N*C*CH$_2$, 2,6-*i*Pr$_2$*C*$_6$H$_3$, *C*$_2$Me$_2$); 154.3 (GeC). EI-MS: m/z (%): 686.22 (11, [M$^+$]), 671.13 (10, [(M-Me)$^+$]), 643.24 (100, [(M-iPr)$^+$]). Elemental analysis calcd (%) for C$_{40}$H$_{60}$N$_4$GeO: C 70.08, H 8.82, N 8.17, found: C 69.78, H 8.66, N 8.13. IR (KBr, cm^{-1}): 430 (W), 456 (W), 543 (w), 593 (w), 670 (w), 703 (w), 730 (w), 760 (m), 787 (w), 803 (m), 870 (m), 897 (w), 908 (w), 936 (w), 974 (w), 1039 (m), 1057 (w), 1109 (m), 1141 (w), 1176 (w), 1201 (m), 1242 (w), 1253 (w), 1278 (w), 1310 (w), 1324 (m), 1353 (m), 1361 (w), 1378 (s), 1438 (s), 1462 (s), 1488 (w), 1598 (w), 1553 (s), 1624 (s), 1637 (m), 2680 (w), 2865 (m), 2927 (m), 2964 (s), 3057 (w), 3110 (w).

B. X-Ray Diffraction Studies

Single-Crystal X-ray Structure Determinations: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of compounds **2a**, **2b**, **3a,** and **3b** 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[3] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. In **3a** one of the isopropyl groups was disordered and thus was refined with restraints for the anisotropic displacement parameters. Additionally, strongly disordered diethyl ether molecules in the data of **3a** were removed using the squeeze command in the Platon Software package,[4] except a disordered diethyl ether molecule which was refined with distance restraints and restraints for the anisotropic displacement parameters. In **3b** one of the isopropyl groups is disordered and refined with restraints for the anisotropic displacement parameters. CCDC 731869-731872.

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Crystallographic data for 2a

Empirical formula	C36 H52 Ge N4	
Formula weight	613.41	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 12.5971(6) Å	α= 90°.
	b = 16.7102(6) Å	β= 105.778(4)°.
	c = 17.2809(6) Å	γ = 90°.
Volume	3500.6(2) $Å^3$	
Z	4	
Density (calculated)	1.164 Mg/m^3	
Absorption coefficient	0.903 mm^{-1}	
F(000)	1312	
Crystal size	0.23 x 0.18 x 0.15 mm^3	
Theta range for data collection	2.96 to 25.00°.	
Index ranges	-14<=h<=14, -19<=k<=19, -20<=l<=20	
Reflections collected	15170	
Independent reflections	6140 [R(int) = 0.0656]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.95990	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6140 / 0 / 383	
Goodness-of-fit on F^2	0.879	
Final R indices [I>2sigma(I)]	R1 = 0.0519, wR2 = 0.0781	
R indices (all data)	R1 = 0.1065, wR2 = 0.0871	
Largest diff. peak and hole	0.643 and -0.521 $e.Å^{-3}$	

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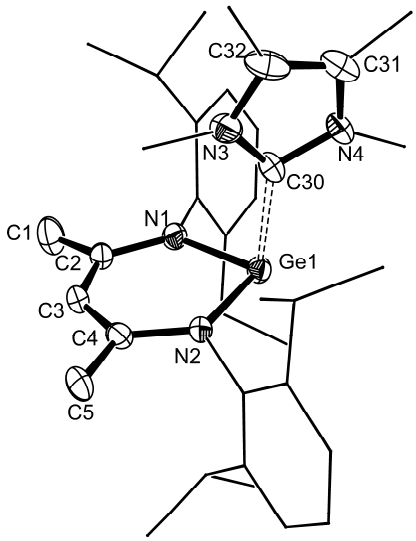

Figure 1. Molecular structure of compound **2a.** Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected interatomic distances and angles of compound **2a**

Interatomic distances (Å)		Angles(°)	
Ge1-N1	1.927(3)	N1-Ge1-N2	95.1(1)
Ge1-N2	1.929(3)	N1-Ge1-C30	95.5(1)
Ge1-C30	2.149(3)	N2-Ge1-C30	97.4(1)
N1-C2	1.385(4)	C2-N1-Ge1	127.7(3)
N2-C4	1.407(4)	C4-N2-Ge1	124.3(2)
N3-C30	1.345(4)	C30-N3-C32	111.1(3)
N3-C32	1.386(5)	C30-N4-C31	111.3(3)
N4-C30	1.355(4)	N1-C2-C3	118.5(3)
N4-C31	1.383(4)	C4-C3-C2	130.8(3)
C1-C2	1.379(5)	C3-C4-N2	123.0(3)
C2-C3	1.430(5)	N3-C30-N4	104.3(3)
C3-C4	1.359(5)	N3-C30-Ge1	134.0(3)
C4-C5	1.471(5)	N4-C30-Ge1	121.1(2)
C31-C32	1.340(5)	C32-C31-N4	106.4(3)
		C31-C32-N3	106.9(3)

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Crystallographic data for **2b**

Empirical formula	C47 H68 Ge N4	
Formula weight	761.64	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	p-1	
Unit cell dimensions	a = 11.1525(4) Å	α= 74.438(3)°.
	b = 14.2463(5) Å	β= 80.643(3)°.
	c = 14.3356(6) Å	γ = 87.108(3)°.
Volume	2164.92(14) Å^3	
Z	2	
Density (calculated)	1.168 Mg/m^3	
Absorption coefficient	0.743 mm^{-1}	
F(000)	820	
Crystal size	0.29 x 0.14 x 0.11 mm^3	
Theta range for data collection	2.96 to 25.00°.	
Index ranges	-13<=h<=11, -16<=k<=16, -16<=l<=17	
Reflections collected	16315	
Independent reflections	7585 [R(int) = 0.0464]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.97301	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7585 / 0 / 485	
Goodness-of-fit on F^2	0.942	
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.0704	
R indices (all data)	R1 = 0.0789, wR2 = 0.0760	
Largest diff. peak and hole	0.566 and -0.549 e.Å^{-3}	

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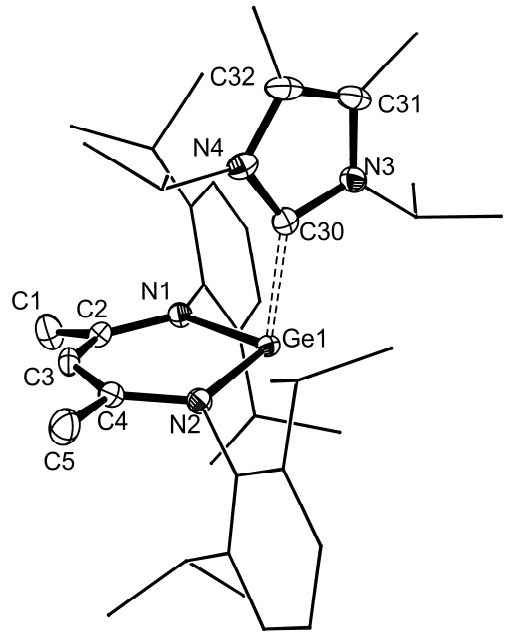

Figure 2. Molecular structure of compound **2b.** Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2 Selected interatomic distances and angles of compound **2b**

Interatomic distances (Å)		Angles (°)	
Ge1-N2	1.912(2)	N2-Ge1-N1	95.35(9)
Ge1-N1	1.943(2)	N2-Ge1-C30	103.29(9)
Ge1-C30	2.192(3)	N1-Ge1-C30	94.85(9)
N1-C2	1.387(3)	C2-N1-Ge1	126.1(2)
N2-C4	1.399(3)	C1-C2-N1	123.3(3)
N3-C30	1.357(3)	C1-C2-C3	118.8(2)
N3-C31	1.398(3)	N1-C2-C3	117.9(2)
N4-C30	1.353(3)	C4-C3-C2	129.3(2)
N4-C32	1.391(3)	C3-C4-N2	123.2(2)
C1-C2	1.356(4)	N4-C30-N3	105.4(2)
C2-C3	1.459(4)	N4-C30-Ge1	137.2(2)
C3-C4	1.350(4)	N3-C30-Ge1	117.4(2)
C4-C5	1.500(3)	C32-C31-N3	106.7(2)
C31-C32	1.345(4)		

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Crystallographic data for **3a**

Empirical formula	C41 H64 Cl2 Ge N4 O2	
Formula weight	788.45	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 11.6635(3) Å	α= 90°.
	b = 24.5936(7) Å	β= 102.959(2)°.
	c = 15.6283(3) Å	γ = 90°.
Volume	4368.76(19) $Å^3$	
Z	4	
Density (calculated)	1.199 Mg/m^3	
Absorption coefficient	0.860 mm^{-1}	
F(000)	1680	
Crystal size	0.36 x 0.23 x 0.19 mm^3	
Theta range for data collection	2.97 to 25.00°.	
Index ranges	-13<=h<=12, -29<=k<=26, -18<=l<=15	
Reflections collected	18717	
Independent reflections	7646 [R(int) = 0.0321]	
Completeness to theta = 25.00°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.97579	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7646 / 76 / 496	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0645, wR2 = 0.1584	
R indices (all data)	R1 = 0.0918, wR2 = 0.1693	
Largest diff. peak and hole	0.977 and -0.690 $e.Å^{-3}$	

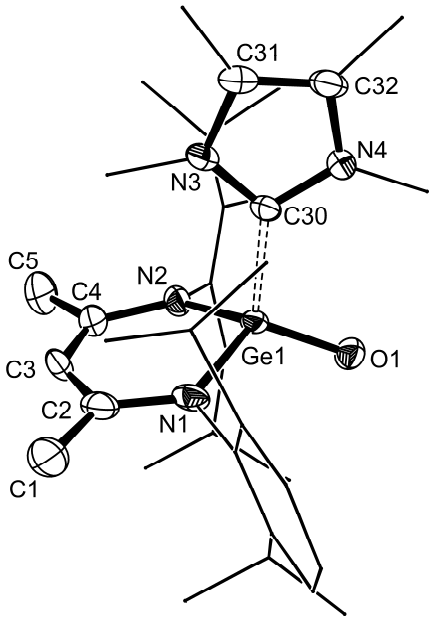

Figure 3. Molecular structure of compound **3a.** Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2 Selected interatomic distances and angles of compound **3a**

Interatomic distances (Å)		Angles (°)	
Ge1-O1	1.672(3)	O1-Ge1-N2	116.1(2)
Ge1-N2	1.854(4)	O1-Ge1-N1	117.3(2)
Ge1-N1	1.859(3)	N2-Ge1-N1	100.5(2)
Ge1-C30	2.020(4)	O1-Ge1-C30	109.7(2)
N1-C2	1.401(6)	N2-Ge1-C30	104.7(2)
N2-C4	1.395(6)	N1-Ge1-C30	107.4(2)
N3-C30	1.347(5)	C2-N1-Ge1	122.0(3)
N3-C31	1.384(6)	C4-N2-Ge1	122.5(3)
N4-C30	1.346(5)	C30-N3-C31	111.3(4)
N4-C32	1.389(5)	C30-N4-C32	111.6(3)
C1-C2	1.395(7)	N1-C2-C3	120.4(4)
C2-C3	1.417(7)	C4-C3-C2	131.0(4)
C3-C4	1.380(7)	C3-C4-N2	121.2(4)
C4-C5	1.441(7)	N4-C30-N3	104.7(3)
C31-C32	1.361(7)		

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Crystallographic data for **3b**

Empirical formula	C40 H60 Ge N4 O	
Formula weight	685.51	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 21.2684(5) Å	α= 90°.
	b = 16.9410(4) Å	β= 94.333(2)°.
	c = 21.6339(5) Å	γ = 90°.
Volume	7772.6(3) $Å^3$	
Z	8	
Density (calculated)	1.172 Mg/m^3	
Absorption coefficient	0.822 mm^{-1}	
F(000)	2944	
Crystal size	0.29 x 0.23 x 0.19 mm^3	
Theta range for data collection	3.04 to 25.00°.	
Index ranges	-25<=h<=25, -16<=k<=20, -25<=l<=25	
Reflections collected	71416	
Independent reflections	13672 [R(int) = 0.0693]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.88750	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13672 / 33 / 859	
Goodness-of-fit on F^2	0.956	
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.0685	
R indices (all data)	R1 = 0.0823, wR2 = 0.0757	
Largest diff. peak and hole	0.592 and -0.536 $e.Å^{-3}$	

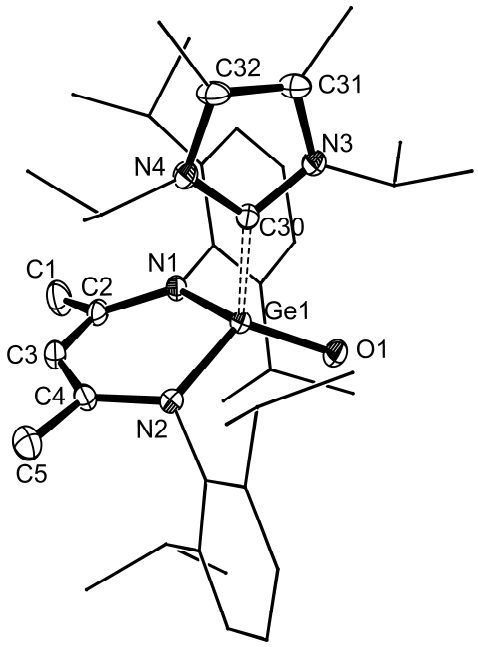

Figure 4. Molecular structure of compound **3b.** Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2 Selected interatomic distances and angles of compound **3b**

Interatomic distances (Å)			Angles (°)		
Molecule 1		Molecule 2	Molecule 1		Molecule 2
Ge1-O1	1.670(2)	1.664(2)	O1-Ge1-N2	115.25(8)	113.88(9)
Ge1-N2	1.852(2)	1.853(2)	O1-Ge1-N1	118.35(8)	118.83(9)
Ge1-N1	1.871(2)	1.866(2)	N2-Ge1-N1	100.47(9)	100.54(9)
Ge1-C30	2.040(2)	2.053(3)	O1-Ge1-C30	108.48(9)	109.0(1)
N1-C2	1.397(3)	1.400(3)	N2-Ge1-C30	111.08(9)	110.3(1)
N2-C4	1.409(3)	1.415(3)	N1-Ge1-C30	102.36(9)	103.5(1)
N3-C30	1.354(3)	1.355(3)	N1-C2-C3	118.4(2)	118.3(2)
N3-C31	1.390(3)	1.388(3)	C4-C3-C2	129.4(2)	129.2(2)
N4-C30	1.357(3)	1.361(3)	C3-C4-N2	123.1(2)	122.9(2)
N4-C32	1.391(3)	1.390(3)	N3-C30-N4	106.1(2)	105.9(2)
C1-C2	1.351(3)	1.356(3)	N3-C30-Ge1	123.4(2)	123.6(2)
C2-C3	1.460(3)	1.464(3)	N4-C30-Ge1	129.4(2)	130.2(2)
C3-C4	1.343(3)	1.348(3)			
C4-C5	1.503(3)	1.488(3)			

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References

[1] Driess, M.; Yao, S.; Brym, M.; van Wüllen, C. *Angw. Chem. Int. Ed.* **2006**, *45*, 4349.
[2] Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561.
[3] G. M. Sheldrick, *SHELX-97 Program for Crystal Structure Determination*, Universität Göttingen (Germany) **1997**.
[4] a) A.L.Spek (2005) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. b) Sluis & Spek, *Acta Cryst.* **1990**, A46, 194).