Products of the Reactions of 2-Diazomalonate and of 2-Diazoindanedione with Germylenes and Stannylenes

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Products obtained in the reaction between germylenes or stannylenes with dimethyl 2-diazomalonate and 2-diazo-1,3-indanedione have been isolated and characterized. Compounds thus prepared are the 2*H*-1,3,4,2-oxadiazagermanine-5-carboxylates **1** and **2**, the indeno[2,1-*e*]-1,3,4,2-oxadiazametallanin-5(2*H*)-ones **7** and **8**, the 6-oxa-3,4-diaza-2,7-digermabicyclo[3.2.0]hept-3-ene-carboxylate **3**, resulting from the thermal treatment of **2**, and the unsymmetrical dimer of **7**, (**7**)$_2$. Furthermore the reaction products of **2** with *t*-BuNCO, **4**, with PhCHO, **5**, and with $H_2C{=}CHCHO$, **6**, and compound **9** obtained by partial hydrolysis of **7** and (**7**)$_2$ were isolated. The compounds were characterized by NMR spectroscopy (^{1}H, ^{13}C, and ^{29}Si and in part ^{15}N and ^{119}Sn), MS (EI or FI), and elemental analyses. X-ray crystal structure determinations are presented for **1**, **2**, **3**, **4**, and (**7**)$_2$.

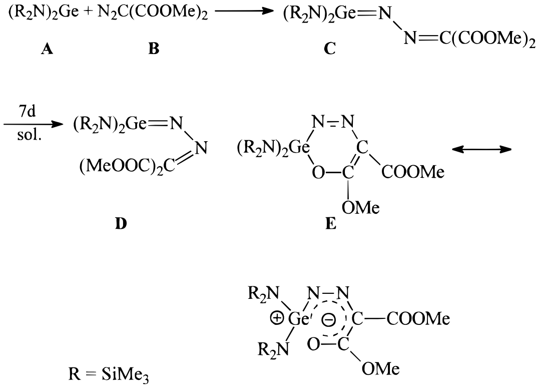
Introduction

In 1987 the formation of a first example of a stable germaimine was described from the reaction of bis[bis(trimethylsilyl)amino]germane(II) with 2-diazomalonate.[1,2] It was reported that the reaction led to the transoid isomer of the germaimine (**C**), which in solution upon storage at room temperature converted to the cisoid conformer (**D**) (Scheme 1).

Structural assignments have been done in accordance with ^{1}H- and ^{13}C-NMR data and are supported by MNDO calculations. Later on a cyclic equilibrium structure (**E**) was also considered (based on MNDO results[3,4]) by the interaction of one of the C═O groups with the germanium atom. The MNDO calculations using a simplified model (SiH_3 for $SiMe_3$, gas phase at 0 K) resulted in enthalpies of formation of $\Delta H_f = -590$ kJ/mol for the germaimine structure (**C**) but $\Delta H_f = -775$ kJ/mol for **E**.[5,6]

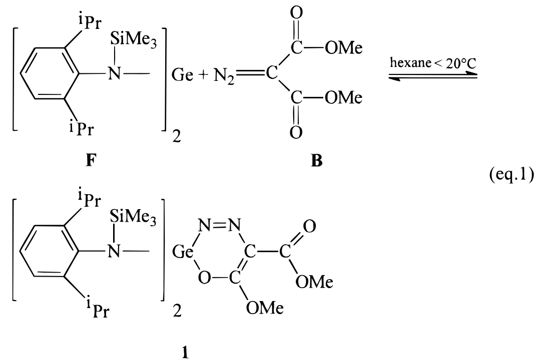
E however cannot be considered as a germaimine anymore. Apparently no further attempts have been made by the original authors to isolate any of the discussed compounds. As we are concerned with the chemistry of germaimines ourself,[7,8] we were interested in characterizing the products of the reactions of germylenes with diazo compounds with additional data including X-ray structure determinations.

Scheme 1



Results and Discussion

As **C** and **D** were only reported in solution but not in the solid state, we suspected that these compounds might be somewhat difficult to crystallize. Therefore **F**[9] was reacted with diazomalonic acid dimethylate,[10] **B**, according to eq 1. The melting point of **F** is 84−85 °C, and the melting point of **A**,[11] bis[bis(trimethylsilyl)amino]germane(II) (used in ref 1), is only 33 °C. Compound **1** was obtained in 55% yield by repeated



[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

(1) Glidewell, C.; Lloyd, D.; Lumbard, K. W.; McKechnie, J. S. *Tetrahedron Lett.* **1987**, *28*, 343.

(2) Glidewell, C.; Lloyd, D.; Lumbard, K. W. *J. Chem. Soc., Dalton Trans.* **1987**, 501.

(3) Glidewell, C. *Struct. Chem.* **1990**, *1*, 317.

(4) Glidewell, C.; Lloyd, D.; Wiberg, N. *Struct. Chem.* **1990**, *1*, 151.

(5) Glidewell, C.; Lloyd, D.; Lumbard, K. W.; McKechnie, J. S.; Hursthouse, M. B.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1987**, 2981.

(6) Glidewell, C.; Hursthouse, M. B.; Lloyd, D.; Lumbard, K. W.; Short, R. L. *J. Chem. Res. (S)* **1986**, 434; *J. Chem. Res. (M)* **1986**, 3501.

(7) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245.

(8) Meller, A.; Ossig, G.; Maringgele, W.; Stalke, D.; Herbst-Irmer, R.; Freitag, S.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1123.

(9) Meller, A.; Gräbe, C.-P. *Chem. Ber.* **1985**, *118*, 2020.

(10) Regitz, M. *Chem. Ber.* **1966**, *99*, 3128.

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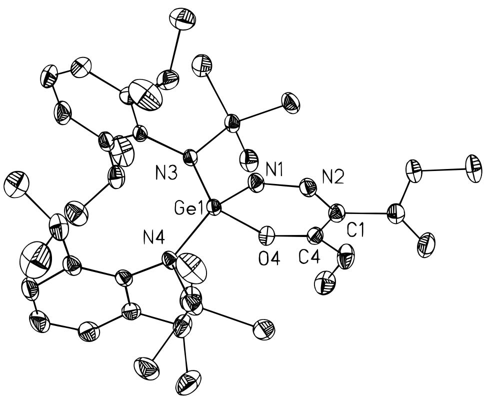
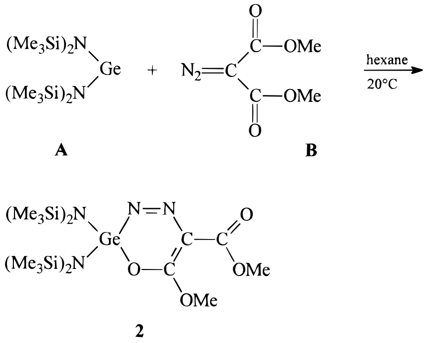


Figure 1. Crystal structure of **1** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms and the single lattice hexane molecule have been omitted for clarity.

crystallization from hexane at -25 °C. However in solution **1** is in equlibrium with **F** and **B** and this equilibrium is shifted in the direction of the educts upon raising the temperature. This can be observed from the intensity of the ^{1}H-NMR signals of **F** and **1**. **1** forms orange-red crystals which decompose above 40 °C.

An X-ray crystal structure analysis confirms its structure as methyl 2,2-bis[2,6-diisopropyl-*N*-(trimethylsilyl)anilino]-6-methoxy-*2H*-1,3,4,2-oxadiazagermanine-5-carboxylate (Figure 1). No other products are formed in the reaction (eq 1).



(eq.2)

Accordingly **2** was obtained from the reaction of **B** and **A** (eq 2). The NMR data for **2** correspond perfectly to those reported[1,2] for **C** (for which a transoid germaimine structure was claimed) and are distinctly different from those reported for **D**. **2** forms orange-red crystals from hexane at -25 °C in 95% yield within 16 h. The structure of **2** has been confirmed by an X-ray-structure analysis (Figure 2). **2** is thermally more stable than **1**; it melts without decomposition at 84 °C. The ^{15}N-NMR signals of the N=N group in **2** appear at δ +102 and δ +184 ppm far away from the ^{15}N-NMR signal of a germaimine (δ -193 ppm).[8] The ^{15}N-NMR signal of the N(SiMe$_3$) groups in **2** at δ -331 ppm (comparable to those of dihydro-1,3,4,2-oxadiazagermines[2]) excludes any ylidic form as postulated for **E**. It can be concluded from the ^{15}N-NMR and the ^{13}C-INADEQUATE data ($^1J(^{13}\text{C}-^{13}\text{C}) = 85.1$ Hz for the sp^2-hybridized C atoms) that conjugation effects in **2** are minimal. We did find the ^{1}H- and ^{13}C-NMR signals assigned by Glidewell et al. to the cisoid isomer of the germaimine **D** in solution but could not isolate a corresponding substance in a pure state. However, as these signals appear[1,2] upon storing the *2H*-1,3,4,2-oxadiazagermanine-5-carboxylate **2** (≡**E**), which is thermodynamically more stable than **D**, the latter structure can be excluded.

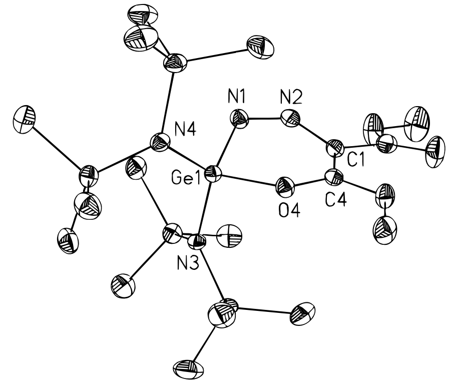


Figure 2. Crystal structure of **2** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

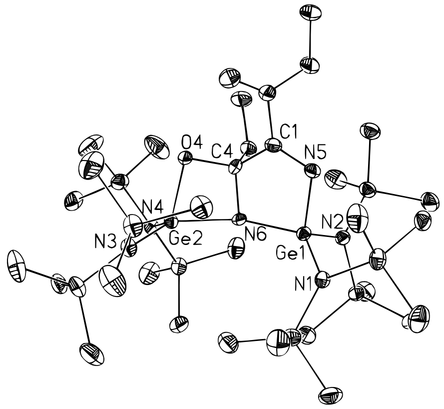


Figure 3. Crystal structure of **3** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

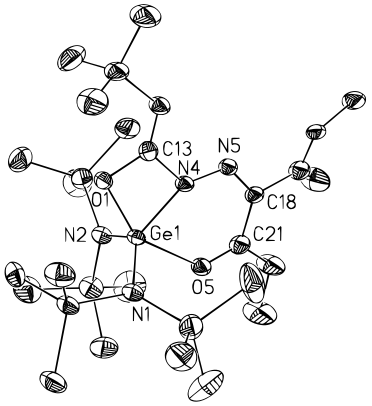


Figure 4. Crystal structure of **4** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms and the hexane molecule have been omitted for clarity.

At elevated temperatures decomposition of **2** is observed in solution. Upon heating of **2** in hexane for 4 h and slow evaporation of the solvent colorless crystals

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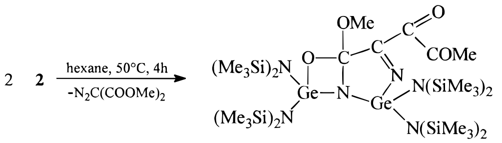
(11) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

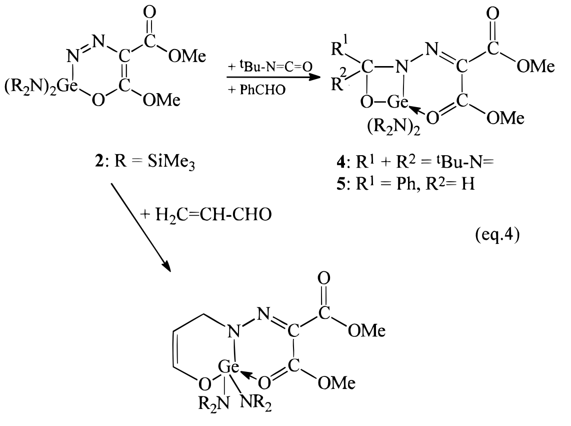
of **3** were obtained, formed according eq 3. The result of an X-ray structure analysis is depicted in Figure 3. The diazomalonate that split off was isolated by high-vacuum distillation at 35 °C. We were not successful in the attempted characterization of the remaining oily residue.



(eq.3)

3

Although **2** is not a germaimine, it reacts with *tert*-butyl isocyanate, benzaldehyde, and acrolein to products which would be expected from a moiety containing a Ge═N double bond (eq 4). Apparently the [2 + 2] cycloadditions to give **4** and **5** and the [2 + 4] cycloaddition leading to **6** proceed via ring opening and isomerization of **2** induced by formation of an O–Ge bond with the reagent. The same mechanism appears to be true for the addition product reported for **C** (or **D**) with weak acids.[5] In this connection one of the reviewers proposed the following interesting mechanism:



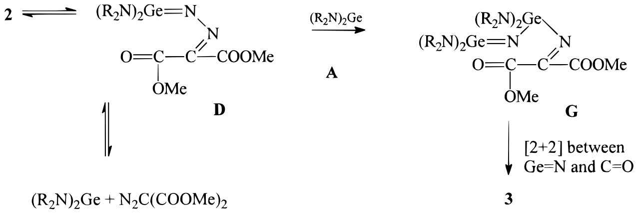
2: R = SiMe₃

4: R¹ + R² = ᵗBu-N=

5: R¹ = Ph, R²= H

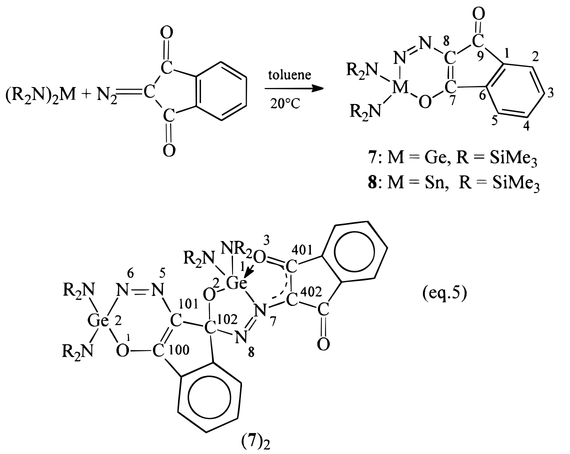
(eq.4)

6



This mechanism rests upon the assumption that there could be an equilibrium between **2** and the cisoid germaimine **D** from which **D** is removed continuously by the reaction with the germylene **A**. The product of this reaction would be **G** (perhaps the unidentified species which has been claimed to be the cisoid germaimine **D**[1,2]). This mechanism also gives a conclusive explanation for the formation of **3**. On the other hand, we find that the substance (still unidentified) which gives the NMR data ascribed for **D** is colorless which—in our opinion—excludes structure **G**. Furthermore the NMR spectra of **2** do not exhibit even traces of signals which could be attributed to **D**. Finally we do not find **3** as a product, if we perform the reactions and manipulations at ambient temperature. It will be difficult to discern if ring opening of **2** is induced by the formation of a donor bond from the reaction partner (thus including a five-coordinate transition state at the germanium atom) or by an equilibrium reaction proceeding via minimal amounts of **D** and **A**. In the formation of **3** (at elevated temperatures) the intermediate **G** is a convincing assumption regardless if its formation (in solution) involves intermolecular coordination between two molecules of **2** or the formation of **A** in the first step. For **4** an X-ray structure analysis was performed (Figure 4). For **5** and **6** $\delta(^{13}C) \sim 103$ ppm for the endocyclic *C*═N atoms indicates conjugation in the six-membered rings.

For comparison purposes we reacted as well bis[bis(trimethylsilyl)amino]germanium(II) and -tin(II) with 2-diazo-1,3-indanedione[12] according to eq 5, thus obtaining the corresponding indeno[2,1-*e*]-1,3,4,2-oxadiazametallanin-5(*2H*)-ones **7** and **8**. Besides **7** also a dimeric compound (**7**)$_2$ crystallized at −25 °C forming an olive solid; by different crystallization procedures, crystals of monomeric (yellow) and dimeric (green) **7** could be separated. At ambient temperature in solution NMR signals of the dimer (**7**)$_2$ are recorded. The signals of the monomeric **7** appear in addition to those of (**7**)$_2$ upon heating in CDCl$_3$ to 50 °C. This means that, in addition to the 22 ^{13}C-resonances for (**7**)$_2$, 10 more signals for **7** are observed. In the ^{15}N-NMR spectrum of (**7**)$_2$ there are 8 signals. Four of them (δ −333.2 to −328.5) can be assigned unequivocally to the (TMS)$_2$N substituents. For the remaining four signals we tentatively propose the following assignments: δ −61.4 (N(7)), 19.4 (N(8)), 163.6 (N(6)), 191.1 (N(5)). In contrast to that, **8** is only obtained in the monomeric form. An X-ray crystal structure analysis gave an unexpected structure for (**7**)$_2$ which includes a four- and a five-coordinated germanium atom (Figure 5).

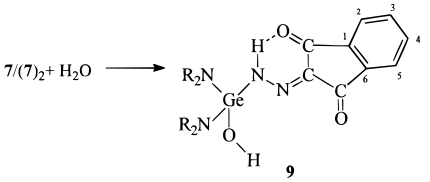


7: M = Ge, R = SiMe₃

8: M = Sn, R = SiMe₃

(eq.5)

(**7**)₂



9

The partial hydrolysis of **7** and (**7**)$_2$ (in toluene) gave **9**. In the dimerization of compound **7**, the first step probably is the formation of a donor bond from a carbonyl group (on C(102)) to Ge(1) which results in

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[12] Regitz, M.; Schwall, H.; Heck, G.; Eistert, B.; Bock, G. *Chem. Ber.* **1966**, *99*, 125.

Table 1. Selected Bond Lengths (pm) and Angles (deg) for 1−4 and (7)$_2$

Compound **1**							
Ge(1)−N(4)	180.6(2)	Ge(1)−N(1)	187.0(2)	N(1)−N(2)	126.6(3)	C(1)−C(4)	138.6(3)
Ge(1)−N(3)	181.1(2)	Ge(1)−O(4)	187.7(2)	N(2)−C(1)	138.3(3)	C(4)−O(4)	129.9(3)
N(4)−Ge(1)−N(3)	120.87(8)	N(4)−Ge(1)−O(4)	109.42(8)	N(2)−N(1)−Ge(1)	122.3(2)	O(4)−C(4)−C(1)	124.5(2)
N(4)−Ge(1)−N(1)	108.31(8)	N(3)−Ge(1)−O(4)	101.80(8)	N(1)−N(2)−C(1)	126.5(2)	C(4)−O(4)−Ge(1)	122.52(14)
N(3)−Ge(1)−N(1)	115.25(8)	N(1)−Ge(1)−O(4)	98.38(7)	N(2)−C(1)−C(4)	125.7(2)		
Compound **2**							
Ge(1)−N(4)	180.3(2)	Ge(1)−O(4)	186.3(2)	N(1)−N(2)	126.5(3)	C(1)−C(4)	139.1(3)
Ge(1)−N(3)	181.2(2)	Ge(1)−N(1)	188.0(2)	N(2)−C(1)	139.2(3)	C(4)−O(4)	130.4(3)
N(4)−Ge(1)−N(3)	119.18(9)	N(4)−Ge(1)−N(1)	112.11(9)	N(2)−N(1)−Ge(1)	119.0(2)	O(4)−C(4)−C(1)	124.3(2)
N(4)−Ge(1)−O(4)	106.63(8)	N(3)−Ge(1)−N(1)	113.35(9)	N(1)−N(2)−C(1)	126.7(2)	C(4)−O(4)−Ge(1)	119.8(2)
N(3)−Ge(1)−O(4)	104.43(8)	O(4)−Ge(1)−N(1)	98.32(8)	C(4)−C(1)−N(2)	124.4(2)		
Compound **3**							
Ge(1)−N(2)	184.0(3)	Ge(1)−N(5)	189.0(3)	Ge(2)−N(4)	183.0(3)	C(1)−C(4)	155.1(5)
Ge(1)−N(1)	184.6(3)	Ge(2)−N(3)	181.9(3)	Ge(2)−N(6)	188.5(3)	C(4)−O(4)	141.0(4)
Ge(1)−N(6)	186.7(3)	Ge(2)−O(4)	182.8(2)	N(5)−C(1)	126.4(4)	C(4)−N(6)	145.6(4)
N(2)−Ge(1)−N(1)	111.82(12)	N(3)−Ge(2)−O(4)	109.05(11)	N(4)−Ge(2)−N(6)	113.52(12)	N(6)−C(4)−C(1)	108.9(3)
N(2)−Ge(1)−N(6)	114.15(12)	N(3)−Ge(2)−N(4)	115.14(12)	C(1)−N(5)−Ge(1)	108.6(2)	C(4)−N(6)−Ge(1)	105.3(2)
N(1)−Ge(1)−N(6)	122.70(11)	O(4)−Ge(2)−N(4)	112.24(11)	N(5)−C(1)−C(4)	118.5(3)	C(4)−N(6)−Ge(2)	87.3(2)
N(2)−Ge(1)−N(5)	110.39(12)	N(3)−Ge(2)−N(6)	124.13(12)	O(4)−C(4)−N(6)	104.2(2)	Ge(1)−N(6)−Ge(2)	161.2(2)
N(1)−Ge(1)−N(5)	102.64(12)	O(4)−Ge(2)−N(6)	75.06(10)	O(4)−C(4)−C(1)	117.2(3)	C(4)−O(4)−Ge(2)	91.0(2)
N(6)−Ge(1)−N(5)	91.67(11)						
Compound **4**							
Ge(1)−N(2)	180.7(2)	Ge(1)−O(1)	194.2(2)	C(13)−N(3)	124.8(4)	N(5)−C(18)	131.0(4)
Ge(1)−N(1)	181.2(2)	Ge(1)−O(5)	215.5(2)	C(13)−N(4)	143.9(4)	C(18)−C(21)	145.5(4)
Ge(1)−N(4)	188.3(2)	O(1)−C(13)	134.4(4)	N(4)−N(5)	129.8(3)	C(21)−O(5)	123.6(4)
N(2)−Ge(1)−N(1)	123.74(11)	N(4)−Ge(1)−O(1)	68.34(9)	C(13)−O(1)−Ge(1)	95.6(2)	N(4)−N(5)−C(18)	121.0(3)
N(2)−Ge(1)−N(4)	119.62(11)	N(2)−Ge(1)−O(5)	91.11(10)	O(1)−C(13)−N(4)	101.0(2)	N(5)−C(18)−C(21)	123.3(3)
N(1)−Ge(1)−N(4)	116.53(11)	N(1)−Ge(1)−O(5)	94.19(10)	N(5)−N(4)−C(13)	123.0(2)	O(5)−C(21)−C(18)	124.5(3)
N(2)−Ge(1)−O(1)	102.21(10)	N(4)−Ge(1)−O(5)	80.91(9)	N(5)−N(4)−Ge(1)	140.1(2)	C(21)−O(5)−Ge(1)	127.9(2)
N(1)−Ge(1)−O(1)	100.92(10)	O(1)−Ge(1)−O(5)	149.19(8)	C(13)−N(4)−Ge(1)	95.0(2)		
Compound (**7**)$_2$							
Ge(1)−N(2)	181.3(4)	Ge(2)−N(3)	181.9(5)	C(100)−C(101)	136.8(7)	N(7)−C(402)	135.7(6)
Ge(1)−N(1)	183.2(4)	Ge(2)−O(1)	183.6(4)	C(101)−C(102)	152.2(7)	O(3)−C(401)	125.5(6)
Ge(1)−O(2)	186.0(3)	Ge(2)−N(6)	189.6(5)	C(102)−O(2)	137.4(6)	C(401)−C(402)	139.8(7)
Ge(1)−N(7)	205.3(4)	N(5)−N(6)	129.0(6)	C(102)−N(8)	152.1(6)	C(402)−C(403)	145.8(7)
Ge(1)−O(3)	215.8(3)	N(5)−C(101)	138.2(7)	N(7)−N(8)	125.5(5)	C(403)−O(4)	121.9(6)
Ge(2)−N(4)	181.5(5)	O(1)−C(100)	134.2(6)				
N(2)−Ge(1)−N(1)	121.0(2)	N(4)−Ge(2)−N(3)	116.8(2)	O(1)−C(100)−C(101)	127.9(5)	C(402)−N(7)−Ge(1)	115.2(3)
N(2)−Ge(1)−O(2)	102.6(2)	N(4)−Ge(2)−O(1)	107.0(2)	C(100)−C(101)−N(5)	128.6(5)	N(7)−N(8)−C(102)	109.9(4)
N(1)−Ge(1)−O(2)	101.7(2)	N(3)−Ge(2)−O(1)	104.0(2)	C(100)−C(101)−C(102)	109.8(5)	C(102)−O(2)−Ge(1)	118.5(3)
N(2)−Ge(1)−N(7)	119.2(2)	N(4)−Ge(2)−N(6)	111.4(2)	N(5)−C(101)−C(102)	121.6(5)	C(401)−O(3)−Ge(1)	110.1(3)
N(1)−Ge(1)−N(7)	118.1(2)	N(3)−Ge(2)−N(6)	112.9(2)	O(2)−C(102)−N(8)	111.0(4)	O(3)−C(401)−C(402)	123.5(5)
O(2)−Ge(1)−N(7)	77.9(2)	O(1)−Ge(2)−N(6)	103.3(2)	O(2)−C(102)−C(101)	117.0(4)	N(7)−C(402)−C(401)	113.3(4)
N(2)−Ge(1)−O(3)	91.3(2)	N(6)−N(5)−C(101)	122.9(5)	N(8)−C(102)−C(101)	104.3(4)	N(7)−C(402)−C(403)	135.7(5)
N(1)−Ge(1)−O(3)	88.1(2)	N(5)−N(6)−Ge(2)	120.2(4)	N(8)−N(7)−C(402)	125.9(4)	C(401)−C(402)−C(403)	110.5(5)
O(2)−Ge(1)−O(3)	155.21(14)	C(100)−O(1)−Ge(2)	115.1(3)	N(8)−N(7)−Ge(1)	118.9(3)	O(4)−C(403)−C(402)	128.8(5)
N(7)−Ge(1)−O(3)	77.4(2)						

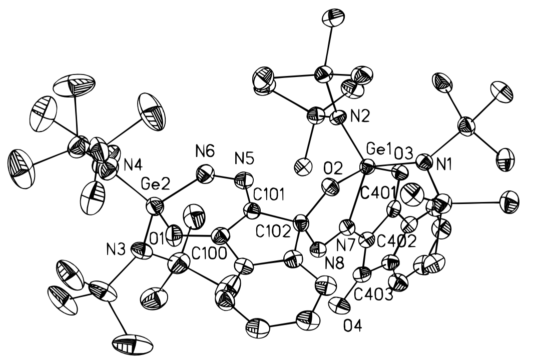

Figure 5. Crystal structure of (**7**)$_2$ with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms and the four lattice THF molecules have been omitted for clarity.

pentacoordination on the Ge atom. The electron withdrawal exerted on C(102) enables nucleophilic attack, and in a concerted rearrangement the Ge−N bond is switched from N(8) to N(7), N(8) now coordinating C(102) (notice the long bond distance, 152.1 pm, between N(8) and C(102)). Apparently this stabilization is advanced by steric effects (from the exocyclic substituents) and electronic effects in the two five-membered rings. Alternatively an intermolecular [2 + 2] cycloaddition between the C=O group and an intermediately formed Ge=N double bond can be discussed, followed by the rearrangement of the four- and six-membered rings into two five-membered rings.

Crystal Structures. Selected bond lengths and angles are compiled in Table 1.

In the structure of **1**, the germanium atom is surrounded by three nitrogen atoms and one oxygen atom in a distorted tetrahedral environment. The angle N(3)−Ge(1)−N(4) is widened due to steric reasons. The six-membered GeN_2C_2O ring is nearly planar (mean deviation 1.4 pm). The bond length between Ge(1) and N(1) (187.0 pm) is longer compared to those between

Ge(1) and N(3) and N(4), respectively, and corresponds to a single bond distance.[5,7] The Ge(1)−O(4) distance (187.7 pm) is on the upper limit of Ge−O bond lengths observed in cyclic compounds containing tetracoordinated germanium and two coordinated oxygen atoms (169.0−187.5 pm).[13] The bond distances between N(1) and N(2) (126.6 pm) and C(1) and C(4) (138.6) represent localized double bonds.

Bond lengths and bond angles in **2** are in full accordance with those determined in **1**, but the six-membered ring shows a distorted boat conformation. Ge(1) and C(1) are positioned 45.9 and 12.1 pm above the plane formed by N(1), N(2), C(4), and O(4).

In **3** all bond lengths at the germanium atoms correspond to covalent single bonds, while the distance between C(1) and N(5) (126.4 pm) stands clearly for a double bond.

In **4** the germanium atom is pentacoordinated (distorted trigonal bipyramidally). The equatorial positions are occupied by the nitrogen atoms, and the axial positions, by the oxygen atoms. The Ge(1)−O(5) distance (215.5 pm) indicates a coordinative bond. In the six-membered ring double bonds are localized between the atoms N(5) and C(18) (131.0 pm) and C(21) and O(5) (123.6 pm).[14] The bond length between N(4) and N(5) (129.8 pm) is remarkably shortened compared to a N−N single bond (135.5 pm).[13]

The structure of $(\mathbf{7})_2$ contains two Ge atoms: Ge(2) is tetrahedrally coordinated like the germanium atom in **1** and **3**. Ge(1) however exhibits pentacoordination, and its geometry corresponds to the Ge atom of **4** (with the oxygen atoms at axial positions). The six-membered ring containing Ge(2) shows structural parameters analogous to those in **1** and **2** (localized double bonds between the nitrogen atoms N(5) and N(6) (129.0 pm) and the carbon atoms C(100) and C(101) (136.8 pm)). The bonding sphere around Ge(1) is somewhat confusing. The Ge(1)−N(7) bond length (205.3 pm) exceeds the Ge−N single bond distances in the structures of **1**−**4** by 20 pm which indicates a quite weak bond. The bond between the Ge(1) and O(3) atoms (215.8 pm) corresponds to the coordinative bond between O(5) and Ge(1) in **4**. Normal covalent bonds exist between Ge(1) and N(1), N(2), and O(2). With consideration of the structural parameters a delocalized electron system extending from N(8) via N(7), C(402), and C(401) to O(3) is likely to be accepted; the bond length between N(8) and C(102) is quite long (152.1 pm) compared to a typical single bond (147 pm).[14]

Experimental Section

All reactions were performed in an inert atmosphere of dry nitrogen in dry solvents saturated with nitrogen. Melting points were determined in sealed capillaries. Elemental analyses were performed by Mikroanalytisches Labor Beller, Göttingen, Germany. NMR spectra were recorded on Bruker AM-250 or MSL-400 instruments. Heteroelement spectra were recorded in the proton-decoupled mode. Solvents and standards used were as follows: ^{1}H, ^{13}C, ^{29}Si ($CDCl_3$/TMS internal; C_6D_6 or toluene-d_8/TMS external); ^{15}N ($CDCl_3$, C_6D_6, or toluene-d_8/CH_3NO_2 external); ^{119}Sn (toluene-d_8/$SnMe_4$ external). Assignments of ^{13}C signals were made using multiplet selection ("Musel", 62.89 MHz) or distortionless enhancement by polarization transfer (DEPT, 100.60 MHz) methods where necessary; $^{13}C-^{13}C$ coupling constants were evaluated by INADEQUATE experiments. Mass spectra were obtained in a Varian CH5 instrument (EI, 70 eV, and FI) and a Finnigan MAT 8230 (EI, 70 eV) spectrometer.

Starting materials were prepared according to the following references: $[(2,6\text{-}{}^iPr_2C_6H_3)(Me_3Si)N]_2Ge$,[9] $[(Me_3Si)_2N]_2Ge$,[11] $[(Me_3Si)_2N]_2Sn$,[11] $N_2C(COOMe)_2$,[10] $N_2C(CO)_2C_6H_4$.[12]

Methyl 2,2-Bis[(2,6-diisopropylphenyl)(trimethylsilyl)amino]-6-methoxy-*2H*-1,3,4,2-oxadiazagermanine-5-carboxylate (1) and Methyl 2,2-Bis[bis(trimethylsilyl)amino]-6-methoxy-*2H*-1,3,4,2-oxadiazagermanine-5-carboxylate (2). To a stirred solution of 2.50 g of bis [(2,6-diisopropylphenyl)(trimethylsilyl)amino]germane(II) (4.39 mmol for **1**) or 8.46 g of bis[bis(trimethylsilyl)amino]germane(II) (21.51 mmol for **2**) in 60 mL of hexane, the molar equivalents of diazomalonic acid dimethylate (0.69 g for **1** at 0 °C, 3.40 g for **2** at 22 °C) were added dropwise with a syringe through a septum. The reaction mixtures have a red color; the one leading to **1** turns yellow upon warming to ambient temperature. **1** is obtained by threefold crystallization (overnight) at −25 °C, manipulations performed below −20 °C. **2** is obtained by a single crystallization at −25 °C. Single crystals (of red color for both products) grow from highly diluted solutions at −25 °C. **1**: yield 1.77 g (2.43 mmol), 55%; orange-red crystals decompose at 40−46 °C. **2**: yield 11.31 g (20.52 mmol), 95%; orange-red crystals; mp 84 °C.

1 is in equilibrium with its educts, depending upon temperature (temperature, °C/% of **1**): −20/27; −30/34; −40/41; −50/44; −60/47; −70/47. ^{1}H NMR (toluene-d_8, −60 °C): δ −0.10, −0.06 (2s, each 9 H, $SiMe_3$), 1.01 (d, $^3J_{HH} = 6.5$ Hz, 3 H), 1.084 (pseudo-t: 2 d at 1.076 + 1.093 Hz, $^3J_{HH} = 6.5$ Hz each d, 6 H), 1.18 (pseudo-t: d at 1.19, 2nd d covered by educt, 6 H), 1.24 (pseudo-t: d at 1.23, 2nd d covered by educt, 6 H), 1.79 (d, $^3J_{HH} = 6.3$ Hz, 3 H) ($CH(C\mathit{H}_3)_2$), 3.09 ($^3J_{HH} = 6.6$ Hz), 3.39 ($^3J_{HH} = 6.4$ Hz), 3.67 ($^3J_{HH} = 6.6$ Hz), 4.21 ($^3J_{HH} = 6.3$ Hz) (4 br sept, each 1 H, $C\mathit{H}(CH_3)_2$), 3.53, 3.76 (2 s, each 3 H, OMe), 6.67−6.76 (m, 2 H), 6.84 (d, $^3J_{HH} = 7.3$ Hz, 1 H), 6.88−6.96 (m, 3 H) (C_6H_3) [C_6H_3 (−80 °C): δ 6.71 (pseudo-t, 2 H), 6.81 (d, 1 H), 6.87 (d, 1H), 6.92 (pseudo-t covered by AB_2 spectra of educt, 2H)]. ^{13}C NMR (toluene-d_8, −40 °C): δ 1.78, 2.08 ($SiMe_3$), 23.7 (covered), 23.84, 24.62, 24.68, 24.77, 25.44, 25.52, 25.93 (8 × $CH(\mathit{C}H_3)_2$), 27.51, 27.88 [(−60 °C): δ 27.88, 27.94 (2 × $\mathit{C}H(CH_3)_2$] (br, 2 C), 28.10 ($\mathit{C}H(CH_3)_2$), 51.27, 52.33 (OMe), 121.24 (OC=*C*N), 124.44 (C-3,3′,5,5′, 1−3, probably 2 signals missing for C-3,3′,5,5′), 126.47, 126.62 (C-4,4′), 140.00, 140.58 (C-1,1′), 146.16, 147.21, 147.46 (2 C) (C-2,2′,6,6′) ppm. Signals of the educts {$[(2,6\text{-}{}^iPr_2C_6H_3)(Me_3Si)N]_2Ge$ and $N_2C(COOMe)_2$}: δ 3.70 ($SiMe_3$, 23.78, 25.83 ($CH(\mathit{C}H_3)_2$), 28.27 ($\mathit{C}H(CH_3)_2$, 51.67 (OMe), $C{=}N_2$ not detected (24 °C: 65.81), 123.90 (C-3,5), 125.51 (C-4), 142.89 (br, C-1), 147.46 (C-2,6) (C_6H_3), 160.59 (br, C=O). ^{29}Si NMR (toluene-d_8, −40 °C): δ 15.24, 16.08 (2 s). MS (EI; 70 eV): *m/z* (relative intensity) 570 (7) [$M - N_2C(COOMe)_2{}^+$], 322 (100) [$^iPr_2C_6H_3NSiMe_3Ge^+$]. MS (FI) *m/z* 570 (100). Anal. Calcd for $C_{35}H_{58}N_4O_4Si_2$ (727.63): C, 57.78; H, 8.03; N, 7.70. Found: C, 57.79; H, 8.14; N, 7.65.

2. ^{1}H NMR (C_6D_6): δ 0.23 (s, 36 H, $SiMe_3$), 3.32, 3.71 (2 s, each 3 H, 2 × O−Me. ^{13}C NMR (C_6D_6): δ 4.84 ($SiMe_3$), 51.10, 52.39 (2 × O−Me), 119.86 (OC=*C*N), 157.78 (O*C*=CN), 165.82 (C=O). ^{13}C NMR (INADEQUATE, C_6D_6): $^1J(C{=}C) = 85.1$ Hz, $^1J(CC{=}O) = 97.1$ Hz, $^2J(COC{=}O) = 9.0$ Hz, $^2J(COCO) = 8.9$ Hz. ^{29}Si NMR (C_6D_6): δ 7.44. ^{15}N NMR (C_6D_6): δ −331 ($^1J(^{29}Si-^{15}N) = 5.0$ Hz, $N(SiMe_3)_2$), 102 (Ge*N*=N), 184 (GeN=*N*). MS (EI; 70 eV): *m/z* (relative intensity) 537 (4) [$M - Me^+$], 277 (100). Anal. Calcd for $C_{17}H_{42}GeN_4O_4Si_4$ (551.48): C, 37.03; H, 7.68; N, 10.16. Found: C, 37.01; H, 7.76; N, 9.99.

Methyl 2,2,7,7-Tetrakis[bis(trimethylsilyl)amino]-5-methoxy-6-oxa-3,4-diaza-2,7-digermabicyclo[3.2.0]hept-3-ene-1-carboxylate (3). A solution of a 2.94 g (5.33 mmol)

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amount of **2** dissolved in 60 mL of hexane is heated with stirring to 50 °C for 4 h. A 40 mL volume of the solvent is evaporated under reduced pressure and the remaining solution slowly evaporated at ambient temperature. Crystals of **3** thus obtained were collected on a glass frit and washed twice with 5 mL of hexane at −78 °C. Dimethyl diazomalonate was distilled from the remaining liquid at 35 °C/0.01 mbar and identified by its MS and IR spectrum. **3** (yield 0.52 g, 0.55 mmol, 21%) forms colorless crystals: mp 149 °C; ^{1}H NMR (C_6D_6) δ 0.38 (s, 18 H), 0.40 (s, 9 H), 0.45 (s, 27 H), 0.49 (s, 9 H), 0.61 (br s, 9 H) ($SiMe_3$), 3.37 (s, 3 H), 3.70 (s, 3 H) (OMe); ^{13}C NMR (C_6D_6) δ 5.55 (3 C), 5.62 (3C), 6.81 (9 C), 6.93 (6 C), 7.52 (3 C) ($SiMe_3$), 51.77, 52.29 (OMe), 115.02 (*C*OMe), 164.83 (C=N), 172.70 (C=O); ^{29}Si NMR (C_6D_6) δ 3.32, 5.38, 5.94 (2 Si), 6.58 (2 Si), 7.55, 9.07 (6 s); MS (EI; 70 eV) *m*/*z* (relative intensity) 929 (5) [M − Me^+], 913 (3) [M − MeO^+], 394 (36) [{$(Me_3Si)_2N$}$_2Ge^+$], 379 (100) [{$(Me_3Si)_2N$}$_2$Ge − Me^+]. Anal. Calcd for $C_{29}H_{78}Ge_2N_6O_4Si_8$ (944.84): C, 36.87; H, 8.32; N, 8.89. Found: C, 36.81; H, 8.24; N, 9.04.

({Dimethyl[*tert*-butylcarbamoyl)hydrazono]malonato}(2−)-*N′*,*O*^{1},*O*^{2})bis(1,1,1,3,3,3-hexamethyldisilazanato-*N*)germanium (4), ({Dimethyl[(hydroxyphenylmethyl)hydrazono]malonato}(2−)-*N′*,*O*^{1},*O*^{2})bis(1,1,1,3,3,3-hexamethyldisilazanato-*N*)germanium (5), and ({Dimethyl[3-hydroxyallyl)hydrazono]malonato}(2−)-*N′*,*O*^{1},*O*^{2})bis(1,1,1,3,3,3-hexamethyldisilazanato-*N*)germanium (6). To the solution (showing a red color) of **2** in 60 mL of hexane, the corresponding reagent is added in slight excess with a syringe through a septum at ambient temperature. For **4**, to 3.60 g (6.53 mmol) of **2** is added 0.7 g (7.1 mmol) of *tert*-butyl isocyanate. For **5**, to 3.36 g (6.09 mmol) of **2** is added 0.8 g (7.5 mmol) of benzaldehyde. For **6**, to 2.32 g (4.21 mmol) of **2** is added 0.25 g (4.5 mmol) of acrolein. The solutions immediately change their color to yellow. **4** and **5** crystallize upon storing at −25 °C, and **6** crystallizes at −80 °C. Single crystals of **4** were grown at 0 °C from a solution in hexane saturated at 50 °C. **4**: yield 3.34 g (5.13 mmol), 79%; yellow crystals; mp 99 °C. **5**: yield 2.43 g (3.70 mmol), 61%; bright yellow crystals; mp 80 °C. **6**: yield 1.75 g (2.88 mmol), 68%; bright yellow crystals; mp 94 °C.

4. ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 36 H, $SiMe_3$), 1.30 (s, 9 H, CMe_3), 3.74, 3.96 (2 s, 2 × 3 H, OMe). ^{13}C NMR ($CDCl_3$): δ 4.98 ($SiMe_3$), 30.32 (CMe_3), 52.25 (CMe_3), 52.19, 53.98 (OMe), 117.96 (NN=C), 148.59 (t-BuN=*C*), 162.85, 165.21 (C=O). MS (EI; 70 eV): *m*/*z* (relative intensity) 493 (1) [M − $N_2C(COOMe)_2^+$], 379 (74) [M − $N_2C(COOMe)_2$ − Me_3CNCO − Me^+], 275 (100) [Me_5Si_2N − $NSi_2Me_4^+$]. FI: *m*/*z* 394 (16) [{$(Me_3Si)_2N$}$_2Ge^+$], 158 (100) [$N_2C(COOMe)_2^+$], 84 (66) [Me_2CNCO^+]. Anal. Calcd for $C_{22}H_{51}GeN_5O_5Si_4$ (650.61): C, 40.61; H, 7.90; N, 10.76. Found: C, 40.44; H, 8.10; N, 10.35.

5. ^{1}H NMR ($CDCl_3$): δ 0.17 (br s, 36 H, $SiMe_3$), 3.80, 4.08 (2 s, each 3 H, OMe), 6.16 (s, 1H, CHO), 7.31−7.37 (m, 2H), 7.69−7.75 (m, 2 H), 7.81−7.85 (m, 1 H) (C_6H_5). ^{13}C NMR ($CDCl_3$): δ 4.83 ($SiMe_3$), 51.02, 54.88 (OMe), 94.45 (CHO), 103.23 (C=N), 126.82 (C-3,5), 127.74 (C-4), 128.03 (C-2,6), 139.71 (C-1) (C_6H_5), 160.70, 171.36 (C=O). ^{29}Si NMR ($CDCl_3$): δ 5.1 (br s). MS (EI; 70 eV): *m*/*z* (relative intensity) 395 (12) ([$Me_3Si)_2N]_2$Ge + H^+), 73 (100) ($SiMe_3^+$). FI: *m*/*z* 394 (8) [{$(Me_3Si)_2N$}$_2Ge^+$], 158 (39) [$N_2C(COOMe)_2^+$], 106 (100) [$PhCHO^+$]. Anal. Calcd for $C_{24}H_{48}GeN_4O_5Si_4$ (657.60): C, 43.84; H, 7.36; N, 8.52. Found: C, 48.11; H, 7.65; N, 8.29.

6. ^{1}H NMR ($CDCl_3$): δ 0.12 (br s, 36 H, $SiMe_3$), 3.76, 4.05 (2 s, each 3 H, OMe), 5.32 (dt, $^{3}J_{HH}$ = 10.4 Hz, $^{2}J_{HH(gem)} \approx {}^{4}J_{HH(allyl)}$ = 1.5 Hz, 1 H, CH=CHC*H*$_2$), 5.60 (dt, $^{3}J_{HH}$ = 17.2 Hz, $^{2}J_{HH(gem)} \approx {}^{4}J_{HH(allyl)}$ = 1.4 Hz, 1 H, CH=CHC*H*$_2$), 5.66 (br d, 1 H), 6.04 (br ddd, 1 H) (2 × CH=CH). ^{13}C NMR ($CDCl_3$): δ 5.04 ($SiMe_3$), 51.27, 55.11 (OMe), 95.76 (CH=*C*HCH$_2$), 103.16 (C=N), 118.47 (CH=CH*C*H$_2$), 135.96 (*C*H=CHCH$_2$), 160.92, 171.44 (C=O). MS (EI; 70 eV): *m*/*z* (relative intensity) 608 (7) [M^+], 593 (5) [M − Me^+], 549 (10) [M − $COOMe^+$], 379 (100) [{$(Me_3Si)_2N$}$_2$Ge − Me^+]. Anal. Calcd for $C_{20}H_{46}GeN_4O_5Si_4$ (607.54): C, 39.54; H, 7.63; N, 9.22. Found: C, 39.48; H, 7.82; N, 9.06.

2,2-Bis[bis(trimethylsilyl)amino]indeno[2,1-*e*]-1,3,4,2-oxadiazagermanin-5(2*H*)-one (7), Bis(1,1,1,3,3,3-hexamethyldisilazanato-*N*){[indane-1,2,3-trione 2-({2,2-bis[bis(trimethylsilyl)amino]-2,5-dihydro-5-hydroxyindeno[2,1-*e*]-1,3,4,2-oxadiazagermanin-5-yl}hydrazanato)](2−)-*N*,*O*^{1},*O*^{2}}germanium (7)$_2$, and 2,2-Bis[bis(trimethylsilyl)amino]indeno[2,1-*e*]-1,3,4,2-oxadiazastannin-5(2*H*)-one (8). To a stirred solution of bis[bis(trimethylsilyl)amino]germane(II) (6.38 g, 16.22 mmol) and -stannane(II) (4.63 g, 10.54 mmol), in 20 mL of toluene, the equivalent amount of 2-diazo-1,3-indanedione (2.79 g for **7** and 1.81 g for **8**) dissolved in 60 mL of toluene is added dropwise at ambient temperature. The reaction mixture of **7** (and (**7**)$_2$) is dark green, and that of **8** is dark brown. Stirring is continued for 2 h. Crystallization is achieved at −25 °C. **8** is obtained in the form of yellow crystals by twice recrystallizing it from toluene: yield 3.60 g (54%); decomposition at about 130 °C. Monomeric **7** was isolated in the form of yellow-brown hexagonal crystals (decomposition at about 170 °C) by slow evaporation of its solution in toluene at ambient temperature. Its dimer (**7**)$_2$ crystallized from very diluted solutions in toluene at −25 °C in the form of green needles (decomposition at 181−182 °C). When the yellow-brown crystals of **7** are dissolved, a green solution results again. The yield of **7** + (**7**)$_2$ is 7.86 g (85%).

7. ^{1}H NMR ($CDCl_3$, 50 °C): δ 0.24 (s, 36 H, $SiMe_3$), 7.65−7.73 (m, 2 H), 7.73−7.81 (m, 1 H), 7.83−7.88 (m, 1 H) (C_6H_4). ^{13}C NMR ($CDCl_3$, 50 °C): δ 4.86 ($SiMe_3$), 121.83, 122.53, 128.94, 130.48, 134.03, 134.83, 136.25, 166.03, 188.37 (C=O). ^{29}Si NMR ($CDCl_3$, 50 °C): δ 8.06. MS (EI; 70 eV): *m*/*z* (relative intensity) 566 (3) [M^+], 523 (4) [M − Me − N_2^+], 379 (80) [{$(Me_3Si)_2N$}$_2$Ge −Me^+], 275 (100) [$Me_5Si_2N_2Si_2Me_4^+$], 172 (64) [$N_2O_2C_3C_6H_4^+$]. Anal. Calcd for **7** $C_{21}H_{40}GeN_4O_2Si_4$ (565.51): C, 44.60; H, 7.13; N, 9.91. Found: C, 44.66; H, 7.24; N, 9.80.

(7)$_2$. ^{1}H NMR ($CDCl_3$): δ 0.17 (br, s), 0.20 (s), 0.29 (s), 0.31 (br, s) (72 H, $SiMe_3$), 7.36−7.77 (6 m, 8 H, C_6H_4). ^{13}C NMR ($CDCl_3$): δ 5.06, 5.18, 5.36 (br), 5.99 (br, $SiMe_3$), 104.48, 116.97, 122.14, 122.47, 123.01, 126.16, 129.96, 131.03, 133.21, 133.66 (br), 134.38, 134.81, 137.40, 138.96, 142.68 (br), 148.59, 179.11, 186.34 (C=O). ^{29}Si NMR ($CDCl_3$): δ 5.89 (br), 6.11 (br), 6.85, 7.25. ^{15}N NMR ($CDCl_3$): δ −332.2, −330.7, −328.6, −328.5 (N($SiMe_3)_2$), −61.4 (N(7)), 19.4 (N(8)), 163.6 (N(6)), 191.1 (N(5)) (assignments tentative). MS (EI; 70 eV): *m*/*z* (relative intensity) 1102 (1) [M − N_2^+], 958(6) [M − $N_2C_3O_4C_6H_4^+$], 566 (4) [M/2^+], 146 (100) [$Me_6Si_2^+$]. Found for $C_{42}H_{80}Ge_2N_8O_4Si_8$ (1131.01): C, 43.07; H, 7.25; N, 9.93.

8. ^{1}H NMR ($CDCl_3$): δ −0.03 (br s, 18 H) ($SiMe_3$), 7.37−7.45 (m, 2 H, 3-H, 4-H), 7.50−7.56 (m, 1 H), 7.64−7.70 (m, 1 H) (2-H + 5-H). ^{13}C NMR ($CDCl_3$): δ 5.80 ($^{3}J_{SnC}$ = 13.2 Hz), 6.36 ($^{3}J_{SnC}$ = 16.0 Hz, $SiMe_3$), 98.80 ($^{3}J_{SnC}$ = 28.5 Hz, C-8), 121.63 (C-4), 126.88 (C-3), 128.55 ($^{2}J_{SnC}$ = 29.4 Hz, C-7), 129.12 (C-5), 132.46 (C-2), 134.98 ($^{3}J_{Sn}$ = 16.1 Hz, C-6), 148.79 ($^{4}J_{SnC}$ = 8 Hz, C-1), 176.69 ($^{4}J_{SnC}$ = 16.7 Hz, C-9). ^{29}Si NMR: δ 6.81 (s), 7.39 (s). ^{119}Sn NMR (toluene-d_8): δ −309.1. MS (EI; 70 eV): *m*/*z* (relative intensity) 440 (2) [M − $N_2C_3O_2C_6H_4^+$], 130 (100) [$Me_4Si_2N^+$]. MS (FD): *m*/*z* (relative intensity) 440 (4), 172 (100) [$N_2C_3O_2C_6H_4^+$]. Molecular mass (cryoscopic method in C_6H_6), found: 615. Anal. Calcd for $C_{21}H_{40}N_4O_2Si_4Sn$ (611.6): C, 41.24; H, 6.59; N, 9.16. Found: C, 41.16; H, 6.35; N, 8.86.

Indane-1,2,3-trione 2-({Bis[bis(trimethylsilyl)amino]hydroxygermyl}hydrazone) (9). Water (0.054 g, 3 mmol) is added to the stirred solution of 1.56 g (2.76 mmol) of (**7**)$_2$ in 20 mL of toluene which causes the green solution to change its color to brown. After evaporation of the solvent in vacuo, the residue is recrystallized from toluene and crystals are collected at −25 °C. The yield is 0.83 g (1.42 mmol, 52%) of a bright yellow solid (decomposition at 182 °C). ^{1}H-NMR ($CDCl_3$): δ 5.06 (s, 36 H, $SiMe_3$), 2.63 (s, 1 H, O-H), 7.72−7.79

Table 2. Crystal Data and Structure Refinement Details for 1−4 and (7)$_2$

	1·$^1/_2C_6H_{14}$	2	3	**4**·$^1/_2C_6H_{14}$	(**7**)$_2$·$4C_4H_8O$
formula	$C_{38}H_{65}GeN_4O_4Si_2$	$C_{17}H_{42}GeN_4O_4Si_4$	$C_{29}H_{78}Ge_2N_6O_4Si_8$	$C_{25}H_{58}GeN_5O_5Si_4$	$C_{58}H_{112}Ge_2N_8O_8Si_8$
M_r	770.71	551.50	944.87	693.71	1419.46
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (pm)	1090.86(7)	1334.5(1)	1161.0(4)	3466.4(4)	1348.2(5)
b (pm)	1134.56(9)	1434.8(1)	1231.5(4)	1240.3(2)	1553.4(5)
c (pm)	1748.9(2)	1520.4(2)	1850.6(7)	1814.9(2)	2029.5(7)
α (deg)	84.184(5)	90	102.76(2)	90	106.38(2)
β (deg)	77.088(5)	101.21(1)	92.67(2)	103.07(2)	106.71(2)
γ (deg)	83.684(5)	90	107.23(2)	90	99.45(2)
V (nm$^{3)}$	2.0904(4)	2.8556(5)	2.447(2)	7.601(2)	3.764(2)
Z	2	4	2	8	2
D_x (Mg/m^3)	1.224	1.283	1.282	1.212	1.252
μ (mm^{-1})	0.831	1.268	1.461	0.969	0.977
F(000)	826	1168	1004	2968	1512
cryst size (mm)	0.5 × 0.4 × 0.3	0.4 × 0.2 × 0.2	0.3 × 0.3 × 0.2	0.7 × 0.5 × 0.5	0.4 × 0.3 × 0.2
2θ range (deg)	8−50	8−45	8−45	8−45	8−45
range of hkl	$-12 \le h \le 13$ $-13 \le k \le 13$ $-13 \le l \le 20$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-16 \le l \le 16$	$-12 \le h \le 12$ $-13 \le k \le 12$ $-17 \le l \le 19$	$-36 \le h \le 37$ $-13 \le k \le 12$ $-19 \le l \le 19$	$-14 \le h \le 14$ $-16 \le k \le 16$ $-11 \le l \le 21$
no. of rflns coll	7814	14 811	7281	12 369	10 321
no. of indep rflns	7422	3717	6373	4948	9775
R(int)	0.0520	0.0373	0.0357	0.0309	0.0621
$T_{\min}$	0.599	0.749	0.773		0.561
$T_{\max}$	0.675	0.805	0.847		0.929
no. of data	7418	3716	6364	4947	9764
no. of params	459	285	468	487	950
no. of restraints	0	0	0	307	1306
S	1.049	1.032	1.061	1.048	1.030
$R1$ [$I > 2\sigma(I)$]	0.0355	0.0251	0.0310	0.0318	0.0548
w$R2$ (all data)	0.0924	0.0539	0.0736	0.0866	0.1541
g_1	0.0354	0.0169	0.0261	0.0355	0.0486
g_2	1.5354	2.4782	3.1706	22.7641	6.8781
largest diff peak	0.392	0.261	0.364	0.814	0.576
largest diff hole (e nm^{-3})	−0.453	−0.193	−0.404	−0.287	−0.339

(m, 3-H + 4-H, 2 H), 7.83−7.87 (m, 1 H), 7.90−7.94 (m, 1 H) (2-H + 5-H) (C_6H_4), 11.78 (s, 1 H, N-H). ^{13}C NMR ($CDCl_3$): δ 5.06 ($SiMe_3$), 122.85, 123.08 (C-3, C-4, C_6H_4), 134.15 (C═N), 134.71, 135.02 (C-2, C-5, C_6H_4), 138.85, 140.24 (C-1, C-6, C_6H_4), 186.40, 188.11 (C═O). ^{29}Si NMR ($CDCl_3$): δ 6.78 (s). MS (EI; 70 eV): m/z (relative intensity) 569 (28) [M − Me$^+$], 277 (100). Anal. Calcd for $C_{21}H_{42}GeN_4O_3Si_4$ (583.52): C, 43.23; H, 7.25; N, 9.60. Found: C, 43.01; H, 7.42; N, 9.41.

X-ray Structure Determinations for 1−4 and (7)$_2$. Data were collected at −120 °C on a Stoe-Siemens diffractometer with monochromated Mo Kα radiation (λ = 71.073 pm). A semiempirical absorption correction was employed for structures **1**−**3**, and an empirical correction was employed for structure (**7**)$_2$. The structures were solved by direct methods using SHELXS-90.[15] All non-hydrogen atoms were refined anisotropically. For the hydrogen atoms the riding model was used. The structures were refined against F^2 with a weighting scheme of $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$ with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL-93.[16] The R values are defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{0.5}$. Figures 1−5 (hydrogen atoms omitted) show 50% probability displacement ellipsoids. Crystal data and structure refinement details are listed in Table 2.

In structure **4** one COOMe group is disordered over two positions with occupancies of 0.5. Distance restraints were used for the refinement. In structure (**7**)$_2$ one $SiMe_3$ group is disordered over two positions with occupancies of 0.6 and 0.4. Again distance restraints and also similarity and rigid bond restraints for the anisotropic displacement parameters were used.

The hexane molecule in structure **1** is ordered on the inversions center, while the hexane in structure **4** is disordered on the 2-fold axis. It was refined with distance restraints and similarity and rigid bond restraints for the anisotropic displacement parameters. Antibumping restraints were used, because there were short distances between the hexane and the disordered COOMe group. In structure (**7**)$_2$ there are four THF molecules, of which two are ordered while two are disordered. They were refined as five-membered carbon rings in two and three positions, respectively (occupancies 0.85:0.15 and 0.4:0.4:0.2). Again distance restraints and similarity and rigid bond restraints were used.

Summary. In the reactions between diazagermylenes and diazastannylenes with diazo compounds carrying non-enolizable substituents, formation of primary and secondary reaction products depends critically on the metal and the substituents. In some cases equilibria between educts and products or between different products can be observed. In none of the systems studied here could formation of a free germaimine species be substantiated, which does not exclude short-lived germaimine intermediates.

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Supporting Information Available: Tables of crystal data, complete fractional coordinates and U values, bond lengths and angles, and anisotropic displacement parameters and fully labeled figures of 50% anisotropic displacement parameters of the structures **1**−**4** and (**7**)$_2$ (32 pages). Ordering information is given on any current masthead page.

OM950599P

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[15] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[16] Sheldrick, G. M. SHELXL-93, program for crystal structure refinement, University of Göttingen, 1993.