

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

Günter Ossig, Anton Meller,* Stefanie Freitag, Olaf Müller,
Heinz Gornitzka, and Regine Herbst-Irmer

Institut für Anorganische Chemie der Universität Göttingen,
Tammannstrasse 4, D-37077 Göttingen, Germany

Received August 1, 1995[®]

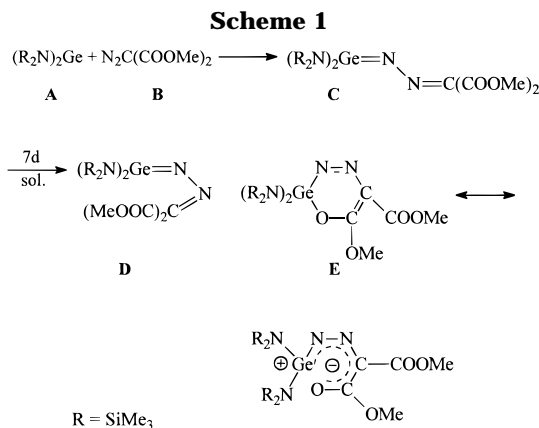
Products obtained in the reaction between germylenes or stannylenes with dimethyl 2-diazomalonate and 2-diazo-1,3-indanedione have been isolated and characterized. Compounds thus prepared are the 2*H*-1,3,4,2-oxadiazagermanine-5-carboxylates **1** and **2**, the indeno[2,1-*e*]-1,3,4,2-oxadiazametallanin-5(2*H*)-ones **7** and **8**, the 6-oxa-3,4-diaza-2,7-digermbicyclo[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 H₂C=CHCHO, **6**, and compound **9** obtained by partial hydrolysis of **7** and (**7**)₂ were isolated. The compounds were characterized by NMR spectroscopy (¹H, ¹³C, and ²⁹Si and in part ¹⁵N and ¹¹⁹Sn), 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 germamine 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 germamine (**C**), which in solution upon storage at room temperature converted to the cisoid conformer (**D**) (Scheme 1).

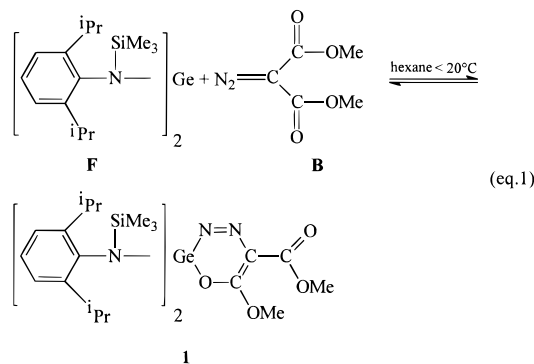
Structural assignments have been done in accordance with ¹H- and ¹³C-NMR data and are supported by MNDO calculations. Later on a cyclic equilibrium structure (**E**) was also considered (based on MNDO results^{3,4}) by the interaction of one of the C=O groups with the germanium atom. The MNDO calculations using a simplified model (SiH₃ for SiMe₃, gas phase at 0 K) resulted in enthalpies of formation of Δ*H*_f = -590 kJ/mol for the germamine structure (**C**) but Δ*H*_f = -775 kJ/mol for **E**.^{5,6}

E however cannot be considered as a germamine 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 germamines ourselves,^{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.



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.

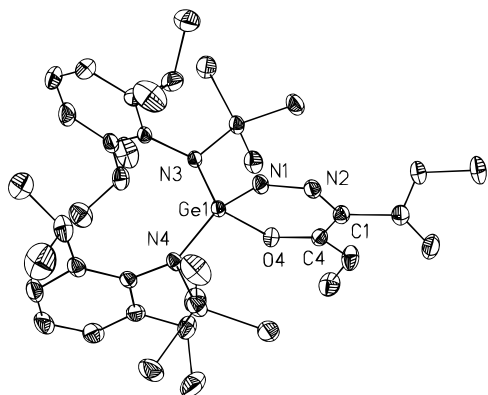
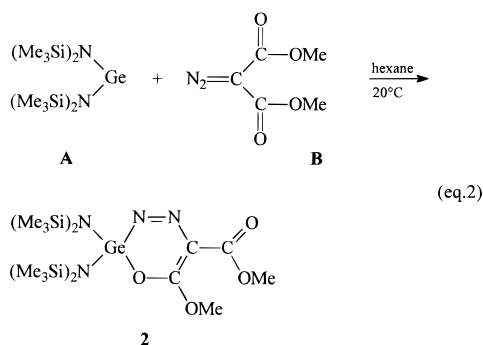


Figure 1. Crystal structure of **1** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms and the single lattice hexane molecule have been omitted for clarity.

crystallization from hexane at $-25\text{ }^{\circ}\text{C}$. However in solution **1** is in equilibrium 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 $^1\text{H-NMR}$ signals of **F** and **1**. **1** forms orange-red crystals which decompose above $40\text{ }^{\circ}\text{C}$.

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

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 germaine structure was claimed) and are distinctly different from those reported for **D**. **2** forms orange-red crystals from hexane at $-25\text{ }^{\circ}\text{C}$ 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 $84\text{ }^{\circ}\text{C}$. The $^{15}\text{N-NMR}$ signals of the $\text{N}=\text{N}$ group in **2** appear at $\delta +102$ and $\delta +184$ ppm far away from the $^{15}\text{N-NMR}$ signal of a germaine ($\delta -193$ ppm).⁸ The $^{15}\text{N-NMR}$ signal of the $\text{N}(\text{SiMe}_3)$ groups in **2** at $\delta -331$ ppm (comparable to those of dihydro-1,3,4,2-oxadiazagermines²) excludes any ylidic form as postulated for **E**. It can be concluded from the $^{15}\text{N-NMR}$ and the $^{13}\text{C-INADEQUATE}$ 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 $^1\text{H-}$ and $^{13}\text{C-NMR}$ signals assigned by Glidewell et

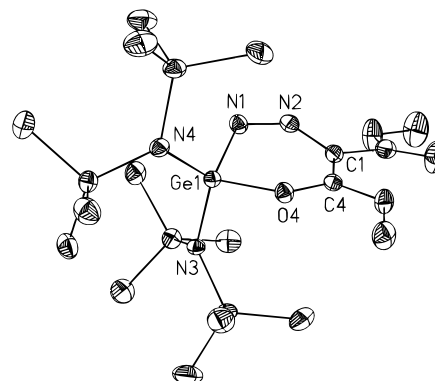


Figure 2. Crystal structure of **2** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

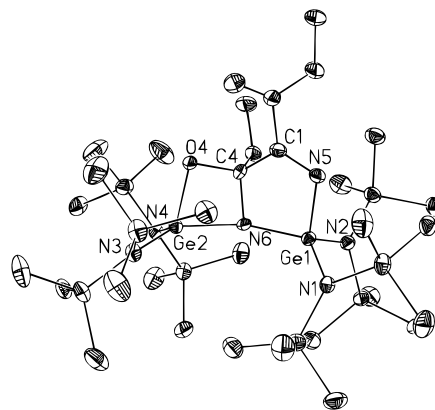


Figure 3. Crystal structure of **3** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms have been omitted for clarity.

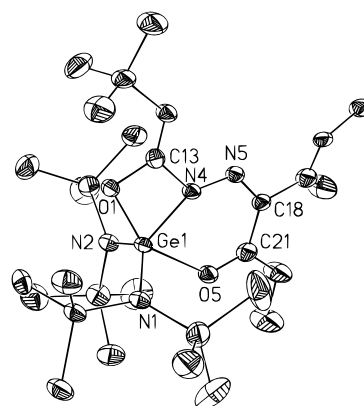


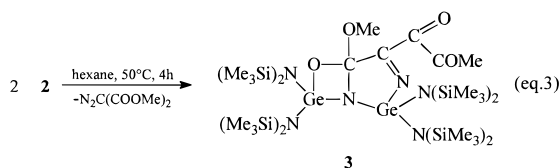
Figure 4. Crystal structure of **4** with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms and the hexane molecule have been omitted for clarity.

al. to the cisoid isomer of the germaine **D** in solution but could not isolate a corresponding substance in a pure state. However, as these signals appear^{1,2} upon storing the 2*H*-1,3,4,2-oxadiazagermanine-5-carboxylate **2** (\equiv **E**), which is thermodynamically more stable than **D**, the latter structure can be excluded.

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

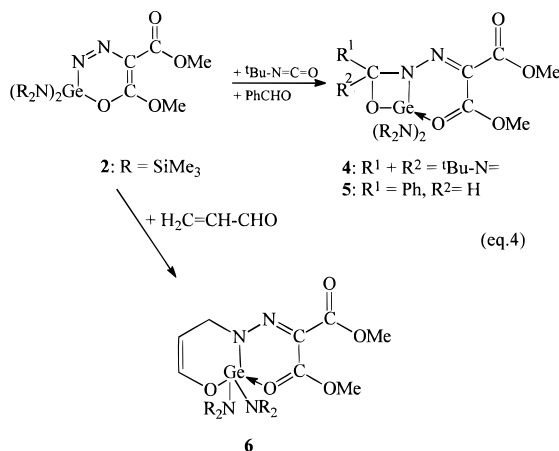
(11) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

of **3** were obtained, formed according eq 3. The result

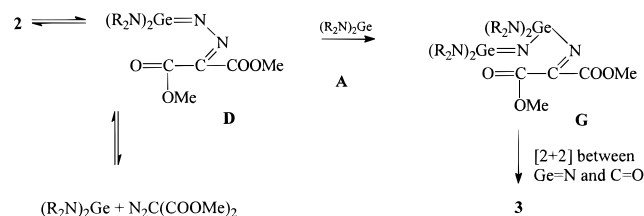


of an X-ray structure analysis is depicted in Figure 3. The diazomalonate that split off was isolated by high-vacuum distillation at 35 °C. We were not successful in the attempted characterization of the remaining oily residue.

Although **2** is not a germaine, 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]



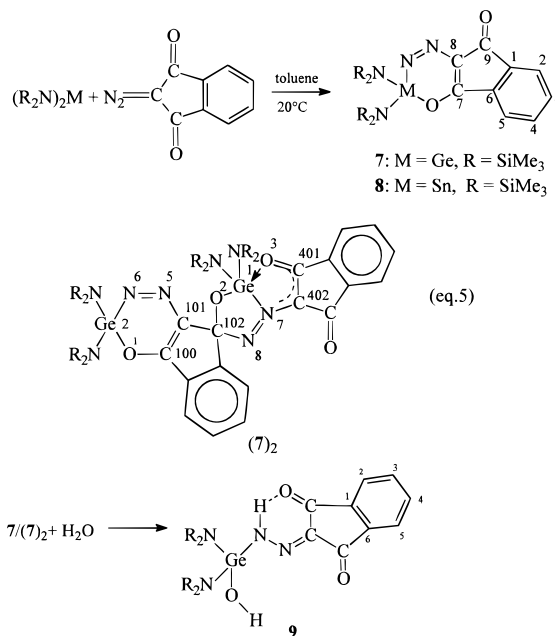
cycloadditions to give **4** and **5** and the [2 + 4] cycloaddition leading to **6** proceed via ring opening and isomerization of **2** induced by formation of an O–Ge bond with the reagent. The same mechanism appears to be true for the addition product reported for **C** (or **D**) with weak acids.⁵ In this connection one of the reviewers proposed the following interesting mechanism:



This mechanism rests upon the assumption that there could be an equilibrium between **2** and the cisoid germaine **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 germaine **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** $\delta(^{13}\text{C}) \sim 103$ 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-indanedione¹² according to eq 5, thus obtain-



ing the corresponding indeno[2,1-*e*]-1,3,4,2-oxadiazametallanin-5(2*H*)-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 CDCl₃ to 50 °C. This means that, in addition to the 22 ¹³C-resonances for (**7**)₂, 10 more signals for **7** are observed. In the ¹⁵N-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)₂N 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).

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

(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)						

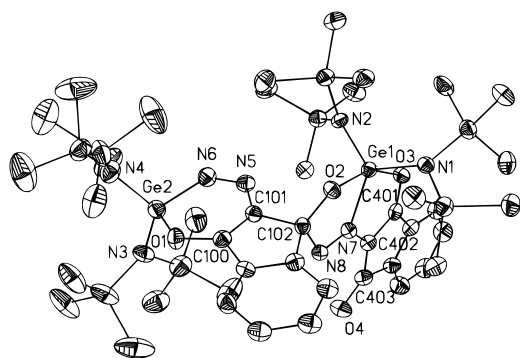


Figure 5. Crystal structure of (7)₂ with anisotropic displacement parameters depicting 50% probability. The hydrogen atoms and the four lattice THF molecules have been omitted for clarity.

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 GeN₂C₂O 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 (**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: ¹H, ¹³C, ²⁹Si (CDCl₃/TMS internal; C₆D₆ or toluene-*d*₈/TMS external); ¹⁵N (CDCl₃, C₆D₆,

or toluene-*d*₈/CH₃NO₂ external); ¹¹⁹Sn (toluene-*d*₈/SnMe₄ external). Assignments of ¹³C signals were made using multiplet selection ("Musel", 62.89 MHz) or distortionless enhancement by polarization transfer (DEPT, 100.60 MHz) methods where necessary; ¹³C–¹³C 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-*i*-Pr₂C₆H₃)(Me₃Si)N]₂Ge,⁹ [(Me₃Si)₂N]₂Ge,¹¹ [(Me₃Si)₂N]₂Sn,¹¹ N₂C(COOMe)₂,¹⁰ N₂C(CO)₂C₆H₄.¹²

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. ¹H NMR (toluene-*d*₈, –60 °C): δ –0.10, –0.06 (2s, each 9 H, SiMe₃), 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(CH₃)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, CH(CH₃)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) (C₆H₃) [C₆H₃ (–80 °C): δ 6.71 (pseudo-t, 2 H), 6.81 (d, 1 H), 6.87 (d, 1H), 6.92 (pseudo-t covered by AB₂ spectra of educt, 2H)]. ¹³C NMR (toluene-*d*₈, –40 °C): δ 1.78, 2.08 (SiMe₃), 23.7 (covered), 23.84, 24.62, 24.68, 24.77, 25.44, 25.52, 25.93 (8 × CH(CH₃)₂), 27.51, 27.88 [–60 °C): δ 27.88, 27.94 (2 × CH(CH₃)₂) (br, 2 C), 28.10 (CH(CH₃)₂), 51.27, 52.33 (OMe), 121.24 (OC=CN), 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-*i*-Pr₂C₆H₃)(Me₃Si)N]₂Ge and N₂C(COOMe)₂]: δ 3.70 (SiMe₃, 23.78, 25.83 (CH(CH₃)₂), 28.27 (CH(CH₃)₂, 51.67 (OMe), C=N₂ 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) (C₆H₃), 160.59 (br, C=O)}. ²⁹Si NMR (toluene-*d*₈, –40 °C): δ 15.24, 16.08 (2 s). MS (EI; 70 eV): *m/z* (relative intensity) 570 (7) [M – N₂C(COOMe)₂]⁺, 322 (100) [Pr₂C₆H₃NSiMe₃Ge⁺]. MS (FI) *m/z* 570 (100). Anal. Calcd for C₃₅H₅₈N₄O₄Si₂ (727.63): C, 57.78; H, 8.03; N, 7.70. Found: C, 57.79; H, 8.14; N, 7.65.

2. ¹H NMR (C₆D₆): δ 0.23 (s, 36 H, SiMe₃), 3.32, 3.71 (2 s, each 3 H, 2 × O–Me). ¹³C NMR (C₆D₆): δ 4.84 (SiMe₃), 51.10, 52.39 (2 × O–Me), 119.86 (OC=CN), 157.78 (OC=CN), 165.82 (C=O). ¹³C NMR (INADEQUATE, C₆D₆): ¹J(C=C) = 85.1 Hz, ¹J(CC=O) = 97.1 Hz, ²J(COC=O) = 9.0 Hz, ²J(COCO) = 8.9 Hz. ²⁹Si NMR (C₆D₆): δ 7.44. ¹⁵N NMR (C₆D₆): δ –331 (¹J(²⁹Si–¹⁵N) = 5.0 Hz, N(SiMe₃)₂), 102 (Ge=N=N), 184 (Ge=N=N). MS (EI; 70 eV): *m/z* (relative intensity) 537 (4) [M – Me⁺], 277 (100). Anal. Calcd for C₁₇H₄₂GeN₄O₄Si₄ (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)

(13) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, I.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr.* **1979**, *B35*, 2331.

(14) Rademacher, P. *Strukturen organischer Moleküle*; VCH: Weinheim, Germany, New York, 1987.

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 diazomalatonate 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; ¹H NMR (C₆D₆) 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) (SiMe₃), 3.37 (s, 3 H), 3.70 (s, 3 H) (OMe); ¹³C NMR (C₆D₆) δ 5.55 (3 C), 5.62 (3C), 6.81 (9 C), 6.93 (6 C), 7.52 (3 C) (SiMe₃), 51.77, 52.29 (OMe), 115.02 (COMe), 164.83 (C=N), 172.70 (C=O); ²⁹Si NMR (C₆D₆) 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) [(Me₃Si)₂N]₂Ge⁺, 379 (100) [(Me₃Si)₂N]₂Ge - Me⁺]. Anal. Calcd for C₂₉H₇₈Ge₂N₆O₄Si₈ (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,O'*bis(1,1,1,3,3,3-hexamethylsilazano-*N*)-germanium (**4**), ({Dimethyl[(hydroxyphenylmethyl)hydrazono]malonato)-(2-)-*N,O',O''*bis(1,1,1,3,3,3-hexamethylsilazano-*N*)-germanium (**5**), and ({Dimethyl[3-hydroxyallyl]hydrazono}malonato)-(2-)-*N,O',O''*bis(1,1,1,3,3,3-hexamethylsilazano-*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. ¹H NMR (CDCl₃): δ 0.21 (s, 36 H, SiMe₃), 1.30 (s, 9 H, CMe₃), 3.74, 3.96 (2 s, 2 × 3 H, OMe). ¹³C NMR (CDCl₃): δ 4.98 (SiMe₃), 30.32 (CMe₃), 52.25 (CMe₃), 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 - N₂C(COOMe)₂]⁺, 379 (74) [M - N₂C(COOMe)₂ - Me₃CNCO - Me⁺], 275 (100) [Me₅Si₂N - NSi₂Me₄]⁺. FI: *m/z* 394 (16) [(Me₃Si)₂N]₂Ge⁺, 158 (100) [N₂C(COOMe)₂]⁺, 84 (66) [Me₂CNCO]⁺. Anal. Calcd for C₂₂H₅₁GeN₅O₅Si₄ (650.61): C, 40.61; H, 7.90; N, 10.76. Found: C, 40.44; H, 8.10; N, 10.35.

5. ¹H NMR (CDCl₃): δ 0.17 (br s, 36 H, SiMe₃), 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) (C₆H₅). ¹³C NMR (CDCl₃): δ 4.83 (SiMe₃), 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) (C₆H₅), 160.70, 171.36 (C=O). ²⁹Si NMR (CDCl₃): δ 5.1 (br s). MS (EI; 70 eV): *m/z* (relative intensity) 395 (12) [(Me₃Si)₂N]₂Ge + H⁺, 73 (100) (SiMe₃⁺). FI: *m/z* 394 (8) [(Me₃Si)₂N]₂Ge⁺, 158 (39) [N₂C(COOMe)₂]⁺, 106 (100) [PhCHO]⁺. Anal. Calcd for C₂₄H₄₈GeN₄O₅Si₄ (657.60): C, 43.84; H, 7.36; N, 8.52. Found: C, 48.11; H, 7.65; N, 8.29.

6. ¹H NMR (CDCl₃): δ 0.12 (br s, 36 H, SiMe₃), 3.76, 4.05 (2 s, each 3 H, OMe), 5.32 (dt, ³J_{HH} = 10.4 Hz, ²J_{HH(gem)}} ≈ ⁴J_{HH(allyl)}} = 1.5 Hz, 1 H, CH=CHCH₂), 5.60 (dt, ³J_{HH} = 17.2 Hz, ²J_{HH(gem)}} ≈ ⁴J_{HH(allyl)}} = 1.4 Hz, 1 H, CH=CHCH₂), 5.66 (br d, 1 H), 6.04 (br ddd, 1 H) (2 × CH=CH). ¹³C NMR (CDCl₃): δ 5.04 (SiMe₃), 51.27, 55.11 (OMe), 95.76 (CH=CHCH₂), 103.16 (C=N), 118.47 (CH=CHCH₂), 135.96 (CH=CHCH₂), 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)

[(Me₃Si)₂N]₂Ge - Me⁺. Anal. Calcd for C₂₀H₄₆GeN₄O₅Si₄ (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-hexamethylsilazano-*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}hydrazano)}(2-)-*N,O',O''*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. ¹H NMR (CDCl₃, 50 °C): δ 0.24 (s, 36 H, SiMe₃), 7.65-7.73 (m, 2 H), 7.73-7.81 (m, 1 H), 7.83-7.88 (m, 1 H) (C₆H₄). ¹³C NMR (CDCl₃, 50 °C): δ 4.86 (SiMe₃), 121.83, 122.53, 128.94, 130.48, 134.03, 134.83, 136.25, 166.03, 188.37 (C=O). ²⁹Si NMR (CDCl₃, 50 °C): δ 8.06. MS (EI; 70 eV): *m/z* (relative intensity) 566 (3) [M⁺], 523 (4) [M - Me - N₂]⁺, 379 (80) [(Me₃Si)₂N]₂Ge - Me⁺, 275 (100) [Me₅Si₂N₂Si₂Me₄]⁺, 172 (64) [N₂O₂C₃C₆H₄]⁺. Anal. Calcd for **7** C₂₁H₄₀GeN₄O₂Si₄ (565.51): C, 44.60; H, 7.13; N, 9.91. Found: C, 44.66; H, 7.24; N, 9.80.

(7)₂. ¹H NMR (CDCl₃): δ 0.17 (br, s), 0.20 (s), 0.29 (s), 0.31 (br, s) (72 H, SiMe₃), 7.36-7.77 (6 m, 8 H, C₆H₄). ¹³C NMR (CDCl₃): δ 5.06, 5.18, 5.36 (br), 5.99 (br, SiMe₃), 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). ²⁹Si NMR (CDCl₃): δ 5.89 (br), 6.11 (br), 6.85, 7.25. ¹⁵N NMR (CDCl₃): δ -332.2, -330.7, -328.6, -328.5 (N(SiMe₃)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 - N₂]⁺, 958(6) [M - N₂C₃O₄C₆H₄]⁺, 566 (4) [M/2]⁺, 146 (100) [Me₆Si₂]⁺. Found for C₄₂H₈₀Ge₂N₈O₄Si₈ (1131.01): C, 43.07; H, 7.25; N, 9.93.

8. ¹H NMR (CDCl₃): δ -0.03 (br s, 18 H) (SiMe₃), 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). ¹³C NMR (CDCl₃): δ 5.80 (³J_{SnC} = 13.2 Hz), 6.36 (³J_{SnC} = 16.0 Hz, SiMe₃), 98.80 (³J_{SnC} = 28.5 Hz, C-8), 121.63 (C-4), 126.88 (C-3), 128.55 (²J_{SnC} = 29.4 Hz, C-7), 129.12 (C-5), 132.46 (C-2), 134.98 (³J_{Sn} = 16.1 Hz, C-6), 148.79 (⁴J_{SnC} = 8 Hz, C-1), 176.69 (⁴J_{SnC} = 16.7 Hz, C-9). ²⁹Si NMR: δ 6.81 (s), 7.39 (s). ¹¹⁹Sn NMR (toluene-*d*₈): δ -309.1. MS (EI; 70 eV): *m/z* (relative intensity) 440 (2) [M - N₂C₃O₂C₆H₄]⁺, 130 (100) [Me₆Si₂N⁺]. MS (FD): *m/z* (relative intensity) 440 (4), 172 (100) [N₂C₃O₂C₆H₄]⁺. Molecular mass (cryoscopic method in C₆H₆), found: 615. Anal. Calcd for C₂₁H₄₀N₄O₂Si₄Sn (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}hydrazono) (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). ¹H-NMR (CDCl₃): δ 5.06 (s, 36 H, SiMe₃), 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 ₆ H ₁₄	2	3	4·1/2C ₆ H ₁₄	(7) ₂ ·4C ₄ H ₈ O
formula	C ₃₈ H ₆₅ GeN ₄ O ₄ Si ₂	C ₁₇ H ₄₂ GeN ₄ O ₄ Si ₄	C ₂₉ H ₇₈ Ge ₂ N ₆ O ₄ Si ₈	C ₂₅ H ₅₈ GeN ₅ O ₅ Si ₄	C ₅₈ H ₁₁₂ Ge ₂ N ₈ O ₈ Si ₈
M _r	770.71	551.50	944.87	693.71	1419.46
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (pm)	1090.86(7)	1334.5(1)	1161.0(4)	3466.4(4)	1348.2(5)
<i>b</i> (pm)	1134.56(9)	1434.8(1)	1231.5(4)	1240.3(2)	1553.4(5)
<i>c</i> (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)
<i>V</i> (nm ³)	2.0904(4)	2.8556(5)	2.447(2)	7.601(2)	3.764(2)
<i>Z</i>	2	4	2	8	2
<i>D</i> _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
<i>F</i> (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
2 θ range (deg)	8–50	8–45	8–45	8–45	8–45
range of <i>hkl</i>	–12 ≤ <i>h</i> ≤ 13 –13 ≤ <i>k</i> ≤ 13 –13 ≤ <i>l</i> ≤ 20	–14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 15 –16 ≤ <i>l</i> ≤ 16	–12 ≤ <i>h</i> ≤ 12 –13 ≤ <i>k</i> ≤ 12 –17 ≤ <i>l</i> ≤ 19	–36 ≤ <i>h</i> ≤ 37 –13 ≤ <i>k</i> ≤ 12 –19 ≤ <i>l</i> ≤ 19	–14 ≤ <i>h</i> ≤ 14 –16 ≤ <i>k</i> ≤ 16 –11 ≤ <i>l</i> ≤ 21
no. of rflns coll	7814	14 811	7281	12 369	10 321
no. of indep rflns	7422	3717	6373	4948	9775
<i>R</i> (int)	0.0520	0.0373	0.0357	0.0309	0.0621
<i>T</i> _{min}	0.599	0.749	0.773		0.561
<i>T</i> _{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
<i>S</i>	1.049	1.032	1.061	1.048	1.030
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0355	0.0251	0.0310	0.0318	0.0548
<i>wR</i> 2 (all data)	0.0924	0.0539	0.0736	0.0866	0.1541
<i>g</i> ₁	0.0354	0.0169	0.0261	0.0355	0.0486
<i>g</i> 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) (C₆H₄), 11.78 (s, 1 H, N-H). ¹³C NMR (CDCl₃): δ 5.06 (SiMe₃), 122.85, 123.08 (C-3, C-4, C₆H₄), 134.15 (C=N), 134.71, 135.02 (C-2, C-5, C₆H₄), 138.85, 140.24 (C-1, C-6, C₆H₄), 186.40, 188.11 (C=O). ²⁹Si NMR (CDCl₃): δ 6.78 (s). MS (EI; 70 eV): *m/z* (relative intensity) 569 (28) [M – Me⁺], 277 (100). Anal. Calcd for C₂₁H₄₂GeN₄O₃Si₄ (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 K α 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 $R1 = \sum |F_o| - |F_c| / \sum |F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{0.5}$. 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 SiMe₃ 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 germainine species be substantiated, which does not exclude short-lived germainine intermediates.

Acknowledgment. Support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

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.

(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.