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Azadigermiridines by Addition of Diazomethane or Trimethylsilyldiazomethane to a Digermene[1]

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Tetrakis(2,4,6-triisopropylphenyl)digermene (**2**), prepared by treatment of germanium bis(trimethylsilyl)amide with 2,4,6-triisopropylphenyllithium, reacts with diazomethane or trimethylsilyldiazomethane in a [2+1] fashion to furnish the *N*-methyleneamino-substituted azadigermiridines **7** and **8**, respectively. The dissociation equilibrium between **2** and bis(triisopropylphenyl)germylene has been confirmed by the trapping reaction with a 1,2-quinone, from which the 1,3-dioxa-2-germaindan **10** was isolated. The structures of **2**, **7**, **8**, and **10** were determined by X-ray crystallography. The sterically congested digermene **2** has a short Ge−Ge double-bond length of 2.213(1) Å.

Introduction

Digermenes now constitute an established class of compounds and have been the topic of several review articles.[2] One of their most interesting modes of reaction involves formal [2+1] cycloaddition at the Ge/Ge double bond to form digermiranes. The latter compounds, consisting of a three-membered ring composed of two germanium atoms and one heteroatom, are not readily accessible by other routes (Scheme 1).

For example, the 2,6-diethylphenyl-substituted digermene **1** reacts with diazomethane to furnish the digermirane **3**, presumably by way of a [2+3] cycloaddition with subsequent elimination of nitrogen. Depending on the reaction conditions, compound **3** is isolated in 72%[3] or even quantitative yield.[4] In contrast, the corresponding reaction of the more voluminously substituted digermene **2** affords the digermirane **4** in only 6% yield.[3] The increased steric shielding in **2** apparently has an adverse effect on the primary [2+3] addition, and thus, perhaps, a further mode of attack of diazomethane on the Ge/Ge double bond needs to be taken into consideration.

With this possibility in mind, we have reinvestigated the reaction of **2** with diazomethane and now report on a novel synthesis of **2**, its reactions with diazomethane and trimethylsilyldiazomethane, and the partial dissociation of **2** into germylene molecules.

Results and Discussion

Up to now the digermene **2** was mostly prepared in a multistage procedure starting from a germanium tetrahalide.[5,6] We have found that the reaction of the germanium(II) amide **5**[7] with the appropriate aryllithium component affords compound **2** in one step and the acceptable yield of 67% (Scheme 2).

An X-ray crystallographic analysis (Figure 1) of the light yellow crystals of **2** gave some unexpected results. Thus, the Ge−Ge separation in **2** is 2.213(1) Å and thus identical with the value found for the sterically appreciably less congested compound **1** [2.213(2) Å].[8] Also the *trans*-bent and torsion angles of 12.3° and 13.7° are comparable with those of **1** (12° and 10°, respectively). These structural similarities are surprising because digermenes have otherwise been found to react very sensitively to changes in the spatial requirements of their substituents. For example, the tetraaryldigermene (*Z*)-Mes(Dip)Ge═Ge(Dip)Mes, Mes = 2,4,6-$Me_3C_6H_2$, Dip = 2,6-$i$$Pr_2C_6H_3$, with appreciably less bulky substituents than **2** exhibits a much longer double-bond length of 2.301(1) Å and a *trans*-bent angle of 36°.[9] Together with **1,** compound **2** has the shortest currently observed Ge/Ge double-bond length, and this fact, together with the steric shielding in **2,** explains why the expected [2+3] cycloaddition processes proceed only with great difficulty.

In fact, the reaction of **2** with diazomethane furnishes a product in 80% yield for which the analytical and spectral data suggest the existence of a 1:1 adduct of the starting materials. An X-ray crystallographic analysis (Figure 2), revealed that the methyleneamino-

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[1] Compounds of Germanium, Tin, and Lead. 33. Part 32: Stürmann, M.; Saak, W.; Weidenbruch, M.; Bernd, A.; Scheschkewitz, D. *Heteroatom Chem.*, in press.

[2] Reviews: (a) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem.* **1991**, *103*, 916; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902. (b) Driess, M.; Grützmacher, H. *Angew. Chem.* **1996**, *108*, 900; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 827. (c) Baines, K. M.; Stibbs, W. G. In *Multiply Bonded Main Group Metals and Metalloids;* West, R., Stone, F. G. A., Eds.; Academic Press: San Diego, 1996, p 275. (d) Power, P. P. *J. Chem. Soc., Dalton Trans* **1998**, 2939. (e) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373.

[3] (a) Ando, W.; Tsumuraya, T. *Organometallics* **1988**, *7*, 1882. (b) Tsumuraya, T.; Sato, S.; Ando, W. *Organometallics* **1990**, *9*, 2061.

[4] Batcheller, S. A.; Masamune, S. *Tetrahedron Lett.* **1988**, *29*, 3383.

[5] Park, J.; Batcheller, S. A.; Masamune, S. *J. Organomet. Chem.* **1989**, *367*, 39.

[6] Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.

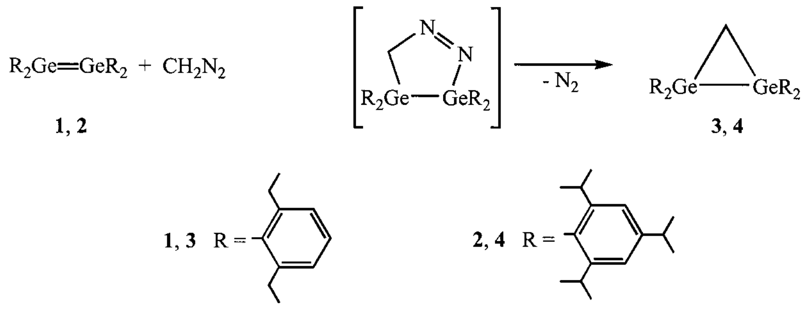
[7] Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

[8] Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. J. *Tetrahedron Lett.* **1984**, *25*, 4191.

[9] Batcheller, S. A.; Tsumuraya, T.; Tempkin, O.; Davis, W. M.; Masamune, S. *J. Am. Chem. Soc.* **1990**, *112*, 9394.

10.1021/om990337d CCC: $18.00

Scheme 1



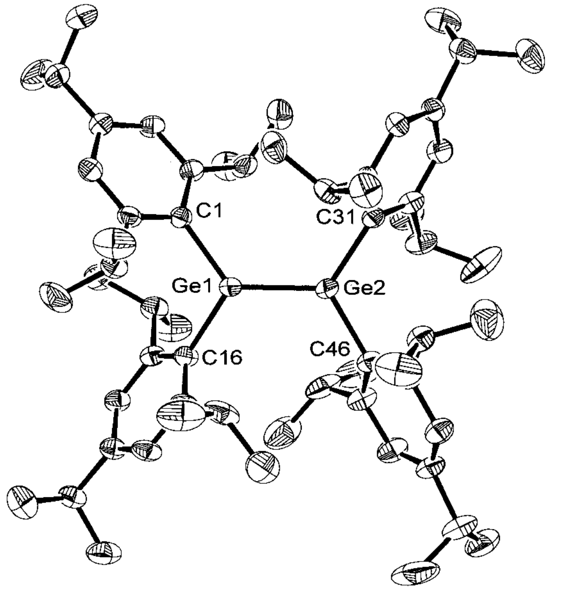
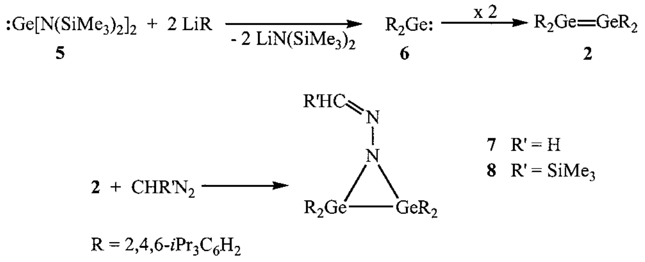


Figure 1. Molecule of **2** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−Ge(2) 2.213(1), Ge(1)−C(1) 1.964(5), Ge(1)−C(16) 1.970(5), Ge(2)−C(31) 1.957(5), Ge(2)−C(46) 1.960(5), C(1)−Ge(1)−C(16) 111.5(2), C(31)−Ge(2)−C(46) 117.0(2).

Scheme 2



substituted azadigermirane **7** had been formed, presumably by a [2+1] cycloaddition without subsequent loss of nitrogen. Interestingly, the digermirane **4** obtained by Ando et al.[3] in low yield could not be observed.

In the three-membered ring, the smaller angles are found at the two germanium atoms and the larger angle is found at the nitrogen atom. As expected, the substituents at the nitrogen atom have a planar arrangement, while, in contrast, the almost planar environments (angular sum in each case 358.5°) of the two *ipso*-carbon atoms and the respective other germanium atom about the ring germanium atoms were not expected. A similar situation was observed for disiliranes with an electronegative atom in the three-membered ring; this, together with the normally considerably shortened Si/Si bond lengths, was interpreted as an indication that these compounds exist in a continuum ranging from the classical three-membered ring structure to a π-interaction between the Si/Si double bond and the heteroatom.[10] However, a comparable bonding situation in **7** can probably be discounted since the Ge/Ge bond length is only slightly shorter than the normal single-bond length of 2.44 Å.

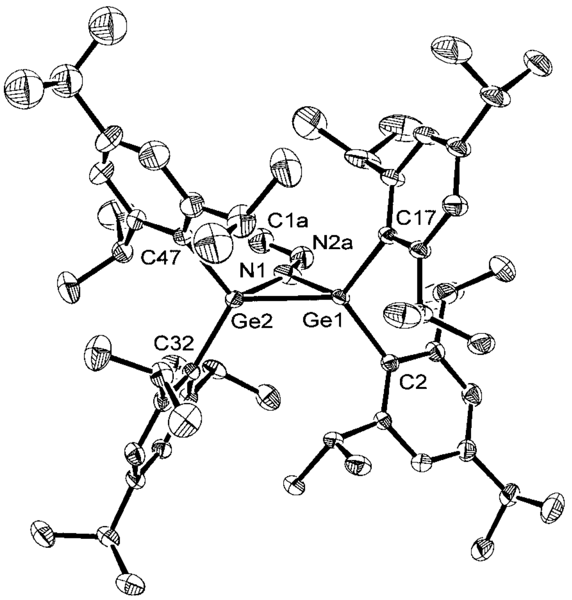


Figure 2. Molecule of **7** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)−Ge(2) 2.4237(4), Ge(1)−N(1) 1.883(2), Ge(2)−N(1) 1.924(2), N(1)−N(2) 1.382(5), N(2)−C(1) 1.297(7), Ge(1)−C(2) 1.982(2), Ge(1)−C(17) 1.983(2), Ge(2)−C(32) 1.983(2), Ge(2)−C(47) 1.970(3), Ge(1)−Ge(2)−N(1) 49.72(6), N(1)−Ge(1)−Ge(2) 51.20(7), Ge(1)−N(1)−Ge(2) 79.08(8), N(1)−N(2)−C(1) 115.9(5), C(2)−Ge(1)−C(17) 111.04(9), C(32)−Ge(2)−C(47) 112.5(1).

The reaction mode demonstrated here was previously unknown in the chemistry of digermenes, although an analogous ring system had been isolated from the reaction of tetramesityldisilene with phenyldiazomethane, albeit without a complete structural characterization.[11]

To determine whether the [2+1] addition process is also realizable with substituted diazomethanes and if the possibly formed compounds exhibit similar struc-

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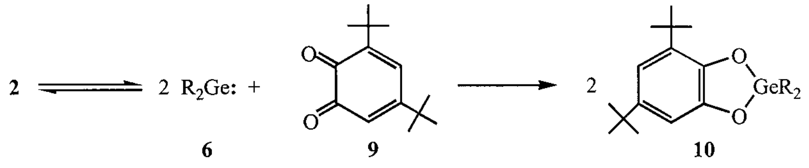
(10) Reviews: (a) Weidenbruch, M. *Chem. Rev.* **1995**, *95*, 1479. (b) Okazaki, R.; West, R. In *Multiply Bonded Main Group Metals and Metalloids*; West, R., Stone, F. G. A., Eds.; Academic Press: San Diego, 1996; p 231.

(11) Piana, H.; Schubert, U. *J. Organomet. Chem.* **1988**, *348*, C19.

Scheme 3



R = 2,4,6-iPr$_3$C$_6$H$_2$

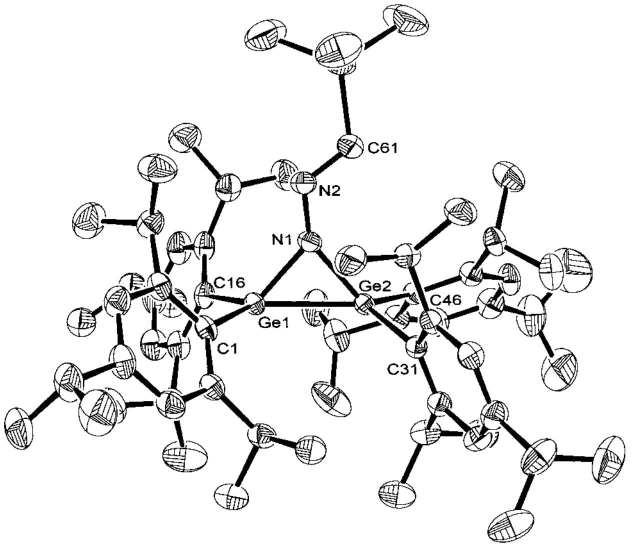


Figure 3. Molecule of **8** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Ge(1)–Ge(2) 2.4415(5), Ge(1)–N(1) 1.866(3), Ge(2)–N(1) 1.914(3), N(1)–N(2) 1.359(4), N(2)–C(61) 1.292(5), Ge(1)–C(1) 2.005(2), Ge(1)–C(16) 2.015(2), Ge(2)–C(31) 2.004(2), Ge(2)–C(46) 2.010(2), Ge(1)–Ge(2)–N(1) 48.93(8), N(1)–Ge(1)–Ge(2) 50.62(9), Ge(1)–N(1)–Ge(2) 80.46(11), N(1)–N(2)–C(61) 120.6(3), C(1)–Ge(1)–C(16) 113.38(9), C(31)–Ge(2)–C(46) 107.66(9).

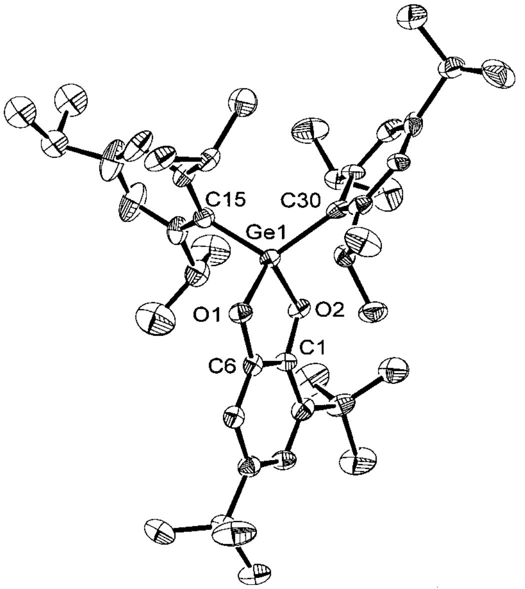


Figure 4. Molecule of **10** in the crystal (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (deg): Ge–O(1) 1.838(5), Ge–O(2) 1.789(4), O(1)–C(6) 1.390(7), O(2)–C(1) 1.436(8), O(2)–Ge–(O(1) 89.6(2), C(1)–O(2)–Ge 103.3(4), C(6)–O(1)–Ge 111.6(4), C(15)–Ge–C(30) 114.1(2).

tural parameters, the digermene **2** was allowed to react with trimethylsilyldiazomethane. Again we obtained colorless crystals in a yield of 67%, the analytical, spectral, and X-ray crystallographic data (Figure 3) of which supported the existence of the [2+1] adduct **8**.

Compound **8** crystallizes as two crystallographically independent molecules with two of each occupying the unit cell. The bond lengths and angles within the three-membered ring of both molecules of **8** are not appreciably different from those of compound **7**. The ring nitrogen atom in **8** also exists in a planar environment with its substituents (angular sum 360°). However, the coordination situations of the *ipso*-carbon atoms and the respective other Ge atom differ at the two germanium atoms. While the atom Ge(1) with an angular sum of 358.9° has an almost planar environment, the angular sum of 346° at Ge(2) is indicative of a significant pyramidalization. This is presumably due to the steric influence of the trimethylsilyl group which forces the aryl groups and hence the *ipso*-carbon atoms out of the plane (Scheme 3).

The cycloaddition processes described here support the conclusions from previous investigations[3] that the digermene **2** also retains at least part of its structural integrity in solution. Okazaki et al. recently studied the bond dissociation energy of a similar, sterically congested digermene using temperature-dependent electron spectroscopy and determined a value of only 61.5 kJ mol^{-1} for the dissociation into germylene molecules.[12] Accordingly, we have performed some trapping reactions in an attempt to detect an at least partial dissociation of **2** to the germylene **6**.

A solution of **2** in DME was heated in the presence of the 1,2-quinone **9**, a compound known for its ability both to participate in [4+2] additions with double-bond systems and to trap carbene analogues.[13] This reaction furnished colorless crystals of the 1,3-dioxa-2-germaindan **10** in 48% yield. The structure of **10** was confirmed unequivocally by its analytical and spectral data as well as by an X-ray crystallographic analysis (Figure 4). This result indicates that, at least under these harsher reaction conditions, digermene **2** at least partially dissociates into two germylene molecules **6**. However, a trapping reaction of the digermene **2** by the 1,2-quinone **9**, followed by extrusion of a germylene molecule **6,** cannot be completely excluded.

Experimental Section

General Procedures. All manipulations were carried out in oven-dried glassware under an atmosphere of dry argon.

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[12] Kishikawa, K.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1998**, 239.

[13] Weidenbruch, M.; Pellmann, A.; Pohl, S.; Saak, W.; Marsmann, H. *Chem. Ber.* **1995**, *128*, 935.

Table 1. Crystallographic Data for 2, 7, 8, and 10

	2	**7**	**8**	**10**
empirical formula	$C_{60}H_{92}Ge_2$	$C_{61}H_{94}Ge_2N_2$	$C_{64}H_{102}Ge_2N_2Si\cdot{}^1/_2DME$	$C_{44}H_{66}GeO_2$
fw	958.52	1000.56	1117.80	699.56
a (Å)	13.0859(5)	10.9205(10)	21.705(1)	16.8443(10)
b (Å)	13.5481(7)	13.5314(11)	21.4197(9)	15.5059(13)
c (Å)	18.2446(11)	22.624(2)	22.3357(14)	17.7051(12)
α (deg)	98.302(7)	77.60(1)	78.088(6)	90
β (deg)	96.916(6)	76.36(1)	75.347(7)	116.515(7)
γ (deg)	111.948(5)	68.380(9)	73.919(6)	90
V (Å^3)	2914.6(3)	2989.9(5)	6909.3(7)	4137.9(5)
Z	2	2	4	4
D(calcd) (g cm^{-3})	1.092	1.111	1.075	1.123
cryst size (mm)	1.10 × 0.65 × 0.38	0.60 × 0.50 × 0.40	0.68 × 0.53 × 0.33	0.46 × 0.15 × 0.14
cryst syst	triclinic	triclinic	triclinic	monoclinic
temp (K)	213(2)	213(2)	193(2)	193(2)
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
$2\theta_{max}$ (deg)	52	52	52	55
no. of rflns measd	24031	40173	54502	40031
no. of unique rflns	10544	10886	25118	7558
lin abs coeff (mm^{-1})	1.064	1.041	0.924	0.773
no. of params	559	581	1186	397
R [$I > 2\sigma(I)$]	0.0767	0.0346	0.0480	0.0804
wR2 (all data)	0.1960	0.0908	0.1270	0.1894
GOF (F^2)	1.110	1.015	0.861	0.867

The ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a Bruker ARX 500 spectrometer using C_6D_6 as solvent. Elemental analyses were performed by Analytische Laboratorien, D-51779 Lindlar, Germany.

Tetrakis(2,4,6-triisopropylphenyl)digermene (2). At 0 °C, a solution of 2,4,6-triisopropylphenyllithium[14] (6.11 g, 29 mmol), prepared from 1-bromo-2,4,6-triisopropylbenzene[15] and *n*-butyllithium, in diethyl ether (50 mL) was added dropwise to a solution of the germanium amide **5** (6.53 g, 16.6 mmol) in diethyl ether (50 mL). The mixture was allowed to warm to room temperature, and stirring was continued for 12 h. The solvent was then removed and all volatile compounds were distilled off at 170 °C/0.05 mbar. The residue was extracted with *n*-hexane (120 mL) and the resulting solution concentrated to a volume of 30 mL. Cooling at −50 °C for 12 h furnished 5.3 g (67% yield) of pale yellow crystals of **2**: mp > 280 °C; for ^{1}H and UV/vis spectra, see ref 4; ^{13}C NMR δ 24.28, 24.39, 24.47, 24.59, 25.03, 25.30, 34.81, 37.89, 38.07, 121.99, 122.99, 143.40, 150.25, 153.47, 153.73. Anal. Calcd for $C_{60}H_{92}Ge_2$: C 75.18, H 9.67. Found: C 75.00, H 9.51.

Methylene[2,2,3,3-tetrakis(triisopropylphenyl)azadigermiridin-1-yl]amine (7). At −30 °C, a solution of diazomethane (approximately 0.13 g, 0.3 mmol, prepared from 1.0 g (4.7 mmol) of *p*-tolylsulfonylmethylnitrosamide[17]) in diethyl ether (18 mL) was added dropwise to a mixture of **2** (0.50 g, 0.52 mmol) and copper powder (40 mg) in DME (9 mL) with stirring. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 36 h. The mixture was then filtered through silica gel, and the filtrate was concentrated to a volume of 2 mL and cooled to −18 °C to afford 0.418 g (80% yield) of colorless crystals of **7**: mp 148 °C (dec); ^{1}H NMR δ 0.55 (d, 6 H, ^3J = 6.6 Hz), 0.59 (d, 6 H, ^3J = 6.6 Hz), 0.76 (d, 6 H, ^3J = 6.6 Hz), 0.99 (d, 6 H, ^3J = 6.6 Hz), 1.10 (d, 12 H, ^3J = 6.6 Hz), 1.21 (d, 6 H, ^3J = 6.6 Hz), 1.22 (d, 6 H, ^3J = 6.6 Hz), 1.33 (d, 6 H, ^3J = 6.6 Hz), 1.45 (d, 6 H, ^3J = 6.6 Hz), 1.46 (d, 6 H, ^3J = 6.6 Hz), 1.51 (d, 6 H, ^3J = 6.6 Hz), 2.67 (sept, 2 H), 2.77 (sept, 2 H), 3.32 (sept, 2 H), 3.53 (sept, 2 H), 3.87 (m, 4 H), 6.48 (m, 2 H, CH_2), 6.99 (s, 4 H), 7.05 (s, 2 H), 7.20 (s, 2 H); ^{13}C NMR δ 23.36, 23.63, 23.96, 24.04, 24.40, 24.94, 25.01, 25.47, 25.74, 33.02, 34.38, 34.63, 35.58, 36.31, 36.62, 37.13, 121.48, 122.09, 122.74, 123.44, 138.85, 140.05, 150.30, 153.04, 153.32, 154.12, 154.77. Anal. Calcd for $C_{61}H_{94}Ge_2N_2$: C 73.22, H 9.47, N 2.80. Found: C 73.04, H 9.46, N 2.65.

[2,2,3,3-Tetrakis(2,4,6-triisopropylphenyl)azadigermiridin-1-yl]trimethylsilylmethyleneamine (8). At 5 °C, 1 mL of a 2 M solution of trimethylsilyldiazomethane (2 mmol) in *n*-hexane (Fluka, D-82041 Deisenhofen, Germany) was added dropwise to a mixture of **2** (0.50 g, 0.52 mmol) and copper powder (40 mg) in DME (5 mL) with stirring. The resulting mixture was allowed to warm to room temperature, and stirring was continued for 36 h. The mixture was then filtered through silica gel, and the filtrate was concentrated to a volume of 2 mL and cooled to −18 °C to furnish 0.375 g (67% yield) of colorless crystals of **8**: mp 108 °C; ^{1}H NMR δ 0.33 (s, 9 H, SiMe$_3$), 0.55 (d, 6 H, ^3J = 6.6 Hz), 0.59 (d, 6 H, ^3J = 6.6 Hz), 0.76 (d, 6 H, ^3J = 6.6 Hz), 0.99 (d, 6 H, ^3J = 6.6 Hz), 1.10 (d, 12 H, ^3J = 6.6 Hz), 1.21 (d, 6 H, ^3J = 6.6 Hz), 1.22 (d, 6 H, ^3J = 6.6 Hz), 1.33 (d, 6 H, ^3J = 6.6 Hz), 1.45 (d, 6 H, ^3J = 6.6 Hz), 1.46 (d, 6 H, ^3J = 6.6 Hz), 1.51 (d, 6 H, ^3J = 6.6 Hz), 2.67 (sept, 2 H), 2.77 (sept, 2 H), 3.12 (s, DME), 3.32 (sept, 2 H, overlapping with the DME signal), 3.33 (s, DME), 3.53 (sept, 2 H), 3.87 (m, 4 H), 6.99 (s, 4 H), 7.05 (s, 2 H), 7.20 (s, 2 H), 7.60 (s, 1 H, N=CH); ^{13}C NMR δ −0.75, 23.59, 23.89, 23.95, 24.10, 24.23, 24.46, 24.86, 25.01, 25.49, 25.83, 32.99, 34.38, 34.65, 35.58, 36.57, 37.01, 58.88 (DME), 72.44 (DME), 121.51, 122.19, 122.74, 123.52, 145.58, 150.28, 150.40, 153.08, 153.38, 154.82. Anal. Calcd for $C_{64}H_{102}Ge_2N_2Si\cdot{}^1/_2DME$: C 70.90, H 9.65, N 2.50. Found: C 70.74, H 9.54, N 2.38.

4,6-Di-*tert*-butyl-2,2-bis(2,4,6-triisopropylphenyl)-1,3-dioxa-2-germaindan (10). At room temperature, solid **9** (0.180 g, 8.2 mmol) was added to a solution of **2** (0.40 g, 0.42 mmol) in DME (5 mL) with stirring. The reaction mixture was heated under reflux for 24 h and then the solvent distilled off. The residue was extracted with *n*-hexane (15 mL), filtered through silica gel, and concentrated to a volume of 3 mL. Cooling at −18 °C afforded 0.28 g (48% yield) of colorless crystals of **10**: mp 102−106 °C; ^{1}H NMR δ 1.12 (d, 12 H, ^3J = 6.6 Hz), 1.18 (d, 12 H, ^3J = 6.6 Hz), 1.20 (d, 12 H, ^3J = 6.6 Hz), 1.32 (s, 9H), 1.59 (s, 9 H), 2.69 (sept, 2 H), 3.87 (sept, 4 H), 7.02 (s, 1 H), 7.09 (s, 4 H), 7.28 (s, 1 H); ^{13}C NMR δ 23.41, 24.32, 24.55, 29.71, 31.51, 34.15, 34.60, 97.27, 109.60, 113.56, 121.78, 132.64, 134.20, 141.51, 150.28, 151.81, 153.46. Anal. Calcd for $C_{44}H_{66}GeO_2$: C 75.55, H 9.51. Found: C 75.31, H 9.56.

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(14) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *J. Organomet. Chem.* **1988**, *341*, 1.

(15) Whitesides, G. M.; Eisenhut, M.; Bünting, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5398.

(16) Sheldrick, G. M. *SHELXL-97. Program for crystal structure refinement*; Universität Göttingen: Göttingen. Germany, 1997.

(17) DeBoer, T. J.; Backer, H. J. *Org. Synth.* **1956**, *36*, 16.

Crystallographic Analyses. Crystal and numerical data of the structure determinations are given in Table 1. In each case, the crystal was mounted in an inert oil. Data collection was performed with a STOE IPDS area-detector using graphite-monochromated Mo Kα radiation (0.71073 Å). The structures were solved by direct phase determinations and refined by full-matrix least-squares techniques against F^2 with the SHELXL-97 program system.[16] Hydrogen atoms were placed in the calculated positions, and all other atoms were refined anisotropically. The N=CH_2 group of **7** is disordered and was refined on two positions with an occupancy factor of 0.5 each. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-118 856 (**2**), CCDC-118 857 (**7**), CCDC-118 859 (**8**), and CCDC-118 858 (**10**).

Acknowledgment. Financial support of our work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Listing of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **2**, **7**, **8**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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