Organometallics **1996,** *15,* 741−746

Bis(2,4,6-tri-*tert*-butylphenyl)germylene Reinvestigated: Crystal Structure, Lewis Acid Catalyzed C−H Insertion, and Oxidation to an Unstable Germanone

Peter Jutzi,* Holger Schmidt, Beate Neumann, and Hans-Georg Stammler

Fakultät für Chemie, Universität Bielefeld, Universitätsstrasse, D-33615 Bielefeld, FRG

Received July 21, 1995[⊗]

Bis(2,4,6-tri-*tert*-butylphenyl)germylene (**1**), which had been reported to undergo an insertion of the germanium atom into a C−H bond of an *o*-*tert*-butyl group at room temperature, was found to be quite stable. Such a C−H insertion does occur in solution, forming germaindane **2**, but only in the presence of a Lewis acid such as the starting material $GeCl_2$. **1** can be stored unchanged at −30 °C for months; at 20 °C it decomposes within several weeks under release of 1,3,5-tri-*tert*-butylbenzene. Compound **1** was characterized by X-ray diffraction methods. The X-ray structure of **1** shows that the two aryl ligands have very different geometries: one aryl group is greatly distorted to give a “boat” form and the Ge atom is remote from any of the ring planes, while the second aryl group is only slightly deformed and the Ge atom lies in the ring plane. UV/vis spectra exhibit an intense absorption at 430 nm in solution and at 405 nm in the solid state, which represents an enormous hypsochromic shift compared to other germylenes with bulky aryl ligands. Oxidation of **1** with trimethylamine *N*-oxide leads to a germanone, which rearranges very rapidly by a C−H insertion process yielding the germaindanol **3**.

Introduction

The synthesis of divalent germanium compounds with organic ligands (germylenes) has now been a goal of organometallic research for two decades. Species with small, nonfunctionalized ligands aggregate quite rapidly to form oligo- and polymeric products.[1] Polymerization can be prevented by kinetic and/or thermodynamic stabilization.

Thermodynamic stabilization is achieved by the use of n- or π-donor ligands, which bring about a reduction of the electron deficiency by donating electrons to the vacant p-orbital of the Ge center. The following classes of donor-stabilized germylenes have been characterized structurally: (i) sandwich compounds of the type $GeCp_2$[2] (Cp = (substituted) cyclopentadienyl); (ii) half-sandwich compounds of the type Cp*GeR (Cp* = pentamethylcyclopentadienyl, R = Cl,[2c] alkyl, aryl, amino[2h,3]) and of the type $Cp^*Ge^+ X^-$;[2h,4] (iii) nitrogen-, phosphorus-, and oxygen-substituted germylenes of the type GeX_2 (X = NR_2,[5] PR_2,[6] OR[7] (R = alkyl, aryl)); (iv) germylenes of the type RGeCl (R = $(N^tBu)SiMe_2(NH^tBu)$,[8] 2,4,6-tri-*tert*-butylphenyl (=Mes*),[9] ((dimethylamino)ethyl)tetramethylcyclopentadienyl[10]).

Kinetic stabilization is also a very important factor in the examples given above. There are only a few germylenes which are stablilized merely through steric effects: Lappert's famous germylene, $Ge(CH(SiMe_3)_2)_2$, is monomeric in solution[11] and in the gas phase,[12] but X-ray crystallography has shown that even the bulky $CH(SiMe_3)_2$ ligands are not able to prevent dimerization in the solid state.[13] We found, however, that the exchange of one ligand by the even bulkier $C(SiMe_3)_3$ group leads to a germylene which is also monomeric in the solid state.[14]

Considering the kinetic effects of aryl groups, the stabilization seems to depend on the steric requirements of these groups. Germylenes with less bulky aryl groups

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

[1] Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311.

[2] (a) Almlöf, J.; Fernholt, L.; Faegri, K., Jr.; Haaland, A.; Schilling, B. E. R.; Seip, R.; Taugbol, K. *Acta Chem. Scand.* **1983**, *A37*, 131. (b) Grenz, M.; Hahn, E.; du Mont, W.-W.; Pickardt, J. *Angew. Chem.* **1984**, *96*, 69. (c) Fernholt, L.; Haaland, A.; Jutzi, P.; Kohl, F.-X.; Seip, R. *Acta Chem. Scand.* **1984**, *A38*, 211. (d) Schumann, H.; Janiak, C.; Hahn, E.; Loebel, J.; Zuckerman, J. J. *Angew. Chem.* **1985**, *97*, 765. (e) Schumann, H.; Janiak, C.; Hahn, E.; Kolax, C.; Loebel, J.; Rausch, M. D.; Zuckerman, J. J.; Heeg, M. J. *Chem. Ber.* **1986**, *119*, 2656. (f) Jutzi, P.; Schlüter, E.; Hursthouse, M. B.; Arif, A. M.; Short, R. L. *J. Organomet. Chem.* **1986**, *299*, 285. (g) Cowley, A. H.; Mardones, M. A.; Avendano, S.; Roman, E.; Manriquez, J. M.; Carrano, C. J. *Polyhedron* **1993**, *12*, 125. (h) Jutzi, P. *Adv. Organomet. Chem.* **1986**, *26*, 217 (review).

[3] (a) Jutzi, P.; Hampel, B.; Hursthouse, M. B.; Howes, A. J. *Organometallics* **1986**, *5*, 1944. (b) Jutzi, P.; Becker, A.; Leue, C.; Stammler, H. G.; Neumann, B.; Hursthouse, M. B.; Karaulov, A. *Organometallics* **1991**, *10*, 3838.

[4] Jutzi, P. *J. Organomet. Chem.* **1990**, *400*, 1 (review).

[5] (a) Lappert, M. F.; Slade, M. J.; Atwood, J. L.; Zaworotko, M. M. *J. Chem. Soc., Chem. Commun.* **1980**, 621. (b) Pfeiffer, J.; Maringgele, W.; Noltemeyer, M.; Meller, A. *Chem. Ber.* **1989**, *122*, 245. (c) Chorley, R. W.; Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P.; Power, P. P.; Olmstead, M. M. *Inorg. Chim. Acta* **1992**, *198−200*, 203. (d) Herrmann, W. A.; Denk, M.; Behm, J.; Scherer, W.; Klingan, F.-R.; Bock, H.; Solouki, B.; Wagner, M. *Angew. Chem.* **1992**, *104*, 1498. (e) Meller, A.; Ossig, G.; Maringgele, W.; Noltemeyer, M.; Stalke, D.; Herbst-Irmer, R.; Freitag, S.; Sheldrick, G. M. *Z. Naturforsch.* **1992**, *47b*, 162. (f) Braunschweig, H.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J.-M. *Angew. Chem.* **1994**, *106*, 1243.

[6] Driess, M.; Janoschek, R.; Pritzkow, H.; Rell, S.; Winkler, U. *Angew. Chem.* **1995**, *107*, 1746.

[7] (a) Cetinkaya, B.; Gümrükcü, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2088. (b) Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J *J. Chem. Soc., Chem. Commun.* **1985**, 939.

[8] Veith, M.; Hobein, P.; Rösler, R. *Z. Naturforsch.* **1989**, *44b*, 1067.

[9] Jutzi, P.; Leue, C. *Organometallics* **1994**, *13*, 2898.

[10] Jutzi, P.; Schmidt, H.; Stammler, H. G.; Neumann, B. *J. Organomet. Chem.* **1995,** *499*, 7.

[11] Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

[12] Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

[13] Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480.

[14] Jutzi, P.; Becker, A.; Stammler, H. G.; Neumann, B. *Organometallics* **1991,** *10*, 1647.

0276-7333/96/2315-0741$12.00/0

have been reported in the literature as transient species.[15] du Mont et al. synthesized the more bulky Mes*$_2$-Ge (**1**) first in 1987 and characterized the compound by IR, NMR, and MS methods.[16] They reported that at room temperature the compound decomposes by insertion of the germanium atom into a C$-$H bond of an *o*-*tert*-butyl group, leading to germaindane **2**. They further noted that the reaction of **1** with sulfur leads to an unstable germathione which then rearranges by a similar C$-$H insertion. Mochida, Udagawa, et al. proved the monomeric character of **1** in solution by EXAFS.[17] Only recently Okazaki et al. synthesized another bulky diarylgermylene GeTb(Tip) (Tb = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl, Tip = 2,4,6-triisopropylphenyl), which was characterized by a UV/vis spectrum in solution although it has not yet been isolated.[18]

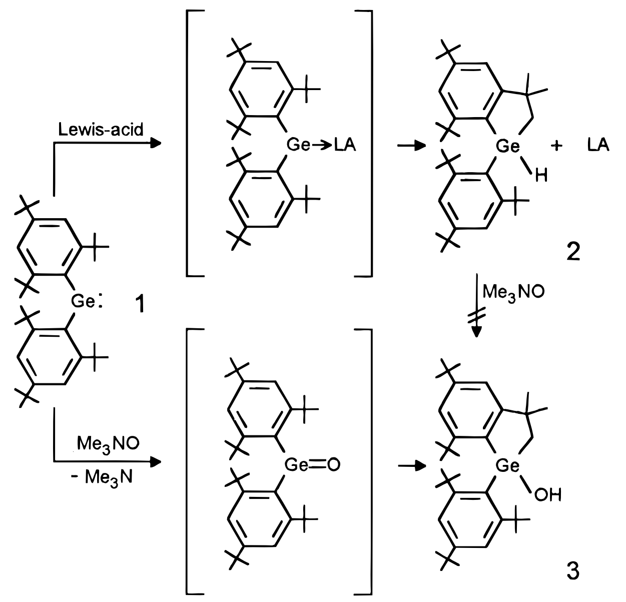
During our research with Mes*-containing germylenes,[3b,9] we found that the stability of **1** is much greater than previously assumed, so that we are now able to report the first fully characterized diarylgermylene which is stable under ordinary conditions.

Results

The title compound **1** was prepared from GeCl$_2$(dioxane) and Mes*Li and isolated as orange-red crystals in good yields. These can be stored unchanged at a temperature of -30 °C for months. At room temperature their color slowly changes; after some days the crystals have turned dark, but ^{1}H NMR spectra show no sign of decomposition. Within several weeks **1** releases Mes*H and forms oligomers of so far unknown structure; seperation and identification of the decomposition products will be the subject of further investigation. The rate of decomposition increases at higher temperatures and is quite fast above the melting point, but C$-$H insertion does not occur. After some days at ambient temperature in various solvents, **1** decomposes, releasing Mes*H; no other products could be traced by ^{1}H and ^{13}C NMR methods. At higher temperatures, this reaction accelerates, but there is no sign of a C$-$H insertion process. When exposed to air, **1** decomposes within some hours. It is very soluble in common aliphatic and aromatic hydrocarbons and in ether solvents but reacts rapidly with chlorinated solvents. ^{1}H and ^{13}C NMR spectra give signals corresponding to four equivalent *o*-*tert*-butyl groups even at -80 °C. UV/vis spectra of **1** dissolved in hexane or THF show an intense absorption maximum at 430 nm; a spectrum of solid **1** shows a maximum at 405 nm.

After addition of catalytic amounts (10 mol %) of a Lewis acid to a stirred solution of **1**, the mixture quickly loses its color. ^{1}H and ^{13}C NMR spectra show the exclusive formation of the C$-$H insertion product **2** (see Scheme 1). The rate of the C$-$H insertion process depends on the Lewis acid and the solvent used; the time for a complete reaction varies from some seconds to several hours. A general trend regarding the strength of the acid or the polarity of the solvent could not be found.[19] Stoichiometric amounts of GeCl$_2$(dioxane) lead to an instantanous C$-$H insertion; the formation of Mes*GeCl [9] via ligand exchange is not observed. It is therefore very important to avoid an excess of GeCl$_2$ during the synthesis of **1** and to extract rapidly the product with hexane. We believe that du Mont's results, which he interpreted in terms of a thermally initiated insertion, were in fact due to an insertion process catalyzed by the presence of GeCl$_2$(dioxane) in the reaction mixture.

Scheme 1. Reactions of 1



The $(2\pi + 4\pi)$ cycloaddition with conjugated dienes can be used to trap unstable germylenes and also to form derivatives of stable compounds such as GeTb(Tip).[18] In contrast to other germylenes, compound **1** does not react with 2,3-dimethylbutadiene even when the diene is used as a solvent and the solution is stirred for several hours.

Oxidation of **1** with trimethylamine *N*-oxide yields germaindanol **3** (see Scheme 1). We have shown that compound **2** is not an intermediate in this process, since **2** does not react at all with Me_3NO.

Crystals suitable for an X-ray crystallographic analysis could be prepared from a solution of **1** in hexane at -30 °C. Figure 1 shows the crystal structure of **1** as an ORTEP plot, and Figure 2 gives a different view in which the methyl groups are omitted. Tables 1$-$3 give selected bond lengths and angles, atomic coordinates, and crystallographic data.

There are no structural data for other diarylgermylenes, and so it is not possible to make precise

---

(15) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759.

(16) Lange, L.; Meyer, B.; du Mont, W.-W. *J. Organomet. Chem.* **1987**, *329*, C17.

(17) Mochida, K.; Fujii, A.; Tsuchiya, N.; Tohji, K.; Udagawa, Y. *Organometallics* **1987**, *6*, 1811.

(18) Tokitoh, N.; Manmaru, K.; Okazaki, R. *Organometallics* **1994**, *13*, 167.

(19) The reaction was carried out in three different solvents (hexane, toluene, THF) with five different Lewis acids (GeCl$_2$(dioxane), GeCl$_4$, AlCl$_3$, BBr$_3$, TiCl$_4$). All combinations of solvent and acid except two gave the same product. In hexane and toluene, TiCl$_4$ reacted with **1** under formation of unsoluble decomposition products which might be the result of a redox process. A suspension of TiCl$_4$·2THF in hexane remained unchanged but also showed no catalytic activity. To examine the influence of the solvent we used GeCl$_4$ and BBr$_3$ (which are both soluble in common solvents) as catalysts under identical conditions. Small amounts of GeCl$_4$ in a solution of **1** in THF lead to a complete decolorization within a few seconds. The same process took some minutes when carried out in toluene and several hours when performed in hexane. BBr$_3$ generally worked much slower: the fastest reaction was achieved in toluene, and there was found no difference between hexane and THF as a solvent.

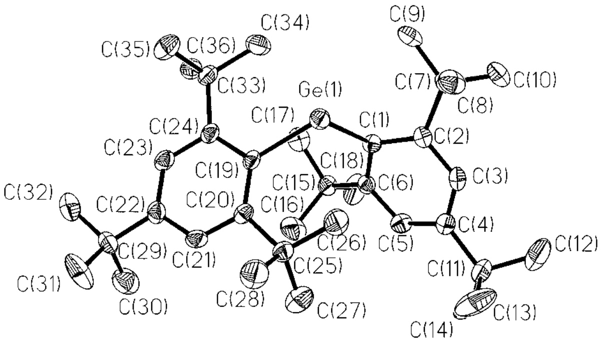


Figure 1. Crystal structure of **1** (ORTEP plot with 50% probability).

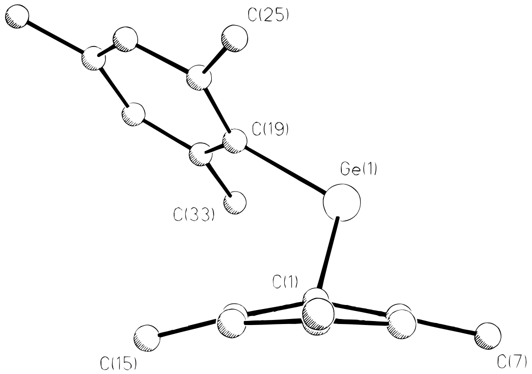


Figure 2. Crystal structure of **1** (methyl groups omitted for clarity).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

Ge−C(1)	2.053(4)	Ge−C(19)	2.041(4)
C(1)−C(2)	1.436(5)	C(2)−C(3)	1.392(5)
C(3)−C(4)	1.380(5)	C(4)−C(5)	1.390(5)
C(5)−C(6)	1.405(5)	C(1)−C(6)	1.422(5)
C(2)−C(7)	1.549(5)	C(4)−C(11)	1.539(6)
C(6)−C(15)	1.562(5)	C(19)−C(20)	1.416(5)
C(20)−C(21)	1.397(5)	C(21)−C(22)	1.394(5)
C(22)−C(23)	1.386(5)	C(23)−C(24)	1.403(5)
C(19)−C(24)	1.421(5)	C(20)−C(25)	1.562(5)
C(22)−C(29)	1.548(6)	C(24)−C(33)	1.548(5)
C(1)−Ge−C(19)	108.0(2)	C(2)−C(1)−Ge	105.1(3)
C(6)−C(1)−Ge	127.4(3)	C(2)−C(1)−C(6)	116.1(4)
C(1)−C(2)−C(3)	118.9(4)	C(2)−C(3)−C(4)	123.6(4)
C(3)−C(4)−C(5)	116.3(4)		
C(4)−C(5)−C(6)	122.4(4)	C(1)−C(6)-C(5)	119.6(4)
C(1)−C(2)−C(7)	123.4(4)	C(3)−C(2)−C(7)	117.5(4)
C(1)−C(6)−C(15)	123.9(4)	C(5)−C(6)−C(15)	116.2(3)
C(20)−C(19)−Ge	122.5(3)	C(24)−C(19)−Ge	119.1(3)
C(20)−C(19)−C(24)	118.1(4)	C(19)−C(20)−C(21)	119.5(4)
C(20)−C(21)−C(22)	123.1(4)	C(21)−C(22)−C(23)	116.6(4)
C(22)−C(23)−C(24)	123.2(4)	C(19)−C(24)−C(23)	119.3(4)
C(19)−C(20)−C(25)	127.0(4)	C(21)−C(20)−C(25)	113.6(4)
C(19)−C(24)−C(33)	126.4(4)	C(23)−C(24)−C(33)	114.1(3)

Table 2. Atomic Coordinates (×10^4) and Isotropic Displacement Parameters *U*(iso) or *U*(eq)[a] (Å^2 × 10^3) for 1

	x	*y*	*z*	*U*(eq)
Ge(1)	1341(1)	3240(1)	1388(1)	29(1)
C(1)	1522(4)	2036(3)	873(1)	23(1)
C(2)	362(4)	2136(3)	526(1)	24(1)
C(3)	470(4)	2241(4)	42(2)	28(1)
C(4)	1633(4)	2189(3)	−131(2)	27(1)
C(5)	2706(4)	1851(4)	195(1)	29(1)
C(6)	2665(4)	1729(4)	689(1)	25(1)
C(7)	−1020(4)	2043(4)	657(2)	29(1)
C(8)	−1716(4)	3219(4)	620(2)	38(1)
C(9)	−1044(4)	1526(4)	1158(2)	36(1)
C(10)	−1814(4)	1225(4)	294(2)	45(1)
C(11)	1729(5)	2467(4)	−659(2)	36(1)
C(12)	577(5)	1965(5)	−997(2)	68(2)
C(13)	1697(6)	3765(4)	−714(2)	76(2)
C(14)	2954(5)	1999(5)	−812(2)	69(2)
C(15)	3861(4)	1136(4)	993(2)	30(1)
C(16)	5099(4)	1850(5)	1023(2)	49(1)
C(17)	3623(4)	851(4)	1499(2)	36(1)
C(18)	4068(5)	−8(4)	743(2)	54(2)
C(19)	3157(4)	3757(4)	1684(1)	25(1)
C(20)	3882(4)	4545(4)	1453(1)	25(1)
C(21)	5128(4)	4850(4)	1674(2)	31(1)
C(22)	5673(4)	4477(4)	2131(2)	30(1)
C(23)	4917(4)	3763(4)	2365(2)	30(1)
C(24)	3674(4)	3399(4)	2158(1)	27(1)
C(25)	3440(4)	5159(4)	962(2)	29(1)
C(26)	2045(4)	4878(4)	733(2)	46(1)
C(27)	4322(5)	4874(4)	596(2)	50(1)
C(28)	3457(5)	6462(4)	1047(2)	48(1)
C(29)	7067(4)	4843(4)	2348(2)	36(1)
C(30)	8024(4)	4344(5)	2042(2)	54(2)
C(31)	7151(5)	6146(4)	2353(2)	63(2)
C(32)	7451(5)	4411(5)	2867(2)	53(2)
C(33)	2957(4)	2703(4)	2502(1)	30(1)
C(34)	1651(4)	2179(4)	2276(2)	41(1)
C(35)	2649(4)	3527(4)	2897(1)	41(1)
C(36)	3794(4)	1704(4)	2742(1)	35(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

comparisons. It is interesting however that the lengths of the Ge−C bonds (2.041(4), 2.053(4) Å) in **1** lie in the same range as those in the dialkylgermylene (Me$_3$Si)$_3$CGeCH(SiMe$_3$)$_2$[14] (2.012, 2.067 Å); the same applies for the C−Ge−C angles (108.0(2) and 111.3°, respectively). The closest Ge−Ge distance in the solid is 8.64 Å, which far exceeds any binding distance.

A striking feature of the structure is the very different conformation of the two Mes* ligands: Ring 1 (containing C(1)−C(18)) is strongly distorted into a "boat" conformation[20] with the ends tipped through about 8 and 15° (see Figure 3 and Table 4). The Ge atom is well out of the plane defined by the ring atoms C(2), C(3), C(5), and C(6) (angle $\alpha + \beta$ in Figure 3). It is also bent by 32.2° out of the plane defined by the ring atoms C(1), C(2), and C(6) (angle α in Figure 3). In ring 1 the *o-tert*-butyl groups are bent away from the Ge atom, so that the angles C(1)−C(2)−C(7) and C(1)−C(6)−C(15) increase from 120° to about 124°. Ring 2 (containing C(19)−C(36)) is nearly planar, and the Ge atom lies almost in the ring plane. The *o-tert*-butyl groups move further away from the Ge atom (indicated by the angles C(19)−C(20)−C(25) (127.0(4)°) and C(19)−C(24)−C(33) (126.4(4)°) but are closer to the ring plane than in ring 1.

The torsional angle between the average ring planes (least-squares method) is 43.2°, and the angles between the ring planes and the C(1)−Ge−C(19) plane are 50.1° (ring 1) and 75.3° (ring 2). An overall view of these distortions is given by Figure 2.

Very close distances between the Ge atom and two of the methyl carbon atoms are found: Ge−C(26) (2.84 Å) and Ge−C(34) (2.77 Å). These short distances are significant, since the sum of the van der Waals radii of a methyl group and a germanium atom is approximately 4 Å.[21−23]

---

(20) A similar deformation of a Mes* ligand has been found in several sterically overcrowded molecules: (a) Yoshifuji, M.;Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *Angew. Chem.* **1980**, *92*, 405. (b) Yoshifuji, M.; Inamoto, N.; Hirotsu, K.; Higushi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1109. (c) Weber, L.; Reizig, K.; Bungardt, D.; Boese, R. *Chem. Ber.* **1987**, *120*, 1421.

Table 3. X-ray Crystallographic Data for 1

formula	$C_{36}H_{58}Ge$
fw	563.41
size	0.3 × 0.3 × 0.3 mm^3
cryst syst	monoclinic
space group	$P2_1/n$
a	10.447(3) Å
b	11.732(4) Å
c	28.150(7) Å
β	99.11(2)°
V	3407(2) Å^3
Z	4
D_{calc}	1.099 g/cm^3
diffractometer	Siemens P2$_1$
T	−100 °C
radiation	Mo Kα (λ = 0.710 73 Å)
monochromator	graphite
range	3° < 2θ < 55°
no. of reflns collcd	8146
no. of indpdt reflns	7739
R_{int}	0.068
scan type	ω
abs corr	ψ-scans
programs	Siemens SHELXTL plus/SHELXL-93
solution	direct methods
refinement	full-matrix least-squares on F^2
H atoms	riding model
params	352
μ	0.919 mm^{-1}
F(000)	1224
goodness-of-fit	1.373
R_F (basing on 4333 reflns with $I > 2\sigma(I)$)	0.080
R_{F^2} (basing on 4333 reflns with $I > 2\sigma(I)$)	0.098
largest diff peak	0.6 e Å^{-3}

Discussion

We have found that two Mes* ligands can kinetically stabilize the Ge(II) compound bis(2,4,6-tri-*tert*-butylphenyl)germylene (**1**). When these two bulky substituents are attached to the germanium atom, the compound is not able to dimerize or polymerize. Furthermore, there are certain structural pecularities which influence both the spectroscopic properties and the chemical behaviour. In the following sections we will discuss the specific features which distinguish **1** from other known germylenes.

(I) Structural Effects. Compared with other compounds of the type Mes*$_2$El (El = Fe, Mg, Mn, Sn, Hg), **1** shows a much greater stereochemical difference between the two Mes* rings. The Mes* groups in Mes*$_2$Fe,[24,25] Mes*$_2$Mg,[25] Mes*$_2$Mn,[25] and Mes*$_2$Sn[26] are essentially equivalent; those in Mes*$_2$Hg[27] show relatively small differences. Obviously, the effect is related with the combination of a short C−El bond and a small C−El−C angle: The C−El bonds in **1** (2.04, 2.05 Å) are among the shortest found in this class of compounds (Mes*$_2$Fe, 2.05 Å; Mes*$_2$Hg, 2.08 Å; Mes*$_2$Mg, 2.11, 2.12 Å; Mes*$_2$Mn, 2.11 Å, Mes*$_2$Sn, 2.26, 2.27 Å), while the C−El−C angle (108.0°) is the second smallest (Mes*$_2$Fe, 158.9°; Mes*$_2$Mg, 158.3, 158.0°; Mes*$_2$Mn, 159.7°; Mes*$_2$Hg, 173.4°; Mes*$_2$Sn, 103.6°). It appears that the unequal deformation of the two Mes* rings in **1** makes it possible to avoid too close contact between nonbonded atoms without a great expansion of the bonding angle or a pronounced lengthening of the bonds.[28]

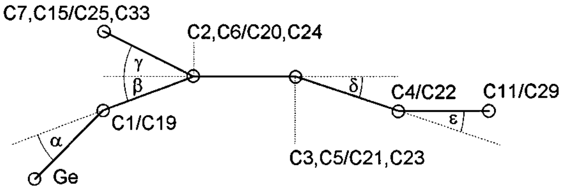


Figure 3. Deformation angles of the supermesityl ligands.

Table 4. Deformation Angles (deg) of the Supermesityl Ligands

	ring 1	ring 2		ring 1	ring 2
α	32.2	4.9	δ	7.8	0.5
β	15.1	5.1	ϵ	1.0	1.2
γ	11.9,13.9	4.5,6.0			

It is noteworthy that the asymmetric nature of compound **1** is not reflected in its solution NMR spectra: Even at −80 °C, there is no evidence for a ring inequivalence between the Mes* groups.

(II) Lewis Acid Catalyzed C−H Insertion. This reaction, shown in Scheme 1, is unique in germylene chemistry. Alkyl C−H bonds are normally stable toward germylenes, even toward such reactive species as Me$_2$Ge.[1] Our proposal for the mechanism for C−H insertion in **1** attributes the activation of the germylene to the inductive effect of the Lewis acid, when it interacts with the lone pair on Ge. A donor−acceptor complex is formed,[29] and the electron density at the Ge atom is decreased. The acceptor ability of the vacant Ge orbital is thereby increased. Because of the very close approach of Ge to a methyl group of an *ortho*-*tert*-butyl group (see discussion of the solid-state structure), an electrophilic attack by Ge on a C−H bond is possible. The system then rearranges to form a Ge−C and a Ge−H bond. At the same time the Lewis acid is released.

More generally, we have not found any other example of a Lewis acid catalyzed C−H insertion which simply leads to a rearranged product.[30]

(III) Lack of Lewis Acidity. Germylenes normally interact with Lewis bases to form adducts. With matrix-isolated unstable germylenes, complex formation has

---

(21) Pauling, L. *The Chemical Bond;* Cornell University Press: Ithaca, NY, 1967.

(22) Emsley, J. *The Elements,* 2nd ed.; Clarendon Press: Oxford, U.K., 1991.

(23) (a) The van der Waals radius of a methyl group is about 2.0 Å.[21] A van der Waals radius for divalent Ge is difficult to define, but the covalent radius is 1.22 Å [22] and van der Waals radii are normally about 0.8 Å longer than covalent radii.[21] (b) A "nonbonded" radius of 1.58 Å has been found for Ge in: Glidewell, C. *Inorg. Chim. Acta* **1979**, *36*, 135.

(24) Müller, H.; Seidel, W.; Görls, H. *Angew. Chem.* **1995**, *107*, 386.

(25) Wehmschulte, R. J.; Power, P. P. *Organometallics* **1995**, *14*, 3264.

(26) Weidenbruch, M.; Schlaefke, J.; Schäfer, A.; Peters, K.; von Schnering, H. G.; Marsmann, H. *Angew. Chem.* **1994**, *106*, 1938. Additional structural data were kindly provided by the authors.

(27) Huffman, J. C.; Nugent, W. A.; Kochi, J. K. *Inorg.Chem.* **1980**, *19*, 2749.

(28) The difference between Mes*$_2$Fe and Mes*$_2$Hg might be due to significantly differing covalent radii of the central atoms (Fe, 1.17 Å; Hg, 1.44 Å).[22]

(29) Stable adducts between germylenes and 16 valence-electron transition metal fragments have been isolated: (a) Marks, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 7090. (b) Marks, T. C.; Newman, A. R. *J. Am. Chem. Soc.* **1973,** *95*, 769. (c) Jutzi, P.; Steiner, W. *Chem. Ber.* **1976**, *109*, 3473. (d) Jutzi, P.; Steiner, W. *Angew. Chem.* **1977**, *89*, 675. (e) Lappert, M. F., Miles, S. J.; Power, P. P.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Chem. Commun.* **1977**, 458. (f) Jutzi, P.; Steiner, W.; König, E.; Huttner, G.; Frank, A.; Schubert, U. *Chem. Ber.* **1978**, *111*, 606. (g) du Mont, W.-W.; Lange, L.; Pohl, S.; Saak, W. *Organometallics* **1990**, *9*, 1395. (h) Veith, M.; Becker, S.; Huch, V. *Angew. Chem.* **1990**, *102*, 186. (i) See ref 18.

Table 5. UV/vis Maxima of Diorganogermylenes[15,18]

germylene	λ_{max}/nm	germylene	λ_{max}/nm
Me_2Ge	420[a]	Mes_2Ge	550[a]
Et_2Ge	440[a]	Tip_2Ge	558[a]
MePhGe	440[a]	Tb(Tip)Ge	580[b]
Ph_2Ge	466[a]	$Mes*_2Ge$	405[c]/430[b]
^{t}BuMesGe	508[a]		

[a] Matrix-isolated. [b] Solution in hexane. [c] Solid state. [d] Mes = 2,4,6-trimethylphenyl, Tip = 2,4,6-triisopropylphenyl, Tb = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl, and Mes* = 2,4,6-tri-*tert*-butylphenyl.

been demonstrated using UV/vis spectra,[15] while stable germylenes with intramolecular base coordination have been characterized by X-ray methods.[8,10] Even the sterically hindered germylene GeTb(Tip) forms a weak adduct with the Lewis base THF, as shown by the color change between solutions in hexane and THF.[18] In contrast, germylene **1** shows no Lewis-acidity: there is no change in the UV/vis absorption maximum when the solvent is similarly changed.

This lack of reactivity is presumably a result of the strong steric shielding around Ge. The same explanation may accound for the lack of reaction with 2,3-dimethylbutadiene.

(IV) Blue-Shifted Visible Spectrum and Structural Consequences. The UV/vis spectrum of **1** shows a dramatic hypsochromic shift of the λ_{max} value when compared with other sterically overcrowded diarylgermylenes. This is illustrated clearly by the data in Table 5. On the basis of previous spectroscopic studies and theoretical treatments for silylenes and germylenes, we propose the following explanation.[15,31-33] The value of λ_{max} depends on the energy difference between the lone-pair orbital (n, HOMO) and the vacant p-orbital (p, LUMO) on germanium. This energy difference depends on two factors. First, when the bond angle at Ge increases as a result of steric interactions, the energy of the lone-pair orbital also increases. Second, when aryl groups are present, the energy of the p-orbital is decreased by interaction with the aryl π^* orbital; for this to occur, however, the aromatic system must be coplanar with the adjacent C(aryl)−Ge−C(aryl) plane. When both these factors are present as in GeTb(Tip), the HOMO−LUMO gap is especially small and λ_{max} is correspondingly large.

In the case of **1**, a λ_{max} value similar to that of GeTb(Tip) (580 nm)[18] might be expected; two Mes* ligands should produce a similar increase in the C−Ge−C angle as the combination of a smaller (Tip) and a larger (Tb) ligand. However, our experimental values of $\lambda_{max} = 430$ nm (solution) and 405 nm (solid state) are far smaller and almost identical with that reported for Me_2Ge (420 nm). This corresponds to a blue shift of at least 150 nm.

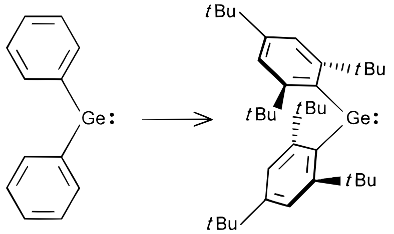


Figure 4. Configurational changes in diarylgermylenes induced by bulky *tert*-butyl substituents.

We believe this effect is due to the configurational change observed in compound **1**. As discussed earlier, this change removes the coplanarity between aryl groups and the C(aryl)−Ge−C(aryl) plane and also allows the bond angle at Ge to decrease (see Figure 4). In terms of the previous discussion, this both raises the energy of the p-orbital and lowers the energy of the n-orbital, hence increasing the HOMO−LUMO gap. A similar argument has been deployed to account for the spectral changes in a series of (trimethylsily)(aryl)-silylenes.[33,34]

As **1** and Me_2Ge exhibit nearly the same value for λ_{max}, the C−Ge−C angle should also be similar. However, calculations on Me_2Ge have proposed an angle of 97°,[12] which is much smaller than the respective angle in **1** (108°). It has to remain the subject of further discussion if additional effects leading to a stabilization of the lone pair or a destabilization of the p-orbital are responsible for the observed extreme blue shift.

(V) Oxidation Process. Oxidation of **1** does not lead to the expected germanone but to the germaindanol **3**. It seems likely that the initial product is a germanone since similar intermediates have been found in the oxidation of other germylenes.[35-37] But unlike these other germanones, $Mes*_2GeO$ does not form dimers,[36] oligomers, or polymers:[35] Instead insertion of the GeO unit into a C−H bond yields **3**, which can be isolated as an air-stable solid. A comparable insertion process was observed by du Mont et al. when **1** reacted with elementary sulfur to produce a germaindanethiol. The rearrangement is so fast that the germanone can neither be isolated as such nor trapped; obviously the insertion process results from the close Ge−methyl distance as discussed earlier.[38] Despite its great steric demand, the Mes* group does not seem to be an appropriate ligand to stablilize double-bonded germanium species.

Experimental Section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dried, oxygen-free argon. Solvents were dried and purified by standard methods. Spectra were recorded on following instruments: ^{1}H-NMR, Bruker AM 300, 300.1 MHz, $CHCl_3$ or C_6D_5H as internal

---

(30) The C−H insertion of a cationic center has been observed in some decomposition reactions: (a) Barclay, L. R. C.; MacDonald, M. C. *Tetrahedron Lett.* **1968**, *7*, 881. (b) Barclay, L. R. C.; Sonawane, H. R.; MacDonald, M. C. *Can. J. Chem.* **1972**, *50*, 281. (c) Cowley, A. H.; Kilduff, J. E.; Norman, N. C., Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 4845. (d) Okazaki, R.; Ishida, T.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1988**, 40.

(31) Apeloig, Y.; Karni, M.; West, R.; Welsh, K. *J. Am. Chem. Soc.* **1994**, *116*, 9719.

(32) Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1048.

(33) Kira, M.; Maruyama, T.; Sakurai, H. *Chem. Lett.* **1993**, 1345.

(34) Bott, S. G.; Marshall, P.; Wagenseller, P. E.; Wang, Y.; Conlin, R. T. *J. Organomet. Chem.* **1995**, *499*, 11.

(35) (a) Barrau, J.; Bouchaut, M.; Lavayssière, H.; Doisse, G.; Satgé, J. *Helv. Chim. Acta* **1979**, *62*, 152. (b) Barrau, J.; Boichaut, M.; Castel, A.; Cazes, A.; Doisse, G.; Lavayssière, H.; Rivière, P.; Satgé, J. *Syn. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 273. (c) Rivière, P.; Satgé, J.; Castel, A.; Cazes, A. *J. Organomet. Chem.* **1979**, *177*, 171.

(36) Veith, M.; Becker, S.; Huch, V. *Angew. Chem.* **1989**, *101*, 1287.

(37) The successful trapping of a diaryl-germanone has been reported in: Matsumoto, T.; Kishikawa, K.; Tokitoh, N.; Okazaki, R. *Phosphorus Sulfur* **1994**, *93−94*, 177.

(38) A similar reaction has been reported for intermediate PO units: Cadogan, F. J. G.; Cowley, A. H.; Gosney, I.; Pakulski, M.; Yaslak, S. *J. Chem. Soc., Chem. Commun.* **1983,** 1408.

standard; ^{13}C-NMR, Bruker AM 300, 75.5 MHz; mass spectra, Autospec, Sison's instruments, where peak groups of Ge-containing fragments are specified by their maxima; solution UV/vis, Shimadzu UV-160 A; solid-state UV/vis, Beckman Acta MIV; FT-IR, Mattson Polaris, Bruker IFS-66. Elemental analyses were carried out by the analytical laboratory of the Universität Bielefeld. Melting points are uncorrected.

Bis(2,4,6-tri-*tert*-butylphenyl)germylene (1). Within 5 min 20 mL of a 1.6 M solution of BuLi in hexane was added to a stirred solution of 10.0 g of Mes*Br (30.7 mmol) in 30 mL of THF at −60 °C . After the mixture was stirred for 1 h at the same temperature, a solution of 3.20 g of $GeCl_2$(dioxane) (13.8 mmol) in 10 mL of THF was added, the solution stirred for further 15 min, and the solvent removed in vacuo. The residue was extracted with hexane. Cooling of the deep red liquid yielded 4.09 g (7.26 mmol) of **1** as analytically pure orange crystals (52.6% referring to $GeCl_2$(dioxane)).

^{1}H NMR (300.1 MHz, C_6D_6): $\delta = 1.31$ (s, 36 H, *o*-*t*-Bu), 1.34 (s, 18 H, *p*-*t*-Bu), 7.39 (s, 4 H, ring H). ^{13}C-NMR (75.5 MHz, C_6D_6): $\delta = 31.5$ (*p*-(C(CH$_3$)$_3$)), 34.2 (*o*-C(CH$_3$)$_3$), 34.7 (*p*-C(CH$_3$)$_3$), 39.2 (*o*-C(CH$_3$)$_3$), 122.4 (*m*-ring C), 150.2 (*p*-ring C), 158.3 (*o*-ring C), 162.1 (ipso-ring C). UV/vis (hexane or THF): $\lambda_{max} = 430$ nm ($\epsilon = 520$ L·mol^{-1}·cm^{-1}). UV/vis (solid state): $\lambda_{max} = 405$ nm. IR (KBr, cm^{-1}): 2962 s, 2903 m, 2865 m, 1593 m, 1577 m, 1476 s, 1464 s, 1390 s, 1360 s, 1243 s, 1209 m, 1197 m, 1120 m, 898 m, 874 s, 743 s, 648 s, 564 m, 478 m. MS [CI] [m/z (I_{rel})]: 563 (11.6%, M$^+$ − H), 319 (21.2%, Mes*Ge$^+$), 246 (38.9%, Mes*H$^+$), 231 (100%, [Mes* − CH$_2$]$^+$). Mp: 61 °C. Anal. Calcd for $C_{36}H_{58}Ge$: C, 76.74; H, 10.38. Found: C, 76.48; H, 10.65.

Reaction of 1 with Lewis Acids (Example).[19] To a stirred solution of 0.20 g of **1** (0.36 mmol) in 2 mL of THF was added a solution of 6 mg of $TiCl_4$ (0.03 mmol) in 0.25 mL of THF. The solution lost its color within 10−15 s. After removal of the volatiles the colorless residue was examined by NMR, IR, and MS methods. These indicate the exclusive formation of germaindane **2** (NMR, IR, and MS data are in accord with the literature[16]).

^{1}H NMR (300.1 MHz, $CDCl_3$): $\delta = 0.77$, 0.89 (2 s, 9 H, *t*-Bu), 1.14, (s, 3 H, Me), 1.27, 1.28, 1.53 (3 s, 9 H, *t*-Bu), 1.59 (s, 3 H, Me), 1.61 (dd, $^2J_{HH} = 14.0$ Hz, $^3J_{HH} = 2.4$ Hz, 1 H, CH$_2$), 1.69 (dd, $^2J_{HH} = 14.0$ Hz, $^3J_{HH} = 5.2$ Hz, 1 H, CH$_2$), 5.87 (m, 1H, Ge−H), 7.14 (d, $^4J_{HH} = 2.1$ Hz, 1 H, ring-H), 7.20 (d, $^4J_{HH} = 1.7$ Hz, 1 H, ring H), 7.23 (d, $^4J_{HH} = 2.1$ Hz, 1 H, ring H), 7.30 (d, $^4J_{HH} = 1.7$ Hz, 1 H, ring H). ^{1}H NMR (300.1 MHz, C_6D_6): $\delta = 1.01$, 1.05 (2 s, 9 H, *t*-Bu), 1.27 (s, 3 H, Me), 1.33, 1.34, 1.65 (3 s, 9 H, *t*-Bu), 1.75 (s, 3 H, Me), 1.78 (dd, $^2J_{HH} = 14.0$ Hz, $^3J_{HH} = 2.4$ Hz, 1 H, CH$_2$), 1.89 (dd, $^2J_{HH} = 14.0$ Hz, $^3J_{HH} = 5.2$ Hz, 1 H, CH$_2$), 6.24 (m, 1H, Ge−H), 7.39 (d, $^4J_{HH} = 1.7$ Hz, 1 H, ring H), 7.41 (d, $^4J_{HH} = 2.1$ Hz, 1 H, ring H), 7.48 (d, $^4J_{HH} = 1.7$ Hz, 1 H, ring H), 7.50 (d, $^4J_{HH} = 2.1$ Hz, 1 H, ring H); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 29.7$ (−CH$_2$−), 31.4, 31.6 (C(CH$_3$)$_3$), 31.9 (−(CH$_3$)$_2$C−Ge), 32.5, 33.6, 34.0 (C(CH$_3$)$_3$), 34.6, 34.9, 37.6, 39.0 (quart C), 39.1 (−(CH$_3$)$_2$C−Ge), 39.2, 43.5 (quart C), 118.8, 122.5, 123.4, 123.7 (tert ring C), 131.2, 133.6, 149.8, 152.2, 154.8, 157.9, 159.5, 160.4 (quart ring C). IR (KBr, cm^{-1}): 2958 s, 2903 m, 2866 m, 2086 s, 1588 s, 1532 m, 1478 m, 1464 s, 1392 s, 1361 s, 1239 m, 1212 m, 1197 m, 1138 m, 875 s, 800 s, 746 s, 741 s, 685 m, 646 m, 575 m, 569 m, 487 m. MS [CI] [m/z (I_{rel})]: 563 (29.0%, M$^+$ − H), 319 (97.9%, Mes*Ge$^+$), 231 (26.3%, [Mes* − CH$_2$]$^+$), 57 (100%, $C_4H_9^+$).

The reaction was further carried out with $GeCl_2$(dioxane), $AlCl_3$, BBr_3, and $GeCl_4$ as catalysts in hexane, THF, and toluene; the rate of the reaction varied over a wide range.

Reaction of 1 with Trimethylamine *N*-Oxide. A solution of 0.36 g of **1** (0.64 mmol) in 5 mL of THF was slowly added to a suspension of 48 mg of Me_3NO (0.64 mmol) in 5 mL of THF, cooled to −60 °C. Within 10 h the mixture was allowed to warm to ambient temperature. The solvent and Me_3N were removed in vacuo, and the residue was dissolved in hexane. Cooling the solution to −30 °C after filtration yielded 0.22 g of **3** as a colorless solid (0.38 mmol, 59%). A reaction in the presence of 2,3-dimethylbutadiene or 2,2-dimethylbutan-3-one as a trapping reagent gave the same product.

^{1}H NMR (300.1 MHz, $CDCl_3$): $\delta = 0.72$ (s, 1H, −OH, gives H/D exchange in CD_3OD/THF), 0.84, 0.93 (2 s, 9 H, *t*-Bu), 1.25 (s, 3 H, Me), 1.28, 1.29, 1.50 (3 s, 9 H, *t*-Bu), 1.56 (s, 3 H, Me), 1.60 (d, $^2J_{HH} = 14.3$ Hz, 1 H, CH$_2$), 1.74 (d, $^2J_{HH} = 14.3$ Hz, 1 H, CH$_2$), 7.18 (d, $^4J_{HH} = 2.0$ Hz, 1 H, ring H), 7.23 (d, $^4J_{HH} = 1.7$ Hz, 1 H, ring H), 7.32 (d, $^4J_{HH} = 1.7$ Hz, 1 H, ring H), 7.33 (d, $^4J_{HH} = 2.0$ Hz, 1 H, ring H). ^{1}H NMR (300.1 MHz, C_6D_6): $\delta = 0.76$ (s, 1 H, −OH), 1.05, 1.06, 1.30 (3 s, 9 H, *t*-Bu), 1.33 (s, 3 H, Me), 1.34 (s, 9 H, *t*-Bu), 1.68 (s, 3 H, Me), 1.71 (d, $^2J_{HH} = 14.4$ Hz, 1 H, CH$_2$), 1.75 (s, 9 H, *t*-Bu), 1.88 (d, $^2J_{HH} = 14.4$ Hz, 1 H, CH$_2$), 7.36 (d, $^4J_{HH} = 1.9$ Hz, 1 H, ring H), 7.44 (d, $^4J_{HH} = 1.6$ Hz, 1 H, ring H), 7.53 (d, $^4J_{HH} = 1.6$ Hz, 1 H, ring H), 7.58 (d, $^4J_{HH} = 1.9$ Hz, 1 H, ring H). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 31.2$, 31.4 (C(CH$_3$)$_3$), 31.6 (−(CH$_3$)$_2$C−Ge), 32.1 (C(CH$_3$)$_3$), 32.6 (−CH$_2$−), 32.9, 33.7 (C(CH$_3$)$_3$), 34.4, 34.8, 37.4, 38.7 (quart C), 39.1 (−(CH$_3$)$_2$C−Ge), 39.3, 42.0 (quart C), 119.1, 122.3, 122.9, 123.7 (tert ring C), 131.7, 134.3, 149.6, 152.5, 153.8, 157.4. 159.0, 159.2 (quart ring C). IR (KBr, cm^{-1}): 3409 s, 2961 s, 2908 m, 2866 m, 1592 s, 1535 m, 1479 m, 1464 s, 1393 s, 1362 s, 1237 m, 1214 m, 1138 m, 904 m, 880 s, 738 s, 693 m, 663 m, 646 m, 623 s, 580 m, 569 m, 489 m, 421 m, 382 m. MS [CI] [m/z (I_{rel})]: 579 (7.1%, M$^+$ − H), 563 (21.8%, M$^+$ − OH), 335 (100%, M$^+$ − Mes*), 57 (79.2%, $C_4H_9^+$). Mp: 175 °C. Anal. Calcd for $C_{38}H_{58}GeO$: C, 74.62; H, 10.09. Found: C, 74.56; H, 9.94.

Acknowledgment. The financial support of the "Deutsche Forschungsgemeinschaft" and the "Fonds der Chemischen Industrie" as well as a gift of germanium from Chemetall GmbH, Frankfurt/Main, Germany, is gratefully acknowledged.

Supporting Information Available: Tables of crystal data and structure refinement, measurement, and program parameters, hydrogen coordinates and isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

OM950558T