

Preparation, Structure, and ^{73}Ge NMR Spectroscopy of Arylgermanes ArGeH_3 , Ar_2GeH_2 , and Ar_3GeH

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Arylgermanes of the types ArGeH_3 , Ar_2GeH_2 , and Ar_3GeH are important precursors for the preparation of oligo- and polygermanes. These precursors are readily prepared in good yields via an in situ Grignard reaction employing tetra(ethoxy)germane, an aryl halide, and magnesium metal in tetrahydrofuran as the reaction medium. The aryl-tri(ethoxy)germanes obtained were reduced to the germane hydrides with LiAlH_4 . This method is also applicable for aryl groups with sensitive substituents, as demonstrated for (4-methoxyphenyl)germane (*p*-anisylgermane, $\text{MeOC}_6\text{H}_4\text{GeH}_3$). With modified stoichiometry, bis(*p*-anisyl)germane is also available. The insertion of GeCl_2 into the C–Br bond of arylbromides using catalytic amounts of anhydrous AlCl_3 proved to be an efficient alternative if the reaction was carried out in the absence of a solvent. After LiAlH_4 reduction of the aryltrihalogermanes, phenyl-, *p*-tolyl-, and mesitylgermane were obtained in good yields. The arylgermanes have been identified by their analytical and spectroscopic data, including ^{73}Ge ($s = 9/2$) NMR spectroscopy. Very surprisingly, sharp multiplet signals were observed with well-resolved $^1J(\text{Ge},\text{H})$ couplings. The molecular structure of *p*- $\text{MeOC}_6\text{H}_4\text{GeH}_3$ was determined from low-temperature X-ray diffraction data collected from a single-crystal grown “in situ” from the melt (mp: 15 °C). The significant distortions observed in the anisyl part of the structure and the conformation of the molecule are in excellent agreement with results of ab initio quantum chemical calculations (MP2/6-31G*) of this compound.

Introduction

For a long time germanium hydrides have been a largely neglected area in preparative and structural chemistry owing to a very limited range of applications. The demand for high-purity germanium and germanium alloys in modern microelectronics has changed this situation very rapidly and there is now a steady growth of pertinent research and development.¹ Application of volatile germanium compounds for the production of thin film devices, in particular by epitaxial growth, has focused renewed attention to germanium hydrides and their derivatives.^{1d,2} The development thus follows, with some delay, the enormous activities in the chemistry and physics of silicon hydrides in the last four decades.^{2b,c}

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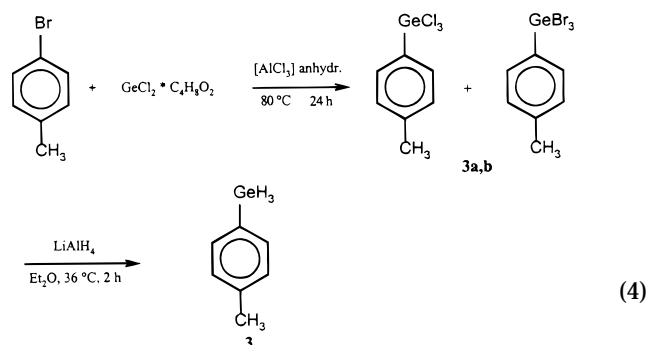
(1) (a) Katz, S. M.; Reichl, J. A.; Berry, D. H. *J. Am. Chem. Soc.* **1998**, *120*, 9844. (b) Joseph, A. J.; Cresler, J. D.; Richey, D. M.; Hasame, D. L. *Technol. Dig.-Int. Electron. Devices Meet.* **1996**, 253. (c) Tanaka, H.; Sadamoto, M.; Ishiguro, N.; Yanagana, N.; Fukuda, S. *Jpn. Kokai Tokyo Koho Patent* 09,191,117 [97,191,117] *Chem. Abstr.* **127**, 193056v. (d) Lesbre, M.; Mazerolles, P.; Satgé, J. *The Organic Compounds of Germanium*; Seyferth, D., Ed.; Wiley-Interscience: New York, **1971**. (e) Riviere, P.; Riviere-Baudet, M.; Satgé, J. *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford **1982**, Vol. 2; Chapter 10. (f) *Comprehensive Organometallic Chemistry II*; Wilkinson, G.; Stone, F. G. A., Abel, E. W., Davies, A. G., Eds.; Pergamon Press: Oxford **1995**, Vol. 2, Chapter 5. (2) (a) Kouvetakis, J.; Haaland, A.; Shorokhof, D. J.; Volden, H. V.; Girichev, G. V.; Sokolov, V. I.; Schmitttinger, S.; Matsunaga, P. *J. Am. Chem. Soc.* **1998**, *120*, 6738. (b) Ritter, S. K.; Nofle, R. E. *Inorg. Chim. Acta* **1999**, *287*, 232. (c) Ritter, S. K.; Nofle, R. E. *Chem. Mater.* **1992**, *4*, 872.

Silicon hydrides have also attracted considerable interest as precursors for optoelectronic and nonlinear optical materials, which can be generated through new techniques including, e.g., dehydrogenative or desilana-tive coupling of arylsilanes.^{2–6} These silicon-based polymers feature conjugated di/polysilane and arene units with enhanced absorption in the UV–Vis region, which has advantages for the production of photoresist and related materials.⁷ This synthetic potential has led to increasing interest in tailored arylsilane molecules with various specific photochemical properties associated with the substitution pattern.⁸

Arylgermanes $\text{Ar}_m\text{GeH}_{4-m}$ have received only very limited attention.^{1d,9} However, very recently two important contributions showed that oligomerization of phenylgermanes by dehydrogenative as well as demeth-anative coupling are facile, easily controlled, high-yield

(3) (a) Aitken, C. T.; Harrod, J. F.; Samuel, E. *Can. J. Chem.* **1986**, *64*, 1677. (b) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059. (c) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863. (4) Sakakura, T.; Kumberger, O.; Tan, R. P.; Arthur, M.-P.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 193. (5) (a) Barbarella, G.; Ostojia, P.; Maccagnani, P.; Pudova, O.; Antolini, L.; Casarini, D.; Bongini, A. *Chem. Mater.* **1998**, *10*, 3683. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (6) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (7) (a) Kakimoto, M.; Kashiwara, H.; Kashiwagi, T.; Takiguchi, T.; Ohshita, J.; Ishikawa, M. *Macromolecules* **1997**, *30*, 7816. (b) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (c) Kakimoto, M.; Ueno, H.; Kojima, H.; Yamaguchi, Y.; Nishimura, A. *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34*, 2753.

liberated in the process (80 °C) to give a mixture of *p*-tolyltrichloro- and -tribromogermane (**3a,b**) in almost quantitative yield (98%, eq 4).

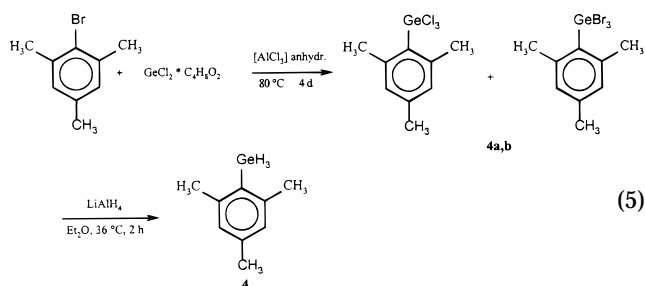


According to NMR spectroscopic and mass spectrometric data, this product is *not* a random distribution of mixed *p*-tolylchloro/bromogermanes [4-MeC₆H₄GeCl_{*n*}Br_{3-*n*}] and is free of the 2-Me- and 3-Me-isomers. Only the two compounds with either three chlorine or three bromine atoms (molar ratio 2:1) at a given germanium atom are present, and the methyl groups remain in the *p*-position. Note that the thermal and catalyzed redistribution reactions between GeCl₄ and (*p*-Tol)₄Ge probed for the synthesis of *p*-tolyltrichlorogermane lead to extensive rearrangements to give complex mixtures of *o*/*m*/*p*-tolylchlorogermanes with different substitution patterns.²⁵

Also note that the insertion of GeI₂ into PhI requires reaction temperatures of 160 °C (sealed tube, 32% yield after reduction to the germane), and that of GeCl₂ into chloro- or bromobenzene requires even higher reaction temperatures of 250 °C (under pressure), the latter proceeding in 37 and 88% yield, respectively.²⁶

The mixture of the two primary products is readily reduced by LiAlH₄ in diethyl ether to give good yields of *p*-tolylgermane (**3**) (76%).

Bromomesitylene can be converted similarly into mesitylgermane (**4**) (76% yield) via mesityltrichloro- or bromogermane (**4a,b**) (80% yield, eq 5).



Phenyl-, diphenyl-, and triphenyl-germane (**5–7**) were synthesized by LiAlH₄ reduction of the corresponding chlorogermanes which are commercially available. All arylgermanes prepared in this work are colorless, distillable liquids as described in the literature: PhGeH₃,¹⁸ Ph₂GeH₂,¹⁹ Ph₃GeH,¹⁹ *p*-TolGeH₃,²⁰ MesGeH₃,²⁰ *p*-Me-OC₆H₄GeH₃,¹⁸ (*p*-MeOC₆H₄)₂GeH₂.¹⁸

The products were identified by their physical constants, and IR and mass spectra. UV spectra of several arylgermanes were reported in a very early study.¹⁸ The conclusions drawn from these preliminary results were based only on a comparison with data of related methyl- and silylarenes, and on a crude model separating inductive and conjugative effects. Ge atoms were thus assumed to be weak σ -donors and strong π -electron acceptors, allegedly owing to their empty d-orbitals. In light of advanced quantum chemical calculations this assumption must be considered untenable.

Where ¹H and ¹³C NMR spectra of the arylgermanes had been recorded previously,^{19,27} the data were confirmed and complemented. There were no obvious anomalies. However, in the absence of any reliable results regarding ⁷³Ge NMR spectroscopy, several ArGeH₃ prototypes have now been investigated in greater detail using state-of-the-art facilities.

⁷³Ge NMR Spectroscopy. Among the various germanium isotopes only the ⁷³Ge nucleus is amenable to high-resolution NMR spectroscopy. Yet its high nuclear spin ($s = 9/2$) and high quadrupole moment suggest extensive line broadening and efficient quenching of spin–spin coupling with neighboring nuclei. Therefore, it was not a surprise that most germanium compounds investigated to date showed either broad resonances with no discernible multiplicity, or no signal at all.

Exceptions to this rule are molecules with high symmetry securing a zero field gradient at the germanium nucleus. Thus, solutions of monogermane GeH₄ in solvents of low polarity show the famous 10-line ¹H NMR signal from which the coupling constant ¹*J*(Ge,H) = 97.6 Hz can be extracted.²⁸ Apart from Et₃-GeH,¹² there is also a series of simple germa/sila-alkanes for which ⁷³Ge NMR spectra of surprisingly good resolution have been obtained.¹¹ ¹*J*(Ge,H) couplings range from 88 to 99 Hz. Tetramethylgermane, GeMe₄, also shows rather sharp resonances, but with no splitting. As a convention, this compound has been used as the standard of ⁷³Ge NMR spectroscopy ($\delta = 0.0$ ppm).

Owing to their low molecular symmetry (point groups *C_s*, *C₂*, or *C₃*), arylgermanes are not expected to give high quality ⁷³Ge NMR spectra, and, in fact, for several series of aryl- and heteroarylgermanes only broad resonances ($w_{1/2}$ 15–600 Hz) have been reported.¹⁴ The chemical shift data show certain correlations with electronegativity increments of the substituent pattern of a given set of molecules.

With this background, it was very surprising that ⁷³Ge NMR spectra of excellent quality (Figures 1–4) were obtained for all arylgermanes reported in this work.

As a representative example, phenylgermane (**5**) shows a well-resolved 1:3:3:1 quartet at $\delta = -190$ ppm [¹*J*(Ge,H) = 98 Hz]. The same pattern is found for *p*-tolyl-, mesityl-, and even *p*-anisylgermane as summarized in Table 1.

Accordingly, diphenyl- and triphenylgermane (**6,7**) show triplet and doublet signals, respectively, at -108.5 [*J* = 94 Hz] and -55.4 ppm [*J* = 98 Hz]. Conversely,

(27) Birchall, T.; Drummond, I. *J. Chem. Soc., Inorg. Phys. Theor.* **1970**, 1401.

(28) Ebsworth, E. A. V.; Rankin, D. W. H.; Cradock, S. *Structural Methods in Inorganic Chemistry*, 2nd ed.; Blackwell Scientific Publication: Oxford, 1987.

(25) Kühlein, K.; Neumann, W. P. *Liebigs Ann. Chem.* **1967**, 702, 17.

(26) Mironov, V. F.; Gar, T. G. *Organic Compounds of Germanium* [in Russian]; Nauka, 1967; pp 164, 173, 181.

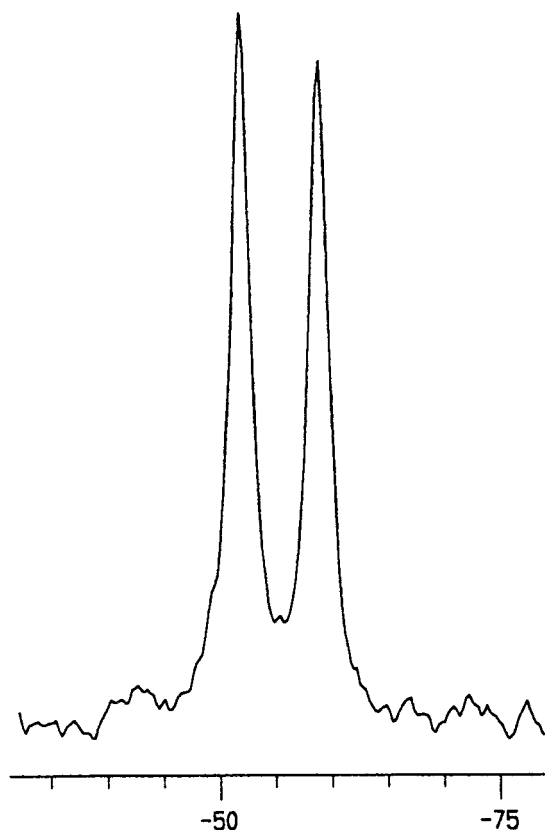


Figure 1. ^{73}Ge NMR spectrum of Ph_3GeH (in C_6D_6 at 20°C).

Table 1. ^{73}Ge NMR Data [ppm, Hz] of Arylgermanes $\text{Ar}_n\text{GeH}_{4-n}$ ($n = 1, 2, 3$)

compound	multiplicity	[ppm]	$^1J_{\text{GeH}}$ [Hz]
<i>p</i> -anisylgermane (1)	quartet	-189.9	97
bis(<i>p</i> -anisyl)germane (2)	broad singlet	-112.0	—
<i>p</i> -tolylgermane (3)	quartet	-190.6	96
mesitylgermane (4)	quartet	-234.3	95
phenylgermane (5)	quartet	-190.0	98
diphenylgermane (6)	triplet	-108.8	94
triphenylgermane (7)	doublet	-55.4	98

none of these $^1J(\text{Ge,H})$ couplings was observed in the ^1H NMR spectra of the compounds. It thus appears that ^{73}Ge NMR spectroscopy is in fact a very helpful tool for the identification and for a more detailed study of alkyl- and arylgermanes. We can offer several suggestions which help to explain this phenomenon: (1) Because of the discontinuities in the electronegativity sequence of group 14 elements, the Ge—C bond has an inherently low polarity. (2) It is known from microwave and vibrational spectroscopy that $\text{H}_3\text{Ge—R}$ bonds have very low barriers of rotation, and this is, of course, particularly true for bonds to sp^2 and sp carbon atoms. Virtually free rotation can be assumed. (3) The line width factor I is a function of both the quadrupole moment Q (^{73}Ge : $0.18 \times 10^{-28} \text{ m}^2$, -0.22 barn) and the nuclear spin I of the isotope under observation (9/2). Apparently, an internal compensation of the two contributions according to $I = (2I + 3)Q_2/[I^2(2I - 1)] = 2.4 \times 10^{-59} \text{ m}^4$ leads to an appreciable sharpness of the lines generated in the spin—spin coupling.²⁹

(29) Harris, R. K. *Proceedings of the NATO Advanced Study on the Multinuclear Approach to NMR-Spectroscopy*; Lambert, J. P., Riedell, F. G., Reidel, D., Eds.; Publishing Company: Dordrecht, 1987.

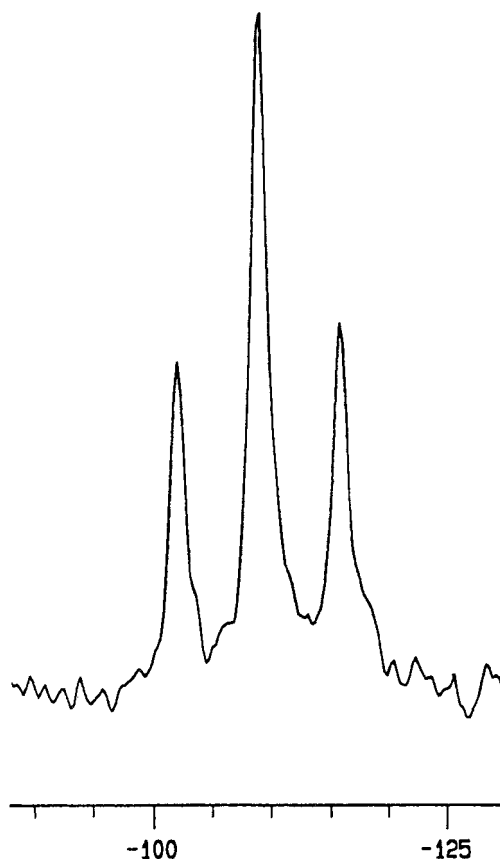


Figure 2. ^{73}Ge NMR spectrum of Ph_2GeH_2 (in C_6D_6 at 20°C).

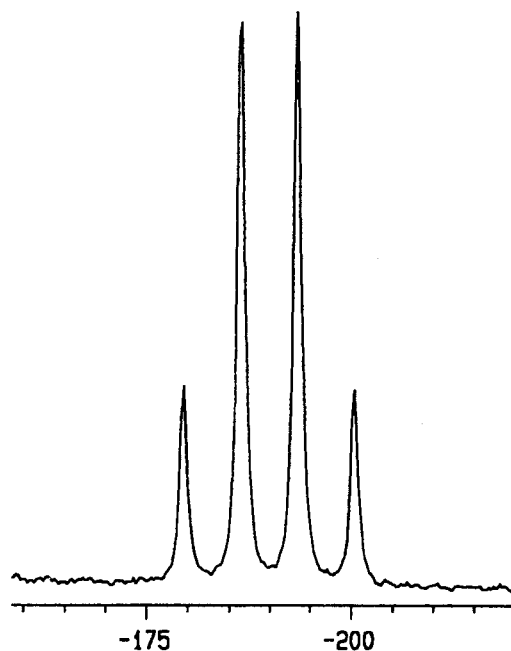


Figure 3. ^{73}Ge NMR spectrum of PhGeH_3 (in C_6D_6 at 20°C).

Note that the sensitivity of the ^{73}Ge nucleus (1.1×10^{-4} rel ^1H) is close to that of frequently observed nuclei such as ^{29}Si (3.7×10^{-4}), but the frequency range is one of the lowest of all nuclei [3.49 MHz, rel. ^1H (100 MHz)].

Structural Studies. Of all the arylgermanes prepared in this work, only *p*-anisylgermane (1) could be obtained in the form of single crystals suitable for X-ray

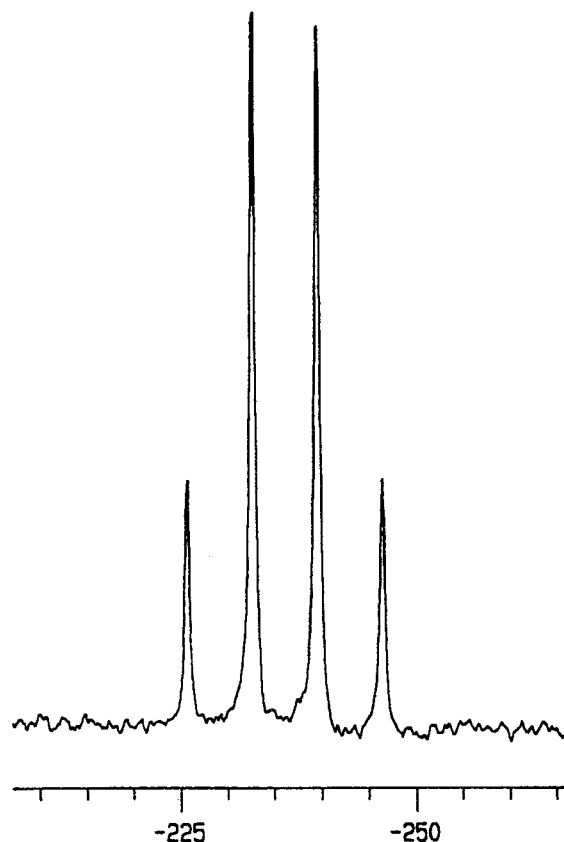


Figure 4. ^{73}Ge -NMR spectrum of MesGeH_3 (in C_6D_6 at 20°C).

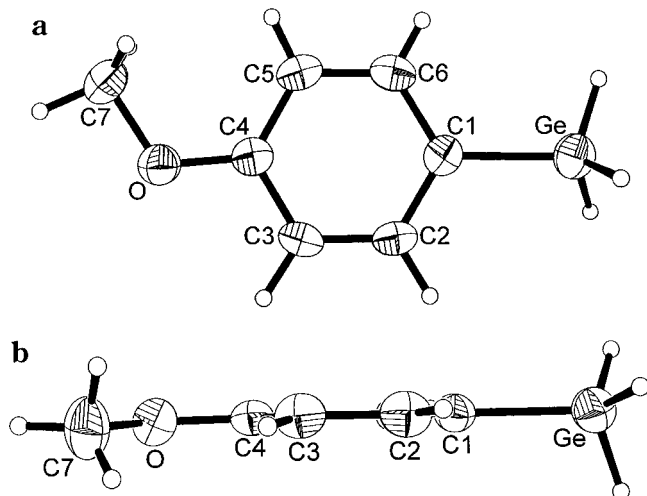


Figure 5. (a and b) Molecular structure of **1** (ORTEP drawing with 50% probability ellipsoids). Projection perpendicular and parallel to the plane of the arene ring.

diffraction studies. Crystals of $4\text{-MeO-C}_6\text{H}_4\text{-GeH}_3$ (mp 15°C , grown from the melt by "in situ" low-temperature crystallization methods in a sealed capillary on the diffractometer) are orthorhombic, space group $Pca2_1$, with $Z = 4$ molecules in the unit cell. An individual molecule is shown in projections perpendicular and parallel to the molecular plane in Figures 5a and b, and the packing of the molecules is presented in Figure 6. Selected bond distances and angles are given in Table 3.

Figure 5b shows that all non-hydrogen atoms are virtually coplanar, which places the methyl carbon atom

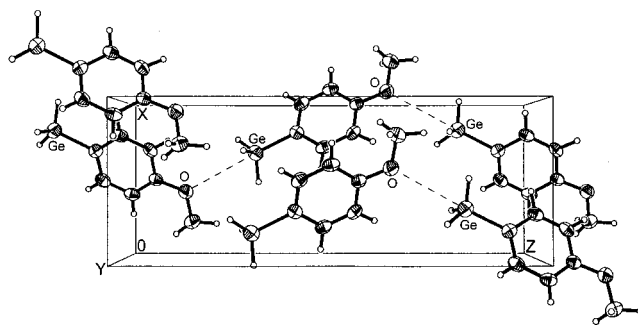


Figure 6. Packing diagram of **1**.

Table 2. Crystal Data, Data Collection, and Structure Refinement for *p*-Anisylgermane **1**

Crystal Data	
empirical formula	$\text{C}_7\text{H}_{10}\text{GeO}$
fw	182.74
cryst syst	orthorhombic
space group	$Pca2_1$
a , Å	6.386(1)
b , Å	7.339(1)
c , Å	17.011(3)
V , Å ³	797.3(2)
D_{calcd} , g cm ⁻³	1.522
Z	4
$F(000)$, e	368
μ (Mo $K\alpha$), cm ⁻¹	37.63
cryst dims, mm	$1.0 \times 0.4 \times 0.4$
Data Collection	
temp, K	203(2)
scan mode	ω
hkl range	$-8 \rightarrow 8; -9 \rightarrow 9; -21 \rightarrow 21$
measured reflns	3440
unique reflns	1723 ($R_{\text{int}} = 0.0693$)
reflns used for refinement	1723
Refinement	
least-squares parameters	103
final R values [$I > 2\sigma(I)$]:	
$R1^a$	0.0345
$wR2^b$	0.0754
goodness-of-fit on F^2	1.124
ρ_{fin} (max/min), e Å ⁻³	0.868/-0.370

^a $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0476$; $b = 0.0000$.

Table 3. Selected Bond Lengths [Å] and Angles [deg] of *p*-Anisylgermane **1** (XRD and MP2/6-31G*)

1 (XRD, crystal data)	1 (ab initio MP2/6-31 G*)
Ge-C1: 1.939(4)	1.929
Ge-H: 1.400 fixed	1.551(2*1.554)
C1-C2: 1.398(5)	1.406
C1-C6: 1.399(5)	1.399
C2-C3: 1.378(6)	1.388
C3-C4: 1.392(5)	1.402
C4-O: 1.370(5)	1.369
O-C7: 1.416(6)	1.425
C7-H(7A): 0.9506	1.089
C7-H(7B): 0.9506	1.095
C7-H(7C): 0.9506	1.095
C6-C1-Ge: 122.4(3)	121.27
C2-C1-Ge: 120.1(3)	120.90
C6-C1-C2: 117.5(4)	117.83
C3-C4-C5: 119.9(4)	119.89
O-C4-C5: 124.4(3)	124.98
O-C4-C3: 115.7(3)	115.12
C4-O-C7: 117.8(3)	116.83
O-C7-H71(av): 109 (4)	—

also in the molecular plane, with the dihedral angle C3-C4-O-C7 close to 0° . The distance Ge-C1 = 1.939(4) Å is a new benchmark value for X-ray data of arylger-

manes. A previous reference value was obtained from gas-phase microwave studies (MW) of phenylgermane ($\text{Ge}-\text{C} = 1.9423 \text{ \AA}$). As expected, an ab initio calculation (4.21G*) for PhGeH_3 gave a much shorter distance of only 1.9054 \AA which refers to the position of the nuclei and not of electron density maxima.¹⁵ Solid-state $\text{Ge}-\text{C}$ distances in polyphenylated germanes, such as Ph_4Ge , are all significantly longer owing to steric congestion at the germanium atoms. For the structure refinement of **1**, the $\text{Ge}-\text{H}$ bond lengths (constrained to idealized tetrahedral geometry) were fixed at $\text{Ge}-\text{H} = 1.40 \text{ \AA}$. For the reason mentioned above, the reference value from MW data of phenylgermane is larger at 1.520 \AA , and the calculated value (4.21G* with corrections) at 1.516 \AA .¹⁵

The H_3Ge group is positioned almost symmetrically between the two ortho carbon atoms with angles $\text{Ge}-\text{C}1-\text{C}2$ and $\text{Ge}-\text{C}1-\text{C}6$ at $120.2(3)^\circ$ and $122.3(3)^\circ$, respectively. The small difference between the two angles is probably due to the orientation of the germyl hydrogen atoms.

By contrast, the methoxy oxygen atom is in a position which strongly deviates from the line bisecting the angle $\text{C}3-\text{C}4-\text{C}5$, as best illustrated by the angles $\text{O}-\text{C}4-\text{C}3 = 115.6(3)^\circ$ and $\text{O}-\text{C}4-\text{C}5 = 124.5(3)^\circ$. The "ethereal angle" $\text{C}4-\text{O}-\text{C}7 = 118.2(4)^\circ$ is not unusual, but together with the aforementioned deformation it is large enough that a close contact of the methyl group and the arene ring is avoided. In *unsubstituted phenol* PhOH and *thiophenol* PhSH , where no crowding is expected, only much smaller differences in the two angles $\text{C}-\text{C}-\text{O}/\text{S}$ were found [PhOH by MW spectroscopy: $117.01(2)^\circ$ and $122.14(2)^\circ$; PhSH : 120.9° and 121.0°].^{30a,b} For methyl phenyl sulfide groups, $\text{C}_6\text{H}_5\text{SMe}$, the deviations from 120° are again much larger, mostly in the range from 117° to 125° .^{30c}

According to a MW study,³¹ gaseous anisole features angles $\text{O}-\text{C}-\text{C}$ of 113.7° and 126.3° (imposed planarity; no error limits given), whereas electron diffraction (ED) data give a deviation of 4° from 120° .³² The latter of the two results is in excellent agreement with the data of the present study [$4.4(3)^\circ$]. Our data also confirm the in-plane (coplanar) orientation of the methoxy group (torsional angle 0°) proposed from MW and ED studies.

A nonplanar structure had been considered on the basis of earlier dipole moment and Kerr constant data (torsional angle $\text{C}-\text{C}-\text{O}-\text{C} = 18^\circ$).³³ Extended Hückel calculations also seemed to indicate an even larger torsional angle (75°),³⁴ but CNDO/2 studies clearly favored the planar structure (0°),³⁵ and, finally, most recent ab initio calculations (STO-3G) gave angles $\text{O}-\text{C}-\text{C}$ of 113.7° and 126.3° (for $\text{C}-\text{O}-\text{C} = 115.2^\circ$) for a fully planar structure (Scheme 1).³⁶

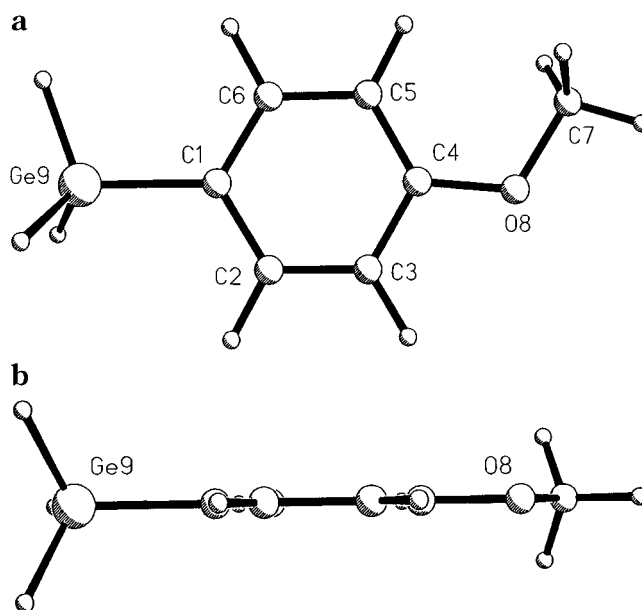
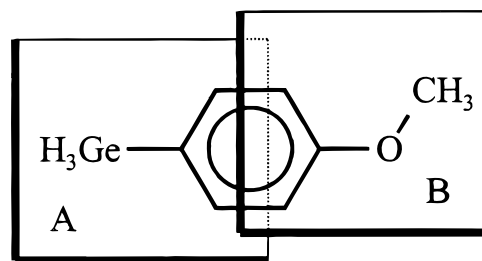


Figure 7. (a and b) Molecular structure of **1** as calculated by ab initio quantum chemical methods (MP2/6-31G*). For geometrical dimensions see Table 3. Projection perpendicular and parallel to the plane of the arene ring.

Scheme 1



In conclusion, therefore, both the phenylgermyl (part A) and the anisyl part (part B) of the *p*-anisylgermane molecule show standard structural patterns with very little, if any, mutual influence.

The packing of the molecules in the lattice shows a parallel stacking of the arenes (Figure 6). Contacts between these stacks are not very intimate, but it is obvious that the methoxy oxygen atoms are oriented toward the germyl groups of molecules in neighboring stacks. The atom sequence $\text{C}1-\text{Ge}-\text{O}$ is almost linear (172.5°) with a distance $\text{Ge}-\text{O} = 3.396 \text{ \AA}$. These parameters may indicate a weak donor-acceptor or dipole-dipole interaction, initiating a trigonal bipyramidal configuration at the germanium atom. These interactions are probably responsible for the rather high melting point of *p*-anisylgermane as compared to phenyl-, *p*-tolyl-, or mesitylgermanes.

Ab Initio Quantum-Chemical Calculations of *p*-Anisylgermane. Ab initio quantum chemical calculations on the MP2/6-31G* level lead to a molecular structure for *p*-anisylgermane (**1**) which is in excellent agreement with the experimental data (Figures 7a and b, and Table 3). Interestingly, the only significant difference between the two structures is the conformation of the GeH_3 group relative to the ring. The calculated structure has the higher symmetry of point group C_s as compared to C_1 (but virtually C_s) for the experimental data. The calculated energy differences

(30) (a) Larsen, N. W. *J. Mol. Struct.* **1979**, *51*, 175. (b) Byrn, M. P.; Curtis, C. J.; Goldberg, I.; Hsiou, Yu.; Khan, S. I.; Sawin, P. A.; Tendick, S. K.; Strouse, C. E. *J. Am. Chem. Soc.* **1991**, *113*, 6549. (c) Parfomy, A.; Tinant, B.; Declercq, J. P.; Van Meenche, M.; Klein, J.; Merenyi, R.; Viehe, H. G. *Bull. Soc. Chim. Belg.* **1987**, *96*, 89.

(31) Onda, M.; Toda, A.; Mori, S.; Yamaguchi, I. *J. Mol. Struct.* **1986**, *144*, 47.

(32) Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1973**, *27*, 4025.

(33) Aroney, M. J.; Le Fevre, R. J. W.; Pierens, R. K.; The, M. C. N. *J. Chem. Soc. B* **1969**, 666.

(34) Tylli, H. *Suom. Kemistiseuran Tied.* **1970**, *79*, 22.

(35) Tylli, H. *Suom. Kemistiseuran Tied.* **1972**, *81*, 19.

(36) Konschin, H. *J. Mol. Struct.* **1983**, *105*, 213.

between C_1 and C_s are very small, however, which suggests that the deviations may indeed be due only to the above-discussed intermolecular contacts between the germanium atom and the oxygen atom of the neighboring molecule in the crystal.

Experimental Section

General Methods. All experiments were carried out under an atmosphere of dry nitrogen using Schlenk techniques. Germanium dichloride·dioxane was prepared and purified according to published procedures.² Solvents were appropriately dried, distilled, and saturated with dry nitrogen; glassware was dried in an oven and filled with nitrogen. All NMR spectra were recorded at 20 °C on a JEOL-JNM-LA 400 spectrometer (^1H at 400.05 MHz, ^{13}C at 100.50 MHz, ^{73}Ge at 13.83 MHz) in sealed tubes with predried C_6D_6 as solvent except where indicated otherwise. Mass spectra were recorded with an analytical gas–liquid chromatography (GLC)–MS Hewlett-Packard 5890 Series II chromatograph (column HP1, cross-linked methylsilicone gum 12 m/0.2 mm, thickness of film 0.33 μm) with a mass-selective detector HP MS 5971 A (electron ionization (EI)–MS 70 eV). Microanalyses were performed in-house by combustion.

(4-Methoxyphenyl)triethoxygermane (1a). A suspension of magnesium chips (0.72 g, 29.7 mmol) in 5 mL of dry THF was stirred for about 10 min and activated with 1,2-dibromoethane. Freshly distilled tetra(ethoxy)germane (5.00 g, 19.8 mmol) in 20 mL of THF was added and the mixture heated to 60 °C with stirring. Ten percent of a solution of 4-bromoanisole (3.70 g, 2.5 mL, 19.8 mmol) in 15 mL of THF was then added slowly, and stirring continued until a mild exothermic reaction commenced. The addition was slowly continued to maintain reflux of the solvent. Afterward, the mixture was refluxed for 2 h. After the mixture cooled to room temperature, 20 mL of pentane was added, the white precipitate was filtered, and the volatile products were removed in vacuo. The residue was extracted with pentane and the solvent was removed in vacuo to give a colorless oil (36%, 2.20 g). ^1H NMR (20 °C): δ = 1.25 (t, $^3J_{\text{HH}}$ = 7 Hz, 9H, CH_3), 3.53 (s, 3H, OCH_3), 4.25 (q, $^3J_{\text{HH}}$ = 7 Hz, 6H, CH_2), 6.96 (d, $^3J_{\text{HH}}$ = 8.5 Hz, 2 H, $\text{H}_{3,5}$), 7.60 (d, $^3J_{\text{HH}}$ = 8.5 Hz, 2H, $\text{H}_{2,6}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (20 °C): δ = 25.8 (CH_3), 59.3 (OCH_3), 67.2 (CH_2), 129.0 ($\text{C}_{2,6}$), 130.7 ($\text{C}_{3,5}$), 133.4 (C_1^{ipso}), 167.5 (C_4^{ipso}). MS (EI, 70 eV): m/z = 316 [M^+ + H], 315 [M^+], 301 [M^+ – CH_3], 271 [M^+ – OEt], 257 [M^+ – CH_3 – OEt], 225 [M^+ – 2 OEt + H], 181 [M^+ – 3 OEt], 151 [M^+ – 3 OEt – OCH_3], 108 [M^+ – $\text{Ge}(\text{OEt})_3$ + H, 100%], 91 [M^+ – $\text{Ge}(\text{OEt})_3$ – CH_3], 78 [C_6H_4^+], 51. Calcd for $\text{C}_{13}\text{H}_{22}\text{GeO}_4$ (314.8): C, 49.61; H, 6.99. Found: C, 49.43; H, 6.96.

(4-Methoxyphenyl)germane, [*p*-Anisylgermane] (1). To a stirred suspension of lithium aluminum hydride (222 mg, 5.9 mmol) in 25 mL of diethyl ether at –78 °C, a solution of (4-methoxyphenyl)triethoxygermane (1a) (2.20 g, 7.1 mmol) in diethyl ether was added dropwise with vigorous stirring. Stirring was continued for 1 h and the mixture was allowed to warm to room temperature. The formation of a white precipitate was observed. Pentane (30 mL) was added and the precipitate was filtered. The filtrate was fractionized to give a colorless liquid (1.1 g, 86.4%, bp 68 °C at 0.05 mbar, mp 15 °C). ^1H NMR (20 °C): δ = 3.27 (s, 3H, OCH_3), 4.27 (s, 3H, GeH_3), 6.72 (d, 2H, $^3J_{\text{HH}}$ = 8.8 Hz, $\text{H}_{3,5}$), 7.25 (d, 2H, $^3J_{\text{HH}}$ = 8.8 Hz, $\text{H}_{2,6}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (20 °C): δ = 54.5 (OCH_3), 114.6 ($\text{C}_{2,6}$), 121.3 (C_4^{ipso}), 136.9 ($\text{C}_{3,5}$), 161.0 (C_1^{ipso}). ^{73}Ge NMR (20 °C): δ = –189.9 (q, $^2J_{\text{Ge-H}}$ = 97 Hz, GeH_3). MS (EI, 70 eV): m/z = 184 [M^+ + H], 183 [M^+], 167 [M^+ – CH_3], 152 [M^+ – OCH_3], 108 [M^+ – GeH_3 + H, 100%], 77 [M^+ – GeH_3 – OCH_3], 138, 123, 65. Calcd for $\text{C}_7\text{H}_{10}\text{GeO}$ (182.7): C, 46.02; H, 5.47. Found: C, 45.92; H, 5.30.

Bis(4-methoxyphenyl)diethoxygermane (2a). A procedure analogous to that described for (4-methoxyphenyl)-

triethoxygermane (1a) was used with 2 equiv of *p*-bromoanisole (5.92 g, 4.0 mL, 31.7 mmol) and 1 molar equiv of tetra(ethoxy)germane (4.00 g, 15.8 mmol). After a reaction time of 1.5 h (with the formation of the product monitored by GC–MS analysis), the product (2a) was separated by extraction of the oily residue with pentane. A slightly yellow oil was obtained (27%, 1.62 g). ^1H NMR (20 °C): δ = 1.32 (t, $^3J_{\text{HH}}$ = 7 Hz, 6H, CH_3), 3.56 (s, 6H, OCH_3), 4.28 (q, $^3J_{\text{HH}}$ = 7 Hz, 4H, CH_2), 6.98 (d, $^3J_{\text{HH}}$ = 8.5 Hz, 4H, $\text{H}_{3,5}$), 7.64 (d, $^3J_{\text{HH}}$ = 8.5 Hz, 4H, $\text{H}_{2,6}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (20 °C): δ = 26.2 (CH_3), 59.6 (OCH_3), 67.9 (CH_2), 129.3 ($\text{C}_{2,6}$), 131.3 ($\text{C}_{3,5}$), 135.2 (C_1^{ipso}), 167.8 (C_4^{ipso}). MS (EI, 70 eV): m/z = 378 [M^+], 333 [M^+ – OEt], 289 [M^+ – 2 OEt], 270 [M^+ – $\text{CH}_3\text{OC}_6\text{H}_4$], 226 [M^+ – $\text{CH}_3\text{OC}_6\text{H}_4$ – OEt], 181 [100%, M^+ – $\text{CH}_3\text{OC}_6\text{H}_4$ – 2 OEt], 152 [M^+ – $\text{CH}_3\text{OC}_6\text{H}_4$ – OEt – Et], 108 [M^+ – $\text{CH}_3\text{OC}_6\text{H}_4$ – $\text{Ge}(\text{OEt})_2$], 89, 64. Calcd for $\text{C}_{18}\text{H}_{24}\text{GeO}_4$ (376.8): C, 57.38; H, 6.37. Found: C, 57.12; H, 6.38.

Bis(4-methoxyphenyl)germane, [Bis(*p*-anisyl)germane] (2). Bis(4-methoxyphenyl)diethoxygermane (2a) (1.62 g, 4.3 mmol) was reduced to bis(4-methoxyphenyl)germane (2) as described for 1 with lithium aluminum hydride (90 mg, 2.4 mmol) in ethereal solution at –78 °C. After fractional trap-to-trap condensation (0 °C, –10 °C) the product was isolated as a colorless liquid in the 0 °C trap (51.8%, 0.64 g). ^1H NMR (21 °C): δ = 3.29 (s, 6H, OCH_3), 5.20 (s, 2H, GeH_2), 6.78 (d, 4H, $^3J_{\text{HH}}$ = 8.7 Hz, $\text{H}_{3,5}$), 7.40 (d, 4H, $^3J_{\text{HH}}$ = 8.8 Hz, $\text{H}_{2,6}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (21 °C): δ = 54.3 (OCH_3), 115.1 ($\text{C}_{2,6}$), 120.9 (C_1^{ipso}), 137.0 ($\text{C}_{3,5}$), 160.8 (C_4^{ipso}). ^{73}Ge NMR (21 °C): δ = –112.0 (bs, GeH_2). MS (EI, 70 eV): m/z = 290 [M^+ + H], 289 [M^+], 273 [M^+ – CH_3], 240 [M^+ – OCH_3 – CH_3], 181 [100%, M^+ – $\text{C}_6\text{H}_5\text{OCH}_3$], 167 [M^+ – CH_3 – $\text{C}_6\text{H}_5\text{OCH}_3$], 151 [M^+ – OCH_3 – $\text{C}_6\text{H}_5\text{OCH}_3$], 108 [M^+ – $\text{C}_6\text{H}_5\text{OCH}_3$ – GeH_2], 77 [M^+ – $\text{C}_6\text{H}_5\text{OCH}_3$ – GeH_2 – OCH_3], 138, 65. Calcd for $\text{C}_{14}\text{H}_{16}\text{GeO}_2$ (288.8): C, 58.23; H, 5.54. Found: C, 58.16; H, 5.50.

(4-Methylphenyl)trichloro-/(4-Methylphenyl)tribromogermane (2:1) (3a,b). A mixture of 250 mL of *p*-bromotoluene (347.50 g, 2.03 mol), 10 g of $\text{GeCl}_2\cdot\text{dioxane}$ (43.2 mmol), and 0.29 g of anhydrous AlCl_3 (2.17 mmol) was heated to 80 °C for 24 h with continuous stirring. After the mixture was cooled to room temperature, it was filtered, the dioxane removed in vacuo, and the unreacted *p*-bromotoluene removed by vacuum distillation (43 °C/0.5 mbar) to leave a white solid (13.33 g, 98% altogether).

***p*-Tolyltrichlorogermane:** MS (GC-coupled, EI 70 eV, 64%): m/z = 270 [M^+], 235 [M^+ – Cl], 126 [M^+ – GeCl_2], 109 [GeCl^+], 91 [C_7H_7^+], 65 [C_5H_5^+].

***p*-Tolyltribromogermane:** MS (GC-coupled, EI 70 eV, 32%): m/z = 403 [M^+], 322 [M^+ – Br], 153 [GeBr^+], 91 [C_7H_7^+], 65 [C_5H_5^+]. Calcd for $\text{C}_7\text{H}_7\text{GeCl}_3$ (270.1)/ $\text{C}_7\text{H}_7\text{GeBr}_3$ (403.1) = 2:1 ratio: C, 26.93; H, 2.24. Found: C, 26.89; H, 2.20.

(4-Methylphenyl)germane, [*p*-Tolylgermane] (3). A portion of the product 3a,b from the preceding experiment (5.85 g, 18.33 mmol) was dissolved in 15 mL of diethyl ether and slowly added to a slurry of 1.54 g of LiAlH_4 (41.64 mmol) in 25 mL of diethyl ether. The reaction mixture was refluxed for 2 h. After the solvent was removed under reduced pressure, 20 mL of pentane was added to the residue. Subsequent filtration and vacuum distillation gave a colorless liquid (yield 2.26 g, 74%, bp 40 °C/2 mbar). ^1H NMR (C_6D_6 , 25 °C) 2.08 [s, 3H, CH_3], 4.77 [s, 3 H, GeH_3], 6.93 [d, 2H, $^3J_{\text{HH}}$ = 8.04 Hz, $\text{H}_{2,6}$], 7.28 [d, 2H, $^3J_{\text{HH}}$ = 8.04, $\text{H}_{3,5}$]. ^{13}C NMR: 21.3 [CH_3], 127.4 [C – GeH_3], 129.4 [$\text{C}_{2,6}$], 135.7 [$\text{C}_{3,5}$], 138.8 [C – CH_3]. ^{73}Ge –NMR: –190.57 [q, $^1J_{\text{GeH}}$ = 95.6 Hz, GeH_3]. MS (GC-coupled, EI 70 eV): m/z = 166 [M^+], 91 [C_7H_7^+], 77 [GeH_3^+]. Calcd for $\text{C}_7\text{H}_{10}\text{Ge}$ (166.2): C, 50.42; H, 6.04. Found: C, 50.31; H, 6.03.

(2,4,6-Trimethylphenyl)trichloro-/(2,4,6-Trimethylphenyl)tribromogermane (2:1) (4a,b). As described for 3a,b, a mixture of 60 mL of bromomesitylene (0.4 mol), 5.2 g

of $\text{GeCl}_2 \cdot \text{dioxane}$ (22.5 mmol), and 0.15 g of anhydrous AlCl_3 (1.2 mmol) was heated to 80 °C for 4 days. The workup procedure was the same as described above, the excess of bromomesitylene being collected at 43 °C/0.05 mbar. The residue was a white solid (yield 7.21 g, 80% altogether).

Mesityltrichlorogermane: MS (GC-coupled, EI 70 eV, 27%): m/z = 298 [M^+], 262 [$\text{M}^+ - \text{Cl}$], 153 [$\text{M}^+ - \text{GeCl}_2$], 118 [$\text{M}^+ - \text{GeCl}_3$].

Mesityltribromogermane: MS (GC-coupled, EI 70 eV, 27%): 432 [M^+], 353 [$\text{M}^+ - \text{Br}$], 198 [$\text{M}^+ - \text{GeBr}_2$], 118 [$\text{M}^+ - \text{GeBr}_3$]. Calcd for $\text{C}_9\text{H}_{11}\text{GeCl}_3$ (298.1)/ $\text{C}_9\text{H}_{11}\text{GeBr}_3$ (431.5) = 2:1 ratio: C, 31.55; H, 3.23. Found: C, 31.53; H, 3.26.

(2,4,6-Trimethylphenyl)germane, [Mesitylgermane] (4). A 5.20 g (15.2 mmol) sample of the above product mixture (**4a,b**) in 15 mL of diethyl ether was added to a slurry of 1.3 g of LiAlH_4 (34.2 mmol) in 20 mL of diethyl ether. After 2 h at reflux, volatiles were distilled in vacuo. Extraction with 20 mL of pentane and vacuum distillation yielded a colorless liquid (2.25 g, 76%, bp 85 °C/4 mbar). ^1H NMR (C_6D_6 , 25 °C): 2.22 [s, 3H, $p\text{-CH}_3$], 2.32 [s, 6H, $o\text{-CH}_3$], 4.15 [s, 3H, GeH_3], 6.74 [s, 2H, $m\text{-CH}$]. ^{13}C NMR: 21.45 [$p\text{-CH}_3$], 24.47 [$o\text{-CH}_3$], 127.19 [C_1], 128.90 [C_3], 138.37 [C_4], 144.08 [C_2]. ^{73}Ge NMR: -234.32 ppm [q, $^1J_{\text{GeH}} = 95.0$ Hz, GeH_3]. MS (GC-coupled, EI 70 eV): 194 [M^+], 179 [$\text{M}^+ - \text{CH}_3$], 118 [$\text{M}^+ - \text{GeH}_3$]. Calcd for $\text{C}_9\text{H}_{14}\text{Ge}$ (194.4): C, 55.49; H, 7.24. Found: C, 55.47; H, 7.26.

For phenylgermane (**5**), diphenylgermane (**6**), and triphenylgermane (**7**), the syntheses followed the literature procedures.^{18,19}

Crystal Structure Determinations. A solid–liquid equilibrium was established at 258 K in a sample of compound **1** held in a capillary. Single crystals grew on cooling at 1 K h^{-1} . The specimens were used for measurement of precise cell constants and intensity data collection on an Enraf-Nonius CAD4 diffractometer (graphite-monochromated $\text{Mo K}\alpha$ radiation, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. The structure was solved by direct methods (SHELXTL-NT³⁷) and completed by full-matrix least-squares techniques against F^2 (SHELXL-97³⁸). The thermal motion of all non-hydrogen atoms was treated anisotropically. The hydrogen atoms of the phenyl ring were found and refined with isotropic contributions. The methyl group was refined as an idealized group with tetrahedral angles and C–H distances that may vary, the same shift being applied along all C–H

bonds. The germyl group was refined as a rigid group with tetrahedral angles and Ge–H distances fixed at 1.4000 Å. Further information on crystal data, data collection, and structure refinement are summarized in Table 2. Important interatomic distances and angles are given in Table 3. For further details, see the Supporting Information. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited at Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. The data are available on request by quoting CCDC No. 129255.

Ab Initio Calculations. Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.³⁹ Geometry optimizations (self-consistent field (SCF) and MP2 level of theory) and vibrational frequency calculations (up to SCF/6-31 G*) were performed from analytical first and second derivatives. Calculations were undertaken at the SCF level using the standard 3-21G*^{40,41} and 6-31G*^{42–44} basis sets, the larger basis sets being used for calculations at the MP2 level of theory.

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Supporting Information Available: Details of crystal data, data collection, and structure refinement and tables of atomic coordinates, isotropic and anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(39) Calculations were performed using standard methods implemented in Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94, Revision C.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(40) Pietro, W. J.; Francel, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(41) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

(42) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(43) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(44) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(37) SHELXTL-NT V5.1; Bruker AXS Inc.: Madison, WI, 1997.

(38) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen: Göttingen, FRC, 1997.