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

Frank Riedmiller, Gerald L. Wegner, Alexander Jockisch, and
Hubert Schmidbaur*

*Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
D-85747 Garching, Germany*

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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, $MeOC_6H_4GeH_3$). 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(Ge,H) couplings. The molecular structure of *p*-$MeOC_6H_4GeH_3$ 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]

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 desilanative 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 Ar_mGeH_{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 demethanative coupling are facile, easily controlled, high-yield

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* To whom correspondence should be addressed.

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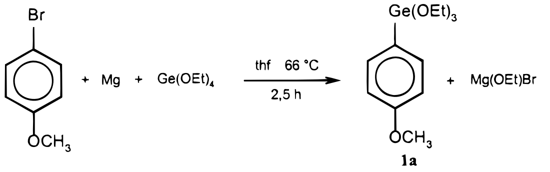
processes which lead to interesting di- and polygermanes.[1a,10] Dimethyltitanocene and tetrakis(trimethylphosphine)ruthenium are employed as catalyst precursors, respectively.

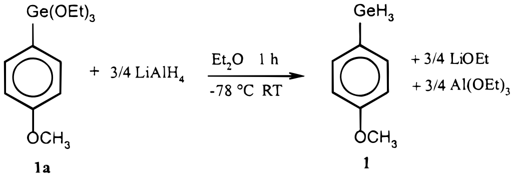
Following some earlier work on alkylgermanes[11] we, therefore, revisited the chemistry of arylgermanes.[1] The program was started with an effort to find new or improved pathways to simple representatives, to determine their molecular structure, and to provide a set of fundamental spectroscopic data. Previous spectroscopic investigations had not employed ^{73}Ge NMR methods. The few attempts gave only poorly resolved spectra or no results at all.[12−14] Recent improvements in the equipment and techniques have now made such studies possible.[11] Structural studies of arylgermanes were limited to gas-phase investigations by microwave spectroscopy, supplemented by vibrational and electronic spectroscopy, and by quantum chemical calculations.[15−17]

Preparation of Arylgermanes. The few arylgermanes described in the literature were prepared by treatment of germanium tetrachloride with aryl Grignard, aryllithium, or arylmercury reagents to give aryltrichlorogermanes.[18−20] The first two mentioned reactions are not very selective and give a range of products in low yields. Reduction of the chlorogermanes with lithium aluminum hydride affords the corresponding hydrides. Arylhalogermane precursors were also obtained by the insertion of germanium dihalides into the aryl−halogen bond of aryl halides, but the procedure in its original form was limited either to GeI_2[21] or to pressurized reactions with $GeCl_2$(L) adducts[22] and thus was not very satisfactory.

In modifications of these early preparations we used tetra(ethoxy)germane as starting material and subjected it to an "in situ Grignard" reaction (in analogy to the well-known synthetic concept for polysilyl-arenes via Si(OR)$_4$[23]) employing magnesium metal and aryl halides in boiling tetrahydrofuran (THF) (eq 1).

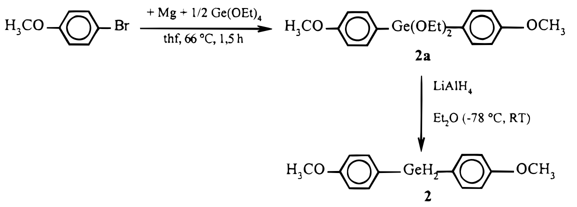


(1)



(2)

This reaction can also be carried out with substituted aryl halides as demonstrated with anisyl bromide (1-bromo-4-methoxybenzene). The anisyl group has proved to be an important substituent in the chemistry of arylsilanes because of its excellent leaving group properties in protodearylation reactions.[24] The primary products, aryl(ethoxy)germanes, can be reduced with $LiAlH_4$ and have been found to give better yields (86%) than the halogenogermanes (29 and 32%, respectively).[18] Equation 2 shows the preparation of 4-methoxyphenylgermane (**1**) as a representative example. Diarylgermanes such as bis(4-methoxyphenyl)germane (**2**) can be synthesized following the same sequence of reactions with modified stoichiometry (eq 3).



(3)

As an alternative synthetic pathway, the insertion of GeX_2 molecules into the C−halogen bond of halobenzenes has been revisited.[24e] The reaction conditions have been optimized to allow the process to be carried out (a) under convenient experimental conditions (no pressure, only slightly elevated temperature), (b) with the most readily available germylene reagent $GeCl_2$(dioxane), (c) with halobenzenes bearing sensitive substituents, and (d) in high yields.

It was found that 4-bromotoluene (as a reagent and as a solvent) reacts with $GeCl_2$(dioxane) in the presence of small amounts of anhydrous $AlCl_3$ as a catalyst already below the reflux temperature of the dioxane

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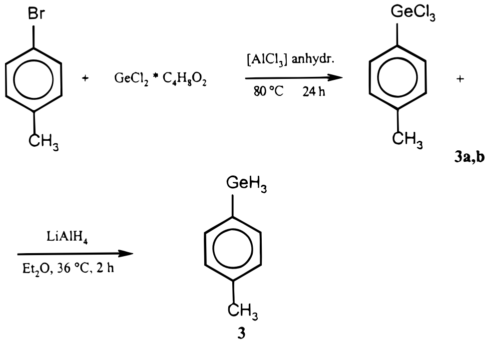
liberated in the process (80 °C) to give a mixture of *p*-tolyltrichloro- and -tribromogermane (**3a**,**b**) in almost quantitative yield (98%, eq 4).



3a,b

3

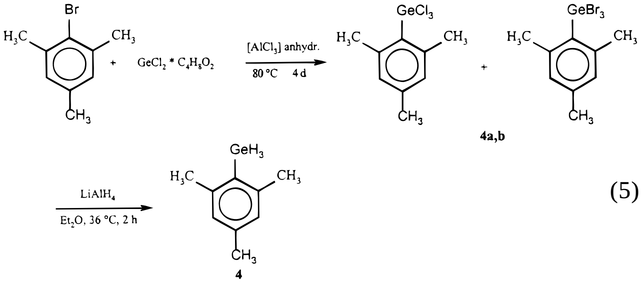
(4)

According to NMR spectroscopic and mass spectrometric data, this product is *not* a random distribution of mixed *p*-tolylchloro/bromogermanes [4-$MeC_6H_4Ge\text{-}Cl_nBr_{3-n}$] 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 $GeCl_4$ and (p-Tol)$_4$Ge 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 GeI_2 into PhI requires reaction temperatures of 160 °C (sealed tube, 32% yield after reduction to the germane), and that of $GeCl_2$ 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 $LiAlH_4$ in diethyl ether to give good yields of *p*-tolylgermane (**3**) (76%).

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



4a,b

4

(5)

Phenyl-, diphenyl-, and triphenyl-germane (**5**−**7**) were synthesized by $LiAlH_4$ reduction of the corresponding chlorogermanes which are commercially available. All arylgermanes prepared in this work are colorless, distillable liquids as described in the literature: $PhGeH_3$,[18] Ph_2GeH_2,[19] Ph_3GeH,[19] *p*-TolGeH_3,[20] MesGeH_3,[20] *p*-Me-$OC_6H_4GeH_3$,[18] (p-$MeOC_6H_4$)$_2GeH_2$.[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 ^{13}C 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 ^{73}Ge NMR spectroscopy, several $ArGeH_3$ prototypes have now been investigated in greater detail using state-of-the-art facilities.

^{73}Ge NMR Spectroscopy. Among the various germanium isotopes only the ^{73}Ge 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 GeH_4 in solvents of low polarity show the famous 10-line ^1H NMR signal from which the coupling constant $^1J(Ge,H) = 97.6$ Hz can be extracted.[28] Apart from Et_3GeH,[12] there is also a series of simple germa/sila-alkanes for which ^{73}Ge NMR spectra of surprisingly good resolution have been obtained.[11] $^1J(Ge,H)$ couplings range from 88 to 99 Hz. Tetramethylgermane, $GeMe_4$, also shows rather sharp resonances, but with no splitting. As a convention, this compound has been used as the standard of ^{73}Ge NMR spectroscopy ($\delta = 0.0$ ppm).

Owing to their low molecular symmetry (point groups C_s, C_2, or C_3), arylgermanes are not expected to give high quality ^{73}Ge 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 ^{73}Ge 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 [$^1J(Ge,H) = 98$ 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,

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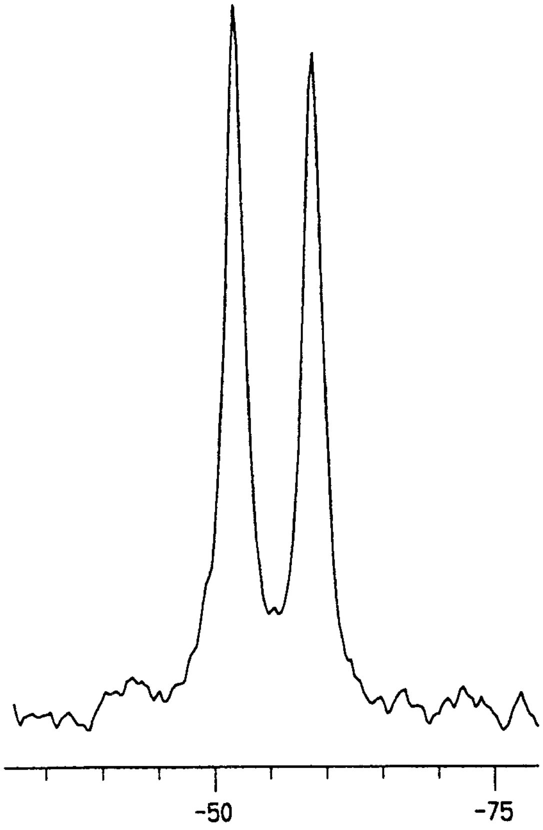

Figure 1. ^{73}Ge NMR spectrum of Ph_3GeH (in C_6D_6 at 20 °C).

Table 1. ^{73}Ge NMR Data [ppm, Hz] of Arylgermanes Ar_nGeH_{4-n} ($n = 1, 2, 3$)

compound	multiplicity	[ppm]	$^1J_{GeH}$ [Hz]
p-anisylgermane (**1**)	quartet	−189.9	97
bis(*p*-anisyl)germane (**2**)	broad singlet	−112.0	−
p-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(Ge,H) couplings was observed in the ^{1}H 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 $H_3Ge{-}R$ 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 l is a function of both the quadrupole moment Q (^{73}Ge: 0.18×10^{-28} 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 $l = (2I + 3)Q_2/[I^2(2I - 1)] = 2.4 \times 10^{-59}$ m^4 leads to an appreciable sharpness of the lines generated in the spin−spin coupling.[29]

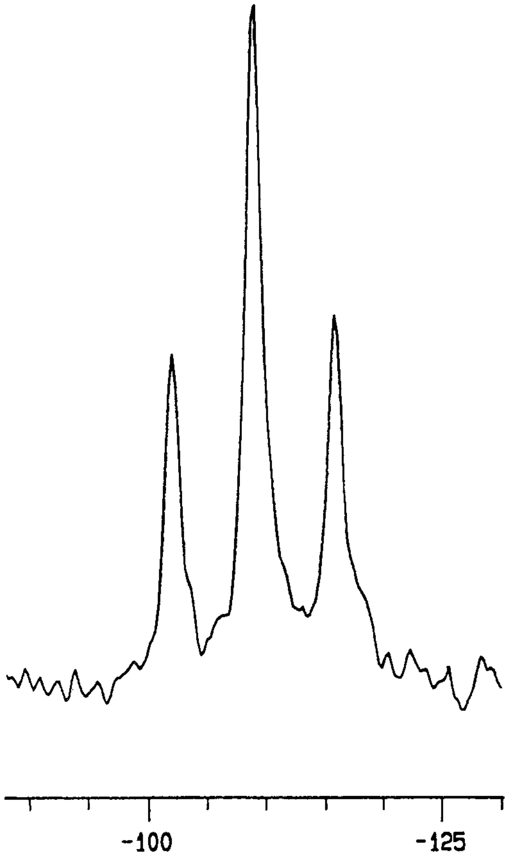

Figure 2. ^{73}Ge NMR spectrum of Ph_2GeH_2 (in C_6D_6 at 20 °C).

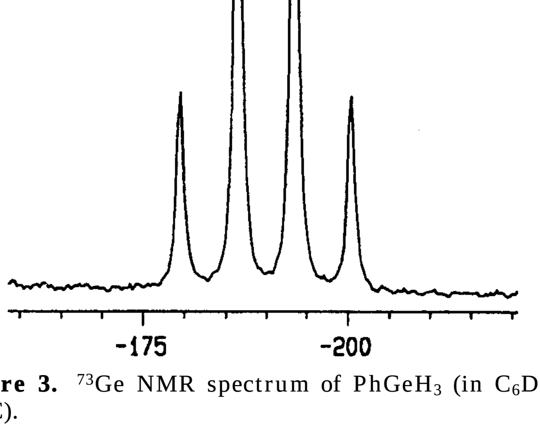

Figure 3. ^{73}Ge NMR spectrum of $PhGeH_3$ (in C_6D_6 at 20 °C).

Note that the sensitivity of the ^{73}Ge nucleus (1.1×10^{-4} rel ^{1}H) 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. ^{1}H (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

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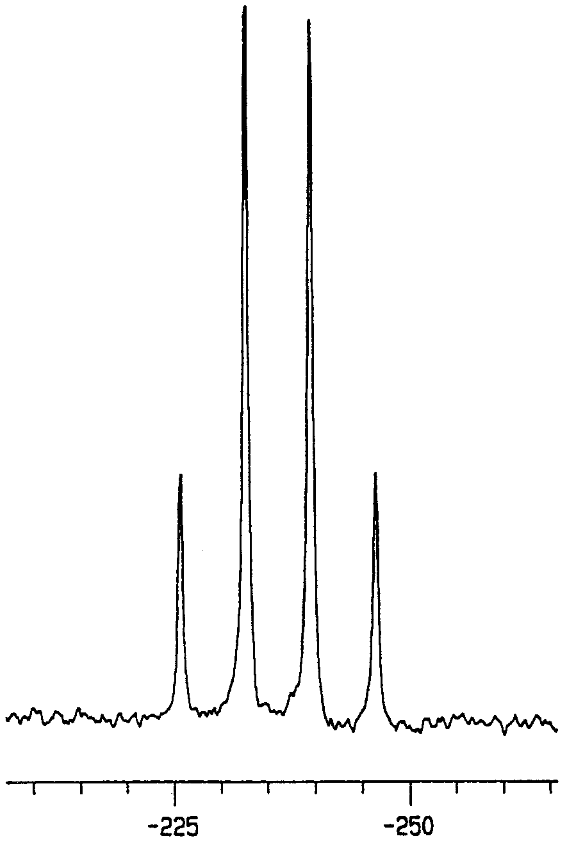


Figure 4. ^{73}Ge−NMR spectrum of MesGeH$_3$ (in C$_6$D$_6$ at 20 °C).

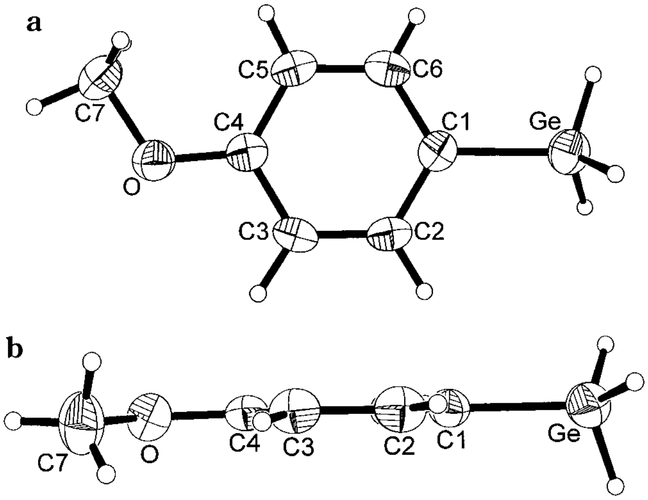


Figure 5. (a and b) Molecular structure of **1** (ORTEP drawing with 50% probability ellipsoids). Projection perpendicular and parallel to the plane of the arene ring.

diffraction studies. Crystals of 4-MeO−C$_6$H$_4$−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 *Pca*2$_1$, 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 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-

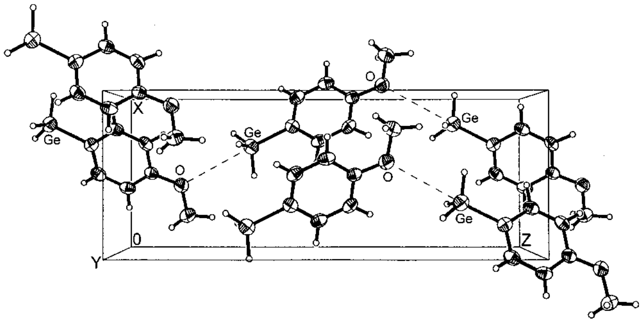


Figure 6. Packing diagram of **1**.

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

Crystal Data	
empirical formula	C$_7$H$_{10}$GeO
fw	182.74
cryst syst	orthorhombic
space group	*Pca*2$_1$
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*α), cm^{-1}	37.63
cryst dimens, mm	1.0 × 0.4 × 0.4
Data Collection	
temp, K	203(2)
scan mode	ω
hkl range	−8→8; −9→9; −21→21
measured reflns	3440
unique reflns	1723 (R_{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 $= \Sigma(||F_o|| - ||F_c||)/\Sigma|F_o|$. ^{b} wR2 $= \{[\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(ap)^2+bp]$; $p = (F_o^2+2F_c^2)/3$; $a = 0.0476$; $b = 0.0000$.

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)	−

manes. A previous reference value was obtained from gas-phase microwave studies (MW) of phenylgermane (Ge−C = 1.9423 Å). As expected, an ab initio calculation (4.21G*) for $PhGeH_3$ gave a much shorter distance of only 1.9054 Å which refers to the position of the nuclei and not of electron density maxima.[15] Solid-state Ge−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 Ge−H bond lengths (constrained to idealized tetrahedral geometry) were fixed at Ge−H = 1.40 Å. For the reason mentioned above, the reference value from MW data of phenylgermane is larger at 1.520 Å, and the calculated value (4.21G* with corrections) at 1.516 Å.[15]

The H_3Ge group is positioned almost symmetrically between the two ortho carbon atoms with angles Ge−C1−C2 and Ge−C1−C6 at 120.2(3)° and 122.3(3)°, 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 C3−C4−C5, as best illustrated by the angles O−C4−C3 = 115.6(3)° and O−C4−C5 = 124.5(3)°. The "ethereal angle" C4−O−C7 = 118.2(4)° 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 C−C−O/S were found [PhOH by MW spectroscopy: 117.01(2)° and 122.14(2)°; PhSH: 120.9° and 121.0°].[30a,b] For methyl phenyl sulfide groups, C_6H_5SMe, 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 O−C−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)°]. 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 C−C−O−C = 18°).[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 O−C−C of 113.7° and 126.3° (for C−O−C = 115.2°) for a fully planar structure (Scheme 1).[36]

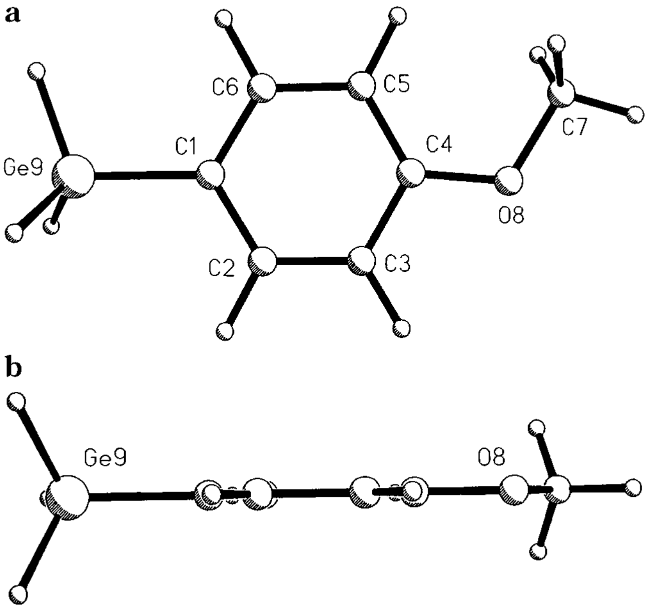
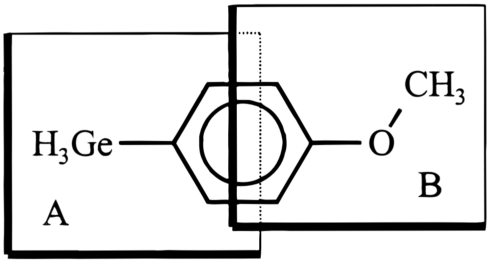


Figure 7. (a and b) Molecular structure of **1** as calculated by ab initio quantum chemical methods (MP2/6-31G*). For geometrical dimensions see Table 3. Projection perpendicular and parallel to the plane of the arene ring.

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 C1−Ge−O is almost linear (172.5°) with a distance Ge−O = 3.396 Å. 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

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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 (^{1}H 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). ^{1}H NMR (20 °C): $\delta = 1.25$ (t, $^3J_{HH} = 7$ Hz, 9H, CH_3), 3.53 (s, 3H, OCH_3), 4.25 (q, $^3J_{HH} = 7$ Hz, 6H, CH_2), 6.96 (d, $^3J_{HH} = 8.5$ Hz, 2 H, $H_{3,5}$), 7.60 (d, $^3J_{HH} = 8.5$ Hz, 2H, $H_{2,6}$). $^{13}C\{^1H\}$ NMR (20 °C): $\delta = 25.8$ (CH_3), 59.3 (OCH_3), 67.2 (CH_2), 129.0 ($C_{2,6}$), 130.7 ($C_{3,5}$), 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 [$M^+ - Ge(OEt)_3 + H$, 100%], 91 [$M^+ - Ge(OEt)_3 - CH_3$], 78 [$C_6H_4^+$], 51. Calcd for $C_{13}H_{22}GeO_4$ (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). ^{1}H NMR (20 °C): $\delta = 3.27$ (s, 3H, OCH_3), 4.27 (s, 3H, GeH_3), 6.72 (d, 2H, $^3J_{HH} = 8.8$ Hz, $H_{3,5}$), 7.25 (d, 2H, $^3J_{HH} = 8.8$ Hz, $H_{2,6}$). $^{13}C\{^1H\}$ NMR (20 °C): $\delta = 54.5$ (OCH_3), 114.6 ($C_{2,6}$), 121.3 (C_4^{ipso}), 136.9 ($C_{3,5}$), 161.0 (C_1^{ipso}). ^{73}Ge NMR (20 °C): $\delta = -189.9$ (q, $^2J_{Ge-H} = 97$ 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 $C_7H_{10}GeO$ (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). ^{1}H NMR (20 °C): $\delta = 1.32$ (t, $^3J_{HH} = 7$ Hz, 6H, CH_3), 3.56 (s, 6H, OCH_3), 4.28 (q, $^3J_{HH} = 7$ Hz, 4H, CH_2), 6.98 (d, $^3J_{HH} = 8.5$ Hz, 4H, $H_{3,5}$), 7.64 (d, $^3J_{HH} = 8.5$ Hz, 4H, $H_{2,6}$). $^{13}C\{^1H\}$ NMR (20 °C): $\delta = 26.2$ (CH_3), 59.6 (OCH_3), 67.9 (CH_2), 129.3 ($C_{2,6}$), 131.3 ($C_{3,5}$), 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 [$M^+ - CH_3OC_6H_4$], 226 [$M^+ - CH_3OC_6H_4 - OEt$], 181[100%, $M^+ - CH_3OC_6H_4 - 2\ OEt$], 152 [$M^+ - CH_3OC_6H_4 - OEt - Et$], 108 [$M^+ - CH_3OC_6H_4 - Ge(OEt)_2$], 89, 64. Calcd for $C_{18}H_{24}GeO_4$ (376.8): C, 57.38; H, 6.37. Found: C, 57.12; H, 6.33.

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). ^{1}H NMR (21 °C): $\delta = 3.29$ (s, 6H, OCH_3), 5.20 (s, 2H, GeH_2), 6.78 (d, 4H, $^3J_{HH} = 8.7$ Hz, $H_{3,5}$), 7.40 (d, 4H, $^3J_{HH} = 8.8$ Hz, $H_{2,6}$). $^{13}C\{^1H\}$ NMR (21 °C): $\delta = 54.3$ (OCH_3), 115.1 ($C_{2,6}$), 120.9 (C_1^{ipso}), 137.0 ($C_{3,5}$), 160.8 (C_4^{ipso}). ^{73}Ge NMR (21 °C): $\delta = -112.0$ (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%, $M^+ - C_6H_5OCH_3$], 167 [$M^+ - CH_3 - C_6H_5OCH_3$], 151 [$M^+ - OCH_3 - C_6H_5OCH_3$], 108 [$M^+ - C_6H_5OCH_3 - GeH_2$], 77 [$M^+ - C_6H_5OCH_3 - GeH_2 - OCH_3$], 138, 65. Calcd for $C_{14}H_{16}GeO_2$ (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 $GeCl_2$·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 $C_7H_7GeCl_3$ (270.1)/$C_7H_7GeBr_3$ (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). ^{1}H NMR (C_6D_6, 25 °C) 2.08 [s, 3H, CH_3], 4.77 [s, 3 H, GeH_3], 6.93 [d, 2H, $^3J_{HH} = 8.04$ Hz, $H_{2/6}$], 7.28 [d, 2H, $^3J_{HH} = 8.04$, $H_{3/5}$]. ^{13}C NMR: 21.3 [CH_3], 127.4 [$C{-}GeH_3$], 129.4 [$C_{2/6}$], 135.7 [$C_{3/5}$], 138.8 [$C{-}CH_3$]. ^{73}Ge−NMR: −190.57 [q, $^1J_{GeH} = 95.6$ Hz, GeH_3]. MS (GC-coupled, EI 70 eV): $m/z = 166$ [M^+], 91 [C_7H_7], 77 [GeH_3]. Calcd for $C_7H_{10}Ge$ (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 $GeCl_2$·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, 53%): $m/z = 298$ [M^+], 262 [$M^+ - Cl$], 153 [$M^+ - GeCl_2$], 118 [$M^+ - GeCl_3$].

Mesityltribromogermane: MS (GC-coupled, EI 70 eV, 27%): 432 [M^+], 353 [$M^+ - Br$], 198 [$M^+ - GeBr_2$], 118 [$M^+ - GeBr_3$]. Calcd for $C_9H_{11}GeCl_3$ (298.1)/$C_9H_{11}GeBr_3$ (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*-CH_3], 2.32 [s, 6H, *o*-CH_3], 4.15 [s, 3H, GeH_3], 6.74 [s, 2H, *m*-CH]. ^{13}C NMR: 21.45 [*p*-CH_3], 24.47 [*o*-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, $^1J_{GeH} = 95.0$ Hz, GeH_3]. MS (GC-coupled, EI 70 eV): 194 [M^+], 179 [$M^+ - CH_3$], 118 [$M^+ - GeH_3$]. Calcd for $C_9H_{14}Ge$ (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 Mo $K\alpha$ radiation, λ(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-NT[37]) and completed by full-matrix least-squares techniques against F^2 (SHELXL-97[38]). 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.

Acknowledgment. This work was supported by Fonds der Chemischen Industrie and by Deutsche Forschungsgemeinschaft. The authors are grateful to Dr. Norbert Mitzel for help with the crystal growth and data collection.

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.

OM990349Z

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