

# Ligand-Protected Strain-Free Diarylgermylenes<sup>†</sup>

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Reaction of 2 molar equiv of 2,6-di(1'-naphthyl)phenyllithium with bis[bis(trimethylsilyl)-amino]germylene afforded the red, crystalline, stable bis[2,6-bis(1-naphthyl)phenyl]germylene [(bisap)<sub>2</sub>Ge, **6**] in good yield. The structure of the solvate **6**·C<sub>6</sub>H<sub>6</sub> was determined by single-crystal X-ray methods. The molecule features a largely strain-free conformation with a C–Ge–C angle of 102.72(9)° and Ge–C distances of 2.036(2) and 2.030(2) Å. These parameters are very close to those calculated for the diphenylgermylene prototype by ab initio methods [101.6°; 2.006 Å]. The two new wing-like 2,6-di(1-naphthyl)phenyl substituents appear to protect the germylene center of **6** in a very efficient way without inducing destabilizing distortions. Bis[2,4,6-triphenylphenyl]germylene [(triph)<sub>2</sub>Ge, **1**] was also prepared. Germylenes **1** and **6** were oxidized to yellow products of the composition (triph)<sub>2</sub>GeO (**2**) and (bisap)<sub>2</sub>GeO (**7**), respectively. The compounds have been characterized by their mass spectra, which show the parent ions in full accordance with the proposed formulas.

## Introduction

There is currently widespread interest in the chemistry of carbenes SiR<sub>2</sub> and their heavy-atom homologues, the silylenes SiR<sub>2</sub> and germylenes GeR<sub>2</sub>, stannylenes SnR<sub>2</sub>, and plumbylenes PbR<sub>2</sub>. Recent reviews<sup>1</sup> reflect the advances in these topical areas of research. In the context of our studies of the preparation and reactivity of germanium hydrides<sup>2a,d–f</sup> and low-valent germanium compounds<sup>2b,c</sup> we became interested in stable diorganogermylenes R<sub>2</sub>Ge as substrates for oxidation, addition, and insertion reactions.

A literature search revealed that only very few diorganogermylenes have been isolated and structurally characterized.<sup>3–7</sup> The first stable dialkylgermylene R<sub>2</sub>Ge reported in 1976 appears to be bis[bis(trimethylsilyl)-methyl]germanium,<sup>3</sup> [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>Ge, but this com-

pound was found to be a monomer only in the gas phase and in solution,<sup>8</sup> but forms a dimer in the solid state.<sup>9</sup> Further increase of the steric crowding by using one tris(trimethylsilyl)methyl group finally afforded a stable germylene, [(Me<sub>3</sub>Si)<sub>3</sub>C]Ge[CH(SiMe<sub>3</sub>)<sub>2</sub>], which is monomeric in all three states of aggregation.<sup>4a</sup>

Three stable diarylgermylenes Ar<sub>2</sub>Ge were isolated with Ar = 2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; 2,4,6-(Me<sub>3</sub>C)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>; 2,6-(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. According to the crystal structure analysis, the tris(trifluoromethyl)phenyl compound features an intramolecular stabilization through short F–Ge contacts.<sup>5</sup> In the tris(*tert*-butyl)phenyl (“super-mesityl”) compound there is structural evidence for considerable strain.<sup>6</sup> The two aryl groups are inequivalent (C–Ge–C 108°) and show significant distortions of the aryl rings. This leads to considerable instability and to facile intramolecular insertion of the germylene unit into one of the C–H bonds. Similar strain is discernible in the 2,6-bis(mesityl)phenyl compound, where the C–Ge–C angle is widened to 114°, the largest value detected in diorganogermylenes, to allow phenyl stacking.<sup>7</sup> An unsymmetrical diarylgermylene with 2,4,6-tris(trimethylsilyl)phenyl and 2,4,6-tri(isopropyl)phenyl groups was also prepared, but its structure is unknown.<sup>10</sup>

<sup>†</sup> Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday.

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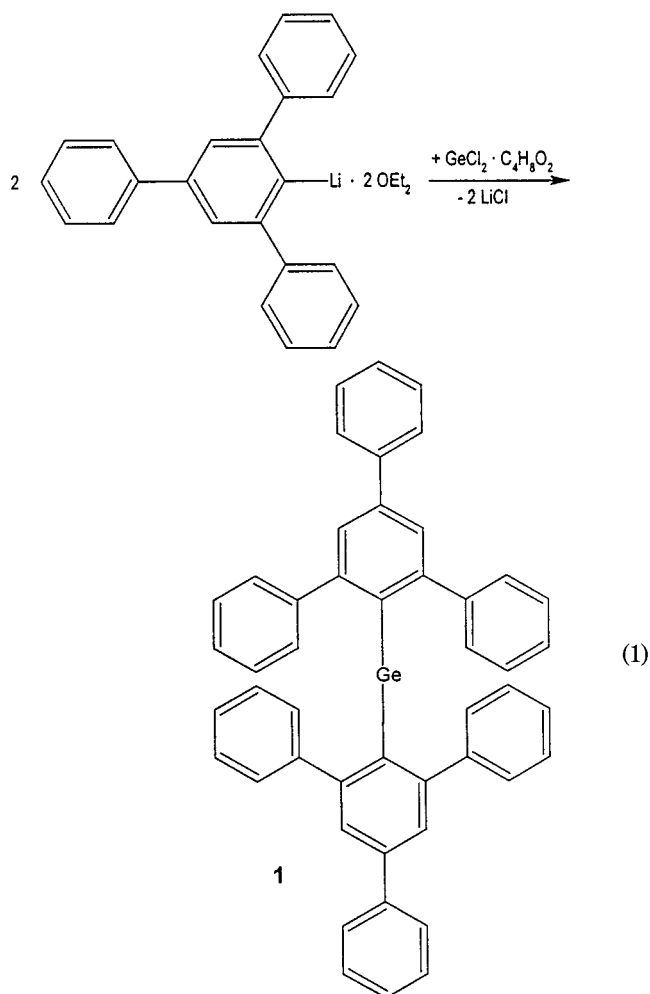
In the present investigation two ligands were introduced which were expected to provide sufficient shielding of the germylene function to impede dimerization, but to leave enough freedom of substituent motion to avoid destabilizing strain at the C–Ge–C core unit. In complementary quantum-chemical studies of the simple model system *diphenylgermylene* the ground state geometry in the gas phase of a diarylgermylene has been calculated, to which the experimentally determined data were to be compared.

A germylene protected in an efficient but not “invasive” way should also allow the preparation of a stable germanone of the formula  $R_2Ge=O$ , for which there is no precedent in the literature.

Germanones are highly elusive species, and the literature has several reports of unsuccessful attempts for their isolation. Simple germanones with  $R = H$  or  $Me$  were trapped in low-temperature argon matrixes and identified via their vibrational absorption spectra.<sup>11</sup> Upon warming to room temperature decomposition or oligomerization was observed. The reaction of bis-(supermesityl)germylene and trimethylamine oxide led only to a germandanol as an insertion product.<sup>6b</sup> The product of the oxidation of {(2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[2,4,6-tri(isopropyl)phenyl]germylene, “(Tbt)Ge(Tip)”, using tribenzylamine oxide gave a short-lived germanone which undergoes rearrangement to form a germacyclobutane.<sup>12</sup> Like many other transient germanones,<sup>13</sup> this germanone was also identified through its cycloaddition compounds with selected reagents.

### Preparative Results

Bis(2,4,6-triphenylphenyl)germylene “(triph)<sub>2</sub>Ge”, **1**, was prepared by reaction of  $GeCl_2$ (dioxane)<sup>14</sup> with 2 equiv of 2,4,6-triphenylphenyllithium bis(diethyl ether)<sup>15</sup> in diethyl ether at  $-60^\circ C$ . An orange-red solid product was obtained in 88% yield. The compound is thermochromic and turns yellow upon cooling to  $-196^\circ C$ . It is soluble in aromatic hydrocarbons and in tetrahydrofuran, but could not be crystallized from these solvents or their mixtures with aliphatic hydrocarbons. For this reason it was not possible to obtain a pure product. The  $^1H$  and  $^{13}C$  NMR spectra show complex arene multiplets or poorly resolved resonance patterns, respectively, which were not assigned, except for the signal due to the ipso-C1 atoms, which appears at 162.7 ppm. In the mass spectrum (CI) the molecular ion was observed at  $m/z$  683.4 followed by  $[(triph)Ge]^+$  ( $m/z = 378.4$ ) and  $[triph]^+$  ( $m/z$  306.3).



Oxidation of the orange-red germylene **1** by trimethylamine oxide in tetrahydrofuran at  $20^\circ C$  gave a yellow solid **2**, which has solubility characteristics similar to those of the parent germylene. In the  $^{13}C$  NMR spectrum the signal of the ipso-C1 carbon atoms is shifted to 168.8 ppm, while all other resonances are largely unchanged. In the mass spectrum (CI) the molecular ion  $[(triph)_2GeO]^+$  appears at  $m/z = 700.2$ , followed by  $[(triph)_2Ge]^+$ ,  $[(triph)GeO]^+$  ( $m/z = 393.3$ ),  $[(triph)Ge]^+$ , and  $[triph]^+$ . The intensity distribution pattern is distinctly different from the mass spectrum of the parent germylene **1**.

Single crystals of **2** could not be grown from common solvents or their mixtures. In the IR spectrum  $Ge=O$  absorptions are expected at ca.  $940\text{ cm}^{-1}$  as calculated and observed (in matrixes) for the  $H_2GeO$  and  $Me_2GeO$  prototypes. For  $[(triph)_2Ge]$  and  $[(triph)_2GeO]$  there are numerous ligand bands in this region, which make reliable assignments extremely difficult. The evidence for the germanone  $[(triph)_2GeO]$  is therefore not fully conclusive.

There is also no fully confirmed evidence for any other monomeric compound of the general type  $X_2Ge=O$ , with  $X$  other than alkyl or aryl. The determination of the crystal structure of the compound with  $X = (Me_3Si)_2N$  has shown that the compound is a dimer with a  $[GeO]_2$  four-membered ring.<sup>16</sup> The sulfur, selenium, and tellurium analogues are also known to be dimers.<sup>17</sup>

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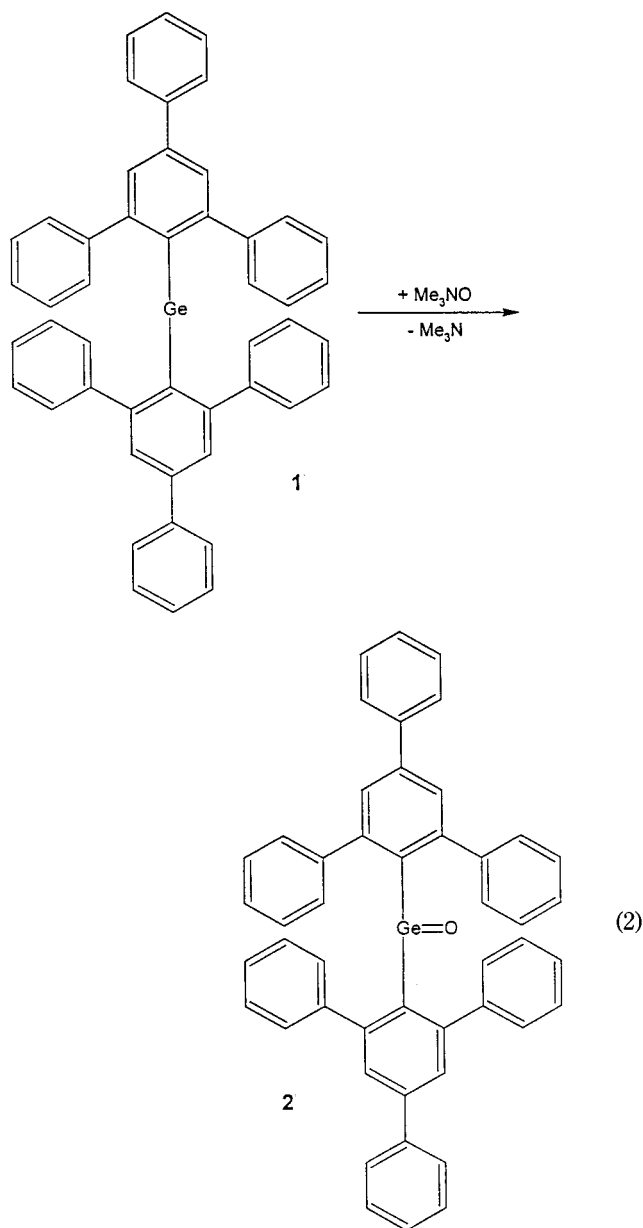
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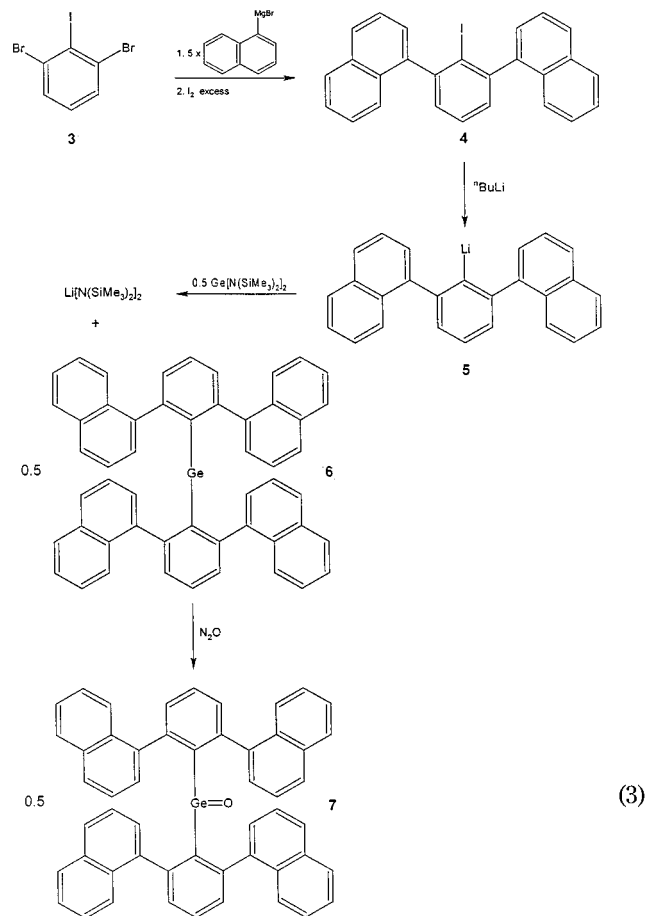
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To synthesize a pure, crystalline germylene, which could be a more convenient starting material for oxidation reactions, it was therefore necessary to design a new ligand. This ligand was required to be amenable neither to germylene insertion reactions nor to nucleophilic substitution or intramolecular rearrangement. 2,6-Bis(1-naphthyl)phenyl, "bisap", was expected to meet all these conditions, because it has no alkyl or substituted alkyl substituents.

2,6-Bis(1-naphthyl)(1-iodo)benzene (**4**) was prepared in 62% yield and lithiated using an equivalent quantity of *n*-butyllithium in hexane/diethyl ether. 2,6-Bis(1-naphthyl)phenyllithium was isolated as a colorless crystalline solid (**5**). A solution of the latter in diethyl ether was treated with bis[bis(trimethylsilyl)amino]germylene in 2:1 molar ratio at  $-50^\circ\text{C}$ . The reaction mixture turned purple, and after evaporation of all volatile components the byproduct  $\text{LiN}(\text{SiMe}_3)_2$  could be



extracted with pentane. Crystallization of the residue from diethyl ether afforded a dietherate of bis[2,6-(1-naphthyl)]germylene (**6**), in 32% yield. The crystal structure of this product could not be refined to a satisfactory level owing to disorder of one of the solvent molecules. However, recrystallization from benzene/*n*-octane gave red crystals of the diarylgermylene (**6**) with 1 equiv of benzene in a fully ordered structure (below).

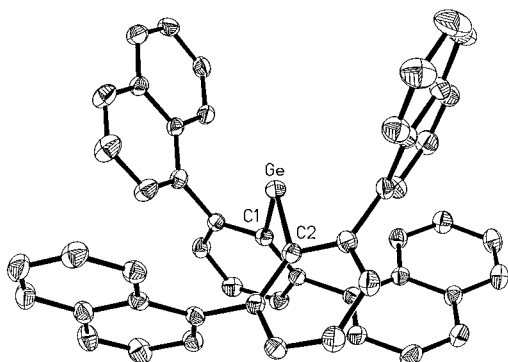
The composition of the product was confirmed by mass spectrometry (chemical ionization), the molecular ion being observed in high intensity. Owing to the low symmetry of the molecule, the compound shows no signal in its  $^{73}\text{Ge}$  NMR spectrum. However, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are in full agreement with the proposed formula. The IR spectrum is extremely rich in absorption bands in the aromatic regions. All assignments are therefore tentative.

Preliminary studies of the oxidation reactions using nitrous oxide provided a colorless product [(bisap) $_2\text{GeO}$ ] (**7**), which has the expected molecular ion in the mass spectrum (CI,  $m/z = 748$ ) with the correct isotope pattern. More extensive investigations are under way.

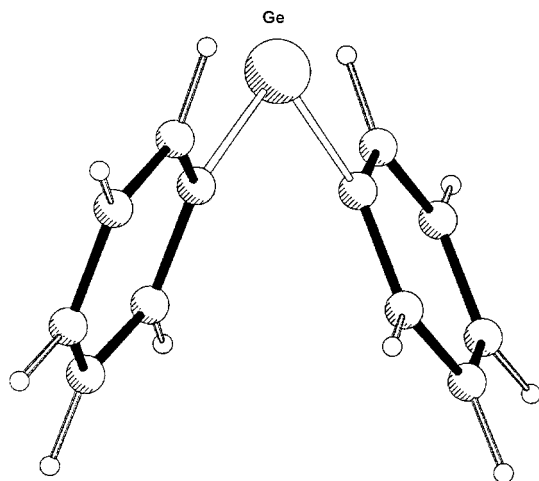
**Molecular Structure of the New Germylene.** Crystals of **6**· $\text{C}_6\text{H}_6$  (from benzene/*n*-octane at  $0^\circ\text{C}$ ) are monoclinic, space group  $P2_1/n$  with  $Z = 4$  germylene and benzene molecules in the unit cell. There are no sub-van der Waals contacts between these components in the lattice. The germylene should therefore be considered strictly as a monomer. The molecule **6** has no crystallographically imposed symmetry, but the structure approaches quite closely the symmetry requirements of a 2-fold axis passing through the Ge atom and

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**Figure 1.** Molecular structure of (bisap)<sub>2</sub>Ge, **6**, in crystals of **6** × benzene with atomic numbering (ORTEP drawing at the 50% probability level; H atoms omitted for clarity). Ge–C1 2.036(2), Ge–C2 2.030(2) Å, C1–Ge–C2 102.72(9)°.



**Figure 2.** Calculated structure of Ph<sub>2</sub>Ge (arbitrary radii). Ge–C 2.006 Å, C–Ge–C 101.6°.

bisecting the C–Ge–C angle. At only 102.72(9)° this angle is the lowest among the data documented in the literature except for the CF<sub>3</sub>-substituted example [99.95(10)°; above] with its intramolecular F–Ge contacts.

An inspection of the structure (Figure 1) shows that the two Ge-bound phenyl groups with their four naphthyl substituents can be readily accommodated in the environment of the Ge atom, suggesting a strain-free conformation. There are no significant distortions of the geometries of any of the arene rings and of the interring angles. The two Ge–C distances [2.036(2) and 2.030(2) Å] and the C–Ge–C angle [102.72(9)°] may therefore be taken as the “natural” or intrinsic parameters of a diarylgermylene.

**Quantum-Chemical Calculations of Diphenylgermylene.** Ab initio calculations at the B3LYP level of theory using standard programs gave data for diphenylgermylene as a simple reference compound. The ground state of the molecule has a structure with C<sub>2</sub> symmetry, as shown in Figure 2. The phenyl groups show a standard geometry. The Ge–C distances were calculated to be at 2.006 Å, the C–Ge–C angle at 101.6°. Both values are very close to the experimental data for germylene **6** in support of the idea that this new diarylgermylene has a largely strain-free geometry at the core unit. Deviations in the torsion angles are not unexpected and reflect the specific steric requirements

of the naphthyl-substituted phenyl groups. Obviously rotations about the Ge–C and aryl–aryl bonds are sufficient to accommodate these ligands.

## Experimental Part

**General Methods.** The experiments were carried out under an atmosphere of dry nitrogen using Schlenk techniques. GeCl<sub>2</sub>·dioxane,<sup>14</sup> Ge[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>,<sup>18</sup> (Triph)Li(Et<sub>2</sub>O)<sub>2</sub>,<sup>15</sup> and Me<sub>3</sub>NO<sup>19</sup> were prepared and purified according to published procedures. 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 (<sup>1</sup>H at 400.05 MHz, <sup>13</sup>C at 100.50 MHz, <sup>73</sup>Ge at 13.83 MHz) in sealed tubes with predried C<sub>6</sub>D<sub>6</sub> as solvent. Mass spectra were recorded with a Finnigan MAT 90 mass spectrometer (chemical ionization (CI)–MS, isobutane) and with an analytical gas–liquid-chromatograph (GLC)–MS Hewlett-Packard 5890 Series II (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.

**(Triph)<sub>2</sub>Ge (1).** To a solution of (triph)Li(OEt)<sub>2</sub> (5.31 g, 11.52 mmol) in 20 mL of diethyl ether was added GeCl<sub>2</sub>·dioxane (1.34 g, 5.78 mmol). The reaction mixture was stirred at –50 °C for 2 h and thereafter allowed to warm to room temperature. After continued stirring for 6 h the volatiles were stripped off in vacuo. The product was extracted from the residue with 20 mL of toluene. Evaporation of the solvent gave an orange solid. Yield: 3.86 g, 98%. <sup>1</sup>H NMR (20 °C): 6.5–7.8 (m). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C): 126.6, 128.6, 128.7, 128.9, 129.1, 129.2, 130.6, 132.8, 134.1, 143.1, 144.2, 162.7 (C<sub>1</sub>). MS (CI, isobutane): *m/z* 683.4 [M<sup>+</sup>], 378.4 [M<sup>+</sup> – triph], 306.3 [triph<sup>+</sup>], 229.3 [triph – Ph]. Calcd for C<sub>48</sub>H<sub>34</sub>Ge (683.39): C, 84.36; H, 5.01. Found: C, 83.38; H, 5.44.

**(Triph)<sub>2</sub>GeO (2).** Me<sub>3</sub>NO (147 mg, 1.96 mmol) was added to a solution of (triph)<sub>2</sub>Ge (1.34 g, 1.96 mmol) in 15 mL of THF. The mixture was stirred at room temperature for 24 h. Volatiles were removed in vacuo. The residue was washed with 10 mL of pentane. Extraction with 10 mL of toluene and evaporation afforded a yellow solid (**2**). Yield: 1.13 g, 83%. <sup>1</sup>H NMR (20 °C): 6.8–7.8 (m). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C): 125.6, 127.3, 127.5, 128.5, 129.1, 129.9, 130.0, 130.1, 141.7, 142.9, 168.8 (C<sub>1</sub>). MS (CI, isobutane): *m/z* 700.6 [(triph)<sub>2</sub>GeO<sup>+</sup>], 683.4 [(triph)<sub>2</sub>Ge<sup>+</sup>], 393.3 [(triph)<sub>2</sub>GeO<sup>+</sup> – Triph], 379.3 [M<sup>+</sup> – triph], 306.4 [triph<sup>+</sup>]. Calcd for C<sub>48</sub>H<sub>34</sub>GeO (699.39) C, 82.43; H, 4.90. Found: C, 83.14; H, 5.44%; N, 0.5. The nitrogen contents suggest the presence of some residual Me<sub>3</sub>NO or NMe<sub>3</sub>.

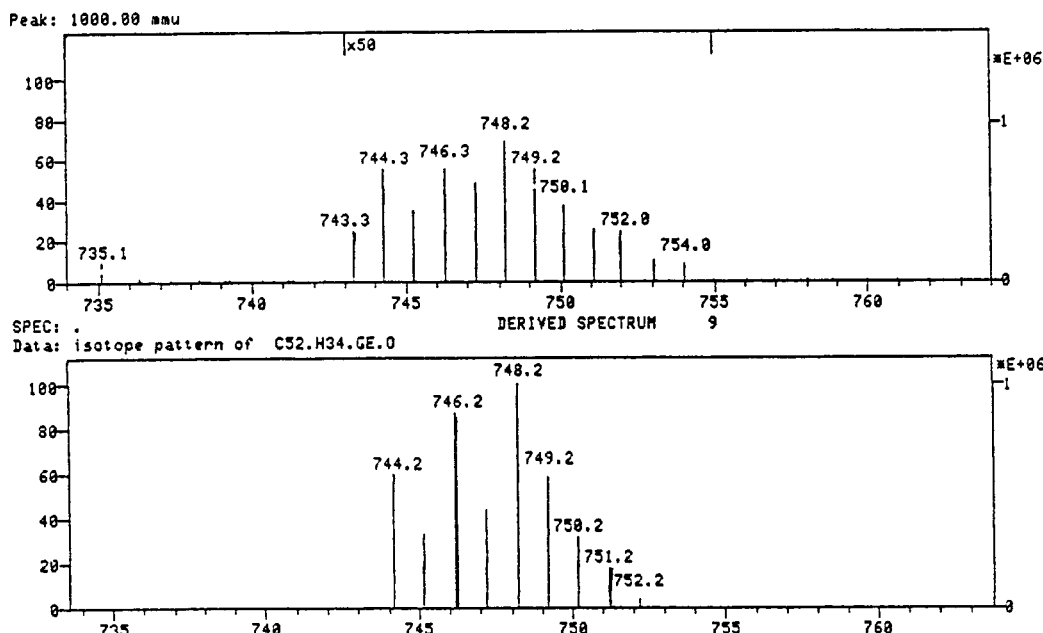
**2,6-Dibromiodobenzene (3).** The compound was prepared following a literature procedure.<sup>20</sup> It was recrystallized twice from 2-propanol instead of benzene–ethanol. The purified product was dissolved in dry THF. The solvent and all volatile components trapped in the crystals were removed in vacuo. <sup>1</sup>H NMR (20 °C): δ 6.12 (t, 1H, <sup>3</sup>J = 7.8 Hz, H<sub>4</sub>), 6.92 (d, 2H, <sup>3</sup>J = 7.8 Hz, H<sub>3/5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (20 °C): δ 96.8 (C<sub>1</sub>), 130.1 (C<sub>4</sub>), 131.0 (C<sub>3/5</sub>), 131.5 (C<sub>2/6</sub>). MS (EI, 70 eV): *m/z* 362 [M<sup>+</sup>]; 235 [M<sup>+</sup> – I]; 155 [M<sup>+</sup> – I – Br]; 75 [M<sup>+</sup> – I – 2Br]. Calcd for C<sub>6</sub>H<sub>3</sub>Br<sub>2</sub>I (361.8): C, 19.92; H 0.83. Found: C, 20.08; H, 0.89.

**2,6-Bis(1'-naphthyl)iodobenzene, [bisapI] (4).** A suspension of magnesium chips (12 g, 0.5 mol) in 100 mL of THF was activated with few drops of 1,2-dibromoethane. Ten

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**Figure 3.** (a) Molecular ion in the mass spectrum (FAB) of  $(\text{bisap})_2\text{GeO}$  (7), (b) calculated isotope pattern for  $\text{C}_{52}\text{H}_{34}\text{GeO}$  (747.45).

percent of a solution of 1-bromonaphthalene (100 g, 0.48 mol) in tetrahydrofuran was then added, and stirring continued until a mild exothermic reaction commenced. The addition was slowly continued to maintain reflux of the solvent. Thereafter the mixture was refluxed for 2 h. A solution of 2,6-dibromiodobenzene (12 g, 66.3 mmol) in 100 mL of THF was added dropwise at room temperature within a period of 2 h. After the reaction mixture had been stirred for 4 h, iodine (95 g, 0.75 mol) was added in small portions with cooling (ice bath), and stirring was continued overnight. A solution of  $\text{Na}_2\text{SO}_3$  (28 g, 0.22 mol) in 400 mL of water was added to destroy the excess iodine. The aqueous layer was separated and washed twice with 100 mL of toluene. The combined organic layers were washed with 300 mL of water and 200 mL of a saturated aqueous  $\text{NaCl}$ .  $\text{MgSO}_4$  was used to dry the organic layer. The solvents were evaporated after filtration. Most of the side product 1-iodonaphthalene was removed by sublimation (150 °C/0.05 mbar). Recrystallization from a 2:1 mixture of 2-propanol and toluene and finally from pure toluene afforded colorless crystals of  $\text{bisapI} \cdot 0.5$  toluene. The toluene can be removed by heating the material to 100 °C in vacuo for several hours to afford pure **4** as a white solid. Yield: 18.76 g, 62%.  $^1\text{H}$  NMR (20 °C): 7.06–7.40 (m).  $^{13}\text{C}\{^1\text{H}\}$  NMR (20 °C): 107.3 ( $\text{C}_1$ ), 125.5 ( $\text{C}_8'$ ), 126.1 ( $\text{C}_3'$ ), 126.1 ( $\text{C}_6'$ ), 126.4 ( $\text{C}_7'$ ), 126.5 ( $\text{C}_4'$ ), 127.5 ( $\text{C}_2'$ ), 128.4 ( $\text{C}_5'$ ), 128.6 ( $\text{C}_4$ ), 129.9 ( $\text{C}_{3/5}$ ), 132.2 ( $\text{C}_{8a}$ ), 134.2 ( $\text{C}_{4a}$ ), 143.7 ( $\text{C}_1'$ ), 147.3 ( $\text{C}_{2/6}$ ). IR ( $\text{cm}^{-1}$ ): 3044, 1593, 1554, 1507, 1391, 1383, 1010, 861, 798, 776, 737, 720, 703, 668, 618, 566, 499. MS (EI, 70 eV):  $m/z$  = 456 [ $\text{M}^+$ ], 329 [ $\text{M}^+ - \text{I}$ ], 202 [ $\text{M}^+ - \text{I} - \text{Naph}$ ], 163 [ $\text{M}^{2+}$ ], 127 [ $\text{Naph}^+$ ]. Calcd for  $\text{C}_{26}\text{H}_{17}\text{I}$  (456.32): C, 63.43; H, 3.76. Found: C, 63.36; H, 3.79.

**(Bisap) $_2\text{Ge}$  (6).** With rapid stirring, 5.2 mL of a 1.6 M solution of *n*-BuLi (8.3 mmol) in hexane was added dropwise to a slurry of  $(\text{bisap})\text{I}$  (3.8 g, 8.3 mmol) in 15 mL of diethyl ether at room temperature. Stirring was continued for 30 min, then the volume of the resulting yellow solution was reduced to incipient crystallization and cooled to –35 °C overnight. The colorless crystals obtained (5 g) were washed twice with 15 mL of pentane. A solution of  $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$  (1.48 g, 3.75 mmol) in 20 mL of diethyl ether was added at –50 °C with stirring. The reaction mixture, which took on an intense purple color, was allowed to warm to room temperature within 2 h and then stirred for a further 12 h at ambient temperature. The volatile materials were removed under reduced pressure, and the

**Table 1.** Calculated [B3LYP/TZV(P)] Cartesian Coordinates of  $\text{Ph}_2\text{Ge}$  in  $\text{m}^{-10}$

Ge	–0.000849	0.003112	–1.401064
C	1.553854	0.030728	–0.134178
C	1.563631	0.616478	1.143071
H	0.654170	1.044938	1.547894
C	2.765730	–0.487734	–0.621116
H	2.803727	–0.918075	–1.617887
C	2.728498	0.672194	1.901716
H	2.716690	1.141562	2.878987
C	3.926555	–0.464126	0.145423
H	4.845675	–0.885573	–0.245380
C	3.909621	0.122879	1.407752
H	4.814722	0.156972	2.002969
C	–1.554055	–0.031831	–0.132921
C	–2.770337	0.472362	–0.624148
H	–2.811507	0.894575	–1.624248
C	–1.558539	–0.606604	1.149280
H	–0.645509	–1.024379	1.557152
C	–3.930377	0.447433	0.143479
H	–4.852303	0.860740	–0.249355
C	–2.722493	–0.663609	1.909197
H	–2.706293	–1.123435	2.890932
C	–3.907565	–0.125706	1.412066
H	–4.812153	–0.162503	2.007940

residue was washed twice with 15 mL of pentane to give a dietherate,  $(\text{bisap})_2\text{Ge} \cdot 2 \text{OEt}_2$ . The remaining red powder was recrystallized from benzene/*n*-octane to afford **6** as red crystals. Yield: 0.97 g, 32%.  $^1\text{H}$  NMR (20 °C):  $\delta$  6.8–8.2 (m),  $^{13}\text{C}\{^1\text{H}\}$  NMR (20 °C):  $\delta$  125.0 ( $\text{C}_8'$ ), 125.2 ( $\text{C}_6'$ ), 125.9 ( $\text{C}_3'$ ), 126.4 ( $\text{C}_7'$ ), 126.5 ( $\text{C}_4'$ ), 126.8 ( $\text{C}_2'$ ), 127.1 ( $\text{C}_5'$ ), 129.8 ( $\text{C}_4$ ), 130.2 ( $\text{C}_{3/5}$ ), 134.2 ( $\text{C}_{8a}$ ), 134.6 ( $\text{C}_{4a}$ ), 143.3 ( $\text{C}_1'$ ), 145.0 ( $\text{C}_{2/6}$ ), 168.6 ( $\text{C}_1$ ).  $^{73}\text{Ge}$  NMR: no signal. MS (CI):  $m/z$  732.3 [ $\text{M}^+$ ], 401.1 [ $\text{M}^+ - \text{bisap}$ ], 330.1 [ $\text{bisap}^+$ ], 202.0 [ $\text{bisap}^+ - \text{Naph}$ ]. IR ( $\text{cm}^{-1}$ ): 3049, 1652, 1617, 1593, 1554, 1507, 1390, 907, 864, 798, 788, 776, 734, 636, 617, 568, 499. Calcd for  $\text{C}_{58}\text{H}_{40}\text{Ge}$  (809.5) C, 86.05; H 4.98. Found: C, 87.25; H, 4.89.

**(Bisap) $_2\text{GeO}$  (7).**  $(\text{Bisap})_2\text{Ge} \cdot 2\text{OEt}_2$  (0.6 g, 0.69 mmol) was dissolved in 3.5 mL of toluene in a 50 mL flask, and the headspace was filled with 45 mL of dry  $\text{N}_2\text{O}$  (20.3 mmol). The flask was kept at 0 °C for 2 days. The red solution was discolored, and a small amount of a precipitate formed. Evaporation of the solvent in vacuo left 0.51 g of a white powder (98% yield). The mass spectrum is shown in Figure 3. Attempts to obtain this product completely free of solvent and to recrystallize it have not yet been successful.

**Crystal Structure of Compound 6·C<sub>6</sub>H<sub>6</sub>.** The data were collected on a Nonius DIP2020 image plate system using graphite-monochromated Mo K $\alpha$  radiation. The structure was solved by a combination of direct methods and difference Fourier syntheses and refined by full matrix least-squares calculations on  $F^2$ . The thermal motion was treated anisotropically for all non-hydrogen atoms. Hydrogen atoms were calculated and allowed to ride on their corresponding C atoms with fixed isotropic contributions. *Crystal data for C<sub>58</sub>H<sub>40</sub>Ge*:  $M_r = 809.49$ , dark red crystals, monoclinic,  $a = 15.901(1)$ ,  $b = 15.175(1)$ ,  $c = 18.335(1)$  Å,  $\beta = 112.96(1)^\circ$ , space group  $P2_1/n$ ,  $Z = 4$ ,  $V = 4073.6(4)$  Å<sup>3</sup>,  $\rho_{\text{calc}} = 1.320$  g cm<sup>-3</sup>,  $F(000) = 1680$ ;  $T = -130$  °C; 9717 measured and unique reflections; 532 refined parameters,  $wR2 = 0.1025$ ,  $R = 0.0574$  for 8064 reflections [ $F_o \geq 4\sigma(F_o)$ ] used for refinement. Residual electron densities:  $+0.51/-0.61$  e/Å<sup>3</sup>. The function minimized was  $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ ;  $w = 1/[\sum^2(F_o^2) + (ap)^2 + bp]$ ;  $p = (F_o^2 + 2F_c^2)/3$ ;  $a = 0.0264$ ,  $b = 5.00$ . Important interatomic distances and angles are given in the Figure 1 caption. Anisotropic thermal parameters and complete lists of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC-148625.

**Computational Details.** The structure of the Ph<sub>2</sub>Ge molecule was calculated with the Turbomole<sup>21</sup> program package (version V5.2). Turbomole's implementation<sup>22</sup> of the Becke

three-parameter hybrid-functional in conjunction with the correlation functional according to Lee, Yang, and Parr<sup>23</sup> was chosen as a suitable level of theory (B3LYP). As basis functions the triple- $\zeta$  split-valence set augmented with polarization functions on Ge and C was used [TZV(P)].<sup>24</sup>

The structure was optimized without any constraints regarding symmetry, and in order to prove the calculated geometry as a local minimum on the energy hypersurface a frequency analysis was carried out.

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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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