

Synthesis and Characterization of a Novel Diarylgermylene Containing Electron-Withdrawing Groups

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Summary: The fluoroarylgermylene bis[2,4,6-tris(trifluoromethyl)phenyl]germanium(II) was synthesized by the reaction of 2 equiv of [2,4,6-tris(trifluoromethyl)phenyl]lithium with GeCl₂·dioxane. This monomeric germylene has good thermal stability, despite having the least sterically encumbering set of stabilizing ligands of any alkyl germylene isolated to date.

Introduction

The chemistry of germylenes has steadily developed over the past 20 years.¹ Approximately 30 stable, isolable σ -bonded germylenes now exist.^{2–9} The majority of these compounds contain heteroatom linkages to germanium, stabilizing the germylene via electron donation from the heteroatom lone pairs to the empty germanium p-orbital.^{2,3a,b,4–9} Comparatively few well-characterized examples of germylenes containing σ -bonds to carbon have been isolated.^{2a,g,3c,d,8} In the absence of supporting ligands containing electron pairs capable of donating electron density to the germanium, these complexes rely on extreme steric bulk and electron-rich

alkyl groups to inhibit oligomerization. These properties, coupled with low thermal stability, have limited their utility as transition-metal ligands.

In the context of our recent studies of the reactivity of transition-metal–germylene complexes,¹⁰ we have encountered the need for (1) a less sterically encumbered, monomeric germylene that can be isolated as a stable, crystalline solid and (2) a germylene that is not easily hydrolyzed, hydrogenated, or otherwise reactive at the Ge–X bond, the major drawback we have found to date in our work utilizing Lappert's extraordinarily useful complex Ge[N(SiMe₃)₂]₂.^{2a} In addition, the bis-(trimethylsilyl)amino groups are quite effective π -bases and compete with filled transition-metal orbitals for the empty germanium p-orbital. To enhance the possibility of significant M–Ge π -bonding, it is important to minimize the π -donation from the germanium-based supporting ligands. Previous work on stannylenes and plumblylenes by Zuckerman et al.,¹¹ Edelmann et al.,¹² and Grützmacher et al.¹³ suggested a possible solution to these problems, the synthesis of Ge[(2,4,6)-(CF₃)₃C₆H₂]₂ (1). We now report the synthesis and characterization of this new germylene complex.

Results and Discussion

Slow addition of an ethereal solution of [2,4,6-tris(trifluoromethyl)phenyl]lithium (12 mmol in 38 mL of ether) to a 0 °C solution of GeCl₂·dioxane (1.10 g, 4.75 mmol) in 25 mL of ether over a period of 5 h resulted in an opaque yellow mixture. All volatiles were removed *in vacuo*, 10 mL of pentane was added, and the mixture was filtered. Recrystallization from pentane at –78 °C resulted in 2.2 g of Ge[2,4,6-(CF₃)₃C₆H₂]₂ (1) as an orange-yellow powder (~85% pure). Compound of analytical purity was obtained by vacuum sublimation (30 °C and 0.1 Torr) as bright yellow, air-sensitive crystals (1.2 g, 41% yield overall). A suitable crystal for X-ray analysis was selected from the sublimed material.

The resulting structure demonstrated that the new germylene is a monomer in the solid state (Figure 1). Additional salient features of the structure include

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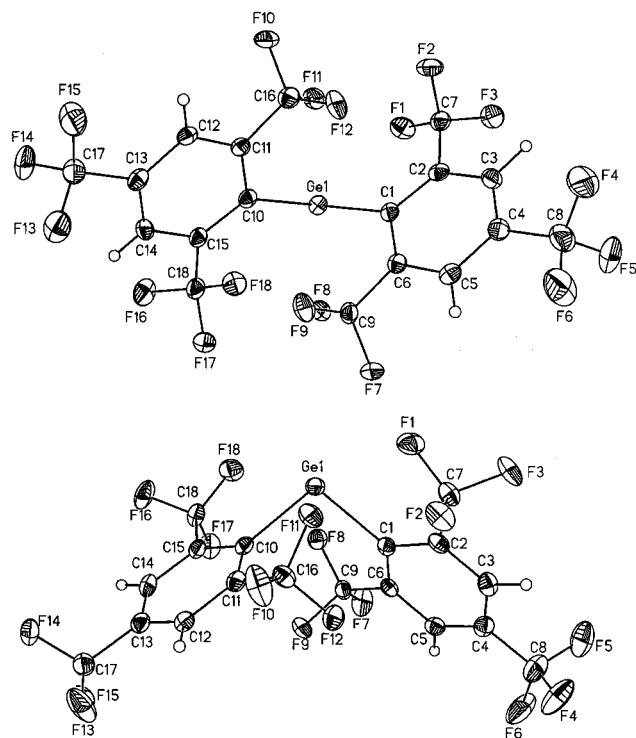


Figure 1. ORTEP diagram for **1** showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Ge–C1, 2.081(3); Ge–C10, 2.072(3); C1–Ge–C10, 99.95; Ge–F11, 2.566(2); Ge–F8, 2.554(1); Ge–F1, 2.790(2); Ge–F18, 2.781(2); F11–C16, 1.372(3); F8–C9, 1.356(3); F1–C7, 1.341(3); F18–C18, 1.346(3); average C–F bond length for CF₃ groups in para position, 1.334(8).

Ge–C bonds of 2.072(3) and 2.081(3) Å and a C–Ge–C angle of 99.95(10)°. The closest Ge–Ge contact of 6.29 Å is much greater than the ~4.4 Å expected for a van der Waals interaction,¹⁴ indicating that there is no Ge–Ge bonding in this structure. For the known σ -bonded monomeric alkyl or aryl germylenes,^{2a,g,3c,d,8} the Ge–C bonds lengths range between 1.80 and 2.05 Å and the C–Ge–C angle varies from 85.9 to 111.4°. Within this class of compounds, **1** has the longest Ge–C bond encountered to date and the least obtuse C–Ge–C angle. *Ab initio* calculations performed by Lappert et al.^{2g} and by Grev and Schafer¹⁵ on simple alkyl germylenes showed that the contraction of the bond angle and the simultaneous lengthening of the Ge–C bond is consistent with increased p-character of the Ge–C bond.

In all three fluoroaryl M(II) compounds isolated to date,^{12,13} the aryl rings are twisted from coplanarity (Ge, 89.5°; Sn, 89.9°; Pb, 111.6°) and four close M–F contacts are observed (Figure 2). Ge–F contacts in **1** are observed at 2.554(1) (Ge–F8), 2.790(1) (Ge–F1), 2.566(2) (Ge–F11), and 2.782(2) Å (Ge–F18). These distances are intermediate between the van der Waals radii estimated by Bondi (Ge–F = 3.66 Å)¹⁴ and a covalent Ge–F bond (1.86 Å). A comparison of the Ge–F contact distances with those published previously for the Sn and Pb homologues reveals that essentially the same degree of interaction is observed for each set of M–F bonds. Inspection of the C–F bond lengths for all three homologous compounds also reveals a slight lengthening (~0.02–0.03 Å) of the C–F bond for those

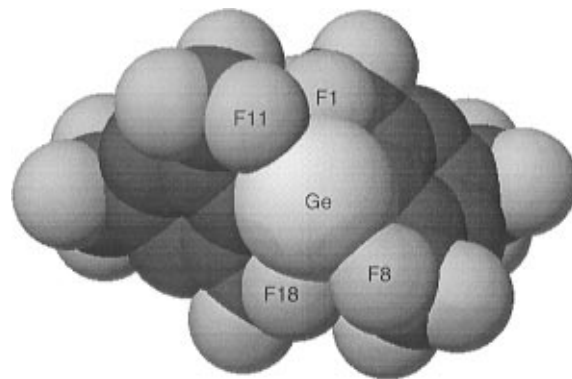


Figure 2. Space filling model of Ge[2,4,6-(CF₃)₃C₆H₂]₂ (**1**) highlighting the four Ge–F close-contacts that play a crucial role in stabilizing this molecule.

fluorines in close contact with the group 14 metal. Grützmacher et al. were able to follow the M–F interaction for the Sn analogue using variable-temperature ^{119/117}Sn–¹⁹F NMR and demonstrated that the coupling constant increased as the temperature was lowered.¹³

The accessible repertoire of stable alkyl and aryl germylenes, previously known only for five extremely encumbered complexes, has now been enriched with the discovery of Ge[2,4,6-(CF₃)₃C₆H₂]₂ (**1**). Despite being only slightly larger in size than bis(mesityl)germylene, known to be stable only in oligomeric form,¹⁶ **1** is a stable monomer, yet still has the more robust Ge–C ligation to help prevent side-reactions of the ligand during transition-metal complex studies.¹⁷ All previously isolated germylene complexes contained heteroatoms capable of donating lone pairs of electrons into the empty germanium p-orbital or multiple bulky electron-donating groups on the alkyl or aryl ligand. By way of contrast, **1** contains strong electron-withdrawing groups on the aryl rings, demonstrating that the supporting ligands need not be strong electron donors to stabilize the Ge(II) fragment. The *ortho*-trifluoromethyl groups do provide a critically important weak internal base to help stabilize the complex. Our ongoing syntheses of transition-metal–germylene complexes containing this ligand and the reactivity of the new complexes will be reported in due course.¹⁸

Experimental Section

All procedures utilized air-free techniques and dry, deoxygenated solvents.¹⁹ [2,4,6-Tris(trifluoromethyl)phenyl]lithium²⁰ and GeCl₂-dioxane²¹ were prepared according to literature procedures. ¹H (300 MHz), ¹⁹F (282 MHz), and ¹³C NMR (90.6 MHz) spectra were taken in C₆D₆ and chemical shifts referenced to the residual protons of C₆D₆ at 7.15 ppm, CFCl₃

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in C_6D_6 at 0.0 ppm, and the natural abundance ^{13}C in C_6D_6 at 128.0 ppm, respectively. IR spectra were taken using a Nicolet 5DXB spectrometer. UV/vis spectra were taken using an HP8450A diode array spectrometer.

Ge[2,4,6-(CF₃)₃C₆H₂]₂ (1). A diethyl ether solution of [2,4,6-tris(trifluoromethyl)phenyl]lithium (12 mmol in 38 mL of diethyl ether) was added dropwise to a 0 °C solution of GeCl₂·dioxane (1.10 g, 4.75 mmoles) in 25 mL of ether over a period of 5 h. The mixture was allowed to warm to 20 °C and stirred for one additional hour. All volatiles were removed *in vacuo*, 10 mL of pentane was added, and the insoluble salts were filtered away. An additional 5 mL of pentane was added, the solution was cooled to -78 °C, and the resulting orange-yellow powder (2.2 g, 85% pure) of crude germylene was isolated via a cold filtration. Sublimation of the solid at 30 °C to an 11 °C probe gave a yellow, crystalline, analytically pure product (1.2 g, 41%). ¹H NMR (C_6D_6): δ 7.71 (s, 4H, *meta-CH*). ¹³C NMR (C_6D_6): δ 165.29 (s, *ipso-C*), 135.59 (q, *para-C*, ²*J*_{F-C} = 36.1 Hz), 132.51 (q, *ortho-C*, ²*J*_{F-C} = 34.3 Hz), 126.35 (m, *meta-C*), 125.60 (q, *ortho-CF*₃, ¹*J*_{F-C} = 277 Hz), 122.96 (q, *para-CF*₃, ¹*J*_{F-C} = 273 Hz). ¹⁹F NMR (C_6D_6): δ -56.56 (s, 12F, *ortho-CF*₃), -63.31 (s, 6F, *para-CF*₃). IR (Nujol): ν 1834 (w), 1623 (m), 1574 (w), 1300 (vs), 1279 (vs), 1202 (vs), 1152 (vs), 1131 (vs), 913 (s), 850 (s), 688 (s) cm⁻¹. UV-vis (hexane): λ_{max} 374 nm (ϵ = 1300 L·mol⁻¹·cm⁻¹). MS (EI 70 eV): *m/z* 617 (M - F). Anal. Calcd for C₁₈H₄F₁₈Ge: C, 34.06; H, 0.64. Found: C, 34.20; H, 0.89.

X-ray Data Collection, Structure Determination, and Refinement of Ge[2,4,6-(CF₃)₃C₆H₂]₂ (1). A crystal was selected with dimensions of 0.40 × 0.38 × 0.20 mm, space group *P2₁/c*, *a* = 12.538(1) Å, *b* = 13.434(1) Å, *c* = 11.775(1) Å, β = 92.71(1)°, *V* = 1981.1(3) Å³, *Z* = 4, μ (Mo K α) = 1.147 mm⁻¹, 3899 reflections measured, $2\theta_{max}$ = 52°, *T* = 178 K, empirical absorption correction (XABS2), 3899 unique reflections, refined in full-matrix on *F*². All non-hydrogen atoms were anisotropically refined, with H atoms in idealized positions. *R*1 = 0.030, *wR*2 = 0.062 (*I* > 2 σ *I*); *R*1 = 0.047, *wR*2 = 0.064 (all data).

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Supporting Information Available: Tables of complete bond lengths and angles, atomic coordinates, and isotropic and anisotropic thermal parameters and ORTEP diagrams (9 pages). Ordering information is given on any current masthead page.

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