o-(Trifluoromethyl)aryl Interactions and Stabilization in Hypervalent Germanium Compounds

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A series of *o*-(trifluoromethyl)phenyl-substituted germanes have been synthesized to study the potential for weak Ge−F bonding interactions. $^{1}H-^{19}F$ coupling constants in these compounds range between 2 and 5 Hz. These coupling magnitudes are consistent with previously reported literature examples in ^{19}F and multinuclear NMR spectra for derivatives of the $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ ligand. Solid-state structural characterization of these germanes consistently reveals Ge−F contacts at 2.8−2.9 Å, midway between the longest single bond and the longest expected van der Waals contact. For the simple unsymmetrical catenate, $[3,5\text{-}(CF_3)_2C_6H_3]_2Ge(H)Ge(H)[2,4,6\text{-}(CF_3)_3C_6H_2]_2$ (**4**), there are close contacts to *both* germanium atoms from the *ortho*-CF_3 groups. **4** is not otherwise sterically constrained to force distal, intramolecular contacts, and thus a weak Ge−F bonding interaction is invoked for the entire series of *o*-(trifluoromethyl)aryl-substituted tetravalent Ge compounds. The synthetic approaches to these germanes make extensive use of Ge(II) precursors, employing both catalytic hydrogenation and insertion reactions of germylenes.

Introduction

The tris(2,4,6-trifluoromethyl)phenyl ligand has been employed to stabilize a wide variety of unusual, σ-bonded main group and transition metal organometallic compounds.[1] Several compounds of the group 14 elements with this ligand have appeared.[2] The combination of unusually short M−F contacts observed in the solid state between the fluorines of the CF_3 groups and the central metal atom to which this ligand is attached and the highly electron-withdrawing character of the ligand appears to be the major contributor to the stabilizing properties typically observed. The ligand provides an interesting foil to the more common classes of sterically bulky and electron-rich σ-bonded ligands[3] and multidentante pincer ligands,[4] often employed to stabilize main group complexes. The only carbon σ-bonded germanium derivative of this ligand, $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$, was first noted in solution by Edelmann[1e] and subsequently isolated and structurally characterized by Bender et al.[5] The germylene was noted to have all four of the *ortho*-CF_3 groups positioned such that a fluorine from each was well within the sum of the van der Waals radii of germanium and fluorine. Two Ge−F contacts were noted at ∼2.6 Å, and two longer contacts were also present at ∼2.8 Å. We wished to further explore the nature of these close contacts in tetravalent germanium species, particularly in germane catenates, where contacts could be made to Ge atoms not directly bonded to the $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ substituent. Reactions of digermanes have generated significant interest recently.[6,7]

Simpler phenyl analogues of $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ containing only one or two CF_3 groups have also been studied, though in much less experimental detail. For the 2-(trifluoromethyl)phenyl and bis(2,6-trifluoromethyl)phenyl groups,[8,9] there is a body of experimental evidence showing weak intramolecular bonding interactions between the central metal atom and the ligand

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(1) (a) Carr, G. E.; Chambers, R. D.; Holmes, T. F.; Parker, D. G. *J. Organomet. Chem.* **1987**, *325*, 13. (b) Scholz, M.; Roesky, H. W.; Stalke, D.; Keller, K.; Edelmann, F. T. *J. Organomet. Chem.* **1989**, *366*, 73. (c) Schluter, R. D.; Cowley, A. H.; Atwood, D. A.; Jones, R. A.; Bond, M. R.; Carrano, C. J. *J. Am. Chem. Soc.* **1993**, *115*, 2070. (d) Edelmann, F. T. in *Inorganic Fluorine Chemistry, Toward the 21st Century;* Thrasher, J. S., Strauss, S. H., Eds.; ACS Symposium Series 555; 1994; p 309. (e) Edelmann, F. T. *Main Group Metal Chem.* **1994**, *17*, 67.

(2) (a) Grutzmacher, H.; Pritzkow, H.; Edelmann, F. T. *Organometallics* **1991**, *10*, 24. (b) Brooker, S.; Buijink, J.-K.; Edelmann, F. T. *Organometallics* **1991**, *10*, 25. (c) Lay, U.; Pritzkow, H.; Grutzmacher, H. *J. Chem. Soc., Chem. Commun.* **1992**, 260. (d) Buijink, J.-K.; Noltemeyer, M.; Edelmann, F. T. *J. Fluor. Chem.* **1993**, *61*, 51. (e) Braddock-Wilking, J.; Schieser, M.; Brammer, L.; Huhmann, J.; Shaltout, R. *J. Organomet. Chem.* **1995**, *499*, 89. (f) Klinkhammer, K. W.; Fassler, T. F.; Grutzmacher, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 124.

(3) (a) Tokitoh, N.; Matsuhashi, Y.; Shibata, K.; Matsumoto, T.; Suzuki, H.; Saito, M.; Manmaru, K.; Okazaki, R. *Main Group Metal Chem.* **1994**, *17*, 55. (b) Lappert, M. F. *Main Group Metal Chem.* **1994**, *17*, 183. (c) Driess, M.; Grutzmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828.

(4) For example see: (a) Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New J. Chem.* **1997**, *21*, 751. (b) Carre, F.; Chuit, C.; Corriu, R. J. P. *Organometallics* **1995**, *14*, 2754.

(5) Bender, J. E.; Banaszak Holl, M. M.; Kampf, J. W. *Organometallics* **1997**, *16*, 2743.

(6) (a) Pigarev, S. D.; Bravo-Zhivotovskii, D. A.; Kalokhman, I. D.; Vyazankin, N. S.; Voronkov, M. G. *J. Organomet. Chem.* **1989**, *369*, 29. (b) Castel, A.; Riviere, P.; Satge, J.; Desor, D.; Ahbala, M.; Abdenadher, C. *Inorg. Chim. Acta* **1993**, *212*, 51. (c) Chaubon-Deredempt, M. A.; Escudie, J.; Couret, C. *J. Organomet. Chem.* **1994**, *467*, 37.

(7) Baines, K. M.; Stibbs, W. G. *Coord. Chem. Rev.* **1995**, *145*, 157.

10.1021/om980430m CCC: $15.00

CF_3 group. Butters et al. and Fernandez et al. noted short M−F contacts in their structural studies of the $[2\text{-}(CF_3)C_6H_4]-$ ligand.[8d,h] Multinuclear NMR experiments have been used to characterized this interaction, and there have been two papers applying ^{119}Sn Mossbauer spectroscopy.[8a,9a] A large literature on the long-range coupling behavior of $^{19}F-X$ (>4 bonds) indicates that the magnitudes can be large (>2.0 Hz); however, they are very sensitive to interatomic separation and orientation. The sensitivity of the couplings to direct F−X contacts has lead some workers in the field to describe the couplings as a “through-space” interaction.[10] Braddock-Wilking and co-workers conducted a detailed multinuclear NMR study of two silicon molecules closely related to the species reported in this paper: $[2,4,6\text{-}(CF_3)_3C_6H_2]_2SiH_2$ and $[2,4,6\text{-}(CF_3)_3C_6H_2]_2SiFH$. The nominal five-bond H−F couplings between the CF_3 groups and Si−H moieties were found to be 5.0 and 4.6 Hz, respectively, perhaps larger than would be expected for coupling nuclei separated by five bonds that are not otherwise fixed close in space.[2e,10] Yet, these couplings are considerably smaller than the $^2J_{H-F}$ coupling of 51 Hz observed for the F−Si−H of $[2,4,6\text{-}(CF_3)_3C_6H_2]_2SiFH$. In a report on the use of the $[2,4,6\text{-}(CF_3)_3C_6H_2]$ substituent to stabilize the first known iminoarsine complex $[2,4,6\text{-}(CF_3)_3C_6H_2]As{=}N[2,4,6\text{-}(CF_3)_3C_6H_2]$, Roesky and co-workers found $^{19}F-^{19}F$ coupling constants of 4.2 Hz.[11] The coupling ^{19}F nuclei of the *ortho*-CF_3 groups are nominally nine bonds apart, yet the six-bond *ortho*−*para* CF_3 coupling is not seen. Empirically, ^{19}F NMR spectra for compounds of $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ often show coupling magnitudes and temperature dependence consistent with a through-space, not through-bond, interaction. The evidence to date suggests against classifying couplings such as those described above as purely classical through-bond interactions. However, no consistent alternative description has been introduced into the literature.

Here we present a system of germanium small molecules, synthesized as structural models for the development of ligand-based approaches to the physical properties of group 14 polymers. A number of methods for synthesizing germanium organometallics is demonstrated, based mostly on novel strategies for the use of the Ge(II) state as a Ge(IV) synthon. The emphasis is on *o*-(trifluoromethyl)aryl substituents that bring a CF_3 group in close proximity to the group 14 element atom (Figure 1). The CF_3 groups exhibit strong influences that are electronically inductive, sterically hindering, and weakly bonding. *Ortho*-CF_3 substitution can provide opportunities for such hypercoordination and potentially create novel tertiary structures in polygermanes through distal, intramolecular Ge−F contacts.

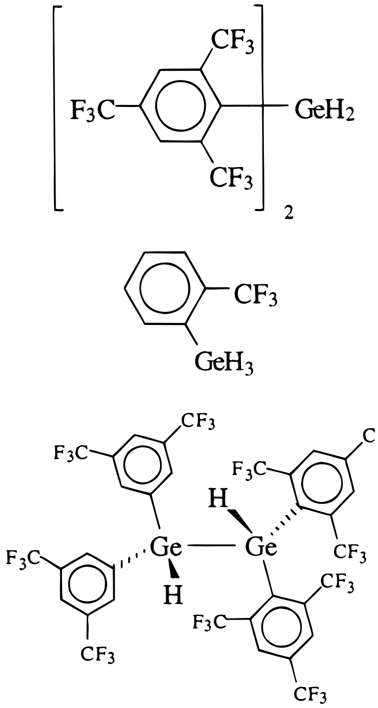

Figure 1. *o*-(trifluoromethyl)arylgermanes **1**, **2**, and **4**.

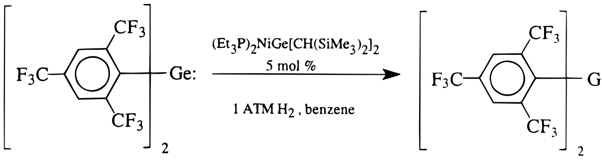

Figure 2. Synthesis of **1** via catalytic hydrogenation of $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$.

Results

$[2,4,6\text{-}(CF_3)_3C_6H_2]_2GeH_2$ (**1**) was synthesized via an application of our previously published metal-catalyzed hydrogenation method (Figure 2).[12] In this particular instance, $Ni(COD)_2$ cannot be used as a catalyst, since it forms an insoluble precipitate upon reaction with $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$. Phosphine substituents must be used to keep the Ni catalyst in solution. The reaction is thus somewhat slower than for other germylenes, but is still efficient.[12] $[2\text{-}(CF_3)C_6H_4]GeH_3$ (**2**) and $[2\text{-}(CF_3)C_6H_4]GeBr_3$ (**3**) were synthesized by established routes from Grignard reagents and $GeBr_4$.[13] Much like $[3,5\text{-}(CF_3)_2C_6H_3]_2GeH_2$,[14] the overall yields of germane **2** from $GeBr_4$ were low (<25%). It was initially feared that such CF_3-substituted compounds may not give stable Grignard agents, particularly $[2\text{-}(CF_3)C_6H_4]MgBr$, which is intramolecularly positioned for the elimination

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(8) (a) Eaborn, C.; Hornfeld, H. L.; Walton, D. R. M. *J. Organomet. Chem.* **1967**, *10*, 529. (b) Chivers, T.; Sams, J. R. *J. Chem. Soc. (A)* **1970**, 928. (c) Chivers, T. *Can. J. Chem.* **1970**, *48*, 3856. (d) Butters, T.; Scheffler, K.; Stegmann, H. B.; Weber, U.; Winter, W. *J. Organomet. Chem.* **1984**, *272*, 351. (e) Sihler, R.; Werz, U.; Brune, H.-A. *J. Organomet. Chem.* **1989**, *368*, 213. (f) Akianiec, B. C.; Young, G. B. *Polyhedron* **1991**, *10*, 1411. (g) Huber, F.; Preut, H.; Scholz, D.; Schurmann, M. *J. Organomet. Chem.* **1992**, *441*, 227. (h) Fernandez, J. M.; Lembrino-Canales, J. J. *Monatsh. Chem.* **1995**, *126*, 129. (i) Driess, M.; Pritzkow, H.; Reisgys, M. *Chem. Ber.* **1996**, *129*, 247.

(9) (a) Bigwood, M. P.; Corvan, P. J.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7643. (b) Escudie, J.; Couret, C.; Ranaivonjatovo, H.; Lazraq, M.; Satgé, J. *Phosphorus, Sulfur, Silicon, Relat. Elem.* **1987**, *31*, 27. (c) Kodaira, K.; Okuhara, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1625.

(10) (a) Emsley, J. W.; Phillips, L.; Wray, V. *Fluorine Coupling Constants*; Pergamon Press: Elmsford, NY, 1977. (b) Schaefer, T.; Sebastian, R.; Veregin, R. P.; Laatikainen, R. *Can. J. Chem.* **1982**, *61*, 29. (c) Burgess, D. A.; Finn, M. F.; Jordan, D.; Rae, I. D.; Walters, B. D. *Aust. J. Chem.* **1984**, *37*, 1769. (d) Kira, M.; Tokura, S. *Chem. Lett.* **1994**, 1459.

(11) Ahleman, J. T.; Kunzel, A.; Roesky, H. W.; Noltemeyer, M.; Markovskii, L.; Schmidt, H.-G. *Inorg. Chem.* **1996**, *35*, 6644.

(12) Litz, K. E.; Bender, J. E.; Banaszak Holl, M. M.; Kampf, J. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 496.

(13) Tabern, D. L.; Orndorff, W. R.; Dennis, L. M. *J. Am. Chem. Soc.* **1925**, *47*, 2039.

(14) Bender, J. E.; Litz, K. E.; Giarikos, D.; Wells, N. J.; Banaszak Holl, M. M.; Kampf, J. W. *Chem. Eur. J.* **1997**, *3*, 1793.

of MgBrF. However, the low yields obtained in some steps of these preparations are consistent with yields normally obtained for Grignard alkylations of $GeBr_4$ with unfunctionalized aliphatic groups.[13,14] Previous work with fluorinated organometallics generally supports the chemical robustness of the aryl−CF_3 functionality observed here;[1b,8i,15] however, there have been recent reports of CF_3 group degradation in silicon compounds.[2d,e,16]

Insertion reactions of both stable and transient germylenes to form new Ge−Ge and Ge−Si bonds have been studied by several groups recently.[17] We have successfully employed this chemistry in the synthesis of unsymmetrical digermanes **4** and **5**. The reactions were carried out using the known, stable germylene complexes $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$ and $[(Me_3Si)_2CH]_2Ge$ as substrates.[5,18] Neither **4** nor **5** exhibited photosensitivity under ambient conditions.

Discussion

A primary characterization tool for this series of *o*-(trifluoromethyl)aryl germanes has been multinuclear (^{19}F and ^{1}H), variable-temperature NMR. Over this range of compounds, certain general trends are observed in the NMR spectra. The number of CF_3 groups coupling to the Ge−H units are always the maximum possible for the system. Complex **2**, which contains only a single *ortho*-CF_3 group, gives a quartet for the GeH_3 protons ($J_{F-H} = 5.2$ Hz) very similar in magnitude to the couplings previously reported for similar silicon compounds by Braddock-Wilking et al.[2e] Once again, the question arises regarding the mechanism of the coupling. Is an interaction of this magnitude consistent with a classical $^5J_{F-H}$ coupling constant? Perhaps it should be considered as a coupling mediated by the weak Ge−F interaction and therefore better described as a $^2J_{F-H}$ coupling constant. Comparison to other coupling constants present in the same molecule is informative. The aromatic protons *ortho*, *meta*, and *para* to the CF_3 group give rise to the possibility of additional $^4J_{F-H}$, $^5J_{F-H}$, and $^6J_{F-H}$ couplings all within the same molecule. This internal comparison is particularly useful because the aromatic protons in question are geometrically constrained so that no close contacts can occur with the CF_3 group; however, they are also located on the same aromatic ring system, so electronic communication of the coupling should be at least as good as that to germane hydrogen. Although some fine structure exists on the quartet observed for the CF_3 group in the ^{19}F NMR spectrum, the coupling constants between the fluorine and the aromatic ring hydrogen atoms are <0.5 Hz, suggesting that the Ge−F close contacts likely play an important role in the 5.2 Hz coupling constant observed between CF_3 and GeH_3 groups. Comparison to *o*-(trifluoromethyl)toluene, which exhibits a quartet ($^5J_{F-H} = 1$ Hz) coupling between the CF_3 and CH_3 groups,[19] is also instructive. This complex has the identical through-bond coupling path except for the replacement of germanium by carbon. The observation of a greatly reduced magnitude for the coupling constant further supports the argument that the Ge−F close contacts play a key role in the observed coupling constants for the germane complexes. Given the large effect the Ge−F interactions appear to cause in the magnitude of the coupling constants, we believe that assigning this interaction as a five-bond coupling is misleading. Therefore, we will use the previously adopted practice of simply referring to these couplings as J_{F-H}.[2]

Compound **1** has four CF_3 groups present, and a 13-line spectrum is observed ($J_{F-H} = 5.2$ Hz) centered at 5.79 ppm. Not only is maximum coupling observed, but also rapid exchange by all groups capable of interacting. Using VT NMR in toluene-d_8, an attempt was made to observe the temperature dependence of the $^{19}F-^{1}H$ coupling constants for molecules **1**, **2**, and **4**. However, upon cooling to −80 °C, the same multiplicities and magnitude of coupling constants were observed. Similar room-temperature NMR spectra were observed for analogous silicon compounds synthesized by Edelmann et al. and Braddock-Wilking et al.: $[2,4,6\text{-}(CF_3)_3C_6H_2]_2SiH_2$ and $[2,4,6\text{-}(CF_3)_3C_6H_2]_2SiF_2$.[2d,e] These compounds showed the same rapid exchange behavior as well, averaging the four *ortho*-CF_3 groups to give 13-line spectra for the proton or fluorine nuclei to which the CF_3 groups are coupled.

The multinuclear VT NMR study of Grutzmacher et al. on $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Sn$ showed a weak temperature dependence for the magnitude of the $^{19}F-^{117}Sn$ and $^{19}F-^{119}Sn$ couplings.[2a] The magnitude of the change seen for the $^1J_{Sn-F}$ coupling of $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Sn$ was only 0.5%/10 °C, an amount we could not reliably resolve for the much smaller magnitude J_{F-H} in **1**, **2**, or **4**. This study provides additional direct evidence that the coupling magnitudes in these $[2,4,6\text{-}(CF_3)_3C_6H_2]$-substituted compounds are sensitive to interatomic separation (through-space or weak F−E bond) and are not simply classical through-bond couplings. A simultaneous differentiation between the four CF_3 groups present on $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Sn$ was not reported in the VT experiment; Schluter et al. failed to freeze out conformations in an attempt at low-temperature ^{19}F NMR studies of In and Ga derivatives of $[2,4,6\text{-}(CF_3)_3C_6H_2]^-$.[1c]

The $^3J_{H-H}$ coupling values for the unsymmetrically substituted digermanes **4** and **5** (4.2 and 7.6 Hz, respectively) are smaller than the $^3J_{HSiGeH}$ coupling of 11 Hz previously reported by Baines et al.[20] The couplings for the Ge−H resonances of **4** are observed as broad multiplets (expected triskadectet of doublets), which we have not been able to resolve sufficiently by selective decoupling. A further comparison of the long-range coupling magnitudes can be made using the CF_3 groups in the *meta* positions in complexes **4** and **5**. The *meta*-CF_3 groups form no close intramolecular contacts, and the nominal five and six through-bond couplings are < 0.1 Hz. Similar to the case described for **2**, the

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(15) Porwisiak, J.; Schlosser, M. *Chem. Ber.* **1996**, *129*, 233.

(16) Weidenbruch, M.; Will, P.; Marsmann, H.; Peters, K.; von Schering, H. G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 15, and references therein.

(17) (a) Haberle, K.; Drager, M. *J. Organomet. Chem.* **1986**, *312*, 155. (b) Baines, K. M.; Cooke, J. A.; Vittal, J. J. *J. Chem. Soc., Chem. Commun.* **1992**, 1484.

(18) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

(19) Tordeux, M.; Langlois, B.; Wakselman, C. *J. Chem. Soc., Perkin Trans.* **1990**, 2293.

(20) Baines, K. M.; Groh, R. J.; Joseph, B.; Parshotam, U. R. *Organometallics* **1992**, *11*, 2176.

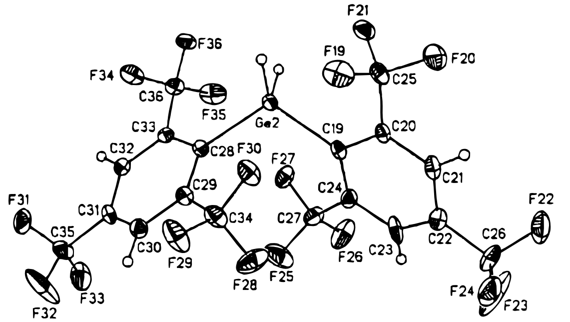

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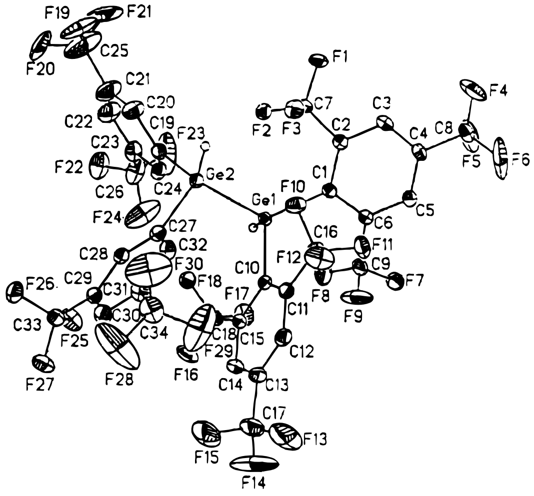
Figure 3. ORTEP of **1** (50% probability). Bond lengths (Å) and angles (deg) for molecule 2: Ge2−C28 = 2.000(5); Ge2−C19 = 2.003(5); C19−Ge2−C28 = 112.5(2); Ge2−F27 = 2.841(3); Ge2−F30 = 2.841(3); Ge2−F36 = 2.943(3); Ge2−F21 = 2.955(3). Average bond length lengths (Å) and angles (deg) for all three molecules: Ge−C = 1.998(5); C−Ge−C = 113.4(8).

Table 1. Crystallographic Data for 1 and 4

	1	4
formula	$C_{18}H_6F_{18}Ge$	$C_{34}H_{12}F_{30}Ge_2$
a, Å	21.2602(9)	21.7553(2)
b, Å	18.0529(7)	10.90780(10)
c, Å	16.4813(7)	16.5229(2)
a, deg	90	90
b, deg	106.3010(10)	102.0390(10)
g, deg	90	90
V, Å^3	6071.4(4)	3834.69(7)
Z	12	4
fw	3696	2200
space group	$P2_1/c$	$P2_1/c$
T, K	133	148
l, Å	0.710 73	0.710 73
r_{calc}, g cm^{-3}	2.090	1.967
R1	0.0773	0.0393
wR2	0.1630	0.0907

nominal five-bond couplings are of sufficient magnitude to detect when a Ge−F close contact effectively shortens the path to a two-bond interaction. However, classical five-bond couplings are not observed in the absence of the Ge−F close contact.

Single-crystal X-ray structure determinations were performed on compounds **1** and **4** (see Table 1). For the previously reported [2,4,6-$(CF_3)_3C_6H_2$]$_2$Ge,[5] four Ge−F contacts were seen, two at 2.6 Å and two at 2.8 Å. So far, this is the only germanium derivative of the [2,4,6-$(CF_3)_3C_6H_2$]− ligand for which we have seen four close contacts and the only one for which contacts at 2.6 Å are seen. In compound **1** (Figure 3), a tetravalent analogue of [2,4,6-$(CF_3)_3C_6H_2$]$_2$Ge with the smallest possible additional groups attached (H), only two contacts are retained at 2.8 Å. In another compound synthesized in our laboratory, $(Ph_3P)_2$NiGe[2,4,6-$(CF_3)_3C_6H_2$]$_2$,[21] the [2,4,6-$(CF_3)_3C_6H_2$]$_2$Ge germylene exists in a dative bonding mode, albeit a very sterically crowded one, and it also retains only two close Ge−F contacts at 2.8 Å. Two additional contacts for **1** and $(Ph_3P)_2$NiGe[2,4,6-$(CF_3)_3C_6H_2$]$_2$, which are also within the sum of the van der Waals radii (3.66 Å),[22] are seen at 2.943 and 2.957 Å and 3.003 and 3.057 Å, respectively. Another major comparison between the Ge(II) [2,4,6-$(CF_3)_3C_6H_2$]$_2$Ge and **1** is the C−Ge−C angle, which is 99.95(10)° in the germylene and 113.4(8)° in **1**.[23] Steric repulsions in this Ge(IV) species easily explain the deviation from 109.4°. This angle has only opened up slightly for $(Ph_3P)_2$NiGe[2,4,6-$(CF_3)_3C_6H_2$]$_2$ to 104.3°, consistent with the expected retention of Ge(II) character in this molecule.[18,24]



4

Figure 4. ORTEP of **4** (50% probability). Bond lengths (Å) and angles (deg): Ge1−Ge2 = 2.4352(3); Ge2−C19 = 1.942(2); Ge2−C27 = 1.952(2); Ge1−C1 = 2.012(2); Ge1−C10 = 2.001(2); C19−Ge2−C27 = 109.04(10); C1−Ge1−C10 = 112.42(9); C27−Ge2−Ge1−C10 = 17.58(10); C19−Ge2−Ge1−C1 = 98.23(10); Ge1−F10 = 2.837(2); Ge1−F18 = 3.024(2); Ge1−F2 = 3.017(1); Ge2−F2 = 2.947(1).

Like **1**, **4** is also tetravalent, with a C−Ge−C angle of 112.42(9)° on the side of the molecule derived from [2,4,6-$(CF_3)_3C_6H_2$]$_2$Ge (C1−Ge1−C10) and 109.04(10)° on the side derived from [3,5-$(CF_3)_2C_6H_3$]$_2$GeH$_2$ (C19−Ge2−C27). Ge−F contacts are still seen, but in completely different form (Figure 4). Ge1 has a close contact at 2.836(2) Å (F10) and three others at 3.013(2), 3.017(1), and 3.025(2) Å. Ge2 experiences a distal Ge−F contact, from an *ortho*-CF_3 group *leaning* over to contact it at 2.947(1) Å (F2), in preference to the expected Ge−F contact at Ge1 based on the other structurally characterized Ge derivatives described in this paper. The closest contact of F2 to Ge1 is 3.017(1) Å. The hydrogen atoms were located in **4** and lie in the expected tetrahedral positions on Ge1 and Ge2. The closest approach of any fluorine to the hydrogens is 2.44 Å, right on the edge for a weak van der Waals contact (2.65 Å).[22] Two weak intermolecular F−H−Ge contacts are observed at 2.82(3) (H1−F28) and 2.73(3) (H2−F25) Å and five weak intramolecular F−H−Ge contacts of 2.53(3) (H1−F8), 2.64(3) (H1−F17), 2.44(3) (H1−F18), 2.89(3) (H2−F2), and 2.62(3) (H2−F3) Å. Finally, the dihedral angle defined by C27−Ge2−Ge1−C10 is only 17.6°, very close to eclipsed, again suggesting that steric interactions are being overcome to satisfy a lower electronic energy state arising from the Ge−F contact. The two different Ge−F contacts seen in **4** are consistent with the solution NMR data, which also show H−F couplings of differing magnitudes. However, it is also clear from the solution

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[21] Bender, J. E.; Litz, K. E.; Banaszak Holl, M. M.; Kampf, J. W. Submitted.

[22] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[23] The average value for the three independent molecules in the unit cell is given.

[24] Grev, R. S.; Schaefer, H. F. *Organometallics* **1992**, *11*, 3489.

NMR data that these couplings are in systems where the CF_3 interactions are averaged, so the fixed bond lengths obtained in the structure determination of **4** cannot be quantitatively related to the NMR data.

Simple force field calculations (CAChe-Mechanics and Spartan−Merck Molecular Force Field) performed on **1**, **2**, and **4** indicate that the spatial constraints imposed by placing a CF_3 group in the *ortho* position bring the Ge and F to within ∼3.1 Å. This value can be used as an upper bound to rule out any bonding character in contacts of that length or greater which appear otherwise to be van der Waals contacts. In a recent review, Plenio empirically derived 3.0 Å as an upper limit for an assignable Ge−F contact.[25] For **1** and **4**, this qualifies several contacts at <3.0 Å as possible bonding interactions. In particular, the preference for a contact between Ge2 and F2 in **4** at 2.947 Å cannot be explained by steric hindrance or crystal-packing arguments. The very acute dihedral angle seen in **4** between C27−Ge2−Ge1−C10 is predicted by force field calculations to be 35°, twice as great as observed experimentally. As is clearly the case for the more Lewis acidic $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$, both **1** and **4** place their CF_3 groups closer to the Ge centers than is necessary by steric requirements alone. We do not believe that weak F−H intermolecular contacts play a significant role in determining the observed dihedral angle. The contacts appear too long to be considered significant bonding interactions, particularly when compared to the short Ge−F contacts and the presence of comparitively shorter F−H−Ge intramolecular contacts.

The literature of weak-bonding interactions of fluorine-containing molecules has become quite active recently.[25] A system of significant relevance is that of the stabilized Ziegler−Natta catalysts, though here the metal centers are cationic and so have enhanced Lewis acidity toward fluorine.[26] Numerous mononuclear compounds containing the $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ unit have been synthesized, though there are few structurally characterized examples with relevance to **4**. A series of papers published by Roesky and co-workers describes multinuclear derivatives of $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ similar to **4**. $[2,4,6\text{-}(CF_3)_3C_6H_2]Se-Se[2,4,6\text{-}(CF_3)_3C_6H_2]$ was reported, and the crystal data reveal that this compound contains a distal M−F contact.[27] This contact is in fact the shortest Se−F contact in the molecule, at 3.07 Å. Such distal contacts are also seen in the compounds $[2,4,6\text{-}(CF_3)_3C_6H_2]S-Tl\cdot dioxane$ (Tl−F at 3.123 and 3.174 Å)[28] and $[2,4,6\text{-}(CF_3)_3C_6H_2]S-Na\cdot 2THF$ (Na−F at 2.434, 2.436, 2.486, and 2.571 Å).[29] These last two compounds crystallize as ladder polymers, where the contacts appear to provide considerable stabilization of the chains. These compounds also leave the CF_3 group with no choice as to which Lewis basic site it may choose to interact with; the relevance here is the ability to conquer conformational flexibility to form the M−F contact. The Se dimer, being homonuclear and essentially a covalent molecule, is most relevant. **4** and $[2,4,6\text{-}(CF_3)_3C_6H_2]Se-Se[2,4,6\text{-}(CF_3)_3C_6H_2]$ certainly have many other conformations available to them that would not involve M−F contacts. There are several other examples of such distal contacts in the polynuclear literature of the $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ substituent, though these remaining examples only involve single metal centers.[30]

Conclusions

The weak Ge−F interaction highlighted by the set of complexes presented herein is quite intriguing. For cases such as **4**, the steric demands of the $[2,4,6\text{-}(CF_3)_3C_6H_2]-$ substituent alone cannot account for such contacts. These data are also consistent with a large amount of previously published work on *o*-(trifluoromethyl)aryl-substituted compounds showing that such groups stabilize unusual low-valent main group complexes, complexes that are not otherwise stable in the absence of *ortho*-CF_3 groups. The series of new germanes presented have F−H coupling constant magnitudes that are highly dependent upon the presence or absence of close Ge−F contacts. Although the couplings mediated by the contacts are significantly weaker than analogous couplings involving more standard covalent bonds, direct comparisons within the set of complexes also show the couplings to be signicantly greater than expected for a classical through-bond pathway. As a prelude to polymerization studies using (trifluoromethyl)aryl-substituted polygermanes, we wished to make a concerted investigation of small molecule model compounds that fills in some of the knowledge gaps existing in the literature of (trifluoromethyl)aryl germanes. The *ortho*-CF_3 group has clearly demonstrated its ability to interact with both the germanium atom to which the ligand is attached as well as neighboring germanium atoms. These interactions hold out the promise of interesting properties in related polygermanes. The excellent thermal stability of these molecules may foreshadow a similar stability being imparted to chains. We are currently pursuing higher level calculations and electronic spectroscopy to examine the electronic effects contributing to the tendency for Ge−F close contacts in these small molecules and in polygermanes.

Experimental Section

All air-free manipulations were carried out using standard vacuum line and drybox techniques. All solvents were distilled from Na/benzophenone just prior to use. $GeBr_4$,[31] $GeCl_2\cdot dioxane$,[32] $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$,[5] $(Et_3P)_2NiGe[N(SiMe_3)_2]_2$,[12] $Ge[CH(SiMe_3)_2]_2$,[18] and $[3,5\text{-}(CF_3)_2C_6H_3]_2GeH_2$[14] were prepared according to literature procedures. $2\text{-}(CF_3)C_6H_4Br$ and Mg

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[25] Plenio, H. *Chem. Rev.* **1997**, *97*, 3363.

[26] For example, see: Karl, J.; Erker, G.; Frohlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 11165, and references therein.

[27] Bertel, N.; Roesky, H. W.; Edelmann, F. T.; Noltemeyer, M.; Schmidt, H. G. *Z. Anorg. Allg. Chem.* **1990**, *586*, 7.

[28] Labahn, D.; Pohl, E.; Herbst-Irmer, R.; Stalke, D.; Roesky, H. W.; Sheldrick, G. M. *Chem. Ber.* **1991**, *124*, 1127.

[29] Brooker, S.; Edelmann, F. T.; Kottke, T.; Roesky, H. W.; Sheldrick, G. M.; Stalke, D.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1991**, 144.

[30] (a) Bertel, N.; Noltemeyer, M.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1990**, *588*, 102. (b) Labahn, D.; Brooker, S.; Sheldrick, G. M.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1992**, *610*, 163. (c) Edelmann, A.; Brooker, S.; Bertel, N.; Noltemeyer, M.; Roesky, H. W.; Sheldrick, G. M.; Edelamnn, F. T. *Z. Naturforsch.* **1992**, *47b*, 305. (d) Labahn, D.; Bohnen, F. M.; Herbst-Irmer, R.; Pohl, E.; Stalke, D.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1994**, *620*, 41. (e) Voelker, H.; Pieper, U.; Roesky, H. W.; Sheldrick, G. M. *Z. Naturforsch.* **1994**, *49b*, 255. (f) Dillon, K. B.; Gibson, V. C.; Howard, J. A. K.; Sequeira, L. J.; Yao, J. W. *Polyhedron* **1996**, *15*, 4173.

[31] Curtis, M. D.; Wolber, P. *Inorg. Chem.* **1972**, *11*, 431.

[32] Viktorov, N. A.; Gar, T. K.; Nikishina, I. S.; Nosova, V. M.; Ivashchenko, D. A.; Mironov, V. F. *Zh. Obshch. Khim.* **1986**, *325*, 13.

turnings were purchased from Aldrich and used as received. ^{1}H NMR spectra were recorded at 400 MHz on a Varian Inova 400 spectrometer and referenced to the residual protons in C_6D_6 at 7.15 ppm, in THF-d_8 at 3.78 ppm and in toluene-d_8 at 2.09 ppm. ^{13}C NMR spectra were recorded at 100.581 MHz and referenced to the natural abundance of ^{13}C in C_6D_6 or THF-d_8 at 128.00 and 67.57 ppm, respectively. ^{19}F NMR spectra were recorded at 376.321 MHz and referenced externally to $CF_3C_6H_5$ in C_6D_6 at −63.73 ppm. IR spectra were recorded on a Nicolet 5DXB spectrometer. UV−vis spectra were recorded on an HP model 8425A diode-array spectrophotometer. Mass spectra were collected on an VG Analytical model 70-S spectrometer. Elemental analyses were performed in-house on a Perkin-Elmer model 2400 analyzer.

$[2,4,6\text{-}(CF_3)_3C_6H_2]_2GeH_2$ (1). A 300 mg (0.473 mmol) sample of $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$ and 30 mg (0.043 mmol) of $(Et_3P)_2NiGe[N(SiMe_3)_2]_2$ were placed in a small, round-bottom flask. A 10 mL sample of benzene was frozen into the flask under vacuum and allowed to thaw under 10+ equiv of H_2 gas at 1 atm. The thawed solution was allowed to stir 16 h, giving a dark brown color. The flask was recharged with H_2 at 1 atm and allowed to stir an additional 16 h. The solvent was then removed under vacuum, taking care not to overdry, as the solid product is highly sublimable at 10^{-3} Torr. Colorless crystals were isolated from the crude solids by sublimation at 25 °C onto a water-cooled probe (165 mg, 55% yield). A crystal suitable for X-ray diffraction was selected from the sublimed material. ^{1}H NMR (C_6D_6): δ 7.76 (s, 4H, *m*-*H*-Ar), 5.79 (triskadectet, 2H, $^2J_{F-H} = 5.1$ Hz, *H*-Ge). ^{1}H NMR (THF-d_8): δ 8.41 (s, 4H, *m*-*H*-Ar), 5.85 (triskadectet, 2H, $^2J_{F-H} = 5.1$ Hz, *H*-Ge). ^{19}F NMR (THF-d_8): δ −55.51 (t, 12F, $^2J_{H-F} = 5.1$ Hz, *o*-C*F*$_3$), −61.95 (s, 6F, *p*-C*F*$_3$). IR (KBr, cm^{-1}): 2186 (Ge−H). CIMS (methane): *m*/*e* 637 $(M - H)^+$, 619 $(M - F)^+$, 357 $(M - C_9H_2F_9)^+$. Anal. Calcd for $C_{18}H_6F_{18}Ge$: C, 33.9; H, 0.95. Found: C, 34.0; H, 1.1.

Structure determination for 1. A crystal was selected with dimensions of 0.08 × 0.16 × 0.18 mm, space group $P2_1/c$, $a = 21.2602(9)$ Å, $b = 18.0529(7)$ Å, $c = 16.4813(7)$ Å, $\beta = 106.3010(10)°$, $V = 6071.4(4)$ Å^3, $Z = 12$, μ(Mo Kα) = 1.684 mm^{-1}, 56 886 reflections measured, $2\theta_{max} = 29.48°$, $T = 133$ K, empirical absorption correction (SADABS), 15 374 unique reflections, refined in full matrix on F^2. All non-hydrogen atoms were anisotropically refined, with H atoms in idealized positions. R1 = 0.0773, wR2 = 0.1630 ($I > 2\sigma I$); R1 = 0.1353, wR2 = 0.1937 (all data).

$[2\text{-}(CF_3)C_6H_4]GeH_3$ (2). A suspension of $LiAlH_4$ (1.00 g, 0.026 mol) in 50 mL of diethyl ether was generated by allowing a pellet to slowly break up with stirring over a period of 4 h at 20 °C under Ar. To this solution was added $2\text{-}(CF_3)C_6H_4\text{-}GeBr_3$ (7.25 g, 0.016 mol) in 10 mL of ether over a period of 30 min. The volume of solution was reduced to 10 mL total and then extracted into a new flask with hexane (2 × 50 mL). The hexane and ether were then removed under vacuum, and the crude oil was further purified by condensing onto a coldfinger under vacuum at −78 °C. **2** was obtained as a colorless, clear liquid in 39% yield (1.34 g). ^{1}H NMR (C_6D_6): δ 7.37 (d, 1H, $J_{H-H} = 3.9$ Hz, *H*-Ar), 7.23 (d, 1H, $J_{H-H} = 4.0$ Hz, *H*-Ar), 6.87 (m, 2H, *H*-Ar), 4.36 (q, $^2J_{F-H} = 5.6$ Hz, Ge*H*$_3$). ^{19}F NMR (C_6D_6): δ −61.48 (q, 3F, $^2J_{H-F} = 5.6$ Hz, C*F*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 138.26 (s), 134.43 (q, $^2J_{F-C} = 30.5$ Hz, *C*-CF$_3$), 131.16 (s), 130.7 (q, $^3J_{F-C} = 5$ Hz, *C*(GeH$_3$), 129.37 (s), 126.08, (q, $^3J_{F-C} = 5.3$ Hz, *C*H−C−CF$_3$), 125.32 (q, $^1J_{F-C} = 274$ Hz, *C*F$_3$). IR (neat, cm^{-1}): 3065 (C−H), 2095 (Ge−H), 1173/1124 (C−F). EIMS (70 eV): 221 $(M - H^{\bullet+})$. CIMS (methane, relative intensity): 238 $(M + CH_4^{\bullet+}$, 9.1). Anal. Calcd for $C_7H_7F_3Ge$: C, 38.1; H, 3.2. Found: C, 37.81; H, 3.18. Overall yield from $GeBr_4$: 23%.

$[2\text{-}(CF_3)C_6H_4]GeBr_3$ (3). $2\text{-}(CF_3)C_6H_4MgBr$ was generated by slowly adding 6.94 g of $2\text{-}(CF_3)C_6H_4Br$ (0.0308 mol) to a suspension of Mg turnings (0.800 g, 0.033 mol) in 50 mL of diethyl ether. The majority of the Mg reacted, and the solution became opaque brown after 3 h. This Grignard solution was then slowly added to a 100 mL diethyl ether solution of $GeBr_4$ (12.2 g, 0.0312 mol) over a period of 1 h and stirred a further 24 h. A brown solution resulted with formation of a salt precipitate. The ether was removed under vacuum, and the crude solids were extracted with 160 mL of hexane. The hexane was removed under vacuum to give 8.4 g of a crude brown oil (59% crude yield). Vacuum distillation at 60 °C gave a clear, colorless liquid in analytical purity (53.5% yield). ^{1}H NMR (C_6D_6): δ 7.75 (d, 1H, $J_{H-H} = 7.2$ Hz, *H*-Ar), 7.12 (d, 1H, $J_{H-H} = 7.6$ Hz, *H*-Ar), 6.75 (t, 1H, $J_{H-H} = 7.2$ Hz, *H*-Ar), 6.68 (t, 1H, $J_{H-H} = 7.6$ Hz, *H*-Ar). ^{19}F NMR (C_6D_6): δ −56.80 (s, 3F, C*F*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 134.93 (s), 132.88 (s), 130.19 (q, $^2J_{F-C} = 31$ Hz, *C*-CF$_3$), 127.17 (s), 123.63 (q, $^1J_{F-C} = 273$ Hz, *C*F$_3$), 120.14 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 134.41 (s), 133.20 (s), 132.77 (q, $^2J_{F-C} = 32.6$ Hz, *C*-CF$_3$), 132.19 (s), 128.14 (q, $^3J_{F-C} = 4.6$ Hz, *C*H−C−CF$_3$), 123.94 (q, $^1J_{F-C} = 274$ Hz, *C*F$_3$). EIMS (70 eV): 439 $(M^{\bullet+})$, 377 $(M - Br^{\cdot+})$. IR (neat, cm^{-1}): 3071 (C−H), 1180/1138 (C−F). Anal. Calcd for $C_7H_4\text{-}Br_3F_3Ge$: C, 18.4; H, 0.8. Found: C, 18.28; H, 0.97.

$[3,5\text{-}(CF_3)_2C_6H_3]_2Ge(H)Ge(H)[2,4,6\text{-}(CF_3)_3C_6H_2]_2$ (4). A 208 mg (0.328 mmol) sample of $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Ge$ and 160 mg (0.328 mmol) of $[3,5\text{-}(CF_3)_2C_6H_3]_2GeH_2$ were refluxed in benzene for 15 h. The solvent was distilled off under vacuum, giving a waxy solid. Side products were sublimed away at 95 °C for 12 h followed by a second sublimation at 120 °C to a water-cooled probe over 2 days, yielding a colorless microcrystalline solid (175 mg, 67% yield). Crystals suitable for X-ray diffraction were grown from slow evaporation of a dilute benzene solution. ^{1}H NMR (C_7D_8): δ 7.81 (s, 4H *o*-C-*H*), 7.74 (s, 4H, *m*-C-*H*), 7.62 (s, 2H, *p*-C-*H*), 6.38 (1H, m, *H*-Ge[2,4,6-(CF$_3$)$_3$C$_6$H$_2$]$_2$), 5.72 (1H, m, *H*-Ge[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_2$). ^{19}F NMR (C_7D_8): δ −57.14 (dd, 12F, $^1J_{F-H} = 5.6$ Hz, $^2J_{F-H} = 1.9$ Hz, *o*-C*F*$_3$), −64.46 (s, 12F, *m*-C*F*$_3$), −65.02 (s, 6F, *p*-C*F*$_3$). Elem. Anal. Calcd for $C_{34}H_{12}F_{30}Ge_2$: C, 36.0; H, 1.1. Found: C, 36.1; H, 1.1.

Structure determination for 4. A crystal was selected with dimensions of 0.20 × 0.32 × 0.38 mm, space group $P2_1/c$, $a = 21.7553(2)$ Å, $b = 10.90780(10)$ Å, $c = 16.5229(2)$ Å, $\beta = 102.0390(10)°$, $V = 3834.69(7)$ Å^3, $Z = 4$, μ(Mo Kα) = 1.742 mm^{-1}, 40 515 reflections measured, $2\theta_{max} = 29.57°$, $T = 148$ K, empirical absorption correction (SADABS), 9906 unique reflections, refined in full matrix on F^2. All non-hydrogen atoms were anisotropically refined, with H atoms in idealized positions. R1 = 0.0393, wR2 = 0.0907 ($I > 2\sigma I$); R1 = 0.0511, wR2 = 0.0980 (all data).

$[(Me_3Si)_2CH]_2Ge(H)Ge(H)[3,5\text{-}(CF_3)_2C_6H_3]_2$ (5). A 235 mg sample of $Ge[CH(SiMe_3)_2]_2$ (0.60 mmol) and 265 mg of $[3,5\text{-}(CF_3)_2C_6H_3]_2GeH_2$ (0.53 mmol) were allowed to stir at 20 °C in hexane for 16 h. The solvent was removed under vacuum; the solids were recrystallized from cold pentane (−78 °C). **5** was obtained as a white, powdery solid after vacuum-drying (305 mg, 68% yield). ^{1}H NMR (C_6D_6): δ 8.12 (s, 4H, *o*-C*H*), 7.73 (s, 2H, *p*-C*H*), 5.31 (d, 1H, $^3J_{H-H} = 7.6$ Hz, *H*-Ge[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_2$), 4.83 (dt, 1H, $^3J_{HGeGeH} = 7.6$ Hz, $^3J_{HGeCH} = 2.4$ Hz, H−Ge[CH(SiMe$_3$)$_2$]$_2$), 0.04 (s, 18H, Si(C*H*$_3$)$_3$), 0.00 (s, 18H, Si(C*H*$_3$)$_3$), −0.19 (d, 2H, $^3J_{HCGeH} = 2.4$ Hz, *H*-C(SiMe$_3$)$_2$). ^{19}F NMR (C_6D_6): δ −67.44 (s, 12F, *m*-C*F*$_3$). ^{13}C {^{1}H} NMR (C_6D_6): δ 140.46 (s, *i*-Ar-*C*H), 135.5 (m, *o*-Ar-*C*H), 131.91 (q, *C*-CF$_3$, $^2J_{F-C} = 33.1$ Hz), 123.81 (q, *C*F$_3$, $^1J_{F-C} = 273.1$ Hz), 123.31 (q, Ar-*C*-C−CF$_3$, $^3J_{F-C} = 4.2$ Hz), 4.67 (s, *C*H(SiMe$_3$)$_2$), 3.20 (s, (*C*H$_3$)$_3$Si), 2.48 (s, (*C*H$_3$)$_3$Si). IR (Nujol, cm^{-1}): 2052, 2003, 1982 (Ge−H). Elem. Anal. Calcd for $C_{30}H_{46}F_{12}Ge_2Si_4$: C, 40.4; H, 5.2. Found, C, 40.0; H, 5.0.

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Supporting Information Available: Complete lists of the crystallographic data for compounds **1** and **4** (27 pages). See any current masthead page for ordering information and Web access instructions.

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