

# Neutral Pentacoordinate Group 14 Compounds with $\beta$ -Diketonato ligands

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A stable neutral pentacoordinate germanium compound substituted with three  $CF_3$  and a dibenzoylmethane ligand was synthesized. Single-crystal X-ray diffraction structure determination proves the presence of two crystallographically independent molecules in the asymmetric unit, one of them deviating somewhat from planarity. Density functional computations show the isolated molecule to be planar, while the computation of a molecule pair yielded a minimum, where the planarity of the two monomeric units differ from each other, with the resulting structure resembling the unit cell in the crystal. Bader analysis revealed this molecule pair to be bound together by hydrogen bonds. The stability of the pentacoordinate bond in this compound is about 23 kcal/mol at the B3LYP/6-31+G\* (31 kcal/mol at the MP2/6-31+G\*//B3LYP/6-31+G\*) level. The stabilizing effect of the trifluoromethyl substituent on the pentacoordinate structure is comparable to that of the fluorine group. Computations on the analogous Si-containing systems reveal similar pentacoordinate structures, even though the relative stabilities of these structures are somewhat different for the two group 14 elements. For example, germanium substituted by three -OEt moieties forms a stable pentacoordinate structure with the acetylacetone (acac) ligand (explaining the role of acac as hydrolysis inhibitor of tetraethoxygermane), while the hypervalent bond of the silicon analogue is unstable at the B3LYP/6-31+ $G^*$  level.

## Introduction

Hypervalent compounds with heavier group 14 elements are known, the first examples of such silicon compounds dating back to the beginning of the 19th century.<sup>1</sup> These compounds are also of contemporary interest (as shown by the rapidly increasing number of publications<sup>2</sup>) due to their reactivity. While many of these hypervalent systems are hexacoordinate,<sup>1,3</sup> pentacoordinate species are also known and their enhanced stability with respect to the analogous carbon compounds has recently been elegantly explained by the different sizes of the central atoms (carbon and silicon).<sup>4</sup> Most of the hypervalent silicon and germanium species, however, either are charged<sup>2</sup> or are often described as zwitterionic compounds.<sup>5–7</sup> In many of the neutral compounds the tetracoordinate group 14 element is loosely complexed by an electron pair donor (among others, see the works of Bassindale and Baukov),<sup>2h,8</sup> as indicated by the 2.3–2.8 Å interatomic distance;<sup>8</sup> thus, the existence of five equally bound moieties can be questioned. For example, in the case of silatranes **1**, with certain substituents a variation of the SiN "bonding" distance from the equilibrium state by

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 $\pm 0.25$  Å has resulted in an energy change of only 1.2 kcal/mol,<sup>9</sup> indicating the weakness of the hypervalent interaction. The ligands of the group 14 elements in the few remaining known neutral pentacoordinate systems are mainly electronegative groups (F, Cl, O, N), such as different amino and phosphino complexes of SiX<sub>4</sub> (X = F, Cl, Br)<sup>10</sup> or **2**,<sup>11</sup> **3**,<sup>12</sup> **4** (R = Cl),<sup>13</sup> **4** (R = ONO<sub>2</sub>),<sup>14</sup> **5** (R' = Cl),<sup>15</sup> **6** (X = F, Cl),<sup>3e</sup> **7**,<sup>16</sup> and real pentacoordinate compounds, where only three

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Scheme 2. Complexes of Interest for Silicon, Gallium, and Germanium Formed with the acac Ligand



Scheme 3. Closed (Hypercoordinate) and Open Forms for the Acetylacetonate Complexes (E:Si, Ge)



carbon atoms are attached to the central group 14 element such as 5 (R' = Me, Ph),<sup>15a</sup> 8,<sup>17</sup> and 9 (R = Ph) are rare.<sup>18</sup>

The aim of the present work was to explore the possibilities of stabilizing pentacoordinate silicon and germanium compounds with at least three carbon substituents. We have selected the bidentate acetylacetone (acac) ligand, which was already used to form a neutral hexacoordinate<sup>19</sup> as well as hexacoordinate ionic<sup>20</sup> complexes (**10**); furthermore, a Ga complex with the acac ligand (**11**) was also reported<sup>21</sup> (Scheme 2). Also, this ligand has been used to synthesize a three-coordinate compound of germanium (**12**).<sup>22</sup> Interestingly, acetylacetonate is also used as an inhibitor in the hydrolysis of tetraethoxygermane when forming GeO<sub>2</sub> nanosheets,<sup>23</sup> and we suspect that this behavior can be explained by the formation of a stabilized pentacoordinate intermediate (see below).

This ligand system has a further advantage, since a direct comparison of the relative energies of the opened (130) and closed forms (13h) provides an estimate for the stability of the hypervalent bond in 13h (Scheme 3). It is worth noting that in most of the stable pentacoordinate structures tridentate ligands were used for complexation.<sup>3g,12-14,24</sup>

#### **Results and Discussion**

In order to assess the stability of the pentacoordinate system with different substituents at the group 14 element, first we have carried out density functional computations at the B3LYP/6-31+G\* level (see Tables 1 and 2 for the germanium and Tables S1 and S2 in the Supporting Information for the silicon species, respectively). We have found recently<sup>3h</sup> that this level of theory provides a conservative estimate of the formation of hypercoordinate silicon-centered systems with respect to experimental observations.<sup>3i,j,15a</sup> As expected, the electronegative substituents stabilize the

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Table 1. B3LYP/6-31+G\* Structural Data (in Å) for the Hypervalent Germanium Species 13h (E = Ge) with Different R Groups  $(R' = H)^{a}$ 



|                                 | R = H | R = Me | $R = CF_3$ | R = F | R = Cl | R = OEt |
|---------------------------------|-------|--------|------------|-------|--------|---------|
| Ge-O <sub>ax</sub>              | 2.579 | 2.744  | 2.189      | 1.972 | 2.042  | 2.089   |
| Ge-O <sub>eq</sub>              | 1.854 | 1.883  | 1.848      | 1.816 | 1.866  | 1.871   |
| $O_{eq}-C_1$                    | 1.312 | 1.307  | 1.309      | 1.300 | 1.302  | 1.301   |
| O <sub>ax</sub> -C <sub>3</sub> | 1.237 | 1.237  | 1.255      | 1.268 | 1.264  | 1.254   |
| $C_1 - C_2$                     | 1.368 | 1.372  | 1.371      | 1.379 | 1.377  | 1.375   |
| $C_2 - C_3$                     | 1.438 | 1.438  | 1.418      | 1.409 | 1.408  | 1.416   |
| $\Delta E$ (kcal/               | +2.0  | +1.4   | -10.9      | -20.5 | -6.1   | -7.5    |
| mol)                            |       |        |            |       |        |         |

<sup>*a*</sup> The relative energies are given with respect to the open forms 130 (E = Ge, R' = H) in kcal/mol.

Table 2. B3LYP/6-31+G\* Structural Data (in Å) for the Hypervalent Germanium Species 13h (E = Ge) with Different R' Groups  $(R = CF_3)^a$ 



|                           | $\mathbf{R}' = \mathbf{H}$ | $\mathbf{R}'=\mathbf{Ph}\left(14\right)$ | $R' = CF_3$ | $R' = CH_3$ |
|---------------------------|----------------------------|--|-------------|-------------|
| Ge-O <sub>ax</sub>        | 2.189                      | 2.038                                    | 2.353       | 2.096       |
| Ge-O <sub>eq</sub>        | 1.848                      | 1.836                                    | 1.826       | 1.841       |
| $O_{eq} - C_1$            | 1.309                      | 1.319                                    | 1.312       | 1.315       |
| $O_{ax} - C_3$            | 1.255                      | 1.280                                    | 1.234       | 1.269       |
| $C_1 - C_2$               | 1.371                      | 1.386                                    | 1.369       | 1.380       |
| $C_2 - C_3$               | 1.418                      | 1.415                                    | 1.439       | 1.419       |
| $\Delta \tilde{E}$ (kcal/ | -10.9                      | -23.1                                    | -13.5       | -16.9       |
| mol)                      |                            |  |             |             |

<sup>*a*</sup> The relative energies are given with respect to the open forms 130 ( $E = Ge, R = CF_3$ ) in kcal/mol.

pentacoordinate structure 13h, and with R = F the pentacoordinate structure becomes more stable than the open-chain isomer 130. The hypercoordinate germanium compounds have an enhanced relative stability with respect to their silicone counterparts in most of the cases; for the heavier analogue the hypercoordinate structure is more stable even for R = Cl. Not only the easily hydrolyzable halogens (note that with di-, tri-, and tetrachlorosilanes the formation of hexacoordinate anionic species was reported<sup>20</sup>) but also the CF<sub>3</sub> group turns out to promote the formation of the hypercoordinate structures in a manner comparable to that of fluorine! The introduction of ethoxy moieties (R =-OEt) on the germanium center also supports the pentavalency; the relative stability of the hypercoordinate form is 7.5 kcal/mol. The stability of this pentacoordinate structure explains the ability of the acac ligand to inhibit the hydrolysis of tetraethoxygermane. Interestingly in the case of the silicon-centered analogue the open chain isomer is more stable (by 6.6 kcal/mol); accordingly, in the hydrolysis reaction of tetraethoxysilane the acac ligand should be a less effective inhibitor. The stability difference between the opened and the closed forms correlates with the axial E-O

bond distance. For the most stable pentacoordinate structures the axial E–O distance (see Ge– $O_{ax}$  in Table 1) is only slightly longer than the equatorial distance (Ge– $O_{eq}$  in Table 1). It is also worth noting that the pairs of C–C and C–O distances tend to equalize as the pentacoordinate character of the silicon or germanium increases, indicating delocalization along the OCCCO framework. Other acetylacetonate complexes of gallium,<sup>21,25</sup> chromium,<sup>26</sup> and lanthanides<sup>27</sup> exhibit a similar bond equalization. According to X-ray crystallographic studies the largest difference between C–O and C–C distances is 0.022 and 0.045 Å for the Lu(III) and Dy(III) complexes,<sup>27</sup> respectively, while the Ga complex 11 is symmetrical.<sup>21</sup>

Since the pentavalency is apparently related to the bonding between the ring carbon atoms, further tuning of the strength of the hypervalent bond should be possible by variation of the substituents of the  $\beta$ -diketonato moiety. For the substituents of the silicon (germanium) we have selected the CF<sub>3</sub> group, which was shown to promote the formation of the hypervalent structures efficiently. The results in Table 2 for the germanium (in Table S2 in the Supporting Information for the silicon) compounds show clearly that the phenyl substitution increases further the stability of the pentacoordinate structure. 13h (E = Ge, R = CF<sub>3</sub>, R' = Ph) is more stable by 23 kcal/mol than its isomer 130 ( $E = Ge, R = CF_3$ , R' = Ph), and this energy difference can be considered as the strength of the hypervalent bond. It is worth noting that at the MP2/6-31+G\*//B3LYP/6-31+G\* level the energy difference between the closed and the opened forms is 31 kcal/ mol. The higher predicted stability of the hypervalent compound at the MP2 level is in agreement with our previous results.<sup>3h</sup> For the analogous silicon compound 13h (E = Si,  $R = CF_3$ , R' = Ph) is more stable by 23.1 kcal/mol than 130 (Table S2), the MP2/6-31+G\*//B3LYP/6-31+G\* stability of the closed form being 23.6 kcal/mol. It is worth noting that the energy difference between 9(R = H) and its isomer with one opened five-membered ring was considerably smaller (8.2 and 13.5 kcal/mol at the HF/6-31G\*\* and MP2/6-31G\*\* levels, respectively).<sup>28</sup> Also, the computed energy difference between an Oacetyl→Si coordinating rotamer of  $XMe_2SiCH_2NAc_2 (X = -OAc, -F, -Cl, -Br, -OCOCF_3)$ with respect to the opened form did not exceed 6 kcal/mol<sup>29</sup> and the QCISD(T)/6-311G\*\*//MP2/6-31G\*+ZPE stability of amino complexes of different substituted silanes even with the most electronegative substituents was less than 5.2 kcal/ mol.<sup>30</sup>

On the basis of the above theoretical results on the synthesizability,<sup>31</sup> **14** (**13h**, E = Ge,  $R = CF_3$ , R' = Ph) was prepared from (CF<sub>3</sub>)<sub>3</sub>GeI and dibenzoylmethane in toluene at -40 °C in the presence of triethylamine as proton acceptor (Scheme 4). The product was isolated after recrystallization from toluene/hexane as moisture-sensitive yellow

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**Figure 1.** Molecular structures and ORTEP<sup>32</sup> representation of the two crystallographically independent molecules of **14** found in the asymmetric unit. The displacement ellipsoids are drawn at the 50% probability level, and heteroatoms are shaded. The upper molecule is **14a**, and the lower molecule is **14b**.

Scheme 4. Preparation of Compound 14



crystals with a yield of 74%. Well formed, pale yellow, prismshaped single crystals of 14 suitable for X-ray diffraction study were obtained by recrystallization from diethyl ether at -30 °C. The diffraction measurement was performed at 100(2) K. Despite the disordered CF<sub>3</sub> groups it was possible to refine the structure to 6.09%. Hydrogen atoms were found on the difference Fourier map.

There are two chemically identical but crystallographically different molecules in the asymmetric unit (Figure 1; crystal data and details of the structure determination are given in the Supporting Information).

The two crystallographically independent molecules differ in their conformation. The six-membered -O-C-C-C-O-Geor-Ge- rings have a mostly delocalized electron system (see also below) shown by the distribution of the bond lengths (Table 3). However, the Ge atom is out of plane of the other five atoms of the ring by 0.588 Å in molecule **14a**, while Ge remains in the plane in molecule **14b** (the distance between Ge and the -O-C-C-C-O- plane is 0.023 Å). The two molecules are shown superimposed in Figure 2 to visualize the conformational difference. The packing arrangement highlighting the molecules of two different conformations is presented in Figure 3.

There is no classic hydrogen bond in the crystal structure. Two weak  $C-H\cdots F$  interactions exist only between the two



Figure 2. Structural overlay of the two molecules in the asymmetric unit showing the conformational difference especially at the Ge atoms. Molecule 14a is green, and molecule 14b is red.



Figure 3. Crystal packing diagram from the *b* crystallographic axis showing the alternating layers of the two conformationally different molecules. Molecule 14a is green, and molecule 14b is red.

moieties (C116–H116···F251 = 0.950 Å, 2.550 Å, 3.384(9) Å, 147.0° and C216–H216···F = 153 0.950 Å, 2.470 Å, 3.361(5) Å, 156.00°). The molecules are arranged in the crystal forming alternating layers of the phenyl rings and the terminal trifluoromethyl groups along the *a* crystallographic axis (Figure 3). The phenyl moieties are not close enough to each other to have a significant  $\pi \cdots \pi$  interaction (C111–C116 and C231–C236 at 3.736(2) Å, C131–C136 and C211–C216 at 3.811(2) Å) because the three terminal CF<sub>3</sub> groups act as spacers. Some of the terminal CF<sub>3</sub> groups have enough free space available in the crystal to be disordered with site occupation factors of 0.670 around C16, 0.6307 around C25, and 0.926 around C26.

The X-ray structure is in good agreement with the computed results (Table 2). The Ge atom remains in the plane in the computed structure for the isolated molecule of 14. Attempts to locate a nonplanar minimum on the B3LYP/  $6-31+G^*$  potential energy surface (starting an optimization from the structure obtained by X-ray crystallography) has failed; only the planar structure was obtained for 14 with different optimization strategies.

Since our attempts at optimizing a nonplanar structure for 14 have failed, we have tried a different approach with the

Table 3. Important Interatomic Distances and Angles of Molecule 14a (Ge out of Plane) and Molecule 14b (Ge in Plane)

|  | measured   | computed <sup>a</sup>                              |  | measured   | computed <sup>a</sup>                              |
|--|--|--|--|--|--|
|  |  | Bond D   | Distances (Å)  |  |  |
| Ge1-O11<br>Ge1-O12<br>O11-C11<br>O12-C13<br>C11-C12<br>C12-C13                         | 1.841(3)<br>1.964(3)<br>1.323(5)<br>1.293(5)<br>1.377(6)<br>1.400(6) | 1.854<br>2.035<br>1.319<br>1.284<br>1.385<br>1.413 | Ge2-O21<br>Ge2-O22<br>O21-C21<br>O22-C23<br>C21-C22<br>C22-C23                         | $1.828(3) \\ 1.967(3) \\ 1.328(4) \\ 1.283(4) \\ 1.372(6) \\ 1.402(5)$ | 1.845<br>2.042<br>1.318<br>1.279<br>1.385<br>1.415 |
| 012 013  | 1.400(0)   | Bond A   | Angles (deg)   | 1.402(3)   | 1.415  |
| O11-Ge1-O12<br>Ge1-O11-C11<br>Ge1-O12-C13<br>O11-C11-C12<br>O12-C13-C12<br>C11-C12-C13 | 87.6(1)<br>128.4(2)<br>126.0(2)<br>123.5(4)<br>122.1(4)<br>122.7(4)  | 85.9<br>133.0<br>129.3<br>123.5<br>122.7<br>122.6  | O21-Ge2-O22<br>Ge2-O21-C21<br>Ge2-O22-C23<br>O21-C21-C22<br>O22-C23-C22<br>C21-C22-C23 | 88.2(1)<br>132.2(2)<br>130.7(3)<br>123.3(4)<br>121.6(3)<br>123.6(4)    | 86.6<br>133.9<br>129.9<br>123.9<br>122.7<br>122.8  |
|  |  | Dihedra  | Angles (deg)   |  |  |
| Ge1-O11-C11-C12  | 16.0(6)  | -14.4  | Ge2-O21-C21-C22  | -2.3(6)  | 3.6  |

<sup>a</sup> Computation refers to the geometric parameters of the optimized "molecule pair" structure.

aim of describing the effects responsible for nonplanarity. We have carried out a B3LYP/6-31G\* geometry optimization for a molecule pair of 14, starting from the solid-state geometry in the crystal (Figure 2). In the optimized structure one of the Ge atoms indeed remained significantly displaced from the six-membered ring (see Table 3), while the deviation from planarity was much less in case of the second molecule. To understand the nature of the interaction, the analysis of the B3LYP/6-31+G\* electron density for the two molecular assemblies (14a and 13b) at the geometry of the crystal structure was carried out by the method developed by Bader.<sup>33</sup> This analysis revealed 11 bond critical points of low electron density (ranging from 0.003 to 0.006 au), all corresponding to F···H interactions. These weak nonclassical hydrogen bonds are likely to be responsible for the special structural features observed in the crystal structure.

For the two oxygens attached to Ge, one is in an apical position, exhibiting a bond length of 1.964 (1.967) Å, while the other one is in an equatorial position, with a bond length of 1.841 (1.828) Å (the data in parentheses refer to the nonplanar molecule 14b). The difference is in agreement with the usual lengthening of the apical bonds in trigonalbipyramidal molecules. For a better understanding of the bonding situation around the germanium (silicon) core, the electron density of 13o and 13h ( $R = CF_3, R' = Ph, E = Si$ , Ge) was analyzed by the Bader method.<sup>33</sup> The results are summarized in Table 4. The C-E electron densities at the critical points are similar for both the opened (130) and closed (13h) forms; furthermore, the values for the axial and equatorial bonds differ only slightly. Among the O-E bonds the one in the opened form exhibits the largest density at the bond critical point, with the relative weakness of the axial bond reflected by the smallest density. This observation is in accordance with the length of the respective bonds given in Tables 2 and S2). The (small) negative Laplacian values indicate that all of the five bonds around germanium and silicon have (polarized) covalent character. It is interesting to

Table 4. Computed Electron Densities (in au/Å<sup>3</sup>) and Their Laplacians for the Open and Hypervalent Forms of 13 ( $R = CF_3, R' =$ Ph. E = Si, Ge)

|         |                   | Е                   | = Si      | E = Ge              |           |  |
|---------|-------------------|---------------------|-----------|---------------------|-----------|--|
| species | bond              | electron<br>density | Laplacian | electron<br>density | Laplacian |  |
| 13h     | O-E <sub>ax</sub> | 0.0795              | -0.0884   | 0.0755              | -0.0605   |  |
|         | $O-E_{eq}$        | 0.1040              | -0.1619   | 0.1137              | -0.1395   |  |
|         | C-E <sub>ax</sub> | 0.1062              | -0.0430   | 0.1117              | -0.0256   |  |
|         | $C-E_{eq}$        | 0.1096              | -0.0411   | 0.1185              | -0.0236   |  |
| 130     | O-E               | 0.1315              | -0.2563   | 0.1321              | -0.1673   |  |
|         | C-E               | 0.1156              | -0.0465   | 0.1248              | -0.0294   |  |

note that for the hitherto investigated hypercoordinate Si complexes large positive Laplacians were reported, <sup>3e,29,30,34</sup> which were considered a consequence of ionic interactions.

The O–Ge–C apical angles in the two molecules are close to each other: 173.4(1)° in molecule **14a** and 172.7(2)° in the planar molecule **14b**. We have investigated computationally the structure with two equatorial Ge–O bonds, which was 10.1 kcal/mol less stable than **14** at the B3LYP/6-31+G\* level, while at the MP2/6-31+G\*//B3LYP/6-31+G\* level an even smaller value (4.1 kcal/mol) was obtained. This has turned out to be a first-order saddle point, which according to an IRC study connects the two (energetically identical) stereoisomeric forms of **14**. This low-energy transition structure allows a facile interconversion of the two structures in solution and indicates a dynamic NMR behavior. Nevertheless, the NMR spectral characteristics at -70 °C did not show any change, in accordance with the low barrier (note the MP2 results).

The <sup>19</sup>F NMR spectrum of **14** shows only a singlet for all fluorine atoms at -56.57 ppm, a slight high-field shift compared to the signals of (CF<sub>3</sub>)GeI (-53.38 ppm). In the <sup>1</sup>H NMR spectrum a singlet appears for the H atom in the

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C11(C12H)C13 framework at 6.42 ppm (for the labeling, see Figure 1). In the <sup>13</sup>C NMR spectrum only a small downfield shift is observed for the C(CH)C framework ( $\delta_{C=O}$  187.42 ppm,  $\delta_{CH}$  95.35 ppm) in comparison to the signals of dibenzoylmethane ( $\delta_{C=O}$  186.55,  $\delta_{CH}$  93.77 ppm). The resonance of the CF<sub>3</sub> groups appears as a septet of a quartet at 130.75 ppm. All these NMR data are in full accordance with the low barrier interconversion of two identical but nonsymmetric structures, obtained from the computations.

The six-membered -O-C-C-C-O-Ge- ring has an apparently highly delocalized electron system according to the single-crystal structural bond lengths, as also concluded from the computed results (see above). This might suggest that the six-membered ring can be aromatic, considering that the Ge center contributes with 0 electrons to the 6- $\pi$ -electron system. Hyperconjugate aromatic systems with different atoms without formal  $p_z$  orbitals (carbon,<sup>35</sup> phosphorus<sup>36</sup>) are known, their aromaticity depending on the electron donor or acceptor properties of the substituents on the saturated center.<sup>35</sup> Nevertheless, the GeO bond lengths in 14 do not show double-bond character, and also the B3LYP/ 6-31+G\* NICS(0) and NICS(1) values (+3.7 and +0.9 ppm, respectively) indicate that no aromaticity is present in the investigated system. Also, the frontier MOs are  $\pi$  orbitals located mainly at the OCCCO fragment without any significant involvement of Ge. The related silicon compound 13h (E = Si, R = CF<sub>3</sub>, R' = Ph) exhibits aromaticity measures similar to those of 14.

#### Conclusions

The bidentate acac ligand and especially its phenyl derivative (dibenzoylmethane) is efficient in complexing Si- and Ge-centered molecules, resulting in neutral pentacoordinate structures. The stabilizing effect of the CF<sub>3</sub> substituents at silicon or germanium is comparable to that of fluorine. With three trifluoromethyl and a bidentate dibenzoylmethane ligand a pentacoordinate germanium-centered molecule could be synthesized and characterized by X-ray crystallography. The resulting structure exhibited somewhat different GeO bond lengths, in agreement with the apical and equatorial arrangement of the two oxygens, while the OCCCO unit exhibits significant delocalization. The stability of the pentacoordinate bond was estimated as 23 kcal/mol, in comparison to the opened isomer. The Laplacians at the bond critical points around the silicon or germanium center indicate polarized covalent bonding. For the tris-(triethoxygermene) center the pentacoordinate complex is stable, while in the case of the silvl analogue the open-chain tetracoordinate system is favored.

### **Experimental Section**

**General Considerations.** All manipulations were performed in flame- or oven-dried glassware under a dry nitrogen atmosphere using standard Schlenk techniques. Toluene, diethyl ether,

triethylamine, and  $C_6D_6$  were dried over sodium/benzophenone. Dibenzoylmethane was dried in vacuo at room temperature for 2 h before use. (CF<sub>3</sub>)<sub>3</sub>GeI was purchased from Aldrich Chemical Co. and used as received.

The <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300.1, 75.5, and 282.4 MHz, respectively, using deuterated solvent ( $C_6D_6$ ) as an internal lock and TMS (<sup>1</sup>H, <sup>13</sup>C) or CFCl<sub>3</sub> (<sup>19</sup>F) as the external standard. Melting points were taken on a Boetius micro melting point apparatus and were uncorrected. Infrared spectra were recorded on a Zeiss Specord IR 75 spectrometer, operating in the region of 4000–400 cm<sup>-1</sup>. IR samples were prepared using Nujol. High-resolution mass spectra were measured on a Varian MAT 8200 mass spectrometer. Elemental analysis determination was performed with an Elementar Vario EL analyzer.

Synthesis of 14. A solution of (CF<sub>3</sub>)<sub>3</sub>GeI (0.813 g, 2.0 mmol) in toluene (10 mL) was added dropwise to a solution of dibenzoylmethane (0.448 g, 2.0 mmol) and triethylamine (0.35 mL, 2.5 mmol) in toluene (10 mL) at -40 °C with stirring over a 1 h period. The reaction mixture was warmed slowly to room temperature and stirred for a further 3 h and then filtered. Removal of volatile materials from the filtrate in vacuo afforded a yellow solid. Recrystallization of the residue from toluene/ hexane at -30 °C yielded the product (0.74 g, 74%) as yellow crystals, mp 111-113 °C. Crystals of X-ray quality were grown from diethyl ether at -30 °C. Anal. Calcd for  $C_{18}H_{11}F_9O_2Ge: C$ , 42.99; H, 2.20. Found: C, 43.08; H, 2.10. <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>):  $\delta$  6.42 (s, 1H, CH), 6.92–6.99 (m, 4H, Ph), 7.06–7.12 (m, 2H, Ph), 7.64–7.71 (m, 4H, Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>):  $\delta$ 95.35 (*C*H), 128.51 (Ph), 128.98 (Ph), 130.75 (qua,  ${}^{1}J_{CF} = 342.4$ Hz, sep,  ${}^{3}J_{CF} = 6.6$  Hz,  $CF_{3}$ ), 134.04 (Ph), 134.70 (Ph), 187.42 (CO) ppm.  ${}^{19}$ F NMR (benzene- $d_{6}$ ):  $\delta$  -56.57 ppm. IR (cm<sup>-1</sup>): 1600 m, 1584 m, 1529 m, 1456 s. EI-MS: m/z 434.986 68 (calcd for C<sub>17</sub>H<sub>11</sub>O<sub>2</sub>F<sub>6</sub><sup>74</sup>Ge 434.987 50) 27.82%, 432.985 10 (calcd for C<sub>17</sub>H<sub>11</sub>O<sub>2</sub>F<sub>6</sub><sup>72</sup>Ge 432.988 40) 20.47%, 430.979 55 (calcd for C<sub>17</sub>H<sub>11</sub>O<sub>2</sub>F<sub>6</sub><sup>70</sup>Ge 430.990 57) 15.05%, [M<sup>+</sup> – CF<sub>3</sub>].

Data for the X-ray structure are as follows. Crystal data:  $C_{18}H_{11}F_9GeO_2$ , formula weight 502.86, yellow, prism, size 0.75 ×  $0.60 \times 0.25$  mm, monoclinic crystal system, space group  $P2_1/c$ , a = 19.612(4) Å, b = 14.042(3) Å, c = 13.579(3) Å,  $\alpha = 90.00^{\circ}$ ,  $\beta = 105.02(3)^{\circ}, \gamma = 90.00^{\circ}, V = 3611.8(12) \text{ Å}^3, T = 100(2) \text{ K},$  $Z = 8, F(000) = 1984, D_x = 1.850 \text{ Mg m}^{-3}, \mu = 1.799 \text{ mm}^{-3}$ crystal was mounted on a loop. Cell parameters were determined by least-squares of the setting angles of 19 570 (2.9612  $\leq$  $\theta \leq 35.8470^{\circ}$ ) reflections. Intensity data were collected on a Rigaku RAxis Rapid diffractometer (graphite monochromator; Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) at 100(2) K in the range  $3.09 \le \theta \le 25.00^\circ$ . A total of 84 243 reflections were collected, of which 6351 were unique ( $R(int) = 0.1146, R(\sigma) = 0.0489$ ); 6021 reflections were obtained with  $I > 2\sigma(I)$ . Completeness to  $2\theta$ : 0.997. A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.3456 and 0.6619). The structure was solved by direct methods (SHELXS-97).<sup>37</sup> Neutral atomic scattering factors and anomalous scattering factors were taken from ref 38. Anisotropic full-matrix least-squares refinement (SHELXL- $(97)^{39,40}$  on  $F^2$  for all non-hydrogen atoms yielded R1 = 0.0609 and wR2 = 0.1695 for 6021  $(I > 2\sigma(I))$  and R1 = 0.0656 and wR2 = 0.1755 for all (6351) intensity data (goodness of fit 1.102; maximum and mean shift/esd 0.105 and 0.004; extinction coefficient 0.0005(3)). The extinction coefficient

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expression is

$$F_{\rm c}^* = kF_{\rm c}[1 + 0.001F_{\rm c}^2\lambda^3/\sin(2\theta)]^{-1/4}$$

The number of parameters is 623. The maximum and minimum residual electron densities in the final difference map was 1.672 and  $-1.047 \text{ e/Å}^3$ . They can be found close to the Ge centers.

The weighting scheme applied was

$$w = 1/[\sigma^2(F_0^2) + (0.1166P)^2 + 2.5390P]$$

where

$$P = (F_o^2 + 2F_c^2)/3$$

Hydrogen atomic positions were located in difference maps. Hydrogen atoms were included in structure factor calculations, but they were not refined.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 746174.

**Calculations.** The structures were fully optimized at the B3LYP<sup>41</sup> functional with the 6-31+G\* basis set, while the "dimer" of 14 was calculated at the B3LYP/6-31+G\*//B3LYP/6-31G\* level using the Gaussian 03 program package.<sup>42</sup> Subsequent calculation of the second derivatives was carried out to characterize the nature of the stationary points

obtained. Transition state structures (one negative eigenvalue of the second derivative matrix) were verified by subsequent optimizing after changing the geometry along the single imaginary frequency. In some cases (see text) further MP2/6-31+G\*//B3LYP/6-31+G\* calculations were carried out. For the visualization of the optimized molecules, the Molden program<sup>43</sup> and the Mercury program were used.<sup>44</sup> Bader analysis<sup>33</sup> was preformed using the AIM2000 software.<sup>45</sup>

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Supporting Information Available: Figure S1, giving the B3LYP/6-31+g\* optimized structure of 14 (14b), Table S1, giving the B3LYP/6-31+G\* structural data (in Å) for the hypervalent silicon species 13h (E = Si) with different R groups ( $\mathbf{R}' = \mathbf{H}$ ), Table S2, giving B3LYP/6-31+G\* structural data (in Å) for the hypervalent silicon 13h (E = Si, R = CF<sub>3</sub>) with different R' groups, Tables S3-S40, giving optimized structures in Cartesian coordinate format with total energies, Table S41, giving crystal data and details of the structure determination for 14a and 14b, Table S42, giving final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms for 14a and 14b, Table S43, giving hydrogen atom positions and isotropic displacement parameters for 14a and 14b, Table S44, giving (an)isotropic displacement parameters for 14a and 14b, Table S45, giving bond distances (Å) for 14a and 14b, Table S46, giving bond angles (deg) for 14a and 14b, Table S47, giving torsion angles (deg) for 14a and 14b, Table S48, giving contact distances (Å) for 14a and 14b, Table S49, giving hydrogen bonds (Å, deg) for 14a and 14b, and a CIF file, giving the structure of 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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