Synthesis of cyclotrigermerenes – Carbon not alone in forming a three-membered unsaturated ring

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The so-called ‘Double-bond rule’ enunciated by Pitzer and Mulliken presaged that the second and subsequent row of elements in the periodic table will not be able to form stable compounds containing $\pi$-$\pi$ multiple bonds among themselves or with the elements of the first row. In line with this theoretical reasoning, multiple bonding was conspicuously absent in the chemistry of heavier Main Group elements until 1970’s when the first stable phospahtaine, RP=NR’, and unconjugated phospahtenes, RP=CR’ (OSiMe₂) were isolated by Niecke and Bocker respectively. Subsequent to these developments, there was sporadic interest in these types of compounds but the situation changed dramatically in 1981 with the isolation of stable double- and triple-bonded compounds featuring Si=S, Si=Si, P=PR and C=CR functionalities. Since then there has been an explosive growth in the area of low-coordinated compounds of Group 14 and Group 15 elements, which continues to this day.

The stabilization of heavier Main Group element multiple bonds has been realized largely by using sterically demanding substituents which presumably exert ‘thermodynamic control’ over oligomerization and ‘kinetic control’ over other reactions to which a double or a triple bond is susceptible. Using the same principle of ‘steric stabilization’, three-membered rings of heavier Group 14 elements such as $(R_2M)_2 (R = Si, Ge or Sn)$ have also been synthesized. However, unsaturated three-membered ring compounds of these elements akin to cyclopropenes are not known so far. Sekiguchi and coworkers have now reported the first successful synthesis of cyclotrigermerenes bearing an unsaturated three-membered ring skeleton and their structural characterization by X-ray crystallography.

The strategy adopted for the synthesis of cyclotrigermerenes is shown in Figure 1. The final products 2a and 2b were obtained as dark red crystals (mp 157°C and 178°C with decomposition, respectively) in low yields (20 and 13% respectively). The mechanism of formation of the unsaturated ring is obscure although the use of bulky silyl or germyl anions $(Bu_3Si or Bu_3Ge)$ is essential to generate the cyclotrigermerene ring. When $GeCl_3 \cdot$ dioxane is treated with RLi $(R = C_6H_5CH_3)$ only germylenes (GeCIR and GeR₂) are formed; on the other hand, the reaction of $(Me_3Si)_3SiLi(THF)_3$ with $GeCl_3 \cdot$ dioxane gives the three-membered ring compound, $(R_3Si)_2GeR (R = SiMe_3)$ containing two silicon and a germanium in the ring skeleton.

The X-ray crystal structures of 2a and 2b reveal trigonal planar geometries around the two sp³-hybridized germanium atoms with a Ge–Ge distance of 2.239(4) Å, which may be compared with the single bond Ge(1)–Ge(2) distance of 2.522(4)Å for 2a and 2.505(6)Å for 2b. These Ge–Ge distances in 2a and 2b and those observed in cyclogermerenes, $(R,Ge)$, $(n = 3, 4$ or 6) and digermerenes, $(R,Ge)^2$, are listed in Table 1. The Ge–Ge single bond distance in cyclotrigermerenes is somewhat longer than those in the higher members of cyclogermerenes $(Ph,Ge)$, while the Ge–Ge double bond distance in digermerenes lies in the range 2.21–2.35 Å. The $Ge(xpy^2)$–$Ge(xpy^2)$ distance in 2a or 2b is intermediate between the $Ge(xpy^2)$–$Ge(xpy^2)$ and $Ge(xpy^2)$–$Ge(xpy^2)$ distances (Table 1).

The cyclotrigermerenes 2a and 2b do not undergo addition reaction with ethanol or diazomethane at room temperature.

REFERENCES


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Figure 1. Synthesis of cyclotrimeranes.

Table 1. Germanium-germanium distances in cyclopolygermanes, cyclotrimeranes, digermeranes and cyclotrimeranes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ge–Ge distance (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ph₂Ge)₄</td>
<td>2.460(3)</td>
<td>19</td>
</tr>
<tr>
<td>(Ph₂Ge)₄</td>
<td>2.465(5)</td>
<td>20</td>
</tr>
<tr>
<td>(Bu₃Ge)₃</td>
<td>2.563(1)</td>
<td>21</td>
</tr>
<tr>
<td>(Bu₃Ge)₃</td>
<td>2.541(1)</td>
<td>22</td>
</tr>
<tr>
<td>(R₂Ge)₃ (R = C₆H₅Me₂-2,6)</td>
<td>2.590</td>
<td>10</td>
</tr>
<tr>
<td>(R₂Ge)₃ (R = C₆H₅Et₂-2,6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R₂Ge=GeR₂ (R = 2,6-ETC₆H₆)</td>
<td>2.213(2)</td>
<td>23</td>
</tr>
<tr>
<td>R₂Ge=GeR₂ (R = CH(SiMe₃)₂)</td>
<td>2.347(2)</td>
<td>24</td>
</tr>
<tr>
<td>Z-RR'Ge=GeRR' (R = 2,6-C₆H₅Me₂)</td>
<td>2.301(1)</td>
<td>25</td>
</tr>
<tr>
<td>2a</td>
<td>2.239(4)₆</td>
<td>18</td>
</tr>
<tr>
<td>2b</td>
<td>2.239(5)₆</td>
<td></td>
</tr>
</tbody>
</table>

₆Ge(sp²)–Ge(sp³); ³Ge(sp³–sp³).

though cyclotrimeranes can be a possible precursor for a digermene RGe=GeR, no evidence for such a species was found when 2a or 2b was heated at 100°C in toluene or irradiated with light of wave length >300 nm. In either case, only products arising from cleavage of the exocyclic Ge–Si or Ge–Ge bonds and the rupture of the three-membered ring were obtained.

The successful synthesis of cyclotrimeranes adds a new dimension to the rapidly expanding chemistry of multiple bonded compounds of heavier Main Group elements. One may anticipate further interesting developments in the synthesis of similar type of compounds incorporating other congeners such as Si or Sn and the reactivity of this new class of cyclotrimetallenenes. A particularly exciting prospect is the synthesis of transition metal complexes of cyclotrimetallenyl cations, (R₃M₃)⁺ analogous to cyclopropenyl cationic ligand, (R₃C)⁺.


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