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 $p_x-p_y$ 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 phosphoramines, $RN=NR$ and uncharged phosphaalkenes, $RP=CR$ (OSiMe$_3$) were isolated by Niecke and Becker 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=C, Si=Si, P=Pt, and C=W functionalities. Since then there has been an explosive growth in the area of low-coordinated compounds of 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 $\text{R}_2\text{M}_3$ ($\text{R} = \text{Si, Ge or Sn}$) have also been synthesized.

However, unsaturated three-membered ring compounds of these elements akin to cyclopropanes 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 ($\text{Bu}_3\text{Si}$ or $\text{Bu}_3\text{Ge}$) is essential to generate the cyclotrigrermene ring. When $\text{GeCl}_3$-dioxide is treated with RLi ($\text{R} = \text{C}_6\text{H}_{28}\text{H}_2$) only gemylenes ($\text{GeCIR}$ and $\text{GeR}_2$) are formed; on the other hand, the reaction of $\text{M}_2\text{Si}_3\text{SiLi}$(THF) with $\text{GeCl}_3$-dioxide gives the three-membered ring compound, $\text{(R}_2\text{Si})\text{GeR}_2$ ($\text{R} = \text{SiMe}_3$) 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 sp$^2$-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 cyclogermanes, $\text{R}_2\text{Ge}$, ($n = 3, 4$ or 6) and digermines, $\text{R}_2\text{Ge}=\text{GeR}_2$ are listed in Table 1. The Ge–Ge single bond distance in cyclogermanes is somewhat longer than those in the higher membered cyclogermanes ($\text{Ph}_2\text{Ge}$)$\text{Ge}_4$, while the Ge–Ge double bond distance in digermines lies in the range 2.21–2.35 Å. The Ge(sp$^2$)–Ge(sp$^2$) distance in 2a or 2b is intermediate between the Ge(sp$^2$)–Ge(sp$^3$) and Ge(sp$^3$)–Ge(sp$^3$) distances (Table 1).

The cyclotrigermerenes 2a and 2b do not undergo addition reaction with ethanol or diazomethane at room temperature.
though cyclotrigermenes 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 cyclotrigermenes 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 cyclotrimetallenes. A particularly exciting prospect is the synthesis of transition metal complexes of cyclotrimetallenylic cations, (R,M)⁺ analogous to cyclopropenyl cationic ligand, (R,C₃H₅)⁺.}