

dustry a profitable business are: i) demand (domestic as well as international) in excess to domestic support, ii) continuing increasing trend in metal prices, iii) an efficient mining vessel/platform with sturdy mining systems capable of operating throughout the year irrespective of weather conditions, iv) ore carriers to shuttle between mining vessel and a nearest Indian port, v) a metallurgical plant to handle/process over 5000 tonnes of nodules a day located at a nearest point to the mining area, most probably on the southernmost coast of Kerala, and vi) well-trained work force. Keeping these basic requirements for an efficient deep-

sea nodule mining process, the efforts are needed to study techno-economic feasibility in the Indian context.

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RESEARCH NEWS

Synthesis of cyclotrigermenes – 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 $p_{\pi}-p_{\pi}$ multiple bonds among themselves or with the elements of the first row¹. 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 phosphimine, $RP=NR'$ and unconjugated phosphalkenes, $RP=CR'$ ($OSiMe_3$) were isolated by Niecke² and Becker³ 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 $Si=C^4$, $Si=Si^5$, $P=P^6$ and $C=P^7$ 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 day⁸⁻¹⁵. The stabilization of heavier Main Group element multiple bonds has been realized largely by using sterically demanding substituents which presumably exert 'ther-

modynamic control' over oligomerization and 'kinetic control' over other reactions to which a double or a triple bond is susceptible¹⁶. Using the same principle of 'steric stabilization', three-membered rings of heavier Group 14 elements such as $(R_2M)_3$ ($R = Si, Ge$ or Sn) have also been synthesized^{10,17}. However, unsaturated three-membered ring compounds of these elements akin to cyclopropenes are not known so far. Sekiguchi and coworkers¹⁸ have now reported the first successful synthesis of cyclotrigermenes bearing an unsaturated three-membered ring skeleton and their structural characterization by X-ray crystallography.

The strategy adopted for the synthesis of cyclotrigermenes is shown in Figure 1. The final products **2a** and **2b** were obtained as dark red crystals (mp 157° 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 (tBu_3Si or tBu_3Ge) is essential to generate the cyclotrigermene ring. When $GeCl_2 \cdot dioxane$ is treated with RLi ($R = C_6H_{21}Bu_3-2,4,6$), only germylenes ($GeClR$

and GeR_2) are formed; on the other hand, the reaction of $(Me_3Si)_3SiLi(THF)_3$ with $GeCl_2 \cdot dioxane$ gives the three-membered ring compound, $(R_2Si)_2GeR_2$ ($R = SiMe_3$) 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 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 cyclogermenes, $(R_2Ge)_n$ ($n = 3, 4$ or 6) and digermenes, $R_2Ge=GeR_2$ are listed in Table 1. The Ge-Ge single bond distance in cyclogermenes is somewhat longer than those in the higher membered cyclogermenes $(Ph_2Ge)_{4,6}$ while the Ge=Ge double bond distance in digermenes lies in the range 2.21-2.35 Å. The $Ge(sp^3)-Ge(sp^2)$ distance in **2a** or **2b** is intermediate between the $Ge(sp^3)-Ge(sp^3)$ and $Ge(sp^2)-Ge(sp^2)$ distances (Table 1).

The cyclotrigermenes **2a** and **2b** do not undergo addition reaction with ethanol or diazomethane at room temperature. Al-

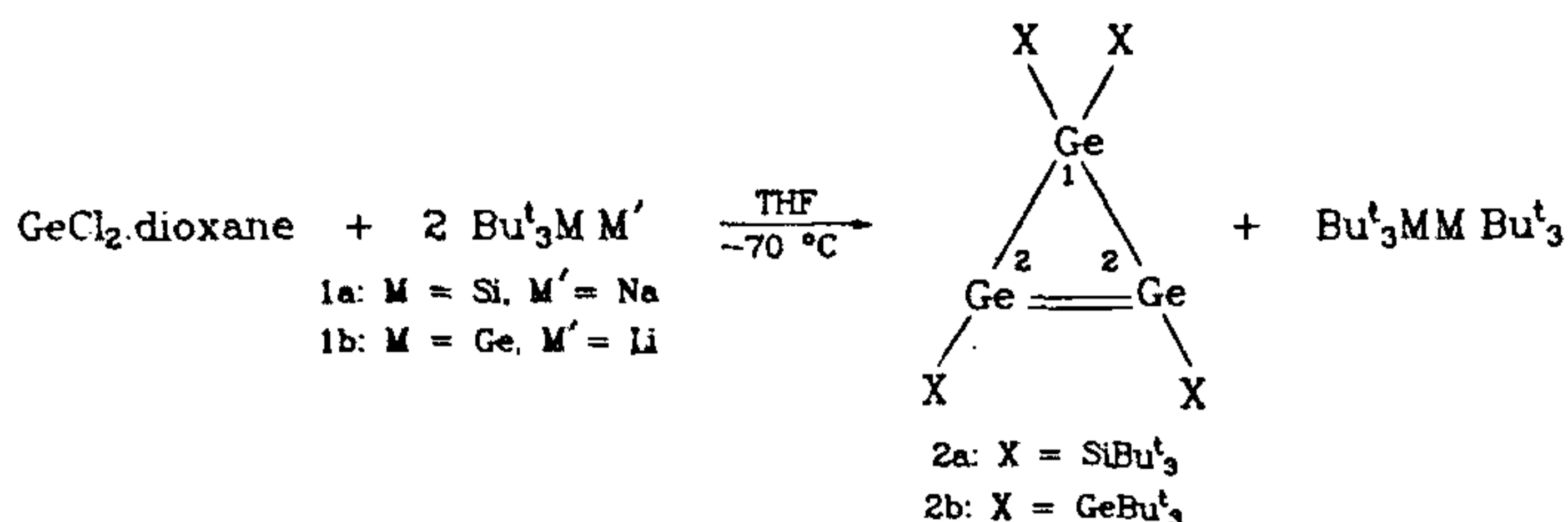


Figure 1. Synthesis of cyclotrigermenes.

Table 1. Germanium-germanium distances in cyclopolygermanes, cyclotrigermenes, digermenes and cyclotrigermenes

Compound	Ge-Ge distance (Å)	Ref.
(Ph ₂ Ge) ₆	2.460(3)	19
(Ph ₂ Ge) ₄	2.465(5)	20
(Bu ₂ Ge) ₃	2.563(1)	21
(R ₂ Ge) ₃ (R = C ₆ H ₃ Me ₂ -2,6)	2.541(1)	22
(R ₂ Ge) ₃ (R = C ₆ H ₃ Et ₂ -2,6)	2.590	10
R ₂ Ge=GeR ₂ (R = 2,6-Et ₂ C ₆ H ₃)	2.213(2)	23
R ₂ Ge=GeR ₂ (R = CH(SiMe ₃) ₂)	2.347(2)	24
Z-RR'Ge=GeRR' (R = 2,6-C ₆ H ₃ Pr ₂ , R' = 2,4,6-C ₆ H ₂ Me ₃)	2.301(1)	25
2a	2.239(4) ^a 2.522(4) ^b	18
2b	2.239(5) ^a 2.505(6) ^b	18

^aGe(sp²)-Ge(sp²); ^bGe(sp³-sp²).

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 wavelength > 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 syn-

thesis 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 cyclotrimetallenylium cations, (R₃M₃)⁺ analogous to cyclopropenyl cationic ligand, (R₃C₃)⁺.

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