Ring of Three Gallium Atoms Displays Aromatic Character

Another Feather in Hückel's Cap

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The simple Hückel rule, which states that conjugated cyclic systems having $4n + 2\ \pi$ electrons (n being an integer) are aromatic, is one of those rules which have really stood the test of time. Many familiar organic molecules and ions can be cited to illustrate the rule. For example, the most elementary aromatic system is a $2\ \pi$ electron system ($n = 0$) and its carbocyclic analogue is the triphenylcyclopropenium cation. Is there an inorganic species which shows similar aromaticity?

Recently, X -W Li, W T Pennington and G H Robinson at Clemson University, USA, have prepared, for the first time, a three membered metallic ring that is isoelectronic with the above mentioned cation (*J. Am. Chem. Soc.*, **117**, *7578, 1995*). The ring consists of three gallium atoms, each substituted with 2,6-dimesitylphenyl group (*Figure 1*). Attachment of such bulky groups close to a reactive site is an old ploy used by chemists to tame molecules which are *kinetically* unstable.[1]

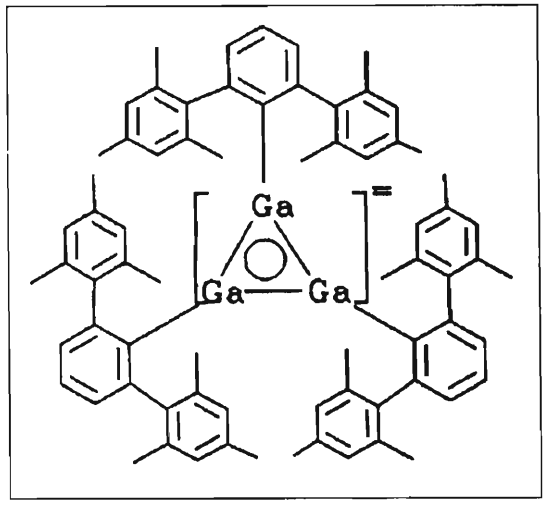

Figure 1 The three membered metallic ring prepared at Clemson University, USA.

The actual synthesis involves the cyclotrimerisation of 2,6-dimesitylphenylgallium dichloride using sodium. Even after coupling, two sodium atoms are perfectly centered above and below the Ga_3 ring. The structure can be represented as a dianion ring, with Na^+ counter-ions. The trivalent gallium atoms are sp^2 hybridised and the ring consists of 2π electrons. The ring is therefore expected to be aromatic. Consistent with this electronic structure, the Ga-Ga bond length of this molecule (2.44 Å) is among the shortest known (for example, the Ga-Ga bond length in $Ga_4[C(SiMe_3)_3]_4$ is 2.69 Å).

[1] Kinetically unstable species are not necessarily high energy species. It just means that the activation barriers for their decomposition pathways are low.

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