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Structure and bonding of MCB_5H_7 and its sandwiched dimer $CB_5H_6M–MCB_5H_6$ ($M = Si, Ge, Sn$): Isomer stability and preference for slip distorted structure

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Abstract

We find sandwiched metal dimers $CB_5H_6M–MCB_5H_6$ ($M = Si, Ge, Sn$) which are minima in the potential energy surface with a characteristic M–M single bond. The NBO analysis and the M–M distances (Å) (2.3, 2.44 and 2.81 for M = Si, Ge, Sn) indicate substantial M–M bonding. Formal generation of $CB_5H_6M–MCB_5H_6$ has been studied theoretically. Consecutive substitution of two boron atoms in $B_7H_7^{-2}$ by M (Si, Ge, Sn) and carbon, respectively followed by dehydrogenation may lead to our desired $CB_5H_6M–MCB_5H_6$. We find that the slip distorted geometry is preferred for MCB_5H_7 and its dehydrogenated dimer $CB_5H_6M–MCB_5H_6$. The slip-distortion of M–M bond in $CB_5H_6M–MCB_5H_6$ is more than the slip distortion of M–H bond in MCB_5H_7. Molecular orbital analysis has been done to understand the slip distortion. Larger M–M bending ($CB_5H_6M–MCB_5H_6$) in comparison with M–H bending (MCB_5H_7) is suspected to be encouraged by stabilization of one of the M–M π bonding MO's. Preference of M to occupy the apex of pentagonal skeleton of MCB_5H_7 over its icosahedral analogue $MCB_{10}H_{11}$ has been observed.

Keywords: Carboranes; Sandwich compounds

1. Introduction

Structure, bonding and reactivity of polyhedral boron clusters are of great interest. Pentagonal-bipyramidal closo-borane $B_7H_7^{-2}$ is highly reactive [1–6]. It can be stabilized by substitution of a vertex by a group 13 metal [7]. Jemmis et al. concluded [8] that optimum overlap between the five membered face of boron ring and group 13 metal leads to a very stable vertex substituted pentagonal-bipyramidal boranes. The stability is even more than the icosahedral analogue. Several isoelectronic molecules of $B_nH_n^{2-}$ ($n = 7, 12$), containing one or two heteroatoms other than carbon in the cage have been prepared [9–20]. In 1995, Hosmane and co-workers synthesized a novel class of compounds where the Ga–Ga bond is stabilized by two 2,4-dicarbo-nido-hexaborate^{2-} carborane ligands [7]. A few inorganic compounds with Ga–Ga bond such as Ga_2Br_3, $[GaC(SiMe_3)_3]_4$ and Ga_2R_4 [$R = (Me_3Si)_2CH$, 2,4,6-$i$$Pr_3C_6H_2$ and 2,4,6-$(CF_3)_3C_6H_2$] have been reported in the literature [21–25]. Multiply bonded Si in RSi≡SiR has been studied by Sekiguchi et al. [26–33].

Recently, Power et al. [34–41] described the compounds RE≡ER (E = Ge–Pb) comprising of bulky aryl ligands. These compounds have *trans*-bend geometries with bond orders less than three. The lone pair character increases down the group. For the heaviest element Pb, E–E bond is essentially single.

Our interest for the search of new kinds of binuclear sandwich compounds, important role of homonuclear metal–metal bonding in chemistry [42] and rich literature of metallacarboranes has lead us to consider the electronic structures of $CB_5H_6M–MCB_5H_6$ ($M = Si, Ge, Sn$). Systematic substitution of two boron atoms in $B_7H_7^{-2}$ by M

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and carbon leads to neutral MCB_5H_7, where M–H fragment occupy the apical position above the pentagonal CB_4H_5 ring with slip distorted geometry. Relative preference of M–H cap between the pentagonal bipyramid (MCB_5H_7) and its icosahedral analogue ($MCB_{10}H_{11}$) has been studied. Dehydrogenation of two neutral MCB_5H_7 may lead to the desired neutral binuclear sandwich dimer $CB_5H_6M–MCB_5H_6$. These dimers also show slip-distorted geometry. Distortion of M–M bond above the pentagonal ring is more than the M–H distortion in MCB_5H_7. The nature and strength of M–M bonds in $CB_5H_6M–MCB_5H_6$ are compared with its bare M_2 dimers and $H_3M–MH_3$ species. Molecular orbital analysis has been done to understand the M–H and M–M slip distortion above the pentagonal ring in mononuclear $CB_5H_6–MH$ and binuclear $CB_5H_6M–MCB_5H_6$, respectively. Three dimensional aromaticity in the conversion from $B_7H_7^{-2}$ to $CB_5H_6M–MCB_5H_6$ has been analyzed. Electronic requirements of all the polyhedral structures reported here follow Wade's Rules [43,44].

2. Theoretical methods

All the structures are fully optimized at B3LYP/LANL2DZ level of theory using GAUSSIAN03 program [45]. All the reported structures are minima and characterized by frequency calculations. B3LYP functional incorporates Becke's three parameter functional [46] with Lee et al. [47] correlation functional. Variation of aromaticity has been probed by Nuclear Independent Chemical Shift (NICS) [48,49] calculations for the optimized geometries. Nature of M–M bonds of the dimers are studied by NBO calculations [50].

3. Results and discussions

Our idea is to substitute one of the boron atoms of $B_7H_7^{-2}$ by group 14 metal M (Si, Ge, Sn). Then in the resultant most stable isomer $MB_6H_7^-$, one boron atom is substituted by carbon to have neutral MCB_5H_7. Dehydrogenation of two MCB_6H_7 molecules may lead to our desired neutral homonuclear sandwich $CB_5H_6M–MCB_5H_6$.

3.1. Relative stability and bonding in the pentagonal bipyramidal systems

The high reactivity of $B_7H_7^{-2}$ (D_{5h}) is attributed to the poor interaction between B_5H_5 ring and the BH fragments [51,52]. Size of B_5H_5 ring is large enough to have optimum overlap between π-MOs of the ring and MOs of the two BH fragments. One of the resulting MOs is shown in Fig. 1a. For hypothetical $B_6H_6^{4-}$ or well-known B_6H_{10}, out of plane bending of B–H bonds indicate the improvement of ring–cap interaction (Fig. 1b). When there are two BH caps, such possibilities do not exist; BH bonds of the ring are forced to be in plane due to symmetry. The ring size can be reduced by substituting boron atoms by carbon atoms. Since B–C bonds are shorter than B–B bonds, the five membered ring in $C_2B_5H_7$ is shorter. As a result more effective overlap between the B–H cap and $C_2B_3H_5$ ring leads to higher stability of $C_2B_5H_7$ over $B_7H_7^{-2}$ (Fig. 1c).

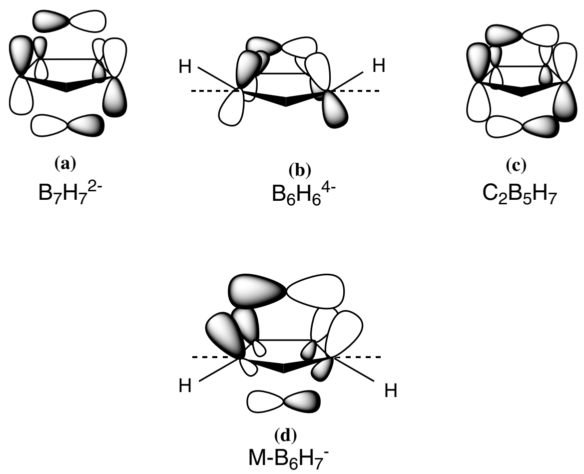

Fig. 1. Ring–cap overlap scheme. M = Si, Ge, Sn.

When one of the boron in $B_7H_7^{-2}$ is substituted by M (Si, Ge, Sn), we found that M prefers to occupy the apical position [shown in Fig. 2a]. Apical isomer of $MB_6H_7^-$ (Fig. 2a) is relatively more stable than the other one (shown in Fig. 2b) by 11.1, 13.2 and 20.8 kcal/mol for Si, Ge and Sn, respectively. Positioning of M in the ring will increase the ring size and leads to poor ring–cap compatibility. Hence due to the larger size down the group, preference to occupy the apical position increases. Variation in the structures of $B_7H_7^{-2}$ (D_{5h}) when an apical boron is substituted by group 14 metals (Fig. 2a) are noteworthy. Ring

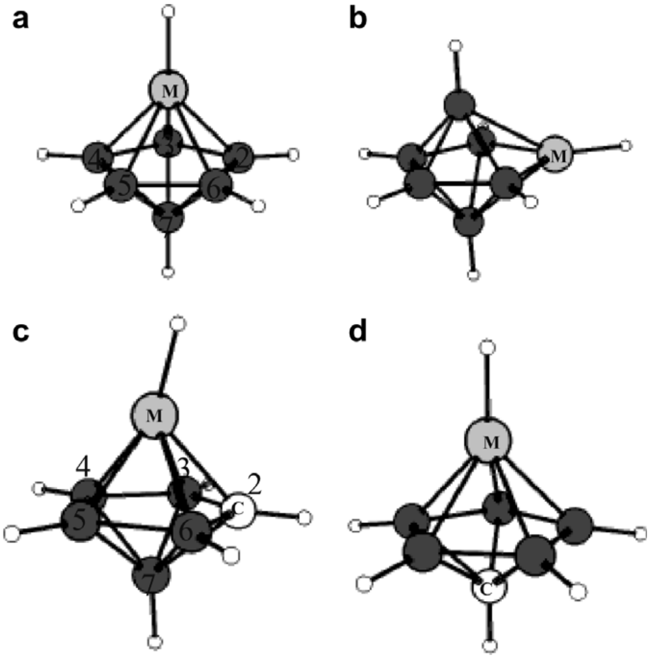

Fig. 2. Two isomers of $MB_6H_7^-$ [(a),(b)] and MCB_5H_7 [(c), (d)], where M = Si, Ge, Sn.