

# Structure and bonding of $\text{MCB}_5\text{H}_7$ and its sandwiched dimer $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$ ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ): Isomer stability and preference for slip distorted structure

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## Abstract

We find sandwiched metal dimers  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ) 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  $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ) indicate substantial M–M bonding. Formal generation of  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  has been studied theoretically. Consecutive substitution of two boron atoms in  $\text{B}_7\text{H}_7^{2-}$  by M (Si, Ge, Sn) and carbon, respectively followed by dehydrogenation may lead to our desired  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$ . We find that the slip distorted geometry is preferred for  $\text{MCB}_5\text{H}_7$  and its dehydrogenated dimer  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$ . The slip-distortion of M–M bond in  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  is more than the slip distortion of M–H bond in  $\text{MCB}_5\text{H}_7$ . Molecular orbital analysis has been done to understand the slip distortion. Larger M–M bending ( $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$ ) in comparison with M–H bending ( $\text{MCB}_5\text{H}_7$ ) is suspected to be encouraged by stabilization of one of the M–M  $\pi$  bonding MO's. Preference of M to occupy the apex of pentagonal skeleton of  $\text{MCB}_5\text{H}_7$  over its icosahedral analogue  $\text{MCB}_{10}\text{H}_{11}$  has been observed.

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## 1. Introduction

Structure, bonding and reactivity of polyhedral boron clusters are of great interest. Pentagonal-bipyramidal closo-borane  $\text{B}_7\text{H}_7^{2-}$  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  $\text{B}_n\text{H}_n^{2-}$  ( $n = 7, 12$ ), 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<sup>2-</sup> carborane ligands [7]. A few inorganic compounds with Ga–Ga bond such as  $\text{Ga}_2\text{Br}_3$ ,  $[\text{GaC}(\text{SiMe}_3)_3]_4$  and  $\text{Ga}_2\text{R}_4$  [ $\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$ , 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> and 2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>] have been reported in the literature [21–25]. Multiply bonded Si in  $\text{RSi}\equiv\text{SiR}$  has been studied by Sekiguchi et al. [26–33].

Recently, Power et al. [34–41] described the compounds  $\text{RE}\equiv\text{ER}$  ( $\text{E} = \text{Ge}-\text{Pb}$ ) 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 metallocarboranes has lead us to consider the electronic structures of  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ). Systematic substitution of two boron atoms in  $\text{B}_7\text{H}_7^{2-}$  by M

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and carbon leads to neutral  $\text{MCB}_5\text{H}_7$ , where M–H fragment occupy the apical position above the pentagonal  $\text{CB}_4\text{H}_5$  ring with slip distorted geometry. Relative preference of M–H cap between the pentagonal bipyramid ( $\text{MCB}_5\text{H}_7$ ) and its icosahedral analogue ( $\text{MCB}_{10}\text{H}_{11}$ ) has been studied. Dehydrogenation of two neutral  $\text{MCB}_5\text{H}_7$  may lead to the desired neutral binuclear sandwich dimer  $\text{CB}_5\text{H}_6\text{M}–\text{MCB}_5\text{H}_6$ . These dimers also show slip-distorted geometry. Distortion of M–M bond above the pentagonal ring is more than the M–H distortion in  $\text{MCB}_5\text{H}_7$ . The nature and strength of M–M bonds in  $\text{CB}_5\text{H}_6\text{M}–\text{MCB}_5\text{H}_6$  are compared with its bare  $\text{M}_2$  dimers and  $\text{H}_3\text{M}–\text{MH}_3$  species. Molecular orbital analysis has been done to understand the M–H and M–M slip distortion above the pentagonal ring in mononuclear  $\text{CB}_5\text{H}_6–\text{MH}$  and binuclear  $\text{CB}_5\text{H}_6\text{M}–\text{MCB}_5\text{H}_6$ , respectively. Three dimensional aromaticity in the conversion from  $\text{B}_7\text{H}_7^{2-}$  to  $\text{CB}_5\text{H}_6\text{M}–\text{MCB}_5\text{H}_6$  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  $\text{B}_7\text{H}_7^{2-}$  by group 14 metal M (Si, Ge, Sn). Then in the resultant most stable isomer  $\text{MB}_6\text{H}_7^-$ , one boron atom is substituted by carbon to have neutral  $\text{MCB}_5\text{H}_7$ . Dehydrogenation of two  $\text{MCB}_5\text{H}_7$  molecules may lead to our desired neutral homonuclear sandwich  $\text{CB}_5\text{H}_6\text{M}–\text{MCB}_5\text{H}_6$ .

### 3.1. Relative stability and bonding in the pentagonal bipyramidal systems

The high reactivity of  $\text{B}_7\text{H}_7^{2-}$  ( $D_{5h}$ ) is attributed to the poor interaction between  $\text{B}_5\text{H}_5$  ring and the BH fragments [51,52]. Size of  $\text{B}_5\text{H}_5$  ring is large enough to have optimum overlap between  $\pi$ -MOs of the ring and MOs of the two BH fragments. One of the resulting MOs is shown in Fig. 1a. For hypothetical  $\text{B}_6\text{H}_6^{4-}$  or well-known  $\text{B}_6\text{H}_{10}$ , 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

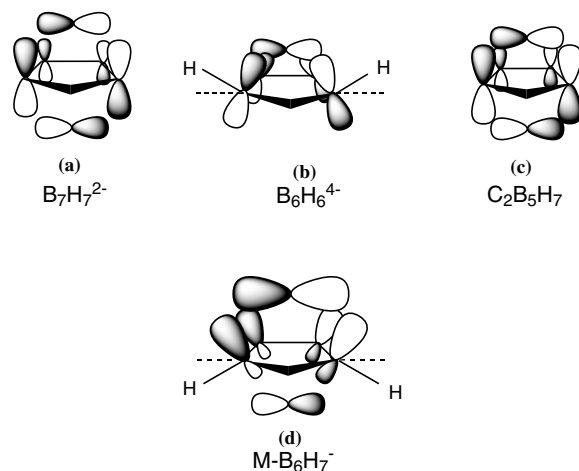


Fig. 1. Ring–cap overlap scheme. M = Si, Ge, Sn.

five membered ring in  $\text{C}_2\text{B}_5\text{H}_7$  is shorter. As a result more effective overlap between the B–H cap and  $\text{C}_2\text{B}_5\text{H}_5$  ring leads to higher stability of  $\text{C}_2\text{B}_5\text{H}_7$  over  $\text{B}_7\text{H}_7^{2-}$  (Fig. 1c).

When one of the boron in  $\text{B}_7\text{H}_7^{2-}$  is substituted by M (Si, Ge, Sn), we found that M prefers to occupy the apical position [shown in Fig. 2a]. Apical isomer of  $\text{MB}_6\text{H}_7^-$  (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  $\text{B}_7\text{H}_7^{2-}$  ( $D_{5h}$ ) when an apical boron is substituted by group 14 metals (Fig. 2a) are noteworthy. Ring

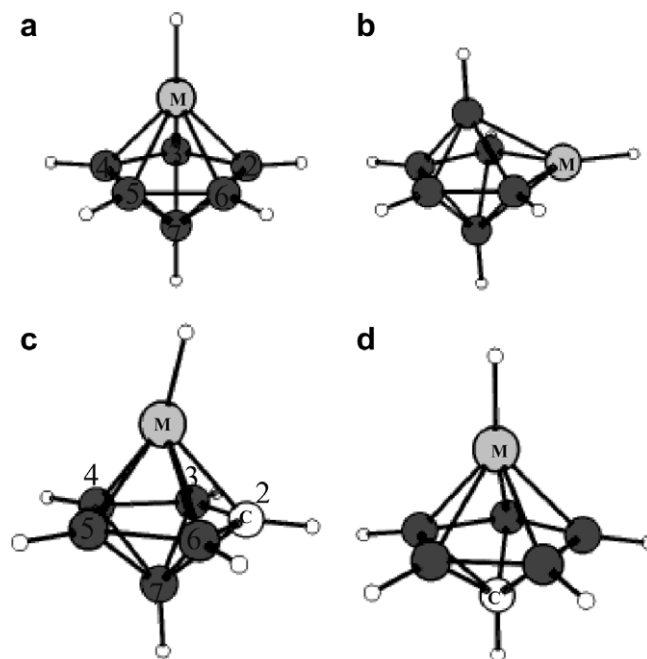


Fig. 2. Two isomers of  $\text{MB}_6\text{H}_7^-$  [(a),(b)] and  $\text{MCB}_5\text{H}_7$  [(c), (d)], where M = Si, Ge, Sn.

hydrogens of  $B_7H_7^{2-}$  bend away from the M–H cap. Fig. 1d pictorially represents the feasible overlap and consequent stabilization of the isomer shown in Fig. 2a. Bending of B–H bonds out of the  $B_5$  plane rehybridize the orbitals, so that larger lobe is directed towards the M–H group to have optimum overlap. As a result B–B bond lengths in the  $B_5$  ring increases and the distance between apical B–H and centroid of the  $B_5$  ring decreases.

In most stable isomers of  $MB_6H_7^-$  (Fig. 2a), the extent of out-of-plane bending of ring B–H bonds are  $2.39^\circ$ ,  $3.39^\circ$  and  $6.15^\circ$  for Si, Ge and Sn, respectively. Bending angles of interest are given in Table 1. B–B bond lengths (Table 2) of the five membered ring of  $B_7H_7^{2-}$  and  $MB_6H_7^-$  for M = Si, Ge, Sn (Fig. 2a) are 1.68, 1.73, 1.74 and 1.76 Å,

Table 1  
Important angles of interest

Molecule	Figure	Angles ( $^\circ$ )	M = Si	Ge	Sn
$MB_6H_7^-$	Fig. 2a	X–M–H	0.0	0.0	0.0
		X–B <sub>1–6</sub> –H	2.39	3.39	6.15
1M–2– $CB_5H_6$	Fig. 2c	X–M–H	14.98	19.26	23.82
		X–C <sub>2</sub> –H	5.37	6.85	10.21
		X–B <sub>3–6</sub> –H	5.20	5.65	7.72
		X–B <sub>4–5</sub> –H	1.52	1.91	3.83
$H_6B_5C-M-M-CB_5H_6$	Fig. 5	X–M–M	15.75	21.41	28.45
		X–C <sub>2</sub> –H	5.28	6.97	10.41
		X–B <sub>3–6</sub> –H	5.13	5.55	7.80
		X–B <sub>4–5</sub> –H	1.09	1.43	3.19

“X” is centroid of the five membered ring. Reported angles are obtained by subtracting from  $180^\circ$ .

Table 2  
Important distances

Molecule	Figure	Distances (Å)	M = Si	Ge	Sn
$MB_6H_7^-$	Fig. 2a	Ring B–B	1.73	1.74	1.76
		M–B <sub>2/6</sub>	2.11	2.18	2.34
		B <sub>7</sub> –B <sub>2/6</sub>	1.83	1.83	1.81
		M–X	1.50	1.60	1.80
		B <sub>7</sub> –X	1.09	1.07	1.03
1M–2– $CB_5H_6$	Fig. 2c	C <sub>2</sub> –B <sub>3/6</sub>	1.60	1.60	1.60
		B <sub>3/5</sub> –B <sub>4/6</sub>	1.73	1.74	1.75
		B <sub>4</sub> –B <sub>5</sub>	1.78	1.80	1.83
		M–C <sub>2</sub>	2.06	2.16	2.35
		M–B <sub>3/6</sub>	2.13	2.21	2.38
		M–B <sub>4/5</sub>	2.08	2.15	2.31
		M–X	1.53	1.63	1.84
		B <sub>7</sub> –X	1.11	1.09	1.06
		$H_6B_5C-M-M-CB_5H_6$	Fig. 5	C <sub>2</sub> –B <sub>3/6</sub>	1.60
B <sub>3/5</sub> –B <sub>4/6</sub>	1.73			1.74	1.75
B <sub>4</sub> –B <sub>5</sub>	1.78			1.80	1.84
M–C <sub>2</sub>	2.05			2.17	2.36
M–B <sub>3/6</sub>	2.14			2.22	2.40
M–B <sub>4/5</sub>	2.09			2.16	2.33
M–X	1.53			1.64	1.86
B <sub>7</sub> –X	1.11			1.09	1.06
M–M	2.3			2.44	2.81

“X” is centroid of the five membered ring.

respectively. Increase in bond length indicates an enlargement of the five-membered ring. Distance between apical boron and centroid (Table 2) of the  $B_5$  ring are 1.2, 1.09, 1.07, 1.03 Å for  $B_7H_7^{2-}$  and  $MB_6H_7^-$  with M = Si, Ge, Sn, respectively.

We substituted one of the boron atoms of  $MB_6H_7^-$  (most stable isomer shown in Fig. 2a) by a carbon and the resulting isomers are shown in Fig. 2c and d. The general structure and bonding remains unaltered in case of neutral carborane  $MCB_5H_7$  derivatives (Fig. 2). Due to lower symmetry of the five-membered ring, the structures of  $MCB_5H_7$  undergo distortion. Carbon atom prefers to sit on the five-membered ring instead of apical position due to optimum overlap of ring–cap orbitals. Isomer shown in Fig. 2c is more stable than the isomer shown in Fig. 2d by 25.9, 26.8, 28.4 kcal/mol for Si, Ge and Sn, respectively. Bending of –MH group towards the carbon side of  $CB_4H_5$  face has been observed in our calculation (Table 1, X–M–H angles, “X” is centroid of the five membered ring), which has also been reported and explained for Ga and In derivatives [53–55]. Fine tuning of ring–cap bonding is reported to be responsible for the distortion.

To understand this distortion we have analyzed the MO's. If the apex MH group is artificially separated from the nido  $CB_5H_6$  unit, then  $p_z$  orbitals of the five membered ring can be used to construct five molecular orbitals, among which three are bonding. The bonding MO's are of proper symmetry for overlap with  $sp_z$ ,  $p_x$ ,  $p_y$  orbitals on the apex M–H. We have identified three filled molecular orbitals which are generated by the interaction of  $sp_z$ ,  $p_x$ ,  $p_y$  orbitals of the cap and three bonding orbitals of the ring (see Fig. 3). Change in energy of these three molecular orbitals with respect to change in X–M–H angle are shown in Fig. 4. We concluded that, deviation of X–M–H angle from  $180^\circ$  leads to stabilization of the bonding molecular orbital shown in Fig. 3B. Due to smaller size of the  $p_z$  orbital on carbon, the M–H group bends towards the C to have optimum overlap. Destabilizing effect of the MO shown in Fig. 3C upon deviation from  $180^\circ$  is smaller than the stabilization effect of the MO shown in Fig. 3B. The MO shown in Fig. 3A has not changed significantly upon distortion. As we go down the group we find that the slip-distortion increases (Table 1, X–M–H angle of 1M–2– $CB_5H_6$ ). To accommodate bigger atom down the group, size of the pentagonal ring increases with increase in bending of C–H and B–H bonds away from the cap (see Table 1, X–C<sub>2</sub>–H and X–B<sub>3/6</sub>–H angle of 1M–2– $CB_5H_6$ ). The X–C–H angle of 1M–2– $CB_5H_6$  (Fig. 2c) are  $5.37^\circ$ ,  $6.85^\circ$ ,  $10.21^\circ$  for Si, Ge and Sn, respectively. Now to have optimum overlap (shown in Fig. 3B), M–H bond bends towards the carbon side of the ring. M–H bending increases as we go from Si to Sn.

Icosahedral boranes are usually considered to be the most stable among polyhedral boranes. Preference of M to sit in the apex between pentagonal bipyramid and its icosahedral analogue has been analyzed by the following isodesmic equation:

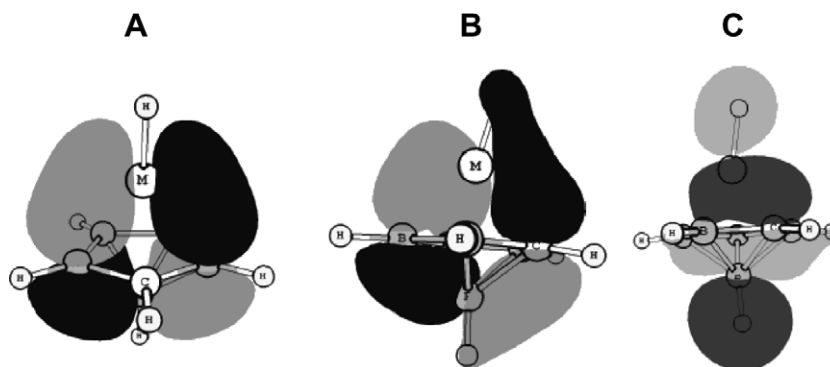
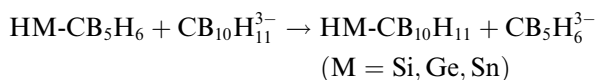


Fig. 3. Molecular orbitals formed by, (A) interaction between  $p_x$  of M and valence  $\pi$  molecular orbital of  $CB_5H_6$  unit. This MO is rotated by  $72^\circ$  from the right to show the absence of interaction between M and carbon clearly, (B) interaction between  $p_y$  of M and valence  $\pi$  molecular orbital of  $CB_5H_6$  unit. Orbital overlap between M and C of the ring is identified, (C) interaction of  $sp_2$  of M and most stable bonding  $\pi$  molecular orbital of  $CB_5H_6$  unit.



$\Delta E$  of the above equation are 97.12, 101.12, 107.78 kcal/mol for Si, Ge and Sn, respectively. Higher endothermicity of the above reaction clearly suggest the thermodynamic preference of M to stay in the pentagonal bipyramidal apex rather than its icosahedral analogue. This preference is more than group 13 metalation of the pentagonal-bipyramid reported [8] in the literature. Optimum ring-cap compatibility is the controlling factor for this preference.

### 3.2. Binuclear complexes

Thermodynamic feasibility for the formation of binuclear sandwich  $CB_5H_6M-MCB_5H_6$  from mononuclear  $MCB_5H_7$  has been analyzed by the following equation:

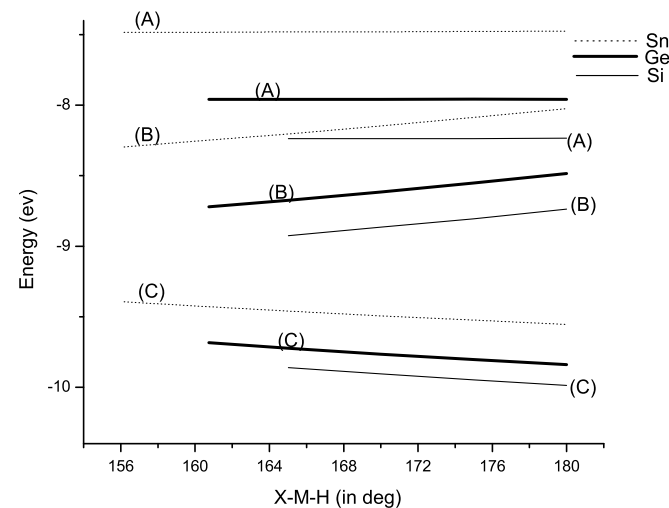


Fig. 4. Change in energy of three MO's shown in Fig. 3A–C with respect to the change in X–M–H angle (M = Si, Ge, Sn). “X” is centroid of the five-membered ring. Lowest value of the abscissa in each set of curves (Si, Ge, Sn) defines the optimized M–H distorted geometry of  $MCB_5H_7$ .

$\Delta E$  of Eq. (1) are 1.53,  $-4.16$ ,  $-12.6$  kcal/mol for Si, Ge and Sn, respectively. Lower bond strength of M–H down the group is reflected in the  $\Delta E$  values. In addition, we have estimated the bond strength of M–M bond by comparing the following equation with the above one.



$\Delta E$  of Eq. (2) are 5.12, 0.72,  $-6.03$  kcal/mol for Si, Ge and Sn, respectively. Higher exothermicity for Eq. (1) in comparison to Eq. (2) suggest stronger M–M bond in  $CB_5H_6M-MCB_5H_6$ . The structures of  $CB_5H_6M-MCB_5H_6$  (M = Si, Ge, Sn) are shown in Fig. 5. HOMO–LUMO gap (in eV) of these compounds are 5.00, 4.29 and 3.26 for Si, Ge and Sn, respectively. High HOMO–LUMO gap indicates the stability of these compounds. We find that, the structures having C–M–C dihedral angle of  $180^\circ$  are stable minima (Fig. 5).

M–M distances (Å) for Si, Ge and Sn are 2.3, 2.44 and 2.81, respectively, which indicate substantial M–M bonding. The M–M distances of experimentally characterized structures (values in parenthesis of Table 3) by Power et al. [56,57] are in good agreement with our results. The M–M distance is shorter than free  $M_2$  and its hydride analogue  $H_3M-MH_3$  (Table 3). Shortening of the M–M distance of bare dimer  $M_2$  upon capping with two

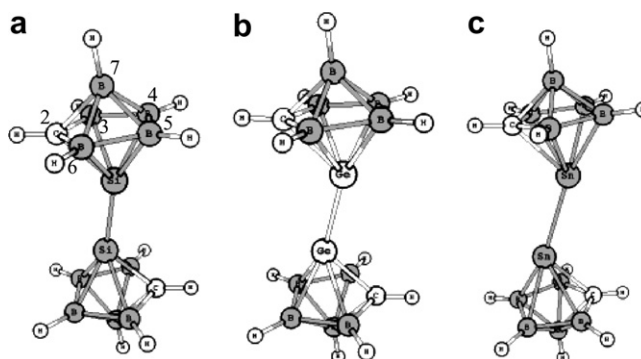


Fig. 5. Binuclear sandwich metal dimer  $CB_5H_6M-MCB_5H_6$  (M = Si, Ge, Sn).

Table 3  
Bond distance, Wiberg bond index and electron occupancy in M–M bond

M	Parameters	CB <sub>5</sub> H <sub>6</sub> M–MCB <sub>5</sub> H <sub>6</sub>	M <sub>2</sub>	H <sub>2</sub> M–MH <sub>2</sub>	H <sub>3</sub> M–MH <sub>3</sub>
Si	Si–Si distance (Å)	2.3	2.37	2.15	2.35
	Wiberg bond index	0.9487	2.00	1.99	1.01
	Occupancy	1.98	4.00	3.97	1.98
Ge	Ge–Ge distance (Å)	2.44 (2.39)	2.55	2.34	2.48
	Wiberg bond index	0.9080	2.00	1.7586	0.9808
	Occupancy	1.93	4.00	3.85	1.97
Sn	Sn–Sn distance (Å)	2.81 (2.81)	2.89	2.75	2.83
	Wiberg bond index	0.8630	2.00	1.4991	0.9450
	Occupancy	1.82	4.00	3.69	1.95

Value in the parentheses indicates geometrical parameter of the corresponding experimentally characterized structures.

nido-carborane is the most convincing proof of CB<sub>5</sub>H<sub>6</sub> stabilizing effect. In bare M<sub>2</sub> dimer, the filled valence  $\sigma$  molecular orbital has more electron density in the antibonding region which leads to elongation of M–M bond [58,59]. Capping with CB<sub>5</sub>H<sub>6</sub> may take away the antibonding electron density from the M nucleus which leads to shortening of M–M bond. Nature of M–M bond in CB<sub>5</sub>H<sub>6</sub>M–MCB<sub>5</sub>H<sub>6</sub> has been analyzed by NBO calculation and the results are given in Table 3.

Wiberg bond index between two metals in CB<sub>5</sub>H<sub>6</sub>M–MCB<sub>5</sub>H<sub>6</sub> is close to one and the electron occupancy is close to two, which indicate that there is a single bond. Formally, it can be concluded that among the 4 valence electrons of M, one is being utilized to form M–M bond and the other three electrons are involved in cluster bonding with nido

CB<sub>5</sub>H<sub>6</sub>. Nido CB<sub>5</sub>H<sub>6</sub> require 3 electrons according to Wade's rule. To understand the nature of bonding between M and CB<sub>5</sub>H<sub>6</sub> moiety, we calculate the activation energy for rotation of CB<sub>5</sub>H<sub>6</sub> ring in the dinuclear sandwich CB<sub>5</sub>H<sub>6</sub>M–MCB<sub>5</sub>H<sub>6</sub>. The ring has been rotated by changing C–M–M–C dihedral angle from the optimized geometry. Single point energy corresponding to the structure has been calculated to estimate the activation energy. Strength of ionic bonding is expected to have inverse dependence to the activation energy. Activation energies for the rotation of CB<sub>5</sub>H<sub>6</sub> ring are 7.18, 10.91, 14.43 kcal/mol for Si, Ge and Sn, respectively. Ferrocene is fluxional with the rotational barrier of nearly 17 kcal/mol. Therefore, these molecules are expected to be fluxional at room temperature. As the rotation is not free, we can conclude that the

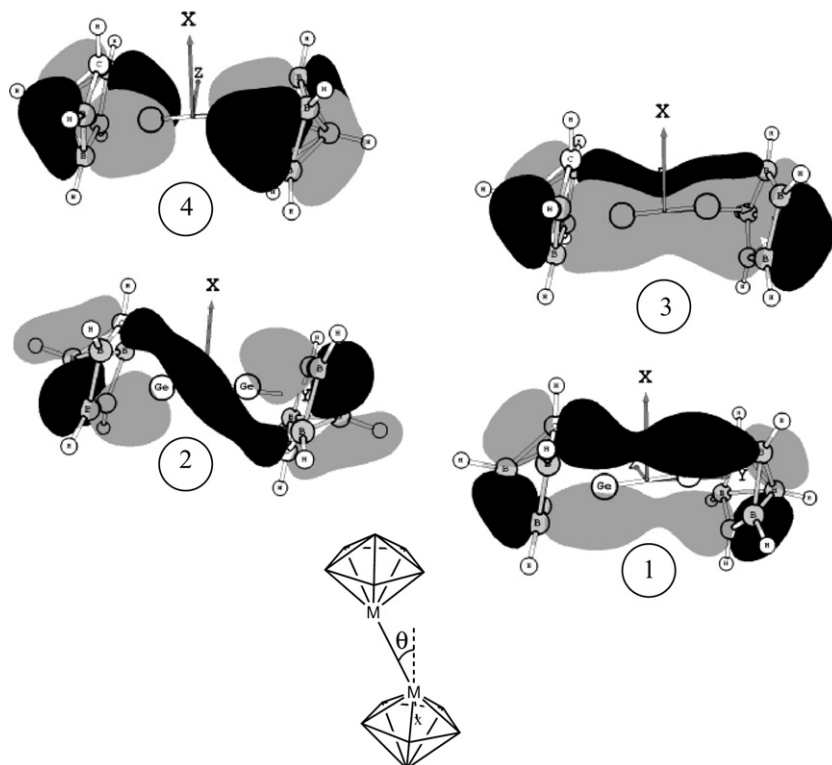


Fig. 6. Four higher energetic filled MO's which indicate M–M interaction by mainly  $p_x$ ,  $p_z$  orbitals of M. Here  $y$  is bonding axis between two M.  $\theta$  defines the extent of slip distortion.

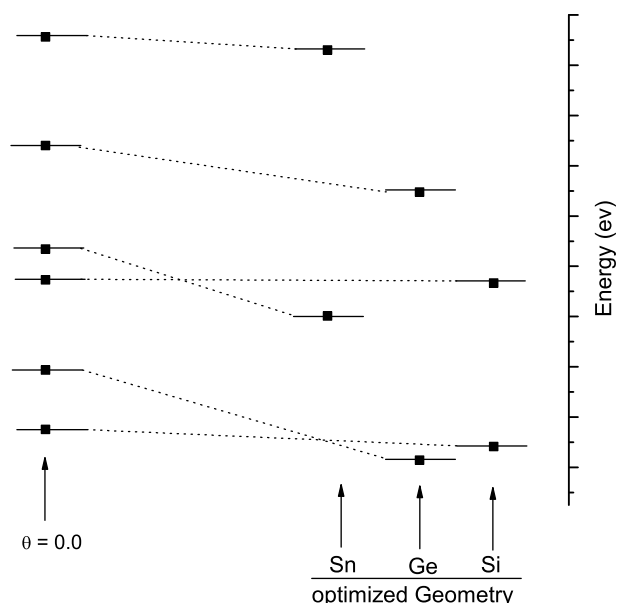


Fig. 7. Change in energy gap between two M–M  $\pi$ -bonding MOs [(1) and (3) of Fig. 6] upon changing  $\theta$  from optimized geometry to  $0.0^\circ$ .

bonding between M and  $\text{CB}_5\text{H}_6$  moiety is essentially a mixture of ionic and covalent in nature.

The interesting feature of  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  is its non-linear *trans*-bend geometry (Fig. 5) [60]. Slip-distortion of M–M bond increases down the group from Si to Sn. X–M–M angle (Table 1) in  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  is greater than its mononuclear hydride analogue  $1\text{M}-2-\text{CB}_5\text{H}_6$  (Table 1, X–M–H angle). This clearly indicates that some additional factor (apart from the explanation given for slip-distortion of M–H bond in  $1\text{M}-2-\text{CB}_5\text{H}_6$ ) is playing a role towards the slip-distortion of M–M bonds in case of binuclear sandwich  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$ . Molecular orbital analysis has been done to understand slip distortion of M–M bond.

We concentrated on four molecular orbitals shown in Fig. 6. Molecular orbitals (1) and (3) show bonding interaction (In M–M bond), which are due to  $p_x$  and  $p_z$  orbitals of M, respectively. Among the other two MO's, (4) is the antibonding analogue (In M–M bond) of (3). The antibonding analogue of (1) gets mixed with  $p_y$  of the metal and produces (2). We have noticed that by changing  $\theta$  (Fig. 6) from  $0.0^\circ$  to slip-distorted stable geometry (shown in Fig. 5), MO (2) is stabilized and the energy gap between the bonding (1) and (3) MO's increases (The energies of these MO's for the stable distorted geometry and  $\theta = 0.0^\circ$  are given in supporting information). Increase in energy gap between the two  $\pi$  bonding MOs [(1) and (3) of

Fig. 6] indicates that one of the  $\pi$  bonding MOs may be favored more upon distortion. The change in energy gap between the two bonding MOs [Between (1) and (3) of Fig. 6] are shown in Fig. 7. We conclude that the stabilization of MO (2) and preference of one of the  $\pi$  bonding MO's [(1) and (3) of Fig. 6] may be the driving force for the extra slippage of M–M in  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$ .

Carboranes are aromatic and three dimensional delocalized bonding leads to exceptional stability of these clusters. Variation of aromaticity (NICS value at the cage center) from  $\text{B}_7\text{H}_7^{2-}$  to  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  (Table 4) has been probed. No considerable change in aromaticity indicates that the same aromatic character is retained from  $\text{B}_7\text{H}_7^{2-}$  to  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$ .

#### 4. Conclusion

Consecutive substitution of two boron atoms of  $\text{B}_7\text{H}_7^{2-}$  by M (Si, Ge, Sn) and carbon followed by dehydrogenation may lead to binuclear sandwich  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$ . M prefers to stay at the apex of pentagonal  $\text{MCB}_6\text{H}_7$  where as carbon prefers to stay at the ring due to optimum overlap between the five membered face of ligand and metal fragment. Thermodynamic feasibility for occupying the apex position in pentagonal bipyramidal systems ( $\text{MCB}_6\text{H}_7$ ) are even larger than their icosahedral analogue. Bending of apex M–H group in  $\text{MCB}_6\text{H}_7$  above the pentagonal face is due to stabilization of one of the ring-cap bonding MO's (shown in Fig. 3B). M–M bond strengths in  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  are large compared to free  $\text{M}_2$  and  $\text{H}_3\text{M}-\text{MH}_3$ . Smaller M–M bond lengths in  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  compared to free  $\text{M}_2$  is convincing proof of  $\text{CB}_5\text{H}_6$  stabilizing effect. NBO analysis indicates a covalent single M–M bonding. Activated rotation of  $\text{CB}_5\text{H}_6$  in  $\text{CB}_5\text{H}_6\text{M}-\text{MCB}_5\text{H}_6$  indicates a mixed ionic-covalent bonding between M and  $\text{CB}_5\text{H}_6$ . Stabilization of MO (2) of Fig. 6 coupled with stabilization of one of the  $\pi$  bonding MO's (between M and M) are suspected to be encouraged by nonlinear *trans*-bend geometry of the sandwiched dimer. Our theoretical investigations invite experimental verification.

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Table 4  
Nuclear Independent Chemical Shift (NICS) at the center of pentagonal cage

M	Figure	M = Si	Ge	Sn
$\text{B}_7\text{H}_7^{2-}$	Fig. 1a			NICS = -19.73
$\text{MB}_6\text{H}_7$	Fig. 2a	-19.51	-19.79	-19.05
$1\text{M}-2-\text{CB}_5\text{H}_6$	Fig. 2c	-19.35	-19.46	-18.93
$\text{H}_6\text{B}_5\text{C}-\text{M}-\text{M}-\text{CB}_5\text{H}_6$	Fig. 5	-19.19	-19.39	-18.42

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.12.034](https://doi.org/10.1016/j.jorganchem.2007.12.034).

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