

## Supporting Information

**Table. S1. Comparison among energies of different isomers of  $[\text{Pd}_3\text{Ge}_{18}(\text{SnMe}_3)_6]^{2-}$  using non-relativistic DFT and all-electron DKH2 calculations**

$\Delta E$ (kcal/mol)	Regular DFT	All-electron DKH2
<i>mm</i> -isomer*	8.9	2.3
<i>tm</i> -isomer*	0.0	0.0
<i>tt</i> -isomer*	18.8	10.3

\* *mm*/*tm*/*tt*-isomer denotes the substitution sites on the two  $\text{Ge}_9$  cages. *m* stands for substitution on middle layer and *t* stands for top layer.

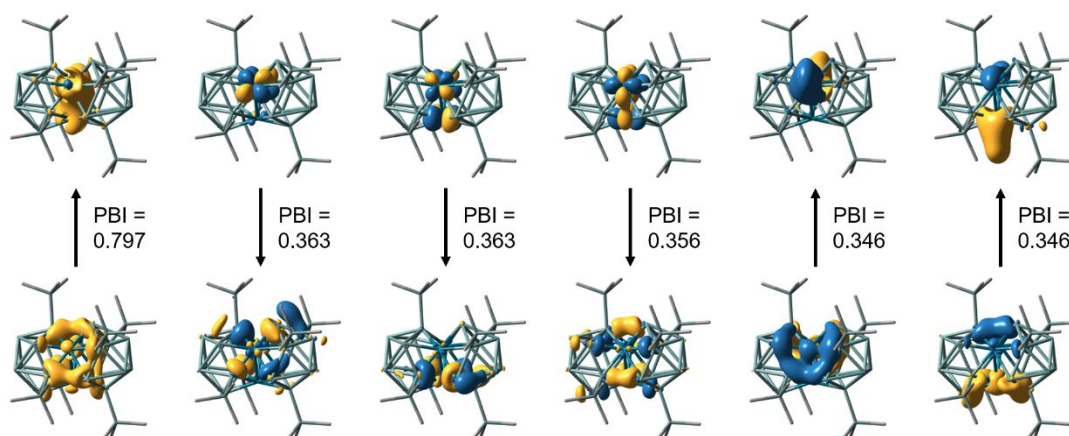


Figure S1. Top PIO pairs of the  $\text{Pd}_3$  triangle and the  $\text{Ge}_{18}(\text{SnMe}_3)_6$  cage with respect to each other in the cluster compound **1'**. Isovalue: 0.035.

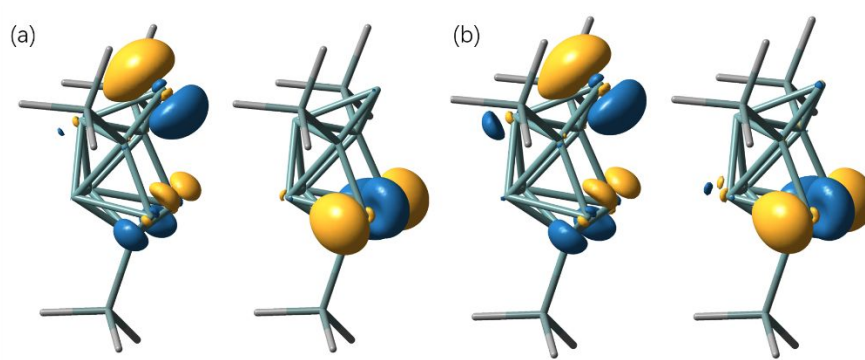


Figure S2. (a) The two singly occupied Spin Natural Orbitals (SNOs) of triplet *m*- $[\text{Ge}_9\text{R}_3]^\cdot$ . (b) Degenerate LUMOs of *m*- $[\text{Ge}_9\text{R}_3]^+$  for comparison. Isovalue: 0.05.

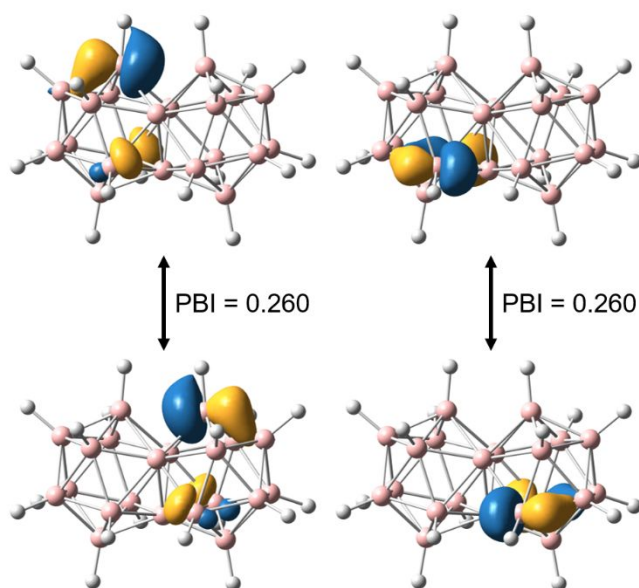


Figure S3. Top two PIO pairs of the two  $B_9H_9$  moieties with respect to each other in the borane cluster compound  $[B_{21}H_{18}]^-$ . Note that the PIOs are similar to those of the  $Ge_9$  cage, while the PIO-based bond indices (PBIs) are significantly smaller than those in cluster **1'** as reported in the main text. Isovalue: 0.10.

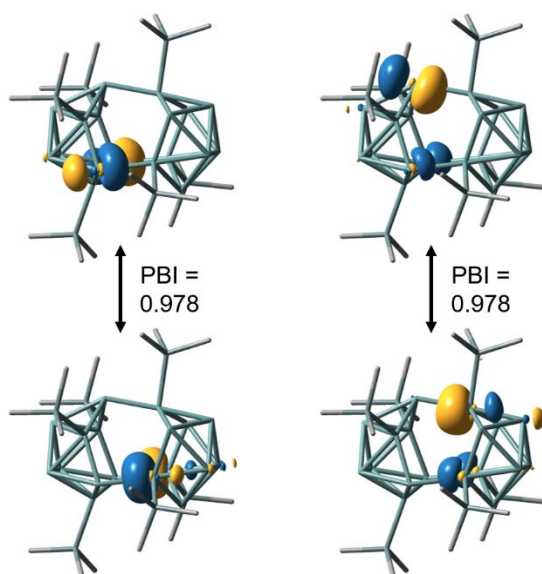


Figure S4. Top two PIO pairs of the two  $Ge_9R_3$  cages with respect to each other in the hypothetical cluster compound  $[Ge_{18}(SnMe_3)_6]^{2-}$ . Note that they are almost the same as those of the  $Ge_9R_3$  fragments in the cluster **1'**. The PBIs are slightly reduced in cluster **1'** because the donor-acceptor interaction between the  $Pd_3$  triangle and the  $Ge$  cage weakens the formal bond between the two  $Ge_9R_3$  fragments. Isovalue: 0.05.

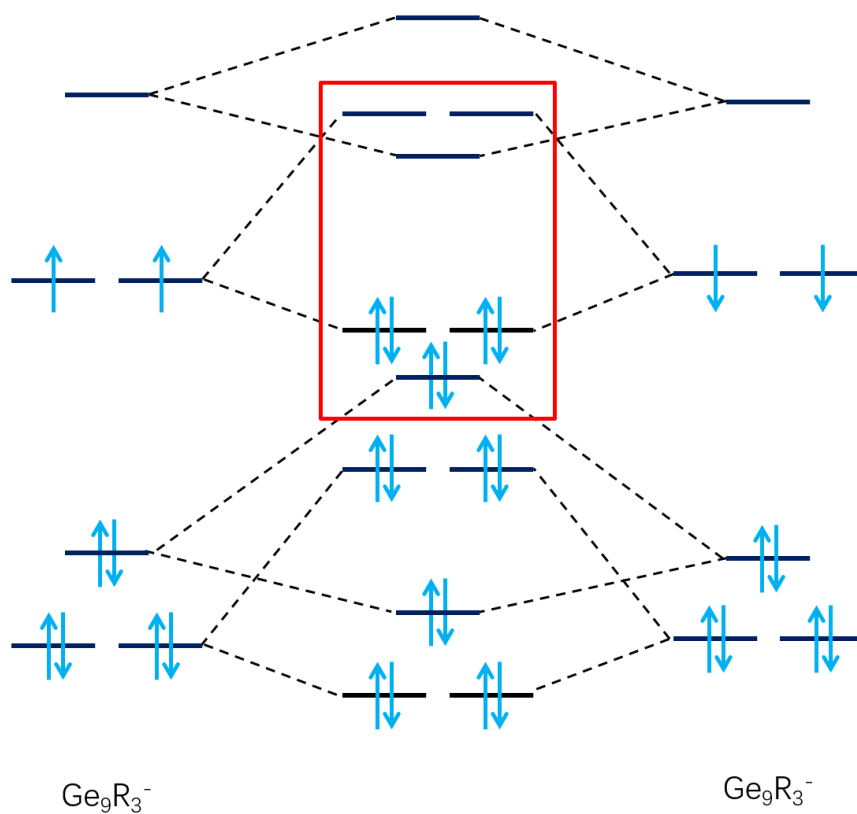


Figure S5. Schematic orbital interaction diagram between two  $\text{Ge}_9\text{R}_3^-$  cages showing more frontier orbitals of each cage. The resulting frontier orbitals highlighted in the red box correspond to the six dominant PIOs of the  $\text{Ge}_{18}\text{R}_6$  cage given in Figure S1.