

# Bonding in Some Unsaturated Compounds of Heavy Group 14 Elements- Importance of Nonbonding Orbital

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Schaefer et al. have shown that the order of relative stabilities of the four isomers **1**–**4** of disilyne ( $\text{HSi}\equiv\text{SiH}$ ) is just opposite to that of the acetylene. The trans-bent structure **2** is more stable than the linear structure **1** which is not a stable minimum. The dibridged structure **4** is the most stable isomer followed by **3** with the order  $4 > 3 > 2 > 1$ . A simple rule of thumb appears to be that the more nonbonding (n) orbitals present at the expense of  $\pi$  bonding orbitals, the more favorable the isomer is. The trans-bent structure **2** has been characterized with the donor-acceptor interactions between the two doublet silynes with an additional  $\pi$  bond as depicted in formula **5**.

With some suitable substituents, the structure **2** may become the global minimum. Our recent study on metallacetylenes,  $\text{R}_1\text{C}\equiv\text{MR}_2$  ( $\text{M}=\text{Si}$ ,  $\text{Ge}$ , and  $\text{Sn}$ ) with bonding mode **5** shows that the nonbonding orbitals are stabilized through highly electronegative substituents such as fluorine. The C-M  $\pi$  bond is switched to  $\sigma$  bond with a local triplet carbene structure on the carbon site for the ground state as indicated in **6**. For the acetylene analogues ( $\text{RM}\equiv\text{MR}$ ,  $\text{M}=\text{Si}$ ,  $\text{Ge}$ ,  $\text{Sn}$ , and  $\text{Pb}$ ), the switch of the  $\pi$  bond to  $\sigma$  bond for the ground singlet shown in **7** is also observed when the nonbonding orbitals are stabilized through either substituent effect or the nature of the heavy element **7**.

