

Multiply Bonded Heavy Main Group Elements

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Once thought to be confined to first row elements, multiple bonding has now been demonstrated in several heavy main group elements.¹ Multiple bonds were originally deemed unlikely for large elements in the main group due to weak $p\pi$ interaction.² The syntheses of distannene and digermene in 1976,³ and the realization of stable silicon and phosphorous double bonds in 1981,^{4,5} however, have shown that such bonding is possible. Studies of these compounds are motivated by insight into bonding, as well as comparison of experimental physical characteristics with theory.

Synthesis in this area entails the use of sterically demanding ligands, and this has become the central theme in the preparation of new multiply bonded heavy main group compounds. These ligands provide kinetic stabilization of the multiple bonds with respect to oligomerization, as well as a general steric barrier to reactions at these sites.

Recent examples of heavy element multiple bonding have validated the success of this approach. Germanium, for example, has provided a variety of multiply bonded compounds. Digermenes have been prepared by reductive coupling and photochemical techniques using bulky groups such as the 2,6-diisopropylphenyl ligand.⁶ X-ray crystal structures of these compounds show significant pyramidalization around each germanium center, the degree of which is dependent upon the ligand. *Ab initio* calculations show a comparable folded geometry for the hypothetical Ge_2H_4 species.⁷ One explanation of the folded shape focuses on the narrowing of the energy gap between the π and σ^* levels of $\text{Ge}=\text{Ge}$ relative to $\text{Si}=\text{Si}$ and $\text{C}=\text{C}$ double bonds. Upon distortion from planar D_{2h} symmetry to a folded C_{2h} configuration, these levels can mix as shown in Figure 1, lowering the energy of the HOMO.⁸



Figure 1.

More recently, a germanium analog of cyclopropenium has been prepared.⁹ Oxidation of a cyclotrigermene containing bulky tri-*tert*-butylsilyl groups¹⁰ yields a 2π electron cation, which has been analyzed by X-ray crystallography. The structure reveals a mean Ge-Ge length of 2.326 Å, which lies between the single (2.522 Å) and double (2.239 Å) bond values of the cyclotrigermene precursor. The planarity and electron delocalization of the species are analogous to cyclopropenium. Aromatic in a Hückel sense ($4n+2$ π electrons), the ring is stable despite considerable strain.

The first example of a heavy Group 4 element forming a triple bond to a transition metal has also involved germanium. Using the sterically bulky 2,6-bis(2,4,6-methylphenyl)phenyl ligand, Power and coworkers have prepared a molybdenum germylyne complex.¹¹ In addition

to having a short Mo-Ge bond length of 2.271 Å, the complex also has a nearly idealized Mo-Ge-C bond angle of 172.2°.

The multiple bonding capability of gallium has also been recently demonstrated. Digallane compounds, first synthesized in 1989,¹² have been reduced to yield radical anions believed to contain one electron π bonds.^{13,14} For example, the species $\text{Trip}_2\text{GaGaTrip}_2$ (Trip = 2,4,6-*i*-Pr₃C₆H₃) has been reduced with lithium to give $\text{Trip}_2\text{GaGaTrip}_2^-$.¹³ Dramatic decreases in bond length and in the torsional angle of the compound upon reduction are indicative of the induced π -bonding character. Gallium-based cyclopropenium analogs have recently been prepared.^{15,16} Reduction of $\text{Mes}_2\text{C}_6\text{H}_3\text{GaCl}_2$ (Mes = 2,4,6-Me₃C₆H₃) with sodium or potassium yields $\text{Na}_2[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$, and $\text{K}_2[(\text{Mes}_2\text{C}_6\text{H}_3)\text{Ga}]_3$, respectively. These cyclogallanes are believed to be aromatic, 2π electron species. Changing the Mes group to the bulkier Mes* (Mes* = 2,4,6-*i*-Pr₃C₆H₃)¹⁷ has produced a novel gallyne compound, which has the shortest gallium-gallium bond distance yet reported at 2.319 Å.¹⁸ Bridged by sodium cations, the triple bond shows nonidealized C-Ga-Ga angles of 128.5° and 133.5°. Theoretical studies have been performed which rationalize the bent geometry of this species.^{18,19}

In perhaps the most dramatic example of heavy main group element multiple bonding, Okazaki and coworkers have recently reported a dibismuthene compound.²⁰ Using the large Tbt ligand (Tbt = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl), researchers have been able to generate the TbtBiBiTbt species, shown in Figure 2. The synthesis involves the formation of a six membered Bi-Se ring, which is deselenated to yield dibismuthene. Amazingly, this compound exhibits a fair degree of air stability, and maintains a double bond both in the solid state and in solution, shown from X-ray crystallography and the UV/Visible spectrum. The nonidealized bond angles of the complex demonstrate the "inert pair effect" experienced by the

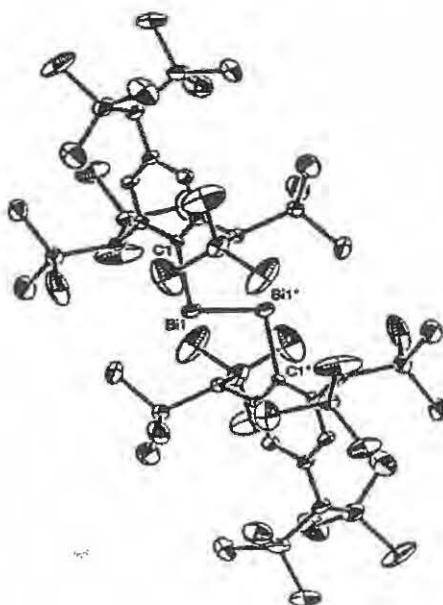


Figure 2.

TbtBiBiTbt: Tbt = 2,4,6-tris(bis(trimethylsilyl)methyl)phenyl

bismuth atoms. At 134 cm^{-1} , the Raman stretch of the bond is 31 cm^{-1} higher than in $\text{Ph}_2\text{BiBiPh}_2$, a shift which correlates well with the theoretically predicted 34 cm^{-1} difference. In addition, the $\pi \rightarrow \pi^*$ transition shows a red shift from diphosphene and diarsine species that is predicted by theory.²¹

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