Dative bonds beyond the second row - Shaping a suitable lone pair

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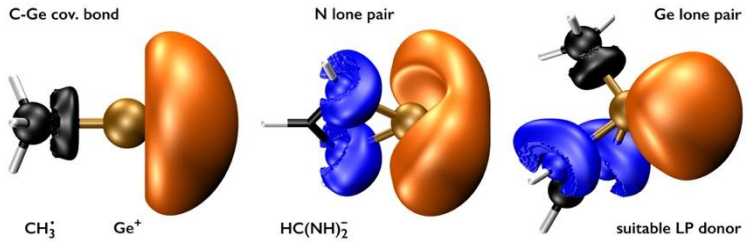
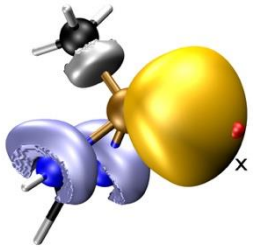
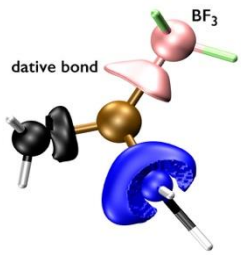
Dative bonds are commonly observed between atoms with different electronegativities. However, the atoms in molecules (AIM) and electron localization function (ELF) analysis of the electron density by B3LYP/6-31G(d,p) in Ge-polycations shows conclusively that geometric and electronic constraints can enforce homonuclear dative bonds.

These bonds base on lone pairs on the Ge ion, but lone pairs suitable to engage in dative bonds are rarely seen on atoms beyond the second row of the periodic table. Calculations show that a designated combination of two ligands of which one forms electrostatic and the other covalent bonds to the Ge ion force the electron density on the Ge ion into a lone pair ready to engage in dative bonds.



The ELF is used to characterize and quantify these lone pairs. For example, the direction of a lone pair can be identified by the point on the ELF iso-value surface furthest away from the central Ge ion (X, marked red). The so defined GeX axis aligns with the dative bond in Ge cluster compounds built with these lone pairs donors.





At the same time, the lone pair acceptors BH_3 and BF_3 can be used to judge whether these lone pairs can participate in homonuclear dative bonds. While the majority of Ge building blocks can bond to BH_3, but only those able to bond to BF_3 can engage in Ge–Ge dative bonds.