HOW LIGAND PROPERTIES AFFECT THE FORMATION AND CHARACTERISTICS OF RECOUPLED PAIR BONDS

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Our group has developed a theoretical framework for understanding hypervalency called recoupled pair bonding. In a recoupled pair bond, a singly occupied orbital of an incoming ligand is able to decouple a pair of electrons on a central atom and form a bond with one of the electrons. The other electron is then free to bond with a second ligand. However, not every ligand is able to induce recoupling and lead to the formation of hypervalent compounds; SF_4 exists, but SH_4 is not stable, for example. We have investigated a large variety of monovalent ligands (including H, F, Cl, OH, NH_2, CH_3, and other radicals) to discover which ligands are capable of recoupling the $3p^2$ electron pair of sulfur and to quantify the strength of these bonds relative to covalent bonds formed with the same ligand. Also of interest is which properties of the various ligands correlate with their ability to recouple a pair of electrons. We have also benchmarked the accuracy of density functional theory in the description of recoupled pair bonds compared to high level MRCI and RCCSD(T) calculations as a possible way to test the recoupling ability of larger ligands such as the phenyl radical (C_6H_5).