

Here is the periodic table of elements! You're probably already familiar with it if you have taken any chemistry classes before. The majority of the high chemistry courses at the very basic level, however, often focus on the following sections on the periodic table but not on the middle section: transition metals. Transition metals are widely used in a variety of catalytic reactions, including hydrogenation, hydrodefluorination, and cross-coupling, due to excellent ability to undergo redox cycles and facilitate complex bond transformations. Such catalysts are essential in both industrial and academic synthetic chemistry because of high efficiency and broad substrate scope.

However, many transition-metal catalysts are expensive, toxic, and environmentally hazardous, which limits sustainable use and poses challenges for large-scale or green chemistry applications.

Bismuth, one of the main-group elements, offers a promising alternative. The advantageous aspects of bismuth are its low toxicity and affordability. Essentially, bismuth is perceived as one of the safest metals since it is often employed for medicinal purposes. Moreover, the comparison of prices of bismuth and other transition metals the best catalytic activities eludes the viability of bismuth as potentially applicable catalysts in the industry. Moreover, it is capable of mediating redox catalysis under mild conditions. Studies by Moon and Cornella (2022) demonstrate that Bi(III)/Bi(I) redox cycles can enable radical polymerization, photocatalysis, hydrodefluorination, and other transformations, while Ramler et al. (2020) show that molecular bismuth complexes can facilitate photochemically induced radical dehydrocoupling. These works highlight bismuth's versatility, low toxicity, and recyclability, suggesting it as a viable replacement for transition metals in sustainable catalysis.

Developing organobismuth catalysts could significantly improve sustainable and efficient catalyst use, reducing reliance on expensive and hazardous transition metals while expanding the toolbox for synthetic chemists. Understanding the structure, stability, and reactivity of these complexes is therefore critical for advancing greener chemistry. Despite these promising results, relatively few studies have explored organobismuth complexes in depth. For instance, Cornella and co-workers noted that the dihydride intermediate is unstable above 0 °C, highlighting challenges in catalyst design. Additionally, mechanistic pathways and ligand effects on Bi-H bond stability remain underexplored, limiting predictive control over catalytic activity. The purpose of my research is to use computational chemistry to investigate the behavior of organobismuth complexes. Molecular structures will be optimized with quantum mechanical methods (Hartree-Fock and DFT), and bonding will be analyzed using quasi-atomic orbital (QUAO) analysis. The study will examine how different ligands affect the Bi-H bond and overall catalyst stability, as well as calculate the energy required for homolytic Bi-H cleavage; according to current literature, the Bi(III)/Bi(I) redox cycle, involving homolytic cleavage of Bi-H bond, is primarily affected by the ligand design. Insights gained will clarify how efficiently the catalyst can cycle between Bi(III) and Bi(II) oxidation states, guiding the rational design of organobismuth catalysts for hydrogenation, radical polymerization, and other applications.

Here are the steps of the computational analysis. First, I optimize molecular geometries with Hartree-Fock and Density Functional Theory methods; it is necessary to confirm local minima on the potential energy surface (PES) by running frequency calculation—if any of the frequency values are imaginary, indicating negative eigenvalues in diagonalized Hessian matrix, then the optimized point is not located in the true local minima on PES. Then, I analyze bonding through quasi-atomic orbitals

(QUAO), focusing on bond order, orbital occupation, and s/p character. I am planning on varying the following three independent variables: substituent types, such as $-F$, $-NH_2$, $-OCH_3$, $-CH_3$, $-SCH_3$, and $-NO_2$; Substituent positions, such as para versus ortho on phenyl groups; and denticity of ligands (e.g., tridentate, tetradentate, etc.)

Here are the input files for geometry optimization, for example. After the results have been obtained, by comparing the QUAO profiles and the bond dissociation energies across these variations, I would see which substituent to employ as well as its exact position in order to synthesize the most stable and efficient organobismuth catalysts.

If successful, my research will clarify how to stabilize and tune Bi-H bonds, helping chemists design more efficient organobismuth catalysts, which could reduce our reliance on hazardous transition metals and expand the toolkit for sustainable catalysis in hydrogenation, radical polymerization, and beyond. In other words, it is one step toward greener, safer, and more affordable chemistry.”