Computational Investigation of Electronic and Geometric Effects of Ligand Architecture on Homolytic Bi–S Bond Cleavage in Diaryl Bismuth Thiophenolate Complexes

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Concerns regarding the toxicity, cost, and sustainability of traditional transition-metal catalysts have driven growing interest in main-group alternatives. Bismuth complexes have emerged as promising candidates; however, ligand design principles governing Bi–X bond homolysis and radical stabilization remain poorly understood. In particular, the relationship between ligand architecture, electronic structure, and homolytic bond dissociation energies (BDEs) has not been systematically established. Herein, we present a computational investigation of diaryl bismuth thiophenolate (Bi(diaryl)SPh) complexes with systematically varied aryl substituents (X = H, CH3, CF3, i-Pr, NH2, NO2, OCH3). Density functional theory (DFT) was used to compute homolytic BDEs, while quasi-atomic orbital (QUAO) analysis probed charge distribution and orbital interactions. Bi–S BDEs vary widely with substituent identity, particularly in systems with ortho- and para-substitution lacking bridging motifs; however, no clear electronic correlation was observed. Instead, steric effects from ortho substituents and conformational flexibility dominate bond strength. When these factors were controlled, BDEs converged across substituents. Charge analysis revealed that electronic effects become significant only with strongly electron-withdrawing groups at both ortho and para positions, increasing positive charge at the bismuth center. These results suggest that optimal ligand design should incorporate rigidifying bridges and small, strongly electron-withdrawing substituents to minimize steric effects. Overall, this work demonstrates how computational approaches disentangle steric and electronic contributions to bond homolysis, providing design principles for sustainable bismuth-based catalysts.

Awards Won:

American Chemical Society: Fourth Award of $1,000