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COLLEGE OF ARTS & SCIENCES
Department of Chemistry

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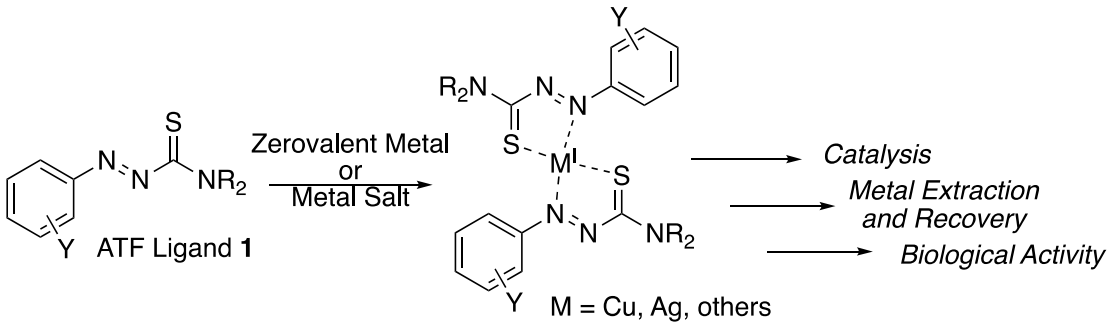
Redox-Active Azothioformamide Ligands: From Coordination to Catalysis

ABSTRACT:

Redox-active azothioformamide (ATF) ligands, with an N=N–C=S 1,3-heterodiene binding moiety, have the unique ability to oxidatively dissolve zerovalent late transition metals forming coordination complexes with singly reduced ligands. Starting from oxidized salts, specifically Cu^{I} salts, the coordination event remains neutral and leads to either 2:1 or 1:1 complexes (found as 2:2 dimers) based on the metal salt source. Extensive UV-Vis titration studies indicate that both the 2:1 and 2:2 dimer complexes fit best with 2:1 binding association models yielding many potential complexation mechanisms which were supported by X-ray crystal structures and computational models. The one-pot ATF synthesis allows for rapid access to a ligand library as to examine the binding effects and potential redox events upon complexation. *Para*-substituted electron-donating group (EDG) appendages provided the strongest binding associations and X-ray crystal data on these complexes compliment the multi-mechanism binding theory. Electron-withdrawing groups (EWG) produced complexes yet with weaker binding association values. Appended ATF ligands were tested as Cu^{I} catalysts and EDG ATFs were found highly effective for the reductive insertion of CO_2 into terminal alkynes to create propiolic acids. Mild conditions also promoted decarboxylation of propiolic acids in the absence of CO_2 to form Glaser-Hay homodiynes using DMSO as both solvent and oxidant. ATF copper complexes were equally successful as CuAAC catalysts. Lastly, a variety of these compounds have been tested for their biological activity with some exuding high cytotoxicity (1.4 µM) against A549 human adenocarcinoma cells. In this seminar, a variety of the merits of ATF ligands will be discussed.



BIO:

My research experiences have been broad but I tend to focus my research on the creative development of strategies towards building complex organic compounds and novel material frameworks. In addition to this ongoing research I also have concurrent projects focused on immunostimulants, and pesticide fate and degradation.