Designed Synthesis and Catalytic Applications of Azo-Based Ligands in Transition Metal Complexes

Abstract

This thesis presents a comprehensive investigation into the synthesis, electronic structure, and applications of azo-based redox-active ligands, specifically diaryl-azo-oxime, amino-azo-quinoline, and 2-(pyridylazo)aniline. The study emphasizes their capacity for ligand-centered redox non-innocence, radical stabilization, catalytic activity and biological relevance in coordination chemistry. The first chapter examines the redox behaviour of phenyl-azo-oxime ligands coordinated to rhodium(III). Structural studies revealed that the orientation of the ligand governs its electronic properties, with the *trans*-isomer exhibiting enhanced electron-accepting ability due to coplanarity and π-π stacking while the *cis*-isomer remains inactive. Reduction with $NaBH_4$ produced a radical complex stabilized by oxime…oximato hydrogen bonding, a finding supported by DFT (Density Functional Theory) and TD-DFT (Time Dependent Density Functional Theory) analyses. The second chapter focuses on an amino-azo-quinoline ligand and its Ni(II) complexes. Single-crystal X-ray diffraction (SCXRD) demonstrated extended hydrogen bonding and π-π stacking. Electrochemical and spectroscopic studies indicated ligand-centered reductions and mixed metal-ligand oxidations. Both ligand and complexes showed anti-cancer activity, with the complexes proving more effective, attributed to their rigid square-planar geometry and stronger DNA binding, corroborated by molecular docking with B-DNA. The third chapter explores catalytic applications of azo-oxime ligands with ruthenium. A ruthenium(II) complex of *p*-chloro-aryl-azo-oxime was synthesized and characterized as a robust ligand-based redox catalyst. It efficiently catalyzed alcohol dehydrogenation and sp^3 C–H activation of fluorene under aerobic conditions, with the azo moiety driving redox steps while the metal acted as a passive spectator. The final chapter investigates a ruthenium(II)-hydride complex with 2-(pyridylazo)aniline ligand for direct dehydrogenative synthesis of bis(indolyl)methanes (BIMs). Mechanistic studies identified hydrogen atom transfer to the azo group as the key step, followed by aldehyde condensation and base induced nucleophilic addition, highlighting ligand-metal cooperation for selective and sustainable catalysis. Overall, this work positions azo-based ligands as versatile platforms for stabilizing radicals, facilitating ligand-assisted electron transfer and promoting transformations with significant bio-relevant catalytic applications. The insights gained contribute to the broader design of redox-active ligands for next-generation catalysts and bioactive complexes.

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