Exploring the Influence of Azo Ligands in Catalysis: Ruthenium-Catalyzed C–C and C–N Bond Formation and Ligand-Catalyzed CO_2 Capture

Abstract

This thesis investigates the rational design, synthesis, and catalytic applications of redox-active azo-based ligands, with a particular emphasis on diaryl-azo-oxime and bis-azo-aromatic amine frameworks. Upon coordination with ruthenium centers, these ligands provide a versatile platform for exploring redox-switchable reactivity, ligand-centered electron transfer, and sustainable catalysis. The research is presented across six chapters, beginning with a comprehensive introduction that outlines the scientific motivation, ligand design strategies, and a suite of characterization techniques including electrochemical, spectroscopic, and computational methods. Chapter 2 and 3 focus on the synthesis of ruthenium(II) complexes of the general formula *trans*-[Ru(L)(CO)Cl(PPh_3)$_2$] incorporating azo-oxime ligands with electronically varied aryl substituents. Structural and redox studies reveal that variations in the Ru–N_{azo} and Ru–N_{oxime} bond lengths and electrochemical behavior are directly influenced by ligand electronics. These complexes exhibit significant catalytic potential in electron transfer mediated transformations, such as the α-alkylation of ketones and the synthesis of 2-substituted quinoline derivatives. Mechanistic investigations suggest that catalysis is driven by ligand-centered redox events, with the ruthenium center functioning primarily as a geometrical anchor. Chapter 4 describes the synthesis and characterization of an air- and moisture-stable Ru(II) complex, *trans*-[Ru(NpL)(CO)Cl(PPh_3)$_2$], which acts as an efficient pre-catalyst for the aerobic dehydrogenative coupling of both aliphatic and aromatic primary alcohols with *o*-amino or N-substituted benzamides to afford quinazolin-4(3H)-ones. Both experimental and theoretical analyses support a hydrogen atom transfer (HAT) mechanism mediated by the azo group, with the Ru center remaining redox-inactive. Chapter 5 highlights the catalytic valorization of CO_2 using a bis-azo-aromatic amine-based complex. The transformation proceeds *via* a unique triplet diradical intermediate that initiates a cascade, converting CO_2 into C_3 products namely acetic acid and acetone *via* glyoxal intermediates. This study underscores the potential of fluxional, electro-active ligand platforms in carbon capture and utilization, offering a promising strategy for sustainable catalysis. The final chapter presents a hexacoordinated Ru(III) complex with a bis-azo-diamido scaffold, effectively catalyzing the direct N-alkylation of aromatic amines using alcohols. The reaction proceeds through ligand-centered dehydrogenation followed by condensation and a borrowing hydrogenation sequence, with the azo moiety driving redox activity and the metal center assisting in hydrogenation. Overall, this work establishes redox active azo ligands as powerful components in the development of advanced transition metal complexes for tunable and sustainable catalysis. The insights gained herein pave the way for future exploration of ligand centered reactivity in small molecule activation and green synthetic methodologies.

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