Design and Synthesis of Rhenium and Ruthenium Complexes and Their Catalytic Applications Towards Sustainable Transformation (Index No. 45/20/Chem./27)

Abstract

The work in this thesis is five folds consisting of an introduction cum literature survey chapter and four chapters based on my Ph.D. work. This work presents a comprehensive investigation into the design, synthesis, and functional evaluation of transition-metal complexes for applications in electrocatalysis, photocatalysis, and organocatalysis, with emphasis on energy conversion and sustainable synthesis. In the 2nd chapter two dinuclear rhenium(V) oxo complexes were developed as homogeneous electrocatalysts for water oxidation in acetonitrile–water mixtures. Oxygen evolution was confirmed by GC-TCD analysis, while controlled potential electrolysis (CPE) at 1.30 V (vs Ag/AgCl, pH ~7) revealed a redox-induced electron transfer (RIET) pathway leading to monocationic species, subsequently oxidized to high-valent Re(VI)=O intermediates. In the 3rd chapter a series of six isomeric rhenium(I) tricarbonyl complexes with asymmetric di-imine ligands were synthesized, structurally characterized, and evaluated for CO_2 reduction. Electrochemical reduction in the presence of trifluoroethanol produced CH_4 and CO, whereas photochemical reduction with TEOA selectively yielded CO. Mechanistic insights from NMR, UV–Vis, and TD-DFT analyses emphasized the influence of ligand design on catalytic efficiency. In the 4th chapter exploration of ruthenium complexes bearing bis(2-picolyl)amine, bipyridine, and BF_2-chelated dipyrromethane (BODIPY) ligands highlighted the impact of electron-donating substituents on light-harvesting and catalytic performance. These self-photosensitizing systems exhibited efficient visible-light-driven CO_2 reduction to CO, with detailed studies of solvent effects, product distribution, and intermediate species elucidating their redox behaviour and guiding future catalyst design. Finally, in the 5th Ru(III) polypyridyl complexes were employed as organocatalysts for dehydrogenative annulation reactions, enabling the atom-economical synthesis of substituted quinolines from 2-aminobenzyl alcohols and secondary alcohols or ketones. The cooperative interplay between the Ru(III) center and redox-active ligands was found to be crucial in hydrogen abstraction and bond construction, underscoring the synthetic versatility of these systems.Overall, this research integrates electrocatalysis, photocatalysis, and organocatalysis to demonstrate how rational ligand and metal center design enables efficient energy-related transformations and sustainable organic synthesis. The mechanistic insights gained offer valuable guidelines for advancing solar-to-fuel conversion and catalytic methodologies.

Uday Shee
26/08/2025

J Rajak 26/08/2025
Dr Kajal Krishna Rajak
Professor of Chemistry
Jadavpur University
Kolkata-700032