

PHOTOREDOX CATALYSIS BY POLYPYRIDYL TRANSITION METAL COMPLEXES: USING VISIBLE LIGHT AS A REAGENT IN ORGANIC SYNTHESIS

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INTRODUCTION

Approaches to photochemistry in organic synthesis have heretofore found niche application due to the requirement for specialized equipment to generate high-intensity ultraviolet light.¹ In contrast, the use of organometallic complexes to capture energy from ubiquitous sources of visible light and transfer it to an organic substrate has recently received significant attention, resulting in the improvement of efficiency and utility of such processes.^{2a-b} Polypyridyl transition metal complexes of ruthenium² and iridium³ have shown significant promise in oxidative and reductive reactivity modes for a variety of different organic transformations (Figure 1).

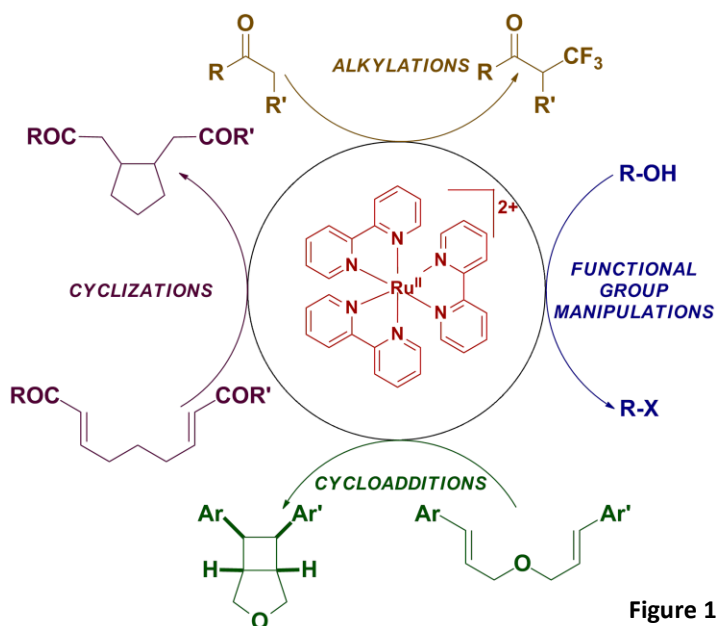


Figure 1

REACTIVITY IN OXIDATIVE MODE

The oxidative quenching of the persistent photoexcited state of Ru(bpy)₃²⁺ generates a ruthenium(III) species, a strong single-electron oxidant (+1.29V v. SCE).² Recently, reactivity has been demonstrated in this mode for efficient conversion of alcohols to alkyl halides by Stephenson and coworkers.⁴ Intramolecular oxidative 2+2 cycloadditions of bis-styrenes to diarylcyclobutanes has also been demonstrated by Yoon and coworkers.⁵ In recent weeks, Yoon has demonstrated oxidative [4+2] cycloadditions of unactivated dienes, demonstrating complementarity to more traditional Diels-Alder methodology.⁶ Sanford has also applied this Pd-mediated oxidative C-H functionalization.⁷

REACTIVITY IN REDUCTIVE MODE

The reductive quenching of photoexcited Ru(bpy)₃²⁺ generates a Ru(I) species, which is a strong single-electron reducing agent (-1.33V v. SCE).² A significant advance in use of this methodology was made by MacMillan and coworkers: SOMO activation of catalytically generated asymmetric enamines for alkylation of aldehydes,⁸ which can be extended to trifluoroalkylation⁹ and benzylation¹⁰ through Ir catalysis. More recently, they have explored this reductive reactivity for perfluoroalkylation of silyl derivatives of ketones, esters, and amides, generated both *in situ* and exogenously, in good yield but

limited stereoselectivity.¹¹ This reactivity mode has also been further developed by Stephenson to perform efficient reductive dehalogenations,¹² radical cyclizations,¹³ and intermolecular C-H alkylations.¹⁴ These methods enabled the total synthesis of Gliocladin C,¹⁵ providing an efficient gateway into this indole alkaloid family. Yoon and coworkers have demonstrated that Ru(bpy)₃²⁺ catalyzes radical enone cyclizations to generate functionalized cyclopentanes,¹⁶ as well as diastereoselective intra-¹⁷ and intermolecular [2+2] cycloadditions of enones to generate functionalized cyclobutanes.¹⁸ Also, formal intramolecular [3+2] cycloadditions of aryl cyclopropyl ketones have been reported to generate functionalized fused 5,5-bicyclic systems,¹⁹ along with formal intramolecular [4+2] hetero-Diels-Alder type reactivity of dienones to generate functionalized dihydropyrans, which can be reduced to substituted cyclohexanes through reductive cleavage.²⁰

CONCLUSIONS

The use of polypyridyl transition-metal complexes to harness visible light as a reagent has emerged as a powerful strategy for a variety of synthetically useful processes. The ability to perform single-electron redox processes catalytically and without the use of stoichiometric radical chain-carrying species will enable photoredox catalysis by polypyridyl transition-metal complexes to become a general solution for radical-mediated reaction pathways.

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