

TERPYRIDINE DIPHOSPHINE RUTHENIUM COMPLEXES AS EFFICIENT PHOTOCATALYSTS FOR THE TRANSFER HYDROGENATION OF CARBONYL COMPOUNDS

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Over the past decade, visible-light photoredox catalysis or photocatalysis has grown to become a commonly employed powerful tool in organic synthesis leading to new unique and valuable molecular transformations, inaccessible from thermally activated processes.^[1] Photocatalysis can be conducted in homogeneous conditions as well as employing heterogeneous transition metal or solid semiconductors.^[2] The commonly employed homogeneous visible-light photocatalysts are homoleptic Ru and Ir polypyridyl complexes, like $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ir}(\text{ppy})_3]$ (bpy = 2,2'-bipyridine; ppy = 2-phenylpyridine). These compounds, when excited by visible light undergo a metal-to-ligand-charge transfer (MLCT) transitions from HOMO and LUMO orbitals of the ligand.^[3] The 2,2':6',2''-terpyridine (tpy) is an NNN-type Pincer ligand, which can give tight chelation of various metal cations in a nearly planar geometry. The presence of the electron-deficient pyridine cycles make it a strong σ -donor and also as a very good π -receptor, moreover the presence of low energetic LUMO levels allows it to participate in the redox reactions as a non-innocent ligand.^[4]

Among the catalytical reactions, the transfer hydrogenation (TH) of carbonyl compounds promoted by Ru complexes is a core process for the synthesis of alcohols in an environmentally friendly and widely accepted method in industry.^[5]

We report herein a practical and innovative procedure for the synthesis of a new class of ruthenium cationic $[\text{RuX}(\text{PP})(\text{tpy})]\text{Y}$ (PP = diphosphine; X = Cl, OAc; Y = Cl, OAc, PF_6) complexes containing tpy and a suitable diphosphine (Figure 1). These cationic complexes are active visible-light photocatalysts for the TH of carbonyl compounds at 30 °C in 2-propanol.

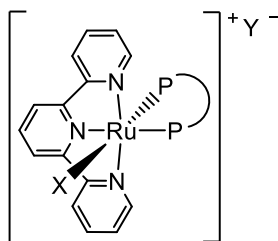


Figure 1. Synthesis of $[\text{RuX}(\text{PP})(\text{tpy})]\text{Y}$ Complexes

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