

ABSTRACT

Ruthenium complexes of selected organic ligands: Synthesis, characterization and reactivity

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Chapter I: In this chapter the scope of the present investigation is delineated briefly along with the aim of the work.

Chapter II: Reaction of $[\text{Ru}(\text{trpy})\text{Cl}_3]$ with 1,4-diazabutadienes ($p\text{-RC}_6\text{H}_4\text{N}=\text{C}(\text{H})\text{-}(\text{H})\text{C}=\text{NC}_6\text{H}_4\text{R-}p$; R = OCH₃, CH₃, H and Cl; abbreviated as **L-R**) in refluxing ethanol in the presence of triethylamine has afforded a family of complexes, isolated as perchlorate salts, of type $[\text{Ru}(\text{trpy})(\text{L-R})\text{Cl}]\text{ClO}_4$ [depicted as complexes **1** (R = OCH₃), **2** (R = CH₃), **3** (R = H) and **4** (R = Cl)]. Crystal structures of complexes **1**, **2** and **4** have been determined, and structure of complex **3** has been optimized by DFT method. The 1,4-diazabutadiene ligand in each complex is bound to ruthenium as a N, N-donor forming five-membered chelate. Complexes **1** – **4** show intense absorptions in the visible and ultraviolet regions, which have been analyzed by TDDFT method. Cyclic voltammetry of complexes **1** – **4** in acetonitrile solution shows Ru(II)-Ru(III) oxidation within 1.03 – 1.12 V vs SCE, and ligand (trpy and L-R) based reductions on the negative side of SCE. Complexes **1** – **4** catalyze transfer hydrogenation of aryl aldehydes to the corresponding alcohols with high ($\sim 10^6$) TON. They are also found to catalyze transfer hydrogenation of aryl ketones to corresponding secondary alcohols, but with much less efficiency. Catalytic transfer hydrogenation of nitroarenes to the corresponding amines has also been achieved.

Chapter III: Synthesis of a ruthenium(II)-aquo complex bearing 2,2':6',2''-terpyridine and a 1,4-diazabutadiene ligand, and exploration of its synthetic utility and catalytic activity are described. Ag⁺-assisted displacement of the coordinated chloride from the previously described $[\text{Ru}(\text{trpy})(\text{L-OCH}_3)\text{Cl}]\text{ClO}_4$ complex in Chapter II [depicted as complex **1**; where L-OCH₃ represents 1,4-di-(*p*-methoxyphenyl)azabutadiene] in aqueous ethanol affords the $[\text{Ru}(\text{trpy})(\text{L-OCH}_3)(\text{H}_2\text{O})]^{2+}$

complex cation, which has been isolated as the perchlorate salt (complex **1a**). Complex **1a** undergoes facile substitution of the aquo ligand by neutral monodentate ligands leading to the formation of complexes of type $[\text{Ru}(\text{trpy})(\text{L-OCH}_3)(\text{L}')^{2+}]$, also isolated as perchlorate salts [$\text{L}' =$ acetonitrile (complex **1b**); $\text{L}' =$ dmsO (complex **1c**); $\text{L}' =$ 4-picoline (complex **1d**) and $\text{L}' =$ PPh_3 (complex **1e**)]. Complexes **1b** – **1e** can also be synthesized directly from complex **1**, via the Ag^+ -assisted displacement of coordinated chloride by the respective monodentate L' ligand. Crystal structures of complexes **1a**, **1b** and **1d** have been determined. The complexes show intense absorptions in the visible and ultraviolet regions, the origin of which have been probed into with the help of TDDFT method. Cyclic voltammetry of the complexes shows an irreversible $\text{Ru}(\text{II})$ - $\text{Ru}(\text{III})$ oxidation within 0.9 – 1.6 V vs SCE, and two ligand (trpy and L-R) based reductions on the negative side of SCE. The aquo-complex (**1a**) is found to serve as an efficient catalyst for the hydration of aryl nitriles to the corresponding amides, and aryl alkynes to aldehydes.

Chapter IV: Reaction of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ with a group of four 1,4-diazabutadiene ligands (p - $\text{RC}_6\text{H}_4\text{N}=\text{C}(\text{H})-\text{C}(\text{H})=\text{NC}_6\text{H}_4\text{R}$ - p ; $\text{R} = \text{OCH}_3, \text{CH}_3, \text{H}$ and Cl ; abbreviated as L-R) in equimolar ratio afforded chloro-bridged di-ruthenium complexes (**1** – **4**) of general type $[\text{Ru}_2(\text{PPh}_3)_2(\text{L-R})_2\text{Cl}_3]\text{Cl}$. Crystal structures of complexes **1** ($\text{R} = \text{OCH}_3$), **2** ($\text{R} = \text{CH}_3$) and **4** ($\text{R} = \text{Cl}$) have been determined, and molecular structure of complex **3** ($\text{R} = \text{H}$) has been optimized by DFT method. Each complex shows four intense absorptions spanning over the visible and ultraviolet regions, the origin of which has been probed into with the help of TDDFT calculations. The complexes are found to serve as efficient catalyst-precursor for the oxidative, as well as deaminative, C-N coupling of a series of primary amines producing the corresponding imines in good yields. Homo-coupling of benzylamines, and cross-coupling of two differently substituted benzylamines, or benzylamine with anilines and other aryl/alkyl amines could be brought about by this catalytic protocol with aerial oxygen as the oxidant.

Chapter V: In this chapter we have discussed about utilization of a phosphine containing mixed-ligand ruthenium(II) complex as catalyst precursor for two types of organic transformations, viz. transfer hydrogenation and C-C coupling reaction.

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