Quinoxaline and Triazole Based Sulfur/Selenium Ligands: Metal Complexes for Catalytic Activation

ABSTRACT

The focus of thesis is on (i) designing of bidentate chalcogenoether ligands (ii) exploring their coordination chemistry with Pd(II), (η⁶-benzene)Ru(II) and (η⁵-pentamethylcyclopentadiene) Rh(III)/Ir(III) and (iii) investigating the designed metal complexes for C–C coupling reactions, NMO based oxidation of alcohols, Oppenauer-type oxidation of alcohols and transfer hydrogenation of carbonyl compounds.

The bidentate 2,3-di[(phenylthio/-seleno)methyl]quinoxaline (L₁ / L₂) synthesized by the reaction PhS⁻/PhSe⁻ with 2,3-bis(bromomethyl)quinoxaline, on reaction with Na₂PdCl₄, results in complexes [Pd₂(L₁−H)₂Cl₂] (1) / [PdL₂Cl₂] (2) respectively. Structures of Single crystals by X-ray diffraction of ligands and complexes have been determined. The 1 is a palladacycle, formed by external base free activation of benzyl group’s C(sp³)−H of L₁ whereas L₂ behaves in 2 as a bidentate. Complexes 1 and 2 were explored to catalyzed Suzuki–Miyaura coupling reactions of several aryl bromides (including deactivated ones). The palladacycle 1 shows better catalytic efficiency than complex 2. The catalysis with 1 / 2 has been found to proceed via in situ generated nanoparticles (size < 2 nm) composed of palladium and sulfur or selenium and protected by L₁ or L₂.

The bidentate 1-benzyl-4-((phenylthio)-/(phenylseleno)methyl)-1H-1,2,3-triazole (L₃ / L₄) and 4-phenyl-1-((phenylthio)-/(phenylseleno)-methyl)-1H-1,2,3-triazole (L₅ / L₆) were synthesized by the 1,3-dipolar cycloaddition of azides to terminal alkynes (click reaction). Their metal complexes (3–8) are formed by direct reaction with [Pd(CH₃CN)Cl₂] and [{(η⁶-benzene)RuCl(μ-Cl)}₂]. The coordination There is a "pseudo-octahedral" half sandwich “Piano-Stool” geometry around the Ru center in 7–8. The Pd(II) complexes were explored for C–C coupling reactions (Suzuki-Miyaura and Heck), whereas Ru(II) complexes were investigated to catalyze oxidation of alcohols and transfer hydrogenation of ketones. Complexes efficient for Suzuki than Heck coupling are pre-catalysts and dispense catalytically active Pd NPs in the course of reaction. NPs (size 3–11 nm) appear to have a role in the catalysis, as they show catalytic activity after isolation also. Catalytic oxidation of alcohols appears to involve the formation of Ru(IV)=O species, whereas catalytic transfer
hydrogenation reactions proceed via formation of a metal-hydride intermediate. The catalytic efficiency orders are supported by HOMO–LUMO energy gaps estimated by DFT calculations.

The half-sandwich Cp*Rh(III) / Ir(III) complexes of bidentate ligands prepared by reacting them with \([\eta^5\text-Cp^*\text{RhCl(\mu-Cl})]_2\), and \([\eta^5\text-Cp^*\text{IrCl(\mu-Cl})]_2\) at room temperature followed by treatment with NH₄PF₆ were characterized by X-Ray crystallography and explored as a catalyst in transfer hydrogenation of carbonyl compounds using 2-propanol as hydrogen donor, N-methylmorpholine-N-oxide (NMO) based and Oppenauer-type oxidation of alcohols. Both the type of oxidation of alcohols reactions involves the formation of metal hydride species. In TH the species formed with loss of Cp* appears to be involved incatalysis.

A multidentate1,2,3-triazole based chalcogen ligands and their Pd(II) and Ru(II) complexes have been synthesized by their reaction with \([\text{Pd(CH}_3\text{CN})\text{Cl}_2]\) and \([\{\eta^6\text-benzene}\text{RuCl(\mu-Cl})\}_2]\) respectively and their structures established by X-Ray crystallography. Pd(II) complexes were explored for Suzuki-Miyaura coupling reactions and Ru(II) complexes in transfer hydrogenation of carbonyl compounds (2-propanol and glycerol as hydrogen donor). The oxidation of alcohols using NMO as an oxidant and Oppenauer-type oxidation of alcohols are also catalyzed by these Ru complexes. DFT calculations on Ru(II) complexes have been made which support experimental results of catalysis and structural aspects of complexes.