**Organometallic and polypyridyl complexes of Ru(II), Ru(III), Pd(II) and Pd(IV); Structural, spectroscopic, electrochemical,**

**spectroelectrochemical and magnetic behaviors;**

**The investigation of their applications such as DNA interaction**

**and C–X (X = C, N) bond formation**

Marzieh Daryanavard

m.daryanavard@ch.iut.ac.ir

September 11, 2013

Department of Chemistry

Isfahan University of Technology, Isfahan 84156-83111, Iran

**1st Supervisor: Prof. H. Hadadzadeh\*, E-mail: hadad@cc.iut.ac.ir**

**2nd Supervisor: Prof. U. Fekl\*\*, E-mail: ulrich.fekl@utoronto.ca**

**Advisor: Prof. S. Mallakpour\***

**Department Graduate Coordinator: Dr. H. Tavakol**

**\*** Isfahan University of Technology, Isfahan 84156-83111, Iran

**\*\*** University of Toronto, Toronto, ON M5S 1A1, Canada

**Abstract**

In the first section, five organometallic and polypyridyl complexes of Ru(II) and

Ru(III), [Ru(phen-diox)2Cl2], [Ru(phen-diox)2(ppy)](PF6), [Ru(tpy)2](PF6)2, [Ru(DMSO)2(AO)2Cl2] and [Ru(bpy)(tppz)Cl](PF6)2 were prepared and fully characterized. Their electrochemical, spectroelectrochemical and magnetic properties were also studied. For synthesis of a new derivative of phen-dione ligand, the condensation of it with a diol was investigated for the first time. This condensation reaction was done by the metal-assisted effect of [Ru(phen-dione)2Cl2]. The DFT calculations showed that the electronic and energy parameters are involved in this unusual condensation reaction. Also, the interaction of [Ru(phen-diox)3](PF6)2 and [Ru(phen-diox)2(H2O)2](PF6)2 with FS-DNA was monitored by UV–Vis, fluorescence and voltammetric techniques. The [Ru(DMSO)2(AO)2Cl2] complex was used for the preparation of the Ru(II)/ZnO/CNTs/CPE nanocomposite modified electrode. The [Ru(tpy)2](PF6)2 complex was used for the preparation of the metal complex-Cloisite nanohybrid (MC-C).

In the second section, five organometallic complexes of Pd(II) and Pd(IV), [PdMe2(COD)],

K[PdMe2(Tp\*)], [PdMe3(Tp\*)], [PdMe2(Tp\*)(pmbd)] and [PdMe2(Tp\*)(pbbd)] were prepared and characterized. The oxidation of K[PdMe2(Tp\*)] was investigated through both of aerobic and anaerobic conditions. In anaerobic oxidation, the stable [PdMe2(Tp\*)(pmbd)] and [PdMe2(Tp\*)(pbbd)] complexes were prepared as the first complexes of Pd(IV) with the aryldiazenido ligand by reaction with pmbd-BF4 and pbbd-BF4 salts, respectively. Also, the aerobic oxidation of K[PdMe2(Tp\*)] complex in acetone led to the formation of [PdMe3(Tp\*)] complex. The reactivity of the Pd(IV) complexes toward the C–X (X = C, N)

bond formation was investigated by 1H NMR through the thermolysis in C6D6 at 70 °C.

**Keywords**: Ru(II) cyclometallated complex, Ru polypyridyl complexes, DNA interaction, , Organopalladium(IV) complexes, Aryldiazonium salts, Aerobic oxidation, Anaerobic oxidation, Modified electrode.