

**Title:** Ruthenium(II) Arene Complexes Bearing Tris(pyrazolyl)methanesulfonate Capping Ligands. Electrochemistry, Spectroscopic, and X-ray Structural Characterization

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**Abstract:** Novel [Ru(L)(Tpms)]Cl and [Ru(L)(Tpms(Ph))]Cl complexes (L = p-cymene, benzene, or hexamethylbenzene, Tpms = tris(pyrazolyl)-methanesulfonate, Tpms(Ph) = tris(3-phenylpyrazolyl)methanesulfonate) have been prepared by reaction of [Ru(L)(μ-Cl)(2)](2) with Li[Tpms] and Li[Tpms(Ph)], respectively. [Ru(p-cymene)(Tpms)]BF<sub>4</sub> has been synthesized through a metathetic reaction of [Ru(p-cymene)(Tpms)]Cl with AgBF<sub>4</sub>. [RuCl(cod)(Tpms)] (cod = 1,5-cyclooctadiene) and [RuCl(cod)(Tpms(Ph))] are also reported, being obtained by reaction of [RuCl<sub>2</sub>(cod)(MeCN)(2)] with Li[Tpms] and Li[Tpms(Ph)], respectively. The structures of the complexes and the coordination modes of the ligands have been established by IR, NMR, and single-crystal X-ray diffraction (for [RuL(Tpms)]X (L = p-cymene or HMB, X = Cl; L = p-cymene, X = BF<sub>4</sub>)) studies. Electrochemical studies showed that each complex undergoes a single-electron R-II → R-III oxidation at a potential measured by cyclic voltammetry, allowing to compare the electron-donor characters of the tris(pyrazolyl)methanesulfonate and arene ligands, and to estimate, for the first time, the values of the Lever E-L ligand parameter for Tpms(Ph), HMB, and cod.

**KeyWords Plus:** Coordination Chemistry; 1,3,5-Triaza-7-Phosphaadamantane PTA; Peroxidative Oxidation; Ferrocene Derivatives; Catalyst Precursors; Crystal-Structures; Rhenium Complexes; Electron-Transfer; Anticancer Drugs; Redox Potentials

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