Title: Oxorhenium Complexes Bearing the Water-Soluble Tris(pyrazol-1-yl)methanesulfonate, 1,3,5-Triaza-7-phosphaadamantane, or Related Ligands, as Catalysts for Baeyer-Villiger Oxidation of Ketones

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Abstract: New rhenium(VII or III) complexes [ReO3(PTA)(2)][ReO4] (1) (PTA = 1,3,5-triaza-7-phosphaadamantane), [ReO3(mPTA)][ReO4] (2) (mPTA = N-methyl-1,3,5-triaza-7-phosphaadamantane cation), [ReO3(HMT)(2)] [ReO4] (3) (HMT = hexamethylenetetramine), [ReO3(eta(2)-Tpm)(PTA)][ReO4] (4) [Tpm = hydrotris(pyrazol-1-yl)methane, HC(pz)(3), pz = pyrazolyl), [ReO3(Hpz)(HMT)][ReO4] (5) (Hpz = pyrazole), [ReO(Tpms)(HMT)] (6) [Tpms = tris(pyrazol-1-yl)methanesulfonate, O3SC(pz)(3)(-)] and [ReCl2{N2C(O)Ph} (PTA)(3)] (7) have been prepared from the Re(VII) oxide Re2O2 (1-6) or, in the case of 7, by ligand exchange from the benzoyldiazenido complex [ReCl2(N2C-(O)Ph}(Hpz)(PPh3)(2)], and characterized by IR and NMR spectroscopies, elemental analysis and electrochemical properties. Theoretical calculations at the density functional theory (DFT) level of theory indicated that the coordination of PTA to both Re(III) and Re(VII) centers by the P atom is preferable compared to the coordination by the N atom. This is interpreted in terms of the Re-PTA bond energy and hard-soft acid-base theory. The oxo-rhenium complexes 1-6 act as selective catalysts for the Baeyer-Villiger oxidation of cyclic and linear ketones (e.g., 2-methylcyclohexanone, 2-methylcyclopentanone, cyclohexanone, cyclopentanone, cyclobutanone, and 3,3-dimethyl-2-butanone or pinacolone) to the corresponding lactones or esters, in the presence of aqueous H2O2. The effects of a variety of factors are studied toward the optimization of the process.

KeyWords Plus: Ray Crystal-Structures; Transition-Metal-Complexes; Hydrogen-Peroxide; Rhenium Complexes; Organometallic Compounds; Coordination Chemistry; Molecular-Oxygen; Mild Conditions; Ionic Liquids; Structural-Characterization

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