

The influence of α,α' -diimine bridging ligand on the reactivity of binuclear *para*-cymene ruthenium(II) complexes. Kinetic, mechanistic and computational study

Abstract.

Substitution kinetics of the aqua ligands in four binuclear ruthenium(II) *para*-cymene complexes with different α,α' -diimine bridging ligands [2-pyridylaldazine (Ru-1), *p*-phenylenebis(picoline)aldimine (Ru-2), *p*-biphenylenebis(picoline)aldimine (Ru-3) and *p*-xylylenebis(picoline)aldimine (Ru-4)] was investigated as a function of nucleophile concentration and temperature under *pseudo*-first order conditions using thiourea nucleophiles. The rates of the simultaneous substitution of the aqua ligands decreased in the order: Ru-1 > Ru-4 > Ru-3 > Ru-2. The reactivity of the complexes is controlled by the inherent electronic and steric contributions of the bridging ligand. The strong π -acceptor bridging ligand is responsible for the high reactivity observed in Ru-1 compared to the rest of the complexes. From Ru-2 to Ru-4, the reactivity increases with decrease in steric congestion around the metal centres. The cage effect plays a role in the enhanced reactivity of Ru-4 compared to Ru-3 and Ru-2. Reactivity trends are excellently supported by computational results. All the complexes showed a stepwise deprotonation of the coordinated aqua ligands except Ru-4 and the pK_a values increased from Ru-1 to Ru-4 due to progressive increase in σ -donicity of the spacers. The activation parameters ($\Delta H^\ddagger > 0$, $\Delta S^\ddagger < 0$) obtained for all the complexes support an associative mechanism of activation.

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