

# Synthesis, spectroscopic characterization and DFT study of dinuclear ruthenium sawhorse-type complexes derived from the reaction of trinuclear aggregates and (Z)-5-arylidenerhodanines

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## Resumen

The synthesis of dinuclear ruthenium sawhorse-type complexes  $[\text{Ru}-2(-\text{ArCH}:\text{Rhod})(2)(\text{CO})(4)](n)$  12a-e and  $[\text{Ru}-2(\text{ArCH}:\text{Rhod})(2)(-\text{ArCH}:\text{Rhod})(2)(\text{CO})(4)]$  13a-e through reaction of  $[\text{Ru}-3(\text{CO})(10)(\text{NCMe})(2)]$  and  $[\text{Ru}-3(\text{CO})(12)]$  and the corresponding (Z)-5-arylidenerhodanines ( $\text{ArCH}:\text{Rhod}$ ) 10a-e, respectively, are reported. These complexes are arranged in a sawhorse structure in which two bridged (Z)-5-arylidenerhodanines coordinate to the metals using sulfur and nitrogen of the rhodanine ring. A Density Functional Theory method was used to gain insight into the polymerization process by calculating dimerization Gibbs energies ( $G(\text{dim})$ ). Values between -10.7 and -5.3 kcal/mol(-1) indicate that dimerization is a spontaneous process. A reaction pathway for formation of the sawhorse compounds  $[\text{Ru}-2(-\text{ArCH}:\text{Rhod})(2)(\text{CO})(4)]$  was calculated and the rate-determining step for the mechanism is coordination of a second (Z)-5-arylidenerhodanine ligand with activation energies between 41.1 and 47.8 kcal/mol(-1). In order to understand the apparent thermodynamic favorability of the fragmentation step, we calculated the fragmentation energy ( $E\text{-Frag}$ ) for the key intermediate and its energetic contributors, the interaction energy,  $E\text{-int}$  and the reorganization energy,  $E\text{-reorg}$ . Low values of  $E\text{-Frag}$  imply that the fragmentation is thermodynamically facile. Large values of  $E\text{-int}$  are countered by opposite and large values of  $E\text{-reorg}$  which indicate that the cleavage of the trimetallic intermediate aggregate is determined by the nature of the ligand and the balance between its interaction with the metal and the extent of structural reorganization.

## Palabras clave

**Palabras clave de autor:** [Sawhorse-type complexes](#); [ruthenium cluster carbonyls](#); [DFT-mechanism](#); [fragmentation energy](#)

**KeyWords Plus:**TRIRUTHENIUM CARBONYL CLUSTERS; AB-INITIO PSEUDOPOTENTIALS; CARBOXYLATE COMPLEXES; CATALYTIC-ACTIVITY; CRYSTAL-STRUCTURE; BASIS-SETS; LIGANDS; RU-3(CO)(12); DERIVATIVES; RU3(CO)12

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