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BOOK OF ABSTRACTS

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Halogen Effect on the Structure and Intermolecular Interactions of Ruthenium(II)-arene Complexes

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The field of quantum crystallography has significantly expanded its output over the past decade [1]. One particularly promising technique is Hirshfeld Atom Refinement (HAR), a refinement model that delivers highly accurate results, especially for hydrogen atom positions, comparable to those obtained from neutron diffraction [2].

This study investigates the structure of ruthenium(II) organometallic complexes, with a focus on hydrogen–halogen bonding interactions. Using single-crystal X-ray diffraction in combination with HAR, two crystal structures were characterized, and their intermolecular interactions thoroughly analyzed. Based on analyses involving Hirshfeld surfaces, fingerprint plots, electron density Laplacians (Lap), and electrostatic potential surfaces (ESP), the results indicate that halogen–hydrogen interactions play a crucial role in the stability of the studied complexes.

Furthermore, structural elucidation provided deeper insights into the relationship between molecular geometry, electronic properties, and the influence of halogen substituents. Analyses of the Laplacian and ESP surfaces revealed that the substitution of halogens (chlorine, bromine, and iodine) induces changes in the donor character of the phosphorous atom in triphenylphosphine. Despite this electronic variation, no significant difference in the Ru–P bond length was observed. This suggests that while the potential over the phosphorous atom becomes more positive in the presence of chlorine as the ancillary ligand, the overall geometry of the complex remains unchanged.

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