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Nature and cooperativity of metal−ligand bonds in groups 5, 7, 9 and 11 half-sandwich cyclopentadienyl complexes

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Half-sandwich complexes that have an metal center attached to a cyclopentadienyl ligand have attracted much attention due to their unique electronic and chemical properties. The term sandwich compound was introduced in organometallic nomenclature in 1956 in a report by Dunitz and co-workers who confirmed the structure of ferrocene by X-ray crystallography [1]. In this work, we investigate the electronic structure and bonding interactions in a set of half-sandwich complexes using advanced computational methods and recently developed methodolgies [2, 3]. The aim of this project is to provide a detailed theoretical investigation of the nature of bond, and cooperativity of bonds for half-sandwich complexes containing cyclopentadienyl and carbonyl ligands with the general formula [M(η^5–Cp)(CO)$_n$] (M=Cu^+, Au^+, Ag^+, n=1, M= Co^+, Ir^+, Ru^+, n=2, Mn^+, Re^+, Tc^+, n=3, V^+, Nb^+, Ta^+, n=4). The geometries of all complexes were fully optimized at the B3LYP, B971, M06-D3, M06L and MP2 levels with the def2-TZVP basis set using the GAUSSIAN-09 program without any symmetry restrictions. Vibrational frequency analysis, calculated at all levels of theory, indicates that the optimized structures are at the stationary points corresponding to local minima without any imaginary frequency.The results indicate that the type and degree of cooperativity of bonds in the series of these complexes depend highly on the type and nature of central metal ion.

Keywords: Theoretical study, Half-sandwich compounds, Cooperativity of bonds, Nature of bonds

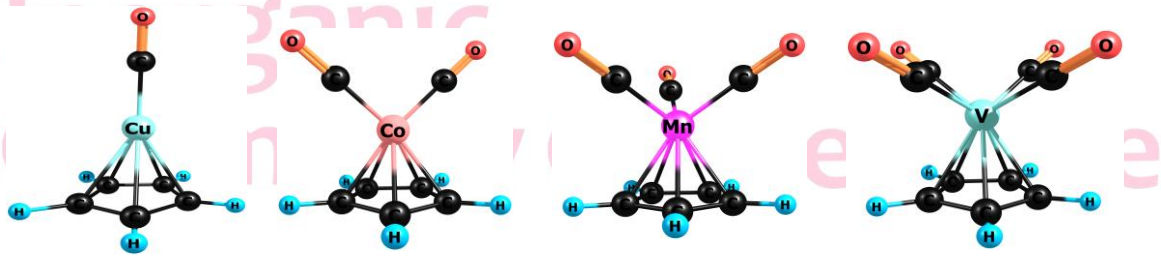


Figure 1. Optimized structure of selected complexes, [Cu(η^5–Cp)(CO)], [Co(η^5–Cp)(CO)$_2$], [Mn(η^5–Cp)(CO)$_3$] and [V(η^5–Cp)(CO)$_4$], at M06L/def2-TZVP level of theory.

References

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