289q Computational Modeling of Group 4 Metallocenes: Geometry Prediction and Reactivities

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Organometallic compounds containing group 4 transition metals are very active and selective catalysts for highly demanded reactions like hydrogenations and polymerizations. Within this work we would like to present the results of DFT calculations of a series of bridged and unbridged cyclopentadienyl (Cp) based metallocenes with varying ligands. In particular, the effects of the bridge, the substituents on the metal and on the Cp ligands on geometry parameters and on the molecular electronic structure are studied. Equilibrium geometries are optimized with the B3LYP method with different basis sets (3-21G, LanL2DZ, 6-31G*, SDD). Selected geometrical parameters like M-X distances (M = Ti, Zr, Hf; X = Cl, F, Me, binol), M-Cp' distances (Cp' = centroid of the five-membered ring for any Cp based ligand), X-M-X angles and Cp'-M-Cp' angles are analyzed in detail and compared with experimentally determined crystal structures. These results and further investigations involving e.g. the examination of the HOMO-LUMO gaps, NBO analyses and comparisons of the M-X frequencies will form the basis for catalyst design (e.g. the best positions for functional tethers to immobilize the complexes onto heterogeneous supports) and will help to provide a better understanding of mechanistic pathways of catalytic reactions like hydrogenations, hydrosilylations, and polymerizations.