Electron transfers and bond weakening in excited and ground states based on bent metallocenes

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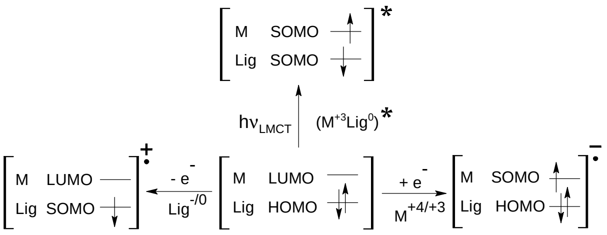
The group 4 bent metallocenes have been a cornerstone in the development of modern coordination organometallic chemistry and catalysis and continue to be a focus of chemical and structural studies giving novel insights into reactivity, optical and thermal electron-transfer properties, structural preferences, and bonding requirements. We have initiated a systematic investigation on the influence the metal core and ligands have on the electronic structure, the fundamental changes that occur in the bonding, electron distribution, and electronic energies in the π-,σ-complexes, especially those aspects of electronic structure that can be probed by reliable physical methods. Here principle experimental investigation is achieved with optical spectroscopy and electrochemistry, the results of which can be complementary. Each of the two methods serves as a probe, more or less direct, of the valence electronic structure; our efforts are under way to draw correspondences between information gained with each of the techniques, directing attention to group 4 bent metallocenes.

Emphasis is given to versatile transformations induced by a first-electron uptake/ loss and properties of the ligand-to-metal charge-transfer (LMCT) excited states based on group 4 metallocenes $(\pi\text{-L})_2\text{M}^{\text{IV}}\text{X}_2$ (M = Ti, Zr, Hf; X = Cl, Me). The study represents a systematic application of the associated spectroscopic and electrochemical approach to probe the frontier orbitals (FMOs) and to unravel origin and the driving force of the loss of structural integrity of the π-organometallics in their reduced/ oxidized ground and thermally (non)equilibrated excited states. Parallels are made for molecular photodissociation and electrochemical/ thermal electron-transfer (withdrawal/ release)-induced chemistry upon a single occupation (e^-) of the LUMO and a hole generation (h^+) on the HOMO:



The associated analysis is implemented by our recent evidence that the same optical and redox FMOs are involved in optical and heterogeneous/ thermal electron-transfer processes of the structurally-related group 4 metal complexes.[1] For organometallic π-complexes, emphasis is for the first time given to very different photo- and electrochemical metal–ligand bond splitting routes; the mechanisms are shown to be strongly affected by the electron-donor and (σ, π)-bonding abilities of the organic/inorganic ligand network and the electronic state as governed by thermodynamic and largely kinetic factors. (Bi)radical behavior of the organometallic LMCT excited states is rationalized to originate largely from a single occupancy (h^+) of the highest ligand-centered orbital (the HOMO in the ground state), rather than a single occupancy (e^-) of the lowest metal-centered orbital (the LUMO in the ground state).

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Reference

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