

High-spin Cyclopentadienyl Complexes, Part 7. Ambivalent Interpretation of the Bonding in Iron-Copper Complexes: Metalated Arene *versus* Carbocyclic Carbene

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The electron distribution within a mesityl ligand bridging a cyclopentadienyliron fragment attached to the mesityl π system and a second metal fragment connected to the *ipso* carbon of the mesityl ring has been probed using a copper(I) halide as a component in $[\text{Cp}^{\text{III}}\text{Fe}(\mu, \eta^5 : \eta^1\text{-C}_6\text{H}_2\text{Me}_3)\text{CuCl}]$ (**2**) and its copper bromide derivative **3**. This approach minimizes steric effects and allows for DFT calculations the results of which are in very good agreement with structural data. The calculations show a significant carbene character already for the bare phenyl anion as a result of electrostatic repulsion of the lone pair pushing the π electrons away from the *ipso* carbon towards the *para* carbon atom of the aromatic ring. π Coordination of a cyclopentadienyliron(II) fragment to the phenyl anion to form a hypothetical sandwich complex does not change this situation. The iron center rather follows the unsymmetric distribution of π charge with an unsymmetrical coordination to the π system. Coordination of a copper(I) chloride moiety to the phenyl anion or to the hypothetical π complex $[\text{CpFe}(\text{C}_6\text{H}_5)]$ in both cases equally lowers that carbene character by attracting the lone pair of the *ipso* carbon and thus decreasing its repulsive influence on the π electrons.

Key words: Iron Complexes, Copper Complexes, Tri(*tert*-butyl)cyclopentadienyl,
DFT Calculations, Carbene