Orbital Analysis of Carbon-13 Chemical Shift Tensors Reveals Patterns to Distinguish Fischer and Schrock Carbenes

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Fischer and Schrock carbenes have M=C bonds that display highly deshielded carbon chemical shifts (greater than 250 ppm), in particular Fischer carbenes (greater than 300 ppm). They are typically described according to the electrophilic and nucleophilic nature of their metal-carbon double bonds. Recently, we have shown that the analysis of ^{13}C NMR chemical shift anisotropy (CSA), defined by its principal components δ_{ii} ($\delta_{ii} = \delta_{11}, \delta_{22}, \delta_{33}$), and the corresponding chemical shielding δ_{ii}, is a powerful tool to understand the nature of M=C bonds in Schrock alkylidenes (**1**).[1] Here, we show how this approach, which combines solid-state NMR spectroscopy and DFT calculations supplemented by localized MO analysis (called NCS analysis), can provide characteristic information about Fischer carbenes (**2**) and Ru-based carbenes (**3**) in comparison with Schrock alkylidenes (**1**) (Figure 1). The highly deshielded ^{13}C isotropic chemical shifts observed for Fischer carbenes result from the particularly low-lying π*(M=C) associated with the CO ligand. The same analysis on Ru-based metathesis catalyst show that they are similar to Schrock alkylidenes, albeit with a high-lying Ru=C σ orbital associated with the d^6 configuration of Ru.

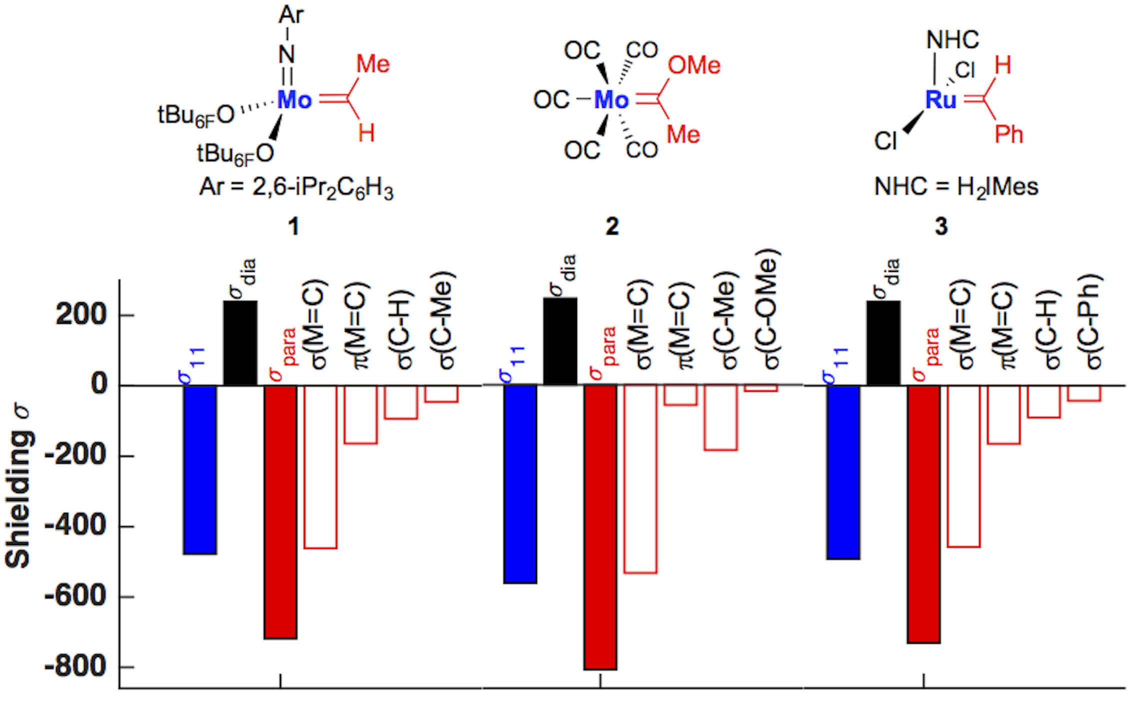

Figure 1. Histgrams of orbital contributions to σ_{11} of M=C complexes based on NCS analysis.

1. Halbert, S.; Copéret, C.; Raynaud, C.; Eisenstein, O. J. Am. Chem. Soc. 2016, 138, 2261.