



Learning from NMR chemical Shifts

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Abstract: NMR spectroscopy is without doubt one of the most useful characterization methods of essentially all chemical species. Despite this extremely wide usage of this spectroscopy, the factors that determine the NMR chemical shifts are still often unclear, especially when a main group element is in the vicinity of a heavy atom. The isotropic chemical shifts that average the chemical shifts in all directions is difficult to analyse indeed.

Solid state NMR, which provides information on the anisotropy of the chemical shift, is actually more amenable to analysis. We will illustrate this on several Schrock alkylidene complexes that are used in olefin metathesis reactions. These alkylidene carbons are nucleophilic but have an NMR signature in the range of that of a carbocation (chemical shift higher than 240 ppm). Using experimental information from solid state NMR while combining state-of-the-art relativistic calculations with an orbital analysis give highly valuable information on the chemical shifts

It appears that

- I. The charge is not a reliable criteria for chemical shifts.
- II. One can divide the NMR shielding in two terms. The diamagnetic is constant for all systems while the paramagnetic term determines the variations in the chemical shifts.
- III. The paramagnetic term to the chemical shift can be analysed easily from the molecular orbitals (and in particular the frontier and near-frontier molecular orbitals) of the chemical species.

References:

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