FROM REACTIVITY TO NMR PHYSICAL PROPERTIES: THE EXAMPLE OF D^0 OLEFIN METATHESIS CATALYSTS

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Computational chemistry is currently used for determining reaction mechanisms and physical properties of chemical systems. While there is a tendency for representing the experimental systems as accurately as possible and for using computational methods that represent strong and weak interactions as precisely as possible, there is also room for trying to determining trends by considering simplified systems that carry the physics of the problem. Questions of the same nature apply for the calculations of physical properties, which are here the NMR chemical shifts.

We will use the d^0 olefin metathesis catalysts of the type M(X)(Y)(ER)(CHR) with M = Mo, W and ER = amido; M = Re and ER = alkylidyne, X, Y = C-, N-, O- anionic ligands. The influence of the ligands and the metal on the efficiency of the catalysis will be presented.[1]

The solid state NMR chemical shifts of the alkylidene ^{13}C for M(X)(Y)(ER)(CHR) with M = Mo, W and ER = amido; M = Re and ER = alkylidyne, M = Ta and ER = alkyl, X, Y = C-, N-, O- anionic ligands were determined by experiment, illustrating the anisotropy of the electronic environment of the alkylidene carbon in the various systems.[2] State-of-the-art fully relativistic 4 components (4c) calculations of the ^{13}C chemical shift tensor reproduce well the experimental values. Calculations show the absence of correlation between the ^{13}C isotropic chemical shifts and NBO charge of the alkylidene carbon. However, an NBO based analysis (Natural Chemical Shift) of the shape and directions of the shielding tensors calculated with 2 components calculations (validated by comparison with 4c calculations) provide a rational of the observed values and demonstrate the role of the paramagnetic contributions in determining the chemical shifts.[3] If time permits, results concerning other systems than the alkylidene complexes will be presented.

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