^{15}N NMR Anisotropy on Transition Metal Imido Complexes: Link between Spectroscopy and Reactivity

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Imido ligands are one of the most fundamental ingredients in organometallic chemistry serving as supporting ligand, which can be typically found in Schrock-type olefin metathesis catalysts, and as a reactive site which facilitates numerous stoichiometric- and catalytic transformations such as cycloaddition with unsaturated bonds, nitrene transfer or C-H bond activation. Despite the diverse reactivity found among transition metal imido complexes across the periodic table, no general reactivity descriptor has been uncovered. In this context, solid-state NMR (ssNMR) has recently emerged as a powerful tool to link the spectroscopic signature, *i. e.* chemical shift tensors (CSTs), of specific nuclei to their electronic structures, which can be further tied with the reactivity.[1] In this work, we uncover the electronic structures of transition metal imido complexes using solid-state NMR augmented with DFT calculations and establish a spectroscopy-reactivity relationship.

The experimentally-collected ^{15}N ssNMR spectrum of the group 5 mono-imido species $V(=^{15}NPh)Cl_3(dme)$, which has inert imido ligand, revealed an axial spectral pattern ($d_{11} \approx d_{22}$) while the highly reactive group 6 bis(imido) species $Mo(=^{15}NPh)Cl_2(dme)$ exhibited an anisotropic spectrum ($d_{11} \neq d_{22}$). Natural Chemical Shift (NCS) analysis anchored on the experimentally-determined chemical shift anisotropy revealed the dominant and highly asymmetric development of p-contribution on the CSTs in $Mo(=NPh)_2Cl_2(dme)$, while s-bond only plays a marginal role. This contrasts with the symmetric distribution of s- and p-orbitals in the unreactive $V(=NPh)Cl_3(dme)$, in which the s(V-N) orbital dominates. The highly developed contribution from the p(Mo-N) orbital in $Mo(=NPh)_2Cl_2(dme)$ points out its high-lying nature. Visualization of the molecular orbitals revealed the competitive p-interaction between two imido ligands sharing the same orbital, which induces an increase HOMO energy and reactivity. Such scenario further supports the so-called concept of the “p-loading effect”,[2] which is often referred as an activation strategy for imido complexes. The thus-obtained results show that ^{15}N chemical shift tensors are useful probe of reactivity for imido complexes.

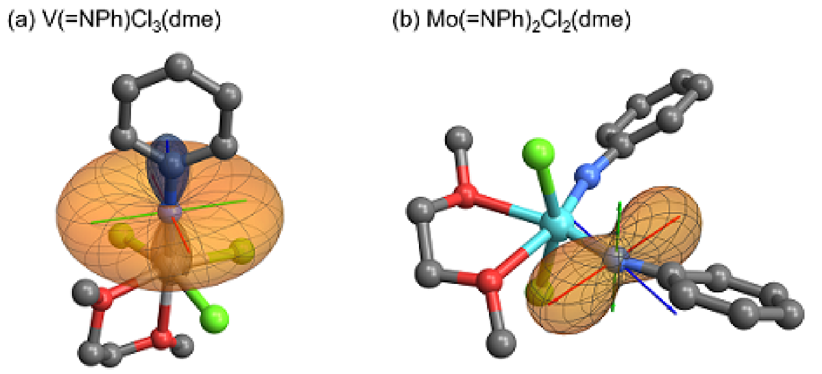

Figure 1. Visualized ^{15}N Chemical Shielding Tensors for selected imido complexes

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[2] Lapina, O. B.; Mats'ko, M. A.; Mikenas, T. B.; Zakharov, V. A.; Paukshtis, E. A.; Khabibulin, D. F.; Sobolev, A. P. *Kinetics and Catalysis*, **2001**, *42*, 553–560.