

**$^{15}\text{N}$  NMR Anisotropy on Transition Metal Imido Complexes: Link between Spectroscopy and Reactivity**Y. Kakiuchi<sup>1</sup>, P. S. Karmakar<sup>2</sup>, C. Copéret<sup>1\*</sup>, I. A. Tonks<sup>2\*</sup>

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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.<sup>1</sup> 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  $^{15}\text{N}$  ssNMR spectrum of the group 5 mono-imido species  $\text{V}(=\text{NPh})\text{Cl}_3(\text{dme})$ , which has inert imido ligand, revealed an axial spectral pattern ( $d_{11} \approx d_{22}$ ) while the highly reactive group 6 bis(imido) species  $\text{Mo}(=\text{NPh})\text{Cl}_2(\text{dme})$  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  $\text{Mo}(=\text{NPh})_2\text{Cl}_2(\text{dme})$ , while s-bond only plays a marginal role. This contrasts with the symmetric distribution of s- and p-orbitals in the unreactive  $\text{V}(=\text{NPh})\text{Cl}_3(\text{dme})$ , in which the s(V-N) orbital dominates. The highly developed contribution from the p(Mo-N) orbital in  $\text{Mo}(=\text{NPh})_2\text{Cl}_2(\text{dme})$  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”,<sup>2</sup> which is often referred as an activation strategy for imido complexes. The thus-obtained results show that  $^{15}\text{N}$  chemical shift tensors are useful probe of reactivity for imido complexes.

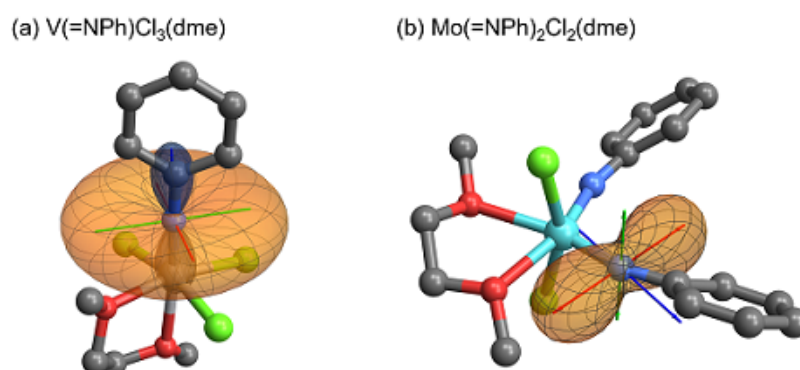


Figure 1. Visualized  $^{15}\text{N}$  Chemical Shielding Tensors for selected imido complexes

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