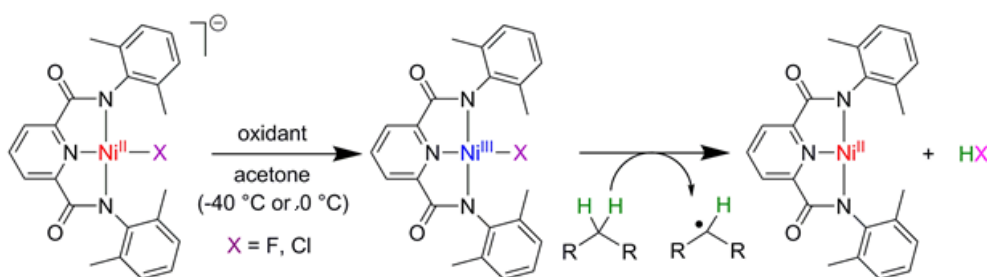


Title of the Talk: High Valent Nickel-Halide Complexes and Their Bioinspired Reactivity

Abstract: The selective oxidative functionalization of the inert C-H bonds in hydrocarbon is an economically and environmentally valuable chemical transformation process. Nature has evolved a number of metalloenzymes that perform such hydrocarbons oxidation, forming hydroxylated, halogenated and desaturated hydrocarbons products.¹ It has been proposed that such reactions involve hydrogen atom transfer (HAT) from an inert C-H bond to a high valent metal based oxidants such as M=O and M-OX (OX = OH, OR, O₂CR, ONO₂).^{2,3} However, the HAT reactivity of the metal-bound halide in C-H activation has not been studied before. To get an idea about the HAT reactivity toward the hydrocarbon oxidation by metal-bound halide, two high valent nickel-halide complexes [Ni^{III}(X)(L)] (X= F, Cl, L = N,N'-(2,6-dimethylphenyl)-2,6-pyridinedicarboxamide) have been prepared by one-electron oxidation of the [Ni^{II}(X)(L)]⁻ precursors (**Scheme 1**) and characterized using electronic absorption, EPR, XAS and mass spectrometry.⁴⁻⁷ Oxidative reactivity of these complexes was investigated with a series of hydrocarbon C-H bonds (**Scheme 1**), having different bond dissociation energy. Exceptional rate constants were determined for the [Ni^{III}(F)(L)] complex, comparable to the most reactive high-valent metal-oxo oxidants. Kinetic analysis of the Hammett, Evans-Polanyi, Marcus plots, KIE and oxidative product study confirmed that oxidation reactions proceed via hydrogen atom transfer (HAT) mechanism. These are the first well studied high valent metal-halide oxidants that perform HAT reaction. These results demonstrate that high valent metal-halides can be a potential strong oxidant for hydrocarbon oxidation and oxidative halogenation reactions.



Scheme 1. Preparation of high valent nickel-halide complexes and their oxidative reaction.

References

1. Saisaha, P.; de Boer, J. W.; Browne, W. R. *Chem. Soc. Rev.* **2013**, *42*, 2059.
2. Borovik, A. S. *Chem. Soc. Rev.* **2011**, *40*, 1870.
3. Dhar, D.; Tolman, W. B. *J. Am. Chem. Soc.* **2015**, *137*, 1322.
4. Mondal, P.; Pirovano, P.; Das, A.; Farquhar, E. R.; McDonald, A. R. *J. Am. Chem. Soc.* **2018**, *140*, 1834.
5. Mondal, P.; Lovisari, M.; Twamley, B.; McDonald, A. R. *Angew. Chem. Int. Ed.* **2020**, *59*, 13044.
6. Mondal, P.; McDonald, A. R. *Chem. -Eur. J.* **2020**, *26*, 10083.
7. McManus, C.;[#] Mondal, P.;[#] Lovisari, M.; Twamley, B.; McDonald, A.R. *Inorg. Chem.* **2019**, *58*, 4515. (# = equal contribution).