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Synthesis, Characterization & Reactivity of Putative High-Valent Nickel-Oxo Species

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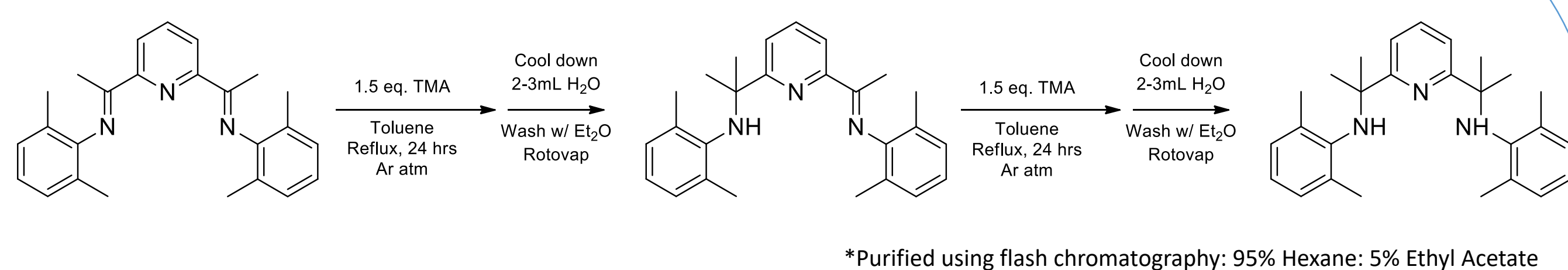
Introduction

The study of terminal high-valent metal-oxo complexes has increased significantly over the years as it is believed to be important intermediates in many biological processes such as the mononuclear non-heme iron (Fe) oxygenases that utilize Fe(IV)-oxo to initiate oxidative transformations. These complexes are also utilized in other reactions such as C-H bond activation, C-X bond formation, etc.¹⁻²

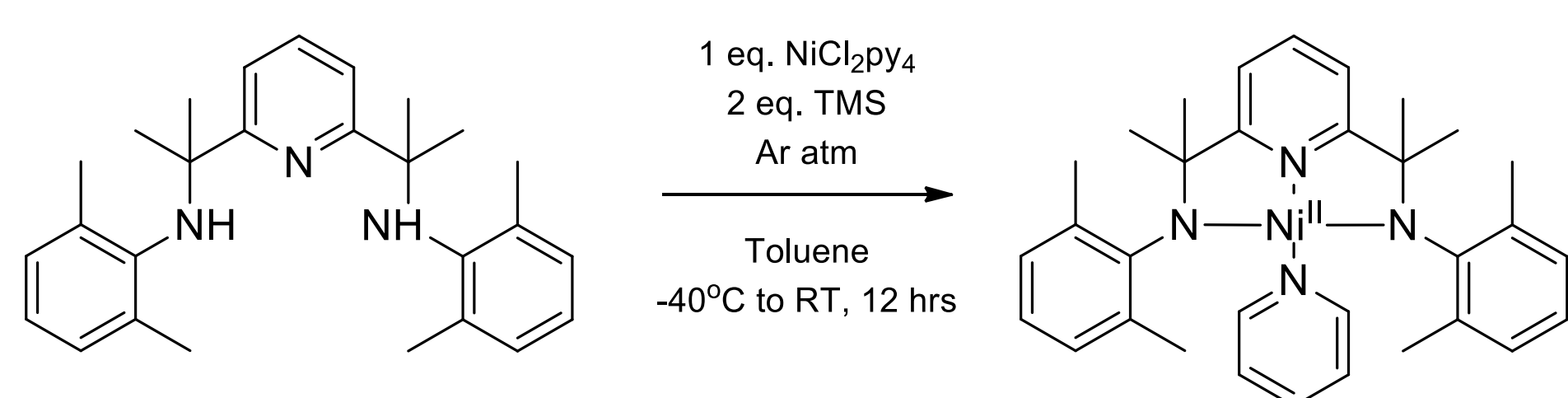
Synthetic models of these complexes will help us to perceive and understand the chemical and physical properties that have remained elusive. The formation of a stable high-valent metal-oxo complex for late-transition metals is challenging synthetically and terminal metal-oxo ligands for metals in Groups 9 through Group 12 are rare. The sudden change of abundance of complexes from Group 8 to Group 9 is a phenomenon referred to as the oxo-wall.³⁻⁴ These complexes beyond the wall should be very reactive and have been seen in oxidation reactions.⁹ Others have been able to create stable high-valent metal oxo complexes, synthesizing the complex in the more important square planar geometry.⁵ Synthesizing these complexes in square planar has opened the pathway to generate stable high-valent oxo species beyond the oxo-wall.

In our research, we aim to study a series of mononuclear nickel complexes with increasing oxidation states of +2, +3, and +4. These Ni complexes do hold a square planar geometry as they are supported by a dianionic, tridentate ligand system.⁶⁻⁷ After a one-electron oxidation of Ni(III)-OH, an EPR silent species was generated. This species has been able to carry out C-H bond cleavage within reactions. These reactivity reactions were observed using various forms of spectroscopic methods. This poster does not contain all data obtained.

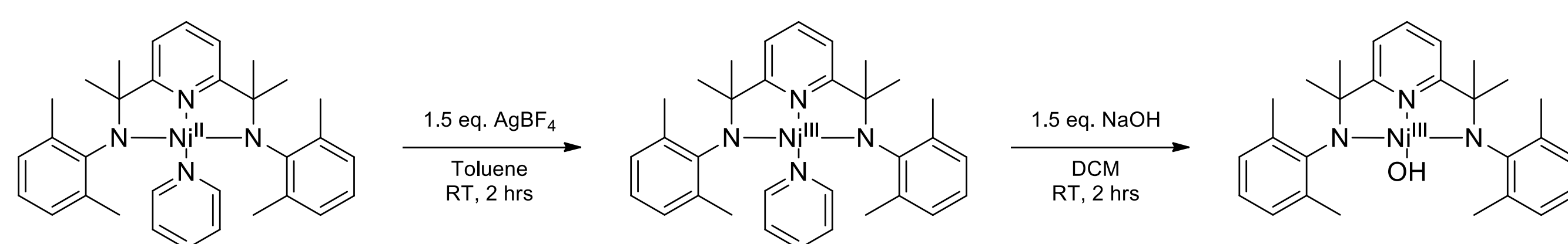
Generation of Ni(II), Ni(III), Ni(IV) Complexes



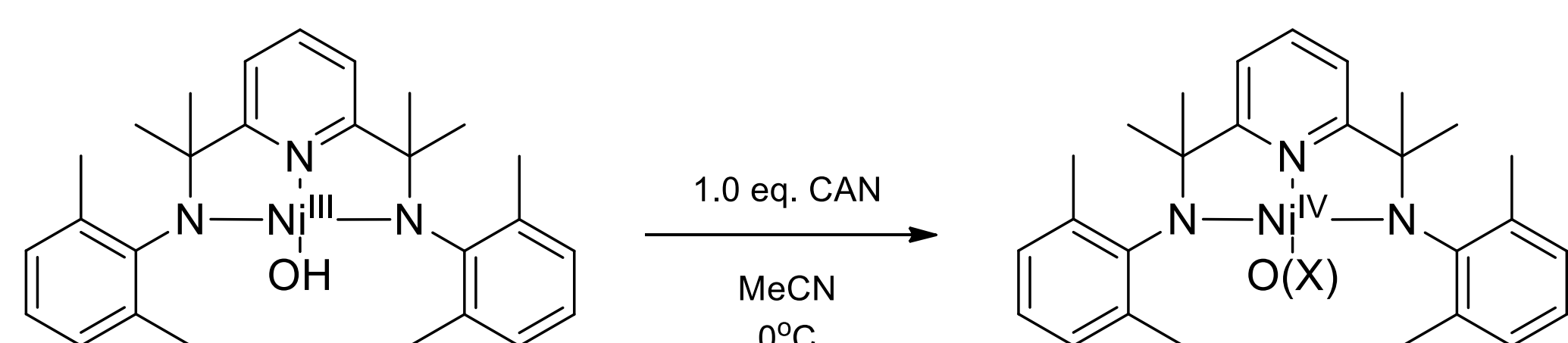
Scheme 1. Synthesis of Ligand Scaffold: $[NNNMe_8]H_2$



Scheme 2. Coordination of and Deprotonation of $[NNNMe_8]H_2$



Scheme 3. Synthesis of Ni(III)-OH



Scheme 4. Generation of Ni(IV)-O(X)

*Crystals of Ni(II) and Ni(III) species have been submitted

Characterization of Ni Complexes

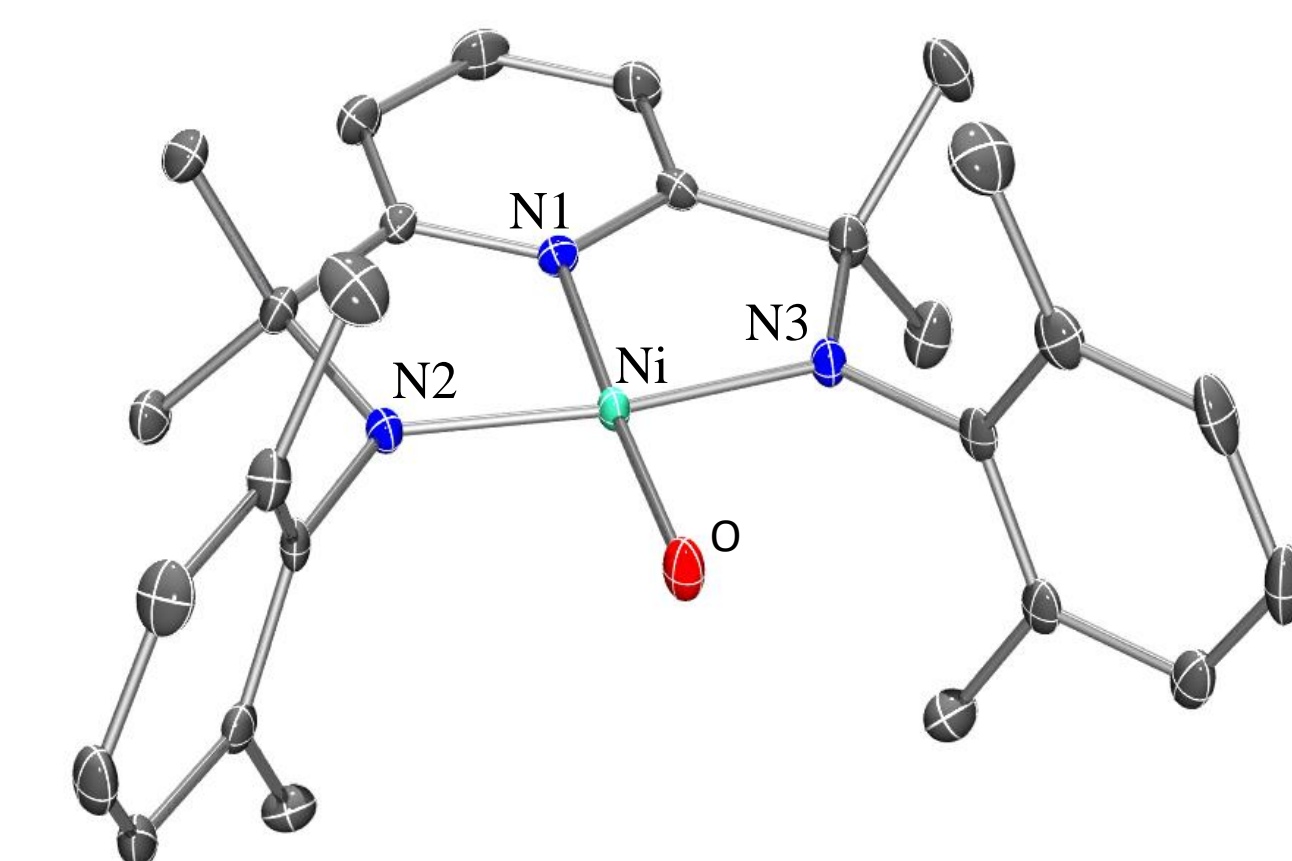
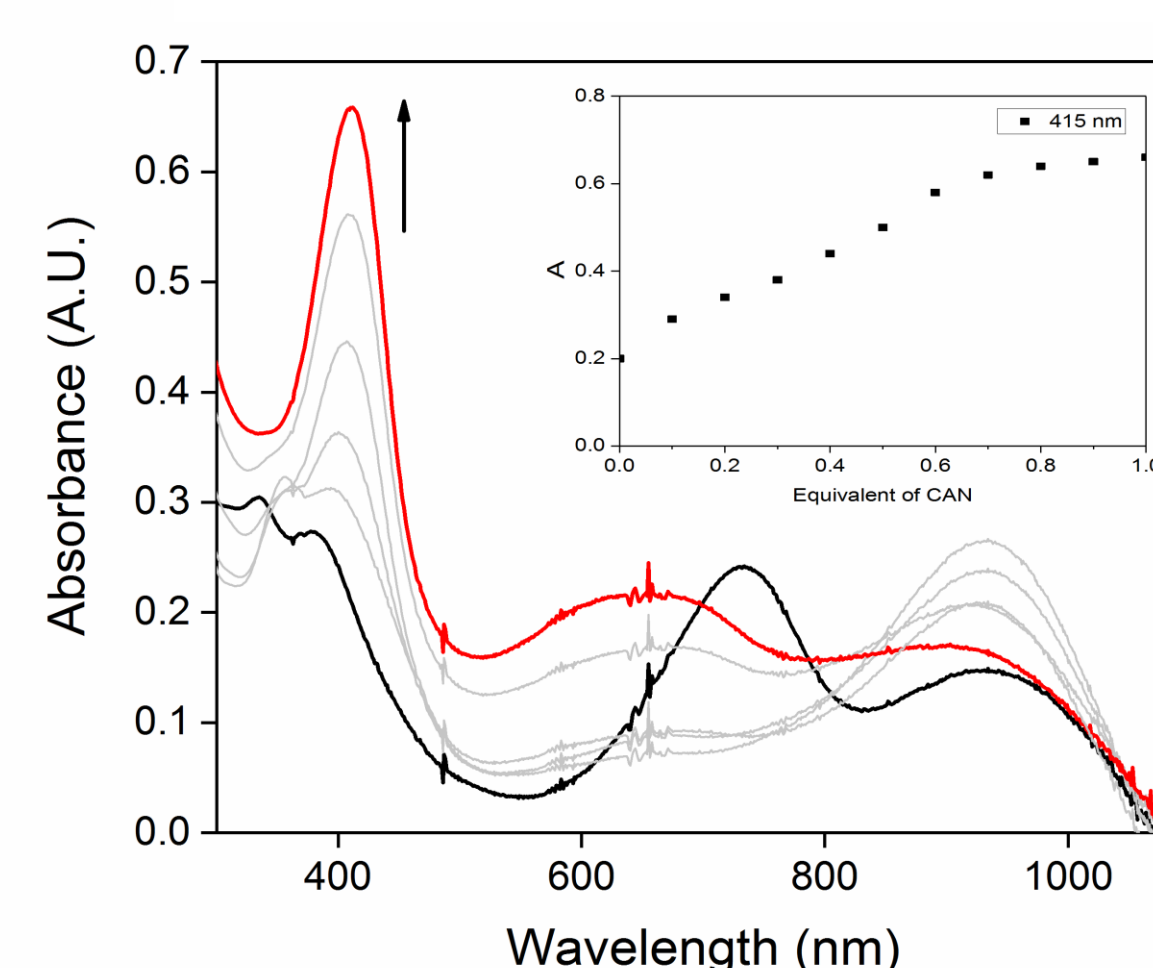
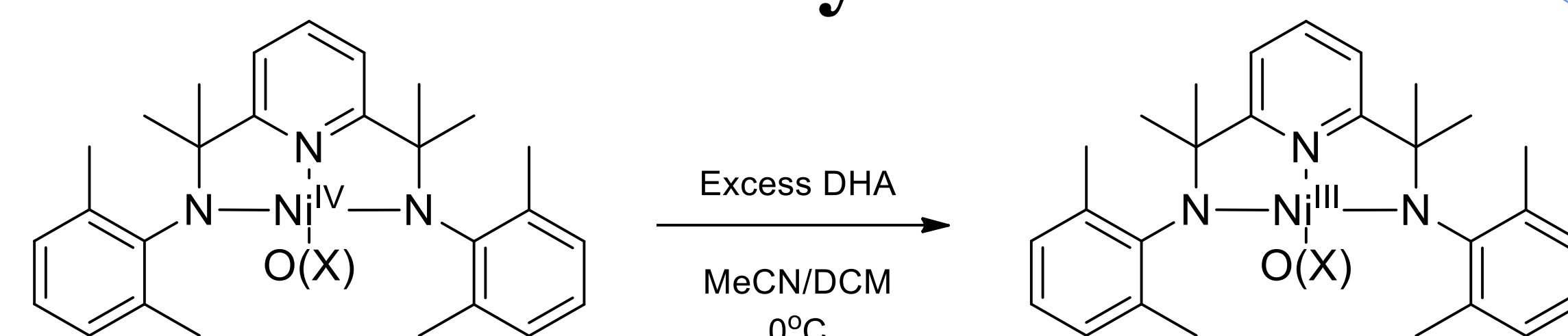


Figure 1. Left: UV-Vis spectrum for the Conversion of Ni(III)-OH (black) to Ni(IV)-O(X) (red) by one equivalence of CAN in Acetonitrile at 0°C. Inset: Titration of CAN monitored at 415 nm.

Right: Crystal Structure of Ni(III)-OH.

Reactivity Studies



Scheme 5. Reactivity of excess substrate with Ni(IV)-O(X)

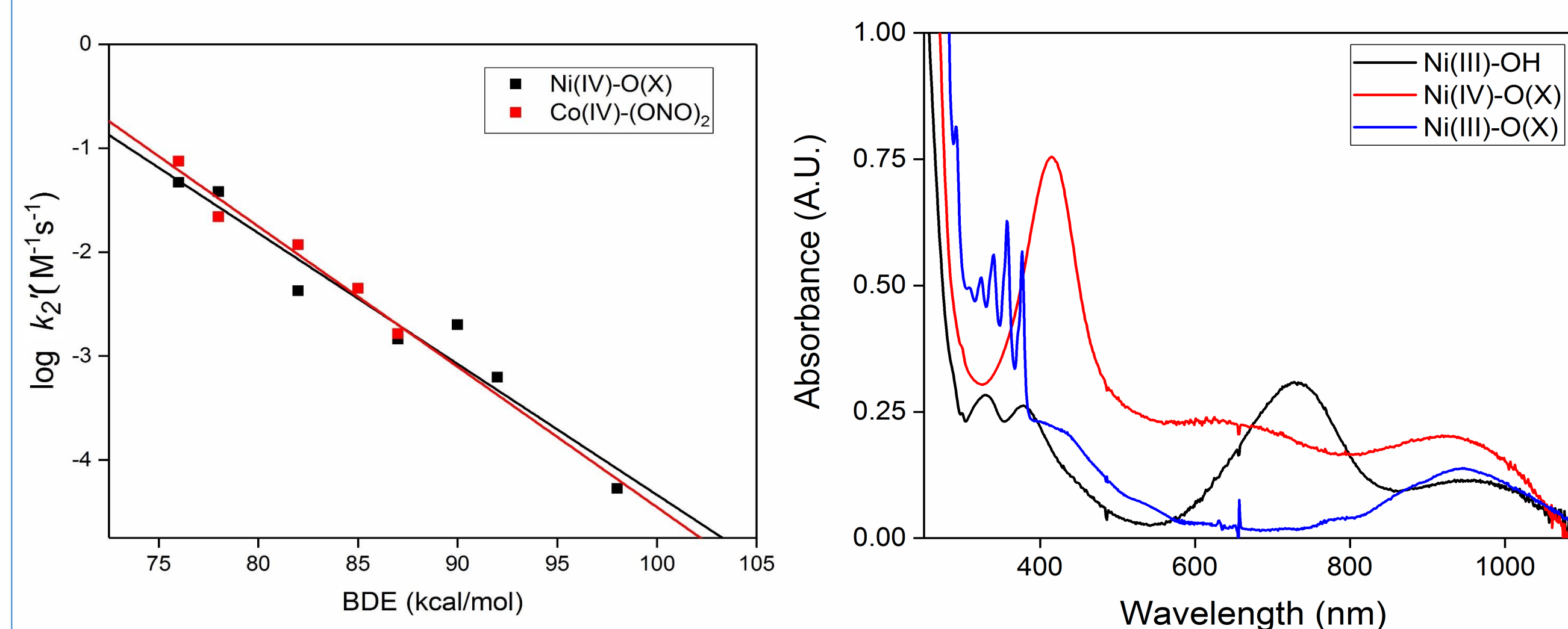


Figure 2. Left: Plots of $\log k_2'$ as a function of the C-H bond strength for substrate oxidation by Ni(IV)-O(X) (black) and Co(IV)-(ONO)₂ (red)⁸

Right: Individual spectrum of the addition of CAN to Ni(III)-OH (black), and the addition of excess DHA to Ni(IV)-O(X) (red), to yield C-H bond cleavage and a Ni(III) species (blue).

Substrate	Xanthene	DHA	Cyclohexene	Ethylbenzene	Toluene	THF	Cyclohexane
BDE (kcal/mol)	76	78	82	87	90	92	99
k_2 ($M^{-1}s^{-1}$)	0.094	0.153	0.0173	0.0029	0.006	0.0025	0.00032

Table 1. Kinetic results for Ni(IV)-O(X) with substrates

Conclusions & Future Work

The successful synthesis of both Ni(II) and Ni(III) species were done according to procedure. UV-Vis spectra followed by raw EPR data were both taken of each complex. From the collected data, we have evidence that upon a one-electron oxidation of Ni(III)-OH species a new species was created. This new species generated an EPR silent species that we propose to be a Ni(IV) species.

We have evidence that adding the substrate, DHA, to this new species has the potential to perform C-H bond cleavage. Immediate reaction of the substrate and the putative Ni(IV) species gives us evidence that we have made a Ni(III) species due to similar UV-Vis feature. With this new finding, we believe that newly generated Ni(IV) species is a high-valent Ni-oxo species. The axial ligand bound to the proposed Ni(IV) species is currently under investigation.

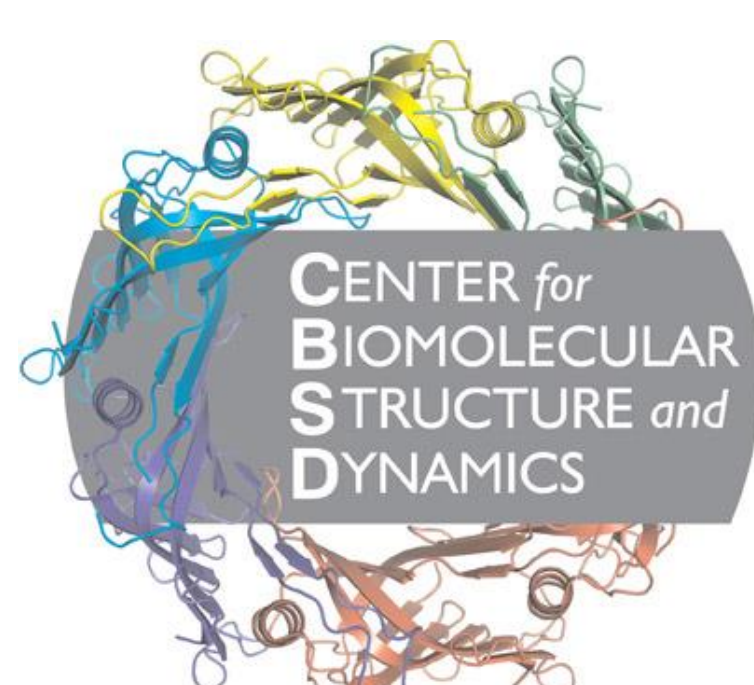
Future work includes obtaining more structural data of all Ni complexes with the oxidation states +2, +3, and +4 through X-ray crystallography, X-ray absorption spectroscopy, EPR spectroscopy, FTIR analysis, elemental analysis. We will continue the reactivity studies of substrate addition.

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Acknowledgments

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