

Final Technical Report DE-SC0009363

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Abstract: This is a Final Technical Report of DOE AWARD NUMBER: DE-SC0009363. PROJECT TITLE: "Controlling High-Valent Reactivity in Earth Abundant Metals". PROJECT PERIOD: AUGUST 16, 2019 TO AUGUST 15, 2022. This report provides a comprehensive summary of all work completed under this award.

1. What were the major goals of the project?

Aim 1) Constructing stable and anionic derivatives of terpyridine ligands for accessing high valent nickel.

The underivatized terpyridine ligand supports a wide range of catalytic reactions mediated by nickel.

Moreover, the electrochemical redox events of nickel terpyridine are well-separated, which benefits the development of electrocatalytic reactions using this metal/ligand combination. We proposed to develop robust and anionic derivatives of the terpyridine ligand in order to expand the chemistry possible with this ligand through electronics, vacant site control, and spin control at metal centers. The electron-rich nature of the ligand makes it appealing for use in the emerging high-valent chemistry at nickel.

Aim 2) Develop catalytic approaches to hydrocarbon functionalization at high valent nickel. We aimed to develop a catalytic system by which nickel(I) complexes oxidatively add organic halides to afford organonickel(III) halide complexes that upon irradiation with visible light eliminate halogen atoms to activate hydrocarbons, which in turn participate in nickel-catalyzed coupling reactions. Ligands and substrates will be identified that enable such transformations, and the salient features of the catalysis will be studied through systematic analysis of individual steps.

Aim 3) Develop electrocatalytic strategies for accessing high-valent metals at reduced potentials using anion-mediated electron transfer. The goal of this Aim is to understand how to generate exceptionally reactive high-valent nickel complexes on-demand and in low concentrations so reactions with hydrocarbons can be performed without the risk of explosions. We sought to understand how anions can modulate redox potentials of well-defined metal complexes so that the energy needed to generate high-valent nickel can be lowered. A long-term goal, based on an understanding of the fundamental parameters required to achieve electrocatalytic fluorination reactions is to understand how we can replace fluoride with other groups such as hydroxide in order to electrochemically convert gaseous hydrocarbons to liquid alcohols for fuels.

2. What was accomplished under these goals?

We have made an interesting discovery for using anionic frameworks to lower the potential at which high valent nickel can be generated. Our initial efforts were guided by the emerging efforts to understand how to develop catalysis with the related high valent copper derivatives $[\text{LCu}(\text{CF}_3)_3]$ and $[\text{Cu}(\text{CF}_3)_4]^-$. We hypothesized that a homoleptic tetra(trifluoromethyl)metal complex bearing a bona fide d^8 ground state electronic configuration may be possible with nickel, as nickel in the +2 oxidation state is more commonly encountered than copper in its +3 oxidation state. Moreover, if $[\text{Ni}(\text{CF}_3)_4]^{2-}$ and $[\text{Ni}(\text{R})(\text{CF}_3)_3]^{2-}$ complexes could be generated, then access to their higher oxidation states would be more facile than for $[\text{Cu}(\text{CF}_3)_4]^-$ and $[\text{LCu}(\text{CF}_3)_2(\text{R})]$ derivatives, which are already highly oxidized molecular species. Access to higher oxidation states would provide the opportunity to explore whether difficult chemical bond forming reactions involving the trifluoromethyl group could be triggered by oxidative means with unsupported architectures at nickel. Nickel fluoroalkyl complexes often exhibit two additional oxidations beyond the formal nickel(II) state and show higher reactivity in their oxidized forms. We found that the nickel anions $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ and $[\text{Ni}(\text{CF}_3)_4]^{2-}$ could be prepared by formal addition of three and four equivalents, respectively, of “ AgCF_3 ” to $[(\text{dme})\text{NiBr}_2]$ in the presence of $[\text{PPh}_4]^+$ counter-ion. The structure of both of these anionic complexes were confirmed by X-ray

crystallography, which verified that such complexes could be prepared without the need for any complicated supporting ligands.

With $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ and $[\text{Ni}(\text{CF}_3)_4]^{2-}$ in hand, we evaluated their electrochemical properties by cyclic voltammetry. We found that oxidation of the monoanionic $[\text{PPh}_4][(\text{MeCN})\text{Ni}(\text{CF}_3)_3]$ is irreversible and occurs at the onset potential of ca. +0.02 V vs the ferrocene/ferrocenium couple. Peak potentials for $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ appear at +0.38 V and +0.76 V. The oxidation of complex $[\text{Ni}(\text{CF}_3)_4]^{2-}$ was more facile, with an onset potential of ca. -0.1 V and peak potentials at +0.10, +0.50 and +0.79 V. Gratifyingly, both of these complexes display oxidations in windows that are easily accessible. A notable difference in shifting the redox potentials to less positive values, as the charge-neutral complex $[(\text{MeCN})_2\text{Ni}(\text{CF}_3)_2]$ displays its first oxidation at +0.76 V. The CVs are also interesting to compare with that of the copper derivative $[\text{NBu}_4][\text{Cu}(\text{CF}_3)_4]$. Because $[\text{NBu}_4][\text{Cu}(\text{CF}_3)_4]$ is already a highly oxidized species (irrespective of whether the holes lie predominantly on the metal or ligand), no oxidation peak was observed in the CV in the region spanning from 0 to +1.5 V vs the ferrocene/ferrocenium couple. Thus, we believe that changing the metal identity from copper to nickel in the $[\text{M}(\text{CF}_3)_4]^{n-}$ (and formally d^8) platform provides exciting opportunities to explore redox triggered-reactions involving this “ligandless” trifluoromethyl source using readily available and practical oxidants.

The knowledge that monoanionic $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ can accommodate an additional trifluoromethyl anion to afford $[\text{Ni}(\text{CF}_3)_4]^{2-}$ prompted us to explore the reactivity of $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ with a different nucleophile to determine if a heteroleptic dianionic complex could be prepared. If so, such structures could potentially be developed as intermediates in catalytic reactions involving high valent nickel, akin to the emerging methodologies involving $[\text{Cu}(\text{CF}_3)_3(\text{R})]^-$. Reaction of $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ with $[\text{NMe}_4][\text{OPh}]$ indeed led to the production of the new dianionic nickel phenoxide complex $[(\text{PhO})\text{Ni}(\text{CF}_3)_4]^{2-}$, which has been structurally characterized. Interestingly, NMR data suggests that when isolated crystals of $[(\text{PhO})\text{Ni}(\text{CF}_3)_4]^{2-}$ are dissolved in MeCN, the phenolate moiety dissociates from nickel and reaffords monoanionic complex $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ in solution. Benzene is generated in the process along with triphenylphosphine oxide, indicating a non-innocent interaction between phenoxide and the phosphonium counter-ion. Control experiments showed that simple reaction of $[\text{NMe}_4][\text{OPh}]$ with $[\text{PPh}_4]\text{Cl}$ in acetonitrile solvent in the absence of nickel indeed leads to $\text{O}=\text{PPh}_3$ plus benzene. The source of the oxygen atom does not appear to be derived from the phenoxide moiety, as reaction of $[\text{NMe}_4][p\text{-fluorophenoxide}]$ with $[\text{PPh}_4]\text{Cl}$ in acetonitrile still yields triphenylphosphine oxide but does not produce any detectable fluorobenzene. Thus, we suspect that adventitious water may be the source of the oxygen atom in $[\text{O}=\text{PPh}_3]$. Changing the counter-ion and reacting $[\text{NBu}_4][(\text{MeCN})\text{Ni}(\text{CF}_3)_3]$ with $[\text{NMe}_4][\text{OPh}]$ gratifyingly leads to a solution stable complex whose ^{19}F NMR signals (CD_3CN , δ –21.2 (septet, J = 4.1 Hz) and –31.3 (quartet, J = 4.1 Hz)) are consistent with the desired $[\text{NR}_4][(\text{PhO})\text{Ni}(\text{CF}_3)_3]$ product. With knowledge of this noninnocent interaction of $[\text{PPh}_4]^+$ with phenoxide, it is clear that judicious choice of counter-ions will be a critical component to catalytic methods development with these “ligandless” complexes of nickel.

In preliminary reactivity studies, we have shown that $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ reacts with the two electron oxidant bis(4-tert-butylphenyl)iodonium hexafluorophosphate to afford trifluoromethylated arene in 54% yield, producing $[(\text{MeCN})_2\text{Ni}(\text{CF}_3)_2]$ in 75% yield as the only detectable nickel containing product. Hypervalent iodine reagents are known to oxidize both Pd(II) and Ni(II) to Pd(IV) and Ni(IV), so we believe that the intermediate in this new chemical bond forming reaction is the high valent $[\text{Ar}-\text{Ni}^{IV}(\text{CF}_3)_3(\text{MeCN})_2]$. Such a species, upon reductive elimination or aryl– CF_3 product would afford

$[(\text{MeCN})_2\text{Ni}(\text{CF}_3)_2]$ as the nickel-containing byproduct. Further experiments with $[\text{Ni}(\text{CF}_3)_4]^{2-}$ shows that oxidation to unsupported and formally nickel(IV) trifluoromethyl derivatives is indeed possible. We observed that a two electron oxidation of $[\text{Ni}(\text{CF}_3)_4]^{2-}$ with potassium persulfate produced a new species detected by ^{19}F NMR spectroscopy (CD_3CN , δ -19.15 (sept, J = 7.3 Hz) and -30.60 (sept, J = 7.3 Hz) in 11% NMR yield along with other fluorine-containing nickel species consistent with $[(\text{SO}_4)\text{Ni}(\text{CF}_3)_2(\text{MeCN})_2]$, $[(\text{MeCN})_2\text{Ni}(\text{CF}_3)_4]$, and $[(\text{MeCN})\text{Ni}(\text{CF}_3)_5]^-$. Fortuitous crystallization of one of the new species from MeCN/ether enabled its solid-state structure determination and confirmed the identity of the crystallized compound as $[\text{PPh}_4]_2[\text{Ni}(\text{CF}_3)_4(\text{SO}_4)]$. To our knowledge, this is the first example of an unsupported trifluoromethyl nickel(IV) complex, and the identification of such a structure lends credence to the proposal that a high-valent nickel(IV) species is a viable intermediate in the exciting trifluoromethylation reaction described above.

Because the unsupported complexes $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ and $[\text{Ni}(\text{CF}_3)_4]^{2-}$ are so unique, we collaborated with a group at Cornell to study their electronic structures. Detailed insights into the electronic properties of these new compounds were obtained through the use of density functional theory (DFT) calculations, spectroscopy-oriented configuration interaction (SORCI) calculations, X-ray absorption spectroscopy. The data collectively show that trifluoromethyl complexes of nickel, even in the most common oxidation state of nickel(II), are highly covalent systems whereby a hole is distributed on the trifluoromethyl ligands and surprisingly rendering the metal to a physically more reduced state. In the cases of $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ and $[\text{Ni}(\text{CF}_3)_4]^{2-}$, these complexes are better described as physically d⁹ metal complexes. We believe these fundamental insights will provide a solid foundation for developing new catalytic reactions of interest to the DOE.

Aim 3 also targets the generation of high valent cobalt in order to test these compounds for the fluorination of hydrocarbons. Towards this goal, synthetic protocols to the new fluoroalkylated cobalt complexes such as $[\text{fac}-(\text{MeCN})_3\text{Co}(\text{C}_2\text{F}_5)_3]$ and $[\text{fac}-(\text{MeCN})_3\text{Co}(\text{CF}_3)_3]$ have been developed. Interestingly, we found that upon standing in pyridine solvent, $[\text{fac}-(\text{MeCN})_3\text{Co}(\text{CF}_3)_3]$ undergoes a C-H bond functionalization of acetonitrile to produce CF_3H and $[(\text{pyr})_2(\text{CF}_3)_2\text{Co}(\mu-\text{CH}_2\text{CN})]_2$ whereby the former acetonitrile ligands bridge the two cobalt centers.

The acetonitrile ligands in this precursor are labile and can be replaced by other ligands such as water and terpyridine. The coordination of water to cobalt in the presence of a large excess of pyridine is remarkable, considering pyridine is typically considered to be a stronger ligand than water in the spectrochemical series. Thus, the aquo complex **2** exhibits an unusual combination of air-stability, affinity for water over a basic solvent like pyridine, and a resistance to undergo hydrolysis of the perfluoroethyls, making it an interesting platform for exploring the reactivity of the metal-bound water ligands in a variety of applications, including water-oxidation. Such studies are ongoing in our labs.

3. What opportunities for training and professional development has the project provided?

The project has supported the full training of two students and partial training of one student towards their Ph.D. degrees. Additional development for the students has been provided by attendance at professional meetings such as the Winter Fluorine Conference and at the European Symposium on Fluorine Chemistry. Two undergraduate students were also trained for this project. These students have collectively written fourteen papers.

4. How have the results been disseminated to communities of interest?

Results have been disseminated via peer-reviewed publications, in-person conference and university presentations, and virtual presentations.

5. What is the impact on the development of the principal discipline(s) of the project?

- We have developed convenient routes to fluoroalkylcobalt precursors. Such precursors with labile solvento ligands were unknown prior to these studies
- We developed a systematic way to prepare fluoroalkylated cuprates
- We showed that electron holes can be distributed on trifluoromethyl ligands even in nickel complexes bearing formally common oxidation states.
- We have developed catalytic methods to perform C-H trifluoromethylation reactions.
- We showed that nickel in various oxidation states can serve as reservoirs for trifluoromethyl ligands (up to six on a single nickel center).
- We identified a ligand environment that better separates oxidation potentials in the anionic Ni perfluoroalkyl complexes, which is expected to aid in the development of new (electro)catalytic methods that target single electron oxidations in order to release trifluoromethyl and perfluoroalkyl radicals.
- We've showed proof-in-principle that simple homoleptic trifluoromethyl nickel complexes can perform stereoselective catalytic trifluoromethylation reactions of complex molecules.

6. What is the impact on other disciplines?

Inexpensive and low toxicity metals like nickel are being employed in fluorocarbon reactions that impact many areas of basic science. The DOE has had a long-standing interest in the chemistry of fluorine ever since it was discovered that uranium hexafluoride exhibits a high vapor pressure and could be used to purify isotopically enriched uranium. Fluorination has become popular for other important reasons, like its known ability to increase the oxidative and thermal stability of new materials and its pervasive role in life sciences. Tailored ligands and counter-ions that allow metals to operate under harsh oxidative conditions often feature fluoroalkyl substituents due to the chemical inertness of the $[\text{CF}_3]$ and $[\text{CF}_2]$ functional groups. Such harsh conditions are often required for hydrocarbon oxidations.

7. What is the impact on the development of human resources?

This project has trained three Ph.D. students. One has graduated so far and has gone on to do a postdoc at University of Pennsylvania. He has now accepted a full-time job at Adhesives Research Co. The project has also trained two undergraduate students. One has received his B.S. and is now a graduate student in chemistry at NYU. The other undergraduate is continuing research in the lab and has received the ACS Division of Fluorine Chemistry Undergraduate Research Award.

8. What is the impact on physical, institutional, and information resources that form infrastructure?

The project produced a significant amount of 3-dimensional crystal structures which have been deposited with the Cambridge Structural Database.

9. What is the impact on technology transfer?

A provisional patent entitled "Methods to Derivatize Brucine with Fluorine and Fluorinated Groups" was submitted by Lehigh University in 2021.

10. What is the impact on society beyond science and technology?

The published works contribute to our understanding of how to use cheap, low-toxic, and environmentally friendly metals to perform catalytic reactions that were once dominated by precious metals that had geopolitical issues associated with their mining.

11. Products

a. Journal articles intellectually driven by this DOE award:

"Transformation of brucine into trifluoromethyl neobrucine using the homoleptic nickel catalyst $[\text{Ni}(\text{CF}_3)_4]^{2-}$ " Shreiber, S. T.; Puchall, G. I.; Vicic, D. A. *Tetrahedron Lett.* **2022**, 97, 153795.

"Synthesis, Structure, and Electrochemical Properties of $[\text{LNi}(\text{R}_f)(\text{C}_4\text{F}_8)]^-$ and $[\text{LNi}(\text{R}_f)_3]^-$ Complexes" Shreiber, S. T.; Amin, F.; Schäfer, S. A.; Cramer, R. E.; Klein, A.; Vicic, D. A. *Dalton Trans.* **2022**, 51, 5515-5523.

"Access to Perfluorometallacyclopentane Complexes of Cobalt through the $[(\text{MeCN})_4\text{Co}(\text{C}_4\text{F}_8)][\text{PF}_6]$ Precursor" Xue, T.; Cramer, R. E.; Vicic, D. A. *Organometallics* **2021**, 40, 3585-3590.

"Synthesis and Characterization of the Dinuclear Cobalt(III) Complex: $[(\text{C}_2\text{F}_5)_3\text{Co}(\mu\text{-F})]_2^{2-}$ " Shreiber, S. T. and Vicic, D. A. *J. Organomet. Chem.* **2021**, 949, 121974.

"Solvated Nickel Complexes as Stoichiometric and Catalytic Perfluoroalkylation Agents" Shreiber, S. T. and Vicic, D. A. *Angew. Chem. Int. Ed.* **2021**, 60, 18162-18167.

"Routes to Acetonitrile-Supported Trifluoromethyl and Perfluorometallacyclopentane Complexes of Cobalt" Xue, T.; Vicic, D. A. *Organometallics* **2020**, 39, 3175-3720. This work was listed as one of the "most-read" articles of the journal during the month of October.

"Synthesis and Oxidative Stability of an Anionic Perfluoroethyl Cobalt(III) Complex" Shreiber, S. T.; Vicic, D. A. *Helv. Chim. Acta* **2020**, 103, e2000149. (Special issue dedicated to Antonio Togni).

" $[(\text{MeCN})\text{Ni}(\text{CF}_3)_3]^-$ and $[\text{Ni}(\text{CF}_3)_4]^{2-}$: Foundations Toward the Development of Trifluoromethylations at Unsupported Nickel" Shreiber, S. T.; DiMucci, I. M.; Khrizanforov, M. N.; Titus, C. J.; Nordlund, D.; Dukina, Y.; Cramer, R. E.; Budnikova, Y.; Lancaster, K. M.; Vicic, D. A. *Inorg. Chem.* **2020**, 59, 9143-9151. This work was listed as one of the "most-read" articles of the journal during the month of June.

"Syntheses, Solution Behavior, and Computational Bond Length Analyses of Trifluoromethyl and Perfluoroethyl Cuprate Salts" Shreiber, S. T.; Kaplan, P. T.; Hughes, R. P.; Vasiliu, M.; Dixon, D. A.; Cramer, R. E.; Vicic, D. A. *J. Fluorine Chem.* **2020**, 109518.

" $[(\text{MeCN})_3\text{Co}(\text{C}_2\text{F}_5)_3]$: A Versatile Precursor to Cobalt(III) Perfluoroethyl Complexes" Shreiber, S. T.; Scudder, J. J.; Vicic, D. A. *Organometallics* **2019**, 38, 3169-3173. This work was listed as one of the "most-read" articles of the journal during the month of August 2019.

b) Jointly funded by the DOE award and other grants but not intellectually driven by the DOE grant:

"The Myth of d^6 Nickel(IV)" DiMucci, I. M.; Titus, C. J.; Nordlund, D.; Bour, J. R.; Kosobokov, M. D.; Martin, C. D.; Nebra, N.; Sanford, M. A.; Vicic, D. A.; Yruegas, S.; MacMillan, S. N.; Shearer, J.; Lancaster, K. M. **2021**, *in preparation*.

"On the Role of the X Coligands in Cyclometalated [Ni(Phbpy)X] Complexes (HPhbpy = 6-phenyl-2,2'-bipyridine)" Vogt, N.; Sandleben, A.; Kletsch, L.; Schäfer, S.; Chin, M. T.; Vicic, D. A.; Hörner, G.; Klein, A. *Organometallics* **2021**, *40*, 1776-1785.

"Nickel-Mediated Trifluoromethylation of Phenol Derivatives via C–O Bond Activation" Hu, W.-Q.; Pan, S.; Xu, X.-H.; Vicic, D. A.; Qing, F.-L. *Angew. Chem. Int. Ed.* **2020**, *59*, 2-9. This work was listed as a "Hot Paper" for the month of June.

"Exploiting the Trifluoroethyl Group as a Precatalyst Ligand in Nickel-Catalyzed Suzuki-Type Alkylations" Yang, Y.; Zhou, Q.; Cai, J.; Xue, T.; Liu, Y.; Jiang, Y.; Luo, G.; Chung, L. W.; Vicic, D. A. *Chem. Sci.* **2019**, *10*, 5275-5282.