

Oxidatively Induced C-H Activation at High Valent Nickel

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Supporting Information

ABSTRACT: This communication describes a series of oxidatively induced intramolecular arene C–H activation reactions of Ni^{II} model complexes to yield Ni^{IV} σ -aryl products. These reactions proceed within 10 min at room temperature, which represents among the mildest conditions reported for C–H cleavage at a Ni center. A combination of density functional theory and preliminary experimental mechanistic studies implicate a pathway involving initial 2e⁻ oxidation of the Ni^{II} starting materials by the F⁺ transfer reagent *N*-fluoro-2,4,6-trimethylpyridinium triflate followed by triflate-assisted C–H cleavage at Ni^{IV} to yield the products.

T ransition metal-mediated C–H activation is a key elementary step in the catalytic C–H functionalization of organic molecules. The vast majority of examples of both stoichiometric and catalytic C–H activation involve low valent metals, such as Pt^{II}, Pd^{II}, and Ni^{II.1} However, there is increasing evidence that higher oxidation state group 10 metal centers can also participate in C–H cleavage reactions.^{2–5} For instance, our group has recently reported several examples of intramolecular C–H activation at Pd^{IV} centers.³ In these systems, the Pd^{II} precursors are unreactive toward cyclometalation. However, upon treatment with a 2e⁻ oxidant, C–H cleavage proceeds rapidly to afford an octahedral Pd^{IV} metallacycle. These stoichiometric studies have motivated the development of a variety of catalytic transformations that leverage C–H activation at Pd^{IV} as a key step in the catalytic cycle.⁴

High oxidation state organonickel complexes (particularly Ni^{IV} species) are far rarer than their Pd^{IV} analogues.^{6,7} Nonetheless, growing evidence supports the feasibility of accessing Ni^{IV} intermediates using various 2e⁻ oxidants.^{6e-g,j} In addition, recent reports have shown that Ni^{IV} compounds can undergo reductive elimination,^{6a-c,e-j} transmetalation,^{6c,j} and group transfer^{6g} reactions to yield a diverse array of organic and organometallic products. The emerging studies of C–H activation at Pd^{IV} led us to hypothesize that Ni^{IV} complexes might also participate in C–H bond cleavage reactions.⁵ Insights into the feasibility and mechanism of this fundamental organometallic transformation could ultimately inform its incorporation into Ni-catalyzed reactions.

We sought to design a Ni^{II} model complex that could undergo C–H cleavage upon treatment with a 2e⁻ oxidant. Previous work has shown that high valent Ni intermediates are stabilized by facial tridentate nitrogen donor ligands such as tris(2-pyridyl)methane (py₃CH) (Scheme 1a).^{6e} We hypothesized that replacing one of the pyridine arms of py₃CH with an aryl group might enable an





intramolecular C–H cleavage reaction to form a product of general structure **2** (Scheme 1b).^{3b} We selected trifluoromethyl ligands as the other supporting ligands in this model system, as fluoroalkyls are well-known to stabilize high valent Ni centers.^{6e,f,j,7c–e,8} Finally, *N*-fluoro-2,4,6-trimethylpyridinium triflate (NFTPT) was selected as the oxidant because it has been used for the 2e⁻ oxidation of Pd^{II} to Pd^{IV},¹⁰ including for a related oxidatively induced C–H activation reaction at Pd^{IV.3b}

We first turned to density functional theory (DFT) to assess the feasibility of the transformation proposed in Scheme 1b.¹¹ As summarized in Figure 1, computational studies reveal that the inner sphere $2e^-$ oxidation of 1a with NFTPT to form Ni^{IV}-F intermediate **B** proceeds with an activation barrier (ΔG^{\ddagger}) of just 10.5 kcal/mol. The steps involved in converting 1a to B are directly related to those previously reported for the oxidation of $(bipy)Pd^{II}(CH_3)(OAc)to[(bipy)Pd^{IV}(CH_3)(OAc)(F)]^+$ using NFTPT.¹⁰ The observation of Ni–aryl interactions in **B** suggests that this Ni^{IV} intermediate is highly electrophilic. Indeed, we observe a low energy pathway for cyclometalation at Ni^{IV} via an S_EAr mechanism.¹² The interaction of the triflate counterion with B lowers the energy of this cation by >5 kcal/mol (to form intermediate C). The TfO⁻ then assists as a base in the cyclometalation step, where D can be viewed as a Ni^{IV}-arenium species involving an electrophilic Caryl-H bond cleavage. This transformation ultimately results in the formation of the Ni^{IV}(aryl) (fluoride) complex 2a as a TfOH adduct (structure F) that is -31.9 kcal/mol lower in energy than the Ni^{II} starting material 1a + NFTPT. Overall, these calculations demonstrate

Received: March 9, 2017



Figure 1. Energy profile for the oxidative transformation of **1a** to **2a** using NFTPT, with all computation employing the solvent used in synthetic studies (dichloromethane). Structures **B** and **C** exhibit short Ni…C_{ipso} interactions (2.408, 2.394 Å) with no indication of C–H agostic interactions (Ni…C_{ortho} 3.010–3.101 Å, Ni…H_{ortho} 3.288–3.383 Å). Energies ΔG (ΔH) in kcal/mol. Bond lengths in Å.

that a pathway involving the $2e^-$ oxidation of 1a with NFTPT followed by $C(sp^2)$ -H cleavage at the resulting Ni^{IV} center is energetically feasible.

These initial DFT studies motivated us to explore this transformation experimentally. The Ni^{II} precursor **1a** was prepared via ligand exchange between $(MeCN)_2Ni^{II}(CF_3)_2$ and



 py_2CFPh (eq 1). Complex 1a was characterized by ¹H, ¹³C, and ¹⁹F NMR spectroscopy and elemental analysis. X-ray quality crystals of 1a were obtained by vapor diffusion of diisopropyl ether into an acetonitrile solution of 1a, and an X-ray structure is shown in Figure 2a. In the solid state, 1a exhibits a square planar



Figure 2. X-ray structures of (a) **1a**, (b) **1b**, and (c) **1d** plotted with 50% probability ellipsoids for non-H atoms.

geometry at the Ni^{II} center. A relatively long distance (2.906(2) Å) is observed between Ni and the *ipso* carbon of the pendant aryl group, suggesting that there is minimal bonding interaction in the Ni^{II} oxidation state.¹³

The treatment of 1a with 1.3 equiv of NFTPT in CH_2Cl_2 at 25 °C resulted in an instant color change from amber yellow to bright yellow.¹⁴ The Ni^{II} starting material was completely consumed

within 10 min, as determined by $^{19}\mathrm{F}$ NMR spectroscopy, and no diamagnetic intermediates were detected. The diamagnetic Ni^V product **2a** (eq 2) shows a Ni–CF₃ resonance at –24 ppm and a



^aNMR yield based on average of two trials. ^bIsolated yield. ^cAt -35 °C

py₂CFAr fluorine signal at -182 ppm. Notably, this latter signal shifts substantially from the starting material (-138 ppm), and this large shift is diagnostic for the formation of Ni^{IV} complexes of this ligand. This new complex also shows a broad resonance at -283 ppm, which is indicative of a M^{IV}-F.^{15,16}

Complex **2a** was purified via an aqueous workup followed by trituration with diethyl ether, and was isolated as an analytically pure yellow solid in 70% yield. Unlike many transition metal fluorides,¹⁷ this complex is stable to ambient air and moisture. Characterization by ¹H, ¹³C, and ¹⁹F NMR spectroscopy as well as X-ray crystallography confirmed that **2a** is the σ -aryl Ni^{IV} product of an oxidatively induced C–H activation reaction. The X-ray structure of **2a** (Figure 3a) shows an octahedral Ni^{IV} complex with the σ -aryl ligand *trans* to the fluoride. To our knowledge, this is the first example of an organometallic Ni^{IV} fluoride complex. Overall,



Figure 3. X-ray structures of (a) **2a**, (b) **2b**, and (c) **2c** plotted with 50% probability ellipsoids for non-H atoms.

this transformation demonstrates the viability of oxidatively induced C-H cleavage at Ni under mild conditions (<10 min, 25 °C). These represent among the mildest conditions reported for a cyclonickelation reaction at any oxidation state of Ni.^{5,13,18-2}

We next probed the scope and mechanism of this transformation. A first set of experiments focused on determining the isotope effect associated with the C-H cleavage event (eq 3). The



reaction proved too fast for rate studies, even at -50 °C. As such, we were unable to obtain an intermolecular KIE. However, the use of substrate la-d afforded a 24:76 ratio of 2a:2a-d, which corresponds to an intramolecular isotope effect of ≈ 3 (DFT computed value ≈ 5). The observed value is significantly smaller than those reported for $C(sp^2)$ -H activation at $Pd^{IV}(7-12)^{3c}$ but comparable to that for related transformations at Pt^{IV} centers (2.3 and $\bar{3}$).^{2a}

We also investigated electronic effects using a series of substituted analogues of 1 bearing OMe, F, and CF₃ substituents on the arene ring (1b-d in eq 2). X-ray structures of the Ni^{II} starting materials 1a, 1b, and 1d are shown in Figure 2. The bond distances and bond angles in these structures are nearly identical, including the Ni-ipso-C distance (2.906(2), 2.923(2), and 2.926(2) Å, respectively). This suggests that the remote substituents have minimal impact on the interaction of the aryl ring with the Ni^{II} center. All three complexes were found to react rapidly with NFTPT at 25 °C. In the case of 1b and 1c, the major product of this reaction is the Ni^{IV} C–H activation product **2b** or 2c (formed in 89% and 84% yield, respectively). These products are formed with high (>20:1) selectivity for activation of the C-H bond para to the substituent (for X-ray structures of 2b and 2c, see Figure 3b,c). This selectivity likely reflects a high sensitivity to the steric environment of the C-H bond. Similar effects have been observed in intramolecular C-H functionalization reactions at Pd.²¹

In contrast, the CF₃-substituted complex 1d afforded <2% of 2d. Instead, the Ni^{II} cation [(py₂CFAr)Ni^{II}(CF₃)(2,4,6-trimethylpyridine)]⁺, 3d, was formed as the major Ni product in 60% yield (see eq 4 for the unsubstituted analogue 3a). As discussed



below, Ni^{II} products of general structure 3 appear to form in these reactions when the C-H activation step is slow.²² Slower C-H activation on the electron deficient CF₃-substituted aryl ring is consistent with the electrophilic C-H activation mechanism proposed in Figure 1.

The DFT studies suggest that triflate plays an important role in the C-H cleavage step. Thus, we next probed the impact of replacing the triflate with a tetrafluoroborate. The treatment of 1a with NFTPB (N-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate) in place of NFTPT under otherwise identical conditions resulted in <2% of the Ni^{IV} C–H activation product **2a**. Instead, the Ni^{II} cation 3a was formed in 87% yield (eq 4), along with a mixture of CF₃H, CF₄, and C₂F₆.^{23,24} Complex 3a was characterized via ¹H, ¹³C, and ¹⁹F NMR spectroscopy as well as X-ray crystallography (eq 4). Further consistent with the importance of triflate, the C-H activation reactivity in this system could be recovered by adding 2 equiv of NBu₄OTf to the NFTPB oxidation. Under these conditions, 2a was formed in 52% vield.

Overall, these results are consistent with the computational studies, which suggest that the triflate is intimately involved in the C-H cleavage step (see TS D/E in Figure 1). DFT also shows that substitution of tetrafluoroborate for triflate in TS D/E raises the barrier for that step by approximately 8 kcal/mol. The rapid formation of Ni^{II} product 3a (along with CF_3H , CF_4 , and C_5F_6) with NFTPB suggests that, when the barrier to C-H cleavage at high valent Ni is relatively high, the rates of other decomposition pathways become competitive and ultimately dominate the observed reactivity. These counterion effects are particularly noteworthy because similar trends have been seen in other Nicatalyzed C-H functionalization reactions. For instance, Chatani reported that diaryliodonium triflates are effective oxidants for Nicatalyzed C-H arylations, whereas the tetrafluoroborate analogues afford essentially no reaction.²⁵

In summary, we describe a series of oxidatively induced arene C-H activation reactions that yield Ni^{IV} σ -aryl products of general structure 2. These reactions proceed within 10 min at room temperature, thereby representing among the mildest conditions reported for C-H cleavage at a Ni center. Preliminary studies suggest the viability of a pathway involving the 2e⁻ oxidation of the Ni^{II} starting materials by NFTPT followed by triflate-assisted electrophilic C-H cleavage at Ni^{IV}. However, it is important to note that a recent report by Mirica implicated the possibility of C-H activation at related Ni^{III} centers.⁵ Furthermore, NFTPT has been proposed to act as a 1e⁻ oxidant in some systems.²⁶ Thus, at this time, we cannot rule out the possibility of sequential 1e⁻ oxidation pathways for this transformation. Nonetheless, this report demonstrates the first example of accessing Ni^{IV} σ -aryl products via oxidatively induced C-H cleavage. This opens up exciting possibilities for this and related transformations to be exploited in catalysis.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b02387.

CIF data for 1a (CIF)
CIF data for 1b (CIF)
CIF data for 1d (CIF)
CIF data for 2a (CIF)
CIF data for 2b (CIF)
CIF data for 2c (CIF)
CIF data for 3a (CIF)
Experimental details, com

plete characterization data for all new compounds, and DFT calculations (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the NSF CHE-1361542. E.C. thanks NSERC for a postdoctoral fellowship.

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(22) We hypothesize that 3 is formed via initial oxidation of 1 followed by decomposition of the resulting high valent Ni intermediate. This decomposition pathway appears to predominate in cases where the substituents on the aryl ring and/or the reaction conditions render C–H activation relatively slow.

(23) Traces of **3a** were also observed in the reactions of **1a** with NFTPT. The formation of this side product could be minimized to <2% by conducting the reaction at -35 °C.

(24) CF₃H (42%), CF₄ (30%), and C₂F₆ (5%) were detected by ¹⁹F NMR spectroscopy when the reaction of **1a** with NFTPB was carried out in CH₂Cl₂ in a sealed J. Young NMR tube at -97 °C. When the analogous reaction was conducted in CD₂Cl₂, the major detectable organic products were CF₃D (2%), CF₄ (43%), and C₂F₆ (2%). These latter results suggest that the H/D derives from the solvent.

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