Nickel(IV) Intermediates in Aminoquinoline-Directed C(sp^2)–C(sp^3) Coupling

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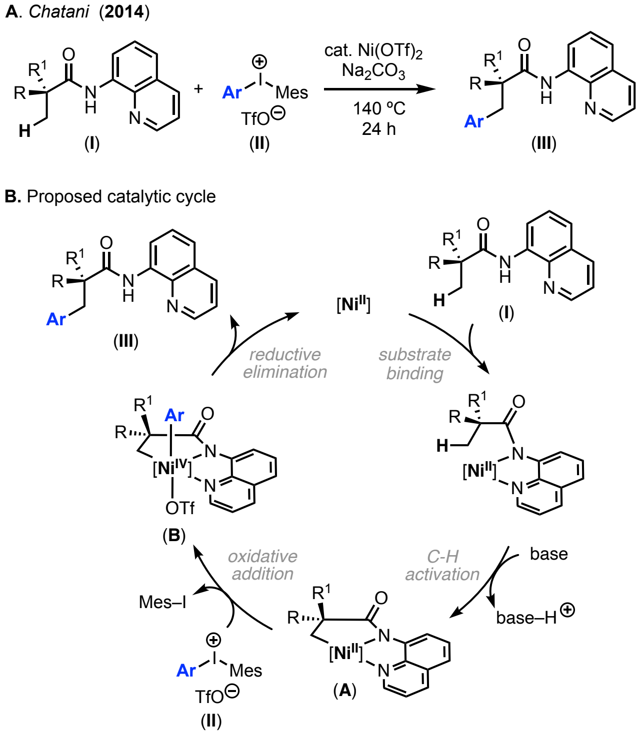
ABSTRACT: We use a ligand-design strategy to isolate a cyclometallated nickel(IV) complex that is directly analogous to a key intermediate proposed in aminoquinoline-directed C–H functionalization catalysis. This nickel(IV) complex is formed by oxidative addition of a diaryliodonium reagent to an anionic nickel(II)-picolinate precursor. The nickel(IV) σ-aryl complex is stable at room temperature but undergoes C(sp^2)–C(sp^3) bond-forming reductive elimination under mild conditions (70 ºC, 120 min). Overall, this study demonstrates the accessibility of long-sought-after nickel(IV) intermediates in C-H functionalization catalysis. Furthermore, it demonstrates that LX-type (bidentate mono-anionic) ligands such as picolinate dramatically stabilize these nickel(IV) species.

Since seminal early work by Daugulis,[1] metal-catalyzed aminoquinoline (AQ) directed C–H functionalization reactions have been widely used for the formation of carbon–carbon and carbon–heteroatom bonds.[2] These reactions most commonly involve Pd or Ni catalysts, an aminoquinoline substrate bearing a tethered C–H bond, and an aryl halide or diaryliodonium-based oxidant. In a representative example relevant to this work, Chatani reported the Ni(OTf)$_2$-catalyzed C(sp^3)–H arylation of substrate **I** with diaryliodonium reagents (**II**) to afford products of general structure **III** (Figure 1a).[3] The proposed catalytic cycle (which is similar for both Pd and Ni catalysts) involves (i) AQ-directed C–H activation to form metallacycle **A**, (ii) oxidative addition of **II** to generate M^{IV} intermediate **B**, and (iii) finally C–C bond forming reductive elimination to release the functionalized product **III** (Figure 1b).[2,4,5]

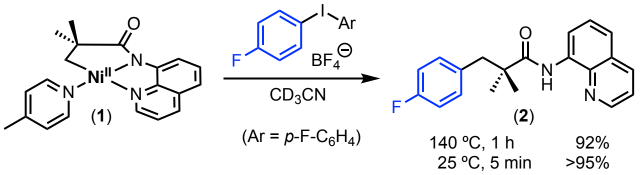

A. *Chatani* (**2014**)

B. Proposed catalytic cycle

Figure 1. (a) Chatani's Ni-catalyzed aminoquinoline-directed C–H arylation of **I** with **II**.[3] (b) Proposed mechanism.

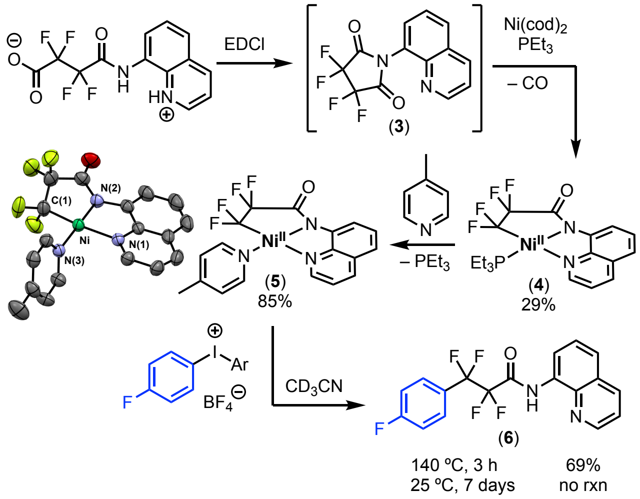
Over the past two decades, numerous studies have interrogated aminoquinoline-directed C–H activation to generate intermediates like **A** (or related σ-aryl species) at Pd^{II} and, more recently, Ni^{II} centers.[4,6,7] In contrast, the oxidative functionalization step has been much less explored. While the stoichiometric reactions of **A** and analogues with aryl electrophiles (ArX) has been shown to yield **III** in several systems (with M = Pd and Ni), M^{IV} intermediates have not been isolated, to date, with either metal.[8,9] As such the accessibility of M^{IV} intermediates like **B** remains speculative, particularly in Ni-based systems that can readily participate in single electron redox cycles.[5a] In this report, we leverage a ligand design strategy to isolate a Ni^{IV} analogue of **B** via the oxidation of a nickel(II)-picolinate precursor with a diaryliodonium reagent. Furthermore, we demonstrate that this intermediate undergoes C(sp^3)–Ph bond-forming reductive elimination under mild conditions. The implications of these results for catalysis are discussed.

We initiated these studies with nickelacycle **1**, a direct analogue of the putative Ni^{II} intermediate **A** in Chatani's catalytic reaction (Scheme 1).[10] The reaction of **1** with Ar$_2$IBF$_4$ (Ar = *p*-FC$_6$H$_4$) at 140 ºC (the temperature used in catalysis)[3] resulted in 92% yield of the C(sp^3)–Ar coupling product **2** within 1 h. In an attempt to detect intermediates in this transformation, the temperature was decreased. However, the reaction remained fast at both 25 ºC (quantitative yield within 5 min) and –25 ºC (18% yield within 10 min). Furthermore, no diamagnetic Ni intermediates were detected by ^{1}H NMR spectroscopy under any conditions. These results suggest that the oxidative addition/reductive elimination sequence is unlikely to be rate-limiting in catalysis. Instead, the high temperatures required for the reaction in Figure 1A may be due to slow C–H activation and/or to the formation of off-cycle Ni species.[7b]



Scheme 1. Reaction of **1** with Ar$_2$IBF$_4$ to afford **2**

We hypothesized that replacing the σ-alkyl ligand in **1** with a fluoroalkyl group could potentially stabilize high oxidation state Ni intermediates. This approach has proven effective for the isolation of other high valent late transition metal complexes of Pd^{IV}, Ni^{III}, and Ni^{IV}.[9,11,12] The fluoroalkyl analogue **5** was synthesized via the route outlined in Scheme 2. The treatment of a mixture of Ni(cod)$_2$ and PEt$_3$ with 3,3,4,4-tetrafluoro-1-(quinolin-8-yl)pyrrolidine-2,5-dione (**3**) resulted in oxidative addition and carbonyl de-insertion to yield nickelacycle **4** in 29% isolated yield over the two steps. Exchange of the PEt$_3$ ligand for picoline then afforded **5**, a direct analogue of **1** bearing a fluoroalkyl ligand. Complex **5** was isolated in 85% yield from this reaction and characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy as well as elemental analysis and X-ray crystallography. Comparison of the solid-state structures of **1** and **5** shows that both assume a square planar geometry with comparable Ni–N bond distances (see Table S6 for complete data). The largest difference between the two structures is that the Ni–C bond in **5** is approximately 0.03 Å shorter than that of **1**. A similar 0.04 Å difference was noted by Vicic when comparing Ni^{II}–CH$_3$ and –CF$_3$ complexes.[13]



Scheme 2. Synthesis and reactivity of Ni^{II} fluoroalkyl aminoquinoline complex **5**

We next examined the reaction of **5** with Ar$_2$IBF$_4$ under analogous conditions to Scheme 1. Overall, **5** showed dramatically lower reactivity. For example, no conversion of **5** was observed at room temperature, even after 7 days (Scheme 2). This is in contrast to the nearly instantaneous reaction between **1** and Ar$_2$IBF$_4$ at room temperature (Scheme 1). Heating a solution of **5** and Ar$_2$IBF$_4$ at 140 ºC did result in 69% yield of **6** after 3 h; however, again, no intermediates were detected in this reaction.

To gain further insight into the relative reactivity of **1** and **5**, cyclic voltamograms (CVs) of the two complexes were compared in CH$_3$CN/NBu$_4$PF$_6$. As shown in Figure 2A, the CVs are qualitatively similar, displaying one quasi-reversible (Ni$^{II/III}$) and one irreversible (Ni$^{III/IV}$) oxidation peak separated by ~1.0 V. However, both of the oxidation peaks of the σ-fluoroalkyl complex **5** (*red*) are shifted by approximately +475 mV relative to those of the σ-alkyl complex **1** (*black*).[14] This large positive shift is consistent with the sluggish reactivity of the σ-fluoroalkyl complex with the Ar$_2$IBF$_4$ oxidant. We hypothesized that a picolinate ligand could displace the picoline of **5** to generate an anionic Ni^{II} intermediate that would be more susceptible (both thermodynamically and kinetically) to oxidation. To test this proposal, we carried out cyclic voltammetry of **5** in the presence of 2 equiv of tetramethylammonium picolinate. As shown in Figure 2B, this resulted in a dramatic ~800 mV negative shift in the oxidation peaks to –0.47 V and 0.59 V, respectively. Remarkably, these couples are significantly more negative than even those of the neutral σ-alkyl complex **1**. Additionally, the Ni$^{III/IV}$ couple (at 590 mV versus Ag/Ag$^+$) is now quasi-reversible, suggesting that Ni^{IV} intermediates might be observable or even isolable in this system under appropriate conditions.

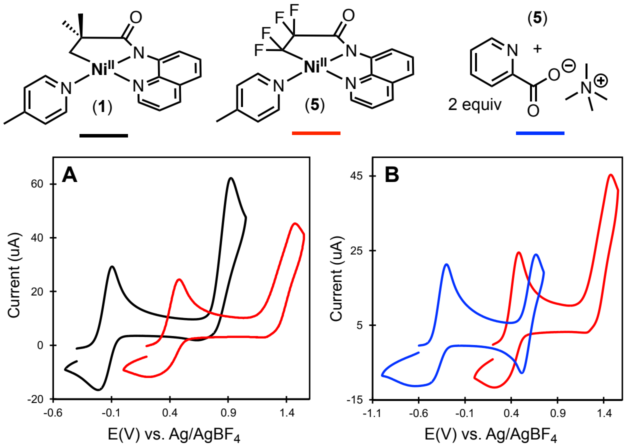
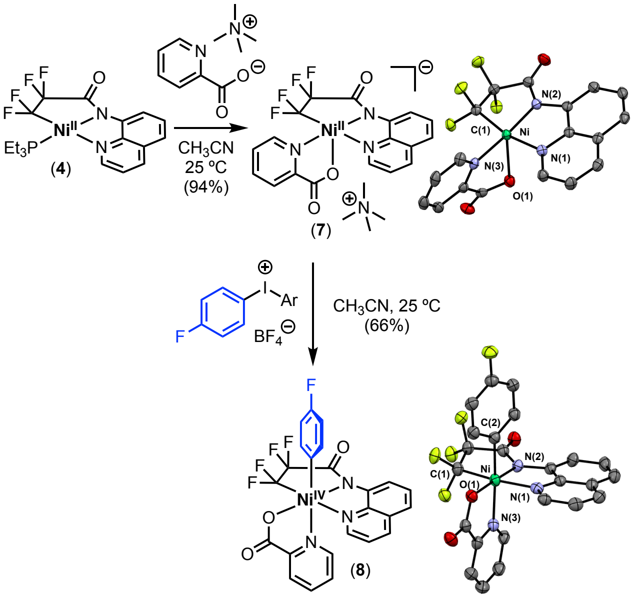


Figure 2. (A) Overlaid CVs of **1** (*black*) and **5** (*red*). (B) Overlaid CVs of **5** (*red*) and **5** + 2 equiv of tetramethylammonium picolinate (*blue*). Conditions: 0.01 mM solution of [Ni^{II}] in 0.1 M NBu$_4$PF$_6$ in CH$_3$CN; scan rate of 100 mV/s.

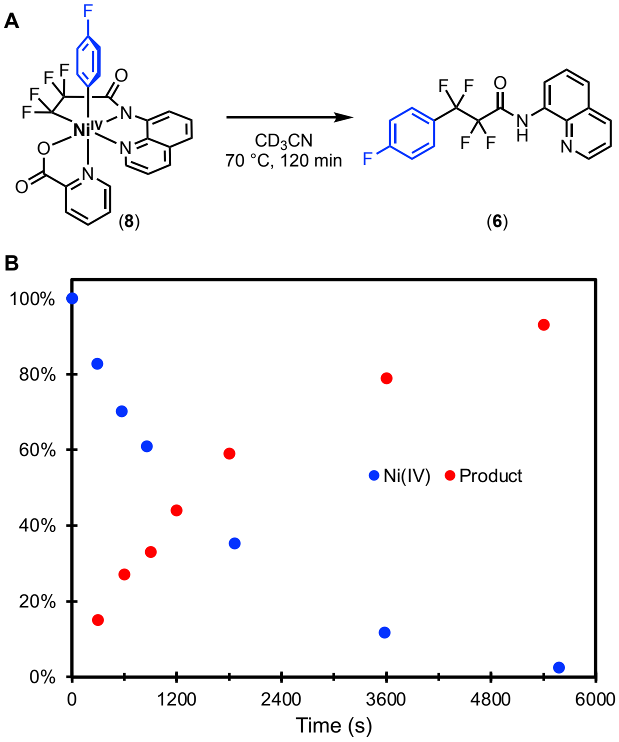
To test whether this shift in redox potential translated to enhanced reactivity with Ar$_2$IBF$_4$, we first synthesized the anionic Ni^{II} picolinate complex **7** via a ligand exchange between of **4** and 1 equiv of tetramethylammonium picolinate in CH$_3$CN at 25 ºC (Scheme 3). The product was isolated in 94% yield and characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy as well as elemental analysis and X-ray crystallography. The X-ray structure of **7** shows a five-coordinate pseudo-square pyramidal anionic Ni^{II} complex. The CNN (carbon-nitrogen-nitrogen) pincer ligand and N of the picolinate are equatorial and show bond distances within 0.015 Å of those in **5** (see Table S6 for full details). The Ni–O bond is in the axial position, and the bond distance of 2.467 Å is consistent with a relatively weak interaction.



Scheme 3. Synthesis of picolinate complex **7** and oxidation with Ar$_2$IBF$_4$.

The treatment of **7** with Ar_2IBF_4 at 25 °C in CH_3CN resulted in a rapid and quantitative reaction to form a new diamagnetic Ni species within 15 min. The product precipitated from the reaction mixture over the course of several hours at room temperature. This Ni^{IV} complex (**8**) was isolated in 66% yield and characterized by ^1H and ^{19}F NMR spectroscopy, elemental analysis, and X-ray crystallography. The X-ray structure confirms that **8** is a neutral octahedral Ni^{IV} complex with the σ-Ar group in the axial position. Notably, the picolinate ligand isomerizes upon oxidation, such that the carboxylate oxygen is now trans to the amide nitrogen of the aminoquinoline. The oxidation results in a significant (nearly 0.1 Å) lengthening of the Ni–fluoroalkyl bond.[15] Overall, this complex is a direct analogue of putative catalytic intermediate **B**. The isolation of this species provides a direct experimental demonstration that M^{IV}-σ-aryl intermediates are accessible with these aminoquinoline CNN pincer-type ligand scaffolds.

Heating solutions of **8** in CD_3CN at 70 °C for 120 min resulted in clean $C(sp^3)$–Ar bond-forming reductive elimination to afford product **6** in 93% yield (Scheme 4A). A time study of this reaction shows that the consumption of **8** occurs at a comparable rate as the appearance of **6**. (Scheme 4B). These results demonstrate the feasibility of product formation from this Ni^{IV} species, providing further evidence that such Ni^{IV} species could be catalytically relevant.



Scheme 4. (a) $C(sp^2)$–$C(sp^3)$ bond-forming reductive elimination from complex **8**. (b) Time study of the reductive elimination.

This study has several implications for the continued development of Ni-catalyzed C–H functionalization reactions. First, it shows that with appropriate ligand design, Ni^{II} complexes of general structure **A** can react with Ar_2IBF_4 to form isolable Ni^{IV} intermediates. This directly confirms the feasibility of a mechanism that has long been proposed in catalysis. Second, bidentate monoanionic ligands (specifically picolinate in this study) form Ni^{II}-ate complexes with dramatically lower redox potentials and faster oxidation rates than their neutral analogues. This insight provides a roadmap for how to further accelerate the oxidation step and promote the generation of Ni^{IV} intermediates in catalysis. Indeed, the formation of related Ni^{II}-ate intermediates could be a key (and largely overlooked) role for the anionic additives (e.g., carbonate and carboxylate salts) that are commonly used in C–H functionalization catalysis of these and related scaffolds. A second equivalent of aminoquinoline substrate (which is in large excess under catalytic conditions) could also potentially play a role as a bidentate mono-anionic donor ligand in this context.[7b] Finally, a σ-fluoroalkyl group participates in facile and high yielding $C(sp^2)$–$C(sp^3)$ bond-forming reductive elimination from complexes of general structure **A**.[16] This suggests the potential feasibility of coupling fluorocarbons (R_F–H) with aryl electrophiles via $Ni^{II/IV}$ pathways. Ongoing work is focused on leveraging these insights for the development and optimization of new Ni-catalyzed C–H functionalization processes.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, NMR spectra, and cyclic voltammograms. The Supporting Information is available free of charge on the ACS Publications website.

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