

Reaction Mechanisms

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Impact of Oxidation State on Reactivity and Selectivity Differences between Nickel(III) and Nickel(IV) Alkyl Complexes

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Abstract: Described is a systematic comparison of factors impacting the relative rates and selectivities of $C(sp^3)-C$ and $C(sp^3)-O$ bond-forming reactions at high-valent Ni as a function of oxidation state. Two Ni complexes are compared: a cationic octahedral Ni^{IV} complex ligated by tris(pyrazolyl)borate and a cationic octahedral Ni^{III} complex ligated by tris(pyrazolyl)methane. Key features of reactivity/selectivity are revealed: 1) $C(sp^3)-C(sp^2)$ bond-forming reductive elimination occurs from both centers, but the Ni^{III} complex reacts up to 300-fold faster than the Ni^{IV} , depending on the reaction conditions. The relative reactivity is proposed to derive from ligand dissociation kinetics, which vary as a function of oxidation state and the presence/absence of visible light. 2) Upon the addition of acetate (AcO^-), the Ni^{IV} complex exclusively undergoes $C(sp^3)-OAc$ bond formation, while the Ni^{III} analogue forms the $C(sp^3)-C(sp^2)$ coupled product selectively. This difference is rationalized based on the electrophilicity of the respective $M-C(sp^3)$ bonds, and thus their relative reactivity towards outer-sphere S_N2 -type bond-forming reactions.

Palladium- and nickel-catalyzed cross-coupling reactions have emerged as powerful methods for the formation of alkyl-alkyl, alkyl-aryl, and alkyl-heteroatom bonds.^[1] A unifying feature of these transformations is the formation of a metal-alkyl intermediate that participates in the product-forming reductive elimination step of the catalytic cycle. Detailed studies of Pd-alkyl species have shown that their reactivity varies dramatically as a function of the oxidation state of the Pd center. For instance, while Pd^{II} -alkyls are typically nucleophilic at carbon, Pd^{IV} -alkyls serve as potent carbon-based electrophiles.^[2] These factors lead to profound differences in relative rates and selectivities of reductive elimination reactions as a function of oxidation state.^[3] As such, $Pd^{0/II}$ and $Pd^{II/IV}$ catalytic cycles often provide highly complementary types of products.^[3,4]

There are three oxidation states that are potentially relevant to the bond-forming step of Ni-catalyzed cross-coupling reactions: Ni^{II} , Ni^{III} , and Ni^{IV} . While the reactivity of

Ni^{II} -alkyl complexes has been studied extensively,^[1a] detailed investigations of analogous Ni^{III} - and Ni^{IV} -alkyls have been impeded by a lack of stable model complexes. However, recent work from our group^[5] and others^[6] has shown that facial tridentate ligands are highly effective for supporting isolable Ni^{III} and Ni^{IV} complexes. This finding opens up opportunities to systematically interrogate the impact of oxidation state on the reactivity of Ni^{III} -alkyls compared to Ni^{IV} -alkyls. Such studies have the potential to unveil reactivity differences as a function of oxidation state that might ultimately be exploited in catalysis.

A key challenge for these studies is to design a model system in which the oxidation state of Ni is the sole difference between the high-valent Ni complexes. Previous reports have accessed Ni^{III} and Ni^{IV} complexes that contain the same facial tridentate ligand [for instance, tris(pyrazolyl)borate (Tp)^[5] or 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn)^[6]]. However, as exemplified for the Tp complexes in Figure 1, these

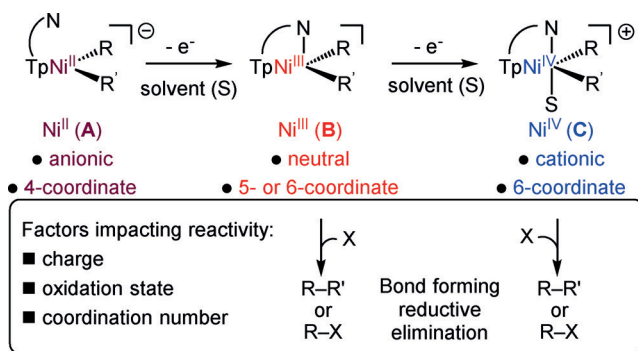


Figure 1. Challenges with comparing the impact of Ni oxidation state on reactivity/selectivity in reductive elimination.

species differ in their overall charge (neutral Ni^{III} versus cationic Ni^{IV}) and coordination geometry (square-pyramidal Ni^{III} versus octahedral Ni^{IV}) as well as their oxidation state.^[5] These differences preclude the direct comparison of the influence of oxidation state on reductive elimination reactions.^[7]

This report describes the design of model complexes that enable a direct comparison of the rate/selectivity of reductive elimination as a function of Ni oxidation state. The first is an analogue of **B** wherein the anionic Tp ligand is replaced with the neutral facial tridentate ligand tris(pyrazolyl)methane (Tpm; Figure 2). Tpm imparts the same primary coordination environment as Tp, but the overall charge of the ligand is neutral.^[8] Thus, it results in a cationic octahedral Ni^{III} complex, **1-Ni^{III+}**. The second complex in this study is the

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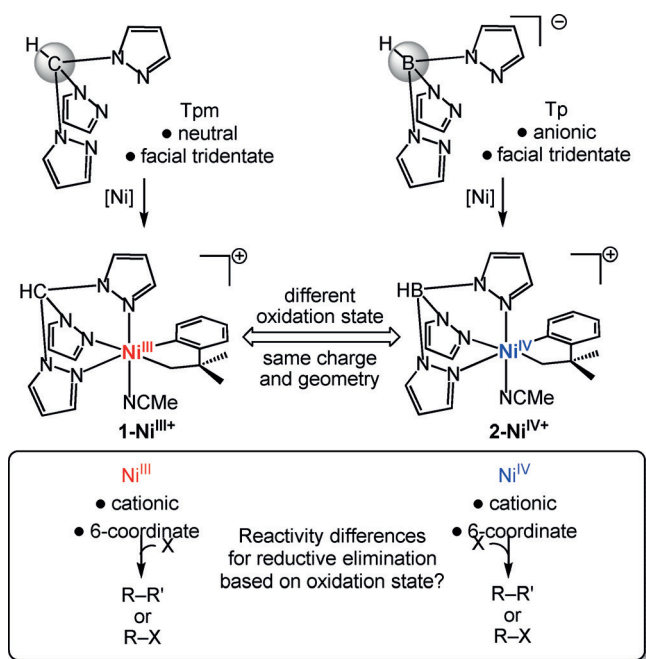


Figure 2. Design of study to test impact of oxidation state on reactivity and selectivity of C–C and C–X coupling from high valent Ni.

previously reported cationic, octahedral TpNi^{IV} adduct **2-Ni^{IV+}** (Figure 2). We report herein that these complexes exhibit dramatically different reactivity towards both $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ and $\text{C}(\text{sp}^3)\text{--oxygen}$ coupling reactions and we provide a rationale for the observed effects.

1-Ni^{III+} and **2-Ni^{IV+}** were synthesized by oxidation of the appropriate Ni^{II} precursor with 1 or 2 equivalents of AgBF_4 (see the Supporting Information for complete details).^[5] The complexes were characterized by ^1H and ^{13}C NMR spectroscopy, cyclic voltammetry, EPR spectroscopy, and X-ray crystallography, and all the data are consistent with the structures shown in Figure 2. The X-ray crystal structures of these complexes are shown in Figure 3. Notably, X-ray quality crystals of **1-Ni^{III+}** were obtained in the presence of pyridine. As such, a pyridine ligand (rather than an acetonitrile) is coordinated in the axial site. In the solid state, both **1-Ni^{III+}** and **2-Ni^{IV+}** are six-coordinate octahedral structures.

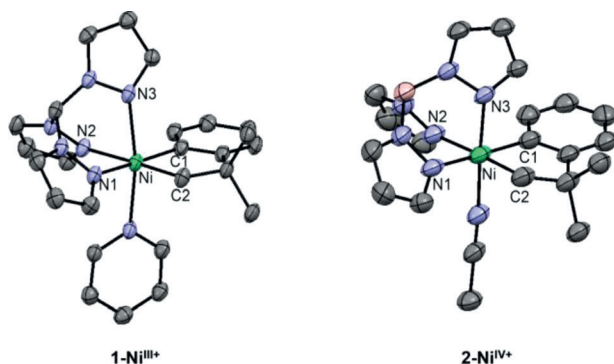


Figure 3. ORTEP structures^[23] of **1-Ni^{III+}** and **2-Ni^{IV+}**. BF_4 and solvent molecules omitted for clarity. Thermal ellipsoids are shown at 50% probability.

We first focused on comparing the rates of inner-sphere $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ bond-forming reductive elimination from **1-Ni^{III+}** and **2-Ni^{IV+}**. There are two opposing factors that could potentially dictate the relative reactivity of these two complexes. On one hand, Ni^{IV} complexes are generally considered to be higher energy intermediates than their Ni^{III} analogues. This difference is reflected, for example, in the redox potentials associated with **1-Ni^{III+}** ($\text{Ni}^{\text{II/III}}$ $E_{1/2} \approx -0.7$ V) and **2-Ni^{IV+}** ($\text{Ni}^{\text{III/IV}}$ $E_{1/2} \approx -1.2$ V; $\text{Ni}^{\text{III/IV}}$ $E_{1/2} \approx -0.1$ V vs. Ag/Ag^+ , see pg S34 of the Supporting Information as well as Ref. [5b]). Based on the Hammond postulate, the relative ground-state energetics could lead to faster reductive elimination from **2-Ni^{IV+}** versus **1-Ni^{III+}**.^[9] On the other hand, the mechanism of $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ coupling from octahedral metal centers often involves a pre-equilibrium ligand dissociation prior to C–C bond formation.^[10] Odd-electron d^7 complexes like **1-Ni^{III+}** generally exhibit much faster rates of ligand dissociation than their even-electron d^6 counterparts.^[11] This behavior could thus result in faster $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ coupling from **1-Ni^{III+}**. Furthermore, if ligand dissociation kinetics were the determining factor, the presence/absence of light would be expected to have an impact on the relative rates of C–C coupling.^[12] For example, a number of literature studies have shown that ligand dissociation (and hence C–C bond-forming reductive elimination) at d^6 octahedral group 10 complexes can be accelerated by at least 10-fold upon exposure to ambient light.^[3b,13]

To experimentally compare the relative reactivities of **1-Ni^{III+}** and **2-Ni^{IV+}**, we first monitored the formation of the benzocyclobutane **3** from each complex at 25 °C in CD_3CN in the dark. As shown in Figure 4, **1-Ni^{III+}** undergoes rapid $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ coupling, affording about 40% yield of **3** within just 20 minutes (and 87% yield after 12 h). Under analogous conditions, **2-Ni^{IV+}** forms less than 1% yield of **3** (and < 5% yield after 12 h). These data represents a more than 300-fold difference in the initial rate of reductive elimination from **1-Ni^{III+}** versus **2-Ni^{IV+}**. These results suggest that ligand dissociation is likely a critical factor in the relative rates of

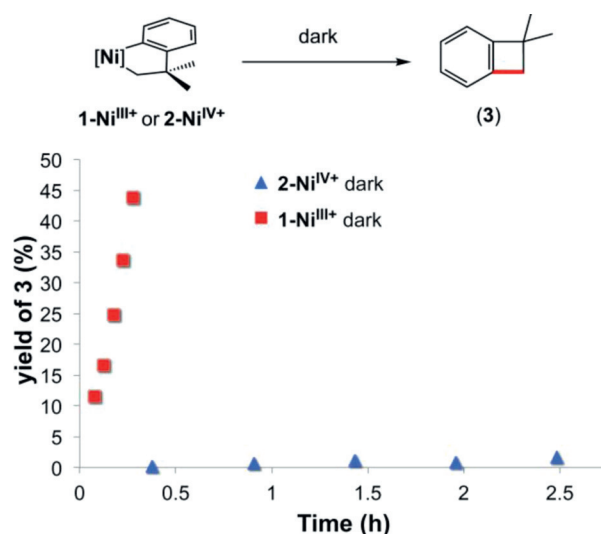


Figure 4. Time study of the formation of **3** in the absence of light $[\text{Ni}] = 0.0023$ M.

this transformation and further experiments were conducted to test this hypothesis.

We next investigated the impact of ambient light on these reactions. As shown in Figure 5, in the time frame measured we could not detect a significant change in the initial rate of C–C reductive elimination from **1-Ni^{III+}** upon exposure to

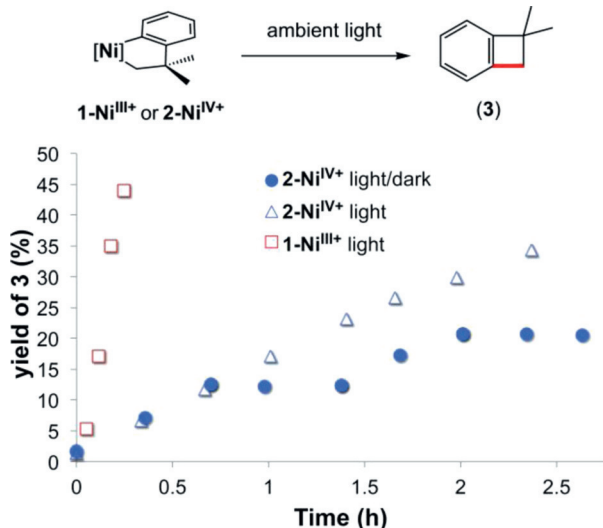


Figure 5. Time study for the formation of **3** in the presence of light $[Ni] = 0.0023$ M.

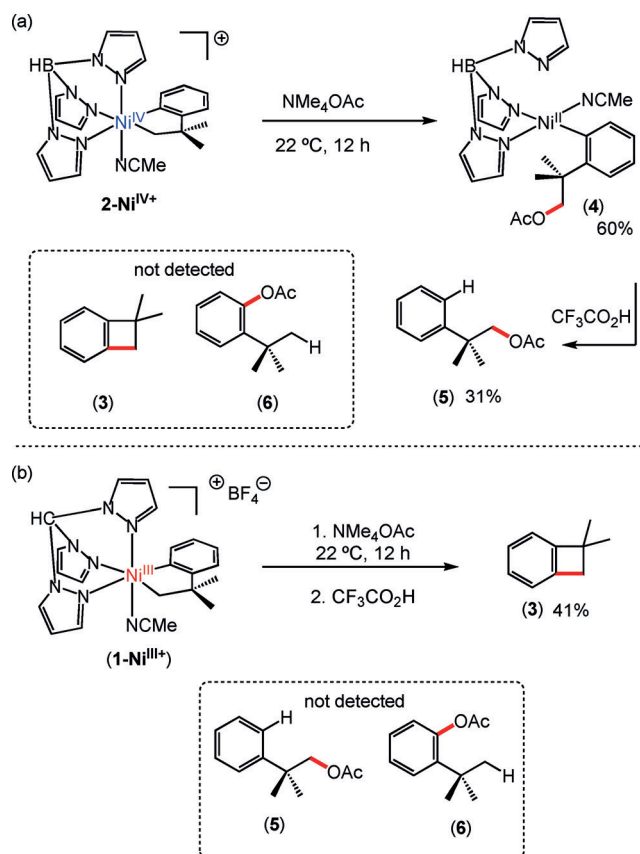
ambient light, and a similar approximate 40% yield of **3** was observed after 20 minutes. After 12 hours, a greater than 95% yield of **3** was observed. In contrast, C–C coupling from the cationic octahedral complex **2-Ni^{IV+}** proved highly sensitive to ambient light. For example, approximately 7% yield of **3** was obtained after 20 minutes, compared to less than 1% in the dark. This reactivity represents a more than 25-fold acceleration of the reaction in the presence of light. When the reaction was run for 12 hours, 65% yield of **3** was obtained. In addition, the C–C coupling from **2-Ni^{IV+}** could be accelerated and then slowed multiple times by sequential exposure to and then removal from ambient light. Throughout this experiment, the observed rate during the light and dark periods is comparable to that seen when analogous reactions are conducted fully in the light or the dark.

As discussed above, we hypothesize that ambient light accelerates C–C reductive elimination from **2-Ni^{IV+}** by promoting dissociation of a ligand (either MeCN or a pyrazole).^[13] To probe the lability of the acetonitrile ligand, we monitored the ¹H NMR resonance associated with coordinated CH₃CN (at $\delta = 2.36$ ppm) throughout the C–C coupling experiments in both the light and the dark. As shown in Figures S3 and S7 (see the Supporting Information), less than 5% exchange with the CD₃CN solvent was observed over 3 hours at 25 °C in both the light and the dark. This result suggests evidence against a pathway involving pre-equilibrium light-promoted dissociation of acetonitrile.^[14] In addition, exchanging the solvent for nitromethane (which has a similar dielectric constant to acetonitrile but should not serve as a ligand to Ni) had minimal impact on time course of C–C

coupling (see Figure S5 for details). Based on these experiments, we propose that the role of the light may be to promote dissociation of a pyrazole arm of the Tp ligand.^[15]

We next examined the relative reactivity of **1-Ni^{III+}** and **2-Ni^{IV+}** towards carbon–heteroatom bond-forming processes. Acetate (AcO[−]) was selected as a representative heteroatom nucleophile based on the relative inertness of C–OAc bonds towards side reactions with low-valent Ni products.^[1a] Literature precedent suggests that C–heteroatom coupling at high-valent group 10 metal centers typically proceeds selectively at M–C(sp³) [versus M–C(sp²)] centers by an outer-sphere S_N2-type pathway.^[2,4,5a,c] The rates/selectivities of these processes are generally dictated by the electrophilicity of the M-bound carbon as well as the relative rates of competing inner-sphere reductive elimination processes.^[3] We note that the Ni^{IV} complex **2-Ni^{IV+}** is expected to have a highly electrophilic Ni–C bond. Furthermore inner-sphere C(sp³)–C(sp²) coupling is slow from this complex. Thus, we hypothesized that **2-Ni^{IV+}** was likely to undergo selective C(sp³)–OAc coupling.

Indeed, the treatment of **2-Ni^{IV+}** with 2 equivalents of NMe₄OAc at 22 °C in MeCN in the dark resulted in rapid conversion of the starting material and the formation of a new diamagnetic Tp-ligated Ni complex within 10 minutes. The ¹H NMR spectrum of this complex contains a pair of diastereotopic resonances at $\delta = 4.59$ and 4.28 ppm, consistent with the formation of the Ni^{II} complex **4** (Scheme 1a). However, **4** (which was formed in 60% yield, as determined



Scheme 1. a) Selective outer-sphere C(sp³)–OAc reductive elimination from **2-Ni^{IV+}**. b) Selective inner-sphere C(sp³)–C(sp²) coupling from **1-Ni^{III+}**.

by ^1H NMR spectroscopic analysis of the crude reaction mixture) proved challenging to isolate cleanly. As such, it was treated with trifluoroacetic acid to protodemetallate the organic ligand(s). Subsequent analysis by ^1H NMR spectroscopy and GCMS revealed the formation of **5** in 31% yield. No trace of either **3** [derived from $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ coupling] or **6** [derived from $\text{C}(\text{sp}^2)\text{--OAc}$ coupling] was detected.^[16] Notably, nearly identical yields and product selectivities were observed in the presence of ambient light. These data are consistent with $\text{C}(\text{sp}^3)\text{--OAc}$ coupling from **2-Ni^{IV+}** proceeding by a different (likely outer-sphere) pathway that is much faster than benzocyclobutane formation.

We next examined the reaction of **1-Ni^{III+}** with NMe_4OAc . As shown in Scheme 1 b, the crude ^1H NMR spectrum of this mixture showed the formation of **3** in 41% yield. The Ni-containing products were paramagnetic and thus could not be readily identified by NMR spectroscopy. As such, trifluoroacetic acid was added to protodemetallate any Ni σ -alkyl or σ -aryl nickel analogues that would form either **5** or **6**. ^1H NMR spectroscopic analysis of the resulting mixture showed no trace of either **5** or **6**, the organic products of $\text{C}(\text{sp}^3)\text{--OAc}$ or $\text{C}(\text{sp}^2)\text{--OAc}$ coupling, respectively. These data demonstrate that C–C bond-forming reductive elimination outcompetes C–OAc coupling at this cationic octahedral Ni^{III} complex. We attribute this difference in reactivity to the lower electronegativity of Ni^{III} versus Ni^{IV} which results in a less electrophilic Ni– $\text{C}(\text{sp}^3)$ bond and thus decreased reactivity in $\text{S}_{\text{N}}2$ -type pathways.

In summary, these studies demonstrate that outer-sphere $\text{C}(\text{sp}^3)\text{--OAc}$ bond-formation is significantly faster than inner-sphere $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ coupling at the Ni^{IV} complex **2-Ni^{IV+}**. This finding is consistent with the mechanism of $\text{C}(\text{sp}^3)\text{--heteroatom}$ reductive elimination from other d⁶ group 10 metals, where $\text{S}_{\text{N}}2$ -type pathways have been proposed at Pt^{IV},^[17] Pd^{IV},^[18] and Ni^{IV}.^[5a,c] Furthermore, inner-sphere $\text{C}(\text{sp}^2)\text{--OAc}$ coupling is not competitive in this system, likely because of the low lability of the MeCN ligand, which precludes acetate coordination to the Ni^{IV} center. An inner-sphere mechanism has been proposed for the vast majority of carbon–carbon and $\text{C}(\text{sp}^2)\text{--heteroatom}$ coupling reactions at Pt^{IV},^[19] Pd^{IV},^[4] Pd^{III},^[20] Ni^{IV},^[21] and Ni^{III} centers.^[3,22] In contrast, the Ni^{III} analogue **1-Ni^{III+}** reacts to selectively form the C–C coupled product **3** in either the presence or absence of the acetate nucleophile. These results demonstrate that the oxidation state of high-valent Ni can play a key role in dictating both the mechanism and selectivity of the favored reductive elimination process in these systems. While this study focuses on model complexes, ongoing investigations in our lab are probing the generality of obtaining complementary bond-forming reactions by manipulating the oxidation state of high-valent Ni intermediates. If these observations prove general, they are likely to find broader applications in catalysis.

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Conflict of interest

The authors declare no conflict of interest.

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- [23] CCDC 1905475 (**1-Ni^{III+}**) and 1905476 (**2-Ni^{IV+}**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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