Connecting Organometallic Ni(III) and Ni(IV): Reactions of Carbon-Centered Radicals with High-Valent Organonickel Complexes

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ABSTRACT: This paper describes the one-electron interconversions of isolable Ni^{III} and Ni^{IV} complexes through their reactions with carbon-centered radicals (R•). First, model Ni^{III} complexes are shown to react with alkyl and aryl radicals to afford Ni^{IV} products. Preliminary mechanistic studies implicate a pathway involving direct addition of a carbon-centered radical to the Ni^{III} center. This is directly analogous to the known reactivity of Ni^{II} complexes with R•, a step that is commonly implicated in catalysis. Second, a Ni^{IV}–CH_3 complex is shown to react with aryl and alkyl radicals to afford C–C bonds via a proposed S_H2-type mechanism. This pathway is leveraged to enable challenging H_3C–CF_3 bond formation under mild conditions. Overall, these investigations suggest that $Ni^{II/III/IV}$ sequences may be viable redox pathways in high-oxidation-state nickel catalysis.

Introduction

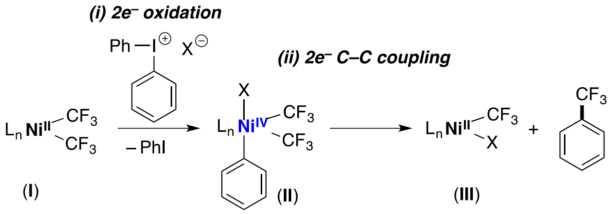
Nickel-catalyzed cross-coupling reactions have emerged as powerful synthetic methods for the mild and selective construction of carbon-carbon and carbon-heteroatom bonds.[1] The vast majority of these transformations are proposed to involve organometallic Ni^{II} and/or Ni^{III} intermediates.[1b-f, 2] Higher oxidation state Ni^{IV} species were historically believed to be inaccessible in these types of catalytic transformations.[1, 2] However, recent studies have shown that organonickel(IV) complexes can be formed at or below room temperature using common oxidants.[3] As such, there is increasing interest in understanding the generation and reactivity of such Ni^{IV} complexes in order to interrogate their potential role(s) in catalysis.[4]

To date, studies of organometallic Ni^{IV} complexes have largely focused on two-electron redox processes that form and/or consume these species.[3] As one example, our group has demonstrated that the net two-electron oxidative addition of diaryliodonium salts to Ni^{II} complex **I** affords Ni^{IV} intermediates of general structure **II** (Scheme 1a, i).[3d] Furthermore, **II** was shown to undergo two-electron C–C bond-forming reductive elimination to afford $PhCF_3$ and Ni^{II} product **III** (Scheme 1a, ii). However, a hallmark of nickel catalysis is the accessibility of one-electron redox events, particularly those involving carbon-centered radicals.[1b-f, 2] For instance, one of the most common elementary steps in Ni-catalyzed cross-coupling reactions involves the formation of a Ni^{III}–alkyl intermediate via the addition of a carbon-centered radical to a Ni^{II} center.[1c,2] Thus, an important outstanding question for the field is whether Ni^{IV} intermediates can be formed and/or consumed via analogous single electron reactions with carbon-centered radicals.

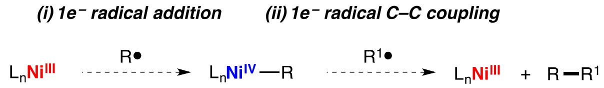
As shown in Scheme 1b, we identified two such reactions for investigation: (i) the addition of carbon-centered radicals to Ni^{III} intermediates to form Ni^{IV} products and (ii) the reaction of organometallic Ni^{IV} complexes with carbon-centered radicals to afford C–C coupling products. Herein, we demonstrate the feasibility of both of these transformations using tris(pyrazolyl)borate-ligated Ni model complexes in combination with thermally-generated carbon-centered radicals. Furthermore, we show that the latter pathway enables challenging carbon–carbon coupling reactions that are not feasible via conventional two-electron inner-sphere C–C bond-forming reductive elimination pathways at Ni.

Scheme 1. (a) Previous work: two electron redox processes to form/consume organometallic Ni^{IV} complexes. (b) This work: one electron redox processes involving carbon-centered radicals that form/consume organometallic Ni^{IV} complexes.

(*a*) Previous work (*2e⁻ redox processes for the formation and reactions of Ni^IV*)



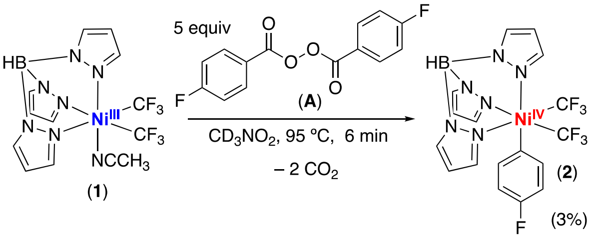
(*b*) **This work** (*1e⁻ redox processes for the formation and reactions of Ni^IV*)



Results and Discussion

Accessing Ni^{IV} via carbon-centered radical addition to Ni^{III} complexes. Recent reports have shown that organometallic Ni^{IV} complexes can be prepared via the net two-electron oxidation of Ni^{II} precursors with oxidants including diaryliodonium salts, aryl diazonium salts, CF_3^+, O^+, Cl^+ and F^+ reagents (for example, Scheme 1a, i).[3,5] These transformations have close analogies to sequences that form high-valent palladium and platinum species.[6] In contrast, the generation of Ni^{IV} intermediates via the reaction of Ni^{III} precursors with carbon-centered radicals has not been demonstrated. This is of particular interest because both Ni^{III} complexes and carbon-centered radicals are common intermediates in Ni-catalyzed cross-coupling. Hence, this pathway, if feasible, could potentially be leveraged in catalytic transformations.

To probe the feasibility of this transformation, we chose the Ni^{III} complex $TpNi^{III}(CF_3)_2(MeCN)$ (**1**, eq. 1) as a model system because our previous work has shown that it is stable and isolable from the $1e^-$ oxidation of $[TpNi^{II}(CF_3)_2]^-$ with $AgBF_4$.[7,8] Additionally, the relevant Ni^{IV} product $TpNi^{IV}(CF_3)_2(Ph)$ (a close analogue of **2**, eq. 1) has been independently formed from the reaction of $[TpNi^{II}(CF_3)_2]^-$ with diaryliodonium salts.[3d] We targeted a method for generating carbon-centered radicals that is compatible with both the organometallic Ni^{III} starting material and the organometallic Ni^{IV} product. The most common carbon-centered radical-forming reactions involve thermolysis, photolysis, reduction, or oxidation of an appropriate precursor.[9] However, high-valent Ni complexes like **1** and **2** generally decompose rapidly at high temperatures, as well as in the presence of light and/or reductants.[3d,5] On the basis of these considerations, we selected diacyl peroxides $[(RCOO)_2]$ as the radical source. These reagents are known to generate carbon-centered radicals under relatively mild conditions (heating at ≤ 95 ºC),[10] without the requirement for light or reductants.[11]



(*1*)

We first studied the reaction of **1** with bis-(4-fluorobenzoyl)peroxide (**A**), which has a $t_{1/2}$ of ~1 h at 90 ºC (eq. 1).[10] Heating the reaction mixture for 15 min at 95 ºC resulted in the complete consumption of **1**[12] along with the formation of **2** in a maximum yield of ~3% (after 6 min). This result suggests the feasibility of the proposed radical addition reaction. However, attempts to improve the yield of **2** by changing the temperature, concentration, or solvent were unsuccessful. A control reaction showed that **1** is unstable at 95 ºC, even in the absence of peroxide. Heating at 95 ºC for 15 min resulted in complete consumption of **1** and the formation of a mixture of products including Tp_2Ni^{II} and HCF_3. This suggests that the low yield of **2** is at least partially due to the instability of the Ni^{III} starting material.

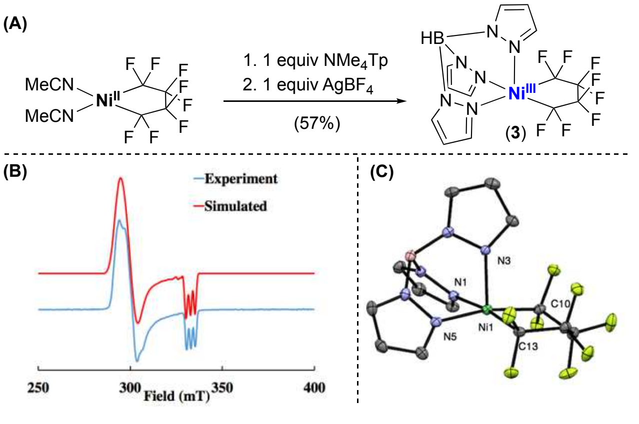
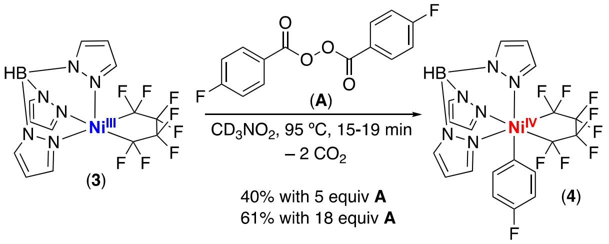


Figure 1. (a) Synthesis of complex **3**. (b) Experimental (blue) and simulated (red) EPR spectra of **3** $G_x = 2.28$; $G_y = 2.22$; $G_z = 2.01$; A_N= 22G. (c) X-ray crystal structure of **3**. Selected bond lengths (Å): Ni1–N3, 2.0314(14); Ni1–N1, 1.9917(14); Ni1–N5, 1.9692(14); Ni1–C13, 1.976 ; Ni1–C13, 1.9420(17). Thermal ellipsoids are drawn at 50% probability

Vicic has reported that Ni^{III} complexes bearing a perfluoronickelocyclopentane ligand are significantly more stable than their trifluoromethyl analogues.[13] As such, we next targeted the analogous reaction of **3**. Complex **3** was synthesized via the reaction of $[TpNi^{II}(C_4F_8)]^-$ with 1 equiv of $AgBF_4$ and was isolated in 57% yield after purification by chromatography on silica gel (Figure 1A). In contrast to **1**, elemental analysis and X-ray crystallography indicate that this is a 5-coordinate Ni^{III} complex. This is further confirmed by EPR spectroscopic analysis (at 100 K in a toluene glass), which shows hyperfine coupling to a single nitrogen.

As predicted, **3** exhibits significantly enhanced thermal stability relative to **1**. Minimal decomposition was observed upon heating a CD_3NO_2 solution of **3** for 15 min at 95 ºC.[14] This suggests that complex **3** should be more compatible with the thermolytic conditions required for R• generation from **A**. Indeed, the treatment of **3** with 18 equiv of **A** at 95 ºC for 19 min produced $TpNi(C_4F_8)(4\text{-}F\text{-}C_6H_4)$ (**4**) in 61% yield, as determined by ^{19}F NMR spectroscopy (eq. 2).[15] Product **4** was purified by column chromatography on silica gel and was isolated in 31% yield as a light orange solid. This octahedral Ni^{IV} complex was characterized by X-ray crystallography (Figure 2a), elemental analysis, and ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy.



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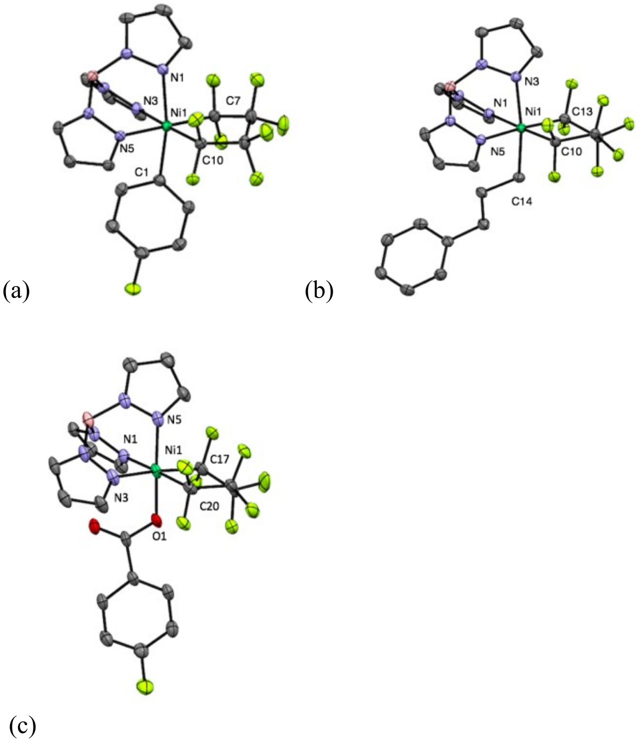
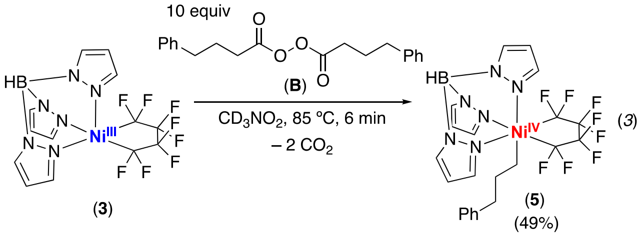


Figure 2. (a) X-ray crystal structure of **4**. Selected bond lengths (A) and angles of **4**: Ni1–N1, 2.089(2); Ni1–N3, 1.980(2); Ni1–C1, 2.031(2); Ni1–C10, 1.978(2); Ni1–C7, 1.967(2); N1–Ni1–C1, 169.31(9)º. (b) X-ray crystal structure of **5**. Selected bond lengths (Å) and angles of **5**: Ni1–N3, 2.1033(13); Ni1–N1, 1.9966(13); Ni1–N5, 1.990(2); Ni1–C13, 1.9787(15); Ni1–C10, 1.9860(16); Ni1–C14, 2.0581(15); N3–Ni1–C14, 171.76(6)º. Thermal ellipsoids are drawn at 50% probability

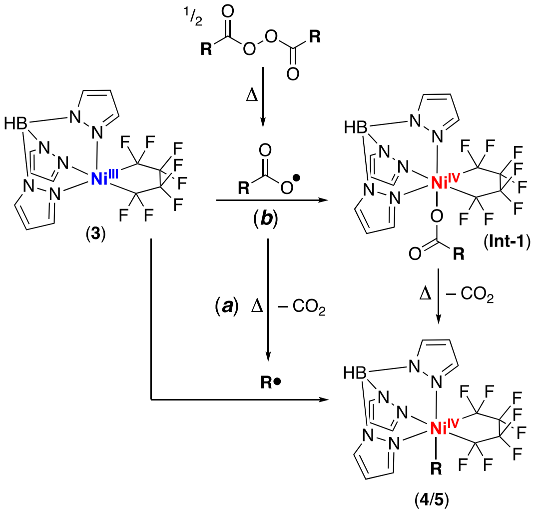
and hydrogen atoms are omitted for clarity. (c) X-ray crystal structure of **Int-1**. Selected bond lengths (Å) and angles of **Int-1**: Ni1–N5, 1.945(4); Ni1–Ni3, 2.012(4); Ni1–N1, 2.006(4); Ni1–O, 1.862(3); Ni1–C20, 1.999(8); Ni1-C17, 2.010(8); N5–Ni1–O1, 178.02(14)º. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms and disorder are omitted for clarity.

We also examined the reaction of **3** with bis-(4-phenylbutyryl)peroxide (**B**).[16] The treatment of **3** with 10 equiv of **B** for 6 min at 85 ºC afforded the Ni^{IV} alkyl product **5** in 49% yield, as determined by ^{19}F NMR spectroscopy (eq. 3).[17] Product **5** was isolated in 17% yield after purification by column chromatography on silica gel, and it was characterized via ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy, as well as by X-ray crystallography (Figure 2b).[18]

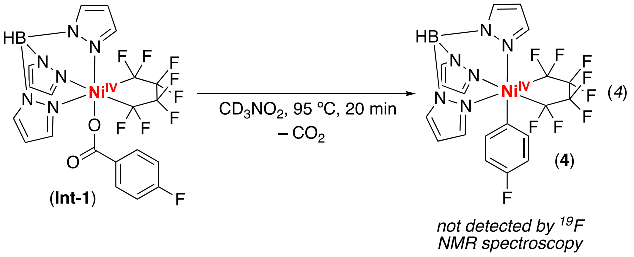


We envision at least two possible pathways for the conversion of **3** to **4**/**5**. The first involves the decarboxylative formation of R• and subsequent addition of this aryl/alkyl radical to **3** (Scheme 2, *a*). The second involves the addition of initially generated RCO$_2$• to **3** to form **Int-1** and subsequent decarboxylation at this Ni^{IV} carboxylate to form **4**/**5** (Scheme 2, *b*). To interrogate this latter possibility, we independently synthesized the Ni^{IV} carboxylate complex **Int-1** (with R = p-FC$_6$H$_4$).[19] **Int-1** was characterized by ^{1}H and ^{19}F NMR spectroscopy (where it exhibits resonances that are clearly distinct from those of **4**) as well as by X-ray crystallography (Figure 2c).

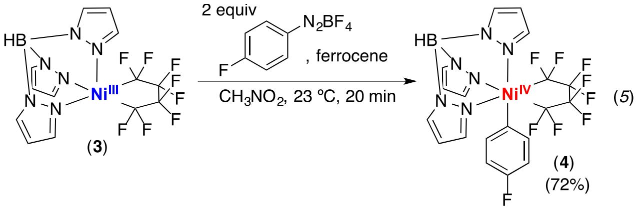
Scheme 2. Possible pathways for conversion of **3** to **4**/**5**



With characterization data for **Int-1** in hand, we reexamined the reaction between **3** and **A**. The crude ^{19}F NMR spectrum of this transformation shows that **Int-1** is formed in approximately 9% yield after 5 min, after which point it rapidly decays. However, this experiment does not establish whether **Int-1** is an intermediate or just a side product formed during this transformation. To distinguish these possibilities, a CD$_3$NO$_2$ solution of **Int-1** was heated at 95 ºC for 20 min (the conditions for the reaction between **3** and **A** to form **4**). This resulted in 67% conversion of **Int-1** to a mixture of products (predominantly 4-fluorobenzoic acid in 55% yield, as determined by ^{19}F NMR).[20] However, no trace of **4** was detected under these conditions (eq. 4). This strongly suggests that pathway b is not operating in this system.



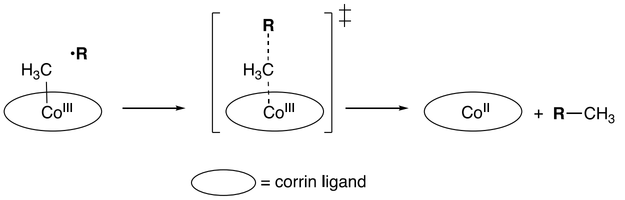
If pathway a were operating then analogous reactivity would be expected using a different source of R•. The combination of aryl diazonium salts and ferrocene is well-known as an alternative route to aryl radicals.[21] As such, we next explored the reaction of Ni^{III} complex **3** with 2 equiv of 4-fluorophenyldiazonium tetrafluoroborate in the presence of 2 equiv of ferrocene (eq. 5). Notably, complex **3** does not react with 4-fluorophenyldiazonium tetrafluoroborate over the course of an hour at room temperature. However, upon the addition of ferrocene, Ni^{IV}-aryl product **4** was formed in 72% yield after just 20 min.[22]



To rule out non-radical pathways, we also conducted radical scavenger experiments using the oxidatively-stable radical trap β-nitrostyrene.[23] We initially confirmed that this reagent does not react with **3** over the timescale of the experiments. When the reaction of **3** with peroxide **A** was performed in the presence of β-nitrostyrene (1 equiv relative to **A**), the yield of **4** dropped dramatically, from 61% to 19%. Similar results were observed using peroxide **B**, with the yield of **5** decreasing from 49% to 14%. This is consistent with the formation (and competitive trapping) of alkyl radicals in the conversion of **3** to **4**/**5**. Collectively, the experiments outlined above are most consistent with pathway a in Scheme 2, involving thermal O–O bond scission, decarboxylation to form R•, and finally capture of R• at **3** to generate Ni^{IV} product **4** or **5**.

One-electron carbon–carbon coupling reactions at Ni^{IV}. We next sought to evaluate the reactivity of Ni^{IV}–alkyl complexes with carbon-centered radicals to generate C–C bonds. Such pathways have precedent in the context of alkyl-Co^{III} systems,[24, 25] but are seldom are considered in high-valent Ni catalysis.[4] In particular methyl–Co^{III} corrinoid cofactors are well-known to react with exogeneous R• to afford R–CH$_3$ via an S$_H$2-type pathway (Scheme 3).[24]

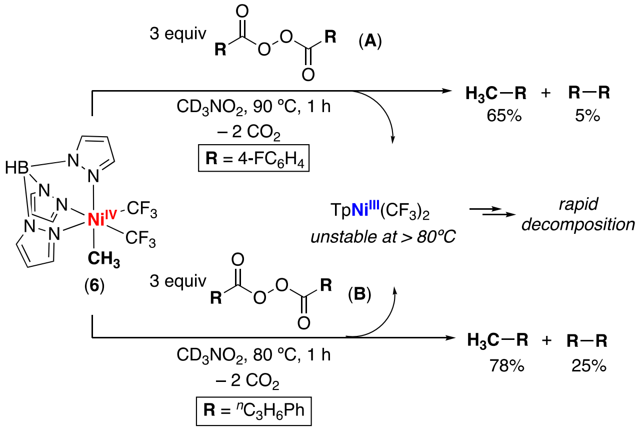
Scheme 3. Reaction of Co^{III}–CH$_3$ adducts with R• to form R–CH$_3$.



To initially probe the viability of this transformation at Ni^{IV}, we evaluated the reactivity of several different Ni^{IV}–alkyl complexes with R• (generated from the thermolysis of **A** or **B**). These studies revealed that the Ni^{IV}–CH_3 complex **6** exhibits the best balance between reactivity with R•, thermal stability, and synthetic accessibility (Scheme 4).[26] Notably, this is similar to the Co systems, in which the methyl variants are typically thermally stable yet highly reactive with carbon-centered radicals.[Error! Bookmark not defined.] As such, complex **6** was selected as the model system for more detailed studies going forward.

Heating a solution of **6** with 3 equiv peroxide **A** at 90 ºC for 1 h resulted in the formation of 4-fluorotoluene in 65% yield along with 5% of 4,4'-difluorobiphenyl, as determined by ^{19}F NMR spectroscopic analysis (Scheme 4).[27, 28] Notably, 44% of **A** (or ~1.3 equiv relative to **6**) was consumed in this reaction. Similarly, the reaction of **6** with 3 equiv of **B** at 80 ºC for 1 h afforded *n*-butyl benzene in 78% yield, as determined by ^{1}H NMR spectroscopy. Notably, 67% of **B** (or ~2 equiv relative to **6**) was consumed in this reaction. In this case, the radical homocoupling product 1,6-diphenylhexane was also detected in 25% yield (Scheme 4). However, neither methane nor ethane was observed in either reaction.

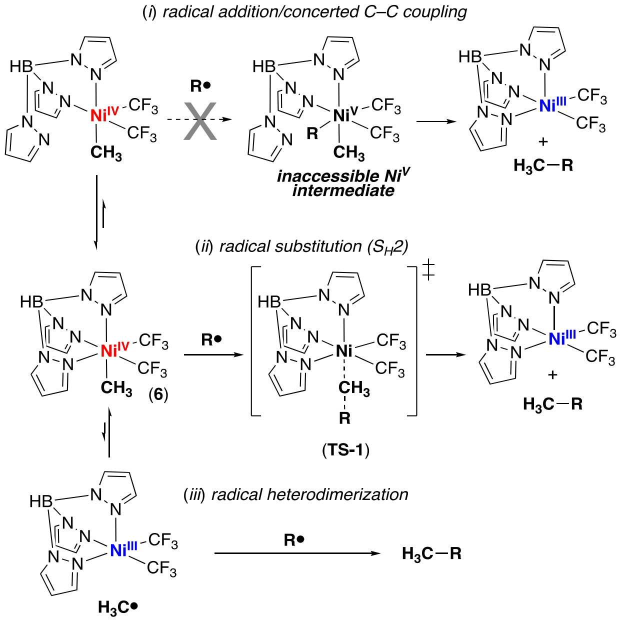
Scheme 4. Reaction of carbon-centered radicals with **6** (yields based on **6** as limiting reagent)



The Ni product of the reaction between **6** and R• is expected to be $TpNi^{III}(CF_3)_2$. However, $TpNi^{III}(CF_3)_2$ is unstable at temperatures ≥ 80 ºC. As such, the reactions with **A** (conducted at 90 ºC) and **B** (conducted at 80 ºC) afforded complex mixtures of Ni by-products that proved challenging to characterize.[29] Analysis of these crude mixtures by ^{11}B NMR spectroscopy revealed the presence of Tp_2Ni.[30]

Scheme 5 shows three pathways that could account for the formation of R–CH_3 in this reaction.[31] The first (Scheme 5, i) involves preequilibrium dissociation of an arm of the Tp ligand followed by radical addition and subsequent concerted inner sphere C–C coupling. Notably, this radical addition/concerted reductive elimination sequence is frequently proposed in reactions of carbon-centered radicals with lower oxidation state coordinatively unsaturated Ni centers.[1c,2] However, it is highly unlikely in the current system, because it requires the formation of a nickel intermediate with a formal +5 oxidation state. The second pathway (Scheme 5, ii) involves outer-sphere radical coupling via a radical substitution (S_H2) pathway.[32] Here, R• reacts directly with the methyl ligand via a transition state of general structure **TS-1**. This pathway is analogous to that proposed for the reaction of methyl–Co^{III} corrinoid cofactors with R• (Scheme 3). Finally, this transformation could proceed via the heterodimerization of R• and methyl radicals formed through spontaneous Ni^{IV}–CH_3 homolysis (Scheme 5, iii).

Scheme 5. Potential mechanisms for C–C coupling reactions between **6** and R•.



The product distribution of these reactions provides initial evidence against the homolysis/radical heterodimerization pathway (mechanism *iii*). Unstabilized carbon-centered radicals are known to dimerize with low selectivity and at near diffusion-limited rates.[33] However, the reaction of **6** with **A** and **B** forms the cross-coupled product, H_3C–R in much higher yield (65% and 78%, respectively) than R–R or H_3C–CH_3 (5% and 25% yield, respectively).[34,35]

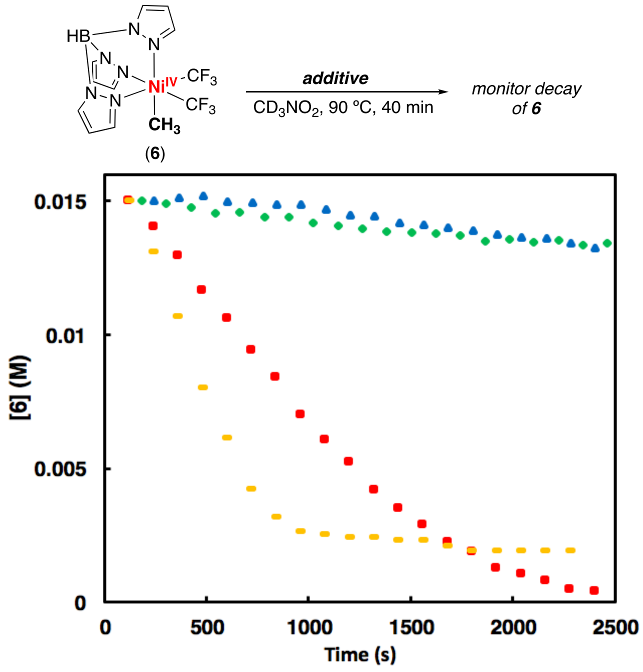
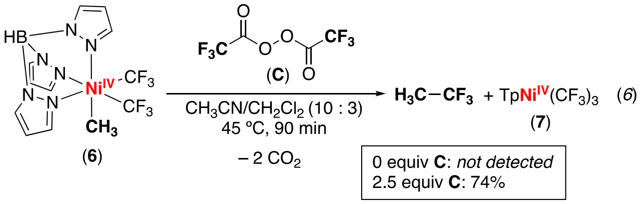


Figure 3. Thermal decomposition of **6** (0.015 M in CD_3NO_2) in the presence of various additives. ▲ = no additive. ◆ = β-nitrostyrene (0.075 M, 5 equiv relative to **6**). ■ = **A** (0.045 M, 3 equiv relative to **6**). ▬ = **B** (0.045 M, 3 equiv relative to **6**)

To further interrogate the viability of mechanism *iii*, we monitored the thermolysis of **6** in the presence of 5 equiv of the radical scavenger β-nitrostyrene. If mechanism *iii* were operating, any free H_3C• that is generated should be rapidly captured by β-nitrostyrene, resulting in fast decomposition of **6**. In contrast, in the event of mechanism *ii*, **6** should be stable in the presence of this reagent. As shown in Figure 3, heating a solution of **6** in the presence of β-nitrostyrene had minimal impact on the decay of **6**. In marked contrast, the addition of **A** or **B** resulted in rapid loss of **6** (with concomitant formation of the respective C–C coupled product). Collectively, the experiments outlined above are most consistent with mechanism *ii.*

Mechanism *ii* is fundamentally different than traditional $2e^-$ inner-sphere C–C bond-forming reductive elimination reactions. As such, we hypothesized that it might enable the formation of $C(sp^3)$–CF_3 bonds, which are challenging to forge via direct inner-sphere pathways.[3c,7,36] For example, heating **6** for 18 h at 100 ºC in MeCN yields <5% of H_3C–CF_3. Instead, other decomposition pathways outcompete H_3C–CF_3 coupling.[37] This result is consistent with the known difficulties associated with direct inner-sphere $C(sp^3)$–CF_3 coupling.

However, in contrast, the treatment of **6** with 2.5 equiv of bis(trifluoroacetyl)peroxide (**C**) at just 45 ºC for 90 min resulted in rapid decay of the Ni^{IV} starting material along with the concomitant formation of H_3C–CF_3 and $TpNi^{IV}(CF_3)_3$ **7** in 74% and 63% yield, respectively (eq. 6).[38] Control reactions show that H_3C–CF_3 is not formed at this temperature unless both **6** and **C** are present. This represents a rare example of metal-mediated $C(sp^3)$–CF_3 coupling.[36,39] In our system, this transformation appears to be enabled by the accessibility of a $1e^-$ outer sphere pathway.



Summary and Conclusions

In summary, this Article describes the first detailed study of the reactivity of high-valent organonickel complexes with carbon-centered radicals (R•). These studies demonstrate that Ni^{IV} compounds can be formed from the reaction of Ni^{III} complexes with R•. They also reveal that Ni^{IV}–methyl complexes can engage R• to form various types of C–C bonds. Preliminary mechanistic studies are most consistent with a pathway involving an S_H2-type reaction of R• with the Ni^{IV}–CH_3 ligand. In contrast, inner-sphere coupling and radical heterodimerization mechanisms are deemed unlikely. This unconventional C–C bond-forming pathway was found to enable $C(sp^3)$–CF_3 coupling, a reaction that is highly challenging through traditional inner-sphere reductive elimination at Ni centers. Overall, these investigations suggest that, with appropriate choice of ligand, $Ni^{II/III/IV}$ sequences involving CCRs could be targeted for the formation of challenging bonds. Future work in our laboratory will seek to extend these insights to the development of new catalytic methods.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details, compound characterization, spectra, and safety considerations (PDF).

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[11] Tp-supported high-valent state organonickel complexes are light sensitive and thus highly unstable under photolytic conditions.

[12] The consumption of **1** was determined by ^{11}B NMR spectroscopic analysis of the crude reaction mixture

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[14] Heating **3** at 100 ºC for 12 h resulted in complete decomposition of the starting material to form a mixture of nickel-containing products including NiTp$_2$.

[15] The yield of **4** appears to be limited by the competitive decomposition of this Ni^{IV} product at 95 ºC. Analysis of the crude reaction between **A** and **3** of revealed that only 11% (~1.8 equiv relative to Ni) of the initial **A** was consumed at the time of maximum Ni^{IV} yield. The remaining mass balance of the reaction was fluorobenzene and 4-fluorobenzoic acid, presumably formed through H-atom abstraction from the solvent (see Figure S3). Using fewer equiv of **A** resulted in lower yields of **4** (11% yield with 1 equiv, 40% yield with 5 equiv).

[16] Diacyl/aroylperoxides are potentially explosive materials and should be handled with appropriate precaution (see Supporting Information for details).

[17] The yield of **5** appears to be limited by the competitive decomposition of this Ni^{IV} product at 85 ºC. Analysis of the crude reaction mixture by ^{1}H NMR spectroscopy and GCMS revealed the formation of 1,6-diphenyl hexane, and allyl benzene. The allylbenzene is formed during the thermal decomposition of **5** via through an apparent net β-hydride elimination.

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[18] Complex **5** was isolated in 17% yield through the reaction of **3** with 5 equiv of **B** at 85 ºC for 6 min. Notably, diacyl peroxides are potentially explosive compounds and should be handled with caution. The equivalents of **B** were reduced to mitigate risk on the preparatory scale.

[19] See Supporting Information, p. S7-S8 for the synthesis and characterization of **Int-1**.

[20] The nature of the primary nickel-containing product of this reaction is currently unclear. The ^{11}B NMR rules out the formation of $NiTp_2$ or free unbound Tp.

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[22] Similarly, complex **1** reacts with 4-fluorophenyldiazonium tetrafluoroborate and ferrocene to yield **2** in 52% yield under these conditions.

[23] A key consideration in the choice of radical scavenger is its stability to the highly oxidizing conditions of this reaction. For example, the use of TEMPO as a radical scavenger resulted in violent decomposition of the peroxides. On this basis, we selected the electron deficient Michael acceptor β-nitrostyrene. Barton, D. H. R.; Togo, H.; Zard, S. R. The invention of new radical chain reactions. Part X. High-yield radical addition reactions of α,β-nitroolefins. An expedient construction of the 25-hydroxy-vitamind D_3 side chain from bile acids. *Tetrahedron* **1985**, *41*, 5507.

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[26] Complex **6** was prepared in 40% yield via the reaction of $NMe_4[TpNi^{II}(CF_3)_2]$ with excess methyl iodide and 1.3 equiv of 2,6-difluorobenzendiazonium tetrafluoroborate (see Supporting Information, p. S9-S10). This Ni^{IV} complex was characterized via ^1H, ^{13}C, ^{19}F, and $^1H/^{19}F$ HMBC NMR spectroscopy as well as elemental analysis. Complex **6** exhibits relatively high thermal stability, with <10% decomposition after 1 h at 90 ºC in CD_3NO_2. This high thermal stability is likely due to the high barrier for CH_3–CF_3 coupling via inner sphere reductive elimination.

[27] A similar yield (58%) was obtained based on ^1H NMR spectroscopic analysis of the crude reaction mixture, confirming that the methyl is not solvent-derived.

[28] The ethyl analogue, $TpNi^{IV}(CF_3)_2(CH_2CH_3)$, reacts with 6 equiv of **A** under analogous conditions to afford 4-fluoroethylbenzene in 7% yield. However, it is important to note that this complex is not very stable at the reaction temperature, and it decomposes competitively at 90 ºC to form ethylene and CF_3H. See Supporting Information pg. S29 for more details.

[29] Attempts to isolate Ni-containing products from the crude reaction mixtures with **A** and **B** (by silica column chromatography or recrystallization) were unsuccessful.

[30] Tp_2Ni was also the major identifiable nickel-containing compound in the thermal decomposition of **1**.

[31] A reviewer suggested that an alternate pathway for the reactions in Scheme 4 and eq. 6 could involve the transmetalation of a methyl group from **6** to reduced nickel byproducts and subsequent C–C coupling from a lower valent Ni center. While we cannot definitively rule out this possibility, we note that this would require a H_3C–CF_3 bond-forming reductive elimination reaction from a lower valent Ni center. This transformation currently does not have precedent from group 10 metal centers. See ref 7

[32] Ingold, K. U.; Roberts, B. P. Free radical substitution reactions: Bimolecular homolytic substitutions at saturated multivalent atoms; Wiley: New York, 1971.

[33] The dimerization of localized and sterically accessible carbon-centered radicals, such as $\bullet CH_3$ and •Ph, is thought to be nearly barrierless. Constentin, C.; Savéant, J-M. Origin of activation barriers in the dimerization of neutral radicals: A “nonperfect synchronization” effect. *J. Phys. Chem. A.* **2005**, *109*, 4125.

[34] Ethane was not detected by ^1H NMR spectroscopy. However, potential loss of ethane to the headspace of the reaction vessel could not be mitigated due to the hazards associated with eliminating reaction vessel headspace in gas-evolving reactions. The mass balance of other methyl-containing products sets the maximum yield as 17% and 11%.

[35] The H-atom abstraction products, fluorobenzene and n-propylbenzene were observed in 30% and <2% yield, respectively.

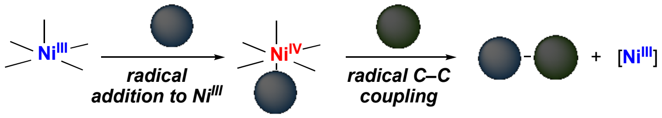
[36] Inner-sphere $C(sp^3)$–CF_3 coupling has recently been proposed to occur from $Cu^{III}(CF_3)_3(CH_3)$ complexes. S_H2 mechanisms involving the direct attack of $\bullet CF_3$ on $Cu^{III}(CH_3)$ were not discussed, see: (a) Tan, X.; Liu, Z.; Shen, H.; Zhang, P.; Zhang, Z.; Li C. Silver-catalyzed decarboxylative trifluoromethylation of aliphatic carboxylic acids. *J. Am. Chem. Soc.* **2017**, *139*, 12340. (b) Paeth, M.; Tyndall, S. B.; Chen, L-Y.; Hong, J-C.; Carson, W. P.; Liu, X.; Sun, X.; Liu, J.; Yang, K.; Hale, E. M.; Tierney, D. L.; Liu, B.; Cao, Z. Cheng, M-C.; Goddard, W. A.; Liu, W. $C(sp^3)$-CF_3 reductive elimination from well-defined Cu(III) complexes. *J. Am. Chem. Soc.* **2019**, *141*, 3153.

[37] In marked contrast, the analogous phenyl complex $TpNi^{IV}(CF_3)_2(Ph)$ undergoes high yielding inner-sphere Ph–CF_3 coupling at 55 ºC over 14 h. See ref. 3d for details.

[38] **7** is likely formed through the addition of $\bullet CF_3$ to $TpNi(CF_3)_2$ which is more stable at these lower temperatures.

[39] Levin, M. D.; Chen, T. Q.; Neubig, M. E.; Hong, C. M.; Theulier, C. A.; Kobylianskii, I. J.; Janabi, M.; O’Neil, J. P.; Toste, F. D. A catalytic fluoride rebound mechanism for $C(sp^3)$-CF_3 bond formation. *Science* **2017**, *356*, 1272.

TOC Graphic


Ni^III
radical addition to Ni^III
Ni^IV
radical C–C coupling
+ [Ni^III]