

## Oxidative C–C Bond Formation Reactivity of Organometallic Ni(II), Ni(III), and Ni(IV) Complexes

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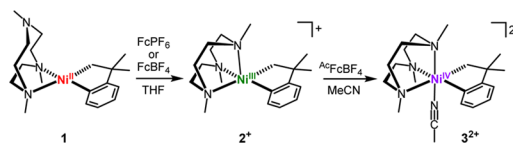
## Supporting Information

**ABSTRACT:** The use of the tridentate ligand 1,4,7-trimethyl-1,4,7-triazacyclononane ( $\text{Me}_3\text{tacn}$ ) and the cyclic alkyl/aryl C-donor ligand  $-\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4-$  (cycloneophyl) allows for the synthesis of isolable organometallic  $\text{Ni}^{\text{II}}$ ,  $\text{Ni}^{\text{III}}$ , and  $\text{Ni}^{\text{IV}}$  complexes. Surprisingly, the five-coordinate  $\text{Ni}^{\text{III}}$  complex is stable both in solution and the solid state, and exhibits limited C–C bond formation reactivity. Oxidation by one electron of this  $\text{Ni}^{\text{III}}$  species generates a six-coordinate  $\text{Ni}^{\text{IV}}$  complex, with an acetonitrile molecule bound to Ni. Interestingly, illumination of the  $\text{Ni}^{\text{IV}}$  complex with blue LEDs results in rapid formation of the cyclic C–C product at room temperature. This reactivity has important implications for the recently developed dual Ni/photoredox catalytic systems proposed to involve high-valent organometallic Ni intermediates. Additional reactivity studies show the corresponding  $\text{Ni}^{\text{II}}$  species undergoes oxidative addition with alkyl halides, as well as rapid oxidation by  $\text{O}_2$ , to generate detectable  $\text{Ni}^{\text{III}}$  and/or  $\text{Ni}^{\text{IV}}$  intermediates and followed by C–C bond formation.

Nickel-based catalysts are commonly employed in a wide range of C–C and C–heteroatom bond formation reactions.<sup>1</sup> Although traditionally these processes have been considered to involve  $\text{Ni}^0$ ,  $\text{Ni}^{\text{I}}$ , and  $\text{Ni}^{\text{II}}$  intermediates,<sup>2</sup> many studies proposed high-valent  $\text{Ni}^{\text{III}}$  species as key intermediates in the C–C/C–heteroatom bond formation step.<sup>3</sup> Moreover,  $\text{Ni}^{\text{IV}}$  species have also emerged as potential intermediates involved in catalytic reactions.<sup>3g,4</sup> However, the number of organometallic  $\text{Ni}^{\text{III}}$ ,<sup>5,6</sup> and  $\text{Ni}^{\text{IV}}$ <sup>7</sup> complexes isolated to date is limited, which hinders detailed reactivity studies to probe their involvement in catalysis.

We have recently reported the use of the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane ( $\text{Me}_3\text{tacn}$ ) to stabilize high-valent organometallic Pd complexes.<sup>8</sup> In addition, the C-donor cyclic ligand  $-\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4-$  (cycloneophyl) has been employed starting more than 2 decades ago by Carmona et al.<sup>9</sup> to stabilize organometallic Ni complexes, because the corresponding Ni(cycloneophyl) species exhibit limited reductive elimination and  $\beta$ -hydride elimination reactivity. Recently, Sanford et al. have elegantly employed the cycloneophyl ligand to isolate novel  $\text{Ni}^{\text{IV}}$  complexes and investigate their C–heteroatom bond formation reactivity.<sup>7f</sup> Herein, we report the synthesis, characterization, and initial reactivity studies of  $\text{Ni}^{\text{II}}$ ,  $\text{Ni}^{\text{III}}$ , and  $\text{Ni}^{\text{IV}}$  complexes

supported by  $\text{Me}_3\text{tacn}$  and containing the cycloneophyl ligand (Scheme 1). To the best of our knowledge, these are the first

Scheme 1. Synthesis of  $(\text{Me}_3\text{tacn})\text{Ni}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)$  Complexes

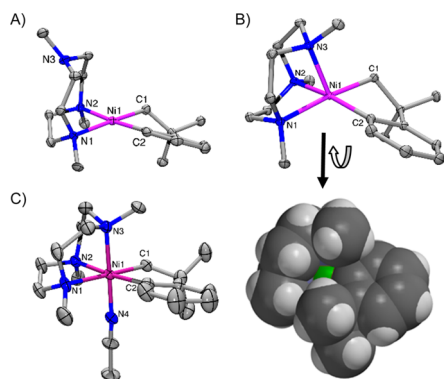
organometallic Ni complexes supported by a 1,4,7-triazacyclononane-derived ligand. Although the isolated five-coordinate  $\text{Ni}^{\text{III}}$  complex is uncommonly stable and exhibits limited C–C bond formation reactivity, the six-coordinate  $\text{Ni}^{\text{IV}}$  complex generates quantitatively the cyclic C–C product upon illumination with blue LEDs, which is relevant to the recently reported dual Ni/photoredox catalytic systems proposed to involve high-valent organometallic Ni intermediates.<sup>10</sup> In addition,  $(\text{Me}_3\text{tacn})\text{Ni}^{\text{II}}(\text{cycloneophyl})$  undergoes oxidative addition with alkyl halides, as well as rapid oxidation by  $\text{O}_2$ , to generate detectable  $\text{Ni}^{\text{III}}$  and  $\text{Ni}^{\text{IV}}$  intermediates followed by reductive elimination to form new C–C bonds. Overall, these studies set the stage for detailed investigations of the reactivity of high-valent organometallic Ni complexes relevant to Ni-catalyzed reactions.

The yellow  $\text{Ni}^{\text{II}}$  complex  $(\text{Me}_3\text{tacn})\text{Ni}^{\text{II}}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)$ , **1**, was synthesized through ligand exchange of  $(\text{py})_2\text{Ni}^{\text{II}}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)$ <sup>11</sup> with  $\text{Me}_3\text{tacn}$  in pentane (Scheme 1).<sup>12</sup> The single crystal X-ray structure of **1** reveals a square planar geometry around the  $\text{Ni}^{\text{II}}$  center with  $\text{Me}_3\text{tacn}$  acting as a bidentate ligand (Figure 1). Moreover, **1** is diamagnetic and its <sup>1</sup>H NMR spectrum reveals only one singlet corresponding to the N–Me groups, suggesting a rapid exchange between the unbound and bound N-donor atoms, as seen before for analogous  $(\text{Me}_3\text{tacn})\text{Pd}^{\text{II}}$  complexes.<sup>8</sup>

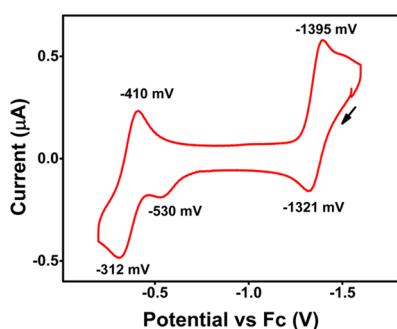
The cyclic voltammogram (CV) of **1** in 0.1 M (*n*Bu<sub>4</sub>N)PF<sub>6</sub>/MeCN shows a pseudoreversible redox event at  $E_{1/2} = -1358$  mV vs ferrocene (Fc), followed by a smaller oxidation wave at  $-530$  mV and a reversible oxidation at  $E_{1/2} = -361$  mV (Figure 2). Because the presence of two anionic carbon ligands is expected to stabilize high-valent Ni centers, the observed reversible oxidations are tentatively assigned to the  $\text{Ni}^{\text{III/II}}$  and  $\text{Ni}^{\text{IV/III}}$

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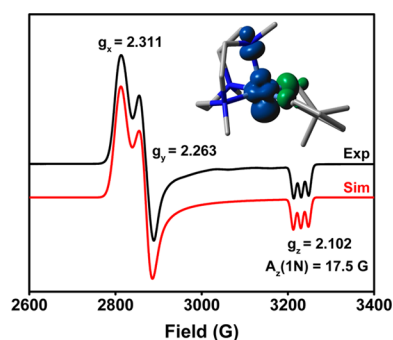


**Figure 1.** ORTEP representation (50% probability thermal ellipsoids) of **1** (A), **2<sup>+</sup>** (B), and **3<sup>2+</sup>** (C, 30% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): **1**, Ni1-C1 1.904(3); Ni1-C2 1.930(3); Ni1-N1 2.059(3); Ni1-N2 2.069(2); C1-Ni1-N1 178.0(2); C2-Ni1-N2 175.1(1); **2<sup>+</sup>**, Ni1-C1 1.976(1); Ni1-C2 1.965(1); Ni1-N1 2.100(1); Ni1-N2 2.100(1); Ni1-N3 2.083(1); C1-Ni1-N1 173.70(3); C2-Ni1-N2 165.33(3); **3<sup>2+</sup>**, Ni1-C1 2.032(8); Ni1-C2 1.973(8); Ni1-N1 2.094(6); Ni1-N2 2.098(6); Ni1-N3 1.977(6); Ni1-N4 1.858(7); C1-Ni1-N1 175.0(3); C2-Ni1-N2 172.4(3). The space filling model of **2<sup>+</sup>** is also shown, as viewed from the bottom along the axial axis.



**Figure 2.** CV of **1** in 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub>/MeCN at RT (100 mV/s scan rate). Redox potentials:  $E_{1/2}(\text{Ni}^{\text{III/II}}) = -1358$  mV;  $E_{1/2}(\text{Ni}^{\text{IV/III}}) = -361$  mV.

redox couples, respectively. The oxidation wave at  $-530$  mV is proposed to correspond to the conformation of **1** in which the Me<sub>3</sub>tacn ligand adopts a  $\kappa^2$  binding mode, and in line with a similar oxidation potential observed by Sanford et al. for the (bpy)Ni<sup>II</sup>(cycloneophyl) complex supported by a bidentate ligand.<sup>7f</sup> As such, the reversible Ni<sup>III/II</sup> redox couple observed at  $-1358$  mV likely corresponds to the conformation of **1** with Me<sub>3</sub>tacn in a  $\kappa^3$  binding mode. Indeed, **1** can be readily oxidized with ferrocenium hexafluorophosphate (FcPF<sub>6</sub>) to yield the orange product [(Me<sub>3</sub>tacn)Ni<sup>III</sup>(CH<sub>2</sub>CMe<sub>2</sub>-*o*-C<sub>6</sub>H<sub>4</sub>)]PF<sub>6</sub>, [**2**]<sup>PF<sub>6</sub></sup> (Scheme 1). The X-ray structure of [**2**]<sup>PF<sub>6</sub></sup> shows a five-coordinate Ni<sup>III</sup> center in a square pyramidal geometry (Figure 1B), as supported by the calculated trigonality index parameter  $\tau = 0.14$ .<sup>13</sup> Interestingly, the Ni-N and Ni-C bond lengths in **2<sup>+</sup>** are longer than those in **1**, which may be due to an increased steric hindrance at the Ni center of **2<sup>+</sup>**, and a likely decrease in orbital overlap upon moving the C/N donor atoms out of the equatorial plane. The five-coordinate geometry is maintained in MeCN, because the EPR spectrum of **2<sup>+</sup>** in 1:3 MeCN:PrCN reveals a rhombic signal with superhyperfine coupling to only one nitrogen atom in the  $g_z$  direction, suggesting that the nitrile solvent does not coordinate to the Ni<sup>III</sup> center (Figure 3). The EPR spectrum also suggests the presence of a Ni<sup>III</sup> d<sup>7</sup> center with a d<sub>2</sub> ground state, which is supported by the

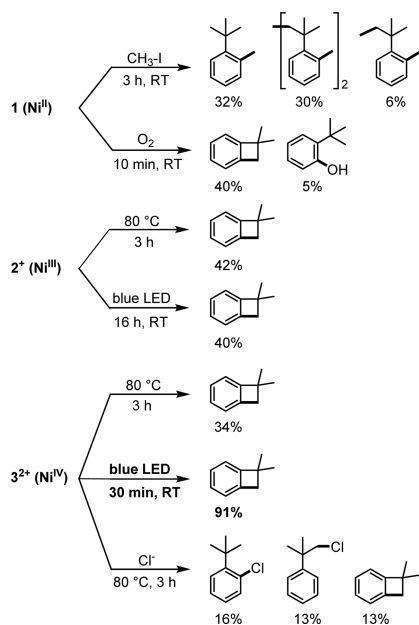


**Figure 3.** Experimental (1:3 MeCN:PrCN, 77 K) and simulated EPR spectra of **2<sup>+</sup>**. The following parameters were used for the simulation:  $g_x = 2.311$ ,  $g_y = 2.263$ ,  $g_z = 2.102$  ( $A_N(1N) = 17.5$  G). Inset: DFT-calculated spin density for **2<sup>+</sup>**, shown as a 0.05 isodensity contour plot.

DFT-calculated spin density for **2<sup>+</sup>** (Figure 3, inset).<sup>12</sup> Finally, **2<sup>+</sup>** is stable at RT for weeks as a solid and for several days in MeCN, which is surprising for a five-coordinate organometallic Ni<sup>III</sup> complex that is usually expected to undergo rapid reductive elimination.<sup>3</sup>

Oxidation of the Ni<sup>III</sup> complex [**2**]<sup>BF<sub>4</sub></sup> with acetylferrocenium tetrafluoroborate (<sup>Ac</sup>FcBF<sub>4</sub>) at  $-30$  °C in MeCN generates a red, diamagnetic product (Scheme 1).<sup>14</sup> NMR analysis suggests the formation of a Ni<sup>IV</sup> species (Figures S16–S20), as exemplified in <sup>1</sup>H NMR by the downfield shift to 5.5 ppm of the peak corresponding to Ni<sup>IV</sup>-CH<sub>2</sub>- protons vs the 2.1 ppm value observed for **1**. Structural characterization confirms the formation of [(Me<sub>3</sub>tacn)Ni<sup>IV</sup>(CH<sub>2</sub>CMe<sub>2</sub>-*o*-C<sub>6</sub>H<sub>4</sub>)(MeCN)](BF<sub>4</sub>)<sub>2</sub>, [**3**](BF<sub>4</sub>)<sub>2</sub>, in which the Ni<sup>IV</sup> center adopts an octahedral geometry with an MeCN molecule as the sixth ligand. Surprisingly, the Ni-C bonds lengths in **3<sup>2+</sup>** are longer than those in both **2<sup>+</sup>** and **1**, likely due to an increased steric hindrance, whereas the axial Ni-N<sub>amine</sub> bond length is shorter than that in **2<sup>+</sup>**, due to the preference of a Ni<sup>IV</sup> d<sup>6</sup> center to adopt an octahedral geometry. Although **3<sup>2+</sup>** is the first dicationic Ni<sup>IV</sup> complex isolated to date and it would be expected to be highly electrophilic,<sup>7f</sup> its uncommon stability is likely due to its coordinatively saturated nature. Overall, **1**, **2<sup>+</sup>**, and **3<sup>2+</sup>** establish an uncommon series of isolable, organometallic Ni<sup>II</sup>, Ni<sup>III</sup>, and Ni<sup>IV</sup> complexes that can be used to compare the reactivity of these Ni oxidation states in organometallic reactions.<sup>15</sup>

With these organometallic Ni<sup>II</sup>, Ni<sup>III</sup>, and Ni<sup>IV</sup> complexes in hand, we set out to probe their reactivity in C-C and C-heteroatom bond formation reactions. First, we studied the ability of the Ni<sup>II</sup> complex **1** to undergo oxidative addition with organic halides, because such a step has been proposed to occur in several catalytic reactions.<sup>3g,4</sup> Gratifyingly, the addition of iodomethane to **1** led to an immediate formation of a deep red solution that faded to pale yellow after 3 h at RT, and analysis of the reaction mixture by GC–MS upon acidic workup revealed the formation of three C-C coupled products that account for 98% of the neophyl ligand (Scheme 2).<sup>12</sup> The 2-methyl-*t*-butylbenzene product likely forms upon oxidative addition of MeI to **1** followed by subsequent C<sub>sp2</sub>-C<sub>sp3</sub> reductive elimination. The dimeric methylated product formed in 30% yield may result upon bimetallic ligand exchange occurring after the first C<sub>sp2</sub>-C<sub>sp3</sub> reductive elimination, followed by a C<sub>sp3</sub>-C<sub>sp3</sub> reductive elimination to yield the observed product. Moreover, the formation of a dimethylated product in 6% yield suggests that more than one oxidative addition of MeI can occur at the same Ni center, and sequential reductive eliminations can form two new

Scheme 2. Reactivity of Complexes 1, 2<sup>+</sup>, and 3<sup>2+</sup><sup>a</sup>

<sup>a</sup>The bonds shown in bold represent new bonds formed in the reaction.

C-C bonds. Alternatively, a methyl group transfer at a high-valent Ni center, followed by reductive elimination, could also account for the dimethylated product.<sup>16</sup> Performing the addition of MeI to **1** in the presence of the radical trap TEMPO leads to no detectable methylation products, instead the cyclized product 1,1-dimethylbenzocyclobutene was formed in 23% yield.<sup>12</sup> This result suggests a single electron transfer (SET) oxidative addition mechanism, as proposed previously for other Ni systems.<sup>3,4</sup> Finally, addition of either iodobenzene or ethyl bromide to **1** leads to the corresponding 2-substituted *t*-butylbenzene products in 50% and 23% yields, respectively, suggesting that the proposed oxidative addition to **1** can occur for a range of organic halides.<sup>12</sup>

Next, we explored the oxidatively induced reactivity of **1** in the presence of mild oxidants. Excitingly, exposure of **1** to O<sub>2</sub> in 9:1 CD<sub>3</sub>CN:D<sub>2</sub>O led to rapid formation of a deep red solution and analysis by <sup>1</sup>H NMR revealed the formation of 1,1-dimethylbenzocyclobutene in 40% yield (Figure S26). GC-MS analysis confirmed the presence of the C-C coupled product, along with 5% of the C-O product 2-*tert*-butylphenol (Scheme 2).<sup>12</sup> Performing the oxidation of **1** with O<sub>2</sub> in 9:1 *d*<sup>6</sup>-acetone:D<sub>2</sub>O at -30 °C allowed the detection by <sup>1</sup>H NMR of chemical shifts that are tentatively assigned to a Ni<sup>IV</sup> complex similar to **3<sup>2+</sup>**, formed in 40% yield (Figure S29). Furthermore, analysis of the reaction mixture by EPR shows the formation of the Ni<sup>III</sup> species in 50% yield (Figure S30). While detailed mechanistic studies of this aerobic reactivity are currently underway, these initial studies suggest O<sub>2</sub> is capable of rapidly oxidizing **1** to generate both Ni<sup>III</sup> and Ni<sup>IV</sup> species, followed by formation of C-C and C-O coupled products, and thus can be potentially employed in catalytic Ni-mediated aerobic transformations. To the best of our knowledge, only two other organometallic Ni<sup>III</sup> complex have been shown to undergo oxidation by O<sub>2</sub> and subsequent C-C bond formation through a high-valent Ni intermediate, although in those cases no C-O bond formation was reported.<sup>7d,16</sup>

Having isolated both Ni<sup>III</sup> and Ni<sup>IV</sup> complexes **2<sup>+</sup>** and **3<sup>2+</sup>**, we then evaluated their C-C bond formation reactivity. Upon heating **2<sup>+</sup>** or **3<sup>2+</sup>** in MeCN at 80 °C, 1,1-dimethylbenzocyclo-

butene was generated in only 42% and 34% yield, respectively (Scheme 2).<sup>12</sup> This is in contrast to related Ni<sup>IV</sup>(cycloneophyl) complexes reported recently by Sanford et al. that undergo almost quantitative formation of the cyclized product, and this may be due to the dicationic nature of **2<sup>+</sup>** and **3<sup>2+</sup>** that leads to less selective reactivity.<sup>7f</sup> Interestingly, the yield of C-C coupled product was found to be dependent on the presence of light, and exposure of **3<sup>2+</sup>** in MeCN to blue LEDs (470 nm) leads to formation of 1,1-dimethylbenzocyclobutene in 91% yield in 30 min at RT. Performing the photolysis in the presence of TEMPO does not affect the yield of product significantly, suggesting that no free radicals are generated during the reaction.<sup>12</sup> We tentatively assign the observed photoreactivity to an LMCT excitation of an electron into an antibonding MO that leads to the dissociation of the axial N donor to yield a 5-coordinate intermediate, which then undergoes rapid reductive elimination.<sup>17</sup> By comparison, exposure of **2<sup>+</sup>** to blue LEDs does not increase the yield of coupled product vs the thermolysis reaction (Scheme 2). Overall, the observed photoreactivity is particularly relevant to the recently reported C-C/C-X bond formation reactions employing dual Ni/photoredox catalysis,<sup>10</sup> and suggests that organometallic Ni complexes can be directly activated by light and undergo rapid reductive elimination.

Finally, the reactivity of both **2<sup>+</sup>** and **3<sup>2+</sup>** in the presence of various nucleophiles was also investigated. Surprisingly, addition of (Et<sub>4</sub>N)Cl, (Et<sub>4</sub>N)OH, (nBu<sub>4</sub>N)OAc, (nBu<sub>4</sub>N)<sub>3</sub>, or (Me<sub>4</sub>N)-NHMs to a CD<sub>3</sub>CN solution of **2<sup>+</sup>** did not lead to formation of any C-heteroatom bond formation product even upon heating at 80 °C, only the C-C product 1,1-dimethylbenzocyclobutene being observed in yields between 24% and 73% (Table S3).<sup>12</sup> The lack of any C-X products could be attributed to the sterically hindered Ni center (Figure 1B). Indeed, no change in the EPR spectra of these solutions was observed upon addition of the nucleophile, supporting the lack of coordination to the Ni<sup>III</sup> center. By comparison, addition of the same nucleophiles to a CD<sub>3</sub>CN solution of **3<sup>2+</sup>** leads to a rapid disappearance of the Ni<sup>IV</sup> complex, yet the yields of C-C coupled products are diminished to 10–25%. The EPR spectra of the reaction mixtures reveal the formation of the Ni<sup>III</sup> complex **2<sup>+</sup>** in up to 50% yield, that could form upon the comproportionation of **3<sup>2+</sup>** with a reductive elimination Ni<sup>II</sup> product.<sup>12</sup> However, the addition of (Et<sub>4</sub>N)Cl to **3<sup>2+</sup>** also generates the products 2-chloro-*t*-butylbenzene and neophyl chloride in 16% and 13% yield, respectively. Although the yields are low, these results suggest that both Cl-C<sub>sp2</sub> and Cl-C<sub>sp3</sub> bond formation reactions can occur, either through coordination of Cl<sup>-</sup> to the Ni<sup>IV</sup> center followed by concerted reductive elimination, or through an S<sub>N</sub>2-type reductive elimination, the latter reaction pathway being also observed by Sanford et al.<sup>7f</sup> Overall, the limited C-heteroatom bond formation reactivity of both **2<sup>+</sup>** and **3<sup>2+</sup>** may be due to their sterically hindered coordination environment, despite being quite electrophilic cationic centers.

In conclusion, reported herein are the first organometallic Ni complexes supported by a triazacyclononane-derived ligand. Moreover, use of the alkyl/aryl C-donor cycloneophyl ligand allowed the isolation of uncommon organometallic Ni<sup>II</sup>, Ni<sup>III</sup>, and Ni<sup>IV</sup> complexes. The five-coordinate Ni<sup>III</sup> complex is surprisingly stable both in solution and the solid state and exhibits limited C-C bond formation reactivity. In contrast, the six-coordinate Ni<sup>IV</sup> complex has an MeCN molecule bound to Ni and it undergoes rapid C-C bond formation upon exposure to blue LEDs. This photoreactivity may have important mechanistic implications for the recently developed dual Ni/photoredox catalytic systems

proposed to involve high-valent organometallic Ni intermediates. Furthermore, the  $(\text{Me}_3\text{tacn})\text{Ni}^{\text{II}}(\text{cycloneophyl})$  complex undergoes oxidative addition with alkyl halides, as well as rapid oxidation by  $\text{O}_2$ , to generate detectable  $\text{Ni}^{\text{III}}$  and  $\text{Ni}^{\text{IV}}$  intermediates and followed by reductive elimination to form new C-C bonds. Current studies are focused on taking advantage of the ability of the  $\text{Me}_3\text{tacn}$  ligand to stabilize high-valent Ni species and employ such organometallic Ni complexes in transformations involving rapid oxidative addition and/or aerobic oxidation steps for catalytic C-C and C-heteroatom bond formation reactions.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10303.

Experimental details (PDF)

Crystallographic data (TXT)

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### Notes

The authors declare no competing financial interest.

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