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Oxidatively-induced aromatic cyanation mediated by Ni(III)<sup>†</sup>Wen Zhou,<sup>a</sup> Nigam P. Rath<sup>b</sup> and Liviu M. Mirica<sup>\*a</sup>

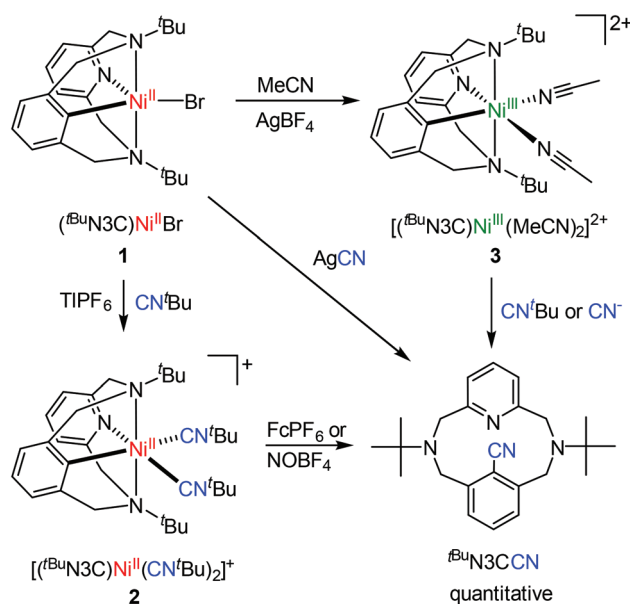
A Ni(II) complex with two *t*-butylisocyanide ligands supported by a N3C<sup>-</sup> type tetradentate ligand was synthesized and characterized. Quantitative generation of the aromatic cyanation product, <sup>t</sup>BuN3C-CN, is observed by reacting this Ni(II) complex with 1 equiv. of an oxidant. Reactivity studies suggest that this oxidatively-induced cyanation involves a heterolytic cleavage of the N-<sup>t</sup>Bu bond and is mediated by Ni(III).

Aromatic cyanation is of great importance as aryl nitriles are integral parts of functional materials, natural products, and pharmaceuticals.<sup>1–3</sup> In addition, the cyano group in organic synthesis can be easily transformed into a variety of functional groups such as amines, amides, ketones or aldehydes.<sup>4,5</sup> Thus, methods of introducing cyano groups into arenes are of great interest. However, traditional approaches such as the Sandmeyer<sup>6</sup> and Rosenmund-von Braun reactions<sup>7,8</sup> usually involve harsh reaction conditions and exhibit limited functional group tolerance. Recently, alternative approaches of transition metal-catalyzed cyanations of arenes have been developed that employ palladium<sup>1,9</sup> or ruthenium complexes<sup>10–12</sup> as catalysts. Also, examples of Ni-catalyzed cyanation reactions involving Ni(0)<sup>13</sup> and Ni(II)<sup>14</sup> oxidation states have been reported, including the reversible cleavage of carbon–cyano bonds in aromatic nitriles through oxidative addition mediated by Ni(0).<sup>15–18</sup> In contrast, no examples of high-valent Ni-mediated cyanation reactions have been published to date, although high-valent Ni(III)<sup>19–21</sup> and Ni(IV)<sup>22,23</sup> complexes have been proposed recently to promote carbon–carbon or carbon–heteroatom bond formation through reductive elimination.

As our group has successfully employed the tetradentate ligand <sup>t</sup>BuN3C<sup>-</sup> to isolate organometallic Ni<sup>III</sup> complexes that

are stable at RT,<sup>20</sup> we set out to study the possibility of Ni<sup>III</sup>-mediated aromatic cyanation reactions. Reported herein is the synthesis, characterization, and reactivity of organometallic Ni(II)-isocyanide complexes that undergo an aromatic cyanation reaction upon addition of an oxidant, suggesting the involvement of Ni<sup>III</sup> intermediates. As this oxidatively-induced aromatic cyanation is rapid and quantitative at RT, we hope that this communication could lead to additional studies on high-valent Ni-mediated cyanation reactions.

Complex (<sup>t</sup>BuN3C)Ni<sup>II</sup>Br (**1**) was prepared following a previously published literature procedure.<sup>20</sup> Debromination of **1** with 1 equiv. of TlPF<sub>6</sub> in the presence of 2 equiv. of *t*-butylisocyanide (CN<sup>t</sup>Bu) in THF leads to the generation of the complex [(<sup>t</sup>BuN3C)Ni<sup>II</sup>(CN<sup>t</sup>Bu)<sub>2</sub>]PF<sub>6</sub> (**2**) at RT (Scheme 1). Complex **2** is paramagnetic with an effective magnetic moment  $\mu_{\text{eff}}$  of 2.89  $\mu_{\text{B}}$



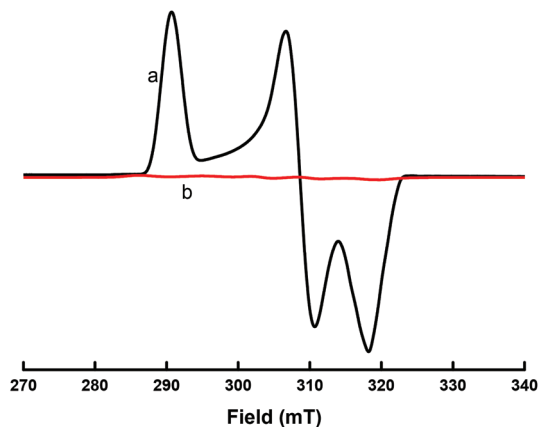
**Scheme 1** Synthesis of complexes **1–3** and oxidatively induced cyanation reactivity.

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**Fig. 2** The experimental EPR spectra of **3** (a, black) and after addition of  $\text{CN}^t\text{Bu}$  (b, red) in  $n\text{PrCN}$  at 77 K. Simulation using the following parameters:  $g_x = 2.236$ ;  $g_y = 2.105$ ;  $g_z = 2.041$  ( $A_{2N} = 13.5$  G).

support an oxidatively-induced cyanation reaction involving the proposed  $\text{Ni}^{\text{III}}$  intermediate **4**. Moreover, when **3** is reacted with 2 equiv. of KCN, the quantitative generation of  $^t\text{BuN}_3\text{CCN}$  is observed within 2 hours (Table 1, entry 4), supporting Zargarian's decomposition mechanism of  $\text{CN}^t\text{Bu}$  and the possible involvement of intermediate **5**. This also suggests that **5** most likely contains two cyanide ligands, although the presence of only one cyanide group cannot be excluded. In contrast, when **1** was reacted with 2 equiv. of KCN under the same conditions, no cyanation product was observed, however,  $^t\text{BuN}_3\text{CCN}$  was generated quantitatively when **1** was reacted with 2 equiv. of  $\text{AgCN}$  in  $\text{MeCN}$  at RT. In the latter case,  $\text{Ag}^+$  serves as both the debromination reagent and the oxidant to promote the cyanation reaction. Overall, the results above strongly support that the oxidatively-induced cyanation is mediated by  $\text{Ni}^{\text{III}}$ .

In conclusion, the first oxidatively-induced aromatic cyanation reaction mediated by  $\text{Ni}^{\text{III}}$  is reported. Both isocyanide and cyanide can serve as the cyano source. In contrast to the other reported cyanation reactions mediated by low-valent Ni systems, this oxidatively-induced aromatic cyanation is rapid and quantitative at RT.

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