Indirect evidence for a Ni^{III}-oxyl oxidant in the reaction of a Ni^{II} complex with peracid

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The reaction of a Ni^{II} complex and *meta*-chloroperoxybenzoic acid (*m*-CPBA) resulted in the formation of a long-lived Ni^{III}–chlorobenzoate complex that is a capable hydrocarbon oxidant. Analysis of the post-reaction decay products showed the formation of oxidised derivatives of the supporting ligand (a benzoxazine), and heterolytic O–O bond scission in *m*-CPBA. This evidence indicates formation of a more potent transient Ni^{III}–oxyl species, which was further supported by DFT calculations.

The study of high-valent transition metal oxidants has attracted recent interest, largely because of their postulated role as highly reactive intermediates in several industrially and biologically relevant oxidation processes.[1] Nickel-oxo (Ni=O) and -oxyl (Ni–O$^{\bullet}$) species have been invoked as the putative oxidants in nickel-catalysed oxidation reactions. Ni=O complexes have been predicted to be the most reactive in a series of metals towards the oxidation of CH_4,[2] although experimental insight into such species is limited.

Early mechanistic studies on Ni-catalysed epoxidation reactions proposed Ni^{IV}=O as an oxidising reagent, on the basis of analysis of product distribution and side reactions.[3] More recently, Itoh and Palaniandavar have demonstrated Ni-catalysed alkane oxidations, and suggested a Ni^{II}–O$^{\bullet}$ or Ni^{III}=O oxidant.[4] Several bis-μ-oxo-Ni^{III}_2 have been reported,[5] but terminal Ni–O$^{\bullet}$ or Ni=O are still largely unknown. The reactions of Ni^{II} complexes with peracids have yielded highly reactive but poorly-defined species, postulated to be Ni^{III}-O(X)[6] or Ni^{III}–O$^{\bullet}$.[7] Itoh and co-workers recently demonstrated the formation of a highly unusual Ni^{II}-aminoxyl radical from the reaction between a Ni^{II} complex and peracid.[8] We recently reported well-characterised examples of Ni^{III}-oxygen adducts, that were proficient hydrogen atom transfer (HAT) reagents.[9] Further exploration of the active oxidants formed in the catalytic reactions would yield precious insights into their mechanisms of oxidation. Herein, we explore the reaction of a Ni^{II} complex (**1**, Scheme 1) towards *meta*-chloroperoxybenzoic acid (*m*-CPBA), and provide evidence for the formation of a transient high valent Ni^{III}–O$^{\bullet}$ oxidant, and trap a thermodynamically more stable Ni^{III}–carboxylate product.

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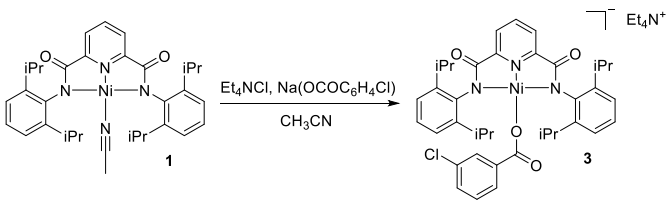
$[Ni^{II}(NCCH_3)(L)]$ (**1**, Scheme 1) was synthesised by deprotonating *N,N'*-(2,6-di*iso*propylphenyl)-2,6-pyridinedicarboxamide (LH_2) with NaH (2 eq.) in THF, and reacting the resulting mixture with $[Ni^{II}(OTf)_2]$, (OTf = trifluoromethanesulfonate). Work-up and re-crystallisation from CH_2Cl_2/diethylether (Et_2O) afforded brown/red crystals of **1**. This replicates a procedure employed for the preparation of $[Ni^{II}(NCCH_3)(L^*)]$ (L* = *N,N'*-(2,6-dimethylphenyl)-2,6-pyridinedicarboxamidate).[9b] Structural assignment and characterisation were achieved by nuclear magnetic resonance (NMR), Fourier transform infra-red (FT-IR), and electronic absorption spectroscopies and X-ray diffraction of single crystals (Figure 1, see supp. info.).



Scheme 1. Preparation of **3** by ligand exchange with **1**.

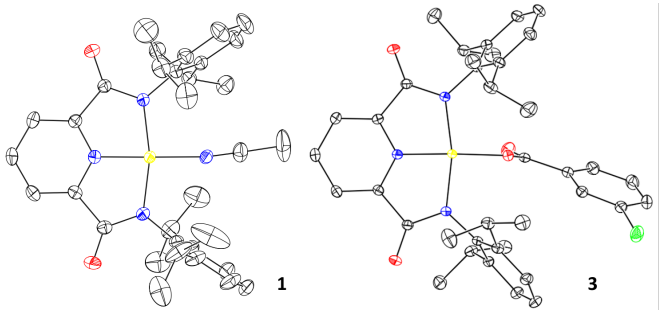


Figure 1. ORTEP plots (at 50% probability level) of the X-ray structures of **1** and **3**. Hydrogen atoms, one molecule of Et_2O in **1,** the tetraethylammonium (NEt_4) counterion and one molecule of CH_3CN in **3** have been omitted for clarity.

Upon addition of *m*-CPBA (2 equiv.) to a solution of **1** at 25 °C (0.5 mM, 2 mL, acetone or CH_3CN), a colour change from orange to dark purple occurred. The maximum yield of the purple species, on the basis of the intensity of the newly formed electronic absorption bands (λ_{max} = 560 nm, 760 nm (shoulder), Figure 2), was obtained after 350 s. The purple species subsequently decayed with a half-life of 2100 s at 25 °C. We previously reported that $[Ni^{III}(OX)(L^*)]$ (OX = OCO_2H, O_2CCH_3, ONO_2) complexes, displayed absorption features in the range λ_{max} = 500-900 nm.[9] The spectrum of the product of

the *m*-CPBA + **1** reaction is reminiscent of these compounds, suggesting a [Ni^{III}(OX)(L)] species had formed.

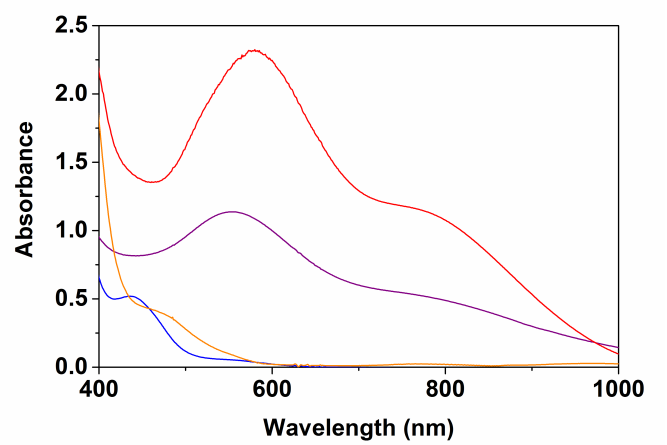


Figure 2. Electronic absorption spectra of **1** (0.5 mM, acetone, 25 °C, blue trace) and the same solution after addition of *m*-CPBA (2 equiv., 25 °C, purple trace); **3** (0.5 mM, acetone, -80 °C, orange trace) and of the oxidation product **2** resulting from the addition of 1 equiv. magic blue (red trace) to **3**.

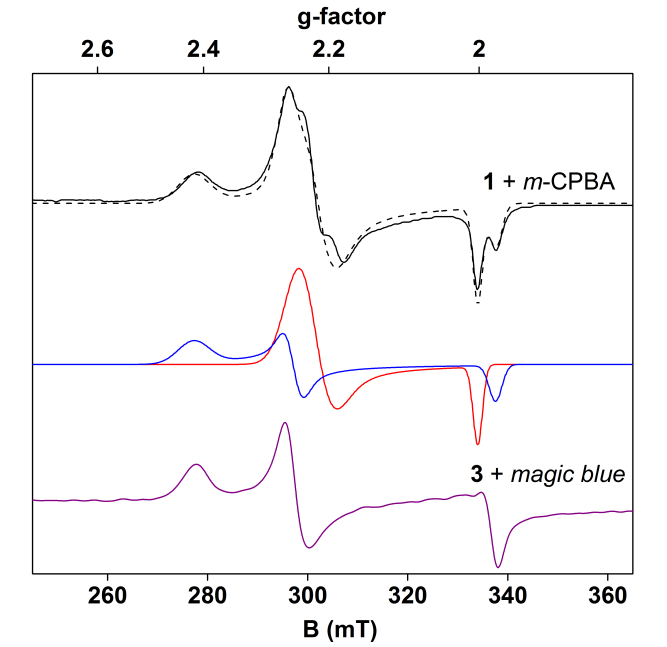


Figure 3. X-Band EPR spectra of the reaction mixture of **1** and *m*-CPBA (top, black line; dashed line = simulated spectrum) and of **3** and magic blue (purple, bottom); measured at 77 K in frozen acetone solution, 2 mW microwave power. Simulated spectra (middle) of the two individual components of the **1** + *m*-CPBA mixture are in red ($g_\perp$ = 2.23, $g_{//}$ = 2.01) and blue (g_x = 2.42, g_y = 2.26, g_z = 1.99).

Electrospray ionisation mass spectrometry (ESI-MS) analysis of the **1** + *m*-CPBA mixture revealed one peak, with an isotopic pattern typical of a Ni-containing species, at *m/*Z = 696, consistent with a [Ni(OCOC$_6$H$_4$Cl)(L)]$^+$ ion (*m/*Z 696.2139, Figure S3); presumably this species results from the ionisation of a neutral [Ni^{III}(O$_2$CC$_6$H$_4$Cl)(L)] species present in solution.

Electron paramagnetic resonance (EPR) analysis of the reaction mixture (Figure 3) displayed a signal suggestive of a mixture of two low-spin S = ½ d^7 Ni^{III} species, similar to previously reported Ni^{III} complexes.[9] We simulated the spectrum as an approximately 1:1 mixture of an axial signal ($g_\perp$ = 2.23, $g_{//}$ = 2.01) and a markedly more rhombic one (g_x = 2.42, g_y = 2.26, g_z = 1.99). Double integration of the signal and comparison with a radical standard (0.5 mM 2,2,6,6-tetramethylpiperidin-1-yl)oxyl, TEMPO) demonstrated a total yield of S = ½ species of ~50% ± 20%, on the basis of the starting concentration of **1**. On the basis of the electronic absorption, mass, and EPR spectra, and in analogy with previously studied [Ni^{III}(OX)(L*)] complexes, we postulated that one of the products was [Ni^{III}(O$_2$CC$_6$H$_4$Cl)(L)] (**2**).

We have previously demonstrated that [Ni^{III}(OX)(L*)] could be prepared by the one electron oxidation of the corresponding [Ni^{II}(OX)(L*)]$^-$.[9] In order to prepare the putative [Ni^{III}(O$_2$CC$_6$H$_4$Cl)(L)] (**2**), we synthesised Et$_4$N[Ni^{II}(O$_2$CC$_6$H$_4$Cl)(L)], **3** (Scheme 1), by the reaction of **1** with crude Et$_4$N(OCOC$_6$H$_4$Cl) (obtained by the metathesis of Et$_4$NCl and NaOCOC$_6$H$_4$Cl in CH$_3$OH, see supp. info). Single crystal X-ray diffraction measurements confirmed the structure of **3** (Figure 1), and was supported by NMR, FT-IR, and ESI-MS (see supp. info.).

The oxidation of **3** with tris(3-bromophenyl)ammoniumyl hexachloroantimonate (magic blue, 1 equiv., -80 °C, acetone) resulted in a purple solution, whose electronic absorption spectrum displayed bands at λ_{max} = 580 and 780 (shoulder) nm (Figure 2). Such features have been identified as typical for [Ni^{III}(OX)(L*)] complexes,[9] allowing us identify this compound as [Ni^{III}(O$_2$CC$_6$H$_4$Cl)(L)] (**2**). Critically, the obtained spectrum possessed a similar profile to that obtained from the **1** + *m*-CPBA mixture, with intense bands in the visible region (Figure 2, Figure S1). However, there was a shift in the λ_{max} values (20 nm), which we ascribe to the presence of at least two Ni^{III} species in the **1** + *m*-CPBA reaction mixture. The EPR spectrum of **2** (Figures 3 and S2) corresponded to a single species (g_x = 2.42, g_y = 2.26, g_z = 1.99). Such signals are typical of [Ni^{III}(OX)(L*)] species.[8] Importantly, **2** displayed EPR features identical to the rhombic component in the mixture obtained from the mixture of **1** and *m*-CPBA (Figure 3). ESI-MS analysis of pure **2** showed a peak at *m/*Z = 696, corresponding to a [**2**]$^+$ ion, which was also observed in the **1** + *m*-CPBA mixture (Figure S4). The same product (**2**, [Ni^{III}(OCOC$_6$H$_4$Cl)(L)]) was thus acquired from the one-electron oxidation of **3**, as from the reaction of **1** with excess *m*-CPBA.

The formation of **2** corresponds to a net one-electron oxidation of **1**. *m*-CPBA can react either as a two- or one-electron oxidant. Two-electron oxidation by *m*-CPBA results from heterolytic O–O bond scission, while a one-electron oxidation derives from homolytic O–O bond scission. It has been previously reported that these two occurrences can be distinguished on the basis of the *m*-CPBA-derived product.[4d,10] In the former a Ni^{IV}=O/Ni^{III}–O$^\bullet$ moiety and *meta*-chlorobenzoic acid (*m*-CBA) would form and in the latter a Ni^{III}=O/Ni^{II}–O$^\bullet$ entity and a *meta*-chlorobenzene carboxyl radical would form. The *meta*-chlorobenzene carboxyl radical would decay further by decarboxylation and further radical-type reactions to yield chlorobenzene, 1,3-dichlorobenzene, or 3-chlorophenol.[10c] We analysed the **1** + *m*-CPBA reaction mixture by GC-MS, after

acidic work-up, but didn't identify any of chlorobenzene, 1,3-dichlorobenzene, or 3-chlorophenol. Moreover, separation by column chromatography of the post-reaction mixture showed recovery of *m*-CBA in high yield (>90%, see supp. Info.). These observations suggest that the reaction of **1** with *m*-CPBA resulted in heterolytic cleavage of the O–O bond, and the formation of a Ni^{IV}=O/Ni^{III}–$O^{\bullet}$ species. **2** is not a Ni^{IV}=O/Ni^{III}–$O^{\bullet}$ complex, and therefore, we assume it derives from the transient Ni^{IV}=O/Ni^{III}–$O^{\bullet}$ species (Scheme S1).

Heterolytic O–O bond scission is further corroborated by DFT calculations (S12g/TZ2P//BP86-D_3/TDZP including COSMO solvation and ZORA relativistic effects[11]) which showed that after binding of *m*-CPBA, the O–O bond broke spontaneously resulting in a hydroxo-Ni^{IV}-carboxylate adduct (Figure S21). Subsequent spontaneous loss of *m*-CBA, after proton transfer from this adduct, lead to the formation of a Ni^{III}–$O^{\bullet}$ species (Figure S22). The Ni^{III}–$O^{\bullet}$ entity (S = 1) was found to be more stable than the Ni^{IV}=O (S = 0) by ca. 9 kcal/mol^{-1}, and carries unpaired spin density on both the metal, nitrogens, and the oxygen atom (Figure 4).

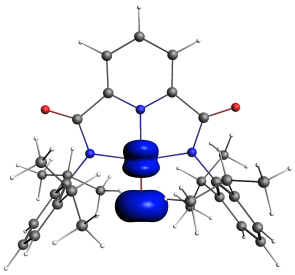


Figure 4. Spin-density of the Ni^{III}-oxyl species (obtained at S12g/TZ2P//BP86-D_3/TDZP, including COSMO solvation and ZORA relativistic effects self-consistently). The MDC-m spin-density charges indicate a total spin of 1.04 on the oxygen, 0.86 on the Ni, 0.04 on the nitrogens, with the remaining spin density scattered over the ligand.

In order to understand the **1** + *m*-CPBA reaction further we performed an acidic work-up of the reaction mixture, which caused demetallation, and isolated all organic products by column chromatography. Alongside non-derivatised ligand (LH_2) one major ligand-oxidised product (**4**) was obtained (Figure 5), as well as traces of other degradation products (see supp. info., Scheme S2). Importantly, none of these ligand-derived organic molecules were formed in the reaction of LH_2 with *m*-CPBA (room temperature, acetone) *or* from the natural decay of the Ni^{III}-carboxylate **2** (prepared with magic blue in acetone, -45 °C to room temperature).

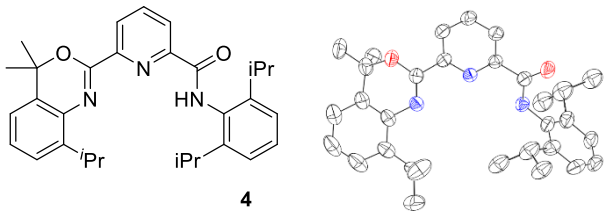
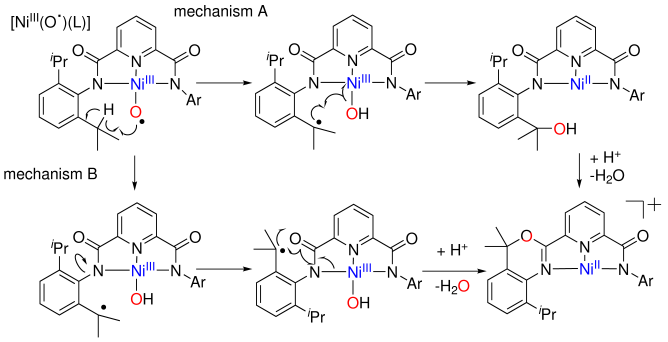


Figure 5. Structure of **4** (left), and ORTEP plot (at 50% probability level) of its X-ray structures. Hydrogen atoms and one molecule of EtOH have been omitted for clarity.

Crystals of **4** that were suitable for X-ray diffraction, obtained from ethanol/H_2O, demonstrated **4** to be a benzoxazine derivative of LH_2 (Figure 5). The yield of **4**, after column chromatography, was 35% relative to the quantity of **1**. We believe there are two plausible mechanisms for the formation of **4** in the reaction of **1** with *m*-CPBA (Scheme 2). In both cases, the putative Ni^{III}–$O^{\bullet}$ presumably abstracts a hydrogen atom from a methine *H*–*C*$(CH_3)_2$, yielding a methine radical and a Ni^{III}–OH. These products could undergo radical rebound to yield a hydroxylated species (mechanism A, Scheme 2). The hydroxylated ligand could then undergo cyclisation-condensation, to yield the benzoxazine product. Alternatively, the methine radical would react directly with the carboxamide oxygen, in a radical coupling fashion, ultimately yielding the benzoxazine (mechanism B, Scheme 2). Analogous benzo-1,3-oxazines have typically been prepared by the acid-promoted cyclisation-condensation of 2-acylamido-benzylalcohols, thus supporting mechanism A.[12] Metal based oxidants such as MnO_2 or PbO_2 have been observed to effect this kind of transformation.[13] To the extent of our knowledge, radical-type mechanisms (as in mechanism B, Scheme 2) have not been investigated.



Scheme 2. Possible mechanisms for the formation of Ni^{II}-bound benzo-1,3-oxazine **4**.

The two mechanisms can be differentiated by the source of the oxygen atom in the product: the putative Ni^{III}–$O^{\bullet}$ oxidant in case A, or the carboxamide O-atom originally present in the ligand in case B. In order to resolve this question, we performed the reaction between **1** and *m*-CPBA in the presence of $H_2{}^{18}O$ (435 equiv.). By ESI-MS, we observed ~30% ^{18}O incorporation in the benzoxazine product **4** (Figure S5). This is a strong indication that the benzoxazine is formed through the intermediate alcohol product, derived from hydroxylation by a putative Ni^{III}–$O^{\bullet}$ species, because such a species is likely to exchange with $H_2{}^{18}O$,[14] whereas the carboxamidate oxygen is unlikely to undergo exchange with $H_2{}^{18}O$.

This was supported by DFT analysis, which showed that although in the Ni^{III}–$O^{\bullet}$ species the methine hydrogen *H*–*C*$(CH_3)_2$ was further away from the oxygen atom (2.95 Å) than the methyl hydrogens HC(CH_3)*C*H_3 (2.51 Å), the barrier for HAT was found to be significantly lower for the methine (8.7 kcal·mol^{-1}) than the methyl (13.8 kcal·mol^{-1}) hydrogen atoms (Figure 6). For the subsequent step (Scheme 2), where either hydroxide radical rebound (mechanism A) or carboxamide O-

atom radical coupling (mechanism B), DFT also supports the experimental observations. The barrier for the rebound pathway was found to be substantially lower (6.5 vs. 14.4 kcal·mol^{-1}, Figure 6), corroborating the results from the isotopic labelling experiments. This allowed us to conclude that a metal-based oxidant, distinct from the Ni^{III}-containing **2**, is transiently formed when **1** was reacted with *m*-CPBA, and causes the oxidation of the supporting ligand.

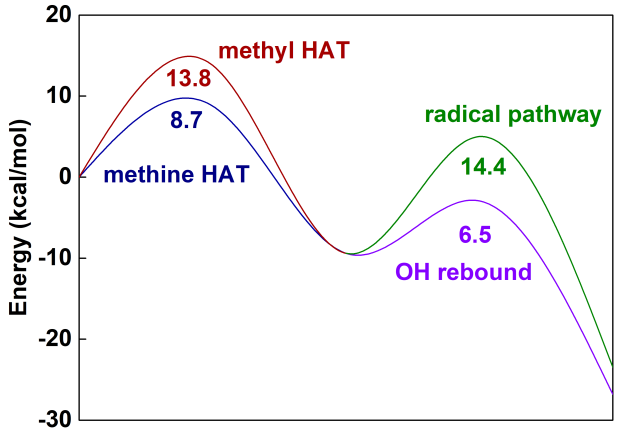


Figure 6. Energy profile (kcal·mol^{-1}, S12g/TZ2P//BP86-D$_3$/TDZP, including COSMO solvation and ZORA relativistic effects self-consistently).

The formation of degradation product **4** demonstrates that the putative Ni^{III}–O$^{\bullet}$ intermediate can be reduced by the transfer of one of the ligand's hydrogen atoms. In the reaction between **1** and *m*-CPBA, we postulate that the observed species **2** is formed by a similar process, in which an exogenous reductant, most likely the solvent, causes the conversion of Ni^{III}–O$^{\bullet}$ to Ni^{III}–OH (Scheme S1). The latter subsequently reacts with *m*-CBA via ligand exchange, to form **2**. While we cannot confirm the structure of the second EPR-active product (axial signal, Figure 3) in the reaction of **1** and *m*-CPBA, we postulate that it is a Ni^{III} species supported by the oxidised ligand (thus a Ni^{III} ion supported by **4**).

We have previously demonstrated[9b] that [Ni^{III}(OX)(L*)] complexes were not capable of oxidising cyclohexane ($BDE_{C\text{-}H}$ = 99 kcal/mol).[15] We believe the putative Ni^{III}–O$^{\bullet}$ will be a more potent oxidant than the [Ni^{III}(OX)(L*)] complexes. We reacted **1** and *m*-CPBA in the presence of excess cyclohexane (80% by volume). Cyclohexanol, the hydroxylated product of cyclohexane, was found in trace amounts by GC-MS. The putative transient Ni^{III}–O$^{\bullet}$ is thus capable of oxidising non-activated, alkylic C-H bonds, and is a superior oxidant compared to well-characterised [Ni^{III}(OX)(L*)] complexes.

In conclusion, the reaction of **1** with *m*-CPBA leads to the formation of a stable [Ni^{III}(L)($O_2C_6H_4Cl$)] species, that previous studies have shown can oxidise substrates with relatively weak C–H bonds (*e.g.* toluene). The analysis of organic decay products led us to surmise the existence of a more powerful, transient Ni^{III}–O$^{\bullet}$ precursor to this Ni^{III} species. The slow reaction of *m*-CPBA and instability of the Ni^{III}–O$^{\bullet}$ prevented its spectroscopic observation. When compared to the previously investigated [Ni^{III}(OX)(L*)], this formally Ni^{IV} entity demonstrated a greater oxidative power, reacting with strong C–H bonds in cyclohexane and effecting the degradation of the supporting ligand. The Ni^{III}–O$^{\bullet}$ mediated ligand oxidation resulted in the unexpected formation of benzoxazine **4**. Future efforts will focus on the stabilisation of the Ni^{III}–O$^{\bullet}$ to facilitate its isolation.

Conflicts of interest: There are no conflicts of interest to declare.

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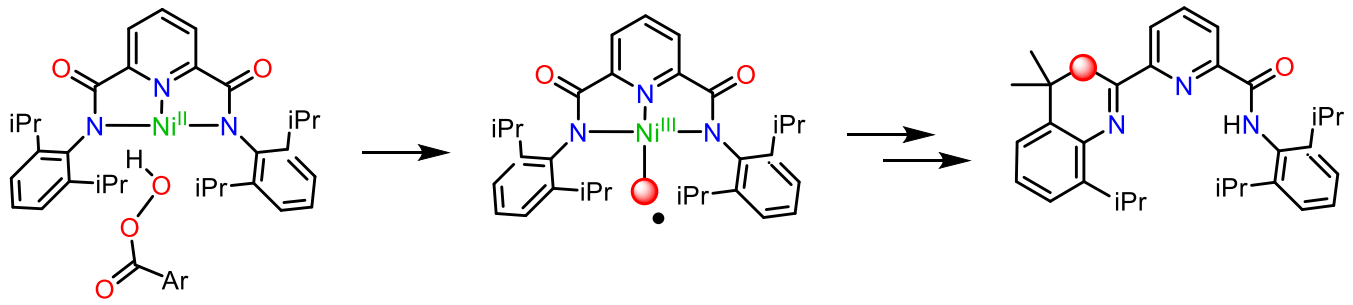
Graphical Abstract



The oxidation of a Ni^{II} complex with *m*-CPBA is shown to promote the formation of a transient Ni^{III}-$O^{\bullet}$ species. Methine C-H bond activation in the supporting ligand led to a benzoxazine product.