

Carboxamidate ligand non-innocence in proton coupled electron transfer

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ABSTRACT: Recent breakthroughs have brought into question the innocence (or not) of carboxamidate donor ligands in the reactivity of high-valent oxidants. To test the reactivity properties of high-valent carboxamidate complexes, $[\text{Ni}^{\text{II}}(\text{'Bu-terpy})(\text{L})]$ (**1**, 'Bu-terpy = 4,4',4''-tri-*tert*-butyl-2,2';6',2''-terpyridine; L = N,N'-(2,6-dimethylphenyl)-2,6-pyridinedicarboxamidate) was prepared and converted to $[\text{Ni}^{\text{III}}(\text{'Bu-terpy})(\text{L})]^+$ (**2**) using ceric ammonium nitrate. **2** was characterized using electronic absorption and electron paramagnetic resonance spectroscopies and electrospray ionization mass spectrometry. **2** was found to be a capable oxidant of phenols and through kinetic analysis was found to oxidize these substrates via a non-concerted or partially concerted proton coupled electron transfer (PCET) mechanism. The products of PCET oxidation of phenols by **2** was phenoxyl radical and the protonated form of **1**, **1H⁺**. **1H⁺** was crystallographically characterized providing convincing evidence of **1**'s ability to act as a proton acceptor. We demonstrate that the complex remained intact through a full cycle of oxidation of **1** to **2**, PCET of **2** to yield **1H⁺**, deprotonation of **1H⁺** to yield **1** followed by re-oxidation of **1** to yield **2**. The N–H bond dissociation energy of the protonated amide in **1H⁺** was determined to be 84 kcal/mol. Our findings illuminate the role carboxamidate ligands can play PCET oxidation.

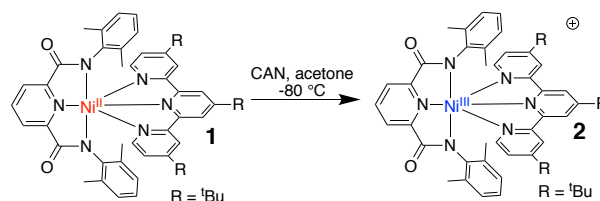
Introduction: The conversion of inert, often saturated, hydrocarbons to high value products relies on our ability to activate strong C–H bonds.^{1–7} Enzymes have evolved to employ an array of high-valent transition-metal oxidants that activate strong C–H bonds. Such species have been identified as containing terminal metal-oxo (M=O) or bridging metal-oxo entities. Great effort has been made to mimic the structural, electronic, and reactivity properties of these metal-based oxidants.^{4, 7–13} Such complexes are designed to imbue sufficient stability into meta-stable high-valent oxidants. Supporting ligands are therefore required to be excellent sigma-donors or containing anionic donors to stabilize metals in high oxidation states.

In this regard, anionic carboxamidate supporting ligands have been used with great success because of their ability to stabilize complexes with metals in high oxidation states. Pioneering work by Collins has demonstrated the stabilizing effect of anionic tetraamidomacrocyclic ligands (TAMLs) to support M=O's.^{14–15} Borovik has similarly employed anionic tris-urea ligands to support a large array of M=O's.^{16–19} Tolman has also demonstrated the use of the 2,6-pyridinedicarboxamidate for supporting high-valent Cu complexes.^{20–22} We and others found that the same ligand was ideal for trapping high-valent Ni species.^{23–30} Most recently Fukuzumi and co-workers have reported a mononuclear non-heme manganese(III)–aqua complex supported by a carboxamidate ligand that was a capable oxidant.³¹ In a similar light, Garcia-Bosch and co-worker reported another carboxamidate supported complex that facilitated the oxidation of benzylalcohol.³² There is thus a very large cohort of carboxamidate complexes that facilitate biomimetic oxidation reactions.

The high-valent oxidants tend to react with hydrocarbon C–H bonds through a proton coupled electron transfer (PCET) oxidation mechanism. PCET represents a class of C–H

oxidation reactions where a proton and electron are transferred in a non-concerted or concerted fashion.^{33–36} M=O complexes, for example, perform hydrogen atom transfer (HAT, a form of concerted PCET) of C–H bonds to yield a one-electron reduced M–O–H and a carbon based radical that will rebound to yield a hydroxylated product and two-electron reduced metal ion. The factors that determine PCET oxidation are the redox potential of the Mⁿ/M^{n–1} couple and the pK_a of the proton accepting entity. For high-valent complexes supported by neutral donor ligands (e.g. polypyridine ligands) the O-atom will always be sufficiently basic to act as a proton acceptor. We were interested in exploring the role that significantly more basic anionic donor ligands (e.g. carboxamidate, amide) may play in PCET oxidation. The recent reports by Fukuzumi, where a carboxamidate-supported Mn–OH₂ complex was surprisingly capable of HAT,³¹ and Garcia-Bosch where a carboxamidate ligand was postulated to act a proton acceptor in PCET,³² and Heyduk, who postulated that a diarylamide ligand could act as an H-atom acceptor,³⁷ heightened this interest. Herein we explore the role, if any, of the 2,6-pyridinedicarboxamidate ligand in PCET reactions.

Scheme 1. Preparation of **2** from **1**, CAN = (NH₄)₂[Ce^{IV}(ONO₂)₆].



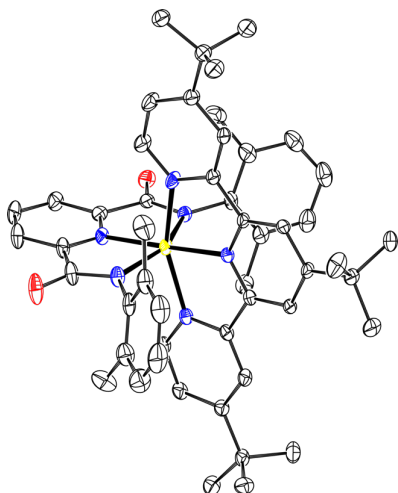


Figure 1. ORTEP plot of **1** with atomic displacement shown at 50% probability. Hydrogen atoms and three co-crystallized CH_2Cl_2 molecules omitted for clarity.

Results and discussion: $[\text{Ni}^{\text{II}}(\text{tBu-terpy})(\text{L})]$ (**1**, tBu-terpy = 4,4',4''-tri-*tert*-butyl-2,2';6',2''-terpyridine; L = N,N'-(2,6-dimethylphenyl)-2,6-pyridinedicarboxamidate, Scheme 1) was prepared from $[\text{Ni}^{\text{II}}(\text{NCCH}_3)(\text{L})]^{26}$ by ligand exchange with tBu-terpy in tetrahydrofuran (THF) (see supporting information for details). The X-ray structure of **1** demonstrated a Ni^{II} ion in a *pseudo*-octahedral geometry (Figure 1), and compared favorably with $[\text{Ni}^{\text{II}}(\text{terpy})(\text{L})]$ (terpy = 2,2';6',2''-terpyridine).³⁰ The ^1H nuclear magnetic resonance (NMR) spectrum of **1** showed broad and shifted peaks, consistent with **1** containing a paramagnetic Ni^{II} ion (Figure S1).^{30, 38} The number of resonances observed (11) was typical of a symmetric molecule, if there were asymmetry in the molecule up to 24 resonances would be expected. A magnetic moment (μ_{eff}) of $2.51 \mu_B$, was determined using the Evan's method, indicating two unpaired electrons (Figure S2).^{30, 38-39} Electrospray ionization mass spectrometry (ESI-MS) confirmed the elemental formula of **1** (observed mass = 831.39 m/z; calculated mass for **1** + H^+ = 831.39 m/z, Figure S4). We thus determined that complex **1** could be assigned the formula $[\text{Ni}^{\text{II}}(\text{tBu-terpy})(\text{L})]$ and contained a $d^8 S = 1 \text{ Ni}^{\text{II}}$ ion in a *pseudo*-octahedral ligand field.

The Ni^{II} complex **1** was oxidized to the Ni^{III} complex **2** in acetone at -80°C using ceric ammonium nitrate (CAN, $(\text{NH}_4)_2[\text{Ce}^{\text{IV}}(\text{ONO}_2)_6]$, 8 equiv., Scheme 1). The reaction was complete within 400 s. **1** displayed weak features at $\lambda_{\text{max}} = 420$ and 820 nm typical of octahedral Ni^{II} complexes.³⁰ while **2** demonstrated an intense and broad band at $\lambda_{\text{max}} = 620$ nm (Figure 2). Similar features in the visible region have been reported for octahedral Ni^{III} complexes, and analogous $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$ complexes.^{23-28, 30, 40-41} **2** could also be generated in the same yield in acetone at -80°C using the one-electron oxidant magic blue (*tris*-(4-bromophenyl)ammoniumyl hexachloroantimonate, Figure S6). ESI-MS of **2** demonstrated a new mass peak at $m/z = 830.37$ (Figure S7), which can be attributed to the $[\text{Ni}^{\text{III}}(\text{tBu-terpy})(\text{L})]^+$ ion. The combined electronic absorption and ESI-MS results led us to assign **2** the formula $[\text{Ni}^{\text{III}}(\text{tBu-terpy})(\text{L})]^+$.

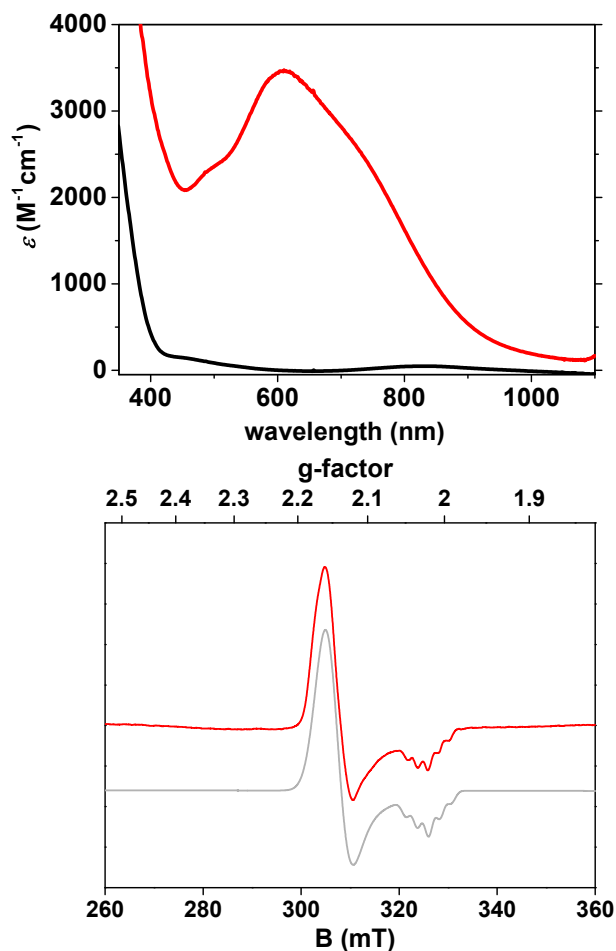


Figure 2. Top: electronic absorption spectra of **1** (black trace, 0.4 mM, acetone) and **2** (red trace, after oxidation of **1** by CAN (8 equiv.) at -80°C . ϵ calculated based on EPR yield. Bottom: X-band EPR spectrum of **2** in a frozen acetone solution (red trace) measured at 77 K, 6.35 mW microwave power with 0.3 mT modulation amplitude, and the simulated spectrum of **2** (grey trace, see the Supporting Information for simulation details).

Electron paramagnetic resonance (EPR) spectroscopy showed that **2** contained an $S = 1/2 d^7 \text{ Ni}^{\text{III}}$ species.^{40, 42-44} The EPR spectrum of **2** exhibited axial symmetry, where $g_{\perp} > g_{\parallel}$ and $g_{\text{av}} = 2.11$ (Figure 2), indicating an axially elongated octahedral geometry, with the unpaired spin density localized on the Ni ion. **2** displayed hyperfine coupling of five lines in the g_{\parallel} component, associated with coupling to two equivalent ^{14}N -donor ligands.³⁰ The EPR signal obtained for **2** was similar to those obtained for all other $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$ complexes, displaying axial symmetry and hyperfine coupling only in g_{\parallel} .^{24, 26, 28, 30} The yield of the Ni^{III} species **2** was calculated to be $70 \pm 20\%$. The obtained spectrum supported the assignment of **2** as $[\text{Ni}^{\text{III}}(\text{tBu-terpy})(\text{L})]^+$.

Complex **2** did not decay over the course of 6 h at -80°C . At 0°C **2** displayed a $t_{1/2} = 2250$ s. It was decided to explore the reactivity of **2** at -80°C to ensure no influence of self-decay on our kinetic analysis. **2** did not react with any hydrocarbons with weak C–H bonds (*e.g.* cyclohexadiene), unlike previous examples of $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$.^{24, 26, 28} In contrast, *para*-substituted 2,6-di-*tert*-butylphenol (4-X-2,6-DTBP, X = H, CH_3 , OCH_3 , tBu) and 2,4-DTBP reacted readily with **2**, allowing us to derive mechanistic insights from the kinetic analysis of these reactions (Figures S8-S16). Substrates containing relatively strong O–H

bonds such as 4-X-2,6-DTBP (where X = Cl, Br, CN, NO₂) did not react with **2** when added in 3000-fold excess. Furthermore, TEMPO-H (1-hydroxy-2,2,6,6-tetramethylpiperidine), containing a relatively weak O–H bond, reacted at such a high rate (10 equiv. reacted within 2 s, Figure S17) with **2** that accurate kinetic analysis was not possible. This demonstrated that a narrow substrate O–H bond dissociation energy (BDE_{O–H}) window existed to explore the reactivity of **2** under the experimental conditions employed.

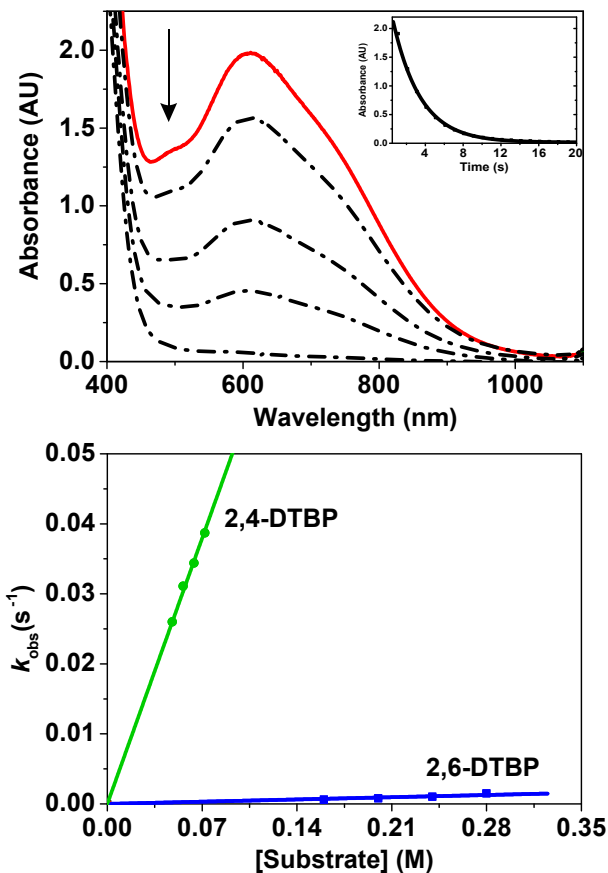


Figure 3. Top: Electronic absorption spectra demonstrating the decay of **2** (red trace) over time upon reaction between **2** and 2,4-DTBP (inset depicts decay of $\lambda_{\max} = 620$ nm feature changes against time). Bottom: Plot of observed rate versus substrate concentration for the reaction of **2** with 2,4-DTBP (green) and 2,6-DTBP (blue).

Upon reaction with 4-H-2,6-DTBP the rate of decay of the characteristic band of **2** ($\lambda_{\max} = 620$ nm) was monitored with time (see Figure 3 for typical reaction). The decay was fitted as first order to obtain a *pseudo*-first order rate constant (k_{obs}) and a plot of k_{obs} against [substrate] gave the second order rate constant for the reaction (k_2 , Figures S10-S16). A k_2 for the reaction between 4-H-2,6-DTBP and **2** of $0.004 \text{ M}^{-1}\text{s}^{-1}$ was measured at -80 °C. We also explored the reaction of **2** with 4-H-2,6-DTBP at -40 °C to allow comparison to previously reported $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$ complexes (Table 1, Figure S15). A k_2 value of $0.06 \text{ M}^{-1}\text{s}^{-1}$ for **2** at -40 °C was determined. The post reaction mixtures for this substrate were analyzed by gas chromatography mass spectrometry (GC-MS), showing peaks corresponding to 3,3',5,5'-tetra-*tert*-butyl-[1,1'-bis(cyclohexane)]-2,2',5,5'-tetraene-4,4'-dione (Figure S8). This product provides a strong indication of PCET by **2**, indicating the formation of a phenoxyl radical that underwent

radical-radical coupling. A kinetic isotope effect (KIE) of 2.1 was measured for the reaction between **2** and 4-*H/D*-2,6-DTBP (Figure S16) which compares favorably to other examples of $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$ complexes oxidatively activating O–H and C–H bonds.^{24, 26, 28, 45} These combined observations suggest the rate-limiting step involved the phenolic O–H hydrogen atom. The products of the reaction suggest the formation of a phenoxyl radical in these reactions, suggesting some form of PCET oxidation by **2**.

Table 1. Phenol BDE_{O–H}, E_{OX} , and k_2 values.

4-X-2,6-DTBP	BDE (kcal/mol) ⁴⁶	$E_{\text{OX}}(\text{V})$ vs Fc/Fc ⁺ ⁴⁷⁻⁴⁸	σ_p ⁴⁹	k_2 ($\text{M}^{-1}\text{s}^{-1}$)
OCH ₃	78.3	0.53	-0.78	89.0
CH ₃	81.0	0.90	-0.31	0.195
C(CH ₃) ₃	81.2	0.93	-0.26	0.165
H	82.1	1.07	0	0.004
2,4-DTBP	82.1	-	-	0.542

The k_2 values determined for the substituted 4-X-2,6-DTBP (X = H, CH₃, OCH₃, ^tBu) that did react with **2** spanned a very wide range (Table 1), with 4-OCH₃-2,6-DTBP (containing the weakest BDE_{O–H}) reacting extremely rapidly, while 4-H-2,6-DTBP (strongest BDE_{O–H}) demonstrated relatively slow reactivity. Furthermore, a k_2 of $0.54 \text{ M}^{-1}\text{s}^{-1}$ was measured for the reaction between **2** and 2,4-DTBP at -80 °C (Figure 3). This represents a 135-fold enhancement for the sterically less encumbered 2,4-DTBP, with both substrates displaying similar BDE_{O–H}.⁵⁰ A plot of $\log(k_2)$ against substrate BDE_{O–H} of the 4-X-2,6-DTBP showed a linear relationship with a negative slope (Figure 4, Table 1). Deriving Gibbs free energies from the k_2 values using the Eyring equation, a $\Delta G^\ddagger/\Delta(\text{BDE})$ value of 0.99 was obtained (Figure S18). A linear Hammett plot was also produced from this data (Figure 4), demonstrating a large and negative slope of $\rho = -5.5$. A plot of $(RT/F)\ln(k_2)$ against E_{OX} (R = gas constant, T = temperature, F = Faraday constant), was also linear with a negative slope with a value of -0.29 (Figure 4).

Discussion on reactivity properties and exploration of mechanism: In order to put the reactivity of **2** into context, we explored the reaction of **2** with 2,6-DTBP at -40 °C to compare it to previously reported $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$ (Table 2: $k_2 = 0.06 \text{ M}^{-1}\text{s}^{-1}$ for **2** at -40 °C; $k_2 = 0.13\text{-}1.96 \text{ M}^{-1}\text{s}^{-1}$ for $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$ at -40 °C). The rate at which **2** reacted would indicate that introducing a neutral donor (^tBu-terpy), unable to act as an H⁺-acceptor, inhibited its reactivity relative to the previously reported $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$ complexes that had anionic H⁺-accepting ancillary donors (Cl[−], OAc[−], ONO₂[−]). Furthermore, at -40 °C **2** was unreactive to hydrocarbons with weak C–H bonds (e.g. 9,10-dihydroanthracene, 1,4-cyclohexadiene), whereas the other $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$ (X = Cl, OAc) were capable of oxidizing such substrates. This demonstrates a marked difference in reactivity properties for **2**: **2** was unable to activate weak C–H bonds, thus rendering it thermodynamically less reactive than previous examples of $[\text{Ni}(\text{X})(\text{L})]$ complexes where X was an anionic donor; **2** was also a kinetically less reactive oxidant of phenols than those complexes with anionic ancillary ligands. Thus, although **2** was a capable oxidant, it should be emphasized that

it was thermodynamically and kinetically less reactive than analogous complexes with ancillary proton acceptors.

2 reacted with 2,4- and 2,6-DTBP with a 135-fold enhancement in reactivity for the sterically less encumbered 2,4-DTBP substrate. Such rate enhancement has previously been ascribed to concerted PCET reactions with phenols (HAT), although is considerably higher than previous examples (values in the range ~30-70).^{24, 26, 28, 50-51} As described below the mechanism by which **2** reacted with phenols may be a non-concerted or partially concerted PCET. The large steric effect observed for these substrates thus could indicate alternative forms of PCET and should not be ascribed simply to concerted PCET. The difference in relative rates could also indicate a difference in reaction mechanism between the two substrates, but we have no evidence for such a change. **2** displayed a KIE value of 2.1 for the reactions between **2** and 4-*H/D*-2,6-DTBP. This compared favorably with many analogous M–O–X oxidants, including all members of the [Ni^{III}(X)(L)] family, where low KIE values (< 7) have been observed in the vast majority of cases.^{24, 26, 28, 45} This observation simply confirms PCET as rate-limiting but does not provide any insight into whether it was concerted or not.

Table 2. Comparison of kinetic and thermodynamic data for a series of [Ni^{III}(X)(L)]^{0/+} complexes.

[Ni(X)(L)] ^{+/0}	k_2 (M ⁻¹ s ⁻¹) ^a	KIE ^b	$\Delta G^\ddagger/\Delta(\text{BDE})$	(RT/F)ln(k_2)/ E_{ox}	Ref.
2	0.06	2.1 ^c	0.99 ^c	-0.29 ^c	This work
Cl	0.18	2.4 ^d	0.66 ^d	-0.15 ^d	28
O ₂ CCH ₃	0.13	2.1 ^d	0.31 ^e	-	26
ONO ₂	1.96	-	-	-	26

All reactions performed in acetone. ^a oxidation of 2,6-DTBP at -40 °C; ^b for oxidation of H- or D-2,6-DTBP; ^c measured at -80 °C; ^d measured at -40 °C; ^e determined for C–H bond activation at 25 °C.

The large $\Delta G^\ddagger/\Delta(\text{BDE})$ value (0.99), Hammett ρ -value (-5.5), and the slope of the plot of (RT/F)ln(k_2) against substrate E_{ox} (-0.29), all suggested a non-concerted PCET mechanism or a mechanism where electron transfer (ET) played a greater role in PCET. First, the large $\Delta G^\ddagger/\Delta(\text{BDE})$ value (0.99) is well in excess of the ideal value predicted by Marcus theory (0.5) and is beyond the range where concerted PCET (HAT) has previously been ascribed (0.15 to 0.7).^{34, 36} For analogous complexes supported by L, we previously observed $\Delta G^\ddagger/\Delta(\text{BDE})$ values of 0.31 ([Ni^{III}(OAc)(L)], hydrocarbon oxidation) and 0.66 ([Ni^{III}(Cl)(L)], phenol oxidation) where concerted PCET (HAT) was implicated in both cases. We conclude that the large $\Delta G^\ddagger/\Delta(\text{BDE})$ value is indicative of a mechanism of O–H bond activation that does not involve concerted PCET, or involves partially concerted (partial transfer of charge simultaneous with PT), or involves PCET towards different locations (so-called multi-site PCET).⁵²⁻⁵³

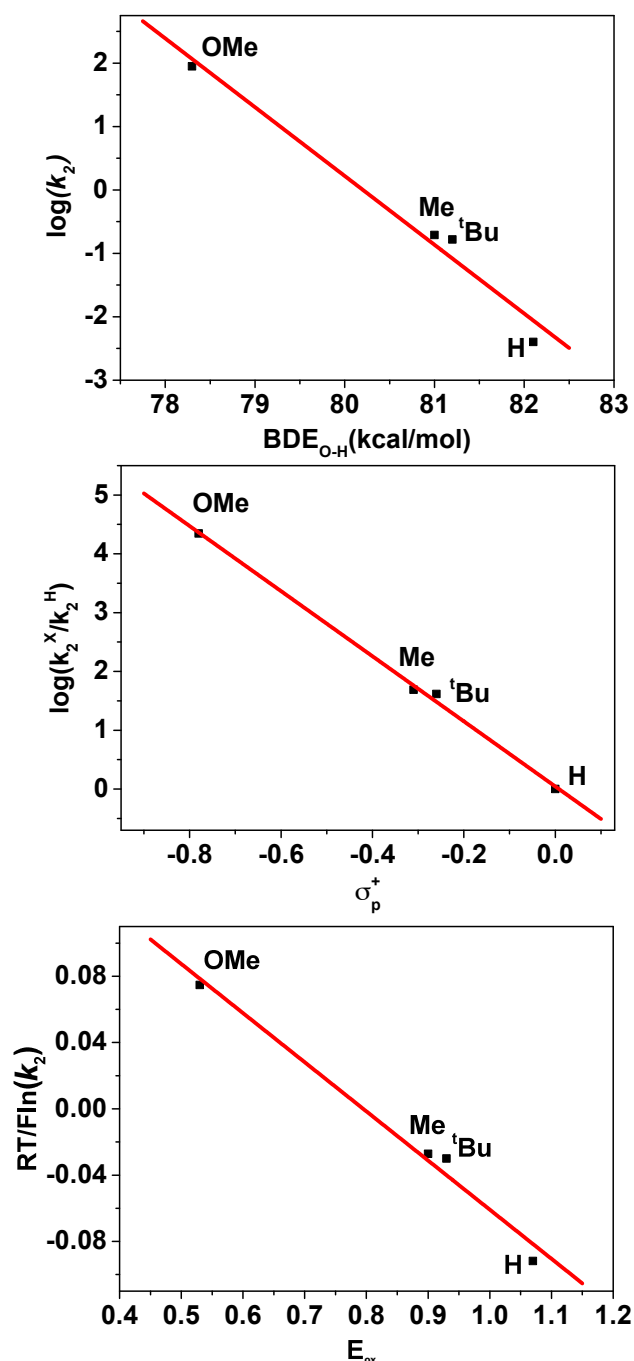


Figure 4. Kinetic data for the reaction between **2** and 4-*X*-2,6-DTBP substrates in acetone: **top**: plot of $\log(k_2)$ versus substrate $\text{BDE}_{\text{O-H}}$; **middle**: Hammett plot, slope = -5.5; **bottom**: plot of (RT/F)ln(k_2) against substrate E_{ox} , slope = -0.29. *Note*: for *p*-Cl/Br/CN/NO₂-2,6-DTBP there was no reaction with **2**, whereas for TEMPO–H, very high rates prevented accurate determination of k_2 .

Second, the slope of the (RT/F)ln(k_2) against substrate E_{ox} plot (-0.29) was higher than would be expected for a concerted PCET reaction. For rate limiting electron transfer (ET), a slope of -0.5 was predicted.^{28, 54-57} If proton transfer (PT) was rate limiting this slope would be closer to -1.0. If the rate determining step was concerted PCET a slope closer to zero is expected. Our results suggest either concerted PCET or rate-limiting ET for the reaction between **2** and phenols, because the slope was closer to the ideal value for rate-limiting ET. We

previously ascribed a slope of 0.18 for $[\text{Ni}^{\text{III}}(\text{Cl})(\text{L})]$ to concerted PCET.²⁸ It is possible that ET was not exclusively rate limiting, with ET and PT demonstrating similar rates. It has previously been suggested that, in cases where the slope is less than -0.5, a partial transfer of charge may occur in the rate-limiting step.^{47, 58} It is also possible that multi-site PCET, where the proton and electron are delivered to different locations, resulted in intermediary (partially concerted) PCET kinetic behavior.⁵²⁻⁵³

The mechanism by which **2** reacted with phenols appeared to be different to previously reported $[\text{Ni}^{\text{III}}(\text{X})(\text{L})]$ oxidants, all of which displayed $\Delta G^\ddagger/\Delta(\text{BDE})$ values closer to 0.5 and $(\text{RT}/F)\ln(k_2)$ against substrate $E_{1/2}$ slopes closer to zero, indicating concerted PCET (Tables 1&2). In those cases, anionic ancillary ligands were deemed to be acting as proton acceptors forming acetic acid and HCl for $[\text{Ni}^{\text{III}}(\text{OAc})(\text{L})]$ and $[\text{Ni}^{\text{III}}(\text{Cl})(\text{L})]$, respectively. The Ni atom was deemed to be accepting the electron. For **2** there are multiple plausible proton acceptor groups (carboxamidate O- or N-atoms, pyridine N-atoms), with the Ni atom acting as the likely electron acceptor.

The fact that **2** was capable of oxidizing phenols indicated that the carboxamidate ligand L may be acid/base non-innocent in PCET reactions, with either N- or O-atoms acting as potential H^+ -acceptors. To probe this further, we explored the acid/base chemistry of complexes **1** and **2**. Ni^{II} complex **1** did not react with any of the (weakly acidic) 4-X-2,6-DTBP substrates (Figure S19), demonstrating that **2** was the only entity reacting with these phenols. Upon exposure of **1** to two equiv. of the more acidic pyridinium triflate (PyHOTf) at -40°C a shift in the near-infra-red (near-IR) features to lower energy was observed by electronic absorption spectroscopy (Figures 6, S20, new species defined as $\mathbf{1H}^+$). Such near-IR features have been attributed to a $d^8 \text{Ni}^{\text{II}}$ ion in an octahedral ligand field. The preservation of these features indicated that $\mathbf{1H}^+$ maintains an octahedral 6-coordinate environment.³⁰ The same shift was observed when HCl (one equiv.) was used as a H^+ -donor (Figure S21), indicating that the same product was obtained with different H^+ -donors. This would suggest that the protonation reaction does not involve replacement of one of the ligands by ^-OTf (from PyHOTf) or ^-Cl (from HCl).

Satisfyingly, we were able to synthesise and isolate $\mathbf{1H}^+$ in the solid state by reacting **1** with two equivalents of pyridinium triflate in CH_2Cl_2 followed by precipitation with excess THF (see supporting information for details). $^1\text{H-NMR}$ analysis comparison of **1** and $\mathbf{1H}^+$ showed the conversion of a highly symmetric paramagnetically shifted spectrum for **1** to another paramagnetically shifted spectrum with much lower symmetry for $\mathbf{1H}^+$ (Figure S22), indicating mono-protonation of the ligand. Fourier transform infra-red (FT-IR) analysis of $\mathbf{1H}^+$ showed a new feature at $\nu = 3235 \text{ cm}^{-1}$ which can be ascribed to an N-H vibrational mode (Figure S23). This feature was absent in **1** (Figure S4), however such N-H resonances were observed in FT-IR spectra of LH_2 (Figure S24). ESI-MS confirmed the elemental formula of $\mathbf{1H}^+$ (Figure S25).

Single crystals of $\mathbf{1H}^+$ were obtained by slow diffusion of THF into a CH_2Cl_2 solution of $\mathbf{1H}^+$ (Figure 5). $\mathbf{1H}^+$ displayed a *pseudo*-octahedral geometry around the Ni^{II} centre with both pyridine dicarboxamide and ^tBu-terpy ligands still bound to the Ni^{II} ion. However, the binding mode of the pyridine dicarboxamide was through the central pyridine donor, one carboxamidate N-donor, and one carboxamide O-donor. One of the carboxamidate N-donors was protonated and no longer bound to the metal ion. The C-O and C-N bond lengths of the

reconfigured carboxamide were consistent with an amide (1.240(3) Å and 1.332(3), respectively). A triflate counterion balanced the charge on the complex ion, confirming no change in the overall oxidation state of the complex during protonation. The X-ray crystal structure of $\mathbf{1H}^+$ confirmed the H^+ -acceptor capability of the 2,6-pyridinecarboxamidate ligand in complex **1**.

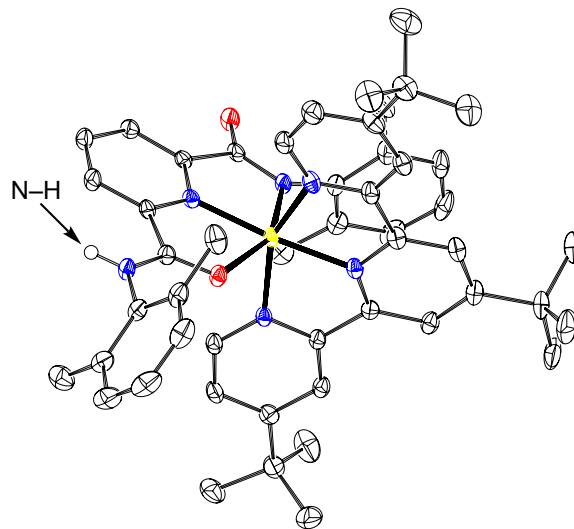


Figure 5. ORTEP plot of $\mathbf{1H}^+$ with atomic displacement shown at 50% probability. Hydrogen atoms (apart from the amide N-H), trifluoromethane sulfonate counterion, and co-crystallized CH_2Cl_2 and THF molecules omitted for clarity.

Critically, the protonation of **1** to yield $\mathbf{1H}^+$ was readily reversed by the addition of a slight excess of base (KOH dissolved in CH_3OH , Figures 6, S27). We tested the reactivity of a series of bases towards $\mathbf{1H}^+$ in CH_3CN and found that the following bases reacted with $\mathbf{1H}^+$ to yield **1**: potassium *tert*-butoxide, KOH, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine (NEt_3), *tert*-butylamine, 4-N,N-dimethylaminopyridine (DMAP), benzylamine, imidazole. The latter five bases reacted slowly with respect to the former three consistent with their relative pK_a values in CH_3CN (Table S2). In contrast the following did not react with $\mathbf{1H}^+$: 2,6-lutidine, aniline, pyridine. This allowed us to estimate the pK_a of the proton in $\mathbf{1H}^+$ to be 15.00 in CH_3CN (Table S2). We then proceeded to more accurately measure the equilibrium constant (K_a) for the reaction $\mathbf{1} + \text{PyHOTf} \rightarrow \mathbf{1H}^+ + \text{Py}$ in order to accurately determine pK_a for $\mathbf{1H}^+$. Titration of **1** with PyHOTf showed a linear decay of the electronic absorption features associated with **1** (Figure S28). However, a plot of $[\mathbf{1H}^+][\text{Py}]/[\mathbf{1}]$ against $[\text{PyHOTf}]$ was not linear, and therefore the slope of the plot and thus K_a could not be determined (Figure S29, see supporting information for details on calculations). The observed non-linear plot suggests that the reaction between **1** and PyHOTf to yield $\mathbf{1H}^+$ was not a simple A-to-B conversion. An isosbestic point was not observed during the titration confirming that this was not a clean **1** to $\mathbf{1H}^+$ conversion (Figure S30). Similar results were obtained for the reverse reaction between $\mathbf{1H}^+$ and KOH (Figure S31). This observation is not unexpected given that the N-atom in **1** must undergo protonation, dissociation from the metal, and rotation around the $\text{C}_{\text{ketone}}\text{-N}$ bond (in no particular order) to yield $\mathbf{1H}^+$.

No reaction was observed upon the addition of CAN to $\mathbf{1H}^+$, indicating that **2** could not be generated from $\mathbf{1H}^+$. CV analysis of $\mathbf{1H}^+$ demonstrated a chemically irreversible wave at 0.93 V

versus Fc/Fc^+ (Figure S26) which is significantly shifted by 0.74 V with respect to **1** (0.19 V versus Fc/Fc^+ , Figure S5). However, **2** was formed in 75% yield when KOH was added to $\mathbf{1H}^+$ followed by CAN (Figures 6, S32). Furthermore, **2** was unreactive towards PyHOTf under the same conditions, showing that it was not capable of acting as a H^+ -acceptor with weak acids. **2** reacted with aqueous HCl yielding a featureless electronic absorption spectrum (Figure S33). Addition of KOH (dissolved in CH_3OH) resulted in the reformation of **2** (Figure S34). Complex **2** was thus capable of acting as a reversible H^+ -acceptor, however, only very strong acids reacted with **2** meaning **2** was unlikely capable of deprotonating 4-X-2,6-DTBP substrates.

Having established that $\mathbf{1H}^+$ was a stable species, it was important to establish its role, if any, in the PCET oxidation of phenols. Analysis of the **2** + 4-OCH₃-2,6-DTBP post-reaction mixture displayed features that were the same as those obtained for $\mathbf{1H}^+$ (Figure 7). In this instance $\mathbf{1H}^+$ was obtained in 70% yield with respect to **2**, as determined by electronic absorption spectroscopy. The same absorption spectrum was obtained for all other substrates (4-X-2,6-DTBP and TEMPO-H, Figure S35). In these spectra, the characteristic electronic absorption features attributed to **1** were absent. No evidence for Ni^{III} (no intense bands in the UV-vis region, EPR silent) was present while ^1H NMR showed only resonances for the substrate (Figure S36). ESI-MS analysis displayed mass ions for $\mathbf{1H}^+$, the substrate, the oxidized product, and fragments of the complex (*i.e.* $\{\text{Ni} + \text{Bu-terpy}\}^+$, $\{\text{Ni} + \text{L}\}^+$, Figure S37). No evidence for oxidative ligand degradation was observed. These observations indicate the $\mathbf{1H}^+$ was the sole product of the reaction between **2** and 4-OCH₃-2,6-DTBP. Addition of KOH to the post reaction mixture yielded absorption features attributed **1** (Figure S31), which could in turn be converted back to **2** again by addition of CAN (Figure S32). These observations demonstrate that $\mathbf{1H}^+$ was the product of PCET oxidation of 4-X-2,6-DTBP by **2**. Furthermore, it demonstrates that the complex remained intact through a full cycle of oxidation of **1** to **2**, PCET of **2** to yield $\mathbf{1H}^+$, deprotonation of $\mathbf{1H}^+$ to yield **1** followed by re-oxidation of **1** to yield **2**.

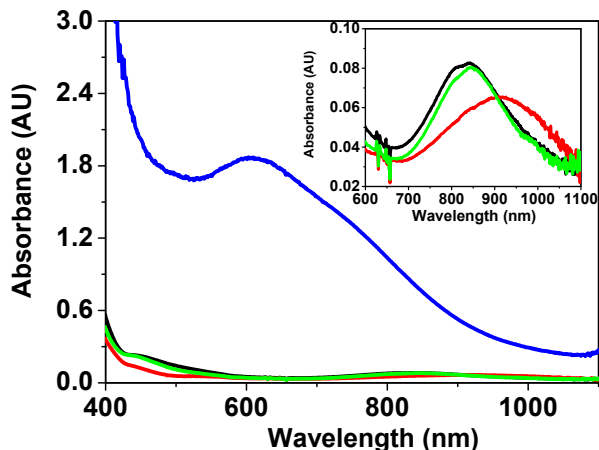


Figure 6. Complex **1** (black trace), complex $\mathbf{1H}^+$ (red trace, **1** + pyridinium (two equiv.)), the re-formation of **1** from the reaction between $\mathbf{1H}^+$ and KOH (green trace, three equiv. KOH), and **2** (blue trace) from the reaction where CAN (8 equiv.) was added to the **1** + pyridinium + KOH mixture.

Our kinetic analysis suggested that $\mathbf{1H}^+$ may have reacted through non-concerted or partially concerted PCET, we therefore decided to assess the driving force for the reaction

between **2** and 4-X-2,6-DTBP should the reaction in fact be concerted PCET (homolytic O–H bond cleavage). This can be analyzed by determining the N–H bond dissociation enthalpy ($\text{BDE}_{\text{N-H}}$) of $\mathbf{1H}^+$. We calculated the $\text{BDE}_{\text{N-H}}$ using methods for metal-based oxidants in PCET pioneered by Mayer and co-workers.^{36,53} The following formula was used to calculate $\text{BDE}_{\text{N-H}}$: $\text{BDE}_{\text{N-H}} = 1.37(\text{p}K_{\text{a}}) + 23.06(E_{1/2}) + C_{\text{H,CH}_3\text{CN}}$; yielding a $\text{BDE}_{\text{N-H}}$ for $\mathbf{1H}^+$ of ~ 84 kcal/mol ($\text{p}K_{\text{a}} = 15.00$; $E_{1/2} = 0.19$ V). The error in this measurement is likely quite high (± 3 kcal/mol) given that the $\text{p}K_{\text{a}}$ was estimated as described above. It is important to note that the reactivity studies were performed in acetone while $\text{BDE}_{\text{N-H}}$ was calculated in CH_3CN because we could not determine the $\text{Ni}^{\text{II/III}} E_{1/2}$ accurately in acetone. Furthermore, the non-linear behavior observed for the reaction between **1** and PyHOTf suggested that other species may form prior to $\mathbf{1H}^+$ in the protonation of **1**, meaning the $\text{BDE}_{\text{N-H}}$ in $\mathbf{1H}^+$ may not be a driver for this reaction. Nonetheless, the calculated $\text{BDE}_{\text{N-H}}$ value is consistent with the observed reactivity patterns, where 4-X-2,6-DTBP substrates with relatively strong O–H bonds did not react with **2** (*e.g.* X = CN, NO_2 ; $\text{BDE}_{\text{O-H}} > 84$ kcal/mol) whereas those with $\text{BDE}_{\text{O-H}} < 84$ kcal/mol did react with **2** (Table 1), demonstrating that thermodynamically the reaction with substrates with strong O–H bonds may not be favourable.

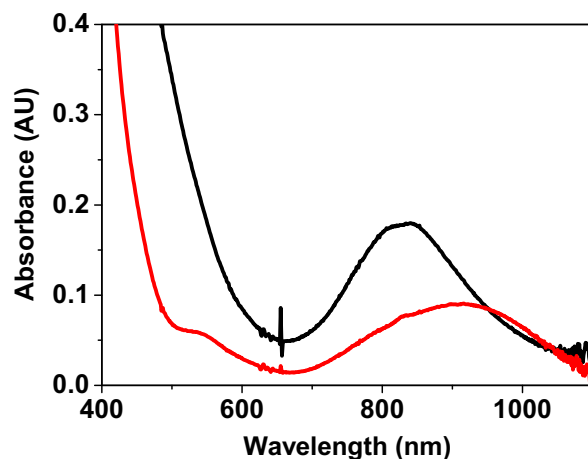
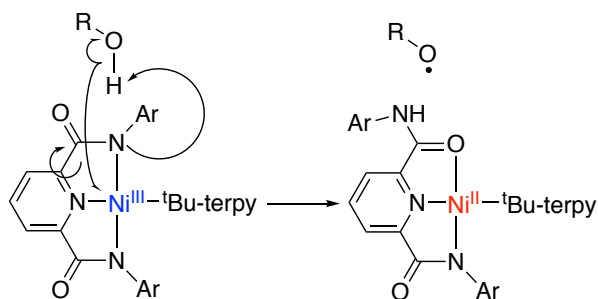


Figure 7. Electronic absorption spectrum of the reaction mixture after the reaction between **2** (3 mM) and 4-OCH₃-2,6-DTBP (red trace, 20 equiv.) and the starting complex **1** (black trace, 3 mM). The red trace is the same as that measured for $\mathbf{1H}^+$.

Carboxamidate complex **2** has thus been shown to be capable of PCET oxidation and the carboxamidate donor group is readily protonated resulting in an amide complex (Scheme 2). We conclude, based on the observation that $\mathbf{1H}^+$ was the product of the PCET oxidation by **2**, that protonation of the carboxamidate N-atom results in decoordination and rotation around the $\text{C}_{\text{ketone}}\text{-N}$ bond. During the PCET reaction the Ni^{III} ion acted as an electron acceptor furnishing Ni^{II} . We believe our results provide some insight to recent studies by Fukuzumi and Garcia-Bosch where carboxamidate complexes have been found to, somewhat unexpectedly, mediate PCET oxidations.³¹⁻³² We postulate that in these cases the carboxamidate ligand could be acting as an H^+ -acceptor (as predicted by Garcia-Bosch using computational methods).

Scheme 2. Ligand acid/base non-innocence in a 2,6-pyridinedicarboxamidate complex.



Conclusion: A coordinatively saturated Ni^{III}-carboxamidate complex (**2**) was synthesized and characterized. **2** reacted with phenols with weak O–H bonds, but not with hydrocarbons in contrast to analogous [Ni^{III}(X)(L)]. **2** reacted with phenols giving rate constants 3–30 times lower than analogous complexes. Thus, **2** was thermodynamically and kinetically less reactive than analogous complexes with ancillary proton acceptors. Analysis of the kinetics of the reaction with a series of *para*-substituted 2,6-di-*tert*-butylphenol substrates showed that the reaction likely proceeded through a non-concerted or partially concerted PCET mechanism. It appeared that ET was not exclusively rate limiting, with ET and PT demonstrating similar rates. The supporting carboxamidate ligand was found to be acid-base non-innocent and thus capable as acting as a H⁺-acceptor (forming complex **1H**⁺). Indeed, we demonstrated that the complex remained intact through a full cycle of oxidation of **1** to **2**, PCET of **2** to yield **1H**⁺, deprotonation of **1H**⁺ to yield **1** followed by re-oxidation of **1** to yield **2**. The N–H bond dissociation enthalpy of the protonated amide in **1H**⁺ was determined to be 84 kcal/mol, and **2** was only capable of oxidizing substrates with O–H bond dissociation enthalpies less than 84 kcal/mol. Our results demonstrate that a carboxamidate ligand can be acid/base non-innocent in PCET oxidation chemistry.

Supporting Information: Included in supporting information file (.pdf): physical methods; synthesis methods; reactivity protocols and results; acid/base studies; further EPR analysis; X-ray crystallography data.

Author Contributions

‡Authors C. McManus and P. Mondal contributed equally.

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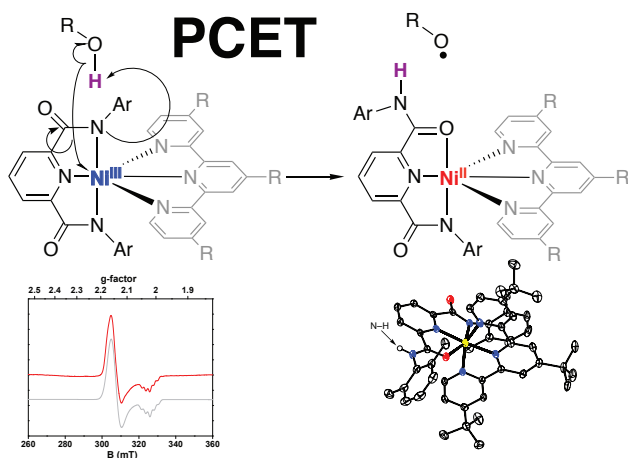
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TOC synopsis:

The 2,6-pyridinedicarboxamidate Ni^{III} complex [Ni^{III}(^tBu-terpy)(L)]⁺ containing a neutral terpyridine ancillary donor was found to be a capable oxidant of phenols. It was found to oxidize these substrates via a proton coupled electron transfer (PCET) mechanism. The products of PCET oxidation were phenoxy radical decay products and the protonated form of the Ni^{II} precursor to [Ni^{III}(^tBu-terpy)(L)]⁺ which was crystallographically characterized. Our findings provide evidence that carboxamidate ligands can act as proton acceptors in PCET oxidations.