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Fast Hydrocarbon Oxidation by a High Valent Nickel-Fluoride Complex

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Abstract: In the search for highly reactive oxidants we have identified high-valent metal-fluorides as a potential potent oxidant. The highvalent Ni-F complex [Ni^{III}(F)(L)] (2, L = N,N'-(2,6-dimethylphenyl)-2,6pyridinedicarboxamidate) was prepared from $[Ni^{II}(F)(L)]^{-}$ (1) by oxidation with selectfluor. 1 and 2 were characterized using ¹H/¹⁹F NMR, UV-vis, and EPR spectroscopies, mass spectrometry, and Xray crystallography. 2 was found to be a highly reactive oxidant in the oxidation of hydrocarbons. Kinetic data and products analysis demonstrate a hydrogen atom transfer mechanism of oxidation. The rate constant determined for the oxidation of 9,10-dihydroanthracene $(k_2 = 29 \text{ M}^{-1}\text{s}^{-1})$ compared favourably with the most reactive highvalent metallo-oxidants. 2 displayed reactions rates 2000-4500-fold enhanced with respect to [Ni^{III}(CI)(L)]. 2 also displayed high kinetic isotope effect values. Oxidative hydrocarbon and phosphine fluorination was achieved. Our results provide an interesting direction in designing catalysts for hydrocarbon oxidation and fluorination.

Introduction

Saturated hydrocarbons remain troublesome to activate due to the strength of the C–H bond, which normally displays bond dissociation enthalpy (BDE) values greater than 100 kcal/mol. In biological systems, a large number of Fe- and Cu-containing metalloenzymes perform saturated hydrocarbon oxidation through oxidative C–H activation, forming hydroxylated, halogenated, and desaturated products.^[11] A high-valent metaloxo or bridging oxo species are most often postulated as the oxidizing entity.^[1a, 2] Man-made catalysts have also demonstrated the ability to oxidatively activate C–H bonds, ^[3] however, very few display the ability to activate strong C–H bonds, presumably because the oxidant does not contain the requisite driving force to activate C–H bonds with high BDE values.

In most of these systems, it was proposed that hydrocarbon oxidation proceeded through an initial hydrogen atom transfer (HAT) mechanism.^[4] The thermodynamic driving force for such reactions is the strength of the X–H bond in the hydrogen atom abstracting product (for Mⁿ=O, the product is Mⁿ⁻¹–O–H, and the strength of the O–H bond drives M=O oxidation).^[4b, 4c, 5] It is thus critical to identify systems where the high-valent oxidant will display a high driving force for C–H activation. To date most synthetic M–O–H complexes display BDE_{O–H} values < 90 kcal/mol.^[5e, 6] Given that most saturated hydrocarbons display BDE_{C–H} values in excess of 100 kcal/mol the thermodynamic driving force for C–H activation is likely low in these systems.

The α -ketoglutarate dependent non-heme iron halogenases are important enzymes that facilitate halogenation of hydrocarbon

substrates through oxidative C-H activation.[7] A non-heme X-Fe^{IV}=O oxidant (X = CI, Br) has been identified to perform HAT from the substrate yielding a X-Fe^{III}-OH entity and a carboncentered radical. Rebound of the halide ligand in X-Fe^{III}-OH entity with the carbon radical produced the halogenated product.^{[8],[9]} Groves and coworker demonstrated the biomimetic fluorination of hydrocarbons catalyzed by high valent manganese-porphyrin complexes.^[10] An F–Mn^V=O entity was postulated to perform HAT through the oxo ligand followed by rebound with a metal-bound fluoride. These systems demonstrated generally low yields of halogenated products and contained some mechanistic ambiguities. It is assumed the low yields of fluorinated product derive from competition with hydroxylation rebound. The elimination of the oxo-ligand could enhance the fluorination yield, which would be achieved through both HAT oxidation and halide radical rebound by a high-valent metal-fluoride complex.

Metal-fluoride species have been implicated in the fluorination of a variety of hydrocarbons and in the electrochemical fluorination of hydrocarbons by HF at Ni electrodes (Simons Process).^[11] As far as we are aware there is limited mechanistic insight into these reactions, and no evidence that they follow PCET or HAT oxidation mechanisms. Exploring the reactivity of high-valent metal-fluorides could provide insight.

We recently discovered high-valent metal-halide oxidants that performed hydrogen atom transfer oxidation.^[12] The high valent nickel-chloride complex [Ni^{III}(CI)(L)] (L = N,N'-(2,6dimethylphenyl)-2,6-pyridinedicarboxamidate) was the first metalhalide complex that performed C-H activation via HAT.^[12] We postulated the product of HAT oxidation of hydrocarbons by [Ni^{III}(CI)(L)] were H–CI and [Ni^{II}(L)], with the BDE_{H–CI} (103 kcal/mol^[13]) providing the thermodynamic driving force for C-H activation. We expect that a high-valent metal-fluoride complex could display enhanced rates of hydrocarbon oxidation due to the strength of the H–F bond (BDE_{H–F} = 135 kcal/mol).^[14] While a few high-valent metal-fluoride complexes have recently been reported,^[15] to the best of our knowledge no report on their HAT reactivity has surfaced. Herein, we describe the preparation of a high-valent Ni-F complex ([Ni^{III}(F)(L)]) which is capable of activating very strong C-H bonds through a HAT mechanism at rates far in excess of those achieved by the corresponding chloride complex.

Results and Discussion

Preparation and Characterization of ${}^{n}Bu_{4}N[Ni^{ll}(F)(L)]$, **1**. The precursor complex [Ni^{ll}(CH₃CN)(L)] (LH₂ = N,N'-(2,6-

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dimethylphenyl)-2,6-pyridinedicarboxamide, Scheme 1) was synthesized by a slight modification of the previously reported procedure (see supporting information for details).^[16] ⁿBu₄N[Ni^{II}(F)(L)] (1, ⁿBu = C₄H₉) was prepared by exchange of CH₃CN for F⁻ through addition of 1.1 equiv. of tetra-*n*-butylammonium fluoride (TBAF) to [Ni^{II}(CH₃CN)(L)] in tetrahydrofuran (THF) at room temperature under an inert atmosphere (Scheme 1). The orange-red complex **1** was crystallized by slow diethylether (Et₂O) diffusion into a N,N-dimethylformamide (DMF) solution of **1** and was obtained in 85 % yield. **1** was characterized by X-ray crystallography, ¹H/¹⁹F/¹³C nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopies, and electrospray ionization mass spectrometry (ESI-MS).



Scheme 1. Preparation of 1 from [Ni^{II}(CH₃CN)(L)], and preparation of 2 from 1.

The ¹H NMR spectrum of **1** showed the expected number of resonances within the chemical shift range of 0.0 - 8.0 ppm for a diamagnetic d⁸ Ni^{II} complex (Figure S1). The ¹⁹F NMR of 1 showed a peak at δ = -421 ppm corresponding to coordinated F⁻ ligand (Figure S3), which was comparable to previously reported metal-fluoride complexes.[15d, 17] Negative mode ESI-MS spectrometry displayed a molecular ion peak at m/z = 448.0787 corresponding to the $[Ni^{II}(F)(L)]^{-}$ ion (expected m/z = 448.0971, Figure S5). The X-ray crystal structure of 1 was similar to the earlier reported [Ni^{II}(X)(L)]⁻ (X = OH, CI, OCO₂H, O₂CCH₃, ONO₂) complexes with the Ni^{II} ion in a slightly distorted square planar geometry (Figure 1).^[16, 18] The metric parameters (Table S2) of the [Ni^{II}(L)] unit in 1 matched well with the previously reported complexes.^[16, 18-19] The Ni-F bond distance (1.808(4) Å) in 1 was comparable with reported values for Ni-F complexes,[17, 20] and considerably shorter than the Ni-Cl bond distance (2.174(2) Å) measured for [Ni^{II}(CI)(L)]^{-,[18a]} which is expected for the smaller F ligand. Spectroscopy and crystallography thus confirmed the composition and structure of 1 as Bu₄N[Ni^{II}(F)(L)].



Figure 1. ORTEP of anionic fragment of 1 with displacement shown at the 50% probability level. Heteroatoms are labelled, while disorder, counter ion ($^{n}Bu_{4}N^{*}$) and hydrogen atoms are omitted for clarity.

Preparation and Characterization of $[Ni^{III}(F)(L)]$, **2**. **1** was oxidized to the corresponding Ni^{III} complex by reaction with one equivalent

of selectfluor (N-chloromethyl-N'-fluorotriethylenediammonium bis(tetrafluoroborate), Scheme 1, 0 °C or -40 °C, acetone, 0.3 mM). An immediate reaction was observed as evidenced by a distinct color change from pale red/orange to deep purple. The reaction was complete within 6 s at 0 °C. The electronic absorption spectrum of the product (defined as **2**) exhibited an intense band at λ = 550 nm along with a shoulder at λ = 700 nm (Figure 2). Such electronic absorption features are similar to those reported for analogous [Ni^{III}(X)(L)] complexes,^[12, 16, 18b] and other high valent nickel complexes.^[18c, 21] The fluoride complex **2** displayed similar absorption features to the previously reported [Ni^{III}(CI)(L)] (Figure S7).^[12] We thus concluded a change in the metal oxidation state had occurred and we defined **2** as having the formula [Ni^{III}(F)(L)].



Figure 2. Electronic absorption spectra of 1 (black trace, 0.3 mM, acetone) and 2 (blue trace, obtained after oxidation of 1 by 1 equiv. selectfluor in acetone (0.3 mM), 0 °C or -40 °C).

Positive mode ESI-MS of **2** showed a peak at m/z = 471.1245 corresponding to the formula [**2** + Na⁺]⁺ (predicted m/z = 471.0878, Figure S8). This peak was not observed in the ESI-MS spectrum of **1**, which exhibited a negative mode molecular ion peak at m/z = 448.0787 ([Ni^{II}(F)(L)]⁻), Figure S5). The peak at m/z = 471.1245 was also not observed in the negative mode ESI-MS of **2**. The mass peak can thus be assigned to the Ni^{III} product [Ni^{III}(F)(L)].

The electronic and magnetic properties of 2 were further explored using X-band electron paramagnetic resonance (EPR) spectroscopy. A frozen acetone solution of 2 was analyzed at 77 K (Figure 3). EPR analysis of 2 exhibited a rhombic signal ($g_x =$ 2.30, $g_y = 2.23$, $g_z = 2.02$) which is typical of a low-spin $S = \frac{1}{2} d^7$ Ni^{III} complex.^[12, 16, 18b, 22] Fluorine hyperfine splitting in the g_z component (A_z = 21 mT, g_z = doublet, Figure 3) was observed, which is due to the interaction of the coordinated F atom (I = $\frac{1}{2}$) with the unpaired spin on Ni^{III}.^[15d, 15e] We observed similar hyperfine coupling for $[Ni^{\rm III}({\rm CI})(L)]$ where CI-hyperfine coupling was observed in the gz component.^[12] The F-hyperfine pattern compared favorably with previously reported paramagnetic Ni-F complexes. $^{\left[15d, \ 15e\right]}$ A minor component was identified in the spectrum ($g_x = 2.37$, $g_y = 2.22$, $g_z = 2.02$, Figure S9) present in a relative ratio of ~9:1 (as determined through simulation of the spectral data, see supporting information). The minor component is an as yet unidentified species, however displayed no Fhyperfine. The total yield of Ni^{III} in the sample was calculated to be 85 ± 20 % by comparison of the double integral of the entire signal to that of a (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) standard. EPR thus confirmed the assignment of 2 as [Ni^{III}(F)(L)].

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Figure 3. X-band EPR spectrum of **2** (blue trace) in a frozen acetone solution, measured at 77 K with 2.02 mW microwave power and 0.7 mT modulation amplitude. Simulated spectrum for **2** (black trace, $g_x = 2.30$, $g_y = 2.23$, $g_z = 2.02$; $A_{zz} = 21$ mT).

The ¹⁹F NMR of *in-situ* prepared **2** displayed a peak at δ = +48 ppm in D₆-acetone at room temperature, while **1** showed a resonance at δ = -421 ppm (Figures 4, S10-S11). The peak at δ = +48 ppm disappeared within 1-2 minutes, on the same timescale as **2** decayed at room temperature, suggesting the feature can be assigned to **2**. The large change in chemical shift on addition of 1 equiv. selectfluor to **1** yielding **2**, was a strong indicator of change of metal oxidation state (diamagnetic Ni^{III} to paramagnetic Ni^{III}), leading to a paramagnetic contact shift effect causing the large downfield sift.^[23] Given the short lifetime of this signal and the large shift we surmise that it must be attributed to a Ni^{III}-bound F-atom and thus further supports the assignment of **2** as [Ni^{III}(F)(L)].



Figure 4. ¹⁹F NMR of 1 (black) and 2 (blue) in D_6 -acetone at room temperature (see Figure S10 for full spectra).

The thermal instability and short lifetime of **2** prevented the growth of crystals of **2** suitable for X-ray diffraction measurements. **2** is a member of a family of $[Ni^{III}(X)(L)]$ complexes and showed remarkably similar electronic absorption and EPR spectroscopic properties to those previously reported examples.^[12, 16, 18b] All of the previously reported $[Ni^{III}(X)(L)]$ complexes displayed very similar X-ray absorption spectroscopy (XAS) properties to eachother.^[12, 16, 18b] We previously demonstrated that the assignment of the electronic structure of $[Ni^{III}(CI)(L)]$ was supported by XAS data.^[12] Given the remarkable similarities in the XAS analysis of this family of complexes we concluded XAS analyses was not warranted for **2**.

Reactivity properties of **2**: **2** was found to be reasonably stable at -40 °C ($t_{1/2} = 6$ h) but decayed more rapidly at 0 °C ($t_{1/2} = 20$ mins). The reactivity of **2** towards different substrates was monitored by

Reaction of **2** with Hydrocarbons. **2** reacted readily with xanthene and 1,4-cyclohexadiene (CHD) at -40 °C in acetone, as evidenced by the disappearance of its characteristic λ = 550 nm band (Figure S12). k_2 values of 4.47 M⁻¹s⁻¹ and 1.19 M⁻¹s⁻¹ were determined for xanthene and CHD, respectively (Figures S13-S14). The products of these reactions were xanthone and benzene, respectively (Figures S15-S16).

Under *the exact same* conditions $[Ni^{III}(CI)(L)]$ reacted very slowly with both substrates demonstrating k_2 values of 1.04 x 10⁻³ M⁻¹s⁻¹ (xanthene) and 5.5 x 10⁻⁴ M⁻¹s⁻¹ (CHD) (Figure 5).^[12] These results show a relative rate enhancement of 4300 and 2200, respectively, for F-containing 2 versus CI-containing $[Ni^{III}(CI)(L)]$. This emphatic rate enhancement would suggest that the postulate that BDE_{H-F} (135 kcal/mol) should induce higher driving force for hydrocarbon oxidation by **2** when compared to $[Ni^{III}(CI)(L)]$ (where the weaker BDE_{H-CI} (103 kcal/mol) drives the reaction) was correct. This demonstrates a facile means to enhance oxidation catalysts by simple halide ligand exchange. It also suggests that high-valent metal-fluoride complexes may represent a class of potent oxidants.



Figure 5. Comparison of $log(k_2)$ for oxidation of xanthene and CHD by **2** (blue) and $[Ni^{III}(CI)(L)]$ (green).

KIE values were measured for the reactions between 2 and D2xanthene and D₄-DHA (Figure 6). High KIE values were obtained (110 and 79, respectively). These KIE values contrast starkly with those obtained for [Ni^{III}(OAc)(L)] which were 3.3 and 3.0, respectively.^[16] A KIE value of 4.5 for the reaction between [Ni^{III}(CI)(L)] and D₂-xanthene was also determined (Figure S17). The greatly increased KIE observed for F-containing 2 represents a massive change and suggests the high rate enhancement observed for 2 versus [Ni^{III}(CI)(L)] is as a result of tunneling. High KIE values from 30-200 were reported for hydrocarbon oxidation by high valent metal-oxo complexes, especially in the large cohort of Fe^{IV}=O complexes.^[5a, 24] A significant tunneling contribution to the reaction rates was attributed to these very high KIE values.^{[24c,} ^{25]} At the moment predicting why the F-atom induced such large KIE changes is difficult, we expect the relative differences in atom size (F vs. Cl) may allow for different angles of substrate approach, thus influencing how the incoming H-atom interacts with the oxidant.

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Figure 6. Plots of k_{obs} versus [H/D-substrate] determined for the reactions between **2** and xanthene (purple), DHA (blue), D₂-xanthene (pink), D₄-DHA (red).

At 0 °C, 2 was sufficiently stable to allow an exploration of its reactivity with a large family of hydrocarbon substrates. 2 readily reacted with xanthene, DHA, fluorene, triphenylmethane, cumene, ethyl benzene, and toluene. The corresponding oxidized products xanthone from xanthene, anthracene and anthrone from DHA, fluorenone from fluorene. triphenylmethanol from triphenylmethane, 2-phenylpropanal and prop-1-en-2-ylbenzene from ethylbenzene were observed (Figures S18-S22). We describe the oxidation of triphenylmethane and ethylbenzene in more detail below, while for toluene it was not possible to clearly identify oxidation products. The reactions all obeyed pseudo-first order kinetics allowing for determination of k_2 values for all of these substrates (Figures S23-S30, Table S3).

The measured k_2 values for these reactions decreased with increasing substrate BDE_{C-H}, demonstrating a linear correlation when $log(k_2)$ was plotted against substrate BDE_{C-H} (Figure S31). Furthermore, in a plot of the free energy of activation (ΔG^{\ddagger}) against substrate BDE_{C-H}, where ΔG^{\ddagger} was calculated from the measured k_2 values, a slope of 0.40 was determined (Figure 7). Note: bond dissociation free energy (BDFE) values are not available for all substrates in the same family of solvents, we therefore use BDE (an enthalpy) throughout this manuscript. With the (limited) available BDFE values we obtain a remarkably similar plot and slope when comparing ΔG^{\ddagger} to BDFE (slope = 0.41, Figure S32). The observed relationship indicates a concerted proton coupled electron transfer (PCET) mechanism which we define as HAT.^[4b, 16, 26] The measured slope is within the appropriate range of the ideal value of 0.5 for a HAT reaction, predicted by Marcus theory, [4a, 4c] and comparable with ([Ni^{III}(OAc)(L)] slope = 0.31).^[16] Furthermore, the slope value sits in the normal range of 0.15-0.69 observed for HAT mediated oxidation by metal-oxygen complexes.[5a, 27]

Analysis of the post reaction mixtures in our substrate reactivity studies showed that there was no incorporation of fluorine atoms in the products when **2** *alone* was reacted with all hydrocarbons. However, if the reaction between **2** and ethylbenzene was performed in the presence of excess selectfluor, TBAF, and AgF (see supporting information for details), fluorinated hydrocarbon products were detected by ¹⁹F NMR of the post reaction mixture. For ethylbenzene one of the products has been identified as 1-fluoro-1-phenylethane amongst several new fluorinated products (Figure S33).^[29] Likewise, in the oxidation of triphenylmethane, fluoro-triphenylmethane was detected by ¹⁹F NMR (Figure S34).^[29b] These products were only detected when **2** was present, all control reactions without Ni

present gave no indication of hydrocarbon fluorination, demonstrating the high-valent metal-fluoride was facilitating hydrocarbon fluorination.



Figure 7. Plot of ΔG^{\ddagger} , for the reactions of **2** with hydrocarbon substrates, measured at 0 °C, against the BDE_{C-H} of the substrates. ΔG^{\ddagger} was determined from k_2 using Eyring equation. BDE references.^[5a, 28]

We postulate the mechanism of this reaction to follow that **2** initially mediated HAT to yield H–F, [Ni^{II}(L)], and a carbon-centred radical (Scheme 2). The carbon-centred radical then presumably rebounds with another molecule of **2**, or the added AgF resulting in C–F bond formation. We observe silver mirror formation in the experiment, suggesting that AgF could be the source of rebounding F-atoms. Furthermore, we never observe fluorination in the absence of AgF. We therefore tentatively assign AgF as the rebounding F-atom donor in this system. This result indicates that high-valent metal-fluoride complexes could be effective oxidants for hydrocarbon fluorination.

In order to explore further the F-atom transfer capabilities of these complexes, we also reacted 2 with triphenylphosphine (PPh₃). An immediate reaction was observed resulting in bleaching of the electronic absorption spectrum of **2**. All of **2** was consumed with 0.5 equiv. of PPh₃, suggesting a 2:1 stoichiometry and that ${\bf 2}$ acts as a single F-atom donor. ^{31}P and ^{19}F NMR provided conclusive proof of the formation of F₂PPh₃ (Figure S35, δ = -54 ppm ³¹P NMR; Figure S36, δ =-39 ppm ¹⁹F NMR), with the product readily identified according to literature precedence.^[30] F₂PPh₃ was obtained in 70% yield according to NMR spectroscopy. [Ni^{III}(CI)(L)] also reacted with PPh₃. The measured k_2 values for these reactions were reasonably close to one another (2: k₂ = 17 M⁻¹s⁻¹; [Ni^{III}(CI)(L)]: k₂ = 9 M⁻¹s⁻¹, Figures S37-S38). The similarity in these values contrasted with the stark differences in k_2 for hydrocarbon oxidation by the same two complexes suggests that the mechanism of reactions were different. It also supports the postulate that the strength of the HF bond is likely the driving force for the oxidation of hydrocarbons, because BDE_{H-F} >> BDE_{H-CI}. Whereas in halogen-atom transfer to phosphines we tentatively define the mechanism as ratelimiting electron transfer, which should not be markedly different between the two complexes, because they display similar Ni^{II/III} potentials (Figure S6). This result also confirms that 2 can act as an F-atom donor (and is thus a plausible rebounding entity in hydrocarbon fluorination).

We postulate that **2** oxidized hydrocarbon substrates by HAT to yield H–F, [Ni^{II}(L)], and a carbon-centered radical (Scheme 2). We postulated similar for the HAT oxidation mediated by [Ni^{III}(CI)(L)] (HCI, [Ni^{II}(L)], and a carbon-centered radical). To explore the products of the oxidation by **2** we added excess TBAF to the post-oxidation reaction mixture (*i.e.* **2** + substrate + TBAF,

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Figures S39-S40) followed by selectfluor. This data showed the reformation of 1 and subsequent regeneration of 2, albeit in slightly lower yield. This result demonstrates that the [Ni^{II}(L)] core remains intact after the HAT reaction by 2. It also demonstrates that 2 is catalytically relevant given that the core remains stable and can be regenerated in the reaction mixture. As a further demonstration of the [Ni^{II}(L)] core remaining intact, we added excess Et₄NCI to the post-oxidation reaction mixture (i.e. 2 + substrate, Figure S41), which gave a distinct electronic absorption spectrum that can be attributed to $[Ni^{II}(CI)(L)]^{-}$ (λ = 456, 498 nm, Figure S41). This demonstrates that [Ni^{II}(L)] is present after HAT oxidation by 2. Addition of ceric ammonium nitrate (CAN) to this mixture resulted in the formation of [Ni^{III}(CI)(L)].^[12] These results clearly show that [Ni^{II}(L)] is the Ni product of HAT oxidation by 2, with H-F presumably the other product which drives HAT oxidation.



Scheme 2. Proposed mechanism of hydrogen atom transfer (HAT) by 2 (top), F-atom rebound under catalytic conditions (middle), F-atom transfer to phosphine (bottom).

Based on literature postulates,^[32] we considered that **2** and [Ni^{III}(CI)(L)] may act in equilibrium with free radical F and CI atoms, respectively, and [Ni^{II}(L)]. The F or CI atom could perform HAT rather than the Ni^{III}-halide complexes. To test this we reacted **2** with CHD in the presence of excess Ni^{II} (**1**). We believed that if such an equilibrium was involved, excess Ni^{II} should retard the rate of substrate oxidation by an F-atom by shifting the equilibrium back towards **2** (preventing the putative free halogen atom from reacting). We observed almost no change in k_2 value (1.42 versus 1.19 M⁻¹s⁻¹) for the reaction performed in the presence of excess Ni^{II} (Figure S42).^[12]

We also determined activation enthalpy and entropy values for the reactions between **2** and [Ni^{III}(CI)(L)] with CHD (Figure S43). The following values were determined: **2**: $\Delta H^{\ddagger} = 6.15$ cal/mol.K; $\Delta S^{\ddagger} = -33.68$ cal.mol-1K-1. [Ni^{III}(CI)(L)]: $\Delta H^{\ddagger} = 8.5$ kcal/mol; $\Delta S^{\ddagger} = -41.11$ cal/mol.K. Mayer and colleagues have demonstrated that metal-based HAT reactions generally display large (<-20 cal/mol.K) and negative entropic values unlike organic radicals (e.g. Cl or F atoms),^[33] because the metal ion induces relatively large reorganization energy. These results demonstrate that the metal-halide complexes likely performed HAT *and* that free halogen atoms are probably not involved.

2 reacted with DHA with a k_2 value in the same range as some of the most reactive oxidants prepared to date (Table 1). Although some of the reactions have been performed at different temperatures, the remarkably high k_2 value identified for Fcontaining **2**, would suggest that identifying high-valent metalfluorides may yield highly reactive oxidants. To the best of our knowledge, **2** represents the first high-valent metal-fluoride to display HAT oxidation reactivity. That it performs this reaction at rates comparable to the most reactive high-valent metal-oxygen adducts indicates that the driving force for HAT by metal-fluorides is likely high. We conclude that the high reactivity of **2** is probably as a result of formation of the strong H-F bond (135 kcal/mol). These results show that high-valent metal-fluoride oxidants display great potential for the development of oxidation catalysis systems that can activate the strongest of saturated C–H bonds.

Table 1. Comparison of high-valent oxidants in the oxidation of DHA.

Complexes	k2	KIE	$\Delta G^{\ddagger /}$ $\Delta (BDE)$	T (°C)
2	29	79	0.40	0
[Mn ^{VII} O ₄] ^{-[27c, 34]}	0.12	-	0.69	-
$[Fe^{IV}(O)(N_4Py)]^{2+[25b, 27a]}$	18	20	0.15	25
[Fe ^{IV} (O)(NTB)] ^{2+ [35]}	78	-	-	-40
[Fe ^{III} (OMe)(PY5)] ^{2+ [36]}	0.0049	5.5	0.17	25
$[Ru^{IV}(O)(bpy)_2(py)]^{3+[5a]}$	125	50-100	0.47	25
[Ni ^{III} (O ₂ CCH ₃)(L)] ^[16]	8.11	3.0	0.31	25

Conclusion

In conclusion, we have prepared the high-valent nickel-fluoride complex 2 ($[Ni^{III}(F)(L)]$), from 1 ($[Ni^{II}(F)(L)]^{-}$) by one electron oxidation with selectfluor. 2 was characterized by UV-vis, NMR, and EPR spectroscopies and mass spectrometry. 2 was found to be highly reactive towards hydrocarbon oxidation via a HAT mechanism as evidenced by kinetic analysis. Fascinatingly, 2 was found to be one of the kinetically most reactive high-valent oxidants prepared and suggests that high-valent metal-fluoride complexes may represent a class of interesting oxidants. We postulate that the strength of the H-F bond may render highvalent metal-fluoride complexes highly reactive. In the oxidation of xanthene and CHD 2 displayed rate constants 4300- and 2200fold greater than those reported for analogous CI-containing oxidants, while demonstrating high KIE values (80-110) for the same reactions. 2 was also capable of facile fluorination of ethylbenzene and triphenylmethane under catalytic conditions. Furthermore, 2 was found capable of oxidizing phosphines to yield the corresponding fluorophosphines in near quantitative yields. Our results demonstrated that high valent metal-fluorides can be a potential strong oxidant for hydrocarbon oxidation and oxidative fluorination reactions.

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Keywords: high-valent oxidants • fluorination • metal-oxo species • oxidation catalysis • reactive intermediates

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Entry for the Table of Contents



A high valent nickel-fluoride complex oxidizes hydrocarbons via a hydrogen atom transfer mechanism while also facilitating oxidative fluorination. The fluoride complex demonstrates a 10³-fold enhanced rate constant for hydrocarbon oxidation when compared to its chloride analogue, demonstrating that fluoride imbues a high driving force for oxidation.

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