

C–H Activation by an Iron-Nitrido Bis-Pocket Porphyrin Species

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Abstract: High-valent iron-nitrido species are nitrogen analogues of iron-oxo species which are versatile reagents for C–H oxidation. Nonetheless, C–H activation by iron-nitrido species has been scarcely explored, as this is often hampered by their instability and short lifetime in solutions. Herein, the hydrogen atom transfer (HAT) reactivity of an Fe porphyrin nitrido species (**2c**) toward C–H substrates was studied in solutions at room temperature, which was achieved by nanosecond laser flash photolysis (LFP) of its Fe(III)-azido precursor (**1c**) supported by a bulky bis-pocket porphyrin ligand. C–H bonds with bond dissociation enthalpies (BDEs) of up to ~84 kcal mol⁻¹ could be activated, and the second-order rate constants (k_2) are on the order of 10²–10⁴ s⁻¹ M⁻¹. The Fe-amido product formed after HAT could further release ammonia upon protonation.

Introduction

High-valent iron-oxo species are critically involved in a number of enzymatic and synthetic oxidative transformations.^[1] A notable example is the active oxidant of cytochrome P450 enzymes, Compound I (Cpd-I), which consists of an Fe(IV)-oxo porphyrin π -radical cation group being capable of activating inert C–H bonds.^[2] Iron-nitrido species^[3] are nitrogen analogues of iron-oxo species and have been proposed as key intermediates in a number of industrial^[4] and biomimetic^[5] nitrogen fixation processes where ammonia can be formed via multiple proton/electron transfer steps onto molecular or surface-bound Fe-nitrido moieties. In the literature, reactivity studies of terminal Fe-nitrido complexes with organic substrates^[6] including phosphines,^[6a, f, g, i] isocyanides,^[6e, l] and alkenes^[6c, h, i, k, m] are mostly studied for trigonal Fe-nitrido complexes^[6a, d, l, 7] having high Fe–N_{nitrido} bond order according to the molecular orbital (MO) diagram (Figure 1a).^[3e, 6a, 7c] On the other hand, Fe-nitrido complexes in tetragonal symmetry^[6c, 8] are generally less stable due to population of Fe d electron(s) in antibonding $d\pi^*$ orbital(s).^[3e, 9] While C–H activation by Fe-nitrido species was investigated computationally,^[10] there have only been a handful of reported experimental studies in which direct hydrogen atom transfer (HAT) from C–H bonds of ligands or organic substrates (such as 1,3- and 1,4-cyclohexadiene) onto trigonal/tetragonal

Fe-nitrido units was proposed as a plausible reaction pathway based on product analysis and/or DFT calculations.^[6c, h, k]

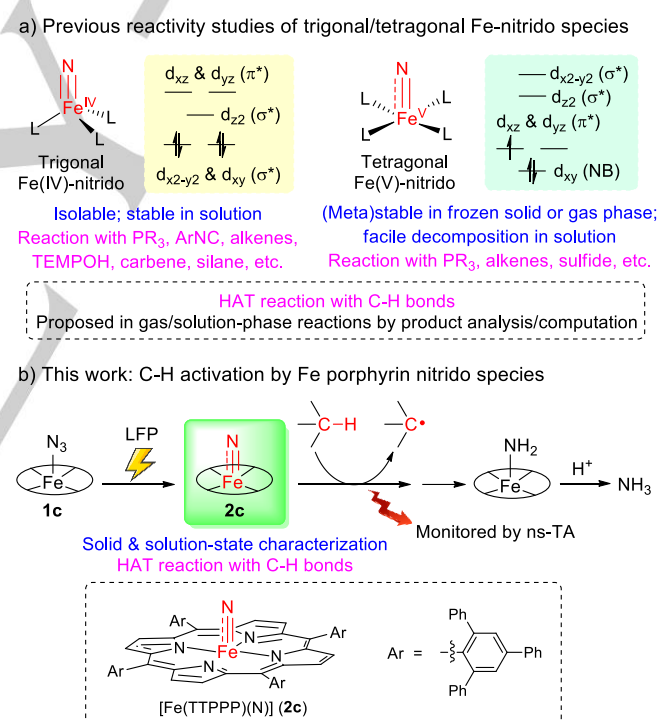


Figure 1. (a) MO diagram, stability, and reactivity study of trigonal Fe(IV)- and tetragonal Fe(V)-nitrido complexes in the literature. (b) HAT reaction between C–H substrates and an Fe-nitrido bis-pocket porphyrin species studied in this work.

A viable candidate for C–H activation is Fe(V) porphyrin nitrido species which have been previously generated via photolysis of the Fe(III)-azido precursors in thin film or frozen solution and characterized at cryogenic temperatures.^[8a, b, 9d] However, reactivity study of such species is hampered by their short lifetime and facile decay (e.g. to μ -nitrido dimers) in solutions.^[3g, 8c, 11] Laser flash photolysis (LFP) is a powerful tool for reactivity studies

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of short-lived species such as metal-oxo porphyrinoid complexes.^[12] Transients with sub-millisecond lifetime could be generated in situ with prior addition of organic substrates in contrast to conventional mixing experiments that require millisecond mixing time. In the literature, LFP coupled with time-resolved Fourier-transform infrared (TR-FTIR) probe was applied to the reactivity study of a tetragonal Fe-nitrido complex, *trans*-[Fe^V(cyclam)(N₃)(N)]⁺ (lifetime \approx 350 μ s in deaerated CH₃CN at room temperature (RT)), yet only nitrogen atom transfer reaction with trialkylphosphane and ligand exchange reaction were reported.^[6g] Herein is described a reactivity study of C–H activation reaction by a tetragonal Fe-nitrido species in solution. This was achieved by using a bulky bis-pocket porphyrin ligand to increase the stability of an Fe porphyrin nitrido species (**2c**), which was generated and studied by employing the LFP method coupled with nanosecond transient absorption (ns-TA) spectroscopy (Figure 1b). Thermodynamic and kinetic data of HAT reactivity of this Fe porphyrin nitrido species are compared to trigonal Fe-nitrido complexes and also to synthetic Cpd-I model complexes.

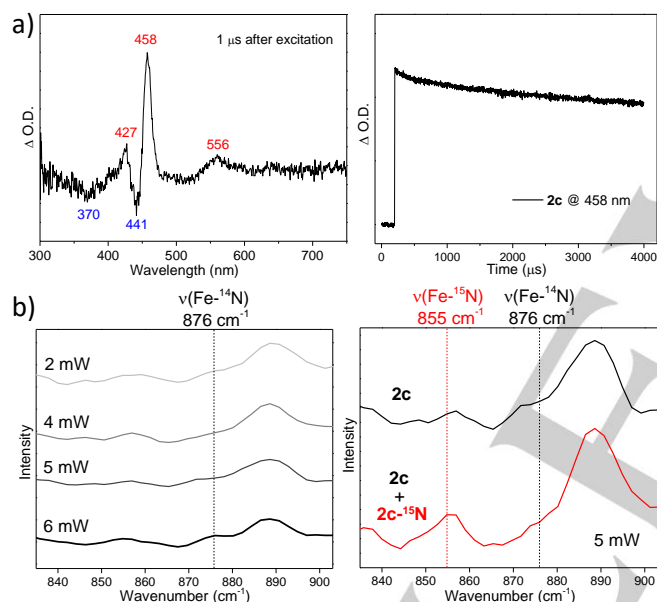


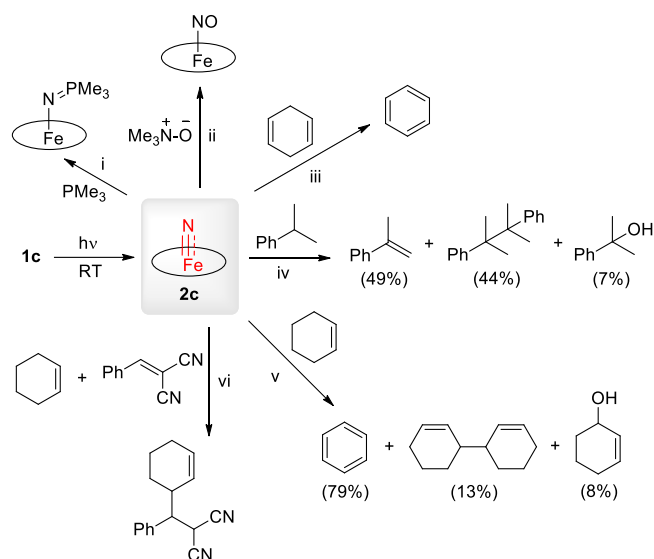
Figure 2. Solution-state characterization of Fe-nitrido species **2c**. a) TA spectrum taken at 1 μ s after photoexcitation (355 nm) of a benzene solution of **1c** (20 μ M) at 298 K (left) and decay of the signal at 458 nm (right). b) Resonance Raman (RR) spectra after photoexcitation (416 nm) of a CH₃CN/DCM solution of **1c** (0.5 mM) at 298 K using different laser powers (left) and comparison between spectra of **1c** and **1c-¹⁵N** using 5 mW laser power (right).

Results

At the outset, we targeted at three Fe porphyrin nitrido species [Fe(Por)(N)] (**2a-c**; **2a**: Por = TPP; **2b**: Por = TMP; **2c**: Por = TTPPP), with **2a,b** previously generated and characterized under cryogenic conditions.^[8a, b, 9d] A bis-pocket porphyrin ligand TTPPP (Figure 1b) was chosen in this study as it is bulky enough to prevent formation of the μ -nitrido dimer and it is devoid of any reactive C–H bonds that could potentially quench the Fe-nitrido group in an intramolecular fashion. Since it was first synthesized,^[13] this sterically demanding ligand has found its

applications in promoting regioselective catalysis^[14] as well as in stabilizing reactive intermediates.^[15] Moreover, its terphenyl scaffolds are known to induce relatively strong London dispersion^[16] and such dispersive interactions with incoming substrates may be advantageous for reactivity studies. In comparison, **2a,b** are conceivably less stable since **2a** is known to form the μ -nitrido dimer in solutions^[11a, c] while **2b** contains reactive benzylic C–H bonds that are in close proximity to the Fe-nitrido unit. The Fe(III)-azido precursor **1c** was prepared from [Fe^{III}(TTPPP)] and NaN₃ according to a procedure similar to that reported for [Fe(TPP)N₃] (**1a**)^[17] and was characterized by IR, MS, ¹H NMR, and UV-vis spectroscopies (Figures S1–4). Its ESI-HRMS spectrum shows a cluster peak at $m/z = 1646.5442$ which corresponds to [M + Na]⁺ (calc. $m/z = 1646.5443$); **1c-¹⁵N** bearing a terminally ¹⁵N-labelled azido ligand resulted in a one mass unit shift to $m/z = 1647.5413$ (Figure S1).

Laser ablation of **1c** under MALDI-MS condition gave a spectrum featuring two new cluster peaks at $m/z = 1582.7$ and 1596.9 (Figure S5). While $m/z = 1582.7$ could be assigned to [Fe^{II}(TTPPP) + H]⁺ (calc. $m/z = 1582.6$) likely arising from homolytic cleavage of the Fe–N_{azido} bond,^[3g] cluster peaks at $m/z = 1596.9$ together with the isotopic pattern are consistent with [**2c** + H]⁺ (calc. $m/z = 1596.6$); using **1c-¹⁵N**, a roughly 1:1 mixture of [**2c** + H]⁺ and [**2c-¹⁵N** + H]⁺ was observed, in accordance with the 50% ¹⁵N-labelling of the nascent nitrido species (Figure S5). Generation of these species in solution at RT was next carried out and monitored by ns-TA spectroscopy. LFP of **1c** at 355 nm in deaerated benzene solution led to a TA spectrum with a major sharp peak at 458 nm together with a broad band at 556 nm (Figure 2a). Assignment of these new spectral features to the Fe-nitrido complex **2c** is favored over other potential photolysis products, such as [Fe^{III}(TTPPP)]⁺ and [Fe^{II}(TTPPP)] resulting from hetero- and homolytic cleavage of the Fe–N_{azido} bond respectively,^[3g] due to the following reasons: 1) these red-shifted Soret and Q bands compared to **1c** (444 and 522 nm, Figure S4) are indicative of the formation of an Fe porphyrin complex in a higher oxidation state;^[18] 2) decay of the signal at 458 nm became faster when a substrate containing allylic/benzylic C–H bond(s) was present (see Figure 3c and the reactivity study below), and among all the possible photolysis products, the Fe-nitrido species is the most likely candidate that could react with C–H bonds whereas no reactivity between [Fe^{III}(Por)]⁺/[Fe^{II}(Por)] and C–H substrates would be expected/has been documented in the literature. Although this species is relatively stable in the timescale of ns-TA (\sim 4 ms, Figure 2a), its UV-vis signals could not accumulate to a detectable amount under steady-state photolysis conditions, inferring that its lifetime is shorter than the detection limit of the UV-vis spectrophotometer (\sim 500 ms). To further corroborate the formation of **2c** in solution, resonance Raman (RR) was performed under 416 nm laser excitation coupled with ¹⁵N-labelling. Photolysis of **1c** in a mixed solvent of CH₃CN/DCM led to a new feature at 876 cm⁻¹ which gradually emerged with increasing laser power from 2 to 6 mW (Figure 2b); this could be assigned to $\nu(\text{Fe-N}_{\text{nitrido}})$ of Fe(V) porphyrin nitrido species which appeared at 873–876 cm⁻¹ in thin film or frozen solution.^[8a, b, 9d] When a solution of **1c-¹⁵N** was used, two weak yet observable new features at 855 and 876 cm⁻¹ appeared with increasing laser power (Figure 2b and Figure S8), and the isotopic shift ($\Delta\nu = 21$ cm⁻¹) is close to the theoretical value ($\Delta\nu = 24$ cm⁻¹) calculated for a diatomic Fe–N moiety. These results lend support to the formation of an Fe-nitrido species **2c** in solution.



Scheme 1. Reactivity of Fe-nitrido species **2c** (product distribution in parentheses).

A reactivity study of the Fe porphyrin nitrido species was carried out at RT. Photolysis of a benzene solution of **1c** in the presence of PMe_3 or trimethylamine *N*-oxide led to the detection of $[\text{Fe}(\text{TTPPP})(\text{N}=\text{PMe}_3)]$ or $[\text{Fe}(\text{TTPPP})(\text{NO})]$ by ESI-MS (Scheme 1, eqs. i–ii); these results are consistent with previously reported reactivities of Fe-nitrido complexes^[69, n] and further supported the generation of **2c** in solution. We next turned to the more challenging C–H activation reaction. In the presence of large excess of 1,4-cyclohexadiene (CHD; BDE = 76.0(12) kcal mol⁻¹),^[19] the lifetime of **2c** decreased with increasing amount of CHD, and the pseudo-first-order rate constant (k_{obs}) showed a linear relationship with the concentration of CHD from which the second-order rate constant (k_2) could be determined as $3.07(10) \times 10^4 \text{ s}^{-1} \text{ M}^{-1}$ (Figure 3a). Partially labelled 1,4-cyclohexadiene-1,2,3,4,5,6-*d*₆ (CHD-*d*₆) gave $k_{\text{HD}} = 1.91(7) \times 10^4 \text{ s}^{-1} \text{ M}^{-1}$ (Figure S18) and hence a kinetic isotope effect (KIE) value of 4.6(16). Steady-state photolysis of a CDCl_3 solution containing **1c** and CHD produced benzene as the sole organic product (Scheme 1, eq. iii). In comparison, no detectable reaction was observed under similar conditions between CHD and **2a,b** generated by the LFP method (Figure 3a). When cyclohexene and cumene bearing stronger C–H bonds (BDE = 81.6 and 83.2(20) kcal mol⁻¹ respectively)^[19] were used as the substrates, slower decays of **2c** were observed with $k_2 = 2.57(18) \times 10^3$ and $1.25(17) \times 10^2 \text{ s}^{-1} \text{ M}^{-1}$ respectively (Figure 3d and Figure S19). Time-resolved TA spectra showed a monotonic decrease in the intensity of the Soret band of **2c** at 458 nm, along with recovery of bleached signals at 370 and 441 nm (Figure 3b). Cyclohexene-*d*₁₀ further retarded the reaction compared to cyclohexene, and a KIE value of 12.9(30) was obtained (Figure 3d). Both primary KIE values determined from CHD and cyclohexene suggest that C–H cleavage is involved in the rate-determining step and disfavor an aziridination mechanism in which secondary KIE values (smaller than unity) would be expected. After steady-state photolysis reactions using cumene and cyclohexene (see SI for experimental details), GC-MS and ¹H NMR analyses revealed that the major organic products were derived from dehydrogenation and radical homocoupling reactions, together with a minor amount of hydro-

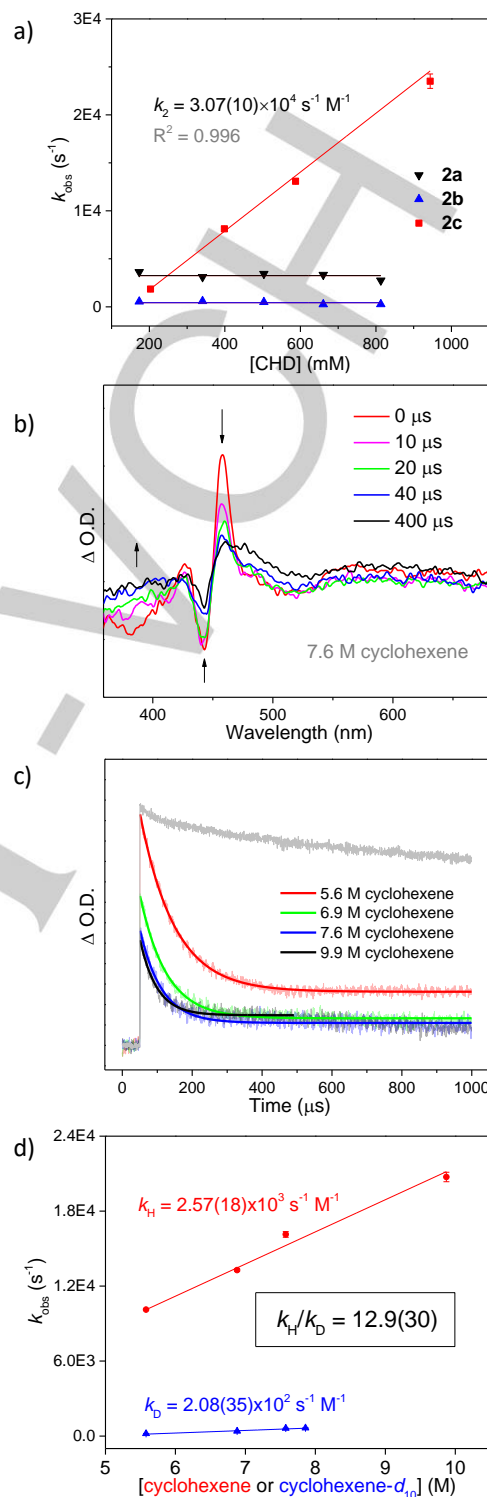


Figure 3. a) Dependence of decay rates of **2a-c** on [CHD]. (b) Time-resolved TA spectra after LFP (355 nm) of a benzene solution containing **1c** (20 μM) and cyclohexene (7.6 M). (c) Decay of signal at 458 nm in the presence of different [cyclohexene]. The grey curve indicates decay of **2c** in the absence of cyclohexene. (d) Linear dependence of k_{obs} on [cyclohexene] and determination of KIE using cyclohexene and cyclohexene-*d*₁₀ as substrates.

xylation products attributable to the presence of adventitious air (Scheme 1, eqs. iv–v). No nitrogen rebound product (e.g. cumylamine or 2-cyclohexen-1-amine) was detected. Formation of an alkyl radical via HAT from cyclohexene has further been

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corroborated by addition of benzylidenemalononitrile into the reaction mixture which led to the radical trapped product (Scheme 1, eq. vi).^[20]

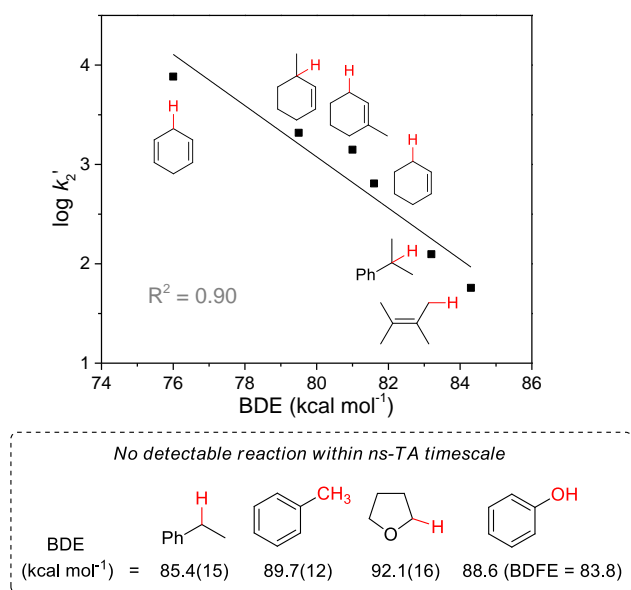


Figure 4. Linear free energy relationship between $\log k_2'$ and C–H BDE in the HAT reaction of **2c**. Inset: non-bulky substrates with stronger C–H/O–H bonds of which the reactions with **2c** were not detected by ns-TA.

Kinetic study revealed that the k_2 values are in the orders of 10^2 – 10^4 $\text{s}^{-1} \text{M}^{-1}$ for the reactions of **2c** with a series of substrates containing allylic or benzylic C–H bonds having BDE < 85 kcal mol^{-1} .^[19] These reactions followed the Bell-Evans-Polanyi behavior^[21] and a good correlation was found between reaction kinetics ($\log k_2'$; k_2' is statistically corrected second-order rate constants) and thermodynamics, i.e. BDEs of C–H bonds (Figure 4). No detectable reaction was observed when xanthene, dihydroanthracene, or fluorene (BDE = 75–82 kcal mol^{-1})^[19] were used as substrates, likely because these C–H bonds flanked by two aryl rings are too bulky to enter the pocket of the TTPPP ligand. Non-bulky yet less reactive substrates such as ethylbenzene (PhEt, 85.4(15) kcal mol^{-1}), toluene (89.7(12) kcal mol^{-1}), and tetrahydrofuran (92.1(16) kcal mol^{-1}) were found not to affect the lifetime of **2c** within the ns-TA timescale even in concentrations of up to ~ 10 M (Figure 4, inset),^[19] which implies that these C–H bonds are beyond the N–H BDE of the resulting parent Fe-imido species **3c** (Figure 5a). By taking into account the BDE values of cumene and PhEt together with their standard deviations (tetramethylethylene is not considered since no standard deviation of its BDE could be found in the literature), the N–H BDE of **3c** was estimated to be in the range of 81–87 kcal mol^{-1} . According to the following equation

$$\text{BDFE}(\text{C–H}) = \text{BDE}(\text{C–H}) - (C_{\text{H,sol}} - C_{\text{G,sol}})$$

where BDFE is the bond dissociation free energy, and $C_{\text{H,sol}}$ and $C_{\text{G,sol}}$ are solvent-dependent constants, as well as the literature value of $(C_{\text{H,benzene}} - C_{\text{G,benzene}}) = 4.8$ kcal mol^{-1} ,^[22] the N–H BDFE value of **3c** in benzene was estimated to be in the range of 76–82 kcal mol^{-1} . This is supported by the use of phenol as a substrate, which is non-bulky and has an O–H bond with a BDFE value of

83.8 kcal mol^{-1} in benzene^[22] yet was not detected to react with **2c** under similar reaction conditions (Figure 4, inset). In comparison, TEMPOH bearing an O–H bond with a BDFE value of 65.2 kcal mol^{-1} in benzene^[22] could be readily activated by **2c** with $k_2 = 8.85(95) \times 10^5$ $\text{s}^{-1} \text{M}^{-1}$ (Figure S23).

In the absence of substrates, steady-state photolysis of **1c** led to the formation of $[\text{Fe}(\text{TTPPP})]^+$ as the major Fe product together with a minor amount of $[\text{Fe}(\text{TTPPP})(\text{NH}_2)]^+$, according to ESI-MS and UV-vis analyses (Figures S9–10). In the presence of cyclohexene, $[\text{Fe}(\text{TTPPP})(\text{NH}_2)]^+$ was formed in an appreciably higher yield (Figure S11), and its molecular mass underwent a two mass unit shift when changing the substrate to cyclohexene- d_{10} (Figure 5b). This is consistent with the formulation of an Fe-amido species **4c** rather than protonated **3c** under the ESI-MS conditions, and is thus supportive of a reaction pathway involving double HAT from the organic substrate to the Fe-nitrido moiety (Figure 5a). After acidic workup of the reaction mixture (see SI for experimental details), ammonia could be detected in the form of NH_4^+ according to ^1H NMR; starting from **1c**- ^{15}N , both $^{14}\text{NH}_4^+$ and $^{15}\text{NH}_4^+$ were detected, showing that ammonia was derived from the N_{nitrido} atom (Figure 5c).

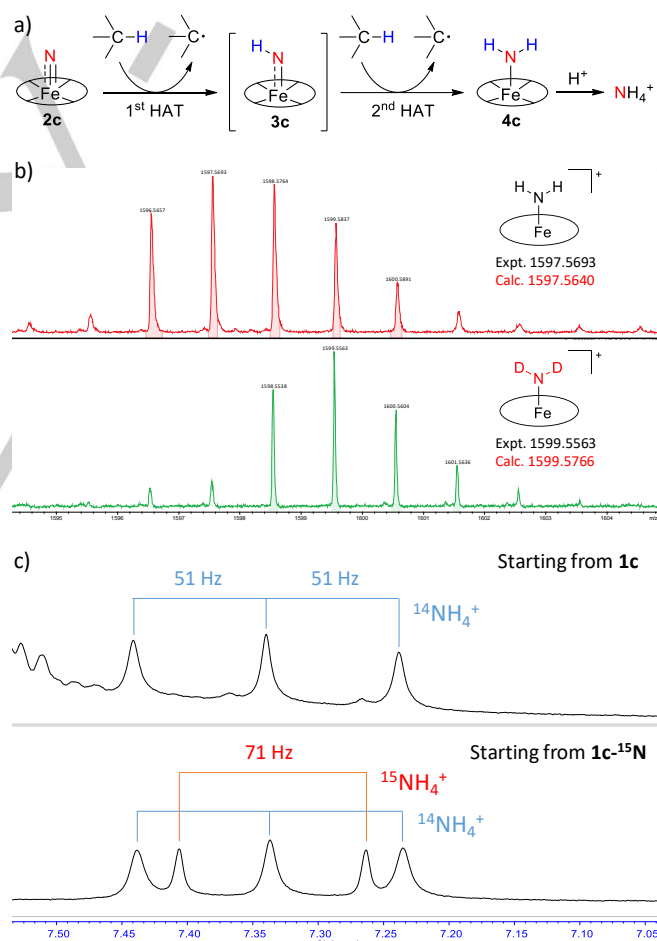


Figure 5. a) Proposed reaction pathway and ammonia formation after acidic workup of **4c** (nitrogens highlighted in red and hydrogens highlighted in blue were investigated by isotopic labelling). b) Detection of **4c** by ESI-HRMS after photolysis of **1c** with cyclohexene (top) and cyclohexene- d_{10} (bottom). c) Detection of ammonia by ^1H NMR after acidic workup of the reaction mixture starting from **1c** (top) and **1c**- ^{15}N (bottom) using cyclohexene as the substrate.

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By DFT calculations, **2c** was calculated to adopt a doublet ground state with a low-spin Fe(V) configuration (Figure 6), and previously such an electronic structure has also been assigned to the TPP analogue **2a** according to spectroscopic and theoretical evidence.^[9d] A structure of Fe(IV)-nitrido porphyrin π -radical cation similar to that of Cpd-I is less favoured since no absorption band of a porphyrin π -radical cation (630–710 nm)^[23] was observed in the ns-TA spectrum (Figure 2a). The calculated Fe–N_{nitrido} distance of 1.59 Å is consistent with a formal bond order of 2.5. The SOMO resides on one of the $\pi^*(\text{Fe}-\text{N}_{\text{nitrido}})$ orbitals (Figure 6), conferring **2c** partial nitridyl radical character. Its HAT reaction with CHD at 298 K in benzene was computed to occur with a kinetic barrier of $\Delta G^\ddagger = 13.2 \text{ kcal mol}^{-1}$ (Figure S24) in a reasonable match with the experimental value of 11.2 kcal mol⁻¹ calculated from the Eyring equation. A middle transition state was predicted, and the C–H bond approaches side-on to the N_{nitrido} atom to interact with one of the $\pi^*(\text{Fe}-\text{N}_{\text{nitrido}})$ orbitals. The resulting Fe-parent imido species **3c** adopts a triplet ground state, with its N–H BDFE value calculated to be 76.4 kcal mol⁻¹.

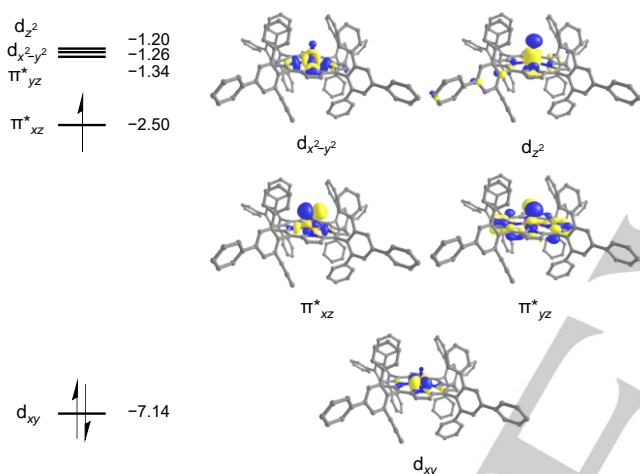


Figure 6. DFT calculated 3d orbital energy levels (in eV) for **2c**. Hydrogen atoms are omitted for clarity.

Discussion

Early works by Taube,^[24] Che,^[25] and Cummins^[26] showed metal-nitrido species as intermediates in N₂ activation processes.^[27] Their roles as nitrogen synthons in organic reactions have aroused increasing interest in recent years.^[3f, 28] While C–H activation has been reported/proposed for a few terminal metal-nitrido species,^[29] reactivity study of this elementary step remains relatively sparse and has so far been limited to an isolable Ru-nitrido complex,^[29g, i] a metastable dinuclear Ru-nitrido complex,^[29f, 30] and the LML'CT excited state of an Os-nitrido complex.^[29m, 31] In this work, we have studied the HAT reactivity of a highly reactive and short-lived Fe porphyrin nitrido species by employing the nanosecond LFP technique. Besides ultrafast spectroscopies, the supporting ligand has also been found to play a pivotal role in this study since only the HAT reactivity of **2c** could be detected. Complex **2a** generated under similar conditions showed a much faster decay compared to **2c** in the ns-TA timescale even in the absence of organic substrates (Figure S6). While for **2b**, its decay was slower (Figure S7) yet not affected by

addition of substrates. We tentatively attribute the observed HAT reactivity of **2c** to the dispersion of substrates with the bis-pocket ligand TTPPP that facilitates the hydrogen atom abstraction process. Titration of CHD or cyclohexene into a solution of **1c** led to slight spectral changes of its Soret band, from which the binding constants were estimated to be 1.31(69) and 0.27(12) M⁻¹, respectively (Figures S14–15); on the other hand, titration of the same substrates into **1b** only resulted in negligible spectral changes under similar conditions (Figure S16).

Based on our reactivity study, N–H BDE of the Fe-parent imido species **3c** was estimated to be in the range of 81–87 kcal mol⁻¹, and this is comparable to the N–H BDE value of 85.6 kcal mol⁻¹ calculated for an *in silico* tetragonal Fe(V)-nitrido complex [Fe^V(NH₃)₄(OH)(N)]⁺.^[10b] DFT calculations predict the 1e⁻ reduction potential of **2c** to be –2.12 V (vs SCE in benzene). The low 1e⁻ reduction potential of Fe-nitrido species has been documented for an isolated trigonal complex [PhB(MesIm)₃Fe^{IV}(N)] which exhibits no reduction wave in its cyclic voltammogram down to –2.5 V (vs Fc⁺⁰ in CH₃CN),^[6d] the Fe(V/IV) redox potential of this Fe-nitrido complex is also relatively low at –0.53 V (vs Fc⁺⁰ in THF).^[7c] This is attributable to the higher negative charge carried by the nitrido ligand compared to the oxo ligand. Stabilization of the high-valent Fe center by multiply bonded nitrogen-donor ligands was recently shown by an Fe(VI)-bis(imido) complex bearing low Fe(VI/IV) redox potential at –0.73 V (vs Fc⁺⁰ in THF).^[32] Experimentally, the reduction potential of **2c** could not be easily determined by the LFP method since prior addition of a strong reductant would directly reduce the Fe(III)-azido precursor **1c**. Nonetheless, addition of ferrocene did not lead to quenching of **2c**, suggesting that Fe porphyrin nitrido species are much less oxidizing than their isoelectronic Fe-oxo analogues ($E_{\text{red}} > 0.4 \text{ V vs Fc}^{+/0}$ for Cpd-I species).^[33] Such a dramatic effect of a nitrogen ligand versus an oxygen ligand on the redox potential has also been reported recently that, the 1e⁻ reduction potential of a Ru(VI)-oxo(alkylimido) complex [Ru(2,6-F₂-TPP)(O)(NAd)] is cathodically shifted by 0.74 V compared to the Ru(VI)-dioxo analogue [Ru(2,6-F₂-TPP)(O)₂].^[34] Due to the lack of a general pH scale in benzene, the pK_a value of **2c** could not be readily estimated, which hampers the depiction of a full PCET thermodynamic square scheme between **2c** and **3c**.

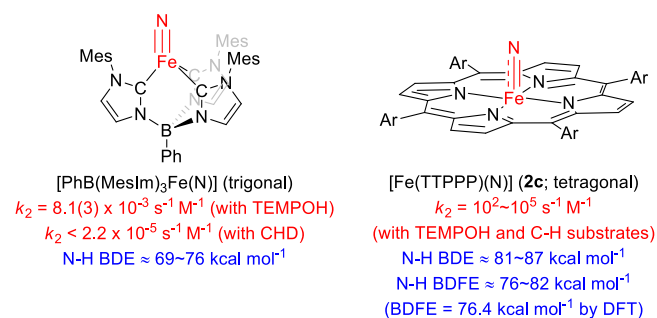


Figure 7. Comparison of kinetics and thermodynamics of HAT reactivity between [PhB(MesIm)₃Fe(N)] and **2c**.

Previously, HAT reactivity of the trigonal Fe(IV)-nitrido complex [PhB(MesIm)₃Fe^{IV}(N)] was studied using TEMPOH as a substrate and the N–H BDE value was estimated to be 69–76 kcal mol⁻¹ being smaller than that of **2c**;^[6d] the same complex was later found reactive toward CHD via a putative HAT process.^[6h] In

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terms of reaction kinetics, **2c** is more reactive than this trigonal Fe-nitrido complex (Figure 7). While the k_2 values of the reactions of **2c** with TEMPOH and CHD were measured as $8.85(95) \times 10^5$ and $3.07(10) \times 10^4 \text{ s}^{-1} \text{ M}^{-1}$ respectively, $[\text{PhB}(\text{MesIm})_3\text{Fe}^{\text{IV}}(\text{N})]$ could only activate the same substrates with rate constants of $8.1(3) \times 10^{-3}$ and $< 2.2 \times 10^{-5} \text{ s}^{-1} \text{ M}^{-1}$ respectively.^[6d, h] Such a large difference in reaction kinetics has also been observed in nitrido transfer reactions with phosphines: the k_2 value of **2c** with PMe_3 was determined to be $2.12(8) \times 10^6 \text{ s}^{-1} \text{ M}^{-1}$ (Figure S17), and although the value is smaller than that reported for *trans*- $[\text{Fe}^{\text{V}}(\text{cyclam})(\text{N}_3)(\text{N})]^+$ (close to the diffusion limit),^[6g] it is at least 2–3 orders of magnitude faster than the reactions between PAr_3 and the trigonal complexes $[\text{PhB}(\text{MesIm})_3\text{Fe}^{\text{IV}}(\text{N})]$ and $[\text{PhB}(\text{Bulm})_3\text{Fe}^{\text{IV}}(\text{N})]$.^[6f]

Table 1. Comparison of rate constants (k_2 in $\text{s}^{-1} \text{ M}^{-1}$; measured at RT unless stated otherwise) among **2c** and synthetic Cpd-I model complexes.

Complexes	Cyclohexene	PhEt
2c	$2.57(18) \times 10^3$	N.D. ^[a] (~ 97) ^[b]
$[\text{Fe}^{\text{IV}}(\text{TMP}^+)(\text{O})(\text{L})]$		
L = <i>p</i> -X-PyO ^[c] (X = OMe, Me, H, Cl)	3.8–43	$(0.6\text{--}4.6) \times 10^{-3}$
L = ClO_4 or Cl ^[d]	68–314	1.6–4.5
$[\text{Fe}^{\text{IV}}(\text{TPFPP}^+)(\text{O})(\text{ClO}_4)]$ ^[d]	225	6.2

[a] N.D. = not determined. [b] Estimated by extrapolation of the linear free energy relationship obtained in Figure 4. [c] Ref [35]. Measured at -40°C . [d] Ref [36].

Comparison can also be made between the isoelectronic Fe porphyrin nitrido and synthetic Cpd-I model complexes, i.e. Fe(IV)-oxo porphyrin π -radical cation species. The thermodynamic driving force for the nitrido species is lower than those of the oxo analogues since the latter species are capable of activating more inert substrates such as unactivated alkanes. In terms of kinetics, the HAT reaction of **2c** with cyclohexene proceeds faster than those of $[\text{Fe}^{\text{IV}}(\text{TMP}^+)(\text{O})(\text{L})]$ and $[\text{Fe}^{\text{IV}}(\text{TPFPP}^+)(\text{O})(\text{ClO}_4)]$ (Table 1).^[35–36] Since some of the cyclohexene oxidation reactions by the Cpd-I species might involve epoxidation rather than pure HAT, comparison of the kinetic data is further made using PhEt. Although the reaction of PhEt with **2c** is not fast enough to be determined under LFP conditions, a k_2 value of $\sim 97 \text{ s}^{-1} \text{ M}^{-1}$ can be estimated by extrapolating the linear free energy relationship depicted in Figure 4, and this value is also larger than those involving $[\text{Fe}^{\text{IV}}(\text{TMP}^+)(\text{O})(\text{L})]$ and $[\text{Fe}^{\text{IV}}(\text{TPFPP}^+)(\text{O})(\text{ClO}_4)]$. Collectively, these imply that the Fe-nitrido species **2c** bearing the TTPPP ligand is kinetically more reactive than the synthetic Cpd-I analogues bearing TMP and TPFPP ligands in HAT reactions. Given the high reactivity of the porphyrinoid Fe-oxo intermediates in catalytic C–H oxidation reactions, it is appealing to extend this methodology to C–H amination reactions via the intermediacy of Fe-nitrido/imido species. Although such catalytic transformations have yet to be developed for Fe-nitrido species, there have been increasing reports on the closely related parent nitrene transfer reactions which can be catalyzed by metalloporphyrinoids and engineered hemoprotein biocatalysts.^[37]

Conclusion

In the present work we have performed a reactivity study on the C–H activation by an Fe porphyrin nitrido species in the solution state using nanosecond laser flash photolysis (LFP) coupled with various spectroscopies (MS, ns-TA, RR, etc.), labelling experiments, and DFT calculations. The current methodology employing the LFP technique is promising in the future study of metal-ligand multiply bonded species especially for those being too reactive to be isolated and bearing chromophoric ligands. The thermodynamic and kinetic data obtained in this work can also shed light on the future development of C–H amination methodologies involving Fe-nitrido intermediates.

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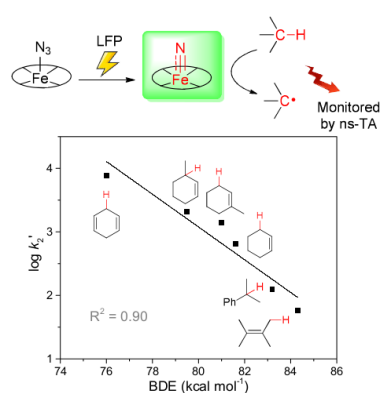
Keywords: C–H activation • Iron • Laser spectroscopy • Nitrides • Porphyrinoids

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C–H activation by Fe-nitrido! A reactivity study on the hydrogen atom transfer (HAT) reaction between C–H substrates and an Fe-nitrido porphyrin species was achieved by employing nanosecond laser flash photolysis and by using a bis-pocket porphyrin ligand. Thermodynamic and kinetic parameters obtained in this study are fundamentally important for designing C–H amination and N₂ fixation reactions involving Fe-nitrido intermediates.