The transfer of protons and electrons to metal-ligand multiply-bonded species is a key step in the mechanism of many bond activation processes. In this regard, terminally-bonded phosphinimides (PN) are isolobal analogues of oxos and imidos and should enable late transition metal complexes featuring terminal PNs to engage in H⁺/e⁻ transfer processes. Recently, we developed a rigid, multidentate PN framework intended to stabilize terminally bonded PN ligands at late, first row transition metals. Herein, we report the synthesis, structure, and spectroscopic characterization of mononuclear FeIII complexes featuring exclusively terminal PN coordination. Magnetic susceptibility and EPR spectroscopic data are consistent with S = 5/2 spin ground states. Proton transfer reactivity both via 1,2-addition across a PN−FeIII moiety and 1,2-elimination from a ferric phosphinimine (PNH) moiety is observed. Hydrogen atom transfer reactivity is observed upon oxidation of the PN−FeIII complex, resulting in formation of a PNH−FeIII species. A combination of electrochemical, pKₐ measurement, and DFT studies support an N−H bond dissociation free energy of ~90 kcal/mol for a PNH−FeIV species, and serve to highlight a reactive, transient PN−FeIV species. Combined, our results highlight terminal, late transition metal-PN moieties as redox-active superbases competent for efficient hydrogen atom abstraction processes.
1. Introduction

Terminal metal-ligand \( \pi \)-bonded species such as metal-oxos and -imidos are important intermediates in many biological and synthetic bond activation processes [1–4]. The isolation and characterization of such intermediates and further understanding of their underlying structure-function relationships are therefore of great interest [5]. In this context, the E–H (e.g. E = O, N) bond dissociation free energy (BDFE) has served as a useful descriptor in categorizing the reactivity of such species, as in the case of the linear free-energy relationship of reaction rates [6]. While certain processes may operate under kinetic control [7], thermodynamic parameters, such as BDFE, can provide critical insight into the intrinsic reactivity of a given functional group and guide design criteria for new synthetic systems.

BDFE’s are related to acidity values and redox potential through the Bordwell equation (Figure 1A) [8]. This relationship provides an experimentally convenient and intuitive definition of BDFE, wherein a simultaneously basic and oxidizing system has a greater thermodynamic driving force for the formation of a particular E–H bond. In this context, we are interested in the unique electronic properties of anionic phosphinimides (PN) as isolobal analogues of oxos and imidos [9,10]. Considering a linear metal-PN motif, two primarily N(2p)-based orbitals can engage in \( \pi \)-bonding with the metal center in two orthogonal planes; an sp-hybridized orbital can engage in \( \sigma \)-bonding with the metal center. The two canonical resonance structures for a linear metal-PN motif highlight the ability of terminal PNs to act as three- or five-electron donors (Figure 1B). The effectiveness of PNs as highly basic, electron-donating ligands has been exploited as ancillary ligands in the synthesis of early transition metal and f-block complexes [11,12]. However, despite the clear isolobal connection to late transition metal oxo and imido complexes, late transition metal PN chemistry remains significantly underdeveloped [13–15]. In particular, we hypothesized that late transition
metal PN complexes may exhibit increased basicity due to $d\pi-p\pi$ repulsive effects, which might lead to high BDFEs and thus a propensity of such complexes to engage in hydrogen atom abstraction. The increased basicity of such PN moieties also explains, in part, the tendency of PNs to act as bridging ligands [16]. In this context, our group has recently developed a new ligand platform that facilitates the isolation of high spin metal complexes with quasi-linear metal-PN linkages, enabling a systematic investigation of their properties and reactivity profiles [17,18].

Herein, we report the synthesis, structure, and spectroscopic characterization of Fe$^{III}$ complexes featuring multiple terminal PN ligands. Driven by the basicity of the PN moiety, 1,2-RH addition (elimination) reactivity is observed across the PN–Fe$^{III}$ bond. Hydrogen atom transfer reactivity is also observed upon oxidation of the PN–Fe$^{III}$ complex, resulting in the formation of a PNH–Fe$^{III}$ species. For the putative PN–Fe$^{IV}$ species, electrochemical, $pK_a$ measurement, and DFT studies indicate an N–H BDFE of ~90 kcal/mol in THF; comparable values have been observed for other Fe$^{IV}$-imido complexes [19]. Combined, our work represents the first systematic study that probes the thermodynamics of N–H BDFE at terminal metal-PN complexes, and our results underscore the previously underappreciated potential of terminal metal-PN moieties as reactive centers in bond activation processes through proton coupled electron transfer.

2. Experimental

2.1. General methods and instrumentation

All reactions were performed in an N$_2$-filled glovebox or by using standard Schlenk techniques. Glassware was oven dried at 150°C for at least 2 h prior to use and allowed to cool under vacuum. All reagents were used as received unless otherwise stated. Anhydrous pentane, diethyl ether, benzene, toluene and THF were purified by sparging with N$_2$ for 30 min, passing under N$_2$ pressure through a column of activated A2 alumina, and stored over freshly activated 3 Å molecular sieves. Fe[N(SiMe$_3$)$_2$]$_2$ and H$_3$L were synthesized according to published procedures [17, 20]. Elemental analyses were performed at the University of California Berkeley. FTIR measurements were
carried out on a Thermo Scientific Nicolet iS20 spectrometer. UV-vis measurements were carried out on a Hewlett Packard 8453 UV-Visible spectrophotometer. Electrochemical measurements were carried out using a BioLogic SP50 potentiostat. Magnetic susceptibility measurements were carried out on a Quantum Design PPMS DynaCool instrument. X-band CW EPR spectroscopic measurements were carried out on a Bruker EMX spectrometer; temperature control was achieved using liquid helium and an Oxford Instruments ESR-900 cryogen flow cryostat and an ITC-503 temperature controller. Spectra were simulated using EasySpin [21] (release 5.2.35) with Matlab R2017a.

2.2. Synthesis

Complete procedures and characterization data can be found in the Supplementary Information.

Synthesis of complex 2: A frozen solution of Fe[N(SiMe3)2]2 (5.25 g, 14 mmol, 1 equiv) in toluene (80 mL) was treated with a solution of TEMPO (2.3 g, 14 mmol, 1 equiv) in toluene (20 mL) and allowed to thaw to room temperature. The resulting dark green solution was stirred at room temperature for 1 h. Subsequently, a suspension of H3L (12.5 g, 13.8 mmol, 1 equiv) in toluene (100 mL) was treated with this dark green solution. The resulting red-brown solution was stirred at room temperature for 18 h. Subsequently, the reaction mixture was filtered through a pad of Celite, and the filtrate was treated with pyridine (20 mL) and stirred for an additional 18 h. The formation of a yellow precipitate was observed. The precipitate was collected on a fritted funnel and washed with copious amounts of Et2O. The yellow solid was dissolved in pyridine and layered with diethyl ether, yielding yellow crystals of 2 (6.06 g, 42%). Analysis calculated for C65H50FeN4P3: C, 75.37; H, 4.87; N, 5.41. Found: C, 75.72; H, 4.85; N, 5.21.

Synthesis of tris-(dimethylamido)benzylphosphonium triflate: tris-(dimethylamido)benzylphosphonium bromide was synthesized according to published procedure [22].
The bromide (94 mg, 1 equiv, 0.28 mmol) was suspended in THF (10 mL). A solution of AgOTf (80 mg, 1.1 equiv, 0.31 mmol) in THF (5 mL) was added in one portion with stirring. The tan suspension was stirred for 18 h and subsequently filtered through a pad of Celite. All volatiles were removed from the filtrate. The residue was rinsed repeatedly with Et₂O to remove the slight excess of AgOTf. After drying under reduced pressure, the phosphonium triflate was isolated as a white solid (80 mg, 71%).

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\text{H NMR (400 MHz, CD₃CN): 7.44–7.35 (m, 3 H), 7.33–7.30 (m, 2 H), 3.79 (d, } J = 16.2, 2 H), 2.65 (s, 9 H), 2.63 (s, 9 H). \]

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\text{31P NMR (162 MHz, CD₃CN): 56.0 ppm.} \]

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\text{19F NMR (376 MHz, CD₃CN): } \\
\text{\#78.6 ppm (Figures S9–S11).} \]

2.3. Crystallography

Suitable crystals were mounted on a nylon loop using Paratone oil, then placed on a diffractometer under a nitrogen stream. X-ray intensity data were collected on a ROD, Synergy Custom DW system, Pilatus 200 K detector employing Mo-Kα or Cu-Kα radiation at a temperature of 100 K. All diffractometer manipulations, including data collection, integration and scaling, were carried out using CrysAlisPro 1.171.40.61a (Rigaku OD, 2019) software. Using Olex2, the structures were solved by intrinsic phasing using ShelXT [23] and refined to convergence by full-matrix least squares minimization using ShelXL [23]. All non-solvent non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. Graphical representations of structures with 50% probability thermal ellipsoids were generated using Diamond visualization software.

2.4. Computational methods

Calculations were performed with Gaussian 09 [24]. Gas phase geometry optimizations were carried out using the BP86 DFT method and the def2-TZVPP basis set for all non-C and -H atoms and SVP for C and H atoms. From this optimized geometry, frequency calculations were performed with the B3LYP DFT method; no imaginary
frequencies were obtained, supporting that the optimized structures represent energetic minima. The sum of the free energies was used to calculate the $\Delta G$ of N–H bond dissociation free energy.

### 3. Results and discussion

On the basis of our previous work describing the synthesis of a high spin Co$^{III}$ complex supported by a rigid tris-PN framework (H$_3$L, Figure 2A), we targeted the synthesis of the analogous Fe$^{III}$ complex in anticipation that a high-valent Fe$^{IV}$ state may be stabilized by the tris-PN framework [17]. The simple combination of H$_3$L with bulky Fe$^{III}$ amide precursors (e.g. Fe[N(SiMe$_3$)$_2$]$_3$) invariably led to complex reaction mixtures. With cursory attempts with Fe[N(SiMe$_3$)$_2$]$_3$ proving unsuccessful, we hypothesized that an alternative approach might involve hydrogen atom abstraction from a PNH/Fe$^{II}$ species [18]. Treatment of H$_3$L with a mixture of Fe[N(SiMe$_3$)$_2$]$_2$ and TEMPO leads to formation of 1. The X-ray crystal structure of 1 is consistent with the (HL)Fe$^{III}$(TEMPO$^-$) formulation (Figure 3A). We hypothesize that an Fe$^{III}$ species with a formula consistent with (TEMPO)Fe[N(SiMe$_3$)$_2$]$_2$ is generated in situ (Figure S1), which subsequently reacts with H$_3$L via protonolysis to afford 1. Consistent with the assignment in which a PN moiety remains protonated, one long Fe–N distance (~2.4 Å) and two shorter Fe–N distances (~1.86 Å) are observed. The Fe$^{III}$ oxidation state assignment is supported by the N(4)–O(1) distance, which is consistent with the reduced nitroxide anion [25]. Further, the IR spectrum of 1 features a broad resonance at 3310 cm$^{-1}$ that can be attributed to the $\nu$(PN–H) stretching vibration (Figure S2). The Fe–N distances in 1 are comparable to those of a recently reported dimeric Fe$^{III}$-PN complex featuring terminal Fe–N distances of ~1.84 Å [14]. For further structural comparison to other $\pi$-basic moieties, Fe$^{III}$–N(ketimide) distances of 1.87 Å have been reported [26]. High spin, three-coordinate Fe$^{III}$-imido complexes feature Fe–N distances of ~1.69 Å; consistent with an Fe–N triple bond, an Fe–N distance of 1.64 Å was reported for a low-spin, four coordinate Fe$^{III}$-imido complex [27–29]. Finally, given that prototypical Fe$^{III}$–N(amide) distances are commonly observed at ~1.92 Å (e.g. those in (THF)FeCl[N(SiMe$_3$)$_2$]$_2$) [30], PN–Fe$^{III}$ distances fall between corresponding Fe-imido and Fe-amido distances, indicating the presence of significant multiple bonding character in terminal PN–Fe$^{III}$ moieties.

![Figure 4](image-url)

**Figure 4.** (A) Reduced magnetization data of 2 in the 2–8 K and 1–8 T range, and corresponding Brillouin function for $S = 5/2$ (red trace). (B) X-band EPR spectrum of 2 (black trace) and simulation (red dotted trace): $T = 5$ K, $S = 5/2$, $g = 2.0$, $D = 0.3$ cm$^{-1}$, $E/D = 0.092$. Data acquisition parameters: frequency = 9.37 GHz, power = 2 mW, conversion time = 80 ms, modulation amplitude = 4 G.
The fully deprotonated FeIII tris-PN complex was obtained via elimination of TEMPO – H from 1. Either in sequential steps or in situ, treatment of 1 with excess pyridine results in the formation of 2 (Figure 2A). The IR spectrum of 2 lacks features ascribable to ν(N – H) vibrations (Figure S3), and the X-ray crystal structure corroborates the LFeIII(py) formulation (Figure 3B). Consistent with the assignment in which all PN moieties are deprotonated, the coordination geometry around Fe in 2 is pseudo-C₃ symmetric, with PN – Fe distances and ∠(PN – Fe – Npy) angles all similar to each other. A tetrahedral character THCDₐ value of 0.42 indicates that the Fe center adopts a squashed-tetrahedral geometry. Notably, the conversion of 1 to 2 does not proceed with THF, suggesting that the 1,2-elimination of TEMPOH from 1 may be assisted by more coordinating ligands such as pyridine. Driven by the basicity of the PN – Fe moiety (vide infra), the reverse 1,2-addition is observed upon treatment of 2 with a phenol, resulting in the formation of 4 (Figure 2B). IR spectroscopic features (Figure S8) as well as the X-ray crystal structure corroborate the (HL)FeIII(PhO) formulation (Figure 3C).

Magnetic susceptibility measurements were performed to obtain further insight into the electronic structure of 2. An ideal Curie behavior was observed in the 2-300 K temperature range with a $\chi T$ value of 4.38 emu K mol⁻¹ (Figure S4), consistent with the expected spin-only value of 4.375 emu K mol⁻¹ ($g = 2$) for an $S = 5/2$ spin ground state. Reduced magnetization data show a saturation magnetic moment of 5 $\mu_B$, further consistent with $S = 5/2$ (Figure 4A). X-band EPR studies were conducted (Figure 4B). Qualitatively, the spectrum of 2 suggests that the weak field regime is operative [31]. In such cases, as illustrated in the rhombograms for half-integer spin states $S > 1/2$, peak positions are primarily determined by the $E/D$ ratio ($|E/D| \leq 0.33$) where $E$ is the transverse component and $D$ is the axial component of the zero-field splitting parameter. The spectrum of 2 features broad signals centered at 92 mT ($g = 7.4$) and 170 mT ($g = 4.0$), which can be assigned to the $|\pm1/2$ Kramers doublet of an $S = 5/2$ spin state with low rhombicity. Additionally, the features at 125 mT ($g = 5$) and 300 mT ($g = 2.3$) can be assigned to the $|\pm3/2$ Kramers doublet. Consistent with these assignments, the spectrum of 2 can be approximated with a rhombicity of $E/D = 0.09$. 

**Figure 5.** Overlay of the cyclic voltammogram (red trace) and the square-wave voltammogram (blue trace) of 2.
Electrochemical studies of \( \text{2} \) were performed to obtain insight into its redox properties (Figure 5). The cyclic voltammogram (CV) of \( \text{2} \) in a THF electrolyte features an irreversible oxidation at \( E_{pa} = 0 \) V versus Fc/Fc\(^{+} \), which can be assigned to the formal Fe\(^{III/IV} \) redox couple. The absence of an observable Fe\(^{II/III} \) redox at potentials as low as \(-1.5 \) V versus Fc/Fc\(^{+} \) indicates a strong stabilization of the Fe\(^{III} \) oxidation state by the tris-PN framework. The absence of a cathodic current \( I_{pc} \) for the Fe\(^{III/IV} \) redox couple suggests that the electrochemical oxidation step is followed by a rapid chemical step. The absence of \( I_{pc} \) at scan rates \( \leq 1 \) V/s and in the presence of a THF-d\(_{8} \) electrolyte indicates a fast rate of decay for the putative Fe\(^{IV} \) species, and suggests either a significant structural reorganization upon oxidation or a rapid reaction with the C–H(D) bonds of THF. On the basis of the square-wave voltammogram (SWV) of \( \text{2} \), the \( E_{1/2} \) of the Fe\(^{III/IV} \) redox couple can be estimated at \(-50 \) mV versus Fc/Fc\(^{+} \).

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Chemical oxidation of \( \text{2} \) was pursued to obtain insight into the identity of the decay product obtained upon oxidation. Treatment of \( \text{2} \) with an equimolar amount of Fc(PF\(_{6} \)) in THF leads to the formation of \( \text{3} \) (Figure 2B). The IR spectrum of \( \text{3} \) features a prominent peak at \( \nu(N–H) = 3300 \) cm\(^{-1} \) (Figure S5), and the X-ray crystal structure corroborates a [(HL)Fe\(^{III} \)(py)]\(^{+} \) formulation (Figure 6D). In addition to EPR analysis (Figure S6) and charge balance considerations, the presence of a unique, elongated PNH–Fe distance of 1.97 Å is consistent with a formal Fe\(^{III} \) oxidation state assignment, and strongly suggests the decay of a transient [LFe\(^{IV} \)(py)]\(^{+} \) species to \( \text{3} \) via a hydrogen atom transfer (HAT) process. Accordingly, the IR spectrum of \( \text{3} \) generated in the presence of dihydroanthracene-d\(_{4} \) features a peak at \( \nu(N–D) = 2290 \) cm\(^{-1} \), in modest agreement with the expected value of 2410 cm\(^{-1} \) from a reduced mass consideration (Figure S7).

To obtain further insight into the thermodynamics of HAT, the \( pK_{a} \) of \( \text{3} \) was determined by spectrophotometric titration of \( \text{2} \) with diverse acids. Treatment of \( \text{2} \) in THF
with the conjugate acid of py, DBU, or TBD ($pK_a = 5.5, 16.9, 21$, respectively) [32,33] leads to effective protonation of 2 to 3. The conjugate acid of Verkade’s base ($pK_a = 26.6$) was not effective, constraining the $pK_a$ of 3 between 21 and 26.6 [34]. Using the phosphonium ylide precursor ($pK_a = 22.7$) shown in Figure 6, an equilibrium was established between 2 and 3, and a value of $pK_a = 24.1$ was obtained after mass balance considerations (Figure S12). Using the experimentally determined values of $E^o$ and $pK_a$, application of the Bordwell equation leads to an estimated $N - H$ BDFE of $92 \pm 2$ kcal/mol in THF. The high BDFE obtained here can be attributed to the simultaneously high oxidation potential and basicity of 2. This is an interesting observation since $E^o$ and $pK_a$ are often inversely proportional; a high basicity is typically related to a low redox potential and vice versa. Considering the lower $pK_a = 19.7$ of the phosphazene base (Me$_2$N)$_3$PNH in THF, the higher $pK_a$ of the PN – Fe$^{III}$ moiety in 2 is noteworthy. A $pK_a$ value of 20.65 has been reported for Ph$_3$PNH, albeit in CH$_3$NO$_2$ [35]. Considering the similar dielectric constants of CH$_3$NO$_2$ and CH$_3$CN (35.9 and 37.5, respectively), a solvent for which $pK_a$ values have been extensively tabulated, we extrapolate the $pK_a$ of Ph$_3$PNH to be in the range of 13–15 in THF using an empirical correlation between $pK_a$ values in CH$_3$CN and THF. Thus, we hypothesize that the much higher $pK_a$ of the PN – Fe$^{III}$ moiety in 2 is intimately connected to its electronic structure (vide infra). While the HOMO of Ph$_3$PNH assumes a weak P – N $\pi$-bonding character, the HOMO of 2 assumes an additional Fe – N $\pi$-antibonding character, resulting in increased basicity. Further inductive effects with the previously described 1-adamantyl-substituted version of H$_3$L may increase the basicity of the corresponding PN – Fe species, and efforts on this front are ongoing. Taken together, these data suggest that certain metal-PN species can behave as redox-active superbases apt to engage in hydrogen atom abstraction processes [36].

To better understand the unique PN – Fe bonding situation in 2, density functional theory (DFT) studies were performed. Consistent with a squashed tetrahedral coordination geometry around the Fe center, the orbitals of d parentage split into a 2-2-1 pattern with two sets of doubly degenerate orbitals. The two degenerate sets correspond to the $d_{xz}/d_{yz}$ and $d_{xy}/d_{x^2-y^2}$ orbitals, with the latter being higher in energy. The orbital of $d_{z^2}$ parentage is lowest in energy, and each orbital of d parentage is half-filled, consistent with the $S = 5/2$ spin ground state. The average, calculated Fe – N distance of 1.87 Å is in excellent agreement with experiment, encouraging additional DFT studies to provide further computational support for the observed BDFE. For the four coordinate [LFe$^{IV}$(py)]$^{+}$ species, in silico geometry optimizations were performed on possible $S = 1$ and 2 spin ground states, with the quintet state found to be significantly lower in energy by approximately 24 kcal/mol. Consistent with this electronic structure, the lowest unoccupied molecular orbital is of $d_{xy}$ (or $d_{x^2-y^2}$) parentage. The average calculated Fe – N distance (1.79 Å) is shorter than comparable distances in 2, consistent with substantial Fe – N multiple bond character. Finally, 3 was optimized as a sextet, and the calculated geometry agrees well with experiment. Considering the calculated free energies of [LFe$^{IV}$(py)]$^{+}$, complex 3, and the hydrogen atom corrected for the energy of dissolution in THF using a CPCM model [28, 37, 38], a BDFE of 88 kcal/mol was calculated, in good agreement with the experimentally determined value (92 kcal/mol).
4. Conclusion

A series of Fe$^{III}$ complexes featuring exclusively terminal PN coordination is reported. Structural, spectroscopic, and reactivity studies show that terminal PN moieties stabilize mononuclear high spin iron complexes that readily engage in proton transfer through 1,2-addition(elimination) processes. Finally, we show that late transition metal complexes featuring terminal PN moieties can exhibit high BDFEs that are driven by both high basicity and oxidation potential; the observed BDFE of 92 kcal/mol in THF is comparable to those of other high-valent metal-oxo(imido) complexes and is currently under consideration as a functional group competent for hydrogen atom abstraction processes.

Acknowledgements

We thank Dr. Nicholas Settineri for assistance with XRD, Prof. Kwabena Bediako and Zhizhi Kong for access to and assistance with SQUID magnetometry, and Prof. R. David Britt and Dr. David Marchiori for access to and assistance with EPR spectroscopy. We thank Dr. Hasan Celik and UC Berkeley’s NMR facility in the College of Chemistry (CoC-NMR) for spectroscopic assistance. Instruments in the CoC-NMR are supported in part by NIH S10OD024998.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This research was supported by the University of California Berkeley. Prof. R. David Britt and Dr. David Marchiori for access to and assistance with EPR spectroscopy (supported by NIH R35 Grant 1R35GM126961-01 to R.D.B.). National Institute of General Medical Sciences.

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