

C–H Bond Amination from a Ferrous Dipyrromethene Complex

Evan R. King and Theodore A. Betley*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, 306E Mallinckrodt, Cambridge, Massachusetts 02138

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In this Communication, we report an intramolecular C–H bond amination reaction of a dipyrromethene ferrous complex with organic azides. Monitoring of the spectral changes (variable-temperature NMR and UV–vis) of the Fe^{II} complex reveals no buildup of an intermediate during conversion of the starting material into the nitrene-inserted product. The rate-determining step appears to be azide addition to the 14-electron Fe^{II} complex, hinting at the potential that these and related platforms may have to effect atom- and group-transfer processes.

Introducing functionality into unactivated C–H bonds remains a significant challenge both in the realm of complex molecule synthesis and in the elaboration of simple hydrocarbon feedstocks into value-added commodity chemicals.¹ The current state-of-the-art C–H bond functionalization techniques mainly utilize late-transition-metal catalysts that facilitate C–H activation and functionalization. Several limitations exist in these methods: C–H bond activation typically requires forcing conditions where oxidation processes can become unselective under the conditions required for bond activation to occur² or C–H bond activation only occurs proximal to substrate-directing groups.³ The development of new inorganic/organometallic catalysts to effect atom- or group-transfer processes will mitigate the reliance on directing groups to activate C–H bonds,⁴ thereby minimizing waste generation during synthetic procedures.⁵ One potential strategy for sequential C–H bond activation and functionalization is to utilize the transient formation of

metal–ligand multiple bonds to effect atom- or group-transfer processes.⁶ Herein we report an intramolecular C–H bond amination mediated by the reaction of a coordinatively and electronically unsaturated dipyrromethene iron(II) complex with organic azides.

A variety of ligand platforms have been employed that utilize strongly donating substituents (e.g., phosphines,⁷ amines,⁸ carbenes,⁹ and β -diketiminates¹⁰), resulting in strongly nucleophilic metal complexes capable of supporting metal–ligand multiple bond formation. To target metal–ligand multiple bonds potentially more reactive toward bond-activating pathways, we sought an oxidatively resistant ligand system that sterically enforces minimal coordination at the metal center while maintaining an electrophilic metal envi-

* To whom correspondence should be addressed. E-mail: betley@chemistry.harvard.edu.

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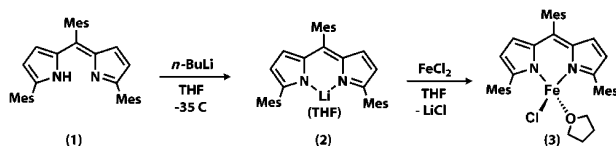
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Scheme 1



ronment, which may confer unique reactivity to the resulting metal complexes. Arylated dipyrromethene ligands are good candidates to satisfy both desired design criteria.¹¹ Using pyridinium *p*-toluenesulfonate as a catalyst (5%), 2-mesitylpyrrole was condensed with mesitaldehyde dimethyl acetal to form the dipyrromethane. Subsequent oxidation with dichlorodicyanoquinone in acetone affords the target 1,5,9-trimesityldipyrromethene [(pyac)H, **1**] in 68% overall yield. Dipyrromethene **1** precipitates from the acetone solution upon oxidation, obviating the need for chromatography as a purification step. Deprotonation of the ligand can be effected by the treatment of **1** with 1.2 equiv of *n*-BuLi in thawing tetrahydrofuran (THF) solutions to produce the solvated lithio complex [pyac][Li(THF)] (**2**), which was, in turn, suitable for installing the pyac moiety onto transition metals.

Reaction of the lithio complex **2** with a thawing slurry of FeCl₂ in THF furnished the four-coordinate, solvated species (pyac)FeCl(THF) (**3**) as a red solid (Scheme 1). The solid-state structure for **3** is provided in Figure 2, confirming the solvated state adopts a pseudotetrahedral environment at iron. THF in **3** is labile and can be exchanged for stronger binding ligands like pyridine to yield (pyac)FeCl(pyr) (**4**). Likewise, the Zn^{II} congener was synthesized by the reaction of **2** with ZnCl₂ in thawing THF, followed by treatment with pyridine to furnish (pyac)ZnCl(pyr) (**5**) as an isolable orange solid. Complexes **3**–**5** could be isolated as analytically pure solids in 75–84% yield. Complexes **4** and **5** adopt geometries similar to that of **3** in the solid state (see the Supporting Information).

Much like their porphyrin congeners, dipyrromethenes and their metal complexes exhibit intense ligand $\pi \rightarrow \pi^*$ transitions afforded by the conjugation and aromaticity of the dipyrromethene ligand system.¹² The dominant charge transfer occurs in the range of 460–500 nm for the parent ligand **1** and its metal complexes (Figure 1) [$\lambda_{\max}$ (ϵ) for **1** 467 nm (49 000 M⁻¹ cm⁻¹); $\lambda_{\max}$ (ϵ) for **2** 499 nm (97 000 M⁻¹ cm⁻¹); $\lambda_{\max}$ (ϵ) for **3** 503 nm (74 000 M⁻¹ cm⁻¹); $\lambda_{\max}$ (ϵ) for **4** 506 nm (69 000 M⁻¹ cm⁻¹); $\lambda_{\max}$ (ϵ) for **5** 501 nm (140 000 M⁻¹ cm⁻¹)]. The observed $\pi \rightarrow \pi^*$ transition for ligand **1** is not unlike other dipyrromethene ligand derivatives that are often employed as fluorescence tags or the parent porphyrin constructs.¹² While the zinc complex **5** is a diamagnetic species, the room temperature solution magnetic moments of complexes **3** and **4** are 5.21(5) and 5.29(1) μ_B , respectively, both consistent with high-spin ($S = 2$) iron centers (Evans method).¹³ Cyclic voltammetry on **3** and **4** reveals fully reversible Fe^{III/II} redox waves centered at –400 mV versus an internal ferrocene reference (Figure 1, inset; scan rate = 100 mV/s). Cyclic voltammetry on complex **5** reveals fully reversible, one-electron reduction (–2.0 V) and oxidation (+0.55 V) events originating from the ligand

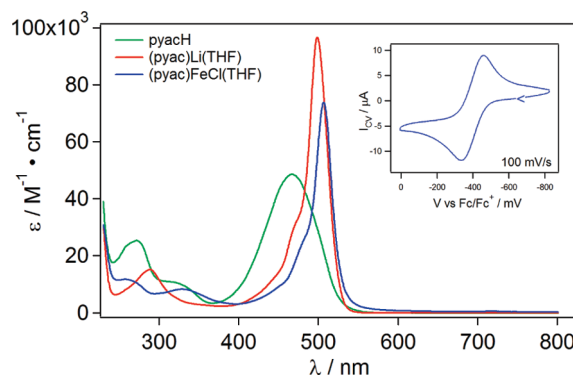


Figure 1. UV-vis spectra of **1**–**3** (THF). The inset shows the cyclic voltammogram of complex **3** in THF (0.1 M) with 0.3 M Bu₄NPF₆; scan rate = 100 mV/s on a glassy carbon electrode.

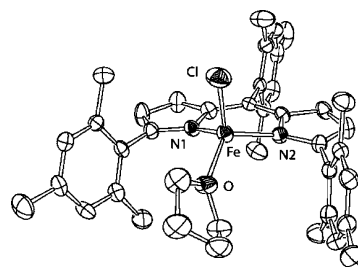


Figure 2. Solid-state structure for **3** with thermal ellipsoids set at the 50% probability level (H atoms omitted for clarity). Bond lengths (Å) for: Fe–N1, 2.017(3); Fe–N2, 2.034(4); Fe–Cl, 2.263(1); Fe–O, 2.029(3).

platform (see the Supporting Information). Reduction waves are observed for complexes **3** and **4** at similar potentials, whereas the onset to oxidation is shifted by ca. –300 mV and the processes are no longer reversible.

To test whether the dipyrromethene ligand could confer the same reactivity at the Fe^{II} center as their porphyrin counterparts, we canvassed the reactivity of **3** with a series of organic azides to examine whether nitrene transfer could be effected.¹⁴ Reacting a thawing solution of **3** in dichloromethane with a stoichiometric amount of 1-azidoadamantane quantitatively produces a new paramagnetic, iron-containing complex, evidenced by the increase of observable proton resonances apparent in ¹H NMR, consistent with desymmetrization of the ligand environment (see the Supporting Information for ¹H NMR details). Solutions of **3** in thawing CH₂Cl₂ react quickly with organic azides (N₃Ph, N₃Mes, and N₃Ad) to expel dinitrogen, as evidenced by the disappearance of the azide stretch in the IR spectrum, and cleanly produce a new high-spin Fe^{II} product distinct from **3** by ¹H NMR, displaying a similar desymmetrization of the ligand proton resonances.

Characterization of crude reaction mixtures by electrospray ionization mass spectrometry revealed parent ions consistent with azide-derived nitrene insertion into a ligand C–H bond (Scheme 2). The masses obtained from the independent reactions of **3** with N₃R (R = ^tBu, 1-Ad, Ph, Mes, Tos) suggest that multiple nitrene insertions into the ligand do not occur,

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