Facile and Regioselective C–H Bond Activation of Aromatic Substrates by an Fe(II) Complex Involving a Spin-Forbidden Pathway

Steven E. Kalman,¹ Alban Petit,² T. Brent Gunnoe,^{3*} Daniel H. Ess,^{3*} Thomas R. Cundari,^{3*} and Michal Sabat[§]

¹Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, United States

²Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, United States

³Department of Chemistry, Center for Advanced Scientific Computing and Modeling (CASCAM), University of North Texas, Denton, Texas 76203, United States

[§]Nanoscale Materials Characterization Facility, Materials Science and Engineering Department, University of Virginia, Charlottesville, Virginia 22904, United States

Supporting Information

ABSTRACT: The Fe(II) complex $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ ($\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$) is shown to mediate facile and highly regioselective C–H activation of aromatic substrates including benzene, furan, thiophene, thiazole, and 2-methylfuran. Experimental and computational evidence suggest a mechanism for C–H activation that involves NCMe dissociation, multiple spin intersystem crossings, C–H bond coordination, and C–H bond cleavage by a σ -bond metathesis reaction.

INTRODUCTION

The majority of homogeneous catalysts for hydrocarbon C–H bond activation and functionalization are based on second- or third-row transition metals.^{1–3} Although first-row transition metal oxo, alkoxide and amide complexes can functionalize C–H bonds,^{4–10} they typically function via net H abstraction and are often limited to relatively weak C–H bonds.⁴ While nature has evolved highly selective enzymes for C–H functionalization using net H abstraction by metal oxo complexes (including Fe oxo complexes), extending the high reactivity and selectivity to synthetic systems has been a substantial challenge.⁴ Thus, it is desirable to develop nonradical, nonoxo metal C–H activation catalysts based on inexpensive Earth-abundant transition metals (Scheme 1). However, there are several challenges associated

with developing catalysts based on the first row of the transition metal series including typically weaker metal carbon bond strengths, propensity toward single-electron chemistry, complications due to the possibility of spin crossover, and access to multiple oxidation states.^{11,12} These challenges have limited the number of examples of nonoxo, nonradical stoichiometric C–H activation reactions based on 3d transition metals.^{13–16} Some examples of catalytic C–H activation and functionalization by first-row transition metals have been disclosed.^{17–19}

Two of our groups have previously reported that $\text{TpRu}(\text{L})(\text{NCMe})\text{Ph}$ [Tp = hydridotrispyrazolylborate; L = CO, PMe_3 , $\text{P}(\text{OCH}_2)_3\text{CEt}$, 2,6,7-trioxa-1-phospha-bicyclo[2,2,1]heptane, $\text{P}(\text{N-pyrrolyl})_3$] complexes readily activate aromatic and olefinic C–H bonds.^{20–24} We envisioned that a similar $(\text{Y})\text{Fe}(\text{L})(\text{NCMe})\text{Ph}$ (Y = monoanionic, six-electron donor ligand) complex with an Fe(II) metal center might also provide entry into C–H activation.²⁵ Because of the similarities between Tp and Cp^* ,²⁶ we chose $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (**2**) as the initial complex. Herein, we report experiments and calculations that showcase the success of this Fe(II) complex for regioselective aromatic C–H activation under mild conditions.

Scheme 1. Oxo Mediated H Atom Abstraction and Fe Mediated C–H Activation

Oxo Mediated H Atom Abstraction

Fe Mediated C–H Activation

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RESULTS AND DISCUSSION

The target complex **2** was prepared by reaction of $\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}^{25}$ with CuOTf and Bu_3SnPh , which gave $\text{Cp}^*\text{Fe}(\text{CO})_2\text{Ph}$ (**1**) in 67% isolated yield. Complex **1** has been previously reported,²⁸ albeit in lower yields. The photolysis of an NCMe solution of **1** produced $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (**2**) in 87% isolated yield (Scheme 2). Complexes **1** and **2** were both characterized by single crystal X-ray diffraction (Figure 1).

Scheme 2. Synthesis of $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (**2**)

Figure 1. ORTEP drawings of $\text{Cp}^*\text{Fe}(\text{CO})_2\text{Ph}$ (**1**) and $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (**2**) (50% probability ellipsoids; H atoms omitted). Complex **1** (left). Selected bond lengths (Å): Fe C7/C7 1.756(1), Fe C8 2.002(2), C7 O1/C7 O1 1.151(2). Selected bond angles (°): C7 Fe C7 95.87(8), C7/C7 Fe C8 91.30(5). Complex **2** (right). Selected bond lengths (Å): Fe C14 1.990(1), Fe C11 1.741(1), Fe N1 1.903(1), C11 O1 1.154(2). Selected bond angles (°): C11 Fe N1 98.00(6), C11 Fe C14 91.79(6), N1 Fe C14 89.76(5).

For an initial test of C–H activation, **2** was heated to 50 °C in C_6D_6 . $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})(\text{Ph}-d_5)$ (**2-d₅**) forms in 80% yield based on NMR spectroscopy (eq 1). The formation of **1**

and **1-d₅** (10%) and other uncharacterized products make up the remaining 20% of Fe complexes. Under pseudo-first-order conditions in C_6D_6 at 49 °C, k_{obs} is $4.6(5) \times 10^{-4} \text{ s}^{-1}$ for the C–D activation of C_6D_6 .

To explore the mechanism of C_6D_6 C–D (modeled as C–H) bond activation by **2**, we utilized M06^{29,30} density functional calculations with SMD solvent corrections to

calculate possible intermediates and transition states.³¹ Comparison of the M06 optimized structure of **2** (Figure 2) shows highly similar bond lengths and angles compared to the X-ray structure shown in Figure 1. Starting from complex **2**, C–H activation begins with NCMe dissociation to create a vacant coordination site. The enthalpic (ΔH) penalty for complete NCMe dissociation along the singlet energy surface is 27.1 kcal/mol. The resulting $\text{Cp}^*\text{Fe}(\text{CO})(\text{Ph})$ singlet complex (**3^s**) shows an unrestricted wave function with a spin contamination $\langle S^2 \rangle$ value of 0.23, which suggests open-shell character and a possible high-spin state of lower energy. Indeed, the triplet $\text{Cp}^*\text{Fe}(\text{CO})(\text{Ph})$ complex (**3^t**) is adiabatically 16.4 kcal/mol more stable than **3^s**. The structures **3^s** and **3^t** show that after complete loss of NCMe, the CO and Ph groups reorient slightly, but the only major bond length change is a decrease in the Fe–Ph bond length from 1.98 Å in **2** to 1.91 and 1.94 Å in **3^s** and **3^t**, respectively. The structures **3^s** and **3^t** are highly similar.

Consideration of spin states and their interconversion is important for first row transition metals.^{32–34} Direct conversion of **3^s** to **3^t** can occur through a singlet–triplet intersystem crossing, called a minimum energy crossing point (MECP). The optimized structure of MECP-1 (Figure 3) connects **3^s** to **3^t** and has an energy and geometry nearly identical to **3^t**. Although it is possible that NCMe completely dissociates before singlet–triplet intersystem crossing, there is a lower energy pathway for conversion of complex **2** to **3^t**. This pathway involves singlet–triplet interconversion with partial NCMe dissociation (Fe–N = 2.18 Å) via MECP-2 with a ΔH value of 9.0 kcal/mol relative to **2**. Optimization of the resulting triplet structure after MECP-2 resulted in the triplet NCMe π complex **4^t** with $\Delta H = 4.6$ kcal/mol. Structure **3^t** is then accessed upon NCMe dissociation. These structures suggest that NCMe dissociation is facile through a dissociative mechanism. An interchange coordination mechanism that remains on the singlet energy surface is unlikely due to the reluctance of the Fe metal center to increase its ligand coordination number.

Scheme 3 outlines the lowest energy pathway calculated for benzene C–H activation by complex **2**. As discussed above, **3^t** is generated via MECP-2 followed by NCMe loss. Although **3^t** is a viable intermediate, Fe–Ph group exchange from this species on the triplet energy surface showed barriers too high to be reasonable, and it is therefore a dead-end intermediate. As a result, a second intersystem crossing step to return to the singlet energy surface is required during the C–H bond coordination/activation mechanistic stage. There are two possible pathways for this intersystem crossing. The first pathway involves conversion of **3^t** to **3^s** via MECP-1 followed

Figure 2. M06 ground-state structures. Bond lengths reported in Å and angles in degrees.

Figure 3. MECPs and triplet π complex. Bond lengths reported in Å and angles in degrees.

Scheme 3. M06/6-311++G(3df,3dp)[LANL2TZ(f)]/M06/6-31G(d,p)[LANL2DZ] Calculated Enthalpies (Free Energies at 298 K) for C–H Activation of Benzene by $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (**2**) in Benzene Solvent (kcal/mol)

by benzene coordination on the singlet surface. The second pathway, which is lower in energy, involves intersystem crossing along with benzene coordination via MECP-3 to give singlet **5^s** directly from **3^t**. The structure and energy of MECP-3 is nearly identical to **5^s** (Figure 4). The enthalpy of triplet **5^t** is 24.0 kcal/mol and confirms that the singlet–triplet crossing point occurs just prior to structure **5^s**.

Figure 4. M06 structures for benzene coordination and C–H bond cleavage. Bond lengths reported in Å and angles in degrees.

Structure **5^s** involves η^2 -C,H-benzene coordination. Because of the orientation of the Fe–Ph group, no true η^2 -C,C-benzene coordination complex could be located. For Ru(II) complexes, η^2 -C,H-benzene coordination in preference to η^2 -C,C-benzene coordination has been taken to imply steric congestion at the metal center.²² From intermediate **5^s**, the lowest energy pathway for C–H bond cleavage occurs via a four-centered σ -bond metathesis type transition state **6-TS** (Figure 4) with a calculated $\Delta H^\ddagger$ of 29.4 kcal/mol. In this transition structure, the Fe–Ph bond length is stretched to 2.04 Å, and the benzene C–H bond partial bond length is 1.49 Å. The transition state **6-TS** directly connects to another η^2 -C,H-benzene coordination complex **5^s**. At this point NCMe can replace coordinated benzene from **5^s** to regenerate **2**. This last step is also susceptible to spin intersystem crossings, but they are not pictorially represented in Scheme 3.

We have ruled out several other C–H activation mechanisms for Fe–Ph group exchange. The first involves the generation of a so-called tuck-in type complex directly from **2**. In this mechanistic pathway a methyl C–H bond of the Cp* group undergoes intramolecular σ -bond metathesis with the Fe–Ph group to give a cyclometalated Cp* group and η^2 -CH-benzene coordination. The calculated $\Delta H^\ddagger$ for this process is 50.9 kcal/mol. The $\Delta G^\ddagger$ for forming the tuck-in complex after dissociation of NCMe is 54.6 kcal/mol. We have observed no

deuterium incorporation into the Cp* methyl resonances (^1H NMR spectroscopy) for the reaction of **2** and C_6D_6 .

We have also considered the Fe(II) to Fe(IV) oxidative addition from **3*** and **3'** to give the seven-coordinate diphenyl hydride intermediate $\text{Cp}^*\text{Fe}(\text{CO})(\text{Ph})(\text{Ph})(\text{H})$. All optimizations starting with seven-coordinate Fe hydride structures reverted back to **5***. Lastly, our calculations suggest several hydrogen abstraction mechanisms from both **3*** and **3'** are unlikely pathways. For example, the H to give $\text{Cp}^*\text{Fe}(\text{CO})(\text{Ph})(\text{H})$ and $\cdot\text{C}_6\text{H}_5$ is 48.4 kcal/mol relative to **3***. Eisenstein et al. have found similar results for their study on the TpFe motif.³⁵

The ability of **2** to activate benzene prompted us to explore the possibility of **2** activating heteroaromatic substrates under similar mild conditions. Indeed, complex **2** regioselectively activates furan, thiophene, thiazole and 2-methylfuran at or below room temperature (Scheme 4). To optimize stability, the

Scheme 4. C–H Activation of Heteroaromatic Substrates by $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (**2**)

products from the C–H activation of furan, thiophene and 2-methylfuran were isolated as their PPh_3 adducts. $\text{Cp}^*\text{Fe}(\text{CO})(\text{PPh}_3)(2\text{-furyl})$ (**7**) and $\text{Cp}^*\text{Fe}(\text{CO})(\text{PPh}_3)(2\text{-thienyl})$ (**8**) were isolated in 96 and 97% yield, respectively, from the reaction of **2** with the furan or thiophene followed by the addition of PPh_3 .

The ^1H and ^{13}C NMR spectra for complexes **7** and **8** exhibit broadened resonances in the aromatic region. A variable-temperature ^1H NMR experiment was performed on **8**, and decoalescence of the Cp^* resonance was observed (Figure 5). When free thiophene (0.5 equiv) was added to a $\text{THF}-d_8$ solution of **8**, no changes to the peak shape or chemical shifts for **8** in the ^1H NMR spectrum were observed. These data, taken in account with only one carbonyl stretching frequency in the IR spectrum and one resonance in the ^{31}P NMR spectrum, implicates that the fluxionality observed is not due to reversible phosphine cyclometalation but possibly a result of hindered rotation of PPh_3 . The structure of **7** has been determined by single-crystal X-ray diffraction (Figure 6), which confirms the regioselectivity of C–H activation at the 2-position.

The reaction of **2** with thiazole produces $\text{Cp}^*\text{Fe}(\text{CO})(\text{thiazole})(2\text{-thiazolyl})$ (**9**) in 36% isolated yield. Calculations suggest the N-bound thiazole complex is more favorable than the S-bound isomer by 13.5 kcal/mol (Scheme 5, see Supporting Information). The formation of **9** proceeds via an intermediate (observed by ^1H NMR spectroscopy), which is likely $\text{Cp}^*\text{Fe}(\text{CO})(\text{thiazole})\text{Ph}$.

The C–H activation of 2-methylfuran by **2** is selective for the 5-position over the methyl group. The reaction of **2** with 2-

Figure 5. ^1H NMR spectra (Cp^* protons) showing the decoalescence of the Cp^* peak for complex **8** (25 to -80°C).

Figure 6. ORTEP drawing of $\text{Cp}^*\text{Fe}(\text{CO})(\text{PPh}_3)(2\text{-furyl})$ (**7**) (50% probability ellipsoids; H atoms omitted). Selected bond lengths (Å): Fe–P1 2.2142(3), Fe–C15 1.730(1), C15–O2 1.159(2), Fe–C11 1.960(1). Selected bond angles ($^\circ$): C11–Fe–C15 89.59(5), C15–Fe–P1 89.65(4), C11–Fe–P1 92.89(4).

Scheme 5. Calculated Relative Enthalpies for the Two Possible Coordination Isomers of $\text{Cp}^*\text{Fe}(\text{CO})(\text{thiazole})(2\text{-thiazolyl})$ (**9**)

methylfuran followed by the addition of PPh_3 produced $\text{Cp}^*\text{Fe}(\text{CO})(\text{PPh}_3)[2\text{-(5-methylfuryl)}]$ (**10**) in 82% isolated yield. Similar to complexes **7** and **8**, complex **10** also exhibits broadened ^1H and ^{13}C NMR resonances in the downfield region of the spectra, which may also be attributed to slow rotation around the Fe– PPh_3 bond. This selectivity, in which Fe activates a stronger aromatic C–H bond in preference to a weaker CH_3 bond, suggests that C–H activation proceeds via a pathway that does not involve the formation of free radicals in accordance with the M06 density functional calculation predictions (see above).

To experimentally probe these C–H activation reactions we studied several kinetic features for the reaction of **2** with furan. Under pseudo-first-order conditions in **2** at 3°C , a plot of $[\mathbf{2}]$ vs time shows a first-order exponential decay (Figure 7). Varying the equivalents of furan relative to **2** revealed that the

Figure 7. Sample first-order decay plot for the reaction of **2** and furan (10 equiv) at 3 °C ($R^2 = 0.99$).

reaction rate has a first-order dependence on the concentration of furan at low concentrations with saturation kinetics at higher concentrations (Figure 8). The rate of reaction is dependent on

Figure 8. Plot of pseudo-first-order rate constants (k_{obs}) versus [furan] for the reaction of **2** with excess furan at 3 °C.

Figure 9. Plot of $1/k_{\text{obs}}$ versus [NCMe] ($R^2 = 0.99$) for the reaction of **2** with excess furan.

the concentration of free NCMe (Figure 9). Treating complex **2** with 10 equiv of a 1:1 molar solution of furan and furan- d_4 and analyzing the relative quantities of C_6H_6 and $C_6H_3D_4$ by GC/MS revealed a kinetic isotope effect of 5.0(4). Additionally, we have examined the kinetic isotope effect with a large excess of furan (50 equiv), and $k_H/k_D = 4.8(1)$, which is statistically equivalent with that determined with 10 equiv of furan. Kinetic data for the C–H activation of furan (10 equiv) were obtained from 12 to 13 °C. An Eyring plot (in which the experimentally determined k_{obs} were corrected to remove

[furan]) gave activation parameters of $H^\ddagger = 23.5(4)$ kcal/mol and $S^\ddagger = 12(2)$ cal/mol·K (Figure 10).

Figure 10. Eyring plot for furan C–H activation (10 equiv) by $Cp^*Fe(CO)(NCMe)Ph$ (**2**) ($R^2 = 0.99$; 12 to 13 °C).

We computed the enthalpy profile for reaction of **2** with furan in THF solvent (Scheme 6). We have found a nearly identical mechanism for benzene and furan C–H activation by **2**. The initial steps of NCMe dissociation and intersystem crossing are identical with the benzene mechanism shown in Scheme 3. The energies of MECP-**2**, **4**[†], and **3**[†] in THF solvent are a few tenths of a kcal/mol lower than in benzene solvent. From **3**[†] furan coordinates via MECP-**4** (Figure 11, $H = 15.9$ kcal/mol) to give singlet **11**[†], which involves the formation of a true η^2 -C,C-complex $Cp^*Fe(CO)(\eta^2$ -C,C-furan) with a H of 13.0 kcal/mol.

The η^2 -C,C-complex **11**[†] is less endergonic than the benzene complex **5**[†] because it involves π forward- and back-bonding in contrast to mainly σ type interactions in **5**[†]. For Lewis basic metals, furan is known to bind stronger than benzene in a dihapto-coordination mode.³⁶ The calculated H for C–H bond cleavage of furan via the σ -bond metathesis transition state **13**-TS is 22.2 kcal/mol, which is in good agreement with the experimental value for H of 23.5(4) kcal/mol. Despite the 8 kcal/mol computed stronger C–H bond strength of furan ($H = 118$ kcal/mol) versus benzene ($H = 110$ kcal/mol), the H value for furan C–H activation is 7 kcal/mol lower than the benzene H value. The lower H for C–H activation of furan could be interpreted as a result of the lower energy η^2 -C,C-complex **11**[†]. However, prior to **13**-TS the η^2 -C,C-complex rearranges to an η^2 -C,H-complex **12**[†] with coordination to the furan σ C–H bond rather than the furan π bond. An alternative explanation for the lower H value for furan C–H activation versus benzene C–H activation is the result from a more stable $Cp^*Fe(CO)(2$ -furyl)(η^2 -C,H-benzene) intermediate **14**[†] ($H = 12.7$ kcal/mol) compared with **5**[†]. The thermodynamic stability of **14**[†] is manifested in **13**-TS as stability gained from formation of a more stable Fe–furyl bond compared with the formation of a Fe–Ph bond in **6**-TS (see Supporting Information for details).³⁷

On the enthalpy surface the furan C–H bond cleavage transition state **13**-TS is higher in energy than MECP-**2** and MECP-**4** points. This suggests that the rate of Fe–Ph group transformation into a Fe–furyl group is controlled by **13**-TS, which is in accordance with the relatively large KIE value (~ 5) observed experimentally.

On the basis of calculations and experimental results, a proposed mechanism and corresponding rate law for the C–H

Scheme 6. Calculated Enthalpies (Free Energies at 298 K) for C–H Activation of Furan by $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (**2**) in THF Solvent (kcal/mol)

Figure 11. Furan C–H activation structures. Bond lengths reported in Å and angles in degrees.

activation of furan by **2** is shown in Scheme 7. Reversible NCMe dissociation via a spin-forbidden pathway yields the coordinatively unsaturated intermediate. After furan coordination and subsequent C–H bond cleavage with concomitant release of benzene, acetonitrile recoordinates completing the transformation. The rate law predicts $1/[\text{NCMe}]$ inhibition (Figure 8) and saturation kinetics in concentration of furan (Figure 9).

Using the proposed rate law, k_1 can be independently determined from the data in Figure 8 and Figure 9. Under saturation conditions (Figure 8), the rate law is reduced to $\text{rate} = k_1[\mathbf{2}]$, and using the data in Figure 8, $k_1 = 8.8 \times 10^{-4} \text{ s}^{-1}$. The value of k_1 can also be determined from the y -intercept of Figure 9, which yields $k_1 = 7.1 \times 10^{-4} \text{ s}^{-1}$. Thus, the two independently determined values of k_1 are in good agreement.

Scheme 7. Proposed Mechanism and Corresponding Rate Law for the C–H Activation of Furan by $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (**2**)

Under saturation conditions in furan, $k_{\text{obs}} = k_1$, which provides the rate of NCMe dissociation from **2** (see above). Thus, an Eyring analysis was performed under saturation conditions (30 equiv of furan, 22 to 3 °C) in order to extract the activation parameters for the NCMe dissociation sequence (Figure 12). For NCMe dissociation, $H^\ddagger = 20.2(3)$ kcal/mol

Figure 12. Eyring plot for furan (30 equiv relative to **2**) C–H activation by $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (**2**) ($R^2 = 0.99$; 22 to 3 °C). Under these conditions, $k_{\text{obs}} = k_1$ (see Scheme 7), which gives the rate of NCMe dissociation.

and $S^\ddagger = 0(2)$ cal/mol·K. Scheme 6 shows that the lowest energy pathway for NCMe dissociation results in **3**[†]. Comparison of the enthalpy of **3**[†] with the measured $H^\ddagger$ shows that the predicted value is 10 kcal/mol too low. We examined the possibility that this discrepancy is due to the M06 density functional. However, all other functionals tested predict lower enthalpy values for **3**[†]. We note that k_1 values have been determined using an indirect method, and despite the discrepancy in experimental and calculated values, the comparison of overall energetics between theory and experiment are a good fit, and the predicted rate limiting C–H activation is in accord with the observed kinetic isotope effects.

We have also explored the kinetics of thiophene activation by **2**. Using 20 equiv of thiophene at 3 °C the k_{obs} is $3.2(4) \times 10^{-4}$ s⁻¹, which is approximately 2.5 times slower than the reaction with furan. Because no intermediates were observed through the course of the reaction (¹H NMR spectroscopy), we speculate that the decrease in rate from the reaction with furan might be explained from the smaller energy stabilization gained from the formation of the Fe–thienyl from the breaking C–H bond versus the analogous transformation with furan.

The regioselective activation of furan^{13,17,38} prompted us to investigate the underlying reasons for this observed selectivity. Calculations show a 3.8 kcal/mol $H^\ddagger$ value between the 13-TS and the regioisomeric transition state at the 3-position of furan. Again, the regioselectivity can be rationalized on the basis of the relative stability gained by formation of an Fe–C2(furyl) bond versus an Fe–C3(furyl) bond in the transition state. The Fe–C2(furyl) intermediate **14**[†] generated from C–H bond cleavage has a $H^\ddagger$ value of 12.7 kcal/mol, while the Fe–C3(furyl) intermediate generated from C–H bond activation has a $G^\ddagger$ value of 17.1 kcal/mol. Quantitative analysis of so-called transition state bond energies³⁷ showed that in 13-TS the Fe–C2(furyl) bond energy is 8 kcal/mol more stable than the Fe–C3(furyl) bond energy in the alternative regioisomeric C–H activation transition state. Eisenstein, Perutz, and Jones

have also suggested thermodynamic influence on the rates of metal-mediated C–H activation.^{39–41}

SUMMARY

We have reported an Fe(II) complex, $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$, that undergoes regioselective C–H activation with a range of aromatic substrates under mild conditions. The furan 2-CH bond (calculated bond dissociation enthalpy = 118 kcal/mol) is readily broken below 0 °C. In addition, we have disclosed a combined experimental and computational mechanistic study for the regioselective C–H activation of furan. The results herein demonstrate a relatively rare example of Fe(II)-mediated C–H activation by a nonradical pathway and demonstrates the potential viability of Fe-based catalysts for the functionalization of inert hydrocarbons and other substrates with strong C–H bonds.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer ($\text{O}_2 < 15$ ppm for all reactions). Tetrahydrofuran and *n*-pentane were dried by distillation from sodium/benzophenone and P_2O_5 , respectively. Diethyl ether was distilled over CaH_2 . Benzene was purified by passage through a column of activated alumina. Benzene-*d*₆, acetone-*d*₆, CD_3CN , and 1,4-dioxane-*d*₈ were used as received and stored under a N_2 atmosphere over 4 Å molecular sieves. For kinetic experiments, THF-*d*₈ was degassed by two conventional freeze pump thaw cycles and stored over 4 Å molecular sieves. ¹H NMR spectra were recorded on a Varian Mercury 300 or Varian Inova 500 MHz spectrometer, and ¹³C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (operating frequency 125 MHz) or Bruker Avance III 800 MHz spectrometer (operating frequency 201 MHz). All ¹H and ¹³C spectra are referenced against residual proton signals (¹H NMR) or ¹³C resonances (¹³C NMR) of the deuterated solvents and are reported in ppm. ³¹P NMR spectra were obtained on a Varian Mercury 300 MHz (operating frequency 121 MHz) spectrometer and referenced against an external standard of H_3PO_4 ($\delta = 0$). GC/MS was performed using a Shimadzu GCMS-QP2010 Plus system with a 30 m × 0.25 mm RTX-Qbond column with 8 μm thickness using electron impact ionization. IR spectra were obtained on a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer. Samples were prepared in solution flow cells. Photolysis experiments were performed using UV vis radiation generated by a 450 W power supply (Model #7830, Ace Glass, Inc.) equipped with a water-cooled 450 W 5 in. arc IMMER UV vis lamp (Model #7825-34, Ace Glass, Inc.). Furan-*d*₄ was purchased from Aldrich and distilled prior to use. All other chemicals were used as purchased from commercial sources. Elemental analyses were performed by Atlantic Microlabs, Inc. $\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}$ ²⁷ was prepared according to the literature procedure.

$\text{Cp}^*\text{Fe}(\text{CO})_2\text{Ph}$ (1**).** A mixture of $\text{Cp}^*\text{Fe}(\text{CO})_2\text{I}$ (0.533 g, 1.43 mmol), CuOTf (0.480 g, 1.91 mmol), Bu_3SnPh (0.610 mL, 1.87 mmol) and 1,4-dioxane (6 mL) was prepared. The mixture was stirred at 60 °C for 4 h during which time the mixture turned from dark brown to orange-beige. After cooling to room temperature, the mixture was filtered through a short plug of silica gel on a fine porosity frit followed by the in vacuo removal of the volatiles from the filtrate. The resulting residue was dissolved in a minimal amount of THF and chromatographed on silica gel eluting with 1:10 (v/v) diethyl ether/hexanes. A yellow band was collected and dried in vacuo. The resulting solid was triturated with a minimal amount of pentane to yield a yellow solid (0.311 g, 67%). A crystal suitable for single crystal X-ray diffraction was grown by the slow evaporation of a pentane solution of **1**. ¹H NMR (300 MHz, C_6D_6): 7.58 (2H, d, ³*J*_{HH} = 6 Hz, phenyl *ortho*), 7.16 (2H, t, ³*J*_{HH} = 6 Hz, phenyl *meta*), 7.07 (1H, t, ³*J*_{HH} = 6

Hz, phenyl *para*), 1.32 (15H, s, C₅Me₅). ¹³C NMR (75 MHz, C₆D₆): 218.3 (CO), 128.6, 143.4, 123.2 (Ph), 96.2 (C₅Me₅), 9.3 (C₅Me₅) (Note: 1 resonance of phenyl is missing presumably from coincidental overlap). IR (NCMe solution): ν_{CO} = 1994, 1937 cm⁻¹. Anal. Calcd for C₁₈H₂₀O₂Fe: C 66.69, H 6.22; found C 66.66, H 6.39.

Cp*Fe(CO)(NCMe)Ph (2). A solution of **1** (0.536 g, 1.67 mmol) in acetonitrile (50 mL) was irradiated in an ice bath with stirring for a total of 3 h. After the first and second hour, photolysis was ceased and 2 conventional freeze pump thaw cycles were performed on the reaction flask. After 3 h, the volatiles were removed in vacuo. The resulting residue was extracted with diethyl ether (50 mL) and filtered through Celite. Removal of volatiles produced a red solid, which was washed with pentane (10 mL in portions) to yield a red-orange solid (0.450 g, 87% yield). This compound is moderately stable at room temperature in the solid state, but was typically stored at 35 °C. A crystal suitable for single crystal X-ray diffraction was grown by the slow evaporation of a pentane solution of **2**. In order to obtain satisfactory elemental analysis, **2** was recrystallized from diethyl ether at 35 °C. ¹H NMR (300 MHz, dioxane-*d*₈): 7.34 (2H, d, ³J_{HH} = 7 Hz, phenyl *ortho*), 6.82 (2H, t, ³J_{HH} = 7 Hz, phenyl *meta*), 6.72 (1H, t, ³J_{HH} = 7 Hz, phenyl *para*), 2.52 (3H, s, NCCH₃), 1.46 (15H, s, C₅Me₅). ¹³C NMR (125 MHz, THF-*d*₆): 223.9 (CO), 172.6, 143.0, 128.9, 126.5 (Ph), 121.4 (CH₃CN), 91.4 (C₅Me₅), 9.6 (C₅Me₅), 3.5 (CH₃CN). IR (NCMe solution): ν_{CO} = 1903 cm⁻¹. Anal. Calcd for C₁₉H₂₃NOFe: C 67.67, H 6.87, N 4.15; found C 67.52, H 6.85, N 4.07.

Cp*Fe(CO)(PPh₃)(2-furyl) (7). To a THF solution (5 mL) of **2** (0.067 g, 0.20 mmol) was added furan (0.29 mL, 4.0 mmol). After stirring at room temperature for 1 h, PPh₃ (0.054 g, 0.21 mmol) dissolved in 2 mL of THF was added. After stirring for an additional 1 h, the volatiles were removed under reduced pressure to leave a red residue. After transferring the residue to a vial with pentane (3 mL) and subsequent removal of the volatiles under reduced pressure, a low density beige solid of **3** was obtained (0.105 g, 96% yield). A single crystal suitable for X-ray diffraction was grown from a saturated pentane solution of **3**. ¹H NMR (300 MHz, acetone-*d*₆): 7.62 (1H, m, furyl 3), 7.35 (15H, br, PPh₃), 5.99 (1H, m, furyl 5), 5.64 (1H, m, furyl 4), 1.42 (15H, s, C₅Me₅). ¹³C NMR (201 MHz, acetone-*d*₆): 224.6 (d, ²J_{CP} = 28 Hz, CO), 177.3 (d, ²J_{CP} = 40 Hz, furyl *ipso*), 148.1 (s, PPh₃), 134.6 (br, PPh₃), 130.3 (br s, PPh₃), 128.6 (s, furyl), 121.7 (s, furyl), 112.1 (s, furyl), 94.0 (s, C₅Me₅), 9.9 (s, C₅Me₅). Note: The *ipso* carbon for PPh₃ could not be located and may be obscured by the broad peaks for the remaining PPh₃ signals. ³¹P{¹H} NMR (121 MHz, acetone-*d*₆): 77.8. IR (C₆H₆ solution): ν_{CO} = 1913 cm⁻¹. Anal. Calcd for C₃₀H₃₄O₂PFe: C 72.27, H 6.06; found C 72.42, H 6.19.

Cp*Fe(CO)(PPh₃)(2-thienyl) (8). Thiophene (0.31 mL, 3.9 mmol) was added to a THF solution (7 mL) of **2** (0.065 g, 0.19 mmol). After stirring at room temperature for 1 h, PPh₃ (0.051 g, 0.19 mmol) dissolved in 2 mL of THF was added. After stirring for an additional 30 min, the volatiles were removed under reduced pressure to leave a light brown residue. After transferring the residue to a vial with a small amount of pentane and diethyl ether and subsequent removal of the volatiles under reduced pressure, a low-density red solid of **4** was obtained (0.109 g, 97% yield). ¹H NMR (300 MHz, acetone-*d*₆): 7.39 (15H, br m, PPh₃), 7.19 (1H, d, ³J_{HH} = 5 Hz, thienyl 3), 6.77 (dd, ³J_{HH} = 5, 3 Hz, thienyl 5), 6.33 (br s, thienyl 4), 1.43 (C₅Me₅). Due to fluxionality, a clean ¹³C NMR spectrum could not be acquired. ³¹P{¹H} NMR (121 MHz, acetone-*d*₆): 74.0. IR (C₆H₆ solution): ν_{CO} = 1913 cm⁻¹. Anal. Calcd for C₃₀H₃₄OSPFe: C 70.21, H 5.89; found C 69.92, H 6.05.

Cp*Fe(CO)(N-thiazole)(2-thiazolyl) (9). Thiazole (0.20 mL, 2.9 mmol) was added to a THF (5 mL) solution of **2** (0.053 g, 0.16 mmol). The solution immediately became dark red and was stirred for 18 h, after which time the volatiles were removed in vacuo. The residue was washed with 3 mL of pentane and collected on a fine porosity frit to give a red-brown solid of **6** (0.026 g, 36% yield). ¹H NMR (300 MHz, acetone-*d*₆): 9.89 (1H, d, ³J_{HH} = 3 Hz, thiazole 2), 8.04 (1H, d, ³J_{HH} = 3 Hz, thiazole/thiazolyl 4), 7.91 (1H, d, ³J_{HH} = 3 Hz, thiazole/thiazolyl 4), 7.65 (1H, dd, ³J_{HH} = 3 Hz, ³J_{HH} = 3 Hz, thiazole 5) 7.08 (1H, d, ³J_{HH} = 3 Hz, thiazolyl 5), 1.42 (15H, s,

C₅Me₅). ¹³C NMR (201 MHz, acetone-*d*₆): 223.1 (s, CO), 205.1 (s, thiazolyl *ipso*), 159.3 (s, thiazolyl/thiazole), 149.9 (s, thiazolyl/thiazole), 144.3 (s, thiazolyl/thiazole), 120.9 (s, thiazolyl/thiazole), 120.7 (s, thiazolyl/thiazole), 92.1 (s, C₅Me₅), 9.3 (C₅Me₅). IR (THF solution): ν_{CO} = 1910 cm⁻¹. Anal. Calcd for C₁₇H₁₇N₂S₂OFe: C 52.58, H 5.19, N 7.21; found C 52.16, H 5.06, N 7.04.

Cp*Fe(CO)(PPh₃)[2-(5-methylfuryl)] (10). To a THF (4 mL) solution of **2** (0.041 g, 0.12 mmol) was added 2-methylfuran (0.11 mL, 1.2 mmol). After stirring the red solution for 1 h, PPh₃ was dissolved in THF (0.032 g, 0.12 mmol) and added to the reaction mixture. The volatiles were removed in vacuo. The subsequent solid was washed with pentane (3 mL) and dried in vacuo to obtain a red solid of **5** (0.056 g, 82% yield). ¹H NMR (300 MHz, acetone-*d*₆): 7.36 (15H, br m, PPh₃), 5.52 (2H, overlapping, methylfuryl 3 and 4), 2.12 (3H, s, methyl), 1.43 (15H, s, C₅Me₅). ¹³C NMR (201 MHz, acetone-*d*₆): 224.8 (d, ²J_{CP} = 27 Hz, CO), 173.5 (d, ²J_{CP} = 32 Hz, thienyl *ipso*), 156.9 (s, PPh₃), 135.0 (br s, PPh₃), 130.3 (s, PPh₃), 128.5 (s, methylfuryl), 122.6 (s, methylfuryl), 108.3 (s, methylfuryl), 94.0 (s, C₅Me₅), 14.2 (s, methylfuryl), 10.1 (s, C₅Me₅). Note: The *ipso* carbon for PPh₃ could not be located likely due to coincidental overlap. ³¹P{¹H} NMR (121 MHz, acetone-*d*₆): 77.7. IR (THF solution): ν_{CO} = 1913 cm⁻¹. Anal. Calcd for C₃₁H₃₇O₂PFe: C 72.60, H 6.27; found C 72.61, H 6.26.

Reaction of Cp*Fe(CO)(NCMe)Ph and C₆D₆. In a screw-cap NMR tube, **2** (0.005 g, 0.02 mmol) and hexamethyldisilane (HMDS, internal standard, 1 μ L) were dissolved in C₆D₆ (0.25 mL). The NMR tube was heated to 50 °C in a temperature-controlled oil bath. The reaction was periodically monitored by ¹H NMR spectroscopy until completion using a delay time of 5 s. During that time, the phenyl resonances decreased in intensity relative to HMDS. Using the integration of the Cp* methyl peaks versus the integration of HMDS, an approximate yield of 80% was determined for the formation of **2-d**₅.

Determination of the Rate of Benzene C D Activation. A stock solution of **2** (0.024 g, 0.071 mmol) and HMDS (3 μ L) was prepared in 1.5 mL of C₆D₆. Three 0.4 mL aliquots of this stock solution were added to three different screw-cap NMR tubes. The samples were frozen until it was time to collect data. Each sample was subsequently monitored by ¹H NMR spectroscopy in a temperature-regulated probe (calibrated at 49 °C) through 2 half-lives, collecting spectra every 5 min (5 s delay). The reaction was monitored through only 2 half-lives due to decomposition at longer reaction times. A plot of [2] vs time was created and fitted to an exponential decay curve. The rate constants were extracted from these plots to yield $k_{\text{obs}} = 4.6(5) \times 10^{-4} \text{ s}^{-1}$ (see Supporting Information).

Dependence on Furan Concentration of the C H Activation of Furan by Cp*Fe(CO)(NCMe)Ph (2). A representative experiment follows. Two stock solutions were prepared in 2 separate 1 mL volumetric flasks. In the first stock solution, complex **2** (0.027 g, 0.080 mmol) was dissolved in 1 mL of THF-*d*₆. In the second stock solution, furan (128 μ L) and HMDS (8 μ L) were added and diluted to 1 mL with THF-*d*₆. From the first stock solution, 275 μ L (0.022 mmol of **2**) aliquots were transferred to 3 separate screw-cap NMR tubes equipped with Teflon-lined septa. The second stock solution was transferred to a 1 dram vial with a Teflon-lined septum cap. Outside the glovebox, one NMR tube was cooled in an ice water bath. Using a microsyringe, a 125 μ L (10 equiv of furan) aliquot of the second stock solution was injected through the cap of the NMR tube. The tube was vigorously shaken and placed in a temperature calibrated NMR probe (3 °C). ¹H NMR spectra (5 s delay, every 2.5 min) were acquired through at least 3 half-lives. By monitoring the disappearance of the *ortho*-phenyl protons of **2** versus HMDS, a plot of [2] vs time was created (see Supporting Information pp. S2–S5). Fitting the data to an exponential decay curve allowed the rate constant to be extracted. This was repeated for the two remaining NMR tubes. The whole procedure was performed for 7, 10, 15, 20, 25, 30, 35 equiv of furan.

Dependence on NCMe Concentration for the C H Activation of Furan by Cp*Fe(CO)(NCMe)Ph (2). A representative experiment follows. Two stock solutions were prepared in 2 separate 1 mL volumetric flasks. In the first stock solution, complex **2** (0.027 g, 0.080 mmol) was dissolved in 1 mL of THF-*d*₆. In the second stock

solution, furan (256 μL), NCMe (18.3 μL , 5% v:v in THF- d_8), and HMDS (8 μL) were diluted to 1 mL with THF- d_8 . From the first stock solution, 275 μL (0.022 mmol of **2**) aliquots were transferred to 3 separate screw-cap NMR tubes equipped with Teflon-lined septa. The second stock solution was transferred to a 1-dram vial with a Teflon-lined septum cap. Outside the glovebox, one NMR tube was cooled in an ice-water bath. Using a microsyringe, a 125 μL (20 equiv of furan, 0.1 equiv of NCMe) aliquot of the second stock solution was injected through the cap of the NMR tube. The tube was vigorously shaken and placed in a temperature calibrated NMR probe (3 $^{\circ}\text{C}$). ^1H NMR spectra (5 s delay, every 5 min) were acquired through at least 3 half-lives. By monitoring the disappearance of the *ortho*-phenyl protons of **2** versus HMDS, a plot of $[\mathbf{2}]$ vs time was created (see Supporting Information pp. S6–S7). Fitting the data to an exponential decay curve allowed the rate constant to be extracted. This was repeated for the two remaining NMR tubes. The whole procedure was performed for 0.05, 0.1, and 0.2 equiv of NCMe. A plot of $1/k_{\text{obs}}$ vs $[\text{NCMe}]$ showed an excellent linear correlation.

Determination of Kinetic Isotope Effect for Furan C(H/D) Activation. A representative experiment follows. In a 4-dram vial with a magnetic stir bar was prepared a THF solution (1.5 mL) of **2** (0.015 g, 0.045 mmol). To this solution was added a 1:1 (molar) mixture of furan and furan- d_4 (35 μL , 10 equiv arene). After 20 min, an aliquot was removed and analyzed by GC/MS. The average mass spectrum for the peak representing benzene was analyzed. Using the relative ratios of $m/z = 78$ and 79 (adjusted for the natural abundance of ^2H), the relative quantities of C_6H_6 and $\text{C}_6\text{H}_5\text{D}$ were determined to give a kinetic isotope effect of 5.43. The reported 5.0(4) is the average of 3 independent reactions as described above. Additionally, the above procedure was performed using 50 equiv of arene, which gave a kinetic isotope effect of 4.8(1). To ensure irreversibility of the reaction, multiple aliquots were analyzed throughout the course of the reaction (over 2 h) with no significant deviation in the relative amounts of C_6H_6 and $\text{C}_6\text{H}_5\text{D}$.

Eyring Plot for the C–H Activation of Furan by $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (2**).** The procedure described above for measuring the dependence of rate of furan activation on furan concentration was repeated at 12, 6, and 13 $^{\circ}\text{C}$ using 10 equiv of furan (3 runs each, see Supporting Information). Plotting $\ln(k_{\text{obs}}/T)$ vs $1/T$ gave an excellent linear fit and allowed the determination of the activation parameters. The plotted k_{obs} value is the value determined after dividing the experimentally determined k_{obs} value by $[\text{furan}]$.

Determination of the Rate of Thiophene C–H Activation. Two stock solutions were prepared in 2 separate 1 mL volumetric flasks. In the first stock solution, complex **2** (0.027 g, 0.080 mmol) was dissolved in 1 mL of THF- d_8 . In the second stock solution, thiophene (281 μL) and HMDS (8 μL) were added and diluted to 1 mL with THF- d_8 . From the first stock solution, 275 μL (0.022 mmol **2**) aliquots were transferred to 3 separate screw-cap NMR tubes equipped with Teflon-lined septa. The second stock solution was transferred to a 1 dram vial with a Teflon-lined septum cap. Outside the glovebox, one NMR tube was cooled in an ice-water bath. Using a microsyringe, a 125 μL (20 equiv of thiophene) aliquot of the second stock solution was injected through the cap of the NMR tube. The tube was vigorously shaken and placed in a temperature calibrated NMR probe (3 $^{\circ}\text{C}$). ^1H NMR spectra (5 s delay, every 2.5 min) were acquired through at least 3 half-lives. By monitoring the disappearance of the *ortho*-phenyl protons of **2** versus HMDS, a plot of $[\mathbf{2}]$ vs time was created (see Supporting Information p. S9). Fitting the data to an exponential decay curve allowed the rate constant to be extracted. This was repeated for the two remaining NMR tubes.

Variable Temperature NMR for $\text{Cp}^*\text{Fe}(\text{CO})(\text{PPh}_3)(2\text{-thienyl})$ (8**).** An NMR sample of **4** dissolved in THF- d_8 was incrementally cooled in a 600 MHz NMR probe. Upon cooling, the resonance assigned to the Cp^* methyl protons decoalesced into 2 singlets. Spectra were acquired at the following temperatures (not calibrated): 25 $^{\circ}\text{C}$, 0 $^{\circ}\text{C}$, 20 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}$, 50 $^{\circ}\text{C}$, 60 $^{\circ}\text{C}$, 80 $^{\circ}\text{C}$.

Monitoring $\text{Cp}^*\text{Fe}(\text{CO})(\text{PPh}_3)(2\text{-thienyl})$ (8**) in the Presence of Excess Thiophene.** Complex **4** (0.011 mg, 0.020 mmol) was dissolved in THF- d_8 (0.4 mL) and transferred to an NMR tube sealed

with a Teflon-lined screw cap. Following the acquisition of an initial ^1H NMR spectrum, thiophene (0.8 μL , 0.010 mmol) was added. A ^1H NMR spectrum of the resulting solution was acquired and revealed the presence of free thiophene and identical chemical shifts and peak shapes of the resonances assigned to **4** as observed in the initial spectrum.

Experimental Evidence against the Formation of a Tuck-In Complex during the Reaction of $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (2**) and C_6D_6 .** While monitoring the reaction of **2** and C_6D_6 , the total integration for the Cp^* peaks relative to HMDS remained constant (within deviation), suggesting there is no H/D exchange into the methyl resonances of the Cp^* ligand during the course of the reaction. The total deviation for the integrations of the Cp^* region is 4%.

Eyring Plot for the C–H Activation of Furan by $\text{Cp}^*\text{Fe}(\text{CO})(\text{NCMe})\text{Ph}$ (2**) Under Saturation Conditions.** Two stock solutions were prepared in 2 separate 1 mL volumetric flasks. In the first stock solution, complex **2** (0.027 g, 0.080 mmol) was dissolved in 1 mL of THF- d_8 . In the second stock solution, furan (384 μL) and HMDS (8 μL) were added and diluted to 1 mL with THF- d_8 . From the first stock solution, 275 μL (0.022 mmol of **2**) aliquots were transferred to 2 separate screw-cap NMR tubes equipped with Teflon-lined septa. The second stock solution was transferred to a 1 dram vial with a Teflon-lined septum cap. Outside the glovebox, one NMR tube was cooled in an ice-water bath. Using a microsyringe, a 125 μL (30 equiv of furan) aliquot of the second stock solution was injected through the cap of the NMR tube. The tube was vigorously shaken and placed in a temperature calibrated NMR probe (22 or 12 $^{\circ}\text{C}$). ^1H NMR spectra (5 s delay, every 15 or 25 min) were acquired through at least 2.5 half-lives. By monitoring the disappearance of the *ortho*-phenyl protons of **2** versus HMDS, a plot of $[\mathbf{2}]$ vs time was created (see Supporting Information p. S10). Fitting the data to an exponential decay curve allowed the rate constant to be extracted. Plotting $\ln(k_{\text{obs}}/T)$ vs $1/T$ gave a very good linear fit and allowed the determination of the activation parameters.

Computational Details. All stationary points were optimized in the gas phase using either restricted or unrestricted M06 density functional theory with the 6-31G(d,p) basis set for all atoms except Fe. The LANL2DZ basis set and pseudopotential was utilized for Fe during optimization. Single point energies were further refined using the M06 functional with the 6-311++G(3df,3dp) basis set for light atoms and LANL2TZ(f) with an f exponent of 2.462 for Fe.^{29,30} Solvent energy corrections were calculated using the SMD solvent model of benzene and furan. Solvation calculations were performed on the gas-phase optimized structures.³¹ Optimization, single point, and solvent calculations were all carried out in Gaussian 09.⁴³ Location of singlet triplet intersystem crossing points, also called minimum energy crossing points (MECPs), was done using the algorithm of Harvey^{44,45} in conjunction with Gaussian 09. Although MECPs are not stationary points, frequency calculations were carried out on these structures to obtain approximate enthalpy and free energy corrections.

■ ASSOCIATED CONTENT

● Supporting Information

Computational details, supporting figures, full reference 43, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dhe@chem.byu.edu (D.H.E.), t@unt.edu (T.R.C.), tb7h@virginia.edu (T.B.G.).

Notes

The authors declare no competing financial interest.

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