

Capturing the Complete Reaction Profile of a C–H Bond Activation

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ABSTRACT: The activation of C–H bonds requires the generation of extremely reactive species, which hinders the study of this reaction and its key intermediates. To overcome this challenge, we synthesized an iron(III) chloride pyridinediimine complex that generates a chlorine radical proximate to reactive C–H bonds upon irradiation with light. Transient spectroscopy confirms the formation of a Cl•|arene complex, which then activates C–H bonds on the PDI ligand to yield HCl and a carbon-centered radical as determined by photocrystallography. First principles molecular dynamics-density functional theory calculations reveal the trajectory for the formation of a Cl•|arene intermediate. Together, these experimental and computational results show the complete reaction profile for the preferential activation of a C–H bond in the solid state.

The discovery and design of chemical transformations build heavily upon our understanding of fundamental reaction steps and intermediates. In particular, research in the field of C–H activation has identified and leveraged highly reactive metal centers,¹ oxos,² nitrides,³ carbenes,⁴ and nitrenes⁵ as key intermediates in C–H functionalization reactions. Moreover, the rapidly growing field of organic photoredox catalysis has exploited the hydrogen-atom abstraction reactivity of short-lived halogen-, oxygen-, and nitrogen-centered radicals.^{6–10} The inherent instability of these reactive intermediates poses significant challenges to obtaining a complete picture of a C–H activation process across an entire reaction landscape. As a consequence, previous work has typically relied on piecing together snapshots from mechanistic, spectroscopic, structural, and computational studies that span a wide range of systems.^{11–15}

To generate and directly observe reactive species relevant to C–H activation, recent studies have coupled transient absorption (TA) spectroscopy with photocrystallography.^{16–18} In particular, we have employed these techniques to follow the photoelimination of halogen radicals from nickel(III) bisphosphine complexes.^{16, 19} Recognizing the chlorine radical as a potent hydrogen-atom abstraction agent, we envisioned that the entire course of a C–H activation reaction could be observed by generating these radicals in proximity to aliphatic C–H bonds within a crystalline lattice.

Toward this end, we report the design of an iron(III) chloride pyridinediimine (PDI) complex (Figure 1A and 1B) ($[\text{Fe}(\text{PDI})\text{Cl}_2]\text{PF}_6$) that situates aromatic groups with multiple reactive C–H bonds in the iron secondary coordination sphere. This complex enables the observation of the reaction of a photoeliminated chlorine radical with methyl C–H bonds on the PDI ligand (Figure 2A) by time-resolved spectroscopy and photocrystallography. These studies coupled with density-functional theory (DFT) and molecular dynamics (MD)

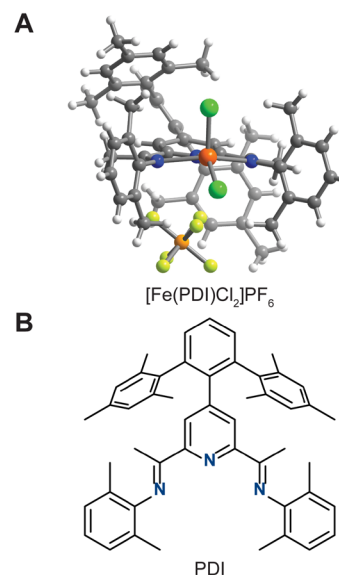


Figure 1. (A) Solid-state structure of $[\text{Fe}(\text{PDI})\text{Cl}_2]\text{PF}_6$ as determined by single-crystal X-ray diffraction at 15 K. Orange, light orange, green, light green, blue, gray, and white spheres represent Fe, P, Cl, F, N, C, and H atoms, respectively. (B) Chemical structure of the PDI ligand.

computations capture the complete course of a C–H activation reaction.

Metalation of the PDI ligand with FeCl_3 in the presence of AgPF_6 in CH_2Cl_2 at room temperature yields the hexafluorophosphate salt of the cationic iron(III) complex $[\text{Fe}(\text{PDI})\text{Cl}_2]^+$, which was isolated as a dark red crystalline solid. The ^{57}Fe Mössbauer spectrum of $[\text{Fe}(\text{PDI})\text{Cl}_2]\text{PF}_6$ (Figure S1A) exhibits a broad asymmetric peak with an isomer shift (δ) of 0.09(2) mm s^{-1} and a quadrupole splitting ($|\Delta E_Q|$) of 0.20(2) mm s^{-1} , which are in line with a five-coordinate $S = 5/2$ iron(III) complex. Crystallographic characterization of

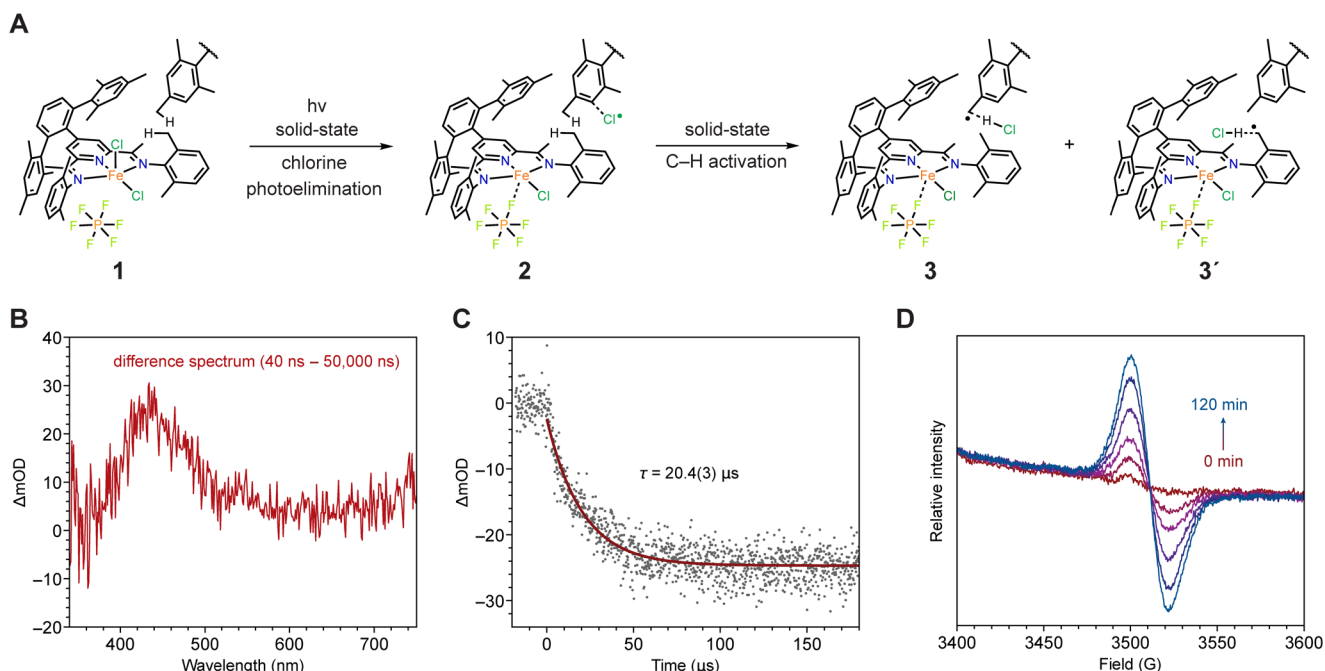


Figure 2. (A) Reaction profile for C–H activation by Cl• upon photoelimination from [Fe(PDI)Cl₂]PF₆ in the solid state. (B) Difference spectrum obtained by subtracting the TA spectrum of a thin film of [Fe(PDI)Cl₂]PF₆ acquired at 50,000 ns from that acquired at 40 ns ($\lambda_{\text{exc}} = 355$ nm). (C) Single-wavelength kinetics trace (gray circles) monitored at 430 nm fit (red line) with a monoexponential lifetime of 20.4(3) μs. (D) Changes in the EPR spectrum (red to blue lines) of a thin film of [Fe(PDI)Cl₂]PF₆ during photolysis with 390 nm light at 298 K.

[Fe(PDI)Cl₂]PF₆ reveals that the complex adopts a distorted square pyramidal geometry with two chloride ligands in the apical and basal positions (Figure 1A and Figure S14A). The absorption spectrum of a thin film of [Fe(PDI)Cl₂]PF₆ (Figure S2) features prominent bands between 300–400 nm. Based on previous work on nickel(III) halide complexes with similar coordination geometries,^{16,19} we assign the prominent absorption feature to ligand-to-metal charge transfer (LMCT) between the apical chloride and the iron(III) center; such a LMCT transition to the 3d_{z²} orbital leads to photocleavage of the Fe–Cl bond and generation of Cl•. In support of this contention, steady-state photolysis of a thin film of [Fe(PDI)Cl₂]PF₆ at room temperature using 390 nm light results in the evolution of a new species with a unique absorption spectrum (Figure S2). The ⁵⁷Fe Mössbauer spectrum (Figure S1B) featuring this photolysis product shows the appearance of a quadrupole doublet with parameters ($\delta = 1.54(2)$ mm s^{−1} and $|\Delta E_Q| = 1.22(3)$ mm s^{−1}) characteristic of a high-spin iron(II) complex. These results are consistent with the reaction pathway in which homolytic cleavage of the metal–halogen bond in [Fe(PDI)Cl₂]PF₆ produces the iron(II) complex (Figure 2A), as has been demonstrated in other first-row transition metal halide complexes that eliminate halogen radicals upon exposure to light.^{16,19,20–24} Notably, five methyl groups, four on the PDI ligand and one on a neighboring iron(III) complex, surround the apical chloride ligand (Figure 1A), providing multiple sites for C–H activation by a photoeliminated chlorine radical.

Previous work has demonstrated that aromatic groups in the secondary coordination sphere stabilize photoeliminated halogen radicals through formation of a X•|arene (X = Cl and Br) charge-transfer complex, which in turn enables detection of the radical species by TA spectroscopy.^{16,19} To probe for Cl•|arene complex formation, nanosecond-resolved TA spectroscopy experiments

were conducted on a thin film of [Fe(PDI)Cl₂]PF₆. The TA spectrum acquired 40 ns after a 355-nm laser pulse is dominated by a permanent bleach signal associated with photolysis of the iron(III) complex. The evolution of the transient spectrum over ~50 μs reveals an intermediate that gives a positive signal superimposed on the bleach signal of the ground state complex (Figure S3). The absorption spectrum of the intermediate (Figure 2B) features a single broad peak with a ~430 nm maximum. Solution-state TA experiments on a [Fe(PDI)Cl₂]PF₆ sample dissolved in acetonitrile show a similar peak with an absorption maximum at ~490 nm (Figures S4A and S4B), indicating that the absence of solvation results in an apparent blue shift of the solid-state signal. The intermediate giving rise to the absorption feature is assigned as the Cl•|arene adduct (Figure 2A, 2) based on its similarity to absorption profiles reported for different Cl•|arene charge-transfer complexes ($\lambda_{\text{max}} = 475\text{--}620$ nm, filled circles in Figure S4B).^{25,26} The persistence of the bleach signal after disappearance of the Cl•|arene adduct suggests that the adduct undergoes a subsequent reaction. Single-wavelength kinetics measurements on the thin film monitored at 430 nm (Figure 2C) show that the adduct decays with a lifetime of 20.4(3) μs. We attribute the decay of the adduct to the irreversible reaction of the chlorine radical with nearby methyl groups in the solid-state structure with a unimolecular rate constant for C–H activation of $4.90(7) \times 10^5$ s^{−1}. The slow rate of C–H activation is attributed to stabilization of Cl• by arene association, consistent with the results of solution-phase reactions between Cl•|arene adducts and alkanes.²⁶

Monitoring the photolysis reaction in a thin film by EPR spectroscopy (Figure 2D) revealed the formation of a long-lived spin 1/2 organic radical ($g \approx 2.006$). This result, along with the absence of EPR signals corresponding to Cl• in the 5000 G range

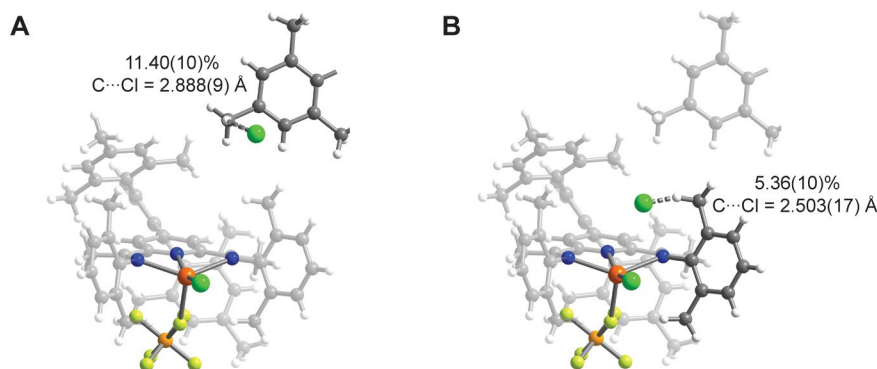


Figure 3. Photoinduced structure of $[\text{Fe}(\text{PDI})\text{Cl}_2]\text{PF}_6$ (16.76(10)% occupancy) as determined by single-crystal X-ray diffraction at 15 K. The Cl atoms of HCl molecules formed after C–H activation were located at sites close to methyl groups on a neighboring iron complex (A) and on the PDI ligand (B), but the H atoms of these molecules could not be located in the electron density difference map. Instead, dashed lines are drawn between the Cl atoms and the H atoms on the methyl groups. Orange, light orange, green, light green, blue, gray, and white spheres represent Fe, P, Cl, F, N, C, and H atoms, respectively.

(Figure S5), supports that the eliminated chlorine radical abstracts a hydrogen atom from the PDI ligand to yield HCl and carbon-centered radical. To further characterize the solid-state photolysis products, a sample was dissolved in CD_2Cl_2 , filtered through metal-scavenging silica, and then analyzed by ^1H NMR spectroscopy and high-resolution mass spectrometry. The appearance of resonances at 4.35 and 4.46 ppm in the ^1H NMR spectrum (Figure S12) and the detection of a major peak with a mass and isotope pattern corresponding to monochlorinated PDI ligand (Figure S13) indicate the chlorination of at least two different methyl groups on the ligand, which likely occurs through Cl-atom transfer from residual iron(III) chloride complex upon dissolution. Encouraged by the evidence for photoinitiated C–H activation in solid $[\text{Fe}(\text{PDI})\text{Cl}_2]\text{PF}_6$, we employed photocrystallography to observe the formation of the C–H activation products. Solid-state structures were obtained by single-crystal X-ray diffraction as a sample was irradiated with 365 nm light at 15 K. These measurements revealed the steady and irreversible formation of a photoinduced structure (Figures 3A, 3B, and S14B) that reaches an occupancy of 16.76(10)% after 9.33 h irradiation (Figure S15). Comparison of the initial and photoinduced structures confirmed that photolysis of the complex leads to $\text{Cl}\cdot$ elimination through cleavage of the apical Fe–Cl bond. The Fe center descends below the plane defined by the three ligand N atoms and forms a weak interaction with the PF_6^- counteranion with an Fe...F distance of 2.3780(19) Å. Furthermore, the Fe–N distances lengthen from 2.0489(9), 2.1653(9), and 2.1739(9) Å in the initial structure to 2.087(2), 2.267(2), and 2.218(2) Å, respectively, in the photoinduced structure, congruous with reduction of the complex from iron(III) to iron(II). Upon elimination, the apical Cl atom migrates to two different sites that are both next to methyl groups in the iron secondary coordination sphere. Critically, the Cl...C distances (2.502(19) and 2.888(9) Å) were found to be considerably shorter than the sum of the van der Waals radii of Cl and C (3.45 Å), indicating the activation of the methyl C–H bonds by $\text{Cl}\cdot$ to form HCl and carbon-centered radicals that remain associated through hydrogen bonding (Figure 2A, 3 and 3'). Remarkably, the methyl group on a mesityl ring of a neighboring iron complex was preferentially activated (11.40(7)% Cl occupancy) over the methyl group directly adjacent to the apical Cl ligand (5.36(6)% Cl occupancy), suggesting that the direction of

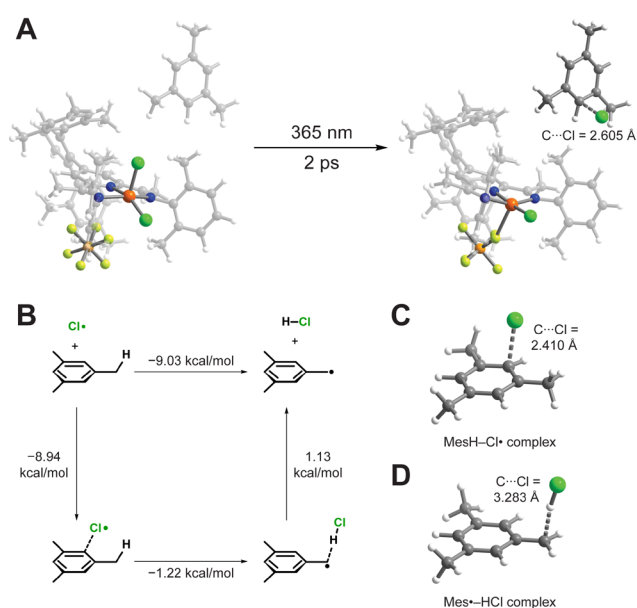


Figure 4. (A) Starting and product structures for chlorine radical photoelimination in a crystal of $[\text{Fe}(\text{PDI})\text{Cl}_2]\text{PF}_6$ simulated over 2 ps using MD-DFT. (B) Relative energies of different intermediates in the reaction of $\text{Cl}\cdot$ with mesitylene (MesH). Structures of the MesH- $\text{Cl}\cdot$ charge-transfer complex (C) and the HCl-Mes $\cdot$ hydrogen-bond adduct (D) determined by DFT calculations.

$\text{Cl}\cdot$ elimination influences C–H activation selectivity in the solid state.

To provide insight into the trajectory of the photoeliminated chlorine radical, we undertook first principles MD-DFT simulations. Computations were performed for the entire lattice, starting with the coordinates of all 452 atoms in the unit cell of the experimental crystal structure. Although computationally expensive, these measures maintain the effects of crystal lattice confinement, which is crucial in modelling the solid-state photoreaction. Chlorine radical elimination was initiated by providing the apical chlorine atom with the energy equivalent to a 365-nm photon directed along the initial Fe–Cl bond vector. A subsequent 2.0 picosecond run (Video S1) revealed the rapid ejection of $\text{Cl}\cdot$ to form an $\eta^1\text{-Cl}\cdot$ |arene

adduct with the mesityl ring that was activated in the photoinduced crystal structure (Figure 4A, 1→2). Consistent with previous computational work on η^1 complexes between halogen radicals and arenes,^{27,28} DFT calculations using the BH&HLYP functional on Cl• and mesitylene (MesH), a simplified model for the PDI ligand, predict that C–H activation to form the hydrogen-bonded Mes•–HCl adduct is thermodynamically favored by 1.22 kcal/mol with respect to the arene complex Cl•|MesH (Figures 4B–4D). The calculated Cl...C distance in Mes•–HCl (3.283 Å) was found to be shorter than the sum of the van der Waals radii of Cl and C (Figure 3D), corroborating the short Cl...C contacts observed in the photoinduced crystal structure. These computational results, in conjunction with the aforementioned solid-state TA and photocrystallography experiments, indicate that the formation of a Cl•|MesH complex leads to the favored activation of the methyl group on the mesityl ring.

The foregoing results describe the key steps and intermediates in a photoinitiated C–H activation reaction (Figure 2A). Photocleavage of the apical Fe–Cl bond in [Fe(PDI)Cl₂]PF₆ results in the generation of a chlorine radical and the concomitant reduction of the iron(III) center. The chlorine radical forms a charge-transfer complex with the mesityl ring on a neighboring iron PDI complex. This intermediate ultimately activates a C–H bond on a nearby methyl group, yielding an HCl molecule and a carbon-centered radical. We anticipate that this intimate understanding of chlorine radical generation and reactivity will inform the development of new paradigms in controlling the outcomes of C–H activation reactions, particularly in the emerging field of photoredox catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Compiled X-ray crystallographic data for [Fe(PDI)Cl₂]PF₆ (ZIP)

MD trajectory of a photodissociation event in a crystal of [Fe(PDI)Cl₂]PF₆ (MP4)

Materials and methods, details on the synthesis of the PDI ligand and [Fe(PDI)Cl₂]PF₆, Mössbauer spectra, UV-Vis absorption spectra, nanosecond-resolved TA spectra, EPR spectra, NMR spectra, crystallographic details and data, and details for the MD-DFT simulations and DFT calculations (PDF)

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The authors declare no competing financial interest.

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