Electronic Supplementary Information

Proton-promoted disproportionation of iron(V)-imido

TAML to iron(V)-imido cation radical and iron(IV) TAML

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Experimental Section

Materials. Commercially available chemicals and solvents were used without further purification unless otherwise indicated. $Na(H_2O)_x[Fe^{III}(TAML)]$ complex was purchased from GreenOx Catalyst Inc. (Pittsburgh, PA, USA). The commercial complex, $Na(H_2O)_x[Fe^{III}(TAML)]$, has been recrystallized from isopropanol/H₂O mixture according to the literature method.^{S1} *N*-tosyliminophenyliodinane (PhINTs) was prepared by previously reported literature method.^{S2}

Instrumentation. UV-vis spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments Cryostat USP-203A for low-temperature experiments. Cold spray ionization time-of-flight mass (CSI-MS) spectral data were collected on a JMS-T100CS (JEOL) mass spectrometer equipped with the CSI source [typical measurement conditions: needle voltage = 2.2 kV, orifice 1 current = 50-500 nA, orifice 1 voltage = 0 to 20 V, ringlens voltage = 10 V, ion source temperature = 5 $^{\circ}$ C, and spray temperature = -40 °C]. X-band CW-EPR spectra were recorded in CH₃CN at 5 K using a X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM) [experimental parameters: microwave frequency = 9.646 GHz, microwave power = 1.0 mW, modulation amplitude = 10 G, gain = 1×10^4 , modulation frequency = 100 kHz, time constant = 40.96 ms, conversion time = 85.00 ms]. Low temperatures were achieved and controlled with an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. Organic product analysis was performed using high performance liquid chromatography (HPLC, Waters 515).

Generation of iron(V)-imido intermediate (1). The nonheme iron(V)-imido complex, $[(TAML)Fe^{V}(NTs)]^{-}(1)$, was prepared by reacting $[Fe^{III}(TAML)]^{-}(1.0 \text{ mM})$ and solid PhINTs (2.0 equiv.) in CH₃CN at room temperature. The reaction solution of Na[(TAML)Fe^{III}] complex and solid PhINTs (2.0 equiv.) was stirred for 30 s, then filtered through a disk filter and kept at -40 °C for further studies.^{S3}

Generation of iron(V)-imido cation radical intermediate (2), iron(IV) TAML complex (3), and iron(IV)-amido species (4). The iron(V)-imido cation radical complex, $[Fe^{V}(NTs)(TAML^{+*})]^{-}$ (2), was prepared by adding one-electron oxidants (1.0 equiv.), such as tris(4-bromophenyl)ammoniumyl hexachloroantimonate (TBPA), $[Fe^{II}(bpy)_3]^{3+}$ (bpy = 2,2' -bipyridine), and $[Ru^{III}(bpy)_3]^{3+}$, to a solution of **1** (0.10 mM) in CH₃CN at -40 °C, as reported previously.^{S4} The iron(IV) TAML complex, $[Fe^{IV}(TAML)]$ (3), was prepared by reacting $[Fe^{III}(TAML)]^{-}$ (0.10 mM) with cerium(IV) ammonium nitrate (CAN; 1.0 equiv.) in CH₃CN at -40 °C, as reported previously.^{S4} The iron(IV)-amido complex, $[Fe^{IV}(NHTs)(TAML)]^{-}$ (4), was generated by reacting **1** (0.10 mM) with 1,4-cyclohexadiene (CHD, 5.0 mM) in CH₃CN at -40 °C, as reported previously.^{S5}

Spectral titration of iron(V)-imido with acids. Spectral titration of **1** with HOTf and HClO₄ was examined in CH₃CN at -40 °C using a Hewlett-Packard 8453 photodiode-array spectrometer with a quartz cuvette (path length = 10 mm). Spectral titration was performed by adding HOTf and HClO₄ (0 – 0.40 mM) in 0.20 equiv. increments to a solution of **1** (0.20 mM) in CH₃CN at -40 °C. As shown in Fig. S1, the titration was monitored with the absorbance change at 520 nm.

Organic Product Analysis. Organic products formed in the reaction solution of **1** upon addition of HOTf was analyzed by HPLC. The complete reaction solution was filtered through a silica gel commun in order to remove inorganic complexes and then filtrate was analyzed by HPLC. Yield of NH₂Ts produced in the reaction solution was calculated by comparison with authentic NH₂Ts sample and quantitative analysis was made on the basis of comparison of HPLC peak integration between product and authentic NH₂Ts sample, resulting that yield of NH₂Ts, which is a major organic product, was ~48% based on **1** used.

Kinetic Measurements. Kinetic measurements were performed on a Hewlett Packard 8453 photodiode-array spectrophotometer at -40 °C. Reactions were run in a 1-cm UV cuvette and followed by monitoring UV-vis spectral changes of reaction solutions. In the C-H bond activation and the nitrene transfer reactions, xanthene and thioanisole

were used as substrates, respectively. For the reactions of 2 with substrates, rate constants were determined under pseudo-first-order conditions by fitting the changes in absorbance at 750 nm due to 2. All reactions were run at least in triplicate, and the data reported represent the average of these reactions.

References

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Fig. S1 UV-vis absorption spectral changes observed in the titration of **1** (0.20 mM) with HOTf [(a) (0 – 0.20 mM) and (b) (0.20 – 0.40 mM)] in 0.20 equiv. increments in CH₃CN at –40 °C.



Fig. S2 EPR spectra of 1 (0.50 mM; blank line) and the complete reaction solution (red line) obtained in the reaction of 1 (0.50 mM) with HOTf (1.0 equiv.) in CH₃CN at -40 °C. EPR spectra were recorded at 5 K.



Fig. S3 Negative mode CSI-MS spectrum of the complete reaction solution obtained in the disproportionation of **1** upon addition of HOTf in CH₃CN at -40 °C. The peak at m/z of 575.2 corresponds to [Fe(TAML)(OTf)]⁻ (*calcd. m/z* of 575.1).



Fig. S4 UV-vis absorption spectral changes observed in the titration of 1 (0.20 mM) with HClO₄ (0 – 0.20 mM) in 0.20 equiv. increments in CH₃CN at –40 °C.



Fig. S5 UV-visible absorption spectral change observed upon addition of TFA (2.0 mM, 10 equiv.) to a solution of 1 (0.20 mM) in CH₃CN at -40 °C.



Fig. S6 UV-vis spectra of **1** (0.20 mM; blank line) and the complete reaction solution (red line) of **1** (0.20 mM) with CH₃COOH (8.0 mM, 40 equiv.) in CH₃CN at -40 °C.



Fig. S7 (a) UV-vis absorption spectral change observed in the reaction of **2** (0.10 mM) with xanthene (20 mM) in CH₃CN at -40 °C. **2** was generated by adding HOTf (0.10 mM) to a solution of **1** (0.10 mM), which was *in-situ* produced by reacting $[Fe^{III}(TAML)]^-$ with a slight excess amount of PhINTs (3.0 equiv.) in CH₃CN at -40 °C. Inset shows the time profile monitored at 750 nm due to **2**. (b) Plot of k_{obs} against the concentration of xanthene to determine a second order rate constant (k_2) in the C-H bond activation by **2** in CH₃CN at -40 °C.



Fig. S8 (a) UV-vis absorption spectral change observed in the reaction of **2** (0.10 mM) with thioanisole (1.0 mM) in CH₃CN at -40 °C. **2** was generated by adding HOTf (0.10 mM) to a solution of **1** (0.10 mM), which was *in-situ* produced by reacting $[Fe^{III}(TAML)]^-$ with a slight excess amount of PhINTs (3.0 equiv.) in CH₃CN at -40 °C. Inset shows the time profile monitored at 750 nm due to **2**. (b) Plot of k_{obs} against the concentration of thioanisole to determine a second order rate constant (k_2) in the sulfimidation reaction by **2** in CH₃CN at -40 °C.



Fig. S9 X-band EPR spectrum of the complete reaction solution obtained upon addition of HOTf (0.50 mM) to a solution of $[(TAML)Fe^{IV}(NHTs)]^-$ (4; 0.50 mM) in CH₃CN at -40 °C. Spectrum was recorded at 5 K.