

## Supporting Information

### *C–H Bond Cleavage by Bioinspired Non-Heme Metal Complexes.*

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### Experimental

#### General Procedures

All reagents were purchased from commercial sources and used as received unless otherwise noted. Solvents were sparged with argon and purified using a JC Meyer Co. solvent purification system with columns containing Q-5 and molecular sieves. Potassium hydride (KH) as a 30 % dispersion in mineral oil was filtered with a medium porosity glass frit and washed 5 times each with pentane and diethyl ether (Et<sub>2</sub>O). Solid KH was dried under vacuum and stored under an inert atmosphere. All synthetic manipulations were conducted in a Vacuum Atmosphere, Co. drybox under an argon atmosphere. TMTACN<sup>1,2</sup> and K[Fe<sup>III</sup>poat(OH)]<sup>3</sup> were synthesized according to previous reports.

#### Physical Methods

Electronic absorbance spectra were recorded with a Cary 50 spectrophotometer using a 1.00 cm quartz cuvette. Solid-state Fourier transform infrared (FTIR) spectra were collected on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. X-band (microwave frequency 9.62 GHz) EPR spectra were recorded on a Bruker EMX spectrometer equipped with an ER041XG

microwave bridge, an Oxford Instrument ESR-900 liquid helium quartz cryostat, and a Bruker bimodal cavity (ER4116DM) for the generation of microwave fields parallel and transverse to the applied magnetic field.

### Synthesis of $[\text{Mg}^{\text{II}}(\text{TMTACN})(\text{OTf})_2]$

Anhydrous  $\text{MgCl}_2$  (27.8 mg, 0.292 mmol) was suspended in 6 mL anhydrous acetonitrile, and TMTACN (56.6  $\mu\text{L}$ , 50.0 mg, 0.292 mmol) was added in one portion using a syringe. The reaction mixture turned clear and was allowed to react overnight. AgOTf (151.5 mg, 0.5896 mmol) was added and let react for an additional 4 h. The solution was filtered through a pad of celite using a fine porosity glass frit, and all volatiles were removed under vacuum. The residue was triturated with  $\text{Et}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$  to afford a white solid (80-90% yield), which was dried further under vacuum. Elemental analysis calcd for  $[\text{Mg}^{\text{II}}(\text{TMTACN})(\text{OTf})_2] \cdot 0.5\text{CH}_2\text{Cl}_2$ ,  $\text{C}_{11}\text{H}_{21}\text{F}_6\text{MgN}_3\text{O}_6\text{S}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ : C, 25.76; H, 4.14; N, 7.84%, found: C, 25.96; H, 4.23; N, 7.84%.

### Synthesis of $[(\text{TMTACN})\text{Mg}^{\text{II}}-(\mu\text{-OH})\text{-Fe}^{\text{III}}\text{poat}]\text{OTf}$

$\text{K}[\text{Fe}^{\text{III}}\text{poat}(\text{OH})]$  (89.8 mg, 0.105 mmol) was dissolved in 3 mL anhydrous  $\text{CH}_2\text{Cl}_2$ .  $\text{NMe}_4\text{OAc}$  (14.7 mg, 0.110 mmol) was added in one portion, and the mixture was allowed to stir for 1 h. The reaction mixture was filtered with a fine porosity glass frit, and the filtrate was added dropwise to a 1 mL  $\text{CH}_2\text{Cl}_2$  solution of  $[\text{Mg}^{\text{II}}(\text{TMTACN})(\text{OTf})_2]$  (51.8 mg, 0.105 mmol). The reaction was allowed to proceed for 1 h, and the mixture was filtered with a medium porosity glass frit to remove any insoluble materials. The filtrate was layered with  $\text{Et}_2\text{O}$  to yield a yellow powder. After the yellow powder was collected and dried, it was redissolved in  $\text{CH}_2\text{Cl}_2$ , and was layered with hexane to yield yellow sheet-like crystals. The crystals were collected on a glass frit and dried under vacuum, affording the product in yields that ranged from 40-50 %. Elemental analysis calcd for  $[(\text{TMTACN})\text{Mg}^{\text{II}}-(\mu\text{-OH})\text{-Fe}^{\text{III}}\text{poat}]\text{OTf} \cdot \text{CH}_2\text{Cl}_2$ ,  $\text{C}_{52}\text{H}_{64}\text{F}_3\text{FeMgN}_7\text{O}_7\text{P}_3\text{S} \cdot \text{CH}_2\text{Cl}_2$ : C, 51.08; H, 5.34; N, 7.87%, found: C, 50.95; H, 5.11; N, 7.88%. FTIR (diamond ATR,  $\text{cm}^{-1}$ ): 3142 (OH), 3062, 3050, 3007, 2994, 2959, 2900, 2859, 2819, 1589, 1493, 1483, 1466, 1441, 1436, 1365, 1300, 1264, 1225, 1173, 1143, 1116, 1103, 1086, 1069,

1063, 1031, 1017, 989, 960, 938, 922, 893, 809, 802, 752, 720, 697, 636. EPR (X-band,  $\perp$ -mode, CH<sub>2</sub>Cl<sub>2</sub>:THF, 10 K):  $g = 9.88, 9.21, 4.98, 3.86$ . UV-vis  $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ): 315 (sh), 375 (5400), 455 (sh).

## References

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