Alkane Oxidation Catalyzed by a Self-Folded Multi-Iron Complex

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Supporting Information

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1. NMR Spectra

Figure S-1: ¹H NMR spectrum of dipicolylpropargylamine **2** (400 MHz, CDCl₃, 298K).

Figure S-2: ¹H NMR spectrum of Tris-pyridyl ligand **5** (400 MHz, CDCl₃, 298K).

Figure S-3: ¹³C NMR spectrum of Tris-pyridyl ligand **5** (400 MHz, CDCl₃, 298K).

Figure S-7: ^{13}C NMR spectrum of Dipicolyl ligand **6** (400 MHz, CDCl_3 , 298K).

Figure S-8: ^1H NMR spectrum of Hexapicolyl complex **4**• $\text{Fe}_3(\text{SO}_4)_3$ (600 MHz, CD_3CN and D_2O , 298K).

Figure S-9: ^1H NMR spectrum of Dipicolyl complex **6**• FeSO_4 (600 MHz, CD_3CN and D_2O , 298K).

Figure S-10: Wide range ¹H NMR spectrum of Hexapicolyl complex **4**•Fe₃(SO₄)₃ (400 MHz, CD₃CN and D₂O, 298K).

2. NMR Spectra of Metal Titrations

Figure S-11: Downfield regions of the ^1H NMR spectra (400 MHz, 298 K, CDCl_3 , 2.5 mM **4**) of the addition of $\text{Zn}(\text{OTf})_2$ to Hexapicolyl ligand **4**.

Figure S-12: Downfield regions of the ^1H NMR spectra (400 MHz, 298 K, CDCl_3 , 2.5 mM **5**) of the addition of $\text{Zn}(\text{OTf})_2$ to Tris-pyridyl ligand **5**.

3. Mass Spectral Data

Figure S-13: ESI-MS full spectrum of Hexapicolyl complex $4\bullet\text{Fe}_3(\text{SO}_4)_3$.

Figure S-14: Top. ESI-MS predicted of 1434 m/z region of Hexapicolyl complex $4\bullet\text{Fe}_3(\text{SO}_4)_2\text{H}^+$.
bottom. ESI-MS of 1434 m/z region of Hexapicolyl complex $4\bullet\text{Fe}_3(\text{SO}_4)_2\text{H}^+$.

Figure S-15: ESI-MS full spectrum of Hexapicolyl complex $4 \cdot \text{Zn}_3(\text{OTf})_6$.

Figure S-16: Top. ESI-MS of 1981 m/z region of Hexapicolyl $4 \cdot \text{Zn}_3(\text{OTf})_6$; bottom. ESI-MS predicted of 1981 m/z region of Hexapicolyl complex $4 \cdot \text{Zn}_3(\text{OTf})_6$

Figure S-17: ESI-MS full spectrum of Tris-pyridyl complex **5**•FeSO₄.

Figure S-18: Top. ESI-MS of 880 m/z region of Tris-pyridyl complex **5**•FeSO₄; **bottom.** ESI-MS predicted of 880 m/z region of Tris-pyridyl complex **5**•FeSO₄.

Figure S-19: ESI-MS full spectrum of Dipicolyl complex $6 \cdot \text{FeSO}_4$.

Figure S-20: Top. ESI-MS of $561 \text{ } m/z$ region of Dipicolyl complex $6 \cdot \text{FeSO}_4$; bottom. ESI-MS predicted of $561 \text{ } m/z$ region of Dipicolyl complex $6 \cdot \text{FeSO}_4$.

4. ICP Analysis

Trial	Mass Fraction of Fe in Ligand 4 (mmol)	(ppm)(vol (l)) / mg total*100	Mass Fraction Ligand 6 (mmol)	(ppm)(vol (l)) / mg total*100
1	0.038	3.806	0.01598	1.6
2	0.0368	3.685	0.0164	1.6
3	0.0378	3.787	0.017	1.7
Average	0.0376	3.76	0.0164	1.64

Table S-1: ICP calculation of Hexapicolyl complex **4**•Fe₃(SO₄)₃ and Dipicolyl complex **6**•FeSO₄ in 1% nitric acid solution.

5. Optical Spectra

Figure S-21: UV-Vis absorption spectrum of Dipicolyl Ligand **6** and Dipicolyl complex **6**•FeSO₄ in H₂O at concentration 500 μM.

Figure S-22: UV-Vis spectrum of Hexapicolyl ligand **4** and Hexapicolyl complex **4**•Fe₃(SO₄)₃ in H₂O at concentration 205 μM.

6. Electrochemical Analysis

Figure S-23: Cyclic Voltammogram of 10mg of Dipicolyl complex $6\bullet\text{FeSO}_4$ in 20% MeCN:H₂O (8 different runs, overlaid, $[6\bullet\text{FeSO}_4] = 1.4 \text{ mM}$).

Figure S-24: Cyclic Voltammogram of Hexapicolyl complex $4\bullet\text{Fe}_3(\text{SO}_4)_3$ in 20% MeCN:H₂O (8 different runs, overlaid, $[4\bullet\text{Fe}_3(\text{SO}_4)_3] = 1.0 \text{ mM}$).

7. Electron Paramagnetic Resonance Analysis

Figure S-25: EPR of Hexapicolyl complex $4\bullet\text{Fe}_3(\text{SO}_4)_3$ at 100K.

Figure S-26: EPR of Hexapicolyl complex $4\bullet\text{Fe}_3(\text{SO}_4)_3$ at 298K.

8. Oxidation Reactions

Instrumentation and General Equipment

The method was used to analyze the samples via GC and/or GC-MS as followed:

GC-MS experiments were performed on GCT premier 7890A Gas Chromatograph with Agilent 7890 TOF detector, using a DB-5 30m x 0.25mm 5% phenyl, 95% methylpolysiloxane column with a film thickness of 0.25 μ m. Helium was employed as carrier gas. A detector temperature of 250 $^{\circ}$ C and an injector temperature of 70 $^{\circ}$ C were used.

8.1 GC Traces of Oxidation Reactions

Figure S-27: GC trace of the products obtained for oxidation of Top: *trans*-decalin oxidation; Bottom: *Cis*-Decalin with 4•Fe₃(SO₄)₃ (see Table 2, entry 5 and 6).

Figure S-28: GC-MS product analysis of the trace shown in Figure S-27. Top: *trans*-decalin oxidation, Bottom: *Cis*-Decalin Oxidation.

8.2 GC-MS Analysis of Oxidation Products

Note: commercially available products (e.g. 2-octanone, etc) were compared against authentic samples in the GC trace and the GC-MS is not included here.

Figure S-29: GC-MS Chromatograph spectrum of *trans*-decalin oxidation results. **Left:** *trans*-decalin oxidation results, **Right:** GC-MS main library.

Figure S-30: GC-MS Chromatograph spectrum of *cis*-decalin oxidation results. **Left:** *cis*-decalin oxidation results, **Right:** GC-MS main library.