

**Carbon-Oxygen Bond Cleavage by Bis(imino)pyridine Iron
Compounds: Catalyst Deactivation Pathways and Observation of Acyl
C-O Bond Cleavage in Esters.**

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Supporting Information

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Experimental Procedures

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.¹ Hydrogen and deuterium gas were passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high vacuum line. Benzene-*d*₆ and toluene-*d*₈ were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves or titanocene, respectively. **1-(N₂)₂**, **1-Br**, and **1-Me** were prepared according to literature procedures.^{2,3} Ethyl acetate, vinyl acetate, allyl acetate, amyl acetate, isopropyl acetate, cyclohexyl acetate, *tert*-butyl acetate, phenyl acetate, methyl benzoate, ethyl formate, isopropyl formate, vinyl bromide, ethyl vinyl ether, allyl ether, and anisole were all purchased from Aldrich and dried over calcium hydride for at least 24 hours before being vacuum transferred onto 4 Å molecular sieves. Methyl acetate and allyl ethyl ether were purchased from Acros and purified in a similar manner. Phenyl formate was purchased from Lancaster and dried over calcium hydride before use.

trans-Methyl-cinnamate was purchased from Aldrich, recrystallized from dry pentane at -35 °C, and dried under vacuum. Hydrocinnamic acid, *trans*-cinnamic acid, and benzoic acid were purchased from Aldrich and dried under vacuum for 16 hours. Allyl alcohol, absolute ethyl alcohol, isopropanol, cyclohexanol, and *tert*-butyl alcohol were purchased from Aldrich and vacuum transferred from sodium before use. Allylmagnesium bromide as a 1.0 M solution in diethyl ether and 10 % palladium on

activated carbon were purchased from Aldrich and used as received. Vinylmagnesium bromide as a 0.7 M solution in tetrahydrofuran was purchased from Acros and used as received.

Ethyl acetate-1,2- d_2 was prepared by deuteration of neat vinyl acetate with 10 % palladium on activated carbon under 4 atmospheres of D_2 and vacuum transferred before use. Methyl 3-phenylpropionate was prepared in a similar fashion from *trans*-methylcinnamate under 4 atmospheres of H_2 . Methyl acetate- d_6 was prepared from D_2SO_4 catalyzed condensation of acetic acid- d_4 and methanol- d_4 . The reaction mixture was extracted with *m*-xylene and the methyl acetate- d_6 was collected by short path distillation. Ethyl benzoate was prepared from acid catalyzed condensation of benzoic acid and ethyl alcohol.

1H NMR spectra were recorded on Varian Mercury 300, Inova 400 and 500 spectrometers operating at 299.76, 399.78 and 500.62 MHz, respectively. 2H NMR spectra were recorded at 20 °C on Inova 500 and 600 spectrometers operating at 76.85 and 92.07 MHz, respectively. ^{13}C NMR spectra were recorded on the Inova 500 spectrometer operating at 125.893 MHz. All 1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using 1H (residual) and ^{13}C chemical shifts of the solvent as a secondary standard. For complexes exhibiting temperature independent magnetism, many assignments were made based on COSY, HSQC, and HMBC NMR experiments. Solution magnetic moments were determined by Evans method⁴ using a ferrocene standard and are the average value of at least two independent measurements. 1H NMR multiplicity and coupling constants are reported where applicable. Peak width at half

height is given for paramagnetically broadened resonances. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox, transferred to a nylon loop and then quickly transferred to the goniometer head of a Bruker X8 APEX2 diffractometer equipped with a molybdenum X-ray tube ($\lambda = 0.71073 \text{ \AA}$). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed using the Bruker SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

Observation of (ⁱPrPDI)Fe(CH₃O₂CCH₃) (1-MeOAc). To a solution of 0.020 g (0.034 mmol) of **1-(N₂)₂** in approximately 0.7 mL of benzene-*d*₆, 2.7 μ L (0.034 mmol) of methyl acetate was added by microsyringe. The resulting reddish-brown solution was transferred to a J. Young tube and quickly analyzed by ¹H NMR spectroscopy. ¹H NMR (benzene-*d*₆, 23 °C): δ = 11.67 (br s, 2H, *m*-pyr), 8.63 (br s, 1H, *p*-pyr), 7.54 (t, 8.0 Hz, 2H, *p*-aryl), 2.57-2.62 (m, 7H, CH(CH₃)₂ and OCH₃), 1.21 (d, 7.0 Hz, 12H, CH(CH₃)₂), 0.59 (s, 3H, COCH₃), -0.13 (d, 7.0 Hz, 12H, CH(CH₃)₂), -4.88 (s, 6H, C(CH₃)), *m*-aryl resonance not located.

Preparation of (ⁱPrPDI)Fe(OCH₂CH₃) (1-OEt). Method A. This complex was prepared in a manner similar to **1-OCH₂CH=CH₂** with 0.050 g (0.084 mmol) of **1-(N₂)₂** and 5 μ L,

(0.084 mmol) of ethanol to yield 0.028 g (57%) of a dark brown foam identified as **1-OEt**. **Method B.** A 20 mL scintillation vial was charged with 0.100 g (0.168 mmol) of **1-(N₂)₂** and approximately 15 mL of pentane. Using a microsyringe, 0.012 g (14 μ L, 0.168 mmol) of ethyl formate was added and the resulting brown solution was allowed to stir for 30 minutes. The solution was filtered through Celite, the solvent was evacuated, and recrystallization of the resulting brown solid from pentane yielded **1-OEt**. Analysis for C₃₅H₄₈FeN₃O: Calcd C, 72.15; H, 8.30; N, 7.21. Found: C, 71.94; H, 8.30; N, 6.99. ¹H NMR (benzene-*d*₆, 20 °C): δ = 84.47 (157 Hz, 2H), 71.68 (67 Hz, 3H), -8.49 (28 Hz, 2H, *m*-aryl), -14.43 (19 Hz, 1H, *p*-aryl), -23.41 (23 Hz, 12H, CH(CH₃)₂), -36.31 (137 Hz, 12H, CH(CH₃)₂), -114.51 (222 Hz, 4H, CH(CH₃)₂), -214.04 (130 Hz, 6H, C(CH₃)), 2 peaks not located.

Observation of (iPrPDI)Fe(OCH₂Ph) (1-OCH₂Ph). This complex was observed along with **1-OAc** from **1-(N₂)₂** mediated cleavage of benzyl acetate. ¹H NMR (benzene-*d*₆, 20 °C): δ = 83.79 (648 Hz, 2H, *phenyl*), 75.20 (314 Hz, 2H, *m*-pyr), 29.58 (154 Hz, 2H, *phenyl*), 24.24 (580 Hz, 1H, *phenyl*), -8.54 (193 Hz, 4H, *m*-aryl), -14.44 (203 Hz, 2H, *p*-aryl), -24.40 (207 Hz, 12H, CH(CH₃)₂), -39.64 (338 Hz, 12H, CH(CH₃)₂), -120.01 (484 Hz, 4H, CH(CH₃)₂), -221.31 (375 Hz, 6H, C(CH₃)), 2 peaks not located.

Preparation of (iPrPDI)Fe(H₂CIN) (1-H₂CIN). This compound was prepared in a manner similar to **1-CIN** with 0.250 g (0.421 mmol) of **1-(N₂)₂** and 0.063 g (0.421 mmol) of hydrocinnamic acid to yield 0.120 g (41%) of a dark green solid identified as **1-H₂CIN**. Analysis for C₄₂H₅₂FeN₃O: Calcd C, 73.46; H, 7.63; N, 6.12. Found: C, 73.38; H,

7.47; N, 5.81. Magnetic susceptibility: $\mu_{\text{eff}} = 4.4 \mu_{\text{B}}$ (benzene- d_6). ^1H NMR (benzene- d_6): $\delta = -284.97$ (270 Hz, 6H, $\text{C}(\text{CH}_3)$), -117.26 (533 Hz, 4H, $\text{CH}(\text{CH}_3)_2$), -30.04 (118 Hz, 12H, $\text{CH}(\text{CH}_3)_2$), -19.89 (29 Hz, 12H, $\text{CH}(\text{CH}_3)_2$), -16.55 (23 Hz, 1H, *p*-aryl), -3.05 (27 Hz, 2H, *m*-aryl), 15.08 (16 Hz, 1H, *p*-phenyl), 17.34 (16 Hz, 2H, *m*-phenyl), 33.60 (42 Hz, 2H, *o*-phenyl), 65.59 (159 Hz, 2H, $\text{CH}_2(\text{C}_6\text{H}_5)$), 119.57 (124 Hz, 2H, *m*-pyr), 181.60 (379 Hz, 2H, COCH_2), 372.36 (116 Hz, 1H, *p*-pyr).

Preparation of ($^{\text{iPr}}$ PDI)Fe(O₂CMe) (1-OAc): Method A. A solution of **1-(EtOAc)** was prepared in a thick-walled glass vessel by adding 21 μL (0.202 mmol) of ethyl acetate to 10 mL of a pentane solution containing 0.120 g (0.202 mmol) of **1-(N₂)₂**. The vessel was sealed and the solution was heated to 65 °C in an oil bath for 16 hours. The resulting brown solution was filtered through Celite and the solvent was removed *in vacuo* to yield a dark brown solid. Recrystallization from pentane yielded 0.044 g (36%) of **1-OAc**.

Method B: A thick-walled glass vessel was charged with 0.100 g (0.170 mmol) of **1-(N₂)₂** and approximately 10 mL of pentane. Upon addition of 0.015 g (16 μL , 0.189 mmol) of methyl acetate, the vessel was sealed, submerged in liquid nitrogen, and evacuated on a high vacuum line. After adding 1 atm of dihydrogen, the solution was thawed and stirred for 4 hrs at ambient temperature. The volatiles were removed and the resulting reddish-brown residue was washed through a Celite fitted frit with diethyl ether. The solvent was removed *in vacuo* and recrystallization from pentane at -35 °C afforded spectroscopically pure **1-OAc**. Analysis for C₃₅H₄₆FeN₃O₂: Calcd C, 70.46; H, 7.77; N, 7.04. Found: C, 70.25; H, 8.04; N, 6.79. ^1H NMR (benzene- d_6): $\delta = -284.76$ (280 Hz, 6H, $\text{C}(\text{CH}_3)$), -114.95 (525 Hz, 4H, $\text{CH}(\text{CH}_3)_2$), -30.37 (170 Hz, 12H, $\text{CH}(\text{CH}_3)_2$), -19.78 (75

Hz, 12H, CH(CH₃)₂), -16.50 (66 Hz, 1H, *p*-aryl), -3.20 (73 Hz, 2H, *m*-aryl), 119.59 (163 Hz, 2H, *m*-pyr), 187.25 (370 Hz, 3H, CO₂CH₃), 372.47 (18 Hz, 1H, *p*-pyr).

Preparation of (iPrPDI)Fe(O₂CPh) (1-OBz). This complex was prepared in a manner similar to **1-CIN** with 0.150 g (0.253 mmol) of **1-(N₂)₂** and 0.031 g (0.253 mmol) of benzoic acid to yield 0.127 g (76%) of a brownish-green solid identified as **1-OBz**. Analysis for C₄₀H₄₈FeN₃O₂: Calcd C, 72.94; H, 7.35; N, 6.38. Found: C, 72.71; H, 7.65; N, 6.16. Magnetic susceptibility: $\mu_{\text{eff}} = 4.9 \mu_{\text{B}}$ (benzene-*d*₆, 20 °C). ¹H NMR (benzene-*d*₆, 20 °C): δ = 373.68 (355 Hz, 1H, *p*-pyr), 119.63 (113 Hz, 2H, *m*-pyr), 69.35 (165 Hz, 2H, *o*-phenyl), 34.43 (25 Hz, 2H, *m*-phenyl), 19.99 (17 Hz, 1H, *p*-phenyl), -3.16 (25 Hz, 2H, *m*-aryl), -16.87 (21 Hz, 1H, *p*-aryl), -20.10 (26 Hz, 12H, CH(CH₃)₂), -30.10 (102 Hz, 12H, CH(CH₃)₂), -117.12 (516 Hz, 4H, CH(CH₃)₂), -284.10 (214 Hz, 6H, C(CH₃)).

Spectroscopic Identification of (iPrPDI)Fe(OCHMe₂) (1-OⁱPr). This complex was observed along with the formation of **1-OAc** upon cleavage of isopropyl acetate with **1-(N₂)₂**. The observation of **1-OⁱPr** was independently confirmed through addition of either isopropanol or isopropyl formate to **1-(N₂)₂**. ¹H NMR (benzene-*d*₆, 20 °C): 86.25 (232 Hz, 6H, OCH(CH₃)₂), 68.38 (72 Hz, 2H, *m*-pyr), -8.74 (26 Hz, 4H, *m*-aryl), -14.42 (22 Hz, 2H, *p*-aryl), -22.88 (26 Hz, 12H, CH(CH₃)₂), -36.90 (152 Hz, 12H, CH(CH₃)₂), -113.00 (373 Hz, 4H, CH(CH₃)₂), -214.30 (150 Hz, 6H, C(CH₃)), 2 resonances not located.

Spectroscopic Identification of (iPrPDI)Fe(OC₆H₁₁) (1-OCy). This complex was observed along with the formation of **1-OAc** upon cleavage of cyclohexyl acetate with **1-**

(N₂)₂. The observation of **1-OCy** was independently confirmed through addition of cyclohexanol to **1-(N₂)₂**. ¹H NMR (benzene-*d*₆, 20 °C): 82.88 (251 Hz, *cyclohexyl*), 68.94 (82 Hz, 2H, *m-pyr*), 62.03 (*cyclohexyl*), 47.79 (128 Hz, *cyclohexyl*), 39.26 (84 Hz, *cyclohexyl*), 28.04 (*cyclohexyl*), -9.00 (26 Hz, 4H, *m-aryl*), -14.46 (20 Hz, 2H, *p-aryl*), -23.14 (29 Hz, 12H, CH(CH₃)₂), -36.81 (164 Hz, 12H, CH(CH₃)₂), -117.09 (391 Hz, 4H, CH(CH₃)₂), -214.32 (166 Hz, 6H, C(CH₃)), *p-pyr* resonance not located.

Spectroscopic Identification of (iPrPDI)Fe(OCMe₃) (1-O^tBu). This complex was observed along with the formation of **1-OAc** upon cleavage of *tert*-butyl acetate with **1-(N₂)₂**. The observation of **1-O^tBu** was independently confirmed through addition of *tert*-butyl alcohol to **1-(N₂)₂**. ¹H NMR (benzene-*d*₆, 20 °C): 84.76 (279 Hz, 9H, C(CH₃)₃), 63.98 (72 Hz, 2H, *m-pyr*), -9.24 (23 Hz, 4H, *m-aryl*), -14.63 (27 Hz, 2H, *p-aryl*), -22.34 (27 Hz, 12H, CH(CH₃)₂), -36.95 (134 Hz, 12H, CH(CH₃)₂), -112.79 (407 Hz, 4H, CH(CH₃)₂), -213.58 (155 Hz, 6H, C(CH₃)), *p-pyr* resonance not located.

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