Ligand-Based Reduction of Nitrate to Nitric Oxide Utilizing a Proton-Responsive Secondary Coordination Sphere.

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Experimental

General Methods. All air sensitive experiments were performed using standard Schlenk procedures or in an MBraun glovebox under N2 atmosphere. Reagents were purchased from commercial sources. All solvents used here were dried and deoxygenated with a PureSolv solvent purification system (CuO and alumina columns). Infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer equipped with an ATR accessory. Gas infrared spectra were obtained on a Thermo Scientific Nicolet 6700 spectrometer equipped with a deuterated triglysine sulfate (DTGS) detector using 10 mm NaCl windows. ¹H NMR was recorded on a Bruker 500 MHz FT-NMR spectrometer. Unless otherwise noted, the data are reported in ppm, using the solvent resonance as the internal standard. The solution magnetic susceptibilities were calculated using Evan's method NMR measurements.[1] Solid-state magnetic susceptibilities were recorded on a Johnson Matthey MSB-1 magnetic susceptibility balance, calibrated with HgCo(SCN)₄. Diamagnetic correction factors were calculated from Pascal's constants.[2] Elemental analyses were performed by ALS in Tucson, AZ. Ion chromatography was performed on a Dionex model 201 DI High Performance Ion Chromatograph (HIPC) with a simple anion column and a conductivity detector. The complex $[Fe(Hdidpa)(CO)_2]^+$ (2) was synthesized according to literature procedures[3].

X-ray Crystallography. Single crystal X-ray diffraction data for **3** was collected on a Rigaku Oxford Diffraction XtaLABPRO X-ray diffractometer equipped with a Pilatus P200K hybrid photon counting (HPC) detector. Reflections were collected at 100(2) K using graphite-monochromated Mo $K_{\alpha 1}$ radiation using a data collection strategy calculated within CrystalClear to ensure

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maximum data redundancy and percent completeness [4]. Data processing, including frame integration, Lorentz-polarization corrections and final cell parameter calculations was completed using CrysAlis^{Pro} [5]. A multi-scan absorption correction was applied using the SCALE3 ABSPACK scaling algorithm integrated into CrysAlis^{Pro} [6]. The crystal structure was solved via intrinsic phasing using ShelXT and refined with least squares minimization with ShelXL in the Olex2 graphical user interface [7]. The space group was unambiguously verified by PLATON [8]. The final structural refinement included anisotropic temperature factors on all non-hydrogen atoms and hydrogen atoms were attached via the riding model at calculated positions using appropriate HFIX commands.

Crystal Data for C₂₉H₄₄F₆FeN₆O₂P (*M* =709.52 g/mol) (**3**): triclinic, space group P-1 (no. 2), *a* = 8.3541(4) Å, *b* = 12.2825(6) Å, *c* = 16.8758(6) Å, *α* = 80.311(4)°, *β* = 85.323(3)°, *γ* = 78.583(4)°, *V* = 1671.05(13) Å³, *Z* = 2, *T* = 100(2) K, μ (MoK α) = 0.569 mm⁻¹, *Dcalc* = 1.410 g/cm³, 27521 reflections measured (4.512° ≤ 2Θ ≤ 54.966°), 7556 unique (R_{int} = 0.0271, R_{sigma} = 0.0236) which were used in all calculations. The final R_1 was 0.0266 (I > 2 σ (I)) and *w* R_2 was 0.0718 (all data).

Mössbauer Spectra. Mössbauer spectra were recorded at room temperature with a constantacceleration spectrometer (Wissel GMBH, Germany) in a horizontal transmission mode using a 50 mCi ⁵⁷Co source. Approximately 0.080 g of sample was crushed in a Mössbauer sample holder and a drop of Paratone-N was used to cover the sample to prevent oxidation. Data acquisition was carried out for two days to get a statistically reasonable spectrum. The velocity scale was normalized with respect to metallic iron at room temperature; hence all isomer shifts were recorded relative to metallic iron. The Mössbauer spectra were fitted by assuming Lorentzian line shapes using the NORMOS (Wissel GMBH) least-square fitting program. The isomer shifts and quadrupole splitting parameters were determined from the fitted spectra.

Electrochemistry. Cyclic voltammetry was carried out using a Pine Wavenow potentiostat with a standard three-electrode electrochemical cell consisting of a glassy carbon working electrode, a platinum auxiliary electrode, and a freshly prepared Ag/Ag⁺ reference electrode with a vycor tip filled with acetonitrile. All potentials were internally referenced to the ferrocene redox couple. Unless otherwise noted, experiments were carried out under a dinitrogen atmosphere at room temperature using 0.001 M acetonitrile solutions of the analyte and 0.100 M tetra(*n*-butyl)ammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. All reversibility studies were carried out at 50, 100, 150, 200 and 250 mV/s.

Synthesis of [Fe(didpa)(NO)₂][PF₆] (3) via reaction of [Fe(Hdidpa)(CO)₂][PF₆] (2) and TBANO₃. In an N₂ filled glovebox, a 20 mL pressure vial was charged with compound 2 (0.050 g, 0.071 mmol), TBANO₃ (0.022 g, 0.071 mmol), and 5 mL of THF. The vial was tightly closed, taken out of the glovebox, and placed in an 80 °C silicone-based oil bath. The solution was left for 12 hours before being brought back into the glovebox. A color change from dark green to dark brown was observed and a liquid IR of the solution was obtained for a yield calculation of 22% of **3**. The remaining solution was transferred to a 20 mL scintillation vial and the solvents were removed *in vacuo*. The brown solid was redissolved in THF and filtered through Celite. The filtrate was layered with pentane and placed in the glovebox freezer to allow for crystallization. An initial crop of white crystals identified as TBAPF₆ by FTIR and X-ray crystallography were manually separated from the brown residue, which was then redissolved in THF, filtered through Celite again, layered with pentane, and placed in the glovebox freezer for final crystallization. Solution yields were determined from FTIR due to contamination with TBAPF₆. FTIR (ATR): 1786, 1714 cm⁻¹ (NO); 837 cm⁻¹ (PF₆⁻). ⁵⁷Fe Mossbauer: δ = 0.348(5) mm/s; ΔE_Q = 0.791(7) mm/s. μ_{eff} = 1.89 μ_B . Anal calcd for C₂₉H₄₄F₆FeN₆O₂P: C, 49.09; H, 6.25; N, 11.84; Found: C, 48.55; H, 6.18; N, 11.71

Synthesis of 3 via reaction of 2 and NaNO₂. In an N₂ filled glovebox, a 20 mL scintillation vial was charged with 2 (0.060 g, 0.083 mmol), a stir bar and 4 mL or THF and stirred for 30 min. In a separate scintillation vial, NaNO₂ (0.0114 g, 0.159 mmol) was dissolved in 1 mL of methanol. The two solutions were mixed together and allowed to stir overnight. The resulting red-brown solution was removed *in vacuo* before redissolving in THF and being filtered through a Celite plug. The solution was carefully layered with pentane, resulting in brown crystals identified as $[Fe(didpa)(NO)_2][PF_6]$ (3), mass: 0.023 g, yield 39%. FTIR (ATR): 1788, 1716 cm⁻¹ (NO); 837 cm⁻¹ (PF₆⁻). ⁵⁷Fe Mossbauer: δ = 0.348(5) mm/s; Δ E_Q = 0.791(7) mm/s. Anal calcd for C₂₉H₄₄F₆FeN₆O₂P: C, 49.09; H, 6.25; N, 11.84; Found: C, 48.55; H, 6.18; N, 11.71

Ion Chromatography. In an N₂ filled glovebox In the glovebox, [Fe(Hdidpa)(CO)₂][PF₆] (**2**) (50.4 mg, 0.069 mmol) and TBANO₃ (21.2 mg, 0.0696 mmol) were added to a 10 mL pressure vial and dissolved in 5 mL of THF. The vial was tightly closed and placed in an 80 °C oil bath overnight. The resulting dark brown solution was transferred to a separation funnel where 20 mL of 0.5 M Na₂SO₄ in water was added (to increase the ionic strength and provide separation from the THF layer) and the solutions were thoroughly mixed. The aqueous layer of the extraction was obtained and filtered through a silica plug. The filtered solution was separated into three separate scintillation vials in 3 mL volumes for each vial. To one of the vials, a small quantity of a solution of 0.03 mM TBANO₃ in 0.5 M Na₂SO₄ was added. To another one of the two remaining vials, a 0.03 mM TBANO₂ in 0.5 M Na₂SO₄ was added. Ion Chromatography was run on these

three samples using a set of three different concentration standards containing F^- , Cl^- , NO_3^- , and $SO_4^{2^-}$.

Reactivity of Fe(didpa)(CO)₂ (1) and TBANO₃. In an N₂ filled glovebox, a 20 mL pressure vial was charged with compound **1** (0.050 g, 0.089 mmol), TBANO₃ (0.027 g, 0.089 mmol), and 5 mL of THF. The vial was tightly closed, taken out of the glovebox, and placed in an 80 °C silicone-based oil bath. The solution was left for 12 hours before being brought back into the glovebox. A liquid IR was obtained to examine the extent of reactivity.

Solution Phase IR Determination of Yield. Solution phase FTIR spectroscopy was utilized to calculate the reaction yields of $[Fe(didpa)(NO)_2][PF_6]$ (**3**). Pristine **3** was independently synthesized and crystallized from the reaction of **2** and NaNO₂ (see above). These samples of **3** were then utilized to prepare a set of standard solutions of **3** in THF. A calibration curve (Fig **S13**) for each NO band was then constructed utilizing a solution FTIR cell with CaF₂ windows and a path length of 0.54 mm. The calibration curves for Peak 1 (1789 cm⁻¹, $\varepsilon = 611 \text{ M}^{-1}\text{ cm}^{-1}$) and Peak 2 (1721 cm⁻¹, $\varepsilon = 976 \text{ M}^{-1}\text{ cm}^{-1}$) were then utilized to calculate the concentration of **3** in the reaction mixtures of **2** and TBANO₃, as well as **2** and NaNO₂.

Stability of TBANO₃ at 80°C. In a control experiment to test the stability of TBANO₃ in THF at 80 °C, a 20 mL pressure vial was charged with TBANO₃ (0.027 g, 0.089 mmol), and 5 mL of THF. A liquid cell IR was obtained. The vial was tightly closed and placed in an 80 °C silicone-based oil bath. The solution was left for 12 hours before being brought back into the glovebox. Another liquid IR was obtained to confirm that the TBANO₃ did not decompose.

Reactivity of 2 with TBA¹⁵NO₃ to form [Fe(didpa)(¹⁵NO)₂][PF₆]. A 20 mL pressure vial was charged with compound **2** (0.050 g, 0.071 mmol), TBANO₃ (0.022 g, 0.071 mmol), and 5 mL of

THF. The vial was placed in an 80 °C silicone-based oil bath overnight. A color change from dark green to dark brown was observed and a liquid IR of the solution was obtained. The remaining solution was transferred to a 20 mL scintillation vial and the solvents were removed *in vacuo*. The brown solids were redissolved in THF and filtered through Celite. The solvents were removed *in vacuo* and IR data were obtained. FTIR (ATR): 1750, 1674 cm⁻¹ (¹⁵NO); 830 cm⁻¹ (PF₆⁻).

Reactivity of 2 with Na¹⁵NO₂ to form [Fe(didpa)(¹⁵NO)₂][PF₆]. In a scintillation vial equipped with a stir bar, **2** (0.050 g, 0.074 mmol)) was dissolved in 5 mL THF and stirred for 30 min. While stirring, a solution of Na¹⁵NO₂ (0.005 g, 0.144 mmol) dissolved in 2 mL of CH₃OH was added drop wise to the solution of **3**. The solution was allowed to stir for 3 hours. The solution turns from a green to red-brown. The solvent was removed *in vacuo*, yielding a brown solid. The solid was redissolved in THF and then filtered through Celite. The solvents were removed *in vacuo* and IR data were obtained. FTIR (ATR): 1755, 1684 cm⁻¹ (¹⁵NO); 830 cm⁻¹ (PF₆⁻).

Reactivity of 2 with TBANO³ **for analysis of NO gas in the headspace.** In an N₂ filled glovebox, compound **2** (0.050 g, 0.071 mmol) and TBANO³ (0.022 g, 0.071 mmol) was dissolved in approximately 5 mL of THF were added to a Fisher Porter tube. The tube was closed with a pressure valve, taken out of the box, and placed in an 80 °C silicone-based oil bath for 12 hours. The Fisher Porter tube and a gas IR cell (NaBr plates) were attached to a T-valve and hooked to a Schlenk line. Once the lines were evacuated and air-free, the headspace from the Fisher Porter tube was allowed to freely flow into the gas cell IR. The valve of the IR cell was closed off and a spectrum was obtained, inspecting for NO gas.



Figure S1. ATR-FTIR of **1** after reaction with TBANO₃ pre-heat (black line) and $Fe(didpa)(CO)_2$ (**1**) after reaction with TBANO₃ for 1 day at 80°C (red line) showing no reaction.



Figure S2. ATR-FTIR of TBANO₃ pre-heat (black line) and TBANO₃ after 1 day at 80°C (red line), showing no decomposition of TBANO₃.



Figure S3. Gas-phase FTIR of the headspace of reaction of $[Fe(Hdidpa)(CO)_2][PF_6]$ (2) with TBANO₃ for 1 day at 80°C (black line) and NO gas (red line). The figure illustrates that NO gas is not present in the headspace. The reaction headspace does contain CO gas at 2147 cm⁻¹ from reacted 2.





Figure S5. ATR-FTIR of 3(¹⁴NO)₂ (red line) and 3(¹⁵NO)₂ (blue line) via synthesis with TBANO₃ and TBA¹⁵NO₃



Figure S6. ATR-FTIR of 3(¹⁴NO)₂ (red line) and 3(¹⁵NO)₂ (blue line) via synthesis with NaNO₂ and Na¹⁵NO₂.



Figure S7. HPIC of aqueous saturated Na₂SO₄ extraction of the reaction mixture of $[Fe(Hdidpa)(CO)_2][PF_6]$ + TBANO₃ (black trace). There is a small amount of Cl⁻ present in the DI water used to make the solutions. Also included are the HPIC standard (red trace, top) showing retention time of NO₃⁻, as well as a NO₃⁻ spike of the reaction mixture (blue trace, 2nd from top) showing the peak at 3.77 minutes is indeed NO₃⁻. The bottom trace (yellow) illustrates the retention time of NO₂⁻ at 2.9 minutes showing that there is undetectable NO₂⁻ in the reaction mixture.



Figure S8. Cyclic voltammogram of 0.010 M [Fe(didpa)(NO)₂][PF₆] (**3**) at $E_{1/2}$ = -1.185 V (left); 0.1 M [(ⁿBu)₄N][PF₆] in CH₃CN; 200 mV/s scan rate and plot of $E_{cathodic}$ peak current versus square root of the scan rate for [Fe(didpa)(NO)₂][PF₆] (**3**).



Figure S9. Plot of Ecathodic peak current versus square root of the scan rate for 3.



Figure S10. Cyclic voltammogram of 0.010 M [Fe(didpa)(NO)₂][PF₆] (**3**) at $E_{1/2}$ = -0.910 V (left); 0.1 M [(ⁿBu)₄N][PF₆] in CH₃CN; 200 mV/s scan rate and plot of $E_{cathodic}$ peak current versus square root of the scan rate for [Fe(didpa)(NO)₂][PF₆] (**3**).



Figure S11. Plot of Ecathodic peak current versus square root of the scan rate for 3.



Figure S12. Zero-field Mössbauer spectrum of $[Fe(didpa)(NO)_2][PF_6]$ (**3**), $[\delta = 0.348(5); \Delta E_Q = 0.791(7) \text{ mm/s}].$



Figure S13. Calibration Curves for determining the yield of the synthesis for compound $[Fe(didpa)(NO)_2][PF_6]$ (3).



Figure S14. Solution FTIR of reaction mixtures of of $[Fe(Hdidpa)(CO)_2][PF_6] + TBANO_3$ in different mole ratios. Included are the 1:1 ratio (black line), 1.5:1 ratio (red line), and 2:1 ratio (blue line).



Figure S15. HPIC of aqueous saturated Na₂SO₄ extraction of the reaction mixture of $[Fe(Hdidpa)(CO)_2][PF_6] + TBANO_3$ in different ratios. There is a small amount of Cl⁻ present in the DI water used to make the solutions. Included are the HPIC standard (blue trace, top) showing retention time of NO₃⁻, as well the reaction of $[Fe(Hdidpa)(CO)_2][PF_6] + TBANO_3$ in a 1:1 ratio (red line, 2nd from top), 1.5:1 ratio (green line, 2nd from bottom), and 2:1 ratio (purple line, bottom).

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