Supporting Information

For

Catalytic Dioxygen Activation by Co(II) Complexes Employing a Versatile Ligand Scaffold

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A. General Considerations

All manipulations were carried out using standard Schlenk techniques or conducted in an MBraun Labmaster 130 drybox under a nitrogen atmosphere. All reagents used were purchased from commercial vendors and used as received unless otherwise noted. Anhydrous solvents were purchased from Sigma-Aldrich and further purified by sparging with Ar gas followed by passage through activated alumina columns. Anhydrous 18O2 was purchased from NexAir and passed through a Drierite™ column before using. 18O2 (99%) was purchased from Icon Isotopes, New Jersey. Elemental analyses were performed by Midwest Microlab, LLC. 1H, 13C, and 31P NMR spectra were recorded on Varian Mercury 300 and Inova 400 MHz spectrometers at ambient temperature. 1H and 13C chemical shifts were referenced to residual solvent peaks. 31P chemical shifts were referenced to phosphoric acid. Infrared spectra were recorded as KBr pellets on a Varian Scimitar 800 Series FT-IR spectrophotometer. UV-Visible absorption spectra were recorded on a Cary50 spectrophotometer using 1.0 cm quartz cuvettes. Solution-state magnetic moments were measured using Evans’ method. Mass spectra were recorded in the Mass Spectrometry Center at Emory University on a JEOL JMS-SX102/SX102A/E mass spectrometer. X-ray diffraction studies were carried out in the X-ray Crystallography Laboratory at Emory University on a Bruker Smart 1000 CCD diffractometer. Cyclic voltammetry experiments were carried out using a CH Instruments (Austin, TX) Model 660C potentiostat. All experiments were conducted in CH2Cl2 with 0.10 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Electrochemical experiments were conducted in a three-component cell consisting of a Pt auxiliary electrode, a non-aqueous reference electrode (Ag/AgNO3), and either a glassy carbon (CV) or reticulated vitreous carbon (bulk electrolysis) working electrode. All electrochemical measurements are referenced and reported versus the ferrocene/ferrocenium couple.

B. Ligand Synthesis

Bis(2-nitrophenyl)amine [HN(o-PhNO2)2]. Prepared using a modified literature procedure. A mixture of 2-nitroaniline (2.0 g, 14.1 mmol) and 1-fluoro-2-nitrobenzene (1.5 mL, 14.1 mmol) was stirred in dimethyl sulfoxide (DMSO, 40 mL) at room temperature. KOtBu (3.3 g, 29.0 mmol) was added slowly and the reaction stirred under N2 at room temperature for 24 h. The reaction mixture was then diluted with water (200 mL) and filtered to give a bright orange solid. The solid was recrystallized from MeOH (500 mL) and dried under vacuum to afford the product as a bright orange, crystalline solid (63%, 2.30 g). 1H NMR (δ, CDCl3, 300 MHz): 11.02 (s, 1H), 8.21 (dd, 2H, J = 1.5 Hz), 7.56 (m, 4H), 7.10 (td, 2H, J = 1.8 Hz, J = 1.5 Hz). 13C NMR (δ, CDCl3, 75.5 MHz): 137.40, 134.30, 127.01, 121.32, 119.20. HRMS(ESI): C12H9N3O4 m/z Calcd. 259.0593, Found 260.06584 [M+1]+. FTIR (KBr, cm−1): ν(NO2) 1514, 1334, ν(NH) 3303. UV-vis (CH2Cl2) λmax, nm (ε, M−1 cm−1): 430 (14100), 268 (35700).

Bis(2-aminophenyl)amine [HN(o-PhNH2)2]. Prepared using a modified literature procedure. To a THF (50.0 mL) solution of HN(o-PhNO2)2 (2.0 g, 7.7 mmol) was added 5 wt.% Pd/C (1.0 g, 0.5 mmol, 6 mol%). The reaction mixture was placed in a pressure-safe reaction vessel and shaken under H2 at 50 psi for 45 min. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo to obtain a thick, colorless oil. The solid was recrystallized from MeOH (500 mL) and dried under vacuum to afford the product as a bright orange, crystalline solid (63%, 2.30 g). 1H NMR (δ, CDCl3, 300 MHz): 11.02 (s, 1H), 8.21 (dd, 2H, J = 1.5 Hz), 7.56 (m, 4H), 7.10 (td, 2H, J = 1.8 Hz, J = 1.5 Hz). 13C NMR (δ, CDCl3, 75.5 MHz): 137.40, 134.30, 127.01, 121.32, 119.20. HRMS(ESI): C12H13N3 m/z Calcd. 199.11095 Found 200.11751 [M+1]+. FTIR (KBr, cm−1): ν(NH) 3413, 3375, and 3344.

2,2'-Bis(isobutyrylamido)diphenylamine (HN(o-PhNHC(O)iPr)2). A suspension of HN(o-PhNH2)2 (1.32 g, 6.6 mmol) in dichloromethane (CH2Cl2, 50 mL) was lowered to 0 °C under an atmosphere of N2. Triethylamine (2.02 mL, 14.5 mmol) was then added, followed by isobutyryl chloride (1.53 mL, 14.5 mmol). The mixture stirred at 0 °C for 1 hour. The reaction mixture was slowly warmed to room temperature and stirred for an additional 20 hours. The resulting pale brown solution was extracted with a saturated aqueous NaHCO3 (3 x 30 mL) solution. The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated in vacuo. The crude solid was recrystallised by layering...
hexanes onto a concentrated CH₂Cl₂ solution of the product (1.78 g, 80%). ¹H NMR (δ, CDCl₃, 300 MHz): 7.83 (s, 2H, NH(CO)), 7.67 (d, 2H, J = 1.6 Hz, ArH), 7.04 (m, 4H, ArH), 6.88 (d, 2H, J = 1.2 Hz, ArH), 5.75 (s, 1H, NH), 2.58 (q, 2H, J = 6.8 Hz, CH), 1.16 (d, 12H, J = 7.2 Hz, CH₃). ¹³C NMR (δ, CDCl₃, 75.5 MHz): 176.48, 136.02, 129.26, 126.27, 124.18, 123.0, 121.11, 36.20, 19.76. HRESI-MS: C₂₀H₂₅N₃O₂ m/z Calcd. 339.19468 Found 340.20150 [M+1]⁺. FTIR (KBr, cm⁻¹): ν(NHamide) 3230, ν(NHamine) 3367, ν(CO) 1660.

C. Complex Syntheses

Synthesis of (Et₄N)₂[1]
To a solution of HN(o-PhNHC(O)iPr₂ (114.0 mg, 0.34 mmol) in DMF, (10 mL) was added potassium hydride (29.67 mg, 0.74 mmol). When gas evolution ceased, CoBr₂ (36.77 mg, 0.17 mmol) was added as a solid. When the reaction mixture became homogenous, tetraethylammonium bromide (70.67 mg, 0.34 mmol) was added to the red solution. After stirring for 3 h, the DMF was removed under high vacuum and the resulting solid was dissolved in CH₃CN (15 mL), filtered through a medium porosity frit, and the filtrate was concentrated to dryness. Bulk recrystallization was obtained by diffusing diethyl ether into a concentrated CH₂Cl₂ solution containing the product. Red, X-ray quality crystals were obtained by slow diffusion of diethyl ether into a concentrated DMF solution of (Et₄N)₂[1] (120 mg, 72%). ¹H NMR (δ, CD₂Cl₂, 400 MHz): -70.03 (s), -63.80 (s), -46.48 (s), -37.23 (s), -16.31 (s), -14.7 (s), -4.11 (s), 1.32 (s), 3.60 (s), 4.90 (s), 6.36 (s), 8.56 (s), 9.22 (s), 12.39 (br), 17.67 (br), 23.44 (s), 27.01 (s), 56.50 (s), 60.54 (s). FTIR (KBr, cm⁻¹): ν(NH) 3388, ν(CO) 1681. Anal. Calcd (found) for (Et₄N)₂[1]·CH₂Cl₂: C, 63.44 (63.27); H, 8.22 (8.50); N, 10.38 (10.02). μₑff = 4.37 μB (Evans Method, CD₂Cl₂, 298K). λmax, nm (ε, M⁻¹cm⁻¹) (DMF): 634 (sh), 569 (640), 535 (sh); λmax, nm (ε, M⁻¹cm⁻¹) (CH₂Cl₂): 636 (sh), 573 (570), 534 (sh); λmax, nm (solid, silicon oil): 211, 255, 360, 573.

Synthesis of (Et₄N)₂[2]
To a solution of HN(o-PhNHC(O)iPr₂ (99.3 mg, 0.29 mmol) in dry dimethylformamide (DMF, 10 mL) was added potassium hydride (41.11 mg, 1.0 mmol). When gas evolution ceased, CoBr₂ (64.06 mg, 0.29 mmol) was added as a solid and the mixture stirred for 1 h. Tetraethylammonium bromide (61.55 mg, 0.29 mmol) was then added to the deep green solution. After stirring for 3 h, DMF was removed under vacuum and the resulting solid was dissolved in CH₃CN (15 mL), filtered through a medium porosity frit, and the filtrate was concentrated to dryness. Dark green, X-ray quality crystals were obtained by slow diffusion of diethyl ether into a concentrated DMF solution of the product (70%, 108 mg). ¹H NMR (δ, CD₂Cl₂, 400 MHz): -46.28 (s), -40.05 (s), -1.12 (s), 0.71 (s), 10.92 (s), 25.99 (s), 28.64 (s), 65.20 (s). FTIR (KBr, cm⁻¹): ν(CO) 1592. Anal. Calcd (found) for (Et₄N)₂[2]: C, 63.98 (63.64); H, 8.05 (7.95); N, 10.66 (11.01). μₑff = 4.73 μB (Evans Method, CD₂Cl₂, 298K). λmax, nm (ε, M⁻¹cm⁻¹) (DMF): 600 (770), 926 (133); λmax, nm (ε, M⁻¹cm⁻¹) (CH₂Cl₂): 636 (sh), 573 (570), 534 (sh); λmax, nm (solid, silicon oil): 253, 343, 455 (sh), 644.

Synthesis of (Et₄N)[1]
To a red solution of (Et₄N)₂[1] (237.6 mg, 0.239 mmol) in acetonitrile (CH₃CN, 10 mL) was added ferrocenium tetrafluoroborate (FcBF₄) (65.23 mg, 0.239 mmol) as an CH₃CN solution (3 mL). After stirring for 12 h, the solvent was removed under vacuum, and the resulting solid was dissolved in THF and filtered to remove Et₄NBF₄. The deep blue filtrate was then concentrated to dryness. The deep blue solid that resulted was washed with hexanes (3 x 5 mL) to remove ferrocene, and the crude solid was collected on a frit. Fine blue crystals can be obtained by layering hexanes onto a concentrated CH₂Cl₂ solution of the product (1.78 g, 80%). ¹H NMR (δ, CDCl₃, 300 MHz): 7.83 (s, 2H, NH(CO)), 7.67 (d, 2H, J = 1.6 Hz, ArH), 7.04 (m, 4H, ArH), 6.88 (d, 2H, J = 1.2 Hz, ArH), 5.75 (s, 1H, NH), 2.58 (q, 2H, J = 6.8 Hz, CH), 1.16 (d, 12H, J = 7.2 Hz, CH₃). ¹³C NMR (δ, CDCl₃, 75.5 MHz): 176.48, 136.02, 129.26, 126.27, 124.18, 123.0, 121.11, 36.20, 19.76. HRESI-MS: C₂₀H₂₅N₃O₂ m/z Calcd. 339.19468 Found 340.20150 [M+1]⁺. FTIR (KBr, cm⁻¹): ν(NHamide) 3230, ν(NHamine) 3367, ν(CO) 1660. HRESI-MS: for [1]⁺ Calcd (m/z): 733.29215, Found 733.29180. Et₄N[1]. Anal. Calcd (found) for (Et₄N)[1]0.25CH₂Cl₂: C, 65.46 (65.11); H, 7.57 (7.53); N, 11.08 (10.87).

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D. Catalytic Oxidation Procedures

Typical procedure for (Et₄N)₂[1]: Under an inert atmosphere, a 25 mL round bottom flask was charged with a stir bar, triphenylphosphine (0.53 g, 2.0 mmol), (Et₄N)₂[1] (0.02 g, 0.020 mmol), and 10 mL of CH₃CN. The mixture was stirred until homogeneous (~3 min) and then the flask was fitted with a septum and removed from the drybox. While stirring at room temperature, a constant slow purge of O₂ (1 atm) was then introduced to flask by connecting it, via 18-gauge needles inserted through the septum, to an O₂ line and to a mineral oil gas bubbler. Reactions were monitored by GC (traces compared to authentic samples of PPh₃ and OPPh₃). After 2 hours, 69% of the PPh₃ had been converted to OPPh₃ (1.38 mmol, 0.39 g). Isolate yield of OPPh₃ confirmed by GC and ³¹P NMR. Catalytic oxidations were run in triplicate and conversion numbers (yields of OPPh₃) in good agreement (±3%).

Typical procedure for (Et₄N)₂[2]: Under an inert atmosphere, a 25 mL round bottom flask was charged with a stir bar, triphenylphosphine (0.498 g, 1.9 mmol), (Et₄N)₂[2] (0.02 g, 0.019 mmol), and 12 mL of CH₃CN. The mixture was stirred until homogeneous (~3 min) and then the flask was fitted with a septum and removed from the drybox. While stirring at room temperature, a constant slow purge of O₂ (1 atm) was then introduced to flask by connecting it, via 18-gauge needles inserted through the septum, to an O₂ line and to a mineral oil gas bubbler. Reactions were monitored by GC (traces compared to authentic samples of PPh₃ and OPPh₃). After 2 hours, 95% of the PPh₃ had been converted to OPPh₃ (0.50 g, 1.81 mmol). Isolated yields of OPPh₃ confirmed by GC and ³¹P NMR. Catalytic oxidations were run in triplicate. Catalytic oxidations were run in triplicate and conversion numbers (yields of OPPh₃) in good agreement (±3%).

Reactions with ¹⁸O₂: Typical experiment: Under an inert atmosphere, a 10 mL round bottom flask was charged with a stir bar, triphenylphosphine (0.030 g, 0.10 mmol), (Et₄N)₂[2] (0.0107 g, 0.010 mmol), and 5 mL of CH₃CN. The mixture was stirred until homogeneous (~3 min) and then the flask was fitted with a septum and removed from the drybox. While stirring, ¹⁸O₂ was then introduced to flask via syringe. Incorporation of ¹⁸O from the ¹⁸O₂ into the oxidized product was confirmed by mass spectrometry.
**Figure S1:** UV-Visible absorption spectra of \((\text{Et}_4\text{N})_2[2]\) (green) and \((\text{Et}_4\text{N})_2[1]\) (red) in \(\text{CH}_2\text{Cl}_2\).

**Figure S2:** UV-Visible absorption spectra of \((\text{Et}_4\text{N})_2[2]\) (green) and \((\text{Et}_4\text{N})_2[1]\) (red) in \(\text{DMF}\).
**Figure S3:** Cyclic voltammogram of (Et₄N)₂[2] recorded in CH₂Cl₂ (0.10 M "Bu₄NPF₆). at room temperature at 100 mV/s.

**Figure S4:** Cyclic voltammogram of (Et₄N)₂[1] recorded in CH₂Cl₂ (0.10 M "Bu₄NPF₆). at room temperature at 100 mV/s (ΔEₚ for E¹/₂, E²/₁₂ and E³/₁₂ are 143.5 mV, 170 mV and 216 mV; i_p/a/i_p are 1.1, 1.3 and 0.86, respectively).
Figure S5: Cyclic voltammogram of electrochemically oxidised (Et₄N)₂[1] after first oxidation in CH₂Cl₂ (0.10 M nBu₄NPF₆) at 100 mV/s.

Figure S6: Cyclic voltammogram of electrochemically oxidised (Et₄N)₂[1] after first oxidation in CH₂Cl₂ (0.10 M nBu₄NPF₆) at 100 mV/s.
Figure S7: Charge vs. time plot for bulk electrolysis of (Et₄N)₂[1] in CH₂Cl₂ at room temperature.

Figure S8: Overlay of UV-Visible absorption spectra of (Et₄N)[1] (blue) and (Et₄N)₂[1] (red) in CH₂Cl₂.
Figure S9. Thermal ellipsoid diagram of (Et₄N)[I] drawn at 50% probability. Hydrogen atoms, tetraethylammonium counter cation, and solvent (CH₂Cl₂) have been removed for clarity. Selected bond distances (Å): Co–N1 1.933(14), Co–N2 1.943(14), Co–N4 1.933(13), Co–N5 1.923(15) and angles (°): N1–Co–N5 132.7(6), N1–Co–N2 87.3(6), N5–Co–N4 85.1(6), N1–Co–N4 114.6(4) N5–Co–N2 111.7(5) N4–Co–N2 131.8(6).  

References & Notes.
5. Crystal data for (Et₄N)[I]: C₄₉₄₇ H₆₈₉₄ Cl₂₉₄ CoN₇O₄, M = 988.85, 0.29 x 0.18 x 0.07 mm³, Triclinic, space group *P*-1, *a* = 12.264(10) Å, *b* = 14.280(12) Å, *c* = 15.642(13), *V* = 2593(4), *Z* = 2, *ρ* = 1.266 g cm⁻³, μ = 531 mm⁻¹, *F*(000) = 1047, *T* = 173(2) K, *R*(*F*² > 2σ) = 0.1377, *wR*² = 0.2424, 9133 independent reflections, [θ range = 1.34 – 25.0°] and 560 parameters, GOF on *F*² = 1.096.