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Co(III) complexes of tetradentate X_3L type ligands: Synthesis, electronic structure, and reactivity

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ABSTRACT

Co(III) complexes of DPP (DPP = (*Z*)-2-(2-((5-(2-hydroxyphenyl)-1H-pyrrol-2-yl)(phenyl)methylene)-2H-pyrrol-5-yl)phenol) and two fluorinated DPP variants are prepared, structurally characterized, and their reactivity explored in the catalytic ring-opening of 1,2-epoxyhexane with alcohols. While the related Co(III) salen and porphyrin complexes are highly active for this catalytic transformation, the Co(III) DPP complexes are shown to be catalytically inert under the conditions studied. Computational characterization of the electronic structure of all the complexes shows that the Co(III) complexes ligated by the DPP ligands (tetradentate X_3L type) do not have sufficient Lewis acidity to activate the epoxide, whereas the Co(III) porphyrin and salen (tetradentate X_2L_2 type) incorporate a counter-ion that draws electron density away from the metal center, creating a more Lewis acidic Co species that is catalytically active for alcohol ring-opening of epoxides. The work thus gives insight into the requirements for effective Lewis acidic epoxide ring-opening catalysts based on cobalt.

1. Introduction

Tetradentate X_2L_2 type ligands are well-established in metal complex catalyzed reactions, with two examples being salen and porphyrin complexes [1–3]. Both are used ubiquitously in catalysis, including for the reactions with CO_2 or isocyanates [4,5], in asymmetric nitroaldol reactions [6], copolymerization of CO_2 and epoxides [7], fluorination of epoxides [8], aziridination [9], C–H oxidative fluorination [10], and olefin epoxidation [11]. One of the most important discoveries in the field of metal salen catalysis was the use of cobalt complexes for the asymmetric ring opening of epoxides with water as nucleophile (hydrolytic kinetic resolution, HKR) [12]. Since then, many papers have focused on the reaction mechanism [13,14] and catalyst engineering [15–17]. In addition to HKR, stereo- and regio-selective ring opening of epoxides with various nucleophiles can also be catalyzed by metal salen and porphyrin complexes [18–20].

We and other groups further examined the catalyst deactivation pathways of epoxide ring opening with water or methanol. For HKR, counter-anion loss is the major reason for the decreased catalytic reactivity, as shown by Jacobsen and Blackmond and verified by others [14,21], while for alcohol ring opening (ARO) of epoxides, Co(III) reduction is also an important contributor [22]. To circumvent the deactivation pathways of counter-anion loss and Co(III) reduction, we explored some quasi-planar tetradentate ligands of the X_3L type, which have tri-anionic character and so do not require a counter-ion when coordinating to Co(III). Here, we report the synthesis of Co(III) complexes with the DPP (DPP = (*Z*)-2-(2-((5-(2-hydroxyphenyl)-1H-pyrrol-2-yl)(phenyl)methylene)-2H-pyrrol-5-yl)phenol) ligand and its derivatives, characterize them experimentally and computationally, and explore their reactivity with terminal epoxides using alcohols as nucleophiles.

2. Materials and methods

2.1. General experimental

Reagents were used as received unless otherwise noted. ^1H and ^{13}C NMR spectra were acquired with a Varian Mercury 400 MHz spectrometer, and chemical shifts are reported in ppm with

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reference to the corresponding residual nuclei of the deuterated solvents. The conversion of epoxides with alcohols and selectivity to β-alkoxy alcohols were determined by using capillary gas-phase chromatography on a Shimadzu GC 2010 equipped with a FID detector and a SHRX5 column (15 m × 0.25 mm × 0.25 μm). UV–Vis absorption spectra were recorded on an Agilent 8453 UV–Vis Spectrophotometer. High resolution ESI mass spectra were obtained using Thermo Instruments Orbitrap.

2.2. Synthesis of ligands

DPP (DPP, dipyrrinphenol, is (*Z*)-2-(2-((5-(2-hydroxyphenyl)-1H-pyrrol-2-yl)(phenyl)methylene)-2H-pyrrol-5-yl)phenol) and F_5DPP (F_5DPP, F_5dipyrrinphenol, is (*Z*)-2-(2-((5-(2-hydroxyphenyl)-1H-pyrrol-2-yl)(perfluorophenyl) methylene)-2H-pyrrol-5-yl)phenol) were prepared according to published procedures [23,24]. Pyrrolylsodium was prepared as reported in the literature [25].

2-(4-fluoro-2-methoxyphenyl)-1H-pyrrole. The title compound was synthesized by adapting a procedure from the literature [25]. In a nitrogen filled glovebox, 0.802 g (9 mmol) pyrrolylsodium and 1.227 g (9 mmol) $ZnCl_2$ were weighed and transferred to a 25-mL Schlenk flask containing a magnetic stir bar. The flask was sealed with a septum, removed from the glovebox, and connected to a Schlenk line. The atmosphere of the tube was evacuated and replaced with nitrogen. Then, 3 mL THF was added via syringe, and the reaction mixture was stirred magnetically for 30 min. The septum was removed under a flow of nitrogen and 3.4 mg (0.5 mol%) of palladium precatalyst and 4.5 mg (0.5 mol%) of 2-(di-tert-butylphosphino)biphenyl, weighed out under air, were quickly added. The flask was then purged under a flow of nitrogen for about 10 min. Subsequently, 0.371 mL (3 mmol) 2-chloro-5-fluoroanisole was added via syringe. The reaction was then heated at 60 °C for 50 h, after which, the reaction mixture was cooled to room temperature. Et_2O (20 mL) and water (20 mL) were then added and the resulting mixture was transferred to a separatory funnel, where the phases were separated. The aqueous layer was extracted with Et_2O (2 × 20 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel. Pure product, as a light bluish liquid, was obtained using 5% ethyl acetate in hexanes as eluent, 0.532 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (br, 1H, N*H*), 7.35 (dd, *J* = 9.8, 3.0 Hz, 1H, C*H*), 6.87–6.90 (m, 2H, C*H*), 6.80–6.86 (m, 1H, C*H*), 6.60–6.62 (m, 1H, C*H*), 6.29–6.31 (m, 1H, C*H*), 3.94 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.72(C), 156.24(C), 128.91(C), 118.32(CH), 112.77(C), 112.65(CH) (d, *J* = 10.0 Hz), 112.50(CH) (d, *J* = 4.0 Hz), 112.24(CH), 109.04(CH), 106.85(CH), 56.26(OCH_3). ^{19}F NMR (400 MHz, $CDCl_3$): δ −114.72.

2-(4-fluoro-2-methoxyphenyl)-5-((5-(4-fluoro-2-methoxyphenyl)-2H-pyrrol-2-ylidene) (perfluro phenyl)methyl)-1H-pyrrole. This compound was synthesized based on a modified procedure from the literature [23]. To a stirred solution containing 2-(4-fluoro-2-methoxyphenyl)-1H-pyrrole (0.55 g, 2.9 mmol) and pentafluorobenzaldehyde (0.18 mL, 1.45 mmol) in CH_2Cl_2 (60 mL) was added trifluoroacetic acid (TFA) (33 μL, 0.44 mmol) under nitrogen atmosphere, and the mixture was stirred for 24 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.33 g, 1.45 mmol) was added, and the resulting solution was stirred overnight. The reaction mixture was washed with saturated $NaHCO_3$ aqueous solution and extracted with CH_2Cl_2. The organic solution was collected, dried over Na_2SO_4, and evaporated to a small volume that was loaded directly onto a short alumina column and eluted with CH_2Cl_2. The first red band was collected and evaporated to a small volume. The pure product, as a very dark solid, was obtained by column chromatography on silica gel using 25% dichloromethane in hexanes as eluent, 0.44 g (54%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.32 (br, 1H, N*H*), 7.70 (dd, *J* = 9.4, 3.2 Hz, 2H, C*H*), 7.00 (dd, *J* = 7.6, 3.2 Hz, 1H, C*H*), 6.97 (dd, *J* = 7.6, 3.2 Hz, 1H, C*H*), 6.91 (d, *J* = 4.4 Hz, 2H, C*H*), 6.89 (d, *J* = 4.4 Hz, 2H, C*H*), 6.43 (d, *J* = 4.4 Hz, 2H, C*H*), 3.84 (s, 6H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.30(C–OCH_3), 155.93, 153.75, 152.97, 140.48, 127.03, 122.82, 121.28, 119.72, 116.55, 116.32, 115.15, 114.91, 113.01, 112.93, 56.43(OCH_3). ^{19}F NMR (400 MHz, $CDCl_3$): δ −123.35 to −123.41 (m, 2F), −138.30 (dd, *J* = 24.0, 8.0 Hz, 2F), −152.83 (t, *J* = 24.0 Hz, 1F), −161.11 to −161.26 (m, 2F).

Synthesis of F_7DPP (F_7DPP is shorthand for F_7dipyrrinphenol = (Z)-5-fluoro-2-(2-((5-(4-fluoro-2-hydroxyphenyl)-1H-pyrrol-2-yl)(perfluorophenyl)methylene)-2H-pyrrol-5-yl) phenol). This compound was synthesized based on a modified procedure from the literature [23]. To a stirred solution of 2-(4-fluoro-2-methoxyphenyl)-5-((5-(4-fluoro-2-methoxyphenyl)-2H-pyrrol-2-ylidene)(perflurophenyl)methyl)-1H-pyrrole (0.44 g, 0.8 mmol) in CH_2Cl_2 (20 mL) was added BBr_3 (16 mL, 1 M in CH_2Cl_2, 16 mmol) at 0 °C under an N_2 atmosphere. The reaction mixture was stirred while allowing the flask to warm up to room temperature and after 50 h the reaction was quenched with methanol (50 mL). The mixture was evaporated and dissolved again with methanol (100 mL). To the obtained mixture conc. HCl (5 mL) was added and refluxed for 3 h. After cooling, the mixture was neutralized with saturated $NaHCO_3$ aqueous solution and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and evaporated to dryness. Pure product, as a very dark solid, was obtained by column chromatography on silica gel using 40% dichloromethane in hexanes as eluent, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 9.0, 3.0 Hz, 2H, CH), 6.84 (d, *J* = 4.4 Hz, 2H, CH), 6.76–6.72 (m, 2H, CH), 6.63–6.60 (m, 4H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.66(C–OH), 152.27, 138.61, 128.83, 117.70, 117.61, 117.37, 117.11, 113.43, 113.19. ^{19}F NMR (400 MHz, $CDCl_3$): δ −123.80 to −123.83 (m, 2F), −138.30 (dt, *J* = 16.0, 8.0 Hz, 2F), −151.55 (t, *J* = 24.0 Hz, 1F), −160.45 to −160.60 (m, 2F).

2.3. Synthesis of complexes *1*–*3*

The Co(III) complexes **1**–**3** (Fig. 1) were all synthesized using a similar procedure. First, 0.1 mmol of DPP, F_5DPP, or F_7DPP was dissolved in 40 mL 1:1 mixture of methanol and dichloromethane in a 250 mL flask. Then, 1 equivalent of $[Co(NH_3)_6]Cl_3$ (26.7 mg) in 20 mL water was added to the above solution. With the flask open, the reaction was heated to 110 °C. In about 30 min, the color turned green and the solution was stirred for another 90 min. After cooling to room temperature, all solvents were removed under vacuum and the remaining solid was redissolved in 50 mL dichloromethane, which was washed with water (3 × 20 mL). **1**–**3** were obtained by removing dichloromethane and dried under high-vacuum overnight. HRMS experimental (calculated): **1** $[CoDPP]^+$ 460.0612 (460.0622); **2** $[CoF_5DPP]^+$ 550.0150 (550.0150); **3** $[CoF_7DPP]^+$ 585.9977 (585.9962). UV–Vis absorbance peak: **1**, 637 nm, **2**, 668 nm and **3**, 655 nm (Fig. 2). Analytically pure complexes were not obtained.

2.4. General procedure for catalytic epoxide ring opening with methanol

2.0 mol% catalyst was dissolved in racemic 1,2-epoxyhexane (2 mmol) with chlorobenzene added as an internal standard for GC analysis. The flask was immersed in a water bath at ambient temperature (295 K), and methanol (4 mmol, 2 equiv) was added to the system to start the reaction. Samples were taken from the reaction mixture at specified times, diluted with anhydrous diethyl ether, and passed through a plug of silica gel in a Pasteur pipet to remove the catalyst. The conversions and selectivity were calculated from data obtained by GC analysis.