Co(III) Complexes of Tetradentate X₃L Type Ligands: Synthesis, Electronic Structure, and Reactivity

Yan Feng,^{a#} Lori A. Burns,^{b,c,#} Li-Chen Lee,^a C. David Sherrill^{b,c,d,*} and Christopher W. Jones^{a,b,*}

^aSchool of Chemical & Biomolecular Engineering, ^bSchool of Chemistry and Biochemistry, ^cCenter for Computational Molecular Science and Technology, ^dSchool of Computational Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

*Christopher W. Jones

telephone number: +1 404 385 1683

e-mail address: cjones@chbe.gatech.edu

postal address: School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive NW, Atlanta, GA 30332-0100, USA

[#]these authors contributed equally to the manuscript.

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 X₃L type) do not have sufficient Lewis acidity to activate the epoxide, whereas the Co(III) porphyrin and salen (tetradentate X₂L₂ 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.

Keywords

Cobalt, Salen, Porphyrin, ARO, B3LYP, ESP

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 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 $\times$ 0.25 mm $\times$ 0.25 μm). UV-Vis absorption spectra were recorded on an Agilent 8453 UV-Visible Spectrophotometer. High resolution ESI mass spectra were obtained using Thermo Instruments Orbitrap.

2.2 Synthesis of ligands

DPP (DPP, dipyrinphenol, is (Z)-2-(2-((5-(2-hydroxyphenyl)-1H-pyrrol-2-yl)(phenyl)methylene)-2H-pyrrol-5-yl)phenol) and F₅DPP (F₅DPP, F₅dipyrinphenol, 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] Pyrrolysodium 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) pyrrolysodium and 1.227 g (9 mmol) ZnCl₂ 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 minutes. 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. Et₂O (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 Et₂O (2 x 20 mL) and the combined organic layers were dried over MgSO₄, 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%). ¹H NMR (400 MHz, CDCl₃):

δ 9.89 (br, 1H, NH), 7.35 (dd, *J* = 9.8, 3.0 Hz, 1H, CH), 6.87-6.90 (m, 2H, CH), 6.80-6.86 (m, 1H, CH), 6.60-6.62 (m, 1H, CH), 6.29-6.31 (m, 1H, CH), 3.94 (s, 3H, OCH₃).

¹³C NMR (100 MHz, CDCl₃): 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(OCH₃). ¹⁹F NMR (400 MHz, CDCl₃): δ -114.72.

2-(4-fluoro-2-methoxyphenyl)-5-((5-(4-fluoro-2-methoxyphenyl)-2H-pyrrol-2-ylidene) (perfluoro 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 CH₂Cl₂ (60 mL) was added trifluoroacetic acid (TFA) (33 μ L, 0.44 mmol) under nitrogen atmosphere, and the mixture was stirred for 24 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.33g, 1.45 mmol) was added, and the resulting solution was stirred overnight. The reaction mixture was washed with saturated NaHCO₃ aqueous solution and extracted with CH₂Cl₂. The organic solution was collected, dried over Na₂SO₄, and evaporated to a small volume that was loaded directly onto a short alumina column and eluted with CH₂Cl₂. 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%). ¹H NMR (400 MHz, CDCl₃): δ 13.32 (br, 1H, NH), 7.70 (dd, $J = 9.4, 3.2$ Hz, 2H, CH), 7.00 (dd, $J = 7.6, 3.2$ Hz, 1H, CH), 6.97 (dd, $J = 7.6, 3.2$ Hz, 1H, CH), 6.91 (d, $J = 4.4$ Hz, 2H, CH), 6.89 (d, $J = 4.4$ Hz, 2H, CH), 6.43 (d, $J = 4.4$ Hz, 2H, CH), 3.84 (s, 6H, OCH₃). ¹³C NMR (100 MHz, CDCl₃): δ 158.30(C-OCH₃), 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(OCH₃). ¹⁹F NMR (400 MHz, CDCl₃): 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 F₇DPP (*F₇DPP* is shorthand for *F₇dipyrroinphenol* = (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)(perfluorophenyl)methyl)-1H-pyrrole (0.44 g, 0.8 mmol) in CH₂Cl₂ (20 mL) was added BBr₃ (16 mL, 1 M in CH₂Cl₂, 16 mmol) at 0 °C under an N₂ 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 NaHCO₃ aqueous solution and extracted with ethyl acetate. The organic layer was dried over MgSO₄ 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, ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): δ 157.66(C-OH), 152.27, 138.61, 128.83, 117.70, 117.61, 117.37, 117.11, 113.43, 113.19. ¹⁹F NMR (400 MHz, CDCl₃): δ 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** (Figure 1) were all synthesized using a similar procedure. First, 0.1 mmol of DPP, F₅DPP, or F₇DPP was dissolved in 40 mL 1:1 mixture of methanol and dichloromethane in a 250 mL flask. Then, 1 equivalent of [Co(NH₃)₆]Cl₃

(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 X 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** [CoF₅DPP]⁺ 550.0150 (550.0150); **3** [CoF₇DPP]⁺ 585.9977 (585.9962). UV-Vis absorbance peak: **1**, 637 nm, **2**, 668 nm and **3**, 655 nm (Figure 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.

2.5 Computational Methods

Figure 3(a) illustrates the metal–ligand complexes employed in electronic structure calculations, where the salen ligand has been truncated such that it is missing its *tert*-butyl groups and the porphyrin ligand is missing its methoxyphenyl groups, the metal center is Co(III), and the complexing species are epoxyp propane (substrate), for **1-3**, the solvent methanol, and for **4** and **5**, the counter-ion hexafluoroantimonate (SbF₆[−]).

Following previous work,[26] which examined the consistency between density functional theory (DFT) and higher order complete active space methods (CASSCF, CASPT3) for d^6 metal salens, the hybrid B3LYP[27, 28] functional, a combination of Becke's 1988 exchange[29] and Lee, Yang, and Parr's correlation components,[30] was selected. B3LYP was used with the LANL2DZ basis set and effective core potentials[31] (ECP) in conjunction with a grid of 100 radial shells and 302 angular points in the Q-Chem 4.1 quantum chemistry package[32] to fully optimize geometries (root-mean-square gradient $< 1 \times 10^{-4}$ au) for the lowest singlet and triplet (unrestricted reference) states of each metal complex. Solvation was modeled implicitly (methanol solvent parameters) through the Poisson-Boltzmann[33] procedure in the Jaguar 5.5 suite of programs[34] using the pseudospectral implementation of DFT[35] with a fine grid and employing the Jaguar LACVP* basis set, which places on Co and Sb the LANL2DZ basis set and ECP and on first-row atoms the 6-31G* basis.[36-39] Binding energies were computed as the electronic energy of the separate Co(III)-ligand-counter-ion and epoxide species less the full Co(III)-ligand-epoxide-counter-ion complex, where each species had a fully relaxed geometry. Atomic charges were derived from a fit of the (solvated) molecular electrostatic potential (ESP)[40, 41] that has been constrained to reproduce the total charge and quantum mechanical dipole moment. Investigation of the role of dispersion employed the dftd3 program of Grimme to compute B3LYP-D3 energies at B3LYP optimized geometries.[42] Visualization of the electron density distribution has been carried out in WebMO[43] by mapping the electrostatic potential (red indicates an electronegative region at $-0.08 e^-$ and blue indicates an electropositive region at $+0.08 e^-$) onto an electron density isosurface (contour at $0.002 e^-/\text{bohr}^3$).

3. Results and Discussion

Co(III)Salen and Co(III)Porphyrin based catalysts are effective catalysts for the ring-opening of epoxides with water,[12] alcohols,[18, 19, 44] and other nucleophiles.[45, 46] While our past work demonstrated that ring-opening with alcohols can be achieved with very high regioselectivity,[19] recent studies identified counter-anion loss and/or reduction from Co(III) to Co(II) as key causes of catalyst deactivation.[22] Counter-anion loss was also implicated as a deactivation pathway for the same Co-salen-counter-ion catalyst in the HKR of epoxides.[13, 14, 21]

DPP ligands were designed to mitigate Co(III) reduction and counter-anion loss for catalytic epoxide ring-opening reactions. As shown in Scheme 1, the blue portion of porphyrin and the green portion of salen were conceptually fused to form DPP, a tri-anionic ligand that requires no mono-anionic (and potentially labile) counter-anion when binding with a Co(III) center. Since DPP is expected to be electron-rich, F₅DPP and F₇DPP variants were prepared with electron-withdrawing fluoro groups (Scheme 1) to bolster the Lewis acidity of the coordinated cobalt center. DPP type ligands were originally derived from BODIPY dyes,[47] and later used in Mn(III),[23] Al(III),[24] as well as with some tetravalent metal chemistries.[48]

Figure 1. Structures of complexes evaluated as catalysts for the ring opening of 1-hexene oxide with methanol. [One-column figure]

Scheme 1. Design of porphyrin- and salen-inspired DPP ligands.

3.1 UV-Vis spectra of DPP, F₅DPP, F₇DPP and their complexes

All the synthesized ligands were very dark red in color. UV-Vis spectra of the ligands were obtained at 1 mM concentrations. Very intense absorbance peaks were observed for the DPP, F₅DPP and F₇DPP ligands at 544 nm, 550 nm and 548 nm, respectively, as shown in Figure 2. Upon coordination to Co(III), the absorbance peaks for **1**, **2** and **3** red shifted to 637 nm, 668 nm and 655 nm, respectively.

Figure 2. UV-Vis spectra of (a) DPP and **1**; (b) F₅DPP and **2**; (c) F₇DPP and **3**. [Two-column figure]

3.2 Magnetic moments for complexes 1- 3

The magnetic moments of complexes **1-3** were determined by NMR, being 2.6, 2.4, and 2.5, respectively. These values indicate that the three complexes are paramagnetic with a triplet state (theoretical value is 2.8).

3.3 Reactivity testing

The new complexes were evaluated in the ring opening of 1,2-epoxyhexane with methanol or phenol (Table 1). At room temperature, complex **1** did not exhibit any catalytic conversion using MeOH as the nucleophile (Table 2, entry 1) or 50 °C (Table 2, entry 2). Phenol was also tested as a nucleophile, but even at 100 °C, the epoxide remained unconverted (Table 2, entry 3). We hypothesized that the tri-anionic DPP ligand provided the Co(III) center with too much electron density, such that it was too poor a Lewis acid to strongly bind the epoxide reagent. To decrease the electron density around the metal center, five fluoro groups were added to the backbone to create the ligand F₅DPP. However, the resulting Co(III) complex, **2**, was still inactive for the ring opening of 1,2-epoxyhexane with methanol. Finally, two more fluoro groups were included in the ligand F₇DPP, and its cobalt complex, **3**, was tested for the ring-opening reaction with methanol at two temperatures, 25 and 60 °C. Under both conditions, the complex was inert. In comparison, the known active catalysts, **4** and **5**, complete the reaction in 4h and 1h at 295 K.[19, 22] Based on the collected results, we hypothesized that the binding of the epoxide to the cobalt center may not be sufficiently strong enough to lead to reaction. To explore this further, we characterized the electronic structure of the suite of Co(III) complexes computationally.

Table 1. Catalytic results for the ring opening of 1,2-epoxyhexane with methanol or phenol^a

Entry	Catalyst	Nucleophile	Temp / °C	Time / h	Conversion / %
1	1	MeOH	25	24	0
2	1	MeOH	50	24	0
3 ^b	1	PhOH	100	24	0
4	2	MeOH	25	24	0
5	3	MeOH	25	24	0
6	3	MeOH	60	24	0
7 ^c	4	MeOH	25	4	99
8 ^d	5	MeOH	25	1	99

^aReaction conditions: 2.0 mol% catalyst was dissolved in racemic 1,2-epoxyhexane (2 mmol) (chlorobenzene was added as an internal reference for the GC analysis). Methanol or phenol (4 mmol, 2 equiv) was added to the system to start the reaction. ^bDMSO as solvent. The concentration of catalyst is 25 mM. ^cResult from ref [22]. ^dResult from ref [19].

3.3 Computational characterization

Gas phase DFT calculations were performed to unravel the cause of the contrasting reactivity patterns observed in the ARO studies of epoxides with the well-established X₂L₂ catalysts, **4** and **5**, which require a counter-ion, and the X₃L catalysts, **1–3**, which are self-contained (methanol ensures full coordination of all coordination sites) but inactive. According to B3LYP computations, our model of the Co(III)-salen-counter-ion complex **4** exhibits a triplet (paramagnetic) ground state, consistent with high-level computations on the bare metal-ligand ion[26] and experimental findings.[49] In contrast, our model of the Co(III)-porphyrin-counter-ion complex **5** was found to have a singlet

(diamagnetic) ground state, consistent with experiments.[19] Complexes **1–3** displayed paramagnetic signals **based on magnetic moments** and were computationally established to support triplet ground states with an appreciably lower singlet-triplet gap (~1 kcal/mol) than the other ligands (~5 kcal/mol). The discussion below compares complexes **1–5** in their ground state forms (triplets **1–4** and singlet **5**).

Figure 3. Computational results for catalysts and catalyst-epoxide complexes. Numerical B3LYP/LANL2DZ results are summarized in (a) including the equilibrium distance between the metal and epoxide (pink), the binding energy of the epoxide to the complex (turquoise), the partial charges on the individual atoms (purple, near C, O, and Co atoms), and the partial charges on the overall Co-ligand, counter-ion/solvent, and epoxide components of the complex (purple, near sectioning brackets). Electrostatic potential plots in (b) reveal an electropositive (deep blue) epoxide binding site for **4** and **5** and an overall neutral (green/light blue) site for **1–3**, correlated with the experimentally observed catalytic activity. [2-column figure]

The magnitude of the positive charge on the cobalt atom might be expected to correlate strongly with reactivity by providing a receptive (sufficiently Lewis acidic) binding site for the epoxide. However, Figure 3(a) shows that the partial charge appears to be primarily determined by the number and nature of the complexing atoms, with porphyrin (**5**: N₄ linking; counter-ion balanced) exhibiting a low value of +0.43 e and the others yielding (**1–3**: N₂O₂ linking; solvent balanced) +0.82 – +0.84 e and (**4**: N₂O₂ linking; counter-ion balanced) +1.00 e. This means that there is no correlation between cobalt partial charge and reactivity, because the inactive complexes **1–3** exhibit cobalt charges intermediate to those of the active complexes **4–5**. Moreover, the addition of electron-withdrawing fluorine atoms across **1–3** does not appreciably alter the cobalt charge.

A more sophisticated analysis of the electrostatic properties of the metal-ligand complexes is afforded by electrostatic potential maps, presented in Figure 3(b). Here, we see a substantial difference in the metal center comparing between the reactive and nonreactive complexes, with the former exhibiting a significantly more electron-poor Co center and the latter a more neutral one. The X₂L₂ ligands support a counter-ion that sequesters negative charge, creating a strongly Lewis acidic binding site for the epoxide. In contrast, the DPP ligands, regardless of the electron-withdrawing propensities of their substituents, are unable to generate substantial separation of charge to form a Lewis acidic binding site at the metal. The sums of atomic charges in Figure 3(a) are consistent with this picture. The counter-ions in complexes **4** and **5** carry substantial negative charge (–0.85 and –0.74 e), and there is a corresponding, appreciable positive charge (+0.76 and +0.55 e, respectively) on the metal-ligand complex. By contrast, the sum of the charges

on the inactive metal-ligand complexes **1-3** is nearly neutral, $-0.03 - -0.07$, in agreement with the lack of a Lewis-acidic binding site for epoxide in the ESP plots.

The distinct reaction site characters between the reactive and unreactive complexes influence other structural and chemical properties. Most importantly, the active catalysts bind more tightly both energetically (epoxide binding energy 15 and 21 kcal/mol for **4** and **5** versus ~ 9 kcal/mol for **1-3**) and structurally (cobalt to epoxide oxygen distance 1.95 Å for **5** versus ~ 2.32 Å for **1-3**). The more polar environment induced by an implicit solvent model loosens the epoxide binding, affecting triplet states more strongly (6–8 triplet vs. 3 kcal/mol singlet) due to their greater ligand-substrate separation. Conversely, dispersion interactions strengthen substrate binding by ~ 10 kcal/mol. Consideration of all effects together (electronic with solvation and dispersion corrections) only slightly modulates the original gas phase trends: 9.6 (**1**), 9.8 (**2**), 10.2 (**3**), 18.5 (**4**), and 28.9 kcal/mol (**5**). Although the interaction with the catalyst might be expected to induce differential charge distributions on the reactant, by comparing the substrate charge distributions in its unactivated versus complexed forms in Figure 3(a), it is apparent that DPP-type ligands are not altering the carbon charge (0.19 – 0.20 e), whereas the partial positive on the tertiary carbon is appreciably greater (0.27 – 0.29 e) in **4-5**.

4 Conclusions

Based on previous deactivation studies of Co(III) salen and porphyrin catalysts for alcohol ring opening of epoxides that showed cobalt reduction and/or counter-ion exchange to be the primary causes of activity loss, trianionic X_3L type ligands were designed to contain some of the features of salen and porphyrin ligands, but without the

need for a counter-ion when binding Co(III) species. However, these complexes are demonstrated here to be inactive in the target reactions, and we therefore utilized computational studies to probe the electronic causes of this differing reactivity. These studies indicated that the electrostatic potential (and hence, Lewis acidity) is very different for the active catalysts, **4** and **5**, compared to the inactive complexes, **1-3**. Substituting more electron-withdrawing fluorine groups to the DPP ligands did not substantially influence this difference. Instead, our studies suggest that the X_2L_2 ligands support a counter-ion that plays the important role drawing electron density away from the metal center and creating a strongly Lewis acidic Co species that is catalytically active for alcohol ring-opening of epoxides. To this end, more stable catalysts that allow for charge separation but mitigate against counter-ion loss might be achieved by use of salen or porphyrin complexes with a pendant anionic arm coordinated from the bottom, which can serve as the counter-ion, like the hangman salen or porphyrin scaffold developed previously.[50-52]

Acknowledgments

This work was funded by the US Department of Energy, Office of Basic Energy Sciences through Catalysis Science contract DE-FG02-03ER15459. The authors thank Prof. Marcus Weck for helpful discussions.

References

- [1] S. Fantauzzi, A. Caselli, E. Gallo, Dalton Trans., 2009 (2009) 5434.
- [2] D. Intriери, A. Caselli, E. Gallo, Eur. J. Inorg. Chem., 2011 (2011) 5071.
- [3] A.K. Shiryaev, Curr. Org. Chem., 16 (2012) 1788.
- [4] T. Baronsky, C. Beattie, R.W. Harrington, R. Irfan, M. North, J.G. Osende, C. Young, ACS Catal., 3 (2013) 790-797.

- [5] D.J. Darensbourg, W.-C. Chung, S.J. Wilson, *ACS Catal.*, 3 (2013) 3050-3057.
- [6] R.I. Kureshy, A. Das, N.H. Khan, S.H.R. Abdi, H.C. Bajaj, *ACS Catal.*, 1 (2011) 1529.
- [7] D.J. Darensbourg, R.M. Mackiewicz, A.L. Phelps, D.R. Billodeaux, *Acc. Chem. Res.*, 37 (2004) 836.
- [8] J.A. Kalow, A.G. Doyle, *J. Am. Chem. Soc.*, 133 (2011) 16001.
- [9] K.H. Hopmann, A. Ghosh, *ACS Catal.*, 1 (2011) 597.
- [10] W. Liu, X. Huang, M.-J. Cheng, R.J. Nielsen, W.A. Goddard III, J.T. Groves, *Science*, 377 (2012) 1322.
- [11] P. Fackler, S.M. Huber, T. Bach, *J. Am. Chem. Soc.*, 134 (2012) 12869.
- [12] M. Tokunaga, J.F. Larrow, F. Kakiuchi, E.N. Jacobsen, *Science*, 277 (1997) 936.
- [13] S. Jain, X. Zheng, C.W. Jones, M. Weck, R.J. Davis, *Inorg. Chem.*, 46 (2007) 8887.
- [14] L.P.C. Nielsen, C.P. Stevenson, D.G. Blackmond, E.N. Jacobsen, *J. Am. Chem. Soc.*, 126 (2004) 1360.
- [15] C.S. Gill, K. Venkatasubbaiah, N.T.S. Phan, M. Weck, C.W. Jones, *Chem. Eur. J.*, 14 (2008) 7306.
- [16] X. Zheng, C.W. Jones, M. Weck, *J. Am. Chem. Soc.*, 129 (2007) 1105.
- [17] X. Zheng, C.W. Jones, M. Weck, *Adv. Synth. Catal.*, 350 (2008) 255.
- [18] J.M. Ready, E.N. Jacobsen, *J. Am. Chem. Soc.*, 121 (1999) 6086.
- [19] K. Venkatasubbaiah, X. Zhu, E. Kays, K.I. Hardcastle, C.W. Jones, *ACS Catal.*, 1 (2011) 489.
- [20] M.H. Wu, E.N. Jacobsen, *J. Org. Chem.*, 63 (1998) 5252.
- [21] K. Venkatasubbaiah, X.-J. Zhu, C.W. Jones, *Top. Catal.*, 53 (2010) 1063.
- [22] K. Venkatasubbaiah, Y. Feng, T. Arrowood, P. Nickias, C.W. Jones, *ChemCatChem*, 5 (2013) 201-209.
- [23] S.E. Ghachtouli, K. Wójcik, L. Copey, F. Szydio, E. Framery, C. Goux-Henry, L. Billon, M.-F. Charlot, R. Guillot, B. Andrioletti, A. Aukauloo, *Dalton Trans.*, 40 (2011) 9090-9093.
- [24] C. Ikeda, S. Ueda, T. Nabeshima, *Chem. Commun.*, 2009 (2009) 2544.
- [25] R.D. Rieth, N.P. Mankad, E. Calimano, J.P. Sadighi, *Org. Lett.*, 6 (2004) 3981.
- [26] T. Takatani, J.S. Sears, C.D. Sherrill, *J. Phys. Chem. A*, 113 (2009) 9231.
- [27] A.D. Becke, *J. Chem. Phys.*, 98 (1993) 5648.
- [28] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.*, 98 (1994) 11623.
- [29] A.D. Becke, *Phys. Rev. A*, 38 (1988) 3098.
- [30] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B*, 37 (1988) 785.
- [31] P.J. Hay, W.R. Wadt, *J. Chem. Phys.*, 82 (1985) 299.
- [32] Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T.V. Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R.Z. Khallulin, P. Klunzinger, A.M. Lee, M.S. Lee, W. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A. Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill, M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 8 (2006) 3172-3191.
- [33] B. Marten, K. Kim, C. Cortis, R.A. Friesner, *J. Phys. Chem.*, 100 (1996) 11775.
- [34] in: Jaguar, Schrödinger LLC, Portland, OR, USA, 1991–2003.
- [35] D. Chasman, M.D. Beachy, L. Wang, R.A. Friesner, *J. Comput. Chem.*, 19 (1998) 1017.
- [36] J.D. Dill, J.A. Pople, *J. Chem. Phys.*, 62 (1975) 2921.
- [37] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, *J. Chem. Phys.*, 77 (1982) 3654.
- [38] P.C. Hariharan, J.A. Pople, *Theoret. Chim. Acta.*, 28 (1973) 213-222.
- [39] W.J. Hehre, R. Ditchfield, J.A. Pople, *J. Chem. Phys.*, 56 (1972) 2257.
- [40] L.E. Chirlian, M.M. Francl, *J. Comput. Chem.*, 8 (1987) 894.
- [41] R.J. Woods, M. Khalil, W. Pell, S.H. Moffat, V.H. Smith Jr., *J. Comput. Chem.*, 11 (1990) 297.
- [42] in: dftd3, Grimme Research Group, Westfälische Wilhelms-Universität Münster, Organisch-Chemisches Institut, Theoretische Organische Chemie, Corrensstrasse 40, D-48149 Münster, pp. See <http://www.uni-muenster.de/Chemie.oc/grimme/> for a FORTRAN program implementing the DFT-D3 method and a file with available C₆ coefficients.
- [43] J.R. Schmidt, W.F. Polik, in: WebMO, WebMO LLC, Holland, MI, USA, pp. version 13.00.

- [44] R.E. Key, K. Venkatasubbaiah, C.W. Jones, *J. Mol. Catal. A: Chem.*, 366 (2013) 1.
- [45] J.A. Kalow, A.G. Doyle, *J. Am. Chem. Soc.*, 132 (2010) 3268.
- [46] G.-P. Wu, S.-H. Wei, R. W.-M., X.-B. Lu, T.-Q. Xu, D.J. Darensbourg, *J. Am. Chem. Soc.*, 133 (2011) 15191.
- [47] H. Kim, A. Burghart, M.B. Welch, J. Reibenspies, K. Burgess, *Chem. Commun.*, 1999 (1999) 1889.
- [48] K. Nakano, K. Kobayashi, K. Nozaki, *J. Am. Chem. Soc.*, 133 (2011) 10720-10723.
- [49] S. Kemper, P. Hrobárik, M. Kaupp, N.E. Schlörer, *J. Am. Chem. Soc.*, 131 (2009) 4172.
- [50] D.K. Dogutan, K. Bediako, T.S. Teets, M. Schwalbe, D.G. Nocera, *Org. Lett.*, 12 (2010) 1036.
- [51] J.Y. Yang, J. Bachmann, D.G. Nocera, *J. Org. Chem.*, 71 (2006) 8706.
- [52] J.Y. Yang, S.-Y. Liu, I.V. Korendovych, E.V. Rybak-Akimova, D.G. Nocera, *ChemSusChem*, 1 (2008) 941-949.