ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

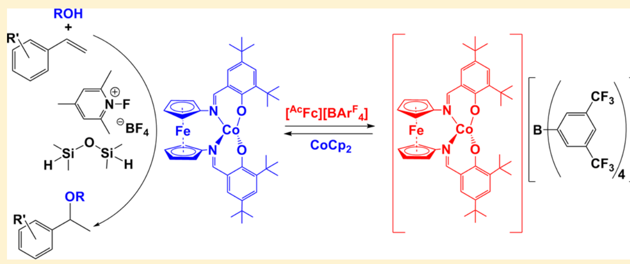
Redox-Switchable Hydroelementation of a Cobalt Complex Supported by a Ferrocene-Based Ligand

Scott M. Shepard and Paula L. Diaconescu*

Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E Young Drive East, Los Angeles, California 90095, United States

Supporting Information

ABSTRACT: The first crystallographically characterized tetrahedral cobalt salen (salen = *N,N*′-ethylenesalicylimine) complex was synthesized by using a 1,1′-ferrocene derivative, salfen (salfen = 1,1′- di(2,4-di-*tert*-butyl-6-salicylimine)ferrocene). The complex undergoes two oxidation events at low potentials, which were assigned as ligand centered by comparison to the corresponding zinc complex. The cobalt complex was found to catalyze the hydroalkoxylation of styrenes, similarly to related square planar cobalt salen complexes, likely due to its fluxional behavior in alcoholic solvents. Furthermore, the one-electron-oxidized species was found to be inactive toward hydroalkoxylation. Thus, the hydroalkoxylation reactivity could be turned on/off *in situ* by redox chemistry.



INTRODUCTION

Hydroelementation, the addition of a hydrogen and a functional group across an unsaturated bond, is a fundamental class of organic chemistry reactions with broad applicability for generating molecular complexity. Additionally, the potential 100% atom economy of these reactions makes them attractive for both green chemistry and low-cost industrial processes.[1] Recent advances in the field of transition metal catalysis have greatly expanded the scope and feasibility of hydroelementation reactions. Milder reaction conditions, greater regioselectivity, stereoselectivity, and a wider functional group tolerance than before are prevalent. This allows the precise formation of complicated products with vital applications ranging from pharmaceuticals to commodity chemical production.[2]

Switchable catalysis is an efficient method that generates multiple, catalytically active species with different reactivity.[3−25] Because these species originate from a single precursor and are readily controlled by external stimuli, rapid production of molecular complexity can be achieved in one pot. Utilizing switchable systems for tandem catalysis is advantageous since problems arising from catalyst compatibility are circumvented. Switchable catalysis has many parallels in biological systems, but it has been less studied in the field of chemical synthesis, largely because of difficulties in regulating multiple catalytically active species in such a way to generate reactions with high levels of substrate selectivity. However, recent developments in chemical,[4] electrochemical,[8] photochemical,[26] mechanochemical,[27] and allosteric[7] control have led to significant advances that have made switchable catalysis possible. An important goal of switchable catalysis is the demonstration of redox switches to be used for creating structural complexity by combining complementary on/off switches.[14,18,24]

Despite the prevalence of hydroelementation chemistry, little if any research has been reported on switchable hydroelementation catalysts. Considering that the carbon−carbon multiple bond is common to all hydroelementation substrates, reversibly switching the activity of a catalyst toward different reactions could provide a novel pathway to important chemicals. Knowles and co-workers recently reported the use of a photoredox catalyst to promote the intramolecular hydroamination of secondary amines.[28] However, their study does not contain an investigation of whether the process is switchable. Another study by Nicewicz and co-workers utilized a photoredox catalyst in the hydrohalogenation of styrenes.[29] However, this study similarly does not investigate switchability.

Recently, Hiroya and co-workers reported a mild and functional group tolerant hydrofluorination reaction with a Co(II) Schiff base complex.[30] This method shows excellent yields for a large variety of substrates with a relatively inexpensive catalyst. Furthermore, this versatile system also leads to hydroalkoxylation in the presence of an alcoholic solvent[31] and intramolecular hydroamination in the presence of a suitable substrate.[32] Dismayed by the lack of switchable hydroelementation reactions in the literature, we sought to develop a redox-switchable catalyst for such processes. A particularly good system to base our work on is the cobalt(II) salen catalyst employed by Hiroya and co-workers for hydrofluorination, hydroalkoxylation, and hydroamination. Not only is this system active toward several different hydroelementation reactions, but it also utilizes a simple salen complex. Salfen (salfen = 1,1′- di(2,4-di-*tert*-butyl-6-

Received: April 19, 2016

DOI: 10.1021/acs.organomet.6b00317
Organometallics XXXX, XXX, XXX−XXX

salicylimine)ferrocene), the Schiff base ferrocene analogue of salen,[33−35] was initially synthesized by Arnold and co-workers[36] and has been used in complexes of cerium[37] and indium[38] for the catalytic ring-opening polymerization of cyclic esters. In this work, we report the synthesis and characterization of a cobalt(II) salfen complex, Co(salfen), and an investigation of its activity toward redox-switchable hydroelementation reactions. The system was found to be active toward the hydroalkoxylation of olefins in its reduced state and inactive in its oxidized state, producing a redox-reversible on/off switch. The complex was not found to be active toward hydroamination of olefins or reactions of alkynes. During this investigation, it was necessary to synthesize and characterize the corresponding zinc(II) complex, Zn(salfen), in order to understand the redox behavior of Co(salfen).

■ EXPERIMENTAL SECTION

General Considerations. All reactions were performed using standard Schlenk techniques or in an MBraun drybox under a nitrogen atmosphere, unless otherwise noted. All glassware and Celite were stored in an oven at >425 K overnight before being brought into the drybox. Solvents, except for methanol, were purified by the method of Grubbs[39] and transferred to the glovebox without exposure to air. Methanol was purified by stirring over calcium hydride overnight followed by distillation under a nitrogen atmosphere and transferred into the drybox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. NMR spectra were recorded at ambient temperature on Bruker AV-300, AV-400, AV-500, and DRX-500 spectrometers. Proton chemical shifts are given relative to residual solvent peaks. Fluorine chemical shifts are given relative to freon. Magnetic susceptibility measurements were performed in either CD_2Cl_2 or $CDCl_3$ using the Evans method.[40,41] UV−vis spectra were obtained on an Agilent Cary 5000 UV−vis−NIR spectrometer. Samples were prepared with dry degassed THF under an inert atmosphere and loaded into a quartz cuvette sealed with a Teflon valve. H_2(salfen), **1**, was prepared according to literature procedures.[36] All other reagents were acquired from commercial sources in the highest available purity and, unless otherwise stated, used as received. Elemental analyses were performed on an Exeter Analytical Inc. CE-440 elemental analyzer.

Co(salfen) (2). Compound **1** (0.29 g, 0.45 mmol) was dissolved in 5 mL of THF and added dropwise to a stirring slurry of potassium hydride (0.04 g, 0.98 mmol) in THF. The dark red solution was stirred for 2 h before filtering through Celite. Then, all volatile substances were removed under reduced pressure. The resulting red solid was washed with hexanes to remove any starting material. The solid was then dissolved in THF, and $CoCl_2$ (0.06 g, 0.45 mmol) was added to the solution. The red solution was stirred for 1 h before the volatiles were removed under reduced pressure. The red solid was dissolved in toluene and filtered through Celite to give a red solution. Evaporation of the toluene under reduced pressure afforded the pure product as a dark red solid (0.28 g, 87.7%). X-ray quality crystals were obtained from the slow evaporation of a benzene solution at ambient temperature. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) −8.94 (s, 1H, N═C*H*), −3.62 (s, 18H, C(CH_3)$_3$), −2.90 (s, 1H, N═C*H*), 9.90 (s, 18H, C(CH_3)$_3$), 10.86 (s, 4H, Cp-*H*), 17.65 (s, 4H, Cp-*H*), 53.70 (s, 2H, aromatic), 60.97 (s, 2H, aromatic). Anal. Calcd for Co(salfen) ($FeCoO_2N_2C_{40}H_{50}$): C, 68.09; H, 7.14; N, 3.97. Found: C, 68.77; H, 6.61; N, 3.72. μ_{eff} = 4.34 μ_B.

[Co(salfen)][BAr^F$_4$] (3). Compound **2** (0.04 g, 0.6 mmol) was dissolved in 3 mL of dichloromethane. To this red solution was added a blue solution of acetylferrocenium [BAr^F$_4$] (Ar^F = 3,5-(CF_3)$_2$-C_6H_3, 0.07 g, 0.06 mmol) in dichloromethane. The resulting black solution was stirred for 30 min before all volatiles were removed under reduced pressure. The black solid was then washed with hexanes until the solution appeared colorless. The product was crystallized by layering a concentrated toluene solution with hexanes. Prolonged standing of this solution at ambient temperature produced X-ray quality crystals (0.07 g, 64.7%). ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) −5.77 (s, 18H, C(CH_3)$_3$), 1.25 (s, 4H, Cp-*H*), 7.59 (s, 12H, B(C_6H_3(CF_3)$_2$)$_4$), 9.30 (s, 18H, C(CH_3)$_3$), 55.60 (s, 2H, aromatic), 61.43 (s, 2H, aromatic). ^9F NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) −62.59 (BAr^F$_4$). Anal. Calcd for [Co(salfen)][BAr^F$_4$] ($FeCoO_2N_2BF_{24}C_{78}H_{62}$): C, 57.09; H, 3.81; N, 1.71. Found: C, 57.22; H, 3.66; N, 1.54. μ_{eff} = 4.80 μ_B.

[Co(salfen)]$_4$ (4). Compound **2** (0.1012 g, 0.14 mmol) was dissolved in 5 mL of THF. To this solution was added 1 mL of MeOH, and the solution was stirred for 4 h. All volatiles were removed under reduced pressure to yield a red solid. The product was purified by layering a concentrated toluene solution of the compound with MeOH. X-ray quality crystals were obtained from prolonged standing of this toluene/MeOH solution at ambient temperature. ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) −8.24 (s, 4H, N═C*H*), −5.11 (s, 36H, C(CH_3)$_3$), −3.83 (s, 36H, C(CH_3)$_3$), −2.89 (s, 4H, N═C*H*), 0.31 (s, 72H, C(CH_3)$_3$), 8.94 (s, 8H, Cp-*H*), 12.86 (s, 8H, Cp-*H*), 49.55 (s, 4H, aromatic), 54.94 (s, 4H, aromatic), 61.43 (s, 4H, aromatic), 64.26 (s, 4H, aromatic). Anal. Calcd for **4** ($Fe_4Co_4O_8N_8C_{160}H_{200}$): C, 68.09; H, 7.14; N, 3.43. Found: C, 68.96; H, 6.49; N, 3.43.

Zn(salfen) (5). Compound **1** (0.09 g, 0.14 mmol) was dissolved in 5 mL of THF and added dropwise to a stirring slurry of potassium hydride (0.01 g, 0.30 mmol) in THF. The dark red solution was stirred for 2 h before filtering it through Celite. Then, all volatiles were removed under reduced pressure. The resulting red solid was washed with hexanes to remove any starting material. The solid was then dissolved in THF, and $ZnCl_2$ (0.02 g, 0.14 mmol) was added to the solution. The red solution was stirred for 1 h before the solvent was removed under reduced pressure. The red solid was dissolved in toluene and filtered through Celite to give a red solution. Removal of all volatiles under reduced pressure afforded the pure product as a dark red solid (0.09 g, 95.9%). ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 1.34 (s, 18H, C(CH_3)$_3$), 1.41 (s, 18H, C(CH_3)$_3$), 3.96−4.14 (d, 2H, Cp-*H*), 4.39−4.64 (d, 2H, Cp-*H*), 7.02−7.03 (d, 2H, aromatic), 7.48−7.49 (d, 2H, aromatic), 8.49 (s, 2H, N═C*H*). ^{13}C NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm)) 29.5 (CH_3), 31.4 (CH_3), 34.1 (CCH_3), 35.8 (CCH_3), 60.7 (Cp), 71.7 (Cp), 72.8 (Cp C═N), 106.3 (aromatic), 117.9 (aromatic), 128.9 (aromatic), 130.3 (aromatic), 142.4 (aromatic), 166.3 (N═CH), 170.1 (CO). Anal. Calcd for Zn(salfen) ($FeZnO_2N_2C_{40}H_{50}$): C, 67.47; H, 7.08; N, 3.93. Found: C, 66.88; H, 6.98; N, 3.90.

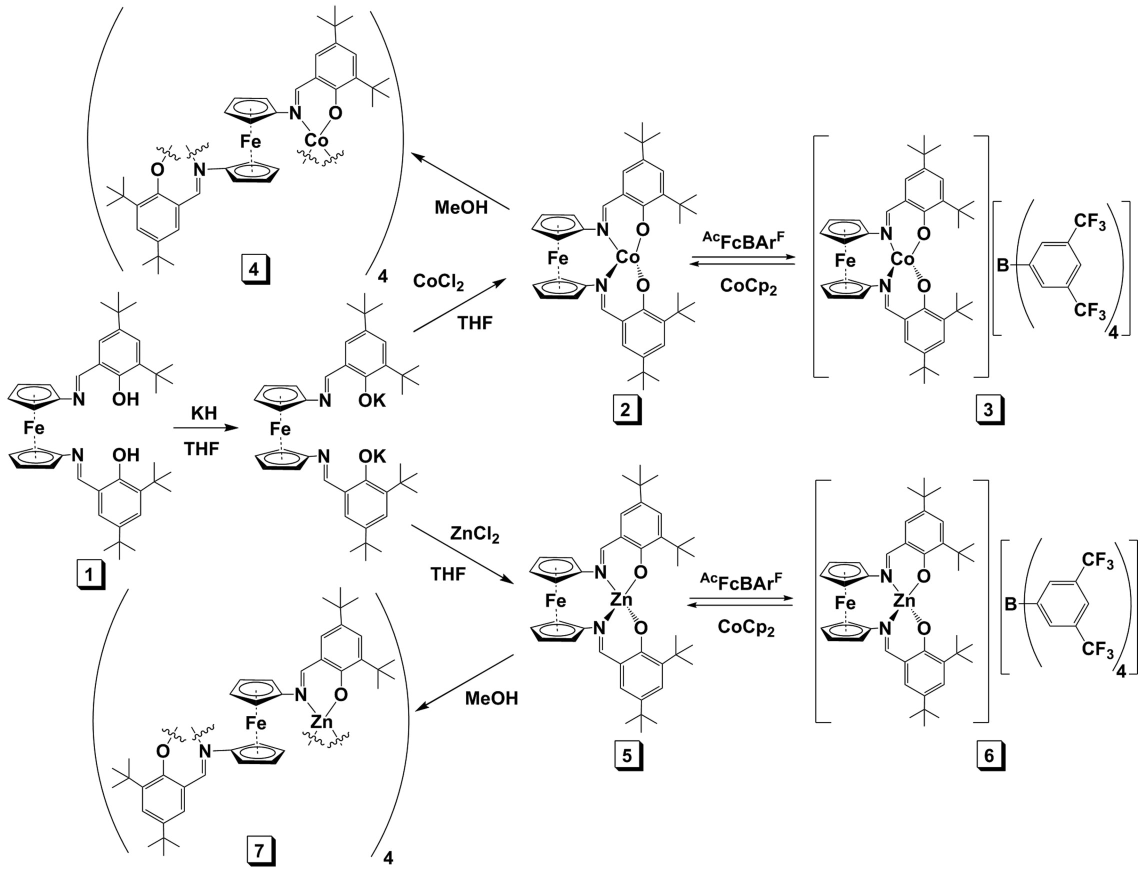
[Zn(salfen)][BAr^F$_4$] (6). Compound **2** (0.004 g, 0.06 mmol) was dissolved in 3 mL of dichloromethane. To this red solution was added a blue solution of acetylferrocenium [BAr^F$_4$] (0.007 g, 0.006 mmol) in dichloromethane. The resulting black solution was stirred for 30 min before the solvent was removed under reduced pressure. The black solids were then rinsed with hexanes to afford the product as a black solid (0.008 g, 90.4%). ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) −2.70, −2.36, 0.06, 1.21, 2.36, 2.56, 3.47, 6.89, 7.72, 13.90, 15.52, 25.0. Anal. Calcd for [Zn(salfen)][BAr^F$_4$] cocrystallized with one molecule of ^{Ac}Fc ($Fe_2ZnO_3N_2C_{84}H_{74}BF_{24}$): C, 54.90; H, 3.97; N, 1.78. Found: C, 54.26; H, 3.60; N, 1.17.

[Zn(salfen)]$_4$ (7). Compound **5** (0.05 g, 0.07 mmol) was dissolved in toluene, and the solution concentrated. This was layered with methanol, and the product formed red crystals upon standing. Recrystallizing in this manner once more afforded a pure product and X-ray quality crystals (0.04 g, 82.1%). ^1H NMR ($CDCl_3$, 500 MHz, 298 K): δ (ppm) 1.13 (s, 36H, C(CH_3)$_3$), 1.28 (s, 36H, C(CH_3)$_3$), 1.37 (s, 36H, C(CH_3)$_3$), 1.57 (s, 36H, C(CH_3)$_3$), 3.67 (s, 8H, Cp-*H*), 3.93 (s, 8H, Cp-*H*), 4.36 (s, 8H, Cp-*H*), 4.50 (s, 8H, Cp-*H*), 4.74 (s, 8H, Cp-*H*), 6.67 (s, 4H, aromatic), 6.86 (s, 4H, aromatic), 7.50 (s, 8H, aromatic), 8.37 (s, 8H, N═C*H*). Anal. Calcd for [Zn(salfen)]$_4$(toluene)$_3$ ($Fe_4Zn_4O_8N_8C_{181}H_{224}$): C, 69.57; H, 7.22; N, 3.59. Found: C, 70.22; H, 7.21; N, 3.18.

General Procedure for Hydroalkoxylation Reactions. Compound **2** (0.01 mmol) was dissolved in 1 mL of dichloromethane. To this solution was added trimethoxybenzene (0.15 mmol) as an internal standard as well as *N*-fluoro-2,4,6-trimethylpyridine tetrafluoroborate

DOI: 10.1021/acs.organomet.6b00317
Organometallics XXXX, XXX, XXX−XXX

Scheme 1. Synthesis of Compounds 2−7



(0.22 mmol), 1,1,3,3-tetramethyldisiloxane (0.22 mmol), the unsaturated substrate (0.20 mmol), and the appropriate alcohol (0.22 mmol). The reaction was allowed to stir until completion and monitored by ^{1}H NMR spectroscopy, by collecting aliquots of the reaction mixture. The volatile substances were removed from the aliquots under reduced pressure, and the solids were dissolved in $CDCl_3$. Product formation and yield were determined by ^{1}H NMR relative integration to trimethoxybenzene.

General Procedure for Redox-Switchable Hydroalkoxylation. Compound **2** (0.01 mmol) was dissolved in 1 mL of dichloromethane. To this solution was added trimethoxybenzene (0.15 mmol) as an internal standard as well as *N*-fluoro-2,4,6-trimethylpyridine tetrafluoroborate (0.22 mmol), 1,1,3,3-tetramethyldisiloxane (0.22 mmol), the unsaturated substrate (0.20 mmol), and the appropriate alcohol (0.22 mmol). The reaction was monitored by ^{1}H NMR spectroscopy, by collecting aliquots of the reaction mixture every hour. The volatile substances were removed from the aliquots under reduced pressure, and the solids were dissolved in $CDCl_3$. After 2 h, acetylferrocenium BAr^F_4 (0.01 mmol) was added to the reaction mixture. After 4 h, cobaltocene (0.011 mmol), *N*-fluoro-2,4,6-trimethylpyridine tetrafluoroborate (0.22 mmol), and 1,1,3,3-tetramethyldisiloxane (0.22 mmol) were added to the reaction mixture.

Electrochemical Studies. Cyclic voltammetry studies were carried out in a 20 mL scintillation vial with electrodes fixed in position by a rubber stopper. The electrolyte used was 0.10 M tetrabutylammonium hexafluorophosphate, which was recrystallized twice from ethanol before use. The solvent used was dichloromethane. A glassy carbon working electrode (planar circular area = 0.071 cm^2), a platinum reference electrode (planar circular area = 0.031 cm^2), and a silver-wire pseudoreference electrode were used and purchased from CH Instruments. Before each cyclic voltammetry experiment, the working and auxiliary electrodes were polished with an aqueous suspension of 0.05 μm alumina on a Microcloth polishing pad. Cyclic voltammograms were acquired with a CH Instruments CHI630D potentiostat and recorded with CH Instruments software (version 13.04) with data processing on Origin 9.2. All potentials are given with respect to the ferrocene/ferrocenium couple.

X-ray Crystallography. X-ray quality crystals were obtained from various concentrated solutions placed in a −40 °C freezer in the glovebox unless otherwise specified. Inside the glovebox, the crystals were coated with oil (STP oil treatment) on a microscope slide, which was brought outside the glovebox. The X-ray data collections were carried out on a Bruker SMART 1000 single-crystal X-ray diffractometer using Mo Kα radiation and a SMART APEX CCD detector. The data were reduced by SAINTPLUS, and an empirical absorption correction was applied using the package SADABS. The structure was solved and refined using SHELXTL (Bruker 1998, SMART, SAINT, XPREP, AND SHELXTL, Bruker AXS Inc., Madison, WI, USA). Tables with atomic coordinates and equivalent isotropic displacement parameters, with all the distances and angles and with anisotropic displacement parameters, are listed in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cobalt and Zinc Complexes. Compound Co(salfen) (**2**) was prepared by salt metathesis between the potassium salt of H_2(salfen) (**1**) and $CoCl_2$ (Scheme 1). Compound **2** is paramagnetic, as expected for a cobalt(II) complex. Its solid-state molecular structure was determined by single-crystal X-ray diffraction (Figure 1), which indicates that the complex adopts a pseudotetrahedral geometry about the cobalt center. The N(1)−Co(2)−O(1) angle of 92.81(9)° and N(2)−Co(2)−O(2) angle of 93.53(9)° are nearly 90°, as expected for a square planar complex, and agree closely with previously reported square planar cobalt salen complexes.[42] However, these two planes are offset by an angle

DOI: 10.1021/acs.organomet.6b00317
Organometallics XXXX, XXX, XXX−XXX

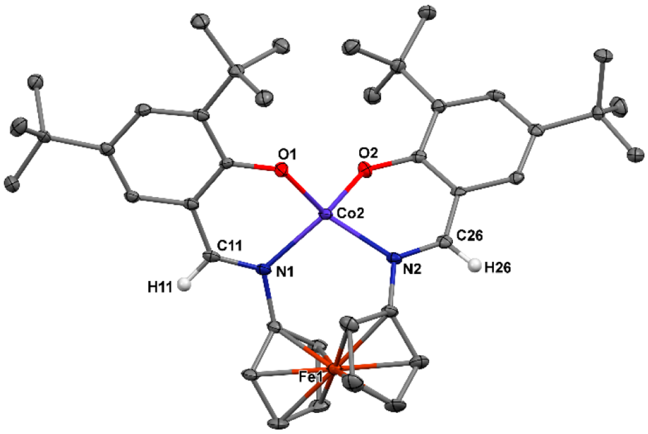


Figure 1. Solid-state molecular structure of Co(salfen) (**2**) with thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances (Å) and angles (deg): N(1)−Co(2), 2.006(2); N(2)−Co(2), 2.009(2); O(1)−Co(2), 1.910(2); O(2)−Co(2), 1.912(2); N(1)−Co(2)−O(1), 92.81(9); O(1)−Co(2)−O(2), 112.37(9); O(2)−Co(2)−N(2), 93.53(9); N(2)−Co(2)−N(1), 107.16(9); O(1)−Co(2)−N(2), 125.50(9); N(1)−Co(2)−N(2), 128.96(9).

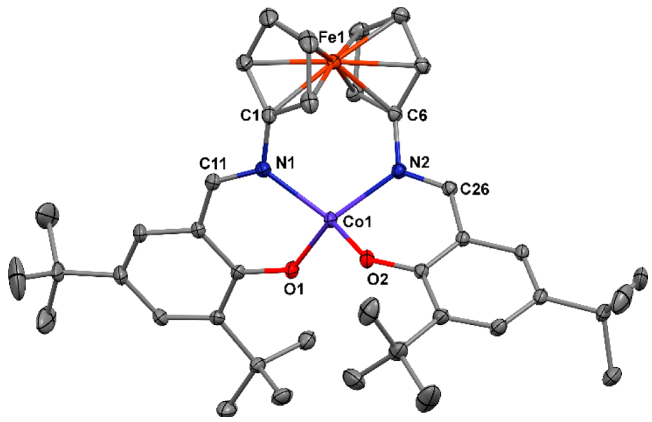


Figure 2. Solid-state crystal structure of [Co(salfen)][BAr^F_4] (**3**) with thermal ellipsoids set at 50% probability. Hydrogen atoms, solvent molecules, and the [BAr^F_4] ion were omitted for clarity. Selected distances (Å) and angles (deg): O(1)−Co(1), 1.8845(13); O(2)−Co(1), 1.8940(13); N(1)−Co(1), 1.9984(15); N(2)−Co(2), 2.0028(15); O(1)−Co(1)−O(2), 112.27(6); O(1)−Co(1)−N(1), 94.09(6); O(1)−Co(1)−N(2), 129.37(6); O(2)−Co(1)−N(2), 92.76(6); O(2)−Co(1)−N(1), 122.74(6); N(1)−Co(1)−N(2), 108.63(6).

of 75.31°. The angle between these two planes in analogous complexes is around 15°.[43] Calculating the τ_4 parameter for the complex yields a value of 0.75, indicating a fairly distorted tetrahedron.[44] The two nitrogen cobalt distances are nearly identical, with a N(1)−Co(2) distance of 2.006(2) Å and a N(2)−Co(2) distance of 2.009(2) Å. Similarly, the oxygen cobalt distances are nearly identical, with an O(1)−Co(2) distance of 1.910(2) Å and an O(2)−Co(2) distance of 1.912(2) Å. All four distances are slightly longer than previously reported for analogous complexes.[42] Four-coordinate cobalt(II) salen complexes typically exhibit a square planar geometry, and a search of the CCSD did not result in any examples of tetrahedral cobalt salen complexes. However, the literature contains one report of tetrahedral coordination in cobalt salen nanoparticles on the basis of EXAFS.[45] This unusual geometry suggests a unique steric and electronic environment. The electronic structure of the compound was investigated by the Evans method, which yielded a magnetic susceptibility of 4.34 μ_B, suggesting an $S = 3/2$ d^7 cobalt, as expected for a tetrahedral geometry. Previously reported square planar cobalt(II) salen complexes exhibit magnetic susceptibilities near 1.7 μ_B, indicative of low-spin, $S = 1/2$ d^7 cobalt.[42,46−48] This unusual geometry is likely due to ferrocene's torsional flexibility relative to common salen ligand backbones.[49]

Compound **2** was found to undergo a one-electron oxidation in the presence of acetylferrocenium [BAr^F_4] (Ar^F = 3,5-$(CF_3)_2$-C_6H_3) to produce the stable and isolable species [Co(salfen)][BAr^F_4] (**3**, Scheme 1). Complex **3** could be reduced back to **2** by the addition of cobaltocene. The solid-state molecular structure of this black oxidized species was determined by single-crystal X-ray diffraction (Figure 2). Similar to the reduced compound **2**, a pseudotetrahedral coordination environment is observed around the cobalt center with the primary structural difference being the presence of the [BAr^F_4] counterion. The nitrogen−cobalt and oxygen−cobalt distances are slightly shorter in **3** than in **2**. The angles around the cobalt center remain relatively unchanged from the reduced species, but the angle between the two nitrogen−cobalt−oxygen planes is slightly larger in **3**, at 77.18°. The τ_4 parameter for the oxidized complex is 0.76, indicating a similar distortion from an ideal tetrahedron as for **2**. The ferrocene moiety in **3** is more distorted than in **2**, with the distance from the Cp centroids to iron of 1.70 Å and an angle between them of 173.10° compared to 1.64 Å and 175.42° in **2**.

Compound **3** is also paramagnetic. The nature of this oxidation was probed by determining the complex's magnetic susceptibility, 4.80 μ_B, using the Evans method. If the oxidation to **3** resulted in a one-electron oxidation of the iron center, the complex would exhibit a theoretical spin-only magnetic susceptibility of 4.24 μ_B for the noninteracting $S = 3/2$ (cobalt) and $S = 1/2$ (iron) spins. For comparison, the theoretical spin-only magnetic susceptibility for an $S = 2$ system, such as high-spin cobalt(III), would be 4.90 μ_B. This suggests that **3** likely contains one more unpaired electron than **2** but does not allow us to assign the first oxidation event unambiguously.

Despite magnetic data showing an additional unpaired electron in compound **3** compared with **2**, we could not assign, on this basis alone, the oxidation states of iron and cobalt in **3**. Thus, we synthesized the zinc complex corresponding to **2**, Zn(salfen) (**5**), by an analogous route (Scheme 1). Compound **5** was also found to undergo a one-electron oxidation in the presence of acetylferrocenium [BAr^F_4] to produce a stable black compound, **6**. Unfortunately, **5** and **6** eluded X-ray crystallographic characterization. However, the zinc complex was found to crystallize in the presence of methanol to form compound **7**. X-ray-quality crystals were obtained for **7** revealing a tetrameric structure analogous to **4**. This suggests that the other zinc complexes likely exhibit geometries comparable to their cobalt analogues.

While studying the reactivity of **2**, we noticed that the corresponding ^1H NMR spectra began to show decomposition. The nature of this decomposition was investigated and found to be the result of methanol present in the drybox atmosphere, a reagent used for hydroalkoxylation reactions (see below). Furthermore, **2** was found to convert cleanly to a new product, **4**, when exposed to methanol and crystallized in its presence. Single-crystal X-ray diffraction studies revealed the solid-state molecular structure of this species to be a tetrameric isomer in

DOI: 10.1021/acs.organomet.6b00317
Organometallics XXXX, XXX, XXX−XXX

which the two phenolate arms of each ferrocene are coordinated to two different cobalt centers (Figure 3).

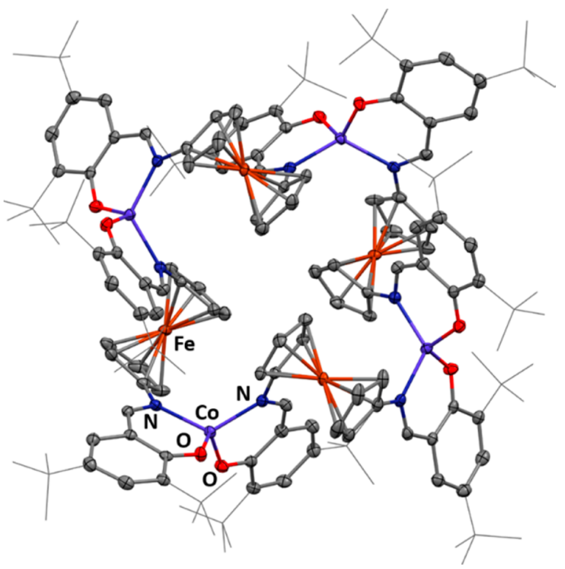


Figure 3. Solid-state crystal structure of [Co(salfen)]$_4$ (**4**) with thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances (Å) and angles (deg): O(1)−Co(1), 1.9005(15); O(2)−Co(1), 1.9102(16); N(1)−Co(1), 1.9866(18); N(2)−Co(1), 1.9967(18); O(1)−Co(1)−O(2), 121.51(7); O(1)−Co(1)−N(1), 95.57(7); O(1)−Co(1)−N(2), 111.76(7); N(1)−Co(1)−N(2), 122.44(7); O(2)−Co(1)−N(2), 95.53(7).

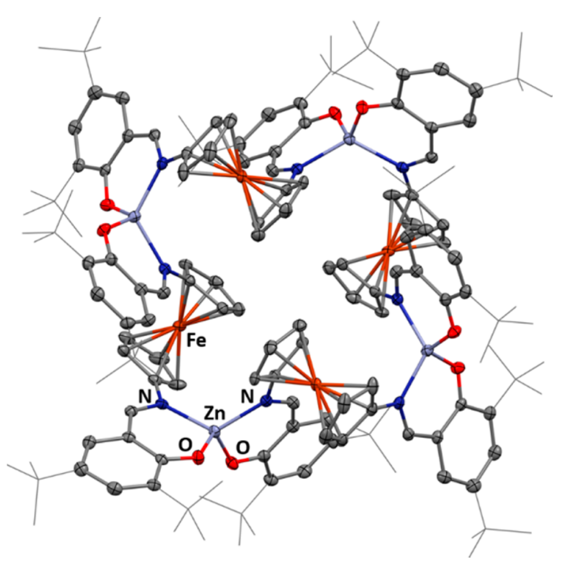


Figure 4. Solid-state crystal structure of [Zn(salfen)]$_4$ (**7**) with thermal ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances (Å) and angles (deg): Zn(1)−N(1), 2.009(2); Zn(1)−N(2), 2.009(2); Zn(1)−O(1), 1.906(2); Zn(1)−O(2), 1.924(2); N(1)−Zn(1)−O(1), 96.27(7); O(1)−Zn(1)−O(2), 112.201(7); N(2)−Zn(1)−N(1), 122.31(8); N(1)−Zn(1)−O(2), 111.78(7); O(1)−Zn(1)−O(2), 120.18(7); N(2)−Zn(1)−O(2), 95.87(7).

The complex retains a pseudotetrahedral coordination environment at each cobalt center. Like the monomeric structure, the angle between the nitrogen and oxygen on the same phenolate arm is nearly 90°, although the angle between these two planes is somewhat larger, 81.70°, in the tetrameric structure. As a result, the τ_4 parameter for the tetrameric structure is 0.82, indicating a geometry significantly closer to a tetrahedron than in the monomer. The nitrogen−cobalt and oxygen−cobalt distances remain almost unchanged from the monomeric structure. Variable-temperature NMR spectroscopy was used to probe whether this tetramer can convert to the monomeric compound with heating. Several peaks in the spectrum coalesce at 80 °C; however, when the sample was returned to ambient temperature, the unchanged tetramer spectrum was observed (Figure S3). This result suggests that the tetrameric structure is more thermodynamically stable. This greater stability presumably arises from less steric congestion, which also allows for a geometry closer to a tetrahedron.

Redox Behavior of Cobalt and Zinc Complexes. Cyclic voltammetry (CV) was employed to investigate the redox behavior of the synthesized compounds. The CV for **2** showed a reversible oxidation event at 0.22 V and a second quasi-reversible oxidation at 0.93 V vs Fc/Fc^+. Compound **5** displays a reversible oxidation at 0.19 V and a second quasi-reversible oxidation at 0.89 V vs Fc/Fc^+. As zinc does not have any easily accessible redox chemistry, we can assign both of these oxidation events as being ligand based. Astoundingly, the cyclic voltammograms for the cobalt and zinc complexes are nearly identical, suggesting that the cobalt(II)/cobalt(III) couple is not observed at these low potentials. Instead these oxidation events must correspond to the iron(II)/iron(III) couple or the formation of organic ligand based radicals. However, the specific assignment of these oxidation processes is ambiguous. The one-electron-oxidized species **3** and **6** are notably EPR silent at room temperature. The fact that ferrocenium EPR signals are usually observable only at liquid helium temperatures[50] coupled with the reversibility of the oxidations suggests that the first oxidation corresponds to the oxidation of the ferrocene moiety. However, UV−vis spectroscopy was used to investigate **2**, **3**, **5**, and **6**, and it indicates that all the compounds have similar absorption spectra (Figures S30−S32). If the first oxidation event corresponded to iron oxidation, the characteristic blue color of ferrocenium would be expected, manifested as an absorption near 600 nm.[51] The lack of this spectral feature for **3** and **6** instead suggests the formation of an organic radical. The formation of phenoxyl radicals upon oxidation of analogous cobalt salen complexes is well known.[46,52] However, no activity was observed between **3** and the common radical traps TEMPO, diphenyl disulfide, and tributyltin hydride (Figures S11−S13).

The redox behavior of **1** was also investigated to ensure that these two remarkably similar cyclic voltammetry profiles are not the result of decomposition, although in neither case was the electrolyte found to decompose the complexes into the free ligand. Furthermore, the CV of the free ligand shows two similar oxidation events; however the first event appears almost 200 mV lower than for the cobalt or zinc complexes (Figure S29). This supports the idea that both of these oxidations are related to the supporting ligand and that these cyclic voltammograms are not the result of decomposition. Furthermore, **1** was investigated by UV−vis spectroscopy before and after an *in situ* oxidation with $[AcFc][BAr^F_4]$, resulting in similar spectra to those of **2**, **3**, **5**, and **6** (Figure S32).

Hydroalkoxylation of Olefins. Inspired by the work of Hiroya and co-workers, compound **2** was investigated for catalytic activity toward the hydroalkoxylation of olefins in the

DOI: 10.1021/acs.organomet.6b00317
Organometallics XXXX, XXX, XXX−XXX

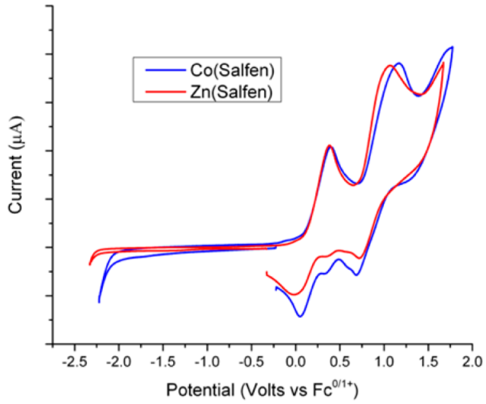
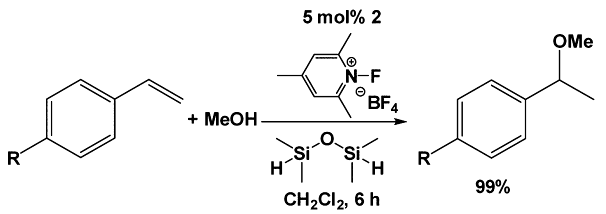


Figure 5. Cyclic voltammograms of Co(salfen), **2**, and Zn(salfen), **5**, recorded in dichloromethane with 0.1 M [^{n}Bu$_4$N][PF$_6$] as the electrolyte. Both CVs are referenced to the Fc/Fc$^+$ couple. The *y* axes of the graphs were normalized to similar dimensions.

presence of a silane and an electrophilic fluorinating agent in trifluorotoluene. With comparable conditions to previous work, the system was shown to be active toward the addition of methanol to 4-methoxystyrene as a model substrate (eq 1), reaching completion in 24 h.



(1)

Optimization of reaction conditions (Table 1) led to the selection of dichloromethane as the optimal solvent, reducing

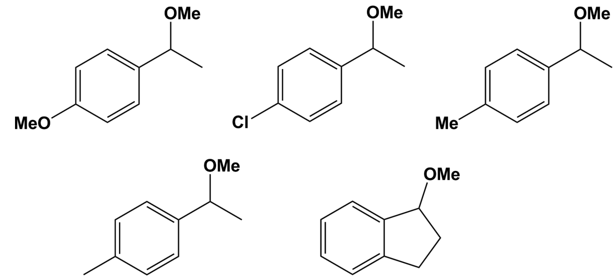
Table 1. Optimization and Control Reactions for the Hydroalkoxylation of 4-Methoxystyrene[a]

entry	silane	fluorinating agent	catalyst	solvent	conv
1	TMDSO	NFPBF$_4$	**2**	$C_6H_5CF_3$	28%
2	TMDSO	NFPBF$_4$	**2**	$C_6H_5CH_3$	14%
3	TMDSO	NFPBF$_4$	**2**	$(CH_2)_4O$	27%
4	TMDSO	NFPBF$_4$	**2**	CH_3OH	56%
5	TMDSO	NFPBF$_4$	**2**	CH_2Cl_2	99%
6		NFPBF$_4$	**2**	CH_2Cl_2	0%
7	TMDSO	NFSI	**2**	CH_2Cl_2	0%
8	TMDSO	NFPBF$_4$		CH_2Cl_2	0%
9	TMDSO	NFPBF$_4$	Et_3N	CH_2Cl_2	0%
10	TMDSO	NFPBF$_4$	**4**	CH_2Cl_2	22%
11	TMDSO	NFPBF$_4$	**5**	CH_2Cl_2	0%

[a]Reaction time of 6 h; conversion determined by ^{1}H NMR integration versus trimethoxybenzene as an internal standard. TMDSO = 1,1,3,3-tetramethyldisiloxane, NFPBF$_4$ = *N*-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate, NFSI = *N*-fluorobenzenedisulfonimide.

reaction times to approximately 6 h. The system demonstrated similar activity toward a variety of styrene derivatives (Chart 1), reaching near-quantitative yields as determined by NMR spectrocopy in a matter of hours. However, little to no activity was observed for a variety of other olefin substrates including alkyl olefins and norbornene derivatives, indicating a need for activated styrene monomers. Various control reactions (Table 1, entries 6–9) were performed in order to confirm that all reagents were necessary for the reaction to proceed. In addition to the standard control experiments (Table 1, entries 6–8), **2** was replaced with an organic base, triethylamine (Table 1, entry 9), as the combination of a silane and halogenation reagent was shown to catalyze intramolecular hydroalkoxylation.[31] Interestingly, the tetrameric cobalt complex, **4**, also showed activity toward hydroalkoxylation, although at a reduced rate compared to the monomeric compound (Table 1, entry 10). When using the zinc complex **5** in place of **2**, no catalytic activity was observed, demonstrating that cobalt is necessary for catalysis rather than just the ferrocene-based ligand or a generic Lewis acid.

Chart 1. Products of the Hydroalkoxylation Reactions



A mechanism for the cobalt salen catalyzed hydroalkoxylation was proposed by Hiroya on the basis of deuterium labeling and radical clock experiments (Scheme S1).[31] The proposed mechanism is consistent with earlier work on cobalt salen catalyzed hydroalkoxylation done by Carreira, in suggesting the formation of a cobalt hydride species capable of undergoing migratory insertion with an olefin substrate.[53] The proposed mechanism notably occurs through a cobalt(III) hydride that would necessitate a five-coordinate metal center. Therefore, we propose that **2** is fluxional in the presence of alcohols, allowing it to adopt a square pyramidal geometry and access the cobalt(III) oxidation state. The formation of the tetrameric species [Co(salfen)]$_4$ (**4**) in the presence of methanol supports this proposal. This rearrangement necessitates a fluxional ligand behavior and is only observed in the presence of methanol; this fact may also explain the complex's activity toward hydroalkoxylation but not toward other types of hydroelementation reactions.

The proposed mechanism notably invokes cobalt(III) intermediates; yet this oxidation state does not appear accessible under cylic voltammetry conditions. Several attempts to generate cobalt(III) complexes were undertaken in order to test this mechanistic proposal. Cobalt(III) salen complexes are typically generated by the aerobic oxidation of the corresponding cobalt(II) complex in the presence of a nucleophile.[54] Such attempts with **2** were unsuccessful, resulting in free ligand due to hydrolysis. Chemical oxidation of **2** in the presence of alkyl phosphines, imidazole, or acetic acid resulted in either a complex mixture of products or free ligand (Figures S14–S16). In contrast to direct oxidation, attempts were also made to generate a cobalt(III) complex by first reducing **2** to cobalt(I) since it is known that cobalt(I) compounds undergo oxidative addition of alkyl halides to generate cobalt(III) alkyl complexes.[55] Reduction with either sodium metal or KC$_8$ afforded a black compound presumed to be a cobalt(I) complex (Figure S17). However, this compound did not undergo any reaction in the presence of alkyl or aryl halides (Figures S18 and S19). Furthermore, a reaction using a

DOI: 10.1021/acs.organomet.6b00317
Organometallics XXXX, XXX, XXX–XXX

cobalt(III) salt, $Na_3[Co(CO_3)_3]$, as a starting material was unsuccessful (Figure S20). These results are expected since cobalt(III) is substitutionally inert[56] and, therefore, rarely used as a starting material. These efforts were further hindered by the insolubility of most simple cobalt(III) salts in common organic solvents.

In addition, cobalt(II) complexes are known to begin cobalt-mediated radical polymerization by generating a cobalt(III) hydride, which can be trapped by olefins.[57] However, heating **2** in the presence of azo-bis-isobutyronitrile and a styrene afforded no reaction (Figure S21), producing neither a cobalt(III) alkyl complex nor a polymeric material. The lack of success in generating a cobalt(III) complex further supports the assignment of the oxidation events described previously as ligand based.

In contrast to **2**, the oxidized compound, **3**, was found to be inactive toward hydroalkoxylation even for styrene substrates. This promising finding coupled with the chemical reversibility of the compound's oxidation and reduction suggested that the cobalt complex could be used as an *in situ* on/off switch. This switch was successfully demonstrated with the hydroalkoxylation of 4-methoxystyrene, beginning with compound **2** (Figure 6). The activity was completely halted upon oxidation

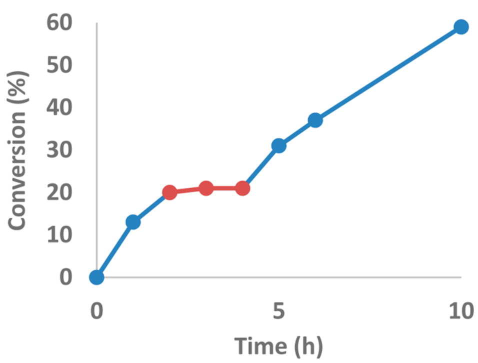


Figure 6. Plot of conversion (as determined by ^{1}H NMR integration versus trimethoxybenzene as an internal standard) versus time of the redox switch for the hydroalkoxylation of 4-methoxystyrene. [AcFc][BAr^F_4] was added after 2 h, and cobaltocene was added after 4 h.

with acetylferrocenium [BAr^F_4]. Subsequent reduction with $CoCp_2$ and the addition of another equivalent of the silane and fluorinating agents nearly restored full activity. If additional silane and fluorinating agent were not added, however, the reaction stalled out sooner. If the two reagents were not added immediately after reduction, they could be added several hours later, when the reaction had stalled, to increase conversion to some degree. Notably, in neither case did the reaction reach the near-quantitative yields observed in the absence of the redox switch. This observation can be attributed to some decomposition of the catalyst or side reactions caused by the *in situ* oxidation and reduction evidenced by the appearance of some unknown ^{1}H NMR signals after the reduction took place (Figure S10).

CONCLUSIONS

Incorporating a ferrocene moiety into the backbone of a cobalt salen, a well-studied class of catalysts, produced a complex with unusual steric, electronic, and electrochemical properties. Co(salfen) exhibits a pseudotetrahedral geometry at the cobalt center, an unusual geometry among salen complexes of any metal and the first crystallographically characterized cobalt example. Magnetic data confirm the presence of three unpaired electrons consistent with a tetrahedral d^7 cobalt(II) species. Furthermore, the compound has two oxidations at potentials low enough to be observed by cyclic voltammetry. Surprisingly, the corresponding zinc complex, which also exhibits a pseudotetrahedral geometry, displays a nearly identical cyclic voltammogram to that of Co(salfen). Accordingly, both of the observed oxidations can be assigned to the supporting ligand. Although the oxidation from cobalt(II) to cobalt(III) is typically easily accessed in square planar cobalt salen complexes, our studies indicate that this process is not facile in the present case. The unique torsional flexibility and redox activity of the ferrocene backbone result in a compound vastly different from previously reported cobalt salen complexes.

Surprisingly, this cobalt complex is able to catalyze the hydroalkoxylation of olefins similar to other cobalt salen complexes, albeit with a much smaller substrate scope. As this reaction was proposed to involve the formation of a cobalt hydride, the complex must exhibit some fluxional behavior in solution to open up a coordination site necessary for the hydride ligand. The possibility of this fluxional behavior is evidenced by the formation of a tetrameric structure in the presence of methanol. Furthermore, oxidation and reduction of the supporting ligand modulates reactivity toward hydroalkoxylation in an on/off manner, where the oxidized compound is inactive.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00317.

NMR spectra and cyclic voltammetry data (PDF)
Crystallographical data (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail (P. L. Diaconescu): pld@chem.ucla.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Mr. Kevin Miller for obtaining single crystals of Co(salfen). This work was supported by NSF, Grant 1362999 to P.L.D. and CHE-1048804 for NMR spectroscopy, and the John Simon Guggenheim Memorial Foundation.

REFERENCES

(1) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368.
(2) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795.
(3) Blanco, V.; Leigh, D. A.; Marcos, V. *Chem. Soc. Rev.* **2015**, *44*, 5341.
(4) Gregson, C. K. A.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; Oxford, P. J.; White, A. J. P. *J. Am. Chem. Soc.* **2006**, *128*, 7410.
(5) Tennyson, A. G.; Lynch, V. M.; Bielawski, C. W. *J. Am. Chem. Soc.* **2010**, *132*, 9420.
(6) Süßner, M.; Plenio, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 6885.
(7) Yoon, H. J.; Kuwabara, J.; Kim, J.-H.; Mirkin, C. A. *Science* **2010**, *330*, 66.

(8) Magenau, A. J. D.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. *Science* **2011**, *332*, 81.
(9) Lorkovic, I. M.; Duff, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 3617.
(10) Allgeier, A. M.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 894.
(11) Abubekerov, M.; Shepard, S. M.; Diaconescu, P. L. *Eur. J. Inorg. Chem.* **2016**, *2016*, 2634.
(12) Wang, X.; Brosmer, J. L.; Thevenon, A.; Diaconescu, P. L. *Organometallics* **2015**, *34*, 4700.
(13) Abubekerov, M.; Diaconescu, P. L. *Inorg. Chem.* **2015**, *54*, 1778.
(14) Wang, X.; Thevenon, A.; Brosmer, J. L.; Yu, I.; Khan, S. I.; Mehrkhodavandi, P.; Diaconescu, P. L. *J. Am. Chem. Soc.* **2014**, *136*, 11264.
(15) Upton, B. M.; Gipson, R. M.; Duhovic, S.; Lydon, B. R.; Matsumoto, N. M.; Maynard, H. D.; Diaconescu, P. L. *Inorg. Chem. Front.* **2014**, *1*, 271.
(16) Broderick, E. M.; Guo, N.; Wu, T.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Cantat, T.; Diaconescu, P. L. *Chem. Commun.* **2011**, *47*, 9897.
(17) Broderick, E. M.; Guo, N.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Mehrkhodavandi, P.; Diaconescu, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 9278.
(18) Biernesser, A. B.; Delle Chiaie, K. R.; Curley, J. B.; Byers, J. A. *Angew. Chem., Int. Ed.* **2016**, *55*, 5251.
(19) Biernesser, A. B.; Li, B.; Byers, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 16553.
(20) Sauer, A.; Buffet, J.-C.; Spaniol, T. P.; Nagae, H.; Mashima, K.; Okuda, J. *ChemCatChem* **2013**, *5*, 1088.
(21) Zhu, Y.; Romain, C.; Williams, C. K. *J. Am. Chem. Soc.* **2015**, *137*, 12179.
(22) Thevenon, A.; Garden, J. A.; White, A. J. P.; Williams, C. K. *Inorg. Chem.* **2015**, *54*, 11906.
(23) Paul, S.; Romain, C.; Shaw, J.; Williams, C. K. *Macromolecules* **2015**, *48*, 6047.
(24) Romain, C.; Williams, C. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 1607.
(25) Neilson, B. M.; Bielawski, C. W. *Chem. Commun.* **2013**, *49*, 5453.
(26) Fors, B. P.; Hawker, C. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 8850.
(27) Paulusse, J. M. J.; Sijbesma, R. P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4460.
(28) Musacchio, A. J.; Nguyen, L. Q.; Beard, G. H.; Knowles, R. R. *J. Am. Chem. Soc.* **2014**, *136*, 12217.
(29) Wilger, D. J.; GrandjeanJean-Marc, M.; Lammert, T. R.; Nicewicz, D. A. *Nat. Chem.* **2014**, *6*, 720.
(30) Shigehisa, H.; Nishi, E.; Fujisawa, M.; Hiroya, K. *Org. Lett.* **2013**, *15*, 5158.
(31) Shigehisa, H.; Aoki, T.; Yamaguchi, S.; Shimizu, N.; Hiroya, K. *J. Am. Chem. Soc.* **2013**, *135*, 10306.
(32) Shigehisa, H.; Koseki, N.; Shimizu, N.; Fujisawa, M.; Niitsu, M.; Hiroya, K. *J. Am. Chem. Soc.* **2014**, *136*, 13534.
(33) Cozzi, P. G. *Chem. Soc. Rev.* **2004**, *33*, 410.
(34) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421.
(35) Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189.
(36) Shafir, A.; Fiedler, D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2002**, 555.
(37) Broderick, E. M.; Diaconescu, P. L. *Inorg. Chem.* **2009**, *48*, 4701.
(38) Quan, S. M.; Diaconescu, P. L. *Chem. Commun.* **2015**, *51*, 9643.
(39) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(40) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(41) Schubert, E. M. *J. Chem. Educ.* **1992**, *69*, 62.
(42) Leung, W.-H.; Chan, E. Y. Y.; Chow, E. K. F.; Williams, I. D.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1996**, 1229.
(43) Räisänen, M. T.; de Almeida, P.; Meinander, K.; Kemell, M.; Mutikainen, I.; Leskelä, M.; Repo, T. *Thin Solid Films* **2008**, *516*, 2948.
(44) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955.
(45) Johnson, C.; Long, B.; Nguyen, J. G.; Day, V. W.; Borovik, A. S.; Subramaniam, B.; Guzman, J. *J. Phys. Chem. C* **2008**, *112*, 12272.
(46) Kochem, A.; Kanso, H.; Baptiste, B.; Arora, H.; Philouze, C.; Jarjayes, O.; Vezin, H.; Luneau, D.; Orio, M.; Thomas, F. *Inorg. Chem.* **2012**, *51*, 10557.
(47) Rhodes, B.; Rowling, S.; Tidswell, P.; Woodward, S.; Brown, S. M. *J. Mol. Catal. A: Chem.* **1997**, *116*, 375.
(48) Clarke, R. M.; Hazin, K.; Thompson, J. R.; Savard, D.; Prosser, K. E.; Storr, T. *Inorg. Chem.* **2016**, *55*, 762.
(49) Abel, E. W.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Šik, V. *J. Organomet. Chem.* **1991**, *403*, 195.
(50) Sixt, T.; Fiedler, J.; Kaim, W. *Inorg. Chem. Commun.* **2000**, *3*, 80.
(51) Xue, G.; De Hont, R.; Münck, E.; Que, L. *Nat. Chem.* **2010**, *2*, 400.
(52) Kurahashi, T.; Fujii, H. *Inorg. Chem.* **2013**, *52*, 3908.
(53) Waser, J.; Carreira, E. M. *J. Am. Chem. Soc.* **2004**, *126*, 5676.
(54) Zhang, Y.-L.; Ruan, W.-J.; Zhao, X.-J.; Wang, H.-G.; Zhu, Z.-A. *Polyhedron* **2003**, *22*, 1535.
(55) Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1.
(56) Chang, C. A.; Huang, C. S.; Tu, C. F. *Anal. Chem.* **1983**, *55*, 1390.
(57) Gridnev, A. A.; Ittel, S. D.; Fryd, M.; Wayland, B. B. *Organometallics* **1993**, *12*, 4871.

DOI: 10.1021/acs.organomet.6b00317
Organometallics XXXX, XXX, XXX−XXX