Supporting Information

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[Supplementary Materials for:]

An Efficient and Exceptionally High Enantio- and Diastereoselective Cyclopropanation of Olefins Catalyzed by Schiff-Base Ruthenium(II) Complexes

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General. GC analyses of cyclopropanation reactions were carried out on Hewlett Packard 5890A and 6890 gas chromatographs equipped with FID detectors. For the determination of the trans:cis ratio of the cyclopropanes, a 30-m HP-5 capillary column with 0.32-mm inner diameter and 0.25-mm film thickness was used. For the determination of enantiomeric excess, Supelco β-DEX series (120 and 225) chiral columns were used. Calibration curves for yield determination were produced using analytically pure samples prepared and characterized by literature methods.1-4 1H, and 13C NMR spectra were recorded on either a Varian Gemini-300 (300.075 and 75.432 MHz for 1H and 13C, respectively) or an Inova-500 FT-NMR (500 and 125.72 MHz for 1H and 13C, respectively) spectrometer. 1H NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), and integration). Chemical shifts for 1H NMR and 13C NMR spectra are reported in ppm downfield from tetramethylsilane (TMS, δ scale) using residual solvent signals in the deuterated solvents as references.

ZINDO calculations of the optimized transition state structure of styrene (following geometry pre-optimization using Augmented MM3) as it approaches the putative (salen)Ru-EDA carbene intermediate was carried out on a Window NT workstation using the CACheWorkSystem Pro Program (V5.02) and INDO/1 parameters.

Chiral 1,2-diaminoalkyl-N,N’-bis(3,5-di-tert-butylsalicylidene) ligands were prepared from the condensation of the corresponding 3,5-di-tert-butylsalicylaldehyde with chiral 1,2-diaminocyclohexane, 1,2-dimino propane, and 1,2-diamino-1,2-diphenylethane. [RuCl2(p-cymene)]2 was prepared by literature method.5 Dichloromethane was distilled over calcium hydride; tetrahydrofuran (THF), toluene, and hexane were distilled over sodium/benzophenone. All solvents were distilled under nitrogen, stored in Strauss flasks, and saturated with nitrogen prior to use. All olefins were purchased from Aldrich Chemical Company, dried over calcium hydride, vacuum distilled, and stored at 0 ºC under nitrogen prior to use. Ethyl diazoacetate was purchased from Aldrich and degassed via three freeze-pump-thaw cycles before used. Deuterated solvents were purchased from Cambridge Isotope Laboratories, distilled over calcium hydride, and vacuum transferred into an air-tight solvent bulb prior to transfer into the inert-atmosphere glovebox. All other reagents were purchased from Aldrich Chemical Company and used without further purification unless otherwise noted. All reactions were carried out either under a dry nitrogen atmosphere using standard Schlenk techniques or in an inert-atmosphere glovebox unless otherwise noted.

General Procedure for the Synthesis of (1,2-diamino-N,N’-bis(3,5-di-tert-butylsalicylidene))dipyridylruthenium(II). A THF (15 mL) solution of (Salen)H2, (738 mg, 1.5 mmol) was treated with LDA (2 mL of a 1.5-M solution of the monotetrahydrofuran complex in cyclohexane, 3.0 mmol) at 0 ºC. After the addition was completed, the solution was allowed to warm up to room temperature and stirred for 1 h. This mixture was then added dropwise to a solution of [RuCl2(p-cymene)]2 (460 mg, 0.75 mmol) and pyridine (1 mL) in THF (15 mL) at 0 ºC. The reaction mixture was allowed to stir overnight, resulting in a dark red solution, which was subsequently evaporated in vacuo. The residue was extracted into toluene (30 mL), filtered via cannula, and
evaporated under reduced pressure. Hexanes (20 mL) was then added to the residue to precipitate a dark red solid which was filtered via cannula and isolated. Further recrystallization using a toluene/hexanes mixture affords analytically pure compounds.

\[ ((R,R)-1,2-Cyclohexanediarnino-N,N'-bis(3,5-di-tert-butylsalicylidene))dipyridylruthenium(II) \] (1-(R,R)): Yield: 74%. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \( \delta \) 0.57 (m, 2H, cyclohexyl), 0.85 (m, 2H, cyclohexyl), 1.29 (m, 2H, cyclohexyl), 1.45 (s, 18H, \( \text{^3} \)Bu), 1.75 (s, 18H, \( \text{^3} \)Bu), 2.13 (m, 2H, cyclohexyl), 2.39 (m, 2H, backbone), 6.07 (m, 4H, \( \text{p} \)-pyridine), 6.44 (m, 2H, \( \text{p} \)-pyridine), 7.41 (d, 2H, aromatics, \( J = 2.6 \) Hz), 7.77 (d, 2H, aromatics, \( J = 2.6 \) Hz), 8.40 (m, 4H, \( \text{o} \)-pyridine), 8.51 (s, 2H, HC=N). MS (EI\(^+\)): m/z 804.4 (Calcd. for M\(^{+}\) = 804.4).

\[ ((R,R)-1,2-Cyclohexanediarnino-N,N'-bis(3-tert-butyl-5-methylsalicylidene))dipyridylruthenium(II) \] (1-(R,R)): Yield: 61%. \(^1\)H NMR (CD\(_2\)Cl\(_2\)): \( \delta \) 0.61 (m, 2H, cyclohexyl), 0.88 (m, 2H, cyclohexyl), 1.32 (m, 2H, cyclohexyl), 1.73 (s, 18H, \( \text{^3} \)Bu), 2.16 (m, 2H, cyclohexyl), 2.39 (m, 2H, backbone), 2.45 (s, 6H, CH\(_3\)), 6.28 (m, 4H, \( \text{m} \)-pyridine), 6.56 (m, 2H, \( \text{p} \)-pyridine), 7.16 (d, 2H, aromatics, \( J = 2.4 \) Hz), 7.48 (d, 2H, aromatics, \( J = 2.4 \) Hz), 8.41 (m, 2H, HC=N), 8.44 (m, 4H, \( \text{o} \)-pyridine). Anal.: Calcd. for C\(_{38}\)H\(_{46}\)N\(_4\)O\(_2\)Ru: C, 66.73; H, 7.0; N, 7.78; Found: C, 66.57; H, 7.18; N, 7.59. MS (EI\(^+\)): m/z 720.3 (Calcd. for M\(^{+}\) = 720.3).

\[ ((S,S)-1,2-Cyclohexanediarnino-N,N'-bis(3-tert-butylsalicylidene))dipyridylruthenium(II) \] (1-(S,S)): Yield: 65%.

\[ ((S,S)-1,2-Cyclohexanediarnino-N,N'-bis(3-tert-butyl-5-methylsalicylidene))dipyridylruthenium(II) \] (1-(S,S)): Yield: 62%.

\[ ((S,S)-1,2-Cyclohexanediarnino-N,N'-bis(3-tert-butylsalicylidene))dipyridylruthenium(II) \] (1-(S,S)): Yield: 32%.

General Procedure for the Asymmetric Cyclopropanation of Styrene with Ethyl Diazooacetate Using Chiral Ruthenium(II) Salen Complexes. A mixture of a chiral ruthenium catalyst (0.005 mmol) and olefin (2.5 mmol) in CH\(_2\)Cl\(_2\) (1 mL) was placed in a 25-mL round-bottom flask under N\(_2\) in a glovebox. A three-times degassed CH\(_2\)Cl\(_2\) (2.5 mL) solution of ethyldiazoacetate (0.50 mmol) and internal standard (0.50 mmol) was slowly added via gas-tight syringe over a period of 23 min under N\(_2\). After the addition was complete the reaction mixture was allowed to stir for 12 h at room temperature.
The solution was then passed through a short plug of silica gel to remove catalyst and washed with CH₂Cl₂ (15 mL). Samples were then analyzed via non-chiral GC with the following method: initial temp = 50 °C, rate = 10 °C/min, final temp = 250 °C, final time = 10 min. GC traces and methods developed for chiral GC analysis follow:

2-Phenyl-cyclopropanecarboxylic acid ethyl ester:

\[ (S,R) \quad (R,S) \]
\[ 50.392 \quad 51.416 \]
\[ 55.969 \quad 55.939 \]
\[ (R,R) \quad (S,S) \]

Cis isomer: Column = β-Dex 120. Head pressure = 20 psi. Temp program: initial temp = 100 °C, initial time = 0.0 min, rate = 0.5 °C/min, final temp = 140 °C, final time = 0.0 min.

Trans isomer: Column = β-Dex 225. Head pressure: 23 psi. Temp program: same as cis isomer.

1-Methyl-cyclopropane-1,2-dicarboxylic acid 2-ethyl ester 1-methyl ester:

\[ (R,R) \quad (S,S) \]

Cis isomer: Column = β-Dex 225. Head pressure = 23 psi. Temp program = 70 °C isothermal for 100 min.
2-Propenyl-cyclopropanecarboxylic acid ethyl ester:

*Cis* and *Trans* isomers: Column = \( \beta \)-Dex 225. Head pressure = 23 psi. Temp program: initial temp = 70 °C, initial time = 0.0 min, rate = 1.0 °C/min, final temp = 140 °C, final time = 0.0 min.

2-Cyano-cyclopropanecarboxylic acid ethyl ester:

*Cis* isomer: Column: \( \beta \)-Dex 225. Head pressure = 23 psi. Temp program: initial temp = 130 °C, initial time = 10.0 min, rate = 10 °C/min, final temp = 170 °C, final time = 10.0 min.

*Trans* isomer: Column: \( \beta \)-Dex 120. Head pressure = 21 psi. Temp program: initial temp = 100 °C, initial time = 20.0 min, rate = 20 °C/min, final temp = 200 °C, final time = 0.0 min.
2-Ethoxy-cyclopropanecarboxylic acid ethyl ester:

Cis and trans isomers: Column: β-Dex 225. Head pressure = 23 psi. Temp program: initial temp = 80 °C, initial time = 17.0 min, rate = 30 °C/min, final temp = 170 °C, final time = 5.0 min.

2-Propyl-cyclopropanecarboxylic acid ethyl ester:

Cis and trans isomers: Column: β-Dex 225. Head pressure = 23 psi. Temp program: initial temp = 50 °C, initial time = 65 min, rate = 30 °C/min, final temp = 170 °C, final time = 10 min.
A ZINDO-optimized model structure of styrene as it approaches the putative (salen)Ru-EDA carbene intermediate. Left: a ball-and-stick model of this structure without a trans axial ligand. Right: a ball-and-stick model of this structure with pyridine as the additional trans axial ligand. Bottom: a top-view space-filling model showing an optimal fit.

References