Synthetic and Structural Studies of Novel 1, 10-Phenanthroline Derivatives

EunJoo Kim

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SYNTHETIC AND STRUCTURAL STUDIES OF NOVEL
1, 10-PHENANTHROLINE DERIVATIVES

by

EunJoo Kim

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Master of Science
Department of Chemistry

Western Michigan University
Kalamazoo, Michigan
April 2005
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2005
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EunJoo Kim
SYNTHETIC AND STRUCTURAL STUDIES OF NOVEL 1, 10-PHENANTHROLINE DERIVATIVES

EunJoo Kim, M.S.
Western Michigan University, 2005

Asymmetric catalysis can provide a general approach to the preparation of enantiomerically enriched compounds in organic synthesis. Very often these asymmetric catalysts consist of a chiral ligand-metal complex. Because of the growing demand to develop enantioselective reactions in organic chemistry one focus of this area of research is the design and characterization of new chiral ligands for asymmetric synthesis.

The focus of my research is in the design, synthesis, and characterization of novel 1, 10-phenanthroline derivatives that could be used as chiral ligands in enantioselective reactions. Central to these studies have been the effect of substituents on the B-ring of 1, 10-phenanthroline. The derivatives were prepared from epoxide via ring opening with various nucleophiles. These fully characterized new compounds were then examined for their ability to coordinate a diverse set of transition metals in order to explore their potential as asymmetric catalysts.
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INTRODUCTION

Importance of Asymmetric Catalysis

The preparation of enantiomERICALLY pure compounds is an important and challenging area of organic synthesis. There are abundant, well-documented cases that highlight the necessity for the preparation of enantiopure compounds. The importance of enantiomERICALLY pure compounds arises from the central role of enantiomer recognition in biological activity.\(^1\) Chiral molecules can exist as pairs of stereoisomers, e. g. enantiomers, like a pair of hands, where one form is left-handed, the other right-handed. These two isomers are structurally identical and have the same physical properties, but are different only in their three-dimensional spatial arrangement. They are non-superimposable mirror images, have no planes of symmetry, and are described as (R) and (S) forms.\(^2\)

Chirality plays a major role in the development of new pharmaceuticals. According to McCarthy and Guitry,\(^3\) two thirds of the 1200 drugs in 1996 were chiral and 51% were being developed as single enantiomer drugs; the rest are sold as racemates. In 1988, the Food and Drug Administration (FDA) required that any company wishing to license a racemic mixture as an active ingredient needed to establish the activity of both
enantiomers and prove that the unwanted isomer does not have side effects.\textsuperscript{3} Well-known painkillers and anti-inflammatory agents such as Advil, Nuprin, Motrin, and Ibuprofen are sold as racemic mixtures of (R) and (S) isomers, even though one of them may be inactive. For example, the inactive (R) enantiomer of Ibuprofen (1, Fig. 1) slows the rate at which the (S) enantiomer takes effect in the body from 12 minutes to 38 minutes.\textsuperscript{2}

Another racemic drug Thalidomide (2, Fig. 1) was first introduced in the 1950s to treat pregnant women for their morning sickness. However, the medication was found to be the cause of severe birth defects in children whose mothers had taken the drug in their first trimester of pregnancy. Laboratory tests in animals showed that the (R) isomer was an effective sedative while the mirror image was teratogenic.\textsuperscript{4} These examples illustrate that it is extremely important to study asymmetric synthesis for the preparation of only desired stereoisomers and to prevent undesirable effects from other forms.

![Figure 1, Examples of Biologically Active Stereoisomers.](image-url)
McCarthy et al. discussed three methods to obtain pure enantiomers, (1) synthesis from the “chiral pool”, (2) resolution of a racemic mixture, and (3) asymmetric synthesis. The latter comprises asymmetric catalysis with the advantage of using small amounts of enantiomerically pure catalyst, capable of producing large amounts of single stereoisomers.

Asymmetric catalysis converts an achiral substrate (S) to enantiomerically pure or enriched chiral product (P*) in the presence of a chiral catalyst, such as a metal-ligand complex (ML*, Fig. 2). The catalytic activity of the latter originates from the metal and the asymmetry of the metal–catalyzed process is almost always induced by the “organic ligand”, favoring a specific stereoisomer. Ligands can control the binding site of reactants, and the subsequent reaction pathways depend on steric and electronic interactions between S and ML*. The design and synthesis of suitable chiral catalytic compounds is a key goal in the field of asymmetric catalysis and a number of very efficient chiral
catalysts have been developed.\textsuperscript{4-7} Among the tremendous number of reported ligands for chiral catalysis, those possessing central chirality,\textsuperscript{8} axial chirality\textsuperscript{9} and planar chirality\textsuperscript{10,11} play a central role.

**Metal - Catalyzed Asymmetric Catalysis**

Palladium-catalyzed allylic substitution reactions are well developed and have been widely applied in synthetic organic chemistry. The reaction proceeds generally via an (\(\eta^3\)-allyl)-palladium complex (4 or 5), which reacts with the nucleophile to give an alkene, as outlined in Scheme 1.\textsuperscript{12}

![Scheme 1, (\(\eta^3\)-Allyl) - Palladium Complex System.](image-url)
The product will be determined by the stereochemistry of the \( \eta^3 \)-allyl complex (syn or anti) and the regiochemistry of the nucleophilic attack. Therefore, nucleophilic addition to the unsubstituted terminus of a syn complex will produce an \((E)\)-alkene (6), and addition to the corresponding anti complex will give a \((Z)\)-alkene (8). Thus, it is possible to prepare \((E)\) or \((Z)\) products by providing suitable ligands that favor a syn or anti \( \eta^3 \)-allyl complex.

A similar mechanism is involved in asymmetric allylic alkylation reactions that can produce enantiomerically pure or enriched isomers.\(^3\)\(^6\) The stereochemistry of the product is determined by the nature of the nucleophiles and the enantio-discrimination ability of the ligand. For the generic example below (Scheme 2), there are two possible pathways that involve different diastereomeric intermediate complexes at different energies, \( \Delta G_B^\dagger \) and \( \Delta G_C^\dagger \) (Fig. 3).

![Scheme 2, Mechanism of Asymmetric Reaction.](image)
The relative rates of formation of each product determine the stereoselectivity, and the product ratio \( \frac{C}{B} \) is given by in Equation 1, where \( k_1 \) and \( k_2 \) are the rate constants for the formations of \( B \) and \( C \), respectively.

\[
\frac{(C)}{(B)} = \frac{k_1}{k_2} = e^{-\Delta G^\ddagger / RT}
\]

Equation 1, The Ratio of Formation of the Products B and C.

\( \Delta \Delta G^\ddagger \) is the difference in the energies of the intermediates for each process, where \( \Delta G_B^\ddagger \) and \( \Delta G_C^\ddagger \) are the free energies for each intermediate in the formation of B and C, respectively.

\[
\Delta \Delta G^\ddagger = \Delta G_B^\ddagger - \Delta G_C^\ddagger
\]

Equation 2, Free Energy Difference between Two Possible Diastereomers.
When the \( k_1/k_2 \) ratio is smaller than 1, product \( \text{B} \) will be favored. However, if it is greater than 1, product \( \text{C} \) will be formed predominately. In other words, whichever intermediate has the smaller \( \Delta G^\ddagger \) will become the major or exclusive stereoisomer. One example is depicted below (Scheme 3) and utilizes a stereodiscriminating phosphinenoxxazoline (71 % ee).

![Scheme 3, 1,3-Dialkylally Asymmetric Alkylation.](image)

Nitrogen Ligands versus Phosphorus Ligands

Chiral phosphines have been widely used in catalytic reactions while nitrogen ligands were long neglected. Recently, Chelucci and Thummel discussed that nitrogen ligands have distinct advantages over phosphines (Fig. 4). First, they are efficient where phosphine may be incompatible with reaction conditions. Second, various nitrogen-containing ligands are now available in enantiomerically pure forms, derived from the "chiral pool" or as cheap industrial intermediates. Third, the production of chiral amines
by resolution of racemates is very easy and the methodology of enantiomer separation is well documented. In addition, nitrogen ligands can bind to a wide variety of transition metals (Rh, Ru, Cu, Ni, Co, Pd, Pt, etc), and many studies address the roles of these ligands in catalytic processes.

Figure 4, Phosphine and Nitrogen Containing Ligands.

1,10-Phenanthroline

The most important and popular nitrogen-containing ligands are those related to pyridine, 2,2'-bipyridine (bpy), 2,2':6',2''-terpyridines (tpy) and 1,10-phenanthroline (phen). 1,10-Phenanthroline is the parent structure of an important class of chelating agents. In contrast to the 2,2'-bipyridyl system, 1,10-phenanthroline (12) has a more rigid structure imposed by the central B-ring. The two nitrogen atoms are always held in juxtaposition, whereas in 2,2'-bipyridine (11) free rotation about the linking bond allows the two nitrogens to separate, in particular under basic or strongly acidic conditions. In
fact, due to the electron repulsion the transoid structure is favored (Fig. 5).\textsuperscript{15} This advantage for 1,10-phenanthroline means that complexes with metal ions can form more rapidly, a property of importance, as discussed by Sammes \textit{et al.}\textsuperscript{16}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig5.png}
\caption{Two Nitrogen Containing Ligands.}
\end{figure}

The chelating ability of 1,10-phenanthrolines has been applied in asymmetric catalysis as illustrated by Chelucci and co-workers who evaluated 5,6-dihydro-1,10-phenanthroline (13) and 1,10-phenanthroline 14 (Scheme 4). The corresponding copper complexes of 13 and 14 catalyzed allylic alkylation reactions of styrene.\textsuperscript{17, 18} The stereoselectivity of these transformations was greatly dependent on the nature of the R-group. Although the yields of the product, a cyclopropane were not affected by the size of complexes, there was a modest increase in enantioselectivity with more bulky substituents.
Research Objectives

In the long term we are interested in determining the utility of 1,10-phenanthroline-based ligands in metal-catalyzed asymmetric reactions. Our immediate goals are to synthesize new phenanthroline derivatives and study their physical properties, including their coordination with metals.

Chelucci et al.\textsuperscript{18} discussed that in 5,6-dihydro-1,10-phenanthrolines the 3,3'-bridge can control the relative orientation of the two rings and, thus, influence the shape of the chelating bite-angle (N-C-C-N dihedral angle, Fig. 6).
Our strategy utilizes the 1,10-phenanthroline framework, where two substituents (X, Y) attached in the B-ring generate stereogenic centers (Scheme 5). Such structural modifications affect the hybridization in the 5- and 6-positions, which change from $sp^2$ to $sp^3$. X and Y subsequently influence the conformational preference and the helicity of 1,10-phenanthroline. The new chiral 5,6-disubstituted 1,10-phenanthroline derivatives will be coordinated to various transition metals and examined as potential catalysts.

Scheme 5, Overall Scheme
RESULTS AND DISCUSSION

To achieve the B-ring functionalization of 1,10-phenanthroline (1), we oxidized the C5 and C6 positions to the corresponding epoxide (2, Scheme 6). This key intermediate was reacted with several nucleophiles (HNBn₂, HNPh₂, H₂NPh) in the presence of a Lewis acid. Subsequently the amino alcohols were protected as their benzyl ether and coordinated with different transition metals to study their chelating properties.

![Scheme 6, Overall Reaction.](image)

Epoxidation

Epoxides are often used as starting materials and intermediates in organic synthesis because of their ease of formation and wide reactivity with nucleophilies. 1,10-
Phenanthroline monohydrate was epoxidized with bleach under biphasic conditions using tetrabutyl ammonium hydrogen sulfate as phase transfer catalyst (PTC, Scheme 7). \(^\text{19, 20}\)

\[
\begin{array}{c}
\text{(1)} \\
\begin{array}{c}
\begin{array}{c}
\text{Phenanthroline monohydrate} \\
\text{NaOCl} \\
0.5 \text{ eq. } n-\text{Bu}_4\text{NHSO}_4 \\
\text{CHCl}_3 \text{ r.t. } 30 \text{ min}
\end{array}
\end{array}
\end{array}
\rightarrow
\begin{array}{c}
\text{(2)} \\
\begin{array}{c}
\text{Epoxide}
\end{array}
\end{array}
\end{array}
\]

Scheme 7, Epoxidation.

Tetrabutyl ammonium hydrogen sulfate was employed to transport the anion \(\text{OC}l^-\) from the aqueous phase into the chloroform layer where oxidation occurs (Scheme 8). \(^\text{21}\)

This procedure employed household bleach and is a convenient, simple, and cheap method for preparing relatively large quantities of epoxide 2.

\[
\begin{array}{c}
(n-C_4H_9)_4N^+\text{HSO}_4 + \text{Na}^+\text{OC}l^- \\
\rightarrow \\
(n-C_4H_9)_4N^+\text{OC}l^- + \text{Na}^+\text{HSO}_4
\end{array}
\]

Scheme 8, Tetrabutyl Ammonium Hydrogen Sulfate as Phase Transfer Catalyst.

The B-ring double bond between carbon 5 and 6 is the most reactive site\(^\text{22}\) and adds Cl\(^+\), as outlined by Antkowiak \textit{et al.}\(^\text{23}\) The corresponding chloronium intermediate 6 is attacked by water to form the chlorohydrine 7. Intramolecular nucleophilic attack of the alcohol on the alkyl halide produces the protonated epoxide 8 that loses a proton to
yield the desired epoxide 2.

Scheme 9, Mechanism of Epoxidation.

As the significance of pH was pointed out in two reports,\textsuperscript{23,24} it is important that the pH of the aqueous hypochlorite was adjusted to 8.6 in order to obtain good yields of the epoxide. At higher pH (above 10) very little epoxidation occurs. The 5,6-dichloro-5,6-dihydro-1,10-phenanthroline (9) was always found at pHs lower than 8.6. Below pH 7 the oxidation products such as 5,5-dichloro-6-oxo-5,6-dihydro-1,10-phenanthroline (10) and 5,6-dioxo-5,6-dihydro-1,10-phenanthroline (11) formed, which were identified by Antkowiak et al. (Scheme 9).\textsuperscript{23}
The same authors observed comparable yields in methylene chloride and chloroform\textsuperscript{23} However, reactions in ethyl acetate or diethyl ether proceeded more slowly. In the absence of phase transfer catalyst, no epoxide was formed while higher concentration led to more rapid product formation\textsuperscript{24}.

Using the reaction condition described in Scheme 7, we prepared the desired epoxide at pH 8.6 in 45 - 70 \% yields after recrystallization. Typically we did not observe any of the side products shown in Scheme 10. However, epoxide purification became more tedious in the presence of additional PTC (1.0 eq.). The oxidation needed to be carefully monitored because longer reaction times promoted side product formation while
shorter times led to recovered starting material, which was difficult to separate.

Ring Opening with Nucleophiles

Epoxide (2) served as a key intermediate and was opened with various nucleophiles, affording the corresponding amino alcohols (3). The preparation is straightforward and we prepared several new 1,10-phenanthroline derivatives by using HNBN₂ for the nucleophilic opening of epoxide 2. 1,10-Phenanthroline-5,6-epoxide and was refluxed in acetonitrile with nucleophilic amines in the presence of a Lewis acid catalyst, such as Mg(ClO₄)₂ or Mg(OTf)₂; the results are shown in Scheme 11. Previous studies in our laboratory have shown that the Mg(ClO₄)₂ procedure is an improvement over epoxide opening in the presence of alumina.²⁵

![Scheme 11, Ring Opening of 1,10-Phenanthroline Epoxide.](image)

To prepare trans-6-aniline-5,6-dihydro-1,10-phenanthrolin-5-ol, 1,10-
phenanthroline-5,6-epoxide was reacted with aniline in acetonitrile at reflux in the
presence of 0.5 eq. Mg(OTf)$_2$ as Lewis acid for 52 - 71 hours and the desired product was
obtained with moderate to good yield (55 - 64 %) after purification. The same
methodology was applied to obtain trans-6-dibenzylamino-5,6-dihydro-1,10-
phenanthroline-5-ol in 55 - 92 % yields.

The formation of the Lewis acid - Lewis base complex between the oxirane
oxygen atom and magnesium activates the epoxide for ring opening by the nucleophilic
amine. Due to the symmetric structure of epoxide 2, the overall reaction sequence led to
the formation of racemic products (3).

We also attempted to use diphenylamine as a nucleophile, and tried various
catalysts (BF$_3$·THF, BF$_3$ in MeOH, Mg(ClO$_4$)$_2$, Mg(OTf)$_2$), and solvents (CH$_3$CN,
CH$_2$Cl$_2$, THF). Even though some reactions produced what appeared to be product, the
result could not easily be reproduced. Therefore, additional studies are necessary.

Chini and co-workers described the catalytic activity of metal salts such as LiClO$_4$,
NaClO$_4$, Mg(ClO$_4$)$_2$, LiBF$_4$ and CaCl$_2$ on the aminolysis of various epoxides.$^{26}$ Metal
triflates have also been used to catalyze the opening of epoxides with amines,\textsuperscript{27-30} however, to the best of our knowledge, Mg(OTf)_2 has not been reported for epoxide openings with aromatic amines. Herein we wish to report the efficiency and compatibility of Mg(ClO_4)_2 and Mg(OTf)_2 as catalysts for the reaction of 1,10-phenanthroline epoxide (2) with dibenzylamine.

Our method was developed by stirring 1.0 eq. of 1,10-phenanthroline-5,6-epoxide and 1.2 eq. of dibenzylamine in acetonitrile as solvent in the presence of different equivalents of Lewis acid at reflux (Scheme 12, Table 1).

Although all reactions were monitored by TLC, reactions in entries 1 - 8, using Mg(ClO_4)_2 showed starting material even after 43 - 72 hours. Therefore, to purify and isolate the target compound, it was necessary to perform silica gel chromatography. On the other hand, reactions in entries 9 - 16, using Mg(OTf)_2 showed complete conversion to product, and the crude reaction mixtures were purified by recrystallization from CHCl_3.
and hexane.

Table 1, Comparison of Mg(ClO₄)₂ and Mg(OTf)₂.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Lewis Acid</th>
<th>Equivalence</th>
<th>Reaction Time (h)a</th>
<th>Isolated Yield (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg(ClO₄)₂</td>
<td>0.5 eq.</td>
<td>53</td>
<td>59</td>
</tr>
<tr>
<td>2</td>
<td>Mg(ClO₄)₂</td>
<td>0.5 eq.</td>
<td>72.0</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>Mg(ClO₄)₂</td>
<td>1.0 eq.</td>
<td>42.5</td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>Mg(ClO₄)₂</td>
<td>1.0 eq.</td>
<td>51</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>Mg(ClO₄)₂</td>
<td>1.2 eq.</td>
<td>42.5</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>Mg(ClO₄)₂</td>
<td>1.2 eq.</td>
<td>59</td>
<td>83</td>
</tr>
<tr>
<td>7</td>
<td>Mg(ClO₄)₂</td>
<td>1.5 eq.</td>
<td>48.5</td>
<td>62</td>
</tr>
<tr>
<td>8</td>
<td>Mg(ClO₄)₂</td>
<td>1.5 eq.</td>
<td>54</td>
<td>66</td>
</tr>
<tr>
<td>9</td>
<td>Mg(OTf)₂</td>
<td>0.5 eq.</td>
<td>48.5</td>
<td>70</td>
</tr>
<tr>
<td>10</td>
<td>Mg(OTf)₂</td>
<td>0.5 eq.</td>
<td>49</td>
<td>85</td>
</tr>
<tr>
<td>11</td>
<td>Mg(OTf)₂</td>
<td>1.0 eq.</td>
<td>48.5</td>
<td>92</td>
</tr>
<tr>
<td>12</td>
<td>Mg(OTf)₂</td>
<td>1.0 eq.</td>
<td>66</td>
<td>85</td>
</tr>
<tr>
<td>13</td>
<td>Mg(OTf)₂</td>
<td>1.2 eq.</td>
<td>48.5</td>
<td>73</td>
</tr>
<tr>
<td>14</td>
<td>Mg(OTf)₂</td>
<td>1.2 eq.</td>
<td>65</td>
<td>89</td>
</tr>
<tr>
<td>15</td>
<td>Mg(OTf)₂</td>
<td>1.5 eq.</td>
<td>50.0</td>
<td>74</td>
</tr>
<tr>
<td>16</td>
<td>Mg(OTf)₂</td>
<td>1.5 eq.</td>
<td>65</td>
<td>74</td>
</tr>
</tbody>
</table>

a Reaction was monitored by alumina TLC, using CHCl₃/3% MeOH as eluant.

b Isolated yields after chromatography or recrystallization.
When using Mg(OTf)$_2$ as the Lewis acid, two factors may contribute to shorter reaction times and complete conversions. First, Mg(OTf)$_2$ produces a homogeneous reaction mixture in acetonitrile when compared to Mg(ClO$_4$)$_2$, which does not completely dissolve. Second, the lower solubility of Mg(ClO$_4$)$_2$ might account for both the longer reaction times and reduced yields. In addition, the triflate ligand would dissociate more readily from the metal center in comparison to the perchlorate ligands, making a greater contribution to reactivity, especially in a homogeneous reaction mixture. Third, the use of Mg(OTf)$_2$ is safer. Perchlorates are potentially explosive and thus dangerous in the presence of combustible substances at high temperature.

Benzylation

Due to the reactivity of the hydroxyl group in trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol (3), we protected it as benzyl ether to prevent side reactions. 

_trans-5-Benzylxyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline_ was prepared by modifying a literature procedure (Scheme 13).$^{31,32}$ The benzylation of alcohol 3 was accomplished with sodium hydride and benzyl bromide in anhydrous CH$_2$Cl$_2$ at reflux under an argon atmosphere. After purification, the desired product was obtained in
moderate to good yield (45 - 86 %).

Scheme 13, Benzylation

The conversion to the desired product was confirmed by NMR and IR spectroscopy. After the alcohol was protected as the benzyl ether, the –OH stretching absorption at 3300 - 3200 cm$^{-1}$ was no longer observed in the IR spectrum.

Figure 7, IR Spectrum of trans-6-Dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol (3) and trans-5-Benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline (4).

Acetylation

We also protected alcohol 3 as its acetate ester. Routinely acetylation is carried
out with acetic anhydride or acetyl chloride in the presence of tertiary amines, such as Et$_3$N or pyridine. Lewis acids such as CoCl$_2$, Me$_3$SiOTf$^{34}$ and Mg(ClO$_4$)$_2$$^{35}$ catalyze this reaction.

*trans*-5-Dibenzylamino-5,6-dihydro-1,10-phenanthroline-6-yl acetate (12) is a new derivative and was prepared by using a solvent-free procedure.$^{35}$ Alcohol 3 was reacted with acetic anhydride in the presence of Mg(ClO$_4$)$_2$ (Scheme 14), although it was necessary to increase the amount of Ac$_2$O (2.0 eq.) to enhance the solubility of Mg(ClO$_4$)$_2$. The desired product was isolated in 54 % yield, after silica gel chromatography.

![Scheme 14, Acetylation.](image)

Substitution of 2,9-Diphenyl-1,10-Phenanthroline

Pena-Cabrera *et al.* have described the special role of C2 and C9 substituents on 1,10-phenanthroline in controlling the stereochemistry of $\eta^3$-allylpalladium complexes.$^{36}$
Disubstituted 1,10-phenanthroline ligands showed an altered syn / anti-stereoselectivity and reactivity of the allyl complex (Scheme 15). This difference may depend on steric interactions between the 1,10-phenanthroline ligand and the allyl fragment (Table 2).\textsuperscript{12}

\begin{equation}
\begin{array}{c}
\text{R=OAc} \\
\text{Pd, L R} \quad \text{\textsuperscript{anti} R}\quad \text{\textsuperscript{syn} R} \\
\text{Nu} \\
\text{Nu} \quad \text{Nu} \\
\text{(E)} \\
\text{(Z)}
\end{array}
\end{equation}

Scheme 15, Palladium Complexes Reactivity.\textsuperscript{36}

Table 2, \textit{anti} / \textit{syn} Ratio for (\eta\textsuperscript{3}-2-Butenyl)-Palladium Tetrafluoroborate Complexes Equilibrated in Dichloromethane.\textsuperscript{12}

<table>
<thead>
<tr>
<th>Entry</th>
<th>\textsuperscript{L} \textsuperscript{L} =</th>
<th>\text{Ratio of anti / syn}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>1 : 9</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>7 : 3</td>
</tr>
<tr>
<td>3</td>
<td>Ph</td>
<td>4 : 6</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>7 : 3</td>
</tr>
</tbody>
</table>

Because substitution in the 2- and 9- position can affect catalytic reactivity, we prepared additional 1,10-phenanthroline derivatives such as 2,9-diphenyl-1,10-phenanthroline, using a modified literature procedure.\textsuperscript{37-40} Under an argon atmosphere, a
PhLi solution was added to anhydrous 1,10-phenanthroline in toluene and THF. The resulting dark red mixture was hydrolyzed with water and re-aromatized with MnO₂ (Scheme 16). After purification, 2,9-diphenyl-1,10-phenanthroline (12) was isolated in good yield (67 %, lit. 70 %³⁷).

![Scheme 16, Preparation of Diphenyl-1,10-Phenanthroline.³⁷](image)

To introduce B-ring chirality, the key intermediate 2,9-diphenyl-1,10-phenanthroline-5,6-epoxide (14) was prepared. Epoxidation was done analogous to the procedure for unsubstituted 1,10-phenanthroline (Scheme 17). However, longer reaction times were necessary (1hr). This may be due to the fact that phenyl substituents on C2 and C9 deactivate the B-ring of 1,10-phenanthroline through electron delocalization.

![Scheme 17, Epoxidation of 2,9-Diphenyl-1,10-Phenanthroline.](image)

After obtaining epoxide 14, we prepared the corresponding trans-amino alcohol.
15. The methodology used for the aminolysis of unsubstituted 1,10-phenanthroline was applied as described before (Scheme 18). Mg(OTf)$_2$ was employed as a catalyst and 2,9-diphenyl-1,10-phenanthroline-5,6-epoxide and HNBn$_2$ were reacted at reflux to obtain trans-6-dibenzyl-2,9-diphenyl-5,6-dihydro-1,10-phenanthroline-5-ol (15). After purification, the desired product was obtained in 16% yield and characterized by $^1$H NMR. Additional characterization is ongoing.

![Scheme 18, Ring Opening of 2,9-Diphenyl-1,10-Phenanthroline Epoxide.](image)

Metal Complexes of 5,6-Disubstituted 1,10-Phenanthroline

The synthetic utility of transition metal-catalyzed reactions in asymmetric syntheses has been soundly demonstrated since they were introduced three decades ago. Transition metal-catalyzed reactions have played an important role, especially in asymmetric catalysis. For example, enantioselective transition metal-catalyzed reactions
can involve transfer of oxygen (epoxidation and dihydroxylation) or molecular hydrogen or the formation of carbon-carbon as well as carbon-heteroatom bonds.$^4$-$^7$ These reactions have been reported with a broad range of metals such as copper, nickel, cobalt, palladium, platinum, rhodium, ruthenium, zinc, tungsten, etc. The differences between the diverse metals employed in the reaction lie in regioselectivity and reactivity toward the different types of substrates and nucleophiles.$^{41}$

The rich coordination chemistry of 1,10-phenanthroline has encouraged the synthesis of new ligand structures that serve as electron donors when chelated to an appropriate metal.$^{42}$ We prepared a variety of new complexes with chiral 1,10-phenanthroline derivatives (Scheme 19) and focused on diamagnetic metal complexes so that they could be characterized by $^1$H and $^{13}$C NMR spectroscopy for structural analysis.

![Scheme 19, Metal Coordination.](image-url)
Copper - 1,10-Phenanthroline Complexes

Copper (I) and (II) complexes of nitrogen containing chiral ligands have become a catalyst of choice for asymmetric aziridination, Michael, and Diels-Alder reactions.\textsuperscript{4-6} Although bidentate nitrogen ligands yield moderately good enantioselectivities, structural improvements are still necessary.\textsuperscript{43} In an effort to examine the coordination chemistry of our ligands, we considered the preparation of copper complexes.

In the past two decades, numerous studies were carried out on the synthesis of copper-1,10-phenanthroline complexes, which are of interest due to their distinct photochemical properties.\textsuperscript{44,45} To familiarize ourselves with the complexation procedure, we first prepared CuCl(2,9-dimethyl-1,10-phenanthroline)\textsubscript{2} following the work by Pallenberg and co-workers.\textsuperscript{44} Commercially available 2,9-dimethyl-1,10-phenanthroline was reacted with cuprous (I) chloride. The product was recrystallized from aqueous methanol to give very fine needles. Our \textsuperscript{1}H NMR, UV, and m.p. data corresponded to the literature values.\textsuperscript{44} Next, we applied this methodology to amino alcohol 3 and benzyl ether 4. However, the preparation of CuCl(\textit{trans}-6-dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol)\textsubscript{2} and CuCl(\textit{trans}-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline)\textsubscript{2} were unsuccessful. We modified another literature procedure\textsuperscript{46,47} by
employing Teflon-lined stainless steel vessels, heat and autogenous pressure, but without success.

Cobalt - 1,10-Phenanthroline Complexes

Nagata et al. examined the asymmetric borohydride reduction of ketones by using a cobalt (II) catalyst with bidentate nitrogen ligands (Scheme 20).\textsuperscript{48} The study employed various substrates and three different cobalt catalysts in order to achieve high enantioselectivity. They obtained excellent enantiomeric excess with several substrates by appropriate choice of the catalysts and mentioned that the enantiofacial selectivity was dependent on the substrate, ligand, and additives.

\[
\begin{array}{c}
\text{O} \\
\text{NaBH}_4 \\
1\text{mol} \% \text{cat.}
\end{array}
\xrightarrow{}

\begin{array}{c}
\text{cat.} = \\
\text{Scheme 20, Asymmetric Reduction of Ketone.}
\end{array}
\]

Various cobalt complexes have been described in the literature\textsuperscript{49, 50} and to
familiarize ourselves with the complexation procedure, we prepared trans-[Co(phen)$_2$Cl$_2$]Cl.$^{51}$ The latter was characterized by 2D COSY NMR, which facilitated peak assignment. Then, we attempted to synthesize [CoCl$_2$(L$^*$)]Cl (L$^*$ = trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthroin-5-ol or trans-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline, but without success. We also followed the work by Schilt and Taylor,$^{52}$ which was not effective. Additional optimization of reaction conditions for cobalt coordination is necessary.

Ruthenium - 1,10-Phenanthroline Complexes

Ruthenium is widely used in coordination chemistry and has been employed in many reactions such as asymmetric cyclopropanation, Diels-Alder, oxidation, hydrogenation, and hydrosilylation reactions.$^{46}$ Nishiyama et al. have used the chiral pybox ligand with Ru (II) as an effective cyclopropanation catalyst with high selectivity ($\geq 95\%$, Scheme 21).
We embarked on developing new Ru (II) complexes with 1,10-phenanthrolines. In the beginning, we followed the literature to prepare the dichloro(1,10-phenanthroline)ruthenium complex,\textsuperscript{53, 54} however, both methods were unsuccessful in our hands. Unfortunately the method for [Ru(phen)\textsubscript{3}I\textsubscript{2} was also without success.\textsuperscript{55} In contrast, the preparation of the analogue bipyridine complex, \textit{cis}-(bpy)\textsubscript{2}RuCl\textsubscript{2}cdot2H\textsubscript{2}O was reproduced in 60 % yield.\textsuperscript{56} Commercial RuCl\textsubscript{3}cdot xH\textsubscript{2}O and bipyridine were dissolved in DMF and stirred at reflux, followed by addition of LiCl. Following the literature,\textsuperscript{57} we then prepared [Ru(bpy)\textsubscript{2}(phen)](ClO\textsubscript{4})\textsubscript{2} in 66 % yield by employing \textit{cis-}(bpy)\textsubscript{2}RuCl\textsubscript{2}cdot2H\textsubscript{2}O as a starting material. The Ru complex was confirmed by comparison with the literature \textsuperscript{1}H NMR and IR data (Scheme 22).\textsuperscript{57}
The same starting material was employed to prepare ruthenium complexes of our 1,10-phenanthroline derivatives.\textsuperscript{58} \textit{cis-}-(Bpy)\textsubscript{2}RuCl\textsubscript{2}-2H\textsubscript{2}O and \textit{trans}-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol or \textit{trans}-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline were refluxed in aqueous ethanol. The flocculent crude precipitates were collected after slowly adding an aqueous NaClO\textsubscript{4} solution, and washing with H\textsubscript{2}O and ether. Attempts to obtain the corresponding hexafluorophosphate complexes through perchlorate exchange were unsuccessful; [Ru(bpy)\textsubscript{2}(L\textsuperscript{*})](PF\textsubscript{6})\textsubscript{2}-xH\textsubscript{2}O (L\textsuperscript{*} = 1,10-phenanthroline, \textit{trans}-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol and \textit{trans}-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline. However, we obtained [Ru(bpy)\textsubscript{2}(L\textsuperscript{*})](PF\textsubscript{6})\textsubscript{2}-xH\textsubscript{2}O complexes through direct addition of an aqueous KPF\textsubscript{6} solution to the mixture of ligand and [Ru(bpy)\textsubscript{2}Cl\textsubscript{2}]-2H\textsubscript{2}O.

Palladium-1,10-Phenanthroline Complexes

Palladium is extensively used in synthetic organic chemistry, including in allylic
substitution reactions.\textsuperscript{5-7} In general, palladium-catalyzed transformations allow the control of regio- and stereoselectivity, depending on the nature of the catalytic species.\textsuperscript{14} For example, Pretot and Pfaltz prepared new chiral ligands derived from binaphthol (Scheme 23) and demonstrated the high selectivities during allylic alkylation with 1- and 3-aryl-2-propenyl acetates (up to 90 \% ee).\textsuperscript{59} We therefore focused on preparing 1,10-phenanthroline-palladium complexes.

\begin{center}
\textbf{Scheme 23, Palladium - Catalyzed Allylic Alkylation.}
\end{center}

Dichloropalladium (II) complexes of 1,10-phenanthroline derivatives were prepared by following a modified literature procedure.\textsuperscript{60-62} Palladium (II) chloride was reacted with \textit{trans}-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol or \textit{trans}-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline in CH\textsubscript{2}Cl\textsubscript{2}, to give quantitative yields of the corresponding dichloropalladium (II) complexes (16 and 17), which were characterized by \textsuperscript{1}H and \textsuperscript{13}C NMR, IR, and m.p. data (Scheme 24).
Platinum complexes have found application in asymmetric hydroformylation reactions. For example, the catalyst PtCl$_2$(BPPM)/SnCl$_2$ was effective for the conversion of styrene and its derivatives, yielding the corresponding 2-arylpropanols (Scheme 25).\(^{63}\)

\[
\text{Ar} \quad \xrightarrow{\text{PtCl$_2$(BPPM)-SnCl$_2$}} \quad \text{Ar-CHO}
\]

Scheme 25, Platinum - Mediated Asymmetric Hydroformylation.

The catalytic cycle of the platinum-promoted hydroformylation in the presence of SnCl$_2$ includes a cationic species. The latter is generated by the removal of a chloride ligand from its precursor, PtCl$_2$L$_2$, via a mixed bimetallic complex, PtClL$_2$(SnCl$_3$).
(Scheme 26). It has been proposed that asymmetric induction occurs during the formation of an alkyl-Pt(CO)L$_2$ intermediate through olefin insertion into the Pt-H bond.$^{64}$

\[
\text{PtCl}_2L_2 + \text{SnCl}_2 \rightarrow \text{L-Pt-SnCl}_3 
\]

\[
\text{H}_2 + \text{L-Pt-SnCl}_3 \rightarrow \text{L-Pt-SnCl}_3 \rightarrow \text{CO} \rightarrow [\text{L-Pt-CO}]^+
\]

active Pt catalyst

Scheme 26, Mechanism for the Formation of Active Pt Catalyst.

Our platinum complexes were prepared by a modified literature procedure; PtCl$_2$(L'), L' = \textit{trans}-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol and \textit{trans}-5-benzzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline.$^{60,62}$ Ethanol solutions of 1,10-phenanthrolines were added to an aqueous solutions of K$_2$PtCl$_4$, from which the products precipitated (Scheme 27). Crude products (18 and 19) were characterized by $^1$H and $^{13}$C NMR, IR, m.p. and elemental analysis.

\[
\text{RO} \quad \begin{array}{c}
\text{N} \\
\text{NR}_2' \\
\text{NR}_2 \\
\end{array} \\
\text{K}_2\text{PtCl}_4 \\
\text{diluted HCl} \\
100^\circ \text{C} \\
\text{RO} \quad \begin{array}{c}
\text{N} \\
\text{NR}_2' \\
\text{NR}_2 \\
\end{array}
\]

(3) R = H, R' = Bn
(4) R = Bn, R' = Bn
(18) R = H, R' = Bn (54 %)
(19) R = Bn, R' = Bn (30 %)

Scheme 27, Platinum Complexation.
We are not aware of crystal structure determinations for any of the specific complexes reported herein. However, we presume that all of the ruthenium complexes possess essentially six-coordinate geometry, while palladium and platinum complexes prefer four coordination sites.

NMR Studies

Methylene Protons

In amino alcohol 3, two proton patterns were observed for the two methylene groups attached to nitrogen, depending on the concentration of the $^1$H NMR samples. At low concentration (A: $1.91 \times 10^{-8}$ M), a singlet was observed, while an AB quartet appeared at higher concentrations (B: $1.27 \times 10^{-7}$ M and C: $1.91 \times 10^{-7}$ M, Fig. 8).
There are two possible explanations for our observations; (1) Deuterated chloroform can contain trace amounts of acid that interacts with the amine moiety. Protonation changes the rate at which the methylene groups interchange and can influence multiplicity. (2) Alternatively, the concentration effect may be due to the interaction between the hydroxyl proton with the adjacent nitrogen in another molecule, which is more frequently detectable at higher concentration than at relatively lower ones. Subsequently, the protons of the two methylene groups are no longer equivalent ($H_a \neq H_b$),
and thus, spin-spin splitting and coupling are observed (Fig. 9).

![Diagram of two amino alcohol molecules with hydrogen bonding]

Figure 9, Interaction between Two Amino Alcohol Molecules.

Benzyl protection of alcohol 3 also influenced the resonance of the methylene groups on the amine (Fig. 10). We observed a doublet of doublet at higher field, 4.40 ppm for 2H and at 3.40 ppm for 4H.
Figure 10, $^1\text{H}$ NMR of \textit{trans}-6-Dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol (3, bottom) and \textit{trans}-5-Benzylxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline (4, top) in CDCl$_3$.

**Methine Protons**

When hydrogens are attached to adjacent carbon atoms the $H_A$-$C$-$C$-$H_B$ interactions (Fig. 11-A) are called \textit{vicinal} couplings (Latin \textit{vicinus} = “neighbor”). These hydrogens generate spin-spin splitting patterns, following the $n+1$ rule in simple aliphatic hydrocarbon chains (Fig. 11-B).\textsuperscript{65}
$^3J_{HH}$ is the vicinal coupling constant and measures the magnitude of the splitting. The actual magnitude of the coupling constant between two adjacent C-H bonds depends on the dihedral angle $\alpha$ between these two bonds (Fig. 11-C).

Martin Karplus studied the variation of coupling constants with an angle $\alpha$ and developed the *Karplus equation* (or *Karplus relationship*) below. It therefore established the theoretical relationship between the vicinal coupling constant $^3J_{HH}$, and the dihedral angle (Eq. 3). This correlation can be illustrated in a graph, the Karplus Curve (Fig. 12). Although the actual experimental data exhibit a wide range as shown by the shaded area of the curve, this graph was accepted to give the best predictions for the relationship between $^3J_{HH}$ and $\alpha$. This information is important for the structural analysis of new 1,10-phenanthroline derivatives.
\[
^3J_{HH} = A + B \cos \alpha + C \cos 2\alpha \\
A = 7 \quad B = -1 \quad C = 5
\]

Equation 3, Karplus Equation.\textsuperscript{65}

![The Karplus Curve](image)

Figure 12, The Karplus Curve.\textsuperscript{65}

Due to the symmetric structure of 1,10-phenanthroline-5,6-epoxide (2), H5 and H6 are equivalent and appear as singlet at 4.61 ppm in CDCl\textsubscript{3}. However, when the epoxide ring was opened with nucleophilic amines, the structure lost that symmetry. As a result, H5 and H6 are non-equivalent and couple with each other. Spin-spin splitting was observed in alcohol 3 and benzyl ether 4, appearing as doublets between 5.30 ppm and 4.23 ppm with various coupling constants \((^3J_{HH} = 2.5 - 9.0 \text{ Hz } \textit{vide infra})\).

For \textit{trans}-6-dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol (3) and \textit{trans}-5-
benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline (4), we calculated the vicinal coupling constants for protons in the 5- and 6- positions and investigated their conformational preferences. For $^3J_{HH}$ compound 3 was 9.0 Hz at room temperature in CDCl$_3$. We determined that the two substituents (amine and alcohol) are either located approximately 180° from each other and in a diaxial position or they are separated by ca. 60° and in a diequatorial arrangement (Fig. 13).

![Figure 13, Two Possible Conformers of trans-6-Dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol (3).](image)

The Karplus equation and computational studies by Professor Miller helped to determine which isomer is preferred.$^{66}$ Coupling constants were calculated for each isomer, which were 1.5 Hz for the diaxial (anti) and 13.0 Hz for the diequatorial (syn) conformers. Subsequently, the ratio of the two isomers was calculated to be $36 / 64 = \text{anti} / \text{syn}$. Thus, the pseudodiequatorial (syn) isomer was favored.
A similar analysis was done for trans-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline (4). The $^3J_{HH}$ value was 2.5 Hz, which indicates that the two B-ring substituents were predominately in a diaxial conformation (anti, Fig. 14). $^3J_{HH}$ values were also calculated for the two possible conformers of ether 4, which were 1.5 Hz for the diaxial conformer (anti) and 12.9 Hz for the diequatorial conformer (syn). Computations provided the ratio of the diaxial and the diequatorial conformers, which were found to be $92 / 8 = \text{anti} / \text{syn}$. Therefore, the diaxial conformer is the preferred conformation (Fig. 14).

![Diagram of conformers of trans-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline (4).]

Calc. $92 / 8 = \text{anti} / \text{syn}$

Figure 14, Two Possible Conformers of trans-5-Benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline (4).

The conformers of derivatives 3 and 4 interconvert rapidly because they are conformationally flexible. Therefore, the observed chemical shifts represent the population-weighted averages of resonances of interconverting conformers. Conformational preference was influenced by the covalent and non-covalent bond...
modifications that change the electronic and steric environment. In particular, the diequatorial conformer of 1,10-phenanthroline alcohol derivative 3 was changed to the diaxial for the benzyl ether 4.

\[^3J_{HH}\] was also recorded for H5 and H6 of the trans-5-dibenzylamino-5,6-dihydro-1,10-phenanthroline-6-yl acetate (5), which was 2.56 Hz. Comparing the \[^3J_{HH}\] of alcohol 3 and benzyl ether 1,10-phenanthroline derivative 4, we presume that the diaxial conformer is preferred for acetate 5.

Ultimately we want to understand how the two substituents on the B-ring of 1,10-phenanthroline influence the ligand chelation site (N-C-C-N, Fig. 15). Angles from ab initio density functional calculations were carried out by Professor Miller at WMU. They imply that the introduction of substituents in the B-ring creates molecular helicity and that the orientation of the helicity is switching depending on the nature of substituents.

Figure 15, Possible 1,10-Phenanthroline Conformers.
In the $^1$H NMR spectrum, we observed that many proton resonances shifted *downfield* when benzyl ether 4 was complexed to palladium ($\delta = 8.84 \text{ Hz} \rightarrow 9.17 \text{ Hz}$ for H$_2$, $\delta = 7.80 \text{ Hz} \rightarrow 8.02 \text{ Hz}$ for H$_4$) (Fig. 16). Similar chemical shifts were observed in the palladium complex of *trans*-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol (16).
In platinum complex 19, resonances also shifted *downfield* relative to the free ligand due to the metal influence ($\delta = 8.84 \text{ Hz} \rightarrow 9.55 \text{ Hz}$ for $H_2$, $\delta = 7.80 \text{ Hz} \rightarrow 8.08 \text{ Hz}$ for $H_4$). Again, this trend was observed for $\text{PtCl}_2(\text{trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol})$ 18.

Coupling constants, $^3J_{HH}$ of the free 1,10-phenanthroline 4 were compared to those of the metal complexes, which were 2.93 Hz and 2.92 Hz for $\text{PdCl}_2(\text{II})(\text{trans-5-benzyloxy-6-dibenzylamino-5,6-1,10-phenanthroline})$ 17 and $\text{PtCl}_2(\text{II})(\text{trans-5-benzyloxy-6-dibenzylamino-5,6-1,10-phenanthroline})$ 19, respectively (Fig. 17). These $^3J_{HH}$ values suggests that diaxial conformers are still preferred but final proof will only be available through solid state analysis.

![Figure 17, $^3J_{HH}$ of Free Ligand and Metal Complexes.](image-url)
SUMMARY AND CONCLUSIONS

We prepared new 1,10-phenanthroline derivatives using 1,10-phenanthroline-5,6-epoxide as a key intermediate. The latter was obtained through biphasic oxidation with bleach. Reaction pH values and time influenced the quality and yields of the product.

To introduce two stereogenic centers on C5 and C6 in the B-ring, nucleophilic ring opening of epoxide 2 was accomplished in the presence of Mg(OTf)$_2$ or Mg(ClO$_4$)$_2$. These Lewis acid methods provided easy access to chiral amino alcohol derivatives in 55 - 92% yields. We found that the aminolysis with magnesium trifluoromethanesulfonate (triflate) gave better results (yields and purity) than with the corresponding perchlorate. To prevent the reactivity of the hydroxyl group in amino alcohol 3, we attached benzyl and acetate groups.

Structural analysis revealed that the new 1,10-phenanthroline derivatives had different conformational preferences, depending on the B-ring substituents. Alcohol derivative 3 preferred a diequatorial arrangement, which switched to a predominately diaxial conformation after benzylation (4). Therefore, B-ring substituents changed the molecular helicity.
1,10-Phenanthroline derivatives 3 and 4 were coordinated to several transition metals to explore their metal binding ability. We synthesized Pd (II) (16, 17) and Pt (II) 
(18, 19) complexes of *trans*-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol (3) and *trans*-5-benzyloxy-6-dibenzyl-amino-5,6-1,10-phenanthroline (4). These complexes are potential catalysts for asymmetric synthesis.
OUTLOOK

Above mentioned 1,10-phenanthroline derivatives were synthesized as racemates. To apply these new compounds in asymmetric catalysis, they need to be separated into single enantiomers. Resolution via formation of diastereomeric salts is a commonly used method and was pioneered by Louis Pasteur. Racemic acids or bases are neutralized with optically pure bases or acids, respectively (tartaric, malic and mandelic acids). These salts can possess significantly different physical properties, such as solubility, boiling point or chromatographic behavior and can thus be separated from each other. After separation, the salts can be converted back to the free base or acid forms.

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\begin{align*}
\text{racemate} & \quad + \quad (R)-\text{mandelic acid} \\
\text{R} = \text{Bn, Ac} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \qu
Scheme 29, Proposed Asymmetric Catalysis.
EXPERIMENTAL

Reagents and Solvents

All reagents and solvents used in this project were obtained from Acros, Lancaster, Aldrich and TCI Chemical Companies. Chemicals were of more than 99 % purity and were used without further purification. All commercial solvents used were of reagent grade. Hexane and THF were dried by distillation from Na / Benzophenone, and dichloromethane was distilled from P₂O₅ before use. Silica gel (32 - 63 mesh, Dynamic Absorbents, LLC) was used for column chromatography. Silica and alumina TLC plates (UV/254) were purchased from AllTech.

Characterization of Compounds and Instrumentation

¹H NMR spectra were recorded with at 400 MHz and ¹³C NMR spectra were obtained with a 100 MHz JEOL Eclipse nuclear magnetic resonance spectrometer, using deuterated chloroform, dimethyl sulfoxide, methanol and acetone. Chemical shifts were reported relative to solvent as an internal standard at 25°C. Melting points, reported in degree Celsius, were determined in open capillaries using a Thomas-Hoover Unimelt
instrument. Infrared (IR) spectra were recorded using a Bruker Equinox 55 and Perkin Elmer 1710 Fourier Transform Infrared Spectrometers. Elemental analyses were done by NuMega Resonance Labs, Inc.

5,6-Dihydro-1,10-phenanthroline-5,6-epoxide (2)

We prepared the epoxide by modifying various literature procedures \(^{19, 20, 23, 24}\). Commercially available bleach (NaOCl, 100 ml) was adjusted to pH 8.6 with concentrated H\(_2\)SO\(_4\). HCl was not used because higher Cl\(^-\) concentration promotes side product formation. To the solution were added tetrabutyl ammonium hydrogen sulfate (1.71 g, 5.05 mmol, 0.5 eq.) as phase transfer catalyst and 1,10-phenanthroline monohydrate (2.00 g, 10.0 mmol, 1.0 eq.) dissolved in chloroform (15 ml) at room temperature. Reaction time and yields varied, depending on the quality of bleach. After the reaction was completed (ca. 30 min) by TLC, the organic layer was separated and washed with several portions of water and brine (3 × 50 ml), respectively. The washed organic layers were combined, dried with anhydrous Na\(_2\)SO\(_4\) and filtered. The solvent was removed by rotary evaporation and the crude epoxide was purified by recrystallization from chloroform and hexane (45 - 70 %). \(^1\)H NMR (400 MHz), \(\delta\) (CDCl\(_3\), ppm): 8.92 (d, J= 1.83 Hz, 1H), 8.90 (d, J= 1.83 Hz, 1H), 8.01 (d, J= 1.83 Hz,
trans-5-Aniline-6-hydroxyl-5,6-dihydro-1,10-phenanthroin-5-ol

The following procedure is a modified literature method.\textsuperscript{26, 27, 30} To a solution of Mg(OTf)\textsubscript{2} (411 mg, 1.27 mmol, 0.5 eq) in CH\textsubscript{3}CN (7 ml) was added 5,6-dihydro-1,10-phenanthroline-5,6-epoxide (500 mg, 2.55 mmol, 1.0 eq.). After stirring for 20 minutes at 40\degree C, H\textsubscript{2}NPh (279 µl, 3.06 mmol, 1.2 eq.) was added to the solution and the reaction mixture was stirred at reflux until TLC analysis indicated complete conversion (2 - 3 days). The mixture was cooled to room temperature, quenched with H\textsubscript{2}O (10 ml) and was extracted with CHCl\textsubscript{3} (3 \times 25 ml). The organic layers were combined and washed with H\textsubscript{2}O and brine (3 \times 50 ml), respectively. The solution was dried with anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated under reduced pressure to give the crude product which was purified by silica gel column chromatography (CHCl\textsubscript{3} / 3 % MeOH) (55 - 64 %). \textsuperscript{1}H NMR (400 MHz), δ (CDCl\textsubscript{3}, ppm) 8.75 (d, J= 3.66 Hz, 1H), 8.72 (d, J= 3.30 Hz, 1H), 8.06 (d, J=
7.69 Hz, 1H), 7.78 (d, J= 7.69 Hz, 1H), 7.38, 7.38 (dd, J= 4.76 Hz, 7.69 Hz, 1H), 7.27, 7.27 (dd, J= 4.76, 8.06 Hz, 1H), 7.25 (s, 1H), 7.19 (t, J= 7.69 Hz, 2H), 6.80 (t, J= 7.69 Hz, 2H), 6.73 (d, J= 7.69 Hz, 2H), 5.06 (d, J= 10.62 Hz, 1H), 4.84 (d, J= 10.25 Hz, 1H) 

$^{13}$C NMR (100 MHz, CDCl$_3$, 25°C) δ 150.5, 149.8, 149.5, 147.4, 135.2, 134.7, 134.3, 133.7, 129.7, 124.5, 124.3, 118.9, 113.7, 70.3, 58.8 IR (NaCl, cm$^{-1}$) 3303, 3056, 1602, 1564, 1498, 1419, 1323, 1264, 1123, 1078, 1041, 798, 746, 694, 420 m.p. 210°C (lit. 206°C).

**trans-6-Dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol (3)**

The following procedure was a modified literature method.$^{26,27,30}$ To a solution of Mg(ClO$_4$)$_2$ (114 mg, 0.510 mmol, 1.0 eq.) or Mg(OTf)$_2$ (164 mg, 0.510 mmol, 1.0 eq.) in CH$_3$CN (3 ml) was added 5,6-dihydro-1,10-phenanthroline-5,6-epoxide (100 mg, 0.510 mmol, 1.0 eq.). After stirring for 20 minutes at 40°C, dibenzylamine (119 µl, 0.612 mmol, 1.2 eq.) was added to the solution and the reaction mixture was stirred at reflux until TLC analysis indicated complete conversion. The mixture was cooled to room temperature and quenched with H$_2$O (5 ml), extracted with CHCl$_3$ (3 × 10 ml) and washed with H$_2$O and brine (3 × 50 ml), respectively. The solution was dried with anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure to give the crude product which was purified by
trans-5-Benzyl oxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline (4)

The following procedure is a modified literature procedure. NaH (61.0 mg, 2.54 mmol, 2.0 eq.) was washed with excess of anhydrous hexane under argon to remove the mineral oil. A solution of 6-dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol (500 mg, 1.27 mol, 1.0 eq.) in anhydrous CH$_2$Cl$_2$ (5 ml) was added to the reaction flask. After stirring for 20 minutes at reflux, BnBr (182 µl, 1.53 mmol, 1.2 eq.) was added and heating continued. After 3 days, the reaction mixture was quenched with H$_2$O and...
extracted with CHCl₃ (3 × 25 ml). The combined organic layers were washed with H₂O and brine (3 × 50 ml), respectively, followed by drying with anhydrous Na₂SO₄, filtration and concentration. The crude product was purified by silica chromatography (CHCl₃ / 3 % MeOH) and obtained in 86 % yield. ¹H NMR (400 MHz), δ (CDCl₃, ppm): 8.84 (d, J= 4.76 Hz, 1H), 8.79 (d, J= 4.76 Hz, 1H) 7.80 (m, J= 6.59 Hz, 1H) 7.63 (m, J= 6.22 Hz, 1H) 7.40 - 7.19 (m, 17H) 4.89 (d, J= 2.20 Hz, 1H) 4.43 (ABq, J= 12.45 Hz, 1H) 4.36 (ABq, J= 12.45 Hz, 1H), 4.28 (d, J= 2.56 Hz, 1H) 3.49 (ABq, J= 13.55 Hz, 2H) 3.35 (ABq, J= 13.55 Hz, 2H) ¹³C NMR (100 MHz, CDCl₃, 25°C) δ 151.5, 151.1, 151.0, 150.1, 139.4, 138.6, 137.7, 137.1, 132.2, 130.9, 128.7, 128.6, 128.4, 128.0, 127.9, 127.3, 124.4, 123.7, 72.7, 69.8, 58.9, 54.5 IR (NaCl, cm⁻¹) 3029, 2834, 2360, 1652, 1559, 1494, 1454, 1426, 1363, 1128, 1065, 1028, 801, 736, 698 E.A. calcd. for C₃₃H₂₉N₃O₂H₂O: C, 76.28; H, 6.40; N, 8.09 found: C, 76.31; H, 6.56; N, 7.85 m.p. 78°C.

trans-5-Dibenzylamino-5,6-dihydro-1,10-phenanthroline-6-yl acetate (12)

The literature method was followed to prepare the desired product.³⁵ Mg(ClO₄)₂ (28.4 mg, 0.127 mmol, 0.5 eq.) was reacted with Ac₂O (50.4 µl, 0.536 mmol, 2.0 eq), following
addition of trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol (100 mg, 0.254 mmol, 1.0 eq.) at room temperature. After 2 - 3 hrs, aqueous NaHCO₃ (5 ml) was added to the reaction mixture and extracted with chloroform (3 x 10 ml). The organic layers were combined and washed with water and brine (3 x 20 ml), respectively, followed by drying with anhydrous Na₂SO₄, filtration and concentration. The crude product was purified by silica chromatography (CHCl₃ / 3 % MeOH) to obtain the desired product (54 %). ¹H NMR (400 MHz), δ (CDCl₃, ppm): 8.80 (d, J= 3.30 Hz, 1H), 8.77 (d, J= 3.30 Hz, 1H), 7.82 (d, J= 7.29 Hz, 1H), 7.75 (d, J= 7.69 Hz, 1H), 7.36, 7.36 (dd, J= 4.76 Hz, 7.69 Hz, 1H), 7.31, 7.31 (dd, J= 4.76 Hz, 7.69 Hz, 1H), 7.25 - 7.16 (m, C₆H₅, 6.52 (d, J= 2.56 Hz, 1H), 4.07 (d, J= 2.56 Hz, 1H), 3.56 (Abq, J= 13.55 Hz, 1H), 3.44 (Abq, J= 13.55 Hz, 1H), 1.89 (s, 3H).

2,9-Diphenyl-1,10-phenanthroline (13)

The following procedure is a modified literature method.³⁷-⁴⁰ A solution of phenyllithium (ca. 1.8 M in di-n-butylether) (1.13 ml, 11.1 mmol, 4.0 eq.) was added by syringe at room temperature to an argon-flashed solution of dried 1,10-phenanthroline (0.500 g, 2.78 mmol, 1.0 eq.) in anhydrous toluene and THF (25 ml, 4:1 vol./vol.). The resulting dark
red mixture was stirred for overnight at room temperature and then hydrolyzed with water at 0°C. The bright yellow organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 10 ml). The crude product was thereafter re-aromatized by addition of MnO₂ (7.5 g) to the combined organic layers, dried (MgSO₄), and filtered. The filtrate was then evaporated to dryness. The crude product was purified by silica gel chromatography, using CH₂Cl₂ / 3 % MeOH (67 %, lit. 70 %).³⁷ ¹H NMR (400 MHz), δ (CDCl₃, ppm): 8.47, 8.45 (d, J = 7.32 Hz, C₆H₅) 8.33, 8.31 (d, J = 8.42 Hz, 2H) 8.17, 8.15 (d, J = 8.42 Hz, 2H) 7.80 (s, 2H) 7.59 (t, J = 7.32 Hz, 7.69 Hz, C₆H₅) 7.50 (t, J = 6.96 Hz, 7.69 Hz, C₆H₅).¹³C NMR (400 MHz, CDCl₃, 25° C) δ 156, 146, 139, 137, 129, 128, 127, 126, 120 IR (NaCl, cm⁻¹): 3058, 1604, 1589, 1505, 1485, 854, 762, 736, 693 m.p. 192° C (lit.184 - 184° C).³⁷

2,9-Diphenyl-1,10-phenanthroline-5,6-epoxide (14)

Commercially available bleach (NaOCl, 12.0 ml) was adjusted to pH 8.6 with conc. H₂SO₄. To this solution were added tetrabutyl ammonium hydrogen sulfate (0.212 g, 6.24 mmol, 0.7 eq.) and 2,9-diphenyl-1,10-phenanthroline (0.296 g, 8.912 mmol, 1.0 eq.) dissolved in chloroform (5 ml) and stirred at room temperature. After 1 hr, the organic
layer was separated and extracted with CHCl₃ (3 x 10 ml). All layers were combined and washed with several portions of water and brine (3 x 10 ml), respectively, following drying with anhydrous Na₂SO₄. After filtration, the solvent was removed by rotary evaporation. The crude epoxide was purified by silica gel chromatography (CH₂Cl₂ / 3 % MeOH) and obtained in 78 % yield. ¹H NMR (400 MHz), δ (CDCl₃, ppm): 8.30 (d, J = 6.96 Hz, C₆H₅) 8.06 (d, J = 7.69 Hz, 2H) 7.88 (d, J = 8.06 Hz, 2H), 7.54 (t, J = 7.51 Hz, C₆H₅) 7.46 (t, J = 7.14 Hz, C₆H₅) 4.67 (s, 2H) ¹³C NMR (400 MHz, CDCl₃, 25°C) δ 158, 149, 139, 138, 129, 128, 127, 127, 120, 55 IR (NaCl, cm⁻¹) 3060, 1565, 1468, 1391, 1218, 1026, 827, 785, 749, 730, 692 E.A. calcd. for C₂₄H₁₆N₂O C, 82.74; H, 4.63; N, 8.04 found: C, 82.43; H, 4.74; N, 8.01 m.p. 178°C.

trans-2,9-Diphenyl-6-dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol (15)

To a solution of Mg(OTf)₂ (30.0 mg, 0.0917 mmol, 1.0 eq.) in CH₃CN (3 ml) was added 2,9-diphenyl-1,10-phenanthroline-5,6-epoxide (100 mg, 0.183 mmol, 2.0 eq.). After stirring for 20 minutes at 40°C, dibenzylamine (34.0 µl, 0.183 mmol, 2.0 eq.) was added to the solution and the reaction mixture was stirred at reflux until TLC analysis indicated complete conversion. The mixture was cooled to room temperature, quenched with H₂O
(5 ml), extracted with CHCl₃ (3 × 10 ml) and washed with H₂O and brine (3 × 25 ml), respectively. The solution was dried with anhydrous Na₂SO₄ and concentrated under reduced pressure to give the crude product which was purified by silica gel column chromatography (CHCl₃ / 3 % MeOH) (16 %). ¹H NMR (400 MHz), δ (CDCl₃, ppm):

8.16 (d, J= 7.36 Hz, 2H), 8.15 (d, J= 7.68 Hz, 2H), 8.03 (d, J= 2.92 Hz, 1H), 8.01 (d, J= 2.56 Hz, 1H), 7.78 (d, J= 6.24 Hz, 1H), 7.76 (d, J= 6.24 Hz, 1H), 7.49 - 7.20 (m, 6H), 5.24 (d, J= 8.44 Hz, 1H), 4.25 (d, J= 8.44 Hz, 1H), 3.96 (ABq, J= 13.91 Hz, 4H)

[CuCl(dmp)₂] (dmp: 2,9-Dimethyl-1,10-phenanthroline)

[CuCl(dmp)₂] was prepared according to a literature procedure.⁴⁴ A vacuum degassed solution of 2,9-dimethyl-1,10-phenanthroline (0.453 g, 2.00 mmol, 2.0 eq.) in absolute ethanol (15.0 ml) was added to cuprous chloride (99.0 mg, 1.00 mmol, 1.0 eq.) under an argon atmosphere. The resulting bright solution was stirred at room temperature for 2 hrs. This mixture was filtered, to remove a small amount of insoluble matter, and evaporated to give 0.304 g of bright red solid (63 %, lit. 100 %⁴⁴). Recrystallization from aqueous methanol gave very fine needles. ¹H NMR (400 MHz), δ (DMSO-d₆, ppm): 8.76 (d, J= 8.42 Hz, 2H), 8.23 (s, 2H) 7.97 (d, J= 8.42 Hz, 2H) 2.39 (s, 6H) m.p 242° C (lit. 238 -
238.5° C\textsuperscript{44}) UV-vis λ\text{max} (CH\textsubscript{2}Cl\textsubscript{2}) 241 nm, 272 nm, 458 nm (lit. 232 nm, 275 nm, 456 nm\textsuperscript{44}).

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\text{[Co(phen)\textsubscript{2}Cl\textsubscript{2}]Cl}
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[Co(phen)\textsubscript{2}Cl\textsubscript{2}]Cl was prepared by following the literature.\textsuperscript{51} 1,10-phenanthroline monohydrate (0.396 g, 2.00 mmol, 2.0 eq.) was added slowly to a vigorously stirred solution of CoCl\textsubscript{2}-6H\textsubscript{2}O (0.238 g, 1.00 mmol, 1.0 eq.) in 0.40 ml of 4 N hydrochloric acid. To the pink slurry were added activated carbon and then 0.20 ml of 35 % hydrogen peroxide solution while stirring constantly. The slurry gradually turned pale brown and was black after about 30 min. After ca. 4 hrs the precipitate was washed with portions of 2 N hydrochloric acid until the filtrate was colorless and then with acetone.\textsuperscript{1}H NMR (400 MHz), δ (DMSO-d\textsubscript{6}, ppm): 10.04 (d, J= 5.13 Hz, 1H), 9.33 (d, J= 8.06 Hz, 1H), 8.84 (d, J= 8.06 Hz, 1H), 7.67, 7.67 (dd, J= 5.48 Hz, 8.04 Hz, 1H), 7.55 (d, J= 5.49 Hz, 1H).
[Ru(bpy)$_2$Cl$_2$]·2H$_2$O

[Ru(bpy)$_2$Cl$_2$]·2H$_2$O was prepared according to a literature procedure. Commercial RuCl$_3$·xH$_2$O (0.178 g, 0.597 mmol, 1.0 eq.) and 2,2'-bipyridine (0.187 g, 1.20 mmol, 2.0 eq.) were refluxed in DMF (60 ml) for 3 hrs. The solvent was evaporated and the reaction mixture was cooled in an ice bath for several hours. The resulting solid was collected by filtration and washed several times with cold water. LiCl (3.0 g) was added to the filtrate. The product was precipitated after evaporating solvents, and washed with several portions of cold water. The dark black microcrystalline product was collected after drying over vacuum (60 %). $^1$H NMR (400 MHz), $\delta$ (DMSO-d$_6$, ppm): 9.98 (d, J= 5.52 Hz, 2H), 8.64 (d, J= 8.08 Hz, 2H), 8.49 (d, J= 7.32 Hz, 2H), 8.07 (t, J= 8.08 Hz, 2H), 7.77 (t, J= 6.96 Hz, 2H), 7.68 (t, J= 8.08 Hz, 2H), 7.52 (d, J= 5.86 Hz, 2H), 7.10 (t, J= 7.32 Hz, 2H).

[Ru(bpy)$_2$(phen)](ClO$_4$)$_2$·xH$_2$O

[Ru(bpy)$_2$(phen)](ClO$_4$)$_2$·xH$_2$O was prepared according to a literature procedure. A
mixture of Ru(bpy)$_2$Cl$_2$$\cdot$2H$_2$O (26.2 mg, 0.0500 mmol, 1.0 eq.) and 1,10-phenanthroline (19.8 mg, 0.100 mmol, 2.0 eq.) in aqueous ethanol (5.0 ml, 1:1 vol./vol.) was heated under argon for 6 hrs at 75°C to give a clear red solution. The ethanol solvent was removed under reduced pressure on a rotary evaporator. To the solution was added an aqueous NaClO$_4$ solution. Upon cooling, the red-orange powder, [Ru(bpy)$_2$(phen)](ClO$_4$)$_2$ was precipitated, collected, washed with ether, and dried in the vacuum oven at 100°C. Recrystallization was accomplished with acetone and ether to obtain the microcrystalline product (66%). $^1$H NMR (400 MHz), δ (CD$_3$COCD$_3$, ppm):

- 8.86 (d, J = 8.04, 2H)
- 8.82 (d, J = 1.44 Hz, 2H)
- 8.80 (d, J = 1.12 Hz, 2H)
- 8.44 (d, J = 1.10 Hz, 2H)
- 8.42 (d, J = 1.46 Hz, 2H)
- 8.40 (s, 2H)
- 8.27 (m, 2H)
- 8.17 (m, 2H)
- 7.93 (dd, J = 5.12 Hz, 2.74 Hz, 2H)
- 7.87 (d, J = 5.12 Hz, 2H)
- 7.65 (m, 2H)
- 7.40 (m, 2H) m.p. 78°C.

[Ru(bpy)$_2$(phen)](PF$_6$)$_2$$\cdot$xH$_2$O

[Ru(bpy)$_2$(phen)](PF$_6$)$_2$$\cdot$xH$_2$O was prepared according to the literature.$^{56-58}$ A mixture of [Ru(bpy)$_2$Cl$_2$]·2H$_2$O (26.2 mg, 0.0500 mmol, 1.0 eq.) and 1,10-phenanthroline (19.8 mg, 0.100 mmol, 2.0 eq.) in aqueous ethanol (5 ml, 1:1 vol./vol.) was heated under an argon atmosphere.
for 6 hrs at 75°C to give a clear red solution. The ethanol solvent was removed under reduced pressure on a rotary evaporator. To the solution was added an aqueous KPF₆ solution. Upon cooling, [Ru(bpy)₂(phen)](PF₆)₂ was precipitated as an orange powder, washed with ether, and dried in the vacuum oven at 100°C. The microcrystalline product was obtained by recrystallization (acetone / ether).

[Ru(bpy)₂(trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol)](ClO₄)₂·xH₂O

The literature⁵⁶-⁵⁸ was followed to prepared [Ru(bpy)₂(trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol)](ClO₄)₂·xH₂O. A mixture of Ru(bpy)₂Cl₂·2H₂O (33.0 mg, 0.0635 mmol, 1.0 eq.) and trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol (50.0 mg, 0.127 mmol, 2.0 eq.) in aqueous ethanol (5.0 ml, 1:1 vol./vol.) was heated under argon for 6 hrs at 75°C to give a clear red solution. The ethanol solvent was removed under reduced pressure on a rotary evaporator. To the solution was added an aqueous NaClO₄ solution. Upon cooling, the orange powder was precipitated, washed with ether, and dried in the vacuum oven at 100°C (70%). ¹H NMR (400 MHz), δ
(CD$_3$COCD$_3$, ppm): 8.81 - 8.72 (m, 4H), 8.43 - 7.84 (m, 6H), 7.64 - 7.11 (m, 10H), 5.85 (m, 1H), 4.51 (m, 2H), 3.96 (d, J = 13.56 Hz, 1H), 3.84 (ABq, J = 13.55 Hz, 4H), 3.60 (d, J = 13.52 Hz, 1H) m.p. 189°C.

The literature method$^{56-58}$ was followed to prepare [Ru(bpy)$_2$(trans-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline)](ClO$_4$)$_2$·xH$_2$O. A mixture of Ru(bpy)$_2$Cl$_2$·2H$_2$O (26.2 mg, 0.0500 mmol, 1.0 eq.) and trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol (50.0 mg, 0.127 mmol, 2.0 eq.) in aqueous ethanol (5.0 ml, 1:1 vol./vol.) was heated under an argon for 3 hrs at 75°C to give a clear red solution. The ethanol solvent was removed under reduced pressure on a rotary evaporator. To the solution was added aqueous NaClO$_4$ solution. Upon cooling, the orange powder was deposited, collected, washed with ether, and dried in the vacuum oven at 100°C. $^1$H NMR (400 MHz), $\delta$ (CD$_3$COCD$_3$, ppm): 8.83 - 8.74 (m, 4H), 8.32 - 7.90 (m, 6H), 7.73 -
6.82 (m, 10H), 5.53 (dd, J= 1.83, 18.5 Hz, 2H), 4.68 - 4.43 (m, 1H), 3.64 (d, J= 13.52 Hz, 1H), 3.63 - 3.48 (m, 4H), 3.41(d, J= 13.16 Hz, 1H) m.p. 170° C.

PdCl₂(5,6-dihydro-1,10-phenanthroline-5,6-epoxide)

Newkome’s procedure was modified to prepare PdCl₂(5,6-dihydro-1,10-phenanthroline-5,6-epoxide). Epoxide 2 (50.0 mg, 0.255 mmol, 1.0 eq.) was added to a solution of PdCl₂ (36.2 mg, 0.204 mmol, 0.8 eq.) in CH₂Cl₂ (2.0 ml), followed by stirring at 40°C overnight. The yellow crystalline precipitate was filtered and washed with CH₂Cl₂ to afford the desired complex. ¹H NMR (400 MHz), δ (DMSO-d₆, ppm): 9.07 (d, J= 5.49 Hz, 2H) 8.74 (d, J= 7.94 Hz, 2H) 7.93 (t, J= 6.22 Hz, 2H) 5.06 (s) ¹³C NMR (100MHz, DMSO-d₆, 25°C) δ 153.7, 152.5, 148.6, 148.5, 141.2, 140.2, 139.6, 139.2, 137.0, 129.0, 128.9, 128.0, 127.9, 127.7, 66.3, 62.1, 54.7 IR (KBr, cm⁻¹) 3435, 2891, 2359, 1577, 1494, 1434, 1285, 1217, 1192, 1113, 1026, 900, 803, 744, 731, 656, 624 m.p. above 300°C.

PdCl₂(trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol) (16)

Two methods were used for the synthesis of this complex. Method A: The following
procedure is a modified literature method. trans-6-Dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol (50.0 mg, 0.127 mmol, 1.0 eq.) was added to PdCl₂ (18.0 mg, 0.102 mmol, 0.8 eq.) in CH₂Cl₂ (2 ml), followed by stirring at 40°C overnight. The yellow crystalline precipitate was filtered and washed with CH₂Cl₂ (61%).

Method B: The following procedure is according to references 60 and 62. To a stirred solution of K₂PdCl₄ (33.3 mg, 0.102 mmol, 0.8 eq.) in H₂O (15 ml and 50 µl conc. HCl) was added trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthrolin-5-ol (50 mg, 0.127 mmol, 1.0 eq.). Temperature was maintained at 100 - 110°C for 24 hrs. A yellow precipitate formed, was filtered and washed with copious amounts of hot H₂O. The product was obtained in 85 % yield. 

¹H NMR (400 MHz), δ (DMSO-d₆, ppm) 8.86 (app t, J= 6.59 Hz, 1H) 8.40 (d, J= 8.06 Hz, 1H) 8.33 (d, J= 7.69 Hz, 1H) 7.82 - 7.78 (m, 2H) 7.30 - 7.23 (m, 10H) 6.19 (d, J= 6.59 Hz, 1H) 5.52 (app t, J= 6.04 Hz, 2H) 4.25 (d, J= 5.86 Hz, 1H), 3.78 (ABq, J= 13.91 Hz, 2H) 3.66 (ABq, J= 13.55 Hz, 2H) 

¹³C NMR (100 MHz, DMSO-d₆, 25°C) δ 153.7, 152.5, 148.6, 148.5, 141.2, 140.2, 139.6, 139.2, 137.0, 129.0, 128.9, 128.0, 127.9, 127.7, 66.3, 62.1, 54.7 IR (KBr, cm⁻¹) 3451, 3059, 2856, 1576, 1492, 1453, 1430, 1213, 1076, 1037, 803, 754, 724, 702 E.A. calcd. for C₂₆H₂₃C₁₂N₃OPd·2.5H₂O C, 50.71; H, 4.58; N, 6.82 found: C, 50.84; H, 3.45; N, 6.89 m.p.
PdCl$_2$(trans-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline) (17)

The following procedure is according to the literature.$^6$1 trans-5-Benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline (100 mg, 0.207 mmol, 1.0 eq.) was added to PdCl$_2$ (29.4 mg, 0.166 mmol, 0.8 eq.) in CH$_2$Cl$_2$ (2 ml), followed by stirring at 40° C overnight. The yellow crystalline precipitate was filtered and washed with CH$_2$Cl$_2$ (10 ml), affording 61 % product. $^1$H NMR (400 MHz), δ (CDCl$_3$, ppm): 9.17 (d, J= 4.39 Hz, 1H) 9.10 (d, J= 4.39 Hz, 1H) 8.02 (d, J= 7.69 Hz, 1H) 7.87 (d, J= 7.69 Hz, 1H) 7.55 - 7.13 (m, 17H), 5.12 (d, J= 2.93 Hz, 1H) 4.49 (s, 2H) 4.41 (d, J= 2.93 Hz, 1H) 3.57 (ABq, J= 13.55 Hz, 2H) 3.49 (ABq, J= 13.55 Hz, 2H) IR (KBr, cm$^{-1}$) 3437, 3027, 2872, 1627, 1493, 1452, 1432, 1140, 1043, 808, 750, 731, 699 m.p. 212 - 220° C.

PtCl$_2$(trans-6-Dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol) (18)

The following procedure is according to the literature.$^{60, 62}$ To a stirred solution of
K$_2$PtCl$_4$ (65.9 mg, 0.159 mmol, 1.25 eq.) in H$_2$O (15 ml and 50 µl conc. HCl) was added

trans-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline-5-ol (50.0 mg, 0.127 mmol, 1.0

eq.), and the temperature was maintained at 100 - 110° C for 24 hrs. A yellow precipitate

formed, which was filtered and washed with plenty of hot H$_2$O (54 %). $^1$H NMR (400

MHz), δ (DMSO-d$_6$, ppm): 9.20 (d, J = 5.49 Hz, 2H) 8.47 (d, J = 7.32 Hz, 1H) 8.38 (d, J =

7.69 Hz, 1H) 7.85, 7.84 (app dd, J$_1$ = 7.32 Hz, J$_2$ = 9.50 Hz, 2H) 7.31 - 7.22 (m, 10H) 6.22

(d, J = 6.96 Hz, 1H) 5.58 (d, J = 6.59 Hz, 1H) 4.31 (d, J = 6.22 Hz, 1H), 3.81 (ABq, J =

13.55 Hz, 2H) 3.67 (Abq, J = 13.55 Hz, 2H) $^{13}$C NMR (100 MHz, DMSO-d$_6$, 25° C) δ

154.5, 153.2, 147.3, 147.2, 140.5, 139.5, 139.4, 137.3, 129.0, 128.9, 128.3, 128.2, 127.7,

66.3, 62.1, 54.6 IR (KBr, cm$^{-1}$) 3443, 2918, 2362, 1635, 1493, 1431, 1076, 803, 754, 722,

701 E.A. calcd. for C$_{26}$H$_{23}$Cl$_2$N$_3$OPt: C, 47.35; H, 3.52; N, 6.37 found C, 47.65; H, 3.49;

N, 6.69 m.p. 250° C.

PtCl$_2$(trans-5-benzylkoxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline) (19)

The following procedure is according to the literature.$^{60, 62}$ To a stirred solution of

K$_2$PtCl$_4$ (34.5 mg, 0.0832 mmol, 0.8 eq.) in H$_2$O (15 ml and 50 µl conc. HCl) was added
trans-5-benzyloxy-6-dibenzylamino-5,6-dihydro-1,10-phenanthroline (50.3 mg, 0.104 mmol, 1.0 eq.), and the temperature was maintained at 100 - 110°C for 24 hrs. A yellow precipitate was formed, which was filtered and washed with copious amounts of hot H2O to give the product as yellow powder (30 %). 1H NMR (400 MHz), δ (DMSO-d6, ppm): 9.55 (d, J= 5.86 Hz, 1H), 9.50 (d, J= 5.13Hz, 1H) 8.08 (d, J= 7.69 Hz, 1H) 7.88 (d, J= 8.42 Hz, 1H) 7.60 - 7. 14 (m, 17H) 5.11 (d, J= 2.92 Hz, 1H) 4.47, 4.46 (m, 3H), 3.56 (ABq, J= 13.91 Hz, 2H) 3.46 (ABq, J= 13.91Hz, 2H) 13C NMR (100 MHz, DMSO-d6, 25°C) δ 153.6, 153.5, 148.2, 148.1, 141.9, 140.8, 139.5, 137.9, 136.2, 134.6, 128.9, 128.9, 128.5, 127.9, 72.2, 70.7, 60.2, 54.9 E.A. calcd. for C33H29Cl2N3OPt; C, 52.88; H, 3.90; N, 5.61 found C, 52.45; H, 3.65; N, 6.01 m.p. 210 - 215°C.
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b.

\[ \text{N, N-} \quad \text{Pt/} \quad \text{(19)} \]

\[ \text{Bn-O} \quad \text{NBn}_2 \]

\[ \text{Cl} \quad \text{Cl} \]