



The asymmetric Rh(I) catalyzed [4+2] cycloisomerization reaction : new homochiral bisphosphine ligands  
by Lydia McKinstry

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry  
Montana State University  
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Abstract:

Intramolecular [4+2] cycloisomerization of ene-dienes and dien-yne was effected with novel Rh(I) templates. The efficiency of cyclization was affected by steric and electronic influences within the ligand sphere. Asymmetric [4+2] cycloisomerization was mediated by Rh(I) complexes modified by ligands. Highly flexible and general procedures for the synthesis of new homochiral bisphosphine ligands have been developed. These new methods were used in the preparation of two generations of carbon-based homochiral bisphosphines. Additionally, a rational approach to the synthesis of a class of homochiral ferrocenyl ligands bearing chirality at phosphorus was introduced.

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APPROVAL  
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Lydia McKinstry

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To Katherine A. and David A. McKinstry  
and Constantine C. Gober

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Abstract

Intramolecular [4+2] cycloisomerization of ene-dienes and dien-yne was effected with novel Rh(I) templates. The efficiency of cyclization was affected by steric and electronic influences within the ligand sphere. Asymmetric [4+2] cycloisomerization was mediated by Rh(I) complexes modified by ligands. Highly flexible and general procedures for the synthesis of new homochiral bisphosphine ligands have been developed. These new methods were used in the preparation of two generations of carbon-based homochiral bisphosphines. Additionally, a rational approach to the synthesis of a class of homochiral ferrocenyl ligands bearing chirality at phosphorus was introduced.

## INTRODUCTION

Current demand for highly enantioenriched biologically active substances, such as pharmaceuticals and pesticides, is exceedingly high. As a result, the demand for efficient synthetic methodologies which can invoke asymmetric selection in chemical transformations is also very high. Presently there are numerous techniques in practice which utilize chiral compounds, as mediators or auxiliaries, to effect such chemical selection. The most common method involves the use of a stoichiometric quantity of a given reagent, for instance a chiral resolving agent. Although this technique has made a significant impact on asymmetric synthesis, it is often disadvantageous because reclamation of the chiral reagent can be both time consuming and costly. Additionally, chiral resolution of a racemic mixture involves the preparation and consumption of *both* the desired and the unwanted enantiomers, rendering the overall process 50% efficient at best. In contrast, the distinguishing feature of a catalyst is the *in situ* reusability of a single molecule. Hence, a single chiral molecule (or a substoichiometric quantity) can generate thousands of chiral products. It is the potential low cost and high efficiency associated with chiral catalysis that has made this methodology particularly attractive for study.

For over three decades, synthetic chemists have participated in the development of homogeneous catalyst

systems that consist of transition metal complexes. The well known Wilkinson's catalyst  $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ , discovered in 1966, is perhaps the most important of these reagents.<sup>1</sup> First used as a homogeneous catalyst for the hydrogenation of olefins, today it is used extensively in many chemical transformations including hydrosilylation, hydroboration, oxidation and double bond isomerization.<sup>2</sup> In order to further the potential of such "Wilkinson-like" complexes, the rhodium center was quickly modified by other alkyl and aryl phosphorus ligands. In fact, the discovery of Wilkinson's reagent initiated extensive research into the catalysis of chemical processes with transition metal-phosphorus complexes.

More importantly, research concerning transition metal catalysts bearing *chiral* phosphine ligands became increasingly widespread. These catalyst systems were designed to effect the stereo- and regiochemical outcome of a wide range of organic reactions. At the forefront of this research was the use of Rh(I)-monophosphine and Rh(I)-bisphosphine catalysts to effect the asymmetric hydrogenation of  $\beta$ -substituted  $\alpha$ -acylaminoacrylic acid derivatives.<sup>3</sup> The successful synthesis of optically pure  $\alpha$ -amino acids constitutes a powerful example of how chiral transition metal complexes could be used as catalysts to generate chiral products.<sup>3</sup>

Popular throughout the last two decades have been investigations of the utility of a vast selection of newly synthesized chiral molecules as ligands for transition metal mediated asymmetric reactions. Much of the current research focuses on the importance of ligand-metal interactions to the efficiency of asymmetric selectivity. These studies should lead to the design of new ligand systems specifically tailored to effect stereocontrol in selected chemical transformations.

Due to our interest in transition metal catalyzed enantioselective processes,<sup>4</sup> the object of the following research was the development of highly flexible and general procedures for the synthesis of three generations of homochiral bisphosphine ligands of determinate structural variation. It was also our goal to determine how ligand structure might influence the efficiency of Rh(I) catalyzed *intramolecular* [4+2] cycloisomerization reactions. In addition, our interest in such ligand-metal interactions led us to an investigation of the stereoinductive strength of several novel homochiral bisphosphine ligands in the Rh(I) catalyzed *asymmetric* [4+2] cycloisomerization of olefins.

## BACKGROUND

A substantial portion of all asymmetric synthesis currently draws upon catalysis with chiral transition metal templates. The employment of this process has become so widespread that it would not be practical to discuss it here in its entirety. The application of asymmetric catalysis to hydrogenation<sup>3</sup> and hydroformylation<sup>7</sup> reactions no longer constitutes the bulk of research into this methodology. In fact, examples of reactions that have more recently been successfully catalyzed by chiral transition metal complexes include hydroboration,<sup>5</sup> double-bond migration,<sup>6</sup> hydrosilylation,<sup>7</sup> hydrocyanation,<sup>8</sup> olefin codimerization,<sup>9</sup> carbon-carbon cross-coupling,<sup>10</sup> cyclopropanation,<sup>11</sup> and epoxidation.<sup>12</sup> As the number of new catalyst systems increases, it is likely that the application of this methodology will continue to expand.

The majority of all the transition metal complexes used in homogeneous catalysis contain manganese, nickel, cobalt, copper, rhodium, ruthenium, palladium or platinum. In addition, although chiral phosphorus ligands are prevalent in these complexes, there are many cases in which amines, amides, alcohols and sulfoxides have proven to be good chiral ligands as well.<sup>13</sup>

## Chiral Phosphine Ligands

The first instance of an optically active phosphorus compound was in 1911, in which Meisenheimer and Lichtenstadt were investigating the bonding properties and stereochemistry of Phosphorus-III, -IV and -V compounds.<sup>14</sup> Despite this early report, it was not until the 1960s that chemists were able to efficiently synthesize compounds containing asymmetric phosphorus atoms.<sup>15</sup> As a result, research into methods for preparing such chiral compounds has increased dramatically over the past two decades.

Chiral phosphines can be divided into three major categories: monophosphines, diphosphines, and polyphosphines. The third category is the youngest of the three and consists mainly of chiral triphosphines, although there have been a few reports on cyclic tetraphosphines.<sup>16</sup> The latter category is omitted from the following discussion.

### Monophosphines

According to Kagan, a chiral monophosphine can contain either a chiral organic unit in the vicinity of an achiral phosphorus (Type I), a chiral phosphorus unit (Type II), or both (Type III) (Figure 1).<sup>13</sup>















































































































































































































































































































































































































































































































































































































































































































































































































