



Reactions of alkyl and alkenyl zirconocene complexes
by Klark Thor Hanson

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemistry

Montana State University

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Abstract:

Zirconacycles have been demonstrated to react sluggishly with acyl chlorides even at elevated temperatures. Studies were undertaken to determine whether or not this reaction could be facilitated via transmetallation of one or both of the carbon-zirconium bonds of the zirconacycle to a more suitable metal. This research demonstrates that zirconacycles will react with acyl chlorides in the presence of secondary metallic reagents. Cuprate reagents and catalytic palladium complexes have been demonstrated to function in this capacity, presumably via stoichiometric and catalytic transmetallation respectively.

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APPROVAL

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Klark Thor Hanson

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Zirconacycles have been demonstrated to react sluggishly with acyl chlorides even at elevated temperatures. Studies were undertaken to determine whether or not this reaction could be facilitated via transmetallation of one or both of the carbon-zirconium bonds of the zirconacycle to a more suitable metal. This research demonstrates that zirconacycles will react with acyl chlorides in the presence of secondary metallic reagents. Cuprate reagents and catalytic palladium complexes have been demonstrated to function in this capacity, presumably via stoichiometric and catalytic transmetallation respectively.

INTRODUCTION

For many years zirconocene reagents have been the subject of extensive study. The wide range of controlled reactivity that these reagents display, coupled with their relatively low cost and toxicity, have made them ideal reagents for many transformations¹. The two most synthetically useful and widely studied classes of reactions involving reagents of this type are the hydrozirconation^{2,3,4} of alkenes and alkynes and the intramolecular reductive coupling of carbon-carbon multiple bonds to form bicyclic products¹ (Figure 1).

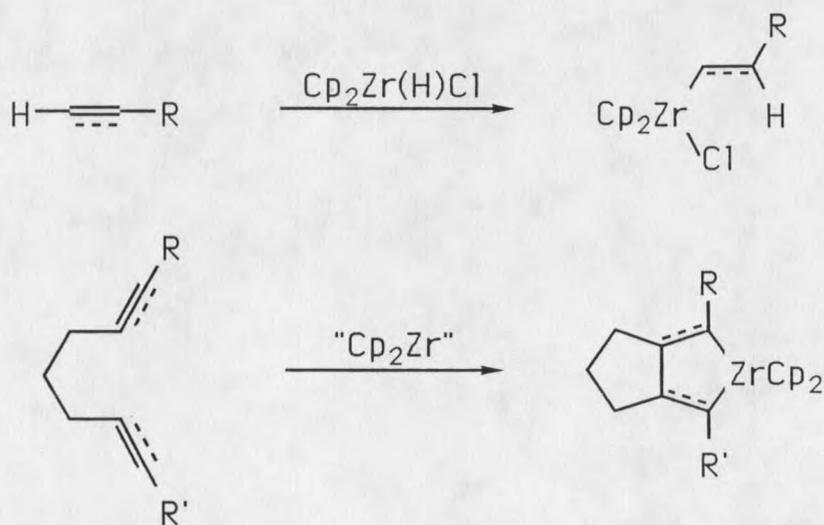


Figure 1. General Zirconium Mediated Processes

Hydrozirconation

Methods

The reagent for effecting hydrozirconation, $\text{Cp}_2\text{Zr(H)Cl}$, is known as Schwartz's reagent². Unfortunately, it readily decomposes when subjected to air or water. It has been shown that Schwartz's reagent can be formed *in situ* by treating zirconocene dichloride with one equivalent of lithium triethylborohydride⁵. This reagent mixture has been shown to give results similar to Schwartz's reagent in many cases but is more desirable than Schwartz's reagent in that it can be prepared immediately before use from readily available and stable precursors. This *in situ* formation of Schwartz's reagent may not always be preferable, however. The presence of stoichiometric quantities of lithium chloride and triethylborane may complicate or impede some processes.

Scope and Limitations

One of the notable factors governing the outcome of these reactions is the propensity of zirconocene to migrate to the terminal carbon during the hydrozirconation of internal, straight chain oleins⁶ (Figure 2).

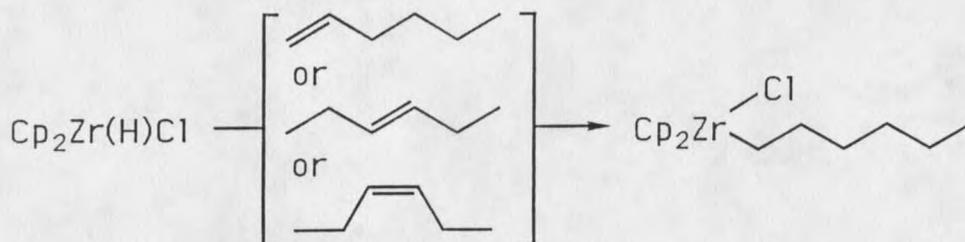


Figure 2. Zirconocene Migration

The order of reactivity for various types of olefins is: terminal > cis internal > trans internal > exocyclic > cyclic, as well as the general trend: monosubstituted > disubstituted > trisubstituted⁷. Tetrasubstituted olefins and trisubstituted cyclic olefins fail to react⁷. Additions to disubstituted alkynes are *cis* with the bulky zirconocene preferring the less hindered terminus⁷. Mixtures of regioisomers readily equilibrate in the presence of a small excess of $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ to a mixture greatly favoring the less hindered product⁷.

Reductive Bicyclization

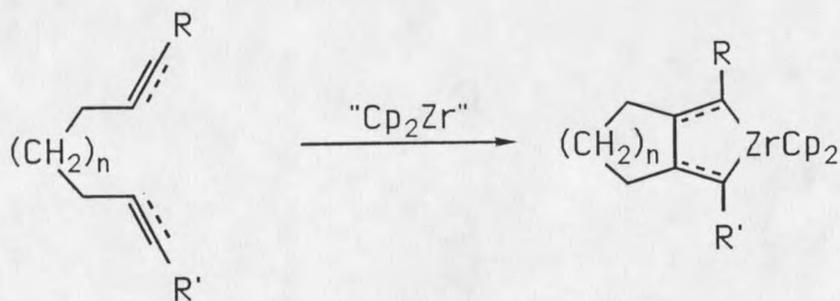
Methods

Intramolecular reductive couplings using zirconocene equivalents are carried out by the *in situ* reduction of zirconocene dichloride by sodium/mercury amalgam⁸, magnesium/mercuric chloride⁹ or, most conveniently, with two

equivalents of *n*-butyllithium followed by reductive elimination of butane¹⁰. The diyne, enyne or diene is then added to this solution and allowed to react to form either the zirconacyclopentadiene, zirconacyclopentene or zirconacyclopentane. Other methods for the *in situ* generation of zirconocene or zirconocene equivalents also exist although they are less frequently applied^{11,12}.

Scope and Limitations

The size of the carbocycle formed can vary from four to seven carbons when coupling diynes to form, following protonation, *E,E* exocyclic dienes¹³. However, dienes^{14,15} and enynes¹⁶ are limited to forming five and six membered carbocycles when reductively coupled (Figure 3).



diyne: $n = 0, 1, 2, 3$
 enyne: $n = 1, 2$
 diene: $n = 1$ (*trans*), 2 (*cis*)

Figure 3. General Intramolecular Reductive Coupling

The stereochemistry of the organic products of diene cyclizations is interesting; when 1,6-heptadiene is cyclized and protonated the product is almost exclusively *trans*-1,2-dimethylcyclopentane (*cis:trans*, 3:97) while 1,7-octadiene affords predominantly *cis*-1,2-dimethylcyclohexane (*cis:trans*, 83:17)^{14,15}. Nugent has shown that by cyclizing 1,6-heptadiene with the reagent formed by treating Cp*ZrCl₃ with sodium/mercury amalgam, *cis*-1,2-dimethylcyclopentanes (*cis:trans*, 99:1) can be formed¹⁴ (Figure 4).

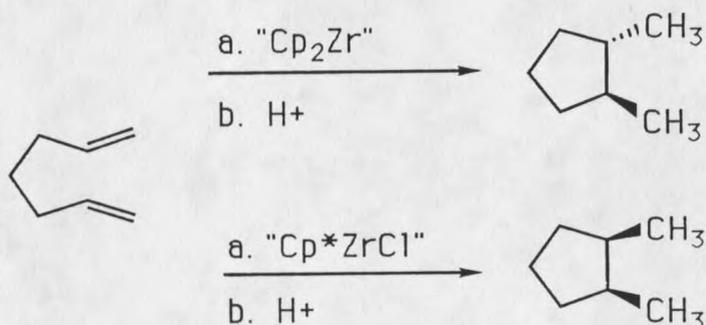


Figure 4. Stereochemistry of Diene Cyclization

These reactions will tolerate a variety of functionality in the precyclic substrate including allylic or propargylic silyl ethers¹⁶, ketals¹⁴, lithium alkoxides^{14,16}, tertiary amines¹, thioethers¹⁶, alkyl silicon, tin and germanium groups¹, and dithio ketals. Nugent¹⁴ and Livinghouse¹⁶ have shown that, when the precyclic diene or

