Communications

1-Zircona-2-cyclohexenes: Novel Synthesis and Preliminary Reactions

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Summary: Six-membered zirconacycles, 1-zircona-2-cyclohexene derivatives, were successfully synthesized via hydrozirconation of C−C double bonds followed by transmetalation. Their chemical properties, including thermal decomposition and carbonylation, were preliminarily studied.

The preparation and reaction chemistry of metallacyclic compounds have attracted much attention in recent years, because many synthetically important transition-metal-assisted reactions proceed via metallacyclic intermediates. As a consequence, metallacyclic compounds have become a large family in organometallic chemistry and are normally generated in situ by a process that involves reductive coupling of two unsaturated organic substrates on a low-valent transition-metal center.[1] In comparison with five-membered metallacycles,[1] relatively fewer reports are known on the preparative methods and reaction chemistry of six-membered metallacycles.[1,2] In general, six-membered metallacycles have been prepared via radical cycloaddition reactions, the reactions of 1,5-dilithium or dimagnesium compounds with metal dihalides, and ring expansion reactions from smaller metallacycles.[2−6] For example, Whitby and co-workers have reported a series of interesting and useful reactions on ring expansion of five- to six-membered zirconacycles by carbenoid insertion.[3]

Hydrozirconation of C−C double bonds has been demonstrated to be a very useful method to afford Zr−C bonds.[7] On the basis of this protocol, followed by transmetalation, as shown in Scheme 1, we have developed a new method to construct zirconacyclohexenes. In this paper we report the preliminary results.

The starting materials, the 1-iodo-1,4-pentadiene derivatives **1a**−**d**, were easily prepared in high yields by following the literature procedure.[8] As demonstrated in Scheme 1, to a suspension of Cp_2ZrHCl (Schwartz reagent) in THF at room temperature was added the 1-iodo-1,4-pentadiene derivative **1a** ($R^1 = R^2 = Bu$), and the reaction mixture was stirred at room temperature for 1 h. This reaction was monitored by GC, which indicated that the diene **1a** disappeared completely within 1 h. Hydrolysis of the reaction mixture afforded the reduced monoiodo compound **3a** in 86% isolated yield. This result

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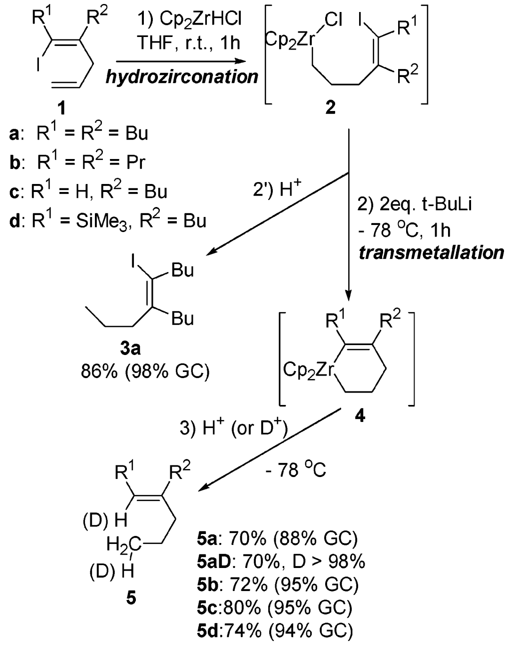
Scheme 1. New Method for the Preparation of Zirconacyclohexenes 4 via Hydrozirconation of Olefin 1 Followed by Transmetalation of 2[a]



[a] Yields given in parentheses are GC yields.

indicated that hydrozirconation indeed took place, as expected, and intermediate **2** must be formed. The in situ generated pale yellow solution of **2** was then cooled down to −78 °C, and 2 equiv of *t*-BuLi was added. The reaction mixture was stirred at the same temperature for 1 h, and the color of the solution changed to brown-red. Hydrolysis of the reaction mixture with 3 N HCl at −78 °C gave the product **5a** in 70% isolated yield (88% GC yield).[9] Products **5b**−**d** were obtained similarly in excellent isolated yields. When the reaction mixture of **1a** was quenched with 20% DCl/D_2O at the same temperature, the dideuterium-substituted compound **5aD** was obtained in 70% isolated yield with a D incorporation of more than 98%.

In addition to the above hydrolysis products, more results have been obtained to support formation of the zirconacyclohexenes **4** and to understand their reaction chemistry. These results also demonstrate that zirconacyclohexenes **4** possess unique properties different from those of five-membered zirconacycles.[1]

First, the intermediate zirconacyclohexene **4a** was found to decompose when the solution temperature was higher than −40 °C.[3j] Products **5a**−**7a** appeared when the reaction mixture was warmed to room temperature and quenched with 3 N HCl (Figure 1); a small amount of a fourth product was also detected, assumed to be **8a** (see Supporting Information). To our surprise, when the reaction mixture was quenched under an N_2 atmosphere, GC-MS analysis showed that product **7a** disappeared, while the amount of product **6a** increased and became a major product. The molar ratio of **5a** to **6a** was 1:3 in 70% combined isolated yield. Pure **6a** was obtained in 42% isolated yield (Scheme 2). This phenomenon indicated that there must be a certain relationship between products **6a** and **7a** and oxygen must play a crucial role in the transformation between precursors of **6a** and **7a**. Indeed, when we admitted oxygen into the reaction vessel, stirred the mixture under an oxygen atmosphere for 1 h, and then quenched it with 3 N HCl, we were delighted to see a complete disappearance of **6a**, resulting in **7a** as the major product (the molar ratio of **7a** to **5a** was 5:4 in 79% combined isolated yield).[10] A proposed reaction mechanism is given in Scheme 2. *β*-H abstraction, which is rare for metallacyclic compounds, might take place to afford **9a**, due to the proper conformation of the six-membered-ring species **4a**.[3j,11,12] Double-bond migration[10,13] and analogous reactions of conjugated diene−zirconocene complexes[14] have been mentioned in the literature by Negishi and co-workers.

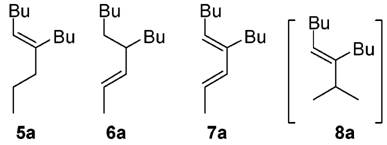
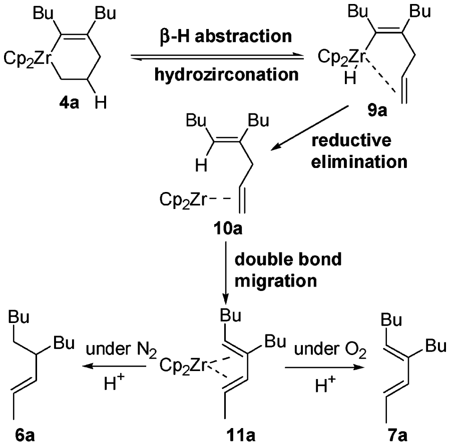
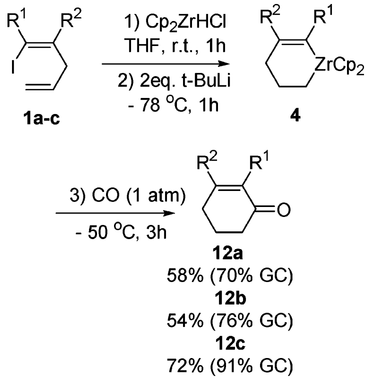


Figure 1. Decomposition of zirconacyclohexene **4a**, to give several products upon hydrolysis.

Scheme 2. Decomposition of Zirconacyclohexene 4a, Proposed To Give the Zirconocene−Diene Complex 11a



Scheme 3. Carbonylation of Zirconacyclohexenes with CO, Affording the Cyclohexenone Derivatives 12



Second, we carried out carbonylation reactions of **4a**−**d** by admitting CO gas into the reaction mixtures. Interestingly, carbonylation reactions of **4a**−**c** took place smoothly to afford their corresponding cyclohexenone derivatives **12a**−**c** in 58% isolated yield (70% GC yield) for **12a**, 54% isolated yield (76% GC yield) for **12b**,[15] and 72% isolated yield (91% GC yield)

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for **12c**, respectively (Scheme 3). No carbonylation reaction was observed for **4d**, for reasons which are not yet clear. These results not only support the formation of the six-membered-ring compound **4** but also provide a good method for the preparation of six-membered cyclic ketones.[16,17] To the best of our knowledge, this is the first example of carbonylation reactions of six-membered zirconacycles affording cyclohexenones.

Further application of this novel synthetic method to six-membered metallacycles and the isolation and further investigation into the chemical properties of zirconacyclohexenes are in progress.

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Supporting Information Available: Text and figures giving experimental details, characterization data, and ^{1}H and ^{13}C NMR spectra for all isolated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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