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Review

Coordination-induced skeletal rearrangements of zirconacyclobutene–silacyclobutene fused complexes

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ABSTRACT

Coordination-induced skeletal rearrangement of transition-metal complexes is of fundamental interest both synthetically and mechanistically. Besides commonly observed ligand substitution, the coordination of ligands may greatly alter the steric and electronic environment around the metal center, thus activating the whole compound, resulting in novel rearrangement or cleavage of chemical bonds. Subsequent formations of chemical bonds would lead to synthetically useful methods for new transition-metal complexes and organic compounds. Zirconacycles have been proved to be very useful for synthetic organic and organometallic chemistry. The present review concentrates on the coordination-induced skeletal rearrangement of zirconacyclobutene–silacyclobutene fused complexes. When treated with nitriles, alkynes, ketones, or other unsaturated organic molecules, the zirconacyclobutene–silacyclobutene fused complexes underwent the coordination-induced rearrangement and new chemical bond forming process, other than the expected direct insertion reactions. Different types of rearrangements were observed depending on the coordinating unsaturated organic molecules. A variety of zirconacycles and organic products were formed efficiently from the zirconacyclobutene–silacyclobutene fused complexes and the unsaturated organic molecules through the coordination-induced rearrangement and new chemical bond forming process.

1. Introduction

Cyclic organometallic compounds (metallacycles) have proved to be prominent in the field of organometallic and coordination chemistry, especially when they are considered as reactive intermediates in metal-promoted or catalyzed reactions [1,2]. Metallacyclobutenes have been proposed as intermediates in

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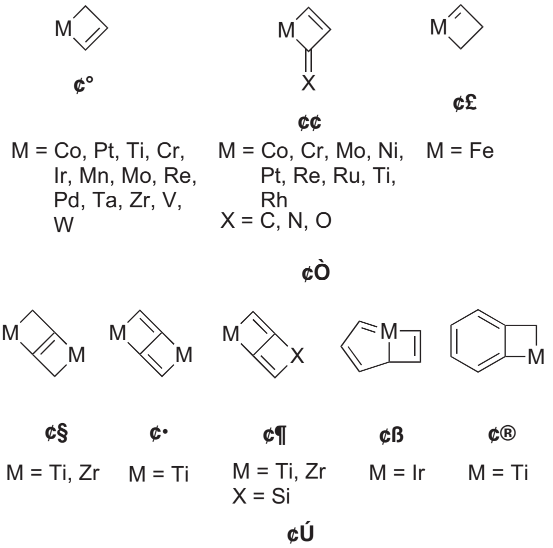
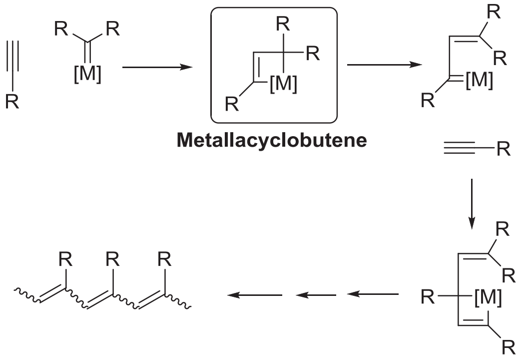


Scheme 1. Two major types of metallacyclobutenes.

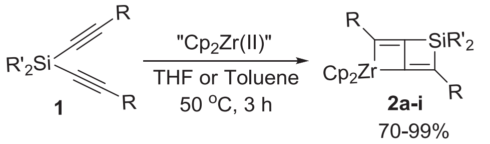


Scheme 2. Metallacyclobutenes in metathesis and polymerization reactions.

numerous metal-catalyzed and promoted reactions [3,4], and have been synthesized based on various pathways, including the [2 + 2] cycloaddition reactions of metal carbene complexes with alkyne, ring-contraction reactions of five-membered metallacycles, oxidative addition reactions of metal complexes into cyclopropene, and radical reactions [5]. Metallacyclobutenes can be divided into two major categories: mono metallacycles (Type I) and fused metallacyclobutenes (Type II). Selected examples are shown in Scheme 1. These two classes of four-membered metallacycles are well investigated and used in a growing number of stoichiometric and catalytic reactions [3,4]. Metallacyclobutenes are involved in processes of metathesis and polymer synthesis (Scheme 2) [6], four-membered heterocyclic synthesis [3c], and ring expansion reactions [3d]. Skeletal rearrangement of metallacyclobutenes may occur upon adding or removing coordinative ligands to/from the metal center, but related reports are rare [3h,4e,4j,4k].

In 1995, Takahashi and co-workers reported the generation of zirconacyclobutene–silacyclobutene fused complexes **2**, from silicon-tethered diynes **1** and low-valent $Cp_2Zr(II)$ species (Scheme 3) [7]. In this process, unexpected skeletal rearrangements occurred to generate the structures which were unambiguously confirmed by single crystal X-ray structural analysis (Fig. 1). Complex **2** is unique for the concomitant presence of two Zr—C bonds and two Si—C bonds in the structure.

Rosenthal and co-workers reported the synthesis of spiro-complexes **4** from the reaction of tetraalkynylsilanes **3** with $Cp_2M(L)(\eta^2\text{-}Me_3SiCCSiMe_3)$(M = Ti, without L, M = Zr, L = THF) (Scheme 4) [8a]. The zirconacyclobutene–silacyclobutene fused complex **2j** could be generated by reductive cleavage and rearrangement of the zirconacyclopentadiene **5** (Scheme 5) [8b].



Scheme 3. Formation of the zirconacyclobutene–silacyclobutene fused complexes **2**.

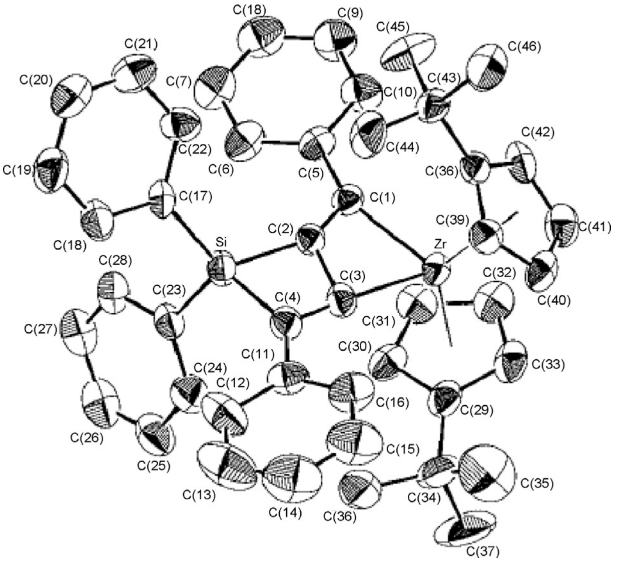
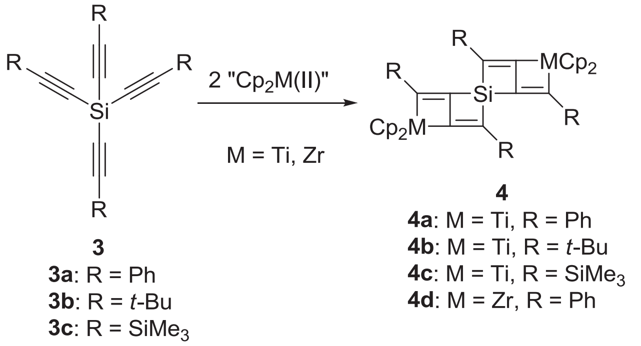
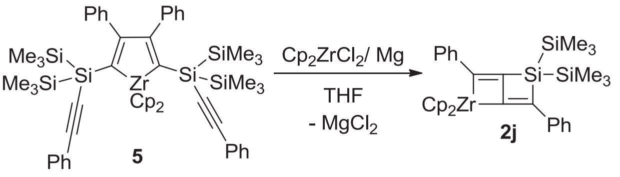


Fig. 1. Molecular structure of a zirconacyclobutene–silacyclobutene fused complex **2** with $(t\text{-}BuC_5H_4)_2Zr$ Moiety. Selected bond lengths [Å]: Zr—C(1) 2.202(4), Zr—C(3) 2.180(4), Si—C(2) 1.883(4), Si—C(4) 1.854(5).



Scheme 4. Reactions of tetraalkynylsilanes with titanocene or zirconocene complexes.

This research group has been studying the reaction chemistry of those zirconacyclobutene–silacyclobutene fused–ring complexes **2a**–**i** shown in Scheme 6 since 2001 [9]. Initially, as our continued interest in the synthetic applications of zirconacycles, we treated complexes **2** with various unsaturated compounds, expecting direct insertion reactions followed by ring-expansion.



Scheme 5. Reductive cleavage and rearrangement of complex **5** to form **2j**.