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Kyoto University
Synthesis of cross-conjugated trienes by rhodium-catalyzed dimerization of monosubstituted allenes

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Full Research Paper

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Abstract
A rhodium(I)/dppe catalyst promoted dimerization of monosubstituted allenes in a stereoselective manner to give cross-conjugated trienes, which are different from those obtained by a palladium catalyst.

Introduction
Cross-conjugated trienes, known as [3]dendralenes [1], are attractive synthetic precursors used for consecutive double [4 + 2] cycloaddition reactions [2-4] to provide a rapid access to polycyclic carbon frameworks. Thus, a number of methods for the preparation of the parent 3-methylenepenta-1,4-diene [5] and its substituted derivatives [6-17] has been developed. Among these, transition-metal-catalyzed dimerization of allenes presents a unique entry to substituted cross-conjugated trienes. For example, a nickel(0)/triphenylphosphine complex catalyzes a dimerization reaction of 3-methylbuta-1,2-diene to afford 2,5-dimethyl-3,4-bismethylenehex-1-ene [18,19]. The nickel-catalyzed reaction, however, leads to a complex mixture of products when monosubstituted allenes such as penta-1,2-diene and 1-phenylpropa-1,2-diene are employed [20]. On the other hand, a palladium-catalyzed dimerization reaction of monosubstituted allenes produces substituted cross-conjugated trienes 2 in high yield (Scheme 1) [21]. We report here that dimerization of monosubstituted allenes is also catalyzed by a rhodium(I)/dppe complex to form cross-conjugated trienes 3, which are different from those obtained with the palladium catalyst.

Results and Discussion
We initiated our study using undeca-1,2-diene (1a) as the model substrate and a rhodium(I) complex as the catalyst (Table 1). When 1a was treated with a catalytic amount of [RhCl(cod)]2 (2.5 mol %, cod = cycloocta-1,5-diene) in toluene at 130 °C for 12 h, 2a was formed in 40% NMR yield along with another minor dimerized product (13% NMR yield) and unidentified...
We propose that the dimerization reaction proceeds through the pathway outlined in Scheme 2. Initially, two molecules of 1a coordinate to a rhodium(I) center at the terminal carbon–carbon double bonds from their sterically less-hindered sides. Oxidative cyclization occurs in a head-to-head manner to form the five-membered rhodacyclic intermediate A [22-25], which is in equilibrium with another rhodacyclic intermediate B via σ–π–σ isomerization. Then, β-hydride elimination takes place with B to form rhodium hydride C stereoselectively. Finally, reductive elimination from C yields 3a together with the catalytically active rhodium(I) complex. It is also conceivable, however, that oxidative cyclization of two molecules of 1a occurs in a tail-to-tail manner to directly furnish B. The other isomer 2a could be formed through allylic 1,3-migration of rhodium from C and subsequent reductive elimination.

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Next, we examined the consecutive double [4 + 2] cycloaddition reaction of the cross-conjugated trienes obtained in the present study. Triene 3a was treated with 4-phenyl-1,2,4-triazoline-3,5-dione (4, PTAD), a highly reactive dienophile, in toluene at 0 °C (Scheme 3). The conversion of 3a was complete within 1 h, and after chromatographic isolation, bisadducts 5a and 5a’ were obtained in 75% and 6% yields, respectively. The major bisadduct 5a resulted from initial addition to the more congested diene moiety of 3a (site β). When tetracyanoethylene (6, TCNE), which was a less reactive dienophile than 4, was used, [4 + 2] cycloaddition also occurred preferentially at site β, but only once on heating at 60 °C for 24 h.

**Conclusion**

In summary, we have developed a new dimerization reaction of monosubstituted allenes catalyzed by a rhodium(I)/dppe complex, allowing the stereoselective formation of substituted cross-conjugated trienes. It is interesting that the rhodium catalyst and the palladium catalyst gave different types of cross-conjugated trienes.

**Experimental**

**General procedure for rhodium-catalyzed dimerization of monosubstituted allenes**

To a side-arm tube equipped with a stirrer bar, was added [RhCl(cod)]2 (4.9 mg, 2.5 mol %) and dppe (7.7 mg, 5 mol %). The tube was evacuated and refilled with argon three times. Then, toluene (4 mL) and substrate 1 (0.4 mmol) were added via syringe and the tube was closed. After heating at 130 °C for 6 h, the reaction mixture was cooled to room temperature, passed through a pad of Florisil® and eluted with ethyl acetate (≈ 90–100 mL). The filtrate was concentrated under reduced pressure and the residue purified by preparative thin-layer chromatography to give product 3. Although the isolated 3 was relatively labile, it could be kept at −30 °C for days without any detectable decomposition or polymerization.
Supporting Information

Supporting Information File 1
Experimental details and spectroscopic data for new compounds.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-67-S1.pdf]

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References


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