

Bicycloaddition of Linear Conjugated Polyenes with Internal Alkynes and the Mechanistic Insights

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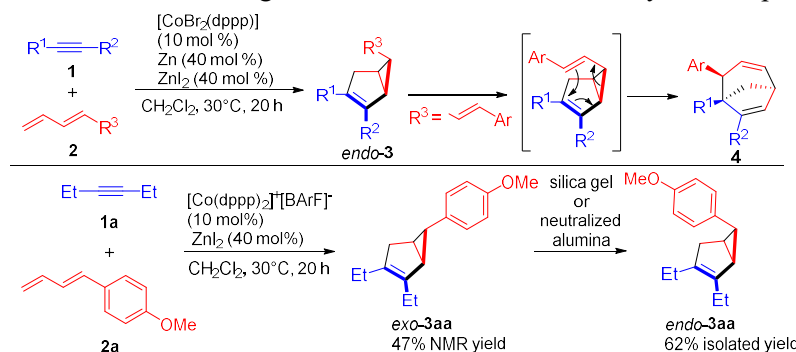
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Keywords: Bicycloaddition; Monovalent Cationic Cobalt Complex; Bicyclo[3.1.0]hex-2-ene; Bicyclo[3.2.1]octa-2,6-diene;

Cross-dimerization of alkynes with conjugated dienes attracted much attention. [CoBr₂(diphosphine)]/Zn/ZnI₂ system catalyzed the [4+2] and [2+2] cycloadditions giving cyclohexenes and alkenylcyclobutenes. In this paper, we disclose the first bicycloadditions of alkynes with conjugated dienes giving bicyclo[3.1.0]hex-2-enes and of alkynes with conjugated trienes giving bicyclo[3.2.1]octa-2,6-dienes.

A cobalt catalyst system [CoBr₂(dppp)]/Zn/ZnI₂ catalyzed diastereoselective bicycloaddition of internal alkynes with conjugated dienes in CH₂Cl₂ at 30°C for 20 h to give bicyclo[3.1.0]hex-2-enes.¹ This is the first bicycloaddition between alkynes and conjugated dienes. To our surprise, a similar treatment of internal alkynes with conjugated trienes produced bicyclo[3.2.1]octa-2,6-dienes as a single diastereomer. This reaction is considered to give *endo*-6-alkenylbicyclo[3.1.0]hex-2-ene as an intermediate followed by the quick and spontaneous vinylcyclopropane rearrangement.

In these catalyst systems, [CoBr₂(dppp)]/Zn/ZnI₂, the initial divalent cobalt species is considered to be reduced by Zn and a cationic monovalent cobalt complex is a possible candidate. Reduction of [CoBr₂(dppp)] with sodium naphthalene followed by the treatment with NaBARF produced a monovalent cationic cobalt complex [Co(dppp)₂]⁺[BARF]⁻ in 36% yield. Treatment of hex-3-yne (**1a**) with (*E*)-1-(4-methoxyphenyl)buta-1,3-diene (**2a**) in the presence of [Co(dppp)₂]⁺[BARF]⁻ (10 mol%)/ZnI₂ (40 mol%) at 30°C for 20 h in CH₂Cl₂ produced *exo*-2,3-diethyl-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-2-ene (*exo*-**3aa**) as a single diastereomer, which isomerized to *endo*-2,3-diethyl-6-(4-methoxyphenyl)bicyclo[3.1.0]hex-2-ene (*endo*-**3aa**) during purification using a silica gel or neutralized alumina. We will discuss about the detailed mechanistic insight for the formation of these bicyclic compounds.



1) Y. Tomita, N. Haraguchi, S. Kiyota, N. Komine, M. Hirano, *Org. Lett.* **2022**, 24, 7774.