



# A practical ruthenium based catalytic system bearing a switchable selectivity between the dimerization and cyclotrimerization reactions of alkynes

Bengi Özgün Öztürk, Solmaz Karabulut\*, Yavuz İmamoğlu

Hacettepe University, Department of Chemistry, 06800 Beytepe, Ankara, Turkey

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## ABSTRACT

In this study, a practical and inexpensive switchable catalytic system (cyclotrimerization vs. dimerization),  $[\text{RuCl}_2(\text{p-cymene})]_2/\text{PR}_3$  has been developed for the catalytic dimerization of terminal alkynes. Bulky and basic phosphine derivatives,  $\text{PCy}_3$  and  $\text{P}(\text{i-Pr})_3$ , were used with  $[\text{RuCl}_2(\text{p-cymene})]_2$  and excess of terminal alkyne to in situ formation of vinylidene intermediates which are active towards dimerization reactions. Effect of phosphine/ruthenium ratio has been investigated. A solvent study was carried out and toluene was found to be the most versatile solvent for both cyclotrimerization and dimerization reactions. A set of aryl and alkyl acetylenes were chosen as substrates to investigate the effect of the nature of the substrates on alkyne dimerization reactions catalyzed by  $[\text{RuCl}_2(\text{p-cymene})]_2/\text{PR}_3$ . In conclusion, we have shown that  $[\text{RuCl}_2(\text{p-cymene})]_2/\text{PCy}_3$  can be used as a practical and inexpensive catalytic system which has a switchable selectivity towards cyclotrimerization and dimerization reactions. Best results in means of regioselectivity and yield were observed by using arylacetylene derivatives in these reactions. This catalytic system emerges as an economical method for the transformation of arylacetylenes to corresponding enyne and arene derivatives in excellent yields and selectivity.

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## 1. Introduction

Transition metal catalyzed carbon–carbon bond formation reactions have proven to be highly selective, and atom-economical synthetic methods have been used to obtain novel organic intermediates which cannot be obtained by other means [1]. Alkynes undergo a great diversity of reactions in the presence of transition metal catalysts, thus making them good candidates as starting materials for the synthesis of both organic and organometallic substances [2]. The catalytic conversion of alkynes yields important organic intermediates like enynes, enol-esters and arene derivatives [3].

Alkyne dimerization reactions are of essential importance because the resulting enyne substructures are important building blocks for organic synthesis and are significant components in various biologically active compounds [4]. Enynes are also potential candidates for making conjugated and light-emitting polymers [5]. It has been reported that enynes can also be used for alkyne dimerization reactions form several possible isomers, among them, (Z)- $\text{RCH}=\text{CH}-\text{C}\equiv\text{CR}$ , (E)- $\text{RCH}=\text{CH}-\text{C}\equiv\text{CR}$  and (gem)- $\text{H}_2\text{C}=\text{CR}-\text{C}\equiv\text{CR}$  are the most common ones. For real and practical applications, one desires a process that exhibits both high

regio- and stereoselectivity towards one isomer. To date, several transition metal complexes have been reported to catalyze the dimerization reactions of alkynes in a selective manner [6]. Among these transition metals, recent studies have focused on ruthenium complexes because they exhibit high functional group tolerance and a wide range of oxidation states and coordination geometries, providing unique properties for catalysis [2a]. A wide range of very different (mechanistically) processes are catalyzed by ruthenium complexes using these unique properties. Each carbon–carbon bond forming reaction has a unique intermediate and mechanism. For example, alkyne dimerization reactions are known to be catalyzed by the formation of vinylidene or acetylidene intermediates [7], whereas inter- or intramolecular [2 + 2 + 2] cyclotrimerization reactions of alkynes proceed by the formation of a metallocyclopentadiene intermediate [8] or in the presence of a metal alkyldiene moiety, the reaction proceeds via cascade metathesis reactions [9].

Due to the growing interest in this field, several research groups have focused their attention on the dimerization reactions of terminal alkynes catalyzed by various ruthenium complexes [10]. Pavlik et al. reported the activity of neutral ruthenium vinylidene  $\sigma$ -alkynyl complexes on alkyne dimerization reactions [11]. Katayama and Ozawa [12] reported an efficient protocol to convert  $[\text{RuCl}_2(\text{p-cymene})]_2$ , in the presence of basic and bulky phosphine ligands and terminal alkynes, to corresponding ruthenium vinylidene complexes with the general formula  $\text{RuCl}_2\{\text{C}=\text{C}(\text{E})\text{R}\}(\text{L})_2$ , where  $\text{E}=\text{H}$ ;  $\text{R}=\text{Ph}$ , and  $\text{Fc}$ ,  $\text{t-Bu}$  and  $\text{L}=\text{PCy}_3$  and  $\text{P}(\text{i-Pr})_3$ . These

\* Corresponding author. Tel.: +90 312 297 60 82; fax: +90 312 299 21 63.  
E-mail address: [solmazk@hacettepe.edu.tr](mailto:solmazk@hacettepe.edu.tr) (S. Karabulut).