



## Catalytic transformation of phenylacetylene mediated by phosphine-free ruthenium alkylidene complexes



Izabela Czeluśniak<sup>a,\*</sup>, Jarosław Handzlik<sup>b</sup>, Maciej Gierada<sup>b</sup>, Teresa Szymańska-Buzar<sup>a</sup>

<sup>a</sup> Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

<sup>b</sup> Faculty of Chemical Engineering and Technology, Cracow University of Technology, ul. Warszawska 24, 31-155 Kraków, Poland

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### ABSTRACT

Phosphine-free ruthenium alkylidene complexes,  $[\text{RuCl}_2(=\text{CH}-o\text{-O}^i\text{PrC}_6\text{H}_4)(\text{IMesH}_2)]$ ,  $[\text{Ru}(\text{CF}_3\text{CO}_2)_2(=\text{CH}-o\text{-O}^i\text{PrC}_6\text{H}_4)(\text{IMesH}_2)]$ , and  $[\text{RuCl}_2(=\text{CHPh})(3\text{-Br-py})_2(\text{IMesH}_2)]$ , were found as catalyst precursors for non-metathesis transformations of phenylacetylene, e.g. cyclotrimerization and dimerization. Selective product formation was affected by modulating the coordination sphere of the catalyst and temperature. An NMR study under various experimental conditions and DFT calculations taken together permitted the conclusion that the degradation of the alkylidene complex took place in the initial step, regardless of the manner of alkyne addition.

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### Introduction

Alkynes are highly reactive building blocks in organic synthesis. They are able to take part in a large number of reactions with transformation of the triple bond. Two examples of the transformation of the terminal alkyne, cyclotrimerization and dimerization, are particularly important since their products can be used as precursors for the synthesis of complex compounds, including natural products [1].

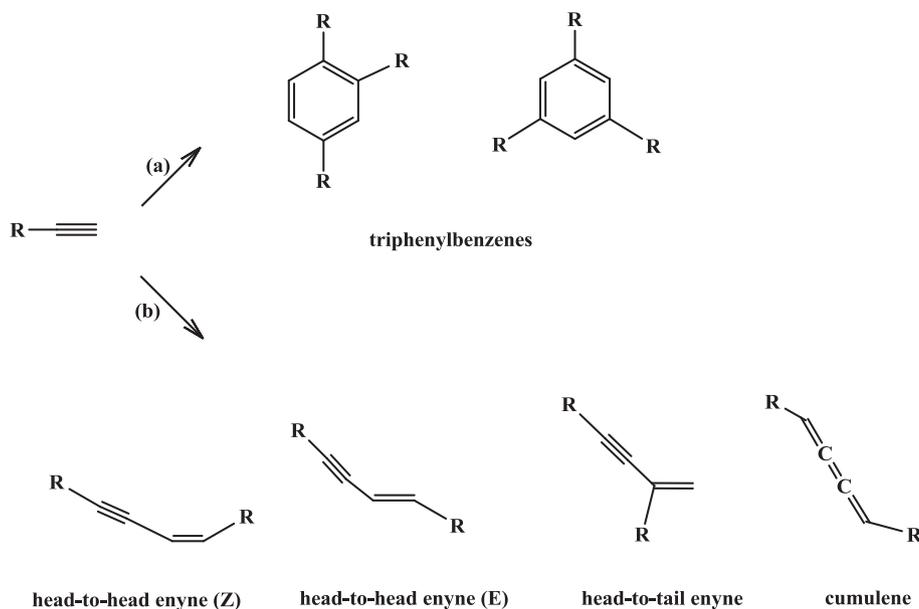
The cyclotrimerization of alkynes catalyzed by transition metals has been recognized as a versatile synthetic approach for highly substituted benzene derivatives [1,2]. A number of homogeneous catalysts mainly containing d-block metals [3–15] have been designed for this transformation. Among them, ruthenium catalysts play an important role due to their functional group tolerance. There are several reports on the catalytic activity of ruthenium complexes toward intra- and intermolecular [2+2+2] cyclizations [8–15]. It has been shown that triynes can isomerize to benzene derivatives using a first-generation Grubbs catalyst,  $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(=\text{CHPh})]$  [9,10]. Alkylidene ruthenium compounds have also been used for crossed [2+2+2] cyclizations of diynes with 1-alkynes [11,12] and

nitriles [13]. Although so far there have been few precedents of the use of alkylidene ruthenium precatalysts to mediate intermolecular cyclotrimerization reactions for the synthesis of the benzene ring [14,15] (Scheme 1, path a), these complexes have received much attention as excellent catalysts for the dimerization of alkynes (Scheme 1, path b) [16–19]. Verpoort et al. reported the unusual catalytic activity of a first-generation Grubbs precatalyst toward the dimerization of phenylacetylene at an elevated temperature [16–18]. The thermal treatment of  $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(=\text{CHPh})]$  in the presence of phenylacetylene leads to the formation of a Ru-vinylidene complex, an excellent precursor for the selective head-to-head addition of terminal alkynes [18]. Vinylidene ruthenium complexes containing bulky electron-donating ligands (e.g. tris(-pyrazolyl)borate or pentamethylcyclopentadienyl) catalyze the dimerization of terminal alkynes into enynes very easily [20,21]. The postulated pathway proceeds via a metal vinylidene species resulting from the isomerization of an  $\eta^2$ -coordinated alkyne [18,22–24]. The migration of the other alkynyl ligand onto the  $\alpha$ -carbon atom of the vinylidene one generates an enynyl ligand which is removed by protonolysis to afford enyne.

However, in the case of cyclotrimerization mediated by alkylidene ruthenium compounds, the mechanism of the reaction should be quite different, and a vinyl carbene complex is postulated as the reactive intermediate of this reaction [9]. Although according to the literature [9,18] the cyclotrimerization and dimerization pathways

\* Corresponding author. Tel.: +48 71 3757 278; fax: +48 71 3282 348.

E-mail address: [izabela.czelusniak@chem.uni.wroc.pl](mailto:izabela.czelusniak@chem.uni.wroc.pl) (I. Czeluśniak).



**Scheme 1.** Two examples of transformation of the terminal alkynes: intermolecular [2+2+2] cyclization (path **a**) and dimerization (path **b**).

are not similar, the complex  $[Cl_2(PCy_3)_2Ru(=CHPh)]$  was reported as an efficient precatalyst for both reactions [9,16–18]. It should, however, be pointed out that Tagliatesta et al. have suggested that vinylidene derivatives are also involved in the formation of cyclo-trimerization products [25].

On the other hand, second-generation ruthenium alkylidene catalysts have also been reported as initiators mediating the hydrosilylation of alkynes [26], the polymerization of *ortho*-substituted phenylacetylenes [27], hydroxyacetylenes [28], and 1,6-heptadiynes [29]. Although second-generation phosphine-free ruthenium catalysts have been reported as inactive in the dimerization of silylacetylenes [19], to the best of our knowledge those complexes have not been used as catalysts for the intermolecular cyclo-trimerization of 1-alkynes.

These results tempted us to investigate the catalytic properties of second-generation phosphine-free ruthenium alkylidene catalysts: a Hoveyda–Grubbs complex (**A**) and its analogue modified by trifluoroacetate (**B**), and the second-generation Grubbs catalyst modified by 3-bromopyridine (**C**), with regard to the non-metathesis transformation of phenylacetylene, e.g. cyclo-trimerization and dimerization (Fig. 1). Because the selectivity of the reactions depends on the intermediates formed by the substrate and the transition metal species, we monitored the reaction between phenylacetylene and complex **C** by means of  $^1H$  NMR spectroscopy in order to obtain more information about the catalytically active species formed in the initiating step of alkyne

transformation. Some mechanistic aspects of initiation were also elucidated with quantum mechanical calculations.

## Experimental

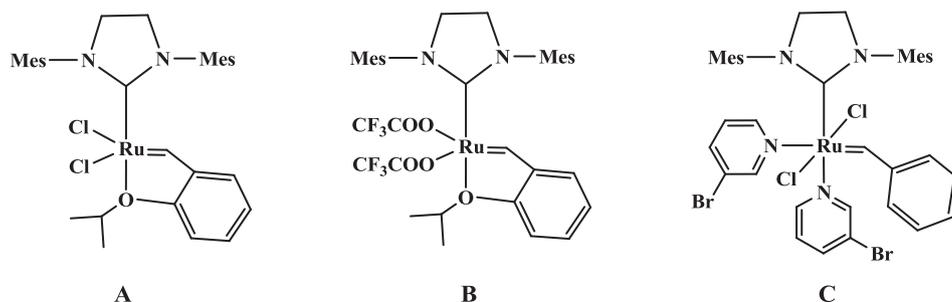
### General

The reactions were carried out under nitrogen using the conventional vacuum/nitrogen line or glove-box techniques. NMR spectra were recorded using a Bruker AMX-300 and 500 spectrometers. All chemical shifts are referenced to residual solvent protons for  $^1H$  NMR ( $\delta$  7.24 chloroform- $d_1$ ; 2.09 toluene- $d_8$ ; 7.16 benzene- $d_6$ ; 5.32 dichloromethane- $d_2$ ) and to the chemical shift of the solvent for  $^{13}C$  NMR ( $\delta$  77.00 chloroform- $d_1$ ).

Mass Spectra were collected on the Hewlett–Packard GC-MS system containing an HP 5890II gas chromatograph equipped with a HP-5MS column (25 mm  $\times$  0.2 mm  $\times$  0.33  $\mu$ m) and an HP 5971A mass detector. Helium was used as the gas carrier. The initial temperature in the column was 70  $^\circ C$ , then increased at 25  $^\circ C$  per min to 290  $^\circ C$  and maintained for 10 min.

### Materials

$[RuCl_2(=CH-o-PrC_6H_4)(IMesH_2)]$  (2nd generation Grubbs–Hoveyda catalyst) (**A**) (Sigma–Aldrich) and triphenylphosphine ( $PPh_3$ ) (Sigma–Aldrich) was used as received.  $[Ru(CF_3CO_2)_2(=CH-$



**Fig. 1.** Phosphine-free second generation ruthenium alkylidene complexes.

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