

New Ru (II)-Catalyzed Cycloaddition Reactions of *o*-(Alkenyl)phenylacetylenes

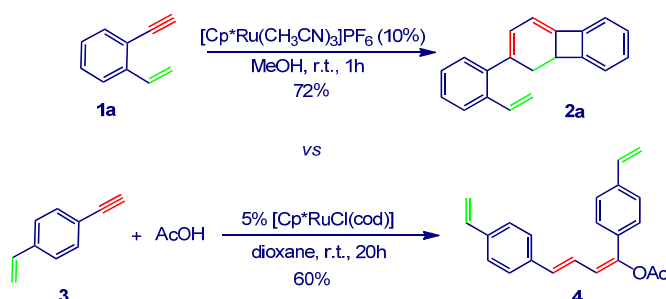
Silvia García-Rubín, Jesús A. Varela and Carlos Saá*

Departamento de Química Orgánica y Centro Singular de Investigación en Química Biológica y Materiales Moleculares (CIQUS).
Universidad de Santiago de Compostela. CP: 15782 Santiago de Compostela, Spain
silvia.garcia@usc.es

Cycloaddition vs Linear Coupling Reactions

In our reserch group, we have recently discovered a new Ru-catalyzed [2+2+2] cycloaddition reaction of *o*-(alkenyl)phenylacetylenes **1a** to give dihydrobiphenylenes **2a**, interesting dimeric structures with a central four-membered ring.

The presence of an alkene *ortho* to the alkyne demonstrated to be crucial for the course of the reaction. In fact, Dixneuf reported that *p*-(alkenyl)phenylacetylenes **3** led to 1,3-dienylacetates **4** through ruthenium-catalyzed linear coupling of the alkynes with incorporation of AcOH.¹

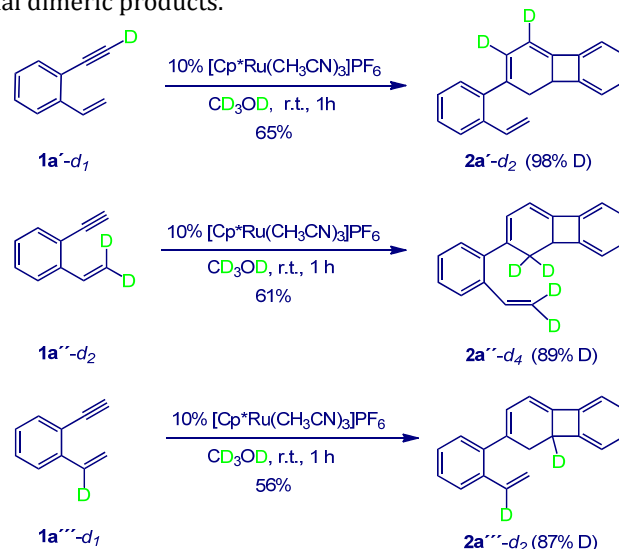


Ru (II)-Catalyzed Cycloaddition Reactions of *o*-(Alkenyl)phenylacetylenes

Substituted 1-ethynyl-2-vinylbenzenes **1** have also participated in the cycloaddition reaction to give the corresponding dihydrobiphenylenes **2**. Also 1-ethynyl-2-allylbenzene **5** gave dihydrofluorene **6** in moderate yield.

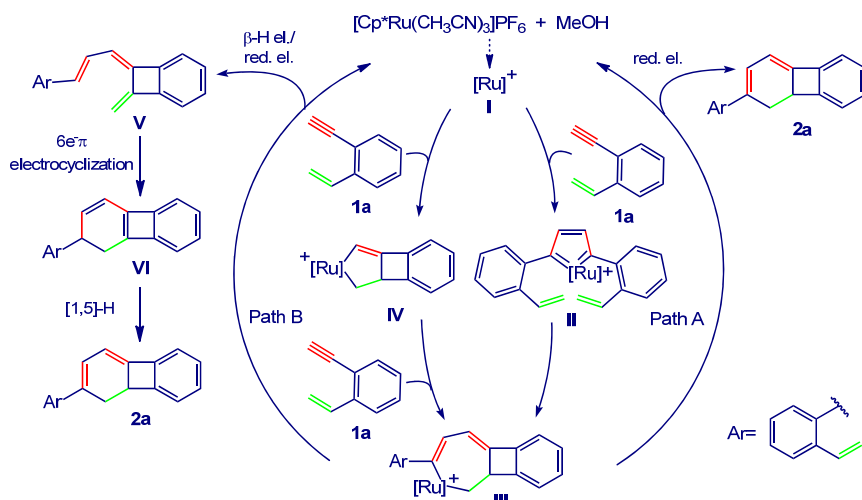
Entry	Substrate	Product	Yield (%)
1			55%
2			63%
3			33%

Deuterium labelling experiments show that the hydrogen of ethynyl and vinyl groups remain in the same position in the final dimeric products.



Mechanistic Proposal

Intermolecular oxidative coupling of two alkyne units to the ruthenium cationic species **I** (formed "in situ" by reaction of the initial catalytic ruthenium complex with methanol) followed by insertion of one vinyl group would afford the ruthenacycloheptadiene **III**. Formation of **III** through intramolecular oxidative coupling of **1a** followed by insertion of an alkyne can not be ruled out. Reductive elimination from **III** would afford the observed product **2a** (Path A). The alternative β -hydride elimination followed by $6e\pi$ electrocyclization and [1,5]-H shift (Path B) can be discarded due to the formation of **2c** from **1c** having a methyl group in the internal vinyl position.



Acknowledgement: This work was supported by the MICINN (CTQ2008-06557), Consolider Ingenio 2010 (CSD2007-00006) and the Xunta de Galicia (2007/XA084 and INCITE08PXIB209024PR). S. G-R. also thanks the M.E.C. for a FPU fellowship.

References: ¹ Le Paith, J.; Monnier, F.; Dérien, S.; Dixneuf, P. H.; Clot, E.; Eisenstein, O. *J. Am. Chem. Soc.* **2003**, *125*, 11964-11975.