



Carlos González-Rodríguez, Jesús A. Varela, Luis Castedo, Carlos Saá*

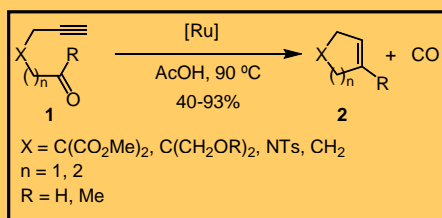
Departamento de Química Orgánica, Facultad de Química,

Universidad de Santiago de Compostela, 15782 Santiago de Compostela, Spain

carlos.gonzalez.rodriguez@usc.es; carlos.saa@usc.es

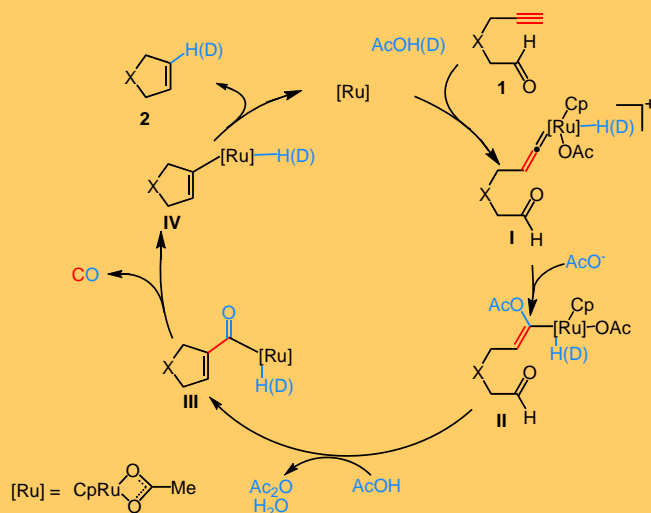
•Decarbonylative cyclization of terminal alkynals

We have recently described the Ru-catalyzed decarbonylative cyclization of terminal 5- and 6-alkynals and 5-alkynones 1 to cycloalkenes 2 in moderate to excellent yields (Scheme 1).¹



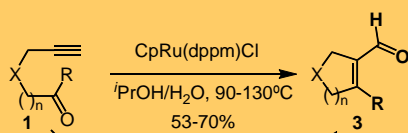
Scheme 1

The likely mechanism of the cyclization involves the formation of Ru(II) vinylidene species I,² which upon nucleophilic addition of the acetic acid affords the vinyl Ru species II. Next, an aldol-type condensation gives the acyl Ru-hydride III, which after decarbonylation followed by reductive elimination affords the observed cycloalkenes 2 (Scheme 2).



Scheme 2

•Cycloisomerization of terminal alkynals



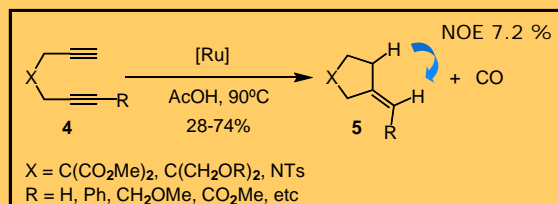
Cycloisomerization of alkynals and alkynones 1 to α,β -unsaturated aldehydes 3 was achieved using CpRu(dppm)Cl as catalyst (Scheme 3). In this case no decarbonylation takes place due to the bidentate nature of dppm ligand, being favored the reductive elimination of III'.

X = C(CO₂Me)₂, etc
n = 1, 2
R = H, Me

Scheme 3

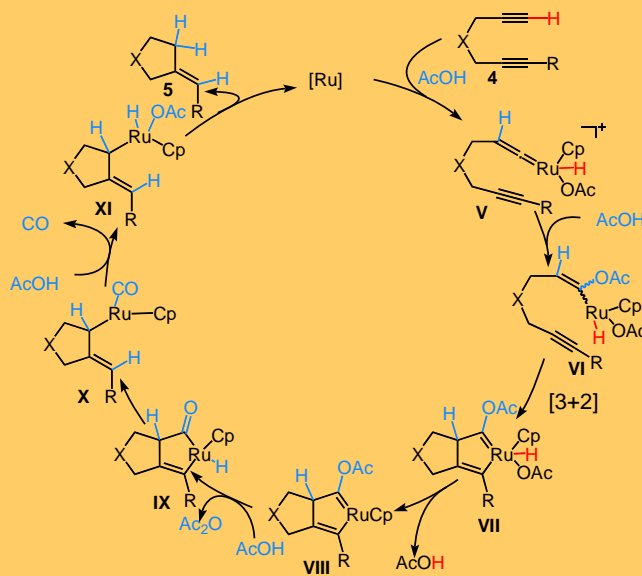
•Decarbonylative cyclization of 1,6-diynes

When 1,6- terminal and monosubstituted diynes 4 were subjected to the Ru/AcOH conditions, *exo*-alkylidenecyclopentane derivatives 5 were obtained in moderate to good yields.³



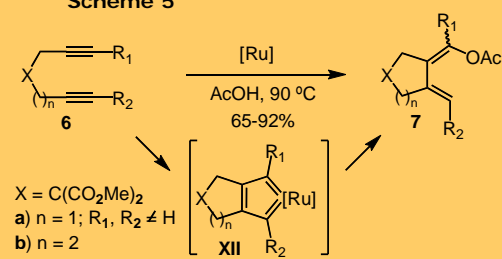
Scheme 4

The proposed mechanism starts with the formation of ruthenium vinylidene V which undergoes nucleophilic addition of AcOH to afford vinyl Ru-hydride VI which, through a [3+2]-type cycloaddition, leads to cyclic carbene Ru-hydride VII. Reductive elimination of AcOH to cyclic carbene VIII, followed by another nucleophilic attack of AcOH gives acyl Ru-hydride IX. Reductive opening of the ruthenacycle IX followed by oxidative addition of AcOH with concomitant decarbonylation of X leads to the Ru-hydride XI, which after reductive elimination affords the observed cyclopentane derivatives 5 (Scheme 5).



Scheme 5

When disubstituted 1,6-diynes 6a or 1,7-diynes 6b were used, dienylacetates 7 were obtained by trapping ruthenacycle-biscarbene⁴ intermediate XII with AcOH (Scheme 6).



Scheme 6

Acknowledgement: This work was supported by the M.E.C. (CTQ2005-08613), Consolider Ingenio 2010 (CSD2007-00006) and the Xunta de Galicia (2007/XA084). C.G.R. and J.A.V. also thanks the M.E.C. for a FPI fellowship and a Ramón y Cajal research contract, respectively.

References: ¹ Varela, J. A.; González-Rodríguez, C.; Rubín, S. G.; Castedo, L.; Saá, C. *J. Am. Chem. Soc.* 2006, 128, 9576.

² Tokunaga, M.; Suzuki, T.; Koga, N.; Fukushima, T.; Horiuchi, A.; Wakatsuki, Y. *J. Am. Chem. Soc.* 2001, 123, 11917.

³ González-Rodríguez, C.; Varela, J. A.; Castedo, L.; Saá, C. *J. Am. Chem. Soc.* 2007, 129, 12916.

⁴ a) LePaih, J.; Monnier, F.; Derien, S.; Dixneuf, P. H.; Clot, E.; Eisenstein, O. *J. Am. Chem. Soc.* 2003, 125, 11964. b) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* 2003, 125, 11516.

