"Formal"-Ru(II) Catalyzed Cycloadditions of 1,6-Diynes to Arenealkylidenes

Silvia G. Rubín, Jesús A. Varela, Luis Castedo and Carlos Saá*

Departamento de Química Orgánica y Unidad Asociada al CSIC, Facultad de Química, Universidad de Santiago de Compostela

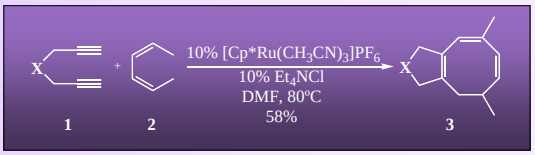
15782 Santiago de Compostela, Spain

qocsaa@usc.es

"Formal"-Ru (II) catalyzed cycloadditions

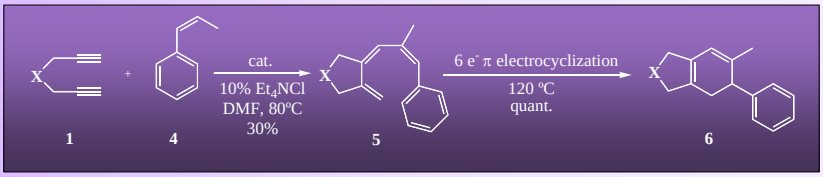
Transition-metal-catalyzed cycloadittion reactions constitute powerful methods for the construction of complex polycyclic systems[1]

We recently described a new "formal" ruthenium-catalyzed [4+2+2] cycloaddition of 1,6-diyne **1** to *cis,cis*-1,4-disubstituted conjugated dienes **2** to give conjugated 1,3,5-cyclooctatrienes **3**.[2]

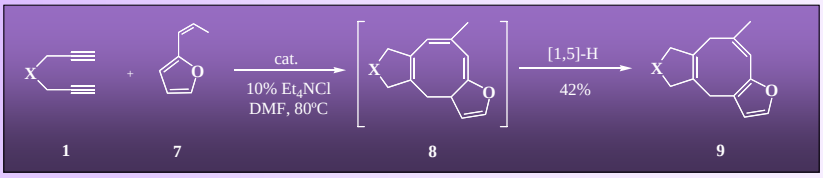


When arenealkylidenes were used as dienes in the "formal" ruthenium-catalyzed [4+2+2] cycloaddition, different cycloadducts were obtained according to the aromatic diene:

In the case of the styrene **4**, aryltriene **5** was obtained, which was cycliced to arylciclohexadiene **6** upon heating.



However, when propenylfurane **7** was used, the cyclooctatriene **9** was obtained as a sole product. Most probably, compound **8** could be the initial product of the "formal" [4+2+2] cycloaddition, followed by a [1,5]-hydrogen shift to the final product **9**.



X = $C(CO_2Me)_2$
cat = 10% $[Cp^*Ru(CH_3CN)_3]PF_6$

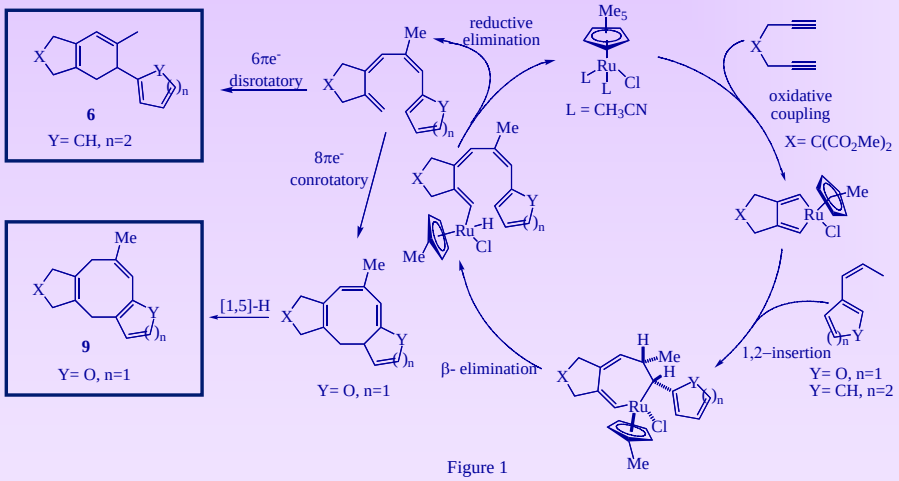
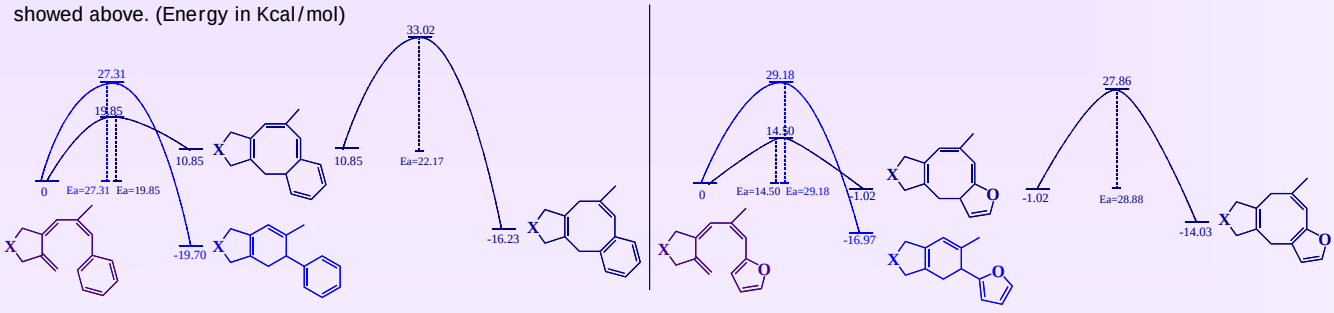


Figure 1

The observed products and the position of the double bonds could be explained if the mechanism showed in the **figure 1** is operating.

The energy surfaces theoretically calculated for these "formal" cycloadditions reactions agree with the experimental results showed above. (Energy in Kcal/mol)



Acknowledgement: This work was supported by the Ministerio de Ciencia y Tecnología (Project BQU2002-02135). J.A.V. also thank the M.C.Y.T. for a research contract under the Ramón y Cajal program.

References: [1] (a) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49; (b) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635.

[2] Varela, J. A.; Castedo, L.; Saá, C. *Org. Lett.* , **2003**, *5*, 2841.