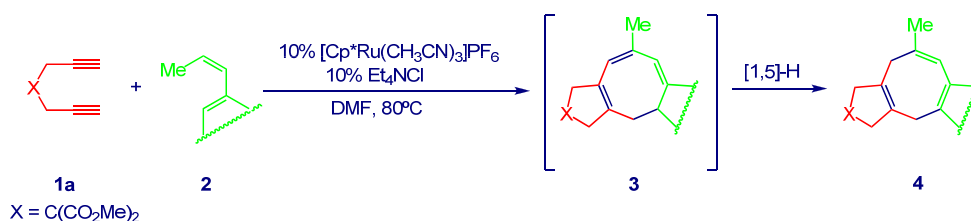


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## "Formal" Ruthenium-Catalyzed [4+2+2] Cycloaddition of 1,6-Diynes to *cis*-Propenylheteroarenes

We have recently developed a new "formal" Ru-catalyzed [4+2+2] cycloaddition between 1,6-diynes **1** to aliphatic *cis*-1,3-dienes **2** to afford 1,3,5-cyclooctatrienes **3**.<sup>1</sup> When *cis*-propenylheteroarenes **2** were used, heterofused cyclooctatrienes **4** were obtained in moderate to good yields.

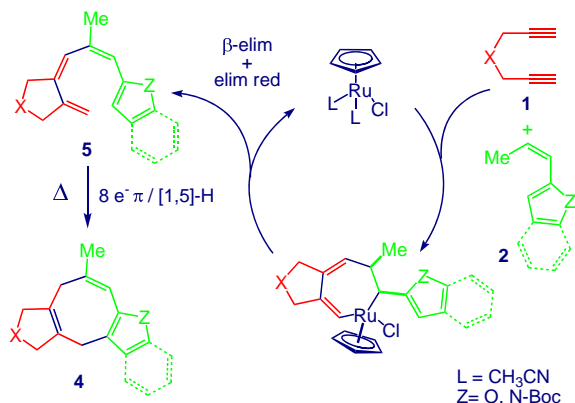


Heteroarene	Product	Yield %
		52
		66
		54

Heteroarene	Product	Yield %
		72
		38
		41

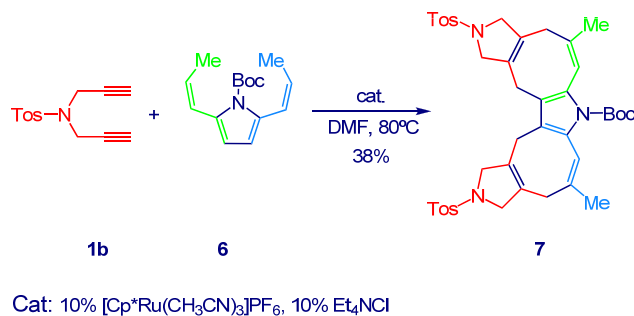
### Mechanism

A plausible mechanism involves the initial Ru-catalyzed linear coupling between diynes **1** and the alkene of heteroarenes **2** to give 1,3,5-hexatrienylheteroarenes **5**. Finally, thermal conrotatory  $8e^- \pi$  electrocyclization of **5** followed by a [1,5]-hydrogen shift affords cyclooctatrienes **4**.



### Double "Formal" [4+2+2] Cycloaddition Reaction

Double Ru-catalyzed cascade reaction of diyne **1b** with bis-propenylpyrrole **6** gives rise to the polycyclic pyrrole derivative **7**, in which pyrrole units are fused to cyclooctene rings.



**Acknowledgements:** This work was supported by the M.E.C. (CTQ2005-08613 and CTQ2008-06557), Consolider Ingenio 2010 (CSD2007-00006) and by the X.U.G.A (2007/XA084 and INCITE08PXIB209024PR). S.G.R. and J.A.V. thanks the M.E.C. for a FPU fellowship and a Ramón y Cajal research contract, respectively.

**References:** <sup>1</sup> J.A. Varela, L. Castedo, C. Saá, *Org. Lett.* **2003**, *5*, 2841.