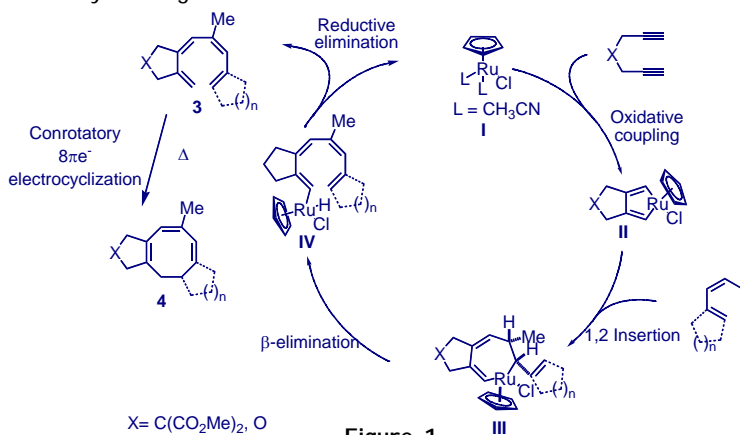


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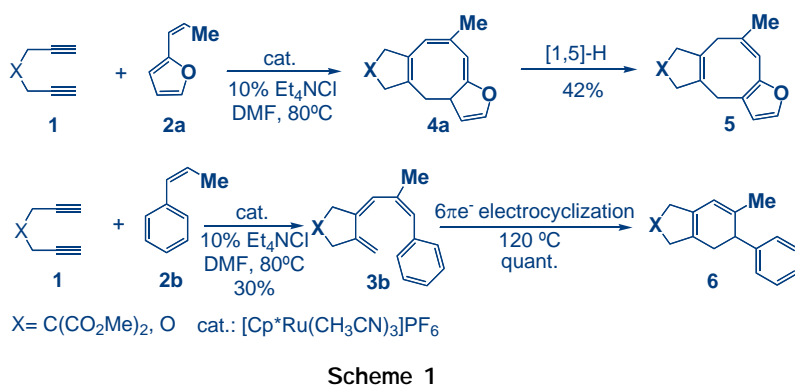
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## "Formal" Ru (II)-Catalyzed [4+2+2] Cycloadditions of 1,6-Diynes to 1,3-Dienes

We recently described a new "formal" ruthenium-catalyzed [4+2+2] cycloaddition of 1,6-diynes to 1,3-dienes to give conjugated 1,3,5-cyclooctatrienes.<sup>1</sup> Their formation could be explained in two steps: initial formation of tetraenes **3** according to the metal-catalyzed cycle showed in **Figure 1** followed by thermal conrotatory electrocyclic ring closure of **3**.

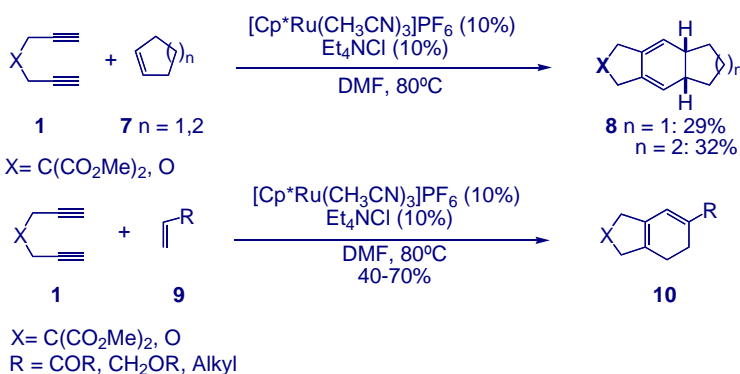


Interestingly, when *cis*-propenylfuran **2a** was used, the tricyclic cyclooctatriene **5** was obtained in acceptable yield. The reaction occurs by initial formation of **4a** followed by a [1,5]-hydrogen shift. However, in the case of the styrene **2b**, the opened aryltriene **3b** was initially obtained, which was quantitatively cyclized to arylcyclohexadiene **6** upon heating (**Scheme 1**).

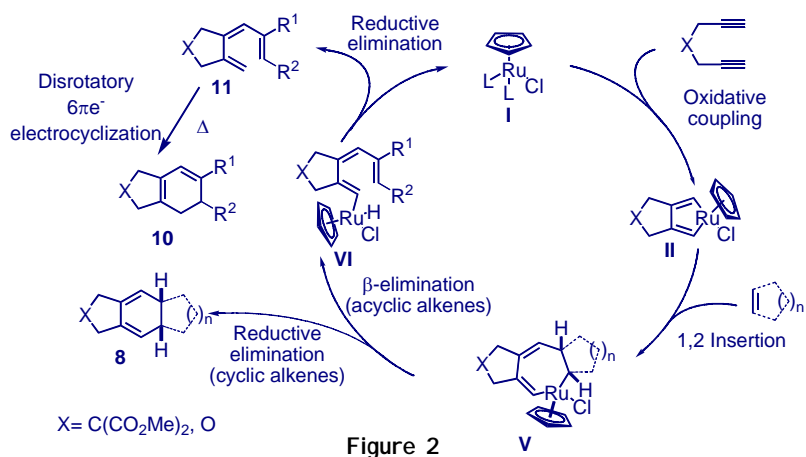


## Ru (II)-Catalyzed [2+2+2] Cycloadditions of 1,6-Diynes to Alkenes

When cyclic alkenes **7** were used, 1,3-cyclohexadienes **8** were obtained in acceptable yields. Surprisingly, when acyclic alkenes **9** were used, isomeric 1,3-cyclohexadienes **10** were obtained in rather good yields (**Scheme 2**).



The likely mechanism for these processes would involve the formation of ruthenacycle intermediate **V**. Depending on the alkene nature, two alternatives could be envisioned from **V**: a) the well-established reductive elimination in the case of cyclic alkenes;<sup>2</sup> b) a new β-elimination + reductive elimination to give 1,3-hexadienes **11** in the case of acyclic alkenes. Final electrocyclization of **11** gave 1,3-cyclohexadienes **10**.



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

<sup>2</sup> a) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Itoh, K. *J. Org. Chem.* 1998, 63, 9610. b) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Kawaguchi, K.; Tatsumi, K.; Itoh, K. *J. Am. Chem. Soc.* 2000, 122, 4310.