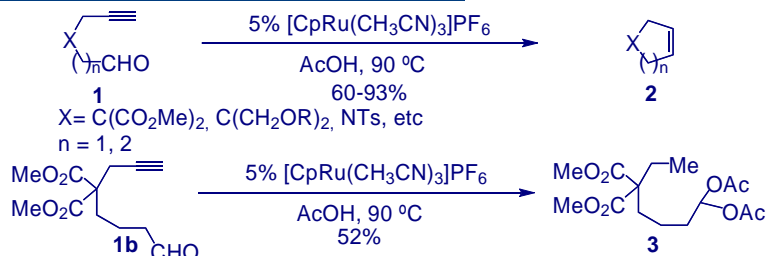
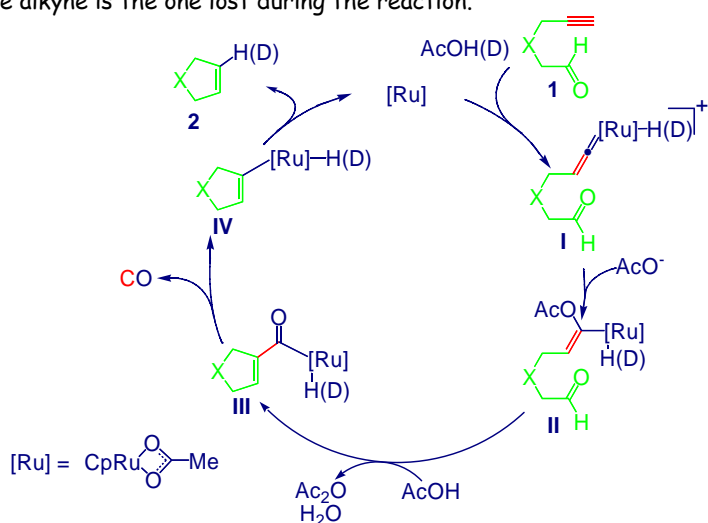


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Ru(II)-Catalyzed Decarbonylative Cyclization of Terminal Alkynals

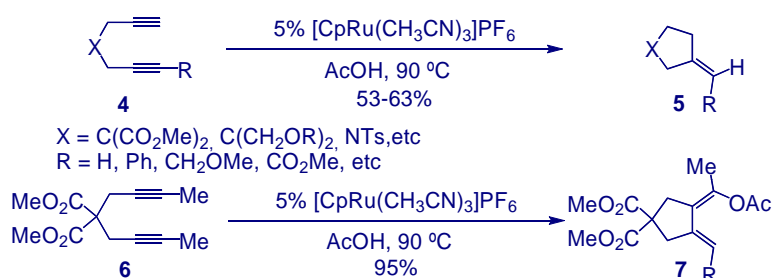
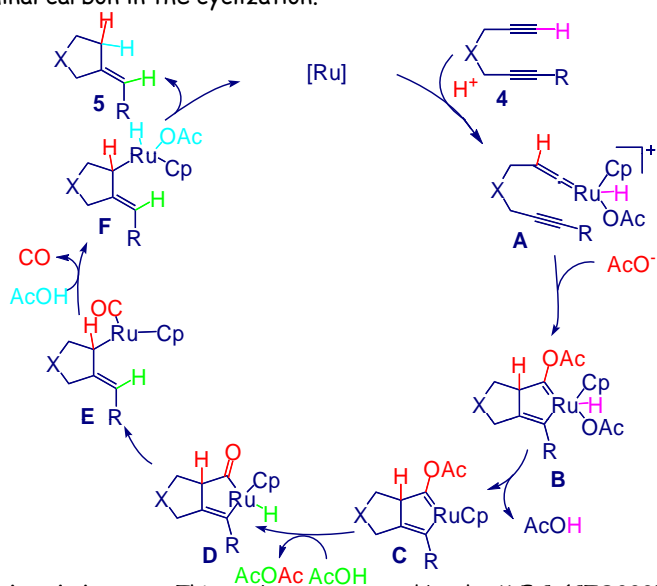
- We recently described a new, efficient Ru(II)-catalyzed cyclization of terminal alkynals **1** to cycloalkenes **2**.¹
- Enlarged alkynals **1b** (n=3) gave rise to non-cyclized compounds **3**, with loss of one carbon, which suggested that the terminal carbon of the alkyne is the one lost during the reaction.



The likely mechanism² would involve the formation of Ru(II) vinylidene species **I**, which upon nucleophilic addition of the acetic acid, would afford the vinyl Ru species **II**. Next, an aldol-type condensation would give the acyl Ru hydride **III**. Then, decarbonylation (*being the terminal carbon of the alkyne the one lost as CO*) followed by reductive elimination would afford the observed cycloalkenes **2**. When CpRu(dppm)Cl was used as catalyst, the conjugated aldehydes were obtained by reductive elimination from **III** (no decarbonylation takes place in this case due to the bidentate nature of dppm ligand).

Ru(II)-Catalyzed Decarbonylative Cyclization of Terminal 1,6-Diynes

- Heating the 1,6-diyne **4a** (X = C(CO₂Me)₂, R = CO₂Me) in a 5% solution of Ru catalyst in AcOH afforded, after 24 h at 90 °C, the *exo*-methylene-cyclopentane derivative **5a**, with one carbon less than **4a**, in quite good yield.
- When 1,7-disubstituted 1,6-diyne **6** was subjected to the same reaction conditions, dienylacetate **7** was obtained in an excellent yield, showing that only a terminal unsubstituted yne unit will lose its terminal carbon in the cyclization.



A possible mechanism for the latter transformation would involve the formation of a ruthenium vinylidene **A**, followed by nucleophilic addition of AcOH to afford the cyclic carbene Ru-hydride **B**. Reductive loss of AcOH of **B** would give the cyclic carbene **C**, which undergoes another nucleophilic attack by AcOH to the acyl Ru-hydride **D**. Reductive opening of the ruthenacycle of **D** followed by oxidative addition of AcOH with concomitant decarbonylation of **E** led to the Ru-hydride **F**. Finally, reductive elimination would then afford the observed cyclopentane derivatives **5**.

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