Theoretical Study of the Ru-Catalyzed Reactions of 1,6-Diynes and Alkenes

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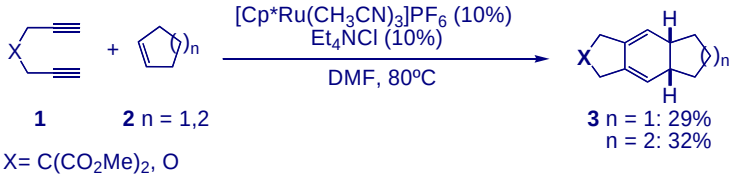
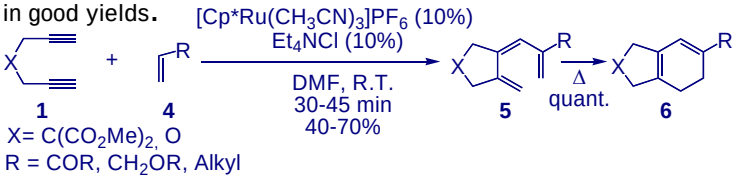
Ru(II)-Catalyzed Cycloaddition of 1,6-Diynes to Cyclic Alkenes

We recently described a Ru(II)- catalyzed cycloaddition of 1,6-diynes **1** to acyclic alkenes **2** to give 1,3-cyclohexadienes **3** in reasonable yields.[1]



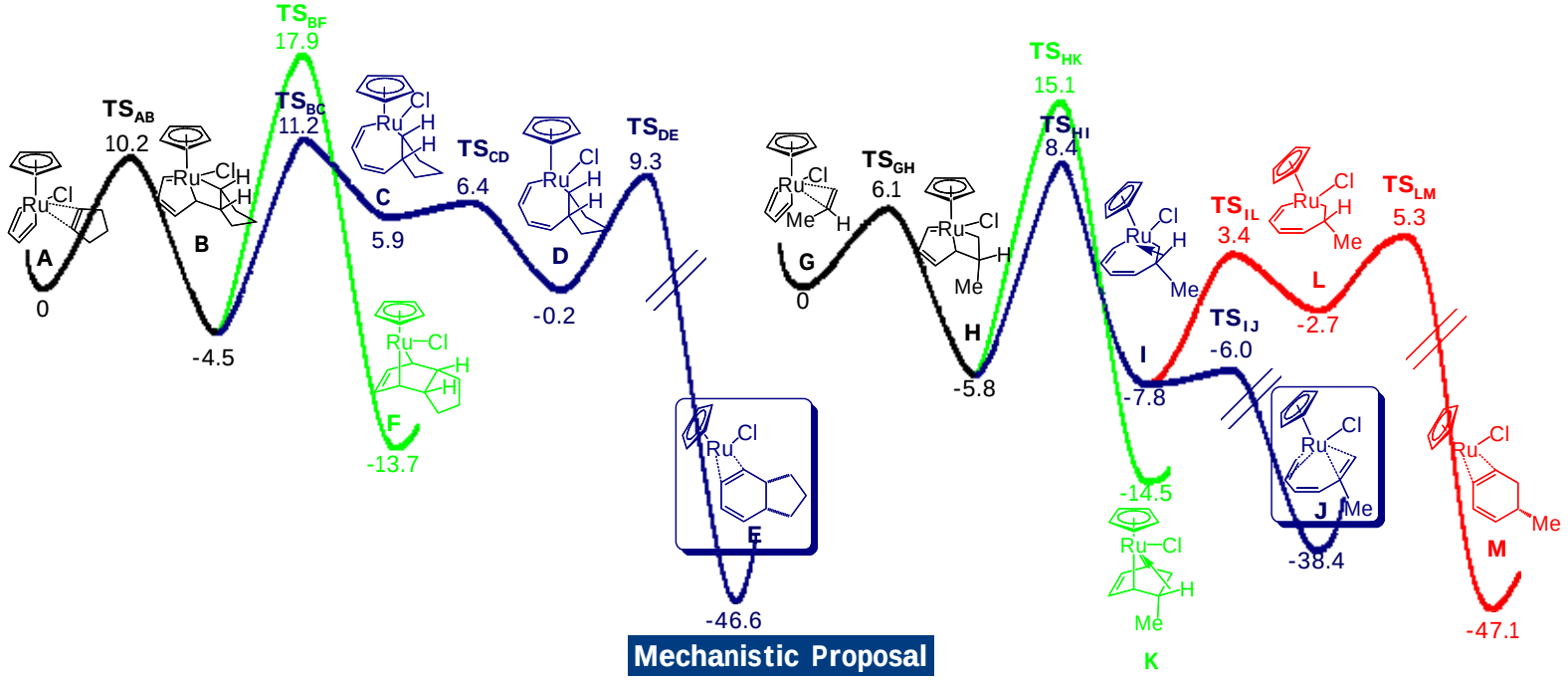
Ru(II)-Catalyzed Cascade Reaction of 1,6-Diynes with Acyclic Alkenes

Remarkably, when acyclic alkenes **4** were used, the open trienes **5** were initially formed, which upon heating underwent a disrotatory 6πe⁻ electrocyclization to give the observed 1,3-cyclohexadienes **6** in good yields.

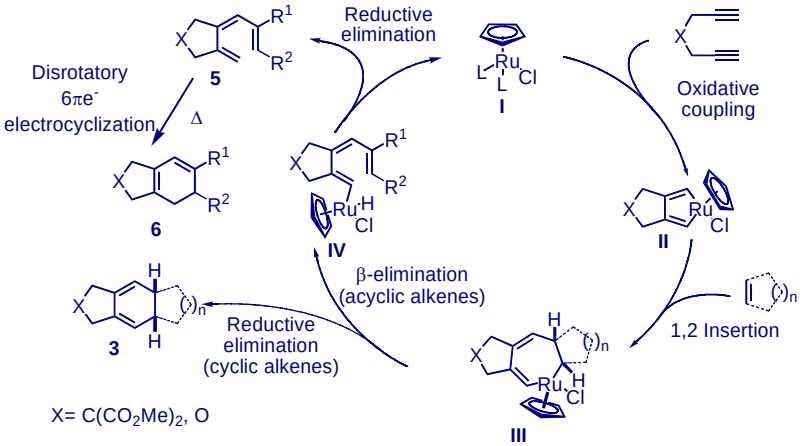


DFT Studies

We have investigated the alkyne-alkene reaction pathway by exploring individual elementary steps using propene and cyclopentene as models for acyclic and cyclic alkenes (calculations at the B3LYP/6-31G(d) (C, H, Cl), LANL2DZ (Ru) level, G and G‡ at 298 K, energies in Kcal mol⁻¹).



Mechanistic Proposal



The likely mechanism for these processes would involve the formation of ruthenacycle intermediate **III**. Depending on the alkene nature, two alternatives could be envisioned: a) the well-established reductive elimination in the case of cyclic alkenes;[2] b) a new β-elimination + reductive elimination to give the open trienes **5** in the case of acyclic alkenes, that undergo disrotatory 6πe⁻ electrocyclization to the observed 1,3-cyclohexadienes **6**.

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References: 1 Varela, J. A.; Rubín, S. G.; González-Rodríguez, C.; Castedo, L.; Saá, C. *J. Am. Chem. Soc.* **2006**, *128*, 9262.

2 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.