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

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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

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References:

DFT Studies

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

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 6π-electrocyclization to the observed 1,3-cyclohexadienes 6.

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