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Abstract:

The mechanism of the trimerization of alkynes in the presence of an Ir complex bearing a hydrotris(pyrazolyl)borate (Tp) ligand has been studied using density functional theory calculations at the B3LYP and M06 levels. In this reaction, the initial oxidative coupling of two alkyne molecules yields an iridacyclopentadiene intermediate, which reacts with a third alkyne molecule to give a benzene TpIr complex. There are two possible mechanisms for the formation of the benzene complex in this reaction, including the intramolecular [4+2] cycloaddition and Schore mechanisms. The formation of unsubstituted benzene was initially investigated using acetylene molecules, and then the oxidative coupling reaction of 1,4-dimethyl-2-butyne-1,4-dioate (CH3OCOCİCCOOCH3) followed by the formation of the substituted benzene complex with 2-butyne (H3CCİCCH3) was studied. It has been possible to clarify the favorable reaction pathway and the effects of different substituents on the reaction mechanism. In the unsubstituted reaction of acetylene the [4+2] cycloaddition is more favorable than the Schore mechanism, whereas the reaction could proceed only via the Schore mechanism in the reactions involving substituted alkynes because of the effect of the substituents. Notably, the effects of additional water molecules on the stability of the reaction intermediates were also evaluated because the water complexes of several intermediates have been experimentally isolated and identified.

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