Dimerization and cyclotrimerization of terminal arylalkynes initiated by a phosphine-free ruthenium alkylidene complex.

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Transformations of alkynes are of great importance in organic synthesis, including formation of natural compounds. Products of CC coupling of terminal alkynes, such as conjugated 1,3- or 1,4-enynes and tri-substituted benzene derivatives are key units of variety natural and biologically active products. Ruthenium catalysts can be effective for such synthesis, however, the mechanisms of these reactions are still not well understood. In this work, dimerization and cyclotrimerization of terminal arylalkyne (phenylacetylene) initiated by the third-generation Grubbs catalyst [$RuCl_2$(CHPh)(3-Br-py)$_2$(H_2IMes)] have been theoretically and experimentally studied. It is shown that ruthenium vinylidene species might be the key intermediate in the catalytic cycle of phenylacetylene dimerization, whereas [$RuCl_2$(H_2IMes)] can be the active species in phenylacetylene cycylotrimerization. Ruthenium alkyne species [$RuCl_2$(η^2PhCCH)(H_2IMes)] is a common intermediate for both competitive reactions. An overall mechanism for terminal arylalkyne transformations is proposed. It includes alkyne-induced decomposition of the phosphine-free ruthenium alkylidene catalyst via ruthenium vinylcarbene to ruthenium vinylidene and [$RuCl_2$(H_2IMes)], followed by the dimerization and cyclotrimerization reactions.

Słowa kluczowe

Cyclotrimerization, DFT calculations, dimerization, Grubbs catalyst, Phenylacetylene

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