

The effect of the oxidation state of molybdenum complexes on the catalytic transformation of terminal alkynes: cyclotrimerization vs. polymerization.

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Streszczenie

Reactions of monosubstituted alkynes ($\text{PhC}\equiv\text{CH}$, $t\text{BuC}\equiv\text{CH}$, $n\text{BuC}\equiv\text{CH}$, $\text{HOCH}_2\text{C}\equiv\text{CH}$, $\text{HO}(\text{CH}_3)_2\text{CC}\equiv\text{CH}$) in the presence of molybdenum(0) and molybdenum(II) carbonyl complexes ($\text{Mo}(\text{CO})_6/h\nu$, $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ (pip = piperidine), $[\text{Mo}(\text{CO})_4(\text{pip})_2]/\text{SnCl}_4$, $[\text{Rpip}]_2\{(\mu\text{-Cl})\text{Mo}(\mu\text{-Cl})(\text{SnCl}_3)(\text{CO})_3\}_2$ ($\text{R} = \text{C}_3\text{H}_5$, H)) lead to the formation of cyclotrimerization and polymerization products, which were characterized by chromatography (GC-MS, GPC) and by ^1H and ^{13}C NMR spectroscopy. The effect of the oxidation state of the molybdenum catalyst on the transformation of the terminal alkynes was observed: cyclotrimerization vs. polymerization. Only molybdenum(II) complexes lead to the formation of polyenic polymers. Moreover, reaction of prop-2-yn-1-ol initiated by $[\text{Mo}(\text{CO})_4(\text{pip})_2]$ in dichloromethane leads to the formation of oligomers containing the vinylidene unit. Mechanistic NMR studies show that η^2 -alkyne complex formation is the principal feature of all transformations of alkynes catalyzed by molybdenum complexes.

Słowa kluczowe

Molybdenum catalysts, Alkynes, Alkynols, Cyclotrimerization, Polymerization, NMR

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