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

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Reactions of monosubstituted alkynes (PhC≡CH, ^{t}BuC≡CH, ^{n}BuC≡CH, $HOCH_2C{\equiv}CH$, $HO(CH_3)_2CC{\equiv}CH$) in the presence of molybdenum(0) and molybdenum(II) carbonyl complexes ($Mo(CO)_6/h\nu$, $[Mo(CO)_4(pip)_2]$ (pip = piperidine), $[Mo(CO)_4(pip)_2]/SnCl_4$, $[Rpip]_2[\{(\mu\text{-}Cl)Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3\}_2]$ (R = C_3H_5, H)) lead to the formation of cyclotrimerization and polymerization products, which were characterized by chromatography (GC–MS, GPC) and by ^{1}H 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 $[Mo(CO)_4(pip)_2]$ 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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