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

Izabela Czeluśniak, Paulina Kocięcka, Teresa Szymańska-Buzar*

Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

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ABSTRACT

Reactions of monosubstituted alkynes (PhC≡CH, ^{t}BuC≡CH, ^{n}BuC≡CH, HOCH$_2$C≡CH, HO(CH$_3$)$_2$CC≡CH) in the presence of molybdenum(0) and molybdenum(II) carbonyl complexes (Mo(CO)$_6$/hv, [Mo(CO)$_4$(pip)$_2$] (pip = piperidine), [Mo(CO)$_4$(pip)$_2$]/SnCl$_4$, [Rpip]$_2$[{(μ-Cl)Mo(μ-Cl)(SnCl$_3$)(CO)$_3$}$_2$] (R = C$_3$H$_5$, 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.

1. Introduction

The [2+2+2] cyclotrimerization of alkynes represents an important strategy for the synthesis of benzene derivatives (Scheme 1), which are useful starting materials for further transformation and building blocks in organic synthesis [1,2]. The transition-metal-catalyzed cyclotrimerization of alkynes was discovered by Reppe and Schweckendick in 1948 [3]. Since then, various metal complexes have been used as catalysts selectively providing two isomers (1,3,5 or 1,2,4) of polysubstituted benzene derivatives [4–7]. In some cases, the transition-metal-catalyzed cyclotrimerization of terminal alkynes is accompanied by polymerization leading to the formation of polyenic polymers, or vice versa, polymerization is accompanied by cyclotrimerization (Scheme 2) [7–10].

Molybdenum complexes, especially those in a low oxidation state, are frequently used as catalysts for the cyclotrimerization of alkynes. Molybdenum (0) complexes such as Mo(CO)$_6$ and its derivatives: [Mo(CO)$_3$(Hpz)$_3$] and [Mo(CO)$_3$(1-Me-im)$_3$], which

contain pyrazole (Hpz) or 1-Me-imidazole (1-Me-im) ligands, cyclotrimerize alkynes like ethyl propiolate (EtOOCC≡CH) and dimethyl acetylenedicarboxylate (MeOOCC≡CCOOMe) to give cyclotrimerization and co-cyclotrimerization reaction products under mild conditions. The latter complexes are also active in the cyclotrimerization of HC≡CPh and HC≡CCMe=CH$_2$ [11]. Moreover, the Mo(CO)$_6$/4-chlorophenol system has been used in the synthesis of alkyne-bridged polymers by the acyclic diyne metathesis (ADIM) of dipropynylated benzenes [12], while alkyne cross-metathesis (ACM) as well as ring-closing alkyne metathesis (RCAM) have been carried out in the Mo(CO)$_6$/2-fluorophenol system [13].

It has also been established that the polymerization of monosubstituted alkynes such as phenylacetylene, 1-chloro-2-phenylacetylene, 2-trimethylsilylphenylacetylene, 2-trifluorome thylphenylacetylene, and *tert*-butylacetylene can be carried out during the photolysis of Mo(CO)$_6$ or W(CO)$_6$ in carbon tetrachloride or other halogenated alkanes [14–16].

In the course of a search for catalytically active species formed in the photochemical reaction of M(CO)$_6$ (M = Mo, W) and alkynes, the η^2-coordination of alkyne to the metal center of the [M(CO)$_5$(η^2-alkyne)] complex and the subsequent rearrangement of the η^2-alkyne ligand to an η^1-vinylidene ligand can be observed by low-temperature matrix studies [17,18]. This transformation may well be the initiation step in the polymerization reaction of

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* Corresponding author. Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland. Tel.: +48 71 375 7221; fax: +48 71 328 2348.
E-mail address: teresa.szymanska-buzar@chem.uni.wroc.pl (T. Szymańska-Buzar).
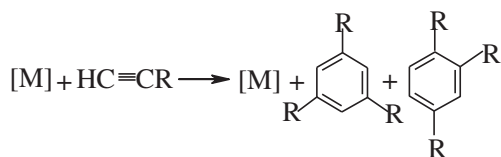
Scheme 1. [2+2+2] cyclotrimerization of alkynes catalyzed by transition-metal complexes [M].
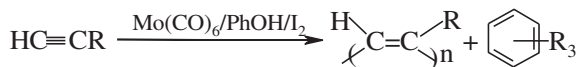
Scheme 2. Cyclotrimerization *vs.* polymerization of terminal alkynes in a catalytic system containing Mo(CO)₆, phenol, and iodine [8].

terminal alkynes in the presence of molybdenum(0) and tungsten(0) complexes [19,20].

In reaction with oxidants such as Cl_2, Br_2, I_2, CCl_4, $GeCl_4$, or $SnCl_4$, molybdenum(0) carbonyl complexes are transformed to seven-coordinate molybdenum(II) complexes [21–23]. These molybdenum(II) complexes readily react with diphenylacetylene in dichloromethane solution at room temperature to give alkyne complexes, but in reaction with terminal alkynes they initiate polymerization and cyclotrimerization reactions [24–27]. As a result of the above-referenced studies, a plausible mechanism for the initiation of alkyne polymerization by molybdenum(II) and tungsten(II) was postulated [28]. It is very probable that an alkylidene ligand initiating the growth of a linear polyenic polymer chain is formed as a result of the rearrangement of the metallacycle formed with three or four molecules of alkyne. The simultaneous formation of cyclotrimerization products of alkynes fits this mechanism very well. It is very interesting that in reaction of [MoI₂(CO)(NCMe)(η^2-MeC≡CPh)₂] with P(O^{i}Pr)₃, the cyclotrimer 1,2,4-trimethyl-3,5,6-triphenylbenzene was isolated [29], but the molybdenum(II) complex, [MoCl(η^3-C₃H₅)(CO)₂(NCMe)₂], catalytically converts PhC≡CPh to a mixture of *E,E*-1,2,3,4-tetraphenylbutadiene and hexaphenylbenzene [30].

However, in contrast to alkyl- and aryl-substituted acetylenes, the cyclotrimerization and polymerization of hydroxyacetylenes have been studied less extensively [31–35], which is probably due to the deactivation of the catalyst by the polar hydroxy group. For that reason, it seems interesting to investigate the catalytic activity of molybdenum complexes in the oligomerization of terminal alkynes containing different substituents.

In this paper, we describe the formation and identification by NMR spectroscopy of the cyclotrimerization and polymerization products formed in reactions of monosubstituted alkynes (PhC≡CH, ^{t}BuC≡CH, ^{n}BuC≡CH, HOCH₂C≡CH, HO(CH₃)₂CC≡CH) catalyzed by molybdenum complexes at room temperature. The effect of the oxidation state of the molybdenum atom on the selectivity of the alkyne reaction is investigated.

2. Experimental

All reactions were performed using standard Schlenk techniques under an atmosphere of nitrogen and with substrates and solvents freshly distilled from calcium hydride. Mo(CO)₆ (**1**) (Sigma-Aldrich) was used as received. *Tert*-butylacetylene (Sigma-Aldrich), 1-hexyne (Fluka), fenylacetylene (ABCR) were distilled from calcium hydride. Prop-2-yn-1-ol (Sigma-Aldrich) was dried with molecular sieves (4A) and distilled. 2-methylbut-3-yn-2-ol (99% Fluka) was used as received. The piperidine (pip) complex

[Mo(CO)₄(pip)₂] (**2**) [36,37] was prepared in the photochemical reaction of Mo(CO)₆ and pip in *n*-hexane. The molybdenum(II) complex [(C₃H₅)pip)₂{(μ-Cl)Mo(μ-Cl)(SnCl₃)(CO)₃}₂] (**3a**) was synthesized in reaction of [Mo(CO)₄(pip)₂] (**2**) and SnCl₄ in dichloromethane in accordance with a previously reported procedure [38]. A small modification of this procedure in the form of a shorter reaction time (2 h) of [Mo(CO)₄(pip)₂] (**2**) and SnCl₄ leads to the formation of an ionic complex of molybdenum(II), [{(μ-Cl)Mo(μ-Cl)(SnCl₃)(CO)₃}₂]²⁻ (**3b**), containing two piperidinium cations [Hpip]⁺ as the counter ions. Anal. Calcd for C₁₆H₂₄Cl₁₀Mo₂N₂O₆ (1124.2): C, 17.09; H, 2.15; N, 2.49. Found: C, 17.70; H, 2.51; N, 2.94.

Photochemical reactions were carried out under an atmosphere of nitrogen in a glass reactor with a quartz window. The photolysis source was an HBO 200 W medium-pressure Hg lamp.

IR spectra were measured with a Nicolet-400 FT-IR instrument in solution, and with a Bruker IFS66 as Nujol mulls or KBr pellets. ¹H, ¹³C NMR, and two-dimensional ¹H–¹H COSY, ¹H–¹³C HMQC, and ¹H–¹³C HMBC NMR spectra were recorded with a Bruker Avance III 600 MHz (¹H, 600.15 MHz; ¹³C, 150.91 MHz) and a Bruker Avance 500 MHz (¹H, 500.13 MHz; ¹³C, 125.76 MHz) instruments. All proton and carbon chemical shifts were referenced to the residual proton signal for ¹H NMR (7.24 CDCl₃, 3.60 C₄D₈O, 3.35 CD₃OD, and 1.40 C₆D₁₂) or the natural abundant carbon signal of the solvent for ¹³C NMR (77.0 CDCl₃, 66.0 C₄D₈O, 49.0 CD₃OD, and 26.4 C₆D₁₂).

Analyses of the reaction products were performed on a Hewlett-Packard GC–MS system containing an HP590II gas chromatograph equipped with a HP-5MS column and an HP5971A mass detector. Mass spectra were measured by electron impact with an ionizing energy of 70 eV and on an apex-Ultra mass spectrometer using the ESI method. The organometallic compounds were analyzed on MicrOTOF-Q Bruker using the ESI method.

Gel permeation chromatography (GPC) data were obtained using a Viscotek GPC max equipped with a Viscotek VE 3580 refractive index detector and 2 × 300 mm Shodex GPC 6 μm KF-802.5 columns for tetrahydrofuran (THF) solutions (10 mg/cm³) of polymers. THF was used as the eluent at a flow rate of 1.0 cm³/min at 30 °C. Polystyrene standards were used for calibration.

Thermogravimetric analyses (TGA) of polymers were conducted under a nitrogen atmosphere at a heating rate of 5 °C/min in the temperature range 30–600 °C with a Perkin Elmer TMA-7 thermal analyzer.

2.1. Photochemical reactions of **1** and alkynes

A hexane, toluene, or tetrahydrofurane solution (20 cm³) of **1** (0.11 g, 0.42 mmol) and the alkyne ^{t}BuC≡CH or HOCH₂C≡CH (*ca.* 0.2 cm³) in a 1:5 molar ratio was stirred and irradiated at room temperature for 1–2 h. The reaction course was investigated by following the IR spectra in solution. All volatile components were then evaporated under reduced pressure at room temperature, and the residue was analyzed by the GC–MS method and NMR spectroscopy, which revealed the conversion of the alkyne to the cyclotrimerization products and their η^6-arene complexes (see Table 1 and Section 2.7.)

2.2. Reaction of prop-2-yn-1-ol in the presence of [Mo(CO)₅(THF)]

2.2.1. Reaction in a round-bottomed flask

The [Mo(CO)₅(THF)] complex, synthesized in photochemical reaction of **1** (0.11 g, 0.42 mmol) in tetrahydrofurane (20 cm³), was isolated by the evaporation of the solvent and then dissolved in dichloromethane (15 cm³). To this solution, prop-2-yn-1-ol (0.55 cm³, 10.4 mmol) was added. The mixture was stirred for 1 h