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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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ABSTRACT

Reactions of monosubstituted alkynes ($PhC{\equiv}CH$, $^{t}BuC{\equiv}CH$, $^{n}BuC{\equiv}CH$, $HOCH_2C{\equiv}CH$, $HO(CH_3)_2CC{\equiv}CH$) 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.

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 $[Mo(CO)_3(1\text{-}Me\text{-}im)_3]$, which contain pyrazole (Hpz) or 1-Me-imidazole (1-Me-im) ligands, cyclotrimerize alkynes like ethyl propiolate ($EtOOCC{\equiv}CH$) and dimethyl acetylenedicarboxylate ($MeOOCC{\equiv}CCOOMe$) to give cyclotrimerization and co-cyclotrimerization reaction products under mild conditions. The latter complexes are also active in the cyclotrimerization of $HC{\equiv}CPh$ and $HC{\equiv}CCMe{=}CH_2$ [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-trifluoromethylphenylacetylene, 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 $[M(CO)_5(\eta^2\text{-alkyne})]$ 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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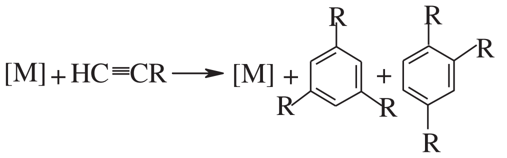
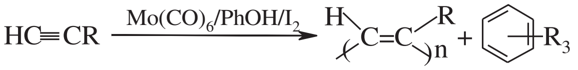


Scheme 1. [2+2+2] cyclotrimerization of alkynes catalyzed by transition-metal complexes [M].



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 $[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC{\equiv}CPh)_2]$ with $P(O^iPr)_3$, the cyclotrimer 1,2,4-trimethyl-3,5,6-triphenylbenzene was isolated [29], but the molybdenum(II) complex, $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$, 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, $HOCH_2C{\equiv}CH$, $HO(CH_3)_2CC{\equiv}CH$) 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 $[(C_3H_5)pip]_2[\{(\mu\text{-}Cl)Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3\}_2]$ (**3a**) was synthesized in reaction of $[Mo(CO)_4(pip)_2]$ (**2**) and $SnCl_4$ 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 $SnCl_4$ leads to the formation of an ionic complex of molybdenum(II), $[\{(\mu\text{-}Cl)Mo(\mu\text{-}Cl)(SnCl_3)(CO)_3\}_2]^{2-}$ (**3b**), containing two piperidinium cations $[Hpip]^+$ as the counter ions. Anal. Calcd for $C_{16}H_{24}Cl_{10}Mo_2N_2O_6$ (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.

${}^{1}H$, ${}^{13}C$ NMR, and two-dimensional ${}^{1}H$–${}^{1}H$ COSY, ${}^{1}H$–${}^{13}C$ HMQC, and ${}^{1}H$–${}^{13}C$ HMBC NMR spectra were recorded with a Bruker Avance III 600 MHz (${}^{1}H$, 600.15 MHz; ${}^{13}C$, 150.91 MHz) and a Bruker Avance 500 MHz (${}^{1}H$, 500.13 MHz; ${}^{13}C$, 125.76 MHz) instruments. All proton and carbon chemical shifts were referenced to the residual proton signal for ${}^{1}H$ NMR (7.24 $CDCl_3$, 3.60 C_4D_8O, 3.35 CD_3OD, and 1.40 C_6D_{12}) or the natural abundant carbon signal of the solvent for ${}^{13}C$ NMR (77.0 $CDCl_3$, 66.0 C_4D_8O, 49.0 CD_3OD, and 26.4 C_6D_{12}).

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/cm^3) of polymers. THF was used as the eluent at a flow rate of 1.0 cm^3/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 cm^3) of **1** (0.11 g, 0.42 mmol) and the alkyne ^{t}BuC≡CH or $HOCH_2C{\equiv}CH$ (*ca.* 0.2 cm^3) 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 cm^3), was isolated by the evaporation of the solvent and then dissolved in dichloromethane (15 cm^3). To this solution, prop-2-yn-1-ol (0.55 cm^3, 10.4 mmol) was added. The mixture was stirred for 1 h

Table 1
Cyclotrimerization reactions of monosubstituted alkynes in the presence of molybdenum complexes [Mo(CO)$_6$] (**1**), [Mo(CO)$_4$(pip)$_2$] (**2**), [Rpip]$_2$[{(μ-Cl)Mo(μ-Cl)(SnCl$_3$)(CO)$_3$}$_2$] (**3**).

Alkyne	Catalytic system	Conversion [a]	Selectivity of cyclotrimerization	Molar ratio of 1,2,4:1,3,5 substituted benzenes
$HOCH_2C{\equiv}CH$	**1**/*hv*	100[b]	99	71:29
$HOCH_2C{\equiv}CH$	[Mo(CO)$_5$(THF)]	5[c]	100	64:36
$HOCH_2C{\equiv}CH$	**3**	64	98	84:16
$HOCMe_2C{\equiv}CH$	**3**	92	9	83:17
$^tBuC{\equiv}CH$	**1**/*hv*	50[d]	100	88:12
$^tBuC{\equiv}CH$	**2**/SnCl$_4$	100	99	0:100
$^tBuC{\equiv}CH$	**3**	100	1	0:100
$^nBuC{\equiv}CH$	**2**/SnCl$_4$	100	100	36:64
$PhC{\equiv}CH$	**2**/SnCl$_4$	100	98	48:52
$PhC{\equiv}CH$	**3**	100	5	50:50

[a] After 24 h of reaction time in CH$_2$Cl$_2$ at room temperature, unless stated otherwise.
[b] 2 h in toluene.
[c] 1 h in CH$_2$Cl$_2$
[d] 2 h in hexane

at room temperature. All volatile components were then evaporated under reduced pressure at room temperature, and the residue was analyzed by NMR spectroscopy and GC–MS. In the GC–MS spectrum, two signals were observed at retention times (r.t.) of 6.5 min ($M^+ = 170$) and 7.5 min ($M^+ = 168$). These signals were assigned to tri(hydroxymethyl)hexatriene and tri(hydroxymethyl) benzene, respectively.

Tri(hydroxymethyl)hexatriene: GC–MS: $C_9H_{14}O_3$, $M_r = 170.21$, r.t. 6.5 min, *m/z* (relative intensity): 170 (M^+, 6), 133 (12), 98 (18), 84 (100), 63 (14), 49 (4).

Tri(hydroxymethyl)benzene: GC–MS: $C_9H_{12}O_3$, $M_r = 168.19$, r.t. 7.5 min, *m/z* (relative intensity): 168 (M^+, 99), 131 (83), 117 (100), 96 (67), 84 (38), 61 (46), 47 (11).

2.2.2. Reaction in the NMR tube

The course of reaction of the [Mo(CO)$_5$(THF)] complex with prop-2-yn-1-ol was followed by ^{1}H NMR spectroscopy. In accordance with the general procedure for NMR experiments, [Mo(CO)$_5$(THF)] (0.05 g, 0.04 mmol) was dissolved in CDCl$_3$ (0.7 cm^3) and transferred to the NMR tube. To this solution, prop-2-yn-1-ol (0.05 cm^3, 1.0 mmol) was added. The tube was periodically monitored by ^{1}H NMR spectroscopy over the desired length of time in the temperature range from −20 to 25 °C. The coordination of prop-2-yn-1-ol to the molybdenum atom was suggested by a signal at 9.74 ppm observed as a triplet with a coupling constant $^4J_{H-H} = 1.9$ Hz, which correlated in the COSY NMR spectrum with a CH$_2$ signal at 2.81 ppm.

2.3. Reaction of alkynes in the presence of 2

A dichloromethane solution (20 cm^3) of **2** (0.076 g, 0.2 mmol) and an alkyne: $^tBuC{\equiv}CH$, $HOCH_2C{\equiv}CH$ or $HO(CH_3)_2CC{\equiv}CH$ (*ca.* 0.3–0.6 cm^3), in a 1:25 molar ratio, was stirred at room temperature for 24 h. All volatile components were then evaporated under reduced pressure at room temperature, and the residue was analyzed by NMR spectroscopy and the GC–MS method.

2.3.1. Reaction of $^tBuC{\equiv}CH$ in the presence of 2

$^tBuC{\equiv}CH$ was recovered essentially unchanged after reaction in the presence of **2**.

2.3.2. Products of $HOCH_2C{\equiv}CH$ transformation in the presence of 2

Analysis of the reaction products by GC–MS showed five signals which appeared with increasing retention times: $C_6H_8O_2$, $M_r = 112.13$, r.t. 7.6 min (7.5%), *m/z* (relative intensity): 112 (M^+, 14), 84 (100), 69 (22), 56 (9), 41 (13); $C_6H_8O_2$, $M_r = 112.13$, r.t. 8.5 min (0.1%), *m/z* (relative intensity): 112 (M^+, 100), 95 (3), 84 (6); 67 (4), 56 (6), 41 (8); $C_6H_8O_2$, $M_r = 112.13$, r.t. 8.6 min (0.2%), *m/z* (relative intensity): 112 (M^+, 100), 98 (3), 84 (8); 67 (2), 56 (5), 41 (5); $C_{15}H_{20}O_5$, $M_r = 280.32$, r.t. 8.9 min (92%), *m/z* (relative intensity): 264 (M^+, −16, 0.2), 180 (3), 166 (3), 152 (24), 136 (3), 122 (3), 112 (13), 98 (100), 84 (16); 67 (4), 55 (10), 41 (11); $C_9H_{12}O_3$, $M_r = 168.19$, r.t. 10.7 min (0.2%), *m/z* (relative intensity): 168 (M^+, 75), 140 (42), 112 (12), 100(12), 98 (42), 84 (100); 67 (18), 59 (43), 41 (30).

Analysis by NMR spectroscopy (^{1}H, ^{13}C, DEPT, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HMQC, and ^{1}H–^{13}C HMBC) revealed the formation as the major product (92% yield by NMR) of two compounds: **a** and **b**, containing vinylidene units and existing in a ratio of 2:1 (**a**:**b**). Another compound (**c**) was identified by NMR analysis (4%) as containing the hydroxymethylvinyl unit, CH=CH(CH$_2$OH). These oily compounds were separated from other products by extraction to hexane.

(**a**) ^{1}H NMR (δ, CDCl$_3$, 600.15 MHz): 4.91 (s, 1H, H$_2$C), 4.73 (s, 1H, H$_2$C), 4.65 (s, 1H, CH), 4.36 (d, $^2J_{H-H} = 12.7$ Hz, 1H, H$_2$C), 4.10 (d, $^2J_{H-H} = 12.7$ Hz, 1H, H$_2$C), 2.96 (dd, $^2J_{H-H} = 11.0$ Hz, $^3J_{H-H} = 6.9$ Hz, 1H, H$_2$C), 2.91 (t, $^3J_{H-H} = 7.4$ Hz, 1H, HC), 2.38 (m, H$_2$C), 2.34 (d, $^2J_{H-H} = 11.0$ Hz, H$_2$C), 2.00 (m, 1H, H$_2$C), 1.86 (m, 1H, H$_2$C), 1.71 (m, H$_2$C), 1.57 (m, H$_2$C), 1.43 (m, H$_2$C). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 150.91 MHz): 141.2 (1C, C), 111.7 (1C, H$_2$C), 81.3 (1C, CH), 68.8 (1C, CH$_2$), 64.7 (1C, CH), 56.3 (CH$_2$), 54.4 (CH$_2$), 47.8 (CH$_2$), 30.3 (CH$_2$), 25.7 (CH$_2$), 18.6 (CH$_2$).

(**b**) ^{1}H NMR (δ, CDCl$_3$, 600.15 MHz): 4.98 (s, 1H, H$_2$C), 4.81 (s, 1H, H$_2$C), 4.44 (s, 1H, CH), 4.22 (d, $^2J_{H-H} = 12.1$ Hz, 1H, H$_2$C), 4.14 (d, $^2J_{H-H} = 12.1$ Hz, 1H, H$_2$C), 3.36 (t, $^3J_{H-H} = 6.9$ Hz, 1H, HC), 2.98 (dd, $^2J_{H-H} = 11.0$ Hz, $^3J_{H-H} = 6.9$ Hz, 1H, H$_2$C), 2.54 (m, H$_2$C), 2.42 (m, H$_2$C), 2.38 (m, H$_2$C), 2.28 (m, H$_2$C), 2.26 (m, H$_2$C), 2.00 (m, 1H, H$_2$C), 1.86 (m, 1H, H$_2$C), 1.71 (m, H$_2$C), 1.50 (m, H$_2$C), 1.43 (m, H$_2$C). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 150.91 MHz): 141.3 (1C, C), 109.4 (1C, H$_2$C), 89.2 (1C, CH), 72.7 (1C, CH$_2$), 61.8 (1C, CH), 55.9 (CH$_2$), 54.5 (CH$_2$), 47.9 (CH$_2$), 30.6 (CH$_2$), 25.4 (CH$_2$), 19.2 (CH$_2$).

(**c**) ^{1}H NMR (δ, CDCl$_3$, 600.15 MHz): 6.23 (d, $^3J_{H-H} = 14.6$ Hz, 1H, HC), 5.81 (dt, $^3J_{H-H} = 14.6$ Hz, $^3J_{H-H} = 5.7$ Hz, 1H, HC), 4.18 (d, $^3J_{H-H} = 5.7$ Hz, 1H, H$_2$C). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 150.91 MHz): 135.5 (1C, HC), 132.5 (1C, HC), 63.0 (1C, CH$_2$).

2.3.3. Products of $HO(CH_3)_2CC{\equiv}CH$ transformation in the presence of 2

Analysis by NMR spectroscopy revealed the formation of compound (**a**) (*ca.* 5%) containing the vinyl unit –CH=CH$_2$, and compound (**b**) (*ca.* 95%) containing the piperidinium cation: (**a**) ^{1}H NMR (δ, CDCl$_3$, 500.13 MHz): 5.84 (dd, $^3J_{H-H} = 17.5$ Hz,

$^3J_{H-H} = 10.7$ Hz, 1H, HC), 5.05 (d, $^3J_{H-H} = 17.5$ Hz, 1H, H_2C), 4.82 (d, $^3J_{H-H} = 10.7$ Hz, 1H, H_2C). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 125.76 MHz): 145.6 (1C, HC), 110.0 (1C, H_2C); (**b**) ^1H NMR (δ, $CDCl_3$, 500.13 MHz): 8.53 (s, 2H, NH_2), 3.02 (s, 4H, H_2C), 1.73 (s, 4H, H_2C), 1.45 (s, 2H, H_2C). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 125.76 MHz): 44.6 (2C, H_2C), 22.0 (2C, H_2C), 21.8 (1C, H_2C). Analysis of the reaction products by the ESI-MS method showed the anion $[C_{30}H_{38}Mo_2O_{14}]^-$ ($M^- = 814.5$) (see Supplementary Data for the experimental and calculated spectra).

2.4. *Reaction of alkynes in the presence of **2** and $SnCl_4$*

A dichloromethane solution (15 cm^3) of **2** (0.02 g, 0.053 mmol), $SnCl_4$ (0.012 cm^3, 0.11 mmol), and an alkyne: PhC≡CH, $^tBuC≡CH$, $^nBuC≡CH$ (*ca.* 0.2–0.3 cm^3), in a 1:2:50 molar ratio, was stirred at room temperature for 24 h. 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 a *ca.* 100% conversion of the alkyne and the formation of cyclotrimers as the major products (see Table 1 and Section 2.7.).

2.5. *Transformation of alkynes in the presence of **3a** or **3b***

A dichloromethane solution (15 cm^3) of **3a** (0.057 g, 0.048 mmol) or **3b** (0.054 g, 0.048 mmol) and an alkyne: PhC≡CH, $^tBuC≡CH$, $HOCH_2C≡CH$ or $HO(CH_3)_2CC≡CH$ (*ca.* 0.2–0.3 cm^3), in a 1:50 molar ratio, was stirred at room temperature for 24 h. 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 formation of polymerization and cyclotrimerization products (see Section 2.7.).

2.5.1. *Characterization of poly($^tBuC≡CH$) (poly-^tBA)*

A white powder of poly-^tBA synthesized in reaction initiated by the molybdenum(II) complex **3a** was purified by crystallization from tetrahydrofurane/methanol solution and next investigated by the GPC, TGA, NMR, and IR methods. The polymer yield was 99%. GPC analysis: M_n 127,251, M_w 147,368, M_w/M_n 1.16. TGA analysis: a one-step degradation process with the onset decomposition temperature at *ca.* 256 °C. ^1H NMR (δ, C_4D_8O, 125.76 MHz): 6.28 (sharp, *cis*-CH), 6.0 (broad, *trans*-CH), 1.20 (^tBu). $^{13}C\{^1H\}$ NMR (δ, C_4D_8O, 125.76 MHz): 145.9 (C^tBu), 129.4 (CH), 39.3, (CMe_3), 32.2 (Me). IR (KBr pellet, ν, cm^{-1} (relative intensity)): 2956 (vs), 2868 (s), 1479 (s), 1391 (m), 1360 (s), 1260 (w), 1199 (m), 1022 (w), 932 (w), 898 (w), 559 (w).

2.5.2. *Characterization of poly(PhC≡CH) (poly-PA)*

Ochre amorphous poly-PA separated by an excess of methanol from dichloromethane solution of the reaction mixture was investigated by the GPC, TGA, NMR, and IR methods. The polymer yield was 95%. GPC analysis: M_n 2418, M_w 4235, M_w/M_n 1.75. TGA analysis: a one-step degradation process with the onset decomposition temperature at *ca.* 200 °C. ^1H NMR (δ, $CDCl_3$, 500.13 MHz); a broad signal in the range 7.5–5.5 with three maximums at 6.93, 6.62, and 5.83 ppm. $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 125.76 MHz); a broad signal in the range 130–124 ppm with a maximum at 127.7 ppm. IR (KBr pellet, ν, cm^{-1} (relative intensity)): 3054 (m), 3025 (m), 2956 (w), 2925 (w), 1597 (s), 1575 (w), 1492 (s), 1473 (w), 1444 (s), 1410 (w), 1261 (m), 1074 (m), 1029 (m), 755 (vs), 696 (vs).

2.5.3. *Characterization of $HOCH_2C≡CH$ transformation products*

The formation of a brown solid was observed from the beginning of the reaction of prop-2-yn-1-ol in the presence of **3a** or **3b**. Analysis of the solution by NMR in $CDCl_3$ revealed several proton signals of very low intensity in the range δ 8–5 ppm, suggesting the formation of compounds containing the olefin bond. Analysis of the brown solid by NMR in C_4D_8O revealed the formation of 1,3,5-tri(hydroxymethyl)benzene and 1,2,4-tri(hydroxymethyl)benzene in the molar ratio of 1:5 (see Section 2.7). The brown solid residue insoluble in any organic solvent was analyzed by IR spectroscopy. IR (KBr pellet, ν, cm^{-1} (relative intensity)): 3180 (vs), 2950 (s), 2870 (m), 1715 (w), 1616 (m), 1574 (s), 1471 (w), 1454 (s), 1473 (w), 1406 (m), 1028 (s), 983 (m), 860 (w), 832 (w), 747 (w), 541 (w), 427 (w).

2.5.4. *Characterization of $HOC(CH_3)_2C≡CH$ transformation products*

In the reaction of 2-methylbut-3-yn-2-ol initiated by **3a** or **3b**, the formation of a brown solid was observed. The solid was isolated from a dark solution and both fractions were analyzed by NMR spectroscopy, which revealed the formation of 1,3,5-tri(2-hydroxyizopropyl)benzene and 1,2,4-tri(2-hydroxyizopropyl) benzene in the molar ratio of 1:5 (see Section 2.7). In the ^1H NMR spectrum measured in $CDCl_3$ solution, in addition to cyclotrimer signals, several proton signals were observed in the range δ 8–5 ppm. The latter signals correlated with carbon signals in the range δ 130–110 ppm, which suggested the formation of compounds containing the olefin bond. Analysis of the latter solution by GC–MS showed the presence of dimers ($C_{10}H_{16}O_2$, $M_r = 168.2$) and cyclotrimers ($C_{15}H_{24}O_3$, $M_r = 252.3$) as well as their hydrogenation products ($C_{10}H_{18}O_2$, $M_r = 170.2$, $C_{15}H_{26}O_3$, $M_r = 254.4$). Analysis by the ESI-MS method revealed the formation of new molybdenum complexes identified as anions M^-: 291 ($C_9H_7MoO_5$), 319 ($C_{10}H_7MoO_6$), 515 ($C_{25}H_{39}MoO_5$), 571 ($C_{13}H_{14}MoO_6Sn$) (see Supplementary Data for the experimental and calculated MS spectra). The brown insoluble solid was analyzed by IR spectroscopy. IR (KBr pellet, ν, cm^{-1} (relative intensity)): 3185 (vs), 3112 (s), 2964 (m), 2872 (w), 1611 (m), 1575 (s), 1473 (w), 1455 (s), 1406 (m), 1389 (w), 1279 (w), 1015 (w), 984 (w), 941 (w), 901 (w), 858 (w), 744 (s), 539 (w), 426 (w).

2.6. *NMR and GC–MS characterization of cyclotrimerization products of alkynes*

1,3,5-triphenylbenzene (1,3,5-TPB) [39,40]: ^1H NMR (δ, $CDCl_3$, 500.13 MHz): 7.77 (s, 3H, HC-Bz), 7.68 (d, $^3J_{H-H} = 7.5$ Hz, 6H, HC_o-Ph), 7.47 (t, $^3J_{H-H} = 7.5$ Hz, 6H, HC_m-Ph), 7.38 (t, $^3J_{H-H} = 7.5$ Hz, 3H, HC_p-Ph). ^{13}C NMR (δ, $CDCl_3$, 125.76 MHz): 142.3, 141.1 (3C, C_i-Ph and 3C, C-Bz), 128.8 (d, $^1J_{C-H} = 160$ Hz, 6C, HC_m-Ph), 127.5 (3C, HC_p-Ph), 127.4 (d, $^1J_{C-H} = 159$ Hz, 6C, HC_o-Ph), 125.2 (d, $^1J_{C-H} = 158$ Hz, 3C, HC-Bz). GC–MS: $C_{24}H_{18}$, $M_r = 306.4$, r.t. 12.7 min, m/z (relative intensity): 306 (M^+, 100).

1,2,4-triphenylbenzene (1,2,4-TPB) [39,40]: ^1H NMR (δ, $CDCl_3$, 500.13 MHz): 7.67 (dd, $^3J_{H-H} = 7.8$ Hz, $^4J_{H-H} = 1.2$ Hz, 1H, HC(5)-Bz), 7.66 (d, $^4J_{H-H} = 1.2$ Hz, 1H, HC(3)-Bz), 7.49 (d, $^3J_{H-H} = 7.8$ Hz, 1H, HC(6)-Bz), 7.43 (t, $^3J_{H-H} = 7.5$ Hz, 2H, HC_m-Ph), 7.36 (t, $^3J_{H-H} = 7.5$ Hz, 1H, HC_p-Ph), 7.22 (d, $^3J_{H-H} = 7.5$ Hz, 4H, HC_o-Ph), 7.21 (d, $^3J_{H-H} = 7.5$ Hz, 2H, HC_o-Ph), 7.21 (t, $^3J_{H-H} = 7.5$ Hz, 2H, HC_p-Ph), 7.18 (t, $^3J_{H-H} = 7.5$ Hz, 4H, HC_m-Ph). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 125.76 MHz): 141.5, 141.1, 141.0, 140.6, 140.4, 139.6 (3C, C_i-Ph and 3C, C-Bz), 131.1 (1C, HC(6)-Bz), 130.0 (2C, HC_m-Ph), 129.9 (2C, HC_m-Ph), 129.4 (1C, HC(3)-Bz), 128.8 (2C, HC_m-Ph), 128.0 (2C, HC_o-Ph), 127.9 (2C, HC_o-Ph), 127.4 (1C, HC_p-Ph), 127.1 (2C, HC_o-Ph), 126.6 (1C, HC_p-Ph), 126.5 (1C, HC_p-Ph), 126.1 (1C, HC(5)-Bz). GC–MS: $C_{24}H_{18}$, $M_r = 306.4$, r.t. 11.4 min, m/z (relative intensity): 306 (M^+, 100).

1,3,5-tri-*t*-butylbenzene (1,3,5-T^tBB) [28]: ^1H NMR (δ, $CDCl_3$, 500.13 MHz): 7.23 (s, 3H, HC-Bz), 1.31 (s, 27H, CH_3-^tBu). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 125.76 MHz): 149.9 (3C, C-Bz), 119.4 (3C, HC-Bz), 35.0 (3C, C-^tBu), 31.6 (9C, CH_3-^tBu). GC–MS: $C_{18}H_{30}$, $M_r = 246.43$, r.t. 6.8 min, m/z (relative intensity): 246 (M^+, 11), 231 (M^+, $-CH_3$, 100).

1,2,4-tri-*t*-butylbenzene (1,2,4-T^{t}BB): ^{1}H NMR (δ, C_6D_{12}, 500.13 MHz): 7.57 (d, $^4J_{H-H} = 2.3$ Hz, 1H, HC(3)-Bz), 7.41 (d, $^3J_{H-H} = 8.4$ Hz, 1H, HC(6)-Bz), 7.02 (dd, $^3J_{H-H} = 8.4$ Hz, $^4J_{H-H} = 2.3$ Hz, 1H, HC(5)-Bz), *ca.* 1.3 (s, 27H, CH_3-^{t}Bu). ^{13}C{^{1}H} NMR (δ, C_6D_{12}, 125.76 MHz): 128.8 (1C, HC(6)-Bz), 126.2 (1C, HC(3)-Bz), 121.9 (1C, HC(5)-Bz), 35.7 (3C, C-^{t}Bu), 31.6 (9C, CH_3-^{t}Bu).

1,3,5-tri-*n*-butylbenzene (1,3,5-T^{n}BB): ^{1}H NMR (δ, $CDCl_3$, 500.13 MHz): 6.79 (s, 3H, HC-Bz), 2.57 (t, $^3J_{H-H} = 7.7$ Hz, 6H, CH_2-^{n}Bu), 1.61 (tt, $^3J_{H-H} = 7.7$ Hz, 6H, CH_2-^{n}Bu), 1.36 (qt, $^3J_{H-H} = 7.5$ Hz, 6H, CH_2-^{n}Bu), 0.93 (t, $^3J_{H-H} = 7.4$ Hz, 9H, CH_3-^{n}Bu). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 125.76 MHz): 142.7 (3C, C-Bz), 125.8 (3C, HC-Bz), 35.7 (3C, CH_2-^{n}Bu), 33.8 (3C, CH_2-^{n}Bu), 22.5 (3C, CH_2-^{n}Bu), 14.0 (3C, CH_3-^{n}Bu). GC–MS: $C_{18}H_{30}$, $M_r = 246.43$, r.t. 8.4 min, *m*/*z* (relative intensity): 246 (M^+, 32), 203 (M^+, $-C_3H_7$, 33), 161 (M^+, $-C_6H_{13}$, 100), 147 (M^+, $-C_7H_{15}$, 11), 105 (M^+, $-C_{10}H_{21}$, 14).

1,2,4-tri-*n*-butylbenzene (1,2,4-T^{n}BB): ^{1}H NMR (δ, $CDCl_3$, 500.13 MHz): 7.02 (d, $^3J_{H-H} = 7.6$ Hz, 1H, HC(6)-Bz), 6.92 (d, $^4J_{H-H} = 1.9$ Hz, 1H, HC(3)-Bz), 6.90 (dd, $^3J_{H-H} = 7.6$ Hz, $^4J_{H-H} = 1.9$ Hz, 1H, HC(5)-Bz), 2.57 (t, $^3J_{H-H} = 7.7$ Hz, 6H, CH_2-^{n}Bu), 1.61 (tt, $^3J_{H-H} = 7.7$ Hz, 6H, CH_2-^{n}Bu), 1.36 (qt, $^3J_{H-H} = 7.5$ Hz, 6H, CH_2-^{n}Bu), 0.93 (t, $^3J_{H-H} = 7.4$ Hz, 9H, CH_3-^{n}Bu). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 125.76 MHz): 140.3, 140.1, 137.6 (3C, C-Bz), 129.7 (1C, HC(6)-Bz), 129.2 (1C, HC(5)-Bz), 125.7 (1C, HC(3)-Bz), 35.7 (3C, CH_2-^{n}Bu), 33.8 (3C, CH_2-^{n}Bu), 22.5 (3C, CH_2-^{n}Bu), 14.0 (3C, CH_3-^{n}Bu). GC–MS: $C_{18}H_{30}$, $M_r = 246.43$, r.t. 8.5 min, *m*/*z* (relative intensity): 246 (M^+, 33), 204 (M^+, $-C_3H_7$, 100), 161 (M^+, $-C_6H_{13}$, 23), 147 (M^+, $-C_7H_{15}$, 43), 105 (M^+, $-C_{10}H_{21}$, 31).

1,3,5-tri(hydroxymethyl)benzene (1,3,5-T($HOCH_2$)B): ^{1}H NMR (δ, C_4D_8O, 500.13 MHz): 7.20 (s, 3H, HC-Bz), 4.57 (s, 6H, H_2C). ^{13}C{^{1}H} NMR (δ, C_4D_8O, 125.76 MHz): 142.0 (3C, C-Bz), 122.5 (3C, HC-Bz), 63.6 (3C, H_2C). GC–MS: (see Section 2.3.1.).

1,2,4-tri(hydroxymethyl)benzene (1,2,4-T($HOCH_2$)B): ^{1}H NMR (δ, C_4D_8O, 500.13 MHz): 7.37 (s, 1H, HC(3)-Bz), 7.31 (d, $^3J_{H-H} = 7.6$ Hz, 1H, HC(6)-Bz), 7.21 (d, $^3J_{H-H} = 7.6$ Hz, 1H, HC(5)-Bz), 4.64, 4.62, 4.56 (s, 6H, H_2C). ^{13}C{^{1}H} NMR (δ, C_4D_8O, 125.76 MHz): 141.2, 139.4, 138.1 (3C, C-Bz), 127.1 (1C, HC(6)-Bz), 125.6 (1C, HC(3)-Bz), 124.4, (1C, HC(5)-Bz), 63.3, 62.0, 61.7 (3C, H_2C). GC–MS: (see Section 2.3.1.).

1,3,5-tri(2-hydroxyizopropyl)benzene (1,3,5-T($HOCMe_2$)B): ^{1}H NMR (δ, $CDCl_3$, 500.13 MHz): 7.14 (s, 3H, HC-Bz), *ca.* 1.3 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 125.76 MHz): 140.5 (3C, C-Bz), 117.8 (3C, HC-Bz). GC–MS: $C_{15}H_{24}O_3$, $M_r = 252.35$, r.t. 7.7 min, *m*/*z* (relative intensity): 252 (M^+, 0.2), 198 (M^+, $-3H_2O$, 100), 183 (9), 143 (12), 128 (13), 115 (11), 77(9), 63 (2), 41 (6).

1,2,4-tri(2-hydroxyizopropyl)benzene (1,2,4-T($HOCMe_2$)B): ^{1}H NMR (δ, $CDCl_3$, 500.13 MHz): 7.47 (d, $^4J_{H-H} = 1.5$ Hz, 1H, HC(3)-Bz), 7.36 (dd, $^3J_{H-H} = 7.8$ Hz, $^4J_{H-H} = 1.5$ Hz, 1H, HC(5)-Bz), 7.02 (d, $^3J_{H-H} = 7.8$ Hz, 1H, HC(6)-Bz), *ca.* 1.3 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 125.76 MHz): 143.7, 143.2, 141.4 (3C, C-Bz), 125.0 (1C, HC(5)-Bz), 120.8 (1C, HC(3)-Bz), 120.5 (1C, HC(6)-Bz), GC-MS: $C_{15}H_{24}O_3$, $M_r = 252.35$, r.t. 6.9 min, *m*/*z* (relative intensity): 252 (M^+, 0.02), 216 (M^+, $-2CH_3$, 2), 201 (M^+, $-3OH$, 100), 183 (7), 155 (3), 128 (4), 115 (4), 91(2), 51(1), 43 (8).

2.7. NMR characterization of [Mo(CO)$_3$(η^6-arene)] complexes

[Mo(CO)$_3$(η^6-1,3,5-T^{t}BB)]: ^{1}H NMR (δ, C_6D_{12}, 500.13 MHz): 5.67 (s, 3H, HC-Bz), *ca.* 1.3 (s, 27H, CH_3-^{t}Bu). ^{13}C{^{1}H} NMR (δ, C_6D_{12}, 125.76 MHz): 95.1 (3C, HC-Bz), 35.0 (3C, C-^{t}Bu), 31.6 (9C, CH_3-^{t}Bu).

[Mo(CO)$_3$(η^6-1,2,4-T^{t}BB)] (δ, C_6D_{12}, 500.13 MHz): 5.93 (d, $^4J_{H-H} = 1.9$ Hz, 1H, HC(3)-Bz), 5.65 (d, $^3J_{H-H} = 7.2$ Hz, 1H, HC(6)-Bz), 5.52 (dd, $^3J_{H-H} = 7.2$ Hz, $^4J_{H-H} = 1.9$ Hz, 1H, HC(5)-Bz), *ca.* 1.31 (s, 27H, CH_3-^{t}Bu). ^{13}C{^{1}H} NMR (δ, C_6D_{12}, 125.76 MHz): 94.8 (1C, HC(3)-Bz), 94.1 (1C, HC(6)-Bz), 90.5 (1C, HC(5)-Bz), 35.7 (3C, C-^{t}Bu), 31.6 (9C, CH_3-^{t}Bu).

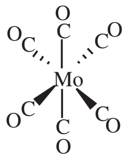
3. Results and discussion

3.1. Reactions of alkynes in the presence of molybdenum(0) complexes **1** and **2**

3.1.1. Photochemical reactions of **1** with alkynes

Broad-band photolysis of *n*-hexane solution of **1** (Chart 1) in the presence of ^{t}BuC≡CH (1:5) gives rise initially to the substitution of one CO group by the alkyne and the formation of the pentacarbonyl complex [Mo(CO)$_5$(^{t}BuC≡CH)], as inferred from IR spectra containing three ν(CO) absorption bands at 2077 (w), 1950 (vs), and 1937 (s) cm^{-1}, characteristic of a molecule with C_{4v} local symmetry [41,42]. Prolonged irradiation causes these bands to disappear. Investigations of the reaction products by ^{1}H NMR allowed us to detect very low-intensity proton signals at *ca.* 10 ppm (Fig. 1), which can be assigned to an η^2-coordinated alkyne ligand, and more intense proton signals in the range 7.5–7.2 assigned to 1,3,5 and 1,2,4-T^{t}BB formed in the molar ratio of 1:7 (Fig. 2, Tables 1 and 2). The cyclotrimers that were formed are very good η^6-arene ligands which can coordinate to the coordinatively unsaturated molybdenum(0) species Mo(CO)$_3$ generated in the photochemical reaction of **1**. The η^6-coordination of 1,3,5 and 1,2,4-T^{t}BB to the molybdenum atom was detected by proton signals in the range 5.9–5.5 ppm (Fig. 2) and carbon signals in the range 96–85. The formation of similar η^6-arene complexes had previously been observed in photochemical reaction of W(CO)$_6$ and propyne [41].

Hydroxysubstituted acetylenes are not soluble in an alkane solution. For that reason, tetrahydrofurane (THF) or toluene were used as solvents in photochemical reaction of **1** and $HOCH_2C$≡CH. However, monitoring the photochemical reaction of **1** and prop-2-yn-1-ol in THF solution by IR spectroscopy allowed us to detect the formation of a fairly stable pentacarbonyl complex, [Mo(CO)$_5$(THF)], which was observed by IR spectra due to three ν(CO) absorption bands at 2078 (w), 1940 (vs), and 1893 (s) cm^{-1}. Thus, the ν(CO) absorption bands of the alkyne pentacarbonyl complex [Mo(CO)$_5$($HOCH_2C$≡CH)] were not detected. Presumably, they were overlapped by more intense bands of the tetrahydrofurane complex. Investigations of the isolated reaction products by NMR showed only low (*ca.* 10%) conversion of prop-2-yn-1-ol. Better results were obtained when the previously synthesized complex [Mo(CO)$_5$(THF)] dissolved in dichloromethane solution was used as an initiator for this reaction. In this reaction, ^{1}H NMR spectroscopy made it possible to detect the η^2-coordination of the



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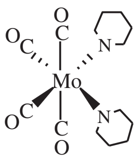

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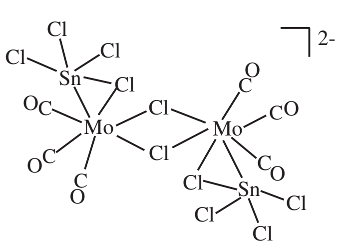

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Chart 1. Schematic view of the molybdenum complexes **1**, **2** and **3**. An ionic complex **3a** contains two allyl piperidinum cations {C_3H_5pip}$^+$ but **3b** contains two piperidinum cations [Hpip]$^+$ as the counter ions.

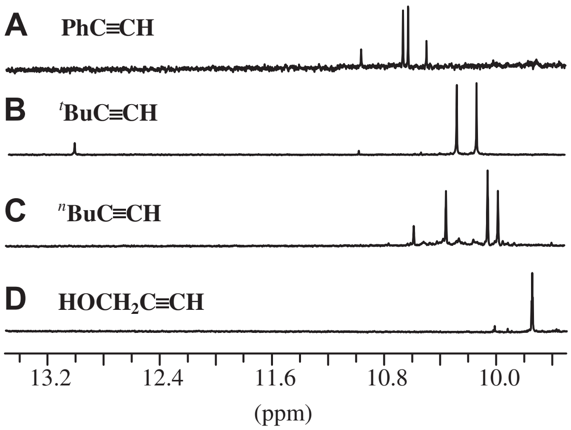
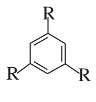
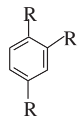


Fig. 1. Selected region of the ^{1}H NMR spectrum showing signals indicating η^2-coordination of terminal alkynes to the molybdenum center observed in the reaction of: (A) PhC≡CH and **2**/$SnCl_4$, (B) ^{t}BuC≡CH and **2**/$SnCl_4$, (C) ^{n}BuC≡CH and **2**/$SnCl_4$, (D) $HOCH_2C$≡CH and $[Mo(CO)_5THF]$.

Table 2
Chemical shift (δ, ppm) of aromatic protons in NMR spectra ($CDCl_3$) of 1,3,5 and 1,2,4 substituted benzenes obtained in reactions of monosubstituted alkynes RC≡CH.

R				
	H(2,4,6)	H(3)	H(5)	H(6)
Ph	7.77	7.66	7.67	7.49
^{t}Bu	7.23	7.57	7.02	7.41
^{n}Bu	6.79	6.92	6.90	7.02
CH_2OH	7.29	7.37	7.30	7.34
CMe_2OH	7.14	7.47	7.36	7.02

C≡C bond of prop-2-yn-1-ol to the molybdenum atom. This coordination was indicated by two proton signals, one observed as a triplet ($^3J_{H-H} = 1.9$ Hz) at $\delta_H = 9.74$ ppm and another observed as a twice-as-intense doublet ($^3J_{H-H} = 1.9$ Hz) at $\delta_H = 2.81$ ppm (Fig. 1). In this reaction, prop-2-yn-1-ol was transformed to cyclotrimers: 1,3,5-T($HOCH_2$)B and 1,2,4-T($HOCH_2$)B (Fig. 3, Tables 1 and 2), observed in this reaction by ^{1}H NMR spectroscopy in a 1:1.8 molar ratio. In the GC–MS spectrum, two signals were detected, one for $M^+ = 168$ (cyclotrimers) and the other one for $M^+ = 170$, thus different by the mass of two hydrogen atoms. This can suggest that during this catalytic reaction, the cyclotrimerization products are formed through a molybdenacycloheptatriene intermediate species (Scheme 4), from which triene may be released in reaction with the source of the hydrogen atom. This is not surprising for a reaction of prop-2-yn-1-ol, containing an active hydrogen at the OH group, which can be oxidatively added to a molybdenum(0) center. The oxidative addition of the H–O bond of phenols to molybdenum(0) in **1** was suggested by McCullough and Schrock for the formation of the first reported homogenous system for the metathesis of alkynes involving **1** as the catalyst precursor [43]. In all the prop-2-yn-1-ol reactions carried out in the presence of molybdenum(0) complexes, two equally intense olefin proton signals at δ 6.23 (d, $^3J_{H-H} = 14.5$ Hz) and δ 5.81 (dt, $^3J_{H-H} = 14.5$ Hz, $^3J_{H-H} = 5.7$ Hz) were detected in ^{1}H NMR spectra. In COSY NMR spectra, the latter signals are correlated, but the signal at δ 5.81correlates with the twice-as-intense proton signal at 4.18 ppm. In HMQC spectra, these three proton signals correlate with the ^{13}C carbon signals at δ 135.5, 132.5, and 63.0 ppm, respectively. Thus, the NMR spectra suggested the formation of species containing the hydroxymethylvinyl –CH=CH(CH_2OH) fragment. Such a fragment may include di(hydroxymethyl)butadiene (hexa-2,4-diene-1,6-diol) or tri(hydroxymethyl)hexatriene. The formation of the latter compound was proved by the GC–MS

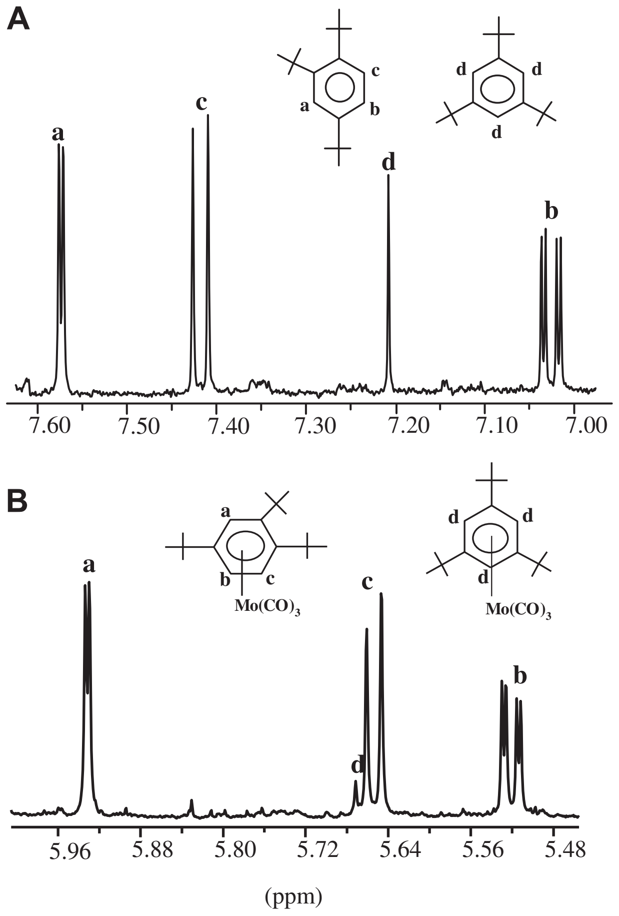


Fig. 2. (A) Partial ^{1}H NMR spectrum (500 MHz, $CDCl_3$) showing signals of *ca.* 1:7 mixture of 1,3,5-T^{t}BB and 1,2,4-T^{t}BB formed in photochemical reaction of ^{t}BuC≡CH in the presence of **1**. (B) Partial ^{1}H NMR spectrum showing signals of 1,3,5-T^{t}BB and 1,2,4-T^{t}BB η^6-coordinated to molybdenum center.

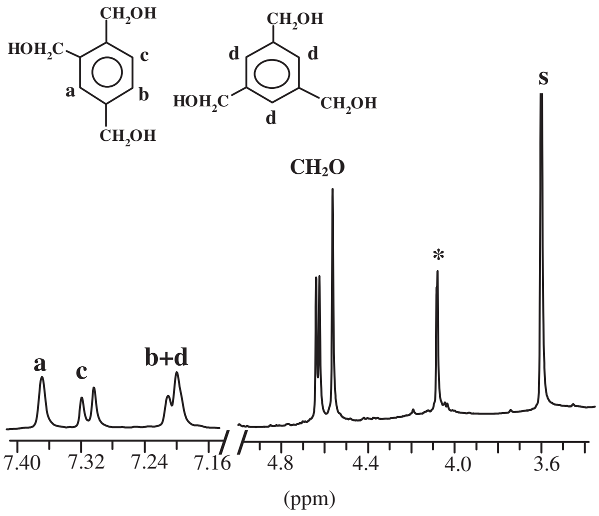


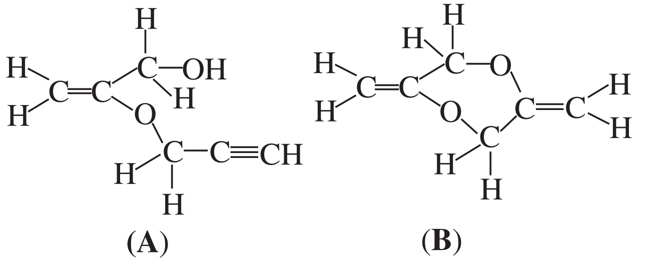
Fig. 3. Partial ^{1}H NMR spectrum (500 MHz, C_4H_8O) showing signals of *ca.* 1:5 mixture of 1,3,5-T($HOCH_2$)B and 1,2,4-T($HOCH_2$)B formed in reaction of $HOCH_2C$≡CH in the presence of **3b**. The proton signal denoted by s is due to C_4H_8O.

method. We observed correlation between the amount of cyclotrimers and the latter species; increasing amounts of this species lowered the amounts of cyclotrimers. Another species containing the hydroxymethylvinyl unit was detected by two equally intense olefin proton signals at δ 6.33 (d, $^{3}J_{H-H} = 16.5$ Hz) and δ 5.91 (dt, $^{3}J_{H-H} = 16.5$ Hz, $^{3}J_{H-H} = 5.4$ Hz). These two signals may be assignable to the dimer $HOCH_2C{\equiv}C{-}CH{=}CH(CH_2OH)$. However, a very low concentration of that species in the reaction products did not make it possible to obtain ^{13}C NMR spectra and interpret it fully. The highest conversion and selectivity of the cyclotrimerization reaction of prop-2-yn-1-ol were detected by NMR in photochemical reaction carried out in toluene solution (Table 1).

*3.1.2. Reactions of alkynes in the presence of **2***

In the process of studying reactions of alkynes with **2** (Chart 1), we observed a relatively fast reaction of hydroxysubstituted alkynes, while alkyl derivatives were almost non-reactive. Thus, in contrast to $^{t}BuC{\equiv}CH$, $HOCH_2C{\equiv}CH$ reacted very smoothly in the presence of complex **2**, and during the first few minutes of the reaction the complete decay of ν(CO) bands of **2** at 2013 (w), 1887 (vs), 1868 (m), and 1819 (w) cm^{-1} was observed by IR spectra. GC–MS analysis of the crude reaction products suggested the formation of oligomers of prop-2-yn-1-ol, such as dimers (7.8%), trimers (0.2%), and pentamers (92%). However, in the mass spectrum of the pentamer, it was impossible to detect the parent molecular ion ($C_{15}H_{20}O_5$, $M^{+} = 280$); only a very low-intensity peak for mass 264 (M^{+}, −16) was observed. The most intense peak in this spectrum was that for mass 98 ($C_5H_6O_2$).

Studies of the crude reaction product by NMR spectroscopy allowed us to detect two similar compounds formed in a 2:1 molar ratio, which can be described as compounds **a** and **b**, both containing the vinylidene unit, like the two dimers **A** and **B** presented in Scheme 3 (see Supplementary Data for the NMR spectra). The methylidene protons of **a** were detected at δ 4.91 and 4.73 ppm. Both proton signals correlate with a carbon signal at δ 111.7 ppm in the HMQC NMR spectrum. Similar correlation was observed between the methylidene proton signals at δ 4.98 and 4.81 ppm and the carbon signal 109.4 ppm of **b**. Two protons of the methylene unit bounded to the tertiary carbon of the vinylidene unit are diastereotopic and were detected as doublets ($^{2}J_{H-H} = 12.7$ Hz) at δ 4.36 and 4.10 ppm for **a** and at δ 4.22 and 4.14 ppm ($^{2}J_{H-H} = 12.1$ Hz) for **b**. In the $^{1}H{-}^{13}C$ HMQC NMR spectra, the correlation between the methylene proton signals at δ 4.36 and 4.10 ppm with carbon signals at δ 68.8 for **a** and proton signals at δ 4.22 and 4.14 ppm with carbon signals at δ 72.7 for **b** was detected. Two tertiary carbons of the vinylidene unit of **a** and **b** were detected at δ 141.2 and 141.3 ppm, respectively. Their assignment was possible due to the observed correlation in the HMBC NMR spectrum, in which the latter carbon signals correlated with the above-discussed methylidene and methylene proton signals as well as with the methine proton signal at δ 2.91 (**a**) and 3.36 ppm (**b**); both signals were observed as pseudo triplets with $J_{H-H} = 7.5$ and 6.9 Hz, respectively. This NMR analysis as well as the very good solubility of these oligomers in hexane suggests their formation pathway through the addition of the polar H–O bond of one alkynol molecule to the triple bond of another one. The first step of this reaction and the formation of vinylidene dimers of prop-2-yn-1-ol is shown in Scheme 3. However, repeated attempts to resolve the structure of the final product by NMR analysis failed. The structure of this compound needs additional studies.



Scheme 3. Proposed structure for two vinylidene dimers (**A**) and (**B**) formed in reaction of prop-2-yn-1-ol in the presence of **2**.

It must be noted that the formation of the vinylidene dimer (**A**) (Scheme 3) has been recently proposed as the first step in the reaction of prop-2-yn-1-ol in the presence of a tetracarbonyl complex of platinum leading to the formation of a formal tetramer of prop-2-yn-1-ol (2,5-dimethyl-2,5-bis(2-propynoxy)-1,4-dioxane) [44]. The addition of the H–O bond of alcohols to the triple bond of alkynes has also been observed in their reactions catalyzed by gold complexes [45].

The very fast reaction of $HO(CH_3)_2CC{\equiv}CH$ in the presence of **2** in dichloromethane solution led to the formation of a brown precipitate which was very slightly soluble in $CDCl_3$ and could not be analyzed by the NMR method. Analysis of compounds soluble in $CDCl_3$ by NMR spectroscopy revealed the formation of a compound (*ca.* 5%) containing a vinyl unit, $CH{=}CH_2$, and another one (*ca.* 95%), containing piperidinium cation ($Hpip^{+}$) [38]. Analysis of the reaction products by the ESI-MS method showed the anion $[C_{30}H_{38}Mo_2O_{14}]^{-}$ ($M^{-} = 814.5$), which may contain a partially hydrogenated tetramer of 2-methylbut-3-yn-2-ol coordinated to two molybdenumpentacarbonyl units ($[Mo_2(CO)_{10}(C_5H_8O)_4H_6]$). This suggests fairly good agreement obtained between the experimental and the calculated mass spectrum (see Supplementary Data). However, the structure of this compound needs additional studies.

*3.1.3. Reactions of alkynes in the presence of **2** and $SnCl_4$ (1:2)*

Reactions of alkyl- or aryl-substituted alkynes ($^{t}BuC{\equiv}CH$, $^{n}BuC{\equiv}CH$, and $PhC{\equiv}CH$) in dichloromethane solution containing the piperidine complex **2** are very slow and after 24 h do not give expected products of alkyne transformation. However, if $SnCl_4$ was first added to a solution containing complex **2** (*ca.* 1:2 molar ratio) and then alkynes were added, the decay of the molybdenum complex could be observed by IR spectroscopy, and the conversion of alkynes ($PhC{\equiv}CH$, $^{t}BuC{\equiv}CH$, $^{n}BuC{\equiv}CH$) reached 100% after 24 h reaction at room temperature. GC–MS and NMR analyses showed that the alkyne is transformed with high selectivity (*ca.* 100%) to cyclotrimerization products (Tables 1 and 2, Figs. 2 and 4). Moreover, analysis of the reaction products by ^{1}H NMR spectroscopy revealed the η^{2}-coordination of the alkyne to the molybdenum atom detected due to ^{1}H proton signals at *ca.* 10 ppm (Fig. 1). In reactions of all of the investigated alkynes, several signals with different but very low intensities compared with the simultaneously observed proton signals of cyclotrimers were observed in this range. Only in reaction of $^{t}BuC{\equiv}CH$ was the concentration of the η^{2}-alkyne complex high enough for the measurement of the $^{13}C\{^{1}H\}$ NMR spectrum. The $^{1}H{-}^{13}C$ HMQC NMR spectra allowed us to detect the correlation of proton signals at 10.15 and 10.27 ppm with carbon signals at 157.7 and 168.6 ppm, respectively. The values of chemical shifts of these carbon atoms are characteristic for complexes in which the alkyne coordinates as a two-electron donor [46–49]. This experiment showed an important role of $SnCl_4$ as an activator of the molybdenum(0) complex **2**. The activation of **2** by $SnCl_4$ results first of all from its Lewis acid properties, which made it possible to remove the piperidine ligand from the coordination sphere of the molybdenum center and to create the possibility of coordinating and activating the alkyne. Two alkynes coordinated to a molybdenum center can be transformed through oxidative coupling to molybdacyclopentadiene and next to a cyclotrimer. The

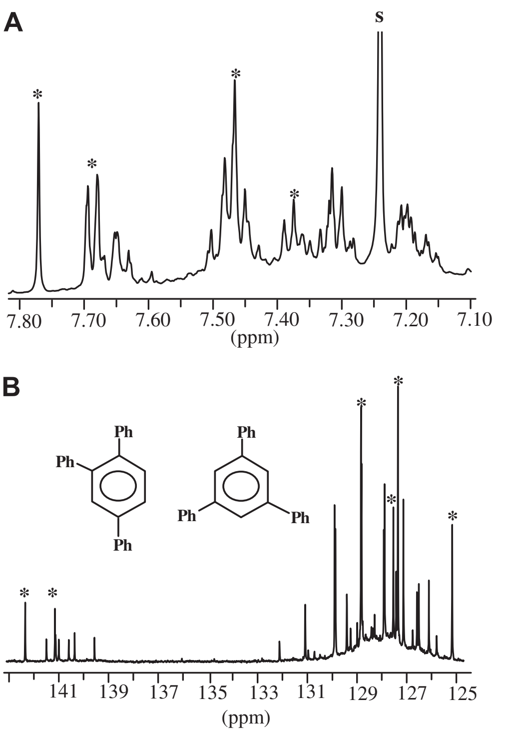
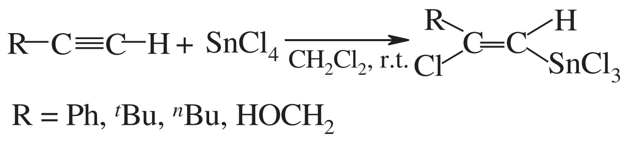


Fig. 4. (A) Partial ^{1}H NMR spectrum and (B) $^{13}C\{^{1}H\}$ NMR spectrum showing signals of *ca.* 1:1 mixture of 1,3,5-TPB and 1,2,4-TPB. Carbon signals of 1,3,5-TPB are denoted by an asterisk (*) and $CDCl_3$ by s.

η^2-coordination of alkyne in the molybdenum complex appears to be the principal feature of all reactions of alkynes catalyzed by molybdenum complexes. Another role of tin tetrachloride is to oxidize molybdenum(0) to molybdenum(II) [38]. This process is always accompanied by the decarbonylation of molybdenum(0) carbonyls [23]. The *in situ* generated coordinatively unsaturated molybdenum(II) species interacts with alkynes to give a bisalkyne complex which can be transformed in the presence of an excess of alkyne to give cyclotrimers. However, at a molar ratio of $SnCl_4$/**2** higher than 2, the simultaneous formation of the recently described stannylation product of alkyne by $SnCl_4$ (chlorovinyltin trichlorides) (Scheme 4) [50] was observed. Thus, tin tetrachloride reacts with the molybdenum(0) complex **2** as well as with alkynes. In summary, we can say that complex **2** initiates the cyclotrimerization reaction only after activation by $SnCl_4$. The activation process of **2** may be effected by the formation of the very reactive binuclear molybdenum(II) complex **3** [38]. A similar effect (an increase in catalytic activity) had been observed before when iodine was added as oxidant to a catalytic system containing a molybdenum(0) complex [8].

3.2. Reactions of alkynes in the presence of the molybdenum(II) complexes *3a* and *3b*

When $^{t}BuC{\equiv}CH$ was added to the solution of the molybdenum(II) complex **3a** (Chart 1) in dichloromethane, the spontaneous precipitation of a white solid was observed. The solid, isolated after 24 h of reaction time, was shown by GPC analysis to be a high-molecular-weight polymer (M_n 127251, M_w 147368) with a low polydyspersity index (PDI = M_w/M_n 1.16). TGA analysis of poly(^{t}butylacetylene) (poly-^{t}BA) showed a one-step degradation process with the onset decomposition temperature at *ca.* 256 °C. Such high thermal stability of poly(^{t}BA) was observed for the first time. As reported previously by Masuda et al. [51], the thermal degradation of poly-^{t}BA started at *ca.* 200 °C. This may be the effect of the polymer structure. Analysis of poly-^{t}BA by NMR spectroscopy showed the exclusively *cis* configuration of the polymer units. This was indicated by one sharp signal at 6.28 ppm in the ^{1}H NMR spectrum and one signal of three equivalent methyl groups at *ca.* 32 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum (Fig. 5) [28,52,53]. Although the preferred *cis* configuration of poly-^{t}BA had been observed before, the *cis* polymer content was never so high.



Scheme 4. Stannylation of terminal alkynes by $SnCl_4$ [50].

In the reaction of PhC≡CH in the presence of catalytic amounts of **3a** or **3b**, the formation of orange polyphenylacetylene (poly-PA) was observed. The number-average molecular weight of this polymer (M_n 2418) is much more smaller than that of poly-^{t}BA, but the PDI is higher, at 1.75, than that for poly-^{t}BA. The thermal degradation of poly-PA started at *ca.* 200 °C, that is at a lower temperature than for poly-^{t}BA. This may be the effect of the polymer structure. The broad signal in the range 7.5–5.5 with three maximums at 6.93, 6.62, and 5.83 ppm in the ^{1}H NMR spectrum and a broad signal in the range 130–124 ppm with a maximum at 127.7 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum suggest no regular structure of the polymer units of poly-PA [52].

When $HOCH_2C{\equiv}CH$ was added to the solution of the molybdenum(II) complex **3b** in dichloromethane, the spontaneous precipitation of a brown solid was observed. Analysis of the soluble compounds by NMR spectroscopy showed a 64% conversion of alkynol and the formation of cyclotrimers with 98% selectivity (1,3,5-T($HOCH_2$)B and 1,2,4-T($HOCH_2$)B in the 1:5 molar ratio). The remaining products included unidentified compounds containing olefin bonds. Among them, compounds containing the hydroxymethylvinyl unit $-CH{=}CH(CH_2OH)$ (see Section 3.1.1.) were detected. Analysis of the brown solid by NMR spectroscopy or GPC was impossible because of its poor solubility in organic solvents, but its IR spectrum showed bands characteristic for the simultaneously formed piperidinium cation of the ionic compound $[Hpip]_2[SnCl_6]$ [54] dominating and obscuring polymer bands. The formation of a brown solid was also observed in the analogous reaction of $HO(CH_3)_2CC{\equiv}CH$ and **3b**. Analysis of the latter solid by NMR spectroscopy or GPC was impossible due to its poor solubility. Analysis of

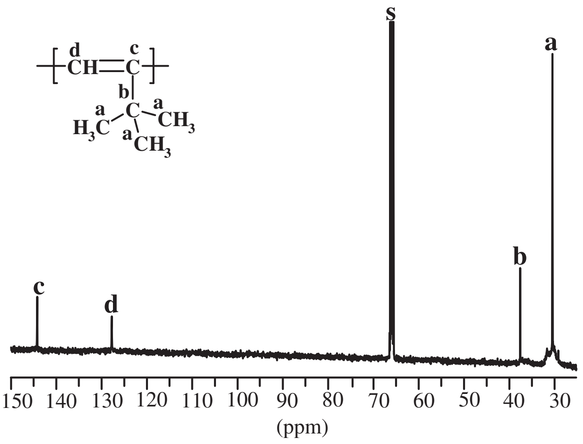


Fig. 5. (a) $^{13}C\{^{1}H\}$ NMR spectrum (125.76 MHz, C_4D_8O) showing signals of poly-*t*-butylacetylene. The carbon signal denoted by s is due to C_4D_8O.

the soluble compounds by NMR spectroscopy showed the formation of 1,3,5-T($HOCMe_2$)B and 1,2,4-T($HOCMe_2$)B in the 1:5 molar ratio. ESI-MS analysis of the solution revealed the formation of several molybdenum compounds identified as anions containing alkynol as a neutral or anion ligand: M^- 291 $[Mo(CO)_4(C_5H_7O)]^-$, 319 $[Mo(CO)_5(C_5H_7O)]^-$, 515 $[Mo(C_5H_8O)_4(C_5H_7O)]^-$, 571 $[Mo(C_5H_7O)_2(SnCl_3)(CO)_3]^-$. These results confirm the ability of $HO(CH_3)_2CC\equiv CH$ to coordinate to the molybdenum center as an anion that is otherwise like the η^2-coordination of the $C\equiv C$ triple bond, identified here by NMR spectroscopy.

4. Conclusions

In summary, we have described an efficient and stereoselective method for the synthesis of substituted benzenes by simple procedures, under mild reaction conditions, and in good yield. The cyclotrimerization products formed in reaction of monosubstituted alkynes ($PhC\equiv CH$, $^tBuC\equiv CH$, $^nBuC\equiv CH$, $HOCH_2C\equiv CH$, $HO(CH_3)_2CC\equiv CH$) have been characterized by ^1H and ^{13}C NMR spectroscopy. It should be noted that benzene derivatives containing the polar functional group OH were obtained for the first time. It is very well known that the polar hydroxyl group has great utility for further transformation and as a building block in organic synthesis. Molybdenum(II) complexes (**3a** and **3b**) formed in reaction of the molybdenum(0) complex **2** and tin tetrachloride appeared particularly effective as catalysts for alkynol cyclotrimerization. However, the reaction of $^tBuC\equiv CH$ and $PhC\equiv CH$ in the presence of a molybdenum(II) complex leads to the selective formation of well-characterized polymers.

The selectivity of alkyne oligomerization reactions depends on the oxidation state of the molybdenum atom of the catalyst. Thus, reactions of monosubstituted alkynes in dichloromethane solution and in the presence of the molybdenum(0) complex **2** never yields benzene derivatives without the addition of $SnCl_4$ as an activator. When $SnCl_4$ was added, benzene derivatives were obtained in good yields (*ca*. 100%). In the presence of complex **2**, prop-2-yn-1-ol transforms to a cyclic oligomer containing a vinylidene unit, which suggests the addition of an H–O bond to the triple $C\equiv C$ bond of alkynol.

It should be noted that regardless of the oxidation state of molybdenum and the substituents present at the triple bond of alkynes, the η^2-coordination of alkynes to the molybdenum center was observed by the NMR method at the initiating step of the reaction.

It is noteworthy that all molybdenum-mediated alkyne reactions take place under very mild conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jorganchem.2012.05.044. These data include MOL files and InChiKeys of the most important compounds described in this article.

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