



Catalytic polymerization of alkynes with the quadruply bonded octachloroditungsten anion

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ABSTRACT

In this work are described the reactions of the quadruply bonded ditungsten complexes $\text{Na}_4[\text{W}_2\text{Cl}_8(\text{THF})_x]$ (**1**) and $[\text{W}_2\text{Cl}_4(\text{PMe}_3)_4]$ (**2**), which contain the W_2^{4+} core and have the $\sigma^2\pi^4\delta^2$ electronic configuration, as well as of the mononuclear $[\text{WCl}_4(\text{THF})_2]$ (**3**) with alkynes $\text{R}^1\text{C}\equiv\text{CH}$, $\text{R}^2\text{C}\equiv\text{CR}^3$ ($\text{R}^1 = \text{Ph}$ (**4**), ^tBu , ^iBu , Me_3Si , C_{10}H_7 (naphthyl), C_{12}H_9 (biphenyl)); $\text{R}^2=\text{R}^3=\text{Me}$, $\text{R}^2=\text{Me}$, $\text{R}^3=^i\text{Pr}$; $\text{R}^2=\text{R}^3=\text{Et}$; $\text{R}^2=\text{Ph}$, $\text{R}^3=\text{Me}$; $\text{R}^2=\text{Ph}$, $\text{R}^3=\text{Et}$; $\text{R}^2=\text{R}^3=\text{Ph}$; $\text{R}^2=\text{R}^3=\text{AcO}$). Complex **1** acts as an efficient single-component initiator for the homogeneous or heterogeneous high-yield polymerization of monosubstituted alkynes. The reaction is very fast in CH_2Cl_2 or heterogeneously and slow in THF. The yield is not significantly affected by the bulk of the alkyl substituents. The reaction is not so efficient with internal alkynes, and is limited to those bearing the less sterically demanding substituents. Polymerization of **4** in THF shows that the reaction comprises three distinct steps. The first is very fast ($t = 3$ min), with consumption of nearly half of **4** (ca. 42%), producing Poly(**4**). The polymer formed is degraded equally fast regenerating **4** (ca. 23%) and oligomeric species ($M_n < 1000$). Subsequent polymerization is slower and complete within 8 h. Direct evidence for the metathetical mechanism of the polymerization was obtained by the in situ examination of the above reaction by ^1H NMR at various temperatures. In contrast, complex **2** alone or activated with EtAlCl_2 is unreactive towards **4**, whereas **3** produces Poly(**4**) in small yield (20%) and very broad polydispersity.

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1. Introduction

Polymerization of alkynes with transition metal complexes has been studied thoroughly because of the unique physicochemical properties of the polyacetylenes (conductivity, ferromagnetism, non-linear optical properties, and permeability) that make them promising materials for several applications [1–3].

The reaction is catalyzed mainly by different mononuclear transition metal catalysts based on Ru, Rh, Ir, Ni, Pd, and especially on Mo and W [4,5]. There is extensive literature for the latter and several general classes of compounds have been identified. These include: (i) high-oxidation state metal halides, e.g. MoCl_5 and WCl_6 ; (ii) high-oxidation state halides activated by co-catalysts, e.g. $\text{WCl}_6/\text{SnPh}_4$, $\text{MoCl}_5/\text{SnBu}_4$; (iii) UV-irradiated solutions of metal carbonyls in a halogenated solvent, e.g. $\text{M}(\text{CO})_6/\text{CCl}_4$, $\text{M} = \text{Mo}$, W ; (iv) alkylidyne or alkylidene complexes of Mo and W formed in situ, as in the cases of (i)–(iii), or discreet ones including the well-

defined Schrock catalysts. Conversely, alkylidynes can be formed by the metathesis of M_2 complexes containing M^2M ($n = 3$) bonds, and an alkyne's $\text{C}\equiv\text{C}$ bond [6].

Although some dinuclear complexes containing M^2M multiple bonds ($n = 2$ or 3), e.g. $[\text{M}_2\text{Cl}_6(\text{tht})_3]$ ($\text{tht} = \text{tetrahydrothiophene}$, $\text{M} = \text{Nb}$, Ta [7], and Mo [8]), and $[\text{M}_2(\text{OR})_6]$ ($\text{M} = \text{Mo}$, $\text{R} = ^i\text{Pr}$, ^tBu , and neopentyl; $\text{M} = \text{W}$, $\text{R} = ^t\text{BuMe}_2\text{SiO}$ [9,10] are capable of inducing metathesis, cyclotrimerization and polymerization of certain alkynes, there is very little information on analogous reactions containing M^2M bonds [11].

The only known examples include: (a) the Mo_2^{4+} complexes $\text{cis-}[\text{Mo}_2(\mu\text{-O}_2\text{CMe})_2(\mu\text{-en})_2(\text{en})_2](\text{MeCO}_2)_2\text{-}(\text{en})$ ($\text{en} = \text{ethylenediamine}$) and $[\text{Mo}_2(\mu\text{-O}_2\text{CMe})_4(\text{Me}_2\text{XCH}_2\text{CH}_2\text{XMe}_2)]_n$ ($\text{X} = \text{N}$, P) which catalyze the coupling, oligomerization and metathesis of internal alkynes ($\text{RC}\equiv\text{CR}'$, R and R' alkyls $\text{C}_1\text{--}\text{C}_{10}$ or aryl) [12–14]; (b) the heterometallic compounds $[\text{Mo}_2(\mu\text{-O}_2\text{CR})_2\{\text{Al}(\mu\text{-OR}')_4\}_2]$ ($\text{R} = \text{Me}$, ^tBu , CF_3 ; $\text{R}' = \text{Ph}$) or analogous species generated in situ from the reaction of homo- or heterodinuclear M^2M complexes ($\text{M} = \text{M}' = \text{Mo}$; $\text{M} = \text{Mo}$, $\text{M}' = \text{W}$) with various alkoxides or phenoxides of aluminum and titanium, which metathesize specific internal alkynes [15]; and (c) the bicomponent system $[\text{Mo}_2(\mu\text{-O}_2\text{CMe})_4]/\text{LA}$ ($\text{LA} = \text{TiCl}_4$, SnCl_4 , GeCl_4 , EtAlCl_2), which was found

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Table 1
Reactions of **1**, **2**, and **3** with mono- and disubstituted alkynes

Entry	Catalyst	Monomer	Solvent	t (h)	Yield (%)	Cis (%)	$M_n \times 10^{-3a}$	M_w/M_n	Colour
1	1	4	–	0.1	95	61	8.7	1.2	Red
2		4	THF	8	93	75	35.7	1.7	Red
3		4	toluene	0.1	96	40	41.2	1.5	Red–orange
4		4	CH ₂ Cl ₂	0.1	97	0	28.2	1.6	Red–orange
5		5	THF	8	92	39	59.1	1.9	Orange
6		5	–	8	96	41	45.8	1.6	Orange
7		6	THF	8	94	42	105	1.5	White
8		7	THF	8	72 ^b	36	22.9	1.4	White
9		8	THF	8	97	5	18.2	1.9	Dark purple
10		9	THF	8	94	27	13.8	1.5	Brown
11		10	THF	8	20 ^b	N/A	–	–	White
12		11	THF	8	17 ^b	N/A	200	1.4	White
13		12	THF	8	12 ^b	N/A	–	–	White
14		13	THF	8	10 ^b	N/A	161	2.2	White
15		14	THF	8	<1 ^b	N/A	–	–	Pale yellow
16		15	THF	8	– ^c	–	–	–	–
17		16	THF	8	– ^c	–	–	–	–
18	2	4	CH ₂ Cl ₂	24	– ^c	–	–	–	–
19	3	4	THF	8	20 ^b	37	–	– ^d	Orange

Conditions: **1**, **2**, or **3** (0.009 mmol), substrate (2.7 mmol)/5.0 mL solvent.

^a By SEC in THF at 40 °C.

^b Same yield after 24 h.

^c No polymerization.

^d Very broad molecular weight distribution.

to induce monosubstituted acetylene (R = Ph, ^tBu) cyclotrimerization and/or polymerization, depending on the solvent and the LA used [16]. Lately, bimetallic metal–metal bonded μ -alkyne derivatives have brought considerable interest from the point of view of bonding and potential catalytic activity, with the first examples usually associated with π -acceptor (η^5 -C₅H₅, CO) or π -donor (OR, NR₂) ligands [17–20]. The isolation and structural characterization of [Mo₂(en)₄(μ -4-MeC₆H₄C≡CH)(μ -O₂CMe)](MeCO₂)₃·(en)₂ [21] and of [W₂(μ -O₂C^tBu)₄(μ -RCCR')₂] (R = R' = Me, Et, Ph; R = Me, R' = Ph) [22], where one or two alkynes are perpendicularly bridging the M₂⁴⁺ bonding axis, has been of vital importance for the identification of the actual catalytic species responsible for the alkyne reactions outlined above.

In view of these findings, and since there exist only a few instances of such complexes supported by halides, e.g. [M₂Cl₄(μ -Cl)₂(μ -RCCR)(THF)₂] (M = Ta, W) deriving from alkyne addition to the doubly (Ta = Ta) [23,24] and triply (W = W) [25] bonded precursors, we have previously attempted to isolate analogous molecules from the reaction of **4** with the quadruply bonded halide anion [W₂Cl₈]⁴⁻ (W₂⁴⁺, $\sigma^2\pi^4\delta^2$), in the form of its sodium salt Na₄[W₂Cl₈(THF)_x] (**1**). Instead, we have found that **1** exhibits high polymerization activity (polymer yield above 90%) and ca. 75% *cis*-stereoselectivity in THF [26]. Indirect evidence concerning the propagation mechanism has been obtained from the reactions of **1** with norbornene (**NBE**) and the copolymerization of equimolar amounts of **4** with **NBE**. In the first case, poly(cyclopentene-1,3-divinylene) with 82% *cis*-selectivity was produced, whereas in the second one, an almost *all-cis* high molecular weight copolymer containing cyclopentene-1,3-divinylene units, which is free of longer sequences of both **4** and **NBE** units, was produced. This suggests that the homopolymerization of **4** with **1** also proceeds by the metathesis mechanism and that the **4**/**NBE** copolymer structure is close to the alternating one.

Herein, we describe the reactions of **1**, [W₂Cl₄(PMe)₄] (**2**), and [WCl₄(THF)₂] (**3**) with **4** in more detail, along with efforts to obtain direct evidence for the metathetical nature of the polymerization and define better this catalytic system. In addition, the reactivity of **1** with a range of monosubstituted alkynes (R¹C≡CH, R¹=ⁿBu (**5**), ^tBu (**6**), Me₃Si (**7**), C₁₀H₇ (naphthyl, **8**), C₁₂H₉ (biphenyl, **9**)) bearing

bulky alkyl substituents including fused aromatic rings, as well as disubstituted ones (R²C≡CR³, R²=R³=Me (**10**), R²=Me, R³=ⁿPr (**11**); R²=R³=Et (**12**); R²=Ph, R³=Me (**13**); R²=Ph, R³=Et (**14**); R²=R³=Ph (**15**); R²=R³=AcO (**16**)), is also reported. The results are summarized in Table 1.

2. Experimental

2.1. General data

Starting materials were purchased from Sigma–Aldrich, except for decahydronaphthalene (*cis* and *trans* mixture of isomers), which was purchased from Riedel de Haën, and are of the highest available purities. Complexes **1** [27], **2** [28] and **3** [29] were prepared according to literature procedures and checked for purity. The alkynes (**4–14**, **16**) were dried by stirring with CaH₂ under argon, distilled under vacuum and stored in the dark under argon. Diphenylacetylene (**15**) was purified by sublimation in vacuo and subsequent elution with hexane through an Al₂O₃ column prior to use. THF and diethyl ether were distilled over Na/Ph₂CO, toluene and hexane over Na, CH₂Cl₂ over CaH₂, methanol over sodium methoxide. Benzaldehyde was purified by distillation under reduced pressure. All solvents were distilled in an inert atmosphere and were degassed by three freeze–pump–thaw cycles, with the exception of methanol, which was degassed by bubbling nitrogen or argon for 0.5 h. All operations were performed under a pure dinitrogen or argon atmosphere, using Schlenk techniques on an inert gas/vacuum manifold or in a drybox (O₂, H₂O < 1 ppm). IR spectra were recorded on a PerkinElmer 883 IR spectrometer. The NMR spectra at room temperature were recorded on a Varian Unity Plus 300 spectrometer and at various temperatures on a Bruker DRX-400 Avance spectrometer. In all cases, chemical shifts are reported in ppm relative to the deuterated solvent resonances. GC–MS experiments were performed on a Varian 3400 CX GC coupled to a Varian Saturn 2000 MS (Column 30 m × 0.25 mm i.d., 0.25 μ m, DB5-MS; injection 1 μ L, 50:1 split; flow 1 mL/min–He, constant flow; oven 50 °C/hold 3.00 min, 7 °C/min to 150 °C, 50 °C/min to 280 °C, 280 °C/hold 2.12 min, 5 °C/min to 300 °C, 300 °C/hold 4.00 min; injector 280 °C; transfer line 280 °C; MSD scan range 10–600 amu).

The samples were prepared in hexane and decahydronaphthalene was used as internal standard for quantitation. Size exclusion chromatography (SEC) experiments were carried out with a modular instrument consisting of a Waters model 600 pump, a Waters model U6K sample injector, a Waters model 410 differential refractometer and a set of 4 μ -Styragel columns with a continuous porosity range of 10^6 – 10^3 Å. The columns were housed in an oven thermostatted at 40 °C. THF was the carrier solvent at a flow rate of 1 mL/min. The instrument was calibrated with PS standards covering the molecular weight range of 4000–900,000.

2.2. Catalytic reactions

A typical procedure is described as follows. To the catalyst (**1**: 7.5 mg, 0.009 mmol; **2**: 7.3 mg, 0.009 mmol; **3**: 4.2 mg, 0.009 mmol) 5 mL of solvent at –20 °C and the substrate (e.g. **4**, 279 mg, 300 μ L, 2.7 mmol) were added. The mixture was left to warm to room temperature and react for a given time (see Table 1). The final reaction mixture was concentrated and treated with excess methanol to precipitate the polymeric products. The resulting solids were filtered and washed repeatedly with methanol. This procedure was repeated twice. The products were dried in vacuo.

The reaction with EtAlCl₂ was carried out as follows. To complex **2** (7.3 mg, 0.009 mmol) in 5.0 mL of CH₂Cl₂ were added EtAlCl₂ (1 M in hexane, 18 μ L, 0.018 mmol) and **4** (279 mg, 300 μ L, 2.7 mmol). The solution was left to react for 24 h. After addition of methanol no polymer was precipitated.

2.3. Catalytic reactions in NMR tubes

Complex **1** (7.5 mg, 0.009 mmol) was placed in an NMR tube. The bottom third of the tube was cooled to –20 °C and the catalyst was dissolved in *d*⁸-THF (0.7 mL, also at –20 °C). The appropriate amount of the substrate (**4**, 46.5 mg, 50 μ L, 0.45 mmol) was added using a microliter syringe. The NMR tube was transferred to a cold bath at the same temperature as used to record the low-temperature NMR spectra.

2.4. Polymer characteristics

The stereochemistry of Poly(**4**) [30] obtained was determined by ¹H and ¹³C NMR. *cis*–*transoidal* Poly(**4**). ¹H NMR (CDCl₃), δ (ppm): 6.95 (very broad, 3H, *m*- and *p*-H_{aro}), 6.80 (shoulder, 2H, *o*-H_{aro}), 5.84 (broad, 1H, =CH). ¹³C NMR (CDCl₃), δ (ppm): 143–139 (m, quaternary carbons), 131.7 (s, =CH), 131–127 (m, *o*- and *m*-C_{aro}), 126.7 (s, *m*-C_{aro}). IR (KBr) (cm⁻¹): 1484, 1438, 1387, 1329, 1068, 1024, 910, 884, 801, 754, 692. Colour: red. *trans*–*cisoidal* Poly(**4**). ¹H NMR (CDCl₃), δ (ppm): 7.02 (very broad, 6H, H_{aro} and =CH). ¹³C NMR (CDCl₃), δ (ppm): 128 (very broad, C_{aro} and =CH). IR (KBr) (cm⁻¹): 1484, 1438, 1387, 1329, 1068, 1024, 910, 884, 801, 754, 738, 692. Colour: red–orange. The *cis* content was calculated according to the generally accepted equation [31]: %*cis* = (A × 10⁴)/(A_{tot} × 16.66), where A, A_{tot} stand for the area of the vinylic protons at 5.84 ppm and the sum of the areas of all the signals of the polyene, respectively.

Poly(*1*-hexyne) (Poly(**5**)) [32]. ¹H NMR (CDCl₃), δ (ppm): 5.92 and 5.81 (broad, 1H, =CH), 2.09 (broad, 2H, =CCH₂(CH₂)₂CH₃), 1.35 (broad, 4H, =CCH₂(CH₂)₂CH₃), 0.93 (broad, 3H, =CCH₂(CH₂)₂CH₃). ¹³C NMR (CDCl₃), δ (ppm): 139.7 (s, =CⁿBu), 127.0 (s, =CH), 31.2 (s, =CCH₂(CH₂)₂CH₃), 28.2 (s, =CCH₂CH₂CH₂CH₃), 23.1 (s, =CCH₂CH₂CH₂CH₃), 14.0 (s, =CCH₂CH₂CH₂CH₃). IR (KBr) (cm⁻¹): 1635, 940, 780. Colour: orange. The *cis* content was calculated as referenced.

Poly(*tert*-butylacetylene) (Poly(**6**)) [33]. ¹H NMR (CDCl₃), δ (ppm): 6.19 (*cis*) and 5.98 (*trans*) (broad, 1H, =CH), 1.14 (broad, 9H,

CH₃). ¹³C NMR (CDCl₃), δ (ppm): 144.55 (s, =CCMe₃), 125.96 (s, =CH), 37.11 (s, =CCMe₃), 32.47, 31.27 and 30.38 (t, CH₃). IR (KBr) (cm⁻¹): 2960, 1611, 1263, 794. Colour: white. The *cis* content of the polymer was calculated from the ¹H NMR integrals [34] and according to the following equation [33]: %*cis* = 100 × H_a/(H_a + H_b + H_c), where H_a, H_b and H_c stand for the heights of the signals at 31.27, 32.47 and 30.38 ppm, respectively.

Poly(*trimethylsilylacetylene*) (Poly(**7**)) [35]. ¹H NMR (CDCl₃), δ (ppm): 6.70 (*cis*) and 6.36 (*trans*) (broad, 1H, =CH), 0.08 (broad, 9H, Me). ¹³C NMR (CDCl₃), δ (ppm): 138.80 (C=C), 1.02 (Me). IR (KBr) (cm⁻¹): 1650–1550, 1257, 820. Colour: white. The *cis* content was calculated as for Poly(**6**) [36].

Poly(*naphthylacetylene*) (Poly(**8**)). ¹H NMR (CDCl₃), δ (ppm): 6.50–8.50 (very broad, 7H, H_{aro}), 6.24 (shoulder, 1H, =CH). ¹³C NMR (CDCl₃), δ (ppm): 137.6 and 132.5 (d, quaternary carbons), 129–121 (very broad, C_{aro} and C=C). IR (KBr) (cm⁻¹): 3039, 2949, 2838, 1635, 1504, 1386, 1331, 1270, 796, 770. Colour: dark purple. The *cis* content was calculated as for Poly(**4**) [37].

Poly(*biphenylacetylene*) (Poly(**9**)). ¹H NMR (CDCl₃), δ (ppm): 7.3 (very broad, 9H, H_{aro}), 6.1 (broad, 1H, =CH). ¹³C NMR (CDCl₃), δ (ppm): 142–137 (broad, quaternary carbons), 128.8–126.6 (broad, C_{aro} and C=C). IR (KBr) (cm⁻¹): 3017, 2955, 1596, 1477, 1401, 1259, 803, 760, 725, 692. Colour: brown. The *cis* content was calculated as for Poly(**4**) [37].

All of the above polymers are soluble in CHCl₃, CH₂Cl₂, and THF.

Poly(*2*-butyne) (Poly(**10**)) [38]. ¹H NMR (CDCl₃), δ (ppm): 1.58 (broad, 3H, CH₃), 1.53 (broad, 3H, CH₃). ¹³C NMR (CDCl₃), δ (ppm): 131.0 (broad, s, C=C) 18.0 (broad, CH₃). IR (KBr) (cm⁻¹): 2960, 2901, 2845, 1630, 1435, 1362, 1258, 1086, 1024, 802. Colour: white. Very sparingly soluble in CHCl₃, CH₂Cl₂, and THF.

Poly(*2*-hexyne) (Poly(**11**)) [39]. ¹H NMR (CDCl₃), δ (ppm): 2.40 (shoulder, 2H, =CCH₂CH₂CH₃), 1.75 (broad, 3H, =CCH₃), 1.53 (broad, 3H, =CCH₃), 1.43 (broad, 2H, =CCH₂CH₂CH₃), 0.9 (broad, 3H, =CCH₂CH₂CH₃). ¹³C NMR (CDCl₃), δ (ppm): 138.0 (broad, C=C), 130.0 (broad, C=C); 37.0 (broad, =CCH₂CH₂CH₃); 22.0 (broad, =CCH₂CH₂CH₃ and =CCH₃); 14.0 (broad, s, =CCH₂CH₂CH₃). IR (KBr) (cm⁻¹): 2952, 2921, 2861, 1628, 1460, 1372, 1257, 1106, 1024, 802. Colour: white. Soluble in toluene, hexane, and THF.

Poly(*3*-hexyne) (Poly(**12**)). ¹H NMR (CDCl₃), δ (ppm): 2.24 (broad, m, 2H, CH₂), 1.11 (broad, 3H, CH₃), 0.89 (broad, 3H, CH₃). ¹³C NMR (CDCl₃), δ (ppm): 140.0 (broad, C=C), 127.0 (broad, C=C), 26.0 (broad, CH₂), 13.0 (broad, CH₃). IR (KBr) (cm⁻¹): 2950, 2925, 2864, 1626, 1460, 1371, 1258, 1095, 1020, 800. Colour: white. Very sparingly soluble in CHCl₃, CH₂Cl₂, and THF.

Poly(*1*-phenyl-1-propyne) (Poly(**13**)) [40]. ¹H NMR (CDCl₃), δ (ppm): 6.95 (broad, 5H, H_{aro}), 1.54 (broad, 3H, CH₃). ¹³C NMR (CDCl₃), δ (ppm): 140.0 (broad, C=C), 133.0 (broad, C_{aro}), 128.0 (broad, C=C), 21.0 (broad, CH₃). IR (KBr) (cm⁻¹): 3070, 3040, 3010, 2930, 2850, 1593, 1486, 1435, 1365, 765, 695. Colour: white. Soluble in CHCl₃, CH₂Cl₂, THF, and toluene.

Poly(*1*-phenyl-1-butyne) (Poly(**14**)). ¹H NMR (CDCl₃), δ (ppm): 7.00 (broad, 5H, H_{aro}), 2.40 (broad, 2H, CH₃), 1.86 (broad, 2H, CH₂), 1.25 (broad, 3H, CH₃), 0.89 (broad, 3H, CH₃). IR (KBr) (cm⁻¹): 2945, 2926, 2845, 1767, 1735, 1712, 1630, 1486, 1435, 1260, 1100, 800, 695. Colour: pale yellow. Soluble in CHCl₃, CH₂Cl₂, and THF.

Quantitative information by NMR on the geometric structure of polymers from disubstituted alkynes is, as far as we know, unavailable [5].

3. Results and discussion

Within the family of the quadruply bonded bimetallic *d*⁴–*d*⁴ complexes those of tungsten are the most reactive towards oxidation and oxidative addition reactions. This sensitivity of the W⁴W

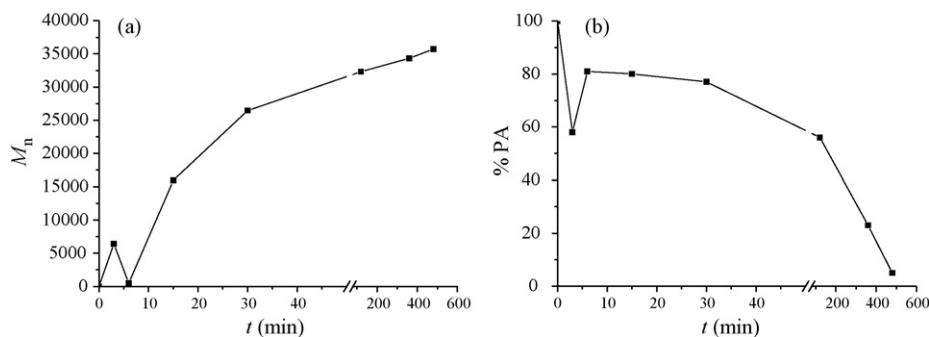


Fig. 1. Polymerization of **4** (279 mg, 300 μ L, 0.45 mmol) with **1** (7.5 mg, 0.009 mmol) in 5.0 mL THF (a) time- M_n plot; (b) time-consumption of **4** plot. The first sample was taken at -5°C and the rest at time intervals while the reaction was warming slowly to room temperature.

bond has been responsible for the difficulties in isolating **1** and the slow development of the W_2^{4+} chemistry in general [11].

Complex **1** is soluble and stable below 0°C in THF, but, above this temperature, decomposes to an insoluble grey material of composition " WCl_2 " and NaCl. Thus, the alkynes were added to THF solutions of **1** at -20°C . In the case of **4**, the blue colour of the solution gradually changes at -5°C to light brown and subsequently to red brown at room temperature, providing Poly(**4**) in high yield (93%) and 75% *cis*-stereoselectivity (Table 1, entry 2). The polymerization is multistage and proceeds in three sequential steps (Fig. 1). The first is fast ($t=3$ min) with nearly half (*ca.* 42%) of **4** consumed producing Poly(**4**) ($M_n \approx 6400$, Fig. 1b). This is followed by fast degradation ($t=6$ min) of the polymer to form **4** ($\sim 23\%$) and oligomers ($M_n < 1000$). Subsequent polymerization is slow and complete after 8 h. These results are reproducible when the same or a different catalyst batch is used.

In dichloromethane, the reaction is very fast and complete within *ca.* 6 min, producing the *trans*-isomer (entry 4), as evidenced by the lack of the 5.84 ppm peak in the ^1H NMR spectrum and the 738 cm^{-1} band in the IR spectrum. Small peaks at $\delta=4.6\text{--}6.2$ ppm in the ^1H NMR spectrum indicate the presence of cyclohexadiene units in the polymer chain [41]. Heterogeneously (addition of neat **4** to solid **1** (caution: highly exothermic) or to a suspension of **1** in toluene) the polymerization proceeds fast affording, in both cases, Poly(**4**) of *cis*-stereochemistry (entries 1 and 3). Control experiments using " WCl_2 " resulting from the decomposition of **1** show no catalytic activity towards the polymerization of this substrate. Under the same conditions, complex **2** alone or activated with EtAlCl_2 (**2**/ EtAlCl_2 : 1/2, 1/4, 1/9, CH_2Cl_2) is inactive, whereas the mononuclear complex **3** produces Poly(**4**) in small yield (20%) and very broad distribution ($M_n \approx 20,000\text{--}100,000$).

The rest of the monosubstituted alkynes react with **1** in a similar manner. The bulk of the alkyl-substituent does not significantly affect the yield of the reaction, except in the case of Poly(**7**) (72%, entry 8). The yield of this reaction is not increased after 24 h. All polymers obtained are soluble in organic solvents (CH_2Cl_2 , CHCl_3 , THF), and have number average molecular weight (M_n) and polydispersity index (M_w/M_n) ranging from 8700 to 105,000 and 1.2–1.9, respectively (entries 1–10).

Disubstituted alkynes are polymerized less efficiently. The reaction is limited to those bearing the less sterically demanding R ligands (entries 11–14), with the yield decreasing by increasing the alkyne's bulk. The polymers are white, except for Poly(**14**), which is pale yellow. The symmetrical ones, Poly(**10**), (**12**), are very sparingly soluble in CH_2Cl_2 , CHCl_3 , THF, whereas the rest are soluble.

All polymers have been characterized from their IR, ^1H and ^{13}C NMR spectra and by correlation with literature data, when available, as referenced.

The difficulty of establishing the mechanism of rapid catalytic polymerization reactions, especially in the absence of isolation of yield-related active intermediates and/or when the concentrations of the catalytically active species are too small to be detected, is well documented. This task becomes even more complicated in bimetallic catalysis, since a variety of potentially active species may be formed, such as: (i) end-on or μ -alkyne adducts, as encountered in $[\text{Cp}_2\text{M}_2(\text{CO})_4]$ [42–44] and $[\text{M}_2(\text{OR})_6]$ [45,46] ($\text{M}=\text{Mo}, \text{W}$); (ii) metal–metal bonded μ -alkylidyne deriving from the alkynes C=C cleavage via addition across a M^2M bond, e.g. $[\text{W}_2(\text{OSi}^t\text{Bu}_3)_4(\mu\text{-CH})(\mu\text{-CPh})]$ [47]; (iii) C–C coupled products, e.g. $[\text{W}_2(\text{O}^i\text{Pr})_6(\mu\text{-C}_4\text{Me}_4)(\eta^2\text{-MeCCMe})]$ [48]; (iv) mononuclear alkyne adducts or alkylidyne from scission or metathesis, e.g. $[(^t\text{BuO})_3\text{W}=\text{CR}]$ ($\text{R}=\text{Me}, \text{Et}, ^i\text{Pr}$ etc) [49–52]; (v) reactive metal carbenes, such as $\{\text{Cl}_{n-2}\text{M}=\text{C}(\text{R})\text{Cl}\}$ or $\{\text{Cl}_{n-2}\text{M}=\text{CHC}(\text{R})\text{Cl}_2\}$ ($\text{M}=\text{W}$) through sequences involving initial alkyne insertion to a M–Cl bond to form a metal–alkenyl $\{\text{Cl}_{n-1}\text{M}-\text{CH}=\text{C}(\text{R})\text{Cl}\}$ followed by HCl loss or ligand (chloride) transfer to the β -position, respectively [53].

With regard to the mechanism of alkyne polymerization, two different pathways are established: alkyne insertion and alkyne metathesis. The intermediates formed are metallacyclic species, alkylidene or alkylidyne complexes, σ -vinyl complexes and metal acetylides. It has been demonstrated that Rh-based catalysis proceeds via the former mechanism, which has been proposed for Ni and Pd derivatives as well [54–56], whereas the polymerization via metathesis is operative for Mo- and W-based catalysts.

Our attempts to isolate intermediates from the reaction of **1** with **4** in THF (**1**/**4**: 1/1–4) always led to formation of small amounts of cyclotrimers, unidentified oligomers (as evidenced by ^1H NMR) and of a very sensitive green solid, which upon slight exposure to air instantly decomposes to blue products insoluble in most common organic solvents. Increasing the amount of **4** just enhances the rate of the polymerization. Despite numerous efforts, we could not crystallize it or satisfactorily characterize it. Specimens of this reaction taken at time intervals after addition of methanol were examined by GC–MS and do not reveal formation of α -chlorostyrene ($\text{PhCl}=\text{CH}_2$) or Cl-containing dimers of **4**, thus excluding coordinated **4** insertion into a W–Cl bond to form an alkenyl-tungsten compound [57].

In order to obtain direct evidence about the metathetical nature of this reaction, we have monitored the polymerization of **4** in situ by ^1H NMR at low temperature (Fig. 2). The substrate was added to a solution of **1** in d^8 -THF at -20°C . The spectrum remained unchanged at temperatures below -5°C . At that temperature, a roll of small peaks, which fall within the region of well-known W-carbene complexes [58–60], or " $\text{W}_2(\mu\text{-RC}\equiv\text{CH})$ " alkynes [25], appeared at $\delta=10.5\text{--}13.5$ ppm. While the reaction was allowed to

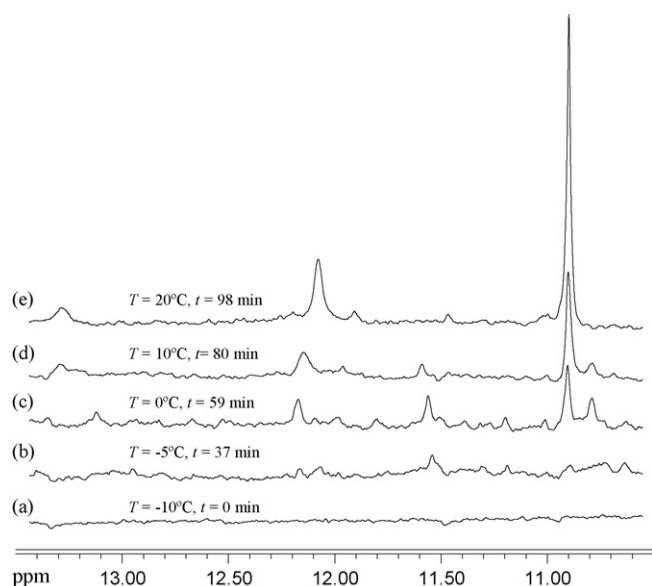


Fig. 2. ^1H NMR spectra (carbene region) of the reaction of **1** (7.5 mg, 0.009 mmol) with **4** (46.5 mg, 50 μL , 0.45 mmol) in d^8 -THF at various temperatures and time intervals, as indicated.

continue, their intensity increased. After 80 min the intensity of some ($\delta = 11.6$, 11.2 and 10.8 ppm) decreased, whereas the intensity of the rest increased and parallel formation of Poly(**4**) was observed. As the polymerization proceeded, these peaks acquired maximum intensity and Poly(**4**) formation increased. The ^{13}C NMR spectrum of this solution did not show any resonances in the W-carbene region, presumably because of the small concentration of these species actually involved in the process. Termination of the reaction with benzaldehyde (PhCHO, **1**/PhCHO: 1/10, $T = 25^\circ\text{C}$) caused slow disappearance of these peaks. Addition of **10** caused also their immediate disappearance and parallel formation of Poly(**10**) sequences. The small solubility of **1** in CD_2Cl_2 did not allow monitoring the events at low temperatures, but at room temperature similar peaks were observed and the same results as above were obtained, except that upon addition of the end-capping reagent (PhCHO) the relevant peaks immediately disappeared. These observations are consistent with the involvement of several active “ W_x -carbene” ($x = 1$ or 2) propagating centers and are compatible with the multistage polymerization of **4** in THF.

The reactivity of **1** differs distinctly from that of the archetypal high-valent chloride WCl_6 (as unicomponent initiator) in terms of reactivity, monomer to catalyst ratio, yield, stereoselectivity and molecular weight in the polymerization of **4**, and resembles more the binary systems $\text{WCl}_6/\text{SnPh}_4$, Sn^nBu_4 or ROH as per reactivity, polymer yield and molecular weight. Also, it differs from the unicomponent chloride catalysts MCl_5 ($M = \text{Nb}, \text{Ta}$), $[\text{MoCl}_3(\text{tht})_3]$, and $[\text{M}_2\text{Cl}_6(\text{tht})_3]$ ($M = \text{Nb}, \text{Ta}, \text{Mo}$), which promote exclusively cyclotrimerization of **4** [4,5].

Further work to establish whether mono- or bimetallic catalysis is in act, as well as to define the precise identity of the active species is in progress.

4. Conclusions

Complex **1** is a highly efficient unicomponent initiator for the polymerization of a range of monosubstituted acetylenes. The reaction is very fast in CH_2Cl_2 and slower in THF. Internal acetylenes are polymerized less effectively with the yield of the reaction decreasing by increasing the steric bulk of the alkyl substituents.

The polymerization of **4** in THF is multistage and consists of: (i) initial fast polymerization yielding Poly(**4**); (ii) equally fast degradation of the polymer formed regenerating **4** and oligomers; (iii) subsequent slower polymerization responsible for the polymer finally obtained. Direct evidence that a metathetical mechanism is in operation has been obtained from the in situ examination of this reaction by ^1H NMR at temperatures ranging from -15 to 25°C , and the observation of several propagating alkylidene active centers.

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