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Polymerization of terminal alkynes with a triply bonded ditungsten halo-complex

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Dedicated to my inspired teacher, Prof. J.M. Brown.

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ABSTRACT

In this work are described the reactions of the triply bonded ditungsten face-sharing bioctahedral (fsbo) halides $A_3[W_2(\mu\text{-}Cl)_3Cl_6]$ ($A^+ = K^+$ (**1**), $^nBu_4N^+$ (**2**)) and $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3$ (**3**), which contain the $(W{\equiv}W)^{6+}$ core and have the $a'^2e'^4$ electronic configuration, with a range of 1-alkynes (RC≡CH, R = Ph (**PA**), C_7H_7 (*o*-methylphenyl), $C_7H_4F_3$ (*o*-trifluoromethylphenyl), ^{n}Bu, ^{t}Bu, Me_3Si, $C_{10}H_7$ (naphthyl)). At ambient temperature complexes **1** and **2** (THF, CH_2Cl_2) are inactive towards **PA**, and when activated with $AlCl_3$ (CH_2Cl_2) give oligomeric products in low yield. In contrast, compound **3** acts as a highly efficient uni-component initiator for the homogeneous or heterogeneous polymerization of the above alkynes providing polymers with high molecular weight. Small amounts of the cyclotrimers are also formed. The reaction is very fast in CH_2Cl_2 or in bulk and slower in oxygen-coordinating solvents (THF, Et_2O). The conditions dictate the microscopic structure of the polymers formed. The yield is not significantly affected by the bulk of the alkyl substituent. The polymerization of **PA** was studied in more detail. In THF it is multimodal involving polymerization and equilibration or degradation steps. Direct evidence in support of the metathetical nature of the polymerization has been obtained from the in situ examination of the reaction at various temperatures ranging from −20 to 20 °C by ^{1}H NMR, and the observation of at least two major active species attributed to the tungsten-carbene propagating polymerization centers.

1. Introduction

Soluble conjugated organic polymers with a well-defined microstructure are of particular importance because of their interesting physicochemical properties (conductivity, ferromagnetism, non-linear optical properties), which make them promising materials in various applications [1–6]. They are accessible via acyclic diene or diyne metathesis polymerization (ADMET [7–9]) or cyclopolymerization [10] starting from α-, ω-dienes or diynes respectively, via ring-opening metathesis polymerization (ROMP) of cyclopolyene precursors [11–14], or more straightforward, via polymerization of 1-alkynes [15–17] (Scheme 1).

Within the different systems based on transition metal complexes (groups IV–X) that catalyze these reactions, and especially the polymerization of alkynes, protagonists are those of Mo, W and Rh [15–19]. The first two operate by a metathesis mechanism and polymerize efficiently sterically crowded alkynes, although in general not stereoselectively. Rh complexes proceed through an insertion mechanism and polymerize almost quantitatively and stereoselectively a rather restricted range of monomers. Whereas Mo and W catalysts are sensitive to polar groups in the monomer, the Rh ones are tolerant to such groups. Under specific conditions, some of the aforementioned systems induce the controlled polymerization of certain alkynes.

There is extensive literature on Mo and W catalysts and the following general classes have been identified: (i) high oxidation state metal halides ($MoCl_5$, WCl_6) alone or activated by co-catalysts, e.g. $WCl_6/SnPh_4$, WCl_6/ROH; (ii) UV-irradiated solutions of metal carbonyls in halogenated solvents, e.g. $M(CO)_6/CCl_4$ (M = Mo, W); (iii) alkylidyne or alkylidene complexes of molybdenum and tungsten formed in situ as in the cases of (i)–(ii), or discreet ones, such as Fischer [20], Casey [20], Rudler [21], and Schrock [22] catalysts. Alternatively, mononuclear alkylidynes can be formed by the M≡M/C≡C metathesis reaction between a M_2-complex and an alkyne [23] Eq. (1). Such six-electron reductive alkyne cleavage transformations are impressively facile, but rare.

$$[(^tBuO)_3W{\equiv}W(O^tBu)_3] + RC{\equiv}CR \rightarrow 2[(^tBuO)_3W{\equiv}CR], \quad R = alkyl \qquad (1)$$

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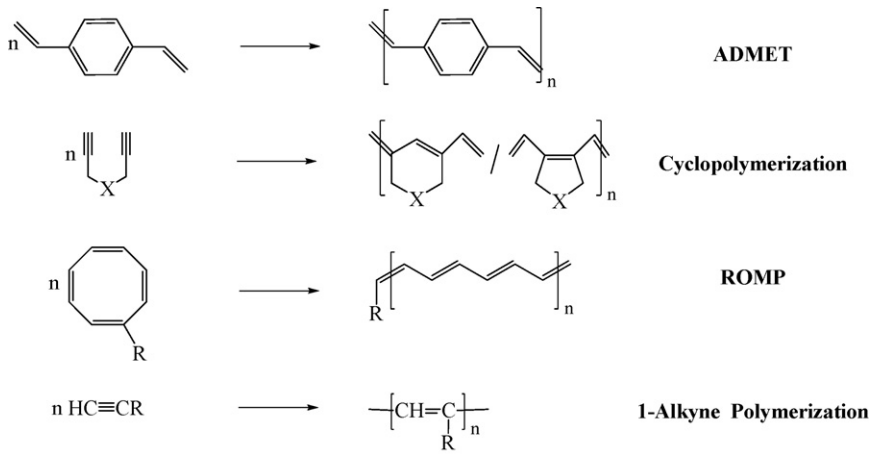


Scheme 1. .

In addition to the above binuclear alkoxides, there exist several other homo- or hetero-bimetallic complexes with formal metal–metal bond orders of 2, 3, and 4, bearing various types of ligands (halide, acetate, allyl, etc.), which are capable as uni- or multi-component initiators to induce metathesis, oligomerization, and polymerization of certain alkynes, albeit with poor selectivity and by unknown mechanisms [24–30].

Bimetallic metal–metal bonded μ-alkyne derivatives have aroused considerable interest from the point of view of bonding and their role in the alkyne transformations outlined above [31–39]. Of particular interest is the ability of $(W\overset{4}{-}W)^{4+}$ complexes to accommodate two *trans* μ-alkyne molecules perpendicularly bound along the W—W bond axis forming bis-(metallocarbotetrahedrane) type adducts, e.g. $\{W_2(\kappa^2\text{-}O_2C^tBu)_4(\mu\text{-}RCCR')_2\}$ (R = R′ = Me, Et, Ph; R = Me, R′ = Ph), which is not encountered in the $(Mo\overset{4}{-}Mo)^{4+}$ analogs [36].

Recently, while we were attempting to isolate analogous species deriving from alkyne addition to the unbridged quadruply bonded $Na_4[W_2Cl_8]\cdot(THF)_x$ (**4**) [$(W\overset{4}{-}W)^{4+}$, $\sigma^2\pi^4\delta^2$] halide, we have discovered that it polymerizes efficiently phenylacetylene (**PA**) and a range of monosubstituted alkynes. Both indirect and direct evidence obtained is indicative of the metathetical nature of the polymerization [40,41]. However, a major disadvantage with this system is the thermal instability of **4** coupled to its high reactivity and sensitivity (H_2O, O_2), therefore an equally efficient but more convenient catalyst would be highly desirable.

Table 1
Reactions of **1**, **2**, **3** with terminal alkynes.

Entry	Catalyst	Monomer	Solvent	*t* (h)	Yield (%)	$M_w \times 10^{-3}$ [a]	M_w/M_n	*Cis* (%)	Colour
1	3[b]	**PA**	THF	8	92	55.8	2.0	90	Red
2		**PA**	Et_2O	8	90	1.5	1.4	78	Orange
3		**PA**	dme	8	90	1.9	1.3	0[c]	Orange
4		**PA**	^{t}BuOH	8	89	14	1.7	68	Red
5		**PA**	CH_2Cl_2	0.1	97	30.1	1.7	45	Red
6		**PA**	Toluene	0.1	96	59.1	1.9	37	Red
7		**PA**	CCl_4	0.1	90	70	1.8	39	Red
8		**PA**	–	0.1	98	159	1.5	54	Red
9	[d]	**PA**	CH_2Cl_2	20	10	9.2	1.8	40	Red
10	[e]	**PA**	CH_2Cl_2	20	55	25.2	1.9	67	Red
11	[f]	**PA**	CH_2Cl_2	20	2	36.5	3.6	61	Red
12		**5**	CH_2Cl_2	8	96	68.1	1.6	53	Red
13		**6**	CH_2Cl_2	8	90	59.7	2.0	N/A	Red
14		**7**	THF	8	20[g]	47.7	2.1	44	Orange
15		**7**	CH_2Cl_2	8	62[g]	8.7	1.9	38	Orange
16		**8**	THF	8	94	85	1.1	36	White
17		**9**	CH_2Cl_2	20	42[c]	23.4	1.3	34	White
18		**10**	CH_2Cl_2	0.1	96	18.1	1.9	6	Brown
19	1 or 2[h]	**PA**	CH_2Cl_2	20	–[i]	–	–	–	–
20		**PA**	THF	20	–[i]	–	–	–	–
21	2[j]	**PA**	CH_2Cl_2	20	30	<2	–[k]	–	Orange

[a] By SEC in THF at 40 °C.
[b] Conditions: **3** (9.0 mg, 0.009 mmol), substrate (2.7 mmol)/5.0 mL solvent.
[c] *trans–cisoidal* structure.
[d] Addition of MeOH (**3**/MeOH = 1/10).
[e] Addition of MeCN (**3**/MeCN = 1/10).
[f] Addition of py (**3**/py = 1/10).
[g] Same yield after 24 h.
[h] Conditions: **1** (7.5 mg, 0.009 mmol) or **2** (12.7 mg, 0.009 mmol), substrate (2.7 mmol)/5.0 mL solvent.
[i] No polymerization.
[j] Conditions: **2** (12.7 mg, 0.009 mmol), $AlCl_3$ (2.4 mg, 0.018 mmol), substrate (2.7 mmol)/5.0 mL solvent.
[k] Very broad molecular weight distribution.

In addition, as part of our studies in exploiting the catalytic activity of multiply bonded clusters [42], we are interested to understand better the intrinsic factors which determine the reactivity of these bonds towards alkynes, e.g. bond multiplicity, tendency to undergo facile oxidative addition reactions, and the effect of bridging ligands. Herein, we report the reactions of the thermally stable triply bonded ditungsten halides $A_3[W_2(\mu\text{-}Cl)_3Cl_6]$ ($A^+ = K^+$ (**1**) [43,44], $^nBu_4N^+$ (**2**) [45,46]) and $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3$ (**3**) [47,48], which contain the $(W{\equiv}W)^{6+}$ core and have the $a'^2e'^4$ electronic configuration, with a range of monosubstituted alkynes RC≡CH, R = Ph (**PA**), C_7H_7 (*o*-methylphenyl) (**5**), $C_7H_4F_3$. (*o*-trifluromethylphenyl) (**6**), ^{n}Bu (**7**), ^{t}Bu (**8**), Me_3Si (**9**), $C_{10}H_7$ (naphthyl) (**10**). 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** [44], **2** [45,46] and **3** [47] were prepared according to literature procedures. The alkynes (**PA**, **5–9**) were dried by stirring with CaH_2 under argon, distilled under vacuum and stored in the dark under argon. THF and diethyl ether were distilled over Na/Ph_2CO, toluene and hexane over Na, CH_2Cl_2 and PhCl over CaH_2, 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 (O_2, H_2O < 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 ID, 0.25 μm, DB5-MS; injection 1 μL, 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 thermostated 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 complex (**1**: 7.5 mg, 0.009 mmol; **2**: 12.7 mg, 0.009 mmol; **3**: 9.0 mg, 0.009 mmol) 5.0 mL of solvent at 25 °C and the substrate (e.g. **PA**, 276 mg, 297 μL, 2.7 mmol) were added. The mixture was allowed to react for a given time (see Table 1). The final reaction mixture was concentrated to half volume and treated with excess methanol to precipitate the polymeric products. In the cases that polymers were formed, the resulting solids were filtered and washed repeatedly with methanol. They were redissolved in THF and the above procedure was repeated. The products were dried in vacuo.

Reaction with $AlCl_3$: To the complex (**2**: 12.7 mg, 0.009 mmol) 5.0 mL of CH_2Cl_2 at 25 °C, $AlCl_3$ (2.4 mg, 0.018 mmol) and **PA** (276 mg, 297 μL, 2.7 mmol) were added. The mixture was allowed to react for 24 h, and then concentrated to half volume. After addition of methanol the solid precipitated was filtered and dried in vacuo.

2.3. Catalytic reactions in NMR tubes

Complex **3** (9.0 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 (**PA**, 46.5 mg, 50 μL, 0.45 mmol) was added using a microliter syringe. The NMR tube was transferred to a cold bath at the same temperature used to record the low temperature spectra.

2.4. Polymer characteristics

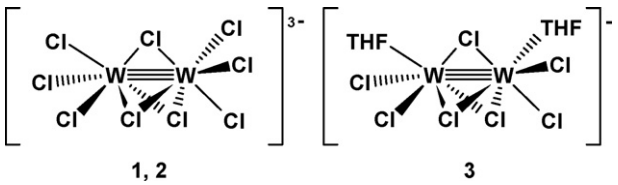
The stereochemistry of poly(phenylacetylene) (**PPA**) [49] obtained was determined by ^{1}H and ^{13}C NMR. *cis–transoidal* ***PPA***. ^{1}H NMR ($CDCl_3$), δ (ppm): 6.95 (very broad, 3H, *m*- and *p*-H_{aro}), 6.80 (shoulder, 2H, *o*-H_{aro}), 5.84 (broad, 1H, =CH). ^{13}C NMR ($CDCl_3$), δ (ppm): 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, 738, 692. Colour: red. *trans–cisoidal* ***PPA***. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.02 (very broad, 6H, H_{aro} and =CH). ^{13}C NMR ($CDCl_3$), δ (ppm): 128 (very broad, C_{aro} and =CH). IR (KBr) (cm^{-1}): 1484, 1438, 1387, 1329, 1068, 1024, 910, 884, 801, 754, 692. Colour: red-orange. The *cis* content was calculated according to the generally accepted equation [50]: $\%cis = (A \times 10^4)/(A_{tot} \times 16.66)$, 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((*o-methylphenyl*)*acetylene*) (*Poly*(***5***)). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.5–6.1 (very broad, 4H, H_{aro}), 6.1–5.0 (broad, 1H, =CH) 2.5–1.0 (broad, 3H, CH_3). ^{13}C NMR ($CDCl_3$), δ (ppm): 140–120 (broad, aromatic and olefinic carbons), 20.4–18.6 (broad, CH_3). IR (KBr) (cm^{-1}): 2955, 1920, 1850, 1620, 1478, 1453, 1364, 1020, 801, 760, 728. Colour: red. The *cis* content of the polymer was calculated from the ^{13}C NMR spectrum [51].

Poly((*o-trifluoromethyl*)*acetylene*) (*Poly*(***6***) [52]). ^{1}H NMR ($CDCl_3$), δ (ppm): 8.0–4.5 (very broad, 4H, H_{aro}, 1H, =CH), ^{13}C NMR ($CDCl_3$), δ (ppm): 138.2–120.4 (broad, aromatic, olefinic carbons and CF_3). IR (KBr) (cm^{-1}): 2955, 1950, 1850, 1295, 1251, 1170, 801, 765 Colour: red. Determination of the microscopic structure of the polymer is prevented by the broad and complex ^{1}H NMR spectrum (4.5–8.0 ppm).

Poly(*1-hexyne*) (*Poly*(***7***)) [53]. ^{1}H NMR ($CDCl_3$), δ (ppm): 5.92 and 5.81 (broad, 1H, =CH), 2.09 (broad, 2H, $=CCH_2(CH_2)_2CH_3$), 1.35 (broad, 4H, $=CCH_2(CH_2)_2CH_3$), 0.93 (broad, 3H, $=CCH_2(CH_2)_2CH_3$). ^{13}C NMR ($CDCl_3$), δ (ppm): 139.7 (s, $=C^n$Bu), 127.0 (s, =CH), 31.2 (s, $=CCH_2(CH_2)_2CH_3$), 28.2 (s, $=CCH_2CH_2CH_2CH3$), 23.1 (s, $=CCH_2CH_2CH_2CH3$), 14.0 (s, $=CCH_2CH_2CH_2CH3$). IR (KBr) (cm^{-1}): 1635, 940, 780. Colour: orange. The *cis* content was calculated as referenced in Ref. [53].

Poly(*tert-butylacetylene*) (*Poly*(***8***)) [54]. ^{1}H NMR ($CDCl_3$), δ (ppm): 6.19 (*cis*) and 5.98 (*trans*) (broad, 1H, =CH), 1.14 (broad, 9H, CH_3). ^{13}C NMR ($CDCl_3$), δ (ppm): 144.55 (s, $=CCMe_3$), 125.96 (s, =CH), 37.11 (s, $=CCMe_3$), 32.47, 31.27 and 30.38 (t, CH_3). IR (KBr) (cm^{-1}): 2960, 1611, 1263, 794. Colour: white. The *cis* content of the polymer was calculated from the ^{1}H NMR integrals [55] and according to the following equation [54]: $\%cis = 100 \times H_a/(H_a + H_b + H_c)$,



1, 2 3

Scheme 2. .

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*(***9***)) [56]. ^{1}H NMR ($CDCl_3$), δ (ppm): 6.70 (*cis*) and 6.36 (*trans*) (broad, 1H, =CH), 0.08 (broad, 9H, Me). ^{13}C NMR ($CDCl_3$), 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(**8**) [57].

Poly(*naphthylacetylene*) (*Poly*(***10***)). ^{1}H NMR ($CDCl_3$), δ (ppm): 6.50–8.50 (very broad, 7H, H_{aro}), 6.24 (shoulder, 1H, =CH). ^{13}C NMR ($CDCl_3$), 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: brown. The *cis* content was calculated from the IR spectrum [58].

All the above polymers are soluble in $CHCl_3$, CH_2Cl_2, and THF.

3. Results and discussion

3.1. Polymerization reactions

Complexes **1** [43], the analogous of **2** as the $HTMPP^+$ salt ($HTMPP^+$ = tris(2,4,6-trismethoxyphenyl)phosphonium)) [59], and **3** [47] have been structurally characterized. They all possess a confacial bioctahedral (fsbo) structure and contain the triply bonded, triply halo-bridged dimetallic core $\{W_2(\mu\text{-}Cl)_3\}$. In **3** two *cis*-chloride ligands are displaced by THF molecules (Scheme 2).

The compounds used have been checked for purity (UV–vis) and an X-ray structure of **3** carried out by us was found to be identical to that reported [47]. At ambient temperature **1** (insoluble in common organic solvents) and **2** (very soluble in CH_2Cl_2, and sparingly soluble in THF) are unreactive towards **PA** (THF, CH_2Cl_2). Activation with $AlCl_3$ (**2**/$AlCl_3$ 1/2–4, CH_2Cl_2, T = 25 °C) gives oligomeric **PPA** (M_w < 2000) in low yield (~30%).

In contrast, complex **3** (soluble in THF, and less soluble in CH_2Cl_2 or $CHCl_3$) is very reactive, and its room temperature reaction in THF provides **PPA** in high yield (92%) and high *cis*-stereoselectivity (*ca.* 90%, Table 1, entry 1). Small amounts of the cyclotrimers are also formed. Diphenylacetylene (PhC≡CPh, **DPA**), as a metathetical product, has not been detected (by GC). Under the same conditions, no cyclotrimers or oligomeric/polymeric polydiphenylacetylene (**PDPA**) are formed from the reaction of **3** with **DPA**.

In Et_2O or dme (1,2-dimethoxyethane) **PPA** yields are high, molecular weights are lower, but in the first case the polymer is *cis*-rich (78%), whereas in the second the *trans–cisoidal* configuration prevails (entries 2, 3), as evidenced by the lack of the 5.84 ppm peak in the ^{1}H NMR spectrum and the 738 cm^{-1} band in the IR spectrum. Small peaks at δ = 4.6–6.2 ppm in the ^{1}H NMR spectrum indicate the presence of some cyclohexadiene units in the polymer chain [60]. In CH_2Cl_2 the reaction is fast and complete within 6 min producing **PPA** containing *cis–transoidal* sequences. Interestingly, if the reaction mixture is left to react longer ($t \approx 2$ h) the polymer is isomerized to the *trans–cisoidal*-isomer [60]. The presence of substituents in the *ortho*-position of the phenyl ring (**5**, **6**) do not improve the polydispersity index (PDI) of the polymers (entries 12, 13). Addition to the reaction mixture of MeOH, CH_3CN, or pyridine lowers the yield and in the last case inhibits polymerization (entries 9–11).

Heterogeneously, addition of neat **PA** to solid **3** (*caution*: highly exothermic) causes fast gelation affording **PPA** having higher molecular weight but lower content in *cis*-units (entry 8). Similar results are obtained when **PA** is added to suspensions of **3** in toluene or CCl_4 (entries 6, 7).

The rest of the alkynes react in a similar manner, except for **7** and **9**, where yields are lower (entries 14, 15, 17). The steric bulk of the substituents does not affect significantly the yield of the reaction. All polymers obtained are soluble in organic solvents (CH_2Cl_2, $CHCl_3$, and THF). They have been characterized from their IR, ^{1}H and ^{13}C NMR spectra and by correlation with literature data, when available, as referenced. Disubstituted alkynes are polymerized less efficiently and details of their reactions will be reported in due course.

3.2. Mechanistic considerations

With regard to the mechanism of alkyne polymerization, two different pathways are established: alkyne insertion and alkyne metathesis. The latter is usually operative for Mo- and W-based catalysts [15,16]. The difficulty of establishing the mechanism of rapid catalytic polymerization reactions in non-well-defined systems, 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 [61]. This is even more complicated in bimetallic alkyne activation, since primarily, a variety of potentially catalytically active species may be formed, such as: end-on or μ-alkyne adducts [39,62–66], μ-alkylidynes [67], C—C coupled products [68], in addition to mononuclear alkyne adducts or alkylidynes from scission or metathesis [69–72].

Attempts to isolate intermediates at low catalyst-to-substrate ratio (**3**/**PA** = 1/4, THF), or even the reported but poorly characterized $[W_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}PhCCH)(THF)_2]$ (**3**/**PA** = 1/6, THF) [39] led to formation of small amounts of cyclotrimers, oligomers (as evidenced by ^{1}H NMR) and of a very sensitive inorganic green solid, which instantly decomposes to blue insoluble products upon exposure to air. Despite our efforts we could not obtain suitable crystals for an X-ray analysis or satisfactorily characterize it. Increasing the amount of **PA** just enhances the rate of the polymerization. Termination of the polymerization with MeOH and examination of the filtrate by GC–MS shows chlorobenzene (PhCl) formation during the reaction course.

In order to obtain information about the mechanism, we have monitored the reaction (**3**/**PA** = 1/50, d^8-THF) in situ by ^{1}H NMR at various temperatures (Fig. 1). As soon as the substrate was added to a solution of **3** at −20 °C, a cluster of weak peaks in the W-carbene area at δ = 11.4–10.4 ppm [61,73,74] along with a very weak unsymmetrical doublet in the $\{W_2\text{-}\mu\text{-}CH\}$ carbyne region at δ = 17.1 ppm appear [67]. The characteristics (shape, intensity) of these peaks change during the reaction course, except for those in the μ-carbynic area, which remain almost unchanged. While the reaction was allowed to continue (t = 72 min, T = 0 °C), the intensity of the roll of peaks in the tungsten-carbene area increases and two additional peaks at δ = 12.3 and 12.4 ppm appear. After 86 min (T = 20 °C) the intensity of those at 12.4–12.3 and 11.3–11.0 ppm increases and **PPA** formation is observed. As the polymerization proceeded (t = 96 min), further changes occurred with the two peaks at δ = 12.3 and 11.0 ppm becoming dominant and acquiring maximum intensity. This is accompanied by parallel increase in **PPA** formation. The ^{13}C NMR spectrum of this solution does not exhibit any signals attributed to the aforementioned peaks, presumably because of the very small concentration of the species involved.

Termination of the reaction with benzaldehyde (**3**/PhCHO = 1/10, T = 25 °C) causes the slow disappearance (t = 65 min) of the low-field

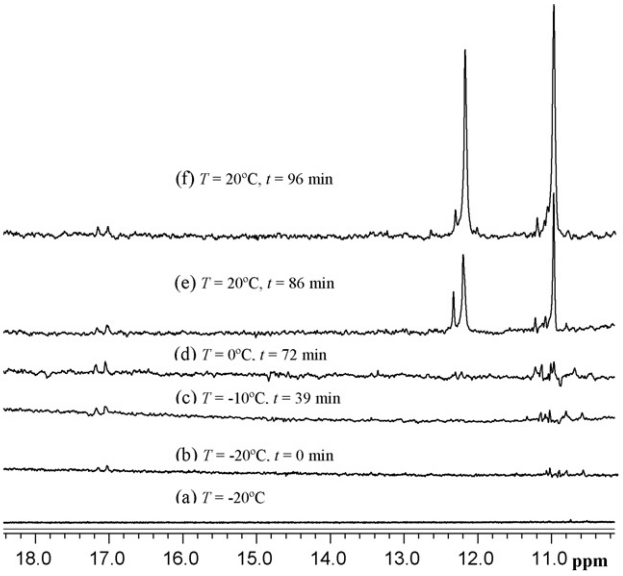


Fig. 1. ^{1}H NMR spectra of **3** in d^8-THF (a) and from the reaction of **3** (9.0 mg, 0.009 mmol) with **PA** (46.5 mg, 50 μL, 0.45 mmol) in d^8-THF at various temperatures and time intervals, as indicated (b–f).

peaks in the ^{1}H NMR spectrum. Also, addition of dimethylacetylene causes fast disappearance of the same peaks with parallel formation of poly(dimethylacetylene). Analogous results were obtained by monitoring the reaction in CD_2Cl_2 or in $CDCl_3$ (T = 20 °C), except that upon addition of the termination reagent, the disappearance of the peaks is immediate. In the case of **8**, termination of the reaction with PhCHO (**3**/**8**/PhCHO = 1/10/5, CH_2Cl_2, T = 25 °C, t = 20 min) and examination (by ^{1}H NMR) of the products reveals the presence of the "Ph(H)C═C" group incorporated in the ω-end of the oligomer chain (δ = 7.1–7.2 ppm (Ph), 6.4 ppm (H, s(br)); integral ratio Ph/H = 5). The spectrum is not sufficiently diagnostic in identifying the α-end chain of the oligomer.

Detection of possibly formed mononuclear carbynes of the type $[W(CR)Cl_4(THF)_n]^-$ (**11**) and $[W(CR)Cl_3(THF)_n]$ (**12**) (R = Ph or H) deriving from a Schrock-type metathesis between **3** and **PA** was not possible because of the masking of the relevant region by the solvents, **PA**, and **PPA** formed. The neopentylidyne complexes are unstable and highly reactive, but form more stable adducts $[W(CCMe_3)(L)Cl_3]$ (L = dme, quiniclidine (quin), pyridine (py) [70,75]). The dme-derivative is reported to polymerize 1-alkynes differently to **3** [76] by an unspecified mechanism. Attempts to detect analogous adducts of **11** and **12** by addition of quin, or py to the reaction mixture (**3**/**PA**/quin or py = 1/10/4) inhibits the polymerization. Dissolution of **3** in dme followed by removal of the solvent in vacuo (twice) leaves back a brown-reddish solid, which does not contain coordinated THF molecules and its ^{1}H NMR spectra indicate that it is the dme-adduct of **3**. Monitoring the polymerization of **PA** with this solid ($CDCl_3$, T = 20 °C) by ^{1}H NMR reveals three major sharp peaks at δ = 18.5, 13.7 and 11.4 ppm (Fig. 2). However, in this case, the intensity of the μ-carbynic peak does not remain constant, but increases during the polymerization progress. No signals in the ^{13}C NMR spectrum of this solution were observed. Addition of PhCHO terminates the polymerization with parallel disappearance of the relevant peaks.

In view of these findings, the polymerization of **PA** in THF, where the reaction is slower, has been examined in more detail and was found to be multistage. The first step ($t \approx 3$ min) is fast with nearly half of the **PA** (44%, Fig. 3a) consumed. At least two active polymerization centers are observed (Fig. 4) corresponding to **PPA**s having molecular weights of 2800 (■, Fig. 3b) and 19 700 (●), respectively. In the second step ($t \approx 6$ min) two active centers are still discernible, but correlate to molecular weights of 3400 (■) and 10 600 (●). In parallel, **PA** evolution (24%) is observed (Fig. 3a). This

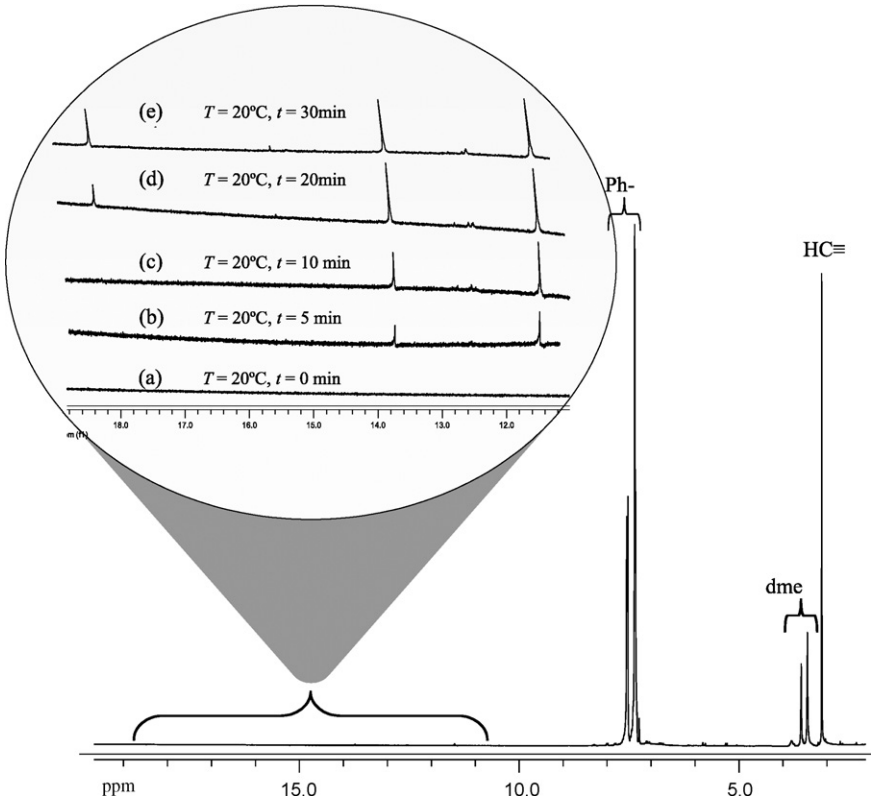


Fig. 2. ^{1}H NMR spectra of the reaction of the dme adduct of **3** (9.0 mg, 0.009 mmol) with **PA** (46.5 mg, 50 μL, 0.45 mmol) in $CDCl_3$ at time intervals, as indicated.

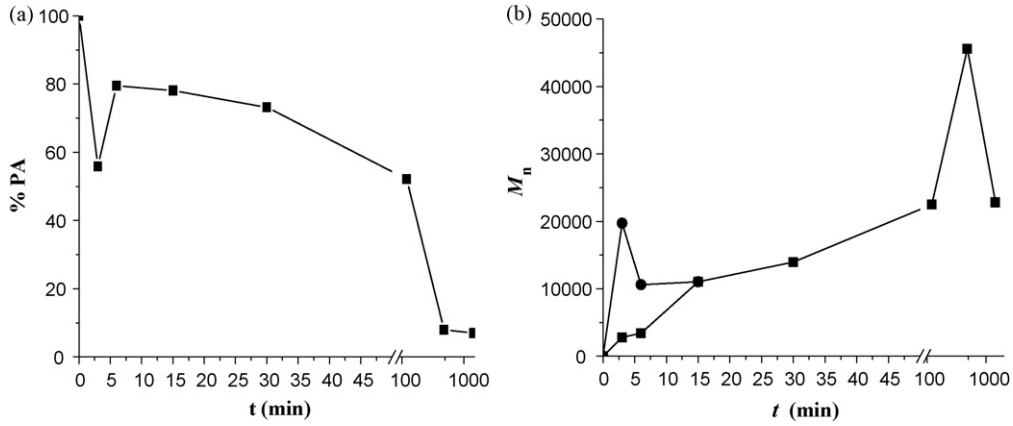


Fig. 3. Polymerization of **PA** (279 mg, 300 μL, 0.45 mmol) with **3** (9.0 mg, 0.009 mmol) in 5.0 mL THF (25 °C). (a) time–consumption of **PA** plot; (b) time–M_n plot.

clearly suggests that in the first case there is an increase in molecular weight, whereas in the second, equilibration and degradation events are in operation. Subsequently, both centers converge or one of them (●) is deactivated ($t \approx 15$ min), and a gradual increase in the molecular weight is observed, with this stage ($t \approx 15$ min–2 h) being responsible for the **PPA** obtained ($M_n = 45\,600$). Longer reaction time ($t \approx 24$ h) causes scission to **PPA** having half the molecular weight ($M_n = 22\,800$). Increasing substrate concentration results in linear increase of the molecular weights of the polymers formed (Fig. 5).

Overall, the results indicate the presence of a multiplicity of active species formed, even at low temperature, which may derive primarily from the reaction of **3** with **PA** via the pathways outlined above, and possibly of additional ones from the secondary metathetical degradation reactions. At room temperature at least two major active {"W_x" = C(H)(P)} ($x = 1$ or 2) carbene propagating centers prevail, which is compatible with the complex multistage nature of the polymerization. The role of the putative {"W_2"(μ-CH)} carbyne remains unclear.

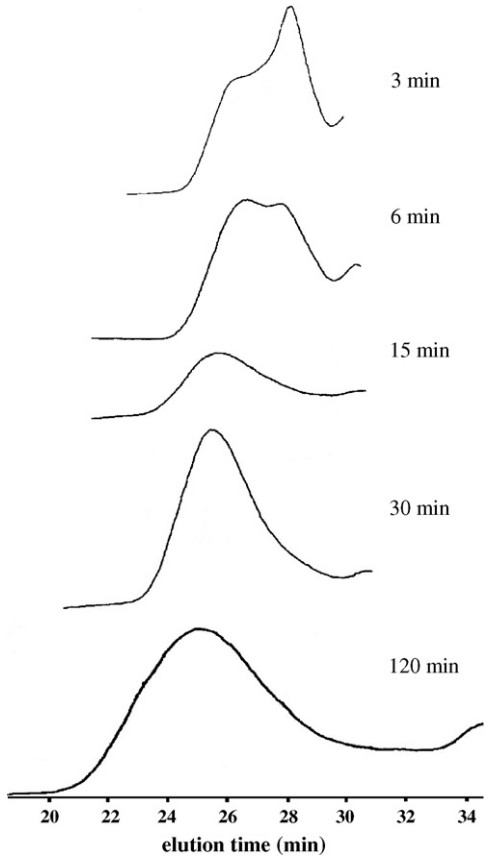


Fig. 4. SEC traces for the evolution of **PA** polymerization (279 mg, 300 μL, 0.45 mmol) with **3** (9.0 mg, 0.009 mmol) in 5.0 mL THF.

3.3. General comments

The reactivity and mechanistic mode of action of the triply bonded, triply bridged **3** and that of the quadruply bonded unbridged $Na_4[W_2Cl_8]\cdot(THF)_x$ (**4**) is remarkably similar. The most distinct differences between them are (a) the formation of the additional carbynic species in the reactions of **3**; (b) the bimodal (**3**) versus the unimodal (**4**) nature of the polymerization (first step); and (c) differences in the M_w, M_w/M_n values and the stereochemistry of the polymers formed. The major advantage of **3** over **4** is its thermal stability and the stability in air for short periods of time (solid state). A general comparison of **3** (reactivity, yield, molecular weight) with the relevant halide-based and other most important Mo and W systems [15–17,25,77] reveals that: (i) it differs distinctly from the uni-component $[MoCl_3(tht)_3]$ (tht = tetrahydrothiophene) and $[Mo_2Cl_6(tht)_3]$ catalysts, which promote mostly **PA** cyclotrimerization or produce mixtures (cyclotrimers/polymers) with other acetylenes; (ii) it is more effective than the uni-component $MoCl_5$, WCl_6 halides,

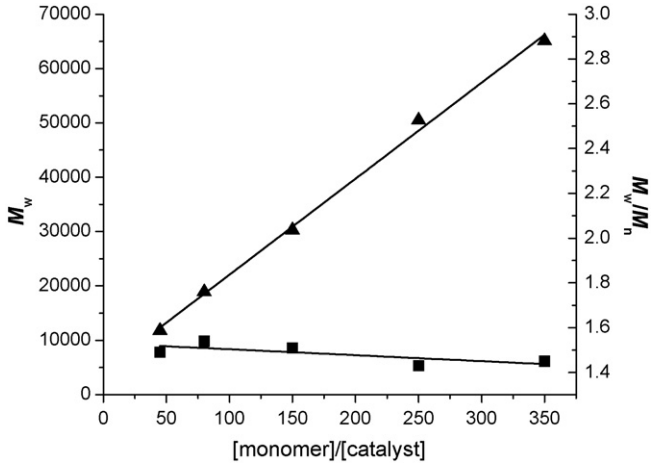


Fig. 5. Effect of initial monomer concentration on the polymerization of **PA** by **3** (9.0 mg, 0.009 mmol) in 5.0 mL THF (25 °C). ▲: M_w – [monomer]/[catalyst] plot; ■ : M_w/M_n – [monomer]/[catalyst] plot.

but resembles to their improved aryloxy or oxo-aryloxy chloro-derivatives (e.g. $[(ArO)_2MoCl_3(THF)_3]$, $[(ArO)_nWCl_{6-n}]$ (n = 1–4), $[WOCl_3(OAr)]$, where Ar is a suitably substituted phenyl ligand), as well as to the alkylidyne $[Cl_3(dme)W{\equiv}C^tBu]$; and (iii) compares to the efficient Masuda type binary (e.g. $MoCl_5$ or WCl_6/co-catalyst ($^nBu_4Sn$, Ph_4Sn, Et_nAlCl_{3-n} (n = 1–3), ^{n}BuLi, Et_2Zn, EtMgBr, Ph_3Bi, etc.), $MoOCl_4$/RLi (R = Me, ^{n}Bu, ^{n}hexyl), $WOCl_4$/co-catalyst (^{n}BuLi or EtMgBr)) or ternary ($MoOCl_4/^nBu_4Sn$ or Et_3Al/EtOH, $WOCl_4/^nBu_4Sn/^tBuOH$) systems, and to the well-defined Schrock's carbenes $(R^1O)(ArN)M{=}CHR^2$ (M = Mo, W; Ar, R^1 and R^2 are bulky substituents) or the carbyne $[(^tBuO)_3W{\equiv}C^tBu]$.

The stereochemistry of **PPA** produced by **3** follows the general trends exhibited by W systems in different solvents [15,78–80], although in our case the effects are more pronounced. Thus, in CCl_4, toluene and CH_2Cl_2 the *trans*-rich geometric structures prevail. Interestingly, when CH_2Cl_2 is used, the polymer has initially a considerable *cis*-content, but if the polymerization is allowed longer, after complete monomer consumption, isomerization to the *trans*-structure occurs. In oxygen-coordinating solvents (THF, Et_2O, ^{t}BuOH) *cis*-rich structures are obtained approaching 90% (THF). Surprisingly and in contrast, in dme the polymer acquires the *trans* geometry. This can be probably attributed to chelation, which substantially affects the structure of the active species. However, since there is no adequate information on their nature, attempting to explain these results is premature.

4. Conclusions

The $[W_2Cl_9]^{3-}$ ion has played an important role in the history of the development of multiple metal–metal bonds and transition metal clusters, but despite efforts for nearly 45 years since its discovery, not any well-documented catalytic activity has been reported [81]. This work constitutes the first example of such activity, with **3** being an efficient, novel and convenient unicomponent initiator for the homogeneous or heterogeneous polymerization of 1-alkynes, which is added to the arsenal of the existing halide-based catalytic systems. The presence of three halides bridging the W≡W bond does not seem to be an obstacle for catalytic activity. In contrast, the presence of two labile ligands (THF) is a prerequisite, as suggested from the difference in reactivity between **2** and **3**. The polymerization is fast in the solid state or in weakly coordinating solvents (CH_2Cl_2) and slower in THF, ether or dme. Direct evidence that a metathetical mechanism is in operation has been obtained from the *in situ* examination of this reaction by ^{1}H NMR (**3**/**PA**/THF) and the observation of several propagating alkylidene active centers. The polymerization is multistage involving polymerization and equilibration or depolymerization steps. The results clearly demonstrate the complexities involved in alkyne polymerizations with non-well-defined systems. Noteworthy is (a) the fast and facile degradation of **PPA** to **PA** at the early stage of the polymerization and its bisection at the end, and (b) the pronounced solvent influence, which dramatically affects the stereochemistry of the polymers (THF, *cis* 90%, entry 1; dme, *cis* 0%, entry 3, Table 1). Further work to define whether the bimetallic integrity of **3** is retained, as well as identifying the nature of the primal active species or the end chain of the polymers is in progress.

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References

[1] H.G. Kiess (Ed.), Conjugated Conducting Polymers, Springer-Verlag, Berlin, 1992.
[2] I.V. Krivoshei, M. Skoroboatov, Polyacetylene and Polyarylenes: Synthesis and Conducting Properties, Gordon and Breach Science, New York, 1991.
[3] P.N. Prasad, D.J. Williams, Introduction in Nonlinear Optical Effects in Molecules and Polymers, Wiley-Interscience, New York, 1991, p. 132.
[4] A.G. MacDiarmid, Angew. Chem. 113 (2001) 2649.
[5] H. Shirakawa, Angew. Chem. 113 (2001) 2642.
[6] T. Masuda, S.M.A. Karim, R. Nomura, J. Mol. Catal. A: Chem. 160 (2000) 125.
[7] E. Thorn-Csányi, P. Kraxner, Macromol. Sympos. 122 (1997) 77.
[8] H. Schlick, F. Stelzer, S. Tasch, G. Leising, J. Mol. Catal. A: Chem. 160 (2000) 71.
[9] U. Anders, O. Nuyken, M.R. Buchmeiser, J. Mol. Catal. A: Chem. 213 (2004) 89.
[10] S.-K. Choi, Y.-S. Gal, S.-H. Jin, H.K. Kim, Chem. Rev. 100 (2000) 1645.
[11] R.R. Schrock, Polyhedron 14 (1995) 3177.
[12] R.R. Schrock, S. Luo, J.C. Lee Jr., N.C. Zanetti, W.M. Davis, J. Am. Chem. Soc. 118 (1996) 3883.
[13] F.J. Schattenmann, R.R. Schrock, Macromolecules 29 (1996) 8990.
[14] M. Buchmeiser, R.R. Schrock, Macromolecules 28 (1995) 6642.
[15] T. Masuda, T. Higashimura, Adv. Polym. Sci. 81 (1986) 121.
[16] T. Masuda, J. Polym. Sci: A: Polym. Chem. 45 (2007) 165.
[17] T. Masuda, F. Sanda, M. Shiotsuki, in: R.H. Crabtree, D.M.P. Mingos (Eds.), Comprehensive Organometallic Chemistry III, Elsevier, Oxford, UK, 2007, Vol. 11, Chapter 11.16.
[18] Y. Kishimoto, P. Eckerle, T. Miyatake, M. Kainosho, A. Ono, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 121 (1999) 12035.
[19] J. Sedláček, J. Vohlídal, Collect. Czech. Chem. Commun. 68 (2003) 1745.
[20] T.J. Katz, S.J. Lee, J. Am. Chem. Soc. 102 (1980) 422.
[21] D.J. Liaw, A. Soum, M. Fontanille, A. Parlier, H. Rudler, Makromol. Chem. Rapid Commun. 6 (1985) 309.
[22] R.R. Schrock, Chem. Rev. 102 (2002) 145.
[23] R.R. Schrock, Adv. Synth. Catal. 349 (2007) 41.
[24] F.A. Cotton, W.T. Hall, K.J. Cann, F.J. Karol, Macromolecules 14 (1981) 233.
[25] P.M. Boorman, M. Wang, M. Parvez, J. Chem. Soc., Dalton Trans. (1996) 4533.
[26] M.C. Kerby, B.W. Eichhorn, U.S. Patent 4,916,222 (1990); Chem. Abstr. 133 (1990) 90360.
[27] M.C. Kerby, B.W. Eichhorn, U.S. Patent 4,965,381 (1990); Chem. Abstr. 114 (1990) 151429.
[28] B.W. Eichhorn, M.C. Kerby, R.C. Haushalter, K.P.C. Vollhardt, Inorg. Chem. 29 (1990) 723.
[29] S.P. Diefenbach, U.S. Patent 4,704,377 (1997); Chem. Abstr. 108 (1987) 96627.
[30] R. Matusiak, A. Keller, J. Mol. Catal. A: Chem. 195 (2003) 29.
[31] R.S. Dickson, P.J. Fraser, Adv. Organomet. Chem, 12 (1974) 323.
[32] K.J. Ahmed, M.H. Chisholm, K. Folting, J.C. Huffman, Organometallics 5 (1986) 2171.
[33] W.E. Buhro, M.H. Chisholm, Adv. Organomet. Chem. 27 (1987) 311.
[34] M.J. Winter, Adv. Organomet. Chem. 29 (1989) 101.
[35] M.C. Kerby, B.W. Eichhorn, L. Doviken, K.P.C. Vollhardt, Inorg. Chem, 30 (1991) 156.
[36] M.J. Byrnes, M.H. Chisholm, J. Gallucci, P.J. Wilson, Organometallics 21 (2002) 2240.
[37] F.A. Cotton, W.T. Hall, Inorg. Chem, 19 (1980) 2352.
[38] F.A. Cotton, W.T. Hall, J. Am. Chem. Soc. 101 (1979) 5094.
[39] S.G. Bott, D.L. Clark, M.L.H. Green, P. Mountford, J. Chem. Soc., Dalton Trans. (1991) 471.
[40] K. Mertis, S. Arbilias, D. Argyris, N. Psaroudakis, J. Vohlídal, O. Lavastre, P.H. Dixneuf, Collect. Czech. Chem. Commun. 68 (2003) 1094.
[41] G. Floros, N. Saragas, P. Paraskevopoulou, I. Choinopoulos, S. Koinis, N. Psaroudakis, M. Pitsikalis, K. Mertis, J. Mol. Catal. A: Chem. 289 (2008) 76.
[42] D. Neuman, P. Paraskevopoulou, N. Psaroudakis, K. Mertis, R.J. Staples, P. Stavropoulos, Inorg. Chem. 39 (2000) 5530.
[43] W.H. Watson Jr., J. Waser, Acta Crystallogr. 11 (1958) 689.
[44] R. Uzel, R. Pribil, Coll. Czech. Chem. Commun. 10 (1938) 33.
[45] F.A. Cotton, M. Shang, Z.S. Sun, Inorg. Chim. Acta 212 (1993) 95.
[46] P. Paraskevopoulou, E. Petalidou, A. Panas, M. Ioannou, S. Koinis, N. Psaroudakis, N. Leventis, P. Stavropoulos, K. Mertis, Polyhedron 27 (2008) 2859.
[47] M.H. Chisholm, B.W. Eichhorn, K. Folting, J.C. Huffman, C.D. Ontiveros, W.E. Streib, W.G. Van Der Sluys, Inorg. Chem. 26 (1987) 3182.
[48] R.R. Schrock, L.G. Sturgeoff, P.R. Sharp, Inorg. Chem. 22 (1983) 2801.
[49] M. Marigo, N. Marsich, E. Farnetti, J. Mol. Catal. A: Chem. 187 (2002) 169.
[50] M. Tabata, T. Sone, Y. Sadahiro, Macromol. Chem. Phys. 200 (1999) 265.
[51] Y. Abe, T. Masuda, T. Higashimura, J. Polym. Sci.: Polym. Chem. 27 (1989) 4267.
[52] T. Sone, R. Asako, T. Masuda, M. Tabata, T. Wada, H. Sasabe, Macromolecules 34 (2001) 1586.
[53] A. Petit, S. Moulay, T. Aouak, Eur. Polym. J. 35 (1999) 953.
[54] T. Masuda, H. Izumikawa, Y. Misumi, T. Higashimura, Macromolecules 29 (1996) 1167.
[55] T. Szymańska-Buzar, I. Czeluśniak, J. Mol. Catal. A: Chem. 160 (2000) 133.
[56] Y. Okano, T. Masuda, T. Higashimura, J. Polym. Sci.: Polym. Chem. 22 (1984) 1603.

[57] H. Izumikawa, T. Masuda, T. Higashimura, Polym. Bull. 27 (1991) 193.
[58] M. Tabata, M. Namioka, K. Yokota, H. Minakawa, Polymer 37 (1996) 1959.
[59] K.R. Dunbar, L.E. Pence, Acta Cryst. Sec. C c47 (1991) 23.
[60] C.I. Simionescu, V. Percec, J. Polym. Sci.: Polym. Chem. 18 (1980) 147.
[61] K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983.
[62] R.J. Klingler, W. Butler, M.D. Curtis, J. Am. Chem. Soc. 97 (1975) 3535.
[63] W.I. Bailey Jr., M.H. Chisholm, F.A. Cotton, L.A. Rankel, J. Am. Chem. Soc. 100 (1978) 5764.
[64] R.F. Gerlach, D.N. Duffy, M.D. Curtis, Organometallics 2 (1983) 1172.
[65] M.H. Chisholm, K. Folting, D.M. Hoffman, J.C. Huffman, J. Am. Chem. Soc. 106 (1984) 6794.
[66] M.H. Chisholm, B.K. Conroy, D.L. Clark, J.C. Huffman, Polyhedron 7 (1988) 903.
[67] R.L.M. Chamberlin, D.C. Rosenfeld, P.T. Wolczanski, E.M. Lobkovsky, Organometallics 21 (2002) 2724.
[68] M.H. Chisholm, D.M. Hoffman, J.C. Huffman, J. Am. Chem. Soc. 106 (1984) 6806.
[69] R.R. Schrock, M.L. Listemann, L.G. Sturgeoff, J. Am. Chem. Soc. 104 (1982) 4291.
[70] M.L. Listemann, R.R. Schrock, Organometallics 4 (1985) 74.
[71] J.H. Wengrovius, J. Sancho, R.R. Schrock, J. Am. Chem. Soc. 103 (1981) 3932.
[72] J. Sancho, R.R. Schrock, J. Mol. Catal. 15 (1982) 75.
[73] J. Kress, J.A. Osborn, R.M.E. Greene, K.J. Ivin, J.J. Rooney, J. Chem. Soc., Chem. Commun. (1985) 874.
[74] V. Percec, J. Künzler, Polym. Bull. 25 (1991) 483.
[75] R.R. Schrock, D.N. Clark, J. Sancho, J.H. Wengrovius, S.M. Rocklage, S.F. Pedersen, Organometallics 1 (1982) 1645.
[76] K. Weiss, R. Goller, G. Loessel, J. Mol. Catal. 46 (1988) 267.
[77] S. Hayano, T. Masuda, Macromolecules 31 (1998) 3170.
[78] T. Masuda, M. Shiotsuki, J. Tabei, in: L.S. Baugh, J.A.M. Canich (Eds.), Stereoselective Polymerization with Single-Site Catalysts, CRC Press, Taylor & Francis Group, Boca Raton, USA, 2008.
[79] J. Vohlídal, J. Sedláček, N. Patev, O. Lavastre, P.H. Dixneuf, S. Cabioch, H. Balcar, J. Pfleger, V. Blechta, Macromolecules 32 (1999) 6439.
[80] J. Sedláček, M. Pacovská, J. Vohlídal, Z. Grubišić-Gallot, M. Žigon, Macromol. Chem. Phys. 196 (1995) 1705.
[81] F.A. Cotton, R.A. Walton (Eds.), Multiple Bonds between Metal Atoms, Third ed., Springer, New York, 2005.