Article

Ring Opening Metathesis Polymerization of Norbornene and Derivatives by the Triply Bonded Ditungsten Complex Na[W₂(*μ*-Cl)₃Cl₄(THF)₂]·(THF)₃

Dedicated to my research colleagues at Sir G. Wilkinson's Laboratory (1972–1980).

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Abstract: In this study, the reactions of the bimetallic compound Na[W₂(W³⁻W)³Cl₄(THF)₂]·(THF)₃ (**1**, (W³⁻W)⁶⁺, a^2e^4) with norbornene (**NBE**) and some of its derivatives (5-X-2-NBE; X = COOH (**NBE–COOH**), OH (**NBE–OH**), CN (**NBE–CN**), COOMe (**NBE–COOMe**), CH=CH₂ (**VNBE**); norbornadiene (**NBD**)) are described. Complex **1** contains a tungsten–tungsten triple bond, bearing three halide bridges and two labile THF ligands, in a *cisoidal* relationship along the metal–metal axis. The complex was found to be a highly efficient room temperature homogeneous and heterogeneous unicomponent initiator for the catalytic ring opening metathesis polymerization (ROMP) of most substrates. **NBE** provides polynorbornene (**PNBE**) of high molecular weight (M_w) in high yields, soluble in organic solvents. The reaction proceeds with high *cis*-stereoselectivity (80%–86% *cis*), independently of the reaction conditions. Strongly coordinating pendant groups (–COOH, –OH, –CN) deactivate **1**, whereas substrates bearing softer ones (–COOMe, –CH=CH₂) are quantitatively polymerized. **NBD** gives

quantitatively insoluble **PNBD**. The polymers have been characterized by ^{1}H, ^{13}C NMR and Size Exclusion Chromatography (SEC). Monitoring the reactions *in situ* by ^{1}H NMR (**1/NBD** or **NBE)** provides direct evidence of the metathetical nature of the polymerization with the observation of the active tungsten alkylidene propagating polymeric chains. Mechanistic aspects of the reactions are discussed.

Keywords: catalysis; metal–metal bonds; norbornenes; ROMP; tungsten

1. Introduction

The olefin metathesis reaction induces the mild cleaving and redistribution of carbon–carbon double bonds, and ever since its discovery, it has been highly utilized in polymer science and organic synthesis (basic chemicals, pharmaceuticals) [1–6]. Important classes of olefin metathesis reactions involve the ring closing metathesis (RCM), ring opening metathesis (ROM), and ring opening metathesis polymerization (ROMP). The last one in particular, apart from being a versatile tool for organic synthesis, is the key process for the preparation of various industrial polyalkenamers [7].

Although the ROMP of bicyclo[2.2.1]hept-2-ene (norbornene, **NBE**) and its derivatives (e.g., bicyclo[2.2.1]hepta-2,5-diene, norbornadiene, **NBD**), providing polynorbornene (**PNBE**) and polynorbornadiene (**PNBD**), respectively (Scheme 1), has been studied for many years and the number of publications is tremendous, the area is still full of challenges [8].

Scheme 1. Ring Opening Metathesis Polymerization (ROMP) of **NBE** and **NBD**.
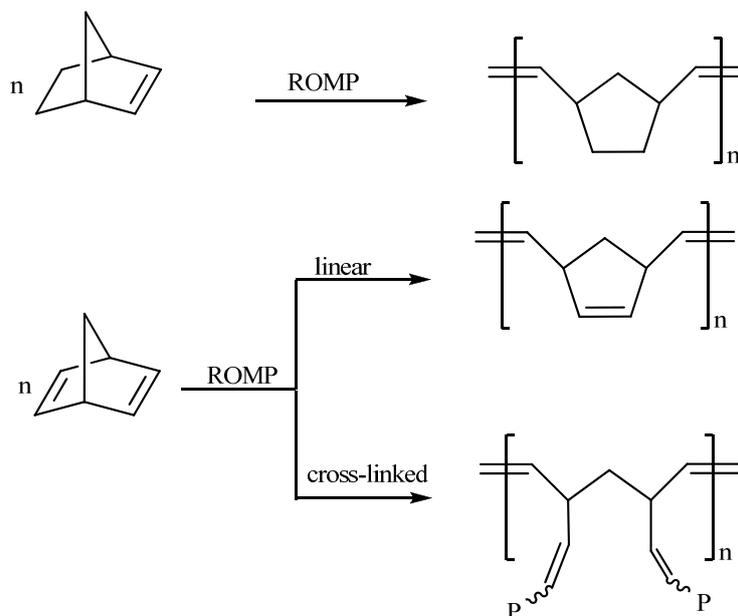
The reaction is catalyzed by a broad range of uni-, bi-, ternary, quaternary and multicomponent catalytic systems based mainly on mononuclear transition metal complexes along the periodic table (Ti, Nb, Ta, Cr, Mo, W, Re, Co, Ru, Os) [1–6]. Among them, protagonists are those of ruthenium,

molybdenum and tungsten. For the last two, the following major categories have been classified [1–6,9–11]:

(i)   ill-defined systems, including the classical high oxidation state halides (e.g., MoCl$_5$, WCl$_6$), oxohalides (e.g., WOCl$_4$), alkoxohalides (e.g., [(RO)$_x$WCl$_{6-x}$], x =1–3) and oxoclusters (e.g., [W$_6$O$_{19}$]$^{2-}$) exhibiting small to moderate activity; these become very reactive when activated by organometallic cocatalysts (e.g., SnMe$_4$, AlEt$_3$);

(ii) discreet alkylidenes, such as the well-defined Katz [(OC)$_5$W=C(Ph)R] (R = OMe, Ph) [12] and Schrock ([M(NAr)(CHR)(OR')$_2$] (M = Mo, W; Ar = aryl; R = aryl or alkyl; R' = CMe$_3$, CMe$_2$CF$_3$, CMe(CF$_3$)$_2$, C(CF$_3$)$_3$) [13] catalysts and their numerous variations.

Despite the abundance of mononuclear catalytic systems, there is only a limited number of bimetallic multiply metal–metal bonded complexes inducing the ROMP of **NBE**. These include: (a) neutral or ionic complexes containing the (Mo$\overset{4}{-}$Mo)$^{4+}$ core with a variety of ligands (acetate, halide, allyl, acetonitrile) [14], which usually are effective when activated with Et$_2$AlCl. The different ligands exert little or no influence on the stereoselectivity of the reaction; (b) the [Cp$^*_2$Os$_2$Br$_4$] ((Os$\overset{3}{-}$Os)$^{6+}$, Cp* = η^5-pentamethylcyclopentadienyl) compound in the presence of MAO (methylaluminoxane) [15]; and (c) the doubly bonded [{W(NR')(OCOMe$_2$CF$_3$)$_2$}$_2$(μ-C$_2$H$_4$)] (R' = 2,6-Me$_2$C$_6$H$_3$), which slowly polymerizes **NBE** [16]. The [W$_2$(OCH$_2^t$Bu)$_6$(py)$_2$] ((W$\overset{3}{-}$W)$^{6+}$, $\sigma^2\pi^4$) alkoxide has been reported for the ROMP of **NBD**, but no detailed data have been presented [17,18].

Current research is more and more directed towards the production of often synthetically very complex functional molecules, the properties of which sensitively depend on their microstructure (primary, secondary, tertiary). This, in effect, is directly related to the stereoselectivity of the reaction, but tuning the configuration of the polymers has been a long-standing problem [19]. A good degree of control of the primary structure (gradient of *cis* and *trans* C=C bonds) can be achieved, either empirically, by using multicomponent systems (catalyst/co-catalyst/additives, such as Michael acceptors or chelating solvents acting as spectator ligands) [2] or by serendipity [20]. Alternatively, elaborate design (steric, electronic) catalysis is employed [19,21]. Mononuclear molybdenum halides (e.g., MoCl$_5$) give predominantly *trans*-**PNBE**, whereas tungsten ones (e.g., WCl$_6$) provide polymers having mixed conformations [2,3]. Industrially produced **PNBE** with the original RuCl$_3$·xH$_2$O/alcohol system is highly *trans* (>90%) [22].

Recently, as part of our studies in exploiting the reactivity of multiply bonded clusters, we have discovered that the ditungsten halide Na[W$_2$(μ-Cl)$_3$Cl$_4$(THF)$_2$]·(THF)$_3$ (**1**, (W$\overset{3}{-}$W)$^{6+}$), a simple derivative of the historic [W$_2$(μ-Cl)$_3$Cl$_6$]$^{3-}$ anion, discovered a century ago (1911) [23] and long considered a kinetic and thermodynamic sink in terms of its redox activity, catalyzes efficiently the metathetical polymerization of monosubstituted alkynes [24]. An interesting aspect of this initiator is its marked predilection to produce highly *cis*-polyacetylenes, which is unusual within the mononuclear tungsten halide analogs.

In this respect, and in view of: (a) the continuing interest on classical-type catalysts in industrial processes for highly active substrates, which may not justify the use of well-defined initiators [1–7,22], and (b) the importance of metal oxidation state in the search for new metathesis catalysts [12], as well as general comparison reasons (W(VI), W$_2^{6+}$ halides), we have extended our investigations into the reactions of **1** with **NBE** and some selected derivatives (5-*X*-2-**NBE**; *X* = COOH (**NBE–COOH**), OH (**NBE–OH**), CN (**NBE–CN**), COOMe (**NBE–COOMe**), CH=CH$_2$ (**VNBE**); norbornadiene (**NBD**)).

Herein, we report its ability to efficiently induce the ROMP of most of these substrates with a high degree of stereoselectivity. The results are summarized in Table 1. Characterization of the polymers formed and mechanistic aspects of these reactions are also presented.

2. Experimental Section

2.1. General

Starting materials were purchased from Sigma-Aldrich and are of the highest available purities. Complexes $Na[W_2(\mu\text{-}Cl)_3Cl_4(THF)_2]\cdot(THF)_3$ (**1**) [25], $(^nBu_4N)_3[W_2(\mu\text{-}Cl)_3Cl_6]$ (**2**) [26] and $(^nBu_4N)[W_2(\mu\text{-}Cl)_3Cl_5(THF)]$ (**3**) [27] were prepared according to literature procedures. **NBE** was dissolved in the solvent used in the reaction, dried by stirring with CaH_2 under argon and was distilled under vacuum prior to use. **NBD** was passed through an Al_2O_3 column. THF and diethyl ether were distilled over Na/Ph_2CO, toluene and hexane over Na, CH_2Cl_2 over CaH_2, and 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).

NMR spectra were recorded on a Varian Unity Plus 300 spectrometer. In all cases, chemical shifts are reported in ppm relative to the deuterated solvent resonances. 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. The substrate (e.g., **NBE**, 423 mg, 4.5 mmol) was added to a solution of complex (e.g., **1**:9.0 mg, 0.009 mmol) in a solvent (2.0 mL). The mixture was allowed to react for a given time (see Table 1), after which it was concentrated to half volume and treated with excess methanol to precipitate the polymeric products. 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*.

2.3. Catalytic Reactions in NMR Tubes

Complex **1** was dissolved in THF-d^8 (8.0 mg, 0.008 mmol) and the green solution was transferred in an NMR tube. The appropriate amount of the substrate (**NBD**: 15.1 mg, 16 μL, 0.16 mmol; **NBE**: 150.6 mg, 1.60 mmol) was added using a microliter syringe.

2.4. Polymer Microstructure

The stereochemistry of the polymers obtained (**PNBE**, **PNBE–COOME**, **PVNBE** and the soluble part of **PNBD**) was determined by ^{1}H and ^{13}C NMR [28–32].

PNBE
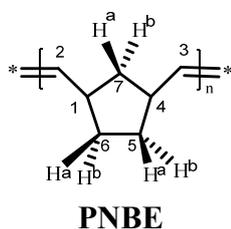
^{1}H NMR (CCl$_4$, 300 MHz): 5.25 (s, 2H, H[2,3] *trans*), 5.10 (s, 2H, H[2,3] *cis*), 2.73 (broad, s, 2H, H[1,4] *cis*), 2.37 (broad, s, 2H, H[1,4] *trans*), 1.95–1.60 (broad, m, 3H, H[5a,6a,7a]), 1.50–1.20 (broad, m, 2H, H[5b,6b]), 1.20–0.85 ppm (broad, m, 1H, H[7b]); ^{13}C NMR (CCl$_4$, 75.4 MHz): 133.99 (s, C[2,3] *ccc*), 133.21 (m, C[2,3] *ctt/ttt/ctc*), 133.08 (s, C[2,3] *ttc*), 43.67 (s, C[1,4] *tc*), 43.44 (s, C[1,4] *tt*), 42.88 (s, C[7] *cc*), 42.25 (s, C[7] *ct/tc*), 41.52 (s, C[7] *tt*), 38.88 (s, C[1,4] *cc*), 38.67 (s, C[1,4] *ct*), 33.39 (s, C[5,6] *cc*), 33.19 (s, C[5,6] *ct*), 32.61 (s, C[5,6] *tc*), 32.43 ppm (s, C[5,6] *tt*).

PNBE–COOME
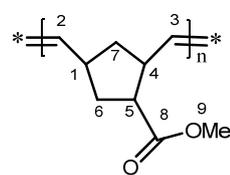
^{1}H NMR (CCl$_4$, 300 MHz): 5.26–5.37 (broad, 2H, H[2,3]), 2.76–3.10 (broad, s, 1H, H[4]), 2.26 (broad, s, 1H, H[5]), 1.80–2.10 (broad, m, 3H, H[9]), 1.10–1.60 (broad, m, 3H, H[1,6,7]); ^{13}C NMR (CCl$_4$, 75.4 MHz): 170.7 (s, C[8]), 140.9–127.4 (m, C[2,3]), 51.1 (s, C[9]), 48.6–34.8 ppm (s, C[1,4,5,6,7]).

PVNBE
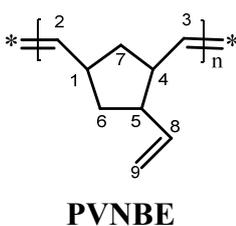
^{1}H NMR (CCl$_4$, 300 MHz): 5.76 (broad, 1H, H[8]), 5.30 (broad, 2H, H[2,3]), 4.89–4.96 (broad, 2H, H[9]), 2.19–3.10 (broad, 3H, H[1,4,5]), 1.10–2.10 (broad, m, 2H, H[6,7]); ^{13}C NMR (CCl$_4$, 75.4 MHz): 141.7, 140.6 (s, C[8]), 135.6–130.3 (m, C[2,3]), 113.6, 113.1 (s, C[9]), 50.1, 47.9 (s, C[5]), 45.6, 37.5 (s, C[1]), 45.6, 41.3 (s, C[4]), 42.8, 41.3, 39.5 (s, C[7]), 41.3 (s, C[6]).

PNBD
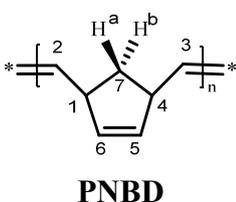
^{1}H NMR (CDCl$_3$, 300 MHz): 5.65 (s, 2H, H[5,6] *trans*), 5.60 (s, 2H, H[5,6] *cis*), 5.40 (m, 2H, H[2,3] *trans*), 5.25 (m, 2H, H[2,3] *cis*), 3.60 (m, 2H, H[1,4] *cis*), 3.20 (m, 2H, H[1,4] *trans*), 2.40 (m, 1H, H$_7$), 1.27 ppm (m, 1H, H$_7$); ^{13}C NMR (CDCl$_3$, 75.4MHz): 134.96 (s, C[5,6] *cc*), 134.88 (s, C[5,6] *tt*), 133.50 (s, C[2,3] *ct*), 133.37 (s, C[2,3] *cc*), 133.20 (s, C[2,3] *tt*), 133.10 (s, C[2,3] *tc*), 48.64 (s, C[1,4] *tc*), 48.58 (s, C[1,4] *tt*), 43.95 (s, C[1,4] *cc*), 43.89 (s, C[1,4] *ct*), 39.85 (s, C[7] *cc*), 39.34 (s, C[7] *tc/ct*), 38.80 ppm (s, C[7] *tt*).

3. Results and Discussion

3.1. Catalyst and Polymerization Reactions

Complex **1** has been isolated and structurally characterized [25]. In the solid state it contains a tungsten–tungsten triple bond, bearing three halide bridges and two THF ligands, one in each tungsten atom, in a *cis* arrangement along the dimetal axis. Such species in solution, in the presence of donor ligands or coordinating solvents, may exist in an equilibrium between the highly symmetric confacial (D_{3h}, fasbo) structure **1** and the edge-sharing (D$_{2h}$, esbo) biooctahedral one **1'** (Scheme S1 in the Supporting Information) [33]. It is air sensitive (oxygen, moisture), but in the solid state, it is stable at room temperature for a few hours. It is soluble in THF, CH$_3$CN and dme, less soluble in CH$_2$Cl$_2$, and

insoluble in toluene, Et_2O and CS_2. The complex has been repeatedly recrystallized and checked carefully for purity (Vis-UV) before use. Polymerization reactions were carried out at room temperature, for a given time. The results are summarized in Table 1.

3.2. Polymerization of **NBE** and Derivatives

The polymerization reactions of **NBE** were carried out in different media and were found to be solvent dependent. They do not proceed in strongly coordinating or chelating solvents (CH_3CN, dimethoxyethane (dme)), indicating the inhibition of substrate coordination. They are slow in THF affording small yields (entry 1), while in CH_2Cl_2 fast gelation is observed and the polymer has low polydispersity index (M_w/M_n, entry 2). Suspension of **1** in toluene gives moderate yield of **PNBE** (entry 5), while suspensions in Et_2O and CS_2 (entries 6 and 7) give high yields of the polymer. After the end of the heterogeneous reactions, the catalyst can be separated and reused (at least four times) with fresh amounts of monomer and solvent, without significant loss of reactivity. The supernatant solution remains colorless during the reaction. The *cis*-stereoselectivity is high (80%–86%) and is not affected by the reaction conditions.

All polymers are soluble in common organic solvents ($CHCl_3$, CH_2Cl_2, THF). Their geometric structure was determined by ^{1}H and ^{13}C NMR spectra (Figure S1) [28]. The relative proportions of double-bond pair sequences, represented as *trans-cis (tc)*, *trans-trans (tt)*, *cis-cis (cc)* and *cis-trans (ct)* units, were determined from the four methine carbon ($C^{1,4}$) signals of the ^{13}C NMR spectrum of **PNBE** at δ_C 43.67 (*tc*), 43.44 (*tt*), 38.88 (*cc*) and 38.67 ppm (*ct*). The fraction of *cis* double bonds ($\sigma_c = 0.85$) estimated from this ^{13}C NMR spectrum is in good agreement with that obtained from the ^{1}H NMR spectrum ($\sigma_c = 0.86$ from the integrals of the signals at δ_H 2.73 ($HC^{1,4}$ *cis*-**PNBE**) and 2.37 ppm ($HC^{1,4}$ *trans*-**PNBE**). The reactivity ratios $r_c = cc/ct = 7.4$, $r_t = tt/tc = 1.3$ and $r_c r_t = 9.6$ were calculated from the heights of the relevant signals in the ^{13}C NMR spectra.

Comparison of **1** (as per reactivity, yield, M_w, and *cis*-selectivity) with other representative catalytic systems revealed that it is much more reactive than the Masuda type W(VI) halides, resembling more to the bicomponent ones (e.g., $WCl_6/AlEtCl_2$, $SnMe_4$ *etc.*) and to the high-valent well-defined Schrock carbenes. Its *cis*-specificity is much more enhanced than that of the aforementioned systems, but it is comparable to that of the low-valent (Katz) and high-valent design catalysts (Schrock, Basset).

Substrates having strongly coordinating substituent groups (–COOH, –OH, –CN) deactivate **1**, while those with softer ones (–COOMe, –CH=CH$_2$) are quantitatively polymerized, albeit with lower rates than **NBE** (Table 1, entries 11 and 12). The polymers are white, elastomeric, soluble in organic solvents and they have been characterized from their ^{1}H and ^{13}C NMR spectra. The broadness of the peak of olefinic protons (5.26–5.37 ppm) of **NBE–COOMe** (because of overlapping signals of *endo*-, *exo*-isomers, possibly presence of HH, HT and TT units) and the complexity of the ^{13}C NMR spectra prevents the estimation of the *cis*-content [29,30]. In the case of **PVNBE**, the peak at 5.30 ppm suggests that the ring-strained C=C bond is cleaved, while the vinylic one is left intact. The overlapping signals of the olefinic protons of the polymeric chain with the vinylic ones prevent the stereoregular assignment for the same reasons as above [30]. **NBE–COOMe** has been polymerized by a variety of catalytic systems (Mo, W, Re, Ru, Os, Ir) with yields varying from 20% to quantitative and molecular weights higher than 800,000 [29]. In contrast, there is only one report for the polymerization

of **VNBE**, namely with the [(OC)$_4$W(μ-Cl)$_3$W(GeCl$_3$)(CO)$_3$] (**4**) complex under controlled conditions, giving high yields of **PVNBE** along with small amounts of side products (~10%) [31]. Both of these monomers are of interest, as their polymers can be easily functionalized by the addition of new side groups.

Finally, it must be noted that the isostructural and isoelectronic perhalocomplex (*^{n}*Bu$_4$N)$_3$[W$_2$(μ-Cl)$_3$Cl$_6$] (**2**) [26] under the same conditions was found inactive towards the ROMP of **NBE**, whereas the monosubstituted W$_2$$^{7+}$ derivative (*^{n}*Bu$_4$N)[W$_2$(μ-Cl)$_3$Cl$_5$(THF)] (**3**) [27] provided very small yield (~10%).

3.3. Polymerization of NBD

The reactions of **NBD** with **1** homogeneously or heterogeneously (bulk or suspension in toluene) occur very fast and in quantitative yields (Table 1, entries 13–16). In a solvent-free regime, the polymer can be detached from the surface of the catalyst, which can be reused for several times. The **PNBD** formed is insoluble in most common organic solvents, indicating extensive cross-linking of the cyclopentene rings. At lower concentrations (**1**/**NBD**: 1/20) a partly soluble polymer (CHCl$_3$) is obtained. The microstructure of the soluble **PNBD** has been analyzed [32] (Figure S2). From the integral ratio of signal due to olefinic protons δ_H = 5.40 (*trans* double bond) and δ_H = 5.60 ppm (*cis* double bond), the value of the *cis* double bond content was calculated to be *ca.* 63%. A *cis* double bond content of *ca.* 68% was calculated from the ^{13}C NMR spectrum. For this purpose, the well-resolved peaks of the methine carbon (C^{1,4}) at δ_C 48.58 (*trans* double bond) and 43.95 ppm (*cis* double bond) were integrated.

Table 1. Reactions of **1** with bicycloolefins [a].

Entry	Monomer	Solvent	t (h)	Yield (%)	$M_w \times 10^{-3}$ [b]	M_w/M_n	*cis* (%)
1		THF	19	12	86.2	1.2	86
2		CH$_2$Cl$_2$	1	96	529	1.2	86
3		dme	48	–[c]	–	–	–
4	**NBE**	CH$_3$CN	48	–[c]	–	–	–
5		toluene	24	37	296	2.9	86
6		Et$_2$O	20	94	422	1.4	86
7		CS$_2$	24	93	1,174	1.4	80
8	**NBE–COOH**	CH$_2$Cl$_2$	–	–[c]	–	–	–
9	**NBE–OH**	CH$_2$Cl$_2$	–	–[c]	–	–	–
10	**NBE–CN**	CH$_2$Cl$_2$	–	–[c]	–	–	–
11	**NBE–COOMe**	CH$_2$Cl$_2$	12	> 99	685	1.15	–
12	**VNBE**	CH$_2$Cl$_2$	8	> 99	974	2.6	–
13		–	0.1	>99	–	–	–
14	**NBD**	THF	4	>99	–	–	–
15		toluene	0.1	>99	–	–	–
16		CH$_2$Cl$_2$	0.1	>99	–	–	–

[a] Conditions: **1** (9.0 mg, 0.009 mmol), monomer (4.5 mmol)/2.0 mL solvent; [b] By SEC in THF at 40 °C;
[c] No polymerization.

3.4. Mechanistic Considerations

Mechanistically, the metal-olefin transformation to active carbenes or metallocyclobutanes in "ill-defined" catalytic systems is an intriguing problem, and several mechanistic pathways concerning mostly mononuclear complexes have been proposed [2,3,34–40]. In the simple case of **NBE**, the rearrangement is believed to be a net 1,2-H-shift along the metal coordinated C=C bond, based on experimental evidence [36–40,41]. The higher unsaturation of **NBD** makes its transformations far more complicated than it had been considered and remain elusive.

In relation to this work, worth noting in some detail are the results reported by Szymańska-Buzar *et al.* on the mechanism of ROMP of **NBE** and **NBD** with a series of heterobimetallic M–M' (M = Mo, W; M' = Sn, Ge) complexes, e.g., [MCl(SnCl$_3$)(CO)$_3$(NCMe)$_2$] (**5**, M = W; **5'**, M = Mo) and [(OC)$_4$Mo(μ-Cl)$_3$Mo(SnCl$_3$)(CO)$_3$] (**6**) [35]. In the case of **5**/**NBD**, the first step of the reaction has been unequivocally established with the isolation and characterization (spectroscopic, structural) of the [WCl(SnCl$_3$)(CO)$_3$(η^4-**NBD**)] (**5a**) adduct, in which the two C=C bonds of the **NBD** ligand are nonequivalently bonded to the tungsten atom. This compound has also been proven to be an efficient precatalyst for the ROMP of **NBD**, along with formation of minor amounts of *exo*-2-chloronorborn-5-ene and *exo*-3-chloronortricyclane [42]. Monitoring (^{1}H and ^{13}C NMR) the reactions (**5** or **5a** in CDCl$_3$ or CDCl$_3$/CD$_2$Cl$_2$, room temperature) does not reveal the carbenic protons of the active species that trigger polymerization (attributed to their very small concentration). Exploratory density functional theory (DFT) calculations on the mechanism of the spontaneous η^4-**NBD** to carbene transformation have been carried out for complexes [MoCl(SnCl$_3$)(CO)$_2$(η^4-NBD)] **5'a** [42], [MoCl(SnCl$_3$)(CO)$_2$(NCMe)$_2$(η^4-NBD)] (**7**) [42], [W(CO)$_3$I$_2$(η^4-NBD)] (**8**) [43] (forty pathways overall have been considered), but the activation energies were found too high. More recent calculations for [W(CO)I(η^2-dppm)(η^4-NBD)] (**9**) taking into account extra important intermediate steps [44], which lower the activation energies by half, favor the mechanism first hypothesized by Handzlik *et al.* [42] (oxidative coupling to form metallacyclopentane, followed by a 1,4-H-shift between the two α-bonded carbons across the face of the metal atom (Scheme S2).

In the case of **NBE** (**4**, **5a**, **6**), the corresponding η^2-**NBE** adducts are not isolable, but can be detected by ^{1}H NMR. Apart from polymer formation, *exo*-2-chloronorbornane and 2,2'-binorbornylidene (**bi-NBE**) were detected. The formation of **bi-NBE** provides direct evidence of η^2-**NBE** transformation to a tungstanorbornylidene species (1,2-hydride shift) capable to initiate either the ROMP of **NBE**, or a carbene–carbene coupling reaction, giving a new olefin (**bi-NBE**) [45–47].

The small initiation efficiency of **1** (it is calculated that only ~10% of **1** is activated by **NBE**) coupled to the sensitivity of the active species, undermined our efforts to isolate adducts of **1** with **NBD** and **NBE** or any other catalytically active yield-related intermediates. Similar was the fate of attempts to establish whether the active species are bimetallic or **1** serves as a precursor to mononuclear compounds (by ESI-MS). Nevertheless, valuable information has been obtained by monitoring *in situ* the reactions of **1** with the substrates by ^{1}H and ^{13}C NMR. Solvent of choice was tetrahydrofuran (THF) because of the rapidity of the polymerizations in halogenated solvents (CHCl$_3$, CH$_2$Cl$_2$, **PNBD** formation even at low ratio (**1**/**NBD**: 1/2), gelation at higher ones) and the insufficient solubility of **1** in the above solvents at lower temperatures.

In the case of **NBD**, as soon as it was added to a catalyst solution (**1**/**NBD** 1/20, THF-d^8; Figures S3 and S4) the peaks at 4.30 and 1.98 ppm, due to the coordinated THF molecules, instantly diminish and gradually disappear, indicating their fast displacement by the substrate, but no peaks due to adduct formation could be detected. Instead, at $t = 0$–1 h, multiple broad unresolved high field peaks in the region 9.80–13.80 ppm, characteristic of the propagating tungsten alkylidene **PNBD** chains [2,48,49] appear simultaneously with peaks at 6.18, 5.90, 3.78 and 2.92 ppm, and one at 3.92 ppm, which could be assigned to the formation of *exo*-2-chloronorborn-5-ene and *exo*-3-chloronortricyclane, respectively [42]. As the reaction progresses, the intensity of the above peaks increases, along with parallel and increasing formation of **PNBD**. Corroborative evidence for the alkylidene ligand(s) by ^{13}C–NMR could not be obtained, presumably as a consequence of their minute concentration. The multiplicity of the signals could be attributed either to formation of several active species deriving from the **1**/**NBD** interaction, to fasbo/esbo equilibria and/or concurrent metathetical reactions. Their broad unresolved nature may be due to paramagnetism of the active species [50], restricted rotation of the alkylidene ligand(s) and/or the existence of several species with nominally similar structural features and slightly differing environments, possibly isomeric alkylidene THF adducts of the type {"W$_x$"(=CHP)(THF)$_y$} (P = polymer chain; x, y = 1 or 2). Quenching the reaction mixture with benzaldehyde (**1**/**NBD**/PhCHO: 1/20/100) causes the disappearance of the high-field peaks.

Interestingly, detection of the **1**/**NBD** interaction has been possible at stoichiometric catalyst to substrate ratio (Figure S5). Under these conditions, ligand (THF) displacement is slower and accompanied with observation of small peaks at 5.44, 5.20 and 4.62 ppm (ratio $\approx$ 2:2:1) indicative of coordinated olefinic protons (absorptions are at higher field than those of free **NBD** by 1.28, 1.50 and 2.10 ppm, respectively). When substitution is nearly complete ($t = 4$ h), the first two nearly disappear, while the third increases and becomes dominant. This peak may be assigned to the equivalently bound olefinic protons of an η^4-**NBD** ligand, either bridging the two tungsten atoms (**1a**) or chelating at one of them (**1'a**, Scheme 2). In support of formation of **1a** is the considerable insight on alkyne activation at bimetallic metal–metal bonded Group 6 centers [33,51,52], and in this particular case, the formation of [W$_2$(μ-Cl)$_3$Cl$_4$(η^2-C$_2$R$_2$)$_2$]$^-$ and dimetallacarbotetrahedrane complexes [W$_2$(μ-Cl)$_2$Cl$_6$(μ-C$_2$R$_2$)]$^{2-}$ (R = Me, Ph) deriving from the reaction of **1** with internal alkynes [53]; also, a limited number of representative alkene and diene interactions [54–60].

Evidently, our findings are remarkably similar to those reported by Szymańska-Buzar *et al.* on the polymerization of **NBE** and **NBD** by **5**, **5'** and **6** [35,42,45–47]. However, the **NBD**-to-carbene transformation in this system is more facile than those occurring in **5a**, and **6**/**NBD**, as this is reflected in the stabilities of the relevant adducts (**4a** stable and isolable; **1a** or **1'a** unstable) and the polymerization reaction rates, respectively (**5** or **5a**/**NBD**/CHCl$_3$ or CHCl$_3$/CH$_2$Cl$_2$ slow; **1**/**NBD**/CH$_2$Cl$_2$ vigorous).

At this stage, our understanding of the system does not allow for the drawing of solid conclusions. However, taking into account the results reported, those obtained in this work, as well as the characteristics of **1** (available coordination sites, W$_2^{6+}$ to W$_2^{8+}$ facile interconversions [26], favoring bimetallacycle formation [44], the synergistic effect of the W$_2^{6+}$ core that may substantially lower the required activation energies) [44,61], and providing that no other events during the reaction course induce rupture of **1** (e.g., disproportionation, excessive substrate binding), tentatively a bimetallic mechanism seems plausible and appears as a particularly attractive possibility (Scheme 2).

Scheme 2. Schematic view of proposed bimetallic mechanism of polymerization of **NBD** with complex **1**.
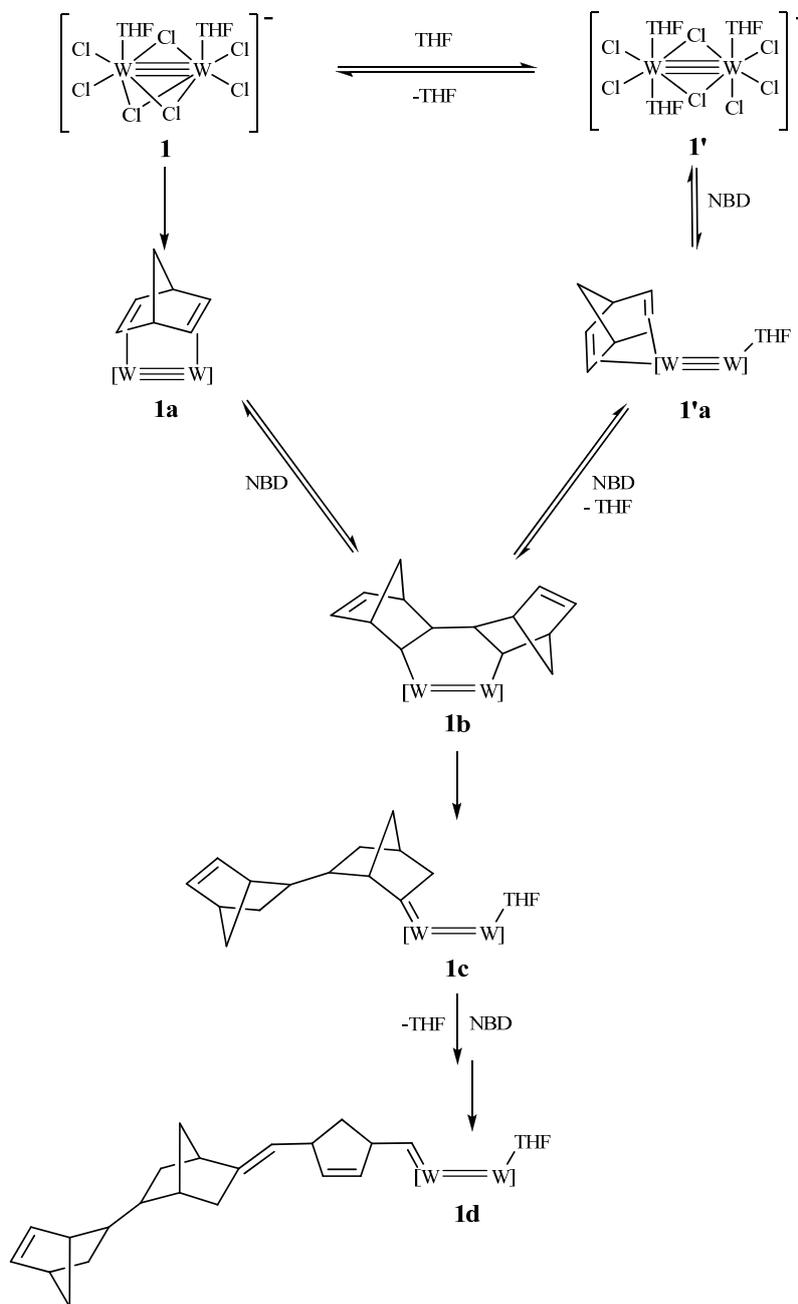
According to this scheme, there is no apparent reason that species **1b**/**1c** should not retain their bimetallic integrity, since they would contain a tungsten–tungsten double bond of formal order of two $(W = W)^{8+}$ supported by halide bridges. Such bridged W(IV)–W(IV) double bonds are strong $([W_2(\mu\text{-}Cl)_2Cl_8)]_n$, (2.688(2) Å) [62], $[K(18\text{-crown-}6)_{1.5}][W_2(\mu\text{-}H)(\mu\text{-}O)(OC^tBu)_6]$ (2.445(1) Å) [63], $[W_2(\kappa\text{-}O_2C^tBu)_4(\mu\text{-}MeCCMe)_2)]$ (2.4888(2) Å) [52], $[W_2(\kappa\text{-}O_2C^tBu)_4(\mu\text{-}PhCCMe)_2)]$ (2.4925(2)Å) [52], $[W_2(OCH_2^tBu)_8]_n$ [56]. The **1b**/**1c** transformation occurring by *a*-H-abstraction induced by the vicinal tungsten atom, followed by ring opening (C–H bond formation), is a possibility worthy of further investigation. Subsequently, propagation may proceed further via a two-center "windscreen" mechanism. Such an hypothesis is not unprecedented and has been previously proposed to explain the

ROMP of **NBE** along an edge of the trinuclear $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ cluster [64]. Alternatively, the possibility of **1c** being bridging cannot be excluded; in such a case, the reaction may occur via a bimetallic mechanism, as encountered in alkyne and cycloolefin polymerization with the $[W_2(CO)_{10}(\mu\text{-}CMe_2)]$ [65] and $[Cp_2Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH(Me))]$ [66] bridging carbenes.

In the case of **NBE**, monitoring of the reactions, apart from the difficulties encountered in CH_2Cl_2, is hampered by additional ones, such as very slow reaction rates even at high **1**/**NBE** (1/200) ratio and the masking of **NBE** and **PNBE** at the fingerprint regions of the ^1H NMR spectra, which makes results interpretation problematic. Competition between THF and substrate for ligation is evident, with the THF ligand displacement being very slow. Coordination of **NBE** could not be detected, but during the course of the reaction ($t = 0$–20 h) appearance of broad high-field peaks at the region 12.80–9.75 ppm (Figure S6), which may be assigned to the tungsten alkylidene **PNBE** propagating chains and of peaks at 3.84, 2.38, 2.30, 2.0–1.9 ppm (Figure S7), typical of *exo*-2-chloronorbornane [46,67], are observed. At longer times ($t = 40$ h) the characteristic peaks of **PNBE** at 5.25 and 5.10 ppm appear, whereas the intensity of the alkylidenic proton signals decay, indicating their decomposition. In this case, the evidence concerning the first step(s) of the reaction and the mechanism overall is much less clear. The process may operate either by the coupling of two η^2-**NBE** ligands in a $[W_2Cl_7(\eta^2\text{-}NBE)_2]^-$ complex, in a manner analogous to that proposed for **NBD**, or with formation of a tungstenonorbornylidene species, deriving from the $[W_2Cl_7(THF)(\eta^2\text{-}NBE)]^-$ anion [45]. This bimetallic mechanism may also explain the high *cis*-efficiency of the reaction, in terms of an enhanced "wall type" [68] steric hindrance along the one side of the dimetal axis. This would oblige the incoming monomer molecule (**NBE**) to approach the metal center minimizing steric repulsions that is favorable for the formation of *cis*- rather than *trans*-junctions in the polymer chain. Such an effect has been considered responsible for the formation of an all-*cis*-**PNBE** polymer from the *in situ* reaction of WCl$_6$/PSLi/**NBE** (PS = polystyrene) [69] and the dramatic stereoselectivity changes of the $[Mo_2(NCMe)_8](BF_4)_4$/EtAlCl$_2$ $((Mo\overset{4}{-}Mo)^{4+})$ system homogeneously (30% *cis*) and heterogeneously (SiO$_2$, 70% *cis*) [14].

4. Conclusions

From this work the following conclusions can be drawn:

(a) Complex **1** is an efficient homogeneous and/or heterogeneous unicomponent initiator for the ROMP of **NBE,** providing high molecular weight polymers in high yields and high stereoselectivity (86% *cis* for **PNBE**). Strongly coordinating pendant groups (–COOH, –OH, –CN) deactivate **1**, softer ones do not affect its reactivity (–COOMe), whereas less strained double bonds remain unaffected (–CH=CH$_2$). **NBD** reacts fast and quantitatively giving insoluble polymers.

(b) The presence of two labile *cis*-THF ligands in **1** seems necessary for catalytic activity, as this derives from the inactivity of **2** or the very small activity of **3** under the same conditions.

(c) *In situ* monitoring of the reactions (**1**/**NBD** or **NBE**) by ^1H NMR allows the observation of the active alkylidenes of the propagating chains, but the in-depth mechanistic aspects of these reactions remain a cloudy landscape.

(d) The reactivity of **1** for the ROMP of **NBE** is higher than that of the classical mononuclear initiators and derivatives thereof, resembling more to the bi- or multicomponent ones (e.g.,

WCl$_6$/organometallic co-catalysts), and to the well-defined high-valent carbenes. Its *cis*-specificity is more enhanced than that of the above mentioned systems, and is comparable to that observed with the low-valent carbenes (Katz) and the high-valent stereoselective design catalysts (Schrock, Basset).

In summary, it could be said that the [W$_2$Cl$_9$]$^{3-}$ anion, which played an important role in the development of metal–metal multiple bonds and transition metal clusters, comes out of its hybernetic inertia and its simple derivative **1** emerges as an interesting precursor for metathesis reactions.

Future studies are planned in order to shed light on mechanism intricacies, and also to survey the reactivity of these initiators towards other ROMPable substrates, as well as in ROMP-related reactions.

Acknowledgments

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