

Stereoselective Ring-Opening Metathesis Polymerization with Tungsten Sulfido Alkylidene *N*-Heterocyclic Carbene Complexes

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A series of cationic tungsten sulfido alkylidene *N*-heterocyclic carbene (NHC) complexes (**W01** – **W09**) of the general formula $[W(S)(CHCMe_3)(X)(NHC)(CMe_3CN)^+B(Ar^F)_4^-]$ (NHC = 1,3-dimesitylimidazol-2-ylidene, IMes; 1,3-dimesityl-4,5-dichloroimidazol-2-ylidene, IMesCl₂; 1,3-bis(2,6-xdiisopropyl)phenyl)imidazol-2-ylidene, IDipp; X = Cl, C₆F₅O, 2,6-Ph₂-C₆H₃; B(Ar^F)₄⁻ = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) are used as initiators in the stereoselective ring-opening metathesis polymerization (ROMP) of (+) 2,3-*endo*, *exo*-dicarbomethoxynorborn-5-ene ((+)DCMNBE, **M1**). *Trans*-isospecificity up to 84% is achieved along with varying percentages of *cis*-syndiospecificity. The different extent of *trans*-ispecificity is compared to the one of related benchmark cationic molybdenum and tungsten imido and tungsten oxo alkylidene NHC complexes. Mechanistic investigations suggest that the *syn*-isomer of a nitrile-free initiator reacts with **M1** presumably in an *ene*_{anti} fashion to yield a *syn*-first insertion product via turnstile rearrangement, which accounts for the predominant *trans*-ispecificity of the polymerization. The *cis*-syndiotactic sequences are proposed to stem from the competing *ene*_{syn} addition of **M1** to a nitrile-containing *syn*-isomer of the initiator.

molybdenum and tungsten alkylidene NHC catalysts bearing imido, oxo and sulfido ligands,^[9–28] respectively, has been developed. Compared to Schrock-type catalysts, this class of catalysts is characterized by a generally increased tolerance toward oxygen, moisture and functional groups^[14,15,29] as well as by higher activities and productivities with turnover numbers exceeding 1.2 million when supported on silica.^[30] So far, molybdenum and tungsten imido alkylidene *N*-heterocyclic carbene (NHC) complexes have been shown to allow for the stereoselective ROMP of various norbornene- (NBE) based monomers, thereby allowing for the selective formation of either *cis-it*, *trans-it*, *cis-st*, or *trans-st* structures.^[11,31,32] More recently, we reported on tungsten sulfido alkylidene NHC complexes.^[13] We were now interested, how this novel class of initiators would perform in stereoselective ROMP and how it compares to other molybdenum and tungsten alkylidenes, i.e., to molybdenum and tungsten oxo as well as tungsten imido alkylidene NHC complexes.

1. Introduction

Group 6 metal alkylidene complexes^[1–6] allow for the ring-opening metathesis polymerization (ROMP) of cyclic olefins such as mono- and disubstituted norbornenes, norbornadienes, or cyclopropenes with high stereocontrol. In many cases, *cis*-isotactic (*cis-it*), *trans*-isotactic (*trans-it*), *cis*-syndiotactic (*cis-st*), or *trans*-syndiotactic (*trans-st*) structures are formed virtually selectively.^[7,8] More recently, the new class of cationic

2. Results and Discussion

In order to allow for a direct comparison with the stereoselectivity of other W alkylidene-based initiators, monomer **M1** was chosen. Its ROMP was accomplished using initiators **W01** – **W10** (**Figure 1**). The stereochemistry of the resulting chiral polymers was determined on the basis of the ¹H NMR spectra. *Cis-st* and *trans-st* polymers possess a C₂-axis in plane of and perpendicular to the double bond, respectively (**Figure 2**). Consequently, the two olefinic protons located at one double bond are not coupled to each other, yet form doublets in the ¹H NMR as a result of the coupling to the neighboring methine protons. The resulting, small ³J-coupling constants typically give rise to pseudo-triplets. *Cis-it* and *trans-it* polymers do not possess any element of symmetry. Consequently, the olefinic protons are coupled and a doublet of doublet (dd) is formed.

Complexes **W01** – **W03** bearing a chloro-ligand show a *trans*-ispecificity between 66 and 84%, which is comparable to the *trans*-ispecificity found in the related W imido alkylidene NHC complexes $[W(N-2-tBu-C_6H_4)(CHCMe_2Ph)Cl](IMes)$

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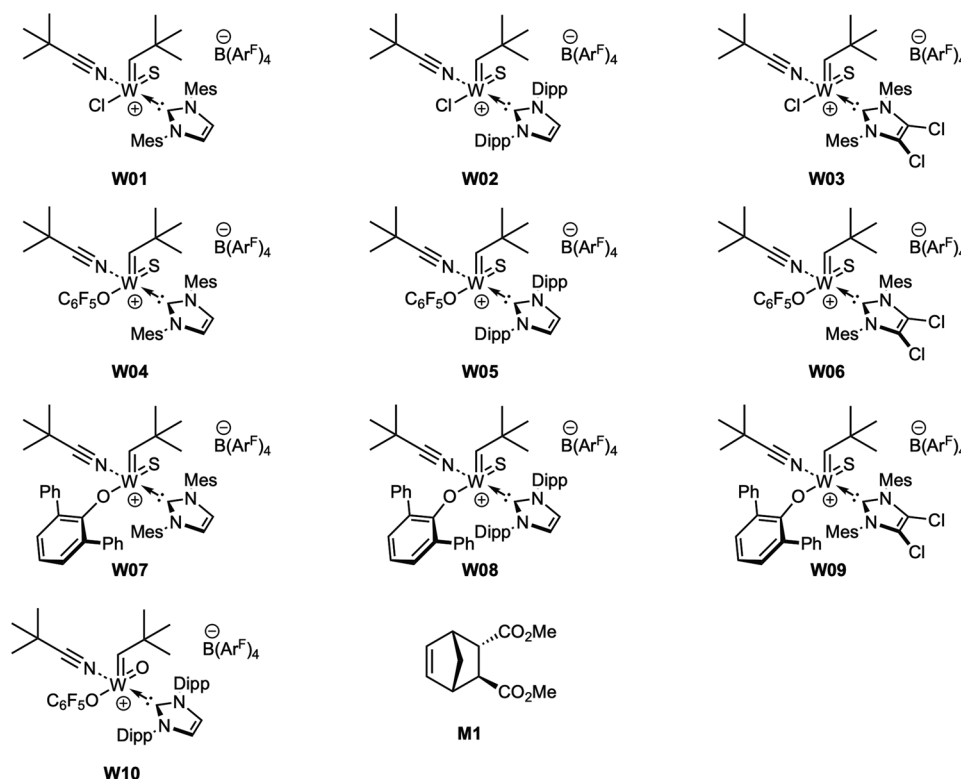


Figure 1. Structure of the tungsten sulfido and tungsten oxo alkylidene NHC complexes W01 – W10 and the monomer (+)-DCMNBE (M1).

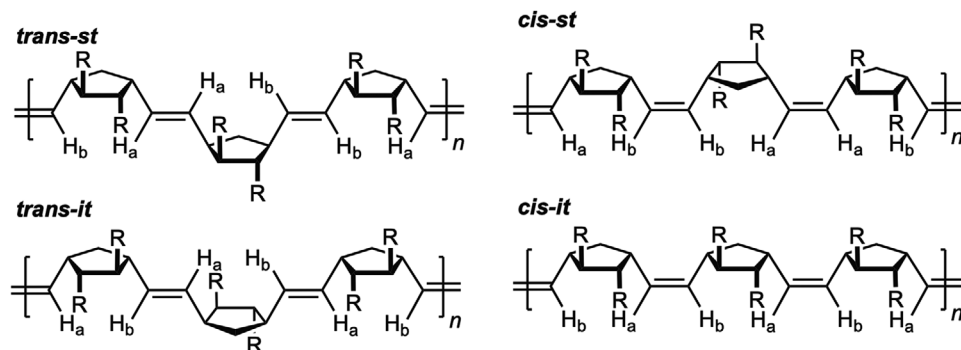


Figure 2. Possible stereoregular structures of poly(M1). R = CO₂CH₃.

(CMe₃CN)⁺B(Ar^F)₄⁻ (81%)^[11] or [W(N-2,6-Cl₂-C₆H₃)(CHCMe₂Ph)Cl(IMes)(CMe₃CN)⁺B(Ar^F)₄⁻] (77%).^[11]

Complexes **W04** – **W06** bearing the pentafluorophenoxide ligand allowed for a *trans*-isospicifity between 16 and 71%, which is, except for **W05**, again comparable to the *trans*-isospicifity observed with related cationic tungsten imido alkylidene NHC complexes [W(N-2,6-*i*Pr₂-C₆H₃)(CHCMe₂Ph)(OC₆F₅)(IMes)(CMe₃CN)⁺B(Ar^F)₄⁻] (88%),^[31] [W(N-2,6-Me₂-C₆H₃)(CHCMe₂Ph)(OC₆F₅)(IMes)(CMe₃CN)⁺B(Ar^F)₄⁻] (52%),^[11] [W(N-2,6-Cl₂-C₆H₃)(CHCMe₂Ph)(OC₆F₅)(IMes)(CMe₃CN)⁺B(Ar^F)₄⁻] (56%),^[11] and [W(N-2-CF₃-C₆H₃)(CHCMe₂Ph)(OC₆F₅)(IMes)(CMe₃CN)⁺B(Ar^F)₄⁻] (63%).^[11] The same accounts for the cationic tungsten oxo alkylidene NHC complex **W10**,^[12] which shows 70% *trans*-isospicifity. Complexes **W07** – **W09** bearing

the 2,6-Ph₂-C₆H₃-ligand allowed for similar *trans*-isospicifities between 57 and 73%. A summary of the *trans*-isospicifity in the ROMP of **M1** by the action of **W01** – **W10** is given in **Table 1**. Clearly, the tungsten sulfido complexes cannot rival the high *trans*-isospicifity of the corresponding Mo imido alkylidene NHC complexes,^[31] which reaches >98%.

The σ -donor capabilities of the NHCs used here, reflected by the Tolman electronic parameter (TEP^[33]), were rather similar and can therefore not be expected to be decisive for the stability of the tungstacyclobutane and thus on its propensity to undergo the turnstile rearrangement (*vide infra*). Thus, complexes **W03**, **W06**, and **W09** based on the NHC with the highest TEP (IMesCl₂, TEP = 2054 cm⁻¹) allowed for similar *trans*-isospicifities than all other complexes bearing the NHC with lower TEP values (Dipp,

Table 1. Conversion and selectivity in the polymerization of M1 with initiators W01 – W10 as well as number-average molecular weights (M_n) and \bar{D} of the polymers prepared.

Cat.	conversion [%]	<i>trans-it</i> [%]	<i>cis-st</i> [%]	M_n [g mol ⁻¹] ¹	\bar{D}	T_g [°C]	TEP ^[44]	X
W01	>99	84	16	2.3×10^4	1.4	79.4	2050.5	Cl
W02	>99	66	34	4.0×10^4	1.2	83.4	2050.5	Cl
W03	>99	70	30	1.1×10^5	1.2	75.5	2054.0	Cl
W04	>99	71	29	1.8×10^5	2.1	85.9	2050.5	OC ₆ F ₅
W05	>99	16	84	3.4×10^4	1.7	55.9	2050.5	OC ₆ F ₅
W06	>99	54	46	6.1×10^4	1.4	71.7	2054.0	OC ₆ F ₅
W07	>99	73	27	1.1×10^4	3.6	84.4	2050.5	O-2,6-Ph ₂ -C ₆ H ₃
W08	95	57	43	1.6×10^5	3.0	87.8	2050.5	O-2,6-Ph ₂ -C ₆ H ₃
W09	88	72	28	1.4×10^5	3.3	84.7	2054.0	O-2,6-Ph ₂ -C ₆ H ₃
W10	>99	70	30	4.0×10^4	1.7	83.7	2050.5	OC ₆ F ₅

¹ M_n (theor.) = 21 100 g mol⁻¹.

TEP = 2050.5 cm⁻¹; IMes, TEP = 2050.5 cm⁻¹). Also, in view of the fact that the NHC is *trans* to the tungstacyclobutane in the transition state, no significant steric effects of the NHC can be expected, the more since the values for the volume buried by the individual NHCs in **W04**, **W05**, and **W06** were very similar (V_{bur} = 29.6, 28.5, and 28.9%, respectively). Buried volumes for the NHCs in complexes **W04** – **W06** were calculated based on their crystal structures^[13] with the web tool SambVca 2.1 developed by Cavallo et al.^[34] For the settings, recommended defaults of a 3.5 Å sphere around the metal center, bond radii scaled by 1.17, and a mesh spacing value of 0.1 Å were used; H atoms were omitted. For a representative illustration, please refer to Figures S24 and S25 (Supporting Information). As found earlier for cationic Mo imido alkylidene NHC complexes,^[31] we again found no significant influence of the nature of the anionic ligand on *trans*-isoselectivity.

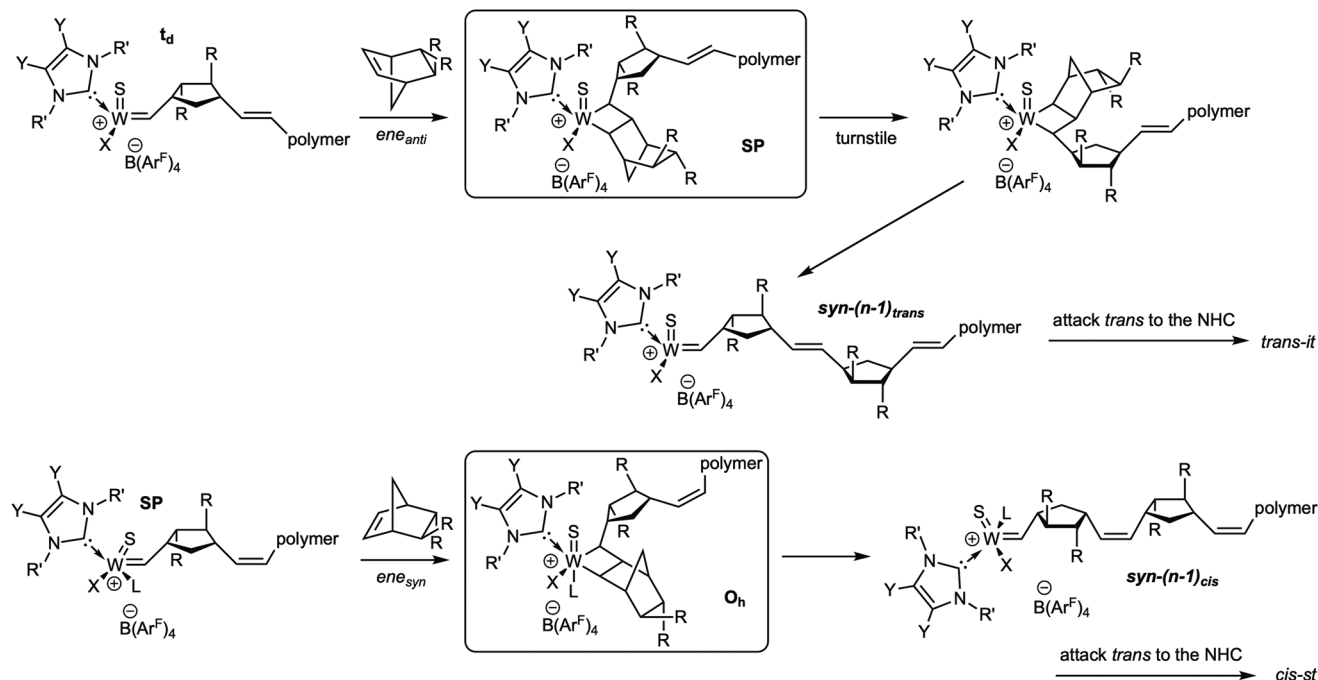
Only the ROMP with complexes **W01**, **W03**, and **W06** yields poly(**M1**) with low polydispersity indices ($\bar{D} \leq 1.4$) and molecular weights close to the theoretical one, suggesting favorable initiation kinetics and controlled, yet not perfectly living polymerizations (Table 1). Initiators **W02** and **W05** produce bimodal distributions while initiators **W07** – **W09** bearing the O-2,6-Ph₂-C₆H₃ ligand produce polymers with $3.0 < \bar{D} < 3.6$. These unusually high \bar{D} -values may be attributed to both, low initiation efficiencies and slow polymerization kinetics, caused by the sterically demanding O-2,6-Ph₂-C₆H₃ ligand, which is in line with the low conversions and high M_n -values found in polymerizations catalyzed by **W08** and **W09**. Poly(**M1**) prepared by any of the initiators was amorphous; the glass transition temperatures were in the range between $55.9 < T_g < 87.8^\circ\text{C}$. Poly(**M1**) with a high *trans-it* base generally possessed higher T_g values than those with a high *cis-st* base (Table 1); however, a strict correlation of T_g with the *trans-it* content of the polymers was in view of the different molecular weights of the polymers not possible.

2.1. Stereoselective ROMP: Mo-Imido versus W-Imido/Oxo/Sulfide Alkylidene NHC Complexes

The proposed reaction sequence that accounts for the formation of *trans-it* structures is outlined in **Scheme 1** (top).^[7,8,11,32,35]

It is based on the finding that we could not observe any signals for the *anti*-isomers in the starting complexes **W01** – **W10**, which is, however, no proof for their non-existence. In the formation of *trans-it* polymers, a monomer adds *ene_{ami}*, i.e., with the C7-carbon of the NBE down, to a *syn*-isomer of the initiator. The intermediary tungstacyclobutane must be stable enough to undergo turnstile rearrangement at tungsten, which consists of several Berry-type rotations. Cycloreversion then leads to a *syn*-first insertion product and, after multiple monomer insertions, to a *trans-it* polymer. With Mo imido alkylidene NHC complexes, this turnstile rearrangement is favored by, e. g. large imido-ligands.^[36] With tungsten oxo/sulfido complexes this is favored by a square pyramidal (SP) transition state in which the NHC is, unlike in Mo-complexes with a trigonal bipyramidal (TBP) transition state, *not* perfectly *trans* to the tungstacyclobutane. Indeed, in a SP transition state the tungstacyclobutane can be expected to have sufficient longevity to “survive” the necessary Berry-type rearrangements.

Generally, cationic Mo imido alkylidene NHC complexes allow for higher stereospecificities in the ROMP of NBE-based monomers for which several factors can be made accountable. In cationic nitrile-free, tetrahedral (t_4) complexes, Mo adopts a trigonal bipyramidal (TBP) transition state with the molybdacyclobutane *trans* to the strongest σ -donor,^[37–39] i.e., the NHC, which allows the steric influence of large anionic ligands such as (substituted) terphenolates that are *trans* to the imido ligand to become most effective, thereby favoring the formation of *cis*-polymers. In the corresponding cationic W imido/oxo/thio alkylidene NHC complexes, the transition state may alternatively adopt a SP geometry (vide supra), which substantially reduces the steric pressure of large anionic ligands and, consequently, stereospecificity. Previous studies also showed that cationic pentacoordinated Mo imido alkylidene NHC complexes bearing an additional acetonitrile can react with a substrate in either an associative or dissociative manner.^[19] Similar can be expected for the analogous cationic W imido/oxo/thio alkylidene NHC complexes. And indeed, the ¹H NMR spectrum of the reaction of two equivalents **M1** with **W06**, which was chosen since it produces almost equal amounts of *trans-it* and *cis-st* polymers, reveals some interesting aspects. Thus, the spectrum shows several new



Scheme 1. Formation of *trans-it* and *cis-st* structures with cationic tungsten imido alkylidene NHC complexes.

alkylidene signals at $\delta = 10.42, 10.39, 10.31, 9.85,$ and 9.83 ppm, all doublets with 3J -coupling constants between 3.3 and 4.1 Hz, assignable to the 3J -coupling of the alkylidene proton to the tertiary hydrogen in the cyclopentane unit. Unfortunately, the $^1J_{\text{CH}}$ coupling constants of the alkylidene protons, which would allow for an unambiguous assignment of *syn*- and *anti*-rotamers, could not be determined. However, based on literature data,^[14,23] we tentatively assign the signals at $\delta = 9.85$ and 9.83 ppm to the nitrile-free *syn*-isomers and those at $\delta = 10.42, 10.39,$ and 10.31 ppm to the nitrile-containing *syn*-isomers. In the olefinic region, several sets of pseudo-triplets and doublets are observed at $\delta = 5.48$ (d, $^3J = 11.4$ Hz), 5.47 (d, $^3J = 12.2$ Hz), 5.12 (t, $^3J = 11.4$ Hz), 4.94 (t, $^3J = 11.4$ Hz), 4.88 (t, $^3J = 11.3$ Hz), 4.87 (t, $^3J = 11.2$ Hz) and 4.81 (t, $^3J = 11.2$ Hz), all assignable to *cis*-configured $-(\text{cyclo-C}_5\text{H}_8)\text{-CH}=\text{CH-R}$ double bonds in the short chain oligomers. In addition, doublets of doublets can be identified at $\delta = 5.23$ ppm (dd, $^3J_1 = 15.7$ Hz, $^3J_2 = 7.5$ Hz), 5.20 ppm (dd, $^3J_1 = 15.9$ Hz, $^3J_2 = 7.0$ Hz) and at $\delta = 5.04$ ppm (dd, $^3J_1 = 16.3$ Hz, $^3J_2 = 6.7$ Hz), assignable to *trans*-configured $-(\text{cyclo-C}_5\text{H}_8)\text{-CH}=\text{CH-R}$ double bonds. According to $^1\text{H}-^1\text{H}$ correlated spectroscopy (Figures S11 and S12, Supporting Information), the corresponding signals (doublets) for the *trans*-configured $-(\text{cyclo-C}_5\text{H}_8)\text{-CH}=\text{CH-CMe}_3$ olefinic proton were in the range of 5.4–5.5 ppm but could not be identified unambiguously.

The occurrence of both, *cis*- and *trans*-configured double bonds together with the alkylidene signals for both, nitrile-containing and nitrile-free propagating species suggests the existence of two polymerization mechanisms being operative at the same time. The first involves a nitrile-free *syn*-configured initiator that reacts with the monomer in an *ene_anti* fashion to yield a *syn*-insertion product with a *trans*-configured double bond via a turnstile mechanism (*syn*-(*n*-1)_{trans}, Scheme 1, vide supra). The second entails a pentacoordinated nitrile-containing *syn*-isomer that inserts the

monomer in an *ene_syn* fashion to yield a *syn*-insertion product with a *cis*-configured double bond (*syn*-(*n*-1)_{cis}, Scheme 1) In the latter case, the transition state is hexacoordinated and cannot undergo a turnstile arrangement that is only observed in pentacoordinated complexes. Since either the nitrile or the anionic ligand is in an apical position in the transition state, an *ene_anti* approach seems less favored for steric reasons while this approach is possible in the solvent-free t_d complexes. Since the chloro-complexes **W01** – **W03** show similar stereoselectivity than **W07** – **W09** bearing a large anionic ligand we propose the nitrile to be in the apical position in the transition state. In view of the observed stereospecificity of complexes **W01** – **W10** and of published data on other cationic W imido/oxo alkylidene NHC complexes, we propose that nitrile dissociation from cationic W imido/oxo/thio alkylidene NHC complexes in the presence of substrate is on the same time scale than coordination of substrate, which leads to both, nitrile-containing and nitrile-free transition states. Indeed, this is different from what is observed at least for some cationic Mo imido alkylidene NHC complexes.^[14] Notably, fast solvent dissociation has also been proposed by Schrock et al. for neutral Mo imido alkylidene complexes.^[40,41] The two different transition states proposed here (penta- vs. hexacoordinated) might also be reason for the different regioselectivity (α - vs. β -insertion) observed in the cyclopolymerization of α,ω -diynes with solvent free- and solvent containing catalysts.^[42,43]

3. Conclusions

Nitrile-containing cationic tungsten sulfido alkylidene N-heterocyclic carbene (NHC) complexes allow for the stereoselective ROMP of *endo*, *exo*-2,3-dicarbomethoxy)norborn-5-ene ((+)-DCMNBE). *Trans*-isospecificities up to 84 % can be obtained and are comparable to those obtained with most other (nitrile-

containing) cationic tungsten imido and tungsten oxo alkylidene NHC complexes. The lower isospecificity compared to nitrile-containing and nitrile-free cationic Mo imido alkylidene NHC complexes is attributed to both, a square-pyramidal instead of a trigonal bipyramidal transition state and the action of a nitrile-free and a nitrile-containing initiator, respectively, which results in penta- and hexacoordinated transition states. Implications of these findings on the regioselectivity in the cyclopolymerization of α,ω -diynes are currently under investigation.

4. Experimental Section

General: All reactions were performed in the absence of moisture and air using standard Schlenk techniques unless indicated otherwise. Reactions with metal complexes were performed in a glove box filled with nitrogen (MBraun Labmaster 130). Glassware was stored overnight at 120 °C and cooled in an evacuated antechamber. CH₂Cl₂, diethyl ether, toluene, pentane, and THF were dried using an MBraun SPS-800 solvent purification system with alumina drying columns and stored over 4 Å Linde-type molecular sieves. Anhydrous benzene was purchased from Sigma-Aldrich; acetonitrile was purchased from Sigma-Aldrich, dried over CaH₂, distilled and stored over 4 Å Linde-type molecular sieves inside a nitrogen filled glove box. Deuterated solvents (Eurisotop) were used as purchased and stored over Linde-type 4 Å molecular sieves in a glove box. Initiators **W01** – **W10** as well as monomer **M1** were prepared according to the literature.^[11,12,31] ¹H and ¹³C NMR spectra were recorded using a Bruker Avance III 400 spectrometer at 400 and 100 MHz, respectively. COSY spectra were recorded on a Bruker Ascent 700 MHz spectrometer. Chemical shifts were given in ppm of tetramethylsilane, with solvent resonance from the remaining solvent protons (CDCl₃: 7.26 ppm, CD₂Cl₂ 5.32 ppm) for reference. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, br = broad, m = multiplet), coupling constant (Hz), and integral. IR spectra were measured on a Nicolet alpha spectrometer. Size exclusion chromatography (SEC) was performed in CHCl₃. The system consisted of a 1260 Infinity system (Agilent Technologies Inc.) equipped with a precolumn (8 × 50 mm) and three consecutive separation columns (8 × 300 mm, PSS, Mainz, Germany, porosities 1000, 100 000, and 1000 000 Å, particle size 5 μm) and an Agilent 1200 Series G1362A RI detector. The flow rate was set to 1.0 mL min⁻¹; the column oven temperature was set to 35 °C. An injection volume of 100 μL was used. The system was calibrated with narrow polystyrene standards (800 ≤ M_n ≤ 3000 000 g mol⁻¹). DSC measurements were carried out on a Perkin Elmer DSC 4000 with a Perkin Elmer Intracooler 2p Cryostate. Data were analyzed with the Pyris software.

Typical Polymerization Procedure: To 0.5 mL of a stock solution of **M1** (500 mM) in CDCl₃ 0.5 mL of a stock solution of the catalyst (5 mM) was added and the reaction was stirred for 24 h at room temperature. The polymers were precipitated in methanol and dried under reduced pressure.

Investigation of the First Insertion Products: A solution of the initiator (17.8 mg, 0.01 mmol) was dissolved in CDCl₃ (0.685 mL), dodecane was added as internal standard and the solution was subjected to ¹H NMR. Then, **M1** (4.18 mg, 0.02 mmol) dissolved in CDCl₃ (0.015 mL) was added and the resulting solution was subjected to ¹H NMR again.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

N-heterocyclic carbene, ring-opening metathesis polymerization, tacticity, tungsten

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