

Tungsten(II)-initiated ring-opening metathesis polymerization and other C–C bond forming reactions of 5-vinyl-2-norbornene

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Abstract

The trichloro-bridged tungsten(II) dimer $[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{GeCl}_3)(\text{CO})_3]$ (**1**) has been demonstrated to be a very effective catalyst for the ring-opening metathesis polymerization (ROMP) of 5-vinyl-2-norbornene (V-NBE). The selectivity of ROMP reaction depends very strongly on properties of solvent in which the reaction is carried out. In CCl_4 solution the ROMP reaction is accompanied by the formation of small amounts of (V-NBE)-(CCl_4) adducts, but in benzene solution 2,2'-bi(vinylnorbornylidene) (bi-(V-NBE)) and (V-NBE)-(C_6H_6) adducts were also detected. In dichloromethane or chloroform- d_1 solution the selectivity of ROMP reaction is low because it is accompanied by formation of bi-(V-NBE). The tungsten(II) compound activates the more strained cyclic double bond of V-NBE. As was shown by ^1H and ^{13}C NMR spectroscopy, the pendant vinyl group is left intact in poly-(vinylcyclopentylenevinylene) as well as in bi-(V-NBE). A mechanism involving C–H bond activation of olefin and the formation of tungsta-vinylnorbornylidene is proposed to explain those results. In dichloromethane and chloroform- d_1 solution a tungsta-vinylnorbornylidene species undergoes a carbene–carbene coupling reaction to give bi-(V-NBE). The reaction products are identified by means of chromatography (GC–MS) and ^1H and ^{13}C NMR spectroscopy.

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1. Introduction

Although transition-metal-catalyzed ring-opening metathesis polymerization (ROMP) of norbornene and functionalized norbornenes have been investigated extensively for many years [1–7], there are no reports of ROMP of 5-vinyl-2-norbornene (V-NBE). Till now the addition polymerization of V-NBE has only been investigated [8,9]. As it is known, the addition of functionalities to a ROMP polymer can greatly enhance the range of reachable properties [1–6].

Recently, the research works in our group and others have indicated that tungsten(II) complexes provide a rich variety of reactions with unsaturated hydrocarbons and can be used as catalysts for the metathesis of acyclic olefins and ROMP of cyclic olefins [10–17]. Among tungsten(II) compounds, the heterobimetallic complexes with a direct W–Sn or W–Ge bond have attracted particular interest owing to their strikingly different reactivity relative to the similar tungsten(II) complexes without metal–metal bond. Heterobimetallic complexes of the

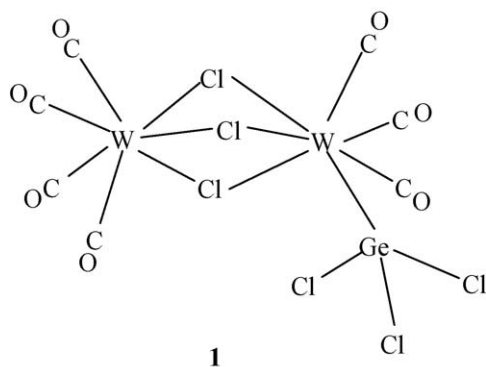
type $[(\text{CO})_4\text{M}(\mu\text{-Cl})_3\text{M}'(\text{Cl}_3)(\text{CO})_3]$, $\text{M} = \text{W}, \text{Mo}$; $\text{M}' = \text{Sn}, \text{Ge}$, have upraised as versatile precursors for synthetically important transformations such as metathesis polymerization of alkynes, ring-opening metathesis polymerization (ROMP), dimerization and hydroarylation of cyclic olefin [15–18]. These complexes have been prepared in photochemical oxidative addition reaction of $\text{W}(\text{CO})_6$ and tin or germanium tetrachloride. The seven-coordinate compound containing a direct W–Ge bond: $[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{GeCl}_3)(\text{CO})_3]$ (**1**) has recently been obtained in a pure crystalline form (Scheme 1) [17,18]. After establishing that **1** initiates the ROMP of NBE, we tested compound **1** as an initiator in ROMP of 5-vinyl-2-norbornene (V-NBE). Here we are reporting the results of our studies in this area. To our knowledge this is the first report of a ROMP of V-NBE.

2. Experimental

2.1. General remarks

All reactions were performed under an atmosphere of nitrogen and with freshly distilled substrates and solvents by standard

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Scheme 1. Schematic view of the ligands arrangement in compound $[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{GeCl}_3)(\text{CO})_3]$ (**1**).

Schlenk techniques. A 5-vinyl-2-norbornene (V-NBE) (95%, mixture of *endo* and *exo*, Aldrich) was dried and distilled from CaH_2 prior to use. The tungsten(II) compound **1** was obtained in photochemical reaction of $\text{W}(\text{CO})_6$ and GeCl_4 in *n*-heptane solution [18]. The photolysis source was an HBO 200 W high-pressure Hg lamp.

^1H , ^{13}C NMR and two-dimensional ^1H – ^1H COSY and ^1H – ^{13}C HMQC NMR spectra were recorded with a Bruker AMX 300 or 500 MHz instrument. All chemical shifts are referenced to residual solvent protons for ^1H NMR (δ 7.24 CDCl_3 , 4.65 D_2O) and to the chemical shift of the solvent for ^{13}C NMR (δ 77.00 CDCl_3). IR spectra of polymers were measured with a Nicolet–400 FT-IR instrument in KBr pellets. Raman spectra of monomers and polymers were measured in CCl_4 solution with a Nicolet Magna 860 FTIR/FT Raman spectrometer. Analyses of the catalytic reaction products were performed on a Hewlett-Packard GC–MS system. The average molecular weights M_n and M_w of the polymers were determined by the gel permeation chromatography (GPC) of the solution in CHCl_3 on a Hewlett-Packard 1090II instrument, equipped with a refractive index detector HP 1047A and Plgel 10 μm MIXED-B or Plgel 5 μm MIXED-C columns, previously calibrated with a use of commercially available polystyrene standards, in the molecular mass range 11.6×10^3 to 2.9×10^6 . A polydispersity ($\text{PDI} = M_w/M_n$) was calculated from the weight average molecular weight (M_w) and the number average molecular weight (M_n) by the non-commercial computer programme examining the peaks at high molecular weight in the gel permeation chromatograms (GPC).

2.2. General polymerization procedure

The *endo/exo* (2/1) V-NBE (ca. 0.43 g, 3.6 mmol) in solution of CCl_4 or C_6H_6 (5 cm^3) was added to compound **1** (ca. 0.03 g, 0.035 mmol) and stirred at 343 K until completion (ca. 3 h in CCl_4 and 6 h in C_6H_6 solution; ^1H NMR monitoring). In CH_2Cl_2 solution the reaction was carried at room temperature for from one to several days. The polymer was then precipitated in methanol, isolated and dried under vacuum. The yield of polymer was determined by mass. The filtrate

obtained after separation of polymer was always analyzed by GC–MS.

2.3. General procedure for NMR experiments

Under a nitrogen atmosphere, complex **1** (0.03 g, 0.035 mmol) was weighed into a NMR tube. The tube was then capped with a septum. A portion of V-NBE (ca. 0.1 g, 0.83 mmol) in (0.7 cm^3) appropriate solution (CDCl_3 , CCl_4) was then added to the NMR tube via a syringe. The tube was shaken very briefly and transferred to the NMR probe. For conversion kinetics, NMR spectra were acquired at the desired time. D_2O was employed as an external standard.

2.4. Spectroscopic characteristics of

poly(5-vinyl-2-norbornene) (poly-(V-NBE))

The microstructure of poly-(V-NBE) was investigated by ^1H and ^{13}C NMR, IR and Raman spectroscopy. ^1H NMR (CDCl_3 , 500 MHz): δ 5.71 (1H, HC^8), 5.23 (2H, $\text{HC}^{2,3}$), 4.89 (2H, H_2C^9), 2.92, 2.82, 2.61, 2.47, 2.20 (3H, $\text{HC}^{1,4,5}$), 1.94, 1.72, 1.60, 1.28, 1.17 (4H, $\text{H}_2\text{C}^{6,7}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 141.66, 140.61 (1C, HC^8), 135.6–130.3 (2C, $\text{HC}^{2,3}$), 113.60, 113.23 (1C, H_2C^9), 50.10–36.19 (5C, $\text{HC}^{1,4,5}$, $\text{H}_2\text{C}^{6,7}$). IR (KBr pellets): $\nu(\text{C}=\text{C})$ 1637 cm^{-1} (vinyl); $\delta(\text{H}-\text{C}=\text{C})$ 994, 910 cm^{-1} (vinyl), 967 cm^{-1} (*trans* vinylene), 754 cm^{-1} (*cis* vinylene). Raman (CCl_4): $\nu(\text{C}=\text{C})$ 1662 cm^{-1} (*trans* vinylene), 1651 cm^{-1} (*cis* vinylene), 1638 cm^{-1} (vinyl).

2.5. GPC analysis of poly-(V-NBE)

The molecular weights of the polymers were determined by GPC (CHCl_3 , r.t.) with polystyrene standards. The polymers samples presented bimodal GPC curves, and the calculated polydispersity index was always higher than 2. Polymers are low molecular weight in the range 1700–2800.

2.6. Formation and identification of

2,2'-bi(vinylnorbornylidene) (bi-(V-NBE))

Bi-(V-NBE) was detected in reaction of V-NBE carried out in a dichloromethane, chloroform- d_1 and benzene solution. The filtrate obtained after separation of polymer was evaporated, and the oily residue analysed by GC–MS showed four signals (a–d) of the bi-(V-NBE) isomers at increasing retention time in a 21:11:46:22% ratio, respectively. ($\text{C}_{18}\text{H}_{24}$, $M_r = 240.38$), m/z (relative intensity): (a) 41 (32), 67 (44), 79 (59), 91 (70), 105 (86), 117 (28), 135 (100), 145 (31), 173 (31), 240 (M^+ , 70); (b) 41 (44), 67 (75), 79 (80), 91 (100), 105 (70), 117 (42), 135 (50), 145 (37), 173 (25), 240 (M^+ , 90); (c) 41 (39), 67 (64), 79 (64), 91 (100), 105 (51), 117 (56), 145 (34), 174 (44), 211 (27), 240 (M^+ , 74); (d) 41 (29), 67 (47), 79 (47), 91 (100), 105 (34), 117 (74), 146 (92), 172 (23), 211 (18), 240 (M^+ , 78). ^1H NMR (CDCl_3 , 500 MHz): δ 5.9–5.7 (m, 1H, HC^8), 5.0–4.8 (m, 2H, H_2C^9), 2.75, 2.73, 2.55, 2.53, 2.50, 2.48, 2.47 (s, 1H, HC^1), 2.30 (s, 1H, HC^4), 2.17–1.12 (m, 5H, H_2C^3 , HC^5 , H_2C^7).

2.7. GC–MS data for (V-NBE)-(CCl₄) 1:1 and 1:2 adducts formed in reaction initiated by **1** in CCl₄ solution

The filtrate obtained after separation of polymer was evaporated and the oily residue analysed by GC–MS showed three groups (a–c) of signals at increasing retention time in a 56:32:12% ratio, respectively. Two groups of signals are belonging to the 1:1 adducts (a and b) and one group of signals (c) belonging to the 1:2 (V-NBE)-(CCl₄) adducts. (a) (C₁₀H₁₂Cl₄, $M_r = 274.01$), m/z (relative intensity): 41 (11), 54 (31), 93 (100), 119 (7), 155 (8), 239 (4), 274 (M^+ , 1). (b) (C₁₀H₁₂Cl₄, $M_r = 274.01$), m/z (relative intensity): 41 (10), 67 (100), 93 (18), 129 (67), 248 (3), 274 (M^+ , 0.2). (c) (C₁₁H₁₂Cl₈, $M_r = 427.83$), m/z (relative intensity): 67 (100), 91 (39), 111 (77), 182 (43), 273 (28), 355 (15), 392 (4).

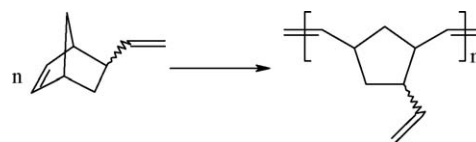
2.8. (V-NBE)-(C₆H₆) 1:1 and 1:2 adducts formed in reaction carried out in C₆H₆ solution

The filtrate obtained after separation of polymer (ca. 90% yield by mass) was evaporated and the residue analysed by GC–MS showed at increasing retention time three groups (a–c) of signals in a 6:91:3% ratio, respectively. One group of signals (b) is belonging to the V-NBE dimers (91%). Two groups of signals are belonging to the (V-NBE)-(C₆H₆) adducts: (a) 1:1 and (c) 1:2. GC–MS one of the most intense signal in the group (a): (C₁₅H₁₈, $M_r = 198.30$), m/z (relative intensity): 41 (23), 91 (81), 104 (100), 144 (50), 170 (6), 198 (M^+ , 34). GC–MS one of the most intense signal in the group (c): (C₂₁H₂₄, $M_r = 276.41$), m/z (relative intensity): 41 (18), 91 (40), 121 (100), 207 (15), 276 (M^+ , 11).

3. Results and discussion

3.1. Reaction of V-NBE in CH₂Cl₂ and chloroform-*d*₁ solution

Monitoring by ¹H NMR spectroscopy the reaction of V-NBE in the presence of **1** in different solvents (CDCl₃, CH₂Cl₂, CCl₄



Scheme 2. Ring-opening metathesis polymerization of 5-vinyl-2-norbornene by **1**.

and C₆H₆) allowed us to observe the decay of proton signals arising from the olefinic protons of V-NBE and the appearing of proton signals at δ 5.2 characteristic for the vinylene protons of polymer chain (Scheme 2, Fig. 1). Simultaneously, the vinyl proton signals at δ 5.71 (HC⁸) and 4.89 (H₂C⁹), left intact during this reaction, which indicates that the W–Ge compound **1** activates the more strained cyclic double bond. The polymer separated from the reaction mixture by precipitation into methanol is not very soluble, but its ¹H and ¹³C{¹H} NMR spectra clearly show the presence of the vinylcyclopentylenevinylene unit (Figs. 1 and 2). All poly-(V-NBE) prepared in different solvents and temperatures are virtually identical with that obtained in CH₂Cl₂ at room temperature (Figs. 1 and 2).

The filtrate obtained after separation of polymer from the dichloromethane solution was evaporated, and the oily residue analysed by GC–MS showed four signals at increasing retention time in a 1.9:1:4.1:1.9 ratio with the same $M_r = 240.38$, calculated for the V-NBE dimer. In ¹H NMR spectrum of this sample, two groups of signals at δ 5.7, and 4.9 in the intensity ratio ca. 1:2 arising from the vinyl protons are observed, indicating that vinyl group is left intact during this dimerization process and suggest the formation of 2,2'-bi(vinylnorbornylidene) (Fig. 3). Three broad signals in the region 2.8–2.5 ppm can be assigned to the methine proton in HC¹ unit in different stereoisomers of bi-(V-NBE) and one broad signal at 2.3 ppm to proton at the methine carbon HC⁴. A singlet at δ 2.17 arises from the proton of the methine group (HC⁵) as was deduced from ¹H–¹H COSY NMR spectrum, where coupling with the proton of HC⁸ groups was observed. Signals of two protons at the methylene carbon H₂C³ are observed as multiplets in the region 2.2–1.8 ppm.

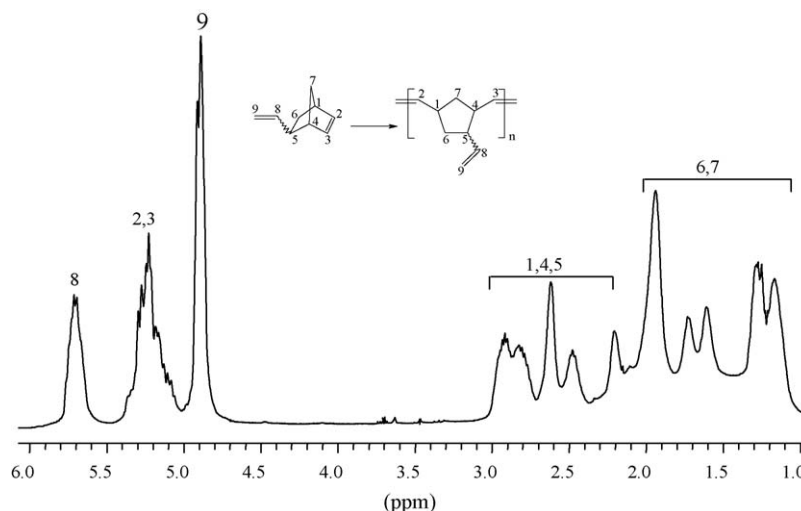


Fig. 1. ¹H NMR spectrum (500 MHz, CDCl₃) of poly-(vinylcyclopentylenevinylene) obtained in reaction of 5-vinyl-2-norbornene initiated by **1** in CH₂Cl₂ solution at r.t.

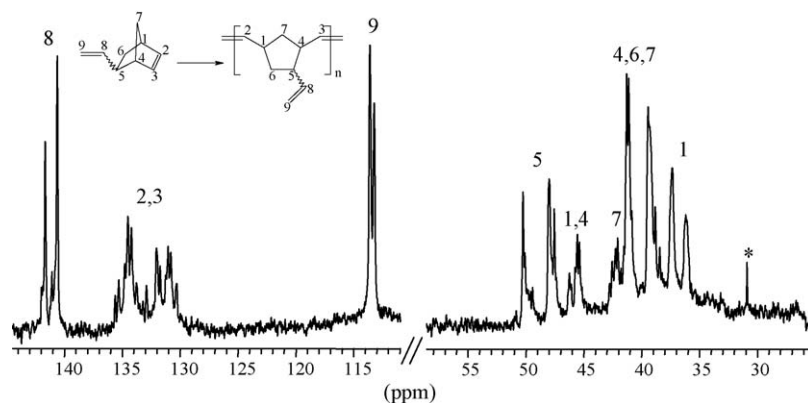


Fig. 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125 MHz, CDCl_3) of poly-(vinylcyclopentylenevinylene) obtained in reaction of 5-vinyl-2-norbornene initiated by **1** in CH_2Cl_2 solution at r.t. (* denoted signal of *n*-heptane).

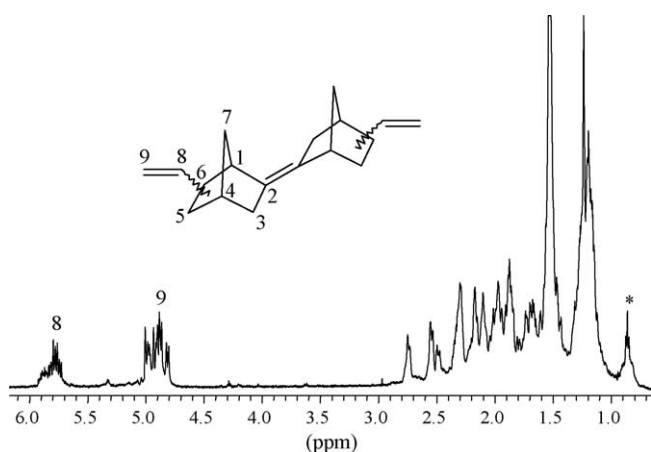
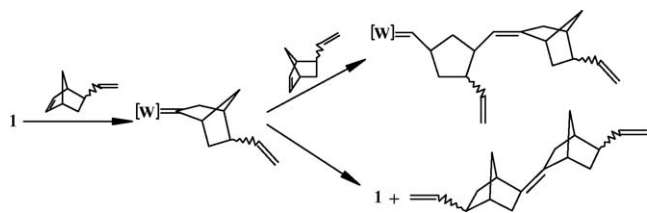


Fig. 3. ^1H NMR spectrum (500 MHz, CDCl_3) of 2,2'-bi(vinylnorbornylidene) (different stereoisomers) formed in reaction of 5-vinyl-2-norbornene initiated by **1** in CH_2Cl_2 solution at r.t. (* denoted signal of *n*-heptane).

The mechanism for the formation of poly-(V-NBE) as well as bi-(V-NBE) involves coordination of V-NBE to the tungsten atom and its transformation to a tungsta-vinylnorbornylidene species as a result of 1,2-hydride shift (Scheme 3). A similar η^2 -olefin to alkylidene rearrangement was proposed by others for such catalytic systems where as the source of alkylidene species was only the olefin ligand [1,4,10,11,19]. The direct evidence for such alkene-to-alkylidene rearrangement was obtained by Wolczanski and co-workers [20]. The bimolecular coupling of the tungsta-vinylnorbornylidene intermediate leads to the formation of bi-(V-NBE) and regenerates the binuclear compound **1** (Scheme 3). Earlier the bimolecular coupling of two



Scheme 3. The initiation of ROMP of V-NBE and the formation of 2,2'-bi(vinylnorbornylidene) in reaction carried out in the presence of **1** in the CH_2Cl_2 , CDCl_3 , or C_6H_6 solution.

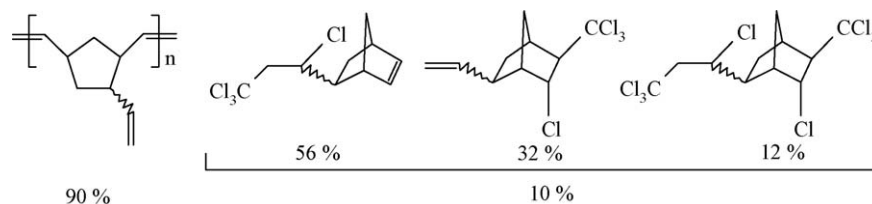
carbene ligands was observed during the mild thermolysis of chromium(0) and tungsten(0) pentacarbonylcarbene complexes [21,22]. Recently, such processes were detected in reaction of alkylidene complexes of molybdenum and tungsten in the higher oxidation states [23,24]. For first time, the carbene–carbene coupling reaction was applied in synthesis of 2,2'-binorbornylidene from a norbornene in reaction catalyzed by a W–Sn compound [25]. The reaction of norbornene in the presence of 2 mol% of a W–Sn compound $[(\text{CO})_4\text{W}(\mu\text{-Cl})_3\text{W}(\text{SnCl}_3)(\text{CO})_3]$ in dichloromethane solution after 24 h at room temperature gave 2,2'-binorbornylidene in 68%. This is a new and straightforward method of synthesis of new olefin. Previously, the Mc Murry and Fleming procedure for reductive dimerization of ketones had been applied for the synthesis of that type of compounds [26,27]. As was shown here the trichloro-bridged tungsten(II) dimer could be used in synthesis of bi-(V-NBE), which is identified by GC–MS analysis as a mixture of at least four isomers.

It is worth pointing out that the detection of bi-(V-NBE) provides direct evidence for the transformation of olefin to metallocarbene promoted by tungsten(II) that is able to initiate the ROMP of V-NBE or to decompose giving a carbene dimer (Scheme 3).

3.2. Reactions of V-NBE initiated by **1** in CCl_4 solution

In the reaction carried out in CCl_4 solution at 343 K the 100% conversion of V-NBE was obtained after 3 h and the yield of ROMP polymer reached ca. 90%. However, in this solvent the (V-NBE)-(CCl_4) adducts (ca. 10%) were also detected (Scheme 4).

The addition of polyhaloalkanes to alkenes is very well known as the Kharasch reaction [28–36]. Various transition-metal complexes, which are known to catalyse this reaction, play a role of the chlorine atom transfer agent. Earlier, that type of carbon–carbon bond forming reaction has been described almost exclusively for the terminal olefins and carried out at relatively high temperatures. Recently, it has been discovered that ruthenium complexes can catalyse the Kharasch reaction at lower temperature [29–36]. The tungsten-catalysed addition of polyhalomethanes such as CCl_4 and CHCl_3 , to norbornene (NBE) were earlier described [37], but here the formation of (V-NBE)-

Scheme 4. The (5-vinyl-2-norbornene)-(CCl₄) adducts formed in reaction carried out in tetrachlorocarbon solution at 343 K.

(CCl₄) adducts accompanied the ROMP reaction. As it could be expected the most efficient is the addition of the C–Cl bond of CCl₄ to the olefin bond of vinyl group, which is formed in about two times greater yield than the adducts to the olefin bond of norbornene. However, the tetrachlorocarbon adducts to both olefin bonds of V-NBE were also detected in a 1:4 ratio to the sum of 1:1 (V-NBE)-(CCl₄) adducts. The yield of (V-NBE)-(CCl₄) adducts is negligible in comparison to the yield of ROMP polymer and proves that the tungsten(II) compound is more effective in activation of the olefin C–H bond than the C–Cl bond of CCl₄.

3.3. The C–C bond forming reactions of V-NBE initiated by **1** in C₆H₆ solution

In benzene solution the ROMP reaction is slower than in CCl₄ (100% conversion in 6 h at 343 K), but occurs with comparable 90% selectivity. In this solvent the additional products such as the V-NBE dimers and phenyl-vinylnorbornane (Ph-V-NBA) in ca. 10:1 ratio were also detected (Scheme 5). Although, in benzene solution the activation of the olefin C–H bond by a tungsten(II) and the formation of tungstavinylnorbornylidene is a predominant reaction, the deactivation of catalytically active carbene species arising from its coupling reaction is lower than in dichloromethane. The simultaneous formation of hydroarylation products of V-NBE implicates the concurrent reaction involving the activation of the C–H bond of arene by tungsten(II) dimer [38–40]. In that way a direct evidence for the activation of the olefin or arene C–H bond by a tungsten(II) compound was obtained.

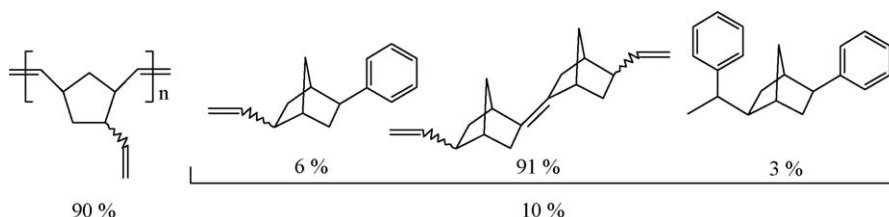
3.4. Characteristic of poly-(V-NBE)

All of the samples of poly-(V-NBE) analyzed by GPC had the similar low molecular weight values in the range 1700–2800 (versus polystyrene standards). GPC chromatograms of V-NBE polymers, obtained in a reaction carried out in a different solution and temperature, showed bimodal curves, which may result from different reactivity of the two tungsten centre created from W₂Ge

binuclear complex **1**. A similar bimodal curve was observed for poly-norbornene obtained in reaction initiated by **1** [37b]. The polydispersity index of polymers was ca. 2 or higher, as is typical for initiators which transform to catalytically active carbene species during the induction period.

As was described earlier, the most useful spectroscopic method applied in elucidation of microstructure of ROMP polymers is ¹H and ¹³C NMR spectroscopy [1,41–44]. In ¹H NMR spectrum of poly-(V-NBE) two broad signal, at δ 5.7 and 4.9 in the intensity ratio 1:2 arising from the vinyl protons and at δ 5.2 due to the aliphatic olefin protons in the polymer chain are observed to indicate that the W–Ge compound **1** activates the more strained cyclic double bond and that the pendant vinyl group is left intact in poly-(V-NBE) (Fig. 1). The same conclusion can be drawn from ¹³C{¹H} NMR spectrum, where signals of the vinyl carbons at δ 141.66, 140.61 (HC⁸), and 113.60, 113.23 (H₂C⁹) are observed (Fig. 2). Analyzing the olefin proton and the olefin carbon region of NMR spectra, we expected to obtain an evidence of the fraction of *cis* double bond in the polymer chain, similarly as for poly-(NBE) [41–44]. However, in ¹H NMR spectrum of poly-(V-NBE), the *cis* and *trans* (–HC=CH–) unit of polymer gives one broad signal at δ 5.2, but in the olefinic carbon region (135.6–130.3 ppm) two groups of signals, due to the olefinic carbons HC² and HC³ containing at least six carbon signals in each group, were detected. Such complicated spectra may result, at first, from the fact that the monomer of V-NBE, being a mixture (2/1) of *endo* and *exo* isomers, gives polymer with a different structure, and secondly, that the V-NBE, as other unsymmetrically substituted cycloalkenes, gives polymer containing head–head, head–tail, tail–tail and tail–head units. For that reason, the three methine (HC^{1,4,5}) units of poly-(V-NBE) give five signals between 2.9 and 2.2 ppm. The ¹³C{¹H} NMR spectrum is also very complicated, although the methine and methylene carbon signals are very well assigned by analysis of ¹H–¹H COSY and ¹H–¹³C HMQC NMR spectra.

To determine the contents of *cis* and *trans* (–HC=CH–) units in poly-(V-NBE), we decided to use the IR and Raman techniques. The IR spectrum (in KBr pellets) of poly-(V-NBE)

Scheme 5. Products of the C–C bond forming reactions of V-NBE initiated by **1** in C₆H₆ solution at 343 K.

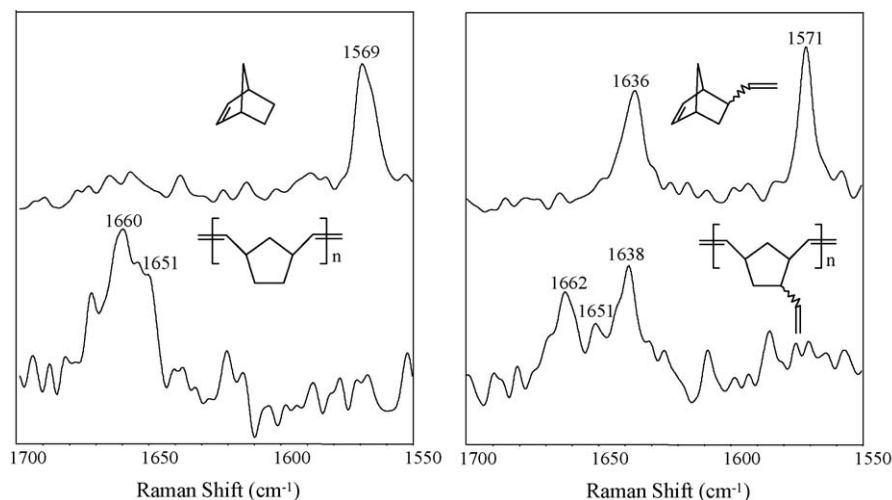


Fig. 4. Comparison of the Raman spectra (CCl_4 solution) of NBE and V-NBE monomers and their ROMP polymers obtained in the presence of **1** at the same reaction conditions (CCl_4 , 343 K).

exhibits three bands for the intact vinyl group; at 1637 cm^{-1} due to the $\nu(\text{C}=\text{C})$ stretching vibration and two bands deriving from the deformation vibration $\delta(\text{H}-\text{C}=\text{C})$ at 991 and 908 cm^{-1} . There are also two bands at 968 and 735 cm^{-1} , indicating olefinic deformation $\delta(\text{H}-\text{C}=\text{C})$, found in *trans* and *cis* olefinic units of polymer chain [45]. Although, it is difficult to calculate the exact intensity ratio of these bands, in all IR spectra their intensity is consistent with the higher content of *trans* (ca. 60%) than *cis* structure of polymer chain. A much more promising was the Raman technique, recently applied with success to analysis of different polymers [46,47]. In the Raman spectrum of the V-NBE monomer two bands, assigned to the $\nu(\text{C}=\text{C})$ stretching vibrations at 1636 and 1571 cm^{-1} due to the vinyl double bond and the cyclic olefin bond, are respectively observed (Fig. 4). After ROMP reaction, the band arising from the cyclic olefin bond decays, while the band of the vinyl group is left almost unchanged. Simultaneously, two new $\nu(\text{C}=\text{C})$ frequencies at 1662 and 1651 cm^{-1} appear, which can be assigned to the aliphatic $\nu(\text{C}=\text{C})$ stretching of the *trans* and *cis* polymer chain. Comparing the Raman spectra of the poly-(V-NBE) and poly-(NBE) obtained in the ROMP reaction carried out at the same conditions, we can see very similar features in the $\nu(\text{C}=\text{C})$ stretching region of the spectrum, which suggests that microstructures of both polymers are very similar (Fig. 4). For sample of poly-(NBE) used in the Raman experiment, the fraction of *cis* double bond ca. 0.4 was determined from ^1H and ^{13}C NMR spectra according to Ivin's method [1,41–43], which is in agreement with the intensity ratio of bands at 1660 and 1651 cm^{-1} in the Raman spectrum.

4. Conclusion

The present study has shown a new possibility of tungsten(II) compound to initiate such a reaction as ROMP of 5-vinyl-2-norbornene and indicated that the selectivity of polymerization reaction depends strongly on the solvent used. In CH_2Cl_2 and chloroform solution the polymerization is diminished due to the

decomposition in the course of carbene–carbene coupling reaction, the already formed vinylnorbornylidene ligand. The later process is not so substantial in such solvent as CCl_4 or benzene, especially at higher temperature (343 K). However, in benzene solution, the ROMP reaction competes with the hydroarylation reaction and in tetrachlorocarbon solution with the Kharasch reaction. These results nicely show what versatile catalytic properties the dimeric tungsten(II) compound possesses.

It is worth pointing out that the detection of bi-(V-NBE) provides direct evidence for the promoted by tungsten(II) transformation of olefin to metallocarbene that is able to initiate the ROMP of V-NBE or to disproportionate giving a carbene dimer.

In that way a direct evidence for the transformation of a cyclic olefin ligand to a carbene species as a result of the activation of the olefin C–H bond by a tungsten(II) compound was obtained.

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