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

Marcin Górski, Teresa Szymańska-Buzar*

Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland

Abstract

The trichloro-bridged tungsten(II) dimer $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ (**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.

Keywords: C–C bond formation; Metathesis; Polymerization; 5-Vinyl-2-norbornene; Tungsten catalyst; Metallacarbene; C–H bond activation

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 $[(CO)_4M(\mu\text{-}Cl)_3M(M'Cl_3)(CO)_3]$, M = W, Mo; M′ = Sn, 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 $W(CO)_6$ and tin or germanium tetrachloride. The seven-coordinate compound containing a direct W–Ge bond: $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ (**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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* Corresponding author. Tel.: +48 71 375 7221; fax: +48 71 328 2348.
E-mail address: tsz@wchuwr.chem.uni.wroc.pl (T. Szymańska-Buzar).

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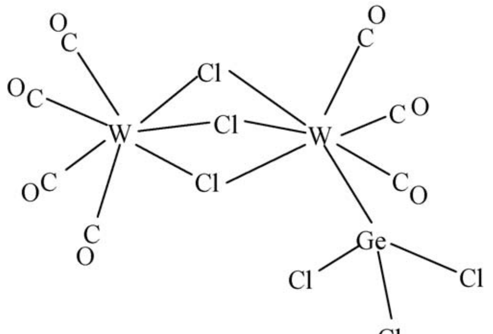

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Scheme 1. Schematic view of the ligands arrangement in compound $[(CO)_4W(\mu\text{-}Cl)_3W(GeCl_3)(CO)_3]$ (**1**).

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 $W(CO)_6$ 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 ($PDI = M_w/M_n$) 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, $HC^{2,3}$), 4.89 (2H, H_2C^9), 2.92, 2.82, 2.61, 2.47, 2.20 (3H, $HC^{1,4,5}$), 1.94, 1.72, 1.60, 1.28, 1.17 (4H, $H_2C^{6,7}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 141.66, 140.61 (1C, HC^8), 135.6–130.3 (2C, $HC^{2,3}$), 113.60, 113.23 (1C, H_2C^9), 50.10–36.19 (5C, $HC^{1,4,5}$, $H_2C^{6,7}$). IR (KBr pellets): ν(C=C) 1637 cm^{-1} (vinyl); δ(H–C=) 994, 910 cm^{-1} (vinyl), 967 cm^{-1} (*trans* vinylene), 754 cm^{-1} (*cis* vinylene). Raman (CCl_4): ν(C=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 polydyspersity 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 curried 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. ($C_{18}H_{24}$, $M_r = 240.38$), *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).