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# A partially serendipitous discovery of thermo-switchable ruthenium olefin metathesis initiator that seem to be well suited for ROMP of monomers bearing vinyl pendant groups

Katarzyna Szwaczko<sup>a§</sup>, Izabela Czeluśniak<sup>b</sup>, Karol Grela<sup>a</sup>\*
 <sup>a</sup> Poland, Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Żwirki i Wigury Street 101, 02-089 Warsaw, Poland
 <sup>§</sup> Current address: Poland Department of Organic Chemistry, Faculty of Chemistry, Marie Curie-Skłodowska University, Gliniana 33, 20-614 Lublin, Poland
 <sup>b</sup> Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland

This paper is dedicated to John Gladysz on the occasion of his 65<sup>th</sup> birthday, in appreciation of his fine friendship, generosity, and approach to science.

#### ABSTRACT:

A latent Ru olefin metathesis catalyst bearing a chelating ligand with an azoxybenzene fragment was obtained and characterized. The complex was inactive in the ring closing metathesis (RCM) reaction of a standard test diene: diethyl diallylmalonate at room temperature but can be subsequently activated by elevated temperature (up to 100 °C). The lack of activity of this azoxy catalyst in RCM of dienes containing terminal C-C double bonds at room temperature and high activity in ring opening metathesis polymerization (ROMP) of bicyclo[2.2.1]hept-2-ene (norbornene, NBE) permitted the ROMP of the challenging monomer: 5-vinyl-2-norbornene yielding soluble polymers with cyclopentenylenevinylene chains with vinyl pendant groups.

KEYWORDS: Olefin metathesis, ring opening metathesis polymerisation (ROMP), ruthenium

# Introduction

Olefin metathesis is widely used as a synthetic methodology in various fields, including synthetic organic chemistry [1], polymer chemistry [2,3], biochemistry [4], and materials science [5]. The application of olefin metathesis in these fields has been facilitated by the development of various increasingly sophisticated and specialised catalysts tailored to the requirements of these

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applications. Due to the huge interest in olefin metathesis, new catalysts are continually developed and the latest trends focus on the development of latent type of metathesis catalysts (Figure 1).



Figure 1. Grubbs-Hoveyda catalyst 1 and selected latent catalysts for olefin metathesis.

The "latent" catalysts are of great importance in the polymer chemistry since it is possible to effectively admix the catalyst in bulk monomer and store until a metathesis reaction is desired [6]. The trigger for initiation can be heat [7], light [8], chemical activation [9] or ultrasound [10]. The use of chelating carbene ligands at the ruthenium centre is the most promising approach to synthesis of a latent catalyst [5a]. Such chelating ligands are bidentate and stabilize the resting state of the catalyst at room temperature while at elevated temperature a coordination site is vacated. The group of Van der Schaaf described thermo-switchable ruthenium complex with 2-pyridylethanyl-carbene ligand [11], the Lemcoff and Grela groups presented latent metathesis initiators with a chelating quinoline, sulfoxide, sulfone and benzylidene thioether ligands [12]. Recently, Sashuk presented a thermo- and photo-switchable ruthenium initiator with *N*-chelating

azo benzene moiety, which coordinates to the ruthenium through either of the two nitrogen atoms [13].

Ring opening metathesis polymerization (ROMP) is among the polymerization techniques of choice, affording polymers exhibiting tailored characteristics [2]. Moreover, ROMP mediated by Ru carbene initiators is reliable, flexible and functional-group tolerant. Highly strained norbornene and its derivatives are the most commonly used monomers for ROMP mainly due to its commercial availability or accessibility via Diels-Alder reaction. Despite ROMP becoming a valuable method for the synthesis of structurally precise polymers, relatively little is known about ROMP of norbornene-type monomers containing vinyl moieties. In this case it is conceivable that the monomers with vinyl groups can also participate in cross-metathesis reaction, which might complicate the polymerization process leading to an insoluble cross-linked polymer. This may especially be true in the presence of a more reactive Grubbs-Hoveyda catalysts. Up to now, the poly(5-vinyl-norbornene) polymers with unsaturated main chain and vinyl pedant groups were achieved almost exclusively with less active W- and V-based initiators [14-18]. According to our best knowledge, there is only one example of ROMP of 5-vinyl-2-norbornene mediated by Grubbs-Hoveyda type Ru alkylidene complex leading to soluble polymers unfortunately with high polydispersity indexes (PDI = 4.6 - 8.5) [19].

In the search for new architectures of potentially thermo-switchable ruthenium-alkylidene complexes we turned our attention to the relatively unexplored class of azoxybenzenes. Herein, we report the synthesis of new ruthenium complex **11** with azoxybenzene ligand, its structural characterization and thermo-switchability assessment in a model ring closing metathesis (RCM) reaction of diethyl diallylmalonate. Finally ring opening metathesis polymerization (ROMP) of norbornene and its vinyl derivative is described, demonstrating the potential usefulness of the newly obtained complex.

#### **Results and discussion**

#### Synthesis of the catalyst

The synthesis of the desired 2-vinylnitrosobenzene precursor was planned *via* a two step reaction starting from commercial 2-bromoaniline. In the first step, the 1-bromo-2-nitrosobenzene dimer 6 was synthesized from 2-bromoaniline in 83% yield according to the

literature [20] by an oxidation with Oxone® in a mixture of dichloromethane (DCM) and water (Scheme 1).



Scheme 1. Synthesis of 2-bromonitrosobenzene dimer.

Next, we attempted to install the vinyl moiety to form a precursor for a chelating azoxybenzylidene ligand. Despite our efforts, we were unable to obtain the desired 2vinylnitrosobenzene (7). Instead we observed formation of a number of partially reduced compounds (Scheme 2). After some experimentation, we were able to establish conditions for the tandem vinylation-reduction yielding vinyl derivative 8 as the major product. Interestingly, only this isomer was formed, i.e. the isomer with the vinyl group exclusively installed at the  $N(\rightarrow O)$ bearing benzene ring. In this reaction bromide 6 was reacted with 1.5 eq. tributyl(vinyl)tin in the presence of catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%) in a toluene (Scheme 2) leading to 8 in 28% yield. As a byproduct (up to 6% of the yield) in this reaction compound 10 was isolated. Surprisingly, the reaction of 2-bromonitrosobenzene with 1.1 eq. or 2.0 eq. of the vinyl donor did not work any better and we observed only the formation of compound 9 (49% of yield). To our knowledge this is the first example of the reduction of a nitrosobenzene to a azoxybenzene derivative with an organic tin compound under Stille reaction conditions.



Scheme 2. Synthesis of ligand precursor 8.

Due to the difficulty of synthesizing 7, we opted to test another design of the chelating Ru complex, derived from compound 8. We considered two possible modes of chelation *via* either *N*- and *O*-chelates. To test this ligand precursor 8 was reacted with  $2^{nd}$ -generation Grubbs catalyst [RuCl<sub>2</sub>(PCy<sub>3</sub>)(SIMes)(CHPh)] in the presence of CuCl, used as a phosphine scavenger. After 'carbene exchange', flash chromatography yielded a brick-red colored microcrystalline solid, later characterized as compound **11** in 48%.



Scheme 3. Synthesis of complex 11 with azoxybenzene motif.

Compound **11** was found to be perfectly stable at room temperature and can be handled under air for a long periods of time (6-12 months).

The complex was characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectra. It contains a *N*-chelating azoxybenzene motif which coordinates to the ruthenium center through both the nitrogen and benzylidene carbene forming a six-membered chelate complex. The NMR spectra exhibited the characteristic features for a  $C_s$  symmetric compound with *trans* dichloro geometry [12e]. The benzylidene proton gave a singlet at  $\delta$  17.9 ppm in <sup>1</sup>H NMR and the corresponding carbon was found at  $\delta$  303 ppm in <sup>13</sup>C NMR, almost the same as those reported for the ruthenium carbene complex **5** bearing azobenzene functionality [13]. For the catalysts with chelating carbone ligands based on imines the corresponding proton was found in the range 18.4-18.7 ppm, while the <sup>13</sup>C NMR spectra shows the alkylidene carbon shifted downfield (341-343 ppm) [7a].

#### X-ray Crystallographic Studies

A single crystal of compound 11 suitable for X-ray diffraction studies was grown at +5°C from a trichloromethane/n-hexane solution. This allowed us to confirm the molecular assignment of the novel catalyst unambiguously (Figure 2). Important bond lengths and angles can be found in the captions of Figure 2. Further crystallographic details are given in the Supporting Information. X-Ray crystal structure analysis reveals that catalyst 11 is a five-coordinate monomeric ruthenium complex chelated by a bromo substituted azoxybenzene ligand. The coordination geometry of ruthenium center is a distorted square pyramid the apex of which is formed by the carbene atom C(4) with Ru–C bond of 1.826(2) Å. The base of the square pyramid is formed by the two chloro ligands Cl(1) and Cl(2) in a mutually trans arrangement while the remaining coordination sites are occupied by the C(1) atom of the NHC ligand and azoxy nitrogen N(3). Azoxy ligand is twisted with a dihedral angle of 116.06° between the two aromatic rings and is bound via a dative interaction through the nitrogen lone pair with Ru(1)-N(3) distance of 2.088(2) Å. The N(3)-N(4) distances of 1.297(2) Å are typical N-N bond lengths in coordinated azoxy molecules (1.279-1.312 Å) [21]. It is noteworthy that the open side of the Ru coordination is comparatively crowded by the presence of the bulky phenyl rings. However, in comparison to earlier presented thermally triggered ruthenium catalysts [7, 22], the geometry of 11 is quite unique. The molecular structure of the azoxy ligand coordinates metal center simultaneously by carbene atom C(4) and additional nitrogen donor N(3). It seems, that the neutral nitrogen donor could be reversible exchange in a metathesis reactions without reorganisation coordination sphere around the metal centre. This should allow to access the ruthenium active site relatively easy and altered its chemical activity as catalyst.



**Figure 2.** The molecular structure of **11** (thermal ellipsoids at 50% probability level; hydrogen atoms and co-crystallized CHCl<sub>3</sub> molecule omitted for clarity); selected bond lengths (Å) and angles (°): Ru(1)–Cl(1) 2.3632(5), Ru(1)–Cl(2) 2.3562(5), Ru(1)–N(3) 2.088(2), Ru(1)–C(1) 2.054(2), Ru(1)–C(4) 1.826(2), C(4)–C(5) 1.450(3), N(3)–N(4) 1.295(2), N(4)–O(1) 1.257(2), Cl(1)–Ru(1)–Cl(2) 164.88(2), C(1)–Ru(1)–N(3) 169.70(7), C(4)–Ru(1)–N(3) 89.15(8), C(5)–C(4)–Ru(1) 124.76(14).

#### Catalytic Performance Tests

The activity of complex **11** was evaluated by employing standard tests for metathesis catalysts. Thus, catalytic performance of **11** was investigated in the ring closing metathesis (RCM) of diethyl diallylmalonate (DEDAM) and the ring opening metathesis polymerization (ROMP) of norbornene (**14**) (Scheme 4). These reactions were selected because they are representative of processes of interest to the organic and polymer chemistry communities.



Scheme 4. RCM of diethyl diallylmalonate (12) and ROMP of norbornene (14) mediated by 11.

Firstly, the RCM of DEDAM was examined at different temperatures in toluene under air (Figure 3). In a demonstration of the latent nature of the azoxybenzene catalyst the RCM reaction of DEDAM was monitored by NMR at 25°C for a one hour, during this time no metathesis product **13** was detected. Even for longer reaction time the lack of catalyst activity was still observed. However, its activity was dramatically increased at elevated temperatures. At a catalyst loading of 1.0 mol % the product **13** was achieved in conversion 60% at 80°C and 81% at 100°C after 60 minutes. Extension of the reaction time up to 90 minutes resulted in conversion 16% at 40 °C and 99% at 80°C (see the Supporting Information).



**Figure 3.** Conversion-time diagram for the RCM of diethyl diallylmalonate **12** (0.1 M) in toluene with 1 mol% catalyst.

It is noteworthy that despite of such extreme reaction conditions (toluene 100°C) catalyst solution remained almost unchanged orange colour, which indicates that the catalyst is still active. Nitrogen containing ligands are strong electron donor in the ruthenium complex, which explains high initiation temperature (80°C-100°C) for the catalyst. Slugovc *et al.* [23] have previously shown that in the case of nitrogen donor ligands six-membered ring size are more stable than 5-membered increasing the precatalyst stability and initiation.

Due to the importance of precatalyst latency for ROMP, we decided to investigate latent catalyst **11** with highly strained ROMP monomer, norbornene (**14**), as detailed in Table 1.

monomer (M)	<b>11</b> mol%	solvent	time (h)	Conv (%) <sup>a</sup>	$M_n^{\ b}$	PDI <sup>b</sup>	cis/trans <sup>c</sup>
14	1	DCM	3	100	20 639	1.29	61/39
14	1	toluene	1	100	18 923	1.21	59/41
14	0.33	toluene	2	100	32 046	1.10	65/35
14	0.1	toluene	5	95	19 240	1.20	58/42
15	1	toluene	6	$80^{d}$	9 917	3.21	-
15	0.1	toluene	24	81 <sup>d</sup>	10 322	3.10	-

Table 1. ROMP of 14 and 15 initiated by complex 11.

Reaction conditions:  $[M] = 0.1 \text{ mol} \cdot \text{dm}^{-3}$ , RT; <sup>a)</sup> conversion determined by <sup>1</sup>H NMR; <sup>b)</sup> determined by GPC in THF relative to polystyrene standard; <sup>c)</sup> *cis/trans* double bonds of poly(**14**) calculated from <sup>1</sup>H NMR; <sup>d)</sup> yield calculated based on the weight of poly(**15**).

Not surprisingly, the monomer was polymerized leading poly(NBE)s with the molecular weights ( $M_n$ ) and polydispersities (PDI) in a range of 32 000 to 19 000 g/mol and 1.10 to 1.29, respectively. The higher than expected Mn of poly(NBE)s and the lack of a linear relationship between the Mn of the polymers and the [14]/[11] ratio suggests high propagation rates and slow initiation rates as well as competing chain-transfer reactions [24]. In fact, monitoring by <sup>1</sup>H NMR spectroscopy the ROMP of 14 (100 equivalents) in the presence of the azoxybenzene catalyst in deuterated benzene at room temperature shows the lack of propagating species and very low conversion of initiator. Moreover, alkylidene protons of propagating species were not detectable during this reaction.

The *cis/trans* ratio of the obtained poly(NBE) by using the investigated initiator **11** is c.a. 60/40 regardless of solvent used, which is typical for  $2^{nd}$  generation Grubbs initiators bearing SIMes ligand [25-27].

The complete lack of activity of the new catalyst in RCM toward terminal C-C double bonds, and at the same time its high activity in ROMP of NBE at room temperature inspired us to test the complex activity in ROMP of 5-vinyl-2-norbornene (**15**, Scheme 5).



Scheme 5. ROMP reaction 5-vinyl-2-norbornene (15) mediated by 11.

First the reaction of **15** mediated by catalyst **11** in  $C_6D_6$  at room temperature was followed by means of <sup>1</sup>H NMR spectroscopy, in order to provide some information about the initiator's activity toward vinyl group of the monomer. During the reaction, the disappearance of signals arising from the internal olefinic protons of **15** and the emergence of signals characteristic for the vinylene protons of polymer chain at  $\delta$  5.24 ppm were observed. Simultaneously, the vinyl protons signals at  $\delta$  5.74 and 4.81 ppm were left intact, indicating that the complex **11** reacts selectively with the internal C-C double bond of the strained bicycle. Careful investigation of alkylidene region (above 20 ppm) revealed that small amount of the catalyst rearranges to propagating species, as in the case of ROMP of **14**.

The catalytic polymerization reactions of **15** in the presence of different ratios of **11** were then studied and the results are detailed in Table 1. To our satisfaction, in the presence of complex **11** the polymerization occurs smoothly at room temperature giving polymers soluble in common organic solvents. Reducing the catalyst's loading lead to the ROMP reaction requiring a longer time to complete. Not surprisingly, the initiator produced poly(**15**) with a broad polydispersites (3.10 - 3.21) due to chain-transfer reactions [24]. However, the obtained  $M_n$  are similar and polydispersities are lower in comparison with polymers prepared by Balcar et al [19].

In order to confirm the structure of the poly(**15**) <sup>1</sup>H NMR and IR spectra were measured (see Supplementary Information, Figures S2 and S3). In the <sup>1</sup>H NMR spectrum two broad signals at  $\delta$  5.68 and 4.86 ppm arising from the vinyl protons and a signal at  $\delta$  5.19 ppm due to the olefinic protons in the polymer chain were observed indicating that the pendant vinyl group was left intact (Fig. S2) [14]. From <sup>1</sup>H NMR spectrum it is possible to estimate if any vinyl groups were consumed. For this, the integration ratio of resonances due to vinyl protons at  $\delta$  4.86 ppm (2H) and aliphatic protons (7H) in a range of 3.2 and 0.8 ppm was calculated giving a value of 2/7.2.

Such good agreement between theoretical and calculated integration ratio supports the lack of pendant vinyl groups metathesis in the presence of complex **11**.

The *cis/trans* double bond ratio in the polymer chain couldn't be assessed due to the overlap of their respective signals with one other [14]. However, IR spectroscopy can permit us to draw some conclusions concerning the microstructure of the polymer (Fig. S3). The spectrum of poly(**15**) exhibits three bands for the pendant vinyl groups; one at 1639 cm<sup>-1</sup> assigned to the stretching vibration v(C=C) and the two other at 993 and 907 cm<sup>-1</sup> arising from the deformation vibration  $\delta(H-C=)$ . This is in close agreement with the results obtained from <sup>1</sup>H NMR spectrum of poly(**15**). Comparing the IR spectra of poly(**15**) and poly(**14**) obtained under the same conditions, the occurrence of bands at 966 and 738 cm<sup>-1</sup> indicating olefinic deformation  $\delta(H-C=)$  of *trans* and *cis* olefinic units in polymer chain was observed [28], suggesting that *cis/trans* ratio of both polymers are similar.

#### Conclusions

In conclusion, we have developed, partially on a serendipitous way, a new latent catalyst system derived from Grubbs 2<sup>nd</sup> catalyst bearing chelating azoxybenzene ligand. The complex was inactive in RCM reaction at room temperature but can be subsequently activated by elevated temperature. Under such conditions, the studied complex was efficient in RCM, had a short initiation period, and led for the reaction under air. Complex **11** readily polymerised norbornene at room temperature. The lack of activity of the catalyst in RCM and high activity in ROMP of NBE at room temperature allowed us to successively carry out ROMP reactions of 5-vinyl-2-norbornene. Metathesis occurs selectively at the internal olefin yielding soluble polymers with cyclopentenylenevinylene main chains with vinyl pendant groups. The apparently lack of cross-linking leaves vinyl pedant groups intact, ripe for further elaboration.

We are continuing to explore the utility of the latent catalyst **11** in the development of new high temperature polymerization applications.

#### **Experimental section**

All reagents were purchased from Sigma-Aldrich, Strem, TCI and Alfa Aesar chemical companies and used without further purification. Toluene was distilled over potassium under atmosphere of argon.  $CH_2Cl_2$  and 5-vinyl-2-norbornene (15) (95%, mixture of *endo* and *exo*,

Sigma-Aldrich) were dried and distilled from CaH<sub>2</sub> and stored under inert atmosphere. For testing the activity of catalyst in RCM HPLC grade solvents (Aldrich), CH<sub>2</sub>Cl<sub>2</sub> and toluene were used as received. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization of TLC plates was performed by UV light either KMnO4 or I2 stains. Flash chromatography was performed using silica gel 60 (230-400 mesh). NMR spectra were recorded on Agilent 400-MR DD2 400 MHz, Bruker AMX-300 or Avance-500 MHz spectrometers. NMR chemical shifts are reported in ppm, and referred to residual solvent peak at 7.26 ppm and 77.16 ppm for <sup>1</sup>H and <sup>13</sup>C in CDCl<sub>3</sub>, 5.32 and 53.84 ppm for  ${}^{1}\text{H}$  and  ${}^{13}\text{C}$  in CD<sub>2</sub>Cl<sub>2</sub>, 2.50 ppm and 39.52 ppm for  ${}^{1}\text{H}$ respectively. The following abbreviations are used in reporting NMR data: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants (J) are in Hz. Spectra are reported as follows: chemical shift ( $\delta$ , ppm), multiplicity, integration, coupling constants (Hz). IR spectra were recorded on a Nicolet 8700A FTIR spectrometer. Wave numbers are in cm<sup>-1</sup>. GC analyses were performed using Clarus 580 chromatograph using durene as an internal standard. Micro-analyses were made using CHN 2400 Perkin-Elmer apparatus. Melting points were recorded on OptiMelt SRS with heating rate 10°C/min. High resolution electrospray mass spectra (ESI-HRMS) were recorded on Quattro LC triple quadrupole mass spectrometer. The mass spectrometer was calibrated with an internal standard solution of sodium formate or sodium iodide in MeOH. IR spectra were measured with a Bruker 113V FTIR instrument in KBr pellets. Gel Permeation Chromatography (GPC) data were obtained using a Viscotek GPC max equipped with a refractive index detector Viscotek VE 3580 and 300 mm Phenomenex Phenogel 5 µm 500 Å column. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min at 30°C. Polystyrene standards were used for calibration.

The reactions were carried out under nitrogen using the conventional vacuum/nitrogen line technique.

#### Synthesis of ligand

1-bromo-2-nitrosobenzene (6). To a solution of 2-bromoaniline (2 g, 11.62 mmol) in DCM



(10ml) Oxone® (7.14 g, 23.24 mmol) dissolved in water (10 ml) was added. The mixture was stirred under argon at room temperature until TLC monitoring indicated complete consumption of the starting material (12-18h). After separation

of the layers, the aqueous layer was extracted with DCM (3x30 ml). The combined organic layers were washed with 3% HCl, saturated sodium bicarbonate solution, water, brine and dried over MgSO<sub>4</sub>. Purification by silica-gel chromatography (c-Hex:EtOAc, 30:1) yielded product as a yellow powder (yield 83%). Crystalline nitrosobenzene was a pale yellow substance due to the formation of dimer, however in organic solvents that dimer dissociates to the corresponding monomer, which was visualized as a change in the color of the reaction mixture from yellow to green. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.98 (dd, 1H, J = 8.0, 4.0, Ar-H), 7.53 (ddd, 1H, J = 9.6, 7.2, 1.6, Ar-H), 7.27 (ddd, 1H, J = 9.6, 7.6, 1.2, Ar-H), 6.21 (dd, 1H, J = 8.0, 7.6, Ar-H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 161.1, 136.6, 135.2, 133.2, 108.9. Anal. Calcd. for C<sub>6</sub>H<sub>4</sub>BrNO: C, 38.74; H, 2.17; N, 7.53; Found: C, 38.38; H, 2.16; N, 7.45.

General procedure for the Stille reaction. The bromide (110 mg, 0.59 mmol), CH<sub>2</sub>=CHSnBu<sub>3</sub> and 5% mol of Pd(PPh<sub>3</sub>)<sub>4</sub> were placed in a Schlenk tube under argon. Dry toluene was added (5ml) and a mixture was refluxed. Progress of the reaction was monitored by TLC (c-Hex:EtOAc, 10:1). After full consumption of the substrates the reaction mixture was cooled down to RT and was stirred with an aqueous solution of KF. The organic phase was separated and water phase was extracted with DCM (3x20 ml). The organic phases were dried over MgSO<sub>4</sub>, filtered and evaporated. The residue was chromatographed with *c*-Hex:EtOAc, 50:1. Depending on the reaction condition, three compounds 8, 9, 10 were obtained.



1-bromo-2-[(2-vinylphenyl)-NNO-azoxy]benzene (8). The compound was isolated as a pale yellow oil, it decomposed very fast. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.90$  (d, 1H, J = 8.0, Ar-H), 7.81 (d, 1H, J = 8.0, Ar-H), 7.76-7.73 (m, 2H, Ar-H), 7.53-7.43 (m, 1H, Ar-H), 7.42-7.41 (m, 2H, Ar-H), 7.24-7.13 (m, 2H, Ar-H, CH), 5.81 (d, 1H, J = 16.0, CH=CH<sub>2</sub>), 5.45 (d, 1H, J = 8.0, CH=CH<sub>2</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.6, 133.4, 131.7, 130.7, 129.4, 128.3, 127.6, 127.2, 124.0,

123.4, 119.1, 117.8; IR (film from CH<sub>2</sub>Cl<sub>2</sub>): v = 3061, 2917, 1568, 1433, 1410, 1259, 1030, 902, 735cm<sup>-1</sup>; Anal. Calcd. for C<sub>14</sub>H<sub>11</sub>BrN<sub>2</sub>O: C, 55.47; H, 3.66; N, 9.24; Found: C, 55.70; H, 3.46; N, 9.65, m/z 325.0, [M+Na]<sup>+</sup>, HRMS calcd. for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>ONaBr 324.9952, found 324.9940.

1-bromo-2-[(2-bromophenyl)-NNO-azoxy]benzene (9). The compound was isolated as a white powder, mp: 111-112 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.96$  (d, 1H, J = 8.0, Ar-H), 7.76-7.69 (m, 3H, Ar-H), 7.49-7.35 (m, 3H, Ar-H), 7.25-7.20 (m, 1H, Ar-H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 142.6$ , 134.1, 133.4, 131.3, 129.7, 128.3, 127.7, 125.2, 123.4, 119.3, 115.0 ; IR (film from CH<sub>2</sub>Cl<sub>2</sub>): v = 3061, 2917, 1606, 1471, 1439, 1410, 1327, 1259, 1030, 902, 735cm<sup>-1</sup>; m/z 376.9, [M+Na]<sup>+</sup>, HRMS calcd. for C<sub>12</sub>H<sub>8</sub>NaBr<sub>2</sub> 376.8901, found 376.8887. The analytical data corresponded to the literature.[29]

**1-vinyl-2-[(2-vinylphenyl)-NNO-azoxy]benzene (10).** The compound was isolated as mixture with compound **9** (5-10%) as a pale yellow oil, it decomposed very fast. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.26-8.24$  (m, 2H, Ar-H), 7.70-7.65 (m, 2H, Ar-H), 7.49-7.32 (m, 4H, Ar-H), 7.21-7.14 (m, 1H, CH=CH<sub>2</sub>), 7.06-7.00 (m, 1H, CH=CH<sub>2</sub>), 5.79 (d, 1H, J = 16.0, CH=CH<sub>2</sub>), 5.74 (d, 1H, J = 20.0, CH=CH<sub>2</sub>), 5.40 (d, 1H, J = 12.0, CH=CH<sub>2</sub>), 5.30 (d, 1H, J = 12.0, CH=CH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 141.0$ , 135.5, 134.3, 133.8, 132.7, 131.7, 130.2, 129.1, 128.3, 128.2,

(100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.0, 135.5, 134.3, 133.8, 132.7, 131.7, 130.2, 129.1, 128.3, 128.2, 127.1, 127.8, 125.9, 123.7, 121.7, 117.7, 116.1; IR (film from CH<sub>2</sub>Cl<sub>2</sub>): v = 1465, 1346, 1045, 1025, 927, 750, 590, 440cm<sup>-1</sup>.

#### Synthesis of ruthenium complex (11)



In a flame dry Schlenk tube  $2^{nd}$  generation Grubbs catalyst (98 mg, 0.11 mmol), CuCl (12.0 mg, 0.12 mmol) and ligand precursor 7 (35.0 mg, 0.11 mmol) were placed. Then, dry DCM was added under atmosphere of argon and a mixture was heated to 30°C. The progress of the reaction was monitored by TLC (*c*-Hex:EtOAc, 2:1). After 20 min the reaction mixture

was cooled down to RT and the solvent was evaporated. Purification by silica-gel chromatography (*c*-Hex:EtOAc, 10:1, followed by *c*-Hex:EtOAc, 3:2) yielded brick-red solid (48%). A single crystal of compound **11** suitable for X-ray diffraction studies was grown at a temperature of +5°C from a trichloromethane/*n*-hexane solution. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 17.9 (s, 1H, Ru=CHAr), 8.50 (d, 1H, *J* = 12.0, Ar-H), 7.87 (dd, 1H, *J* = 16.0, 8.0, Ar-H), 7.45-6.88 (m, 10H, Ar-H), 4.28-4.04 (m, 4H, CH<sub>2</sub>× 2), 2.67-2.34 (br, 15H, CH3 × 5), 2.01 (s, 3H, CH3); <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 303.9, 210.9, 142.8, 140.3, 136.8, 134.5, 132.7, 130.5, 129.5, 128.7, 128.0, 125.7, 125.0, 123.0, 116.6, 77.5, 52.2, 51.1, 20.9, 19.9, 19.8, 18.4, 17.6; IR (film from CH<sub>2</sub>Cl<sub>2</sub>): v = 2913, 1607, 1481, 1414, 1258, 1013, 924, 849, 806, 763, 645, 576, 552 cm<sup>-1</sup>; Anal. Calcd. for C<sub>34</sub>H<sub>36</sub>BrCl<sub>2</sub>N<sub>4</sub>ORu: C, 53.13; H, 4.72; N, 7.29; Found: C, 53.81; H, 4.76; N, 7.27, m/z 791.0, [M+Na]<sup>+</sup>.

#### Crystallography.

Selected single crystals of **11** were mounted in inert oil and transferred to the cold gas stream of the diffractometer. Diffraction data was measured at 120.0(2) K with mirror monochromated Mo–K $\alpha$  radiation on the Oxford Diffraction Gemini A Ultra diffractometer. Cell refinement and data collection as well as data reduction and analysis were performed with the crysalis<sup>pro</sup> [30]. Absorption effects were corrected analytically from the crystal shape. The structures were solved by direct methods and subsequent Fourier-difference synthesis with shelxs–97 [31]. Full-matrix least-squares refinement method against F<sup>2</sup> values were carried out by using the shelx1–2013 [31] and olex2 [30] programs. All non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. The unit cell of **11** contains molecules of solvents: CHCl<sub>3</sub>. Crystal data and structure refinement parameters are given in Table S4 (Supplementary data). Crystallographic data were deposited in Cambridge Crystallographic Database Centre (CCDC 1537635).

#### Activity data

**RCM reaction of diethyl diallylmalonate (DEDAM) monitored by** <sup>1</sup>**HNMR.** In a NMR tube DEDAM (34.4 mg, 0.143 mmol) was weighed. Then, the tube was filled with non-distilled and non-degassed toluene (0.5 ml). Pre-catalyst (**11**) (7.1  $\mu$ mol) was weighed in the 2 ml flask and the toluene was added (1.0 ml). The aliquot of the pre-catalyst (0.2 ml, 1.4  $\mu$ mol) was injected into a solution of substrate in NMR tube. Data points were collected over an appropriate period of time using Varian array function at 25°C, 80°C, and 100°C.

**RCM reaction of diethyl diallylmalonate (DEDAM) monitored by GC.** In a Schelnk tube DEDAM (34.4 mg, 0.143 mmol) was weighed. Then, the tube was filled with non-distilled and non-degassed toluene (0.7 ml). Pre-catalyst (**11**) (1 mol % or 5 mol %) was weighed and added into a solution of the substrate. Reaction was carried out at 25°C, 40°C, and 80°C. Small amounts of the reaction mixture were removed from the flask time to time, diluted with  $CH_2Cl_2$ , and quenched with ethyl vinyl ether before GC analysis.

**Procedure for ROMP of 14 and 15.** In a typical experiment, monomer  $(0.1 \text{ mol} \cdot \text{dm}^{-3})$  dissolved in toluene or DCM was added to the initiator **11** dissolved in 0.5 cm<sup>3</sup> of the same solvent. The reaction was allowed to run for an appropriate time at room temperature under nitrogen. The course of the reaction was monitored by sampling  $(0.1 \text{ cm}^3)$  and analysis by <sup>1</sup>H NMR. Next, the

reaction was quenched with ethyl vinyl ether ( $c.a. 0.5 \text{ cm}^3$ ). The polymer was precipitated into an excess of methanol, isolated and dried under vacuum.

**Procedure for ROMP of 14 and 15 in NMR tube.** Under a nitrogen atmosphere, complex **11** (0.7 mg, 0.0009 mmol) was weighted into a NMR tube. The benzene- $d_6$  was then added to the NMR tube via a syringe. Next the relevant monomer (100 equiv.) was added to the NMR tube. The reactions were monitored by <sup>1</sup>H NMR spectroscopy at room temperature.

Poly(norbornene) (poly(14)). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 5.23$  (2H, trans HC<sup>2,3</sup>), 5.18 (2H, cis HC<sup>2,3</sup>), 2.76 (2H, cis HC<sup>1,4</sup>), 2.41 (2H, trans HC<sup>1,4</sup>), 1.74 (3H, HC<sup>5,6,7</sup>), 1.33 (2H, H<sub>2</sub>C<sup>5,6</sup>), 1.02 (1H, HC<sup>7</sup>). IR (KBr pellets, cm<sup>-1</sup>): 966 trans vinylene  $\delta$ (H-C=), 738 cis vinylene  $\delta$ (H-C=).

**Poly(5-vinyl-2-norbornene) (poly(15)).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 5.71$  (1H, HC<sup>8</sup>), 5.27



(2H,  $HC^{2,3}$ ), 4.90 (2H,  $H_2C^9$ ), 5.27 (2H,  $HC^{2,3}$ ), 2.92, 2.81, 2.62, 2.49, 2.22 (3H,  $HC^{1,4,5}$ ), 1.95, 1.71, 1,61, 1.29, 1.19 (4H,  $H_2C^{6,7}$ ). IR (KBr pellets, cm<sup>1</sup>): 1639 v(C=C), 993 and 907  $\delta$ (H-C=), 966 *trans* vinylene  $\delta$ (H-C=), 749 *cis* vinylene  $\delta$ (H-C=).

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## Supplementary data

The supporting information associated with this article can be found at

## Corresponding author

\*Karol Grela

Phone: +48-22-8220211 ext. 420, Fax: +48-22-8220211

e-mail address: klgrela@gmail.com

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- Thermo-switchable ruthenium alkylidene complex were isolated and characterized.
- The complex was inactive in RCM and active in ROMP at room temperature.
- ROMP of 5-vinyl-2-norbornene yielding soluble polymers with vinyl pendant groups.
- It provides one-step synthesis of polymers carrying C=C bonds in side chains.