S. Karabulut, B. Ö. Öztürk, Y. İmamoğlu / Hacettepe J. Biol. & Chem., 2012, 40 (1), 75-84

Ruthenium-initated Ring Opening Metathesis Polymerization of O-containing Norbornene Derivatives

O-içeren Norbornen Türevlerinin Rutenyum-başlatıcı ile Halka Açılımı Metatez Polimerizasyonu

Research Article

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ABSTRACT

In this study, several homobimetallic ruthenium complexes were synthesized by using monometallic ruthenium alkylidene complexes. The ligands in monometallic fractions were modified by phosphine, N-heterocyclic carbene and Schiff Base ligands. The effect of the ligands on formation of homobimetallic complexes and their ROMP (Ring Opening Metathesis Polymerization) activity were investigated. The synthesized complexes and ROMP polymers were characterized by ^{1}H-NMR and FT-IR and the activity results were compared with corresponding monometallic analogs.

Key Words
O-containing norbornene derivatives, Olefin metathesis, Ruthenium alkylidene, Organometallic catalyst, ROMP.

ÖZET

Bu çalışmada, monometalik rutenyum alkiliden kompleksleri kullanılarak homobimetalik rutenyum kompleksleri sentezlendi. Ligandlardaki monometalik kısımlar fosfin, N-heterosiklik karben ve Schiff Bazı ligandları ile değiştirildi. Homometalik komplekslerin oluşumuna ligandın etkisi ve bunların ROMP (Halka Açılımı Metatez Polimerizasyonu) aktiviteleri araştırıldı. Sentezlenen kompleksler ve polimerler ^{1}H-NMR ve FT-IR teknikleri ile tanımlandı ve aktivite sonuçları monometalik türlerle karşılaştırıldı.

Anahtar Kelimeler
O-içeren norbornen türevleri, Olefin metatez, Rutenyum alkiliden, Organometalilk katalizör, ROMP.

Article History: Received June 7, 2011; Revised October 14, 2011; Accepted January 10, 2012; Avaliable Online: March 5, 2012.

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INTRODUCTION

Cyclic olefins such as norbornene (NBE) and its derivatives can be polymerized via three different routes: ring-opening metathesis polymerization (ROMP) [1], cationic or radical polymerization [2], and vinylic polymerization [3]. The increasing interest in the ring-opening metathesis polymerization (ROMP) of norbornene derivatives containing functional groups has developed in recent years. Because these monomers are quite cheap and readily available [4,5] and obtaining polymer structures have attractive properties such as high glass transition temperature, high optical transparency and low birefringence [6-9]. The functional derivatives of some cycloolefins cannot be polymerized but norbornene can be easily polymerized under the same conditions. Because the high ring strain of the norbornene structure may compensate to some degree for the retarding effect caused by the interaction of functional substituents with active centers of metathesis.

The structure and properties of polymers received are dependent on the catalyst used. In the presence of catalysts on the basis of WCl_6 [10], $RuCl_3$ [11], and Re_2O_7/Al_2O_3 [12], as well as well-defined Schrock [13-15] and Grubbs [16-20] initiators ring-opening metathesis polymerization (ROMP) takes place with formation of cyclolinear structures. We previously reported many scientific studies on the application of W and Mo-based catalyst system to olefin metathesis reactions [21-29]. In this study, we report the activity of Ru-based initiators on the ring opening metathesis polymerization of O-containing norbornene derivatives.

MATERIALS AND METHOD

Chemicals

All manipulations were carried out under an nitrogen atmosphere using Schlenk techniques. Nitrosalicylaldehyde, 4-bromo-2, 4-dimethylanilin, norbornene, 5-norbornene-2yl- acetate, 5-norbor-nene-2-carboxaldehyde and 5-norbornene-2-metha-nol were purchased from Sigma-Aldrich and used as received. $[(PCy_3)_2Cl_2Ru{=}CHPh)]$ and $[RuCl_2(p\text{-cymene})]_2$ were purchased from Sigma-Aldrich and used as received. [(p-cymene)(Cl)Ru(μ-Cl)2Ru(Cl)(PCy_3)-(CHPh)] were synthesized according to the literature [30]. The ligand (IPr: 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene) and the Ru complex $[RuCHPhCl_2(PCy_3)$(IPr)) were synthesized according to previous literature methods [31-33]. Toluene, THF, dichloromethane and chlorobenzene (Sigma-Aldrich) were distilled under Na/benzophenone, P_2O_5 and $CaCl_2$, respectively and stored under an inert atmosphere .

Instrumentation

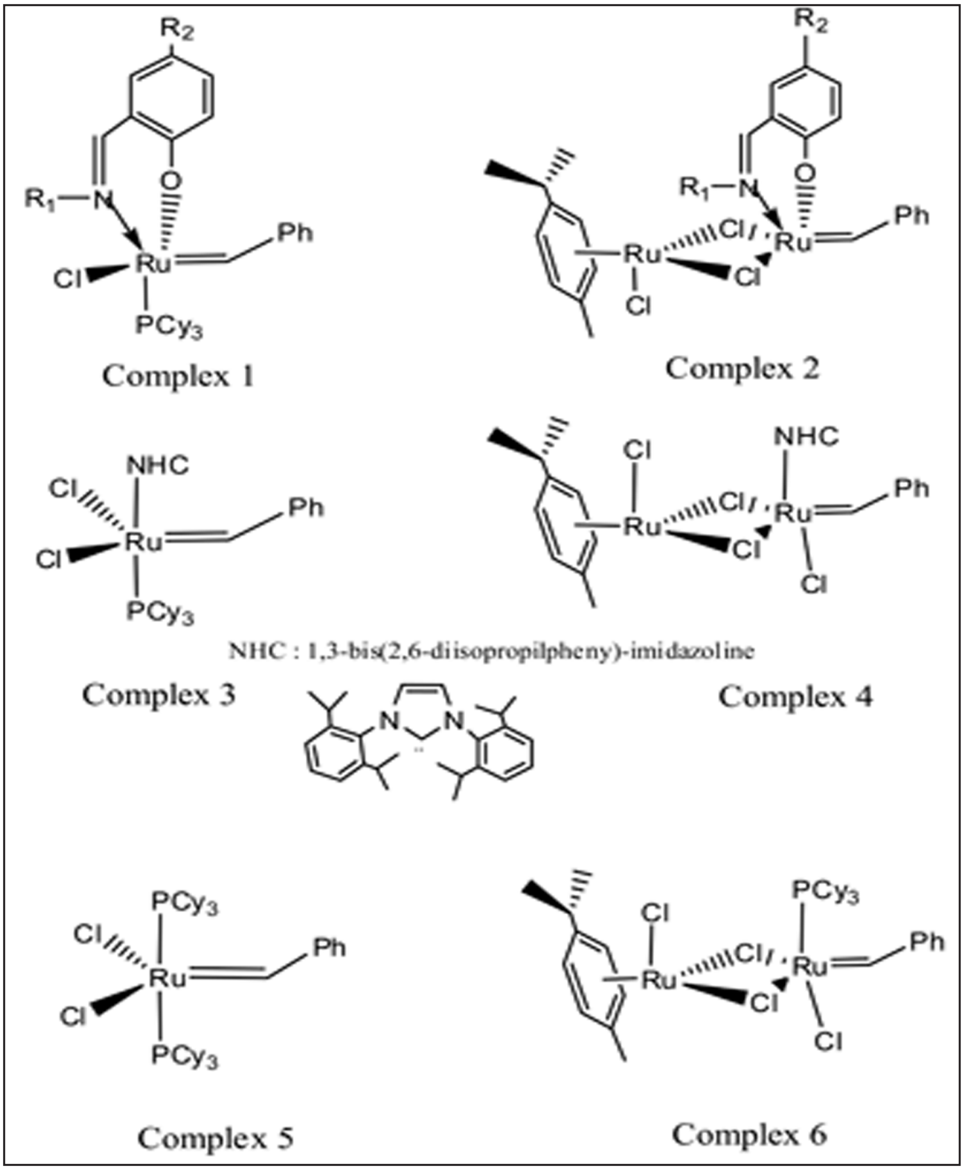
^1H and ^{31}P NMR spectra were recorded at 25 ºC with a Bruker GmbH 400 MHz high performance digital FT NMR spectrometer using $CDCl_3$ as solvent. Tetramethylsilane was used for the reference. ^{31}P NMR was only used to confirm the cleavage of tricyclohexylphosphine. Infrared spectra were obtained with KBr pellets using a Perkin-Elmer FTIR spectrometer.

Synthesis of Schiff Base Ligands

Nitrosalicylaldehyde (0.67 g, 4.0 mmol), 4-bromo-2,6-dimethylaniline (0.80 g, 4.0 mmol) and 15 mL ethanol were refluxed for two hours. The mixture was cooled to 0°C overnight. The solution was filtered and resulting yellow product was washed with cold ethanol twice and dried under high vacuum. Yield: %91, m.p.: 194-196 °C. ^1H NMR (CDCl3): 13.96 (s, 1H), 8.41 (s, 1H), 8.35 (d, 1H), 8.30 (d, 1H), 7.28 (s, 2H), 7.13 (d, 1H), 2.19 (s, 6H). The resulting yellow solid was dissolved in 10 mL of THF and a 5 mL solution of thallium ethoxide was added to reaction medium dropwise, till the all Schiff base-thallium salts were precipitated.

Synthesis of Schiff Base Containing Ruthenium Alkylidene Complex (Complex 1)

$(PCy_3)_2Cl_2Ru{=}CHPh)$ (0.5 g, 0.610 mmol) and thallium salt of Schiff base (0.46 g, 0.825 mmol) were weighted into a two neck 100 mL flask under nitrogen atmosphere. 20 mL THF was added and reaction mixture were stirred at room temperature for two hours. The resulting mixture was filtered under nitrogen atmosphere to remove unreacted Schiff base and thallium chloride salts. Solvent was evaporated under high vacuum and resulting red crystals were dried.



Scheme 1. Homobimetallic and monometallic ruthenium complexes which were used in this study.

Synthesis of Homobimetallic Schiff Base Ruthenium Alkylidene Complex (Complex 2)

Dichloro(p-cymene)ruthenium(II) dimer (0.5 g, 0.820 mmol) and complex 1 (0.7g, 0.850 mmol) were weighted into a two neck round bottom flask under a nitrogen atmosphere. 20 mL of CH_2Cl_2 were introduced into the flask and stirred at room temperature for two hours. Solvent was evaporated under high vacuum. The resulting yellow-dark red solid mixture was washed with 30:1 acetone:toluene mixture to remove unreacted starting materials and ruthenium arene by-product. The complex was characterized by 1H-NMR (Figure 1).

Synthesis of Homobimetallic NHC Ruthenium Alkylidene Complex (Complex 4)

Dichloro(p-cymene)ruthenium(II) dimer (0.5 g, 0.820 mmol) and complex 3 (0.75g, 0.850 mmol) were weighted into a two neck round bottom flask under a nitrogen atmosphere. 20 mL of toluene were introduced into the flask and stirred at room temperature for two hours. Solvent was evaporated under high vacuum. The resulting yellow-dark red solid mixture was washed with 30:1 acetone:toluene mixture to remove unreacted starting materials and ruthenium arene by-product. The complex was characterized by ^{1}H-NMR (Figure 2).

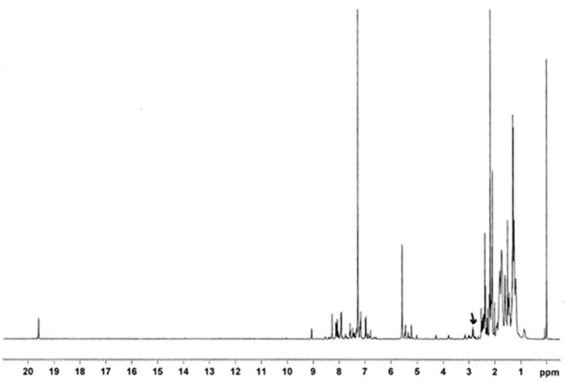


Figure 1. ^{1}H-NMR spectrum of Complex 2

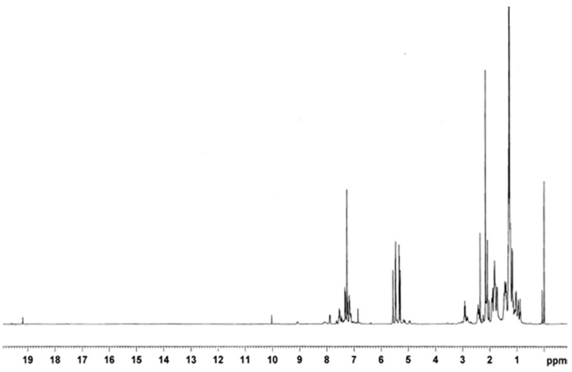


Figure 2. ^{1}H-NMR spectrum of Complex 4

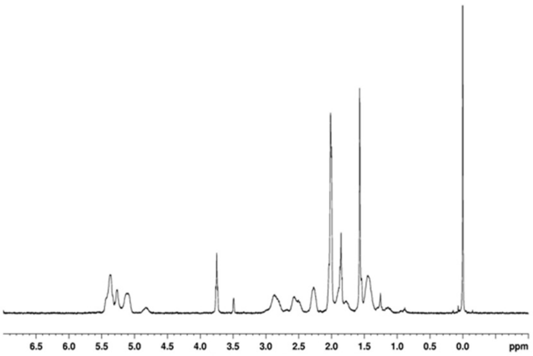


Figure 3. ^{1}H-NMR spectrum of poly(5-norbornene-2yl-acetate)

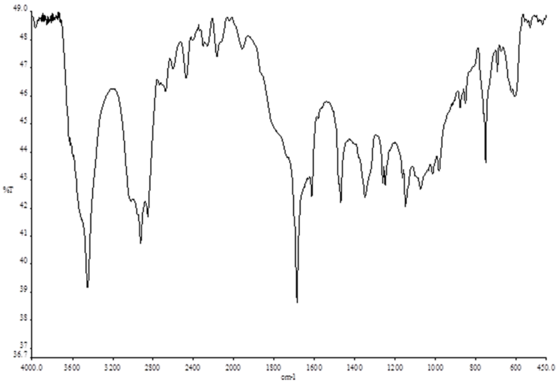


Figure 4. FT-IR spectrum of poly(5-norbornene-2yl-acetate)

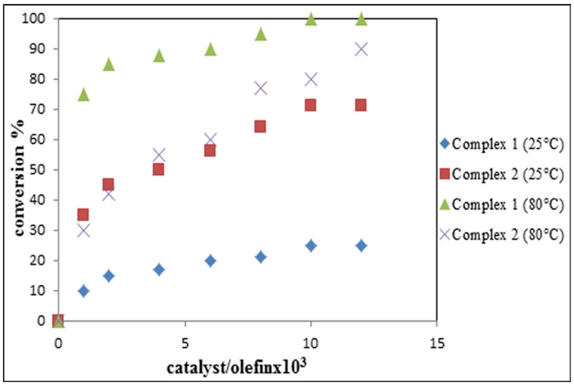


Figure 5. The comparative results concerning the ROMP of 5-norbornene-2yl-acetate, catalyzed by Complex 1 and 2 at 25°C and 80°C

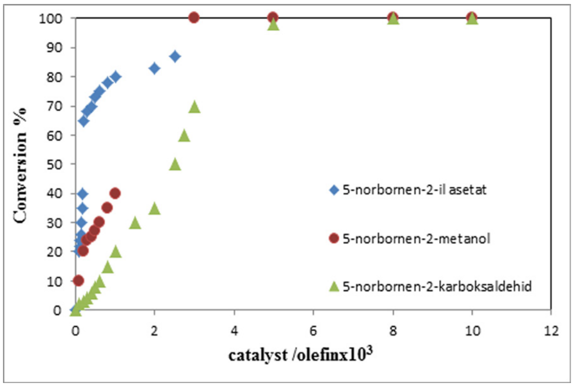
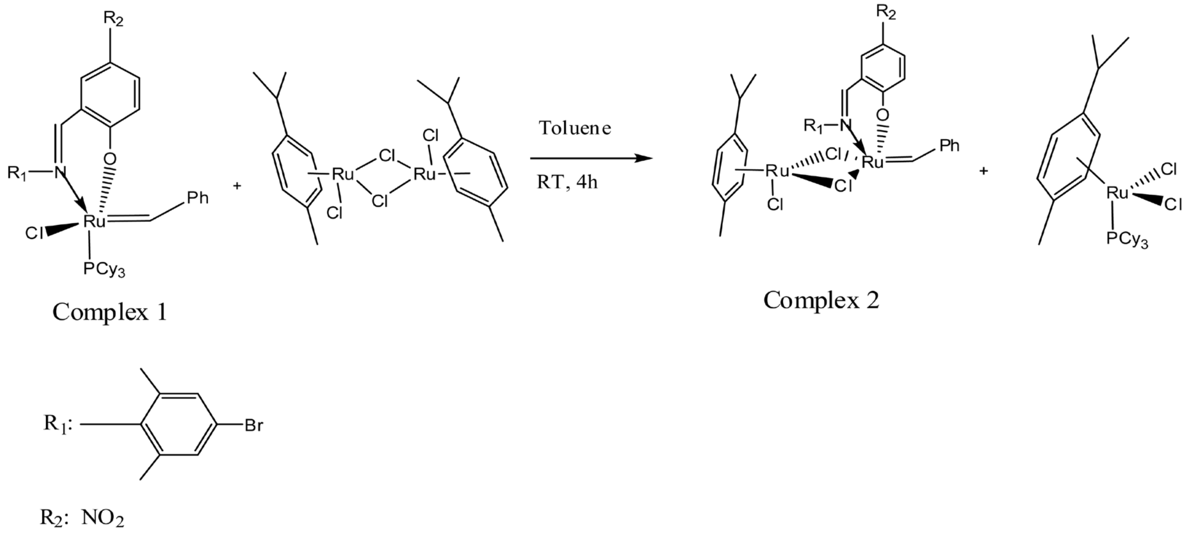
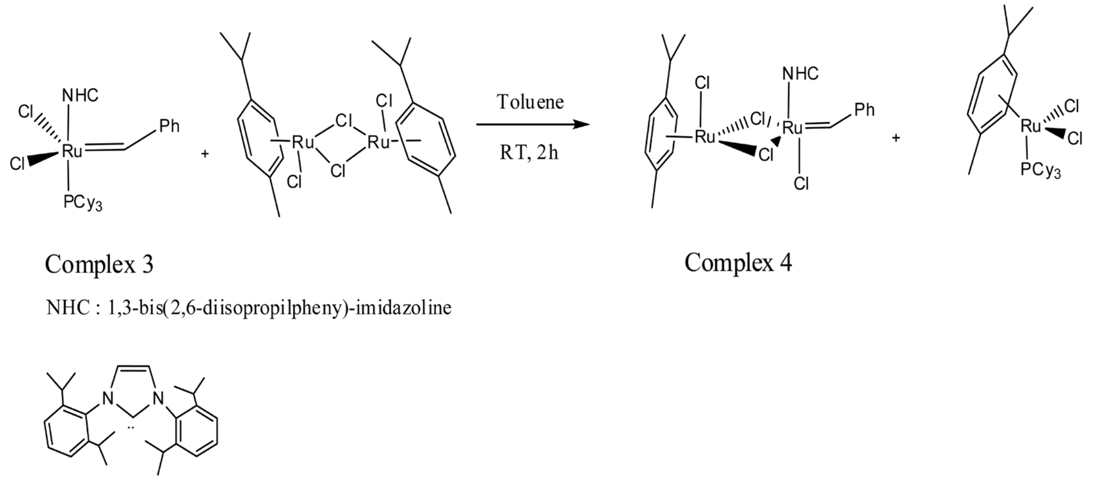


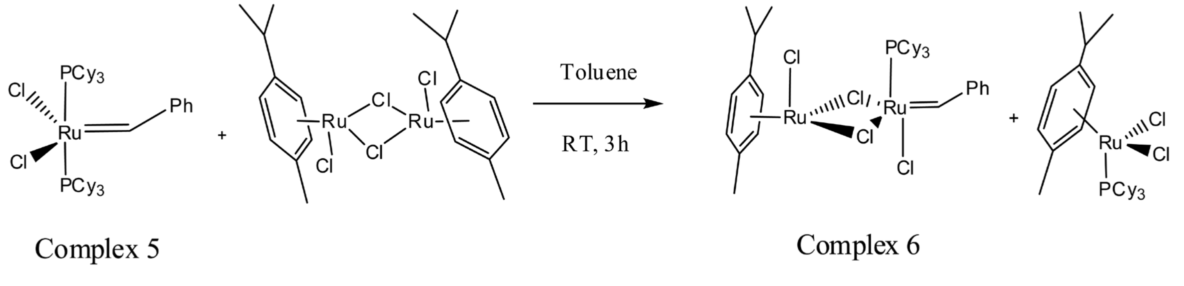
Figure 6. ROMP of various norbornene derivatives catalyzed by Complex 4 at 25°C.



Scheme 2. Synthesis of Complex 2



Scheme 3. Synthesis of Complex 4



Scheme 4. Synthesis of Complex 6

General Procedure for ROMP Reactions

The complexes (Scheme 1) was dissolved in dry CH_2Cl_2 and stirred. To this solution, 5 mL solution of norbornene derivatives (0.024 mol) was added and stirred at room temperature till the viscosity of the solution gradually increases. 20 mL of cold methanol was added to mixture dropwise. The mixture was filtered and polymer was dried under high vacuum.

RESULTS AND DISCUSSION

Synthesis of Ruthenium Complexes

The Schiff base ligands obtained with high yields by condensation reactions of primary amines with sallicaldehyde derivatives in ethanol at 80°C. The reaction proceeded smoothly by using 5-nitrosalicylaldeyhde with 4-bromo-2,6-dimethyl aniline in ethanol with 91% yield. The synthesized Schiff bases must be priory deprotonated before coordination into ruthenium complexes. The hydroxyl group on Schiff base ligands can be deprotonated by using strong bases such as thallium ethoxide and potassium tert-butoxide. The latter one, which is a typical sterically hindered strong base, gave rise to potassium salts of the corresponding ligand that doesn't readily react with ruthenium center at room temperature sufficiently. In some cases catalyst decomposition was observed. Thallium ethoxide salt of the corresponding ligands doesn't give rise to the negative effects that is associated with latter potassium salt derivative. Thallium salt of the ligand reacts completely with ruthenium center at room temperature for two hour. The Schiff base was dissolved in THF and deprotonated in the presence of thallium ethoxide and the resulting thallium salt used without further purification. The synthesized Schiff base salt reacted with $((PCy_3)Cl_2Ru{=}CHPh)$ at room temperature in dry THF. The reaction was monitored by 1H-NMR. The alkylidene proton (Ru=CHPh) of the starting material appears at 20.00 ppm in 1H-NMR. By coordination of Schiff base, the corresponding alkylidene proton peak shifts to lower fields. The completion of the reaction was confirmed by disappearance of alkylidene proton signal at 20.00 ppm and appearance of a new alkylidene proton peak of resulting complex 1 at 19.55 ppm. The isolated complex 1 was reacted with equivalent amount of $(RuCl_2p\text{-cymene})2$ in toluene at room temperature in a fashion to obtain a new homobimetallic complex (Complex 2). Complex 2 was formed by substitution of one of the ruthenium dichloro p-cymene fragment with PCy_3 ligand on complex 1 (Scheme 2). Equivalent amount of $RuCl_2PCy_3(p\text{-cymene})$ was formed as a by-product of the reaction. The resulting by-product, $[RuCl_2(PCy_3)p\text{-cymene}]$ and unreacted starting materials were removed from reaction mixture by washing the crude product with acetone:toluene (30:1) mixture, resulting in a pure complex (Complex 2). N-heterocyclic carbene containing homobimetallic alkylidene complex (Complex 3) was prepared with a similar procedure described above. 1,3-bis-(2,6-diisopropylphenyl) imidazolinium chloride was deprotonated by using potassium bis(trimethylsilyl)amide. During deprotonation process, precipitation of yellow KCl salt was observed by subsequent addition of base to the suspension of 1,3-bis-(2,6-diisopropylphenyl) imidazolinium chloride in toluene. At this point, $((PCy_3)Cl_2Ru{=}CHPh)$ was added and reaction was monitored by the same method described above. The alkylidene proton peak belonging to monometallic NHC-Ru complex gave signal at 19.65 ppm. The resulting complex 3 was reacted with $[RuCl_2(p\text{-cymene})]_2$ in a similar procedure that for complex 2 (Scheme 3). The alkylidene proton signal of the homobimetallic analog of this complex (complex 4) appears at 19.10 ppm. PCy_3 ligand containing homobimetallic ruthenium complex (complex 6) was observed by reacting $((PCy_3)Cl_2Ru{=}CHPh)$ with $(RuCl_2p\text{-cymene})_2$, confirmed by shifting of alkylidene proton peak from 20.00 ppm to 19.68 ppm (Scheme 4). The alkylidene proton shifts in ^{1}H-NMR, associated with monometallic and homobimetallic ruthenium complexes were listed on Table 1.

Activity Studies

The activity of synthesized ruthenium complexes were tested on ROMP reactions of oxygen containing norbornene derivatives Norbornene, 5-norbornene-2-methanol, 5-norbornene-2yl-acetate and 5-nor-bornene-2-carboxaldehyde were successfully polymerized by both mono and homobimetallic ruthenium complexes. A comparison of the ring opening metathesis polymerization results of oxygen containing monomers 5-norbornene-2-methanol, 5-norbornene-2yl-acetate and 5-norbornene-2-carboxalydehyde using various Ru-based catalyst systems is reported in Table 2. As stated on Table 2, no difference in catalytic activity was observed between two catalytic systems, complex 4 and 6, in different catalyst / olefin loadings such as 1/100 and 1/500. At relatively low catalyst/olefin ratio such as 1/1000, complex 2 was shown lower ROMP activity towards the selected monomers. 5-norbornene-2yl-acetate reaches 85% yield at high olefin loadings 1 / 1000 (catalyst/olefin), wherever 5-norbornene-2-carboxaldehyde yields 20% and 5-norbornene-2-methanol yields 70% using complex 6.

5-norbornene-2yl-acetate was polymerized in 100% yield within 4 hours at room temperature with a catalyst/olefin loading of 1/1000. Poly(5-norbornene-2yl-acetate) are soluble in common solvents, thus enabling the fully characterization of the polymer. The ^{1}H-NMR of poly(5-norbornene-2yl-acetate) was given in Figure 3.

Terminal olefinic hydrogen peaks can be seen at 4.95 ppm, whereas internal olefinic signals belonging to cis-protons appear at 5.42 ppm. The protons of cyclopentene ring appear at 1.40, 1.65, 2.20 and 2.40 ppm, respectively. The methyl protons of acetyl group gave rise to a single peak at 1.98 ppm. FT-IR spectrum of polymer can be seen at Figure 4. Cis out-of-plane bending bands of C=C double bond appears at 753.65 cm^{-1}. When compared to cis double bond peak, trans out of plane bending peaks of C=C bond have low intensity, denoting the high cis-double bond content in the polymer. The C=C stretching band at 1687.12 cm^{-1} indicates that the reaction was proceeded with a metathetic pathway. The sharp peak at 1736 cm^{-1} confirms the presence of C=O functional group. The peaks at 2924 cm^{-1} and 2846 cm^{-1} reveals the C-H stretching bands of cyclopentene.

Table 1. Benzilidenic proton NMR shifts in monometallic and homobimetallic complexes in different ligand enviroment

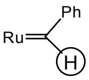
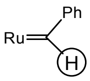
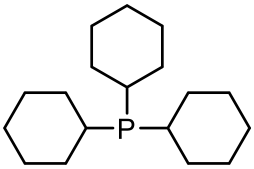
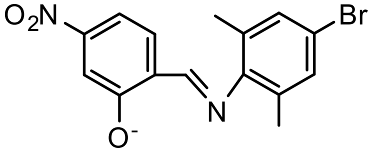
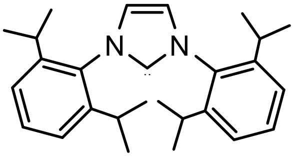
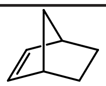
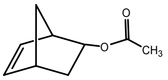
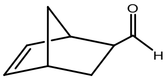
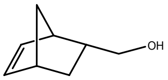
Ligand	Monometallic ^{1}H-NMR  	Homobimetallic ^{1}H-NMR 
	20.00 ppm	19.68 ppm
	19.60 ppm	19.50 ppm
	19.65 ppm	19.10 ppm

Table 2. ROMP reactions of norbornene derivatives catalyzed by Complexes 2, 4 and 6.

			Conversion, %		
Olefin	Olefin/catalyst	Time, min.	Complex 2	Complex 4	Complex 6
	100	5	80	100	100
	500	10	63	100	100
	1000	20	58	100	90
	100	10	65	100	100
	500	20	42	100	100
	1000	75	30	90	85
	100	60	50	100	100
	500	100	30	100	100
	1000	180	10	40	20
	100	20	55	100	100
	500	30	30	100	100
	1000	45	15	80	70

Poly(5-norbornene-2-carboxalydehyde) are not soluble in common solvents. The resulting polymer swells with time, indicating the cross-linking of polymer chains in the sample. Due to undesired cross-linking, characterization of the polymer were made by only FT-IR.

The characteristic C=C bond cis out of plane bending bands appeared at 795.66 cm^{-1}. No trans out of plane bending band was observed in the spectrum. C=C stretching peak appeared at 1673.53 cm^{-1}. The sharp peak at 1706 cm^{-1} confirms the presence of C=O functional group in polymer. C-H stretching bands gave signals at 2924 cm^{-1} and 2846 cm^{-1}.

5-norbornene-2-methanol which contains -OH functional group, was polymerized under the same conditions in high yields, resulted a gelly product. The polimeric structure are not dissolve in solvents such as THF, toluene, chlorobenzen and chloroform. Polymer was swelled when exposed to excess THF overnight, denoting the cross-linking in polymer. The trans-out of plane bending were appeared at 801.15 cm^{-1} whereas cis-out of plane bending band didn't observed, indicating the high trans double bond content. C=C stretching band also present and appears at 1624.15 cm^{-1}. The presence of –OH functional group was confirmed with peak appearing at 3650 cm^{-1}.

Complex 1 which cooperate a Schiff base ligand, exhibits high thermal stability, thus higher activity towards metathesis reactions observed at relatively higher temperature (80°C). ROMP reactions catalyzed by complex 1 proceeds at higher temperatures, whereas at room temperature, the reaction reveals poor metathesis activity. The comparative results concerning the ROMP of 5-norbornene-2yl-acetate, catalyzed by both complex 1 and 2 at 25°C and 80°C were given in Figure 5. The reaction catalyzed by complex 1 yielded 25% of the corresponding polymer at room temperature. The result denoted the need for heating up the reaction mixture to higher temperatures to obtain reasonable yields. At 80°C, reaction proceeded with 100 % yield. The homobimetallic analog, complex 2, catalyzed this reaction at 25°C with 71% yield and at 80°C with 90% yield. Thermal stability of the monometallic ruthenium alkylidene Schiff base complex can be altered by preparing their homobimetallic analogs, enabling the Schiff base complex to catalyze ROMP reactions at both room and high temperature in moderate yields.

Complex 4 and complex 6 showed high ROMP activity at 25°C to both of the monomers. Heating up the reaction didn't result in an increase in both conversion yield and decrease in time. Relatively, NHC containing homobimetallic complex 4 showed slightly better ROMP activity in high catalyst/olefin loadings (Figure 6). When compared to their monometallic analogs, complex 3 and complex 5, homobimetallic analogs revealed slightly high activity towards ROMP reactions. This difference in catalytic activity can be explained by ability of Ru-Cl-Ru bridge bond to change the electron density of the metal center. It is possible that chlorine bridge bond makes the ruthenium center more electron defficient, thus activating the metal center.

CONCLUSION

Most common metathesis catalysts have low tolerance towards aldehyde and acetate functional groups in norbornene derivatives such as 5-norbornene-2yl-acetate and 5-norbornene-2-carboxaldehyde. The experiments which were carried out with complex 1, 2 and 3 revealed that our catalytic systems exhibit high tolerance towards these functional groups and ROMP reactions proceed with high olefin loadings and high yields. The activity of monomers towards ROMP reaction follows this order; 5-norbornene-2yl-acetate>5-norbornene-2-methanol > 5-norbornene-2-car-boxalydehyde.

ACKNOWLEDGEMENTS

This work was supported by a grant provided by the Hacettepe University Research Fund (Grant No: 08A601002).

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