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Ring-Opening Metathesis Polymerization of Norbornene Catalyzed by a Ru(II)-Vinylidene Complex[†]

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Abstract

Highly selective ring opening metathesis polymerization (ROMP) of norbornene can be achieved using a new Ru(II)-vinylidene complex as catalyst precursor. The polymerization reaction proceeds in 1,2-dichloroethane at 80 °C in absence of co-catalysts with high turnover frequencies. The molecular weight and molecular weight distribution of the polymers obtained indicate that different species are active in the catalytic process.

Keywords: catalysis; polymerization; olefin metathesis; ruthenium complexes.

Ru-carbene and Ru-vinylidene complexes have been proven to be highly efficient catalysts for a variety of olefin transformations. These include examples of ring-opening metathesis polymerization (ROMP) [1-7], ring-closing metathesis (RCM) [8,9], polycyclization reactions [9,10] and synthesis of natural compounds with important biological activity [11,12]. In the case of olefin metathesis reactions, this class of compounds usually present lower activities when compared with early transition metal complexes. However, they can tolerate a large variety of functional groups without leading to deactivation of the catalyst. In addition to this, reactions can in some cases take place in polar solvents such as methanol or even water, leading to cleaner and cheaper processes [13-16]. In this paper we report the use of a well-defined Ru-vinylidene complex for selective polymerization of norbornene *via* a ring-opening process.

In a recent paper we reported the synthesis of a series of Ru(II) complexes containing the terdentate ligand 2,6-bis[(dimethylamino)methyl]pyridine (NN'N) [17]. Some of these

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[†] Dedicated to Dr. Jaap Boersma on occasion of his 60th birthday.

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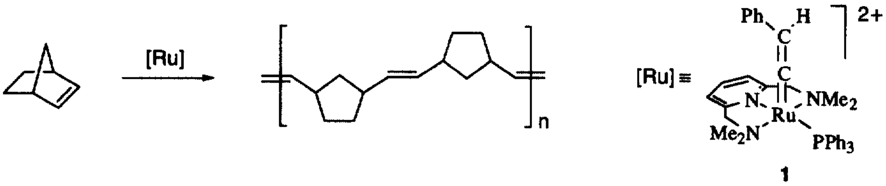
complexes were shown to be efficient catalysts for the (cyclo)alkylation reaction of aromatic amines with alcohols [18]. During the search for new catalytic applications for this type of complex, we synthesized in high yields the vinylidene derivative $[Ru(=C=CHPh)(NN'N)(PPh_3)][BF_4]_2$ (**1**, Scheme 1) [19].[1] Complex **1** was found to promote the ring-opening metathesis polymerization of norbornene (NBE) to afford polynorbornene (PNBE, Scheme 1). The polymerization reaction takes place under mild conditions in absence of co-catalysts. The IR, ^1H and $^{13}C\{^1H\}$ NMR data of the PNBE so obtained indicate that it contains 90-95 % *trans* C=C bonds, in accordance with similar previously reported examples [1-7]. The polymerization results are summarized in Table 1.



Scheme 1

Table 1

Entry	time (h)	solvent	T (°C)	yield (%)	catalyst:monomer ratio	TON[a]	TOF[b]	%	M_w[c] (× 10^3)	M_n[c] (× 10^3)	PDI[c]
1	12	DCM	25	0	1 : 856	–	–	–	–	–	–
2[d]	24	DCM	40	1.6	1 : 856	14	0.6	12.5	1262	1047	1.20
								69.8	96.9	43.7	2.21
								17.7	2.9	2.8	1.03
3[e]	1.25	DCE	80	8.5	1 : 5163	439	351	48.1	1136	845	1.34
								51.9	119	82.7	1.44
4[e]	1	DCE	80	100	1 : 795	795	795	44.9	1119	968	1.16
								55.1	143	114	1.26
5	20	MeOH	60	traces	1 : 1025	–	–	–	–	–	–

Polymerization of norbornene using **1** as catalyst precursor. [a] Turnover number: mol monomer converted × mol $catalyst^{-1}$. [b] Turnover frequency: mol monomer converted × mol $catalyst^{-1}$ × $hour^{-1}$. [c] Molecular weight (M_w), Molecular weight distribution (M_n) and polydispersity index ($PDI = M_w/M_n$) data are based on polystyrene standards. [d] Trimodal molecular weight distribution. [e] Bimodal molecular weight distribution.

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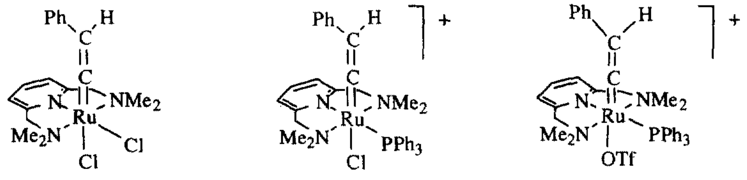
[1] Complex **1** was readily prepared by treatment of $[RuCl_2(NN'N)(PPh_3)]$ [17] with 2 equiv of $Ag[BF_4]$ in CH_2Cl_2 (DCM) in the presence of an excess of phenylacetylene (95% isolated yield). Selected ^1H NMR data (300.113 MHz, CD_2Cl_2) δ: 2.29 (s, 6H, NMe_2), 2.49 (s, 6H, NMe_2), 4.12 (d, *J*= 16.6 Hz, 2H, CH_2), 4.36 (d, *J*= 16.6 Hz, 2H, CH_2), NN'N ligand; 5.61 (d, *J*= 2.4 Hz, 1H, C=C*H*Ph) ppm. $^{31}P\{^1H\}$ NMR data (121.486 MHz, CD_2Cl_2) δ: 38.8 ppm. Selected $^{13}C\{^1H\}$ NMR data (75.453 MHz, CD_2Cl_2) δ: 53.2 (NMe_2), 55.6 (NMe_2), 74.3 (CH_2), 122.2 (*m*-C), 142.8 (*p*-C), 158.5 (*o*-C), NN'N ligand; 120.4 (C=*C*HPh), 358.7 (d, *J*= 12.9 Hz, *C*=CHPh) ppm.

The presence of a vacant coordination site in complex **1** may be an explanation for its high catalytic activity, since this may facilitate the coordination of the incoming olefin to the Ru center, initiating in this way the ROMP process. The best solvent for the polymerization reaction apeared to be 1,2-dichloroethane (DCE) at reflux temperature. Attempts to perform the reaction using alcohols or water as solvents failed, probably due to decomposition of the vinylidene precursor, which reacts readily with water to give complex mixtures from which no pure compound could be identified.[2]

The related vinylidene complexes *cis,mer*-$[Ru(=C=CHPh)Cl_2(NN'N)]$ (**2**), *mer*-$[Ru(=C=CHPh)Cl(NN'N)(PPh_3)][BF_4]$ (**3**) and *mer*-$[Ru(=C=CHPh)(OTf)(NN'N)(PPh_3)][OTf]$ (**4**; OTf = trifluoromethane sulfonate, Figure 1) [19], were also tested as catalyst precursors in this polymerization process. However, **2** appeared to be inactive, while the use of **3** or **4** led to lower turnover numbers. These results may be explained by the fact that **1** is a 16 e^- complex with a vacant coordination site, while complexes **2**-**4** are 18 e^- complexes with a saturated coordination sphere around the metal. The dicationic nature of **1** may be also responsible for its higher activity when compared with **2**-**4**.



2 **3** **4**

Figure 1

Complex **1** appeared to be highly selective for the polymerization of norbornene, being inactive when other cyclo-olefins such as norbornadiene, cyclopentene, cyclohexene or cyclooctene were used. The polymers obtained in the different runs present similar characteristics, with a polymodal molecular weight distribution, ranging from very high molecular weights to oligomers. These data suggest that the polymerization process is not living [20], and that diverse mechanisms and/or active species are operative in this reaction. Attempts to isolate or characterize the active species present in solution were unsuccesful. The very high molecular weights obtained for some of these polymers, which are significantly larger than those expected from the catalyst to monomer ratio, seem to indicate a very high propagation rate for some of the active species present, resulting in the formation of polymers with both high M_w and M_n.

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[2] A typical polymerization reaction (entry 3 in Table 1) proceeds as follows: 70 mg (0.084 mmol) of complex **1** and 6.5 g (69 mmol) of norbornene were dissolved in $ClCH_2CH_2Cl$ (DCE, 50 mL) and the mixture stirred at reflux temperature for one hour. The brownish gel formed was poured into vigorously stirred methanol to give a white precipitate and a brown solution. The solid was dried under reduced pressure to afford 6.5 g of polynorbornene (100 %). The polymers were analyzed by GPC using THF as a solvent and polystyrene standards.

In conclusion, we present here an example of highly selective ROMP of norbornene catalyzed by a Ru(II) vinylidene complex. The polymerization reaction is not living and different mechanisms are operative in the process, leading to the formation of polymers which range from very high to low molecular weights. Polar solvents such as alcohols or water appear to inhibit the polymerization reaction.

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