Benefits of donor solvents as additive on ROMP of norbornene catalyzed by amine Ru complexes

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Abstract

With the aim of understanding the influence of donor solvents on the reactivity of the amine complexes [RuCl$_2$(PPh$_3$)$_2$(piperidine)] (**1**) and [RuCl$_2$(PPh$_3$)$_2$(imidazole)$_2$] (**2**) in the presence of ethyldiazoacetate, and on the properties of the resulting polymer, a ring opening metathesis polymerization of norbornene was carried out in the presence of small amounts of common solvents such as additives (isopropanol, THF, *N*,*N*-dimethylformamide, 2,6-lutidine, isopropanethiol, acetonitrile, dimethyl sulfoxide, NEt$_3$, NH$_2$Me and pyridine). From observations, typical coordinating solvents like DMSO, NEt$_3$, NH$_2$Me and pyridine, hardly affected the yields when either complex was employed. With other additives, the major advantage was the decrease in the polydispersity indices. On using complex **1** with 2,6-lutidine, observed values of M_w/M_n were as low as 1.3, while the yield decreased from 99% to about 20–30% at RT for ~1 min in pure solution. In the case of complex **2**, which is almost inactive to ROMP (19% at 50 °C for 5 min with $M_w/M_n = 6.30$), the yield was three-fold (60% at 50 °C for 5 min with $M_w/M_n = 1.95$) compared to that of without THF. Further, the M_w/M_n was observed to decrease to 1.34 with 200 eq. of THF.
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1. Introduction

Besides the success of those well-defined phosphine–Ru based carbene complexes [1–4], such as the second-generation Grubbs-type catalyst [RuCl$_2$(NHC)(PCy$_3$)(=CHR)], where NHC is an N-heterocyclic carbene, amines have been investigated for use as ancillary ligands in catalysts for reactions of ROMP (ring opening metathesis polymerization). Studies of the complex [RuCl$_2$(PPh$_3$)$_2$(pip)] (**1**), pip = piperidine, a versatile precursor in ROMP of norbornene (99% yield at room temperature for less than 1 min with $M_n \sim 10^6$ and $M_w/M_n = 1.05$) and norbornadiene (48% yield at 50 °C for 5 min with $M_n \sim 10^3$ and $M_w/M_n = 3.40$) using [monomer]/[Ru] up to 5000 and 5 μL of ethyldiazoacetate (EDA) in CHCl$_3$, were recently published [5]. Further, the influence of 4-X-pyridines (X = H, C(O)NH$_2$, CH$_3$ or NH$_2$) on the metal center during ROMP reactions continues

to be investigated [6], where six-coordinated complexes such as [RuCl$_2$(PPh$_3$)$_2$(amine)$_2$] have been isolated. The results show that the yields are greater than 70% in CHCl$_3$ when [norbornene]/[Ru] = 3000 and 5 μL of EDA ($M_n \sim 10^4$–10^5 and $M_w/M_n \sim 1.2$–2.0) at 50 °C for 5 min. Considering the complex with isonicotinamide (X = C(O)NH$_2$) under similar conditions but for [norbornene]/[Ru] = 5000, the yield reaches 94% of isolated polymer with $M_w/M_n = 1.20$.

From NMR experiments, as in the case of the bis-amine six-coordinated complexes, it has been observed that one amine molecule remains coordinated to the metal center while other ligands dissociate when the substrate is present, permitting us to investigate the behavior of the amines as ancillary ligands [5,6]. However, much emphasis has to be placed on how to improve rapid dissociation of the ligands from the Ru(II) coordination sphere. It has also been observed that a PPh$_3$ molecule undergoes dissociating in these complexes [5,6].

In other research works, PCy$_3$ was replaced by substituted-pyridines resulting in a fast-initiation version of the second-

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generation Grubbs catalysts [7]. In these cases, the amines were eliminated by the N-heterocyclic carbene, which presents a large steric hindrance and an elevated σ-donor character [4]. Solvents were also used as additives to observe the influence of functional groups present in the reaction medium on the reactivity of Grubbs-type catalysts [3,8]. The present study was stimulated by the above-mentioned results obtained by Grubbs and Slugovc. Based on these observations amine complexes can behave as good starting material and some molecules working as additive can be used to control the rates of polymerization.

Thus, in the present paper, with the aim of understanding the influence of donor solvents on the reactivity of the amine complexes **1** and [RuCl$_2$(PPh$_3$)$_2$(imN)$_2$] (**2**), imN = imidazole, and on the properties of the resulting polymer, polymerization reactions of norbornene in the presence of small amounts of common solvents such as additives were carried out. Additives employed in the reaction include isopropanol (^{i}PrOH), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), 2,6-dimethylpyridine (2,6-lutidine), isopropanethiol (^{i}PrSH), acetonitrile (MeCN), dimethyl sulfoxide (DMSO), triethylamine (NEt$_3$), methylamine (NH$_2$Me) and pyridine (py). The choice of the complexes **1** and **2** was due to their large difference in behavior in the ROMP of norbornene. Whereas complex **1** is very active, complex **2** attains a yield less than 20% at 50 °C for 5 min. Thus, by observing the different ancillary ligands, the benefits of the additive can be compared. Besides, a major concern was the fact that these additives can be present in the reaction medium as impurity, thus affecting the reactivity of the catalyst initiators.

2. Experimental

2.1. General remarks

Unless otherwise cited, all manipulations were carried out under argon and room temperature (RT) of 24 ± 1 °C. All solvents used were of analytical grade and were distilled from the appropriate drying agents immediately prior to use. RuCl$_3$·xH$_2$O from Stream, norbornene (NBE) from Across, piperidine (pip), ethyldiazoacetate (EDA; N$_2$CHC(O)OEt), imidazole (imN) and triphenylphosphine from Aldrich were used as archived.

2.2. Synthesis of the complexes

The ruthenium complexes **1** [5] and **2** [9] were prepared following methods cited in literature by adding 1.23 mmol of amine to a solution of 0.47 mmol of [RuCl$_2$(PPh$_3$)$_3$] [10] in acetone (50 mL) and the mixture stirred for 1 h under argon at RT. The volume was then reduced (~5 mL) under vacuum, obtaining a solid that was filtered, washed with ethyl ether and dried in a vacuum. The analytical data for [RuCl$_2$(PPh$_3$)$_2$(pip)] is 63.08% C, 5.16% H and 1.79% N;

found: 63.01% C, 5.05% H and 1.69% N (65% yield). The analytical data for [RuCl$_2$(PPh$_3$)$_2$(imN)$_2$] is 62.70% C, 4.40% H and 6.40% N; found: 62.40% C, 4.10% H and 6.10% N (65% yield). These complexes were EPR silent.

2.3. Instrumentation

Elemental analyses were carried out using an EA 1110 CHNS-O Carlo Erba Instrument. EPR was carried out at RT using a Bruker ESP 300C apparatus (X-band) equipped with a TE102 cavity and HP 52152A frequency counter. ^{1}H NMR spectra were obtained in a CDCl$_3$ solution with TMS at 25.0 ± 0.1 °C using a Bruker AC-200 spectrometer equipped with a probe operating at 200.13 MHz. M_n (number-average molecular weight), M_w (weight-average molecular weight) and M_w/M_n (polydispersity index) were obtained by gel permeation chromatography (GPC) analyses using a Shimadzu 77251 spectrometer system equipped with a PL gel column (5 μm MIXED-C: 30 cm, Ø = 7.5 mm). The retention time was calibrated with respect to standard monodispersed polystyrene using HPLC-grade CHCl$_3$ as eluent.

2.4. Polymerization procedure

To a solution of either complex ([Ru] = 1 μmol) in CHCl$_3$ (2 mL) and under an atmosphere of argon, 1, 10 or 200 eq. of additive was added, and the solution left for 5 min at RT in the case of complex **1**, and at 50 °C in the case of complex **2**. A 5000 eq. of norbornene and 5 μL of EDA were then added. In the case of complex **1**, the reaction was quenched with MeOH, while for complex **2**, the reaction was kept for 5 min at 50 °C and then stopped by adding 5 mL of methanol. The polymers were then washed with methanol and dried in a vacuum. Obtained yields are given for the isolated polymers.

3. Results and discussion

Table 1 summarizes the results from the polymerization reaction in the presence of different additives used with either complex **1** or **2**.

Fig. 1 shows the data with a view to better compare the influence of the additives on the reactivity of the complexes.

Considering the complex **1**, the results of yield were lower in presence of the additives, a fact that is more pronounced as the amount of additive increased. Whereas less influence is observed with ^{i}PrOH, THF and DMF on one extreme, the amines NEt$_3$, NH$_2$Me and pyridine on the other extreme drastically poison the reaction. 2,6-lutidine, ^{i}PrSH, MeCN and DMSO were shown to reduce the activity to 60–20%. The only fact capable of justifying the behavior of these additives is their coordination to the metal center, responsible for poising the start of the polymerization reaction. The synthesis of the six-coordinated complex **2** from [RuCl$_2$(PPh$_3$)$_3$] in itself suggests that the five-coordinated complex **1** is sensitive

Table 1
Influence of the additives in the ROMP of norbornene catalyzed by different complexes in $CHCl_3$

Additive	ε	pK_a	$[RuCl_2(PPh_3)_2(pip)]$[a]				$[RuCl_2(PPh_3)_2(imN)_2]$[b]			
			eq.	Yield (%)	M_w	M_w/M_n	eq.	Yield (%)	M_w	M_w/M_n
–			–	99	228,000	1.90	–	19	33,900	6.30
^iPrOH	20.2	17.1	1	90	198,300	2.51	1	27	30,100	4.30
			10	78	203,600	2.42	10	21	43,600	5.15
			200	70	245,700	2.05	200	18	50,100	5.22
THF	7.6	−2.1	1	85	276,500	2.39	1	50	30,700	1.98
			10	69	274,700	2.72	10	60	40,200	1.95
			200	65	216,300	2.46	200	65	53,600	1.34
DMF	38.3	−0.3	1	83	96,900	1.53	1	20	38,500	2.79
			10	78	337,700	3.03	10	17	37,100	2.58
			200	45	438,000	2.09	200	12	35,600	2.37
2,6-Lutidine	7.3	6.6	1	62	254,700	1.54	1	38	43,300	4.33
			10	45	222,600	1.55	10	17	38,600	4.93
			200	30	210,500	1.34	200	15	20,200	4.30
^iPrSH			1	45	158,500	1.95	1	28	27,500	3.08
			10	30	137,400	2.19	10	17	28,600	2.79
			200	23	112,300	2.25	200	8	23,700	2.75
MeCN	36.7	−4.3	1	43	120,600	2.19	1	32	80,300	1.97
			10	32	127,700	1.90	10	24	71,200	2.06
			200	27	115,400	1.85	200	20	30,300	2.03
DMSO	47.3		1	40	120,600	1.37	1	13	27,600	4.00
			10	35	152,300	2.41	10	5	19,500	5.11
			200	20	185,300	2.45	200	3	14,800	5.08
NEt_3	2.4	10.8	1	10	198,900	2.26	1	7	58,200	3.78
			10	4	122,700	1.48	10	3	35,800	3.56
NH_2Me	16.7	10.7	1	NP			1	7	45,300	3.52
							10	2	38,200	3.27
Pyridine	12.3	5.2	1	3	136,600	1.71	1	NP		
			10	NP						

$[Ru] = 1\,\mu mol$, $[NBE]/[Ru] = 5000$; $5\,\mu L$ of EDA to start the reaction. ε: Dielectric constant and NP: no polymerize.

[a] Room temperature (condition of reactions).

[b] $50\,°C$ (condition of reactions).

to the coordination of a sixth ligand. This sixth coordination explains why the use of NEt_3, NH_2Me and pyridine and also MeCN and DMSO as additives results in lower yields. However, it does not explain the behavior of 2,6-lutidine that shows a large steric hindrance and attempts to isolate any complex from $[RuCl_2(PPh_3)_3]$ have been unsuccessful [6]. Perhaps a combination of the electronic and steric effects could explain the results since THF and DMF are also known as coordinating compounds. In addition, the behavior of ^iPrOH or ^iPrSH is not fully understood.

In general, the values of M_w and M_w/M_n were roughly unaffected in the presence of additives when complex 1 was used (Fig. 1). It is very interesting to observe that observed values of M_w/M_n when 2,6-lutidine is used as additive are as low as 1.3. A similar decrease in M_w/M_n was observed with 2,6-lutidine in presence of $[RuCl_2(NHC)(PCy_3)(=CHR)]$ [3,8]. The influence of these molecules on polydispersity indices and the molecular weights of the polymers could be explained by the enhancement of the initiation efficiency and an attenuation of the rate of polymerization due to competi-

tion between the additive and either the leaving PPh_3 ligand or the monomer for the Ru(II) center during initiation and propagation as stated by Grubbs and co-workers [11] and Slugovc [3,8].

With respect to the six-coordinated complex 2, which is almost inactive to ROMP, only the typical coordinating compounds DMSO, NEt_3, NH_2Me and pyridine hardly affected the yields. Otherwise, some gain in yield occurred in the presence of 1 eq. of additive. The molecular weights were roughly unaffected. The great advantage is the decrease in polydispersity indices; in some cases the values are close to 2. In the presence of THF, the yield was three-fold, unaffecting the M_w while the M_w/M_n ratio decreased to less than 2. With 200 eq. of THF, the M_w/M_n was 1.34. It is interesting to observe that the values of yields increased with increase in the amount of THF. Nonetheless, the reaction did not occur in pure THF when either complex 2 or 1 was employed.

In contrast to the five-coordinated complex 1 where the additive probably blocks the formation of the carbene com-
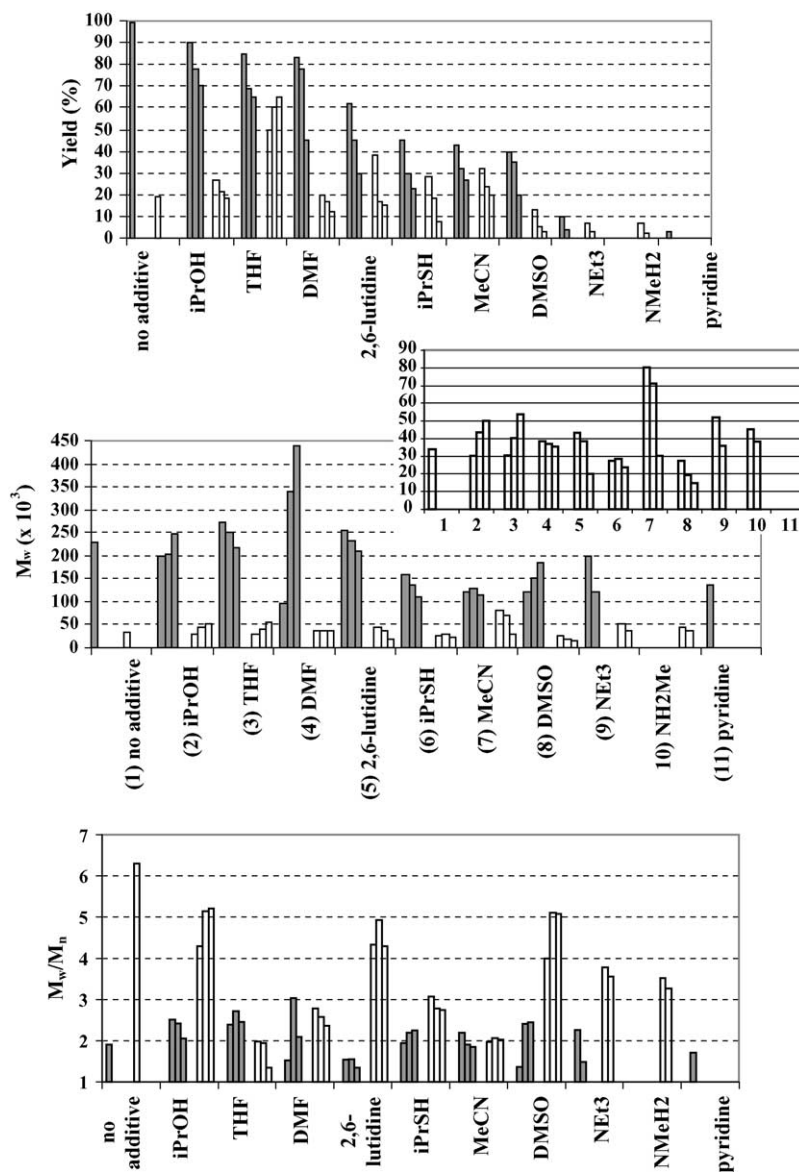
Fig. 1. Yields, weight-average molecular weight and polydispersity indexes of the polynorbornene obtained in the presence of increased amounts of additives (1, 10 or 200 eq.). Gray bars for complex **1** and empty bars for complex **2**. The insert shows the M_w values for complex **2** in a large scale.

plex and/or the coordination of the olefin thus regulating the initiation reaction, for complex **2**, the nature of the mechanism is dissociative up to the generation of the first active monomeric carbene specie, translating in the occurrence of the first turnover. Thus, this could explain why the additives do not affect the reaction in most of the cases studied using the complex **2**. However, as could be expected the case of THF, a molecule that could better stabilize the intermediate complexes acting as a poor coordinating solvent during the substitution mechanism, would permit the ROMP reaction to proceed. This could also be the case with ^{i}PrOH, 2,6-lutidine and ^{i}PrSH which tend to promote an increase in the yield, probably due a protection of the intermediates by their steric hindrances, but their excess impairs the yield thus hardly affecting the M_w/M_n ratio probably due their σ-

donor character. A direct relationship between large values of M_w/M_n and a high donor capacity of the molecules can be observed from the results obtained for DMSO, NEt$_3$ and NH$_2$Me. These results are similar to those of the complex itself (Fig. 1).

An alternative explanation could be associated to the dissolution of the leaving molecules, but this is uncertain since the amounts of additive are very low (1–200 eq. in relation to the complex). This could be the case with complex **2** in the presence of THF, which was the only case where the yields where unaffected by any increase in the amount of additive and the polymer chain are much more monodisperse.

Another interesting additive when using complex **2** is MeCN, which is known to be a poor π-acceptor ligand. A high yield and high M_w values compared to those obtained

in the absence of additive are observed, and the values of M_w/M_n being around 2.

The influence of the additive is not correlated to the values of pK_a. The values of dielectric constant must not affect the results since the volume added to the solution is very low (0.04–20 μL).

Complex **1** is very reactive with an instantaneous quantitative reaction at room temperature for a molar ratio [NBE]/[Ru] = 5000, but the molecular weight distribution is significantly affected if the monomer is either added to the solution in a single batch resulting in $M_w/M_n = 1.90$, or successively added in several batches resulting in a monodisperse polymer ($M_w/M_n = 1.05$) [5]. Thus, the experiments were programmed to observe by how much the presence of the additive affected the reactivity of the complexes and the reaction product. First, the complexes were kept for 5 min in contact with the additives and the polymerization reaction later carried out as usual. In the case of complex **1**, the polymer was isolated just after the addition of EDA and monomer while for complex **2**, the polymer was isolated 5 min later at 50 °C after the addition of monomer and EDA. It was thus possible to verify the amount of monomer consumed in terms of turnover number (TON) during a short period of time by observing values of turnover frequency (TOF) without extending the time. In similar studies with the second-generation Grubbs catalysts, the polymer was isolated after 20 h in most cases [3,8], resulting in high yields and high TON, but the TOF values were very low ($\ll 1$ min^{-1}). Based on the above comparison, it can be concluded that the system in the present work was much more active even though affected by an additive. As earlier mentioned, it is assumed that the additive coordinates to the Ru(II) center. If this occurs, the high TOFs obtained are good results, even though the reaction is very slow, which would explain the decrease in the yields. What seems evident in the present case is a decrease in the yield during a short period of time. It is believed that the TON would increase with time thus decreasing the TOF, since the propagation reaction would increase the polymer chains, and the additive molecules losing the interaction with the metal center.

In the case of the experiments with complex **1**, values of yields were reproduced in the presence of 10 eq. of THF (68%), 2,6-lutidine (47%) or NH$_2$Me (no polymer formed) when NBE and EDA were immediately added to the solution just after the addition of the additive. This shows the sensibility of the five-coordinated initiator **1** in the presence of other molecules. On the other hand, it is important to highlight the importance of the temperature of 50 °C in the case of six-coordinated complex **2**. When this complex was left in presence of THF for 5 min at 50 °C and the solution cooled down to room temperature, no polymer was formed upon the addition of NBE and EDA. However, reducing the period of time in the presence of an additive for 2 min at 50 °C followed by the addition of NBE and then leaving the solution for another 3 min at 50 °C, the solution became very viscose with 57% of polymer isolated upon addition of EDA, a result similar to that obtained before. The results were also repro-
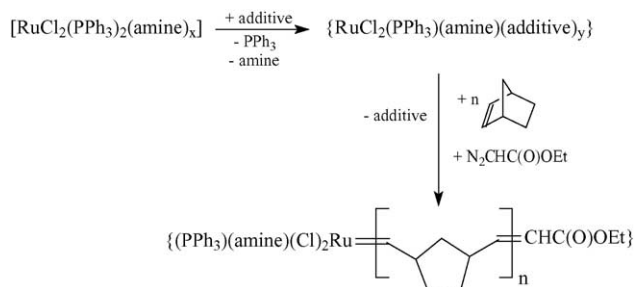
Scheme 1.

duced using 2,6-lutidine (20%). In conclusion thereof, the most probable effect of temperature is to discoordinate the imidazole ligand, to which the Ru(II) center has great affinity.

The presence of addictives did not affect the *trans*-form content in the obtained polymers (58–62%), as observed from the ^{1}H NMR spectra.

4. Conclusions

Based on the results obtained, it can be concluded that small amounts of the donor solvents used such as additives can hardly affect the reactivity of the complexes **1** and **2**. It is suggested that the donor atom of these molecules coordinate to the metal center, hence poisoning its reactivity. However, some additives such as THF, MeCN, or 2,6-lutidine showed benefits in the yield, M_w and M_w/M_n values, since they seem to stabilize the intermediates with low coordination number because they are poor σ/π-coordinating molecules or present a large steric hindrance, propitiating the reaction with EDA and monomer. This fact probably increases the number of Ru species capable of initiating the ROMP reaction at the same time, thus favoring the M_w/M_n values. This means, that such poor coordinating molecules rearrange the initiation of the polymerization process. A proposed sequence of reactions is illustrated in Scheme 1.

On the whole, the results of the present study suggest that additives, when used in polymerization reactions, can modify the values of M_w and M_w/M_n. Notwithstanding, this assumption deserves a closer attention since these solvents can be present as impurity, changing the results of the reactions.

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