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Ring-opening metathesis polymerization of norbornene catalyzed by a [Hydridotris(pyrazolyl)borato]vinylideneruthenium complex

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Abstract

A vinylideneruthenium complex bearing a hydridotris(pyrazoyl)borate ligand, TpRuCl(=C=CHPh)(PPh_3) serves as a catalyst precursor for the ring-opening metathesis polymerization of norbornene. The catalytic activity is efficiently enhanced by adding Lewis acid such as $BF_3 \cdot Et_2O$ to the catalytic system. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hydridotris(pyrazolyl)borate; Vinylideneruthenium; Ring-opening metathesis polymerization (ROMP); Norbornene

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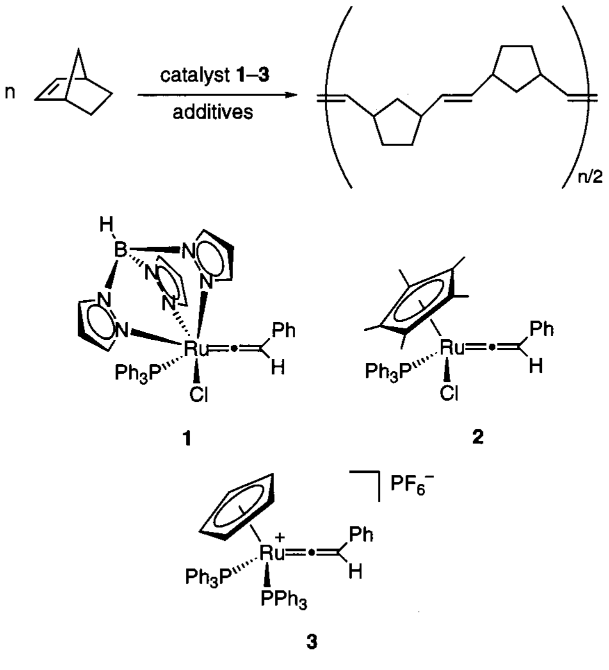
1. Introduction

Transition-metal complexes coordinated with hydridotris(pyrazolyl)borate (Tp) and its derivatives have attracted significant recent interest in organometallic chemistry [1]. The Tp ligand bears a strong resemblance to a cyclopentadienyl ligand (Cp) in terms of the anionic six-electron donation and the facial occupation of three coordination sites. However, Tp complexes frequently exhibit unique chemical properties which are not observed for Cp-coordinated complexes. For example, the Tp complexes tend to possess higher stability than the Cp analogs. This is mainly due to a difference between the cone angles of Tp (199°) and Cp (100°) ligands [2]. Furthermore, the Tp ligand is a better electron-donor than Cp ligand [3]. In these respects we have been interested in the reactivity of Tp-coordinated organometallic complexes, particularly in catalytic systems [4,5].

We have recently reported that vinylideneruthenium complexes of the type $RuCl_2(=C=CHR')(PR_3)_2$ serve as efficient catalyst precursors for the ring-opening metathesis polymerization (ROMP) of norbornene and its derivatives [6,7]. As a continuation of this work, we



Scheme 1.

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Table 1
Polymerization of norbornene catalyzed by vinylideneruthenium(II) complexes **1**–**3** [a]

Entry	Catalyst	Additive (equiv.)[b]	Temp. (°C)	Time (h)	Yield (%)	$M_n/10^4$	M_w/M_n
1	**1**	None	80	24	76	3.0	5.01
2	**1**	None	80	72	99	5.9	5.00
3	**2**	None	80	24	19	—[c]	—[c]
4	**3**	None	80	24	0	—	—
5	**1**	$BF_3 \cdot Et_2O$ (3)	40	72	97	—[d]	—[d]
6	**1**	$Al(OPr^i)_3$ (3)	40	24	9	8.3	3.13
7	**1**	CuCl (3)	40	24	8	12.6	5.02
8	**1**	AgOTf (1)	80	24	Trace	—	—
9	**2**	$BF_3 \cdot Et_2O$ (3)	40	24	32	—[c]	—[c]
10	**3**	$BF_3 \cdot Et_2O$ (3)	40	24	0	—	—
11	**1**	$PdCl_2(NCMe)_2$ (0.5)	r.t.	24	90	0.1	1.78
12	**2**	$PdCl_2(NCMe)_2$ (0.5)	r.t.	24	2	—	—

[a] Initial concentration: $[\text{catalyst}]_0 = 10$ mM, $[\text{norbornene}]_0 = 1.0$ M. Solvent: $ClCH_2CH_2Cl$ (entries 1–4, 8), CH_2Cl_2 (entries 5–7, 9–12). Molecular weights were determined by GPC based on polystyrene standards [8].

[b] Based on catalyst.

[c] Not determined.

[d] GPC analysis was infeasible due to insolubility of the polymer.

examined in this study the catalytic activities of the other types of vinylideneruthenium complexes bearing Tp or Cp ligand: TpRuCl(=C=CHPh)(PPh_3) (**1**), Cp*RuCl(=C=CHPh)(PPh_3) (**2**; Cp* = η^5-C_5Me_5), and [CpRu(=C=CHPh)$(PPh_3)_2$][PF_6] (**3**) (Scheme 1). The Tp complex **1** was found to exhibit much higher reactivity than the Cp analogs **2** and **3**, especially in the presence of Lewis acid.

2. Results and discussion

The results of ROMP of norbornene catalyzed by **1**–**3** are summarized in Table 1. The reaction was first examined in 1,2-dichloroethane at 80°C using 1 mol% of TpRuCl(=C=CHPh)(PPh_3) (**1**) (10 mM) relative to the amount of the monomer (1.0 M). The initially reddish brown solution gradually became viscous as the reaction proceeded. After 24 h, the reaction mixture was poured into vigorously stirred MeOH containing 0.1% of 2,6-di-*tert*-butyl-4-methylphenol to give a white precipitate of poly(norbornene), which was subsequently purified by column chromatography (SiO_2, CH_2Cl_2). These procedures provided 76% yield of polymer (entry 1). The yield was improved to 99% by elongating the reaction time to 72 h (entry 2). The molecular weight (M_n) of the polymer isolated in entry 1 was 3.0×10^4 as confirmed by GPC analysis [8], the value being significantly larger than that expected from the monomer to catalyst ratio. The molecular weight distribution was monomodal, while the polydispersity ($M_w/M_n = 5.01$) was rather high. These GPC data suggest the following features of polymerization. (1) The chain growth proceeds at one kind of reaction center. (2) The efficiency of catalyst precursor is low. (3) Chain transfer reactions including back-biting take place besides the chain propagation reaction.

$^{13}C\{^1H\}$-NMR data of the polymer were identical to those previously reported for poly(norbornene) prepared by a ring-opening metathesis process [9]. Two signals assignable to vinylic carbons of the main chain were observed at δ 133.9 (*cis*) and 133.0 (*trans*) and relative peak integration of these signals indicated *trans* content of the polymer in ca. 90% [9]. This stereoregularity was also supported by the IR spectrum [10], in which the absorption of *trans*-CH=CH out-of-plane bending was much stronger than the *cis*-CH=CH in-plane bending absorption. The ^1H-NMR spectrum exhibited two doublets at δ 5.34 and 5.20, which are corresponding to vinylic protons of the main chain in *trans* and *cis* geometries, respectively [11].

The catalytic activity of Cp* complex **2** was significantly lower than **1**, and the ROMP of norbornene with **2**, which was performed under the same reaction conditions as entry 1, afforded only 19% yield of polymer (entry 3). Cationic Cp complex **3** exhibited no catalytic activity (entry 4). $^{31}P\{^1H\}$-NMR investigations on the catalytic systems provided a part of the reasons for the difference in catalytic activity. In the reaction solution with Tp complex **1**, most of the complex was observed unchanged during the reaction course. This observation is consistent with the low efficiency of catalyst precursor suggested from the GPC data (*vide supra*). On the other hand, the ^{31}P signals of **2** and **3** were gradually reduced under the reaction conditions and disappeared within 24 h. The higher stability of **1** than **2** and **3**, which may be provided by effective steric congestion by the Tp ligand, would serve to maintain the catalysis for long period even under the heated condition.

Since **1** is a coordinatively saturated 18-electron complex, dissociation of one of the ligands is needed for the interaction between ruthenium center and monomer. In order to facilitate the dissociation of the ligand, a variety of Lewis acid were added to the catalytic systems (Table 1, entries 5–8) [12]. Consequently, the addition of $BF_3 \cdot Et_2O$ to the system was found to improve the catalytic activity of **1** to a great extent (entry 5). In this case, the polymerization proceeded even at 40°C and poly(norbornene) was isolated in almost quantitative yield. Among the other Lewis acid tested, $Al(OPr^i)_3$ and CuCl slightly improved the catalytic activity and the polymerization took place at 40°C (entries 6 and 7). In contrast, the addition of AgOTf showed almost no effect, though the precipitation of AgCl was observed in the system (entry 8). Since the catalytic reaction was effectively retarded by addition of free PPh_3 to the system, it is convincing that the catalytic process involves dissociation of PPh_3, which is facilitated by addition of $BF_3 \cdot Et_2O$ to the system. A similar enhancement of the catalytic activity was observed for Cp* complex **2** (entry 9), while Cp complex **3** was still inactive even in the presence of $BF_3 \cdot Et_2O$ (entry 10).

It has been noted that the polymerization of norbornene proceeds at room temperature when $PdCl_2(MeCN)_2$ is added to the catalytic system using **1** (entry 11). On the other hand, the addition of $PdCl_2(MeCN)_2$ did not enhance the polymerization with **2** (entry 12). GPC analysis revealed that the product in entry 11 was an oligomer composed of approximately ten norbornene units. However, the ^1H- and $^{13}C\{^1H\}$-NMR spectra exhibited only small signals corresponding to vinylic protons and carbons. Therefore, the polymerization was concluded to proceed mainly via a conventional insertion process, not via a ring-opening metathesis process. Since it is known that cationic palladium complexes serve as good catalyst precursors for the insertion polymerization of norbornene [13], the polymerization most probably takes place at a palladium center. Although it is possible that the catalytically active species is formed only from $PdCl_2(MeCN)_2$ without participation of **1**, the following NMR observation suggested the presence of a bimetallic species. Thus the reaction of **1** with 0.5 equivalent of $PdCl_2(MeCN)_2$ in CH_2Cl_2 instantly took place at room temperature. In the $^{31}P\{^1H\}$-NMR spectrum, the signal of **1** (δ 37.2) disappeared and a new singlet appeared at δ 48.7, the chemical shift differed from that of $PdCl_2(PPh_3)_2$ (δ 23.9). Several attempts to isolate this unknown species have been unsuccessful.

The ring-opening polymerization of norbornene could be also performed without isolation of **1**. Thus heating a mixture of norbornene (1.0 M), $TpRuCl(PPh_3)_2$ (1 mol%), PhC≡CH (10 mol%), and $BF_3 \cdot Et_2O$ (6.5 mol%) in dichloromethane at 40°C for 24 h gave 28% yield of poly(norbornene). Similarly, the polymerization using (*p*-acetylphenyl)acetylene in place of phenylacetylene under otherwise the same reaction conditions provided poly(norbornene) in 29% yield. IR spectrum of the resulting polymer showed a sharp absorption at 1641 cm^{-1}, which is assignable to n(CO) band of acetyl group. Hence the presence of *p*-acetylphenyl group at the terminus of polymer chain was evidenced.

In conclusion, we have found the catalytic activity of $TpRuCl(=C=CHPh)(PPh_3)$ (**1**) toward ROMP of norbornene. The polymerization is effectively accelerated by addition of $BF_3 \cdot Et_2O$. The catalytic activity of **1** is much higher than the cyclopentadienyl analogs **2** and **3**.

3. Experimental

3.1. General procedures

All reactions and manipulations were performed under a nitrogen atmosphere by using conventional Schlenk-tube techniques. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). 1,2-Dichloroethane and dichloromethane were dried over CaH_2, distilled, and stored over activated molecular sieves (MS-4A) under a nitrogen atmosphere. $CDCl_3$ was dried over activated MS-4A. Norbornene was distilled from sodium prior to use. $TpRuCl(=C=CHPh)(PPh_3)$ [5]a, $Cp^*RuCl(=C=CHPh)(PPh_3)$ [14], $[CpRu(=C=CHPh)(PPh_3)_2][PF_6]$ [15], $TpRuCl(PPh_3)_2$ [16], and (*p*-acetylphenyl)acetylene [17] were prepared by published methods. All other reagents and solvents were used as received from commercial sources.

^1H- and $^{13}C\{^1H\}$-NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.11 MHz (^1H), 75.47 MHz (^{13}C), and 121.49 MHz (^{31}P). The chemical shifts are reported in δ (ppm), referred to ^1H (of residual protons) and ^{13}C signals of the deuterated solvents (^{13}C). Infrared spectra were recorded at room temperature on a JASCO FT/IR-410 instrument. The number- and weight-average molecular weights (M_n and M_w) and polydispersity (M_w/M_n) of polymers were determined by gel permeation chromatography (THF, 38°C) using polystyrene standards. The GPC instrument used is a Tosoh 8000 system equipped with TSK gel columns.

3.2. ROMP of norbornene

3.2.1. Without additives

A typical procedure (Table 1, entry 1) is as follows. To a solution of $TpRuCl(=C=CHPh)(PPh_3)$ (**1**) (13.6 mg, 19.0 mmol) in $ClCH_2CH_2Cl$ (1.9 ml) was added norbornene (175 mg, 1.86 mmol) at room temperature.

The reddish brown solution was stirred at 80°C for 24 h, during the time the mixture gradually set to gel. The resulting viscous mixture was poured into a vigorously stirred MeOH (80 ml) containing 0.1% of 2,6-di-*t*-butyl-4-methylphenol (BHT) to give white precipitate, which was collected by filtration. The solid was suspended in CH_2Cl_2 (10 ml, containing 0.1% BHT) and ethyl vinyl ether (0.2 ml), and stirred at room temperature until the system became homogeneous. The resulting, slightly colored solution was passed through a silica gel column (5 × 40 mm) by using CH_2Cl_2 containing 0.1% BHT as eluent. The eluate was poured into a vigorously stirred MeOH (100 ml, containing 0.1% BHT) to give a white solid of poly(norbornene), which was collected by filtration and dried under vacuum (133 mg, 76%). IR (KBr disk): 2944, 2864, 1445, 1034, 966, 746 cm^{-1}. ^1H-NMR ($CDCl_3$, 21°C): δ 5.35 (d, $J=2.1$ Hz), 5.33 (d, $J=2.1$ Hz), 5.21 (d, $J=1.7$ Hz), 5.19 (d, $J=1.7$ Hz), 2.45–2.32 (m), 1.91–1.70 (m), 1.44–1.24 (m), 1.12–0.97 (m). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 21°C): δ 133.9, 133.0, 43.4, 43.1, 42.1, 41.4, 38.4, 32.3, 32.2.

3.2.2. With additives

A typical procedure (Table 1, entry 5) is as follows. To a solution of **1** (23.9 mg, 33.5 μmol) in CH_2Cl_2 (3.4 ml) were added norbornene (315 mg, 3.35 mmol) and $BF_3 \cdot Et_2O$ (12 μl, 0.098 mmol) at room temperature with stirring. The color of solution rapidly changed from reddish brown to orange. The solution was stirred at 40°C for 72 h, and then subjected to the workup-procedure described above. Poly(norbornene) was isolated as a white solid in 97% yield (305 mg).

Using $PdCl_2(NCMe)_2$ as the additive (Table 1, entry 11), poly(norbornene) formed by the insertion process was obtained. ^1H-NMR ($CDCl_3$, 21°C): δ 2.50–0.90 (broad multiplet) [13]d.

3.2.3. With in situ generated catalyst precursors

To a solution of $TpRuCl(PPh_3)_2$ (50 mg, 57 μmol) in CH_2Cl_2 (6 ml) were successively added $PhC{\equiv}CH$ (63 μl, 0.57 mmol), $BF_3 \cdot Et_2O$ (45 μl, 0.37 mmol), and norbornene (538 mg, 5.72 mmol) at room temperature with stirring. The orange solution was stirred at 40°C for 24 h. After the workup-procedure described above, poly(norbornene) was isolated as a white solid (149 mg, 28%).

The reaction with $p\text{-}CH_3COC_6H_4C{\equiv}CH$ was similarly carried out. The crude product was washed with CH_2Cl_2 (50 ml × 2) and a white solid was obtained (29%). The product was insoluble in common organic solvents and characterized by IR spectroscopy. IR (KBr disk): 2937, 2864, 1641, 1542, 1464, 1263, 965, 686 cm^{-1}.

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