# Catalytic Synthesis of Polynorbornene and Polynorbornadiene of Low Polydispersity Index by [Ru($\eta^5$-$C_9H_7$)Cl(COD)] (COD = 1,5-Cyclooctadiene)

Patricia Alvarez, José Gimeno,* and Elena Lastra

*Departamento de Química Orgánica e Inorgánica, Facultad de Química, Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Universidad de Oviedo, C/ Julián Clavería, s/n, 33006 Oviedo, Spain*

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*Summary: Thermal ROMP of norbonene and norbornadiene can be achieved at room temperature and stereoselectively using as initiator the indenyl complex [Ru($\eta^5$-$C_9H_7$)Cl(COD)]. The polymers are obtained in high yields showing a low polydispersity index, in the range 1.1−4.7, and high $M_n$ and $M_w$ values in a monomodal distribution. Catalytic polymerization of norbornadiene also takes place in the presence of air. A mechanism for the formation of the active carbene species via deprotonation of the cyclooctadiene ligand is proposed.*

Ring-opening metathesis polymerization (ROMP) has emerged as a convenient tool for the preparation of synthetic macromolecules starting from cyclic alkenes.[1] In particular, polymers derived from norbornene have attracted special interest due to their applications in oil spill recovery or as a sound barrier.[2] Among the most efficient transition-metal catalysts, ruthenium complexes have been established as versatile initiators for the olefin metathesis reactions.[3] Especially, the pentacoordinate carbene complexes [$RuCl_2$(=CHR)($PR_3$)$_2$] have been reported to be highly active catalysts with excellent tolerance to various functional groups.[4] In the search to improve catalytic performance under thermal conditions many other ruthenium(II) phosphine complexes have been used as initiators,[5] including a series of half-sandwich derivatives bearing $\eta^5$ ligands such as hydridotris(pyrazolyl)borate (Tp), cyclopentadienyl (Cp), pentamethylcyclopentadienyl (Cp*), and indenyl ($C_9H_7$).[6] It is apparent that the catalytic efficiency and the polymer properties are strongly dependent on the electronic and/or the steric properties of the $\eta^5$ ring.

We have recently reported the catalytic activity of the indenyl complex [Ru($\eta^5$-$C_9H_7$)Cl(COD)] (**1**) in [2 + 2] and [4 + 2] cycloadditions[7] and the hydration of terminal alkynes which shows an improved efficiency with respect to that of [Ru($\eta^5$-$C_9H_7$)Cl($PPh_3$)$_2$][8] These results prompted us to compare the catalytic activity of both complexes in ROMP. It has been previously reported that [Ru($\eta^5$-$C_9H_7$)Cl($PPh_3$)$_2$] (**4**) shows a remarkable catalytic activity under radical conditions,[9] although the polymerization of norbornene under thermal conditions is only achieved in a moderate yield (55%) at 60 °C and in the presence of diazomethane.[6a] In this paper we report that the cyclooctadiene complex **1** efficiently catalyzes the ROMP of norbornene and norbornadiene at room temperature. This initiator belongs to a rather short series of phosphine-free derivatives which are among the more effective species in the catalytic ROMP of cycloolefins.[10]

The results of ROMP of norbornene and norbornadiene are summarized in Tables 1 and 3, respectively. The polymerization of norbornene (Scheme 1) using 1 mol % of **1** as the catalyst was first examined in $CH_2Cl_2$ at 25 °C (Table 1, entry 1). The viscosity of the solution increased strongly while being stirred at 25 °C for the desired reaction time. After 1 h the resulting mixture was diluted and poured into stirred MeOH, affording the polymer as a white solid precipitate in almost quantitative yield (95%). In contrast, no significant catalytic activity is shown by complex **2** (precursor of complex **1**) and the analogous norbornadiene ruthenium(II) complex **3** (Table 1, entries 8 and 9). The catalytic activity remains unchanged in the presence of the radical inhibitor BHT (2,6-di-*tert*-butyl-4-methylphenol), indicating the nonradical nature of the polymerization.[11]

Polynorbornene has been unambiguously characterized by $^1H$ and $^{13}C\{^1H\}$ NMR, FT-IR, GPC, and its glass transition temperature (see the Supporting Informa-

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* To whom correspondence should be addressed. E-mail: jgh@sauron.quimica.uniovi.es. Fax: 985103446.

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[11] The reaction has been carried out in $CH_2Cl_2$ under the general conditions of adding 0.2 mol of BHT to afford 90% of the polymer in 1 h of reaction.

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**Table 1. Polymerization of Norbornene**[a]

| entry | cat. | *t* (h) | solvent | monomer/cat. | yield (%) | $M_w$ ($\times 10^3$)[b] | $M_n$ ($\times 10^3$)[b] | IPD[b] | % trans[d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | $CH_2Cl_2$ | 144 | 95 | 130.4 | 27.4 | 4.7 | 90 |
| 2 | 1 | 3 | $CH_2Cl_2$[c] | 144 | 90 | 1020.9 | 928.8 | 1.1 | 91 |
| 3 | 1 | 12 | THF | 144 | 30 | 36 | 12.7 | 2.8 | 87 |
| 4 | 1 | 12 | diethyl ether | 144 | 49 | 35 | 15.6 | 2.2 | 85 |
| 5 | 1 | 12 | $Br_2(CH_2)_2$ | 144 | 37 | 66.2 | 18.9 | 3.4 | 87 |
| 6 | 1 | 3 | MeBr | 144 | 85 | insol | | | |
| 7 | 1 | 36 | MeOH | 20 | 12 | insol | | | |
| 8 | 2 | 24 | $CH_2Cl_2$ | 200 | 3 | 8.4 | 3.7 | 2.2 | |
| 9 | 3 | 48 | $CH_2Cl_2$ | 200 | trazes | | | | |

[a] Reactions at room temperature. [b] Molecular weight ($M_w$), molecular weight distribution ($M_n$), and polydispersity index (IPD = $M_w/M_n$) date are based on polystyrene standards. [c] 0.1% mol $[NH_4][PF_6]$ as cocatalyst. [d] Percentage of trans double bonds from $^{13}C\{^1H\}$ NMR measurements.

**Table 2. Polymerization of Norbornene in Air Using 1 as Initiators**[a]

| entry | solvent | *t* (h) | yield (%) | $M_w$ ($\times 10^3$)[b] | $M_n$ ($\times 10^3$)[b] | IPD[b] |
|---|---|---|---|---|---|---|
| 1 | THF | 12 | 24 | 76 | 27 | 2.5 |
| 2 | $CH_2Cl_2$ | 1.5 | 92 | insol | | |
| 3 | MeBr | 3 | 40 | insol | | |
| 4 | diethyl ether | 12 | 51 | insol | | |

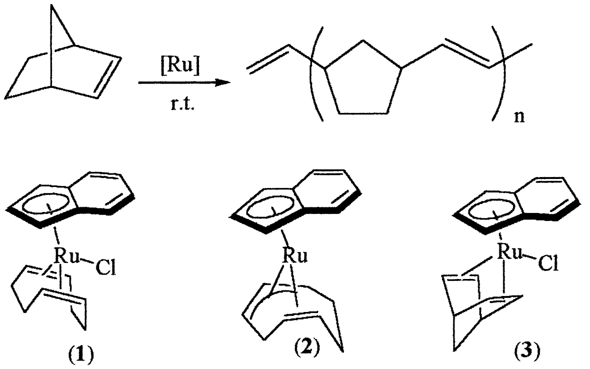
[a] Reactions at room temperature. [b] Molecular weight ($M_w$), molecular weight distribution ($M_n$), and polydispersity index (IPD = $M_w/M_n$) data are based on polystyrene standards.

**Table 3. Polymerization of Norbornadiene Using 1 as Initiators**[a]

| entry | solvent | *t* (h) | yield (%) | $M_w$ ($\times 10^3$)[b] | $M_n$ ($\times 10^3$)[b] | IPD[b] |
|---|---|---|---|---|---|---|
| 1 | THF | 9 | 60 | 66 | 18 | 3.4 |
| 2 | $CH_2Cl_2$ | 1.3 | 93 | 1264 | 1214 | 1.1 |
| 3 | diethyl ether | 7 | 75 | 102 | 42 | 2.4 |
| 4 | MeBr | 3.7 | 90 | 1458 | 1298 | 1.1 |

[a] Reactions at room temperature. [b] Molecular weight ($M_w$), molecular weight distribution ($M_n$), and polydispersity index (IPD = $M_w/M_n$) data are based on polystyrene standards.

**Scheme 1**



tion).[12] In particular, the $^{13}C\{^1H\}$ NMR spectrum shows the typical resonances of trans and cis isomers in a relative ratio of ca. 9/1 and also indicates the formation of a stereoregular and high blockness polymer.[12] Number average molecular weight ($M_n$) and weight average molecular weight ($M_w$) determinations by GPC of the soluble polymers vary from oligomers to high-molecular-weight polymers in a monomodal distribution, with moderate polydispersity index (2.2−4.7). In some cases, the material was insoluble.

The catalytic activity of **1** has been also studied in the presence of $NH_4PF_6$ (Table 1, entry 2). Although the conversion slightly decreases (90% yield after 3 h), a significant increase of polymer molecular weights is achieved along with very narrow molecular weight distributions ($M_n/M_w$ = ca. 1). These results seem to indicate a stabilization of any ionic intermediate of reaction, which avoids the degradation of the active species.[13]

The influence of the solvent and reaction time has been also investigated (Table 1, entries 1−7). However no significant improvements in the yields, stereochemistry, and molecular weights have been observed. In general, halogenated solvents lead to the best results. It is interesting to note that complex **1** does not require any additional activation to show catalytic activity with maximum conversions. This is in sharp contrast to the reported catalytic studies with other phosphine-free ruthenium complexes such as allyl ($[Ru(allyl)_2(NCMe)_2Cl][BF_4]$[13]) and cyclopentadienyl complexes ($[Os_2Cp^*{}_2Br_4]$[12]), which only exhibit activity in the presence of cocatalysts. Thus, the addition of diazo compounds or alkylating agents ($ZnMe_2$, $AlMe_3$, MAO), which act as sources of carbene moieties, is required in the catalytic performance. The addition of a variety of Lewis acids to facilitate the formation of 16-electron catalytic species from the coordinatively saturated vinylidene complexes $[RuTpCl(=C=CHPh)PPh_3]$ and $[RuCp^*Cl(=C=CHPh)PPh_3]$[6b] have also been used.

Following the standard procedure, we have determined the nonliving nature of the polymerization.[14] Thus, molecular weight distributions obtained at different norbornene concentrations show a nonlinear dependence (see the Supporting Information), indicating that the metal fragment attached to the polymeric chain is eliminated while the polymerization proceeds.

Assuming that solutions of complex **1** are stable in the presence of oxygen, the catalytic runs have been also checked in the presence of air (Table 2). In general, lower conversions and insoluble polymers are obtained, indicating probably degradation or cross-linking processes which are favored in the presence of oxygen. Although the reactions in THF lead to soluble polynorbornene, a lower efficiency is achieved (entry 1).

Complex **1** is also active in the ROMP of norbornadiene. The results are summarized in Table 3. The process (Scheme 2) has been performed under similar conditions and with solvents similar to those described

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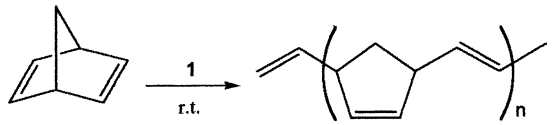
**Scheme 2**



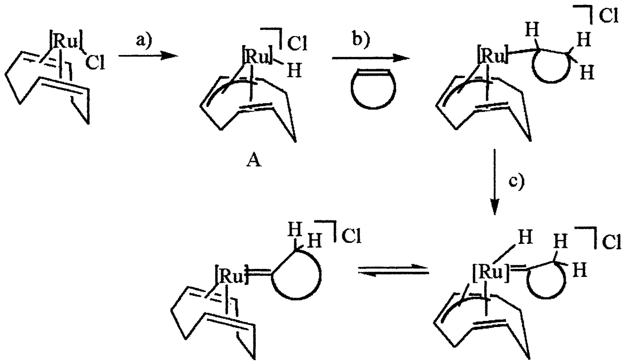
for norbornene and also leads to the highest conversions in halogenated solvents (90−93%).

The white materials which have been fully characterized as polynorbornadiene[15] (IR, NMR, and GPC; see the Supporting Information) were also found to have high molecular weights with polydispersity indexes ($M_n$/$M_w$) near 1 in halogenated solvents (Table 3, entries 2 and 4). Much lower yields and molecular weight distributions are found in THF and diethyl ether (Table 3, entries 1 and 3).

The indenyl phosphine free complex [Ru($\eta^5$-$C_9H_7$)Cl(COD)] is capable of undertaking ROMP of strained cycloolefins such as norbornene and norbornadiene at room temperature. In contrast, the analogous osmium complex [Os($\eta^5$-$C_5Me_5$)Cl(COD)] shows a significantly lower efficiency and selectivity, affording only oligomers ($M_w$ = 1200) at a higher temperature (78 °C) and longer reaction time (18 h).[12] This probably reflects not only the change in the metal center but also the electronic and steric effects of the indenyl ligand which allow the catalytic process to occur at room temperature. The remarkable efficiency of the catalytic activity of **1** can be compared with that reported for the vinylidene ruthenium(II) complexes [RuTpCl(=C=CHPh)$PPh_3$] and [RuCp*Cl(=C=CHPh)$PPh_3$].[6b] However, higher temperatures (40−80 °C) and longer reaction times (24 h) are required for the latter.

As was mentioned above, the polymerization does not proceed through a radical mechanism, since no change is observed when the process takes place in the presence of a radical inhibitor.[11] As has been previously proposed in the catalytic ROMP of olefins performed in the absence of cocatalysts, the required species for metathesis activity is a transient ruthenium carbene initiator generated in situ.[1] However, all attempts to characterize by $^1H$ NMR the actual transient active species of **1** have failed. The spectra of the catalytic reaction mixture show no further signals besides those of the catalyst **1** and the resulting polymers, indicating that the formation of the active species is too fast to be observed on the NMR time scale. Although a simple isomerization of one of the coordinated double bonds of the cyclooctadiene ligand in **1** into a carbene species cannot be discarded,[16] we propose the reaction sequence shown in Scheme 3 for the ROMP initiation. Thus, the carbene species may be formed via intramolecular deprotonation of cyclooctadiene to form the Ru(IV) hydride complex A, containing the $\eta^2$:$\eta^3$-$C_8H_{11}$ ligand (step a), subsequent insertion of norbornene into the Ru−H bond (step b), and α-elimination of the resulting norbornyl group (step c). Although intermediate species A has not been isolated, the analogous complex **2**, containing a $\eta^2$:$\eta^3$-$C_8H_{11}$ ligand, has been isolated.[7] Complex **2** in the presence of HCl is also active in the polymerization of norbornene. However, $^1H$ NMR experiments only show the presence of complex **1**. The catalytic inactivity of the analogous norbornadiene complex **3** also supports the role of the COD ligand in the active catalytic species.

**Scheme 3**



The actual polymerization may follow the typical growing chain involving the metallacyclization and cycloreversion steps. According to the GPC data, the molecular weight distribution is monomodal, suggesting that only one mechanism is involved in the catalysis.

In summary, we have shown that the indenyl complex [Ru($\eta^5$-$C_9H_7$)Cl(COD)] (**1**) is an excellent catalyst precursor in the thermal nonliving ROMP of norbornene and norbornadiene at room temperature. A high trans stereochemistry is also obtained. The best results are obtained using $CH_2Cl_2$ as solvent, and the addition of $NH_4PF_6$ affords polymers with high molecular weight and polydispersity index near 1.

## Experimental Section

The catalytic experiments were performed under a nitrogen atmosphere using standard Schlenk techniques or in the presence of air. Complexes **1**−**3** were synthesized according to previously published procedures.[7] Details of the polymer analysis are given in the Supporting Information.

**General Procedure for ROMP.** To a solution of the complex **1**, **2**, or **3** (0.2 mol) in the desired solvent (10 mL) under nitrogen was added norbornene or norbornadiene (3 mol), and the solution was stirred at room temperature. Once the reaction had finished, the viscous solution was filtered and precipitated over vigorously stirred MeOH. The white resulting polymers were isolated by filtration, washed several times with MeOH, and dried under vacuum.

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**Supporting Information Available:** Figures giving NMR, ATG, and DSC data obtained for polynorbornene and polynorbornadiene and living ROMP of norbornene results. This material is available free of charge via the Internet at http://pubs.acs.org.

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