# Ring-Opening Metathesis Polymerization of Norbornene by $Cp^*{}_2Os_2Br_4$ and Related Compounds

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*Received May 26, 1998*

The dinuclear complex $Cp^*{}_2Os_2Br_4$ (Cp* = pentamethylcyclopentadienyl) and related mono(pentamethylcyclopentadienyl)osmium compounds are catalysts for the ring-opening metathesis polymerization (ROMP) of norbornene. The most active catalyst prepared to date is made by treatment of $Cp^*{}_2Os_2Br_4$ with methylaluminoxane. This catalyst polymerizes norbornene with yields up to 167 kg of polymer per mol of catalyst at room temperature. The $^{13}C$ NMR spectra show that the polymer is slightly blocky and that cis double bonds predominate. The polymer is insoluble in organic solvents but is swelled by many of them.

## Introduction

Olefin metathesis reactions are widely used in industry.[1] The largest application of this reaction is found in the Shell higher olefin process (SHOP), which produces more than $10^5$ tons of $C_{10}-C_{20}$ alkenes annually.[2] One subset of olefin metathesis reactions is known as ring-opening metathesis polymerization (ROMP), in which a cyclic alkene is metathesized to form a ring-opened polymer.[3] Homogeneous ROMP is used industrially to produce specialty polymers such as polycyclooctene (polyoctenamer), polydicyclopentadiene, and polynorbornene. Polynorbornene, $(C_7H_{10})_n$ ($n > 20\,000$), in particular, is a useful polymer with interesting physical properties.[4,5] In its powdered form, the polymer particles are highly porous and are capable of absorbing of up to 15 times their weight in solvent. This property, and the insolubility of polynorbornene in water, makes this polymer useful in cleaning up oceanic oil spills. When polynorbornene is incorporated into dense sheets, its porous structure lends itself to use as a sound barrier and for vibration dampening in engines. Polynorbornene can also be cross-linked to form an unsaturated, deformation-resistant elastomer, which can be molded into soft seals and gaskets.

The first ROMP catalysts were discovered in the mid 1950s and were prepared from early transition metal halides or oxides and cocatalysts such as $AlMe_3$ and $EtAlCl_2$.[6] Ten years later, in 1965, the later transition metal salts $RuCl_3$, $OsCl_3$, and $IrCl_3$ were also found to be active ROMP catalysts.[7] Unlike the catalysts based on the early transition metals, which are highly sensitive to oxygen and water, the later metal catalysts are effective in alcoholic solvents and water emulsions.[8] In addition, cocatalysts are often not required to effect the polymerization. The catalytic activity of these later transition metal salts has been described in several patents and papers.[9−18]

Subsequent work with these later transition metal catalysts led to the development of ruthenium- and iridium-based catalytic systems that are able to catalyze ROMP of not only the highly strained monomer norbornene but also less strained monomers such as cyclopentene and cyclooctene.[19−23] Porri and co-workers

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10.1021/om980434r CCC: $18.00
Publication on Web 04/08/1999

found that treatment of $Ru(C_{12}H_{18})Cl_2$ and $Ru(C_{12}H_{18})(O_2CCF_3)_2$ ($C_{12}H_{18}$ = dodeca-2,6,10-triene-1,12-diyl) with dihydrogen affords a species that catalyzes the polymerization of cyclopentene.[19] They also discovered that $Ir_2Cl_2(COE)_2$ (COE = cyclooctadiene) reacts with a mixture of silver trifluoroacetate and trifluoroacetic acid to afford a product that could polymerize $C_5$ to $C_8$ cycloalkenes.[20] Demonceau and co-workers found the dimeric ruthenium catalyst ($p$-cymene)$_2$$Ru_2Cl_2$ was capable of polymerizing cyclopentene and cyclooctene in the presence of $P(c\text{-}Hx)_3$ and various diazoester cocatalysts.[21] Investigations of the catalytic activity of the related ($p$-cymene)$RuCl_2(P(c\text{-}Hx)_3)$ complex was taken one step further by Stumpf et al., who reported polymerizing functionalized norbornenes and cyclooctenes using (trimethylsilyl)diazomethane as the cocatalyst.[22] Similarly, the ruthenium(II) complex $Ru(H_2O)_6(O_3SC_7H_7)_2$ can polymerize cyclooctene, cyclopentene, and also the functionalized alkene 7-oxanorbornene.[23] New classes of ruthenium-based ROMP catalysts have also been synthesized, including the fragment "Cp*Ru($SnCl_3$)",[24] $[(allyl)_2Ru(NCCH_3)_2Cl][BF_4]$,[25] and the $\eta^2$-(O,P)-chelated ether-phosphine complexes $[(\eta^6\text{-}C_6H_6)RuH(P{-}O)][BF_4]$ (P−O = $Ph_2PCH_2CH_2OCH_3$, $Ph_2PCH_2C_4H_7O_2$, $Ph_2PCH_2C_3H_5O_2$).[26]

There has also been renewed interest in carrying out ROMP catalysis in aqueous solutions, and, in fact, the presence of water is known to increase the activity of certain catalysts such as $OsCl_3$. Methods to control molecular weight and polydispersity of polynorbornenes generated in aqueous solvents are continually being developed.[27−30]

It is generally accepted that the resting state in ROMP reactions is either a metal−carbene or a metallacyclobutane, depending on the precatalyst used.[3] Studies to elucidate the initiation mechanism,[23,31] propagation mechanism,[32−36] and overall kinetics of the polymerization process[37−39] have appeared. Despite these studies, for many ROMP catalysts the carbene or metallacyclobutane complex responsible for the catalysis has never been observed, and the mechanisms by which the active species is formed, the polymer chain is lengthened, and the catalytic cycle is terminated remain unclear. Consequently, Grubbs's recent synthesis of isolable ruthenium carbene complexes that are active ROMP catalysts for norbornene and other monomers has attracted much interest.[40−48]

The first isolable carbene catalyst reported was the five-coordinate species $RuCl_2(PR_3)_2({=}CHCH{=}CPh_2)$.[40−42] When R = Ph, this compound polymerizes norbornene and the strained monomer bicyclo[3.2.0]heptene.[43] When R = c-Hx, the catalyst is more active and can polymerize norbornene, 7-oxanorbornene, cyclopentene, cyclooctene, and cyclooctadiene.[44] Grubbs also synthesized a second class of carbene compounds with the general formula $RuCl_2(PR_3)_2({=}CHR')$, where R = Ph or c-Hx and R′ = Me, Et, Ph, or $p$-$C_6H_4Cl$, which are capable of polymerizing cyclobutenes and functionalized cycloalkenes.[45−47,49,50] By attaching water-soluble phosphines such as $P(c\text{-}Hx)_2(CH_2CH_2NMe_3)^+$ instead of $PPh_3$ or $P(c\text{-}Hx)_3$ to the ruthenium center, Grubbs has shown that highly substituted norbornenes can be polymerized in aqueous solutions.[51−53] Chen and co-workers have shown that these water-soluble ruthenium complexes can also catalyze ROMP in the gas phase.[54] In addition, substitution of the phosphine ligands with bidentate Schiff-base ligands makes these catalysts more tunable and air and water stable.[55] Herrmann et al. have also reported a similar complex with *N*-heterocyclic carbene ligands instead of the phosphine ligands on Grubbs's catalyst.[56] This new ruthenium ROMP catalyst polymerizes substituted norbornenes and cyclooctene. Most recently, Grubbs has reported the synthesis of heterobimetallic ruthenium alkylidene complexes with greater ROMP reaction rates.[57]

Several osmium carbene complexes are known,[41,58] but few studies of their ROMP catalytic ability have been described.[59−62] In fact, few studies of osmium

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compounds other than $OsCl_3$ as ROMP catalysts have been reported. An ill-defined osmium ROMP catalyst capable of polymerizing norbornene was obtained when $OsCl_3$ was heated with cyclooctadiene for several days,[32] and both $OsO_4$[63] and $OsO_2$ supported on $Al_2O_3$[64] were also found to have ROMP catalytic activity. The complex (*p*-cymene)$OsCl_2(P(c\text{-}Hx)_3)$, which is the osmium analogue of a known ruthenium catalyst, is an active ROMP catalyst after activation by ultraviolet light.[65] We now describe our discovery of a new osmium-based ROMP catalyst.

## Results

**ROMP Activity of $Cp^*_2Os_2Br_4$.** The ability of $OsCl_3$ to serve as a ROMP catalyst[7] suggests that other haloosmium(III) species might exhibit similar activity. We have recently prepared the dinuclear osmium(III) complex $Cp^*_2Os_2Br_4$[66] and have shown that it is a useful starting material for the preparation of other organoosmium complexes.[66,67] We now find that this dinuclear complex is active for the ring-opening metathesis polymerization (ROMP) of certain cycloalkenes in both protic and aprotic solvents.

To survey the catalytic ability of $Cp^*_2Os_2Br_4$, we treated solutions of this complex with 1000 equiv of several cycloalkenes (norbornene, 5-norbornen-2-yl acetate, norbornadiene, cyclopentene, cyclooctene, and cyclooctatetraene) both at room temperature and under refluxing conditions. After several hours, the polymer was collected either by filtration or by removing the solvent under vacuum. Under the conditions studied, only norbornene (NBE), the ester-functionalized 5-norbornen-2-yl acetate, and norbornadiene (NBD) were polymerized. The best yields of polymer per mole of catalyst, 30.3 kg of polynorbornene, 5.8 kg of poly(5-norbornen-2-yl acetate), and 4.4 kg of polynorbornadiene, were obtained in refluxing aqueous ethanol after 18 h.

The analogous ruthenium complex $Cp^*_2Ru_2Cl_4$[68,69] also polymerized only NBE and NBD in refluxing ethanol, but the yields were about 5 times lower than those seen for the osmium compound. A similar reactivity trend was also observed by Michelotti and Keaveney in their comparison of the ROMP activity of $OsCl_3$ and $RuCl_3$.[7]

The osmium(II) cyclooctadiene complex $Cp^*Os(COD)Br$[67] was also tested for its ability to serve as a ROMP catalyst. When treated with 1000 equiv of monomer in refluxing ethanol, this complex yielded 15.4 kg of polynorbornene per mol of catalyst, a yield that is comparable to that obtained with the osmium(III) complex, $Cp^*_2Os_2Br_4$. As will be shown below, however, the properties of the polymer obtained from this catalyst are significantly different from those obtained from $Cp^*_2Os_2Br_4$.

**Table 1. Characterization of Polynorbornene Formed from the $Cp^*_2Os_2Br_4$ Precatalyst**

| reaction solvent | cocatalyst | temp, °C | yield[a] | % cis | $r_c$ | $r_t$ |
|---|---|---|---|---|---|---|
| $H_2O$/EtOH (3:1) | none | reflux | 30.3 | 61 | 2.0 | 1.0 |
| $^t$BuOH | none | reflux | 26.5 | 55.6 | 1.8 | 1.3 |
| EtOH | none | reflux | 21.0 | 54.3 | 2.3 | 1.2 |
| $CH_2Cl_2$ | none | reflux | 29.5 | 52 | 1.7 | 0.9 |
| THF | none | reflux | 11.3 | 37 | 1.0 | 1.7 |
| $CHCl_3$ | none | reflux | 20.7 | 63.0 | 2.1 | 0.72 |
| $CH_2Cl_2$ | $AlMe_3$ | 25 | 58.7 | 56 | 1.4 | 0.9 |
| toluene | MAO | 25 | 77.2 | 59 | 1.7 | 0.9 |

[a] kg polymer/mol precatalyst. The monomer:precatalyst ratio was 1000:1 in all cases. A 100% yield would correspond to 94 kg polymer/mol precatalyst.

In addition to the Cp*Os complexes, the osmium(IV) species $H_2OsBr_6$[66] also polymerized norbornene in refluxing ethanol with a yield of 86.9 kg of polymer per mole of catalyst (92.8% of the total NBE added).

**Effect of Cocatalysts on the Polymerizations.** The rate-limiting step in many ROMP processes is the conversion of the precatalyst to the active catalytic species. Consequently, much work has focused on the addition of cocatalysts to accelerate this process.[3]

We tried several different alkylating cocatalysts such as $ZnMe_2$, $AlMe_3$, methylaluminoxane (MAO), and the diazo compound $N_2CHCO_2CH_2CH_3$. Although all of these cocatalysts increased the yield of polymer, we found that addition of either $AlMe_3$ or MAO to $Cp^*_2Os_2Br_4$ generates the most active catalyst. In the presence of $AlMe_3$ and MAO cocatalysts, the polymerization of norbornene occurs readily at room temperature (rather than at reflux) and the yield of polymer is improved dramatically (Table 1).

Unlike Ziegler−Natta catalysts, which require several hundred equivalents of MAO per catalytic center, 2 equiv of MAO per $Cp^*_2Os_2Br_4$ unit are sufficient. In toluene with $Cp^*_2Os_2Br_4$/MAO as the catalyst, 1000 equiv of NBE is polymerized at room temperature to give 77 kg per mole of catalyst, which corresponds to 81% conversion. When 2000 equiv of NBE are added to a toluene solution of $Cp^*_2Os_2Br_4$ and MAO, 167 kg of polymer per mole of catalyst (86% of the theoretical amount of polymer) is generated. This result indicates that the rate of catalyst deactivation is slow when the monomer concentration is high. Once the monomer concentration drops below the level necessary to sustain chain propagation, side reactions that result in catalyst deactivation evidently occur. No reaction occurred when MAO alone was added to norbornene.

Similar increases in the yield of poly(5-norbornen-2-yl acetate) and poly(norbornadiene) are seen when $AlMe_3$ or MAO is present. For example, when 1000 equiv of 5-norbornen-2-yl acetate is added to a $Cp^*_2Os_2Br_4$/$AlMe_3$ catalyst in $CH_2Cl_2$, the polymerization reaction occurs at room temperature and yields 58.2 kg of polymer per mole of catalyst. In contrast, $AlMe_3$- or MAO-activated $Cp^*_2Os_2Br_4$ is not able to polymerize cyclooctene.

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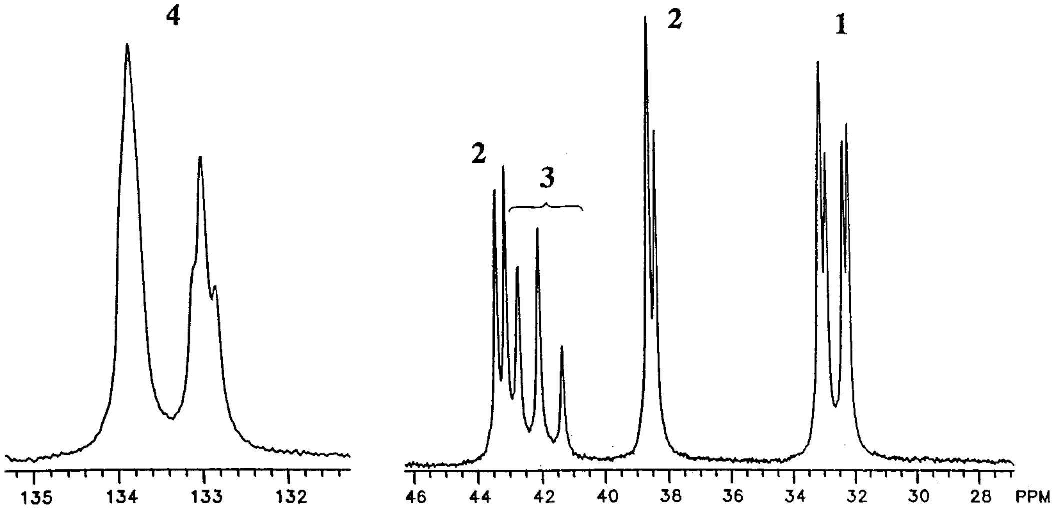


**Figure 1.** 75 MHz $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of polynorbornene generated from the $Cp^*_2Os_2Br_4$ catalyst in aqueous ethanol. Peak numbers correspond to polymer carbon atoms (see text).

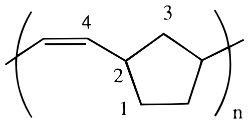
MAO also increases the activity of Cp*Os(COD)Br so that the polymerization of NBE can be carried out at room temperature. Polymerization of norbornene at room temperature in toluene with MAO as a cocatalyst afforded 5.1 kg of polymer per mole of catalyst. The yield of polymer is significantly lower than that obtained under identical conditions from a $Cp^*_2Os_2Br_4$/MAO catalyst.

**Characterization of the Polynorbornene.** The microstructure of the polynorbornene produced can afford insights into the nature of the catalyst and the details of the catalytic mechanism.[70] We will first discuss the properties of the polynorbornene generated in refluxing aqueous ethanol with $Cp^*_2Os_2Br_4$ as a catalyst.

A differential scanning calorimetry plot shows a small endothermic feature at 40 °C which is assigned to the polynorbornene glass transition. This value for the glass transition temperature indicates that the polynorbornene formed is atactic.[1,4] For polynorbornene, the tacticity refers to the stereochemistries of the two tertiary carbon atoms of the cyclopentane rings in the polymer. In an atactic polymer, R,S and S,R disubstituted cyclopentane rings occur randomly along the polymer chain. Thermogravimetric analysis shows that the polynorbornene is stable up to a temperature of 450 °C. A slight (2%) weight gain occurs at 125 °C.

The infrared spectrum of the polynorbornene shows broad bands at 2900 $cm^{-1}$ (C−H stretch), 1778, 1712, 1650 $cm^{-1}$ (C═C stretch), and several bands in the fingerprint region (see Experimental Section). By taking the ratio of the absorptivities of the bands near 960 $cm^{-1}$ (bending mode due to trans disubstituted C═C double bonds) and 730 $cm^{-1}$ (bending mode due to cis disubstituted C═C double bonds), we can determine the relative amounts of these two functional groups in the polymer.[71] For the polynorbornene formed in refluxing ethanol with $Cp^*_2Os_2Br_4$ as a catalyst, the cis/trans ratio is roughly 1:1.

The polynorbornene is completely insoluble in organic solvents, and this property has prevented us from characterizing the molecular weights of the polymers by techniques such as gel permeation chromatography. The polynorbornene, however, swells in the presence of organic solvents. The samples swelled with $CDCl_3$ afford useful $^{13}C\{^{1}H\}$ NMR spectra (Figure 1; the numbering scheme is shown in the diagram below).



For each of the four different kinds of carbon atoms present in the diagram above, the $^{13}C$ NMR chemical shift is sensitive to the configurations about the nearby C═C double bonds.[72,73] For carbon C-4 (the vinylic carbon), two envelopes of resonances are seen: one for carbon atoms situated in trans RHC═CHR groups and one for carbon atoms situated in cis RHC═CHR groups. The corresponding resonances are labeled 4 in Figure 1 (fine structure within each of these resonances is attributed to differing triad structures in the polymer).[33] In contrast, four separate C-1 and four separate C-2 resonances can be observed. These resonances correspond to each of the four possible dyad structures, tt, tc, ct, and cc, where the first index indicates the configuration (cis or trans) about the *nearest* C═C double bond, and the second index indicates the configuration about the *next-nearest* C═C double bond. For carbon C-3, three resonances are seen. These also correspond to dyad structures, but here the tc and ct dyads are identical because the two nearest double bonds are equidistant from this carbon atom.

Peak fitting of the $^{13}C$ NMR spectra allows us to determine accurately the relative amounts of cis and trans C═C double bonds in the polynorbornene (Table 1). The result (61% cis) agrees with that estimated from the IR spectrum. The relative populations of the various dyads, however, afford additional information. In particular, we can determine the “blockiness” of the poly-

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mer, which is related to the frequency of cc or tt double-bond strings relative to alternating ct or tc sequences in the polymer. Of particular interest are the following rate constants:

$$P_c + M \xrightarrow{k_{cc}} P_c$$

$$P_c + M \xrightarrow{k_{ct}} P_t$$

$$P_t + M \xrightarrow{k_{tt}} P_t$$

$$P_t + M \xrightarrow{k_{tc}} P_c$$

The rate constant $k_{ct}$, for example, describes the rate at which a metal-bound polymer chain with a cis C=C double bond adjacent to the metal ($P_c$) reacts with a monomer (M) to give a metal-bound polymer chain with a trans C=C double bond adjacent to the metal ($P_t$).

The two ratios $k_{cc}/k_{ct}$ ($=r_c$) and $k_{tt}/k_{tc}$ ($=r_t$) are measures of the blockiness of the polymer. If both ratios $r_c$ and $r_t$ are 0, then the polymer alternates ···ctctct···. If both ratios are equal to 1, then the polymer has a random sequence of cis and trans double bonds. As both ratios increase without bound, the polymer increasingly consists of long ···cccccc··· or ···tttttt··· strings. The determination of the rate constants from the NMR intensities is described in the Experimental Section.

A summary of the blockiness ratios is given in Table 1. For the polynorbornene prepared in refluxing aqueous ethanol with $Cp^*_2Os_2Br_4$ as a catalyst, $r_c = 2.0$ and $r_t = 1.0$. Thus, a cis C=C double bond is twice as likely to be followed by a cis C=C double bond than by a trans C=C double bond; a trans bond is equally likely to be followed by a C=C double bond of either configuration. The combined effect of $r_c$ and $r_t$ is to afford a polymer with more cis double bonds.

When the polymerization of norbornene is carried out in refluxing dichloromethane with $Cp^*_2Os_2Br_4$ as the catalyst, the polynorbornene generated is very similar to that obtained in refluxing ethanol: cis double bonds slightly predominate (52% cis), and the distribution of cis and trans double bonds is more random than blocky (Table 1). In THF, however, the polymer contains only 38% cis double bonds. This result suggests that coordination of THF to the active species changes the nature of the polymerization sites so that the polymer forms trans double bonds preferentially.

The polynorbornene produced by $H_2OsBr_6$ was very similar to that produced by $Cp^*_2Os_2Br_4$: it has 58% cis double bonds by $^{13}$C NMR spectroscopy, and the distribution of cis double bonds is slightly blocky ($r_c = 1.76$, $r_t = 0.71$). As was true with the polymer produced by $Cp^*_2Os_2Br_4$, the polynorbornene produced by this catalyst is not soluble in conventional solvents, preventing analysis of this polymer by gel permeation chromatography.

When the polymerization of norbornene is performed in toluene in the presence of the $AlMe_3$ or MAO cocatalysts, the polynorbornene generated is essentially identical to that obtained in ethanol in the absence of a cocatalyst. This result suggests that $Cp^*_2Os_2Br_4$ converts to the same active species as that generated in the absence of alkylating cocatalysts, but that the conversion occurs with greater speed or efficiency (or both) when the cocatalysts are present.

When the polymerization of norbornene is performed in refluxing ethanol with Cp*Os(COD)Br as the catalyst, the polynorbornene contains more cis double bonds (73%) and is blockier ($r_c = 6.59$, $r_t = 1.48$) than the polymer produced by $Cp^*_2Os_2Br_4$. Because the polynorbornene produced with the Cp*Os(COD)Br catalyst was soluble, the molecular weight of the polymer could be determined by gel permeation chromatography. The polynorbornene formed was found to be oligomeric ($M_w = 1200$), with an average of 20 monomer units per chain.

**In Situ Attempts to Characterize the Active Catalyst.** All attempts to isolate an active osmium–carbene complex directly from the ROMP reaction solutions were unsuccessful. We also carried out polymerizations in NMR tubes in an attempt to detect the active species by $^1$H NMR spectroscopy. Two samples were prepared in $CD_2Cl_2$: one with no cocatalyst and one with 3 equiv of MAO per $Cp^*_2Os_2Br_4$. In neither case could a signal for an osmium carbene be observed. There was, however, one new peak in the spectra that could not be ascribed to solvent, NBE, or the precatalyst: a broad resonance at $\delta$ 24.8 (fwhm = 286 Hz). This resonance indicates the presence of a paramagnetic species, and we propose that it is a mononuclear osmium(III) species formed when NBE coordinates to (and cleaves) the dinuclear complex $Cp^*_2Os_2Br_4$. This peak is not present when either $Cp^*_2Os_2Br_4$ or $Cp^*_2Os_2Br_4$/MAO is dissolved in the same solvent.

Similar in situ studies of Cp*Os(COD)Br were undertaken, and no signals from any osmium carbene or paramagnetic compounds were observed. Polymerization did occur, however. This result indicates that the active catalyst is formed in amounts too small to be observed by NMR spectroscopy.

## Discussion

**Nature of the Osmium-Based ROMP Catalysts.** The dinuclear osmium complex $Cp^*_2Os_2Br_4$ is capable of effecting the ring-opening metathesis polymerization of strained alkenes such as norbornene. This osmium compound is 5 times more active than its ruthenium analogue $Cp^*_2Ru_2Cl_4$. For norbornene, the activity of $Cp^*_2Os_2Br_4$ is higher than that of the respective chloride salts $OsCl_3$ and $RuCl_3$,[7] which polymerize norbornene in refluxing alcoholic solvents. The osmium(II) complex Cp*Os(COD)Br is also capable of polymerizing norbornene in yields similar to those seen for $Cp^*_2Os_2Br_4$, but the polymer obtained has a much lower molecular weight.

Although the precatalyst, $Cp^*_2Os_2Br_4$, is dinuclear, the active species is almost certainly mononuclear. The presence of paramagnetic species is demonstrated by in situ $^1$H NMR studies; it is not clear, however, whether this species, which is probably a mononuclear osmium(III) complex, is the active catalyst or not.[74] In the absence of cocatalysts, the conversion of the precursor to the active catalyst is probably the rate-determining

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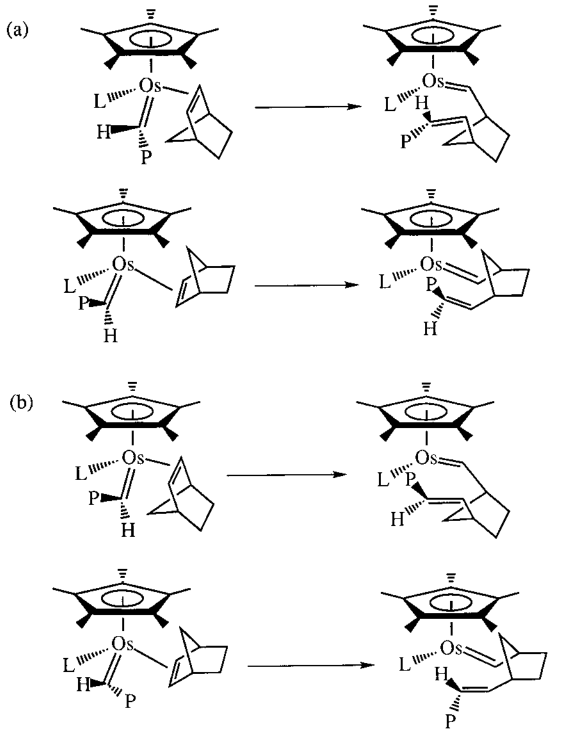
(74) Although we cannot rule out the possibility of formation of an osmium(III) species by the disproportionation of $Cp^*_2Os_2Br_4$ into $[Cp^*_2Os][Br]$ and $OsBr_3$, we think that this possibility is remote. The reaction conditions are relatively mild, and we have studied the chemistry of many other Cp*Os compounds and have never seen evidence for Cp* transfer in these compounds.

**Scheme 1. (a) Formation of Cis Double Bonds; (b) Formation of Trans Double Bonds**



step. As has been proposed by others,[3] a possible activation mechanism in the absence of a cocatalyst involves coordination of the alkene, followed by a 1,2 hydrogen shift to generate a metal carbene species. The addition of $AlMe_3$ or MAO does not change the nature of the polynorbornene formed, but these cocatalysts considerably increase the polymerization rates. Presumably, the cocatalysts alkylate the osmium center, and subsequent α-hydrogen abstraction generates the catalytically active carbene species. These catalysts remain active as long as monomer is present, but in the absence of monomer, the catalysts deactivate.

**Nature of the Polymers and the Polymerization Mechanism.** All of the norbornene polymers formed from $Cp^*_2Os_2Br_4$ in these experiments were atactic, indicating that the catalytically active species is not stereoselective. The solvent used for the polymerization reactions does not greatly affect the nature of the polymer formed. In aqueous ethanol and dichloromethane, the polymers produced are only slightly blocky and 50−60% of the double bonds are cis. When the polymerization is carried out in THF, however, fewer than 40% of the double bonds are cis. The catalyst generated in THF must differ in some significant but unknown way from those generated in other solvents.

A probable mechanism for the formation of cis and trans double bonds in the polymer is shown in Scheme 1. The configurations of the double bonds in the polymer depend on both the orientation of the coordinated NBE and the orientation of the polymer chain in relation to the Cp* ring. In theory, because the steric bulk of the Cp* group blocks one side of the active catalyst, the growing polymer chain is more likely to point away from the Cp* ligand. In addition, the norbornadiene monomer is more likely to bind to the osmium center with the methylene bridge pointing away from the Cp* ligand. Thus, this type of ROMP catalyst should be more capable of catalyzing metathesis reactions with high regioselectivity. In practice, however, the catalysts we have studied are remarkably nonselective, giving polymers with similar amounts of cis and trans double bonds.

## Experimental Section

**General Details.** All experiments were performed under argon or vacuum by using standard Schlenk techniques unless otherwise specified. Solvents were distilled under nitrogen from magnesium (ethanol), calcium hydride (dichloromethane, chloroform), or sodium benzophenone (pentane, diethyl ether, tetrahydrofuran). Water was degassed with argon and distilled before use. Norbornene (Aldrich), 5-norbornen-2-yl acetate (mixture of *exo* and *endo* isomers, Aldrich), and *tert*-butyl alcohol (Aldrich) were distilled before use, whereas methylaluminoxane (1.5 M in toluene; Aldrich) and $AlMe_3$ (2.0 M in toluene; Aldrich) were used as received. The precatalysts $Cp^*_2Os_2Br_4$,[66] $Cp^*Os(COD)Br$,[67] $H_2OsBr_6$,[66] and $Cp^*_2Ru_2Cl_4$[68,69] were prepared by following the literature procedures.

The IR spectra of the polymers were obtained on a Nicolet Impact 410 instrument as a pressed and annealed sample. The $^1H$ and $^{13}C$ NMR data were recorded on a General Electric GN300WB spectrometer at 300 and 75 MHz, respectively. In situ $^1H$ NMR experiments were performed on a General Electric GN500 instrument at 500 MHz. Chemical shifts are reported in parts per million ($\delta$) relative to $SiMe_4$; positive chemical shifts correspond to resonance frequencies higher than that of the reference. Gel permeation chromatography was performed on a Millipore Waters 501 HPLC with a polystyrene column having a pore size of 100 Å. Differential scanning calorimetry measurements and thermogravimetric analyses were made on Perkin-Elmer instruments, models DSC7 and TGA7, respectively. Microanalyses were carried out by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois.

**Polymerization of Norbornene in Aqueous Ethanol with $Cp^*_2Os_2Br_4$ Catalyst.** To a solution of $Cp^*_2Os_2Br_4$ (0.030 g, 0.031 mmol) in water (60 mL) was added a solution of norbornene (2.88 g, 30.6 mmol) in ethanol (20 mL). The resulting mixture was heated to reflux, and a mass of white solid began to appear. After 18 h, the white solid was separated from the yellow supernatant by filtration, and the solid polymer was dried under vacuum overnight. Yield: 0.94 g (33%; turnover number = 320). Anal. Calcd for $(C_7H_{10})_n$: C, 89.4; H, 10.7. Found: C, 87.4; H, 10.9. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 32.2 (1tt), 32.4 (1tc), 32.9 (1ct), 33.1 (1cc), 38.4 (2ct), 38.6 (2cc), 41.3 (3tt), 42.1 (3tc = 3ct), 42.7 (3cc), 43.1 (2tt), 43.4 (2tc), 132.8 (4t), 133.0 (4t), 133.1 (4t), 133.8 (br, 4c).

**Polymerization of Norbornene in *tert*-Butyl Alcohol with $Cp^*_2Os_2Br_4$ Catalyst.** The procedure above was followed except that the solvent was *tert*-butyl alcohol. Yield: 0.81 g (28%; turnover number = 281).

**Polymerization of Norbornene in Ethanol with $Cp^*_2Os_2Br_4$ Catalyst.** The procedure above was followed except that the solvent was ethanol. Yield: 0.59 g (22%; turnover number = 223).

**Polymerization of Norbornene in Dichloromethane with $Cp^*_2Os_2Br_4$ Catalyst.** The procedure above was followed except that the solvent was dichloromethane. Upon bringing the solution to reflux, the solution color remained red-brown and after 18 h the solution was very viscous. The solvent was removed under vacuum to give a solid. Yield: 0.95 g (29%; turnover number = 310).

**Polymerization of Norbornene in Tetrahydrofuran with $Cp^*_2Os_2Br_4$ Catalyst.** The procedure above was followed except that the solvent was tetrahydrofuran. Upon bringing the solution to reflux, the solution color remained brown-orange. Shiny polymer was isolated by removal of the solvent under vacuum. Yield: 0.35 g (13%; turnover number = 120).

**Polymerization of Norbornene in Chloroform with $Cp^*{}_2Os_2Br_4$ Catalyst.** The procedure above was followed except that the solvent was chloroform. Upon bringing the solution to reflux, the solution color remained brown-orange. Shiny polymer was isolated by removal of the solvent under vacuum. Yield: 0.65 g (22%; turnover number = 220).

**Polymerization of Norbornene in Dichloromethane with $Cp^*{}_2Os_2Br_4$ /$AlMe_3$ Catalyst.** To a solution of $Cp^*{}_2Os_2Br_4$ (0.032 g, 0.036 mmol) in $CH_2Cl_2$ (40 mL) was added a solution of norbornene (3.1 g, 32.6 mmol) in $CH_2Cl_2$ (40 mL). Trimethylaluminum (35 $\mu$L of a 2.0 M solution in toluene, 0.070 mmol) was added to the brown reaction mixture, which caused the solution color to become a lighter orange-brown. After being stirred for 10 min at room temperature, the solution had become a gel. After an additional 18 h, the solvent was removed under vacuum and the resulting polymer was further dried overnight. Yield: 2.1 g (68%; turnover number = 620).

**Polymerization of Norbornene in Toluene with $Cp^*{}_2Os_2Br_4$/MAO Catalyst.** To a solution of $Cp^*{}_2Os_2Br_4$ (0.032 g, 0.036 mmol) in toluene (40 mL) was added a solution of norbornene (3.1 g, 32.6 mmol) in toluene (40 mL). A solution of methylaluminoxane (50 $\mu$L of a 1.5 M solution in toluene, 0.075 mmol) was added, which caused the color of the reaction mixture to become dark orange. The mixture immediately became viscous and after 30 min could no longer be stirred. The mixture was washed with acetone (40 mL), and the resulting wet polymer was dried under vacuum to afford a solid. Yield: 2.5 g (81%; turnover number = 820). A repetition of this experiment with $Cp^*{}_2Os_2Br_4$ (0.015 g, 0.015 mmol), norbornene (2.9 g, 31 mmol; 2000 equiv), and MAO (20 $\mu$L of a 1.5 M solution in toluene, 0.030 mmol) afforded 2.5 g (86%) of product; turnover number = 1710.

**Polymerization of Norbornene in Ethanol with Cp*Os(COD)Br Catalyst.** To a solution of Cp*Os(COD)Br (0.020 g, 0.039 mmol) in ethanol (50 mL) was added a solution of norbornene (3.67 g, 39.0 mmol) in ethanol (30 mL). The solution was refluxed for 18 h. The white precipitate was collected by filtration and dried under vacuum overnight. Yield: 0.60 g (16%; turnover number = 164).

**Polymerization of Norbornene in Toluene with Cp*Os(COD)Br/MAO Catalyst.** To a solution of Cp*Os(COD)Br (0.020 g, 0.039 mmol) in toluene (60 mL) was added a solution of norbornene (3.67 g, 39.0 mmol) in toluene (20 mL). A solution of methylaluminoxane (30 $\mu$L of a 1.5 M solution in toluene, 0.045 mmol) was added. The mixture was stirred for 18 h, and the solution became slightly viscous. The solvent was removed under vacuum, and the resulting white polymer was dried under vacuum overnight. Yield: 0.2 g (5.4%; turnover number = 55).

**Polymerization of Norbornene in Ethanol with $Cp^*{}_2Ru_2Cl_4$ Catalyst.** To a solution of $Cp^*{}_2Ru_2Cl_4$ (0.023 g, 0.037 mmol) in ethanol (40 mL) was added a solution of norbornene (3.5 g, 37.2 mmol) in ethanol (40 mL). The brown mixture was refluxed for 18 h, and a small amount of precipitate formed. The off-white polymer was collected by filtration and dried under vacuum overnight. Yield: 0.13 g (4%; turnover number = 37).

**Polymerization of Norbornene in Ethanol with $H_2OsBr_6$ Catalyst.** To a solution of $H_2OsBr_6$ (0.020 g, 0.030 mmol) in ethanol (60 mL) was added a solution of norbornene (2.80 g, 29.8 mmol) in ethanol (20 mL). The solution was refluxed for 18 h, and a white solid precipitated. During the same time, the orange supernatant became colorless. The solid was collected by filtration and dried under vacuum overnight. Yield: 2.60 g (92.8%, turnover number = 923).

**Polymerization of 5-Norbornen-2-yl Acetate in Ethanol with $Cp^*{}_2Os_2Br_4$ Catalyst.** To a solution of $Cp^*{}_2Os_2Br_4$ (0.030 g, 0.031 mmol) in ethanol (80 mL) was added 5-norbornen-2-yl acetate (4.5 mL). The solution was refluxed for 18 h, and a precipitate formed. The solvent was removed under vacuum to afford a brown, oily solid. Pentane (30 mL) was added to the oily solid, and the mixture was allowed to stand for 24 h. The liquid was removed, and the resulting solid polymer was dried under vacuum overnight. Yield: 0.18 g (4%; turnover number = 38).

**Polymerization of 5-Norbornen-2-yl Acetate in Dichloromethane with $Cp^*{}_2Os_2Br_4$/$AlMe_3$ Catalyst.** To a solution of $Cp^*{}_2Os_2Br_4$ (0.030 g, 0.031 mmol) in dichloromethane (80 mL) was added trimethylaluminum (30 $\mu$L of a 2.0 M solution in toluene, 0.06 mmol) and 5-norbornen-2-yl acetate (4.5 mL). The solution was stirred at room temperature for 18 h. The solvent was removed under vacuum to afford a brown, oily solid. Pentane (30 mL) was added to the oily solid, and the mixture was allowed to stand for 24 h. The liquid was removed, and the resulting solid polymer was dried under vacuum overnight. Yield: 2.64 g (56.2%; turnover number = 560).

**In Situ $^1$H NMR Experiments with $Cp^*{}_2Os_2Br_4$.** Two 5 mm NMR tubes were each charged with norbornene (0.01 g, 100 $\mu$mol) and then with a solution of $Cp^*{}_2Os_2Br_4$ (0.01 g, 10 $\mu$mol) in $CD_2Cl_2$ (1 mL). To one sample was added MAO (20 $\mu$L of a 1.5 M solution in toluene, 30 $\mu$mol). The two samples were immediately frozen in liquid nitrogen to prevent polymerization and thawed immediately before insertion into the spectrometer.

**In Situ $^1$H NMR Experiments with Cp*Os(COD)Br.** Two 5 mm NMR tubes were each charged with norbornene (0.01 g, 100 $\mu$mol) and then with a solution of Cp*Os(COD)Br (0.01 g, 19 $\mu$mol) in $CD_2Cl_2$ (1 mL). To one sample was added MAO (20 $\mu$L of a 1.5 M solution in toluene, 30 $\mu$mol). The two samples were immediately frozen in liquid nitrogen to prevent polymerization and thawed immediately before insertion into the spectrometer.

**Polymer Characterization by $^{13}$C NMR Spectroscopy.** The polynorbornene samples were prepared in 10 mm NMR tubes with $CDCl_3$ as the solvent. The tubes were loaded with ~0.020 g of polymer and 2 mL of solvent. The samples were capped and stored for at least 24 h to allow the polymer to swell. After the NMR spectra were acquired, the relative areas of the peaks were determined by the line-fitting algorithm in NUTS (Acorn NMR).

The fraction of cis double bonds in the polymer was calculated independently four times, once each from the relative areas of the $^{13}$C NMR peaks for the four different carbon sites. The pertinent equations are[72]

$$\text{(a)}\qquad \chi_{\text{cis}} = [I_{1\text{cc}} + {}^1/_2(I_{1\text{ct}} + I_{1\text{tc}})]/(I_{1\text{cc}} + I_{1\text{ct}} + I_{1\text{tc}} + I_{1\text{tt}})$$

$$\text{(b)}\qquad \chi_{\text{cis}} = [I_{2\text{cc}} + {}^1/_2(I_{2\text{ct}} + I_{2\text{tc}})]/(I_{2\text{cc}} + I_{2\text{ct}} + I_{2\text{tc}} + I_{2\text{tt}})$$

$$\text{(c)}\qquad \chi_{\text{cis}} = [I_{3\text{cc}} + {}^1/_2 I_{3\text{ct}}]/(I_{3\text{cc}} + I_{3\text{ct}} + I_{3\text{tt}})$$

$$\text{(d)}\qquad \chi_{\text{cis}} = I_{4\text{c}}/(I_{4\text{c}} + I_{4\text{t}})$$

The four values obtained from the equations above, which generally agreed to within 3%, were averaged to give the reported fraction of cis double bonds in the polymer.

The polymer blockiness ratios $r_c$ and $r_t$ were determined from the ratio of peak areas ($r_c = I_{cc}/I_{ct}$, $r_t = I_{tt}/I_{tc}$) for carbons 1 and 2 only.

**Acknowledgment.** We thank the Department of Energy under Grant DEFG02-96-ER45439 for support of this work. J.L.B. thanks the University of Illinois Department of Chemistry for a departmental fellowship.

OM980434R