

Radical Polymerization of Styrene and Methyl Methacrylate with Ruthenium(II) Complexes

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Received October 21, 2002

Methylation of $[\text{TpRu}(\text{CO})_2(\text{THF})][\text{PF}_6]$ yields the Ru(II) complex $\text{TpRu}(\text{CO})_2(\text{Me})$, and reaction of $\text{TpRu}(\text{CO})_2(\text{Me})$ with Me_3NO in refluxing acetonitrile yields $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCMe})$ (Tp = hydridotris(pyrazolyl)borate). Reactions of $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCCH}_3)$ with $\text{CD}_3\text{-CN}$ indicate that the bound acetonitrile ligand undergoes exchange to yield $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCCD}_3)$, and the rates of the exchange reactions are independent of CD_3CN concentration. At elevated temperatures catalytic quantities of $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCMe})$ in the presence of styrene result in the production of polystyrene. The dependence of polystyrene molecular weight on benzene/cumene molar ratios indicates a radical polymerization mechanism. Styrene polymerization also occurs in the presence of carbon tetrachloride or methyl dichloroacetate. In addition, the polymerization of methyl methacrylate in the presence of $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCMe})$ with carbon tetrachloride or methyl dichloroacetate has been observed at 90 °C.

Introduction

Living polymerization reactions of olefins that incorporate early transition metal catalysts have resulted in significant advances in the polyolefin field due to the ability to control polymer molecular weight, polydispersity, and stereochemistry.^{1–6} However, the intolerance of early transition metal catalysts toward Lewis basic functionality limits the application of early transition metal catalysts in the area of polar olefin polymerization.^{7–13} The development of atom transfer radical polymerization (ATRP) techniques has afforded access to “living” radical polymerization reactions that yield polymers with relatively narrow polydispersities. For example, copper salts are frequently incorporated as catalysts for the ATRP of olefins.^{14–19} In addition,

complexes of iron, molybdenum, rhenium, nickel, palladium, and rhodium have been utilized as radical polymerization catalysts.^{20–30} Recent studies have extended such efforts to include catalysts based on ruthenium.^{31–42}

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Late transition metal systems are typically inactive for olefin polymerization via insertion pathways due to strong metal-to-olefin π -back-bonding or lead to the formation of low molecular weight oligomers as a result of facile β -elimination reactions. However, recent efforts have demonstrated that late transition metal complexes can catalyze olefin polymerization to yield high molecular weight polymers.⁴³ Thus, late transition metal systems can initiate olefin polymerization via competitive pathways (i.e., radical vs insertion), and the electronic nature of the metal center can control the mechanism of olefin polymerization. Herein, we report the synthesis of $\text{TpRu}^{\text{II}}(\text{CO})(\text{NCMe})(\text{Me})$ (Tp = hydridotris(pyrazolyl)borate) and its use as a catalyst for the polymerization of styrene or methyl methacrylate (MMA). $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ could initiate olefin polymerization via a radical or insertion pathway, and evidence consistent with a radical polymerization has been obtained.

Experimental Section

General Methods. All procedures were performed under inert atmosphere (nitrogen) in an Innovative Technologies glovebox or using standard Schlenk techniques. The glovebox atmosphere was maintained by periodic nitrogen purges and monitored by an oxygen analyzer $\{\text{O}_2(\text{g}) < 15 \text{ ppm for all reactions}\}$. Methylene chloride, acetonitrile, and hexanes were purified by passage through a column of activated alumina. THF was purified by passage through a column of activated alumina followed by distillation from sodium/benzophenone and storage over 4 Å molecular sieves. Benzene was purified by distillation from sodium/benzophenone. All solvents were purged with nitrogen for at least 10 min prior to use. Benzene- d_6 was purified by distillation from CaH_2 , degassed, and stored over 4 Å molecular sieves. CDCl_3 and CD_2Cl_2 were degassed via three freeze-pump-thaw cycles prior to use and stored over 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on a General Electric 300 MHz, Varian Mercury 300 MHz, or Varian Mercury 400 MHz spectrometer. All ^1H and ^{13}C NMR chemical shifts are reported in ppm and are referenced to tetramethylsilane using residual proton signals or the ^{13}C signals of the deuterated solvents. Peaks in the ^1H NMR spectra due to pyrazolyl resonances are listed by chemical shift and multiplicity only (all coupling constants are 2 Hz). Infrared spectra were recorded on a Mattson Genesis-II spectrometer as thin films on KBr plates (unless otherwise noted). Gas chromatography was performed on a Hewlett-Packard 5890 GC using a J&W Scientific Cyclosil-B capillary column and a FID detector. GC-FID settings for analysis of styrene: injector temperature, 220 °C; detector temperature, 280 °C; oven temperature, 100 °C; initial temperature, 100 °C; initial time, 2 min; rate, 10 °C/min; final temperature, 130 °C; final time, 2 min. GC-FID settings for analysis of methyl methacrylate: injector temperature, 220 °C; detector temperature, 280 °C; oven temperature, 50 °C; initial temperature, 50 °C; initial time, 3 min; rate, 20 °C/min; final temperature, 130 °C; final time, 2 min. Chromatograms were produced using

a Hewlett-Packard 3396A integrator. Gel permeation chromatography (GPC) analyses of polymer molecular weights was performed on a Jasco system comprised of a PU-1580 HPLC pump, a RI-1530 refractive index detector, and a Borwin-GPC control system. The molecular weight was calibrated with polystyrene standards. Two PL-Gel mixed columns were used for analysis with chloroform at a flow rate of 1.0 mL/min. Electrochemical experiments were performed under a nitrogen atmosphere using a BAS Epsilon potentiostat. Cyclic voltammograms were recorded in a standard three-electrode cell from +2.00 to -2.00 V with a glassy carbon working electrode and tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. All potentials are reported versus NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78 \text{ V}$) as internal standard. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA. KTp and $[\text{TpRu}(\text{CO})_2(\text{THF})][\text{PF}_6]$ were prepared according to previously reported procedures.^{44,45} Styrene was purified by passage through a column of activated alumina under an atmosphere of dinitrogen. Methyl methacrylate was purified via passage through a plug of alumina and vacuum distilled twice over CaH_2 . All other reagents were used as purchased from commercial sources.

Preparation of $\text{TpRu}(\text{CO})_2(\text{CH}_3)$ (1). A THF solution (approximately 50 mL) of $[\text{TpRu}(\text{CO})_2(\text{THF})][\text{PF}_6]$ (2.6642 g, 4.54 mmol) was cooled using an EtOH/liquid nitrogen bath. MeLi (1.6 M in Et₂O, 4.2 mL, 6.7 mmol) was added dropwise to this solution via syringe. The solution turned a dark yellow from bright yellow upon addition of MeLi. After stirring for approximately 15 min, the solution was warmed to room temperature. The solvent was removed in vacuo, and the crude reaction mixture was purified on neutral alumina with flash chromatography (~200 mL of methylene chloride). Volatiles were removed from the eluent in vacuo, and the resulting pale yellow solid was dried under vacuum. The solid was then stirred in hexanes, filtered, and dried under vacuum (1.2482 g, 71%). IR (THF solution): ν_{CO} 2030, 1958 cm^{-1} . ^1H NMR (C_6D_6 , δ): 7.36, 7.28 (3H, 2:1 integration, each a d, Tp CH 3 and 5 position), 7.21 (3H, overlapping d's, Tp CH 3 and 5 position), 5.76, 5.71 (3H, 1:2 integration, each a t, Tp CH 4 position), 0.75 (3H, s, Ru-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 201.3 (CO), 143.7, 142.2, 135.3, 135.0 (Tp 3 or 5 position), 106.2, 105.8 (Tp 4 position), -12.1 (Ru-CH₃). CV (CH_3CN , 100 mV/s): Oxidation and reduction waves were not observed between 2.0 and -2.0 V. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{BN}_6\text{O}_2\text{Ru}\cdot 1/2\text{THF}$ (1/2 molecule of THF was observed in ^1H NMR spectrum of the analysis sample): C, 40.11; H, 3.61; N, 20.05. Found: C, 40.27; H, 4.00; N, 20.32.

$\text{TpRu}(\text{CO})(\text{NCMe})(\text{Me})$ (2). $\text{TpRu}(\text{CO})_2(\text{Me})$ (0.5239 g, 1.36 mmol) and Me_3NO (0.2040 g, 2.72 mmol) were refluxed in approximately 25 mL of acetonitrile for 40 min. The solution was cooled to room temperature, neutral alumina (5 g) was added to the solution, and the volatiles were removed under reduced pressure. The green-yellow crude reaction mixture was flashed on a plug of neutral alumina using methylene chloride (~200 mL). Volatiles were removed from the eluent, and the resulting solid was washed with hexanes to give a white solid. The solid was collected and dried under vacuum (0.3601 g, 67% yield). In addition, the product can be recrystallized from methylene chloride/hexanes. IR (KBr): $\nu_{\text{CO}} = 1919 \text{ cm}^{-1}$, $\nu_{\text{CN}} = 2278 \text{ cm}^{-1}$, $\nu_{\text{BH}} = 2484 \text{ cm}^{-1}$. ^1H NMR (CD_2Cl_2 , δ): 7.73 (3H, overlapping d's, Tp CH 3 and 5 position), 7.71, 7.65, 7.46 (3H, 1:1:1 integration, Tp CH 3 and 5 position), 6.29, 6.25, 6.15 (3H, 1:1:1 integration, each a t, Tp CH 4 position), 2.26 (3H, s, Ru-NCCCH₃), 0.19 (3H, s, Ru-CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 206.7 (CO), 143.4, 142.3, 139.9, 135.3, 134.6 (Tp 3 or 5 position, one overlap), 121.7 (Ru-NCCCH₃), 105.6, 105.3, 105.2 (Tp 4 position), 4.2 (Ru-NCCCH₃), -10.5 (Ru-CH₃). CV

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(CH₃CN, 100 mV/s): $E_{1/2} = 0.95$ V (RuIII/II). Anal. Calcd for C₁₃H₁₆BN₇O₁Ru: C, 39.21; H, 4.05; N, 24.62. Found: C, 39.36; H, 4.04; N, 24.74.

Styrene Polymerizations. In a representative reaction, 20 mg (0.005 mmol) of TpRu(CO)(CH₃)(NCMe) (**2**) was dissolved in approximately 9.2 mL of benzene in a thick-walled pressure tube. Styrene (2.9 mL, 25 mmol) and decane (4.9 mL, 25 mmol) were added to this solution, and the reaction vessel was sealed and heated to 90 °C in an oil bath. Periodically, aliquots of the reaction were analyzed by GC-FID and GPC. Details of polymer preparation for GPC analysis are given below. For reactions in the presence of an alkylhalide, 2 equiv (based on complex **2**) of the appropriate initiator was added prior to polymerization. Polymerization reactions using TpRu(CO)(Ph)(NCMe) were performed using analogous procedures. For reactions in the presence of carbon tetrachloride or methyl dichloroacetate, the initiator (2 equiv) was added before heating.

Polymerization of Methyl Methacrylate. TpRu(CO)(Me)(NCMe) (**2**) (20 mg; 0.005 mmol) was dissolved in 9.4 mL of benzene in a thick-walled pressure tube. Methyl methacrylate (2.7 mL, 25 mmol) and decane (4.9 mL, 25 mmol) were added to this solution, and the reaction vessel was sealed. The reaction mixture was heated to 90 °C in an oil bath. Periodically, aliquots of the reaction were analyzed by GC-FID and GPC. Details of polymer preparation for GPC analysis are given below. For reactions in the presence of carbon tetrachloride or methyl dichloroacetate, the initiator (2 equiv) was added prior to heating.

Sample Preparation for Polymer Analysis by GC-FID and GPC. The homogeneous reaction solution was cooled in an ice bath, purged into a nitrogen-atmosphere glovebox, and an aliquot was removed. A small portion of the aliquot was transferred to a vial, diluted with 10 mL of benzene, and analyzed by GC-FID. Approximately 10 mL of methanol was added to the remainder of the aliquot in order to precipitate the polymer. The supernatant was decanted, and the resulting white solid was collected and dried in vacuo at 60 °C. The dried sample was analyzed by GPC by dissolving approximately 10 mg of the polymer in 1 mL of chloroform.

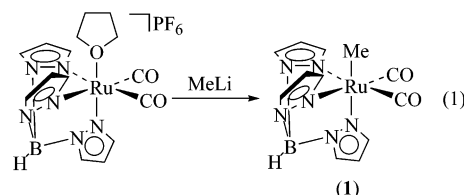
Styrene Reactions with Cumene. In five separate pressure tubes, complex **2** (20 mg, 0.05 mmol) and styrene (2.9 mL, 25 mmol) were combined. Variable amounts of cumene ranging from 0 to 4 equiv (0–100 mmol) were added to each tube, and benzene was added to bring the total solution volume to 5 mL. The resulting solutions were heated to 90 °C for 24 h. After 24 h, the resulting polystyrene was precipitated with methanol, collected via vacuum filtration, dried in vacuo at 60 °C, and analyzed by GPC.

X-ray Diffraction Study of TpRu(CO)(CH₃)(NCCH₃) (3**).** A crystal of dimensions 0.36 × 0.20 × 0.16 mm was selected from a bulk recrystallization from methylene chloride/hexanes. The crystal was mounted on the end of a glass fiber using a small amount of silicon grease and transferred to the diffractometer. Using a nitrogen cold stream, the temperature was maintained at approximately –75 °C. All X-ray measurements were made on an Enraf-Nonius CAD4-MACH diffractometer. The unit cell dimensions were determined by a fit of 25 well-centered reflections and their Friedel pairs with θ between 34° < 2 θ < 36°. An octant of unique data and their Bijvoet pairs were collected using the omega scan mode in a nonbisecting geometry. The adoption of a nonbisecting scan mode was accomplished by offsetting ψ by 20° for each data point collected. The Bijvoet pairs were collected using the negative theta position for the $-h -k -l$ reflection. Three standard reflections were measured every 4800 s of X-ray exposure time. Scaling the data was accomplished using a 5 point smoothed curved routine fit to the intensity check reflections. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ scan data was applied. The structure was solved using

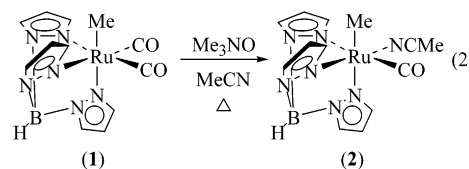
SIR92.⁴⁶ All hydrogen atoms were placed at idealized positions and were allowed to refine isotropically. Refinement of the structure was performed using full matrix least-squares based on F . All non-H atoms were allowed to refine with anisotropic displacement parameters. A secondary extinction correction was included in the final cycles of refinement. The absolute structure was confirmed by both the refinement of the Flack parameter and the analysis of the 200 most sensitive Bijvoet pairs. The molecule exhibited an isomeric disorder in which the positions of the methyl group and the carbonyl group were interchanged. The difference map showed two carbonyl-like groups. The carbon positions for C12 and C13 were intermediate between average bond lengths (using a search of the CSD for similar structural fragments) for Ru–CH₃ and Ru–CO structures. The C–O bond lengths were also slightly short for a CO triple bond. The C12 and C13 positions were allowed to refine anisotropically at full occupancy. During the intermediate refinement cycles the occupancies of the O1 and O2 atoms were allowed to refine and were normalized to 1.0. The oxygen atoms were allowed to refine anisotropically thereafter. The partially occupied methyl hydrogen positions were introduced at idealized positions on both C12 and C13. The occupancies of these hydrogens were made to complement the corresponding oxygen occupancies. These hydrogen atom positions were allowed to ride on the parent carbon shifts. The model refined smoothly with no excessive correlations between the parameters.

Results and Discussion

Methylation of the cationic Ru(II) complex [TpRu(CO)₂(THF)][PF₆] is accomplished upon treatment with MeLi at –100 °C in THF (eq 1). The Ru(II) methyl



complex TpRu(CO)₂(Me) (**1**) can be isolated in approximately 70% yield after column chromatography. NMR data of **1** are consistent with C_s molecular symmetry, as indicated by 2:1 integration patterns for the pyrazolyl rings of the Tp ligand, and the IR spectrum (THF solution) exhibits two CO absorptions at 2030 and 1958 cm⁻¹. The reaction of complex **1** with Me₃NO in refluxing acetonitrile results in oxidative removal of a single CO ligand and coordination of acetonitrile to yield TpRu(CO)(NCMe)(Me) (**2**) in 60–70% yield after workup (eq 2). The conversion of **1** to **2** is indicated by the



appearance of a single CO stretching frequency at 1919 cm⁻¹ using IR spectroscopy. CO stretching frequencies of TpRu(CO)(R)(PPh₃) (R = H, Me, Et, Pr, or Ph) are in the range 1916–1928 cm⁻¹.⁴⁷ ¹H and ¹³C NMR spectra of complex **2** reflect the chiral metal center (i.e., all

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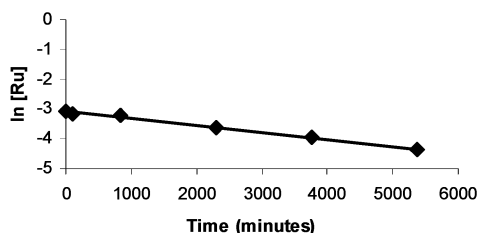


Figure 1. Pseudo-first-order kinetic plot of exchange reaction for $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ (**2**) in the presence of 20 equiv of CD_3CN {50 °C; $[\text{Ru}]$ refers to the concentration of $\text{TpRu}(\text{CO})(\text{Me})(\text{NCCH}_3)$ }.

Scheme 1. Acetonitrile Ligand Exchange Occurs via a Dissociative Mechanism

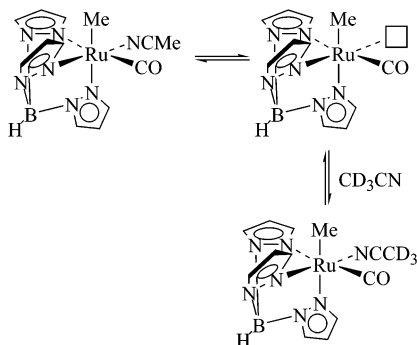


Table 1. Selected Bond Distances (Å) and Angles (deg) for $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCMe})$ (2**)**

Bond Distances			
Ru–N7	2.033(3)	Ru–N1	2.064(3)
Ru–N3	2.166(3)	Ru–N5	2.165(2)
Ru–C12	1.972(4)	Ru–C13	1.967(4)
C12–O1	1.054(8)	C13–O2	1.085(6)
N7–C10	1.133(5)	C10–C11	1.465(6)
Bond Angles			
Ru–N7–C10	172.2(3)	N7–C10–C11	177.1(5)
N1–Ru–N3	86.97(12)	N1–Ru–N5	84.86(14)
N1–Ru–N7	175.31(12)	N3–Ru–N5	84.15(12)
N3–Ru–N7	88.34(12)	N5–Ru–N7	94.65(14)

pyrazolyl rings are inequivalent) with the Ru–Me and acetonitrile methyl groups resonating at 0.19 and 2.26 ppm in the ^1H NMR spectrum, respectively.

Complex **2** undergoes ligand exchange in CD_3CN at 50 °C. The ligand exchange is likely dissociative, as indicated by the zero-order dependence on CD_3CN concentration. For example, monitoring ligand exchange in CDCl_3 with 20, 40, and 80 equiv of CD_3CN yields first-order kinetic plots with nearly identical rate constants ($k = 4.40(4) \times 10^{-6} \text{ s}^{-1}$ at 50 °C). A pseudo-first-order kinetic plot in the presence of 20 equiv of CD_3CN is shown in Figure 1. The dissociative ligand exchange indicates that complex **2** provides access to the coordinatively unsaturated $\{\text{TpRu}(\text{CO})(\text{CH}_3)\}$ fragment (Scheme 1).

A solid-state X-ray diffraction study of **2** confirms its identity (Figure 2). Selected bond distances and angles and data collection parameters are listed in Tables 1 and 2. The molecule exhibited an isomeric disorder in which the positions of the methyl and carbonyl groups were interchanged, and the positions for C(12) and C(13) yield distances that are intermediate for Ru– CH_3 and

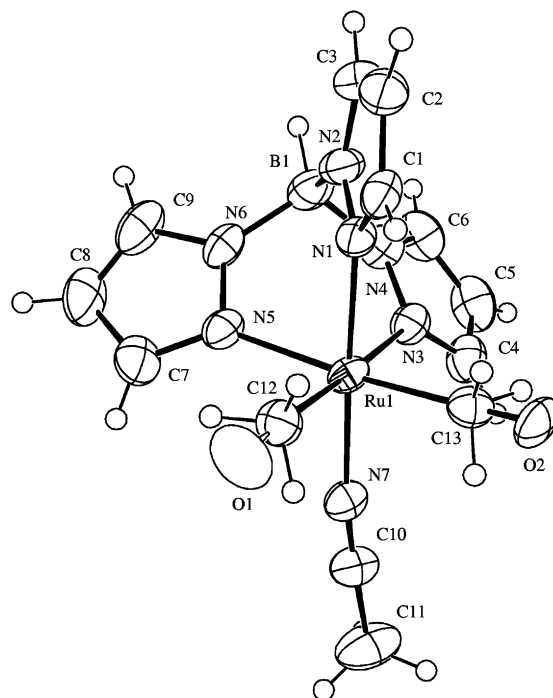


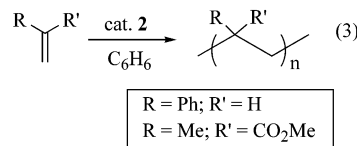
Figure 2. ORTEP diagram of $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ (**2**).

Table 2. Selected Crystallographic Data and Collection Parameters for $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCMe})$ (2**)**

formula	$\text{C}_{13}\text{H}_{16}\text{BN}_7\text{ORu}$
mol wt	398.19
cryst syst	$\text{Pna}2_1$
space group	orthorhombic
<i>a</i> , Å	14.437(5)
<i>b</i> , Å	13.117(3)
<i>c</i> , Å	8.802(3)
<i>V</i> , Å ³	1666.8(9)
<i>Z</i>	4
<i>D</i> _{calcd} , g cm ⁻³	1.587
total no. of reflns	3110
unique reflns	2902
<i>R</i>	0.027
<i>R</i> _w	0.034

Ru–CO bond lengths (see Experimental Section). The Ru to nitrogen bond distance for the bound acetonitrile is 2.033(3) Å. Previously reported Ru–NCMe bond distances range from 2.028(1) to 2.083(1) Å.^{48–50} The Ru–N(7)–C(10) linkage is nearly linear with a bond angle of 172.2(3)°.

Styrene was polymerized with complex **2** as catalyst in benzene at 90 °C (eq 3). For example, heating a



benzene solution of **2** with 500 equiv of styrene results in the isolation of polystyrene after precipitation using MeOH (Table 3). GPC analysis of the polymer isolated

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Table 3. Polymerization Results of Styrene and Methyl Methacrylate Using Complex 2^a

monomer/initiator	reaction time (h)	M_n (g/mol)	M_w/M_n
styrene	24	44404	1.9
styrene	72	16200	2.6
styrene/ CCl_4	72	3373	2.2
styrene/methyl dichloroacetate	72	4691	2.2
neat styrene	24	290443	1.8
MMA	48	788676	1.5
MMA/ CCl_4	48	9748	1.9
MMA/methyl dichloroacetate	48	19553	2.7
styrene ^b	24	74427	1.7

^a Unless otherwise noted, reactions were performed with a 500:1 monomer:2 ratio in benzene at 90 °C. ^b Reaction catalyzed using $\text{TpRu}(\text{CO})(\text{Ph})(\text{NCMe})$.

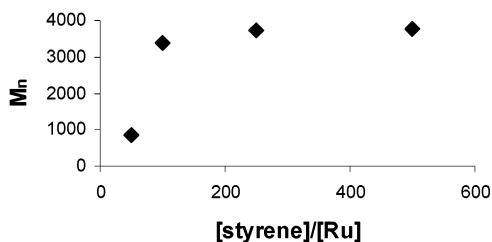
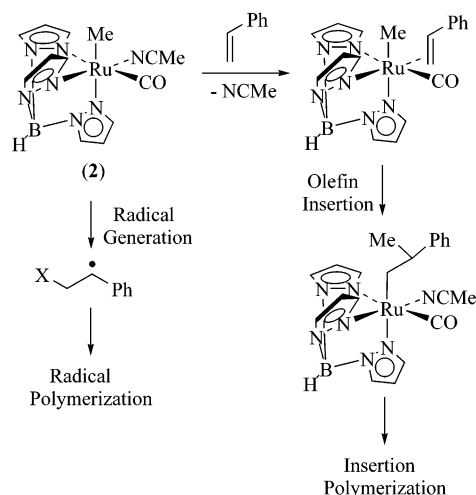


Figure 3. Plot of M_n versus ratio of [styrene]/[catalyst] for the polymerization of styrene at 90 °C in benzene with 2 equiv of CCl_4 (based on catalyst; $[\text{Ru}] = 3 \times 10^{-4}$ M). The polymers were isolated after 24 h of reaction.

after 72 h of reaction reveals $M_w/M_n = 2.6$. Both ^1H and ^{13}C NMR spectroscopy are consistent with atactic polymer. Control reactions in which styrene was heated under identical conditions in benzene in the absence of **2** did not yield polystyrene. In addition, complex **1** does not initiate styrene polymerization. Thus, the Ru(II) complex $\text{TpRu}(\text{CO})(\text{NCMe})(\text{Me})$ (**2**) likely initiates the styrene polymerization. Variation of the [styrene]/[**2**] ratio reveals that lower catalyst loading increases polymer molecular weight; however, the relationship is not linear (Figure 3).

Given the presence of the Ru–methyl bond of complex **2**, the Ru(III/II) potential of 0.95 V (versus NHE), and the lability of the acetonitrile ligand of **2**, we questioned whether the styrene polymerization occurs via a radical mechanism or if the polystyrene forms via olefin binding and insertion into Ru–alkyl bonds (Scheme 2). Other Ru(II) systems that catalyze atom transfer radical polymerization exhibit Ru(III/II) potentials in the range 0.42–0.55 V versus SCE (using a potential for SCE of 0.2444 V versus NHE, the potentials of the Ru(III/II) couples are 0.66–0.79 V vs NHE).³⁵ Thus, single-electron oxidation of complex **2** is more difficult than other Ru(II) systems that initiate radical polymerization via conversion to Ru(III). Brookhart et al. have reported the synthesis of Ru(II) methyl–ethylene complexes that possess diketiminopyridine ligands for which ethylene polymerization reactions do not occur at temperatures up to 70 °C (at 80 °C the slow formation of 1-butene was noted).⁵¹ In contrast, the Ru(II) complex (Pybox)- $\text{RuCl}_2(\text{ethylene})$ (Pybox = 2,6-bis[4*S*-isopropyl-2-oxazolin-2-yl]pyridine) has been reported to polymerize ethylene in the presence of 500 equiv of methylaluminumoxane, and $\text{HRuCl}(\text{PPh}_3)$ polymerizes ethylene and butadi-

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Scheme 2. Radical and Olefin Insertion Mechanisms for Styrene Polymerization

ene.^{52,53} The mechanisms of these transformations are uncertain. In addition, Flood et al. have reported that the Rh(III) complex $[\text{CnRh}(\text{Me})(\text{OH})(\text{H}_2\text{O})]^+$ ($\text{Cn} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane) slowly polymerizes ethylene.⁵⁴ It has been speculated that the presence of a facially coordinating triazacyclononane ligand (Cn) for the Rh(III) system (versus the meridional coordination of the Brookhart diketiminopyridine Ru(II) complex) might play an important role in the ability of the Rh(III) system to catalyze ethylene insertion reactions.⁵¹ Given the presence of the facially coordinating Tp ligand in complex **2** and the isostructural/iselectronic relationship of **2** with $[\text{CnRh}(\text{Me})(\text{OH})(\text{H}_2\text{O})]^+$, the possibility of insertion polymerization reactions seemed feasible. Although the formation of atactic polystyrene is consistent with radical polymerization, it is also potentially consistent with an olefin insertion mechanism in which the polymer stereochemistry would be determined by the facial selectivity of olefin binding.⁵⁵ Fragments of the type $\{\text{TpRu}(\text{CO})(\text{R})\}$ might be expected to exhibit poor stereoselectivity for olefin coordination since closely related $\{\text{TpRe}(\text{CO})(\text{L})\}$ systems exhibit low diastereoselectivity for η^2 -aromatic binding.^{56,57}

The kinetics of chain transfer for radical polymerization of styrene in the presence of various chain transfer reagents have been determined.⁵⁸ Reactions of complex **2** with 500 equiv of styrene in benzene in the presence of 0, 1, 2, 3, and 4 equiv of cumene (based on catalyst concentration) were performed (90 °C). Styrene and catalyst concentrations were kept constant in these reactions. The resulting polymer molecular weights decreased with increasing concentration of cumene (Figure 4). *These results are consistent with a radical polymerization mechanism.*

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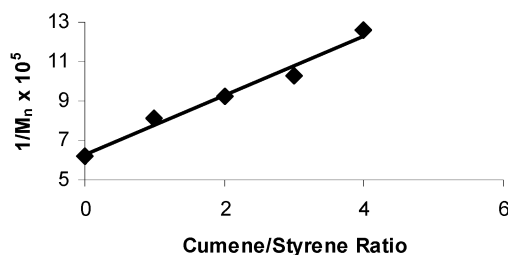


Figure 4. Plot of $1/M_n \times 10^5$ versus molar ratio of cumene/styrene for styrene polymerization catalyzed by $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ (**2**). Reactions were performed with a 500:1 styrene:**2** ratio at 90°C in benzene ($[\text{Ru}] = 3 \times 10^{-4}\text{ M}$), and polymers were isolated after 24 h of reaction.

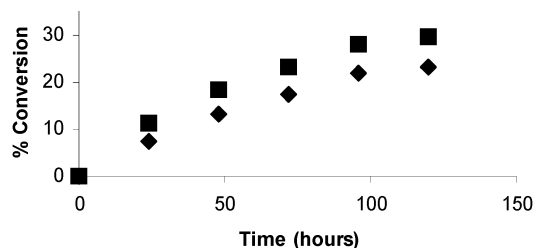


Figure 5. Styrene percent conversion versus time for reaction that is catalyzed by $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ (**2**) in the presence of methyl dichloroacetate (\blacklozenge) or carbon tetrachloride (\blacksquare). Reactions were performed with 500:1 styrene:**2** ratio in benzene at 90°C ($[\text{Ru}] = 3 \times 10^{-4}\text{ M}$).

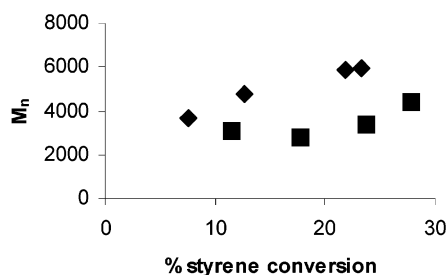


Figure 6. Plot of percent conversion versus M_n for the polymerization of styrene catalyzed by $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ (**2**) in the presence of 2 equiv of methyl dichloroacetate (\blacklozenge) or carbon tetrachloride (\blacksquare). Reactions were performed with 500:1 styrene:**2** ratio in benzene at 90°C ($[\text{Ru}] = 3 \times 10^{-4}\text{ M}$).

Transition metal-mediated radical polymerization reactions can often be controlled via the addition of alkylhalides. Such additives can serve to initiate the polymerization reaction upon metal abstraction of the halogen, and the reversible formation of radicals in such systems keeps the concentration of active radical species low and can afford living polymerizations. Styrene polymerizations were performed in the presence of carbon tetrachloride or methyl dichloroacetate (2 equiv based on complex **2**; Table 3). Figure 5 shows the percent conversion of styrene versus time for both additives, and Figure 6 displays M_n versus percent conversion for polymerizations in the presence of initiators. The polymer molecular weights are lower than for reactions in the absence of alkylhalide (Table 3), and the M_n does not increase linearly with reaction time. Similar observations have been made for other Ru(II)-catalyzed radical polymerizations in the absence of a metal cocatalyst (see below), as has been observed with other Ru-based radical polymerizations of olefins.^{39,59–61}

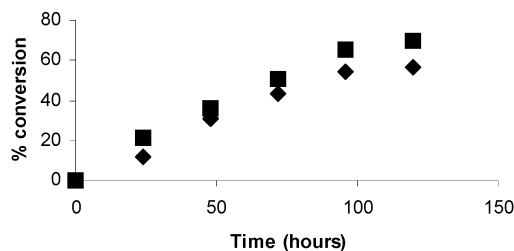


Figure 7. Methyl methacrylate percent conversion versus time for reaction that is catalyzed by $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ (**2**) in the presence of methyl dichloroacetate (\blacklozenge) or carbon tetrachloride (\blacksquare). Reactions were performed with 500:1 MMA:**2** ratio in benzene at 90°C ($[\text{Ru}] = 3 \times 10^{-4}\text{ M}$).

For both initiators, the M_w/M_n ratio is approximately 2.2 after 72 h of polymerization.

Similar to styrene, the combination of 1 mol % of complex **2** with MMA and 2 equiv (based on **2**) of carbon tetrachloride or methyl dichloroacetate results in the formation of poly-MMA. Figure 7 shows the percent conversion of MMA versus time, and consistent with other Ru(II) radical polymerization systems the conversion of MMA is more rapid than analogous polymerizations of styrene. After 48 h of reaction, GPC analysis of the poly-MMA indicates $M_w/M_n = 1.9$ for reactions with carbon tetrachloride and 2.7 for methyl dichloroacetate. Similar to the styrene polymerizations, M_n does not increase linearly with reaction time. The addition of $\text{Al}(\text{O}i\text{-Pr})_3$ (4 equiv based on catalyst) to the polymerization of MMA does not significantly impact polymerization rate, polydispersity, or M_n versus reaction time. The conversion rates of MMA polymerization in the presence of carbon tetrachloride and 2 equiv of $\text{Al}(\text{O}i\text{-Pr})_3$ are almost identical to that in the absence of aluminum cocatalyst. In addition, after 48 h M_w/M_n is 1.8 (cf. 1.9 in the absence of the aluminum reagent).

The detailed mechanism of the radical polymerization reactions remains ambiguous. We have previously reported that **2** reacts with benzene to yield $\text{TpRu}(\text{CO})(\text{Ph})(\text{NCMe})$ and methane,⁶² and the combination of $\text{TpRu}(\text{CO})(\text{Ph})(\text{NCMe})$ with styrene in benzene at 90°C results in the production of polystyrene (Table 3). However, the reaction of $\text{TpRu}(\text{CO})(\text{Me})(\text{NCMe})$ in neat styrene also yields polystyrene. Thus, conversion of the Ru(II) methyl complex to $\text{TpRu}(\text{CO})(\text{Ph})(\text{NCMe})$ is not necessary for polymerization. The only definitive statement that can be made concerning the mechanism is that the polymerization proceeds via a radical rather than insertion mechanism.

Summary and Conclusions

The acetonitrile ligand of the Ru(II) complex $\text{TpRu}(\text{CO})(\text{CH}_3)(\text{NCMe})$ (**2**) is susceptible to ligand exchange reactions at elevated temperatures. Thus, complex **2** can provide access to the coordinatively unsaturated fragment $\{\text{TpRu}(\text{CO})(\text{CH}_3)\}$. Heating a catalytic amount of

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2 with styrene results in the formation of polystyrene. Access to a coordinatively unsaturated metal center and the presence of the Ru–alkyl bond could allow olefin polymerization via olefin binding and insertion into Ru–alkyl bonds. However, reactions in the presence of cumene indicate that the polymerization reactions proceed via a radical mechanism.

Acknowledgment. The National Science Foundation (CAREER Award; CHE 0238167) and North Carolina State University are acknowledged for support of this research. Professor Maurice Brookhart provided

useful discussions, and the research group of Professor Bruce Novak is gratefully acknowledged for use of GPC instrumentation. The authors also wish to thank the National Science Foundation (NSF) for funding (CHE 9509532) to obtain the X-ray diffractometer.

Supporting Information Available: Complete tables of atomic coordinates, anisotropic thermal parameters, complete list of bond distances and angles, and least-squares planes and atomic deviations for TpRu(CO)(Me)(NCMe) (**2**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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