

Ring-Opening Metathesis Polymerization via Ruthenium Complexes of Chelating Diphosphines

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Received November 8, 1999; Revised Manuscript Received January 24, 2000

ABSTRACT: High activity and low polymer polydispersity are found in ring-opening metathesis polymerization (ROMP) of norbornene by ruthenium complexes containing chelating diphosphine ligands. Treatment of compounds with general formula $\text{RuCl}_2(\text{PP})(\text{PPh}_3)$ ($\text{PP} = \text{dppb}$ (**3b**), binap (**3c**), dcyph (**3d**)) or $[\text{RuCl}_2(\text{PP})_2]$ ($\text{PP} = \text{dppb}$ (**4b**)) with PhCHN_2 generates carbene complexes of the type $\text{RuCl}_2(\text{PP})(\text{CHPh})$, which exhibit high ROMP activity *without* halide or phosphine abstraction. Investigations into the role of dissociated PPh_3 have shown that free phosphine acts as a poison, dramatically retarding the rate of polymerization via **3** relative to catalysts derived from **4**.

Introduction

Transition-metal-catalyzed olefin metathesis reactions have received much attention for their power and versatility in C–C bond-forming reactions such as ring-opening metathesis polymerization (ROMP), ring-closing metathesis (RCM), and acyclic diene metathesis (ADMET).¹ Among the catalysts in use for such processes, ruthenium complexes of monodentate phosphines have attained a high profile, owing to their robustness and functional group tolerance. Recent advances in diversifying the Ru ligand scaffold, including examples of bidentate Schiff bases,² allylic groups,³ Wanzlick–Arduengo carbenes,⁴ hydridotris(pyrazolyl)borate, Cp, and Cp*,⁵ have augmented the utility of Ru-based metathesis catalysts.

To date, a single experimental study in the burgeoning ROMP literature focuses on chelating diphosphine complexes of Ru.⁶ The potential scope of this approach, which affords a direct extension of the exceptionally diverse metathesis chemistry of Grubbs' catalyst $\text{RuCl}_2(\text{PR}_3)_2(\text{CHR})$ (**1a**, $\text{R} = \text{Cy}$; **1b**, $\text{R} = \text{Ph}$),⁷ is underlined by the plethora of readily accessible chelating diphosphines, including chiral versions, that have been used to remarkable effect in asymmetric catalysis. Despite the prominent place of such complexes of ruthenium in, for example, asymmetric hydrogenation, Ru ROMP lags far behind Mo-catalyzed ROMP in terms of definition of the active site (the ultimate expression of which is stereocontrolled polymerization). The neglect of this potentially rich area stems in part from the well-established requirement for phosphine loss in ROMP via catalysts of type **1**,⁸ reinforced by a report describing the complete inactivity of $\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2$ ($\text{R} = \text{Ph}$, Pr^i) ligands⁹ within the $\text{RuCl}_2(\text{arene})_2/\text{TMSCHN}_2$ system. (The latter result, however, is almost certainly an artifact of the *in situ* catalyst synthesis. The overwhelming tendency of phosphines affording five-membered Ru chelates to disproportionate into well-characterized, very unreactive $\text{RuCl}_2(\text{PP})_2$ species, long established for $\text{RuCl}_2(\text{PPh}_3)_3$,¹⁰ was more recently demonstrated with $\text{Ru}_2\text{Cl}_4(\text{arene})_2$ complexes.¹¹) Hofmann's recent demonstration of ROMP activity via complexes of the type $\text{RuCl}_2(\text{PP})(\text{CHR})$ (**2a**, $\text{PP} = \text{bis}(\text{di-}t\text{-butylphosphino})\text{-methane}$, dtbpm) is thus a breakthrough in this field.⁶ A notable requirement in this system, however, is the

requirement for chloride loss in order to attain high activity. Much of the gain in definition of the metal coordination sphere resulting from use of a chelating diphosphine is thereby lost. We now report the development of a family of highly active ROMP catalysts of type **2**, which exhibit high polymerization activity without phosphine or halide abstraction and which afford polymers characterized by very low polydispersities.

Experimental Section

Materials. 1,4-Bis(diphenylphosphino)butane (dppb), 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (binap), dicyclohexylphosphine (HPCy₂), and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ were purchased from Strem. Norbornene was purchased from Aldrich and distilled from sodium under N_2 . Methanol was distilled from $\text{Mg}(\text{OCH}_3)_2$ under N_2 and stored over Linde 4 Å molecular sieves. 1,4-Dibromobutane was purchased from Aldrich and used as received. CDCl_3 and C_6D_6 were dried over activated sieves (Linde 4 Å) and degassed by consecutive freeze/pump/thaw cycles. Phenylhydrazomethane, PhCHN_2 ,¹² benzaldehyde tosylhydrazone,¹² 1,4-bis(dicyclohexylphosphino)butane (dcyph),¹³ $\text{RuCl}_2(\text{dppb})(\text{PPh}_3)$,¹⁰ $\text{RuCl}_2(\text{binap})(\text{PPh}_3)$,¹⁴ $\text{Ru}_2\text{Cl}_4(\text{dppb})_2$,¹⁴ and $\text{RuCl}_2(\text{dcyph})(\text{PPh}_3)$ ¹⁵ were prepared according to literature procedures.

Techniques. All manipulations were carried out under N_2 using standard Schlenk or drybox techniques. ^1H NMR (200 MHz) spectra were recorded on a Varian Gemini 200 MHz spectrometer. Chemical shifts are listed downfield from TMS in parts per million and were referenced to the residual solvent proton peak. ^{31}P NMR (121.4 MHz) spectra were recorded on a Varian XL-300 MHz spectrometer and reported relative to 85% aqueous H_3PO_4 . Gel permeation chromatography (GPC) data were obtained with THF as eluent (flow rate 1.0 mL/min; samples 1–2 mg/mL) using an HPLC system equipped with a Waters model 610 pump, a Rheodyne model 7125 injector with a 100 μL injection loop, Waters HR-4, HR-6, and HR-3 columns in series, and a Waters model 410 diffraction refractometer. Molecular weights and polydispersities are reported versus commercially available polystyrene standards ranging from 1.3×10^3 to 3.15×10^6 g/mol MW. Computational results were obtained using software programs from Molecular Simulations Inc. Dynamics calculations were carried out with the Discover programs, using the OFF force field; graphical displays were generated using the Cerius² molecular modeling system.

***t,t*-Benzaldehyde Azine.** To a stirring solution of sodium (0.420 g, 18.3 mmol) in triethylene glycol (23 mL) at 65 °C was added benzaldehyde tosylhydrazone (0.25 g, 9.1 mmol). The solution was stirred for 24 h. Addition of 20 mL of cold distilled water afforded a yellow precipitate, which was filtered

Rates of polymerization are strongly dependent on phosphine bulk and basicity (Figure 2), as in the monodentate systems of type **1**.⁸ Thus, the strongly basic dcyphb catalyst system was most active in the series examined. The decreased reactivity of **3c**/PhCHN₂ is expected on the basis of the greater bulk and rigidity of the binap ligand. The latter system, though slower, was of particular interest for its potential control over polymer microstructure. It yields a notably low propor-

Table 1. Ru-Catalyzed ROMP of Norbornene^a

precursor	M_n	yield (%)	M_w/M_n	trans (%)
2a ^{6b}	n/a	55	2.75	71
3b	90 900	100	1.05	81
3c	102 000	96	1.06	68
3d	188 300	100	1.16	83
4b	80 000	100	1.11	75

^a Reaction conditions: norbornene/Ru = 200, PhCHN₂/Ru = 5, [Ru] = 0.0015 M, 24 h; GPC measured by refractometry vs polystyrene standards.

tion of trans-olefinic linkages for Ru-catalyzed ROMP: the found value of 68% is the lowest in the systems under investigation and represents a drop of 22% relative to that obtained with **1** (R = Ph).⁷ Unlike early-metal catalysts, which give preferentially cis-olefins, virtually all Ru ROMP systems yield *principally* trans-linkages (though at least 10% cis-olefin is invariably obtained). We attribute this phenomenon to the larger size of the late metal and the low degree of steric definition characteristic of existing Ru catalysts, which accommodates expression of the steric preference of the growing chain. The lower proportion of trans-olefin in poly(norbornene) prepared via **3c** is consistent with increased spatial definition of the active site.

ROMP catalysts **1** and **2a**, despite their coordinative unsaturation, require ligand loss in order to attain high polymerization activity. Thus, rate accelerations have been reported for polymerization via **1a** following addition of CuCl as a phosphine scavenger (though catalyst lifetimes were decreased)⁸ and for ROMP via **2a** on addition of trimethylsilyl triflate as a halide scavenger.^{6b} In sharp contrast, we find an approximately 5-fold rate decrease for ROMP via **4b**/PhCHN₂ in the presence of either halide or phosphine scavengers (AgPF₆ and CuCl, respectively). Addition of 1 equiv of CuCl to the **3b**/PhCHN₂ catalyst system has a marked accelerating effect. This is due to removal of free PPh₃ generated via equilibrium (2),¹⁰ as indicated by the near identity of this rate curve with that observed for ROMP via isolated¹⁴ **4b** and PhCHN₂ (vide infra).

The implied poisoning effect of PPh₃ is examined in more detail below. The absence of any rate acceleration in this CuCl experiment, relative to experiments with **4b**/PhCHN₂, suggests, however, that ROMP is not mediated in our systems by a complex containing a "dangling" dppb ligand that could compete with free PPh₃ for complexation of CuCl.

The broad polydispersities found for **2a** (M_w/M_n = 2.75), a function of the higher rate of propagation than initiation,^{6a} are consistent with a preequilibrium involving halide loss. In the present work, markedly low polydispersities are measured for the polymer products (Table 1), supporting the inference that no preequilibrium—whether dechelation to give a "dangling" phosphine or loss of halide—is required to generate the catalytically active species. The catalytic competence of systems **2b–d** is perhaps less surprising than the requirement for ligand loss in **1** and **2a**: the discrepancy suggests a barrier to monomer coordination or to isomerization to place monomer cis to the carbene, which inhibits productive metathesis in the latter systems. The bulk of the trans-phosphine substituents in **1** may be implicated; modeling suggests that small chelate size and rigidity are also factors for **2a**.

The convenience of in situ catalyst generation is frequently undermined by unanticipated side reactions. Potential interference by "contaminating" PPh₃, PhCHN₂

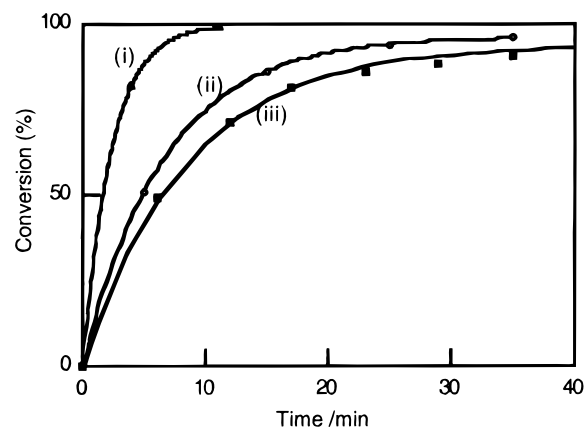
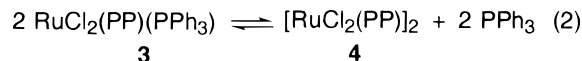


Figure 3. Dependence of ROMP activity of **4b**/PhCHN₂ on diazoalkane:Ru ratio: (i) 1 equiv of PhCHN₂ per Ru; (ii) 0.5 equiv of PhCHN₂ per Ru; (iii) 5 equiv of PhCHN₂ per Ru.

(used in excess in our standard ROMP procedures), and *t,t*-PhCHN=NCHPh (formed in trace amounts in the synthesis of PhCHN₂) was therefore assessed.

Dimers [RuCl₂(PP)]₂ (**4**) exist in spectroscopically observable equilibrium¹⁰ with **3** (eq 2), much of the



chemistry of which they mediate. Catalysis via isolated¹⁴ **4** permits evaluation of the activity of **2** unperturbed by PPh₃. The **4b**/PhCHN₂ catalyst system is approximately 5 times more active than **3b**/PhCHN₂ (Figure 1). Addition of PPh₃ (2 equiv) to solutions of **4b** and norbornene after ROMP has been initiated with PhCHN₂ reduces the rate of polymerization by more than an order of magnitude, implying that poisoning of **2b** by free PPh₃⁸ is implicated in the lower activity of **3b**/PhCHN₂. Competition of free PPh₃ with diazoalkane for the metal center in **4b** is improbable: despite the fact that equilibrium (1) lies strongly in favor of **3b**, the active catalyst is rapidly formed, as evidenced by the absence of an induction period in Figure 1. The amplified metathesis activity of systems derived directly from **4** is of particular interest given the popularity of in situ methods in Ru ROMP and RCM.

Also relevant to such efforts is the often-overlooked effect of diazoalkane concentration (Figure 3). Decreasing the PhCHN₂:Ru ratio from 5:1 to 1:1 in ROMP via **4b** causes a sharp increase in activity, effecting complete polymerization within less than 10 min. The implied attack of phenyldiazomethane on the Ru—carbene unit is supported by the appearance of an increased proportion of stilbene in the ¹H NMR spectrum for the 5:1 experiment. The rate of reaction of **2b** with PhCHN₂ must be slower than attack of norbornene itself, however, as the 5:1 system still shows high ROMP activity (Figure 2). A similar inverse dependence on diazoalkane concentration was reported for the allylruthenium(IV)/EtCO₂CHN₂ system.³ This is unsurprising given the relative bulk of PhCHN₂ and the monomer itself; competing attack of diazoalkane on the [Ru=CHR] moiety is likely to be a complicating factor whenever diazoalkane is used in excess. Finally, use of 1/2 equiv of PhCHN₂ per Ru causes a rate decrease relative to a 1:1 ratio, supporting the formulation **2** versus a Ru₂—monocarbene alternative.¹⁸ It should be noted that while PhCHN₂ can in principle act as a phosphine scavenger

via ylide formation, this reaction is very slow relative to the rate of polymerization.

Synthesis of PhCHN_2 results in coproduction of trace amounts of Ph(H)C=N-N=C(H)Ph , removal of which is precluded by the instability of the diazoalkane. Azine poisoning studies were undertaken to assess the effect of this potentially coordinating ligand. Reaction of **4b** with isolated azine is very slow: no reaction is observed at room temperature over 24 h in solution, even at equimolar concentrations. Consistent with this, ROMP via **3b** or **4b** in the presence of azine (1 equiv per Ru) shows no deterioration in rate. Interference by this common contaminant may be problematic for less active catalysts, or unreactive monomers, where more forcing conditions are required. Thus, gentle thermolysis (50 °C) of **4b** with 1 equiv of azine generates a complex ^{31}P NMR pattern, and a benzonitrile derivative of ruthenium has been crystallographically analyzed. Details of the coordination chemistry will be reported separately.¹⁹

Conclusions

The foregoing demonstrates the first example of ROMP via Ru-phosphine complexes that do not require ligand abstraction in order to achieve high activity. Exceptionally narrow polydispersities are obtained, as well as, in the case of the binap derivative, a high proportion of cis-olefin linkages. Triphenylphosphine and excess diazoalkane emerge as potent catalyst poisons in these systems. Current investigations focus on structural refinements that limit decomposition and enhance stereoselective metathesis.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation (CFI), and the Ontario Research and Development Challenge Fund (ORDCF) for financial support.

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MA9918856