Highly Efficient Ring-Opening Metathesis Polymerization (ROMP) Using New Ruthenium Catalysts Containing N-Heterocyclic Carbene Ligands**

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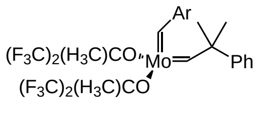
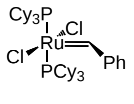
Ring-opening metathesis polymerization (ROMP) has become an effective tool for the preparation of a wide variety of macromolecular architectures.[1] To date, the most widely used catalysts for ROMP and other metathesis reactions are the well-defined complexes based on molybdenum[2] (**1**) and ruthenium[3] (**2**). The former complex displays much higher activity than the latter, thus permitting polymerization of many sterically hindered or electronically deactivated cyclic olefins.[1a, 2] However, the latter catalyst is stable under ambient conditions and tolerates a much larger range of protic and polar functional groups including alcohols, acids, and aldehydes.[1a, 4]



1: Ar=C_6H_3-2,6-(*i*Pr)



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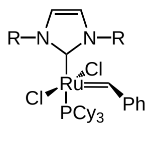
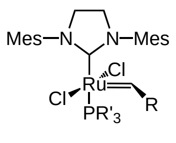


3a: R=*i*Pr or Cy
3b: R=mesityl (Mes)



4a: R=Ph, R'=Cy
4b: R=$CHC(CH_3)_2$, R'=Cy
4c: R=$CHC(CH_3)_2$, R'=Cp

Replacement of one of the phosphane ligands with a more electron-donating N-heterocyclic carbene ligand produced ruthenium complexes **3a**,**b** which displayed dramatically improved metathesis activity, thermal stability, and inertness towards oxygen and moisture when compared to **2**.[5] Recently, complexes[6, 7] **4a**–**c** have been prepared which utilize N-heterocyclic carbene ligands with saturated backbones. These complexes display catalytic activity in ring-closing metathesis[6–8] (RCM) and cross-metathesis[7, 9] (CM) that not only exceed that of **3a**, **b** in many cases, but also begin to rival molybdenum complex **1**, while maintaining the functional group compatibility of **2**. Herein, we report that complexes **3a**, **b** and **4a**–**c** are *more active* than **1** in ROMP and demonstrate their utility in the synthesis of a variety of polymeric structures.

An effective method for comparing relative activities between various catalysts is through monitoring the ROMP of a low-strain cyclic olefin such as *cis*,*cis*-cycloocta-1,5-diene (COD).[5c–d, 10, 11] The ROMP of COD was initiated with **1**, **3b**, and **4a**–**c** and the percent monomer converted to polymer was monitored over time using ^{1}H NMR spectroscopy (Figure 1).[12] The polymerization rate of COD when initiated with **4a** was found to be significantly higher than when initiated with the molybdenum complex **1** at 20 °C. In addition to activity trends observed in RCM and CM,[6–9] complex **4a**, which contains a saturated N-heterocyclic carbene ligand, also displayed increased activity in ROMP relative to its unsaturated analogue (**3b**). When elevated temperatures (50 °C) were employed, complexes **3b**, **4b**, and **4c** also exhibited activities greater than **1** (Figure 2). Interestingly, the activity of the various ruthenium complexes appears to be related to both the phosphane ligands and alkylidene moiety substitution. For example, the discrepancy in polymerization rates between **4a** and **4b** may be related to the initiation rate,[13]

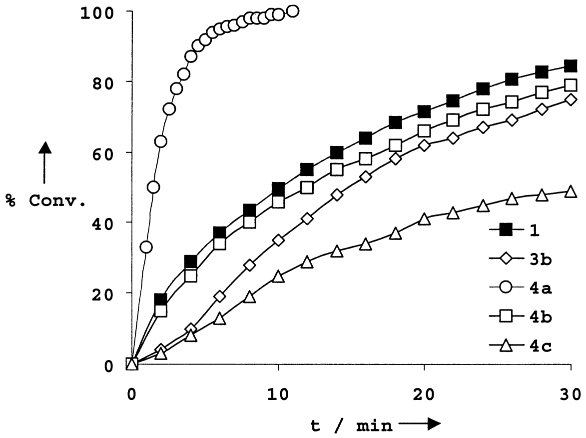


Figure 1. ROMP of COD using catalysts **1**, **3b**, and **4a**–**c**. Conditions: 20 °C, monomer/catalyst ratio 300:1, [catalyst] = 0.5 mM, CD_2Cl_2 as solvent. Conversion determined by ^{1}H NMR spectroscopy.

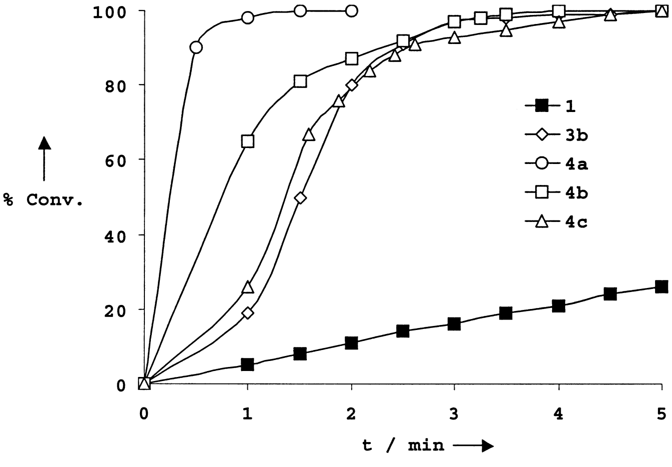


Figure 2. ROMP of COD using catalysts **1**, **3b**, and **4a**–**c**. Conditions: 50 °C, monomer/catalyst ratio 300:1, [catalyst] = 0.5 mM, CD_2Cl_2 as solvent. Conversion determined by ^{1}H NMR spectroscopy.

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[**] C.B. is grateful to the National Science Foundation for a pre-doctoral fellowship. The authors thank Dr. Matthias Scholl for providing catalysts **4a** and **4c**.

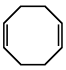
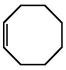
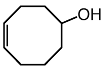
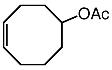
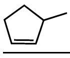
since the propagating species resulting from both catalysts is identical. Thus, the bulkier benzylidene ligand may facilitate phosphane dissociation to a greater extent than the dimethylvinyl carbene ligand, thereby enhancing initiation. In addition, the bulkier tricyclohexyl phosphane (PCy_3) in **4b** may dissociate to a higher degree than the tricyclopentyl phosphane (PCp_3) in **4c**,[14] thereby providing a relatively higher concentration of the highly active (phosphane dissociated) species.

As shown in Table 1, catalysts **4a**–**c** polymerized a variety of low-strain cyclic olefins with extremely low catalyst loadings (up to a monomer/catalyst ratio of 100000).[15] In agreement with the results obtained above, elevated temperatures (50 °C) generally increased the yields of polymer while reducing reaction times. Monomers such as 5-hydroxy- or 5-acetoxycyclooctene were also efficiently polymerized, providing access to polymers with a high degree of backbone functionality.[16, 17] In general, ^1H NMR spectroscopy indicated a predominately (75–95%) *trans*-olefin microstructure in these polymers. As expected for an equilibrium-controlled polymerization in which chain transfer occurs, longer polymerization times resulted in higher *trans*-olefin values.[1a]

Close examination of Table 1 reveals that these highly active ruthenium systems do not form well-defined polymeric structures.[1a] The polydispersity indices (PDIs) of the resulting polymers are relatively high and strongly suggest that significant chain transfer occurred during the polymerization. The percent *trans* olefin in the polymer backbone gradually increased with time which suggests that secondary metathesis isomerizations are also occurring. In addition, monitoring the ROMP of COD (50 equivalents) using catalyst **4a** by ^1H NMR spectroscopy (CD_2Cl_2, 25 °C) indicated that less than 5% of the catalyst initiated before the ROMP was complete (<1 min). After 15 min at 55 °C, complete conversion of unreacted initiator to propagating species ($\delta = 18.60$) through chain transfer was observed. The slow initiation rate explains the relatively high experimental molecular weights when compared to their theoretical values (based on initial monomer/catalyst ratios).

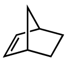
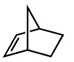
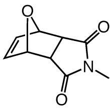
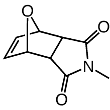
However, the molecular weights were easily regulated through the inclusion of acyclic olefins which effectively act as chain transfer agents (CTAs; Table 1).[1] This technique is extremely useful when poorly soluble polymers are obtained by polymerizing monomers such as cyclooctene in bulk. Including functionalized CTAs during the ROMP of cyclic olefins has been shown to afford end-functionalized (telechelic) polymers,[18] which are useful as intermediates in the syntheses of triblock copolymers and in the formation of polymeric networks.[19] Owing to its high functional group tolerance, complex **2** has been the catalyst of choice when preparing telechelic polymers using this approach; however, only low-strain monomers have been used.[1a, 18] When 1,4-diacetoxy-2-butene was included as a CTA during the **4a**-catalyzed ROMP of highly strained monomers such as norbornene (**5**) and *N*-methyl-7-oxanorbornenedicarbimide (**6**),[20] acetoxy end-terminated polymer was obtained (Table 2). Excellent agreement between theoretical and experimental molecular weights (based on the initial monomer/CTA ratio) were observed when norbornene was employed as the monomer and led to the formation of bis(acetoxy) end-terminated polymer. However, in the case of the oxanorbornene derivative **6**, the CTA did not completely incorporate and produced polymer with a higher-than-expected molecular weight. The monomer is a cyclic ether that may coordinate to the catalyst and sufficiently attenuate its ability to transfer polymer chains. Nevertheless, the molecular weight could still be regulated and an acetoxy endgroup was observed on the polymer chains. These results are particularly notable since end-functionalized polymers composed of highly strained monomers are relatively difficult to obtain using other methods. For example, a metathesis degradation approach using tungsten-based metathesis catalysts has been used to prepare telechelic poly(oxanorbornene)s and poly(norbornene)s.[21] However, the catalyst's tolerable range of func-

Table 1. ROMP of various low-strain cyclic olefins.[a]

Monomer	M/C[b]	T [°C]	t [h]	Yield [%]	M_n[c]	PDI[c]	*trans* [%][d]
	100000	55	0.5	85	112400	2.3	70
	10000	25	24	85	92900	2.5	85
	25000[e]	55	24	89	10700	2.1	90
	100000	55	< 0.1	[g]	[g]	[g]	[h]
	10000	25	0.5	[g]	[g]	[g]	[h]
	25000[e,f]	55	24	75	2200	1.6	85
	100000	55	< 0.1	[g]	[g]	[g]	[h]
	10000	25	0.5	[g]	[g]	[g]	[h]
	25000[e,f]	55	24	85	2600	2.3	85
	10000	55	< 0.1	50	103900	2.8	85
	1000	25	1	60	79300	3.2	90
	1000	25	24	50	23000	2.5	50
	1000	25	24	52	9000	2.5	90

[a] Bulk polymerizations using catalyst **4c**. Catalyst **4a** gives similar results. [b] Initial monomer/catalyst ratio. [c] Determined by CH_2Cl_2 or THF GPC and results are reported relative to poly(styrene) standards. [d] Percent *trans* olefin in the polymer backbone, as determined by ^1H and ^{13}C NMR analysis. [e] 1,4-Diacetoxy-cis-2-butene was included as a CTA. Monomer/CTA ratio 80:1. [f] Monomer/CTA ratio 10:1. $[\text{Monomer}]_0 = 4.5\,\text{M}$ in $C_2H_4Cl_2$. [g] Polymer was insoluble. [h] Not determined.

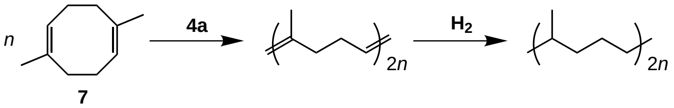
Table 2. Synthesis of acetoxy end-terminated polymers composed of highly strained monomers.[a]

Monomer	M/CTA[b]	Yield [%]	X_n (NMR)[c]	M_n (GPC)[d]	PDI[d]
 **5**	5	95	6	800	2.0
 **5**	20	97	20	2100	2.0
 **6**	1	90	[e]	4200	2.0
 **6**	10	98	[e]	12500	1.9

[a] General polymerization conditions: $T = 55\,°C$; 12 h; $C_2H_4Cl_2$ as solvent; $[\mathbf{4a}]_0 = 10-30$ mM; [monomer] = 3–5 M; nitrogen atmosphere. 1,4-bis(acetoxy)-*cis*-2-butene was included as CTA. [b] Initial monomer/CTA ratio. [c] Average number of monomer units per polymer chain. Determined by endgroup analysis using ^1H NMR spectroscopy and assumes the number of functional groups per polymer chain is exactly two. [d] Determined by CH_2Cl_2 GPC and results are reported relative to poly(styrene) standards. [e] Not determined.

tional groups limits the choice of CTAs. The "pulsed addition" approach has also been employed using catalysts **1** and **2**, but requires carefully timed additions of monomer and/or CTA, thereby reducing the ease of performing these polymerizations.[22]

As shown in Scheme 1, **4a** initiated the ROMP of 1,5-dimethyl-1,5-cyclooctadiene (**7**),[23] a sterically hindered, trisubstituted cyclic olefin, affording poly(isoprene) ($M_n = 10000$, PDI = 2.3) in 90% yield (monomer/catalyst ratio 1000:1, 55 °C, 24 h). Subsequent hydrogenation using *p*-toluenesulfonhydrazide as the hydrogen source afforded an ethylene–propylene copolymer (as determined by NMR analysis) in quantitative yield.[24] Previously, a six-step synthesis was necessary to obtain a similar copolymer by a metathetical route.[25] To the best of our knowledge, this is the first ROMP of this monomer.



Scheme 1. Synthesis of an ethylene–propylene copolymer by ROMP of 1,5-dimethyl-1,5-cyclooctadiene (**7**) followed by hydrogenation.

We have demonstrated that complexes **4a–c** are high-performance ROMP catalysts that can be used to synthesize a variety of polymeric materials including functionalized, telechelic, and trisubstituted polymers. Importantly, these catalysts are late transition metal complexes and demonstrate high functional group tolerance. Through careful tuning of the ligand environment and reaction conditions, these catalysts display metathetical activity that exceeds both previous ruthenium-based catalysts and the early transition metal catalyst **1**.

Received: March 9, 2000 [Z14828]

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[4] Initial investigations using $RuCl_3$ salts as metathesis catalysts demonstrated the high functional group tolerance of ruthenium, see: a) H. H. Thoi, K. J. Ivin, J. J. Rooney, *J. Mol. Catal.* **1982**, *15*, 245–270; b) B. M. Novak, R. H. Grubbs, *J. Am. Chem. Soc.* **1988**, *110*, 960–961.

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[12] The molybdenum catalyst **1** was purchased from Strem Chemicals and recrystallized from pentane at −40 °C prior to use. For the ROMP kinetics experiments, COD and CD_2Cl_2 were distilled from CaH_2 and degassed prior to use. The ruthenium catalysts **3** and **4** were prepared as previously reported.[5–7] All polymerizations were performed under an atmosphere of nitrogen.

[13] A similar observation is obtained when comparing the ROMP activity of **2** (~300 equiv COD per hour) and its dimethylvinyl carbene derivative (~200 equiv COD per hour, catalyst structure not shown).

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[16] Polymers of this type have been prepared by using **2**, see: M. A. Hillmyer, W. R. Laredo, R. H. Grubbs, *Macromolecules* **1995**, *28*, 6311–6316.

[17] Other functionalized cyclooctenes have been polymerized by using a cyclometalated aryloxy(chloro)neopentylidenenetungsten complex, see: a) J.-L. Couturier, C. Paillet, M. Leconte, J.-M. Basset, K. Weiss, *Angew. Chem.* **1992**, *104*, 622–624; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 628–631; b) J.-L. Couturier, K. Tanaka, M. Leconte, J.-M. Basset, J. Ollivier, *Angew. Chem.* **1993**, *105*, 99; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 112–115.

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[23] The 1,5-dimethyl-1,5-cyclooctadiene (**6**) employed in this study contained 1,6-dimethyl-1,5-cyclooctadiene (20%) as an inseparable mixture.

[24] The ethylene–propylene copolymer obtained was not "perfectly" alternating because of the impurity in 1,5-dimethyl-1,5-cyclooctadiene (**6**).[25] We believe that if pure **6** was polymerized, the poly(isoprene) obtained would have perfectly alternating head-to-tail microstructure, since trisubstituted alkylidenes have not been observed to form. Thus, a perfectly alternating ethylene–propylene would be obtained after hydrogenation.

[25] Z. Wu, R. H. Grubbs, *Macromolecules* **1995**, *28*, 3502–3508.

The Phenylsulfonyl Group as an *endo* Stereochemical Controller in Intramolecular Pauson–Khand Reactions of 3-Oxygenated 1,6-Enynes**

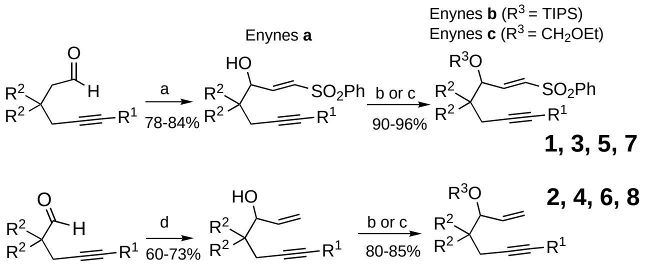
Javier Adrio, Marta Rodríguez Rivero, and
Juan C. Carretero*

Dedicated to Prof. José Barluenga
on the occasion of his 60th birthday

The intramolecular Pauson–Khand (PK) reaction of enynes has become one of the most powerful tools for the construction of cyclopentenone-fused bicyclic compounds. In particular, due to the reliability and efficiency of the cyclization of 1,6-enynes, this reaction has been widely applied to the synthesis of complex products with bicyclo[3.3.0]octane skeletons.[1] In the case of 3-substituted 1,6-enynes, it is well known since the pioneering work of Magnus et al.[2] that the reaction occurs with moderate to high *exo* stereoselectivity[3] (the substituent at the allylic position on the starting enyne ends up on the less sterically crowded *exo* face of the bicyclic product).

Although it is generally assumed that electron-poor alkenes are unsuitable substrates for PK reactions,[1, 4] we recently reported that certain 1-sulfinyl-1,6-enynes undergo intramolecular PK cyclizations in acceptable yields and in a highly stereoselective manner.[5] Encouraged by these results, we envisioned the use of other electron-poor sulfur-substituted olefins, such as vinyl sulfones.[6] Here we report that the readily available racemic or enantiopure 1,6-enynes with γ-oxygenated α,β-unsaturated phenylsulfone structures are not only excellent substrates in intramolecular PK reactions, but also that cyclization takes place with a reversal selectivity, that is, *endo* instead of *exo* selectivity.[7]

Following our usual method of synthesis of (E)-γ-hydroxy-α,β-unsaturated phenyl sulfones,[8] several differently substituted 1-phenylsulfonyl-3-hydroxy-1,6-enynes (substrates **1a**, **3a**, **5a**, and **7a**[9]) were prepared in one step by the piperidine-promoted condensation of the corresponding aldehydes with phenylsulfonyl p-tolylsulfinylmethane in acetonitrile at 0°C (78–84% yield, Scheme 1). Next, to study the effect of substitution at the γ-position, the hydroxy group of these enynes was protected as the triisopropylsilyl (TIPS) ether (substrates **b**) and ethoxymethyl ketal derivatives (substrates **c**). To evaluate precisely the effect of the sulfonyl group on the reactivity and stereoselectivity of the PK reaction, the corresponding 1-unsubstituted 3-oxygenated 1,6-enynes were readily prepared by addition of vinylmagnesium bromide to the appropriate aldehyde (synthesis of alcohols **2a**, **4a**, **6a**, and **8a**[9]) followed by protection of the hydroxy group (substrates **2b–c**, **4b–c**, **6b–c**, and **8b–c**) (Scheme 1).



Scheme 1. Synthesis of the starting 1,6-enynes **1**–**8**. a) $PhSO_2CH_2SOTol$, piperidine, CH_3CN, 0°C; b) TIPSOTf, 2,6-lutidine, CH_2Cl_2, RT; c) $ClCH_2OEt$, DIPEA, CH_2Cl_2, RT; d) vinylmagnesium bromide, THF, −78°C. TIPSOTf = triisopropylsilyl trifluoromethanesulfonate; DIPEA = N,N-diisopropylethylamine.

Table 1 summarizes the results of the PK cyclizations of enynes **1**–**8** under the usual conditions with an amine N-oxide promoter:[10] initial formation of the alkyne dicobalt complex by reaction with $[Co_2(CO)_8]$ in CH_2Cl_2 at room temperature followed by addition of 6 equiv of trimethylamine N-oxide (TMANO). Incomplete conversion was observed under these standard conditions with enynes **7**, and so the reaction was performed in the presence of TMANO and molecular sieves[11] (entries 15, 17, and 19).

Remarkably, in spite of the electron-poor character of the C=C double bond of the vinyl sulfones **1**, **3**, **5**, and **7**, these compounds reacted completely after 2–3 h to give the corresponding bicyclic PK adducts, in most cases as the only detectable compounds (^{1}H NMR) after removal of the cobalt by-products by filtration through Celite. From a synthetic viewpoint, it is noteworthy that the yields of PK products from 1-sulfonylated 1,6-enynes (70–79% yields for cyclopentenones **9**, **11**, **13**, and **15**) are generally higher than those obtained from the corresponding 1-unsubstituted enynes (cyclopentenones **10**, **12**, **14**, and **16**; 38–79% yield), and that there is no significant decrease in efficiency on going from the 4,4-dimethyl series **5** and **7** (Thorpe–Ingold effect) to the 4-unsubstituted series **1** and **3**.[12]

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[**] Financial support of this work by the Ministerio de Educación y Cultura (DGES, project PB96-0021) and Comunidad de Madrid (project 07B/28/1999) is gratefully acknowledged.

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