J|A|C|S
COMMUNICATIONS

A Tandem Approach to Photoactivated Olefin Metathesis: Combining a Photoacid Generator with an Acid Activated Catalyst

Benjamin K. Keitz and Robert H. Grubbs*

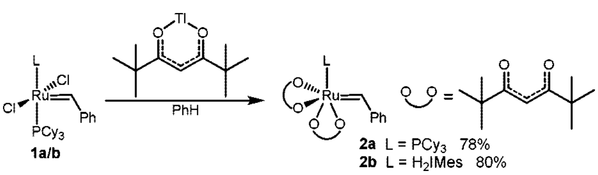
Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received September 10, 2008; E-mail: rhg@caltech.edu

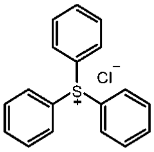
During the past several years, olefin metathesis has evolved into a powerful tool for both materials and synthetic chemistry.[1] Recently, latent olefin metathesis catalysts which require an external stimulus to become active have gained in popularity, particularly for applications in materials science.[2] Latent catalysts activated with light are especially promising for applications such as photolithography[3] and roll to roll coating.[4] Photoinitiated ring opening metathesis polymerization (ROMP) is fairly well-known and occurs with a variety of metals including ruthenium,[4,5] tungsten,[6] molybdenum,[7] and rhenium.[8] On the other hand, there are comparatively few examples of photoinitiated ring closing metathesis (RCM) due to the relatively low activity of current catalyst systems toward acyclic substrates.[9] This low activity for the known systems is most likely due to the fact that a suitable alkylidene for metathesis must be generated *in situ* after either cymene or nitrile ligand dissociation has taken place.[5c] We believed that catalyst activity, especially toward RCM, could be increased by including an alkylidene moiety from the beginning instead of relying on its generation from substrate. Herein, we report our efforts to develop a versatile photoinitiated catalytic system effective at both RCM and ROMP.

Previous work has shown a metathesis inactive Ru-alkylidene complex ligated by acetylacetonate (acac) may be converted into a metathesis active system by protonation and subsequent displacement of the labile *acac* ligands.[10] Treatment of bisphosphine complex **1a** with Ag(Me_6acac) resulted in complete ligand exchange, but the desired product **2a** resisted all attempts at further purification. Fortunately, ligand exchange using thallium as a more capable transmetalation element provided the desired complex **2a** cleanly and in excellent yield (Scheme 1). *N*-Heterocyclic carbene complex **2b** could be obtained in excellent yield by heating a benzene solution of **1b** and Tl(Me_6acac) at 60 °C for 1 h.

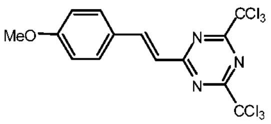
Scheme 1. Synthesis of Catalyst **2a/b**



Combining precatalyst **2a** or **2b** with photoacid generator (PAG) **3** in the presence of sub-300 nm light resulted in extremely active metathesis catalysts that were each capable of RCM and ROMP. Interestingly, switching the PAG counterion from chloride to the non-nucleophilic nonaflate resulted in a complete loss of activity indicating that chloride substitution is a key step in catalyst activation. Reactions run in the absence of UV light or PAG showed no metathesis activity, while irradiation of a solution containing only PAG and precatalyst resulted in eventual precatalyst decomposition.



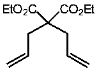
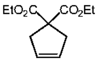
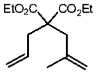
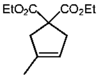
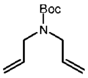
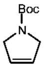
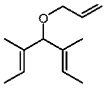
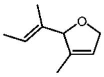
3



4

The tandem system of acid activated precatalyst **2a/b** and PAG **3** was very efficient at RCM as shown in Table 1. Simple substrates (entries 1 and 3) closed in excellent conversion within 1 h of irradiation.[9b] For the substrate of entry 1, we also found 2-(4-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (**4**) to be an effective PAG although its lower quantum yield ($\Phi_f = 0.01$[11] compared to $\Phi_f = 0.6$ for **3**[12]) necessitated a longer exposure time of 2 h to reach 80% conversion. More difficult substrates (entries 2 and 4) cyclized in moderate conversion using PAG **3**.

Table 1. RCM with Precatalyst **2a/b** and PAG **3**[a]

Entry	Substrate	Product	Time (h)	Catalyst	Conv. (%)[b]	Yield (%)[c]
1	 **5**	 **6**	1	**2a**	>95	77
			2	**2b**	>95	83
2	 **7**	 **8**	1	**2a**	55	42
			2	**2b**	93	88
3	 **9**	 **10**	1	**2a**	>95	70[d]
			1	**2b**	>95	93
4	 **11**	 **12**	3	**2a**	47	23
			3	**2b**	71	62

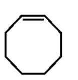
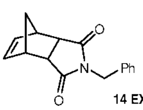
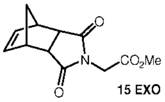
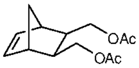
[a] Reaction conditions were **2** (5 mol%) and **3** (10 mol%) in a quartz NMR tube with CD_2Cl_2 (0.1 M) and substrate. [b] Measured by ^1H NMR spectroscopy. [c] Isolated after column chromatography. [d] Average yield over three runs.

Many common monomers such as norbornene derivatives and cyclooctene underwent ROMP in excellent conversion using the combination of **2a** and **3** (Table 2). Curiously, molecular weights (M_n), determined by GPC, were consistently higher than those predicted which is indicative of incomplete catalyst activation. After irradiation for 2 h, a catalyst solution under reaction conditions displayed peaks in both the ^1H and ^{31}P NMR spectra characteristic of precatalyst **2a**. Integration relative to the free *acac* in solution revealed that ca. 10% of the catalyst activated during the reaction time which is consistent with the higher M_n's obtained by GPC. Addition of HCl as a 1.0 M solution in diethyl ether to a solution of **2a** or **2b** also resulted in incomplete precatalyst activation.

Based on the tandem systems success at ROMP and with an eye toward potential industrial applications, we attempted to form

10.1021/ja807187u CCC: $40.75

Table 2. ROMP of Various Monomers with Precatalyst **2a** and PAG **3**[a]

Entry	Monomer	Catalyst	Time (h)	Conv. (%)[b]	theo. M_n (kDa)	exp. M_n[c] (kDa)	PDI
1	 **13**	2a	2	>95	2.2	13.9	1.38
		2b	2	>95	2.2	8.5	1.56
2	 **14 EXO**	2a	1	>95	5.2	57.5	1.33
		2b	1	>95	5.8	127	1.25
3	 **15 EXO**	2a	1	>95	4.7	59.9	1.44
		2b	1	>95	4.9	187	1.29
4	 **16 MIX**	2a/b	1	>95	4.6	-[d]	-

[a] Reaction conditions were **2a** (5 mol%) and **3** (10 mol%) in a quartz NMR tube with CD_2Cl_2 (0.1 M) and substrate. [b] Determined by ^1H NMR spectroscopy. [c] Measured by MALLS GPC. [d] Insolubility precluded GPC analysis.

Figure 1. Quartz vial containing gel resulting from ROMP of DCPD using precatalyst **2a** and PAG **3**.

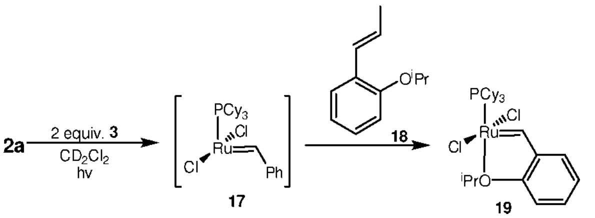
a cross-linked solid from the ROMP of dicyclopentadiene (DCPD). Irradiation of a solution of DCPD, **2a**, and **3** in a minimal amount of CH_2Cl_2 resulted in complete gelation within 1 h (Figure 1). Attempted melting and solvation confirmed that the gel was not a solidified monomer.

Finally, in an effort to improve catalyst performance, we investigated the nature of the catalytically active species via trapping experiments. After 5 h of irradiation, a CD_2Cl_2 solution of **2a**, **3**, and **18** (Scheme 2) clearly showed the formation of catalyst **19** in the ^1H and ^{31}P NMR spectra.

The above result indicates that at least one of the catalytically active species is the 14 electron complex **17**. However, at this time, we cannot rule out the presence of other active metathesis species which may be present in solution.[13]

In summary, we have described a robust light activated catalytic system capable of both RCM and ROMP in good to excellent conversions. Our mechanistic studies indicate that the tandem system goes through the same intermediate as the well-known metathesis catalysts **1** and **19** and the high activity of the system appears to be a result of this similarity. To the best of our knowledge, this is the first example of an organometallic reaction triggered by a PAG and as such has a number of potential advantages over current photoinitiated metathesis systems. For example, the acid activated catalyst can be modified to increase activity in addition to improving stability, latency, and ease of synthesis.[14] Similarly, the PAG may be modified to create a complex with improved solubility and a chromophore tuned to a specific wavelength of light. Exogenous sensitizers can also be added to further improve the sensitivity and quantum yield of the PAG.[12,15]

Scheme 2. Trapping of Reactive Intermediate



Acknowledgment. We thank Prof. C. Grant Willson, Dr. A. J. Boydston, and Dr. Cheol K. Chung for helpful discussions and the NSF for funding. B.K.K. thanks the NDSEG for a graduate fellowship.

Supporting Information Available: Experimental details and spectral data for catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413. (b) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3013. (c) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.
(2) (a) Ung, T.; Hejl, A.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2004**, *23*, 5399. (b) Slugovc, C.; Burtscher, D.; Stelzer, F.; Mereiter, K. *Organometallics* **2005**, *24*, 2255. (c) Hejl, A.; Day, M. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 6149.
(3) Ito, H.; Willson, C. G. *ACS Symposium Series* **1984**, *242*, 11.
(4) Zhang, Y.; Wang, D.; Lonnecke, P.; Scherzer, T.; Buchmeiser, M. R. *Macromol. Symp.* **2006**, *236*, 30.
(5) (a) Delaude, L.; Demonceau, A.; Noels, A. F. *Chem. Commun.* **2001**, 986–987. (b) Delaude, L.; Szypa, M.; Demonceau, A.; Noels, A. F. *Adv. Synth. Catal.* **2002**, *344*, 749. (c) Wang, D.; Wurst, K.; Knolle, W.; Decker, U.; Prager, L.; Naumov, S.; Buchmeiser, M. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 3267.
(6) (a) van der Schaaf, P. A.; Hafner, A.; Muehlebach, A. *Angew. Chem., Int. Ed.* **1996**, *35*, 1845. (b) Tarasov, A. L.; Shelimov, B. N.; Kazansky, V. B. *Kinet. Catal.* **1998**, *39*, 86.
(7) Subbotina, I. R.; Shelimov, B. N.; Kazansky, V. B. *Kinet. Catal.* **1997**, *38*, 678.
(8) Tarasov, A. L.; Shelimov, B. N.; Kazansky, V. B.; Mol, J. C. *J. Mol. Catal. A: Chem.* **1997**, *115*, 219.
(9) For a comparison of photoactivated RCM involving similar substrates see: (a) Picquet, M.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **1998**, 2249. (b) Fürstner, A.; Ackermann, L. *Chem. Commun.* **1999**, 95.
(10) Lynn, D. M.; Dias, E. L.; Grubbs, R. H.; Mohr, B. (California Institute of Technology, USA). U.S. Pat No. 6,486,279 and 6,284,852.
(11) (a) Pohlers, G.; Scaiano, J. C.; Sinta, R. *Chem. Mater.* **1997**, *9*, 3222. (b) Pohlers, G.; Scaiano, J. C.; Sinta, R.; Brainard, R.; Pai, D. *Chem. Mater.* **1997**, *9*, 1353.
(12) Selvaraju, C.; Sivakumar, A.; Ramamurthy, P. *J. Photochem. Photobiol., A* **2001**, *138*, 213.
(13) For an example of other possible active species, see: Samec, J. S. M.; Grubbs, R. H. *Chem.—Eur. J.* **2008**, *14*, 2686.
(14) For other acid activated catalysts, see: (a) Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627. (b) Sanford, M. S.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 5384. (c) Sanford, M. S.; Henling, L. M.; Day, M. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3451. (d) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601. (e) Hahn, F. E.; Paas, M.; Fröhlich, R. *J. Organomet. Chem.* **2005**, *690*, 5816. (f) Gulajski, L.; Michrowska, A.; Bujok, R.; Grela, K. *J. Mol. Catal. A: Chem.* **2006**, *254*, 118. (g) Samec, J. S. M.; Grubbs, R. H. *Chem. Commun.* **2007**, 2826. (h) Gawin, R.; Makal, A.; Wozniak, K.; Mauduit, M.; Grela, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 7206. (i) P'Pool, S. J.; Schanz, H. J. *J. Am. Chem. Soc.* **2007**, *129*, 14200.
(15) (a) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Part A: Polym. Chem.* **1978**, *16*, 2441–2451. (b) Dektar, J. L.; Hacker, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 6004.

JA807187U