# **ORGANOMETALLICS**

# Photogeneration of a Phosphonium Alkylidene Olefin Metathesis Catalyst

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**Supporting Information** 

**ABSTRACT:** Treatment of ruthenium carbide (H<sub>2</sub>IMes)-(Cl)<sub>2</sub>(PCy<sub>3</sub>)RuC (1) with the photoacid generator (PAG) [Ph<sub>3</sub>S][OTf] (3) under 254 nm light results in a highly efficient catalyst for ring-closing metathesis (RCM) and ringopening metathesis polymerization (ROMP) reactions. The reactions proceed via formation of the ruthenium phosphonium alkylidene complex [(H<sub>2</sub>IMes)(Cl)<sub>2</sub>Ru=C(H)PCy<sub>3</sub>]-[OTf] as the active catalytic species. In the case of ROMP



[OTf] as the active catalytic species. In the case of ROMP of cycloalkenes, reactions do not require addition of PAG and protonation of 1 proceeds via allylic C-H bond activation of the substrate under UV light.

T he development of olefin metathesis catalysts<sup>1</sup> that require external activation is an attractive avenue of research from the viewpoint of the materials/polymer chemical community.<sup>2–5</sup> For example, latent metathesis catalysts that can be activated thermally offer some advantages in ring-opening metathesis polymerization (ROMP), in that the stability of monomer/precatalyst mixtures under ambient conditions allows for the storage and "curing" of these mixtures prior to polymerization.<sup>3</sup>

Ólefin metathesis initiated by UV light<sup>4,5</sup> opens a broad range of possibilities for materials chemistry focused on surface modification, for example in photolithography or thin film generation. Such masked catalysts potentially allow for more control over patterning processes or device manufacturing.<sup>2a,d,f</sup> Photoinduced ROMP catalysis is fairly well known<sup>4</sup> and usually proceeds via photodissociation of auxiliary ligands to give highly reactive unsaturated intermediates<sup>4b-h</sup> or via UVinduced intraligand rearrangement to generate in situ alkylidene species.<sup>4a,g</sup> Recently, Grubbs et al. demonstrated an alternative tandem approach to photoactivated olefin metathesis that is based on the combination of an acid-sensitive precatalyst and a photoacid generator (PAG) under sub-300 nm light.<sup>5d</sup> Although such catalysts are typically employed in ROMP applications, photoinitiation of ring-closing metathesis (RCM) reactions, while scarce,<sup>4g,5</sup> is also potentially useful in mechanistic studies.

In 2004, we reported the rapidly initiating phosphonium alkylidene catalysts  $[(H_2IMes)(Cl)_2Ru=C(H)PCy_3][X]$  (2-X) formed via protonation of Heppert's ruthenium carbide  $(H_2IMes)(Cl)_2(PCy_3)RuC$  (1)<sup>6</sup> using acids with weakly coordinating borate anions (Scheme 1).<sup>7,8a,b</sup> With more coordinating anions such as OTf<sup>-</sup> or Cl<sup>-</sup>, the five-coordinate precatalyts 2-OTf and 2-Cl are formed, but in the case of 2-OTf, significant activity is maintained.<sup>8c-e</sup> Herein, we report the photochemical generation of 2-OTf via irradiation of a mixture of carbide 1 with the commercially available PAG [Ph<sub>3</sub>S][OTf] (3).

Exposure of a mixture of carbide 1 and PAG 3 to 254 nm light results in a highly efficient catalyst for both RCM and ROMP with virtually full conversion of substrates within 5 min (Table 1). The combination of 1 and 3 shows improved activity in comparison with previously reported photoinitiated metathesis catalysts.<sup>4,5</sup> For instance, exposure of dicyclopentadiene (DCPD) containing 1 and 3 (1 and 2 mol %, respectively) in CH<sub>2</sub>Cl<sub>2</sub> (9.9 mol/L) to 254 nm light for 35 min leads to a complete solidification of the mixture as a result of ROMP (Figure S1a). Interestingly, ROMP of cyclooctadiene (COD), cyclooctene (COE), norbornene, and DCPD (Table 1, entries 5-8; Table 2, entry 1) does not require addition of PAG and, presumably, proceed via protonation of 1 through allylic C-H bond activation of the substrate under UV light (see discussion below). Nevertheless, faster ROMP reactions with increased yields of the resulting polymers were observed when 3 was present (see Table 1). For example, increasing the concentration of 3 (from 0 to 2 mol %) in 1-mediated (1 mol %) photoinitiated ROMP of COD leads to increased yield as well as increased molecular weights (determined by GPC) of the resulting polymer (Table 2, entries 1-3). Assuming, to a first approximation, the polymerization reaction consists of catalyst initiation, chain propagation, and chain termination and the rate of initiation is much slower than the propagation process (see discussion below), this observation suggests that at constant reaction time addition of the PAG accelerates the catalyst initiation step, resulting in a longer chain propagation process.<sup>9</sup> Further increases in the concentration of 3 (2-10 mol %) do not seem to affect the yield or molecular weight of the polymer (Table 2, entries 3-5), suggesting no further influence of the PAG concentration on the rate of formation of 2-OTf. Gel permeation chromatography (GPC) analysis of poly(cyclooctadiene) (Figure S1b) obtained with variable

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Scheme 1

Entry



Table 1.	RCM and	l ROMP	Reactions	with 1	and	PAG	3'
Table 1. 1	RCM and	l ROMP	Reactions	with 1	and	PAG	3

Entry	Substrate	1, mol %	<b>3</b> , mol %	<i>t</i> <sub>irr</sub> , min	Conversion, % <sup>t</sup>
1	EtO2C CO2Et	1	2	5	>99
2	EtO <sub>2</sub> C CO <sub>2</sub> Et	1	2	5	>99
3	EtO <sub>2</sub> C CO <sub>2</sub> Et	1	2	5	98
4	EtO <sub>2</sub> C CO <sub>2</sub> Et	3	6	5	>99
5	$\bigcirc$	1 1	2	5 10	>99 94
6	$\bigcirc$	1 5	2 -	5 10	>99 77
7	A	1 1	2	5 5	>99 >99
8	A	1 1	2	5 5	>99 60

<sup>a</sup>Conditions: CD<sub>2</sub>Cl<sub>2</sub> (0.1 mol/L), 254 nm. <sup>b</sup>Determined by <sup>1</sup>H NMR spectroscopy.

Table 2. Photoinduced R	COMP of COD
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entry	3, mol %	yield, % <sup>b</sup>	$M_{ m n}$ , kDa <sup>c</sup>	$M_{ m w}$ , kDa	PDI
1	0	13	85.3	181.2	2.1
2	1	17	152.2	253.1	1.7
3	2	59	180.8	445.6	2.5
4	5	50	214.6	423.6	2.0
5	10	51	160.6	447.5	2.8

<sup>a</sup>Conditions: 1 mol % of 1, 0–10 mol % of 3, CH<sub>2</sub>Cl<sub>2</sub> (0.1 mol/L), 254 nm, 10 min. <sup>b</sup>Isolated yield after precipitation from THF solution. <sup>c</sup>Theoretical  $M_{\rm p} = 10.8$  kDa (at 100% conversion).

concentrations of 3 suggested incomplete catalyst activation. Thus, the molecular weights  $(M_n)$  of poly(cyclooctadiene) formed when 0–10 mol % of 3 was employed were found to be consistently higher than those predicted (85-160 versus 10.8 kDa (calcd); Table 2). Incomplete catalyst activation is also suggested on the basis of <sup>1</sup>H NMR analysis of the catalytic reaction mixture, which showed the presence of 1 even after catalytic ROMP reactions were complete.

To probe the mechanism of catalyst activation and nature of the active catalytic species, we performed several control experiments. First, none of the RCM reactions of entries 1-4 (Table 1) took place in the absence of one component of UV

irradiation, 1 or PAG 3.<sup>10</sup> Also, no ROMP reactions occurred in







 $CD_2Cl_2$  solution of 1 to  $1.0 \times 10^{-3}$  mol/L leads to a faster reaction with 3, and full conversion of 1 to 2-OTf under 254 nm light was observed within 5 min.<sup>10</sup> The diaryl sulfides that form as byproducts when 3 is irradiated under UV light<sup>11</sup> do not appear to affect the stability (or reactivity) of 2-OTf. However, prolonged exposure of a mixture of 1 and 3 to UV light leads eventually to decomposition of 2-OTf. After 3 h at 254 nm, the  ${}^{31}P{}^{1}H$  NMR spectrum showed formation of a mixture of decomposition products, one of which was tentatively assigned to [MePCy<sub>3</sub>][OTf],<sup>8e</sup> suggesting some of this decomposition may be via thermally induced pathways. Therefore, we performed a competitive study of thermal stability<sup>8e</sup> versus photostability of 2-OTf. Decomposition of 2-OTf in  $CD_2Cl_2$  (1.8 × 10<sup>-2</sup> mol/L) was followed by <sup>1</sup>H NMR spectroscopy for samples under both ambient and 254 nm irradiation at room temperature; the disappearance of 2-OTf exhibited first-order kinetic behavior with  $k_{\text{ambient}} = (8.2 \pm 1.1) \times 10^{-6} \text{ s}^{-1}$  and  $k_{254} = (1.9 \pm 0.1) \times 10^{-5} \text{ s}^{-1}$ , respectively.<sup>10</sup> The ratio of the rate constants  $(k_{254}/k_{\text{ambient}} = 2.3 \pm 0.3)$  shows an increase of the decomposition rate under UV light; however,

this increase is most likely induced by a significant temperature increase due to the prolonged irradiation time (24 h).<sup>8e</sup>

In an effort to prevent any side-reactions associated with the thermal decomposition of **2-OTf**, a mixture of **1** and **3** (1:1) in  $CD_2Cl_2$  (2.2 × 10<sup>-2</sup> mol/L) was treated with excess 1isopropoxy-2-vinylbenzene (ca. 7 equiv) under 254 nm light to afford alkylidene complex 4<sup>12</sup> with the release of  $[CH_2 = C(H)PCy_3][OTf]$  (Scheme 2).<sup>8,10</sup> However, after 12 h of UV irradiation, <sup>1</sup>H NMR spectroscopy showed only 50% conversion of **1** to **4**, which is accounted for by the polymerization of 1-isopropoxy-2-vinylbenzene under UV light.<sup>13</sup>

To examine the mechanism of catalyst activation in ROMP of cycloalkenes in the absence of a PAG, the stability of 1 and its reactivity with COD under UV light were studied by NMR spectroscopy. First, 1 was found to be stable under UV light in the absence of PAG, and no decomposition of the carbide solution in  $CD_2Cl_2$  (1.0 × 10<sup>-3</sup> mol/L) was observed upon exposure to 254 nm light within 30 min. Second, no photoinduced dissociation of PCy<sub>3</sub> ligand from 1 was detected. Thus, treatment of 1 with 10 equivalents of PEt<sub>3</sub> under either ambient conditions or UV light showed no intermolecular phosphine exchange. Further, exposure of a solution of  $1 (1.6 \times$  $10^{-2}$  mol/L) and 10 equivalents of COD in CD<sub>2</sub>Cl<sub>2</sub> to 254 nm light for 30 min results in 13% conversion of the starting carbide to a mixture of unknown alkylidene derivatives, along with full conversion of COD to the ROMP product. Formation of  $[MePCy_3]^{+8e,10}$  and  $[CH_2=C(H)PCy_3]^{+8e,10,14}$  was also observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, suggesting the intermediacy of the phosphonium alkylidene derivative  $[(H_2IMes)(Cl)_2Ru=C(H)PCy_3]^+$ . Presumably, the latter species forms via ruthenium-assisted C-H activation (most likely allylic C–H activation) of COD under 254 nm, as further control experiments indicated no polymerization of COD when either 1 or UV irradiation is absent.

In conclusion, we developed a highly efficient catalytic system of 1 and 3 for ROMP and RCM reactions that can be triggered by 254 nm light. Control experiments indicate the light-induced formation of ruthenium phosphonium alkylidene complex 2-OTf as an active catalyst.

#### EXPERIMENTAL SECTION

General Procedures and Equipment. An argon-filled MBraun glovebox was employed for manipulation and storage of all oxygenand moisture-sensitive compounds. The reactions were performed in a glovebox and on a double-manifold high-vacuum line using standard techniques. Dichloromethane was dried and purified using the Grubbs/Dow purification system.  $^{15}$  CD\_2Cl\_2 was dried over 4 Å molecular sieves and distilled. NMR spectra were obtained with a Bruker RDQ-400 spectrometer. NMR-scale reactions under ambient light were performed using J. Young NMR tubes. Photochemical NMR scale reactions were performed in Wilmad quartz NMR tubes (5 mm, 7 in., 600 MHz) under an argon atmosphere in a Luzchem LZC 4 V photochemical reactor using USHIO G8T5 254 nm lamps. The samples were prepared in a glovebox using dry CD<sub>2</sub>Cl<sub>2</sub>. Gel permeation chromatography analysis was carried out on a Waters Breeze instrument equipped with two styragel HR4E and HR5 columns. THF solutions for GPC analysis were eluted at 30 °C and at a flow rate of 1.0 mL/min and analyzed using a UV detector. Molecular weights and molecular weight distributions were reported against polystyrene standards (Sigma). Complexes (H<sub>2</sub>IMes)-(Cl)<sub>2</sub>(PCy<sub>3</sub>)RuC (1)<sup>6,8d</sup> and [(H<sub>2</sub>IMes)(Cl)<sub>2</sub>Ru=C(H)PCy<sub>3</sub>][OTf] (2-OTf)<sup>8c</sup> were synthesized according to literature procedures. [Ph<sub>3</sub>S][OTf] (3) was purchased from Sigma-Aldrich and used without further purification. Organic substrates were purchased from SigmaAldrich and additionally distilled prior to utilization. Phosphonium salt byproducts were identified by <sup>31</sup>P NMR spectroscopy.<sup>14</sup>

**Photoinduced NMR-Scale RCM Reactions.** In a glovebox, substrate  $(6.0 \times 10^{-2} \text{ mmol})$ , 1  $(6.0 \times 10^{-4} \text{ mmol})$ ; in the case of diethyl 2-allyl-2-(3-methylbut-3-en-1-yl)malonate  $1.8 \times 10^{-3}$  mmol of 1 was used), and 3  $(1.2 \times 10^{-3} \text{ mmol})$ ; in the case of diethyl 2-allyl-2-(3-methylbut-3-en-1-yl)malonate  $3.6 \times 10^{-3}$  mmol of 3 was used) were mixed together in 0.6 mL of CD<sub>2</sub>Cl<sub>2</sub> in a quartz NMR tube. The sample was kept in the dark and checked by NMR spectroscopy before exposure to UV light. The mixture was exposed to 254 nm light for 5 min and then checked by NMR analysis once again, showing full conversion of the substrates. Only for diethyl 2-allyl-2-(but-3-en-1-yl)malonate was 98% conversion detected by <sup>1</sup>H NMR spectroscopy. Conversions of the substrates were calculated from integration of <sup>1</sup>H NMR spectra.

Photoinduced ROMP Reactions: NMR-Scale Reactions. In a glovebox, substrate ( $6.0 \times 10^{-2}$  mmol), (H<sub>2</sub>IMes)(Cl)<sub>2</sub>(PCy<sub>3</sub>)RuC (1) ( $6.0 \times 10^{-4}$  mmol), and [Ph<sub>3</sub>S][OTf] (3) ( $1.2 \times 10^{-3}$  mmol) were mixed together in 0.6 mL of CD<sub>2</sub>Cl<sub>2</sub> in a quartz NMR tube. The sample was kept in the dark and checked with NMR spectroscopy before exposure to UV light. The sample was placed in a photochemical reactor with 254 nm lamps for 5 min and then checked again by NMR spectroscopy, showing full conversion of the substrates. Conversions of substrates were calculated from integration of <sup>1</sup>H NMR spectra.

Photoinduced ROMP Reactions: Polymerization of Cyclooctadiene with 1 and 3. In a glovebox, cyclooctadiene (61  $\mu$ L, 0.5 mmol), 1 (solution in CH<sub>2</sub>Cl<sub>2</sub> (0.1 M), 297  $\mu$ L, 5.0 × 10<sup>-3</sup> mmol), and various amounts of 3 (ratio to COD: 0, 1, 2, 5, and 10 mol %) were mixed together in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> in a quartz tube. The reaction mixture was left under 254 nm light for 10 min. All volatiles were removed under vacuum, and the residue was dissolved in a minimal amount of THF and precipitated into cold MeOH. The white precipitate was collected by filtration and dried in high vacuum for 2 days.

Photoinduced ROMP Reactions: Polymerization of Cyclooctadiene with 1 and COD. COD (9.6  $\mu$ L, 7.8 × 10<sup>-2</sup> mmol) was added in one portion at room temperature to a solution of 1 (7.8 × 10<sup>-3</sup> mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) in a quartz NMR tube. No reaction was observed within 1 h at RT. The mixture was exposed to 254 nm light for 30 min, showing by <sup>1</sup>H NMR 13% conversion of 1 to a mixture of unknown alkylidene species (diagnostic <sup>1</sup>H NMR signals of Ru=CH in 17.73–18.72 ppm region) and full conversion of COD to poly(cyclooctadiene). <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy also revealed the presence of [MePCy<sub>3</sub>]<sup>+</sup> (32.5 ppm) and [CH<sub>2</sub>=C(H)PCy<sub>3</sub>]<sup>+</sup> (26.7 ppm).<sup>14</sup>

Photoinduced ROMP Reactions: Polymerization of Dicyclopentadiene. In a glovebox, dicyclopentadiene (0.4 mL, 3.0 mmol), 1 (23.0 mg, 0.03 mmol), 3 (25.0 mg, 0.06 mmol), and 0.3 mL of  $CH_2Cl_2$  were mixed together in a quartz tube. The mixture was exposed to 254 nm light for 35 min, resulting in visible gelling of the solution upon polymerization.

Photogeneration of  $[(H_2|Mes)(Cl)_2Ru=C(H)PCy_3][OTf]$  (2-OTf). In a glovebox, 1 (4.6 mg, 6.0 × 10<sup>-3</sup> mmol) and 3 (5.9 mg, 9.6 × 10<sup>-3</sup> mmol) were mixed together in 0.6 mL of  $CD_2Cl_2$  in a quartz NMR tube. The mixture was kept in the dark and checked by NMR spectroscopy before exposure to UV light. No reaction was observed. The reaction mixture was exposed to 254 nm light with monitoring by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy for 1.2 h. The reaction was complete within this time; however, formation of  $[(H_2IMes)-(Cl)_2Ru=C(H)PCy_3][OTf]$  (2-OTf) was observed after 5 min (Figures S2–7). Further exposure of a mixture to 254 nm light for 2 h results in decomposition of 2-OTf to form  $[MePCy_3][OTf]$ . Decreasing concentration of 1 (from  $1.0 \times 10^{-2}$  mol/L to  $1.0 \times 10^{-3}$  mol/L) leads to a faster reaction: full conversion of 1 to 2-OTf under 254 nm light was observed within 5 min.

**Trapping Experiment Procedure.** Carbide 1 (10.0 mg, 1.3 ×  $10^{-2}$  mmol), 3 (5.5 mg,  $1.3 \times 10^{-2}$  mmol), and 2-isopropoxystyrene (16.0 mg,  $9.1 \times 10^{-2}$  mmol) were mixed together in 0.6 mL of CD<sub>2</sub>Cl<sub>2</sub> in a quartz NMR tube. The mixture was kept in the dark and checked

by NMR spectroscopy before exposure to UV light. No reaction was observed. The reaction mixture was then exposed to 254 nm light overnight. NMR spectroscopic analysis after that showed disappearance of the starting material and formation of complex 4 (ca. 50%) and vinylphosphonium salt  $[CH_2=CHPCy_3][OTf]$ .<sup>14</sup> Formation of poly(isopropoxystyrene) was also observed by <sup>1</sup>H NMR spectroscopy.

# ASSOCIATED CONTENT

# **Supporting Information**

Further experimental details, kinetic plots, and selected NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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# 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) Ito, H.; Willson, C. G. Applications of Photoinitiators to the Design of Resists for Semiconductor Manufacturing. In *Polymers in Electronics*; Davidson, T., Ed.; ACS Symposium Series, Vol. 242; ACS Publications: Washington, DC, 1984; pp 11–23. (b) Ung, T.; Hejl, A.; Grubbs, R. H.; Schrodi, Y. *Organometallics* **2004**, 23, 5399. (c) Slugovc, C.; Burtscher, D.; Stelzar, F.; Mereiter, K. *Organometallics* **2005**, *24*, 2255. (d) Harris, R. F.; Ricci, M. J.; Farrer, R. A.; Praino, J.; Miller, S. J.; Saleh, B. E. A.; Teich, M. C.; Fourkas, J. T. *Adv. Mater.* **2005**, *17*, 39. (e) Hejl, A.; Day, M. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 6149. (f) Toohey, K. S.; Sottos, N. R.; Lewis, J. A.; Moore, J. S.; White, S. R. *Nat. Mater.* **2007**, *6*, 581. (g) Monsaert, S.; Ledoux, N.; Drozdzak, R.; Verpoort, F. J. Polym. Sci. A: Polym. Chem. **2010**, *48*, 302. (h) Samec, J. S. M.; Keitz, B. K.; Grubbs, R. H. J. Organomet. Chem. **2010**, 695, 1831.

(3) For example: (a) Ben-Asuly, A.; Tzur, E.; Diesendruck, C. E.; Sigalov, M.; Goldberg, I.; Lemcoff, N. G. Organometallics 2008, 27, 811. (b) Szadkowska, A.; Grela, K. Curr. Org. Chem. 2008, 12, 1631. (c) Monsaert, S.; Lozanno Vila, A.; Drozdzak, R.; Van Der Voort, P.; Verpoort, F. Chem. Soc. Rev. 2009, 38, 3360. (d) Szadkowska, A.; Gstrein, X.; Burtscher, D.; Jarzembska, K.; Wozniak, K.; Slugovc, C.; Grela, K. Organometallics 2010, 29, 117. (e) Yu, Z.; Rogan, Y.; Khosravi, E.; Musa, O. M.; Hobson, L.; Batsanov, A. S. J. Organomet. Chem. 2011, 696, 1591. (f) Diesendruck, C. E.; Iliashevsky, O.; Ben-Asuly, A.; Goldberg, I.; Lemcoff, N. D. Macromol. Symp. 2010, 293, 33. (g) Diesendruck, C. E.; Vidavsky, Y.; Ben-Asuly, A.; Lemcoff, N. G. J. Polym. Sci, A: Polym. Chem. 2009, 47, 4209.

(4) For examples of photoinduced ROMP, see: (a) Van Der Schaaf, P. A.; Hafner, A.; Mühlebach, A. Angew. Chem., Int. Ed. Engl. **1996**, 35, 1845. (b) Delaude, L.; Demonceau, A.; Noels, A. F. Chem. Commun. **2001**, 986. (c) Delaude, L.; Szypa, M.; Demonceau, A.; Noels, A. F. Adv. Synth. Catal. **2002**, 344, 749. (d) Zhang, Y.; Wang, D.; Lonnecke, P.; Scherzer, T.; Buchmeiser, M. R. Macromol. Symp. **2006**, 236, 30. (e) Wang, D.; Wurst, K.; Knolle, W.; Decker, U.; Prager, L.; Naumov, S.; Buchmeiser, M. R. Angew. Chem., Int. Ed. 2008, 47, 3267. (f) Wang, D.; Wurst, K.; Buchmeiser, M. R. Chem.—Eur. J. 2010, 16, 12928. (g) Vidavsky, Y.; Lemcoff, N. G. Beilstein J. Org. Chem. 2010, 6, 1106, and references therein. (h) Buchmeiser, M. R.; Wang, D. Latent Photoactivatable Precatalysts for Metathesis Polymerization. U.S. Patent 0,003,905, January 6, 2011.

(5) For examples of photoinduced RCM, see: (a) Picquet, M.; Bruneau, C.; Dixneuf, P. H. Chem. Commun. **1998**, 2249. (b) Fürstner, A.; Ackermann, L. Chem. Commun. **1999**, 95. (c) Ben-Asuly, A.; Aharoni, A.; Diesendruck, C. E.; Vidavsky, Y.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G. Organometallics **2009**, 28, 4652. (d) Keitz, B. K.; Grubbs, R. H. J. Am. Chem. Soc. **2009**, 131, 2038.

(6) Carlson, R. G.; Gile, M. A.; Heppert, J. A.; Mason, M. H.; Powell, D. R.; van der Velde, D.; Vilain, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 1580.

(7) Romero, P. E.; Piers, W. E. Transition Metal Carbene Complexes Containing a Cationic Substituent as Catalysts of Olefin Metathesis Reactions. *International Patent Appl.* WO 2005/121158 A1, December 22, 2005.

(8) (a) Romero, P. E.; Piers, W. E.; McDonald, R. Angew. Chem., Int. Ed. 2004, 43, 6161. (b) Dubberley, S. R.; Romero, P. E.; Piers, W. E.; McDonald, R.; Parvez, M. Inorg. Chim. Acta 2006, 359, 2658. (c) van der Eide, E. F.; Romero, P. E.; Piers, W. E. J. Am. Chem. Soc. 2008, 130, 4485. (d) Leitao, E. M.; Dubberley, S. R.; Piers, W. E.; Wu, Q.; McDonald, R. Chem.—Eur. J. 2008, 14, 11565. (e) Leitao, E. M.; van Der Eide, E. F.; Romero, P. E.; Piers, W. E.; McDonald, R. J. Am. Chem. Soc. 2010, 132, 2784. (f) van der Eide, E. F.; Piers, W. E. Nat. Chem. 2010, 2, 571.

(9) Odian, G. *Principles of Polymerization*, 4th ed.; Wiley-Interscience: Hoboken, NJ, 2004.

(10) See Supporting Information for details.

(11) The process by which triphenylsulfonium PAGs release protons under UV irradiation is complex and produces several organic byproducts; see: (a) Araki, S.; Ito, H.; Butsugan, Y. J. Org. Chem. **1988**, 53, 1833. (b) Dektar, J. L.; Hacker, N. P. J. Am. Chem. Soc. **1990**, *112*, 6004. For clarity, this chemistry is not depicted in the schemes herein, but for a more complete picture the reader is directed to these references.

(12) (a) Kingsbury, J. S.; Harrity, J. P. A.; Bonitatebus, P. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 791. (b) Garber, S. B.; Kingsbury, J. S.; Gray, B. L.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 8168.

(13) For an example of UV-induced polymerization of styrenes, see: Deng, J.-P.; Yang, W.-T.; Rånby, B. *Macromol. Rapid Commun.* **2001**, 22, 535.

(14) (a)  $[CH_2=C(H)PCy_3][Br]$ : Rabinowitz, R.; Henry, A. C.; Mercus, R. J. Polymer Sci: A **1965**, 3, 2055. (b)  $[CH_2=C(H)PCy_3]$  $[BF_4]$ : Esteruelas, M. A.; Lahoz, F. J.; Martin, M.; Martinez, A.; Oro, L. A.; Puerta, M. C.; Valerga, P. J. Organomet. Chem. **1999**, 577, 265. (c) Jung, S.; Brandt, J. W.; Werner, H. Dalton Trans. **2004**, 375. (d)  $[CH_2=C(H)PCy_3][B(C_6F_5)_4]$ : Romero, P. E.; Piers, W. E. J. Am. Chem. Soc. **2005**, 127, 5032.

(15) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Organometallics **1996**, *15*, 1518.