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Latency for All: Enabling Latency of Hoveyda−Grubbs Second-Generation Catalysts by Adding Phosphite Ligands

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ABSTRACT: The Hoveyda−Grubbs catalyst (**HG2**, M720 Umicore) is among the most widely used catalysts in olefin metathesis reactions. Given the usefulness of **HG2** and the great interest in developing latent olefin metathesis catalysts for numerous applications, we developed a method to introduce phosphite molecules as ancillary ligands into the precatalyst framework. This modification alters the geometry of the complex from an active *trans*-dichloro form to a latent *cis*-dichloro species. Most unusually, the ligands coordinate to **HG2** only in solidified solutions (most likely due to entropic factors), providing latent catalysts that can be activated on demand by heat or light by regenerating the original **HG2** catalyst. Of particular interest is the use of these latent catalysts in ring-opening metathesis polymerization (ROMP) reactions and 3D printing methods. Indeed, the novel complexes displayed the required latency toward ROMP monomers, even the most reactive dicyclopentadiene. Irradiation with 405 nm light readily results in the expedited formation of the desired polymers. This novel approach provides a general and straightforward way to access efficient and well-defined latent olefin metathesis catalysts.

The commercialization of what is colloquially called the "Hoveyda−Grubbs Second Generation" catalyst (Umicore M720, **HG2**, Figure 1) impacted the olefin metathesis field[1,2] by introducing an extremely stable precatalyst used to produce rubbers,[3] natural products,[4−6] and pharmaceuticals.[7−9] Indeed, **HG2** is still today one of the most widely used precatalysts in olefin metathesis.[10] Inspired by the beneficial effects brought about by oxygen chelation (phosphine-free), countless modifications to the structure of **HG2** have been proposed. Changes to the ligand sphere greatly affect the properties of the precatalysts;[11−14] for example, exchanging the chelating oxygen atom in **HG2** with a sulfur atom provides a complex where the anionic ligands rearrange to a *cis* configuration due to a strong *trans* effect (**Ru-1**, Figure 1).[15,16] In this special configuration, the precatalyst is latent and needs to be activated by external stimuli. Although to the casual eye it may seem counterintuitive to suppress the precatalysts' initiation, latency can be a desirable trait.[17,18] A common method for latent catalyst activation is simple heating.[19,20] In addition to thermal stimulus, irradiation with light is another widely used mode for activation.[21,22] Our research group's interest has focused on the development of latent olefin metathesis complexes that can be directly[23] or indirectly[24] activated by light, including using Cazin-type phosphite-containing complexes (e.g., **M220** and **Ru-2**, Figure 1).[25−28]

Aiming to develop novel precatalysts with controlled activity, we envisioned the introduction of phosphite ligands into **HG2** to inhibit its initiation. Displacing the oxygen-chelating moiety with a phosphite ligand was expected to induce a change in the geometry from the *trans*-dichloro form to a latent *cis*-dichloro species.[16] Notably, this modification would provide direct access to the original **HG2** catalyst upon activation.

To synthesize the complexes, an excess of tribenzylphosphite or triethylphosphite was added to a solution of **HG2** in benzene. After mixing, coordination of phosphite to **HG2** was observed in both cases via ^{1}H NMR (Figures S9−S10). Unfortunately, these newly formed complexes were unstable in solution, regenerating **HG2** upon standing together with phosphite decomposition. We hypothesized that a stronger sigma-electron donor, such as triphenylphosphite (**1a**), should provide a stronger P−Ru bond and, accordingly, a more stable compound.[29] However, mixing **1a** with **HG2** in benzene did not lead to the formation of the expected complex (Figure S11). Intuiting steric hindrance as the reason for this outcome, the steric bulkiness of **1a** was reduced by exchanging one of the phenyl groups for an ethyl group. Unfortunately, mixing ethyldiphenylphosphite (**1b**) with **HG2** in benzene provided only trace amounts of the expected 16-electron ruthenium species (**HG‡-EDPP**, Figure 1), even after 24 h. In between attempts, the reaction mixture was stored over the weekend at −20 °C for further experimentation. The frozen mixture was then thawed and examined by ^{1}H NMR to ensure purity of the compounds. To our surprise and completely counterintuitively, after this period of cooling, **HG‡-EDPP** was obtained in relatively large amounts. Moreover, **HG‡-EDPP** was stable in a benzene solution at room temperature over prolonged periods. More puzzling, cooling a mixture of **1b** and **HG2** to −20 °C in

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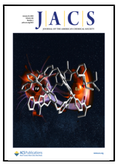

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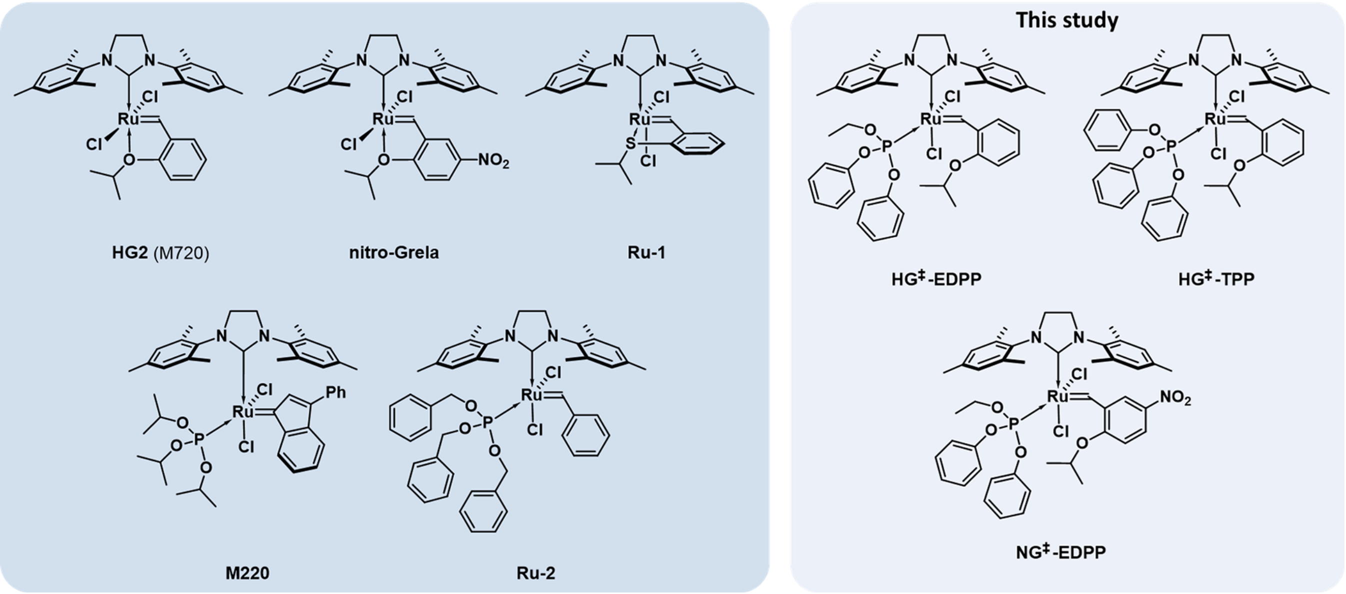


Figure 1. Examples of ruthenium precatalysts (left), including latent precatalysts produced in this study (right).

solvents that do not freeze (e.g., methylene chloride or toluene) did not result in phosphite binding (Figure S13).

To further scrutinize the observation that solidification of the mixture was needed to promote phosphite binding, molten naphthalene was probed as a solvent. Notably, mixing **1a** and **HG2** for 24 h at 90 °C in molten naphthalene did not lead to the formation of the desired phosphite complex. However, to our great satisfaction and surprise, cooling the naphthalene mixture to RT for 96 h provided the new complex **HG‡-TPP** (Figure 2) in high yields.

Thus, these experiments provide strong support for the claim that the solidification of the mixture promotes the formation of these novel complexes. One plausible explanation for this very unusual observation is that the more dominant entropic contribution in solution, as compared to the lower entropy influence in the solid state, hinders the coordination of the phosphite ligand (a higher entropy state).[30] After the desired coordination is achieved, the energetic barrier is high enough to prevent dissociation from happening in solution at room temperature. Accordingly, we considered that an electron-withdrawing group on the benzylidene ring could weaken the oxygen−ruthenium bond, facilitating ligand exchange and lowering the susceptibility to the entropic contribution. To test this assumption, commercially available nitro-Grela catalyst[14] was mixed with **1b** in benzene. After 24 h at room temperature, conversion to the new ruthenium complex indeed occurred in solution, as intended (75% yield).

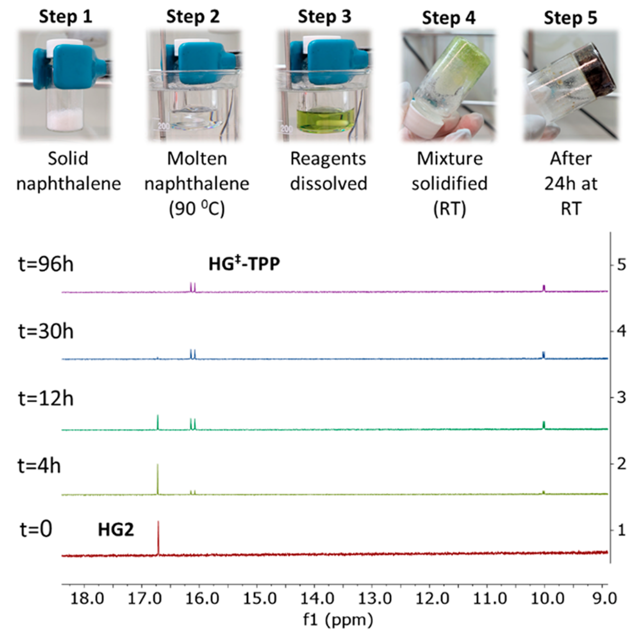


Figure 2. Preparation of **HG‡-TPP** (top) (note the color change from step 4 to 5). Reaction progress was monitored by ^{1}H NMR (bottom, see Figure S15 for full spectra).

The facile ligand exchange with the nitro-Grela catalyst eloquently demonstrates how thermodynamic parameters can subtly influence the synthetic methodology required to produce these complexes. Finally, by optimizing the solid-state synthesis protocol, **HG‡-EDPP** and **HG‡-TPP** could be readily isolated in 75% and 60% total yields, respectively. All novel complexes were characterized by NMR, HR-MS, UV−vis, and single-crystal X-ray diffraction analyses (Figure 3).

Once this was in hand, the photodissociation efficiency of **HG‡-EDPP** and **HG‡-TPP** was studied by irradiation. Thus, the complexes were dissolved in CD_2Cl_2. Then, a stripped and sandblasted optical fiber conveying the output of a 405 nm laser was introduced into NMR tubes (Figure 4, right inset) for in situ monitoring of the complexes' behavior during irradiation.[31] Figure 4 displays phosphite dissociation over time, revealing the disappearance of the original benzylidene peak (16.0 ppm) and the appearance of the new benzylidene signal (16.5 ppm) during the transformation from **HG‡-TPP** to **HG2**. In addition, a distinct color change in the solution from brown to green was observed. Monitoring the dissociation in **HG‡-EDPP** afforded similar results (Figures S16−18).

After confirmation of the complexes' photodissociation efficiency, the photoinduced olefin metathesis activity was probed. To determine the optimal wavelength of activation, a series of benchmark ring-closing metathesis (RCM) experi-

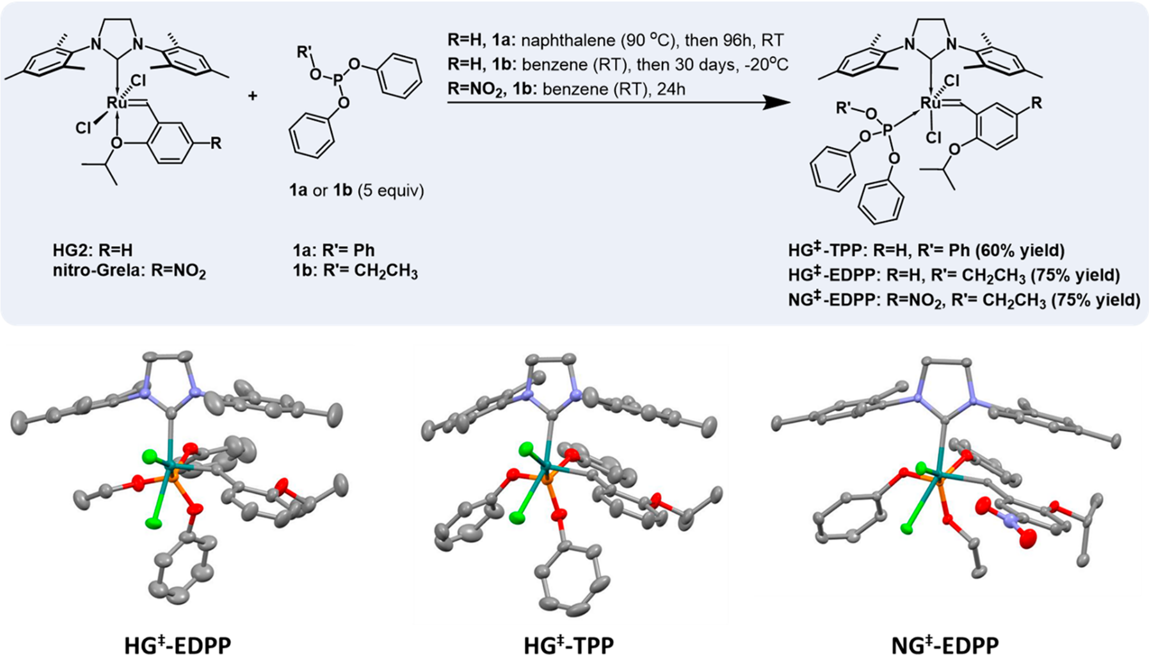


Figure 3. Synthesis of the ruthenium complexes **HG‡-EDPP**, **HG‡-TPP**, and **NG‡-EDPP** (top) and their single crystal X-ray structures (bottom). Ellipsoids are at 50% probability; hydrogens are omitted for clarity.

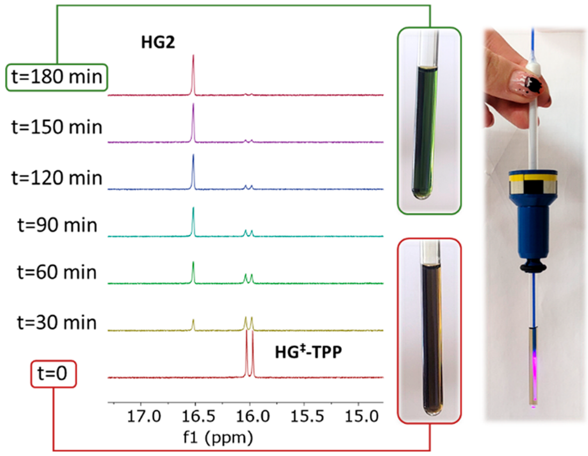
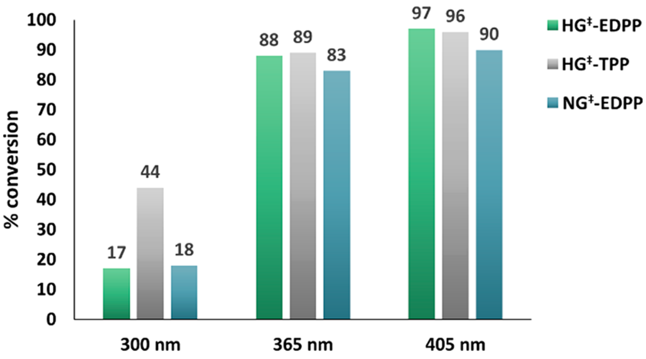


Figure 4. Irradiation of complex **HG‡-TPP** in a CD_2Cl_2 solution (405 nm light, left). ^1H NMR irradiation setup (right).

Chart 1. Photoinduced RCM Profiles with HG‡-EDPP, HG‡-TPP, and NG‡-EDPP



[a]Reaction conditions: 0.5 mL of 0.1 M DEDAM solution and 1 mol % catalyst (added as 50 μL CD_2Cl_2 stock solution) in benzene-d_6 were irradiated for 1 h.

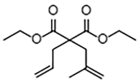
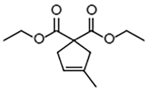
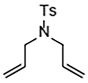
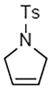
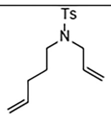
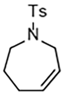
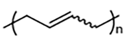
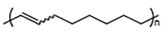
ments with diethyldiallyl malonate (DEDAM) were conducted (Chart 1). **HG‡-EDPP**, **HG‡-TPP**, and **NG‡-EDPP** showed excellent activity under illumination with 365 and 405 nm light. As expected, almost no metathesis activity was observed without irradiation. Solvent screening determined that a 9:1 ratio of benzene:CH_2Cl_2 provided the best results (improving the catalyst solubility).

A wider scope for photoinduced olefin metathesis activity under 405 nm light was probed with a series of RCM and ROMP substrates (Table 1). Excellent conversions with much shorter irradiation times, compared to previously reported phosphite-bearing catalysts, were obtained.[25−27] Notably, thermally induced reactions (80 °C) were also possible, although **HG‡-EDPP** required longer heating periods, and the overall conversions were usually lower when compared to the photochemically induced process (Table S1).

A curious observation was that continued irradiation of the complex−monomer mixture decreased the final polymer sizes. Consequently, the polymers derived from 1,5-*cis*,*cis*-cyclooctadiene (COD) were analyzed over 15 min intervals up to 1 h to assess the effect of irradiation time. The number (M_n) and weight (M_w) average molecular weights, polymer dispersities, and hydrodynamic radii (R_h) were analyzed by multiple detector size exclusion chromatography (SEC). Indeed, polymer sizes decreased with both **HG‡-EDPP** (Figure 5) and **HG‡-TPP** initiators under prolonged irradiation. We suggest that this decrease may be due to backbiting during irradiation,[32] or to further activation of latent initiators that may cleave the main polymer backbone.[33]

To further scrutinize the observed reduction of polymer molecular size under irradiation, the same reaction was repeated using **M220**.[25] As expected, also in the case of **M220**, the polymer size decreased with prolonged irradiation. In contrast, when nonlatent **Grubbs third generation** (bispyridine) or **HG2** were used, the polymers resulting from these ROMP reactions did not decrease in size over time (Table S3).

Table 1. Photoactivity under 405 nm Light Irradiation[a]

Entry	Substrate	Product	Time (min)	Loading (% mol)	Catalyst	% Conversion (Dark control)	E/Z ratio	M_n(KDa) (M_w/M_n)
1			60	1	**HG‡-EDPP**	77 (5)		
			60	1	**HG‡-TPP**	88 (9)		
2			60	1	**HG‡-EDPP**	96 (1)		
			60	1	**HG‡-TPP**	97 (3)		
3			60	1	**HG‡-EDPP**	87 (6)		
			60	1	**HG‡-TPP**	88 (9)		
4			15	0.1	**HG‡-EDPP**	88 (1)		83 (1.45)
			5	0.1	**HG‡-TPP**	-	1:1	
			10	0.1	**HG‡-TPP**	-	1.5:1	
			15	0.1	**HG‡-TPP**	100 (2)	2:1	79 (1.37)
5			15	0.1	**HG‡-EDPP**	97 (1)		237 (1.23)
			15	0.1	**HG‡-TPP**	91 (13)		226 (1.22)

[a] Reaction conditions: 0.5 mL of a 0.1 M substrate (RCM) or 0.5 M substrate (ROMP) solution and 1 mol % catalyst (added as 50 μL of a CD_2Cl_2 stock solution) in benzene-d_6 were irradiated with 405 nm light. Mesitylene was added as an internal standard to measure ROMP conversions. Reaction conversions were measured by ^{1}H NMR.

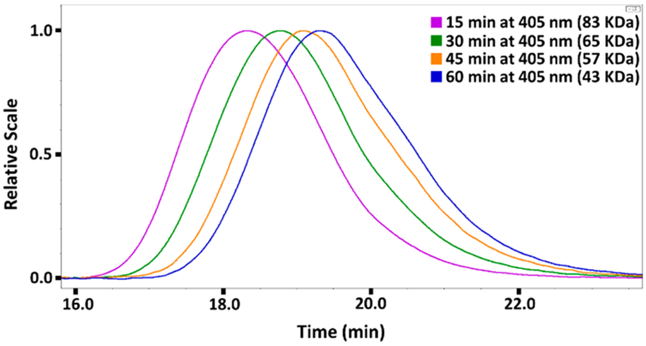


Figure 5. 90° light scattering detector SEC trace for polymers obtained with **HG‡-EDPP**. Reaction conditions: 0.5 mL of a 0.1 M COD solution and 0.1 mol % catalyst (added as 50 μL CD_2Cl_2 stock solution) in benzene-d_6 were irradiated with light for 15−60 min and then quenched with 10 μL of ethylvinyl ether.

An additional control experiment was conducted by using a 118 kDa (M_n) poly(COD) sample. The polymer was dissolved in THF and irradiated for 15−90 min. The polymer size did not change as a function of time, verifying that the presence of a latent ruthenium catalyst is necessary for the size reduction, and that close monitoring of photoinduced ROMP progress is crucial with latent catalysts/initiators to prevent secondary metathesis polymer degradation.

One of the most widely used and valuable ROMP polymers is polydicyclopentadiene (poly(DCPD)), produced by the polymerization of dicyclopentadiene (DCPD).[34] Because of the highly exothermic reaction of DCPD with olefin metathesis catalysts, many researchers have tried to subdue the reaction by using latent catalysts or adding inhibitors. For example, Cazin, Slugovc et al. have used **M220** to achieve a longer processing window.[35] Moore and co-workers used alkyl phosphites as inhibitors in DCPD-**G2** formulations for frontal ring-opening metathesis polymerization (FROMP) applications.[36,37] However, this pioneering work by Moore et al. also showed that adding **HG2** to formulations containing phosphites and DCPD resulted in instantaneous polymerization. We propose, based on the knowledge acquired in this work, that the phosphite ligands need to be precoordinated to the ruthenium center in order to inhibit the metathesis reaction. As we have shown, **HG2** simply does not undergo ligand exchange in solution with phosphites, probably resulting in the immediate polymerization observed by Moore and co-workers. To further validate this result, DCPD, or (even the less reactive) norbornene dicarboxylate, was mixed with 100 ppm of **HG2** and 100 ppm of triphenylphosphite or ethyldiphenylphosphite. Indeed, fast polymerizations (less than 2 min) ensued. However, formulations containing neat DCPD and 100 ppm of **HG‡-EDPP** or **HG‡-TPP** remained in liquid form for 9 or 3 h at room temperature, respectively. Moreover, polynorbornene dicarboxylate and polyhydroxydicyclopentadiene films could also be prepared using similar formulations (Figure 6c, for detailed procedures, see Figure S22). Another attractive use for latent olefin metathesis catalysts is their application in 3D-printing technologies for tough ROMP-derived polymers.[38] Thus, the new initiators were explored for stereolithographic processing. To our great satisfaction, these complexes performed superbly well in layer-by-layer 3D-printing sequences (Figure 6d−f).

By balancing an intricate correlation between thermodynamic parameters, novel latent phosphite precatalysts based on the widely used **HG2**, could be readily synthesized by

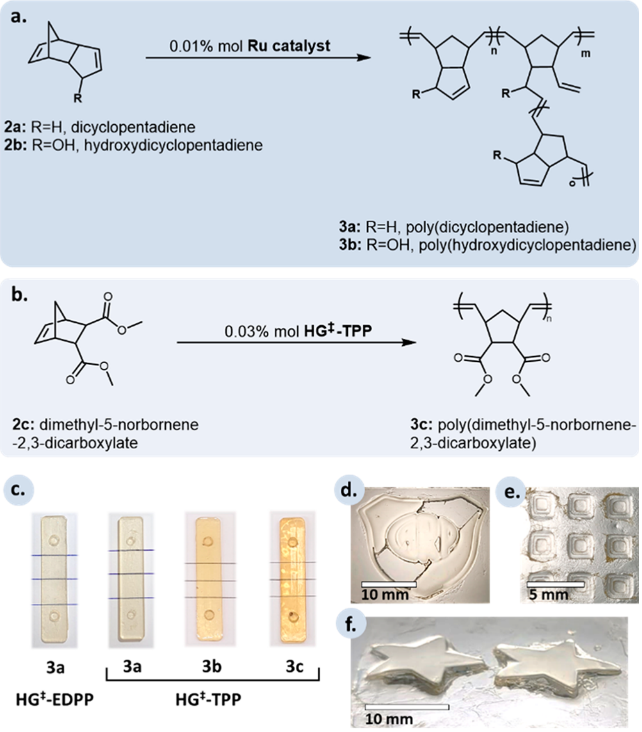


Figure 6. (a, b) Reaction schemes for the polymerizations. (c) Polymer films made in steel molds. (d) Symbol of Argentinian football club River Plate printed in 3 layers using 100 ppm of **HG‡-EDPP** in DCPD. (e) Pyramids were printed in 4 layers using 80 ppm of **HG‡-TPP** in DCPD, with an average layer thickness of 200 μm. (f) Stars were printed in 4 layers using 100 ppm of **HG‡-TPP** in DCPD.

conducting the ligand coordination in the solid state. These phosphite-containing complexes provided excellent olefin metathesis reactivity in various RCM and ROMP reactions when activated by light and were amenable to 3D-printing ROMP processes. In addition, it was discovered that prolonged irradiation times in the presence of photolatent initiators decreased the molecular sizes of ROMP-derived polycyclooctadienes, providing an additional tool to control the molecular weight of these polymers. The facile synthesis, utilizing commercially available **HG2** and phosphites, provides a very convenient methodology for practitioners of the art to experiment with latent olefin metathesis catalysts that can be activated by light or heat for numerous applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c10826.

General information, synthetic procedures, and supplemental data (PDF)

Accession Codes

CCDC 2284872−2284873 and 2284927 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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