

Subscriber access provided by BIU Pharmacie | Faculté de Pharmacie, Université Paris V

Latent Ruthenium Benzylidene Phosphite Complexes for Visible Light Induced Olefin Metathesis

Or Eivgi, Anna Vaisman, Noy B. Nechmad, Mark Baranov, and N. Gabriel Lemcoff

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.9b05079 • Publication Date (Web): 27 Dec 2019

Downloaded from pubs.acs.org on December 28, 2019

Just Accepted

Letter

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Latent Ruthenium Benzylidene Phosphite Complexes for Visible Light Induced Olefin Metathesis

Or Eivgi^{†‡}, Anna Vaisman^{†‡}, Noy B. Nechmad[†], Mark Baranov[†] and N. Gabriel Lemcoff^{†*}

⁺Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105

[‡] Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, Israel, 84105

[‡]These authors contributed equally

lemcoff@bgu.ac.il

photocatalysis, olefin metathesis, photochemistry, 3D printing, phosphites.

ABSTRACT: Herein we report two ruthenium benzylidene complexes with benzylphosphite ligands for olefin metathesis. Unlike the previously reported benzylidene phosphite complexes, the benzylphosphite complexes adopt a *cis*-dichloro configuration making them latent at ambient temperatures. Irradiation with visible light (420 nm and blue LED) prompts activation of the complexes and induces catalysis of olefin metathesis reactions. One of the complexes, *cis*-Ru-1, was found especially suitable for 3D printing of multilayered polydicyclopentadiene structures with excellent spatial resolutions. Additionally, complex *cis*-Ru-2 was designed with a chromatic orthogonal 'kill switch' based on the 2-nitrobenzyl chemistry, allowing the destruction of the catalyst upon exposure to UVC light.

Olefin metathesis is one of the most important reactions for the transmutation of carbon-carbon double bonds in organic synthesis and is routinely utilized in academic research as well as the pharmaceutical and polymer industries.1 Extensive research invested in studying the ligand sphere of the metal complexes yielded a plethora of specialized complexes for task specific applications; for example, third generation fast initiating complexes for precision polymerizations² or the variety of cyclic alkyl amino carbene (CAAC) containing complexes to increase activity, selectivity and reduce double bond isomerization side reactions.³ Slow initiating, or latent, complexes are a notable class of complexes, where external stimuli (heat, pH, ultrasound, etc.) are required to activate an otherwise dormant catalyst.⁴ The use of light to initiate a reaction catalyzed by a latent complex is of particular interest, as light can be conveniently applied with relatively low costs and great specificity.5 Additionally, the option to use light with good spatial resolution and the development of continuous flow techniques for photochemistry, provides the opportunity to apply photoinduced olefin metathesis on an industrial setting and scale.⁶ In the past decade, our group has developed a series of sulfur chelated ruthenium benzylidene complexes that adopt a dormant *cis*-dichloro configuration and can isomerize to the active trans form when irradiated with UV-A light.7 The sulfur chelated complexes have been tested for their heat and photolatent ring closing metathesis (RCM) and ring opening metathesis polymerization (ROMP) activities, including in sterically demanding reactions⁸ and even for chromatic orthogonal applications.9 Originally reported by Cazin et al. in 2010, commercially available phosphite containing ruthenium indenylidene complex cis-Caz-1 (Figure 1, bottom right) also prefers the cis-dichloro configuration and just as its sulfur-chelated and other phosphinechelated counterparts, is latent towards olefin metathesis reactions at ambient temperatures.¹⁰ When heated in toluene cis-Caz-1 exhibited remarkable activity and thermal stability, efficiently completing sterically demanding olefin metathesis reactions with low catalyst loadings and under air." Recently, we reported that cis-Caz-1 may also be activated by UV-A light (350 nm) at room temperature.¹² Irradiation of *cis*-Caz-1 with UV-A light promoted a variety of olefin metathesis reactions (RCM, CM and ROMP) with high efficiency. Interestingly, the benzylidene complexes synthesized by Cazin et al., trans-Ru-P(OEt)₃ and trans-Ru-P(OiPr)₂, featured transdichloro geometries and catalyzed olefin metathesis reactions at room temperature (Figure 1).¹³ Aiming to expand the field of photoinduced olefin metathesis, a chelating phosphite ligand was introduced to produce *cis*-PhosRu-1 (Figure 1).¹² The chelation effect imposed a cis configuration, leading to a latent benzylidene phosphite complex that could be activated with visible light in toluene; however, the activity of this complex for several olefin metathesis reactions was disappointingly low, possibly due to the strong chelation.

ACS Paragon Plus Environment

60



Figure 1. Ruthenium indenylidene complex *cis*-Caz-1¹⁰ (bottom right) and ruthenium benzylidene complexes bearing phosphite ligands reported in the literature by Lemcoff¹² and Cazin¹³ (top) and (bottom, left).

In this work, we report the synthesis of two novel photonon-chelated ruthenium benzylidene switchable complexes, bearing benzylphosphite ligands: cis-Ru-1 and Notably, unlike the previously cis-Ru-2 (Figure 2). reported *trans*-dichloro ruthenium benzylidene phosphites (Figure 1, top),¹³ these complexes adopt the latent cis-dichloro configuration. Upon irradiation with visible light (420 nm lamps or Blue LEDs), photoinduced activity for a variety of olefin metathesis reactions was observed. Additionally, complex cis-Ru-2 was equipped with a chromatic orthogonal 'kill switch'¹⁴ based on the rich 2-nitrobenzyl photochemistry.15 This feature, installed directly on the phosphite ligand, enables the destruction of the catalyst by UV-C light, making it compatible for chromatic orthogonal applications.9ª

The synthesis of the required phosphite ligands 1 and 2 was carried out by alcoholysis reactions of commercially available tris(dimethylamino)phosphine with the corresponding benzyl alcohols under neat conditions (Scheme 1).¹⁶ Mixing 1 and 2 with Grubbs 3rd Generation complex (pyridine) in CH₂Cl₂ for two hours afforded the corresponding complexes *cis*-**Ru**-1 and *cis*-**Ru**-2. (Figure 2).

Scheme 1. Synthesis of phosphite ligands 1 and 2



1: R = H , 45% yield 2: R = NO₂, 30% yield

Reaction progress was monitored by 'H-NMR, presenting new benzylidene signals at 15.27 ppm and 15.22 ppm for *cis*-**Ru-1** and *cis*-**Ru-2** respectively. Moreover, ³¹P-NMR experiments showed signals at 130.5 ppm and 133.8 ppm for *cis*-**Ru-1** and *cis*-**Ru-2**, indicating complexation of the phosphite ligands. The complexes were purified by a series of precipitations (see detailed protocol in the SI) and obtained as purple powders. ¹³C-NMR analysis disclosed a ²*J*_{C-P} coupling constant between the phosphorous and the SIMes carbene of 13 Hz for both *cis*-**Ru-1** and *cis*-**Ru-2**, supporting a *cis*-dichloro geometry.^{10a} Indeed, this assumption was corroborated in the solid state by single crystal X-ray crystallography of the target complexes (Figure 2, bottom).



Figure 2. (top) Synthesis of ruthenium benzylidene benzylphosphite complexes *cis*-**Ru**-1 and *cis*-**Ru**-2. (bottom) Single crystal X-ray structures of complexes (a) *cis*-**Ru**-1 and (b) *cis*-**Ru**-2. Ellipsoids are at 50% probability and the hydrogens are omitted for clarity.

With the new complexes in hand, their photoactivation behavior was studied. To determine the optimum wavelength of activation, a series of experiments using benchmark RCM substrate diethyl diallylmalonate (DEDAM, Figure 3) were conducted. Complex *cis*-**Ru**-1 showed clear activity under illumination with UV-A and visible light. As designed, complex *cis*-**Ru**-2, bearing the photosensitive 2-nitrobenzyl phosphite moiety showed low to negligible activity with UV light. On the other hand, *cis*-**Ru**-2 reported good activity when illuminated with 420 nm light, albeit lower than that obtained with *cis*-**Ru**-1.

60

2

3

4

5

6

7

8

9

10

11

12

13

14

15 16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

58 59

60



Figure 3. Photoactivity of complexes *cis*-**Ru**-1 and *cis*-**Ru**-2 for the RCM reaction of diethyl diallyl malonate in different wavelengths. Conversions measured using ¹H-NMR.

To probe the scope of the photoinduced metathesis, a variety of RCM and ROMP reactions were conducted at 420 nm (Table 1). Moreover, given the surprisingly good results of complex *cis*-Ru-2 with the blue LED (450-470 nm), an uncommon light source for direct photoactivation of latent ruthenium olefin metathesis complexes, the scope of reactions with complex cis-Ru-2 was extended to blue LED activation as well (Table 2). The findings indicate that *cis*-Ru-1 can efficiently catalyze RCM and ROMP reactions using visible light at low catalyst loadings in ambient temperature and under air. In addition, the activity of *cis*-Ru-1 was compared to the state-of-the-art catalyst cis-Caz-1 for di and tri-substituted RCM reactions, highlighting the superior activity of cis-Ru-1 at 420 nm (Figure S7, SI). Complex cis-Ru-2 also showed good activity at similar conditions; however, due to the slow decomposition of the complex occurring at 420 nm, the catalyst loadings had to be doubled to reach good reaction conversions.

37 The efficiency of the UV-C kill switch embedded in 38 complex cis-Ru-2, was then tested by a series of 39 experiments. First, the RCM reaction of N,N-diallyl-4methylbenzenesulfonamide was studied (Figure 4). 40 Reaction mixtures that were exposed to UV-C light, 41 42 followed by 420 nm showed no conversion at all; while, control experiments that were covered with aluminum foil 43 when irradiated by UV-C, showed almost complete 44 conversion upon exposure to 420 nm light; demonstrating 45 the efficacy of the method. Furthermore, ROMP of cis-1,5-46 cyclooctadiene (COD) was also investigated (Figure S8, SI). 47 Exposure of a 0.1 M COD solution in toluene to 254 nm for 48 45 minutes resulted in 18% conversion. Further exposure 49 to 420 nm for 1 h did not lead to additional monomer 50 consumption, indicating the destruction of the catalyst. 51 Once again, control experiments where the reaction 52 mixture was covered at 254 nm and exposed to 420 nm for 53 1h led to almost complete conversion (92%). The kill switch 54 was also tested for bulk polymerization. A formulation 55 containing 1 g of cyclooctene (COE) and 0.005% mol of cis-56 Ru-2 was placed in a steel mold and exposed to 254 nm 57

light for 0.5 h resulting in an amorphous dark gel. On the other hand, exposure of the same formulation to 420 nm yielded solid elastic rubbers (Figure S9, SI).



Figure 4. NMR study of the "kill switch" efficiency of complex *cis*-**Ru-2** for RCM reaction of N,N-diallyl-4-methylbenzenesulfonamide. (a) Control experiment, sample covered with aluminum foil during irradiation at 254 nm and then exposed to 420 nm for 6h (86% conversion). (b) Sample exposed 45 minutes to 254 nm light and then 6h to 420 nm light (o% conversion).

The lower activity of complex *cis*-Ru-2 compared to *cis*-**Ru-1** at 420 nm could probably be related to an accelerated decomposition of the complex. We hypothesized that the competition between two distinct photochemical reactions - the activation of the complex at 420 nm and the photo removal of 2-nitrobenzyl moiety (that may still occur slowly at this wavelength) - could be the cause for the lower activity. To test our hypothesis, molecular UV filters were used.9b Thus, a dichloromethane solution containing DEDAM and cis-Ru-2 was irradiated with 420 nm light using different concentrations of an external solution of 1-pyrene carboxaldehyde. Indeed, the conversion of the reaction was significantly increased from 49% to 77% simply by protecting the reaction with a 10 mM of external solution of pyrene carboxaldehyde as a "molecular UV filter" (Figure S10 and Figure S11, SI).

Table 1. Catalytic activity of complexes <i>cis</i> -Ru-1 and <i>cis</i> -Ru-2 with 420 nm irradiation. ^a
--

entry	substrate	product	time (h)	loading (% mol)	catalyst	% conversion (dark control) ^b	M _n (g/mol) (M _w /M _n)
1	EtO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et	8 8	1 2	cis-Ru-1 cis-Ru-2	92 (4) 80 (14)	-
2	Ts N	Ţs ⟨N⟩	8 8	1 2	cis-Ru-1 cis-Ru-2	92 (o) 86 (o)	-
3	EtO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et	8 8	1 2	cis-Ru-1 cis-Ru-2	73 (6) 46 (3)	-
4	s N	Ts N	8 8	1 2	cis-Ru-1 cis-Ru-2	92(6) 80 (4)	-
5	\bigcirc	(mu)	1 1	0.1 0.05	cis-Ru-1 cis-Ru-2	100 (4) 94 (4)	1.49*10 ⁴ (1.99) 1.67*10 ⁴ (2.01)
6		\$~~~\$	1 1	0.05 0.05	cis-Ru-1 cis-Ru-2	94 (5) 97 (14)	1.76*10 ⁵ (1.52) 1.65*10 ⁵ (2.05)
7	∠ CO₂tBu	f CO2tBu	1 1	0.1 0.2	cis-Ru-1 cis-Ru-2	100 (40) 100 (16)	9.89*10 ⁵ (1.57) 6.62*10 ⁵ (1.66)
8	OAc	₩ Ann	1 1	0.1 0.2	cis-Ru-1 cis-Ru-2	95(0) 94 (3)	n.d ^c n.d ^c

^aReaction conditions: All reactions were carried out in a Luzchem LZC-org photoreactor equipped with 10 LZC-420 lamps. RCM: In an NMR tube under air, 0.1M of substrate dissolved in 0.45 mL tol-d₈ and 0.05 mL of catalyst stock solution in dichloromethaned₂ were irradiated for 8 hours. Reaction conversions were monitored using ¹H-NMR spectroscopy. ROMP: 0.5M of monomer in 0.45 mL tol-d₈ and 0.05mL of catalyst stock solution in dichloromethane-d₂ were irradiated for 1 hour. Reaction conversions were monitored using ¹H-NMR using 10 µL of mesitylene as internal standard. ^b Dark control experiments are covered with aluminum foil to prevent exposure to light ^c not determined due to insolubility of the obtained polymer.

entry	substrate	product	time (h)	loading (% mol)	% conversion (dark control) ^b	M_n (g/mol) (M_w/M_n)
1	EtO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et	8	2	70 (11)	_
2	Ts N	Ts ∧	8	2	80 (1)	-
3	EtO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et	20	2	65 (2)	-
4	Ts N	N N	8	2	79 (5)	-
5	\bigcirc	(marting)	1	0.2	100 (15)	2.24*104 (1.64)
6		\$~~~\$	3.5	0.05	92 (16)	1.62*10 ⁵ (1.70)
7	CO ₂ tBu	f () f n CO₂/Ви	2	0.2	100 (9)	8.30*10 ⁵ (1.99)
8	OAc	Aco Aco	2	0.2	98 (4)	n.d ^c

^aReaction conditions: All reactions were carried out in a Luzchem LZC-org photoreactor equipped with 10 LZC-Blue LED lamps. In an NMR tube under air, solutions as specified in Table 1 were irradiated for the time specified. Reaction conversions were monitored using ¹H-NMR using 10 µL of mesitylene as internal standard. ^b Dark control experiments are covered with aluminum foil to prevent exposure to light. ^c Not determined due to insolubility of the obtained polymer.

Finally, to assess the efficiency of the phosphite complexes for industrial applications, the possibility to print 3D materials by stereolithography was perused.¹⁷ The patterning of polymeric materials using photoinduced olefin metathesis was first explored by Grubbs and co-workers who developed a photolithographic olefin metathesis polymerization (PLOMP) method based on a negative photoresist consisting of COD and a curable bifunctional 5-ethylidene 2-norbornene monomer.¹⁸ Other recent approaches to photoinduced ROMP include the work by Rovis et al. who used a photoredox activated bis-NHC catalyst to polymerize dicyclopentadiene (DCPD) using a mask^{5c} and Chemtob et. al. that generate the NHC by using light in the presence of $([RuCl_2(p-cymene)]_2)$ to initiate the reaction.¹⁹ We are also interested in printing polyDCPD based materials, as this polymer is known for its excellent thermal and mechanical properties.²⁰ Moore and coworkers have shown that phosphite additives can be used to modulate the reactivity of a Grubbs 2nd generation catalyst to prepare bench stable mixtures of catalyst and DCPD.²¹ Thus, we anticipated that cis-Ru-1 could form a processable formulation with a relatively long pot life when mixed with DCPD. Thus, cis-Ru-1 (200 ppm) in a small amount of dichloromethane (35 µl per 1 g of bulk monomer) was mixed

with DCPD (mixture of *endo-* and *exo-* isomers). The mixture was drop casted on a microscope slide and different patterns were irradiated with a programmable LED based light source (DLP projector, 385 nm) for short exposure times (approx. 30-60 seconds per layer, see SI for details). This process was repeated for the desired number of layers and the excess of the non-polymerized formulation was rinsed with acetone to afford the printed structures (Figure 5).



2

3 4

5

6

7

8

9 10 11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

Figure 5. 3D DCPD structures printed in layers using complex *cis*-**Ru**-**1**. a) Pyramids consisting of four layers of squares in decreasing size, b) zoom in on a single square c) Ben-Gurion University logo printed in two layers d) 3D image of River Plate club symbol.

In conclusion, the preparation, characterization and photoactivity of two new ruthenium benzylidene complexes bearing phosphite ligands, cis-Ru-1 and cis-Ru-2 is presented. Both benzylidene complexes adopt the *cis* dichloro configuration and are latent at ambient temperatures. Visible light (420 nm and blue LED) activates these complexes and promotes photoinduced catalysis of several olefin metathesis reactions. Moreover, cis-Ru-1 was found suitable for 3D printing applications of metathesis-based polymers allowing the preparation of a stable multilayered poly-DCPD designs using a programmable light patterning projector. Given the exceptional physical properties of poly-DCPD this application should have wide-ranging practical implications. In addition, complex *cis*-Ru-2 was equipped with a chromatic orthogonal 'self-destruct' switch based on the photoreactive 2nitrobenzyl protecting group and could be decomposed under irradiation of shortwave UV light, expanding the capabilities for one pot divergent photochemical processes.

AUTHOR INFORMATION

Corresponding Author

* lemcoff@bgu.ac.il.

Author Contributions

OE and AV synthesized the complexes and conducted all the experiments, NBN assisted with the 3D printing experiments.MB solved the crystal structures. The manuscript was written by OE and NGL. All authors have given approval to the final

version of the manuscript. ‡These authors contributed equally.

ACKNOWLEDGMENT

The Israel Science Foundation and the Kamin program from the Israel Innovation Authority are acknowledged for funding. We thank Zvi Kotler, Gil Bernstein Toker and Asaf Levy from the Orbotech Company for valuable discussions on material requirements for target 3D applications and technical assistance in carrying out the 3D-printed structures.

ASSOCIATED CONTENT

Supporting Information. General information, synthetic procedures, and supplemental data. This material is available free of charge via the Internet at http://pubs.acs.org."

REFERENCES

1. (a) Grela, K.; Preface In *Olefin Metathesis*, ; Grela, K. (Ed.) John Wiley & Sons, Inc.:Hobiken, NJ, **2014**; pp i-xiv; (b) Wenzel, A. G.; O'Leary, D. J.; Khosravi, E.; Grubbs, R. H. Front Matter, Volume 2: Applications in Organic Synthesis. In *Handbook of Metathesis*, Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, **2015**; pp I-XXVI; (c) Higman, C. S.; Lummiss, J. A. M.; Fogg, D. E., Olefin Metathesis at the Dawn of Implementation in Pharmaceutical and Specialty-Chemicals Manufacturing. *Angew. Chem. Int. Ed.* **2016**, 55, 3552-3565.

2. (a) Choi, T.-L.; Grubbs, R. H., Controlled Living Ring-Opening-Metathesis Polymerization by a Fast-Initiating Ruthenium Catalyst. *Angew. Chem. Int. Ed.* **2003**, *42*, 1743-1746; (b) Yasir, M.; Liu, P.; Tennie, I. K.; Kilbinger, A. F. M., Catalytic living ring-opening metathesis polymerization with Grubbs' second- and third-generation catalysts. *Nat. Chem.* **2019**, *11*, 488-494.

3. (a) Marx, V. M.; Sullivan, A. H.; Melaimi, M.; Virgil, S. C.; Keitz, B. K.; Weinberger, D. S.; Bertrand, G.; Grubbs, R. H., Cyclic Alkyl Amino Carbene (CAAC) Ruthenium Complexes as Remarkably Active Catalysts for Ethenolysis. Angew. Chem. Int. Ed. 2015, 54, 1919-1923; (b) Gawin, R.; Tracz, A.; Chwalba, M.; Kozakiewicz, A.; Trzaskowski, B.; Skowerski, K., Cyclic Alkyl Amino Ruthenium Complexes—Efficient Catalysts for Macrocyclization and Acrylonitrile Cross Metathesis. ACS Catal. 2017, 7, 5443-5449; (c) Butilkov, D.; Frenklah, A.; Rozenberg, I.; Kozuch, S.; Lemcoff, N. G., Highly Selective Olefin Metathesis with CAAC-Containing Ruthenium Benzylidenes. ACS Catal. 2017, 7 (11), 7634-7637; (d) Nascimento, D. L.; Gawin, A.; Gawin, R.; Guńka, P. A.; Zachara, J.; Skowerski, K.; Fogg, D. E., Integrating Activity with Accessibility in Olefin Metathesis: An Unprecedentedly Reactive Ruthenium-Indenylidene Catalyst. J. Am. Chem. Soc. 2019, 141, 10626-10631.

4. (a) Hejl, A.; Day, M. W.; Grubbs, R. H., Latent Olefin Metathesis Catalysts Featuring Chelating Alkylidenes. *Organometallics* 2006, 25, 6149-6154; (b) Szadkowska, A.; Grela, K., Initiation at Snail's Pace: Design and Applications of Latent Olefin Metathesis Catalysts Featuring Chelating Alkylidene Ligands. *Curr. Org. Chem.* 2008, 12 (18), 1631-1647; (c) Monsaert, S.; Ledoux, N.; Drozdzak, R.; Verpoort, F., A highly controllable latent ruthenium Schiff base olefin metathesis catalyst : Catalyst activation and mechanistic studies. *J. Polym. Sci. Part A : Polym. Chem.* 2010, 48, 302; (d) Thomas, R. M.; Fedorov, A.; Keitz, B. K.; Grubbs, R. H., Thermally Stable, Latent Olefin Metathesis Catalysts. *Organometallics* 2011, 30, 6713-6717; (e) Vidavsky, Y.; Anaby, A.; Lemcoff, N. G., Chelating alkylidene ligands as pacifiers for ruthenium catalysed olefin metathesis. *Dalton Trans.*

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58 59

60

2012, *41*, 32-43; (f) Jakobs, R. T. M.; Sijbesma, R. P., Mechanical Activation of a Latent Olefin Metathesis Catalyst and Persistence of its Active Species in ROMP. *Organometallics* **2012**, *31*, 2476-2481.

5. (a) Eivgi, O.; Lemcoff, N. G., Turning the Light On: Recent Developments in Photoinduced Olefin Metathesis. *Synthesis* **2018**, 50, 49-63; (b) Pinaud, J.; Trinh, T. K. H.; Sauvanier, D.; Placet, E.; Songsee, S.; Lacroix-Desmazes, P.; Becht, J.-M.; Tarablsi, B.; Lalevée, J.; Pichavant, L.; Héroguez, V.; Chemtob, A., In Situ Generated Ruthenium–Arene Catalyst for Photoactivated Ring-Opening Metathesis Polymerization through Photolatent N-Heterocyclic Carbene Ligand. *Chem. Eur. J.* **2018**, *24*, 337-341; (c) Theunissen, C.; Ashley, M. A.; Rovis, T., Visible-Light-Controlled Ruthenium-Catalyzed Olefin Metathesis. *J. Am. Chem. Soc.* **2019**, *141*, 6791-6796.

6. (a) Skowerski, K.; Wierzbicka, C.; Grela, K., Olefin Metathesis Under Continuous Flow Mode. *Curr. Org. Chem.* 2013, 17, 2740-2748; (b) Drop, M.; Bantreil, X.; Grychowska, K.; Mahoro, G. U.; Colacino, E.; Pawłowski, M.; Martinez, J.; Subra, G.; Zajdel, P.; Lamaty, F., Continuous flow ring-closing metathesis, an environmentally-friendly route to 2,5-dihydro-1H-pyrrole-3-carboxylates. *Green Chem.* 2017, 19, 1647-1652; (c) Cambié, D.; Bottecchia, C.; Straathof, N. J. W.; Hessel, V.; Noël, T., Applications of Continuous-Flow Photochemistry in Organic Synthesis, Material Science, and Water Treatment. *Chem. Rev.* 2016, 106, 10276-10341; (d) Su, Y.; Straathof, N. J. W.; Hessel, V.; Noël, T., Photochemical Transformations Accelerated in Continuous-Flow Reactors: Basic Concepts and Applications. *Chem. Eur. J.* 2014, 20, 10562-10589.

7. (a) Ben-Asuly, A.; Aharoni, A.; Diesendruck, C. E.; Vidavsky,
Y.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G., Photoactivation of Ruthenium Olefin Metathesis Initiators. *Organometallics* 2009,
28, 4652-4655; (b) Ginzburg, Y.; Anaby, A.; Vidavsky, Y.; Diesendruck, C. E.; Ben-Asuly, A.; Goldberg, I.; Lemcoff, N. G.,
Widening the Latency Gap in Chelated Ruthenium Olefin Metathesis Catalysts. *Organometallics* 2011, 30, 3430-3437.

8. Ivry, E.; Frenklah, A.; Ginzburg, Y.; Levin, E.; Goldberg, I.; Kozuch, S.; Lemcoff, N. G.; Tzur, E., Light- and Thermal-Activated Olefin Metathesis of Hindered Substrates. *Organometallics* **2018**, 37, 176-181.

9. (a) Levin, E.; Mavila, S.; Eivgi, O.; Tzur, E.; Lemcoff, N. G., Regioselective Chromatic Orthogonality with Light-Activated Metathesis Catalysts. *Angew. Chem. Int. Ed.* **2015**, *54*, 12384-12388; (b) Eivgi, O.; Sutar, R. L.; Reany, O.; Lemcoff, N. G., Bichromatic Photosynthesis of Coumarins by UV Filter-Enabled Olefin Metathesis. *Adv. Synth. Catal.* **2017**, *359*, 2352-2357; (c) Sutar, R.; Sen, S.; Eivgi, O.; Segalovich, G.; Schapiro, I.; Reany, O.; Lemcoff, N. G., Guiding a divergent reaction by photochemical control: bichromatic selective access to levulinates and butenolides. *Chem. Sci.* **2018**, *9*, 1368-1374.

10. (a) Bantreil, X.; Schmid, T. E.; Randall, R. A. M.; Slawin, A. M. Z.; Cazin, C. S. J., Mixed N-heterocyclic carbene/phosphite ruthenium complexes: towards a new generation of olefin metathesis catalysts. *Chem. Commun.* 2010, 46, 7115-7117; (b) Lexer, C.; Burtscher, D.; Perner, B.; Tzur, E.; Lemcoff, N. G.; Slugovc, C., Olefin metathesis catalyst bearing a chelating phosphine ligand. J. Organomet. Chem. 2011, 696, 2466-2470.

II. (a) Guidone, S.; Songis, O.; Nahra, F.; Cazin, C. S. J., Conducting Olefin Metathesis Reactions in Air: Breaking the Paradigm. ACS Catal. 2015, 5, 2697-2701; (b) Bantreil, X.; Poater, A.; Urbina-Blanco, C. A.; Bidal, Y. D.; Falivene, L.; Randall, R. A. M.; Cavallo, L.; Slawin, A. M. Z.; Cazin, C. S. J., Synthesis and Reactivity of Ruthenium Phosphite Indenylidene Complexes. Organometallics 2012, 31, 7415-7426.

12. Eivgi, O.; Guidone, S.; Frenklah, A.; Kozuch, S.; Goldberg, I.; Lemcoff, N. G., Photoactivation of Ruthenium Phosphite Complexes for Olefin Metathesis. *ACS Catal.* **2018**, *8*, 6413-6418. 13. Schmid, T. E.; Bantreil, X.; Citadelle, C. A.; Slawin, A. M. Z.; Cazin, C. S. J., Phosphites as ligands in ruthenium-benzylidene catalysts for olefin metathesis. *Chem. Commun.* **2011**, *47*, 7060-7062.

14. Sutar, R. L.; Levin, E.; Butilkov, D.; Goldberg, I.; Reany, O.; Lemcoff, N. G., A Light-Activated Olefin Metathesis Catalyst Equipped with a Chromatic Orthogonal Self-Destruct Function. *Angew. Chem. Int. Ed.* **2016**, 55, 764-767.

15. (a) Patchornik, A.; Amit, B.; Woodward, R. B., Photosensitive protecting groups. *J. Am. Chem. Soc.* **1970**, *92*, 6333-6335; (b) Il'ichev, Y. V.; Schwörer, M. A.; Wirz, J., Photochemical Reaction Mechanisms of 2-Nitrobenzyl Compounds: Methyl Ethers and Caged ATP. *J. Am. Chem. Soc.* **2004**, *126*, 4581-4595; (c) Solomek, T.; Mercier, S.; Bally, T.; Bochet, C. G., Photolysis of ortho-nitrobenzylic derivatives: the importance of the leaving group. *Photochem. & Photobiol. Sci.* **2012**, *11*, 548-555.

16. Bertran-Vicente, J.; Schümann, M.; Schmieder, P.; Krause, E.; Hackenberger, C. P. R., Direct access to site-specifically phosphorylated-lysine peptides from a solid-support. *Org. Biomol.Chem.* **2015**, *13*, 6839-6843.

17. (a) Boydston, A. J.; Cao, B.; Nelson, A.; Ono, R. J.; Saha, A.; Schwartz, J. J.; Thrasher, C. J., Additive manufacturing with stimuli-responsive materials. *J. Mater. Chem. A* **2018**, *6*, 20621-20645; (b) Nadgorny, M.; Ameli, A., Functional Polymers and Nanocomposites for 3D Printing of Smart Structures and Devices. *ACS Appl. Mater. Interfaces* **2018**, 10, 17489-17507.

18. Weitekamp, R. A.; Atwater, H. A.; Grubbs, R. H., Photolithographic Olefin Metathesis Polymerization. *J. Am. Chem. Soc.* **2013**, *135*, 16817-16820.

19. Trinh, T. K. H.; Schrodj, G.; Rigolet, S.; Pinaud, J.; Lacroix-Desmazes, P.; Pichavant, L.; Héroguez, V.; Chemtob, A., Combining a ligand photogenerator and a Ru precatalyst: a photoinduced approach to cross-linked ROMP polymer films. *RSC Adv.* **2019**, *9*, 27789-27799.

20. (a) Vallons, K. A. M.; Drozdzak, R.; Charret, M.; Lomov, S. V.; Verpoest, I., Assessment of the mechanical behaviour of glass fibre composites with a tough polydicyclopentadiene (PDCPD) matrix. *Composites Part A* 2015, *78*, 191-200; (b) Vidavsky, Y.; Navon, Y.; Ginzburg, Y.; Gottlieb, M.; Lemcoff, N. G., Thermal properties of ruthenium alkylidene-polymerized dicyclopentadiene. *Beilstein J. Org. Chem.* 2015, *11*, 1469-1474.

21. (a) Robertson, I. D.; Dean, L. M.; Rudebusch, G. E.; Sottos, N. R.; White, S. R.; Moore, J. S., Alkyl Phosphite Inhibitors for Frontal Ring-Opening Metathesis Polymerization Greatly Increase Pot Life. *ACS Macro Lett.* **2017**, *6*, 609-612; (b) Robertson, I. D.; Yourdkhani, M.; Centellas, P. J.; Aw, J. E.; Ivanoff, D. G.; Goli, E.; Lloyd, E. M.; Dean, L. M.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; White, S. R., Rapid energy-efficient manufacturing of polymers and composites via frontal polymerization. *Nature* **2018**, 557, 223-227.

TOC - Graphic

