PHOTOSWITCHABLE RUTHENIUM-BASED CATALYSIS FOR OLEFIN METATHESIS

Reported by Tony Zhang   November 27, 2023

INTRODUCTION

Since its discovery in the 1950s, olefin metathesis has been a significant and powerful tool in organic chemistry owing to the ability to combine parts from two olefins, including Ring-Closing Metathesis (RCM), Cross-Metathesis (CM), and Ring-Opening Metathesis Polymerization (ROMP). For example, RCM is used in the preparation of Simeprevir, a hepatitis C treatment. At the same time, a bio-refinery plant in Indonesia uses CM to process seed oil to access olefins and related chemicals.[1] Because the outcome of an olefin metathesis reaction relies heavily on catalyst properties, catalysts have been developed to deliver higher turnover numbers, stereoselectivity, or stability. In addition, a new class are latent precatalysts that require external stimuli to activate. Among all the external stimuli, light has the advantages of being green, easily accessible, and convenient for temporal and spatial control. An efficient photocatalyst for ROMP can enable precise and accessible stereolithography.[2]

These photocatalysts have modified pathways to reach the active form compared with the traditional olefin metathesis catalysts, and they respond differently to irradiation according to the design logic and, therefore, have different impacts on olefin metathesis reactions in the presence of light.

MODULATING THE COORDINATING ATOM

Ruthenium olefin metathesis precatalysts usually have square-pyramidal structures and share a common trans geometry of the X-type and the n-type ligands while the carbene stays in the apical position. However, after exchanging the oxygen in the Hoveyda−Grubbs catalyst with a sulfur atom, Lemcoff, and coworkers discovered that the two chlorides give a more stable cis geometry at room temperature, and the catalyst is inactive.[3] However, UV radiation at room temperature activates the catalyst by photoisomerization to the active trans isomer and catalyzes the RCM reaction of diethyl diallylmalonate. The trans isomer can then be heated to transform back to the cis conformer and lose catalytic activity. The conversion reacts rapidly to the light/heat stimuli (Scheme 1).

Using this strategy, new catalysts were developed, including sulfur-chelated derivatives with improved properties, chelated sulfoxide catalysts, and ruthenium phosphite complexes.[4]
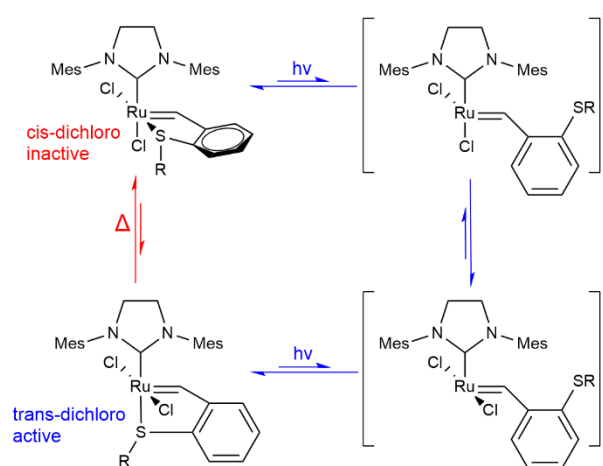
Scheme 1. Proposed isomerization mechanism

SINGLE-ELECTRON TRANSFER PATHWAYS

Instead of using light to isomerize the catalyst, another approach is to couple a latent catalyst with a photocatalyst, which, upon irradiation, can then complete the olefin metathesis catalytic cycle through a single-electron transfer (SET) pathway. In 2019, Rovis and coworkers reported a bis(NHC)-ruthenium complex that is inactive at room temperature but can be activated with photocatalyst TPPT or analogs under blue light, which helps with cleavage of one NHC ligand.[5] Early this year, they also reported a deep red to near-infrared radiation in conjunction with an osmium(II) photocatalyst to activate the latent solvent-coordinated, cationic precatalyst (**Scheme 2**).[6] In both cases, the activated photocatalyst will take one electron from the precatalyst which activates it to complete the catalytic cycle.
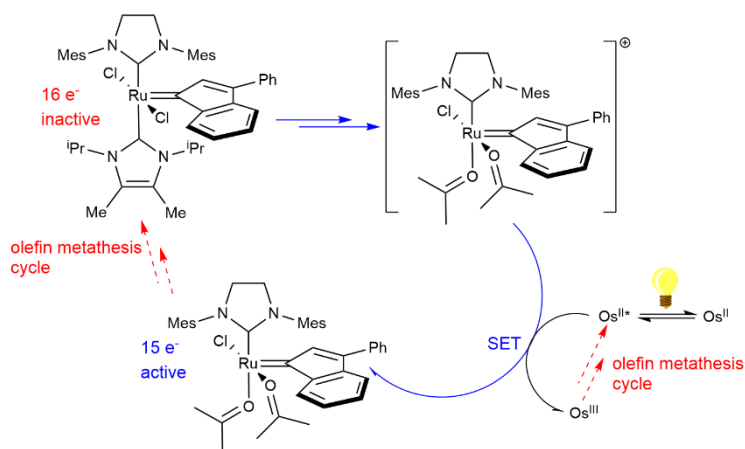
Scheme 2. Proposed SET pathway to activate the catalyst.

PHOTOSWITCHABLE LIGANDS

One of the most straightforward yet rarely studied strategies is incorporating photoswitch motifs in the ligand. In 2017, Bielawski and coworkers reported a catalyst with an NHC ligand bearing an annulated photochromic dithienylethene (DTE) that would cyclize upon irradiation and change the catalyst performance.[7] In 2021, Hong and coworkers incorporated an azobenzene motif in its cyclic(alkyl)(amino)carbene (CAAC) ligand. The new catalyst could rapidly turn the reaction on and off under different wavelengths through photoisomerization of azobenzene.[8]

REFERENCES

(1) Ogba, O. M.; Warner, N. C.; O'Leary, D. J.; Grubbs, R. H. *Chem. Soc. Rev.* **2018**, 47 (12), 4510–4544.

(2) Leguizamon, S. C.; Monk, N. T.; Hochrein, M. T.; Zapien, E. M.; Yoon, A.; Foster, J. C.; Appelhans, L. N. *Macromolecules* **2022**, 55 (18), 8273–8282.

(3) Ben-Asuly, A.; Aharoni, A.; Diesendruck, C. E.; Vidavsky, Y.; Goldberg, I.; Straub, B. F.; Lemcoff, N. G. *Organometallics* **2009**, 28 (16), 4652–4655.

(4) Eivgi, O.; Phatake, R. S.; Nechmad, N. B.; Lemcoff, N. G. *Acc. Chem. Res.* **2020**, 53 (10), 2456–2471.

(5) Theunissen, C.; Ashley, M. A.; Rovis, T. *J. Am. Chem. Soc.* **2019**, 141 (17), 6791–6796.

(6) Cabanero, D. C.; Nguyen, J. A.; Cazin, C. S. J.; Nolan, S. P.; Rovis, T. *ACS Catal.* **2023**, 13 (7), 4384–4390.

(7) Teator, A. J.; Shao, H.; Lu, G.; Liu, P.; Bielawski, C. W. *Organometallics* **2017**, 36 (2), 490–497.

(8) Park, S.; Byun, S.; Ryu, H.; Hahm, H.; Lee, J.; Hong, S. *ACS Catal.* **2021**, 11 (22), 13860–13865.