Homogeneous Catalysis

Fluorescent Dyes

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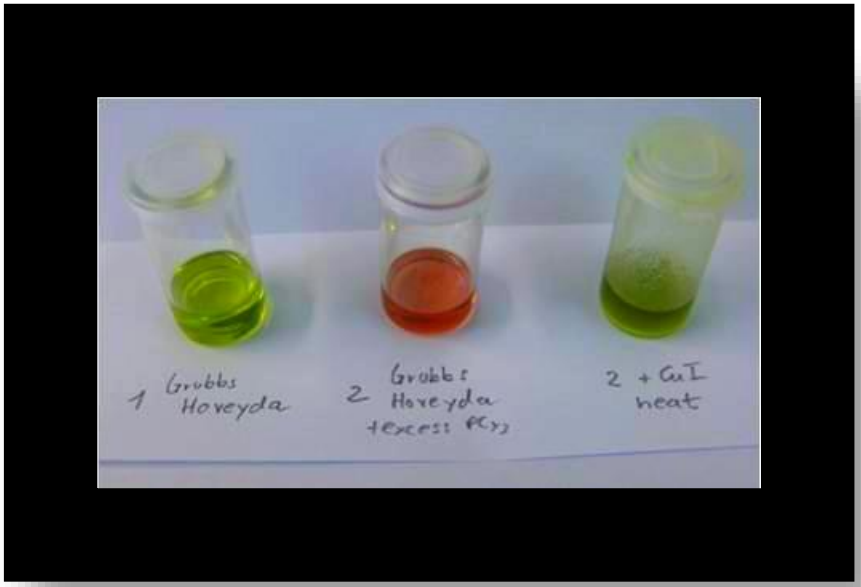

- **Better Tools for the efficient synthesis of Organic Molecules and Polymers**
- **Understanding the mechanism**
- **Using Fluorescent Dyes to understand Homogenous Catalysis**

Please contact: Prof. Dr. Herbert Plenio, Organometallic Chemistry, Alarich-Weiss-Str. 12, TU Darmstadt, 64287 Darmstadt, Germany,

plenio@tu-darmstadt.de

Better Tools for the Conversion of Molecules

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RESEARCH TOPICS

superior synthetic tools =

Development of new catalysts

better synthesis =

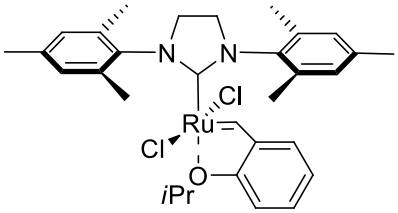
new approaches for the synthesis of organic molecules and polymers

Mechanistic understanding =

mechanistic studies of transition-metal catalyzed transformations

www.lego.com

fast and low-loading RCM catalysis



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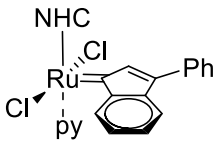
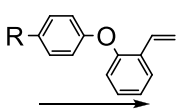
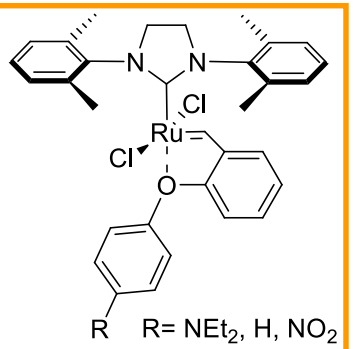
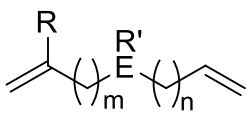


Umicore M31
(or M20)

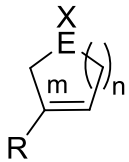


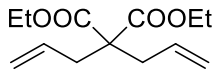


R= NEt_2, H, NO_2

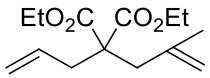


[Ru]
toluene
50 °C
15 min

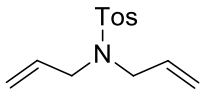




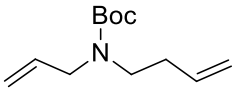
100 ppm 88%



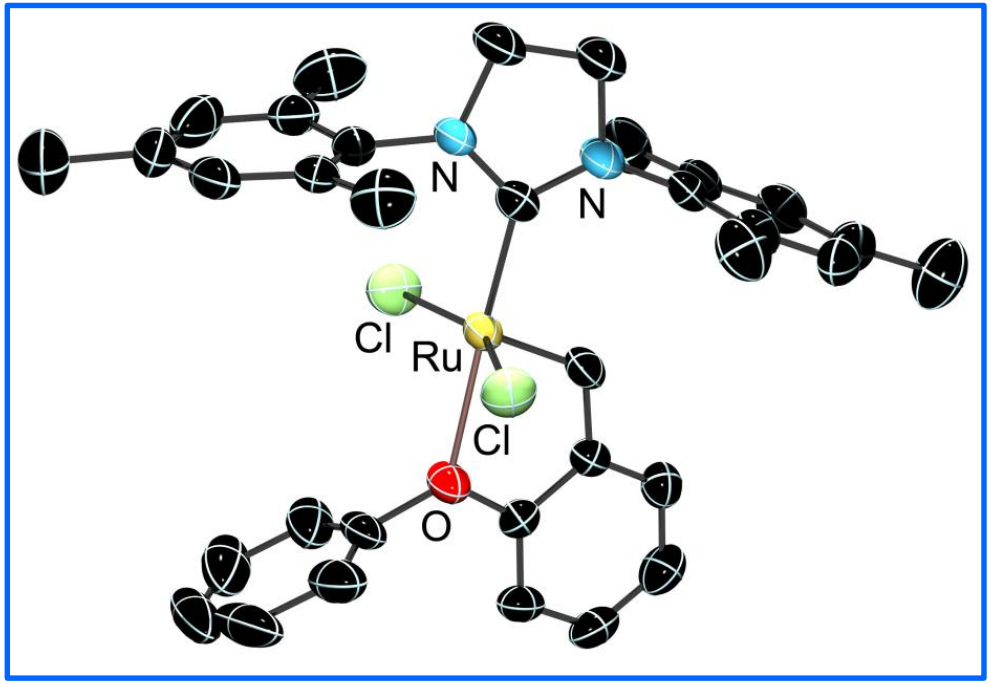
100 ppm 89%



15 ppm 91%



50 ppm 89%



P. Kos, R. Savka, H. Plenio, *Adv. Synth. Catal.* **2013**, *355*, 439
http://onlinelibrary.wiley.com/doi/10.1002/adsc.201200956/abstract

Research Topic: Renewables

Ethenolysis of natural rubber and tire rubber

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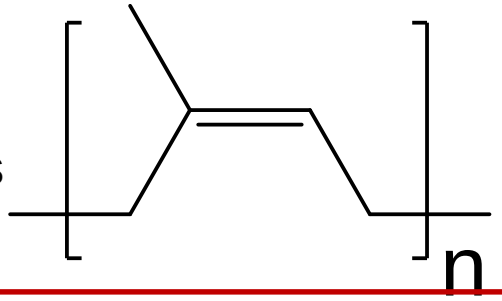
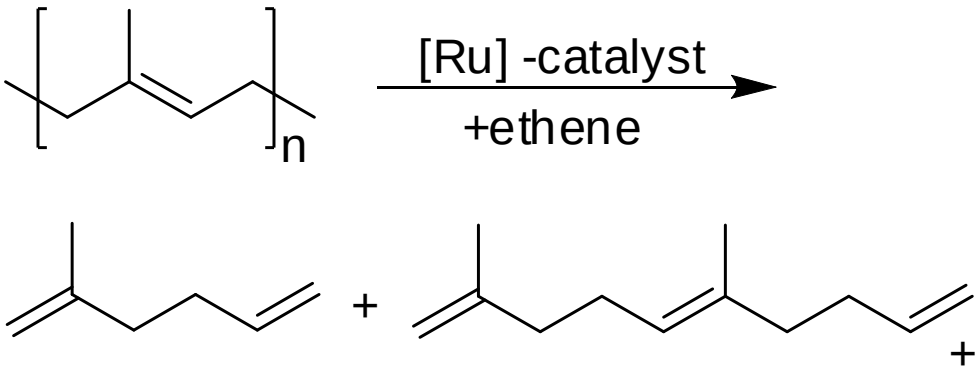
natural rubber
cis-Polyisoprene
Hevea brasiliensis

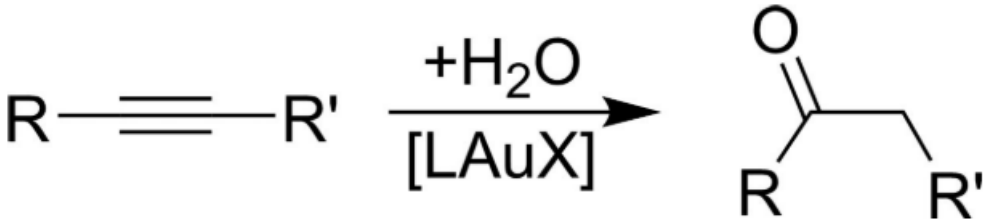


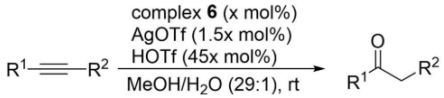
The ethenolysis of natural rubber or tire rubber granulate leads to the depolymerization of the polymer, resulting in the facile formation of small terpenes, which might be suitable for the synthesis of fragrances.

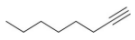
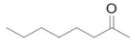
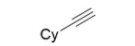
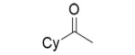
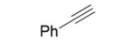
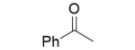
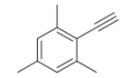
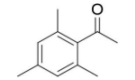
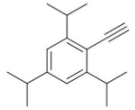
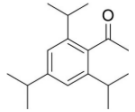
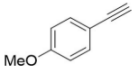
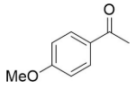
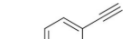
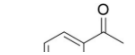


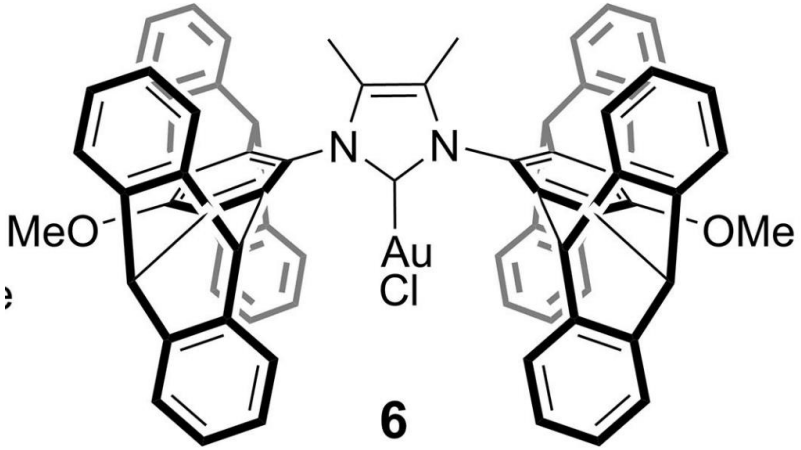
On the ethenolysis of end-of-life tire granulates
S. Wolf, H. Plenio, *Green Chem.* ***2013, 15, 31***; http://dx.doi.org/10.1039/C2GC36417D

Gold-catalyzed Hydration of Alkynes





entry	substrate	product	6 (mol%)	time (h)	Conversion (%)[a]	yield (%)[a]
1			0.01	1	>99	55[b]
2			0.01	2.5	>99	67[b]
3			0.02	3	>99	96
4			0.02	20	>99	96
5			0.02	20	92	91
6			0.02	1	>99	96
7			0.02	20	>99	99



M. Heidrich, M. Bergmann, D. Müller-Borges, H. Plenio, *Adv. Synth. Catal.* **2018**, *360*, 3572, https://onlinelibrary.wiley.com/doi/full/10.1002/adsc.201800605

organic solubles obtained after ethenolysis of ELT powder

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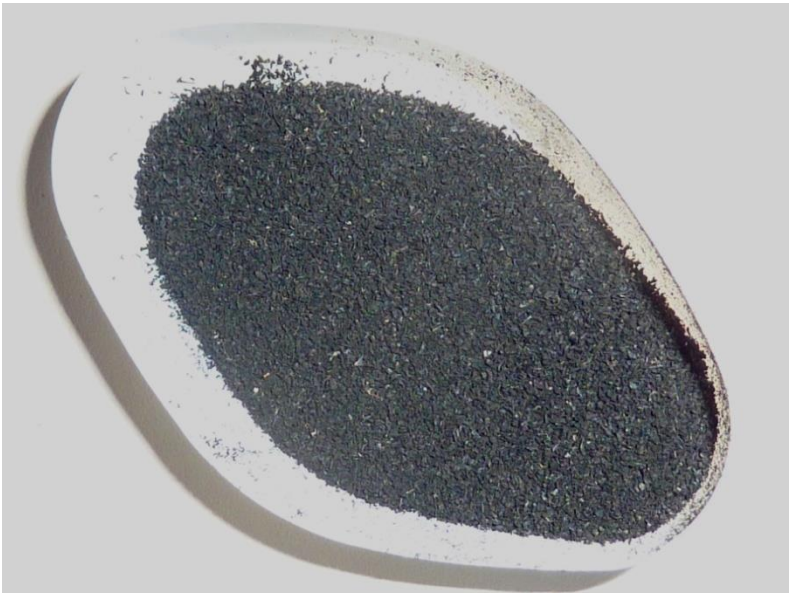

[Ru]
80 °C
7 bar
ethene
toluene

10 g of ELT yield up to 5 g of organic solubles

10 g of ELT require 0.04 g of ruthenium complex

Understanding the mechanism

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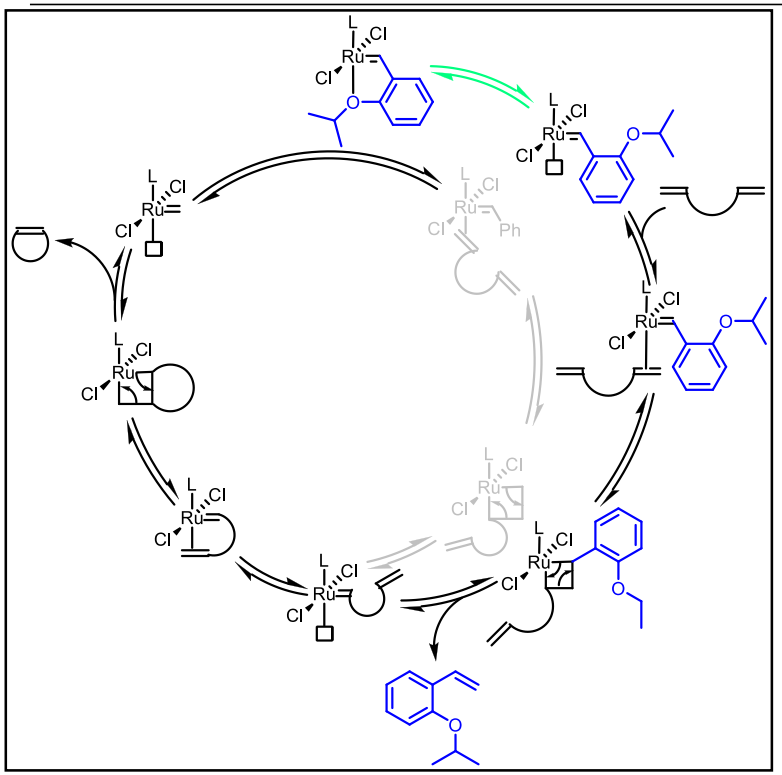
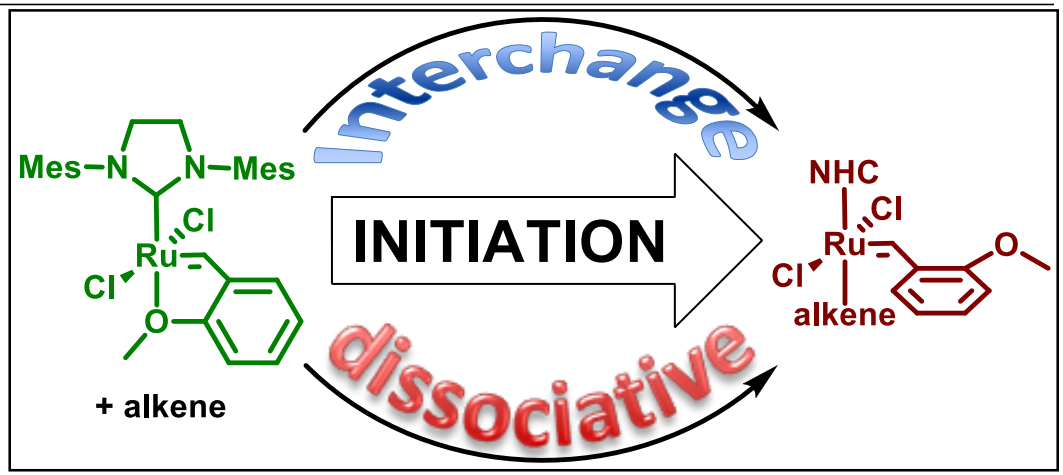
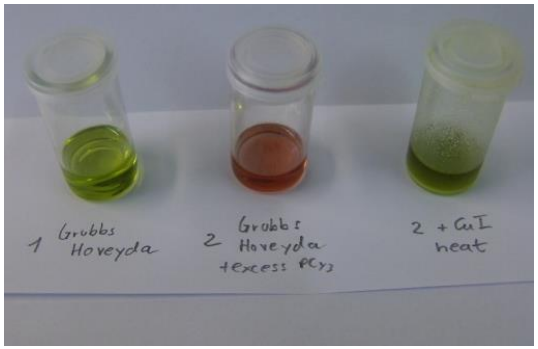


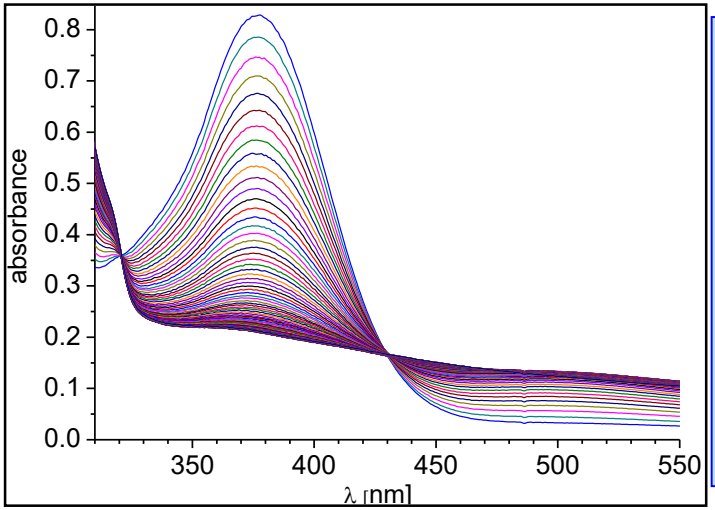


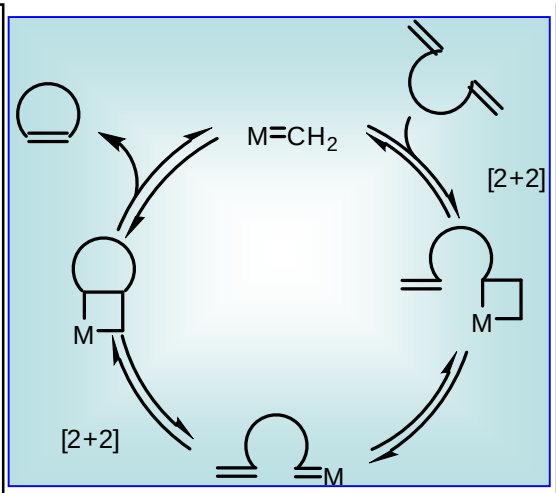


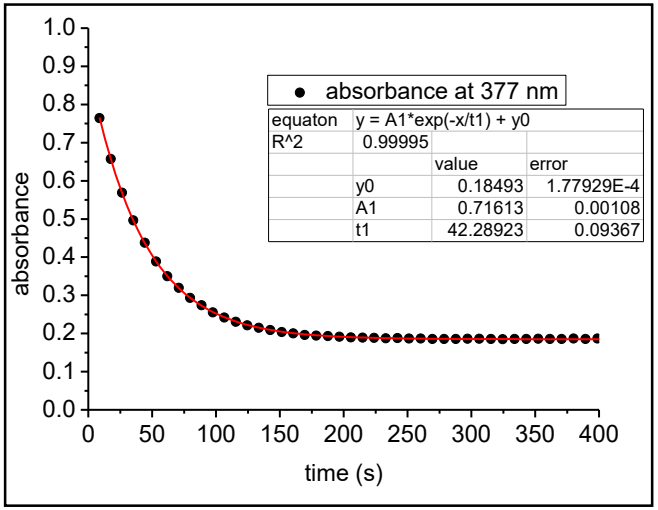
Progress in catalysis critically relies on detailed mechanistic understanding. The development of olefin metathesis over the last decades from ill-defined, low-activity catalysts to powerful synthetic tools is an excellent example for this.

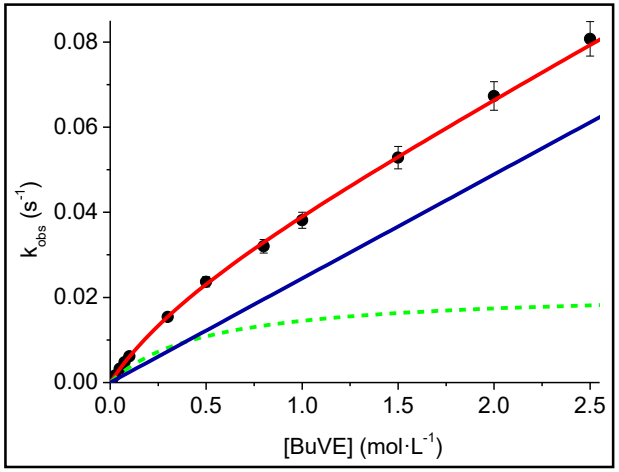
On the Mechanism of the Initiation Reaction in Grubbs-Hoveyda Complexes
V. Thiel, M. Hendann, K. J. Wannowius, H. Plenio, *J. Am. Chem. Soc*. **2012**, *134*, 1104; ACS Catal. 2019, 9, 951 https://doi.org/10.1021/acscatal.8b03445

Understanding the Mechanism









The activation of precatalysts leads to the generation of a catalytically active species. Analysis of initiation kinetics with time-dependent spectroscopic techniques provides a clearer picture of the elementary steps of precatalyst activation.

$k_{obs} = a \cdot [olefin]/(1+b \cdot [olefin]) + c \cdot [olefin]$

Bodipy-tagged Crabtree Catalysts

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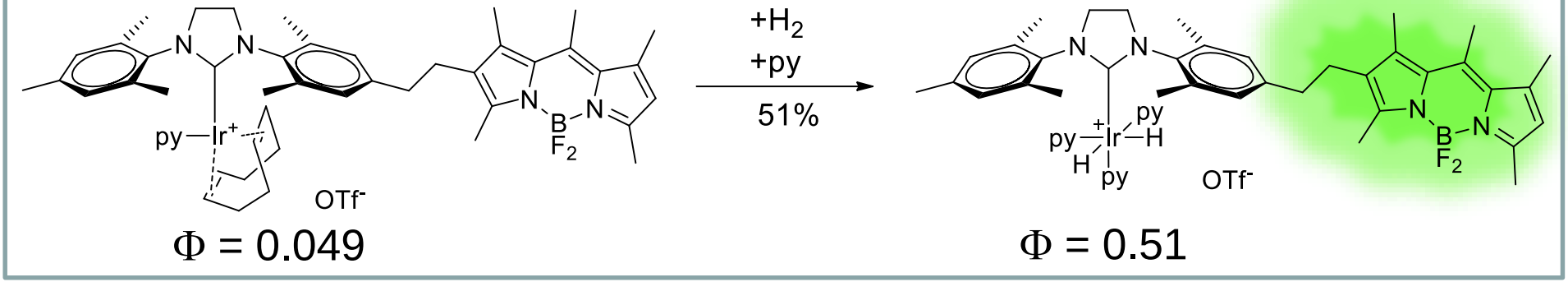
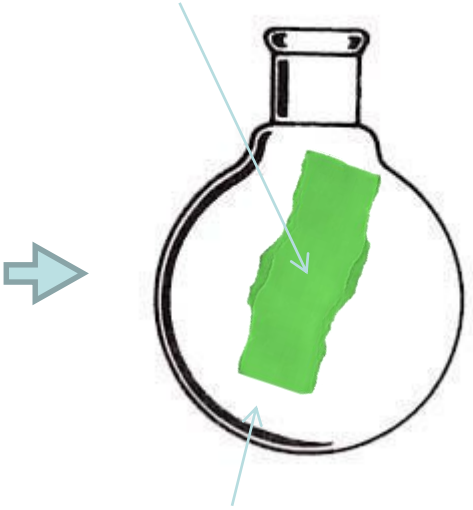
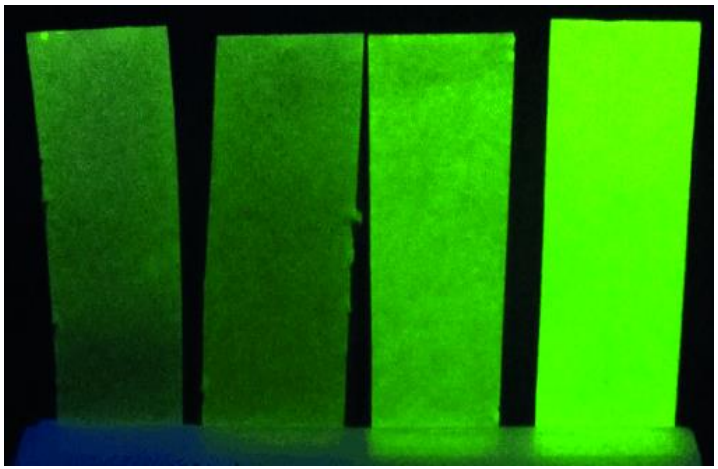


$\Phi = 0.049$ $\Phi = 0.51$

impregnated with complex filter paper strip



H_2



H_2, vol %: 0 1 4 100

Paper strips for H_2 detection

P. Kos, H. Plenio, *Angew. Chem. Int. Ed.* **2015**, *54*, 13293-13296
http://onlinelibrary.wiley.com/doi/10.1002/anie.201506918/abstract

FRET for the detection of dimeric Gold Catalysis

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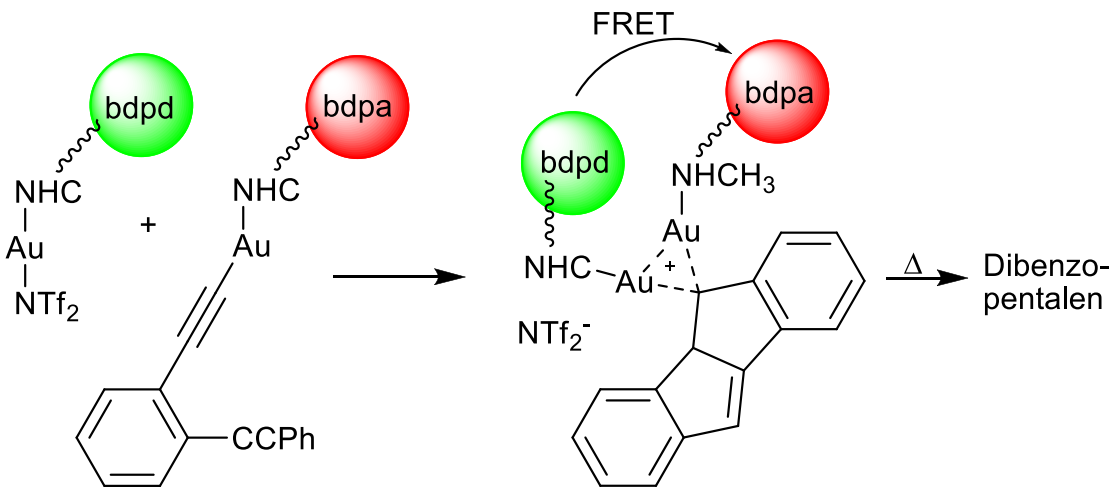
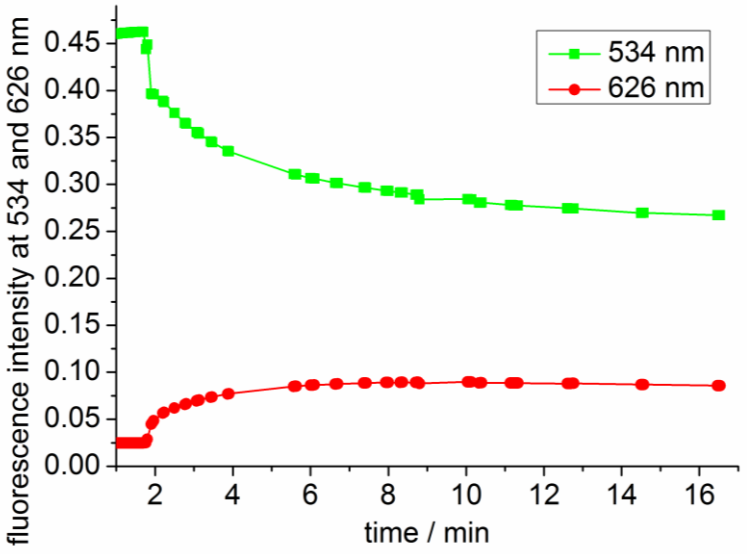
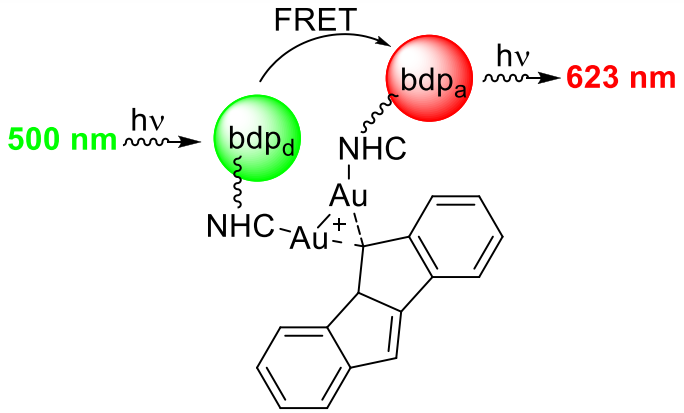
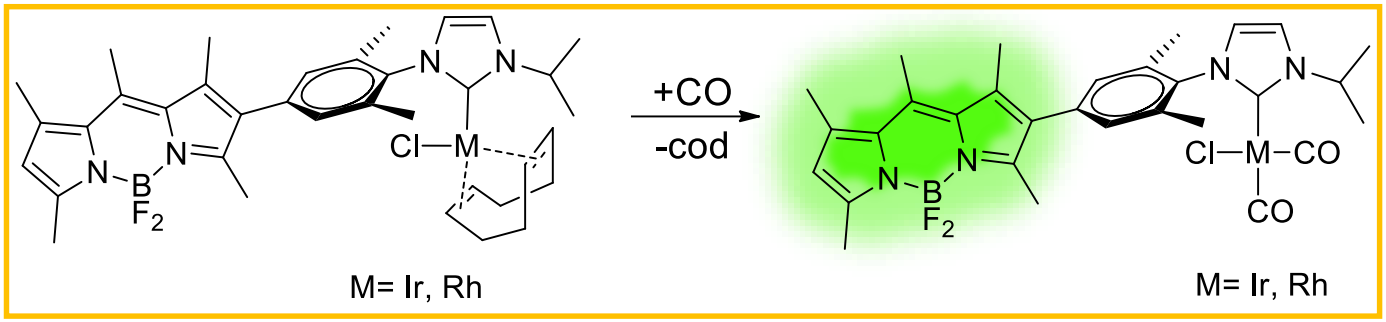


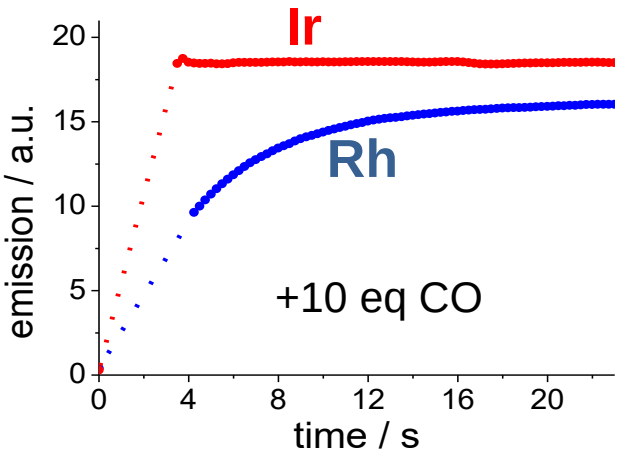


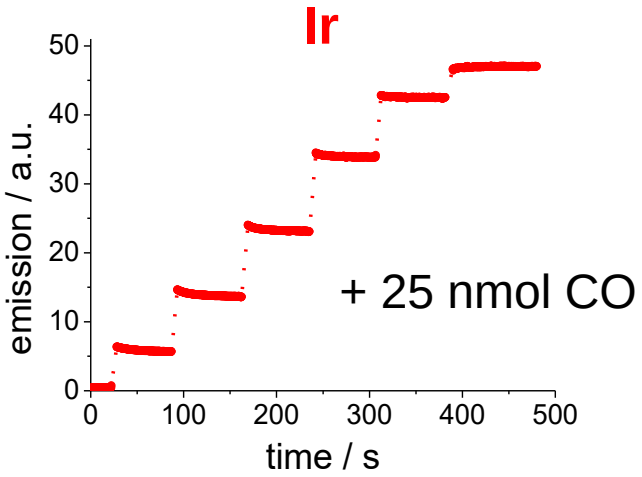


O. Halter, H. Plenio, Chem. Commun. **2017**, *53*, 12461,
http://pubs.rsc.org/en/content/articlepdf/2017/cc/c7cc07018g

Detecting CO a few nanomols of CO

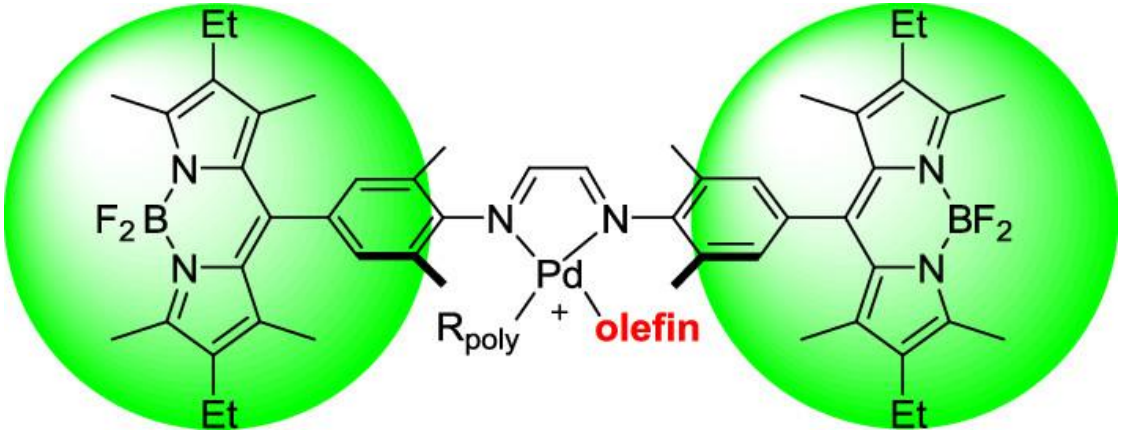


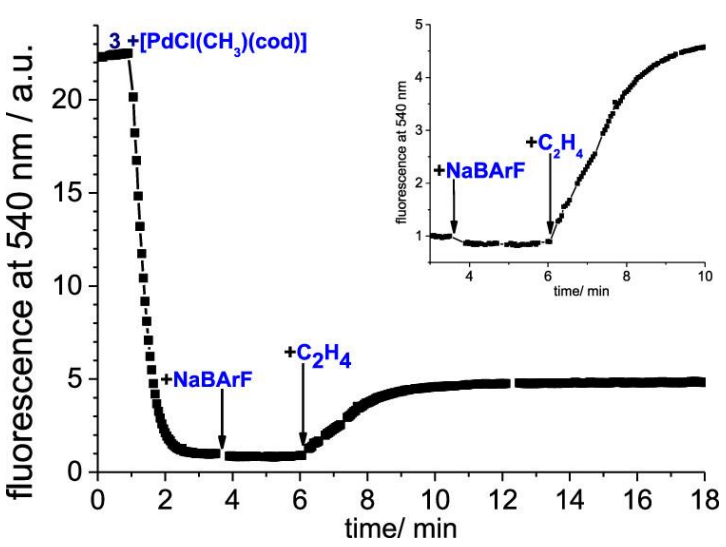


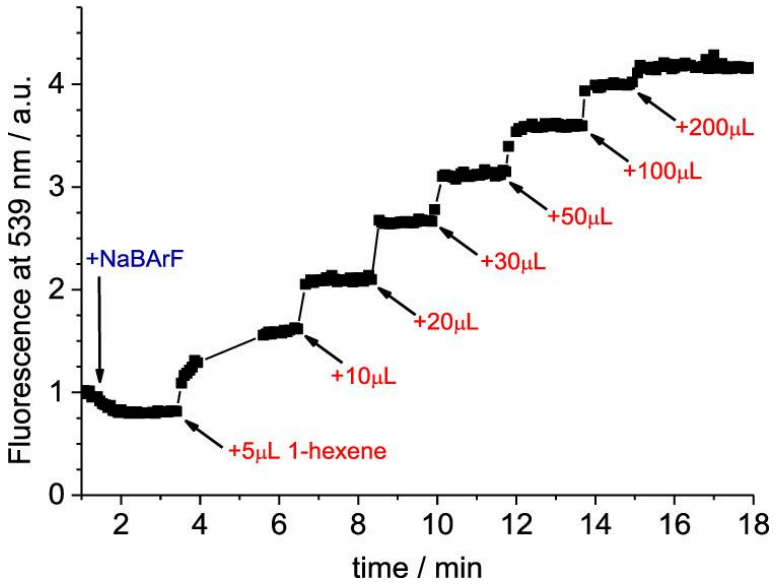


- **80-fold** fluorescence increase for iridium complex
- Complete conversion in **less than 4 s** for Ir
- Detection of less than 1 nanomol of CO

Observing Ethene Insertion in Olefin Polymerization Catalyst







O. Halter, J. Spielmann, Y. Kanai, H. Plenio, *Organometallics* **2019**, 38, 2138, https://doi.org/10.1021/acs.organomet.9b00130