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Latent Ruthenium Olefin Metathesis Catalysts and methods of activation.

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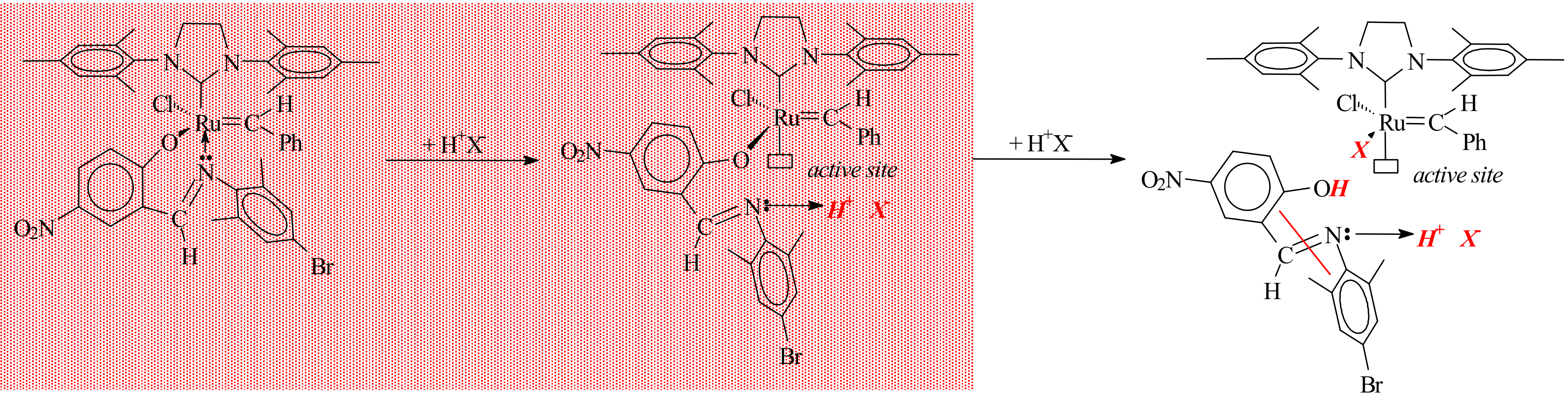
General mechanism of acid activation

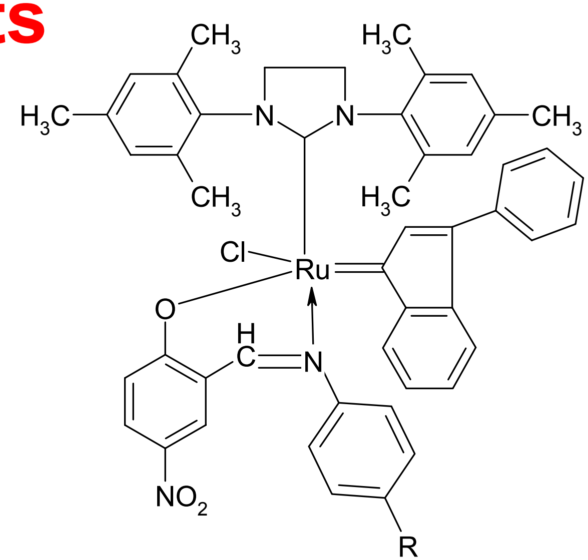


Dry conditions

1. Protons prevent the imine ligand to coordinate, liberating the active site
2. The imine-bond hydrolysis
3. The Ru-O bond can be broken, due to acidolysis

Optimization of some indenylidene catalyst

Influence of para-substituents



R= tert butyl

R=isopropyl

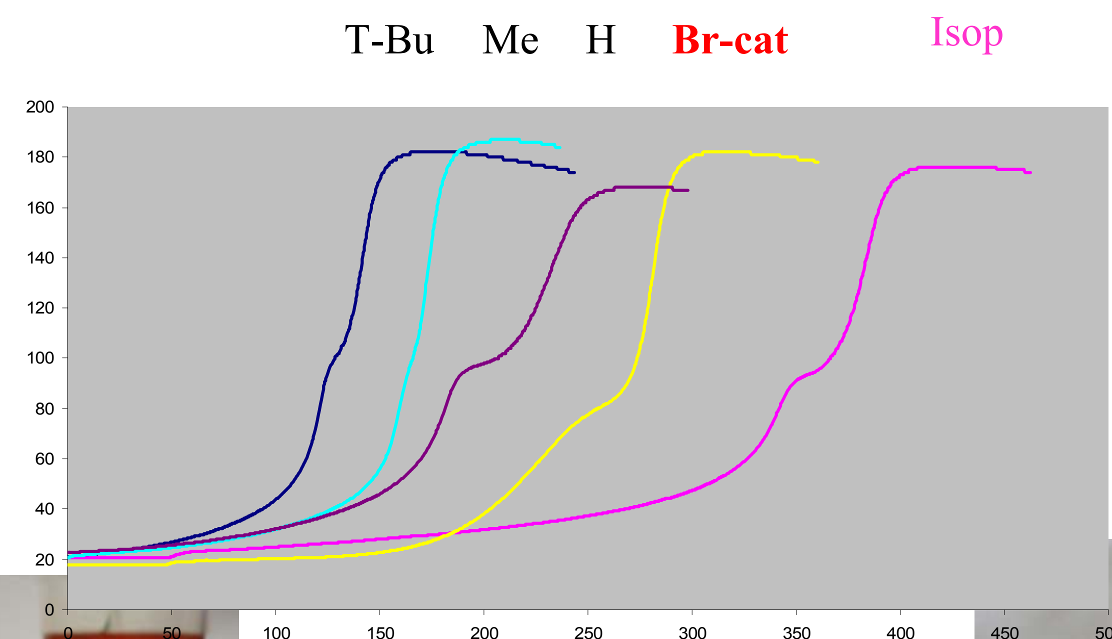
R=methyl

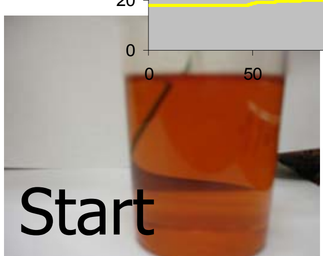
R=H

<u>Conditions:</u>

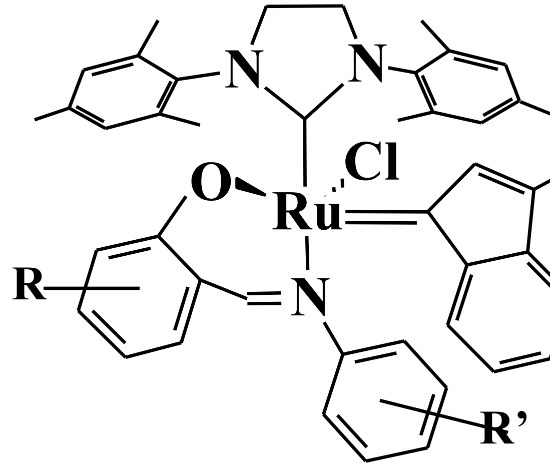
Cat/30000 eq DCPD (10ml)

20 eq, 30 eq, 10 eq HCl, R.T





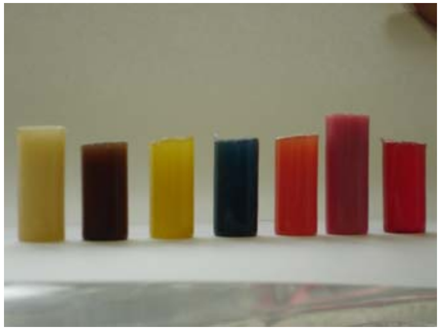
- Schiff base catalyst



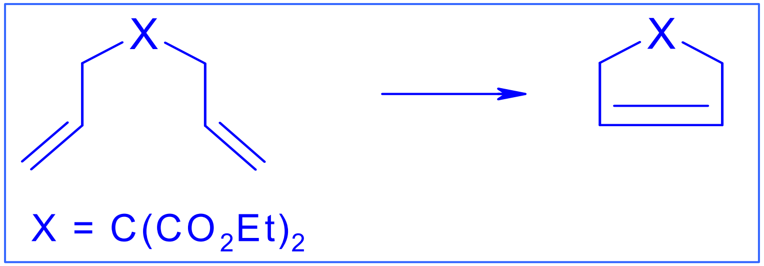
Neolyst M4-type

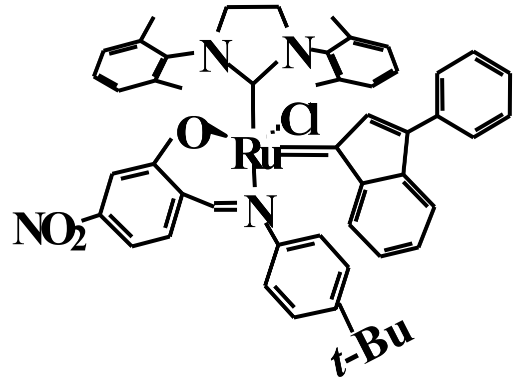
Advantages

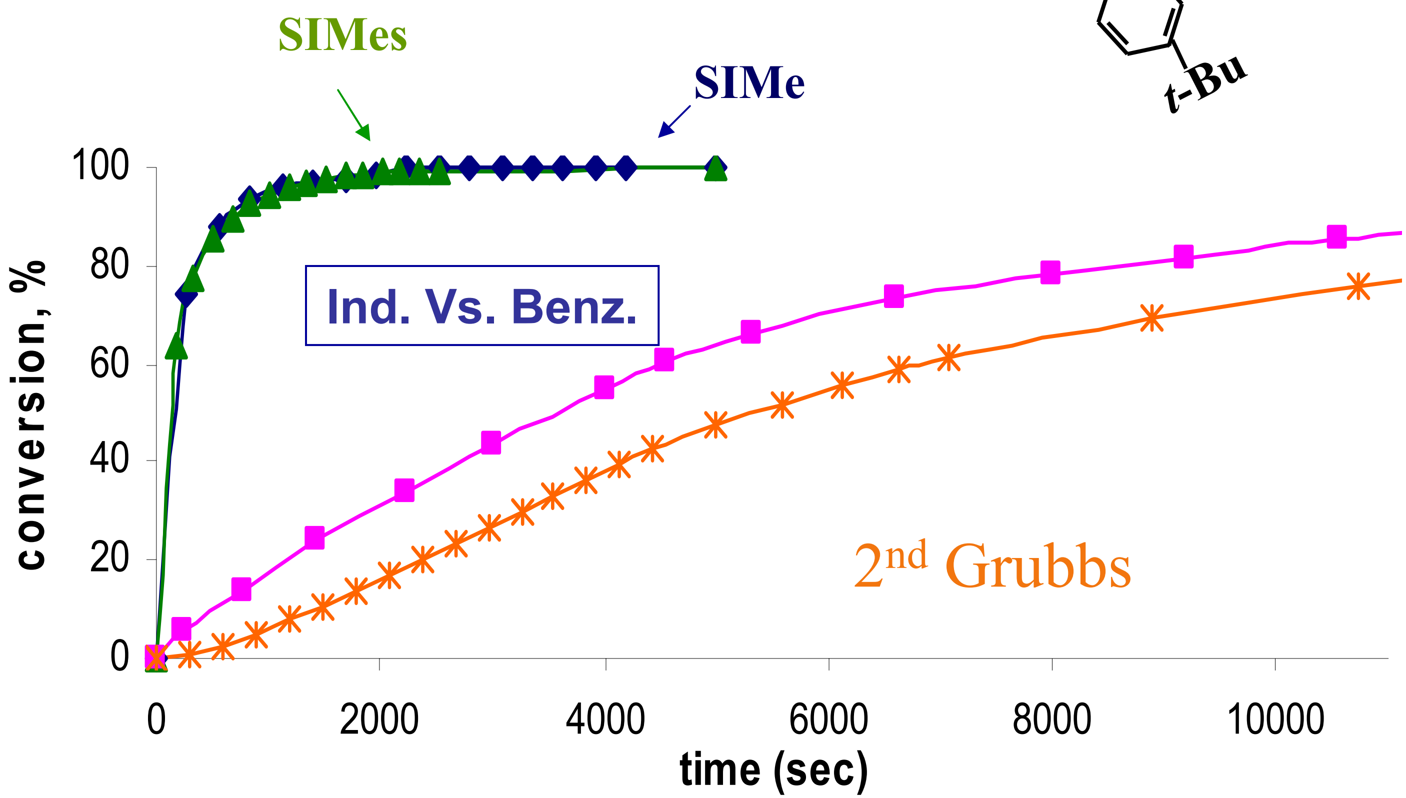
- 1st Ru-catalyst with pot-life for DCPD
- Easily tuneable
- easily activated in a controlled way
- opens new field in PDCPD chemistry

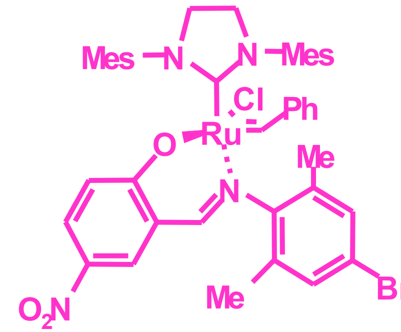


RCM of DEDAM









cat/substrate/$PhSiCl_3$=1/200/1, (19 °C),
2nd G no cocatalyst

Conclusion

The tested Schiff base catalysts

- display excellent stability
- act as precatalysts which are on-demand chemically activated by HCl

A ^{1}H NMR study elucidated the activation mechanism of Schiff base ligated olefin metathesis precursors, comprising protonation and decondensation of the imine bond and cleavage of the Ru-O bond.

High TON's were reached for the ROMP of DCPD using the acid activated catalyst.
This feature, on-demand chemical activation, is very attractive for industrial processes.

Highly active catalyst for RCM.