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## Functionalization of Vinylsubstituted (poly,cyclo)siloxanes and Silsesquioxanes via Cross-metathesis vs. Silylative Coupling

Our previous reports have demonstrated that Grubbs type ruthenium alkylidene complexes effectively catalyze the cross-metathesis (CM) of vinylsubstituted silanes, siloxanes and silsesquioxanes with styrene, alkenes and numerous allyl derivatives [1]. Efficient ADMET copolymerization of divinyltetraethoxydisiloxane with 1,9-decadiene and divinylbenzene as well as ROM/ADMET copolymerization of divinyltetraethoxydisiloxane with cyclooctadiene have also been reported [2]. Recently, we have proposed a general scheme of vinylsilane reactivity in the presence of Grubbs catalyst [3].

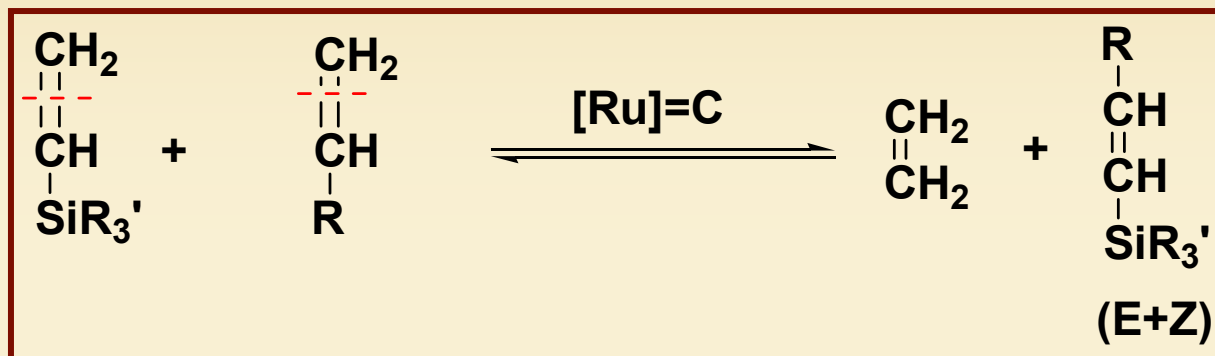
In the lecture we report recent results on effective cross-metathesis of a variety of olefins and dienes with vinyl substituted (poly)siloxanes, cyclosiloxanes and silsesquioxanes. The two reactions [1,4] offers an attractive general and complementary synthetic routes leading to functionalized (poly)siloxanes, cyclosiloxanes and silsesquioxanes of great practical importance as precursors and/or components of nanomaterials as well as organometallic reagents for organic synthesis.

### References:

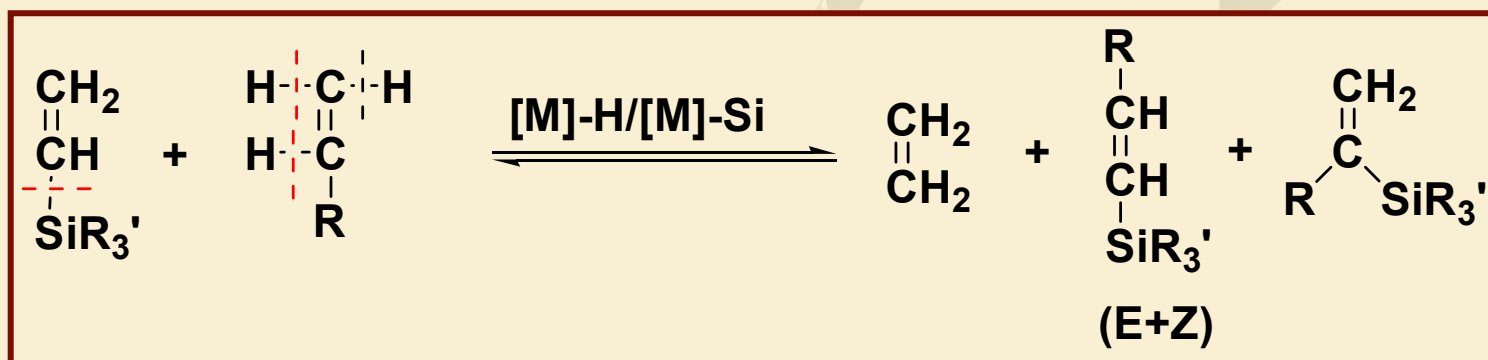
- [1] (a) Marciniec, B.; Pietraszuk, C. *Curr. Org. Chem.* 2003, 7, 691-735; (b) Marciniec, B.; Pietraszuk, C. *Handbook of metathesis*, Grubbs, R.H. (ed.), Wiley-VCH, Weinheim, 2003, chapter 2.13.
- [2] (a) Malecka, E.; Marciniec, B.; Pietraszuk, C.; Church, A.C.; Wagener, K.B. *J. Mol. Catal. A: Chem.*, 2002, 190, 27-31; (b) Marciniec, B.; Majchrzak, M. *J. Organomet. Chem.*, 2003, 686, 228-234.
- [3] Pietraszuk, C.; Marciniec, B.; Rogalski, S.; Fischer, H. *J. Mol. Catal. A: Chem.*, 2005, 240, 67-71.
- [4] (a) Marciniec, B. *Coord. Chem. Rev.*, 2005, 249, 2374-2390; (b) Marciniec, B. *Acc. Chem. Res.*, 2007, (in press).

# Cross-metathesis vs. silylative coupling of olefins with vinylsubstituted silicon compounds

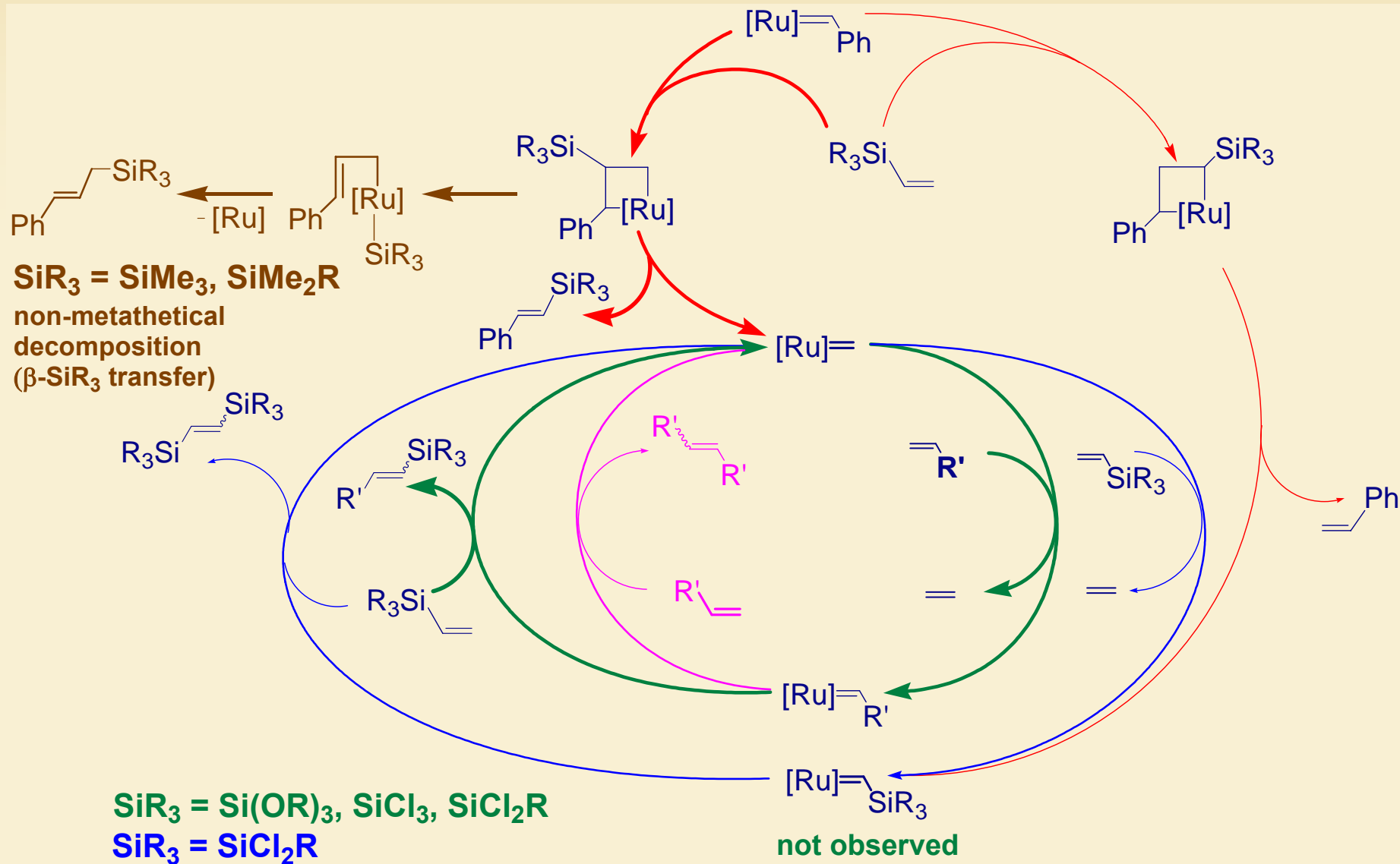
## Cross-metathesis



## Silylative Coupling (*trans*-silylation)

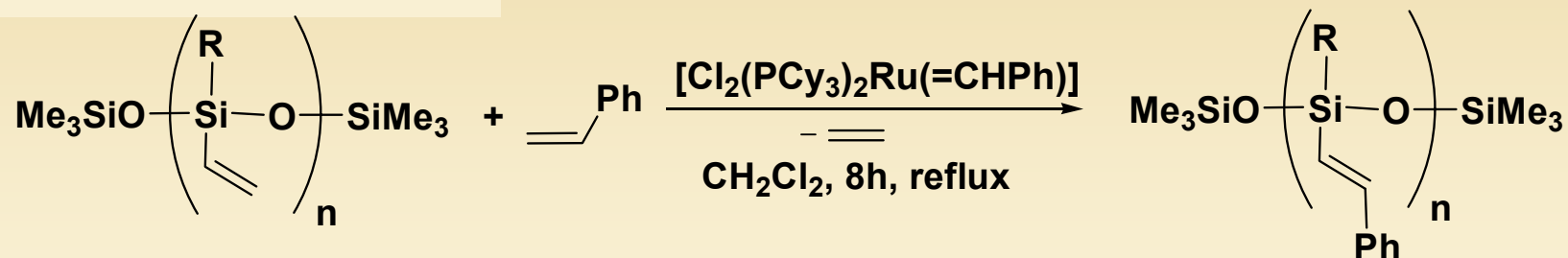


# Reactivity of Grubbs catalysts towards vinylsilanes implications for catalysis



# Modification of (poly)vinylosiloxanes

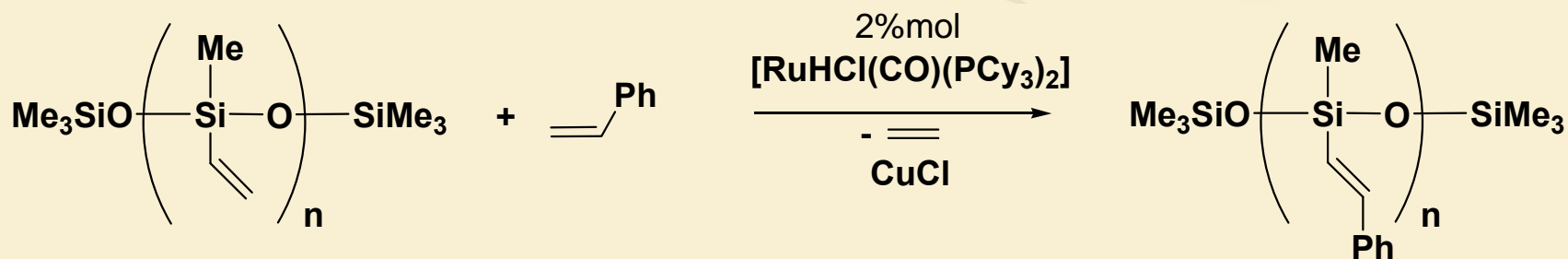
## via cross-metathesis



$n = 14 - 18$

| R  | yield [%]   |
|--|-------------|
| CH <sub>3</sub>                                  | no reaction |
| C <sub>6</sub> H <sub>5</sub>                    | no reaction |
| C <sub>6</sub> H <sub>4</sub> OMe-4              | 32          |
| C <sub>6</sub> H <sub>4</sub> CF <sub>3</sub> -4 | 100         |

## via silylative coupling

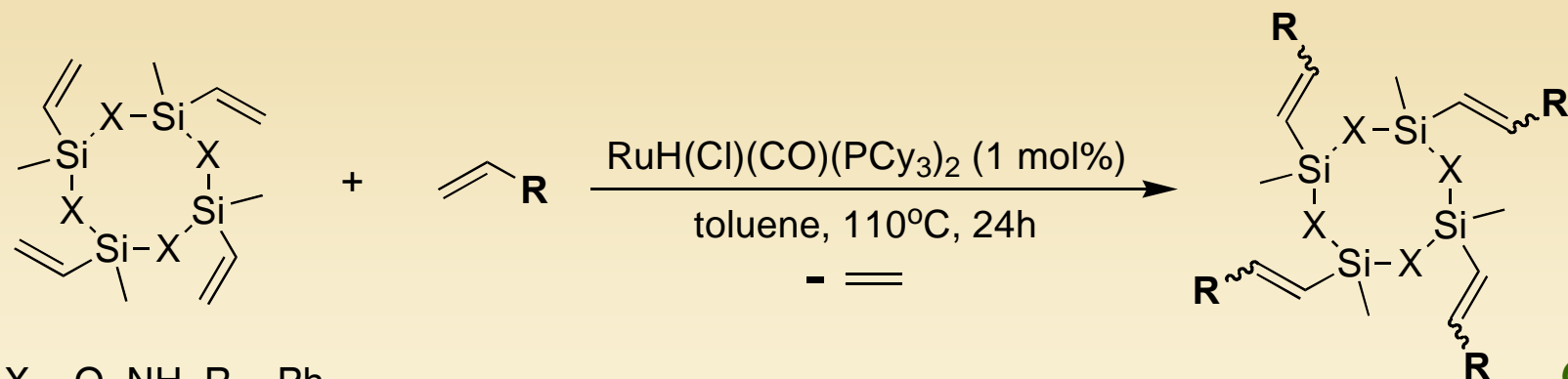


Reaction conditions:

CH<sub>2</sub>Cl<sub>2</sub>, reflux, 8h, Ar, [H<sub>2</sub>C=CH] : [styrene] = 1 : 3, [Ru] : [Cu] = 1 : 5

100%, exclusively E

# Functionalization of tetravinylcyclotetrasiloxanes via silylative coupling



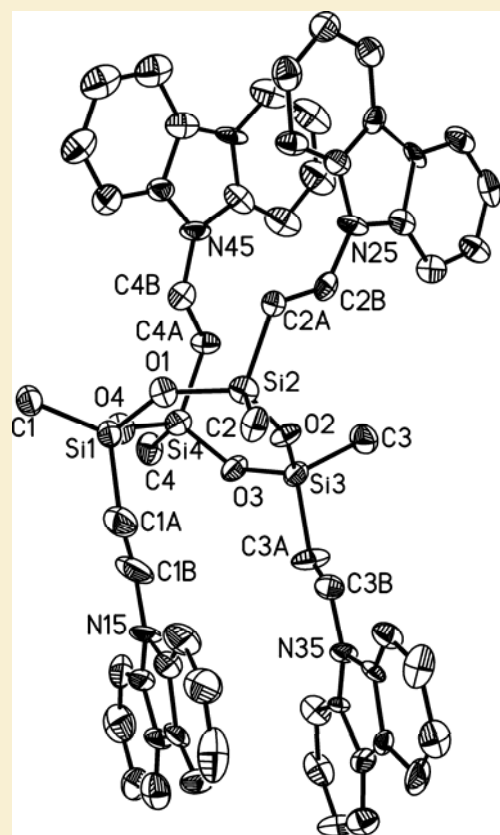
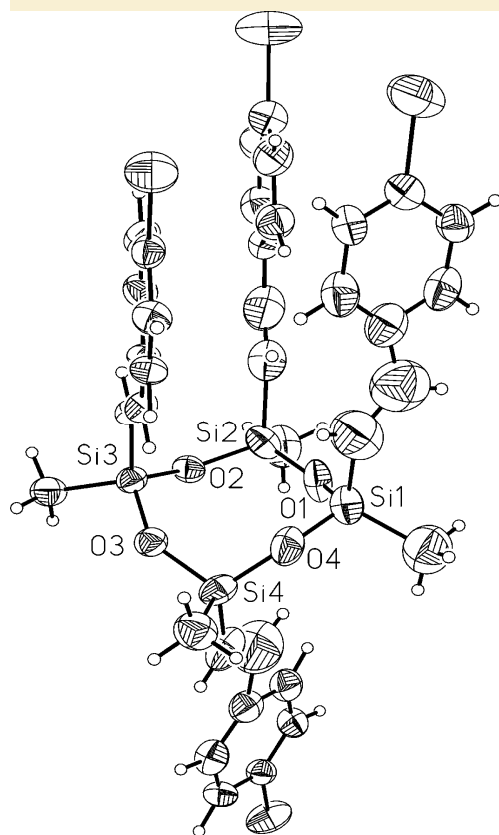
X = O, NH, R = Ph

R = 4-PhBr

R = 9-carbazole

Y.Itami,  
 B.Marciniec,  
 M.Kubicki,  
*Organometallics*,  
 2003, 22, 3717  
 74-92%

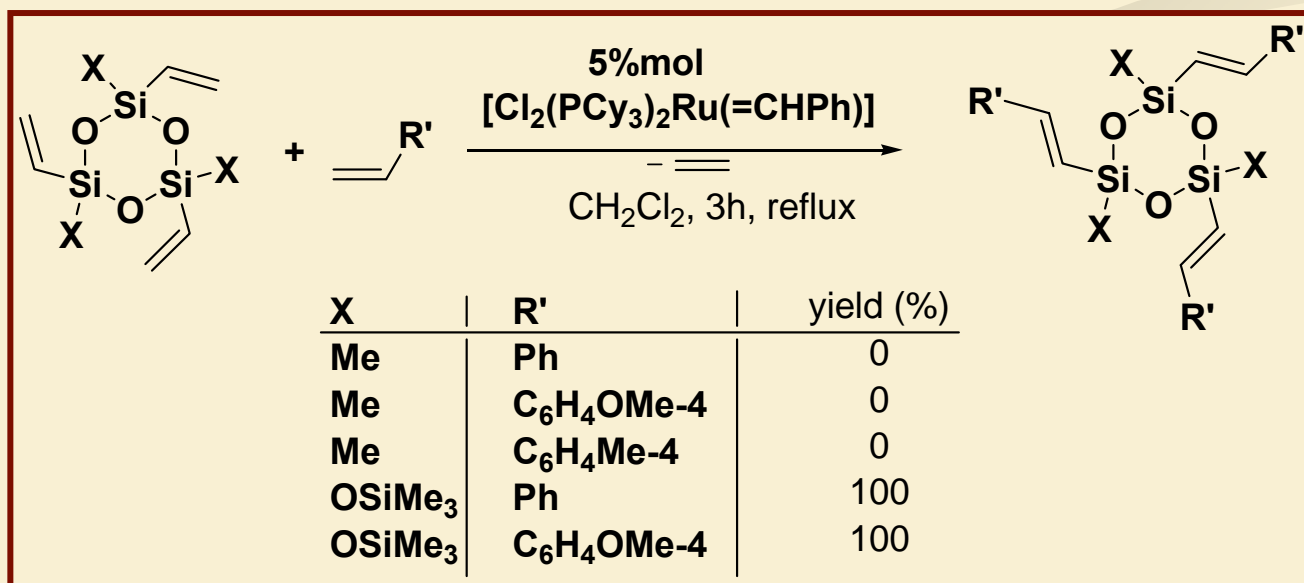
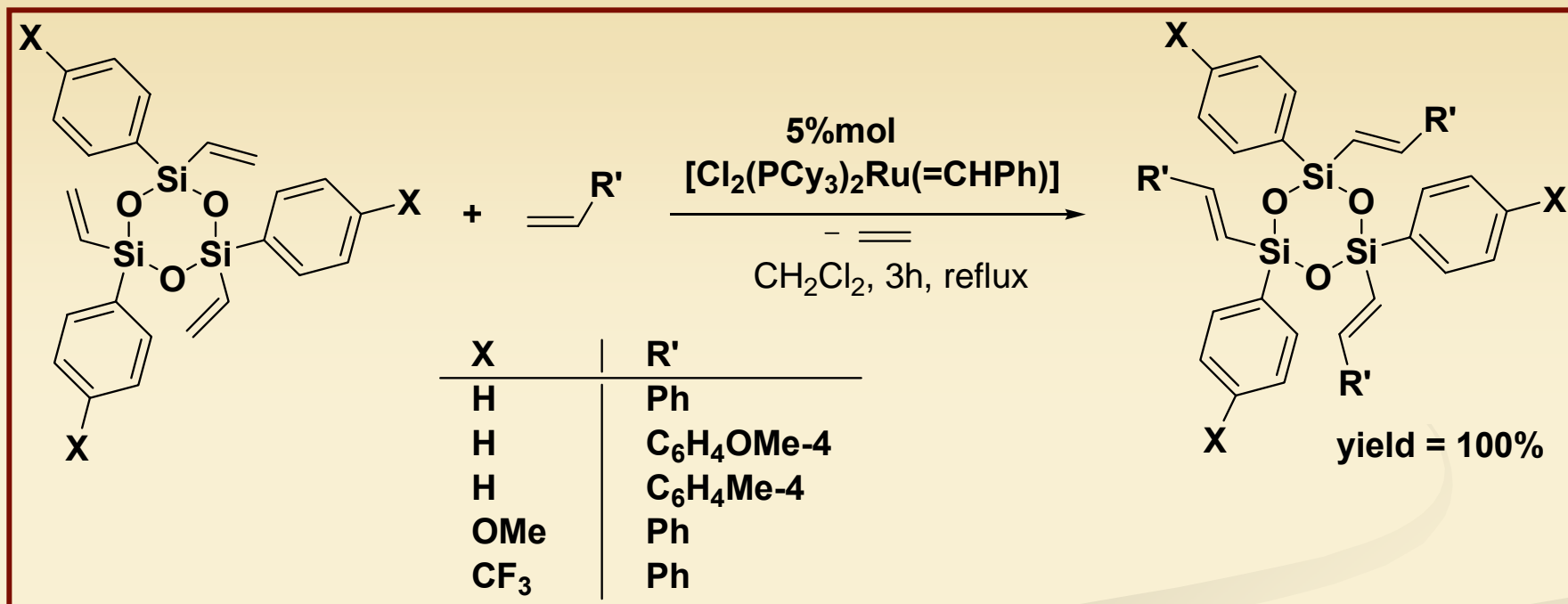
X = O



| R   | Conversion [%] | Selectivity [E/Z]   | Yield [%] |
|---|----------------|---------------------|-----------|
| Ph, 4-PhBr,<br>4-PhOMe,<br>4-PhMe                                       | >99            | 100/0               | 91-93     |
| n-BuO,<br>t-BuO, SiMe <sub>3</sub> ,<br>N-pyrrolidinone,<br>9-carbazole | 93-99          | 95-98 %<br>isomer E | 87-94     |

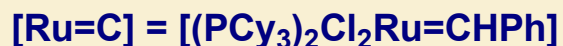
B.Marciniec, J.Waehner, P.Pawluc, M.Kubicki,  
*J.Mol.Catal.*, 2007, 265, 25

# Modification of vinylcyclosiloxanes via cross-metathesis



P.Wrzesniak, C.Pietraszuk,  
 B.Marciniec, *J.Mol.Catal.*,  
 (submitted for publication)

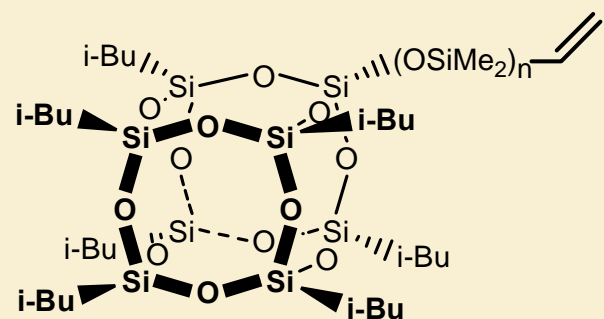
# Functionalization of vinylsubstituted silsesquioxane and spherosilicate



## Cross Metathesis

R = Ph, p-C<sub>6</sub>H<sub>4</sub>Me, pC<sub>6</sub>H<sub>4</sub>OMe  
 p-C<sub>6</sub>H<sub>4</sub>Cl, p-C<sub>6</sub>H<sub>4</sub>Br, p-C<sub>6</sub>H<sub>4</sub>Ph  
 Yield = 90-99%

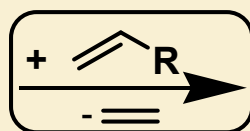
n = 0



n = 0, 1

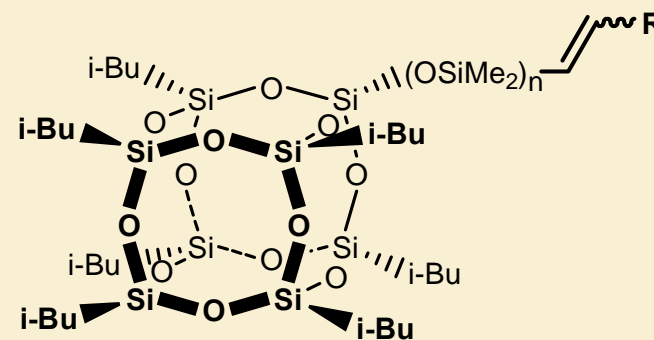
[Ru=C] 1-2 mol %

40°C, 24h, CH<sub>2</sub>Cl<sub>2</sub>



80°C, 24h, toluene

[Ru-H] 1 mol%



R = Ph, <sup>n</sup>Bu, O<sup>n</sup>Bu, O<sup>t</sup>Bu,  
 SiMe<sub>3</sub>, C<sub>12</sub>H<sub>8</sub>N, C<sub>4</sub>H<sub>6</sub>NO  
 Yield = 92-95%

## Silylative Coupling

n = 0, 1

# Functionalization of octavinylsilsesquioxane and spherosilicate

## Cross Metathesis

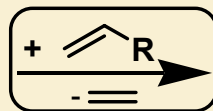
R = Ph, Bu, CH<sub>2</sub>SiMe<sub>3</sub>, S<sup>t</sup>Bu  
Yield = 56-96%

n = 0

Y.Itami, B.Marciniec,  
M.Kubicki, *Chem., Eur.J.*,  
2004, 10, 1239

[Ru=C] 2-4 mol %

r.t.-60°C, 18h  
CH<sub>2</sub>Cl<sub>2</sub>/benzene



80-110°C, 48h,  
benzene/toluene

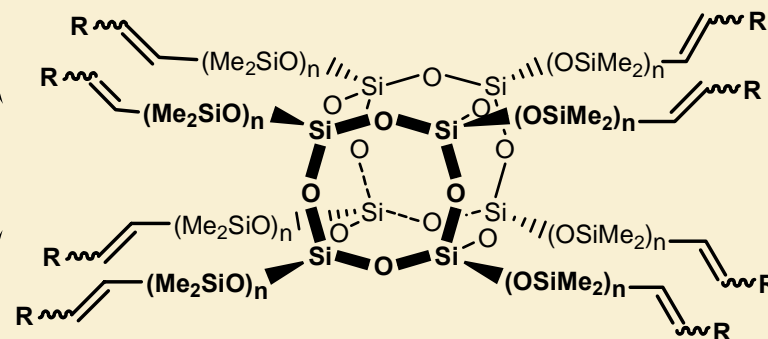
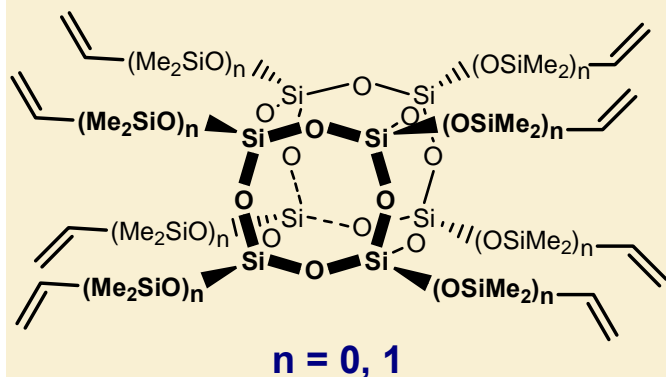
[Ru-H] 0.5-2 mol%

R = Ph, Bu, O<sup>t</sup>Bu, OSiMe<sub>3</sub>,  
CH<sub>2</sub>SiMe<sub>3</sub>, C<sub>12</sub>H<sub>8</sub>N, C<sub>4</sub>H<sub>6</sub>NO  
Yield = 80-91%

## Silylative Coupling

n = 0, 1

J.Waehner, B.Marciniec  
P.Pawluc, *Eur.J.Inorg.  
Chem.*, 2007, 2975



# Conclusions

1. **Cross-Metathesis** and **Silylative Coupling** catalyzed by ruthenium complexes constitute two complementary synthetic routes leading to functionalized poly(siloxanes), cyclosiloxanes and silsesquioxanes of great practical importance as precursors and/or components of nanomaterials as well as organometallic reagents for organic synthesis.
2. While functionalization of commercially available methylsubstituted vinylsilicon compounds can proceed efficiently via **silylative coupling** reaction, the **cross-metathesis** of olefins with vinylsubstituted siloxanes, cyclosiloxanes and polysiloxanes occurs only in the presence of electron-withdrawing substituents at silicon (Cl, OR, C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>, OSiMe<sub>3</sub>).
3. Functionalization of cubic monovinylheptaalkyl- and octavinyl-silsesquioxanes occurs quite efficiently via **cross-metathesis** with  $\alpha$ -olefins, styrene and t-butylvinylsulfide and functionalization of silsesquioxanes by **silylative coupling** proceeds effectively with styrene but additionally with various heteroatom substituted vinyls. Contrary to silsesquioxanes, functionalization of vinylspherosilicates occurs effectively only by ruthenium catalyzed **silylative coupling** reactions.