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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].

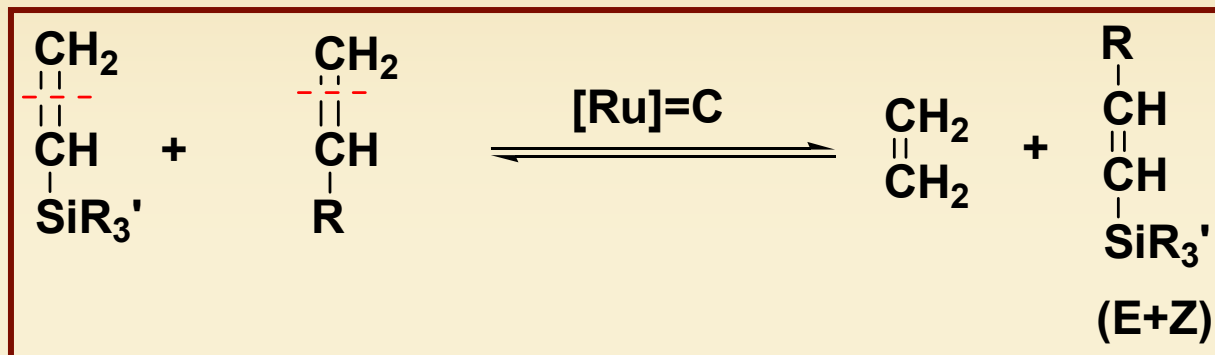
In the lecture we report recent results on effective cross-metathesis of a variety of olefins and dienes with vinyl substituted (poly)siloxanes, cyclosiloxanes and silsesquioxanes. The two reactions [1,4] offers an attractive general and complementary synthetic routes leading to functionalized (poly)siloxanes,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

References:

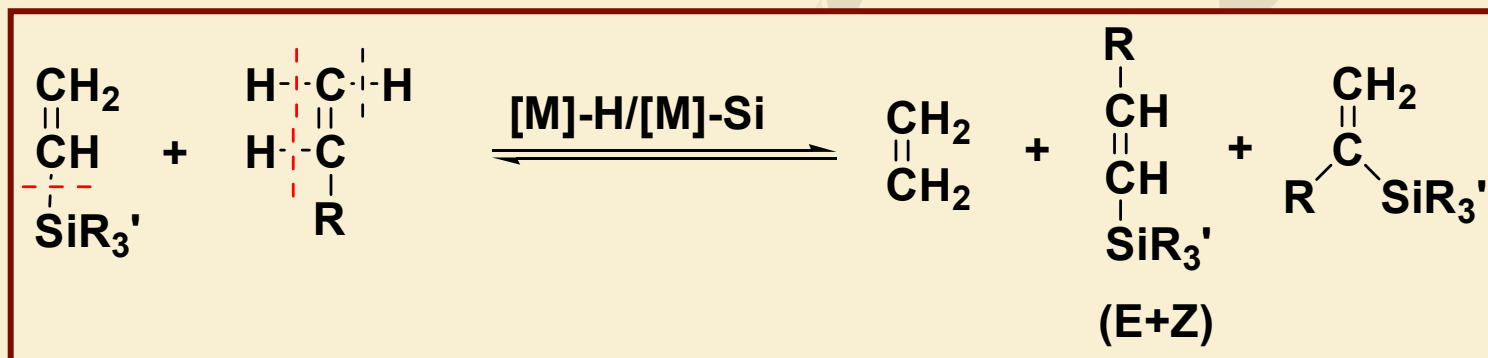
- [1] (a) Marciniec, B.; Pietraszuk, C. *Curr. Org. Chem.* 2003, 7, 691-735; (b) Marciniec, B.; Pietraszuk, C. *Handbook of metathesis*, Grubbs, R.H. (ed.), Wiley-VCH, Weinheim, 2003, chapter 2.13.
- [2] (a) Malecka, E.; Marciniec, B.; Pietraszuk, C.; Church, A.C.; Wagener, K.B. *J. Mol. Catal. A: Chem.*, 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

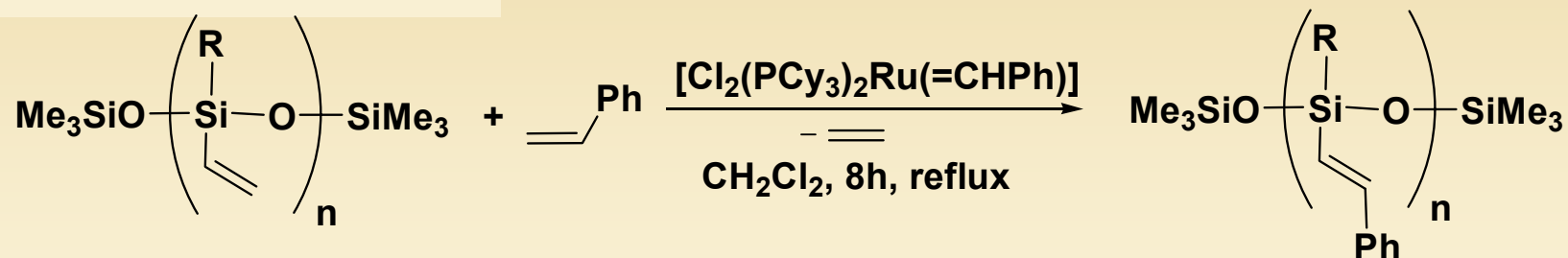


Silylative Coupling (*trans*-silylation)



Modification of (poly)vinylosiloxanes

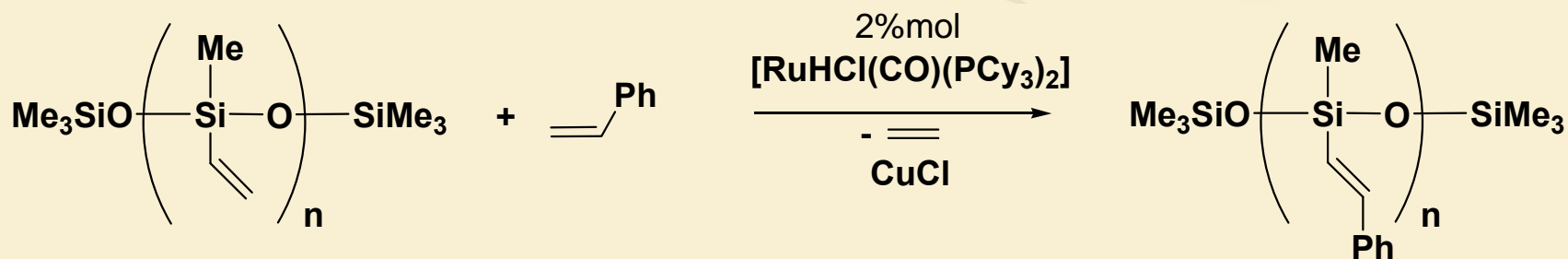
via cross-metathesis



$n = 14 - 18$

R	yield [%]
CH ₃	no reaction
C ₆ H ₅	no reaction
C ₆ H ₄ OMe-4	32
C ₆ H ₄ CF ₃ -4	100

via silylative coupling

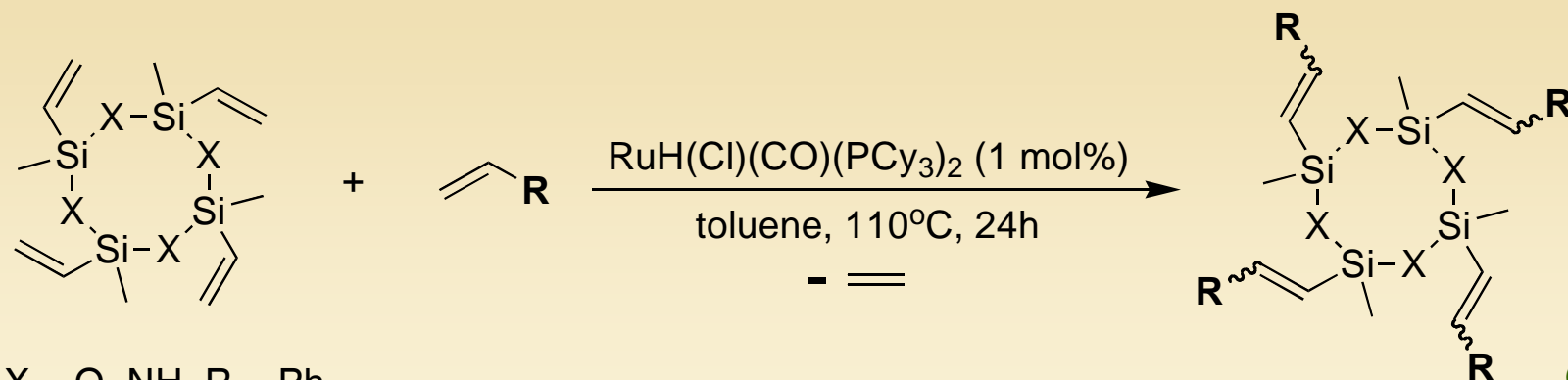


Reaction conditions:

CH₂Cl₂, reflux, 8h, Ar, [H₂C=CH] : [styrene] = 1 : 3, [Ru] : [Cu] = 1 : 5

100%, exclusively E

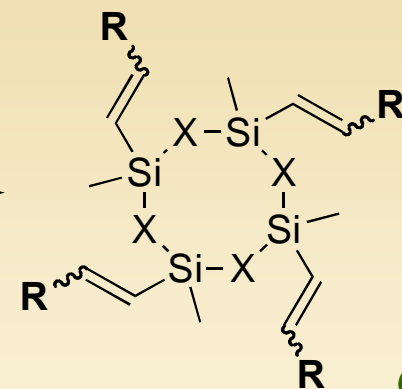
Functionalization of tetravinylcyclotetrasiloxanes via silylative coupling



X = O, NH, R = Ph

R = 4-PhBr

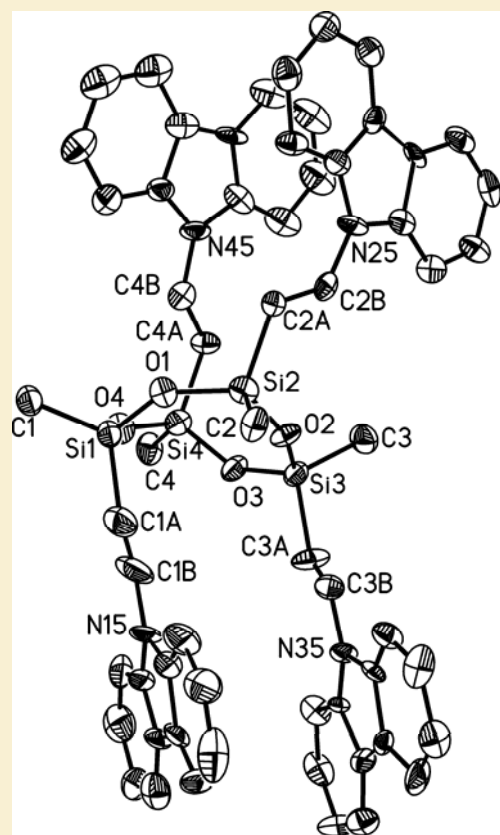
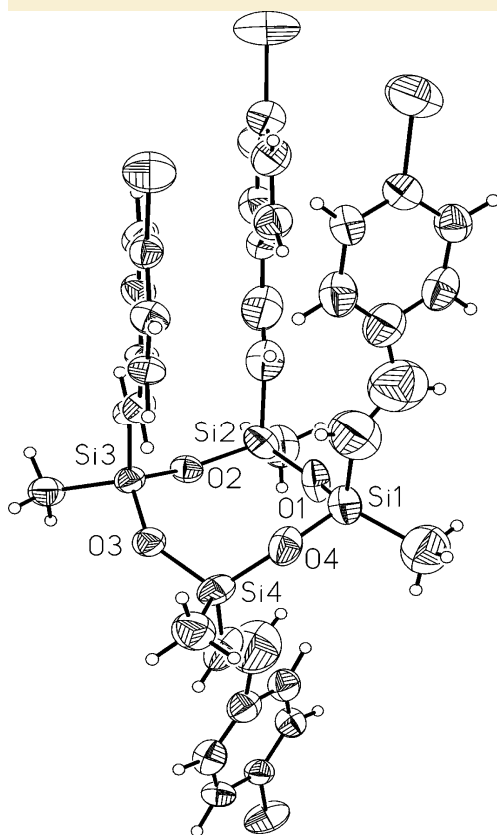
R = 9-carbazole



74-92%

X = O

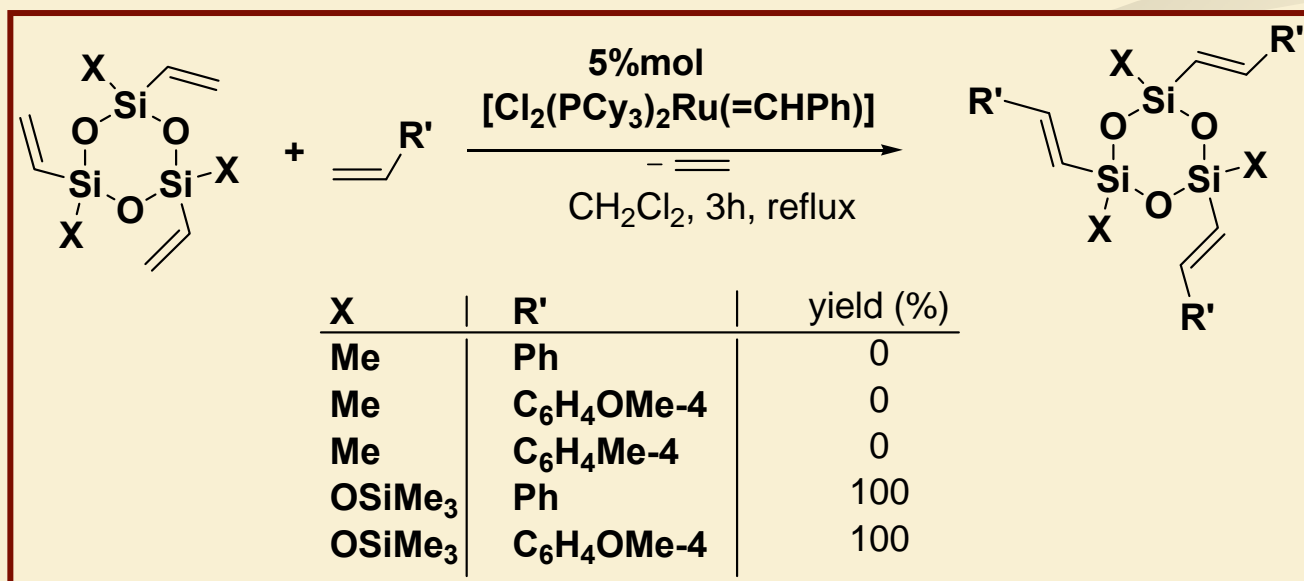
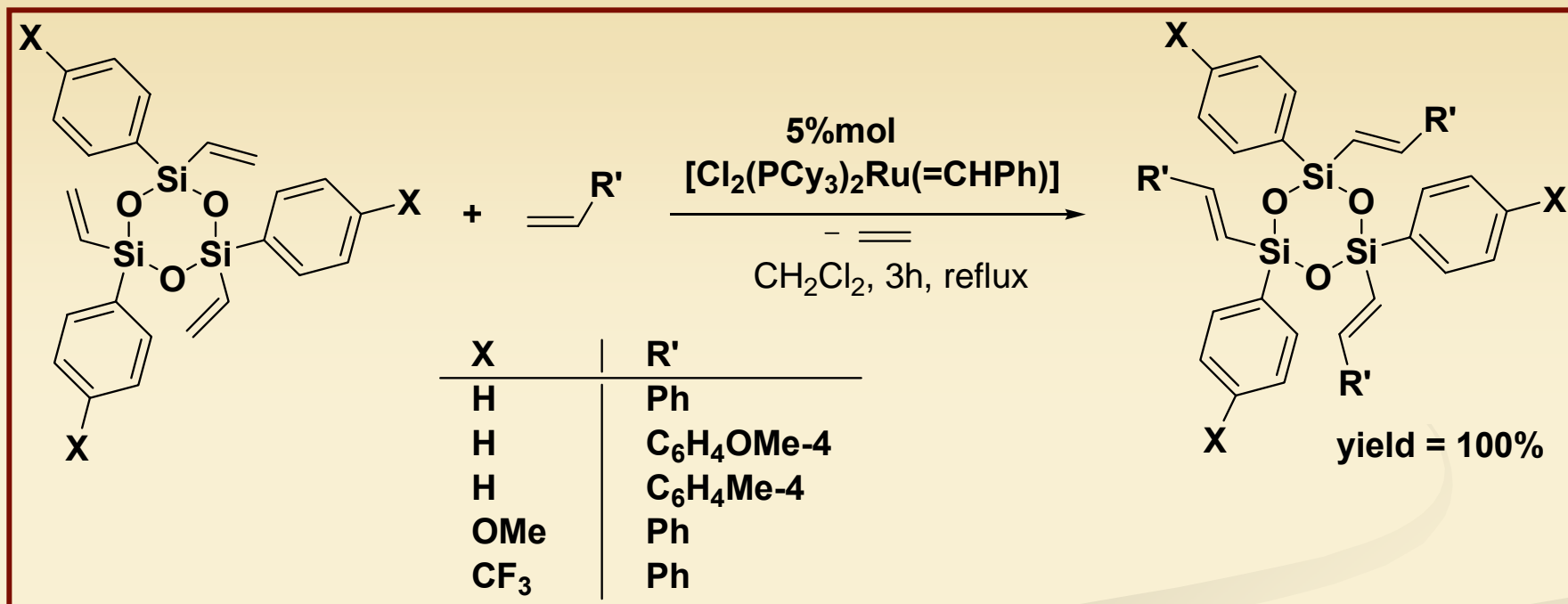
Y.Itami,
B.Marciniec,
M.Kubicki,
Organometallics,
2003, 22, 3717



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

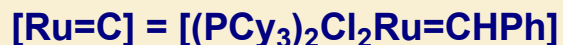
B.Marciniec, J.Waehner, P.Pawluc, M.Kubicki,
J.Mol.Catal., 2007, 265, 25

Modification of vinylcyclosiloxanes via cross-metathesis



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

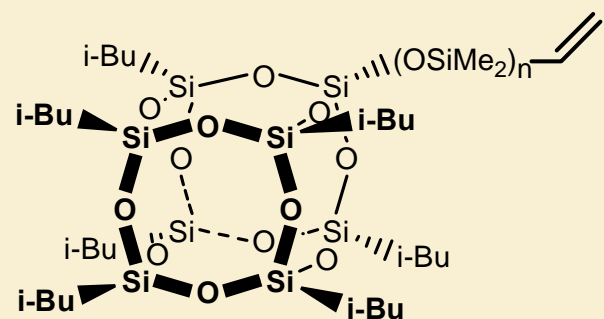
Functionalization of vinylsubstituted silsesquioxane and spherosilicate



Cross Metathesis

R = Ph, p-C₆H₄Me, pC₆H₄OMe
p-C₆H₄Cl, p-C₆H₄Br, p-C₆H₄Ph
Yield = 90-99%

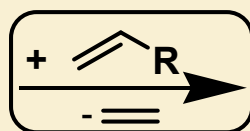
n = 0



n = 0, 1

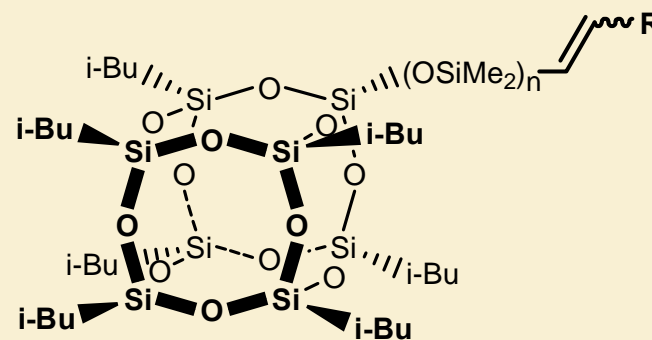
[Ru=C] 1-2 mol %

40°C, 24h, CH₂Cl₂



80°C, 24h, toluene

[Ru-H] 1 mol%



n = 0, 1



R = Ph, ⁿBu, OⁿBu, O^tBu,
SiMe₃, C₁₂H₈N, C₄H₆NO
Yield = 92-95%

Silylative Coupling

Functionalization of octavinylsilsesquioxane and spherosilicate

Cross Metathesis

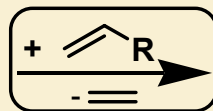
R = Ph, Bu, CH₂SiMe₃, S^tBu
Yield = 56-96%

n = 0

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

[Ru=C] 2-4 mol %

r.t.-60°C, 18h
CH₂Cl₂/benzene



80-110°C, 48h,
benzene/toluene

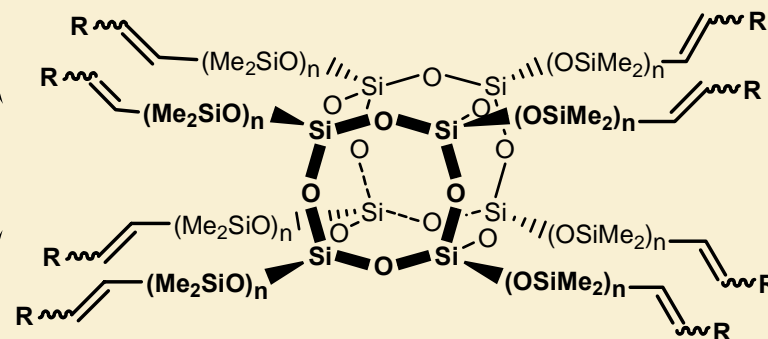
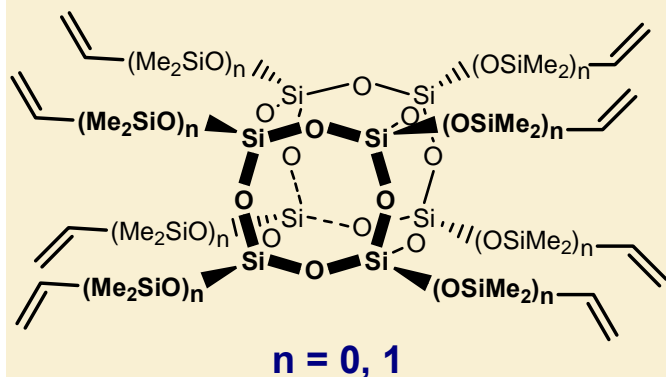
[Ru-H] 0.5-2 mol%

R = Ph, Bu, OBU, O^tBu, OSiMe₃,
CH₂SiMe₃, C₁₂H₈N, C₄H₆NO
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, C₆H₄CF₃, OSiMe₃).
3. Functionalization of cubic monovinylheptaalkyl- and octavinyl-silsesquioxanes occurs quite efficiently via **cross-metathesis** with α -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.