Functionalization of Octavinylsilsesquioxane by Ruthenium-Catalyzed Silylative Coupling versus Cross-Metathesis

Y. Itami, B. Marciniec,* and M. Kubicki[a]

Abstract: Functionalization of octavinylsilsesquioxane (Vi_8T_8, **1**) by two reactions catalyzed by ruthenium complexes is reported: a silylative coupling reaction catalyzed by [RuHCl(CO)(P-Cy$_3$)$_2$] (**I**) and cross-metathesis catalyzed by first- (**II**) and second-generation (**III**) Grubbs' catalysts. The two reactions of **1** with styrene take place highly regio- and stereoselectively (the X-ray structure of the product **2** has also been obtained); the cross-metathesis of 1-hexene and allyltrimethylsilane occurs quite effectively, whereas the silylative coupling with these compounds gives a mixture of isomers. Functionalization of **1** with heteroatom-substituted vinyl derivatives (Si, O, N) by silylative coupling reaction has been found to be highly efficient, but cross-metathesis appears to be the more effective method for the synthesis of S-substituted vinyl-silsesquioxane.

Keywords: metathesis · ruthenium · silsesquioxanes · silylative coupling · vinylsilanes

Introduction

Polyhedral silsesquioxanes (POSS/T_n) of the general formula $(RSiO_{3/2})_n$, as well as spherosilicates (especially silyl-substituted ones), $(R_3SiO)_8Si_8O_{20}$ (Q_8^M), have attracted widespread attention as precursors and components of a variety of inorganic/organic hybrid materials such as POSS polymers, POSS cross-linking polymers, liquid crystals, dendrimers, and others.[1] Generally, silsesquioxanes and spherosilicates may best be described as an interface between inorganic silicates and carbosilanes composed of a rigid silicate core and chemically useful peripheral organic functionalities.

The structure of cubic octahedral silsesquioxanes $(RSiO_{1.5})_8$ resembles the skeletal frameworks found in crystalline forms of silica, particularly in zeolites, and these compounds can be treated as though they were built of the smallest silica particle possible.[2] They are also of great interest because of their nanoscale inorganic core (Si_8O_{12}: 0.5–0.7 nm) and highly symmetric and dimensional octafunctionality, which make these compounds ideal for use in the construction of inorganic/organic hybrid nanomaterials.

Although numerous functionalized octasilsesquioxanes have been synthesized, (mainly by hydrosilylation processes), few alkenyl-substituted silsesquioxanes have been reported so far. There is the platinum-catalyzed hydrosilylation of H_8T_8 with phenylacetylene[3] for the synthesis of monostyryl H_7T_8, the hydrosilylation of H_8T_8 and H_8Q_8M with propargyl methacrylate,[4] and finally the cross-metathesis of Vi_8T_8 and $Vi_8Q_8M_8$ with various olefins.[5] In the latter, reported by Feher et al., Schrock's molybdenum catalyst [Mo(=CHCMe$_2$Ph){NC$_6$H$_3$-2,6-(iPr)$_2$}{OCMe(CF$_3$)$_2$}$_2$] is used in an effective and regioselective process. In all reactions except that with styrene, a complex mixture of stereoisomers has been obtained.[5] The same authors have also used Grubbs' catalyst [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] for two reactions with olefins that have functional groups (4-penten-1-ol and 5-bromopent-1-ene), but the conversions were quite low.

In the last 15 last years we have developed a new type of transition-metal-catalyzed reaction of vinyl-substituted organosilicon monomers and polymers with a variety of olefins, called silylative coupling, "*trans*-silylation", or "silyl group transfer", which has become a useful alternative reaction for the functionalization of the vinyl–silicon group to give novel and well-known silicon-containing olefins (for a review see reference [6]). This reaction occurs by cleavage of the =C–H bond of the olefin and the C–Si bond of vinylsilanes, contrasting with cross-metathesis, which starts with the same substrates and ends mostly with the same products but proceeds by cleavage of the C=C bonds (Scheme 1).

Various transition-metal complexes (i.e. Ru,[7] Rh,[8] Ir,[9] Co[10]), having M–H or M–Si bonds initially or generated in situ, catalyze this process. The mechanism of catalysis proved by Wakatsuki et al.[7a] and corrected by us[7b,c] proceeds by insertion of vinylsilane and β-silyl transfer to the

[a] Dr. Y. Itami, Prof. B. Marciniec, Dr. M. Kubicki
Faculty of Chemistry, Adam Mickiewicz University
Grunwaldzka 6, 60–780 Poznan (Poland)
Fax: (+48) 61-829-1508
E-mail: marcinb@main.amu.edu.pl

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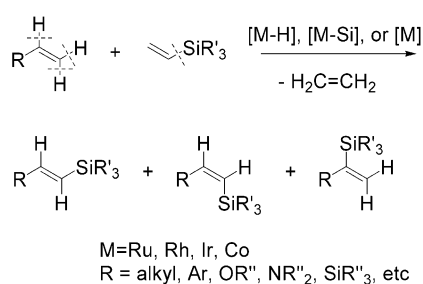
Scheme 1. Bond cleavage in the silylative coupling of olefins and vinylsilanes.

metal center with elimination of ethylene to generate M−Si species, followed by insertion of olefin and β-H transfer to the metal with elimination of substituted vinylsilane (Scheme 2).
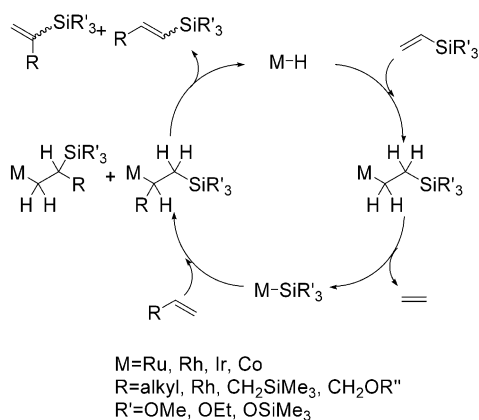

Scheme 2. Mechanism for transition-metal-catalyzed silylative coupling of olefins and vinyl silanes.

A notable peculiarity of this reaction is the silylation of vinyl alkyl ethers with vinylsilanes[11] to give β-alkoxy-substituted vinylsilanes, which are difficult to synthesize by other transition-metal-catalyzed reactions. A functionalization of vinyl-substituted cyclosiloxane and cyclosilazane,[12] as well as novel starburst compounds based on highly stereo- and regioselective reaction of tris(dimethylvinylsilyl)benzene with p-substituted styrenes to give a new core for dendritic compounds,[13] are recent examples of this new synthetic route catalyzed by ruthenium complexes.

We have also reported the first significant cross-metathesis of vinyl-substituted (vinyltrialkoxy)- and (vinyltrisiloxy)-silanes catalyzed by a ruthenium carbene complex (Grubbs' catalyst) with various olefins,

such as styrene,[14] terminal alkenes,[15] p-substituted styrenes,[15] allyl ethers,[16] allyl esters,[17] and allylsilanes.[15] However, the alkyl-substituted vinylsilanes appear to be quite inactive in ruthenium-catalyzed cross-metathesis.[14,18,19] Even one alkyl group on the silicon atom interrupts the catalytic cycle by β-silyl elimination of intermediate β-silyl-ruthenacyclobutane to give allylsilane and Ru⁰ species (Scheme 3).[18]
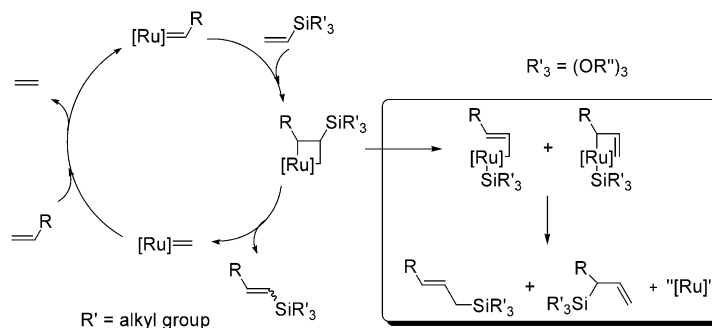

Scheme 3. Mechanism for ruthenium-catalyzed cross-metathesis, including deactivation of the catalyst by β-silyl elimination from ruthenacyclobutane.

Herein we report the effective functionalization of octavinylsilsesquioxane (Vi_8T_8, 1) by employing both types of reactions catalyzed by ruthenium carbene complexes—silylative coupling and cross-metathesis—on a wide range of substituted silsesquioxanes with diverse β-substituted vinyl (especially β-heteroatom-substituted) groups (Scheme 4). The efficiencies of these two reactions have been compared.

Results and Discussion

Compound 1 was first functionalized with styrene to obtain the styryl-substituted silsesquioxane 2 (see Table 1; [RuHCl(CO)(PCy₃)₂] (I) and [RuCl₂(=CHPh)(PCy₃)₂] (II)). The silylative coupling reaction occurred quite efficiently. The cross-metathesis also occurred readily, because the substituent environment of the silicon atoms of 1 involves three

Silylative-Coupling Reaction

Cross-Metathesis

R = alkyl, Ph, SiR'₃, OR', NR'₂, SR'
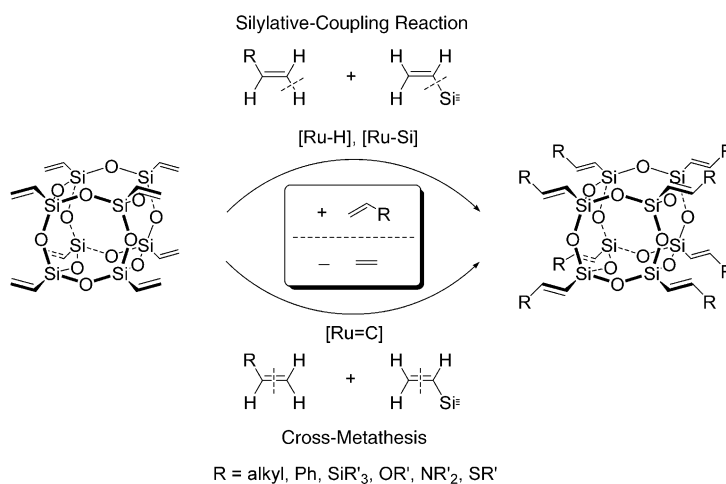
Scheme 4. Combined reaction schemes for silylative coupling and cross metathesis.

Table 1. Functionalization of **1** with styrene.
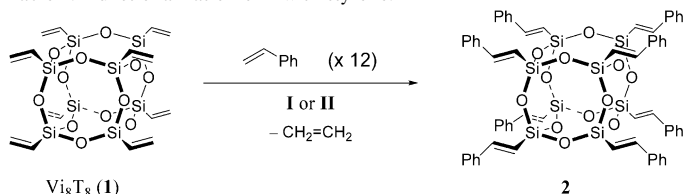
Catalyst	mol %[a]	Temperature	Conversion[b] [%]	Yield [%]	Selectivity (*trans/cis*)[b]
I	0.5	80 °C	> 99	92	> 99 % *trans*
II	0.5	RT	> 99	96	> 99 % *trans*

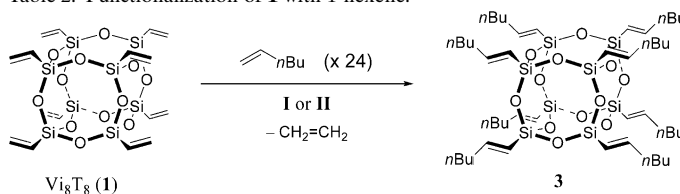[a] mol % per vinyl silyl group. [b] Calculated by ¹H NMR spectroscopy.

alkoxy or siloxy groups, which is a crucial prerequisite for the ruthenium-catalyzed cross-metathesis of vinyl-trisubstituted silane.[14] It is noteworthy that both processes offer quantitative conversion with rather low catalytic loading (0.5 mol % per vinyl silyl group), whereas 3 mol % of the expensive Mo carbene catalyst was employed in the Feher reaction (Table 1).[5]

Both the silylative coupling reaction and cross-metathesis occurred with high regio- and stereoselectivity, giving exclusively the *trans* product. The product was isolated in high yield in both cases, and its structure was characterized by X-ray crystallography (Figure 1).

It has been established that vinylpyridines (2-vinylpyridine and 4-vinylpyridine) are unfavorable for functionalization in both silylative coupling reactions and cross-metathesis, since no reaction occurs, regardless of the catalyst used; even the second-generation Grubbs' catalyst [(H₂IMes)-

RuCl₂(=CHPh)(PCy₃)] (**III**, H₂IMes = 1,3-dimesityl-4,5-dihydroimizadol-2-ylidene) showed no catalytic activity. This seems to be due to the high tendency of pyridine to coordinate to transition metals, which yields pyridine-coordinated catalytically inactive species.[20]

When aliphatic α-alkene (1-hexene) was used as the counter-substrate, the course of these two reactions was different (Table 2). The cross-metathesis of **1** occurred fairly well, although the reactivity of 1-hexene was less than that in the reaction with styrene, owing to the homo-metathesis of 1-hexene. A small amount of the *cis* isomeric fragment was also formed, but the stereoselectivity (*trans/cis* = 94:6) was higher than the selectivity in the Mo-catalyzed cross-metathesis of **1** with 1-pentene (85:16).[5] Meanwhile, the silylative coupling reaction proceeded with low conversion, and a complex mixture of products, consisting of not only

Table 2. Functionalization of **1** with 1-hexene.

Catalyst	mol %[a]	Temperature	Conversion[b] [%]	Yield [%]	Selectivity (*trans/cis*)[b]
I	0.5	80 °C	39		
	2		> 99	74	complex mixture
II	1	RT	72		
	2		> 99	72	94/6

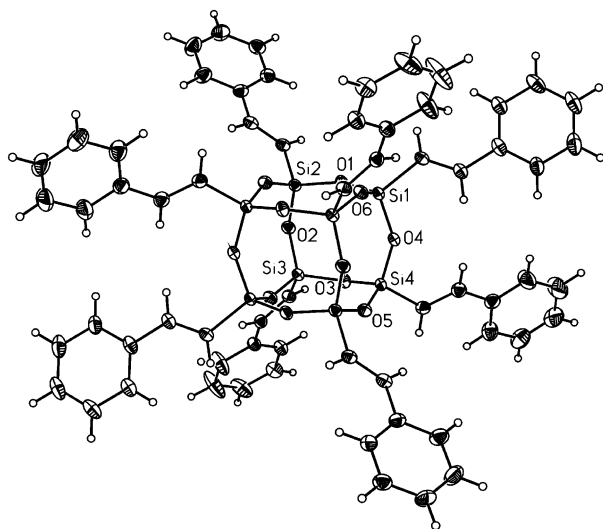[a] mol % per vinyl silyl group. [b] Calculated by ¹H NMR spectroscopy.

Figure 1. Structure of **2** (thermal-ellipsoid representation[32] of non-disordered molecule A, ellipsoids are drawn at 50 % probability level; for clarity only O and Si atoms from asymmetric part are labeled, hydrogen atoms are shown as spheres with arbitrary radii). Selected bond lengths [Å] and angles [°] for non-disordered molecule: <Si−O> 1.621(3), <Si−C> 1.828(2), <C=C> 1.331(5), <C$_{ar}$−C$_{ar}$> 1.384(7); <O-Si-O> 108.9(6), <Si-O-Si> 147.6(17), O-Si-C 110.0(19).

trans and *cis* stereoisomers of the 1-hexenylsilyl components but also 2-hexenylsilyl components, was formed. A plausible mechanism for the formation of the complex mixture is proposed in Scheme 5.

A key step in the formation of isomeric components is the β-H transfer in the intermediate **4**, which should be formed in the course of the silylative coupling reaction as a result of the insertion of 1-hexene into the Ru−Si bond of the ruthenium–silsesquioxane species. The β-H transfer in **4** can give four isomeric components, since there are four different H atoms in the β-position relative to the Ru atom of **4**, two in the α-position relative to Si and the other two in the γ-position. The β-H transfer of H(α) gives a (*trans* and *cis*)-1-hexenylsilyl moiety, while transfer of H(γ) leads to a 2-hexenylsilyl group.

No reaction of **1** occurs with 3,3-dimethylbutene, owing to the bulky substituents at the vinyl group. Similarly, cross-metathesis with its silicon analogue, trimethylvinylsilane, has also been found to be ineffective. In contrast the silylative coupling reaction with trimethylvinylsilane proceeded in the presence of the Ru−H complex **I** (Table 3).
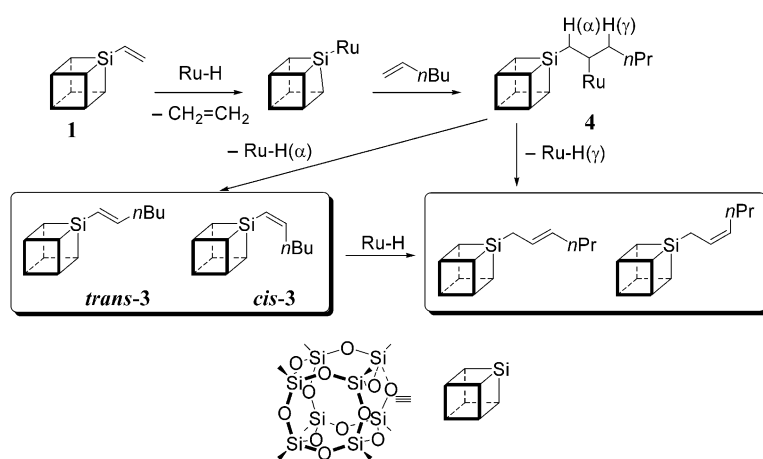
Scheme 5. Proposed mechanism for the silylative coupling of **1** with 1-hexene. The multiple possible products resulting from β-H transfer in **4** are highlighted.

Table 3. Functionalization of **1** with vinyltrimethylsilane.

Catalyst	mol %[a]	Temperature	Conversion[b] [%]	Yield [%]	Selectivity (trans/gem)[b]
I	0.5	80 °C	57		
	2		> 99	95	76/24
II	0.5	RT	trace		
	2				

[a] mol % per vinyl silyl group. [b] Calculated by ^{1}H NMR spectroscopy.

trimethylvinylsilane into the silyl-ruthenium species based on silsesquioxane, or 2) by the insertion of Vi_8T_8 into the trimethylsilyl ruthenium species formed in the reaction of ruthenium hydride **I** with trimethylvinylsilane. Both pathways give the same key intermediates, bis(silyl)ethylruthenium species (1,2- and 2,2-), and the *gem* isomeric component, which derives from β-H migration in the 2,2-bis(silyl)-ethylruthenium species.

Functionalization of **1** with allyltrimethylsilane displays a combination of characteristics of the reaction with aliphatic olefins (1-hexene) and that with trimethylvinylsilane (Table 4). Similar to the reaction with 1-hexene, cross-metathesis proceeded fairly well to give the product **6** in satisfactory yield. Notably, the cross-metathesis occurred with high stereoselectivity, giving exclusively *trans*-3-trimethylsilyl-1-propenyl-substituted silsesquioxane (see ^{1}H NMR spectrum in Figure 2c). This contrasts with both the reaction with 1-hexene, which produces a small number of *cis*-isomeric components, and with the Mo-catalyzed functionalization with allyltrimethoxysilane,[5] which gives a mixture of isomers (88:12) under higher catalyst loading (5 mol %). We also determined the structure of **6** by X-ray crystallography (Figure 3).

In contrast to the cross-metathesis, the silylative coupling reaction with allyltrimethylsilane gave a mixture of isomeric

As determined from ^{1}H NMR experiments, product **5** (Figure 2a) is a mixture of two isomeric components, one of which is assumed to be *trans* on the basis of the approximate coupling constant ($J \approx 19$ Hz). The ^{1}H NMR signal assigned to the second isomeric component in the spectrum does not come from the *cis* isomer, which would have been coupled ($J \approx 14$ Hz). DEPT analysis of the ^{13}C NMR spectrum (see Supporting Information), shows a signal for a $=CH_2$ carbon atom, thus providing direct evidence for the presence of a *gem* isomeric component, which is a characteristic feature of silylative homocoupling reactions.[7b,8a,21]

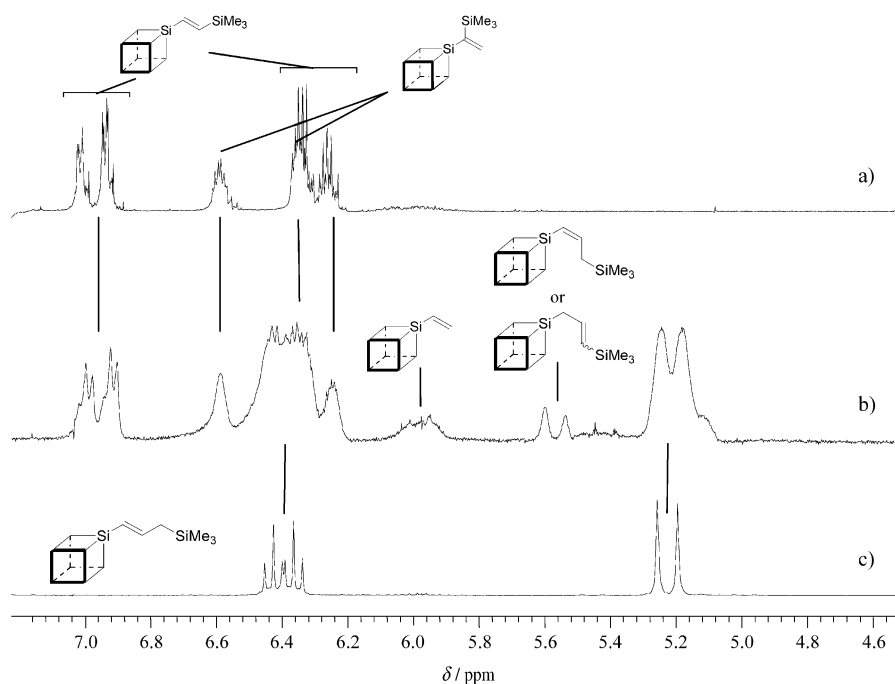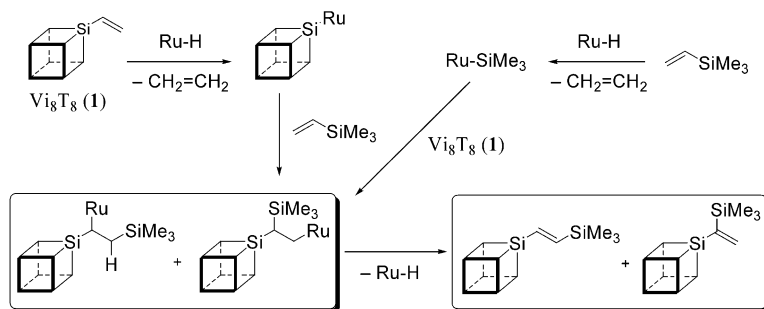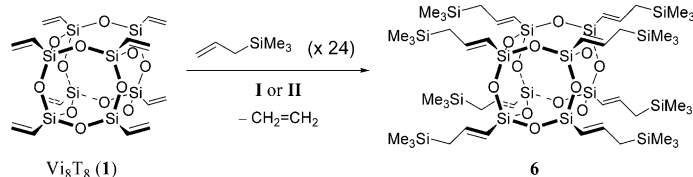The reaction may proceed by two different pathways (Scheme 6): 1) by the insertion of

Figure 2. ^{1}H NMR spectra of a) **5**, b) **6** (silylative coupling), and c) **6** (cross-metathesis).

Scheme 6. Possible reaction routes for the silylative coupling of **1** with trimethylvinylsilane, catalyzed by **I**.

Table 4. Functionalization of **1** with allyltrimethylsilane.

Catalyst	mol %[a]	Temperature	Conversion[b] [%]	Yield [%]	Selectivity (trans/cis)[b]
I	2	80 °C	97	69	complex mixture
II	1	RT	78		
	2		>99	69	>99 % trans

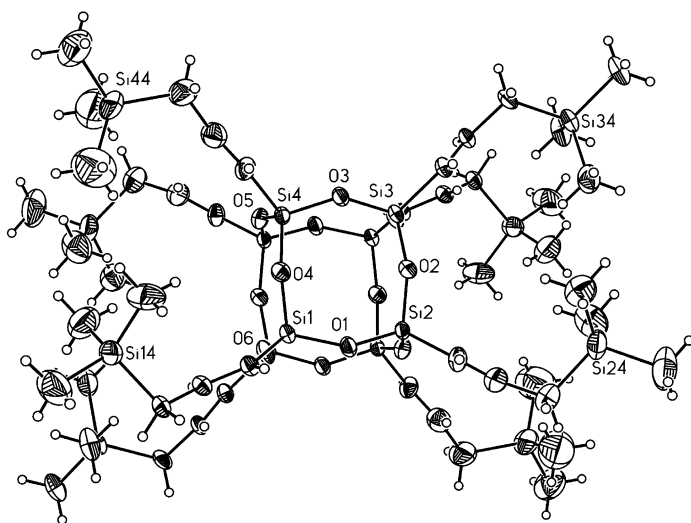[a] mol % per vinyl silyl group. [b] Calculated by ^{1}H NMR spectroscopy.

Figure 3. Structure of **6** (thermal-ellipsoid representation,[32] ellipsoids are drawn at 50 % probability level; for clarity only O and Si atoms from asymmetric part are labeled, hydrogen atoms are shown as spheres with arbitrary radii). Selected bond lengths [Å] and angles [°]: Si–O 1.624(2), <Si(cage)–C> 1.835(4), <Si–C(methyl)> 1.862(17), <C=C> 1.326(8); <O-Si-O> 108.9(6), <O-Si-C> 110.2(12), Si1-O1-Si2 142.43(16), Si2-O2-Si3 153.90(18), Si3-O3-Si4 143.24(16), Si1-O4-Si4 154.60(17), Si4-O5-Si2^i 149.02(16), Si1-O6-Si3^i 149.34(16).

components, which was much more complex than that obtained in the reaction with 1-hexene. Comparison of the ^{1}H NMR spectra of the mixture (Figure 2b) with that of the regio- and stereochemically pure analogue **6** prepared by cross-metathesis (Figure 2c), and with **5** (Figure 2a), suggests

the incorporation of trimethylsilylvinyl silicon fragments instead of trimethylsilylpropenyl silicon fragments. A possible mechanism for a side reaction, comprising silylation of **1** by trimethylsilylruthenium species generated in the reaction of **I** with allyltrimethylsilane to eliminate propene, is shown in Scheme 7. This additional side reaction gives silylvinyl-substituted fragments instead of silylpropenyl fragments, which are formed in the silylation with allyltrimethylsilane.

The ESI-MS plot for the complex mixture (Figure 4) provides direct evidence for the existence of the silylvinyl fragments, showing peaks ([*M*+K]$^+$) for the partially (mono-, bis-, tris-, and tetrakis-) silylvinyl-substituted silsesquioxanes.

While vinyl-substituted hetero-(O, N, Si) organic olefins readily undergo silylative coupling, the corresponding allyl derivatives successfully undergo cross-metathesis with vinylsilanes.[11, 16] Therefore, the functionalization of vinyl-substituted silsesquioxane **1** with various heteroatom-substituted vinyls by means of silylative coupling seems a promising synthetic method for the preparation of silsesquioxanes with β-heteroatom-substituted vinyl functionalities.

Initially, functionalizations of **1** with O-substituted vinyls (vinyl ethers and esters) were performed (Table 5). The results of the experiments were identical to the functionalization of trivinylcyclotrisiloxane with vinyl ethers,[13] that is, effective silylative coupling reactions in the presence of Ru–H catalyst **I**, no cross-metathesis (Table 5, entries 2, 5, 9) even in the presence of the second-generation Grubbs' catalyst **III** (Table 5, entry 6), and catalytic activity of the Ru–carbene complex **II** in silylative coupling by thermal transformation of Fischer carbene species into Ru–H species (Table 5, entries 3, 7, 10). Unfortunately, in all of the reactions, the product is actually a complex mixture of stereoisomeric components. In contrast to the reactions with vinyl ethers, functionalization of **1** with vinyl ester (vinyl acetate) does not proceed effectively (Table 5, entries 11–13).

As an example of N-functionalization of **1**, the silylative coupling reaction with 1-vinyl-2-pyrrolidinone proceeded in the presence of **I** (Table 6). In contrast to the cross-metathesis with vinyl ethers, no reaction of *N*-vinylpyrrolidinone with **1** was observed in the presence of ruthenium–carbene complexes **II** and **III**, even at a higher reaction temperatures.

It has been reported that Ru–carbene complexes react with this olefin to give an N-Fischer-type complex, which is
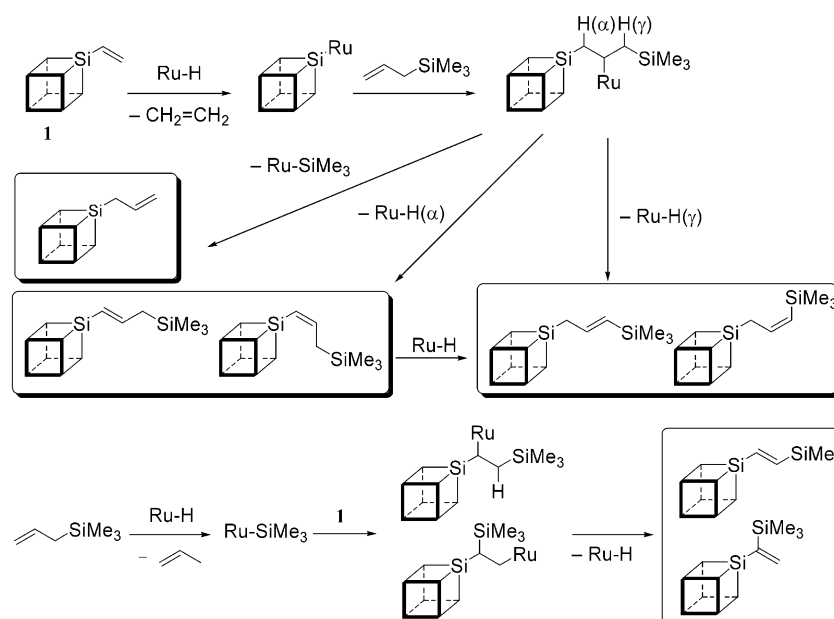
Scheme 7. Silylative coupling reaction of **1** with allyltrimethylsilane. Possible side reaction leads to silyl-vinyl-substituted fragments.
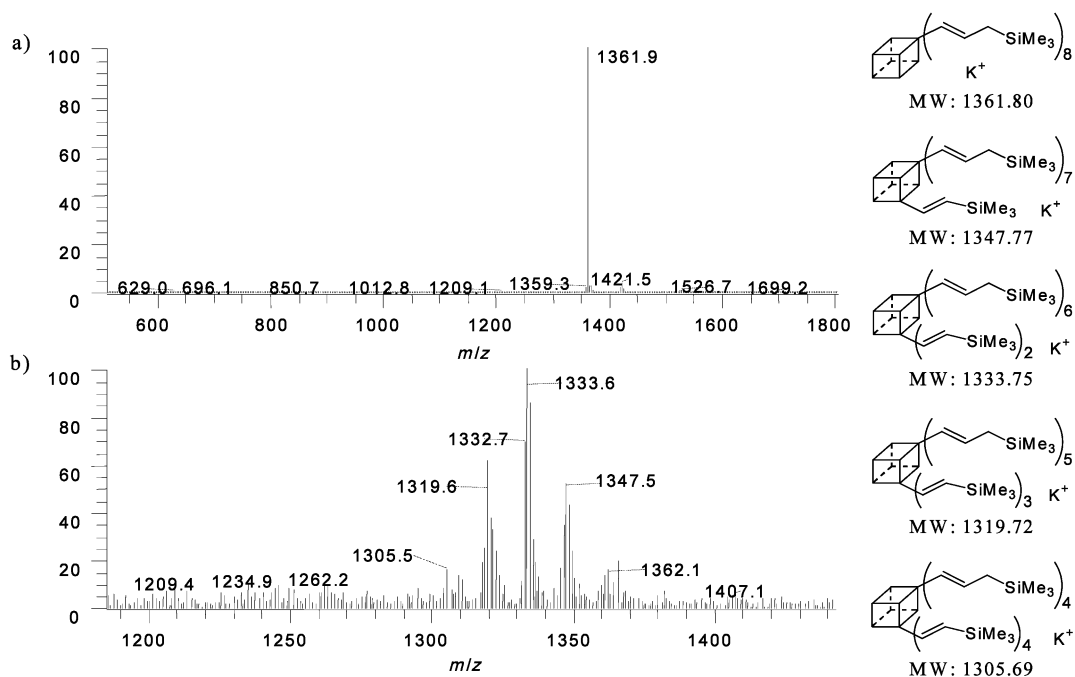

Figure 4. ESI-MS plots of **6**. a) Cross-metathesis, b) silylative coupling reaction.

catalytically inactive in metathesis (Scheme 8).[22] This inactivity follows from the contribution of species **b′**, in which the intramolecular coordination of the carbonyl group reduces the catalytic activity by blocking approach of the olefins towards the coordination sphere. The lack of conversion at a higher reaction temperature suggests that the N-Fischer-type complexes (**a, b, b′**) are stable and thus inactive at higher temperature, or decompose without generation of Ru−H species.

It had been assumed that the reaction of **1** with vinyl sulfide would occur in the same manner as the reaction with vinyl ethers or vinyl pyrrolidinone, exhibiting active silylative coupling and inactive cross-metathesis. However, the reverse was the case (Table 7). Contrary to expectation, the silylative coupling of **1** with *tert*-butyl vinyl sulfide gave no conversion of Vi_8T_8. The NMR spectrum of a mixture of complex **I** and three equivalents of *tert*-butyl vinyl sulfide showed the generation of ethylene (singlet at $\delta = 5.2$ ppm). This implies the occurrence of β-sulfide transfer with elimination of ethylene leading to the formation of the ruthenium sulfide species [Ru−S*t*Bu] (**IV**), which appears to be catalytically inactive towards the silylative coupling reaction

Table 5. Functionalization of **1** with vinyl ethers.
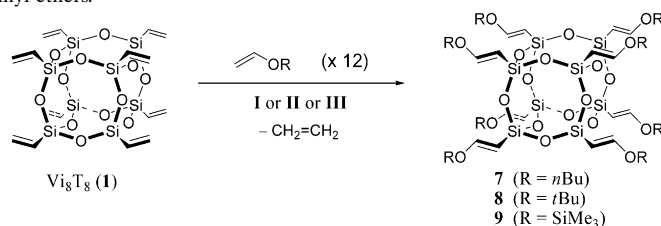
Entry	OR	Catalyst	mol %[a]	Temperature	Yield [%]	trans/cis[b]
1	OnBu	[Ru–H] **I**	0.5	80°C	>99[c] (86)[d]	57/43
2	OnBu	[Ru=C] **II**	1	RT	trace	
3	OnBu	[Ru=C] **II**	1	80°C	70[c]	55/45
4	OtBu	[Ru–H] **I**	0.5	80°C	>99[c] (91)[d]	79/21
5	OtBu	[Ru=C] **II**	1	RT	trace	
6	OtBu	[Ru=C] **III**	1	50°C	trace	
7	OtBu	[Ru=C] **II**	1	80°C	72[c]	68/32
8	OSiMe₃	[Ru–H] **I**	0.5	80°C	>99[c] (81)[d]	45/55
9	OSiMe₃	[Ru=C] **II**	1	RT	trace	
10	OSiMe₃	[Ru=C] **II**	1	80°C	61[c]	37/63
11	OAc	[Ru–H] **I**	0.5	80°C	trace	
12	OAc	[Ru=C] **II**	1	RT	trace	
13	OAc	[Ru=C] **II**	1	80°C	trace	

[a] mol % to vinyl silyl group. [b] Calculated by ¹H NMR spectroscopy. [c] Yield determined from NMR spectra. [d] Yield of isolated product.

Table 6. Functionalization of **1** with 1-vinyl-2- pyrrolidinone.
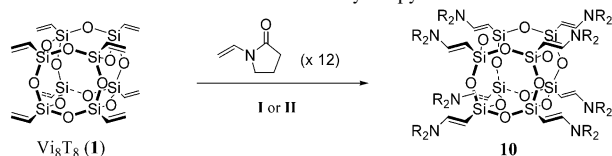
Catalyst	mol %[a]	Temperature	Conversion[b] [%]	Yield [%]	Selectivity (trans/cis)[b]
I	0.5	80°C	36		
	4		>95	69	>95/5
II	2	RT	trace		
II	2	80°C	trace		
II	2	60°C	trace		

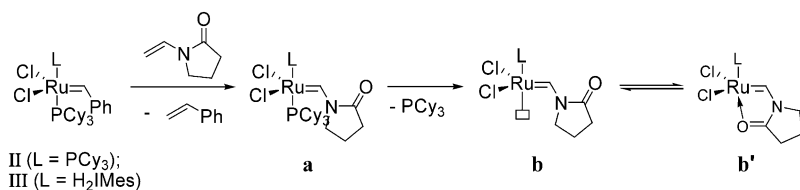[a] mol % to vinyl silyl group. [b] Calculated by ¹H NMR spectroscopy.

Table 7. Functionalization of **1** with *tert*-butyl vinyl sulfide.
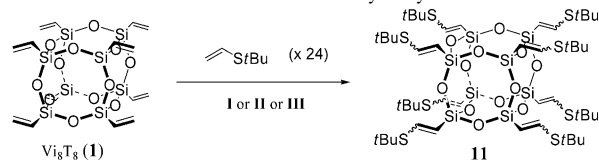
Catalyst	mol %[a]	Temperature	Yield [%]	Selectivity (trans/cis)[b]
I	2	80°C	trace	
II	2	RT 40°C 80°C	trace	
III	2	60°C	56	
	4	60°C	95 (91)[c]	97/3

[a] mol % to vinyl silyl group. [b] Calculated by ¹H NMR spectroscopy. [c] Yield of isolated product.

(Scheme 9a). Analogous formation of ruthenium sulfide Ru–S*t*Bu species has been reported in a reaction of [RuHCl(CO)(PPh₃)₃] with allyl alkyl sulfides involving the elimination of propene (Scheme 9b).[23]

Ozawa et al. have recently reported the ring-opening cross-metathesis of norbornene derivatives with vinyl sulfides catalyzed by S-Fischer-carbene complexes (Scheme 10).[24] Their results suggest that vinyl sulfides (and consequently S-Fischer-carbene complexes) are reactive in cross-metathesis.

Nevertheless, Grubbs′ catalyst **II**, which immediately transforms into S-Fischer-carbene complex **V** in the course of the reaction, proved completely inert in the reaction between **1** and *tert*-butyl vinyl sulfide, even at elevated temperatures (40 and 80°C). This result implies a negative aptitude of vinylsilane for these reactions; however, the second-generation Grubbs′ catalyst **III**, reacted to give the β-(*tert*-butylthio)vinyl-substituted product **11**.

Conclusion

Functionalization of octavinyl-silsesquioxane Vi₈T₈ (**1**) by ruthenium–carbene catalyst **I** in a cross-metathesis with aliphatic α-olefins (1-hexene and allyltrimethylsilane) and styrene occurs quite efficiently,
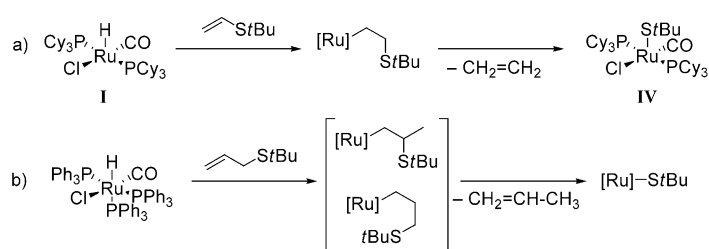

Scheme 8. Proposed mechanism for the formation of the inactive N-Fischer-type complex in the attempted cross-metathesis reaction of **1** with *N*-vinylpyrrolidinone.
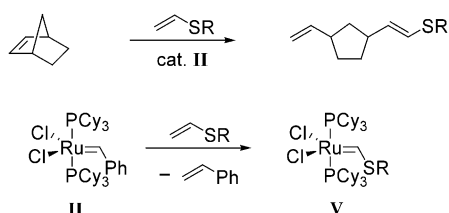
Scheme 9. β-Sulfide transfer a) in the reaction of **I** with *tert*-butyl vinyl sulfide, and b) in the reaction of [RuHCl(CO)(PPh$_3$)$_3$] with allyl alkyl sulfides.

Scheme 10. Transformation of catalyst **II** by vinyl sulfides.

and is superior to Mo-catalyzed functionalization, owing to the higher cost of the Mo catalyst, lower catalyst loading for **I**, and higher stereoselectivity of **I**.

Functionalization of **1** with styrene by silylative coupling is also highly efficient, although in the reaction with aliphatic α-olefins (1-hexene and allyltrimethylsilane) it gives a complex mixture of isomeric components.

Functionalization of vinyl-substituted silsesquioxane **1** with various heteroatom-substituted (Si, O, N) vinyls by employing the silylative coupling reaction has been found to be efficient for preparing silsesquioxanes with β-heteroatom-substituted vinyl functionalities. In contrast, cross-metathesis has emerged as an efficient method for the synthesis of S-substituted vinyl silsesquioxanes.

Experimental Section

General methods: ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian XL 300 MHz spectrometer in CDCl$_3$ or C$_6$D$_6$ solution. Chemical shifts are reported in δ (ppm) with reference to the residual protio solvent (CHCl$_3$ or C$_6$H$_6$) peak for ^{1}H and ^{13}C NMR spectra, and to TMS (Me$_4$Si) for ^{29}Si NMR spectra. ESI-MS spectra were recorded on an LCQ mass spectrometer (Finnigan). Samples for the ESI-MS analyses were prepared as a solution in THF/MeOH = 10:1 and potassium iodide (KI) was added for effective ionization. Elemental analyses were performed on a Vario EL III instrument (Elementar GmbH). Thin-layer chromatography (TLC) was performed on plates coated with 250-mm thick silica gel (Aldrich), and column chromatography was performed with silica gel 60 (70–230 mesh; Fluka). In some cases, silica gel was deactivated with hexamethyldisilazane prior to use.

Styrene, 1-hexene, allyltrimethylsilane, vinyltrimethylsilane, vinylpyridines, vinylalkylethers, vinylpyrolidinone, and *tert*-butyl vinyl sulfide were purchased from Aldrich. [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] (**II**) and [(H$_2$IMes)-RuCl$_2$(=CHPh)(PCy$_3$)] (**III**, H$_2$IMes = 1,3-dimesityl-4,5-dihydroimizadol-2-ylidene) were purchased from Strem Chemicals. [RuHCl(CO)-(PCy$_3$)$_2$] (**I**) was prepared according to a literature procedure.[25] Diethyl ether (Et$_2$O) and tetrahydrofuran (THF) were dried, fllowing distillation over sodium/benzophenone. Similarly, benzene and toluene were distilled

over sodium hydride and 1,2-dichloroethane over calcium hydride under argon. Dichloromethane was dried and neutralized by passing through an Al$_2$O$_3$ column, and degassed (deoxidized) under vacuum while frozen in liquid nitrogen. All of the liquid substrates were dried and degassed by bulb-to-bulb distillation over 4 Å molecular sieves unless otherwise stated. All of the reactions were performed under an argon atmosphere. Octavinylsilsesquioxane, Vi$_8$T$_8$ (**1**) (1,3,5,7,9,11,13,15-octavinylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane), was prepared according to the literature procedure.[26]

Catalytic tests: In the typical procedure an oven-dried flask equipped with a condenser and a magnetic stirrer was charged with octavinylsilsesquioxane (**1**) and olefin in a 1:24 or 1:12 ratio. The reaction was carried out in a 0.1 M solution of catalyst **I** in toluene (silylative coupling) heated to 80°C for 18 h, or in CH$_2$Cl$_2$ for catalysts **II** and **III** (cross-metathesis) at room temperature under a slow argon flow.

General procedure for synthesis of functionalized silsesquioxanes 2–11: In a typical silylative coupling reaction, octavinylsilsesquioxane (**1**) and olefin were added to a solution of the catalyst [RuHCl(CO)(PCy$_3$)$_2$] (**I**) in toluene, and the mixture was heated at 80°C for 18 h. In the cross-metathesis process the substrates were added to [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] (**II**) or [(H$_2$IMes)RuCl$_2$(=CHPh)(PCy$_3$)] (**III**) in CH$_2$Cl$_2$ and the mixture was stirred at room temperature for 18 h. After the disappearance of the signal assigned to vinylsilyl was confirmed by ^{1}H NMR spectroscopy, the volatiles were evaporated and the residue was subjected to short column chromatography (silica gel, hexane). The volatiles were evaporated and the residue dried in vacuo to afford the product.

Octa(β-styryl)silsesquioxane (2): From silylative coupling: white powder, 92% yield. From cross-metathesis: 96% yield. ^{1}H NMR (CDCl$_3$): δ = 6.34 (d, J = 19.2 Hz, 8H; =CH-Si), 7.31–7.39 (m, 24H; Ph), 7.40 (d, J = 19.2 Hz, 8H; =CH-Ph), 7.51 ppm (dd, J = 1.4, 8.0 Hz, 16H; Ph); ^{13}C NMR (CDCl$_3$): δ = 117.44 (SiCH=CHPh), 126.97 (o-Ph), 128.60 (p-Ph), 128.94 (m-Ph), 137.42 (ipso-Ph), 149.25 ppm (PhCH=CHSi); ^{29}Si NMR (CDCl$_3$): δ = −78.35 ppm; ESI-MS: m/z: 1280.5 [M+K]$^+$; elemental analysis calcd (%) for C$_{64}$H$_{56}$O$_{12}$Si$_8$: C 61.90, H 4.55; found: C 61.88, H 4.60.

Octa(hex-1-enyl)silsesquioxane (3): From silylative coupling, 74% yield. ^{1}H NMR (CDCl$_3$): δ = 0.80–0.95 (m, 24H), 1.18–1.49 (m, 26.3H), 1.51–1.68 (m, 8.9H), 1.71–1.75 (m, 0.6H), 1.79–1.88 (m, 1.0H), 1.90–2.05 (m, 8.2H), 2.10–2.15 (m, 5.7H), 5.32–5.48 (m, 13.2H), 6.35–6.51 (br d, 2.7H), 6.55 ppm (br, 0.9H). From cross-metathesis, 72% yield. ^{1}H NMR (CDCl$_3$): δ = 0.92 (t, J = 7.1 Hz, 24H; CH$_3$–CH$_2$), 1.28–1.47 (m, 32H; CH$_3$CH$_2$CH$_2$CH$_2$), 2.13–2.19 (m, 0.91×16H; CH$_2$–CH= (trans)), 2.21–2.31 (m, 0.09×16H; CH$_2$–CH= (cis)), 5.35 (d, J = 14.3 Hz, 0.09× 8H; =CH−Si (cis)), 5.46 (d, J = 18.7 Hz, 0.91×8H; =CH−Si (trans)), 6.46 ppm (dt, J = 6.6, 18.7 Hz; 8H; =CH−CH$_2$); ^{13}C NMR (CDCl$_3$): δ = 13.89 (CH$_3$), 22.20 (CH$_3$CH$_2$CH$_2$CH$_2$CH= (trans)), 22.28 (CH$_3$CH$_2$CH$_2$CH$_2$CH= (cis)), 30.38 (CH$_2$CH$_2$CH$_2$CH= (cis)), 31.50 (CH$_2$CH$_2$CH$_2$CH= (trans)), 33.15 (CH$_2$CH= (cis)), 36.00 (CH$_2$CH= (trans)), 119.47 (SiCH=CHCH$_2$), 153.16 (CH$_2$CH=CHSi (trans)), 153.94 ppm (CH$_2$CH=CHSi (cis)); ^{29}Si NMR (CDCl$_3$): δ = −79.10; ESI-MS: m/z: 1121.00 [M+K]$^+$; elemental analysis calcd (%) for C$_{48}$H$_{88}$O$_{12}$Si$_8$: C 53.29, H 8.20; found: C 52.98, H 8.59.

Octakis(2-trimethylsilylvinyl)silsesquioxane (5): From silylative coupling: white powder, 95% yield. M. p. 320°C (decomp); ^{1}H NMR (CDCl$_3$): δ = 0.05, 0.06, 0.07, 0.08, 0.09, 0.10 (s, 72H), 6.27–6.39 (m(d), J = 22.4 Hz, (0.76+0.24)×8H = 8H; =CH-SiMe$_3$+H$_2$C= (trans-H from SiMe$_3$ group)), 6.60–6.62 (m(d), 0.24×8H; H$_2$C= (cis-H from SiMe$_3$ group)), 6.96–7.05 ppm (m, J = 22.4 Hz, 0.76×8H; =CH-SiO$_3$); ^{13}C NMR (CDCl$_3$): δ = −1.98, −1.94, −1.03 (Me$_3$Si), 138.27, 138.37, 138.43, 138.56 (=CHSiMe$_3$), 144.61 (=CH$_2$), 145.28 (=CSi$_2$), 157.32, 157.36, 157.43, 157.49, 157.56 (=CHSiO$_3$); DEPT (^{13}C): CH$_3$ carbon −1.98, −1.94, −1.03 (Me$_3$Si); CH$_2$ carbon 144.61 (=CH$_2$); CH carbon 138.27, 138.37, 138.43, 138.56, 157.32, 157.36, 157.43, 157.49, 157.56 ppm (=CH-Si); ^{29}Si NMR (CDCl$_3$): δ = −82.45, −82.18, −81.89 (O$_3$Si−C=CH$_2$), −78.13, −77.81 (O$_3$Si−CH=CHSi), −6.28 (Me$_3$Si−CH=CHSi), −3.43, −3.32, −3.19 ppm (Me$_3$Si−C=CH$_2$); ESI-MS: m/z: 1250.1 [M+K]$^+$; elemental analysis calcd (%) for C$_{40}$H$_{88}$O$_{12}$Si$_{16}$: C 39.69, H 7.33; found: C 39.43, H 7.54.

Octakis(3-trimethylsilyl-1-propenyl)silsesquioxane (6): From silylative coupling: white powder, 69% yield. M. p. 204–206°C; ^{1}H NMR (CDCl$_3$): δ = −0.02, 0.00, 0.02, 0.06, 0.07, 0.08 (s, 72H, Me$_3$Si), 1.65 (br, 0.56×

16H; $CH_2(SiMe_3)-CH=$ (*trans*)), 1.66–1.84 (br m, 0.05×16H; $CH_2(Si-Me_3)-CH=$ (*cis*)); $CH_2(SiO_3)$-CH=), 5.16–5.18 (br, 0.05×8H; $(O_3Si)HC=$CH−CH$_2$ (*cis*)), 5.22 (br d, $J = 18.7$ Hz, 0.56×8H; $(O_3Si)HC=CH-CH_2$ (*trans*)), 5.57 (br d, $J = 18.7$ Hz, 0.05×8H; $(Me_3Si)HC=CH-CH_2$ (*trans*)), 6.21–6.28 (br m, 0.29×8H; Me$_3$Si$CH=$CHSiO$_3$, 6.25–6.50 (br m), 0.66×8H; $(CH_2)HC=$CHSiO$_3$ + H$_2$C=CSi$_2$ (*trans*-H from SiMe$_3$)), 6.59 (br, 0.10×8H; H$_2$C=CSi$_2$ (*cis*-H from SiMe$_3$)), 6.91–7.06 ppm (d(m, br), $J = 22.4$ Hz, 0.29×8H; O$_3$Si$CH=$CHSiMe$_3$); ESI-MS: m/z: 1362.1 $[M+K]^+$, 1347.5 $[M-CH_2+K]^+$, 1333.6 $[M-2CH_2+K]^+$, 1319 $[M-3CH_2+K]^+$. From cross-metathesis: yield 89%. ^{1}H NMR (CDCl$_3$): $\delta = 0.89$ (br m, $J = 6.8$ Hz, 24H), 0.00 (s, 72H), 1.64 (d, $J = 8.0$ Hz, 16H; CH$_2$−CH=), 5.23 (d, $J = 18.4$ Hz, 8H; =CH−Si), 6.40 ppm (dt, $J = 8.0$, 18.4 Hz, 8H; =CH−CH$_2$); ^{13}C NMR (CDCl$_3$): $\delta = -1.97$ (Me$_3$Si), 28.36 (Me$_3$SiCH_2CH=), 118.37 (Si$CH=$CHCH$_2$), 149.29 ppm (CH$_2$CH=CHSi); ^{29}Si NMR (CDCl$_3$): $\delta = -79.86$ (SiO$_3$), 0.81 ppm (SiMe$_3$); ESI-MS: m/z: 1361.9 $[M+K]^+$; elemental analysis calcd (%) for C$_{48}$H$_{104}$O$_{12}$Si$_{16}$: C 43.59, H 7.93; found C 43.71, H 8.12.

Octakis(2-*n*-butoxyvinyl)silsesquioxane (7): From silylative coupling: colorless oil. Yield 86%. ^{1}H NMR (CDCl$_3$): $\delta = 0.87$–0.94 (m, 24H, CH$_3$−CH$_2$), 1.37–1.42 (m, 16H, CH$_2$−CH$_3$), 1.53–1.64 (m, 16H, CH$_2$−CH$_2$O), 3.68–3.73 (m, 0.43×16H, CH$_2$−OCH=(*cis*)), 3.77 (t, 0.57× 16H, CH$_2$−OCH=(*trans*)), 4.05 (dd, $J = 2.2$, 8.5 Hz, 0.43×8H,=CH−O-(*cis*)), 4.31 (d, $J = 14.8$ Hz, 0.57×8H,=CH−O(*trans*)), 6.59–6.63 (m, 0.43×8H,=CH−Si(*cis*)), 6.76–6.81 ppm (m, 0.57×8H,=CH−Si(*trans*)); ^{13}C NMR (CDCl$_3$): $\delta = 13.71$ (CH$_3$), 18.86 (CH$_2$CH$_3$(*cis*)), 19.13 (CH$_2$CH$_3$(*trans*)), 30.94 (CH$_2$CH$_2$O(*trans*)), 31.74 (CH$_2$CH$_2$O(*cis*)), 67.47, 67.63, 67.82 (CH$_2$-O(*trans*)), 72.11, 72.24, 72.29, 72.35 (CH$_2$-O(*cis*)), 86.52, 86.84, 86.97 (=CH−Si(*trans*)), 90.80, 91.07, 91.26 (=CH−Si(*cis*)), 160.59, 160.66, 160.75 (=CH−O(*trans*)), 161.59, 161.33, 161.45, 161.62, 161.76, 161.92 ppm (=CH−O(*cis*)); ^{29}Si NMR (CDCl$_3$): $\delta = -79.22$, −79.10, −78.88 (Si−CH = (*cis*)), −74.67 (Si−CH = (*trans*)); ESI-MS: 1249.1 ($[M+K]^+$); elemental analysis calcd (%) for C$_{48}$H$_{88}$O$_{20}$Si$_8$: C 47.65, H 7.33; found: C 47.28, H 7.54.

Octakis(2-*tert*-butoxyvinyl)silsesquioxane (8): From silylative coupling: white powder, 91% yield. M.p. 135–1347°C; ^{1}H NMR (CDCl$_3$): $\delta = 1.24$ (s, 0.18×72H; *tert*-Bu−OCH= (*cis*)), 1.27 (s, 0.82×72H; *tert*-Bu−OCH= (*trans*)), 4.16–4.21 (m, 0.18×8H; =CH−Si (*cis*)), 4.50 (d, $J = 14.2$ Hz, 0.82×8H; =CH−Si (*trans*)), 6.80 (d, $J = 14.2$ Hz, 0.82×8H; =CH−O (*trans*)), 6.77–6.83 ppm (m, 0.18×8H; =CH−O (*cis*)); ^{13}C NMR (CDCl$_3$): $\delta = 27.93$, 27.97, 28.24, 28.27 ((CH$_3$)$_3$COCH= (*trans*)), 29.69 ((CH$_3$)$_3$COCH= (*cis*)), 76.77, 76.87 ((CH$_3$)$_3$C), 90.14, 90.30, 90.35, 90.45, 90.71 (=CH−Si (*trans*)), 93.30, 93.42 (=CH−Si (*cis*)), 155.41, 155.53, 155.57, 155.67 (=CH−O (*trans*)), 156.04, 156.21, 156.39 ppm (=CH−O (*cis*)); ^{29}Si NMR (CDCl$_3$): $\delta = -75.76$, −76.94, −76.01 ppm; ESI-MS: m/z: 1249.3 $[M+K]^+$; elemental analysis calcd (%) for C$_{48}$H$_{88}$O$_{20}$Si$_8$: C 47.65, H 7.33; found: C 47.43, H 7.56.

Octakis(2-trimethylsiloxyvinyl)octasilsesquioxane (9): From silylative coupling: pale yellow gum, 81% yield. ^{1}H NMR (CDCl$_3$): $\delta = 0.15$, 0.16, 0.17, 0.18, 0.19, 0.20 (s, 72H; SiMe$_3$), 4.26–4.32 (m, 0.55×8H; =CH−Si (*cis*)), 4.50 (d, $J = 14.1$ Hz, 0.45×8H; =CH−Si (*trans*)), 6.69 (d, $J = 14.1$ Hz, 0.45×8H; =CH−O (*trans*)), 6.77–6.83 ppm (m, 0.55×8H; =CH−O (*cis*)); ^{13}C NMR (C$_6$D$_6$): $\delta = 1.35$ (SiMe$_3$), 95.42–97.17 (=CH−Si (*cis*)), 97.95–99.54 (=CH−Si (*trans*)), 154.35–156.12 ppm (=CH-O); ^{29}Si NMR (C$_6$D$_6$): $\delta = -80.35$, −80.14, −79.47, −75.80, 20.03, 20.16, 20.23, 20.35, 20.49, 20.87, 21.17 ppm; ESI-MS: m/z: 1377.54 $[M+K]^+$; elemental analysis calcd (%) for C$_{40}$H$_{88}$O$_{20}$Si$_{16}$: C 35.89, H 6.63; found C 35.43, H 6.88.

Octakis(2-pyrrolidin-2-onyl-vinyl)octasilsesquioxane (10): From silylative coupling. ^{1}H NMR (CDCl$_3$): $\delta = 2.12$ (q, $J = 8.6$ Hz, 16H; NCH$_2$CH$_2$), 2.50 (t, $J = 8.6$ Hz, 16H; COCH$_2$), 3.52 (t, $J = 8.6$ Hz, 16H; NCH$_2$), 4.50 (d, $J = 14.2$ Hz, 8H; =CH−Si), 7.48 ppm (d, $J = 14.2$ Hz, 8H; =CH−N); ESI-MS: m/z: 1336.4 $[M+K]^+$; elemental analysis calcd (%) for C$_{48}$H$_{64}$N$_8$O$_{20}$Si$_8$: C 44.42, H 4.97; found C 44.53, H 5.09.

Octakis(2-*tert*-butylsulfanylvinyl)silsesquioxane (11): From cross-metathesis: white powder, 91% yield. M.p. 122–124°C; ^{1}H NMR (CDCl$_3$): $\delta = 1.38$ (s, 72H; *tert*-Bu), 5.64 (d, $J = 18.4$ Hz, 8H; =CH−Si), 7.16 ppm (d, $J = 18.4$ Hz, 8H; =CH−S); ^{13}C NMR (CDCl$_3$): $\delta = 31.21$ (CH$_3$), 44.29 (C(CH$_3$)$_3$), 115.49 (=CH−Si), 145.19 ppm (=CH−S); ^{29}Si NMR (CDCl$_3$): $\delta = -80.10$ ppm; ESI-MS: m/z: 1377.4 $[M+K]^+$; elemental analysis calcd (%) for C$_{48}$H$_{88}$O$_{12}$S$_8$Si$_8$: C 43.07, H 6.63; found: C 45.81, H 6.96.

Crystal structure determinations: Diffraction data were collected by the ω-scan technique up to $2\theta = 54°$, on a KUMA-KM4CCD diffractometer[27] with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The temperature (90(1) K for **2** and 100(1) K for **6**) was controlled by an Oxford Instruments cryosystem cooling device. The data were corrected for Lorentz-polarization effects[28] as well as for absorption by using the SORTAV program.[29] The structures were solved with SHELXS97[30] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97.[31] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were located at the calculated positions and refined as a riding model with isotropic thermal parameters fixed at 1.2 times the U_{eq} values of appropriate carrier atoms (1.3 for methyl groups). For **6** one of the symmetry-independent molecules was disordered: two vinyl fragments were refined in two alternative positions with the site occupation factors set at 0.67 and 0.33. All disordered atoms were also refined with anisotropic thermal displacement parameters. Further crystal data are given in Table 8.

Table 8. Crystal data and details of data collections and structure refinements for compunds **2** and **6**.

Compound	2	6
chemical formula	C$_{64}$H$_{56}$O$_{12}$Si$_8$	C$_{48}$H$_{104}$O$_{12}$Si$_{16}$
M_r	1241.81	1322.75
crystal habit	colorless block	colorless block
crystal size [mm]	0.3×0.2×0.2	0.4×0.35×0.35
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	11.8521(8)	11.6865(12)
b [Å]	13.2751(8)	11.7984(15)
c [Å]	21.8301(11)	16.596(2)
α [°]	96.063(4)	99.795(10)
β [°]	98.916(5)	104.786(10)
γ [°]	111.381(6)	111.188(11)
V [Å^3]	3110.2(3)	1973.7(5)
Z	2	1
ρ_{calcd} [g cm^{-3}]	1.326	1.113
$F(000)$	1296	712
T [°C]	−183	−173
μ(Mo$_{K\alpha}$) [mm^{-1}]	0.234	0.302
transmission	0.94, 0.92	0.93, 0.91
no. of reflections measured	22623	19189
no. of unique reflections	10797	8480
R_{int}	0.025	0.045
$R^{[a]}$ ($F>4\sigma(F)$)	0.0504	0.0697
$wR2^{[b]}$ (F^2, all refl.)	0.1083	0.1646
no. of reflections used	10797	8480
no. of parameters	865	343
no. of restraints	0	36
$S^{[c]}$	1.03	1.22
max $\Delta\rho$ [e Å^{-3}]	1.11; −1.67	1.00; −0.69

[a] $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $wR(F^2) = [\Sigma\{w(F_0^2-F_c^2)^2\}/\Sigma\{w(F_0^2)^2\}]^{1/2}$; $w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $P = (F_0^2 + 2F_c^2)/3$ and a and b are parameters chosen to obtain the best reflections statistics. [c] $S = [\Sigma\{w(F_0^2-F_c^2)^2/(n-p)\}]^{1/2}$, where n is the number of data and p is the number of parameters.

Perspective views of compounds **2** and **6** are shown in Figures 1 and 3, respectively. Both molecules have exact C_i symmetry and occupy special positions in the space group $P\bar{1}$ (the centre of symmetry). In the case of **2** the asymmetric part of the unit cell contains two halves of symmetry-independent molecules that lie on opposite centers of symmetry. Bond lengths and angles are within the expected ranges, and do not show significant differences between the chemically equivalent bonds and angles (see Figure captions). The only exception is the asymmetry of the Si-O-Si angles in compound **6**. The values of these angles can be divided into three pairs: O1 and O3 (mean value of Si-O-Si angle 142.8(4)°), O5 and O6 (149.2(1)°), and O2 and O4 (154.3(3)°). This asymmetry can be related to the differences in the orientation of the side chains with respect to the Si-O-Si fragments, as can be visualized by the values of improper torsion

angles O−Si···C−Si. For example, the O3−Si4···C43−Si44 angle is 175.8(3)°, O6−Si1···C13−Si14 is −102.4(2)°, and O2−Si2···C23−Si24 is −13.7(3)°. Therefore, the largest steric strain would be observed on O2, the medium one at O6, and the smallest on O3, which is consistent with the determined values of the Si-O-Si angles.

CCDC-215894 and CCDC-215895 contain the supplementary crystallographic data. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; or deposit@ccdc.cam.ac.uk).

Acknowledgement

[1] a) R. H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev.* **1995**, *95*, 1409; b) S. Yamaguchi, K. Tamao in *Silicon-Containing Polymers* (Eds.: R. G. Jones, W. Ando, J. Chojnowski), Kluwer, **2000**, Chapter 17; c) S. W. Krska, D. Y. Son, D. Seyferth, *Silicon-Containing Polymers* (Eds.: R. G. Jones, W. Ando, J. Chojnowski), Kluwer, **2000**, Chapter 23; d) B. Boutevin, F. Guida -Pietrasanta, A. Ratsimihety in *Silicon-Containing Polymers* (Eds.: R. G. Jones, W. Ando, J. Chojnowski), Kluwer, **2000**, Chapter 3; e) A. Soum in *Silicon-Containing Polymers* (Eds.: R. G. Jones, W. Ando, J. Chojnowski), Kluwer, **2000**, Chapter 11; f) R. H Baney, X. Cao in *Silicon-Containing Polymers* (Eds.: R. G. Jones, W. Ando, J. Chojnowski), Kluwer, **2000**, Chapter 6; g) F. J. Feher, T. A. Budzichowski, *Polyhedron* **1995**, *14,* 3239; h) Organic/Inorganic Hybrid Materials, *Mater. Res. Soc. Symp. Proc.* **2000**, *628*, whole volume*;* i) Organic/Inorganic Hybrid Materials. *Mater. Res. Soc. Symp. Proc.* **2002**, *726*, whole volume*;* j) C. J. Brinker, G. W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing,* Academic Press, San Diego, **1990**; k) I. M. Saez, J. W. Goodby, R. M. Richardson, *Chem. Eur. J.* **2001**, *7*, 2758; K. M. Kim, Y. Chujo, *Polym. Bull.* **2001**, *46*, 15, and references therein; l) N. Auner, B. Ziemer, B. Herrsheft, W. Ziche, P. John, J. Weis, *Eur. J. Inorg. Chem.* **1999**, 1087.

[2] M. Bartsch, P. Bornhauser, G. Calzeferri, *J. Phys. Chem.* **1994**, *98,* 2817.

[3] Marcolli, R. Imhof, G. Calzaferri, *Microchim. Acta.* **1997**, *14,* 493.

[4] a) A. Sellinger, R. M. Laine, *Macromolecules,* **1996**, *29*, 2327; b) A. Sellinger, C. Zhang, R. M. Laine, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1995**, *36*, 282 and reference therein.

[5] F. J. Feher, D. Soulivong, A. G. Eklund, K. D. Wyndham, *Chem. Commun.* **1997**, 1185.

[6] a) B. Marciniec, in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, Germany, **2002**, Chapter 2.6; b) J. Reichl, D. H Berry, *Adv. Organomet. Chem.* **1998**, *43*, 203; c) B. Marciniec, *Appl. Organomet. Chem.* **2000**, *14*, 527; d) B. Marciniec, C. Pietraszuk, *Curr. Org. Chem.* **2003***, 7*, 691.

[7] a) Y. Wakatsuki, H. Yamazaki, M. Nakano, Y. Yamamoto, *J. Chem. Soc. Chem. Commun.* **1991**, 703; b) B. Marciniec, C. Pietraszuk, *Chem. Commun.* **1995**, 2003; c) B. Marciniec, C. Pietraszuk, *Organometallics* **1997**, *16*, 4320, and references therein; d) C.-S. Yi, D.-W. Lee, *Organometallics* **2000**, *19*, 2036.

[8] a) B. Marciniec, E. Walczuk-Gušciora, C. Pietraszuk, *Organometallics* **2001**, *20*, 3423; b) B. Marciniec, E. Walczuk-Gušciora, P. Błażejewska-Chadyniak, *J. Mol. Catal. A: Chem.* **2000**, *160*, 165; c) B. Marciniec, E. Walczuk-Gušciora, C. Pietraszuk, *Catal. Lett.* **1998**, *55*, 125.

[9] B. Marciniec, I. Kownacki, M. Kubicki, M. *Organometallics* **2002**, *19*, 3263.

[10] B. Marciniec, I. Kownacki, D. Chadyniak, *Inorg. Chem. Commun.* **1999**, *2*, 581.

[11] a) B. Marciniec, M. Kujawa, C. Pietraszuk, *Organometallics* **2000**, *19*, 1677; b) B. Marciniec, M. Kujawa, C. Pietraszuk, *New J. Chem.* **2000**, *24*, 671.

[12] Y. Itami, B. Marciniec, M. Kubicki, *Organometallics* **2003**, *22*, 3717.

[13] Y. Itami, B. Marciniec, M. Majchrzak, M. Kubicki, *Organometallics* **2003**, *22*, 1835.

[14] C. Pietraszuk, B. Marciniec, H. Fischer, *Organometallics* **2000**, *19*, 913.

[15] C. Pietraszuk, H. Fischer, M. Kujawa, B. Marciniec, *Tetrahedron Lett.* **2001**, *42*, 1175.

[16] M. Kujawa-Welten, C. Pietraszuk, B. Marciniec, *Organometallics* **2002**, *21*, 840.

[17] M. Kujawa-Welten, B. Marciniec, *J. Mol. Catal.* **2002**, *190*, 79.

[18] C. Pietraszuk, H. Fischer, *Chem. Commun.* **2002**, 2463.

[19] B. Marciniec, C. Pietraszuk in *Handbook of Methathesis* (Ed.: R. Grubbs), Wiley-VCH, **2003**, Chapter 2.13, p. 455.

[20] a) Pyridine-coordinated ruthenium–carbene complexes: M. S. Sanford, J. A. Love, R. H. Grubbs, *Organometallics* **2001**, *20*, 5314; b) pyrydine-coordinated ruthenium–carbene complexes as reactive catalysts: J. A. Love, J. P. Morgan, T. M. Trnka, R. H. Grubbs, *Angew. Chem.* **2002**, *114*, 4207; *Angew. Chem. Int. Ed.* **2002**, *41,* 4035.

[21] B. Marciniec, C. Pietraszuk, M. Kujawa, .*J. Mol. Catal. A: Chem.* **1998**, *133*, 41.

[22] J. Louie, R. H. Grubbs, *Organometallics* **2002**, *21*, 2153.

[23] N. Kuźnik, S. Krompiec, T. Bieg, S. Baj, K. Skutil, A. Chrobk, *J. Organomet. Chem.* **2003**, *665,* 167.

[24] H. Katayama, M. Nagao, F. Ozawa, *Organometallics* **2003**, *22*, 586.

[25] C. S. Yi, D. W. Lee, Y. Chen, *Organometallics* **1999**, *18*, 2043.

[26] P. G. Harrison, C. Hall, R. Kannengiesser, *Main Group Met. Chem.* **1997**, *20*, 515; M. G. Voronkov, T. N. Martynova, R. G. Mirscov, V. I. Beleyi, *Zh. Obshch. Khim.* **1979**, *49,* 1522.

[27] *CrysAlis v.169*, KUMA Diffraction, Wrocław, Poland, **2001**.

[28] *CrysAlisRed v. 169*, KUMA Diffraction, Wrocław, Poland, **2001**.

[29] R. H. Blessing, *J. Appl. Crystallogr.* **1989**, *22*, 396.

[30] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[31] G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.

[32] Siemens, *Stereochemical Workstation.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1989**.