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Efficient Functionalisation of Cubic Monovinylsilsesquioxanes *via* Cross-Metathesis and Silylative Coupling with Olefins in the Presence of Ruthenium Complexes

Patrycja Żak,[a] Cezary Pietraszuk,[a] Bogdan Marciniec,[a,]* Grzegorz Spólnik,[b] and Witold Danikiewicz[b]

[a] Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
Fax: (+48)-61-8291-508; phone: (+48)-61-8291-509; e-mail: bogdan.marciniec@amu.edu.pl
[b] Institute of Organic Chemistry PAS, M. Kasprzaka 44/52, 01-224 Warsaw, Poland

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Abstract: Monovinylheptaisobutylsilsesquioxane undergoes efficient cross-metathesis and silylative coupling with styrenes. Allyl derivatives were successfully tested in cross-metathesis in the presence of first generation Grubbs' catalyst, while heteroatom-substituted vinyl derivatives (vinyl ethers, 9-vinylcarbazole) efficiently undergo silylative coupling catalysed by ruthenium hydride complexes. Both reactions proceed highly stereoselectively and lead to nearly quantitative formation of *E* isomers. Only when vinyl ethers are used does the reaction lead to a mixture of stereoisomers. Atmospheric pressure photoionisation has been successfully used for recording mass spectra of the functionalised silsesquioxanes.

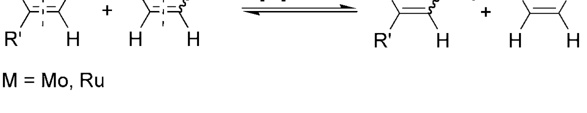
Keywords: catalysis; metathesis; ruthenium complexes; silsesquioxanes; silylative coupling

Introduction

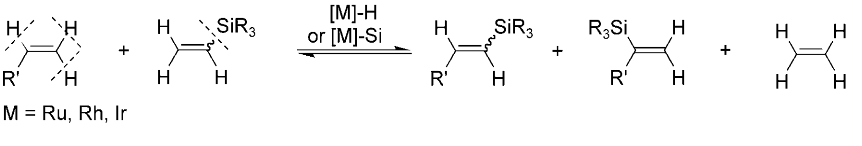
Polyhedral oligosilsesquioxanes of the general formula $(RSiO_{1.5})_n$ constitute a class of organosilicon compounds that currently have a strong impact on both catalytic research and materials science.[1] A rapid growth in interest in the chemistry of polyhedral oligosilsesquioxanes has been observed for the last two decades, stimulated by the increasing number of actual and postulated applications. Substituted cubic silsesquioxanes containing a nanosized inorganic core $(RSiO_{1.5})_8$, similar to the other octasilsesquioxanes, offer considerable potential for producing hybrid materials as the vertices of the cube can be easily functionalised.[1] The vinyl group as substituent at the silsesquioxane core $(ViSiO_{1.5})_8$ is particularly interesting for producing hybrid materials as it can be easily functionalised by a variety of transformations.

In our group two universal, effective and synthetically attractive methods for the functionalisation of molecular and macromolecular compounds with vinylsilicon functionality have been developed. Both methods, i.e., silylative coupling (Scheme 1) and cross-metathesis (Scheme 2), are based on catalytic transformations of vinylsilicon compounds with olefins and lead to the synthesis of the respective functionalised vinylsilicon reagents.[2]

Cross-metathesis proceeds *via* the carbene mechanism and is catalysed by well-defined alkylidene complexes of W, Mo or Ru.[3] In the presence of the first generation Grubbs' catalysts (**1**), second generation Grubbs' catalyst and Hoveyda–Grubbs' catalysts we have demonstrated the efficient cross-metathesis reac-

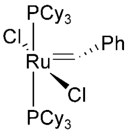


Scheme 2.

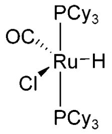


Scheme 1.

tions of vinyltris(trimethylsiloxy)silane, vinyltrialkoxysilanes, trichloro- and generally electron-withdrawing group-substituted vinylsilicon compounds with olefins.[4] The reaction proceeds efficiently for a broad variety of vinylsilicon derivatives which do not bear a methyl group at the vinylsilicon unit. Thus divinyldiaryldisiloxanes undergo cross-metathesis with styrenes and 1-decene,[5] while linear and cyclic vinylaryl-substituted oligosiloxanes are efficiently functionalised upon cross-metathesis with styrene, substituted styrenes, 1-alkene and selected allyl derivatives.[6]



First generation
Grubbs catalyst
(**1**)



(**2**)

The silylative coupling of olefins with vinylsilanes proceeds according to a mechanism involving the activation of =C–H and Si–C= bonds (Scheme 1) and is catalysed by complexes containing or generating hydride ([M]-H) or silyl ([M]-Si) ligands (silicometallics) (where M = Ru, Rh, Ir, Co).[7] A wide variety of vinyl-substituted silanes,[2] cyclosiloxane trimers[8] and tetramers[9] and, recently, linear vinyl-substituted oligo- and polysiloxanes[10] have been effectively functionalised *via* silylative coupling with styrene and some other olefins in the presence of ruthenium hydride complexes, e.g., $[RuHCl(CO)(PPh_3)_3]$ or $[RuHCl(CO)(PCy_3)_2]$ (**2**).

There is a limited number of reports on the application of cross-metathesis for modification of vinyl-substituted silsesquioxanes. In 1997 Feher reported the functionalisation of cubic $(ViSiO_{1.5})_8$ *via* cross-metathesis with selected olefins in the presence of Schrock's catalyst.[11] A highly efficient cross-metathesis of octavinylsilsesquioxanes with selected olefins in the presence of Grubbs' catalyst (**1**) has also been realised in our laboratory.[12] Moreover, we have demonstrated the high activity of ruthenium hydride complexes in the silylative coupling of vinyl-substituted silsesquioxanes[12] and spherosilicates[13] with styrene and some other olefins.

In this paper, we report the synthesis of monovinyl-substituted octasilsesquioxane and its efficient and stereoselective functionalisation *via* cross-metathesis and silylative coupling with styrenes, vinyl- and allyl-organic derivatives. Monofunctionalised octasilsesquioxanes are commonly used as organic-inorganic hybrid monomers, e.g., building blocks for luminescent model substances.[14]

Results and Discussion

Synthesis

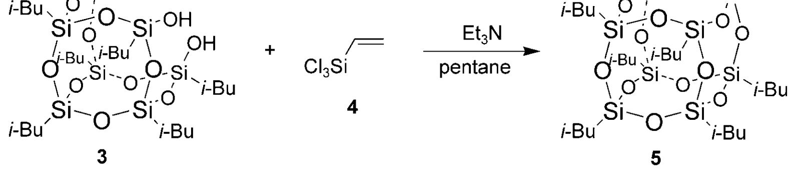
Monovinylsilsesquioxane was synthesised *via* the hydrolytic condensation of incompletely condensed silsesquioxane $(i\text{-Bu})_7Si_7O_9(OH)_3$ (**3**) with vinyltrichlorosilane (**4**) (Scheme 3). This synthetic methodology is well-documented for the synthesis of monosubstituted silsesquioxane [1]. We applied the modified procedure described earlier[15] and were able to get an analytically pure sample with an isolated yield of 92% (see the Experimental Section).

Functionalisation

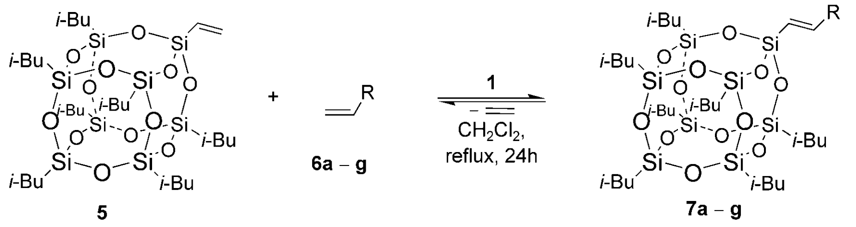
Cross-Metathesis

Treatment of the 1:1 mixture of monovinylheptaisobutyl-substituted silsesquioxane and styrene in CH_2Cl_2 at 40 °C with 1 mol% of first generation Grubbs' catalyst (**1**) gave rise to the slow evolution of ethene and formation of the substituted silsesquioxane (Scheme 4).

Monitoring of the reaction course by gas chromatography showed the gradual consumption of the substrates. Application of a small (one and a half-fold) excess of styrene resulted in complete conversion being observed after 6 h of the reaction. ^1H NMR analysis of the reaction mixture revealed selective formation of the cross-metathesis product. The cross-metathesis was highly stereoselective. The exclusive formation of *E*-isomers was observed for all olefins tested (Scheme 4). A number of substituted styrenes were screened in the cross-metathesis with monovinylheptaisobutyl-substituted silsesquioxane. In all

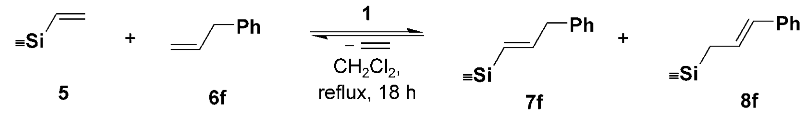


Scheme 3.



R = Ph (**a**), C_6H_4OMe-4 (**b**), C_6H_4Br-4 (**c**), C_6H_4Cl-4 (**d**), C_6H_4Me-4 (**e**), CH_2Ph (**f**), CH_2SiMe_3 (**g**)

Scheme 4.



Scheme 5.

cases complete conversion was observed after 6 or 18 h of reaction in refluxing dichloromethane (Table 1). In the reaction of **5** with 4-methyl-substituted styrene, a three-fold excess of styrene was used to increase the reaction rate and ensure complete conversion.

Allylbenzene and allyltrimethylsilane, exemplary allyl-substituted olefins, undergo efficient and stereoselective cross-metathesis with **5**. ^{1}H NMR spectroscopic analysis of the post-reaction mixture demonstrated the exclusive formation of *E*-isomers. However, in the reaction of **5** with allylbenzene, besides the expected product (**7f**), the formation of its isomer (**8f**) (yield 15%) was observed (Scheme 5). A similar isomerization was not observed for the reaction with allyltrimethylsilane.

The high stereoselectivity of the cross-metathesis of allylbenzene and allylsilanes with vinylsilanes agrees well with our previous observations.[4b] Moreover, efforts have been made to perform the cross-metathesis of **5** with vinylanthracene and vinylphthalimide. However, under the conditions used (temperature up to 110 °C and catalyst concentration up to 4 mol%) no transformation was observed. The inactivity of the ruthenium carbene complex in reactions with these reagents is very likely caused by the formation of stable alkylidene complexes: anthracenyl-substituted ruthenium alkylidene and Fischer-type N-stabilized alkylidene with intramolecular coordination of the carbonyl group to ruthenium as it was postulated by Grubbs for pyrrolidone.[16] Reactions of silsesquioxane (**5**) with vinyl ethers have not been tested in the pres-

Table 1. Cross-metathesis and silylative coupling of monovinyloctasilsesquioxane (**5**) with olefins.

Olefin	Cross-metathesis[a]		Silylative coupling[b]	
	[**5**]:[**6**] (time)	Yield [%] (isolated)	[**5**]:[**6**] (time)	Yield[c] [%] (isolated)
6a	1:2 (6)	100 (97)	1:1.5 (6)	100 (95)
6b	1:1.5 (6)	100 (97)	1:1.5 (6)	100 (95)
6c	1:1.5 (6)	100 (95)	1:1.5 (6)	100 (95)
6d	1:1.5 (6)	100 (96)	1:1.5 (6)	100 (92)
6e	1:3 (6)	100 (94)	1:3 (6)	100 (94)
6f	1:2 (18)	100 (87)[d]	–	–
6g	1:3 (18)	85[e]	–	–
6h	–	–	1:2 (18)	100 (88)[f,g]
6i	–	–	1:2 (18)	100 (93)[f]
6j	–	–	1:3 (24)	100 (85)[h]

[a] *Cross-metathesis:* CH_2Cl_2, reflux, argon, $[RuCl_2(PCy_3)_2(=CHPh)]$ (1 mol%).

[b] *Silylative coupling:* CH_2Cl_2, reflux, argon, $[RuHCl(CO)(PCy_3)_2]/CuCl$, $[RuHCl(CO)(PCy_3)_2]$ (1 mol%), [Ru]:[Cu] = 1:5.

[c] Isomer *E* if not otherwise indicated.

[d] **1** was used as catalyst (2 mol%).

[e] 15% of **8f** was formed (see text).

[f] Toluene, 80 °C, mixture of isomers formed $E/Z = 6/1$.

[g] Isolated sample contains 10 mol% of **5**.

[h] Toluene, 110 °C, **2** was used as catalyst (4 mol%), closed high-pressure Schlenk flask.

ence of a ruthenium alkylidene catalyst. It was demonstrated earlier that, under the conditions used, instead of metathesis, silylative coupling takes place, which is catalysed by ruthenium hydride complexes formed *via* thermal decomposition of ruthenium alkoxybenzylidene complexes.[17]

Silylative Coupling

Heating of the 1:1.5 mixture of monovinylheptaisobutyl-substituted silsesquioxane and styrene in CH_2Cl_2 at 40 °C with 1 mol% of (**2**) (in relation to a molar amount of vinylsilsesquioxane) and five-fold excess of CuCl (in relation to a molar amount of catalyst) led to the evolution of ethene and formation of the substituted silsesquioxane (Scheme 6), similarly as observed for cross-metathesis. ^{1}H NMR analysis of the reaction mixture revealed the selective formation of the functionalised silsesquioxane.

A number of styrenes were tested in the silylative coupling reaction performed in the presence of a catalytic system consisting of $[RuHCl(CO)(PCy_3)_2]$ (**2**) and copper(I) chloride.[18] A nearly quantitative formation of functionalised silsesquioxane was observed after 6 h of reaction in boiling CH_2Cl_2. Similarly to cross-metathesis, silylative coupling proceeds highly regio- and stereoselectively and results in the exclusive formation of *E*-isomers. More forcing conditions (80 °C, toluene) and a two-fold excess of olefin were required when vinyl alkyl ethers were tested as reaction partners. Under optimised conditions, complete conversions were observed after 18 h of the reaction. However, the ^{1}H NMR spectrum of the reaction mixture revealed the formation of a mixture of stereoisomers ($E/Z = 6/1$). An efficient transformation of 9-vinylcarbazole was obtained by using relatively harsh conditions (refluxing toluene, 4 mol% of **2**). Such conditions ensure the highly stereoselective formation of carbazole-functionalised silsesquioxane **7j**.

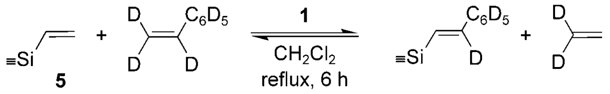
Silylative coupling of allyl derivatives in the presence of ruthenium hydride complexes is always accompanied by isomerisation (migration of the C=C double bond and *cis-trans* isomerisation) leading to a mixture of products. As the isomerisation cannot be avoided, the silylative coupling of isomerising olefins has no synthetic potential. The results of our catalytic examinations are summarized in Table 1. These results were obtained in the reaction conditions (catalyst concentration, solvent, temperature and time) optimised on the basis of a number of catalytic experiments.

The mechanism explaining the effect of copper(I) chloride addition on the reaction course was not examined. The reasonable explanation reported in the literature for similar systems indicates that copper salt acts as a phosphine scavenger and thus facilitates the formation of catalytically active species.[19]

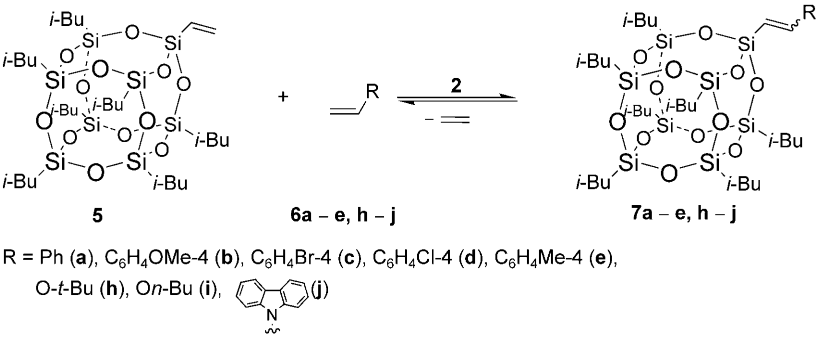
Labelling Studies

Present knowledge of the reactivity of the Grubbs' type ruthenium catalyst indicates the possibility of interconvertions of alkylidene and hydride complexes.[20] Therefore, in order to distinguish between the carbene mechanism (characteristic of olefin metathesis) and non-carbene mechanism (characteristic of silylative coupling) operating in the presence of hydride and silyl complexes,[2] the reaction of **5** with styrene-d_8 was performed in the presence of **1** and in a separate experiment in the presence of **2**.[7b] If the reaction followed the carbene mechanism, it should result in formation of silylstyrene-d_6 and ethylene-d_2 (Scheme 7). In contrast, the insertion-elimination mechanism[7c] should afford the formation of silylstyrene-d_7 and ethylene-*d* (Scheme 8), at least at the initial stage of the reaction.

^{1}H NMR spectroscopic analysis of the products formed in the reaction performed in the presence of **1**

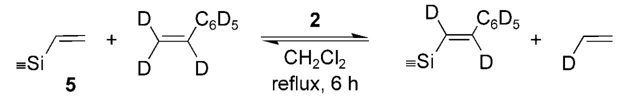


Scheme 7.



R = Ph (**a**), C_6H_4OMe-4 (**b**), C_6H_4Br-4 (**c**), C_6H_4Cl-4 (**d**), C_6H_4Me-4 (**e**), O-*t*-Bu (**h**), O*n*-Bu (**i**), (**j**)

Scheme 6.



Scheme 8.

revealed the formation of silylstyrene-d_6 accompanied by small amount of silylstyrene-d_0 as the product of stoichiometric metathesis of monovinylsilsesquioxane with benzylidene complex (**1**). On the other hand, when the reaction was catalysed by **2**, *E*-1-phenyl-2-(silyl)ethene-d_7 was produced. The results of experiments with deuterium labelled styrene clearly demonstrate that functionalisation of **5** actually can be performed *via* two different mechanisms depending on the catalyst used.

Conclusions

Cubic monovinyl-substituted silsesquioxane undergoes efficient functionalisation *via* cross-metathesis and silylative coupling with styrenes and selected vinyl and allyl derivatives in the presence of ruthenium complexes. Both reactions proceed highly stereoselectively for all olefins tested. Cross-metathesis and silylative coupling are convenient and complementary synthetic routes leading to the functionalisation of vinyl-substituted silicon derivatives. It was found that the best ionisation method for recording mass spectra of silsesquioxanes was an atmospheric pressure photoionisation (APPI) procedure with or without a dopant, depending on the structure of the analysed compound.

Experimental Section

General Methods and Chemicals

^{1}H NMR and ^{13}C NMR spectra were recorded in C_6D_6 on a Varian Gemini 300 instrument at 300 and 75 MHz, respectively. ^{29}Si NMR spectra were recorded in C_6D_6 on a Varian Avance 600 instrument at 119.203 MHz. Atmospheric pressure photoionisation mass spectra (APPI-MS) were recorded on a 4000 Q Trap mass spectrometer (Applied Biosystems) equipped with a PhotoSpray ion source. Compounds with an aromatic substituent were dissolved in dichloromethane (~1 mg in 5 mL) and diluted with methanol about ten thousand times. Flow rate was 100 μL min^{-1}, IS = 1500 V, source temperature = 200 °C and DP = 20 V. No dopant was used. Samples without aromatic substituents (**5**, **7g** and **7i**) were dissolved and diluted as described above using hexane instead of methanol. Flow rate was 100 μL min^{-1}, IS = 1500 V, source temperature = 300 °C and DP = 60 V. Toluene was used as a dopant with a flow rate at 10 μL min^{-1}. The main signal in all spectra corresponds to the protonated molecule ($M+H^+$), however for compounds **7f**, **7g** and **7j** the $M^{+\cdot}$ ion is also observed. Elemental analyses were performed by the analytical laboratory of the Institute of Organic Chemistry PAS in Warsaw.

The chemicals were obtained from the following sources: vinyltrichlorosilane, allyltrimethylsilane and vinyltrimethylsilane from ABCR, styrene, 4-chlorostyrene, 4-methoxystyrene, 4-bromostyrene, 4-methylstyrene, allylbenzene, *tert*-butyl vinyl ether, butyl vinyl ether, 9-vinylcarbazole, dichloromethane, benzene-d_6, decane, dodecane, copper(I) chloride, anhydrous magnesium sulphate, calcium hydride and first generation Grubbs' catalyst from Aldrich, triethylamine and silica gel 60 from Fluka, trisilanolisobutyl POSS from Hybrid Plastics,[21] toluene, acetone, *n*-hexane and *n*-pentane from Chempur. $[RuHCl(CO)(PCy_3)_2]$ was prepared according to the literature procedure.[22] All solvents were dried prior to use over CaH_2 and stored under argon. CH_2Cl_2 was additionally passed through a column with alumina and after that it was degassed by repeated freeze-pump-thaw cycles. All syntheses and catalytic tests were carried out under dry argon.

Synthesis of Monovinylheptaisobutylsilsesquioxane

A two-necked, 500-mL flask equipped with reflux condenser and connected to gas and vacuum line was charged under argon with trisilanol (**3**) (3 g, 3.8×10^{-3} mol), pentane (300 mL) and triethylamine (1.6 mL, 12.0 equiv.). The mixture was cooled down in an ice bath to 0 °C and $ViSiCl_3$ (0.52 mL, 4.0×10^{-3} mol) was quickly added in one portion, which results in the formation of a white precipitate. The suspension was stirred for 24 h at room temperature and filtered on a glass frit. The precipitate was washed with pentane (3 × 50 mL). The filtrate, reduced to 100 mL in volume, was extracted three times with 30 mL of water to remove residues of ammonium salt. The organic phase was dried with $MgSO_4$. Evaporation gave the analytically pure product as a white powder; yield: 2.95 g (92%). ^{1}H NMR (C_6D_6): $\delta = 0.80–0.87$ (m, 14 H, CH_2), 1.05–1.12 (m, 42 H, CH_3), 2.03–2,15 (m, 7 H, CH), 5.97–6.26 (m, 3 H, $-CH{=}CH_2$); ^{13}C NMR (C_6D_6): $\delta = 22.9$, 23.1 (CH_2), 24.3, 24.4 (CH), 25.9, 26.0 (CH_3), 130.3 (=CHSi), 136.4 (=CH_2); ^{29}Si NMR (C_6D_6): $\delta = -66.9$, -67.4 (core), -80.9 (=CHSi); APPI-MS: *m/z*-($[M+H]^+$, % intensity) = 843 (100), 844 (77), 845 (59), 846 (30), 847 (14); anal. calcd. for: $C_{30}H_{66}O_{12}Si_8$ (%): C 42.72, H 7.89; found: C 42.61, H 8.16.

General Procedure for Catalytic Tests

Cross-metathesis: A 5-mL glass reactor equipped with reflux condenser and connected to gas and vacuum line was charged under argon with monovinylsilsesquioxane (**5**) (0.05 g, 5.93×10^{-5} mol), CH_2Cl_2 (2 mL), decane or dodecane (20 μL) and olefin (amounts depending on the olefin, see details under Table 1). The mixture was warmed up to 45 °C in an oil bath and first generation Grubbs' catalyst (0.0005 g, 5.93×10^{-7} mol) or (0.001 g, 1.19×10^{-6} mol) (amounts depend on the olefin, see details under Table 1) was added to the mixture under argon. The reaction mixture was heated under reflux for 24 h. Conversion of the substrate was monitored by gas chromatography. Reaction yields were calculated on the basis of the ^{1}H NMR spectra of the reaction mixture.

Silylative coupling: A 5-mL glass reactor equipped with reflux condenser and connected to gas and vacuum line was charged under argon with monovinylsilsesquioxane (**5**) (0.05 g, 5.93×10^{-5} mol), CH_2Cl_2 (2 mL; or toluene for reaction with vinyl ethers), decane or dodecane (20 µL) and olefin (amount depends on the required silsesquioxane:olefin molar ratio). The mixture was warmed up in an oil bath to 45 °C (for reaction performed in with CH_2Cl_2) or 80 °C (for the reaction performed in toluene) and $[RuHCl(CO)(PCy_3)_2]$ (0.0004 g, 5.93×10^{-7} mol) was added. After 5 min of the reaction copper(I) chloride (0.0003 g, 2.97×10^{-6} mol) was added. The reaction mixture was heated for 24 h. Conversion of the substrate was monitored by gas chromatography. Reaction yields were calculated on the basis of the ^{1}H NMR spectra of the reaction mixture.

Synthesis of Functionalised Monovinylsilsesquioxanes

Via cross-metathesis with olefins (general procedure): A 5-mL glass reactor equipped with reflux condenser and connected to argon/vacuum line was charged under argon with monovinylsilsesquioxane (0.1 g, 1.19×10^{-4} mol), CH_2Cl_2 (3 mL) and olefin (amounts depend on the required silsesquioxane:olefin molar ratio). The mixture was warmed up to 45 °C in an oil bath and first generation Grubbs' catalyst (0.001 g, 1.19×10^{-6} mol) or (0.002 g, 2.37×10^{-6} mol) was added under argon. The reaction mixture was heated under reflux for 24 h. Then the solvent was evaporated under vacuum and cold acetone (2 mL) was added to remaining to form a colourless precipitate. The precipitate was filtered off, dissolved in hexane and purified by column chromatography (silica gel 60/hexane) to remove ruthenium complexes. Evaporation of the solvent gives an analytically pure sample (white powder).

Via silylative coupling with olefins (general procedure): A 5-mL glass reactor equipped with reflux condenser and connected to gas and vacuum line was charged under argon with monovinylsilsesquioxane (0.1 g, 1.19×10^{-4} mol), CH_2Cl_2 (or toluene for reaction with vinyl ethers, 3 mL) and olefin (the amount depends on the required silsesquioxane:olefin molar ratio). The mixture was warmed up in an oil bath to 45 °C (for reaction performed in with CH_2Cl_2) or 80 °C (for reaction performed in toluene) and $[RuHCl(CO)(PCy_3)_2]$ (0.0009 g, 1.19×10^{-6} mol) was added. After 5 min of reaction copper(I) chloride (0.0006 g, 5.93×10^{-6} mol) was added. The reaction mixture was heated for 24 h. Then the solvent was evaporated under vacuum and acetone (2 mL) was added to the remaining contents to form a colourless precipitate. The precipitate was filtered off, dissolved in hexane and purified by column chromatography (silica gel 60/hexane) to remove ruthenium complexes. Evaporation of the solvent gives the analytically pure sample (white powder).

Silylative Coupling of Monovinylsilsesquioxane with 9-Vinylcarbazole

A 10-mL high-pressure Schlenk vessel connected to gas and vacuum line was charged under argon with monovinylsilsesquioxane (0.1 g, 1.19×10^{-4} mol), toluene (2 mL) and 9-vinylcarbazole (0.0688 g, 3.56×10^{-4} mol). The mixture was warmed up in an oil bath to 110 °C and $[RuHCl(CO)(PCy_3)_2]$ (0.0034 g, 4.74×10^{-6} mol) was added. After 5 min of reaction copper(I) chloride (0.0023 g, 2.37×10^{-5} mol) was added. The reaction mixture was heated in the closed vessel for 24 h. Then the solvent was evaporated under vacuum and acetone (2 mL) was added to the remaining contents to form a colourless precipitate. The precipitate was filtered off, dissolved in hexane and purified by column chromatography (silica gel 60/hexane) to remove ruthenium complexes. Evaporation of the solvent gives the analytically pure sample (white powder).

Analytical Data of Isolated Products

7a: ^{1}H NMR (C_6D_6): $\delta = 0.86$–0.91 (m, 14 H, CH_2), 1.08–1.13 (m, 42 H, CH_3), 2.05–2.21 (m, 7 H, CH), 6.47 (d, 1 H, $J = 19.2$ Hz, =CHSi), 7.05–7.1 (m, 3 H, Ph), 7.3–7.4 (m, 2 H, Ph), 7.56 (d, 1 H, $J = 19.2$ Hz, =CHPh); ^{13}C NMR (C_6D_6): $\delta =$ 22.9, 23.1 (CH_2), 24.3, 24.4 (CH), 25.9, 26.0 (CH_3), 118.6 (=CHSi), 127.1, 128.9, 129.0 (C_6H_5), 137.8 (*ipso*-C of C_6H_5), 149.3 (=CHPh); ^{29}Si NMR (C_6D_6): $\delta = -66.9$, -67.3 (core), -79.0 (=CHSi); APPI-MS: m/z ($[M+H]^+$, % intensity) = 919 (100), 920 (89), 921 (68), 922 (36), 923 (18), 924 (7); anal. calcd. for $C_{36}H_{70}O_{12}Si_8$ (%): C 47.02, H 7.67; found: C 46.89, H 7.89; mp 157–158 °C.

7b: ^{1}H NMR (C_6D_6): $\delta = 0.87$–0.92 (m, 14 H, CH_2), 1.09–1.14 (m, 42 H, CH_3), 2.08–2.20 (m, 7 H, CH), 3.23 (s, 3 H, OMe), 6.36 (d, 1 H, $J = 19.2$ Hz, =CHSi), 6.68 (d, 2 H, $J = 8.8$ Hz, C_6H_4), 7.33 (d, 2 H, $J = 8.8$ Hz, C_6H_4), 7.56 (d, 1 H, $J = 19.2$ Hz, =C*H*Ar); ^{13}C NMR (C_6D_6): $\delta = 23.0$, 23.1 (CH_2), 24.4, 24.5 (CH), 25.9, 26.0 (CH_3), 54.7 (OMe), 114.4 (*m*-C of C_6H_4OMe), 115.6 (=CHSi), 128.6 (*o*-C of C_6H_4OMe), 130.7 (*ipso*-C of C_6H_4OMe), 148.9 (=*C*HC_6H_4OMe), 160.8 (*ipso*-C at OMe of C_6H_4OMe); ^{29}Si NMR (C_6D_6): $\delta = -66.91$, -67.32 (core), -78.51 (=CHSi); APPI-MS: m/z ($[M+H]^+$, % intensity) = 949 (100), 950 (82), 951 (56), 952 (29), 953 (13); anal. calcd. for $C_{37}H_{72}O_{13}Si_8$ (%): C 46.80, H 7.64; found: C 46.88, H 7.58; mp 183–184 °C.

7c: ^{1}H NMR (C_6D_6): $\delta = 0.87$–0.91 (m, 14 H, CH_2), 1.08–1.13 (m, 42 H, CH_3), 2.07–2.21 (m, 7 H, CH), 6.32 (d, 1 H, $J = 19.2$ Hz, =CHSi), 6.93 (d, $J = 8.2$ Hz, 2 H, C_6H_4Br), 7.16 (d, $J = 8.2$ Hz, 2 H, C_6H_4Br), 7.33 (d, 1 H, $J = 19.2$ Hz, $<$C$=$$>$CHAr); ^{13}C NMR ($C_6D_6$): $\delta = 22.9$, 23.1 (CH_2), 24.4, 24.5 (CH), 25.9, 26.0 (CH_3), 119.6 (=CHSi), 123.2 (*ipso*-C at Br of C_6H_4Br), 128.6 (*o*-C of C_6H_4Br), 132.05 (*m*-C of C_6H_4Br), 136.6 (*ipso*-C of C_6H_4Br), 147.8 (=CHAr); ^{29}Si NMR (C_6D_6): $\delta = -66.86$, -67.29 (core), -79.38 (=CHSi); APPI-MS: m/z ($[M+H]^+$, % intensity) = 997 (65), 998 (53), 999 (100), 1000 (72), 1001 (51), 1002 (23), 1003 (10); anal. calcd. for $C_{36}H_{69}BrO_{12}Si_8$ (%): C 43.30, H 6.97; found: C 43.29, H 6.98; mp 200–201 °C.

7d: ^{1}H NMR (C_6D_6): $\delta = 1.02$–1.06 (m, 14 H, CH_2), 1.23–1.28 (m, 42 H, CH_3), 2.20–2.35 (m, 7 H, CH), 6.46 (d, 1 H, $J = 19.1$ Hz, =CHSi), 7.30–7.33 (m, 4 H, C_6H_4Cl), 7.50 (d, 1 H, $J = 19.1$ Hz, =CHAr); ^{13}C NMR (C_6D_6): $\delta = 23.0$, 23.1 (CH_2), 24.4, 24.5 (CH), 25.9, 26.0 (CH_3), 119.5 (=CHSi), 128.8 (*o*-C of C_6H_4Cl), 129.1 (*m*-C of C_6H_4Cl), 134.8 (*ipso*-C at Cl of C_6H_4Cl), 136.2 (*ipso*-C of C_6H_4Cl), 147.7 (=*C*HC_6H_4Cl); ^{29}Si NMR (C_6D_6): $\delta = -66.86$, -67.31 (core), -79.38 (=CHSi); APPI-MS: m/z ($[M+H]^+$, % intensity) = 953 (100), 954 (78), 955 (86), 956 (53), 957 (32), 958 (15), 959 (6); anal. calcd. for $C_{36}H_{69}ClO_{12}Si_8$ (%): C 45.32, H 7.29; found: C 45.33, H 7.35; mp 192–193 °C.

7e: ^{1}H NMR (C_6D_6): $\delta=0.86$–0.92 (m, 14H, CH_2), 1.08–1.13 (m, 42H, CH_3), 2.05 (s, 3H, C_6H_4-CH_3) 2.06–2.21 (m, 7H, CH), 6.46 (d, 1H, *J*=19.2 Hz, =CHSi), 6.91 (d, 2H, *J*=8.1 Hz, C_6H_4Me), 7.33 (d, 2H, *J*=8.1 Hz, C_6H_4Me), 7.59 (d, 1H, *J*=19.2 Hz, =CHC_6H_4Me); ^{13}C NMR (C_6D_6): $\delta=23.0$, 23.1 (CH_2), 24.4, 24.5 (CH), 25.9, 26.0 (CH_3), 24.4 ($C_6H_4CH_3$), 118.6 (=CHSi), 127.2 (*o*-C of $C_6H_4CH_3$), 128.9 (*m*-C of $C_6H_4CH_3$), 129.1 (*ipso*-C at CH_3 of $C_6H_4CH_3$), 137.8 (=$CHC_6H_4CH_3$), 149.3 (=CHAr); ^{29}Si NMR (C_6D_6): $\delta=-67.40$, -67.85 (core), -79.27 (=CHSi); APPI-MS: *m/z* ($[M+H]^+$, % intensity)=933 (100), 934 (76), 935 (59), 936 (30), 937 (15), 938 (6); anal. calcd. for $C_{37}H_{72}O_{12}Si_8$ (%): C 47.60, H 7.77; found: C 47.41, H 7.82; mp 184–186 °C.

Mixture of isomers 7f/8f = 7/1: $\delta=$ ^{1}H NMR (C_6D_6): $\delta=0.80$–0.88 (m, 14H, CH_2), 1.04–1.11 (m, 42H, CH_3), 2.00–2.18 (m, 7H, CH), 3.30 (dd, 2H, *J*=6.2 Hz, 1.6 Hz, =$CHCH_2$), 3.78 (d, *J*=7.6 Hz, =$CHCH_2$ in **8f**), 5.73 (dt, partially overlapped, *J*=14.0 Hz, 1.1 Hz, =CHC_6H_5 in **8f**), 5.74 (dt, 1H, *J*=18.6, 1.7 Hz, =CHSi), 6.56 (dt, *J*=14.1 Hz, 7.6 Hz, =$CHCH_2$ in **8f**), 6.82 (dt, 1H, *J*=18.6 Hz, 6.2 Hz, =$CHCH_2$), 7.01–7.2 (m, 5H, Ph), 7.56 (d, 1H, *J*=19.2 Hz, =CHPh); ^{13}C NMR (C_6D_6): $\delta=22.9$, 23.1 (CH_2), 24.3, 24.4 (CH), 25.9, 26.0 (CH_3), 118.6 (=CHSi), 127.1, 128.9, 129.0 (C_6H_5), 137.8 (*ipso*-C of C_6H_5), 149.3 (=CHPh); ^{13}C NMR (C_6D_6): $\delta=22.9$, 23.0 (CH_2), 24.3, 24.4 (CH), 25.9, 26.0 (CH_3), 43.0 ($CH_2C_6H_5$), 121.7 (=CHSi), 126.5, 128.8, 129.1 (C_6H_5), 139.2 (*ipso*-C of C_6H_5), 151.6 (=CHPh); ^{29}Si NMR (C_6D_6): $\delta=-67.49$, -67.64, -67.84, -67.90 (core), -80.55 (=CHSi); APPI-MS: *m/z* (overlaid $M^{+\cdot}$ and $[M+H]^+$ profiles, % intensity)=932 (25), 933 (100), 934 (62), 935 (44), 936 (24), 937 (11), 938 (4); 116–119 °C.

7g: ^{1}H NMR (C_6D_6): $\delta=-0.04$ (s, 9H, $SiMe_3$), 0.83–0.87 (m, 14H, CH_2), 1.07–1.11 (m, 42H, CH_3), 1.58 (dd, 2H, *J*=8.1, 1.0 Hz, =$CHCH_2$), 2.03–2.18 (m, 7H, CH), 5.54 (dt, 1H, *J*=18.5, 1.0 Hz, =CHSi), 6.71 (dt, 1H, *J*=18.5, 8.1 Hz, =$CHCH_2$); ^{13}C NMR (C_6D_6): $\delta=-2.0$ ($SiMe_3$), 23.0, 23.1 (CH_2), 24.4 (CH), 25.9, 26.0 (CH_3), 28.6 (CH_2Si), 118.6 (=CHSi), 150.2 (=$CHCH_2$); ^{29}Si NMR (C_6D_6): $\delta=-67.65$, -67.91 (core), -80.28 (=CHSi); APPI-MS: *m/z* (overlaid $M^{+\cdot}$ and $[M+H]^+$ profiles, % intensity)=928 (34), 929 (100), 930 (88), 931 (69), 932 (41), 933 (24), 934 (9); anal. calcd. for $C_{34}H_{76}O_{12}Si_9$ (%): C 43.92, H 8.24; found: C 43.94, H 8.40; mp 135–136 °C.

7i (mixture of isomers *E*/*Z* = 6/1): ^{1}H NMR (C_6D_6): $\delta=0.74$ (t, 3H, *J*=7.4 Hz, CH_3), 0.84–0.89 (m, 14H, CH_2), 1.07–1.13 (m, 42H, CH_3), 1.16–1.33 (m, 2H, CH_3CH_2), 1.36–1.42 (m, 2H, $CH_3CH_2CH_2$), 2.06–2.19 (m, 7H, CH), 3.39 (t, 2H, *J*=6.5 Hz, CH_2O *cis*), 3.48 (t, 2H, *J*=6.5 Hz, CH_2O *trans*), 4.3 (d, 1H, *J*=8.6 Hz, =CHSi *cis*), 4.7 (d, 1H, *J*=15.0 Hz, = CHSi *trans*), 6.4 (d, 1H, *J*=8.6 Hz, =CHO *cis*), 7.2 (d, 1H, *J*=15.0 Hz, <C=>CHO *trans*); ^{13}C NMR (C_6D_6): $\delta=13.8$ [$O(CH_2)_3CH_3$], 19.4 [$O(CH_2)_2CH_2CH_3$], 23.0, 23.1 (CH_2), 24.3, 24.4 (CH), 25.9, 26.0 (CH_3), 31.1 (OCH_2CH_2), 68.0 (=CHSi *trans*), 102.1 (=CHSi *cis*), 153.5 (=CHO *cis*), 161.2 (=CHO *trans*); ^{29}Si NMR (C_6D_6, ppm): $\delta=-67.53$, -67.72 (core *trans*), -67.78, -67.79 (core *cis*), -80.18 (=CHSi); APPI-MS: *m/z* ($[M+H]^+$, % intensity)=915 (100), 916 (67), 917 (57), 918 (33), 919 (16), 920 (7); anal. calcd. for $C_{34}H_{74}O_{13}Si_8$ (%): C 44.60; H 8.15; found: C 44.72, H 8.25; mp 142–144 °C.

7j: ^{1}H NMR (C_6D_6): $\delta=0.87$–0.91 (m, 14H, CH_2), 1.08–1.12 (m, 42H, CH_3), 2.09–2.17 (m, 7H, CH), 5.95 (d, 1H, *J*=17.2 Hz, =CHSi), 7.15 (*pseudo* t, 2H, Ar), 7.28 (*pseudo* t, 2H, Ar), 7.62 (d, 2H, *J*=8.2 Hz, Ar), 7.84 (d, 1H, *J*=17.2 Hz=CHN), 7.85 (d, *J*=7.64 Hz, 2H, Ar); ^{13}C NMR (C_6D_6): $\delta=23.0$, 23.1 (CH_2), 24.3, 24.4 (CH), 25.9, 26.0 (CH_3), 110.9, 111.3, 120.5, 121.7, 125.1, 126.7 (Ar), 138.6 (=CHSi), 139.7 (=CHN); ^{29}Si NMR (C_6D_6): $\delta=-67.20$, -67.63 (core), -77.63 (=CHSi); APPI-MS: *m/z* (overlaid $M^{+\cdot}$ and $[M+H]^+$ profiles, % intensity)=1007 (92), 1008 (100), 1009 (81), 1010 (52), 1011 (25), 1012 (9); anal. calcd. for $C_{42}H_{73}NO_{12}Si_8$ (%): C 50.01, H 7.29; found: C 50.12, H 7.33; mp 186–187 °C.

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References

[1] a) P. D. Lickiss, F. Rataboul, *Adv. Organomet. Chem.* **2008**, *57*, 1–116; b) R. H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev.* **1995**, *95*, 1409–1430; c) S. Sulaiman, A. Bhaskar, J. Zhang, R. Guda, T. Goodson III, R. M. Laine, *Chem. Mater.* **2008**, *20*, 5563–5573.

[2] a) B. Marciniec, C. Pietraszuk, in: *Handbook of Metathesis*, Vol. 2, (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**, pp 463–490; b) B. Marciniec, C. Pietraszuk, *Curr. Org. Chem.* **2000**, *7*, 691–743; c) B. Marciniec, *Coord. Chem. Rev.* **2005**, *249*, 2374–2390; d) B. Marciniec, C. Pietraszuk, in: *Green Metathesis Chemistry: Great Challenges in Synthesis Catalysis and Nanotechnology*, (Eds.: V. Dragutan, A. Demonceau), Springer, Berlin, **2009**, in press.

[3] *Handbook of Metathesis*, (Ed.: R. H. Grubbs), Wiley-VCH, Weinheim, **2003**.

[4] a) C. Pietraszuk, B. Marciniec, H. Fischer, *Organometallics* **2000**, *19*, 913–917; b) C. Pietraszuk, H. Fischer, M. Kujawa, B. Marciniec, *Tetrahedron Lett.* **2001**, *42*, 1175–1178; c) C. Pietraszuk, B. Marciniec, H. Fischer, *Tetrahedron Lett.* **2003**, *44*, 7121–7124; d) C. Pietraszuk, H. Fischer, S. Rogalski, B. Marciniec, *J. Organomet. Chem.* **2005**, *690*, 5912–5921.

[5] C. Pietraszuk, S. Rogalski, M. Majchrzak, B Marciniec, *J. Organomet. Chem.* **2006**, *691*, 5476–5481.

[6] P. Zak, C. Pietraszuk, B. Marciniec, *J. Mol. Catal. A: Chem.* **2008**, *285*, 1–8.

[7] a) Y. Wakatsuki, H. Yamazaki, M. Nakano, Y. Yamamoto, *J. Chem. Soc. Chem. Commun.* **1991**, 703–704; b) B. Marciniec, C. Pietraszuk, *J. Chem. Soc. Chem. Commun.* **1995**, 2003–2004; c) B. Marciniec, C. Pietraszuk, *Organometallics* **1997**, *16*, 4320–4326.

[8] Y. Itami, B. Marciniec, M. Kubicki, *Organometallics* **2003**, *22*, 3717–3722.

[9] B. Marciniec, J. Waehner, P. Pawluć, M. Kubicki, *J. Mol. Catal. A: Chem.* **2007**, *265*, 25–31.

[10] P. Żak, M. Skrobańska, C. Pietraszuk, B. Marciniec, *J. Organomet. Chem.* **2009**, *694*, 1903–1906.
[11] F. J. Feher, D. Soulivong, A. G. Eklund, K. D. Wyndham, *Chem. Commun.* **1997**, 1185–1186.
[12] Y. Itami, B. Marciniec, M. Kubicki, *Chem. Eur. J.* **2004**, *10*, 1239–1248.
[13] J. Waehner, B. Marciniec, P. Pawluć, *Eur. J. Inorg. Chem.* **2007**, 2975–2980.
[14] C. Marcolli, G. Calzaferri, *Appl. Organomet. Chem.* **1999**, *13*, 213–226.
[15] C. Jost, A. Kuehnle, H. C. L. Abbenhuis, (Creavis Gesellschaft Fuer Technologie Und Innovation m. b. H., Germany), Patent WO 2003042223, **2003**; *Chem. Abstr.* **2003**, *138*, 385570.
[16] J. Louie, R. H. Grubbs, *Organometallics* **2002**, *21*, 2153–2164.
[17] B. Marciniec, M. Kujawa, C. Pietraszuk, *Organometallics* **2000**, *19*, 1677–1681.
[18] C. Pietraszuk, B. Marciniec, M. Jankowska, (Adam Mickiewicz University), Polish Patent PL 195453, **2007**; *Chem. Abstr.* **2008**, *149*, 448545.
[19] E. L. Dias, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.* **1997**, *119*, 3887–3897.
[20] B. Schmidt, *Eur. J. Org. Chem.* **2004**, 1865–1880.
[21] Monovinylsilsesquioxane purchased from Hybrid Plastics Inc. and used as received does not undergo silylative coupling. Preliminary purification by extraction of its pentane solution with water followed by standard work-up produces a reagent that can be successfully used in the process.
[22] C. S. Yi, D. W. Lee, Y. Chen, *Organometallics* **1999**, *18*, 2043–2045.