

Cross-metathesis of vinyl-substituted linear and cyclic siloxanes with olefins in the presence of Grubbs catalysts

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Abstract

Efficient cross-metathesis (CM) of linear and cyclic vinyl-substituted oligosiloxanes with selected olefins in the presence of Grubbs type ruthenium alkylidene complexes is described. Treatment of styrene or 4-substituted styrenes with vinyl group at siloxane skeleton results in the formation of respective cross-metathesis products with good yields and selectivities.

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Keywords: Cross-metathesis; Grubbs catalysts; Vinylsiloxanes

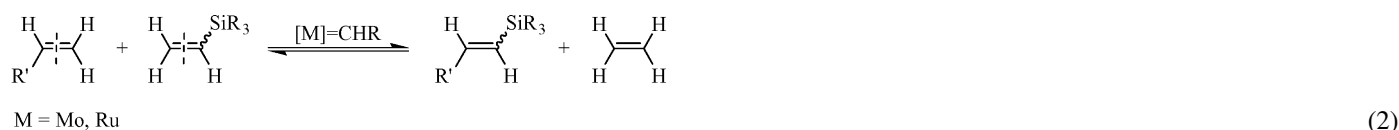
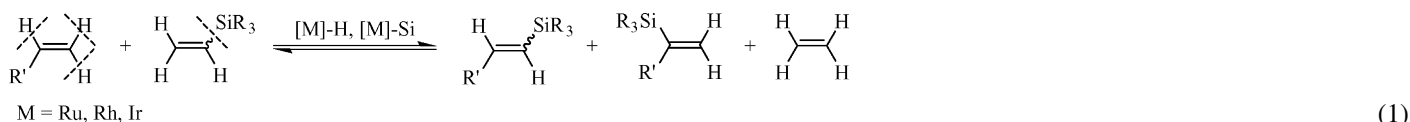
1. Introduction

Substituted vinylsilanes constitute a class of unsaturated organosilicon compounds of prospective wide applicability in organic synthesis [1], especially in the fast developing palladium-catalysed coupling of vinylsilanes with organic derivatives [2]. In last two decades we have developed two universal, effective and synthetically attractive methods for synthesis of well-defined molecular compounds with vinylsilicon functionality. Both methods i.e. silylative coupling (also called *trans*-silylation or silyl group transfer) (Eq. (1)) and cross-metathesis (CM), are based on catalytic transformations of vinyl-silicon compounds with olefins (Eq. (2)) and lead to synthesis of respective functionalized vinyl-silicon reagents [3]

The silylative coupling (SC) is catalysed by complexes containing or generating hydride or silyl ligands ([M]-H or [M]-Si, where M = Ru, Rh, Ir) and proceeds by a mechanism involving activation of =C-H and Si-C= bonds (Eq. (1)) [4,5]. On the other hand, cross-metathesis proceeds via the carbene mechanism and is catalysed by well-defined alkylidene complexes, mostly Ru and Mo [6]. The development of a family of ruthenium-based catalysts, (Fig. 1) tolerant of the majority of functional groups and typical organic and polymer processing conditions has allowed a great number of new applications [6].

Both silylative coupling and cross-metathesis provide universal and complementary routes for the synthesis of well-defined vinylsilicon derivatives [3].

Despite the progress in the study of metathetical reactivity of vinylsilanes, the area of vinylsiloxanes is relatively unexplored.



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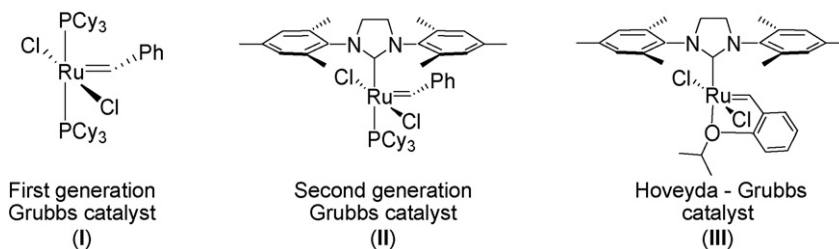


Fig. 1. Grubbs type ruthenium alkylidene complexes.

Vinyltris(trimethylsiloxy)silane [7], methylvinyl-substituted cyclosiloxane trimers [8] and tetramers [9], vinyl-substituted silsesquioxanes [10] and spherosilicates [11] have been effectively functionalized via SC with styrene and some other olefins. On the other hand, effective metathesis transformations have been observed for vinyltris(trimethylsiloxy)silane [12], chlorosubstituted vinyldisiloxanes [13] and vinyl-substituted silsesquioxanes [10]. $\text{ViSi}(\text{OEt})_2\text{OSi}(\text{OEt})_2\text{Vi}$ can be metathetically copolymerized with 1,9-decadiene [14,15] and divinylbenzene [16] and undergoes ROM/ADMET copolymerization with cyclooctadiene [14]. Recently, we described effective conversion of divinylsiloxanes in cross-metathesis with styrenes and 1-decene [17].

Now, we report the metathetical reactivity of linear and cyclic vinyl-substituted oligosiloxanes in cross-metathesis with styrene, substituted styrenes, 1-alkene and selected allyl derivatives in the presence of Grubbs type ruthenium alkylidene complexes (Fig. 1). We discuss advantages and drawbacks of the reaction as a general synthetic route for the synthesis of substituted vinylsiloxanes.

2. Experimental

2.1. General methods and chemicals

All syntheses and catalytic tests were carried out under dry argon. ^1H NMR and ^{13}C NMR spectra were recorded in C_6D_6 on a Varian Gemini 300 at 300 and 75 MHz, respectively. Mass spectra of the products were obtained by the GC–MS analysis (Varian Saturn 2100T, equipped with a DB-1 capillary column – 30 m and ion trap detector). GC analyses were performed on a Varian CP 3800 with a 30 m column and TCD. The chemicals were obtained from the following sources: vinyltris(trimethylsiloxy)silane, vinylmethylbis(trimethylsiloxy)silane, sodium silanolate, and vinylphenyldichlorosilane from ABCR, Grubbs benzylidene catalyst $[\text{Cl}_2(\text{PCy}_3)(\text{H}_2\text{IMes})\text{Ru}(\text{=CHPh})]$, 4-chlorostyrene, 4-methoxystyrene, styrene, *tert*-butyl vinyl ether, allyltrimethylsilane, trichlorovinylsilane, benzene- d_6 , dichloromethane, decane, dodecane, 4-bromoanisole, 4-bromobenzotrifluoride and magnesium from Aldrich, trimethylchlorosilane decene from Fluka and tetraethylammonium hydroxide from Roth. Grubbs first generation benzylidene catalyst was prepared according to the literature procedure [18]. 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.

2.2. General procedure for catalytic tests

The oven dried 10 mL glass reactor equipped with a condenser and magnetic stirring bar was charged under argon with CH_2Cl_2 3 mL, vinylsilane (2.54×10^{-4} mol), decane or dodecane 20 μL (internal standard) and olefin (amounts depend on the $[\text{ViSi}]:[\text{olefin}]$ ratio). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 °C). Then ruthenium benzylidene complex (2.54×10^{-6} mol) was added under argon. The reaction progress was monitored by gas chromatography.

2.3. Synthesis of $\text{H}_2\text{C}=\text{CHSi}(\text{OSiMe}_3)_2(\text{C}_6\text{H}_4\text{CF}_3-4)$

The following procedure is representative for synthesis of vinylsiloxanes.

An oven dried 250 mL flask equipped with a condenser with a bubbler and a magnetic stirring bar was charged under argon with 50 mL of dry pentane and 1.8 mL (9.03×10^{-3} mol) of vinyl[4-(trifluoromethyl)phenyl]dichlorosilane. Then the solution of sodium silanolate (1.86×10^{-2} mol) in 100 mL of pentane was added dropwise in 2 h to the reacting mixture. The mixture was stirred for 24 h at room temperature. Next the resulting suspension was filtered off and the precipitate was rinsed with pentane (2 \times 50 mL). The product was obtained by vacuum distillation (collected fraction 67–75 °C/1 mmHg) (yield = 70%).

^1H NMR (C_6D_6 , δ , ppm): 0.15 (s, 18H, OSiMe₃), 5.84–6.19 (m, $\text{H}_2\text{C}=\text{CHSi}$), 7.42 (d, 2H, $J_{\text{HH}} = 8.0$ Hz, $\text{C}_6\text{H}_4\text{-CF}_3$), 7.64 (d, 2H, $J_{\text{HH}} = 8.0$ Hz, $\text{C}_6\text{H}_4\text{-CF}_3$); ^{13}C NMR (C_6D_6 , δ , ppm): 1.92 (OSiMe₃), 124.63 (q, CF_3), 134.53 ($\text{CH-CH-C}_i\text{-CF}_3$), 135.1 ($\text{C}_i\text{-Si}$), 135.23, 135.34 ($\text{H}_2\text{C}=\text{CHSi}$), 141.6 ($\text{C}_i\text{-CF}_3$); ^{19}F NMR (C_6D_6 , δ , ppm): –61.79 (s, CF_3); MS: m/z (rel. intensity): 45 (16), 59 (19), 73 (100), 74 (10), 77 (24), 141 (10), 225 (41), 85 (16), 359 (12), 363 ($\text{M}^+ - 15$, 40).

2.4. Spectroscopic data for

$\text{H}_2\text{C}=\text{CHSi}(\text{OSiMe}_3)_2(\text{C}_6\text{H}_4\text{OMe-4})$ (isolated yield = 80%)

^1H NMR (C_6D_6 , δ , ppm): 0.21 (s, 18H, OSiMe₃), 3.3 (s, 3H, $\text{C}_6\text{H}_4\text{-OMe}$), 5.95–6.34 (m, $\text{H}_2\text{C}=\text{CHSi}$), 6.87 (d, 2H, $J_{\text{HH}} = 8.7$ Hz, $\text{C}_6\text{H}_4\text{-OMe}$), 7.72 (d, 2H, $\text{C}_6\text{H}_4\text{-OMe}$); ^{13}C NMR (C_6D_6 , δ , ppm): 2.30 (OSiMe₃), 54.6 (OMe), 113 ($\text{CH-CH-C}_i\text{-OMe}$), 134.4 ($=\text{CH-Si}$), 135.9 ($\text{CH-CH-C}_i\text{-OMe}$), 136.1 ($\text{C}_i\text{-CF}_3$), 136.6 ($=\text{CH}_2$), 161.6 ($\text{C}_i\text{-OMe}$); MS: m/z (rel. intensity): 45 (22), 60 (17), 73 (8), 74 (15), 76 (10), 92 (13), 134 (9), 191 (10), 233 (10), 234 (8), 236 (8), 237 (18), 239 (11), 296 (13), 314 (8), 325 (22), 326 (100), 327 (31), 340 (M^+ , 5).

2.5. Synthesis of $Me_3Si(OSiViPh)_nOSiMe_3$

The following procedure is representative of the synthesis of linear vinyl-substituted oligosiloxanes. A three-necked flask (100 mL) equipped with a condenser and a magnetic stirring bar was charged under argon with dry toluene (50 mL), vinyl[4-(methoxy)phenyl]dichlorosilane 1.5 mL (7.98×10^{-3} mol), tetraethylammonium hydroxide (25% solution in water) 5.6 mL (3.99×10^{-2} mol) and 0.2 mL trimethylchlorosilane (1.60×10^{-3} mol). The reaction mixture was stirred at room temperature for 48 h and washed with water (5×10 mL). The organic phase was dried with magnesium sulphate. Evaporation of the solvent under vacuum affords white powder. 1H NMR (C_6D_6 , δ , ppm): 0.18 (s, $SiMe_3$), 5.87–6.39 (m, $CH=CH_2$), 7.04–7.24 (m, Ph), 7.70–7.93 (m, Ph); $Me_3Si[OSiVi(C_6H_4OMe-4)]_nOSiMe_3$: 1H NMR (C_6D_6 , δ , ppm): 0.21 (s, $SiMe_3$), 3.20–3.29 (m, OMe), 5.87–6.39 (m, $HC=CH_2$), 7.04–7.24 (m, Ph), 7.70–7.93 (m, Ph); $Me_3Si[OSiVi(C_6H_4CF_3-4)]_nOSiMe_3$: 1H NMR (C_6D_6 , δ , ppm): 0.31 (s, $SiMe_3$), 5.66–6.29 (m, $HC=CH_2$), 7.22–7.7 (m, C_6H_4).

2.6. Synthesis of 1,3,5-triphenyl-1,3,5-trivinylcyclotrisiloxane

The following procedure is representative of the synthesis of trivinylcyclotrisiloxanes. A three-neck flask (250 mL) equipped with condenser was charged under argon with dried, degassed pentane 200 mL, pyridine 1.92 mL (23.52×10^{-3} mol) and dichlorophenylvinylsilane 2 mL (11.76×10^{-3} mol). Then, water 0.212 mL was added slowly to the vigorously stirred mixture and the reaction was carried out at room temperature for 24 h. Then reaction mixture was filtered through a plug of Celite and the solvent was evaporated in vacuum. The residue was distilled under high vacuum. The product in the form of dense liquid was obtained in the amount of 1.308 g, which is equivalent to a 75% yield. 1H NMR spectroscopy reveals the presence of two isomers *cis* and *trans* at the molar ratio of 1:3.

1H NMR (C_6D_6 , δ , ppm): 5.85–6.46 (m, 9H, $-CH=CH_2$), 7.00–7.29 (m, 6H, Ph), 7.63–7.95 (m, 9H, Ph); ^{13}C NMR (C_6D_6 , δ , ppm): 128.14, 128.17, 128.21, 128.26, 128.30, 130.75, 130.81, 130.86, 134.31, 134.35, 134.39, 136.10, 136.13, 136.70, 136.83, 136.94; MS: *m/z* (rel. intensity): 45 (46), 50 (41), 51 (71), 73 (39), 77 (56), 78 (67), 79 (29), 89 (29), 91 (22), 103 (26), 104 (50), 147 (28), 165 (37), 191 (25), 207 (30), 209 (31), 211 (27), 235 (28), 262 (36), 263 (26), 285 (25), 287 (33), 288 (40), 289 (30), 312 (35), 313 (37), 314 (34), 339 (100), 340 (99), 341 (46), 342 (26), 366 (81), 367 (33), 368 (25), 416 (33), 417 (35), 443 (20), 444 (M^+ , 43).

2.7. Synthesis of $[(Me_3SiO)_3Si]CH=CH(C_6H_4OMe-4)$

The following procedure is representative for synthesis of substituted vinylsiloxanes.

An oven dried 20 mL Schlenk flask equipped with a condenser with a bubbler and a magnetic stirring bar was charged under argon with 10 mL of dichloromethane, vinyltris(trimethylsiloxy)silane (3.22×10^{-3} mol) and 4-methox-

ystyrene (6.4×10^{-4} mol). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 45 °C). Then 0.027 g (3.2×10^{-5} mol) of ruthenium benzylidene complex **II** was added under argon. Intensive bubbling was observed. A gentle flow of argon was applied from the top of the column. The progress of reaction was monitored by gas chromatography. After the reaction had been completed, dichloromethane was distilled off and the resulting product was purified by column chromatography (silica gel MN60/hexane).

2.8. Spectroscopic data for

$[(Me_3SiO)_3Si]CH=CH(C_6H_4OMe-4)$ (isolated yield = 87%)

1H NMR (C_6D_6 , δ , ppm): 0.27 (s, 27H, $OSiMe_3$), 3.3 (s, 3H, C_6H_4-OMe), 6.28 (d, 1H, $J_{HH} = 19.1$ Hz, $=CH-Si$), 7.33 (d, 1H, $J_{HH} = 19.1$ Hz, $=CH-C_6H_4-OMe-4$), 6.71 (d, 2H, $J_{HH} = 8.7$ Hz, $C_6H_4-OMe-4$), 7.32 (d, 2H, $J_{HH} = 8.7$ Hz, $C_6H_4-OMe-4$); ^{13}C NMR (C_6D_6 , δ , ppm): 2.3 ($OSiMe_3$), 54.9 (OMe), 114.4 ($CH-CH-C_i-OMe$), 120.1 ($=CH-Si$), 128.3 ($CH-CH-C_i-OMe$), 131.3 ($=CH-C_i$), 146.5 ($=CH-C_6H_4-OMe-4$), 160.5 (C_i-OMe); MS: *m/z* (rel. intensity): 184 (10), 185 (11), 186 (12), 187 (17), 188 (19), 189 (26), 190 (26), 191 (45), 192 (49), 193 (13), 265 (10), 274 (10), 275 (12), 276 (18), 277 (25), 278 (25), 279 (75), 280 (100), 281 (37), 282 (11), 339 (17), 340 (41), 341 (10), 411 (11), 412 (11), 413 (67), 414 (29), 415 (17), 427 (12), 428 (M^+ , 74).

2.9. Spectroscopic data for

$[(OSiMe_3)_2(C_6H_4-OMe-4)]SiCH=CH(C_6H_5)$ (isolated yield = 82%)

1H NMR (C_6D_6 , δ , ppm): 0.26 (s, 18H, $OSiMe_3$), 3.3 (s, 3H, C_6H_4-OMe), 6.64 (d, 1H, $J_{HH} = 19.2$ Hz, $=CH-Si$), 6.92 (d, 2H, $J_{HH} = 8.7$ Hz, C_6H_4-OMe), 7.05 – 7.35 (m, 5H, Ph), 7.33 (d, 1H, $J_{HH} = 19.2$ Hz, $=CH-Ph$), 7.81 (d, 2H, $J_{HH} = 8.7$ Hz, $C_6H_4-OMe-4$); ^{13}C NMR (C_6D_6 , δ , ppm): 2.4 ($OSiMe_3$), 54.7 (OMe), 114 ($CH-CH-C_i-OMe$), 125.34 ($=CH-Si$), 127.1, 128.2, 128.7, 128.9 (Ph), 136.03 ($CH-CH-C_i-OMe$), 138.4 (C_i-Si), 147.4 ($=CH-Ph$), 161.7 (C_i-OMe); MS: *m/z* (rel. intensity): 45 (8), 73 (16), 91 (7), 145 (8), 207 (6), 209 (12), 210 (100), 211 (33), 212 (10), 251 (6), 265 (6), 267 (7), 293 (40), 294 (12), 297 (14), 309 (7), 313 (6), 325 (14), 401 (17), 402 (7), 416 (M^+ , 17).

2.10. Spectroscopic data for

$(C_6H_5CH=CH)Si(OSiMe_3)_2(C_6H_4-CF_3-4)$ (isolated yield 79%)

1H NMR (C_6D_6 , δ , ppm): 0.2 (s, 18H, $OSiMe_3$), 6.48 (d, 1H, $J_{HH} = 19.2$ Hz, $=CH-Si$), 7.23 (d, 1H, $J_{HH} = 19.2$ Hz, $=CH-Ph$), 7.07–7.33 (m, 5H, Ph), 7.46 (d, 2H, $J_{HH} = 8.5$ Hz, $C_6H_4-CF_3$), 7.72 (d, 2H, $J_{HH} = 8.5$ Hz, $C_6H_4-CF_3$); ^{13}C NMR (C_6D_6 , δ , ppm): 2.2 ($OSiMe_3$), 123.68 ($=CH-Si$), 124.75 (q, CF_3), 127.1, 128.9, 129.06, 138 (Ph), 142.03 (C_i-CF_3), 148.2 ($=CH-Ph$); MS: *m/z* (rel. intensity): 45 (13), 73 (100), 74 (7), 75 (5), 77 (11), 91 (5), 103 (5), 115 (5), 127 (7), 141 (7), 145 (5), 189 (5), 191 (15), 209 (10), 210 (5), 225 (99), 226 (24), 227 (15), 228 (7), 229 (80), 230 (15), 231 (6), 248 (5), 335 (5), 435 (22), 439 (6), 454 (M^+ , 1).

2.11. Spectroscopic data for

$[(Me_3SiO)_3Si]CH=CH(C_6H_4Br-4)$ (isolated yield = 90%)

1H NMR (C_6D_6 , δ , ppm): 0.25 (s, 27H, OSiMe₃), 6.27 (d, 1H, J_{HH} = 19.1 Hz, =CH-Si), 6.93 (d, 2H, J_{HH} = 8.4 Hz, C₆H₄-Br), 7.12 (d, 1H, J_{HH} = 19.1 Hz, =CH-Ph), 7.19 (d, 2H, J_{HH} = 8.4 Hz, C₆H₄-Br); ^{13}C NMR (C_6D_6 , δ , ppm): 2.2 (OSiMe₃), 122.7 (C_i-Br), 124.0 (=CH-Si), 128.4 (CH-CH-C_i-Br), 132.0 (CH-C_i-Br), 137.1 (C_i-CH=), 145.4 (=CH-C₆H₄-Br); MS: m/z (rel. intensity): 45 (19), 73 (55), 159 (10), 207 (16), 239 (34), 240 (89), 241 (100), 242 (23), 243 (8), 279 (41), 280 (14), 281 (8), 293 (16), 373 (8), 375 (12), 397 (16), 461 (13), 463 (18), 476 (M⁺, 8).

2.12. Spectroscopic data for

$[(Me_3SiO)_3Si]CH=CH(C_8H_{17})$ (isolated yield = 75%)

1H NMR (C_6D_6 , δ , ppm): 0.24 (s, 27H, OSiMe₃), 0.92 (t, 3H, J_{HH} = 6.9 Hz, CH₂-CH₃), 1.24 (s, 14H, (CH₂)₇), 1.37 (q, 2H, J_{HH} = 6.9 Hz, CH₂-CH₃), 2.06–2.13 (m, 2H, =CH-CH₂), 5.66 (d, 1H, J_{HH} = 18.7 Hz, =CH-Si), 6.48 (dt, 1H, J_{HH} = 18.7 Hz, 6.0 Hz, =CH-CH₂); ^{13}C NMR (C_6D_6 , δ , ppm): 1.98 (OSiMe₃), 14.36, 23.08, 28.91, 29.54, 29.71, 29.84, 32.25, 36.78 (CH₂), 124.55 (=CH-Si), 150.62 (=CH-CH₂); MS: m/z (rel. intensity): 45 (20), 59 (30), 73 (100), 75 (24), 81 (17), 193 (15), 197 (29),

198 (97), 199 (11), 207 (11), 208 (43), 209 (25), 295 (47), 296 (14), 419 (M⁺-15, 24).

2.13. Synthesis of *cis* and *trans*-1,3,5-tris-(*E*)-(2-phenylethenyl)-1,3,5-triphenylcyclotrisiloxane

A 5 mL glass reactor equipped with a condenser, magnetic stirrer and an attachment permitting connection to the gas-vacuum line, was charged with 3 mL CH₂Cl₂, cyclosiloxane (0.33 g; 7.4×10^{-4} mol) and styrene (0.64 mL; 5.6×10^{-3} mol). The system was heated to the boiling point of the reaction mixture (near 45 °C) in an oil bath, and then Grubbs catalyst (**I**) was added. (4.44×10^{-5} mol). The reaction was conducted at the boiling point of the reaction mixture for 48 h. The course of the reaction was monitored by 1H NMR. Then the catalyst was removed by using column chromatography (silica MN60/hexane). The mixture of isomers *cis* and *trans* at the molar ratio of 1:3 was obtained (composition was calculated on the basis of 1H NMR spectroscopy). Isomer *trans* was isolated from the mixture of isomers by precipitation with hexane from CH₂Cl₂ solution.

Spectroscopic data (isomer *trans*): 1H NMR (C_6D_6 , δ , ppm): 6.66 (d, J = 18.0 Hz, 2H, =CHSi), 6.75 (d, J = 18.0 Hz, 4H, =CHSi), 6.99–7.21 (m, 15H, Ph), 7.51 (d, J = 18.0 Hz, 4H, =CHPh), 8.00–8.12 (m, 15H, =CHPh); ^{13}C NMR (C_6D_6 , δ ,

Table 1
Cross-metathesis of vinylsiloxanes with olefins

Siloxane R=	Olefin X=	Catalyst	Conversion of olefin [%]	Yield (isolated) [%]	<i>E/Z</i>	Yield XHC=CHX [%]
OSiMe ₃	C ₆ H ₅	I	97 ^a	97 ^a	<i>E</i> ^a	0
	C ₈ H ₁₇	I	90	89	10/1	Trace
	CH ₂ OBu	I	99 ^b	95 ^b	7/1 ^b	4 ^b
	C ₆ H ₅	II	93	93	<i>E</i>	0
	C ₆ H ₄ -OMe-4	II	100	95 (87)	<i>E</i>	5
	C ₈ H ₁₇	II	100	96	10/1	4
C ₆ H ₅	CH ₂ SiMe ₃	II	95	94	25/1	Trace
	C ₆ H ₄ OMe-4	I	35 ^a	34 ^a	<i>E</i> ^a	Trace ^a
	C ₈ H ₁₇	I	38 ^a	21 ^a	10/1 ^a	17 ^a
C ₆ H ₄ OMe-4	C ₆ H ₅	II	94	93 (82)	<i>E</i>	Trace
	C ₄ H ₄ -OMe-4	II	95	94	<i>E</i>	Trace
	C ₈ H ₁₇	II	93	93	10/1	0
	CH ₂ SiMe ₃	II	80	80	25/1	0
C ₆ H ₄ CF ₃ -4	C ₆ H ₅	I	86 ^a	86 ^a (79) ^a	<i>E</i>	0
	C ₆ H ₅	I	97	97	<i>E</i>	0
	C ₆ H ₄ -OMe-4	I	94 ^a	94 ^a	<i>E</i>	0
	C ₆ H ₅ -Cl-4	I	80 ^a	80 ^a	<i>E</i>	0
	C ₈ H ₁₇	I	100	95	10/1	5
	CH ₂ OBu	I	100 ^b	100 ^b	8/1	0
	C ₆ H ₄ -OMe-4	II	99	95	<i>E</i>	4
	C ₈ H ₁₇	II	100	95	10/1	5
	CH ₂ SiMe ₃	II	100	100	25/1	0
	CH ₂ OBu	II	100	95	7/1	5
Me	C ₆ H ₄ OMe-4	I	45 ^a	44 (42) ^a	<i>E</i> ^a	Trace ^a
	C ₈ H ₁₇	I	20 ^a	16 ^a	10/1 ^a	4 ^a
	C ₆ H ₄ OMe-4	II	44	43	<i>E</i>	Trace
	C ₈ H ₁₇	II	33	22	10/1	11

Reaction conditions: CH₂Cl₂, reflux, [ViSi]:[C=C]: [Ru] = 5:1:0.05, 5h.

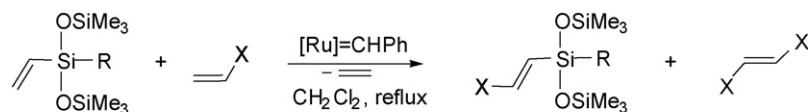
^a [ViSi]:[C=C] = 1:1.

^b [ViSi]:[C=C] = 2:1.

ppm): 122.08, 122.41, 126.44, 126.76, 127.08, 127.38, 128.71, 128.74, 129.00, 130.86, 134.58, 134.63, 135.22, 137.76, 149.7.

3. Results and discussion

A series of vinyltrisiloxanes were synthesised and tested in cross-metathesis with styrenes, substituted styrenes, 1-alkenes or selected allyl derivatives. Treatment of a mixture of vinyltrisiloxane and olefin in the presence of 5 mol% of catalyst **I** or **II** in boiling CH_2Cl_2 for 5 h gives rise to evolution of ethene and formation of 1-silyl-2-organylenes (Eq. (3)).



R = OSiMe₃, Me, C₆H₅, C₆H₄OMe-4, C₆H₄CF₃-4
X = C₆H₅, C₆H₄OMe-4, C₆H₄Cl-4, C₈H₁₇, CH₂SiMe₃, CH₂OBu

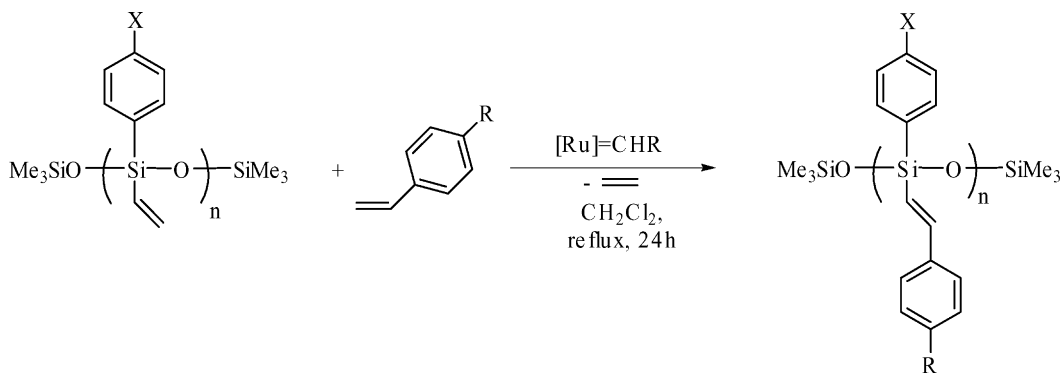
The reaction is accompanied by competitive olefin homo-metathesis. However, the latter process can be easily retarded by application of a five-fold excess of vinylsiloxane. In such conditions the reactions lead to selective formation of the

somewhat unexpected as we did not observe metathetical conversion of vinylsilicon derivatives bearing methyl group [3,12a,20]. The high yields of the cross-metathesis products obtained for vinyl-substituted trisiloxanes have encouraged us to check the reactivity of siloxanes with longer chains. In order to do this, we synthesised by hydrolytic polycondensation three oligosiloxanes containing vinyl and phenyl (or substituted phenyl) groups at each internal silicon atom in the chain and the terminal trimethylsilyl groups (Fig. 2).

(3)

Molecular masses were determined on the basis of ¹H NMR spectra.

The oligosiloxanes prepared were tested in the reaction with styrene or 4-methoxystyrene in the presence of Grubbs catalyst **I** or **II**. The expected reaction course is illustrated in Eq. (4). The results obtained are collected in Table 2.



(4)

cross-metathesis products. High chemo-selectivity of the process is also related to the lack of vinylsilanes activity in the process of homometathesis [19]. The results of the catalytic study are summarised in Table 1.

Very high yield is observed for vinyltrisiloxysilane [see also 12]. The yield of the reaction with phenylsubstituted vinylsiloxanes strongly depends on the substituents. Introduction of an electron-withdrawing substituent in position 4 of the phenyl ring strongly improves the yield of the obtained products. Similar phenomenon was observed for metathesis reactivity of vinylsilanes [13]. Although the cross-metathesis in many systems is known to suffer from low stereoselectivity, analysis of the results obtained indicates stereoselective formation of the products expected. Especially, the reactions with styrenes give exclusively E-isomers of the products.

Moderate yields (up to 44%) were obtained for the reaction of methylsubstituted vinylsilanes. This result was

The results have shown the very high sensitivity of the reaction to the properties of substituent at silicon. No reaction was observed for phenyl-substituted siloxanes. Introduction of the methoxy group to the phenyl ring results in an increase in the observed substitution of the vinyl groups. Finally, introduc-

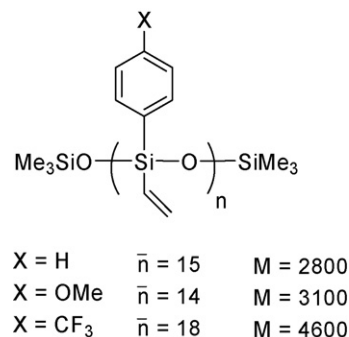


Fig. 2. Linear oligosiloxanes tested in cross-metathesis with styrenes.

Table 2
Cross-metathesis of oligovinylsiloxanes with styrenes

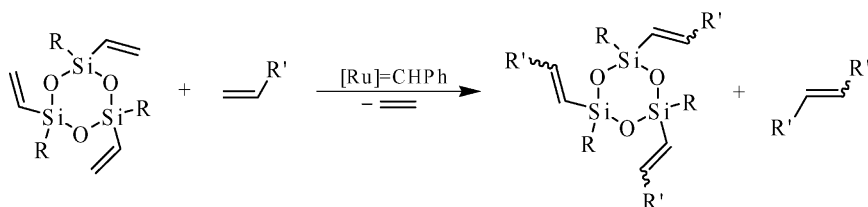
X=	R=	Cat.	Yield ^a [%]
H	H	I	0
	H	II	0
OMe	H	I	32
	H	II	32
	OMe	I	33
	OMe	II	35
CF ₃	H	I	100
	H	II	100
	OMe	I	100
	OMe	II	100

Reaction conditions: CH₂Cl₂, reflux, 24 h, [H₂C=CH]:[styrene]:[Ru] = 1:5:0.05 (for cat. = **I**), [H₂C=CH]:[styrene] = 1:10 (for cat. = **II**).

^a Calculated on the basis of ¹H NMR spectroscopy.

tion of the strongly electron-withdrawing trifluoromethyl group ensured quantitative transformation.

Effective metathesis transformation has been observed when trivinyl-substituted cyclotrisiloxanes were treated with olefins in the presence of metathesis catalyst **I**, **II** or **III** (Eq. (5)).



R = OSiMe₃, Ph, C₆H₄OMe-4

R' = Ph, C₆H₄OMe-4, C₆H₄Cl-4, C₈H₁₇

(5)

The reaction requires an excess of olefin. Therefore, formation of olefin homometathesis products could not be avoided. However, the proper choice of the substrates permits getting high yields and selectivities of the substituted cyclosiloxanes at least for

Table 3
Cross-metathesis of trivinylcyclotrisiloxanes with olefins

Siloxane R=	Olefin R'=	Cat.	Reaction conditions ^a	Conversion of siloxane [%]	Yield (isolated) [%]	E/Z
OSiMe ₃	C ₆ H ₅	I	1:3/4	100	95	E
	C ₆ H ₅ -Cl-4	I	1:3/4	100	96	E
	C ₆ H ₄ -OMe-4	I	1:3/2	100	96	E
	C ₈ H ₁₇	I	1:3/3	79	78	8/1
	C ₆ H ₄ -Cl-4	II	1:15/2	100	90	E
	C ₆ H ₄ -OMe-4	II	1:15/2	100	93	E
	C ₈ H ₁₇	II	1:15/2	100	82	8/1
C ₆ H ₅	C ₆ H ₅	I	1:3/18	100	96 (90)	E
	C ₆ H ₄ -Cl-4	I	1:3/2	100	95	E
	C ₆ H ₄ -OMe-4	I	1:3/4	100	95	E
	C ₈ H ₁₇	I	1:3/5	100	90	8/1
C ₆ H ₄ OMe-4	C ₆ H ₅	I	1:3/2	100	96	E
	C ₈ H ₁₇	I	1:3/3	100	91	10/1
Me	C ₆ H ₅	I	1:3/5	5	0	–
	C ₆ H ₅	II	1:3/5	5	0	–

Reaction conditions: CH₂Cl₂, reflux, [V₁Si]:[Ru] = 1:0.05.

^a [V₁Si]:[C=C]/time [h].

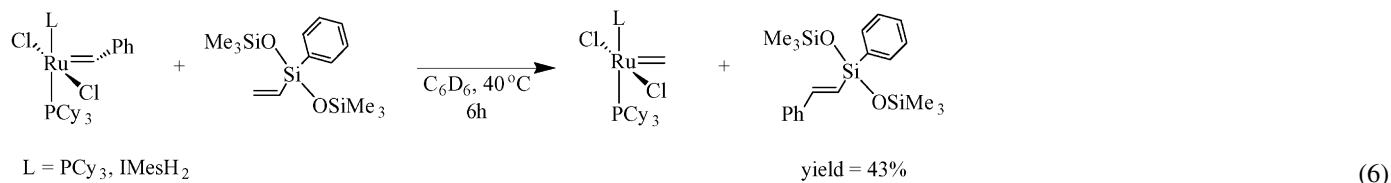
selected reaction systems. The results obtained are presented in Table 3.

The optimum catalyst of the reactions conducted in the presence of excessive amount of olefin is complex **I**, which is a consequence of its low activity in the process of homometathesis of the olefins studied, in particular styrenes, in the conditions of the process. In the presence of **I** in the optimised conditions of the process, the selective products of cross-metathesis were obtained in the yields up to 96%. The reaction is accompanied by formation of trace amounts of the products of olefin homometathesis (up to 5% relative to the concentration of the product of the cross-metathesis). In the presence of **II** the reaction takes place with high yields but the products of the cross-metathesis are accompanied by considerable amounts of those of olefin homometathesis.

3.1. Mechanistic considerations

In order to get more information on the mechanism of the process, the equimolar reactions of Grubbs catalysts **I** and in a separate experiment of Grubbs catalyst **II** with ViSi(OSiMe₃)₂Ph were performed. The reactions were monitored by ¹H NMR spectroscopy and they resulted in formation of

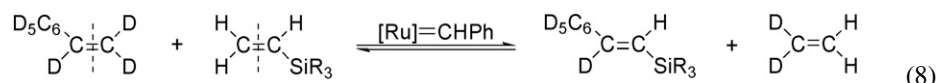
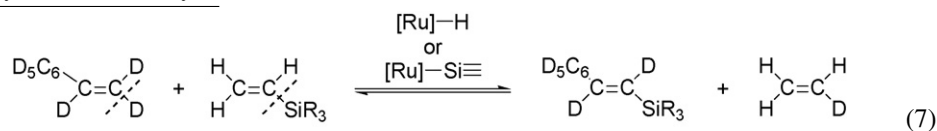
methylidene complex and styryl-substituted siloxane, which was consistent with the results of analogous studies performed for vinylsilanes (Eq. (6)) [12a].



L = PCy₃, IMesH₂

Present knowledge on the reactivity of Grubbs type ruthenium catalyst indicates the possibility of interconversions of alkylidene and hydride complexes [6,21]. Moreover, low to moderate yields of products were observed for methylsubstituted vinyls

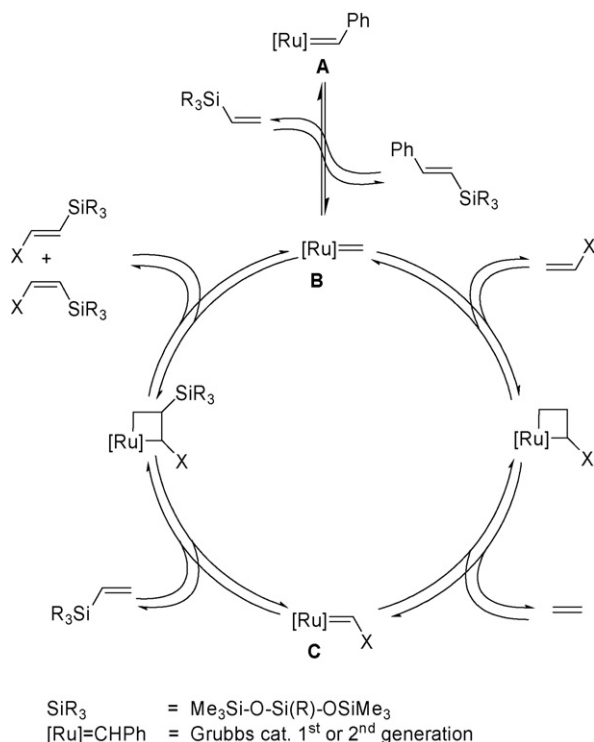
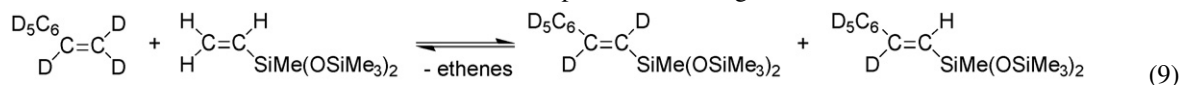
formation of silylstyrene-d₇ and ethylene-d is to be expected (Eq. (7)). In contrast, the carbene mechanism should afford silylstyrene-d₆ and ethylene-d₂ (Eq. (8)).



lanes, which was unexpected in the context of our earlier reports indicating the inactivity of vinylmethylsilanes in metathesis transformation [3,12a,20].

Therefore, in order to distinguish between the non-metallacarbene mechanism (characteristic of silylative coupling) catalysed by hydride complexes, and the carbene mechanism of olefin metathesis, the reactions of selected vinylsiloxanes with styrene-d₈ in the presence of **I** or **II** were investigated [5b]. In the case of the non-metallacarbene mechanism, the

Analysis of the products formed in the reactions of styrene-d₈ with H₂C=CHSi(OSiMe₃)₂Ph in the presence of **I** and with triphenyltrivinylcyclotrisiloxane in the presence of **II** revealed the exclusive formation of *E*-1-phenyl-2-(silyl)ethene-d₆, which strongly supports the carbene mechanism of the reaction. The results obtained for the reaction of styrene-d₈ with H₂C=CHSi(OSiMe₃)₂Me in the presence of **I** indicate the formation of *E*-1-phenyl-2-(silyl)ethene-d₆ (Eq. (9)) and its isotopomer containing seven deuterium atoms.



Scheme 1. Carbene mechanism of cross-metathesis of vinylsiloxane with olefins.

Apparently, in the case of this particular vinylsilane both mechanisms are responsible for the product formation.

On the basis of the results of the equimolar reactions and tests with deuterium labelled reagents the carbene mechanism of the reaction of vinyl-substituted siloxanes with olefins in the presence of Grubbs catalyst is postulated (Scheme 1).

The benzylidene complex **A** reacts with vinylsiloxane to form the metallacyclobutane complex **B** and silylstyrene [12a]. Compound **B** then reacts with the olefin to give the metallacyclobutane complex **C** and ethylene. By reaction of vinylsiloxane with **C** the cross-metathesis product is obtained. Only for linear vinylmethylsiloxanes the carbene mechanism is accompanied by the hydride one, characteristic of silylative coupling.

The crucial point in the metathetical reactivity of vinylsilanes and vinylsiloxanes is the introduction of the proper set of substituents at silicon. Two siloxy groups OSiR₃ bonded to vinyl-substituted silicon atom act as withdrawing substituents and form a skeleton of the potentially reactive molecule. In such a molecule the third substituent determines the reactivity. If it is a methyl group, the reaction has been demonstrated to give the expected products with low to moderate yield and proved to proceed according to the carbene and the hydride mechanisms. The difference in the reactivity between the phenyl and substituted phenyl rings demonstrates the activating role of the electron-withdrawing substituents. The presence of both methoxy and trifluoromethyl group in position 4 of the phenyl ring leads

to a substantial increase in the conversion and yields of the cross-metathesis products.

4. Conclusions

The cross-metathesis of vinyl-substituted linear and cyclic oligosiloxanes with styrenes, alkenes and selected allyl derivatives proceeds efficiently in the presence of Grubbs catalysts. Respective products have been obtained with high yields and selectivities. The reactions with styrenes give exclusively E-isomer. A pronounced effect of the properties of substituents at silicon on the metathesis reactivity of vinylsiloxanes has been demonstrated. The moderate yields were obtained when methyl-substituted vinylsiloxanes were used as substrates. On the other hand, the presence of electron-withdrawing substituent resulted in a very efficient transformation. From the point of view of the application in synthesis of organosilicon compounds, the cross-metathesis along with the silylative coupling make efficient and complementary synthetic routes leading to functionalized linear and cyclic oligo(siloxanes) of great practical importance. The two processes are complementary and the choice of the optimum method depends on the specific character of the reaction system.

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