Cross-metathesis of divinylsubstituted silanes and disiloxanes in the presence of Grubbs catalysts

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Abstract

Efficient cross-metathesis of divinylsilanes and divinyldisiloxanes, carrying different electron-withdrawing substituents at silicon, with selected olefins in the presence of the first and second generation Grubbs catalyst and Hoveyda–Grubbs catalyst is described. The reaction was proved to be a valuable method for synthesis of unsaturated organosilicon derivatives and a model for the study of synthesis of oligo- and polymeric products via ADMET copolymerization of divinylsubstituted silanes and disiloxanes with dienes.
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Keywords: Cross-metathesis; Grubbs catalyst; Alkylidene complexes; Divinylsilanes; Divinyldisiloxanes

1. Introduction

Olefin metathesis has become an important synthetic tool in organic and polymer chemistry. The family of ruthenium-based catalysts (e.g., **I**, **II** or **III**, Fig. 1), tolerant of normal organic and polymer processing conditions and preserving their catalytic properties in the presence of the majority of functional groups has allowed a great number of new applications [1].

Metathesis transformations have also found many applications in organosilicon chemistry [2]. A number of papers appeared on the metathesis reactivity of vinylsilanes as they constitute a class of unsaturated organosilicon compounds of prospective wide applicability in organic synthesis [3], especially in the fast developing palladium-catalyzed coupling of vinylsilanes with organic derivatives [4]. In vinylsilanes stereoelectronic properties of substituents at silicon strongly affect the reactivity of C=C double bond. We have previously shown that Grubbs type catalysts effectively catalyse the cross-metathesis (CM) of trialkoxy-, trisiloxy- [5], trichloro- and generally electron-withdrawing group substituted vinylsilanes [6] and vinylsilsesquioxanes [7] with styrenes, alkenes and numerous allyl derivatives. Recently, we have proposed a general scheme of vinylsilane reactivity in the presence of Grubbs catalyst [8]. Despite the fast development in the study of reactivity of unsaturated organosilicon compounds, there are still limited data available on the reactivity of divinylsubstituted silanes and disiloxanes. Wagener reported ADMET copolymerization of Vi_2SiMe_2 with 1,9-decadiene in the presence of a tungsten alkylidene complex [9]. We previously reported the reactivity of $ViSi(OEt)_2OSi(OEt)_2Vi$ in ADMET copolymerization with 1,9-decadiene [10a,10b] and divinylbenzene [10c] and with ROM/ADMET copolymerization with cyclooctadiene [10a] in the presence of Grubbs catalyst.

Now, we report on the effective transformations of divinylsubstituted silanes and disiloxanes with olefins in the presence of Grubbs type ruthenium alkylidene complexes (Fig. 1). The reaction offers an attractive synthetic route leading to diunsaturated organosilicon derivatives. We discuss advantages and drawbacks of cross-metathesis of vinylsilanes with olefins as a general synthetic method for the synthesis of vinyltrisubstituted silanes and finally search for a mechanistic scheme of catalysis of the reaction. On the other hand, this reaction is a model to study the activity of divinylsilanes and divinyldisiloxanes in effective ADMET (co)polymerization.

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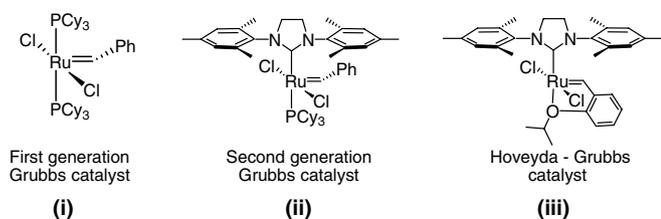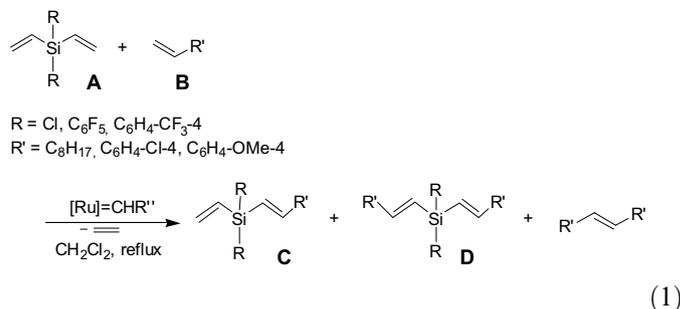 *E-mail address:* marcinb@amu.edu.pl (B. Marciniec).

Fig. 1. Grubbs type ruthenium alkylidene complexes.

$$\text{(1)}$$

2. Results and discussion

Recently, we revealed that only vinylsilanes bearing at least two electron-withdrawing group at silicon can efficiently undergo cross-metathesis with olefins [8], while vinylsilane homometathesis was restricted only to dichloroderivatives ViSiCl$_2$R where R = alkyl, aryl, OSiMe$_3$ [11]. Therefore, we tested a series of electron-withdrawing groups containing divinylsilanes (Fig. 2a) and divinyldisiloxanes (Fig. 2b) with respect of their reactivity in olefin metathesis.

Treatment of a mixture of divinylsilane and olefin in the presence of 5–10 mol% of catalyst **I**, **II** or **III** in boiling CH$_2$Cl$_2$ gives rise to evolution of ethene and formation of mono- and disubstituted vinylsilanes (Eq. (1)).
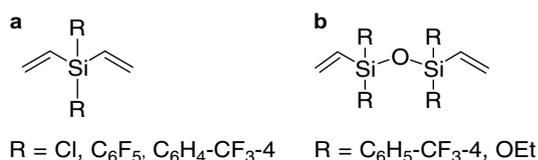

Fig. 2. Divinylsubstituted silanes and disiloxanes.

The reaction is accompanied by competitive olefin homometathesis. On the contrary, no vinylsilane homometathesis was observed. The results of the catalytic studies are summarized in Table 1.

When Vi$_2$SiCl$_2$ was used as a reaction partner very high activity and exclusive formation of disubstituted product **D** was observed in the presence of catalyst **II**. On the other hand, catalyst **I** underwent fast decomposition in the presence of Vi$_2$SiCl$_2$ [12]. Cross-metathesis of other divinylsilanes tested with olefins resulted in a formation of both mono- and a disubstituted product. Therefore, high efforts were undertaken to find conditions of more selective course of the reactions. It was found that 10-fold excess of styrene must be used to ensure high conversion and selectivity towards a disubstituted products. However, even then formation of the monosubstituted product could not be avoided. Interestingly, reactions of Vi$_2$Si(C$_6$H$_4$–CF$_3$–4)$_2$ and Vi$_2$Si(C$_6$F$_5$)$_2$ with 1-decene in the presence of catalyst **I** led to selective formation of monosubstituted product in moderate yields. Introduction of additional catalyst loading led to further improvement in the obtained yield to 63%. The Hoveyda–Grubbs catalyst exhibited similar behaviour to that of catalyst **II** in the reactions tested. 1-Decene

Table 1
Cross-metathesis of divinylsilanes with olefins

Divinylsilane R=	Olefin R′=	Cat.	Reaction conditions[a]	Conversion of A (%)	Yield of C (%)	C E/Z	Yield of D (%)	D[b] E, E/E, Z
Cl	C$_8$H$_{17}$	**II**	1:4/1/5	100	0	25/1	99	15/1
	C$_6$H$_4$–Cl-4	**II**	1:4/3/5	100	0	E	98	E
C$_6$H$_4$–CF$_3$–4	C$_8$H$_{17}$	**I**	1:4/5/5	42	42, 63[c], 50[c,d]	25/1	0	E
	C$_8$H$_{17}$	**II**	1:4/3/5	95	38	25/1	57	15/1
	C$_8$H$_{17}$	**II**	1:10/3/5	100	4	25/1	96, 75[d]	15/1
	C$_8$H$_{17}$	**III**	1:10/3/5	90	32	25/1	56	15/1
	C$_6$H$_4$–Cl-4	**I**	1:4/5/5	10	10	E	0	–
	C$_6$H$_4$–Cl-4	**II**	1:4/5/5	48	34	E	14	E
	C$_6$H$_4$–Cl-4	**II**	1:10/5/10	80	15	E	64	E
	C$_6$H$_4$–Cl-4	**III**	1:10/3/10	98	2	E	96	E
	C$_6$H$_4$–OMe-4	**II**	1:10/5/10	88	16	E	70	E
C$_6$F$_5$	C$_8$H$_{17}$	**I**	1:4/5/5	38	38	25/1	0	E
	C$_8$H$_{17}$	**II**	1:10/3/5	100	2	25/1	98, 78[d]	15/1
	C$_6$H$_4$–Cl-4	**II**	1:10/5/10	88	15	E	72	E
	C$_6$H$_4$–Cl-4	**III**	1:10/3/10	99	1	E	98	E
	C$_6$H$_4$–OMe-4	**II**	1:10/5/10	92	18	E	74	E

Reaction conditions: CH$_2$Cl$_2$, reflux.
[a] [ViSi]:[C=C]/time (h)/catalyst conc. (mol%).
[b] Third possible isomer Z, Z was not observed.
[c] Another loadings of catalyst **I** was added after 5 h and reaction was run for next 3 h.
[d] Isolated yield.

reacted more readily than styrenes in cross-metathesis with divinylsilanes tested. The reactions with styrenes led to selective formation of *E*-isomer. The cross-metathesis of vinylsilanes with 1-decene gave a mixture of *E* and *Z* isomers, with *E* isomer in predominant amounts. The reaction permits synthesis of substituted silylethenes with moderate to high yields, under mild reaction conditions.

The cross-metathesis of divinylsubstituted disiloxanes with olefins proceeds in the presence of 5–10 mol% of catalyst **I**, **II** or **III** in boiling CH_2Cl_2 producing a mixture of mono- and disubstituted vinylsilanes and ethene (Eq. (2)). Also in this case reaction is accompanied by competitive olefin homometathesis. The results of the catalytic studies are summarized in Table 2.

$$R = C_6H_5\text{-}CF_3\text{-}4, OEt$$
$$R' = C_8H_{17}, C_6H_4\text{-}Cl\text{-}4, C_6H_4\text{-}OMe\text{-}4$$

(2)
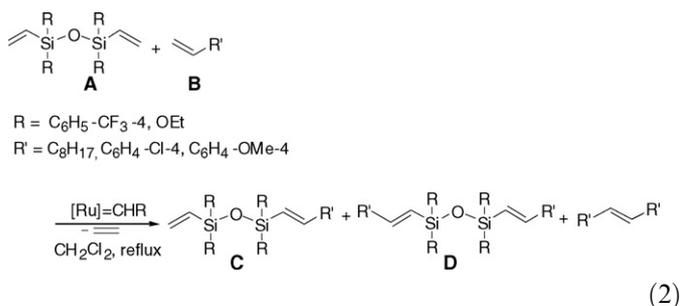
Divinyltetraphenyldisiloxane exhibited almost no reactivity. Only traces of monosubstituted product were found, irrespective of the olefin used. Introduction of the electron-withdrawing group to phenyl ring resulted in a drastic change in reactivity. In most cases nearly quantitative conversion of $ViSi(C_6H_4–CF_3–4)_2OSi(C_6H_4–CF_3–4)_2Vi$ was observed [13]. High conversion of divinyltetraethoxydisiloxane observed for cross-metathesis agrees well with its previously reported activity in ADMET copolymerization [10].

To achieve a high conversion of all divinyldisiloxanes used and a satisfactory selectivity of disubstituted products olefins must be taken at a 10-fold excess. Generally, high stereoselectivity of cross-metathesis was observed. The reactions led to selective formation of *E*-isomer (when styrenes were used as olefins) or a mixture of isomers with high excess of the *E* compound (when 1-decene was used).

2.1. Labelling studies

There are two processes leading to formation of silylolefins and ethene via catalytic transformation of vinylsilanes with olefins, i.e., silylative coupling (Eq. (3)) and cross-metathesis (Eq. (4)) [2]. Both reactions proceed via different mechanisms and are catalyzed by different reactive species.

(3)

(4)
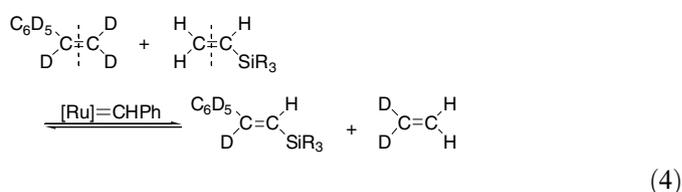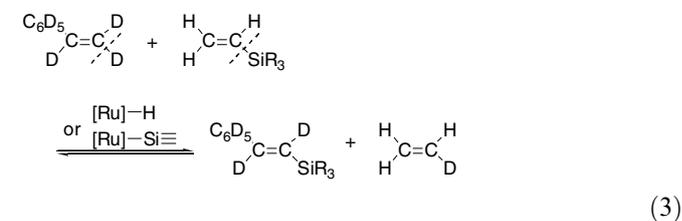
Therefore, in order to distinguish between the non-carbene mechanism (Eq. (3)) and the metallacarbene mechanism (Eq. (4)), divinylbis(pentafluorophenyl)silane and 1,3-divinyl-1,1,3,3-tetraethoxydisiloxane were tested in the reac-

Table 2
Cross-metathesis of divinyldisiloxanes with olefins

Disiloxane R=	Olefin R'=	Cat.	Reaction conditions[a]	Conversion of **B** (%)	Yield of **C** (%)	**C** *E/Z*	Yield of **D** (%)	**D**[b] *E, E/E, Z*
Ph	C_8H_{17}	**II**	1:4/3/5	12	12	*E*	0	–
	$C_6H_5–Cl–4$	**II**	1:4/5/5	4	4	*E*	0	–
$C_6H_4–CF_3–4$	C_8H_{17}	**I**	1:4/3/5	95	51	25/1	44	15/1
	C_8H_{17}	**I**	1:10/3/5	98	32	25/1	66	15/1
	C_8H_{17}	**II**	1:10/3/5	100	8	25/1	92	15/1
	C_8H_{17}	**III**	1:10/3/5	100	10	25/1	88	15/1
	$C_6H_4–Cl–4$	**II**	1:10/5/10	98	25	*E*	73	*E, E*
	$C_6H_4–Cl–4$	**III**	1:10/5 /10	99	12	*E*	87, 75[c]	*E, E*
	$C_6H_4–OMe–4$	**II**	1:10/5 /10	98	20	*E*	78	*E, E*
OEt	C_8H_{17}	**I**	1:4/5/5	63	54	*E*	5	*E, E*
	$C_6H_4–Cl–4$	**I**	1:4/24/5	99	10	*E*	86	*E, E*
	$C_6H_4–Cl–4$	**II**	1:10/3/5	99	2	*E*	95	*E, E*
	$C_6H_4–Cl–4$	**III**	1:10/5/5	88	20	*E*	66	*E, E*

Reaction conditions: CH_2Cl_2, reflux.
[a] [ViSi]:[C=C]/time (h)/catalyst conc. [mol%].
[b] Third possible isomer *Z, Z* was not observed.
[c] Isolated yield.

tions with styrene-d_8 in the presence of **II**. In the case of the non-metallacarbene mechanism, the formation of styrylsilane-d_7, bis(styryl)silane-d_{14} and ethylene-d_1 is to be expected (Eq. (5), in contrast, the carbene mechanism should afford styrylsilane-d_6, bis(styryl)silane-d_{12} and ethylene-d_2 (Eq. (6)).

$$(5)$$

$$(6)$$

Analysis of the products formed revealed formation of styrylsilane-d_6 and bis(styryl)silane-d_{12} which strongly supports the carbene mechanism of the reaction presented previously for vinylsubstituted silicon compounds [5a,8].

3. Experimental

3.1. General

All manipulations were carried out under dry argon using standard Schlenk techniques. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Gemini 300 at 300 and 75 MHz, respectively. GC-MS analyses were made on Varian Saturn 2100T (DB-1, 30 m capillary column). Complexes **II** and **III**, decane, dodecane, CH_2Cl_2 and C_6D_6, were purchased from Aldrich. Catalyst **I** was prepared according to the literature procedure [14].

3.2. Synthesis of divinylbis[4-(trifluoromethyl)phenyl]silane

An oven dried 100 mL flask equipped with a condenser with a bubbler and a magnetic stirring bar was charged under argon with 30 mL of dry THF, 0.52 g (2.1×10^{-2} mol) of magnesium shavings. Then the solution of Br–C_6H_4–CF_3–4 (2.1×10^{-2} mol) in 20 mL of THF was added dropwise to the reacting mixture. The mixture was refluxed for 3 h and cooled down to room temperature. An oven dried 100 mL flask equipped with a condenser with a bubbler and a magnetic stirring bar was charged under argon with 20 mL of dry THF, 3 g (2×10^{-2} mol) of divinyldichlorosilane. Then the solution of BrMg–C_6H_4–CF_3–4 in THF was added dropwise to the mixture. The reacting mixture was stirred for 5 h and the solvent was distilled off. Then 100 mL of pentane was added to precipitate magnesium salt. The salt was filtered off and the product was obtained by vacuum distillation (collected fraction 145–148 °C/1 mm Hg).

The product of 97% purity was obtained with the yield of 75%.

Spectroscopic data: ^{1}H NMR (C_6D_6, δ, ppm): 5.67 (dd, 2H, $J_{HH} = 19.8$, 3.9 Hz, =CH–Si), 6.10 (dd, 2H, $J_{HH} = 14.4$, 3.9 Hz, =CH_2), 6.25 (dd, 2H, $J_{HH} = 19.8$, 14.4 Hz, =CH_2), 7.31–7.40 (m, 8H, C_6H_4–CF_3–4); ^{13}C NMR (C_6D_6, δ, ppm): 124.3 (q, $J_{CF} = 272.1$ Hz, CF_3), 124.2–124.3 (m, $\underline{C}H$–C_i–CF_3), 131.7 (=CH–Si), 135.5 (s, $\underline{C}H$–CH–C_i–CF_3), 137.3 (=CH_2), 138.1 (C_i–Si), (C_i–CF_3) not found; ^{19}F NMR (C_6D_6, δ, ppm): −61.95 (s, CF_3); MS: m/z (rel. intensity): 47 (29), 50 (27), 51 (23), 53 (28), 57 (21), 62 (15), 63 (27), 69 (25), 75 (31), 77 (25), 81 (15), 87 (16), 89 (15), 95 (13), 103 (16), 107 (28), 108 (15), 115 (18), 125 (21), 126 (27), 127 (72), 133 (83), 134 (55), 151 (18), 153 (91), 154 (14), 165 (15), 219 (26), 226 (25), 227 (23), 173 (14), 175 (15), 183 (18), 193 (18), 201 (21), 219 (26), 226 (25), 227 (23), 252 (19), 271 (18), 319 (56), 320 (18), 344 (25), 345 (20), 353 (100), 354 (30), 372 (13).

$Vi_2Si(C_6F_5)_2$ was synthesized according to similar procedure to that presented above.

Isolated yield 80%; ^{1}H NMR (C_6D_6, δ, ppm): 5.69 (dd, 2H, $J_{HH} = 20.2$, 2.8 Hz, =CH_2), 6.01 (dd, 2H, $J_{HH} = 14.2$, 2.8 Hz, =CH_2), 6.45 (dd, 2H, $J_{HH} = 20.2$, 14.2 Hz, =CH–Si); ^{13}C NMR (C_6D_6, δ, ppm): 129.7 (=CH–Si), 137.8 (=CH_2), 137.5 (dm, $J_{CF} = 248.8$ Hz, C_6F_5), 142.9 (dm, $J_{CF} = 256.2$ Hz, C_6F_5), 149.3 (dm, $J_{CF} = 244.8$ Hz, C_6F_5); ^{19}F NMR (C_6D_6, δ, ppm): −159.44 (m, *meta*), −147.56 (tt, $J_{FF} = 20.6$, 4.2 Hz, *para*), −125.14 (m, *ortho*); MS: m/z (rel. intensity): 47 (44), 48 (100), 62 (19), 67 (28), 75 (29), 79 (68), 80 (17), 85 (26), 86 (29), 87 (62), 88 (20), 92 (18), 93 (60), 98 (31), 99 (33), 110 (15), 111 (53), 112 (18), 117 (88), 129 (29), 133 (32), 156 (21), 164 (15), 182 (32), 183 (46), 248 (49), 258 (17), 322 (10), 416 (2, M$^+$).

3.3. Synthesis of 1,3-divinyl-1,1,3,3-tetra-[4-(trifluoromethyl)phenyl]disiloxane

An oven dried 100 mL flask equipped with a condenser with a bubbler and a magnetic stirring bar was charged under argon with 30 mL of dry THF, 1.56 g (6.4×10^{-2} mol) of magnesium shavings. Then the solution of 14.46 g (6.4×10^{-2} mol) Br–C_6H_4–CF_3–4 in 20 mL of THF was added dropwise to the reacting mixture. The mixture was refluxed for 3 h and cooled down to room temperature. An oven dried 100 mL flask equipped with a condenser with a bubbler and a magnetic stirring bar was charged under argon with 20 mL of dry THF, 5.19 g (3.2×10^{-2} mol) of divinyldichlorosilane. Then the solution of BrMg–C_6H_4–CF_3–4 in THF was added dropwise to the mixture. The reacting mixture was stirred for 5 h and the solvent was distilled off. Then 100 mL of pentane was added to precipitate magnesium salt. The salt was filtered off and the product

(H_2C=CH–Si(C_6H_4–CF_3–4)$_2$Cl) was obtained by vacuum distillation (collected fraction: 140–144 °C/1 mm Hg). In the next step a 100 mL flask equipped with a magnetic stirring bar was charged with 20 mL of pentane, 2.75 g (7.2×10^{-3} mol) of H_2C=CH–Si(C_6H_4–CF_3–4)$_2$Cl, 3.0 g (0.17 mol) of distilled water. The mixture was stirred for 2 days at room temperature. Then the mixture was filtered on celite. After evaporation of solvent and water (under vacuum) product of 97% purity was obtained with a total yield of 68%.

Spectroscopic data: ^{1}H NMR (C_6D_6, δ, ppm): 5.71 (dd, 2H, J_{HH} = 20.1, 3.6 Hz, =CH–Si), 6.03 (dd, 2H, J_{HH} = 15.0, 3.6 Hz, =CH_2), 6.22 (dd, 2H, J_{HH} = 20.1, 15.0 Hz, =CH_2), 7.33–7.40 (m, 18H, C_6H_4–CF_3–4); ^{13}C NMR (C_6D_6, δ, ppm): 124.4 (q, J_{CF} = 271.2 Hz, CF_3), 126.0 (q, J_{CF} = 24.7 Hz, $\underline{C}H$–C$_i$–CF_3), 132.7 (q, J_{CF} = 37.5 Hz, $\underline{C}_i$–CF_3), 133.2 (CH_2), 135.2 ($\underline{C}H$–CH–C$_i$–CF_3), 138.2 (=CH–Si), 138.9 (C$_i$–Si); ^{19}F NMR (C_6D_6, δ, ppm): −62.04 (s, CF_3); MS: m/z (rel. intensity): 50 (11), 75 (13), 103 (11), 115 (16), 125 (12), 126 (18), 127 (45), 133 (21), 134 (14), 153 (100), 154 (13), 183 (11), 201 (10), 271 (23).

3.4. Catalytic tests

An oven dried 4 mL Schlenk flask with side neck closed with a septum, equipped with a condenser and a magnetic stirring bar was charged under argon with 3 mL of CH_2Cl_2, divinylsilane (5.9×10^{-5} mol), 1-decene or styrene (5.9×10^{-4} mol) and 20 μL of decane or dodecane (internal standard). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 43 °C). Then 0.0025 g (2.94×10^{-6} mol) of ruthenium benzylidene complex **II** was added under argon. A gentle flow of argon was applied. The reaction was followed by gas chromatography.

3.5. Procedure for the synthesis of dialkenylsilanes and dialkenyldisiloxanes

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 CH_2Cl_2, vinylsilane (2.4×10^{-4} mol) and olefin (2.4×10^{-3} mol). The reaction mixture was stirred and heated in an oil bath (ca. 45 °C) to maintain a gentle reflux. Then 0.01 g (1.2×10^{-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 course of the reaction was followed by gas chromatography. After a given reaction time dichloromethane was distilled off and the catalyst was separated from the mixture using small silicagel column. Then the solvent and homometathesis product of the olefin was distilled off and the pure product was obtained.

Spectroscopic data of selected products:
Si(C_6H_4–CF_3–4)$_2$(CH=CHC$_8$H$_{17}$)$_2$, isolated yield 75%; ^{1}H NMR (C_6D_6, δ, ppm): 0.88–0.92 (m, 6H, CH_3), 1.27–

1.40 (m, 24H, CH_2), 2.14–2.21 (m, 4H, =CH–C$\underline{H}_2$), 5.99 (dt, 2H, J_{HH} = 18.7, 1.5 Hz, =CH–Si), 6.28 (dt, 2H, J_{HH} = 18.7, 6.2 Hz, =C$\underline{H}$–CH_2), 7.50 (dd, 8H, J_{HH} = 18.7, 7.9 Hz, C_6H_4–CF_3–4); ^{13}C NMR (C_6D_6, δ, ppm): 15.0 (CH_3), 23.7, 29.5, 30.24, 30.35, 30.46, 32.88 (CH_2), 38.05 (=CH–$\underline{C}H_2$), 123.3 (=CH–Si), 125.1–125.3 (m, $\underline{C}H$–C$_i$–CF_3), 136.5 (s, $\underline{C}H$–CH–C$_i$–CF_3), 125.3 (q, J_{CF} = 271.6 Hz, CF_3), 132.2 (q, J_{CF} = 32.0, $\underline{C}_i$–CF_3), 141.0 (C$_i$–Si), 155.01 (=$\underline{C}H$–CH_2); ^{19}F NMR (C_6D_6, δ, ppm): −61.8 (s, CF_3); MS: m/z (rel. intensity): 55 (52), 57 (50), 67 (66), 69 (28), 79 (27), 81 (64), 82 (20), 83 (24), 95 (43), 97 (22), 109 (32), 115 (22), 122 (31), 123 (23), 127 (99), 128 (27), 140 (35), 147 (20), 153 (53), 165 (42), 173 (26), 179 (21), 191 (21), 265 (23), 276 (23), 319 (100), 320 (31), 310 (23), 371 (29), 372 (33), 457 (35), 483 (23), 577 (21).

Si(C_6F_5)$_2$(CH=CHC$_8$H$_{17}$)$_2$, isolated yield 78%; ^{1}H NMR (C_6D_6, δ, ppm): 0.86–0.92 (m, 6H, CH_2–C$\underline{H}_3$), 1.26 (s, 24H, CH_2), 2.13–2.20 (m, 4H, =CH–C$\underline{H}_2$), 6.21 (d of broad signals 2H, J_{HH} = 18.6 Hz, =C$\underline{H}$–CH_2), 6.41 (dt, 2H, J_{HH} = 18.6, 6.1 Hz, =CH–Si); ^{13}C NMR (C_6D_6, δ, ppm): 14.7 (CH_3), 23.5, 29.0, 29.9, 30.1, 30.2, 32.6 (CH_2), 37.5 (=CH–$\underline{C}H_2$), 121.18 (=CH–Si), 138.3 (dm, J_{CF} = 256.8 Hz, C_6F_5), 143.4 (dm, J_{CF} = 255.6 Hz, C_6F_5), 149.7 (dm, J_{CF} = 248.8 Hz, C_6F_5), 155.4 (=$\underline{C}H$–CH_2); ^{19}F NMR (C_6D_6, δ, ppm): −159.71–(−159.49) (m, *meta*), −148.16 (tt, J_{FF} = 20.6, 3.9 Hz, *para*), −125.28 (dd, J_{FF} = 11.8, 3.4 Hz, *ortho*); MS: m/z (rel. intensity): 53 (13), 55 (77), 57 (65), 67 (100), 69 (38), 79 (26), 81 (92), 82 (26), 83 (38), 95 (64), 96 (24), 97 (31), 109 (39), 111 (17), 123 (23), 137 (15), 151 (23), 259 (15), 277 (45), 278 (16), 431 (15).

[(C_6H_4–OMe–4)HC=CH]Si(C_6H_4–CF_3–4)$_2$OSi(C_6H_4–CF_3–4)$_2$[CH=CH(C_6H_4–OMe–4)], isolated yield 75%; ^{1}H NMR (C_6D_6, δ, ppm): 3.30 (s, 6H, OMe), 6.56 (d, 2H, J_{HH} = 19.2 Hz, =CH–Si), 7.20 (d, 2H, partially hidden, =C$\underline{H}$–C_6H_4–OMe), 7.20–7.28 (m, 8H, $C_6\underline{H}_4$–OMe), 7.48 (pseudo d, 8H, CH–C$_i$–CF_3), 7.67 (pseudo d, 8H, CH–C$_i$–Si); ^{13}C NMR (C_6D_6, δ, ppm): 54.9 (OMe), 114.5 ($\underline{C}H$–C$_i$–OMe), 118.2 (=CH–Si), 123.8 (q, J_{CF} = 285.2 Hz, CF_3), 124.9–125.1 (m, $\underline{C}H$–C$_i$–CF_3), 128.7 ($\underline{C}H$–CH–C$_i$–OMe), 130.1 ($\underline{C}_i$–CH=), 132.6 (q, J_{CF} = 32.0 Hz, $\underline{C}_i$–CF_3), 135.4 ($\underline{C}H$–CH–C$_i$–CF_3), 150.4 (C$_i$–Si), 161.4 (=$\underline{C}H$–C_6H_4–OMe), ^{19}F NMR (C_6D_6, δ, ppm): −61.95 (s, CF_3).

4. Conclusions

A variety of divinylsilanes and divinyldisiloxanes have been tested in cross-metathesis in the presence of Grubbs catalysts. Stereoselective course of cross-metathesis of vinylsilanes with styrenes and 1-alkenes was indicated. Under the optimum conditions the products required were synthesized with moderate to high yields. The reaction was proved to be a valuable method for the synthesis of unsaturated organosilicon derivatives and a model for the study of synthesis of oligo- and polymeric products via ADMET copolymerization of divinylsubstituted silanes and disiloxanes with dienes.

Acknowledgements

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