Metathesis of Vinyl-Substituted Silicon Compounds with Dienes and Cycloalkenes

Cezary Pietraszuk, Bogdan Marciniec*, Magdalena Jankowska

Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland
Fax: (+48)-61-8291508, e-mail: marcinb@main.amu.edu.pl

Received: March 6, 2002; Accepted: May 10, 2002

Abstract: Metathesis of 1,9-decadiene and cyclooctene with trialkoxy- and trisiloxy-substituted vinylsilanes in the presence of Grubbs catalyst leads to a formation of 1-(silyl)deca-1,9-dienes and 1,10-bis(silyl)deca-1,9-dienes. Under optimised conditions, the reaction is a convenient method for synthesis of disubstituted dienes and a model process for the development of syntheses of silylene(siloxylene)-vinylene-alkenylene copolymers *via* the metathesis transformations of divinyl-substituted silicon compounds with terminal dienes and cycloalkenes.

Keywords: carbene ligands; cycloalkenes; dienes; Grubbs catalyst; metathesis; ruthenium; vinylsilanes

Introduction

Tremendous progress in catalyst design has established metathesis as a significant tool for organic synthesis and polymer chemistry.[1] Extremely impressive developments have been observed for the reactions involving functionalised olefins.[1,2]

Silylolefins, particularly vinyl- and allylsilanes, which have become common silyl reagents used in regio- and stereoselective organic synthesis,[3] have also been tested in metathesis.

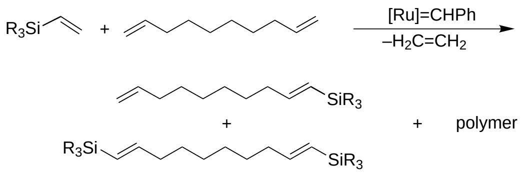
Unlike alkenyl-substituted silanes (e.g., allylsilanes), which can be effectively transformed in homo- and cross-metathesis reactions in the presence of molybdenum and ruthenium carbene complexes[4] and ADMET (co)polymerisation in the presence of molybdenum catalyst,[5] the generation and transformation of vinylsilanes through the use of the cross-metathesis reaction has met with limited success.[6] Only recently was a well-defined functional group-tolerant molybdenum catalyst reported to be active in the ring opening cross-metathesis (AROM/CM) of norbornene,[7] RCM of acyclic silyl ether dienes,[8] and cross-metathesis of vinyl-substituted silsesquioxanes with alkenes.[9] We have recently reported a highly efficient cross-metathesis of trialkoxy- and trisiloxy-substituted vinylsilanes with styrene,[10] *p*-substituted styrenes, l-alkenes, and allyl derivatives[11], particularly allyl alkyl ethers[12] and esters[13], which demonstrates a new opportunity for the common use of the olefin cross-metathesis in the synthesis of unsaturated organosilicon compounds. Divinyl derivatives of organosilicon compounds, which are inert to produce ADMET self-polymerisation, were found to be active in copolymerisation with 1,9-decadiene in the presence of a Schrock-type tungsten catalyst.[5]

In this paper we report on metathetical transformations of vinylsilanes and vinylsiloxanes in reaction with dienes and cycloolefins in the presence of Grubbs-type ruthenium carbene complexes as a method for the synthesis of α,ω-bis(silyl)dienes. The fundamental aim of the study was to estimate the possibility to apply the ruthenium carbene complexes-catalysed metathetic transformation of divinyl-substituted silanes (or siloxanes) with diene (or cycloalkene) for the synthesis of silylene(siloxylene)-vinylene-alkenylene copolymers.

Results and Discussion

The cross-metathesis reactions of trisubstituted vinylsilanes and vinylsiloxane with a variety of terminal dienes were studied. No reactions were found with 1,4-pentadiene and 1,5-hexadiene. In the case of 1,7-octadiene a high diene conversion was detected but the reaction led to selective formation of cyclohexene even when a 10-fold vinylsilane excess was used. Obviously, the ring closing metathesis of 1,7-octadiene is much faster than the cross-metathesis with vinylsilane.

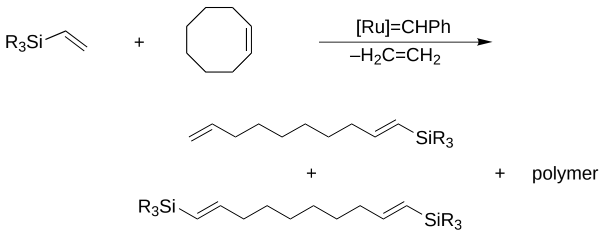
When a mixture containing vinylsilane (vinylsiloxane) and 1,9-decadiene was heated in the presence of Grubbs catalyst, the formation of ethylene was observed. Detailed analysis of the reaction mixture reveals the formation of mono- and bis(silyl)dienes accompanied by the polymeric product. On the basis of analytical data, the following reaction scheme can be proposed (Equation 1).



(1)

The results are collected in Table 1.

Similar products were observed in the Grubbs complex (**I**)-catalysed reaction of vinylsilane (vinylsiloxane) with cyclooctene. The products imply that tandem ring opening metathesis/cross-metathesis took place in the system. The reaction can be illustrated by the following scheme (Equation 2).



(2)

The results obtained are collected in Table 2.

No products were observed when cyclopentene, cyclohexene, cyclododecene or indene were used as reagents.

In the first stage of both reactions, a formation of mono(silyl)-substituted dienes is observed. Monosubstituted products were not isolated, but their presence was confirmed by GC-MS analysis. Continuation of the process led to conversion of the monosilyl derivative and formation of the bis(silyl)-subsituted diene. Removal of ethylene from the system, achieved as a consequence of running the reaction at the boiling point of the reaction mixture (~40 °C) and under a delicate argon flow was observed to favour not only effective cometathesis but also ADMET polymerisation.

Both processes (i.e., the reaction with 1,9-decadiene and that with cyclooctene) were carried out in an excess of vinylsilane in order to reduce the formation of the polymeric product via ADMET polymerisation or ROMP of the cycloolefin, respectively. The use of a higher excess of vinylsilane (10-fold and more) does not result in a significant increase of selectivity. The use of $Cl_2(PCy_3)(IMesH_2)Ru(=CHPh)$ as an initiator did not lead to higher yields of (silyl)-substituted products, but on the contrary, it leads to an increase in the yields of the polymeric products. The conditions proposed ensured a 100% diene conversion at the possibly lowest contribution of the undesirable process of metathetical polymerisation.

For vinylsilanes containing at least one methyl substituent no metathesis was observed either with 1,9-decadiene or with cyclooctene. Presumably decomposition of Grubbs catalyst in the presence of vinylmethylsilanes occurs as reported earlier.[10,14]

^1H and ^{13}C NMR spectra of the polymeric by-products confirm the formation of polyoctenamers.[15] No silyl

Table 1. Cross-metathesis of vinylsilanes with 1,9-decadiene.[a]

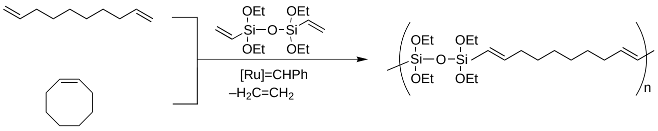
SiR_3	Reaction time [h]	Conv. of diene [%]	Yield of monosubst. [%]	Yield of disubst. [%]	Yield of polymer [%]
$Si(OMe)_3$	0.17	84	60	11	13
	2	100	7	73	20
$Si(OEt)_3$	0.17	88	50	18	20
	2	100	11	58	31
$Si(OSiMe_3)_3$	0.17	83	40	13	30
	2	100	15	45	40

[a] Reaction conditions: open system, CH_2Cl_2, reflux, $[H_2C{=}CHSiR_3]:[\text{diene}]:[Cl_2(PCy_3)_2Ru(=CHPh)] = 6:1:5 \times 10^{-2}$.

Table 2. Ring opening metathesis/cross-metathesis of cyclooctene with vinylsilanes.[a]

SiR_3	Reaction time [h]	Conv. of Cyclooctene [%]	Yield of monosubst. [%]	Yield of disubst. [%]	Yield of polymer [%]
$Si(OMe)_3$	0.17	96	43	35	18
	2	100	8	72	20
$Si(OEt)_3$	0.17	81	47	8	26
	2	100	10	60	30
$Si(OSiMe_3)_3$	0.17	94	29	35	30
	2	100	2	60	38

[a] Reaction conditions: open system, CH_2Cl_2, reflux, $[H_2C{=}CHSiR_3]:[\text{cyclooctene}]:[Cl_2(PCy_3)_2Ru(=CHPh)] = 3:1:5 \times 10^{-2}$.



Scheme 1.

groups were detected, although their presence at a small concentration cannot be excluded.

E,E-1,10-Bis(silyl)-substituted dienes were isolated with medium yields (40–60%) and characterised spectroscopically.

High efficiency of the cross-metathesis of 1,9-decadiene with vinylsilanes indicates the possibility of an effective run of the ADMET copolymerisation of divinylsilanes with diene. This supposition was fully confirmed by the effective ADMET copolymerisation of divinyltetraethoxydisiloxane with 1,9-decadiene leading, in the presence of Grubbs initiator, to the formation of a siloxylene-vinylene-alkenylene polymer.[16] Similarly, tandem ROM/CM of divinyltetraethoxydisiloxane with cyclooctene led to the formation of silicon-containing polymeric material. Analytical data are collected in the experimental section. Both reactions represent a general method for the synthesis of siloxylene-vinylene-alkenylene polymers and oligomers (Scheme 1). In recent years, considerable interest has been given to the study of similar silicon-containing polymers due to their mechanical, thermal, electronic and optical properties.[17]

Conclusions

Metathesis of 1,9-decadiene and cyclooctene with trialkoxy and trisiloxy-substituted vinylsilanes in the presence of Grubbs catalyst carried out in the optimised conditions leads to the formation of 1,10-bis(silyl)-deca-1,9-dienes with relatively high yield. Similar processes performed with divinyl-substituted siloxane lead to the formation of silicon-containing polymers and have been proved to be a convenient method for the synthesis of silylene(siloxylene)-vinylene-alkenylene copolymers.

Experimental Section

General Methods and Chemicals

All syntheses (with isolation procedures) and catalytic tests were carried out under argon. ^{1}H and ^{13}C NMR spectra of isolated products were recorded in C_6D_6 on a Varian Gemini 300 VT spectrometer (300 and 75 MHz, respectively). Mass spectra of the products and substrates were obtained by GC-MS analysis (Varian Saturn 2100T, equipped with a DB-5, 30 m capillary column and ion trap detector). GC analyses were performed on a Hewlett-Packard HP 5890 Series II with a 30 m Megabore HP-1 column and TCD. Gel permeation chromatography (GPC) was performed using a Gilson HPLC system equipped with UV absorbance detector and RI detector. All molecular weights are relative to polystyrene standards. Polymer samples were dissolved in HPLC grade THF (approximately 0.1% w/v) and filtered before injection (a volume of 20–40 μL). The GPC was equipped with a phenogel column 300 × 7.80 mm, 50, 500, 10^4 Å. HPLC grade THF was used as the eluent at a constant flow of 0.7 mL/min. The chemicals were obtained from the following sources: 1,9-decadiene, vinyltriethoxysilane, methylene chloride from Fluka, dodecane from Aldrich, vinyltris(trimethylsiloxy)silane from ABCR, CD_2Cl_2 from Dr. Glaser A.G., $Cl_2(PCy_3)_2Ru(=CHPh)$ (**I**) and $Cl_2(PCy_3)$(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)Ru(=CHPh) were purchased from Strem Chemicals, vinyltrimethoxylsilane was prepared by standard procedures.[18] Prior to use all reagents and solvents were dried and distilled over CaH_2 in argon. CH_2Cl_2 was additionally passed through a column with alumina. Reagents were degassed by repeated freeze-pump-thaw cycles.

Representative Procedure for Catalytic Reaction

An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under argon with CH_2Cl_2 (5 mL), dodecane (internal standard) (0.015 mL), the vinylsilane (vinylsiloxane) (4.78×10^{-3} mol) and 1,9-decadiene (7.97×10^{-4} mol). The reaction mixture was stirred and heated to maintain a gentle reflux. Then ruthenium benzylidene complex **I** (3.98×10^{-5} mol) was added and the progress of the reaction was monitored by GC or GC-MS. In the reaction with cyclooctene the following amounts of chemicals were used $ViSiR_3$ (4.78×10^{-3} mol), cyclooctene (1.59×10^{-3} mol), complex **I** (7.97×10^{-5} mol).

The conversion of the olefin (diene) was calculated using the internal standard method. Polymer content was calculated on the basis of ^{1}H NMR spectra.

Synthetic Procedures

An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under argon with CH_2Cl_2 (20 mL), the $ViSiR_3$ (1.91×10^{-2} mol), and 1,9-decadiene (3.18×10^{-3} mol). The reaction mixture was stirred and heated to maintain a gentle reflux. Then ruthenium benzylidene complex **I** (1.59×10^{-4} mol) was added and the reaction was carried out for 3–6 h.

In the reaction with cyclooctene the following amounts of chemicals were used $ViSiR_3$ (1.91×10^{-2} mol), cyclooctene (6.37×10^{-3} mol), and complex **I** (3.18×10^{-4} mol).

When the diene was fully consumed, $H_2C{=}CHOEt$ (3 equivalents relating to initiator used) was added and the mixture was heated for another 15 min.

Purification Procedure for Tris(trimethylsiloxy)silyl Derivative

CH_2Cl_2 was evacuated in vacuum, the catalyst was removed by passing the reaction mixture through a column with silica using pentane as an eluent, the eluted solution was concentrated and polymeric products were precipitated by dropping the mixture into ice-cold methanol. Then the remaining vinylsiloxane and monosilyl derivative were distilled off in high vacuum. This procedure gives $(Me_3SiO)_3SiCH{=}CH(CH_2)_6CH{=}CHSi(OSiMe_3)_3$ of 98% purity. Isolated yields: 40% for the reaction with 1,9-decadiene and 54% for the reaction with cyclooctene.

Purification Procedure for Trialkoxysilyl Derivatives

The catalyst was removed by adding 10-fold excess of CH_3CN (relating to initiator used), stirring overnight, removing CH_2Cl_2, and precipitating the Ru complex with ice-cold pentane. Then polymer was removed as described above. The reaction mixture (still containing some amount of Ru complexes) was distilled in high vacuum. In all cases the *E*,*E*-isomers were isolated. This procedure gives $(MeO)_3SiCH{=}CH(CH_2)_6CH{=}CHSi(OMe)_3$ of 97% purity (^{1}H NMR). Isolated yields: 60% in the reaction with 1,9-decadiene, 61% in the reaction with cyclooctene.

$(EtO)_3SiCH{=}CH(CH_2)_6CH{=}CHSi(OEt)_3$ of 97% purity (^{1}H NMR) was obtained with isolated yields of 50% and 54%, respectively.

Spectroscopic Data for Isolated Products

$(Me_3SiO)_3SiCH{=}CH(CH_2)_6CH{=}CHSi(OSiMe_3)_3$: ^{1}H NMR ($C_6D_6$): $\delta = 0.24$ (s, 18H, $SiCH_3$), 1.10 – 1.40 (m, 8H, CH_2), 1.90 – 1.22 (m, 4H, CH_2), 5.52 (dt, $J = 18.6$, $J = 1.5$ Hz, 2H, $=CHSi$), 6.34 (dt, 2H, $J = 18.6$, J = 6.9 Hz, 2H, $=CH$); ^{13}C NMR (C_6D_6): $\delta = 2.2$ ($SiCH_3$), 29.0, 29.5, 36.9 (CH_2), 124.6 ($=CHSi$), 150.5 ($=CH$); MS: *m/z* (%) = 549 (11), 475 (10), 416 (13), 401 (12), 327 (9), 295 (68), 281 (15), 253 (13), 221 (28), 207 (100), 179 (20), 73 (87).

$(MeO)_3SiCH{=}CH(CH_2)_6CH{=}CHSi(OMe)_3$: ^{1}H NMR ($C_6D_6$): $\delta = 1.19 – 1.40$ (m, 8H, CH_2), 1.90 – 2.11 (m, 4H, CH_2), 3.52 (s, 18H, OCH_3), 5.53 (dt, $J = 18.6$, $J = 1.5$ Hz, 2H, $=CHSi$), 6.55 (dt, 2H, $J = 18.6$, $J = 6.3$ Hz, 2H, $=CH$); ^{13}C NMR (C_6D_6): $\delta = 2.2$ ($SiCH_3$), 28.7, 29.4, 37.1 (CH_2), 50.5 (OCH_3), 118.8 ($=CHSi$), 154.2 ($=CH$); MS: *m/z* (%) = 378 (M, 3), 346 (13), 299 (4), 227 (32), 197 (25), 121 (100), 91 (36).

$(EtO)_3SiCH{=}CH(CH_2)_6CH{=}CHSi(OEt)_3$: ^{1}H NMR ($C_6D_6$): $\delta = 1.16$ (t, $J = 6.9$ Hz, 18H, CH_3), 1.18 – 1.42 (m, 8H, CH_2), 1.95 – 2.08 (m, 4H, CH_2), 3.86 (q, 12H, OCH_2), 5.55 (dt, $J = 18.3$, $J = 1.5$ Hz, 2H, $=CHSi$), 6.54 (dt, 2H, $J = 18.3$, $J = 6.3$ Hz, 2H, $=CH$); ^{13}C NMR (C_6D_6): $\delta = 2.2$ ($SiCH_3$), 18.8 (CH_3), 28.7, 29.4, 37.1 (CH_2), 58.7 (OCH_2), 120.4 ($=CHSi$), 153.3 ($=CH$); MS: *m/z* (%) = 462 (M, 9), 416 (13), 387 (7), 343 (18), 297 (39), 253 (32), 163 (100), 119(23).

Mono(silyl)-substituted products were not isolated. Identification was made basing on GC-MS data.

$(Me_3SiO)_3SiCH{=}CH(CH_2)_6CH{=}CH_2$: MS: *m/z* (%) = 432 (M, 4), 417 (16), 295 (33), 265 (7), 207 (100), 193 (21), 153 (15), 139 (14), 125 (13), 113 (24), 99 (13).

$(MeO)_3SiCH{=}CH(CH_2)_6CH{=}CH_2$: MS: *m/z* (%) = 258 (M, 1), 226 (5), 162 (5), 136 (7), 121 (100), 117 (6), 91 (27).

$(EtO)_3SiCH{=}CH(CH_2)_6CH{=}CH_2$: MS: *m/z* (%) = 300 (M, 2), 254 (5), 213 (5), 189 (6), 171 (4), 163 (100), 147 (9), 135 (12), 119 (29).

Copolymerisation of Divinyltetraethoxydisiloxane with Cyclooctene

An 25 mL flame-dried, round-bottomed flasks equipped with a magnetic Teflon stirring bar was charged in a glovebox with divinyltetraethoxydisiloxane (3.0 g, 9.8×10^{-3} mol) and cyclooctene (0.18 g, 1.63×10^{-3} mol) in a glove box under an Ar atmosphere. Then the ruthenium carbene complex (Grubbs' catalyst) (0.0670 g, 8.17×10^{-5} mol) was added. The flask was removed from the glove box and placed on a high-vacuum line. The reaction mixture was stirred at 40 °C with intermittent application of vacuum. After 48 hours, the reaction was terminated by addition of vinyl ethyl ether (39 μL, 4.08×10^{-4} mol). The polymeric product was dissolved in dry methylene chloride, precipitated with ice cold methanol, and dried under vacuum until constant weight was reached. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.15 – 1.23$, (m, CH_3), 1.87 – 2.24, (m, CH_2), 3.72 – 3.83, (m, OCH_2), 5.30 – 5.44, (m, $=CH$ internal); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.15$ (CH_3), 28.22, 29.02, 29.63, 32.61, 36.54 (CH_2), 58.37 (OCH_2), 119.72, (Si-$\underline{C}$H=CH), 129.90 (=CH, *cis*), 130.38 (=CH, *trans*), 153.20 (Si-CH=$\underline{C}$H); GPC: $M_N = 4500$; PDI = 3.20.

Acknowledgements

This work was supported by a grant No K026/T09 from the State Committee for Scientific Research (Poland).

References

[1] For recent reviews see: a) K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, **1997**; b) *Alkene Metathesis in Organic Synthesis*, (Ed.: A. Fürstner), Springer, Berlin, **1998**; c) R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413 – 4450; d) M. Schuster, S. Blechert, *Angew. Chem.* **1997**, *109*, 2124 – 2144; *Angew. Chem. Int. Ed.* **1997**, *36*, 2036 – 2056; e) A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140 – 3172; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012 – 3043.

[2] For exemplary recent papers, see a) F. C. Engelhardt, M. Schmitt, R. Taylor, *Org. Lett.* **2001**, *3*, 2209 – 2212; b) K. Grela, M. Bieniek, *Tetrahedron Lett.* **2001**, *42*, 6425 – 6428; c) A. K. Chatterjee, T-L. Choi, R. H. Grubbs, *Synlett* **2001**, SI, 1034 – 1073; d) S. Imhof, S. Randl, S. Blechert, *Chem. Commun.* **2001**, 1692 – 1693; e) A. Smulik, S. T. Diver, *Tetrahedron Lett.* **2001**, *42*, 171 – 174.

[3] a) E. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, **1998**, Chapter 3; b) *The Chemistry of Organosilicon Compounds*, (Eds.: Z. Rappoport, Y. Apeloia), Wiley, Chichester, **1998**.

[4] S. E. Gibson (nee Thomas), S. P. Keen, in *Alkene Metathesis in Organic Synthesis*, (Ed.: A. Fürstner), Springer, Berlin, **1998**, pp. 155 – 181.

[5] K. B. Wagener, W. D. Smith Jr., *Macromolecules*, **1991**, *24*, 6073 – 6078.

[6] a) See, for example: E. Sh. Finkelshtein, N. V. Ushakov, E. B. Portnykh, *J. Mol. Catal.* **1992**, *76*, 133; b) Recently this subject was reexamined: T. Kawai, K. Shiga, T.

Suzuki, T. Iyoda, *J. Mol. Catal. A: Chemical* **1999**, *140*, 287–292, and references cited therein.

[7] D. S. La, J. G. Ford, E. S. Sattely, P. J. Bonitatebus, R. R. Schrock, A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 11603–11604.

[8] S. Chang, R. H. Grubbs, *Tetrahedron Lett.* **1997**, *38*, 4757–4760.

[9] F. J. Feher, D. Soulivong, A. G. Eklund, K. D. Wyndham, *Chem. Commun.* **1997**, 1185–1186.

[10] C. Pietraszuk, B. Marciniec, H. Fisher, *Organometallics* **2000**, *19*, 913–917.

[11] C. Pietraszuk, H. Fischer, M. Kujawa, B. Marciniec, *Tetrahedron Lett.* **2001**, *42*, 1175–1178.

[12] M. Kujawa-Welten, C. Pietraszuk, B. Marciniec, *Organometallics* **2002**, *21*, 840–845.

[13] M. Kujawa-Welten, B. Marciniec, *J. Mol. Catal. A: Chemical* **2002** (in press).

[14] C. Pietraszuk, H. Fischer, *Chem. Commun.* **2000**, 2463–2464.

[15] Ref.[1a], p. 241.

[16] E. Małecka, B. Marciniec, C. Pietraszuk, A. C. Church, K. B. Wagener, *J. Mol. Catal. A: Chemical* **2002** (in press).

[17] *Inorganic and Organometallic Polymers* (*Macromolecules containing Silicon, Phosphorus and other Inorganic elements*), (Eds.: M. Zeldin, K. J. Wynne, H. R Allcock), American Chemical Society, Washington, DC, **1988**.

[18] R. Nagel, C. Tamborski, H. W. Post, *J. Org. Chem.* **1951**, *16*, 1768–1771.