

Homo-metathesis of vinylsilanes catalysed by ruthenium carbene complexes

Cezary Pietraszuk^{a,b,*}, Bogdan Marciniec^a, Szymon Rogalski^a, Helmut Fischer^b

^a Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

^b Fachbereich Chemie, Universität Konstanz, Fach M 727, 78457 Konstanz, Germany

Received 30 December 2004; received in revised form 30 April 2005; accepted 22 June 2005

Available online 1 August 2005

Abstract

Effective homo-metathesis of a series of dichloro-substituted vinylsilanes $H_2C=C(H)SiCl_2R$ (where $R = Me, OSiMe_3, C_6H_5, C_6H_4-Me-4, C_6H_4-CF_3-4$) in the presence of second generation Grubbs catalyst $[Cl_2(PCy_3)(IMesH_2)Ru(=CHPh)]$ (**I**) and Hoveyda–Grubbs catalyst (**II**) leads to selective formation of *E*-1,2-bis(silyl)ethenes and ethene. On the basis of the results of experiments with deuterium-labelled reagents, a metallacarbene mechanism has been suggested for these reactions.

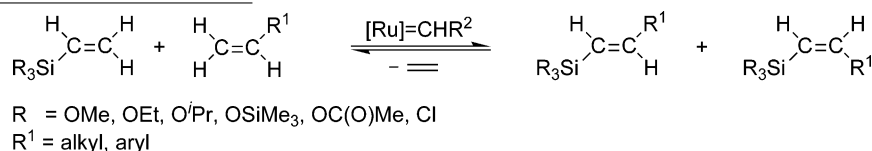
© 2005 Elsevier B.V. All rights reserved.

Keywords: Homo-metathesis; Dichloro-substituted vinylsilanes; Metallacarbene mechanism

1. Introduction

The olefin metathesis has become an important and powerful reaction in organic and polymer synthesis [1] as a result of

with styrenes, alkenes, numerous allyl derivatives (Eq. (1)). Metathesis of vinylsilanes with dienes and cycloalkenes catalysed by Grubbs type complexes has also been demonstrated [10].



development of well-defined, functional group tolerant metal carbene complexes, e.g. **I** (Fig. 1a) and **II** (Fig. 1b), which can act directly as metathesis initiators [1].

A considerable increase in the number of reports on the application of metathesis in organosilicon chemistry demonstrates its great potential as an efficient tool for the transformation of organosilicon compounds [2,3]. Recently, we have shown that Grubbs type catalysts effectively catalyse the cross-metathesis (CM) of trialkoxy-, trisiloxy- [4–7], trichloro- and generally electron withdrawing group-substituted vinylsilanes [8] and vinylsilsesquioxanes [9]

In search for new routes to silyl olefins of the type $R_3SiC(H)=C(H)SiR_3$, which constitute a class of vinylsilanes of prospective wide applicability in organic synthesis [11,12], we studied the homo-metathesis of vinylsilanes. The main catalytic routes to bis(silyl)ethenes involve hydrosilylation of silylacetylenes by hydrosilanes [13], bis(silylation) of acetylenes [14] and homo-coupling (trans-silylation) of vinylsilanes [2,3]. However, all these methods led to mixtures of isomers. Although the number of reports on the metathesis transformation of vinylsilanes is still increasing, very little information on the effective homo-metathesis has been reported until now [2,3]. Early results on the reaction catalysed by ill-defined heterogeneous systems have been summarised [2,3,15] and demon-

* Corresponding author. Tel.: +48 61 8291 366; fax: +48 61 8291 508.
E-mail address: pietrasz@main.amu.edu.pl (C. Pietraszuk).

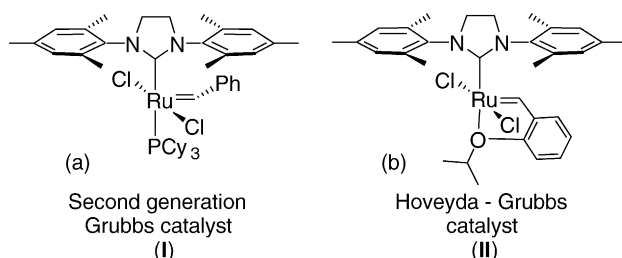


Fig. 1.

strate trace to small conversions of vinylsilane. Effective homo-metatheses occurring in the presence of a number of ruthenium complexes have been shown to proceed by a non-metallacarbene mechanism [16]. Only a single example of an effective vinylsilane homo-metathesis in the presence of $[\text{Mo}(\text{NO})_2(=\text{CHMe})(\text{O}^i\text{Pr})_2(\text{AlCl}_2)_2(\text{EtAlCl}_2)]$ is known [17]. However, no mechanistic evidence for a metallacarbene mechanism of the reaction has been provided.

We now report on the efficient and selective homo-metathesis of some vinylsilanes $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{R}$, (where $\text{R}=\text{Me}$, OSiMe_3 , C_6H_5 , $\text{C}_6\text{H}_4\text{-Me-4}$, $\text{C}_6\text{H}_4\text{-CF}_3\text{-4}$) proceeding under mild conditions in the presence of $[\text{Cl}_2(\text{PCy}_3)(\text{IMesH}_2)\text{Ru}(=\text{CHPh})]$ (I) and the Hoveyda-Grubbs catalyst (II).

2. Experimental

2.1. General

All manipulations were carried out under dry argon using standard Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC250 spectrometer at 250 and 62.9 MHz, respectively, or on a Varian Gemini at 300 and 75 MHz. GC-MS analyses were made on a HP 6890 gas chromatograph (HP-5MS 30 m capillary column) equipped with a HP 5973 mass selective detector or AMD 604/402. The chemicals were obtained from the following sources: complexes I and II, decane, dodecane, CH_2Cl_2 , C_6D_6 , $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{Me}$ from Aldrich. The other substituted vinylsilanes were prepared by literature methods, $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2(\text{OSiMe}_3)$ [18], $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{Ph}$ [19], $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2(\text{C}_6\text{H}_4\text{-X-4})$ (where $\text{X}=\text{Me}$, CF_3) were synthesized using the same methodology as in case of $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{Ph}$.

2.2. 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 , vinylsilane (1.18×10^{-4} mol) and 10 μL of decane or dodecane (internal standard). The reaction mixture was stirred and heated in an oil bath to maintain a gentle reflux (ca. 40°C). Then 0.005 g (5.89×10^{-6} mol) of ruthenium

benzylidene complex II was added under argon. A gentle flow of argon was applied. The reaction was controlled by GC.

Before the chromatographic analysis, the sample of the reaction mixture was treated with an excess of absolute ethanol in the presence of pyridine in order to transform chlorosilanes into ethoxy derivatives.

2.3. Reaction of $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{Me}$ with $\text{D}_2\text{C}=\text{C}(\text{D})\text{C}_6\text{D}_5$

2.3.1. In a closed system

$[\text{Cl}_2(\text{PCy}_3)(\text{IMesH}_2)\text{Ru}(=\text{CHPh})]$ 0.001 g (1.18×10^{-6} mol), C_6D_6 (0.35 mL), $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{Me}$ (3.0 μL , 2.3×10^{-5} mol), and styrene- d_8 (2.7 μL , 2.3×10^{-5} mol) were added under argon to an NMR tube. The sample was heated at 40°C and the reaction progress was controlled by NMR spectroscopy.

2.3.2. In an open system

A Schlenk flask (20 mL) equipped with condenser was charged with 10 mL of CH_2Cl_2 , 30.6 μL of $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{Me}$ (2.36×10^{-4} mol), and 27.0 μL styrene- d_8 (2.36×10^{-4} mol). The mixture was heated at 40°C in an oil bath with intensive stirring. Then 0.01 g of $[\text{Cl}_2(\text{PCy}_3)(\text{IMesH}_2)\text{Ru}(=\text{CHPh})]$ (1.18×10^{-5} mol) was added under argon. The reaction progress was controlled by NMR spectroscopy.

2.4. Representative procedure for the synthesis of *E*-1,2-bis(silyl)ethenes

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 and vinylsilane (4.0×10^{-2} mol). The reaction mixture was stirred and heated in an oil bath (50°C) to maintain a gentle reflux. Then 0.0339 g (4.0×10^{-5} mol) of ruthenium benzylidene complex I or II was added under argon. Intensive bubbling was observed. A gentle flow of argon was applied from the top of the column. After 3 h, or 10 h for $\text{H}_2\text{C}=\text{C}(\text{H})\text{SiCl}_2(\text{C}_6\text{H}_4\text{-X-4})$, dichloromethane was distilled off and the product was obtained by vacuum distillation with the use of a microdistillation set.

- *E*- $\text{MeCl}_2\text{Si}(\text{H})\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{Me}$ [20]: collected fraction 126–130 $^\circ\text{C}/1$ mmHg
 ^1H NMR (C_6D_6 , ppm): 0.30 (s, 6H, SiMe), 6.74 (s, 2H, =CH); ^{13}C NMR (C_6D_6): 4.1 (SiMe), 147.6 (=CH);
- *E*- $\text{Me}_3\text{SiOC}_2\text{Si}(\text{H})\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{OSiMe}_3$: collected fraction 91–93 $^\circ\text{C}/1$ mmHg
 ^1H NMR (C_6D_6 , ppm): 0.05 (s, 18H, SiMe₃), 6.99 (s, 2H, =CH); ^{13}C NMR (C_6D_6): 1.1 (SiMe₃), 146.6 (=CH);
- *E*- $\text{PhCl}_2\text{Si}(\text{H})\text{C}=\text{C}(\text{H})\text{SiCl}_2\text{Ph}$ [21]: collected fraction 161–163 $^\circ\text{C}/1$ mmHg

Table 1
Homo-metathesis of dichloro-substituted vinylsilanes

Entry	H ₂ C=C(H)SiCl ₂ R; where R=	Cat.	Conversion of H ₂ C=C(H)SiCl ₂ R (%)	Yield (isolated) (%)	E/Z	Yield (other products) (%)
1	Me	I	100	95 (70)	25/1	3
2	Me	II	60 ^a	57 ^a	E ^a	Trace ^a
3	Me	II	60	57	E	Trace
4	Me	II	80 ^b	76 ^b	E ^b	4 ^b (siloxanes)
5	OSiMe ₃	I	100	93 (70)	E	5
6	OSiMe ₃	II	100 ^b	100 ^b	E ^b	0 ^b
7	C ₆ H ₅	I	100 ^b	80 ^b (60) ^b	E ^b	5 ^b
8	C ₆ H ₅	II	100 ^b	100 ^b	E ^b	0 ^b
9	C ₆ H ₄ -Me-4	I	100 ^b	80 ^b	E ^b	5 ^b
10	C ₆ H ₄ -Me-4	II	100 ^b	100 ^b	E ^b	0 ^b
11	C ₆ H ₄ -CF ₃ -4	I	40 ^b	20 ^b	E ^b	5 ^b

Reaction conditions: CH₂Cl₂, reflux, 3 h, [vinylsilane]:[cat.] = 20:1.

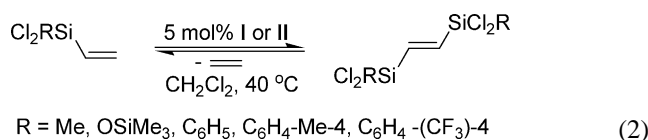
^a [vinylsilane]:[cat.] = 33:1

^b 10 h.

¹H NMR (C₆D₆, ppm): 6.95–7.11 (m, 6H, Ph), 7.2 (s, 2H, =CH), 7.48–7.57 (m, 4H, Ph); ¹³C NMR (C₆D₆): 128.7, 130.8, 132.2, 133.9 (Ph), 148.1 (=CH).

3. Results and discussion

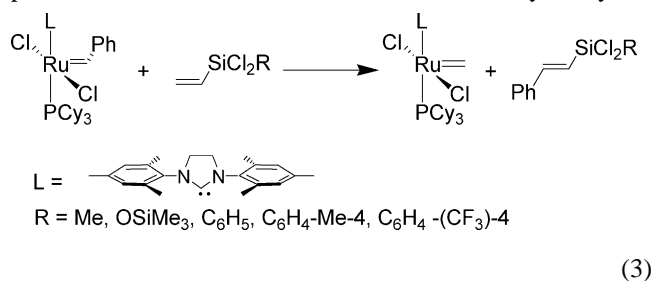
Recently we observed that chloro-substituted vinylsilanes undergo effective cross-metathesis with styrene, alkenes and some allyl derivatives in the presence of **I** [8]. Unexpectedly, when H₂C=C(H)SiCl₂Me was used as the reaction partner, besides CM products minor amounts of *E*-1,2-bis(dichloromethylsilyl)ethene were detected. Following this observation a series of vinylsilanes was screened with the aim to evaluate their activity in homo-metathesis. It was found that only vinylsilanes containing two chloro substituents at silicon underwent highly stereoselective homo-metathesis in the presence of **I** or **II**. The reactions permitted complete conversion of vinylsilanes and led to moderate to high yields of *E*-1,2-bis(silyl)ethenes (Eq. (2)). The results were summarized in Table 1.



The efficient homo-metathesis of vinylsilanes was achieved by performing the reaction in refluxing CH₂Cl₂ in an open system in the presence of **I** or **II**.

For R = Me and OSiMe₃ (Table 1, entries 1–6) catalyst **I** makes it possible to achieve complete conversion already after 3 h, whereas in the case of **II** it was necessary to perform the reaction for 10 h. For phenyl- and 4-(methyl)-phenyl-substituted dichlorovinylsilanes (Table 1, entries 7–10) extensive reaction times were necessary to achieve complete conversions, irrespective of the catalyst used. Low conversions and yields were obtained in homo-metathesis of H₂C=C(H)SiCl₂(C₆H₄-CF₃-4) (Table 1, entry 11).

Both catalysts allow highly selective synthesis of *E*-1,2-bis(silyl)ethenes. However, in the case of reaction catalysed by **I** formation of a trace (up to 4%) of *E*-1-phenyl-2-(silyl)ethenes could not be avoided. Their formation results presumably from the reaction of complex **I** with vinylsilane (Eq. (3)). The formation of *E*-1-phenyl-2-(silyl)ethenes in similar systems was described earlier [4]. Analogous by-products were not observed in the reactions catalysed by **II**.



Removal of ethene was found to be critical for efficient conversions. Only traces of products were observed in closed systems. A gentle flow of argon was found to improve the conversion and yield.

The reaction is very sensitive to water. Much care should be taken to avoid traces of water in the system. Under the conditions used the reaction of moisture traces with chlorosilane leads to rapid hydrolysis of Si–Cl bond and formation of HCl. The reaction is catalysed by free phosphine (which decoordinates from complex **I**). This catalytic side-reaction can significantly decrease product yield and selectivity. Moreover, the loss of phosphine due to the reaction with HCl increases the activity of the catalyst but also accelerates its thermal decomposition. Such effects caused by “phosphine scavengers” (e.g. CuCl) have been documented in the literature [22,23]. We found that in the presence of chlorosilane and traces of water, under similar conditions, first generation Grubbs catalyst undergoes a very fast decomposition.

In order to exclude the non-metallacarbene mechanism of the reaction, proved for vinylsilane disproportionation catalysed by ruthenium hydride or ruthenium silyl complexes (Eq. (4)) [16], or the generation of catalytically active hydride

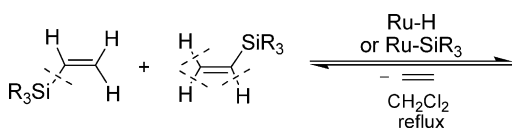
Table 2
Cross-metathesis of vinyl dichloromethylsilane with styrene- d_8

Conditions	Conversion (%)		Yield (%)	
Closed system ^a	20	20	20	Trace
Open system ^b	50	Trace	40	10

^a Reaction condition: NMR tube, C_6D_6 , 40 °C, 3 h, [styrene- d_8]:[vinylsilane] = 1:1.

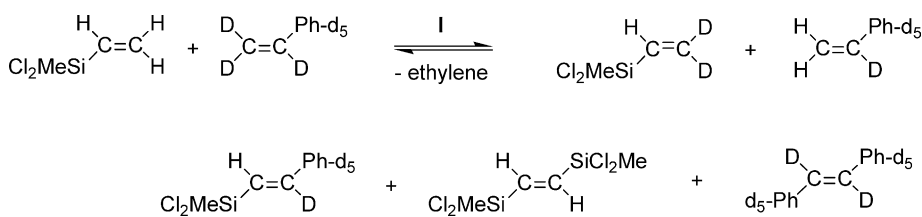
^b Reaction condition: Schlenk flask, CD_2Cl_2 , 40 °C, 3 h, [styrene- d_8]:[vinylsilane] = 1:1.

complexes in situ as in the case of silylation of vinyl ethers with vinylsilanes [24] and a number of other



R' = alkoxy, alkyl, aryl,

reports [25,26], the catalytic cross-metathesis of $H_2C=C(H)SiCl_2Me$ with deuterium labelled styrene $D_2C=C(D)Ph-d_5$ was performed (Eq. (5)). The results were collected in Table 2.



The experiment permitted exclusion of the C–H bond activation. No H/D exchange was observed in any component of the reaction mixture under the conditions used. On the contrary, activation of the C=C bond was confirmed on the basis of CH_2/CD_2 exchange observed in styrene- d_8 and vinylsilane by NMR spectroscopy. The experiment demonstrated that in the presence of catalyst **I** and chloro-substituted vinylsilanes, under the conditions used, only metathesis transformations are observed. Identification of $Cl_2MeSiC(H)=C(H)SiCl_2Me$ containing no deuterium indicate metallacarbene mechanism of its formation because no other isotopomers of 1,2-bis(silyl)ethene can be formed via homo-metathesis in the system studied.

The differences observed between open and closed systems confirmed the critical significance of ethene removal for effective run of the reaction. In a closed system only traces of metathesis products were formed.

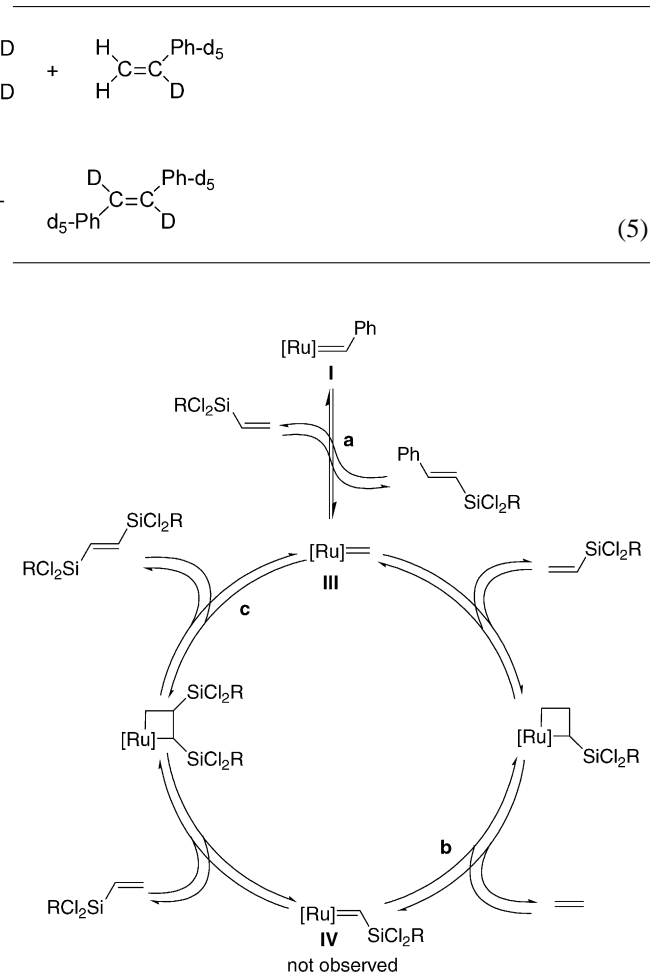
On the basis of the results of our earlier studies on metathesis transformations of vinylsilanes [4], and of the results of the experiment with deuterium-labelled styrene, a metallacarbene mechanism for homo-metathesis is postulated (Scheme 1).

The benzylidene complex **I** reacts with vinylsilane with the formation of methylidene complex **III** and *E*-1-phenyl-2-(silyl)ethene (Scheme 1, pathway a) [4]. Then vinylsi-

lane molecule $H_2C=C(H)SiCl_2R$ coordinates to **III**, the olefin complex formed undergoes oxidative cyclization and



decomposes metathetically to give the silylcarbene complex **IV** and ethene (Scheme 1, pathway b). All attempts to detect **IV** (by 1H NMR spectroscopy) failed, presumably



Scheme 1. Proposed catalytic cycle for the homo-metathesis of dichlorovinylsilanes.

due to the high reactivity of **IV** or its small concentration in the reaction mixture. By coordination of vinylsilane to **IV**, oxidative cyclization and metathesis decomposition of putative bis(silyl)ruthenacyclobutane complex the *E*-1,2-bis(silyl)ethene and methylidene complex (**III**) are formed (Scheme 1, pathway c). A relatively high concentration of **I** or **II** has to be employed because of the instability of the methylidene complex **III** [23] and presumably also of **IV** under the conditions used.

4. Conclusions

Efficient and selective homo-metathesis of dichloro-substituted vinylsilanes occurring in the presence of **I** or **II** offers an attractive route to *E*-1,2-bis(silyl)ethenes. These reactions are the first reported examples of vinylsilanes homo-metathesis.

Acknowledgment

We thank the European Commission (contract number ICA1-CT-2002-70001) for the financial support of this investigation.

References

- [1] (a) R.H. Grubbs (Ed.), *Handbook of Metathesis*, Wiley-VCH, Weinheim, 2003;
(b) A. Fürstner (Ed.), *Alkene Metathesis in Organic Synthesis*, Springer, Berlin, 1998.
- [2] B. Marciniak, C. Pietraszuk, in: R.H. Grubbs (Ed.), *Handbook of Metathesis*, Wiley-VCH, Weinheim, 2003, p. 13 (Chapter 2).
- [3] B. Marciniak, C. Pietraszuk, *Curr. Org. Chem.* 7 (2003) 691.
- [4] C. Pietraszuk, B. Marciniak, H. Fischer, *Organometallics* 19 (2000) 913.
- [5] C. Pietraszuk, H. Fischer, M. Kujawa, B. Marciniak, *Tetrahedron Lett.* 42 (2001) 1175.
- [6] M. Kujawa-Welten, C. Pietraszuk, B. Marciniak, *Organometallics* 21 (2002) 840.
- [7] M. Kujawa-Welten, B. Marciniak, *J. Catal. Mol. A Chem.* 190 (2002) 79.
- [8] C. Pietraszuk, B. Marciniak, H. Fischer, *Tetrahedron Lett.* 44 (2003) 7121.
- [9] Y. Itami, B. Marciniak, M. Kubicki, *Chem. Eur. J.* 10 (2004) 39.
- [10] C. Pietraszuk, B. Marciniak, M. Jankowska, *Adv. Synth. Catal.* 344 (2002) 789.
- [11] (a) T.H. Chan, I. Fleming, *Synthesis* (1979) 761;
(b) W.P. Weber, *Silicon Reagents for Organic Synthesis*, Springer, Berlin, 1983 (Chapter 7);
(c) E.W. Colvin, *Silicon Reagents in Organic Synthesis*, Academic Press, London, 1988 (Chapter 3);
(d) T.-Y. Luh, S.-T. Liu, in: Z. Rappoport, Y. Apeloig (Eds.), *The Chemistry of Organosilicon Compounds*, Wiley, Chichester, 1998 (Chapter 30).
- [12] For recent reviews on the use of silyl olefins in cross-coupling reactions see;
(a) R.S. Denmark, R.F. Sweis, in: A. de Meijere, F. Diederich (Eds.), *Metal Catalyzed Cross-coupling Reactions*, Wiley-VCH, Weinheim, 2004 (Chapter 4);
(b) S.E. Denmark, R.F. Sweis, *Acc. Chem. Res.* 35 (2002) 835;
(c) T. Hiyama, *J. Organomet. Chem.* 653 (2002) 58.
- [13] *Hydrosilylation of silylacetylenes*;
(a) B. Marciniak (Ed.), *Comprehensive Handbook on Hydrosilylation*, Pergamon Press, Oxford, 1992 (Chapter 5.4);
(b) I. Ojima, Z. Li, J. Zhu, in: Z. Rappoport, Y. Apeloig (Eds.), *The Chemistry of Organic Silicon Compounds*, vol. 2, Wiley, Chichester, 1998 (Chapter 29).
- [14] For review see;
(a) B. Marciniak, *Appl. Organomet. Chem.* 14 (2000) 527;
(b) H.K. Sharma, K.H. Pannel, *Chem. Rev.* 95 (1995) 1351.
- [15] E.S. Finkelshtein, B. Marciniak, in: B. Marciniak, J. Chojnowski (Eds.), *Progress in Organosilicon Chemistry*, Gordon and Breach, Amsterdam, 1995 (Chapter 26).
- [16] (a) Y. Wakatsuki, H. Yamazaki, M. Nakano, Y. Yamamoto, *J. Chem. Soc. Chem. Commun.* (1991) 703;
(b) B. Marciniak, C. Pietraszuk, *J. Chem. Soc. Chem. Commun.* (1995) 2003.
- [17] A. Keller, R. Matusiak, *J. Mol. Catal. A Chem.* 104 (1996) 213.
- [18] N. Auner, C.-R. Heikenwaelder, W. Ziche, *Chem. Ber.* 126 (1993) 2177.
- [19] R. Tacke, R. Strecker, M. Lambrecht, G. Moser, E. Lachdl, *Liebigs Ann. Chem.* 6 (1983) 922.
- [20] (a) V.F. Mironov, A.D. Petrov, *Izv. Akad. Nauk. SSSR, Ser. Khim.* (1958) 787;
(b) H. Matsumoto, S. Nagashima, T. Kato, Y. Nagai, *Angew. Chem. Int. Ed. Engl.* 17 (1978) 279;
(c) E. Liepins, I. Birgele, E. Lukevics, V.D. Sheludyakov, V.G. Lahtin, *J. Organomet. Chem.* 385 (1990) 185.
- [21] E.A. Chernyshev, G.F. Pavelko, *Izv. Akad. Nauk. SSSR, Ser. Khim.* (1966) 2205.
- [22] E.L. Dias, S.T. Nguyen, R.H. Grubbs, *J. Am. Chem. Soc.* 119 (1997) 3887.
- [23] M. Ulman, R.H. Grubbs, *J. Org. Chem.* 64 (1999) 7202.
- [24] B. Marciniak, M. Kujawa, C. Pietraszuk, *Organometallics* 19 (2000) 1677.
- [25] For review see B. Schmidt, *Eur. J. Org. Chem.* (2004) 1865.
- [26] S.H. Hong, M.W. Day, R.H. Grubbs, *J. Am. Chem. Soc.* 126 (2004) 7414.