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Cross-metathesis of vinylsilanes carrying electron-withdrawing substituents with olefins in the presence of the second-generation Grubbs catalyst

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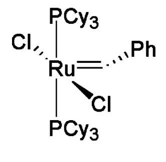
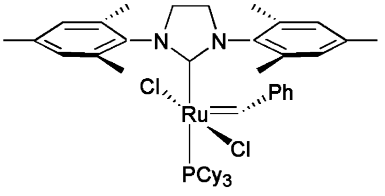
Abstract—The efficient cross-metathesis of vinylsilanes carrying electron-withdrawing substituents with various olefins is described. High yields and selectivities were obtained when styrene, 1-hexene, and selective functional allyl derivatives were used as the olefins.

Recently, the olefin metathesis has become an important and powerful tool in organic and polymer synthesis[1] due to the development of well defined metal carbene complexes (e.g. compounds **I** and **II**) that are tolerant to functional groups and can act directly as metathesis initiators.[2]



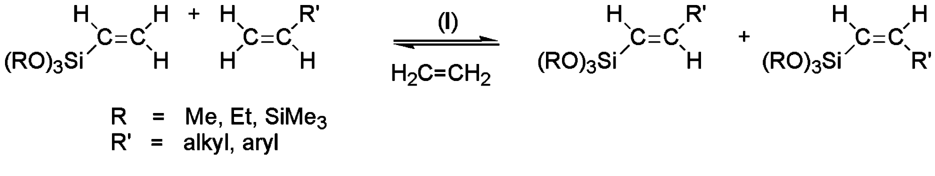
I



II

The growing number of reports on the application of metathesis in organosilicon chemistry proves the large potential of the reaction for the efficient transformation of organosilicon compounds.[3] Vinylsilanes of the type $R_3SiCH{=}C(H)R'$ constitute a class of compounds more and more widely applied in organic synthesis.[4,5] Therefore, we studied the cross-metathesis of terminal vinylsilanes ($H_2C{=}C(H)SiR_3$) with olefins with the purpose of developing new routes to these internal vinylsilanes. Recently, we showed that the Grubbs catalyst **I** effectively catalyses the metathesis of vinylsilanes with styrenes,[6,7] substituted styrenes, alkenes,[7] and numerous allyl derivatives[7,8] (Scheme 1) as well as of dienes and cycloalkenes.[9]

These metatheses were limited to vinylsilanes containing three alkoxy or siloxy substituents at silicon. For organosilicon chemistry, however, the cross-metathesis of chloro-substituted vinylsilanes[10] with alkyl-, aryl-, and silyl-substituted olefins would be especially attractive. The resulting chloro-substituted metathesis products constitute very useful starting compounds for a series of transformations since the chloride at silicon can easily be replaced by a variety of groups.[11] In addition, the organochlorosilicon products are valuable (co)monomers for the synthesis of polysiloxanes and



Scheme 1.

Keywords: vinylsilanes; cross-metathesis; ruthenium; olefins.

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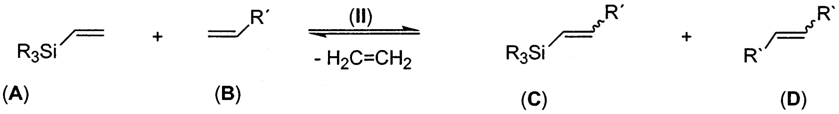
are intermediates in a great number of organic syntheses, especially in the fast developing field of the palladium-catalysed coupling of vinylsilanes with organic derivatives.[5]

We now report that the limitations encountered when using ruthenium catalyst **I** can be overcome by employing the second-generation Grubbs catalyst **II**. In contrast to **I**, complex **II** effectively catalyses the cross-metathesis of di- and trichloro-substituted vinylsilanes[10] with alkyl-, aryl-, and silyl-substituted olefins at room temperature or at slightly elevated temperatures. Effective stirring and heating of the reaction mixture in CH_2Cl_2 to a gentle reflux for 1 h is sufficient for the reactions to proceed quickly (Scheme 2). Only very small amounts of the catalyst (0.5 mol% relative to olefins) are required for a fast and in most cases complete conversion of the olefins. Since vinylsilanes are usually inactive to conversion to self-metathesis products, the vinylsilanes can be used in excess to minimise the formation of olefin self-metathesis products **D**. For reactions of 1-hexene with allyltrimethylsilane a 5-fold excess of the vinylsilane appears to be sufficient. Since styrene, allyl ethyl ether, and allyl bromide tend to form olefin self-metathesis products, a 15-fold excess of the vinylsilanes is recommended. However, even a 15-fold excess of the vinylsilane is not enough to completely suppress the formation of the olefin self-metathesis product **D** (Table 1, entries 3–5 and 8–10).

High yields of cross-metathesis products (Table 1, entries 1, 2, 6, and 7) were obtained in the reactions of 1-hexene and of allyltrimethylsilane with the vinylsilanes $H_2C{=}C(H)SiCl_3$ and $H_2C{=}C(H)SiCl_2Me$. The reactions proceeded highly stereoselectively with a pronounced preference for the formation of the *E* isomer.[12] In contrast, chlorodimethylvinylsilane, and triphenylvinylsilane did not react with 1-hexene (Table 1, entries 11 and 12) suggesting that for efficient cross-metathesis silyl groups are required that carry strongly electron-withdrawing substituents at silicon. In accord with this conclusion displacing triphenylvinylsilane by $H_2C{=}C(H)SiR_3$ ($SiR_3 = Si(C_6H_4CF_3\text{-}p)_3$ or $SiCl(C_6H_4CF_3\text{-}p)_2$) again led to high yield and high stereoselectivity of cross-metathesis products (Table 1, entries 13 and 14).



R' = Ph, C_4H_9, CH_2SiMe_3, CH_2OEt, CH_2Br
n = 2, 3

Scheme 2.

Table 1. Cross-metathesis of vinylsilanes with olefins (approximate concentrations of **B**: 0.7 mol l^{-1} (1-hexene) and 0.4 mol l^{-1} (styrene))

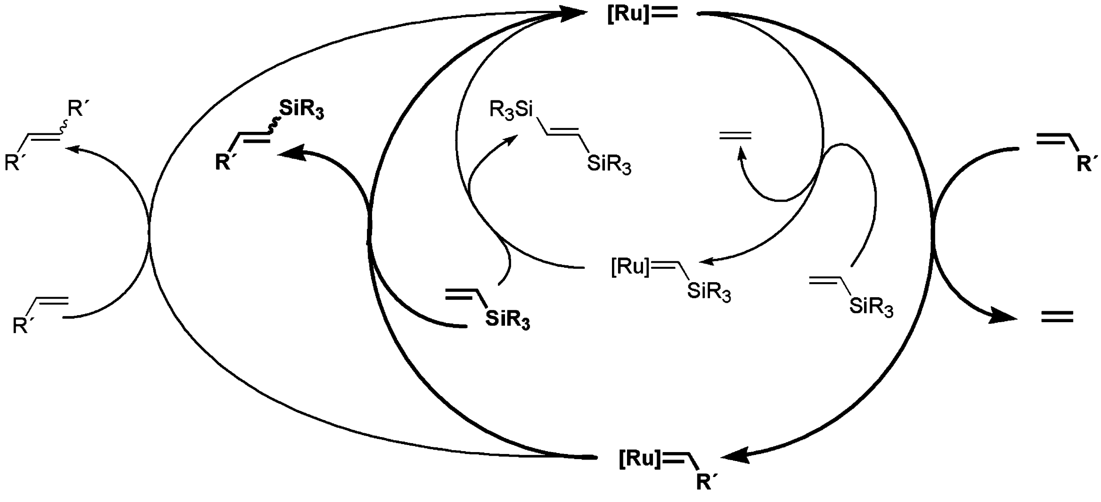
Entry	Vinylsilane (**A**) $R_3Si=$	Olefin (**B**) $R'=$	Conversion of olefin[a] [%]	Yield of **C**[a] (isolated) [%]	*E*/*Z*[a]	Yield of **D**[a] [%]
1	$SiCl_3$	n-C_4H_9[b]	100	100 (90)	20/1	0
2		CH_2SiMe_3[c]	100	100 (92)	25/1	0
3		CH_2OEt[c]	100	92	8/1	8
4		CH_2Br[c]	70	63	>25/1	7
5		Ph[c]	85	83 (70)	>25/1	5
6	$SiCl_2Me$	n-C_4H_9[b]	100	100 (80)	20/1	0
7		CH_2SiMe_3[b]	100	100 (80)	22/1	0
8		CH_2OEt[c]	100	95	11/1	5
9		CH_2Br[c]	60	55	>25/1	5
10		Ph[c]	80	78 (65)	>25/1	Trace
11	$SiClMe_2$	n-C_4H_9[b]	Trace	0	–	0
12	$SiPh_3$	n-C_4H_9[b]	Trace	0	–	0
13	$Si(C_6H_4CF_3\text{-}p)_3$	n-C_4H_9[d,e]	100	97	>25/1	Trace
14	$SiCl(C_6H_4CF_3\text{-}p)_2$	n-C_4H_9[b]	100	100	25/1	0
15	$Si(OAc)_3$	n-C_4H_9[b]	100	100 (70)	20/1	0
16		CH_2SiMe_3[b]	100	100 (70)	25/1	0

Reaction conditions: CH_2Cl_2, reflux (or 50°C), 1 h.

[a] Determined by ^1H NMR spectroscopy.

Molar concentrations ratios: [b] [**A**]:[**B**]:[**II**] = $5:1:5\times10^{-3}$; [c] [**A**]:[**B**]:[**II**] = $15:1:5\times10^{-3}$; [d] [**A**]:[**B**]:[**II**] = $5:1:2\times10^{-2}$.

[e] Reaction complete after 3 h.



Scheme 3.

These reactions required a higher concentration of the catalyst and/or extended reaction times. When 2 mol% of **II** were used in the reaction with $H_2C{=}C(H)Si(C_6H_4CF_3\text{-}p)_3$ the complete conversion of the olefin was observed only after 3 h. Displacement of one 4-trifluoromethylphenyl- by a chloro-substituent led to substantial increase in cross-metathesis reactivity (Table 1, entries 13 and 14).

The crucial role of electron-accepting substituents at silicon is further supported by comparing the reactivity of the series $H_2C{=}C(H)Si(OAc)_nMe_{3-n}$ ($n=1$–3). $H_2C{=}C(H)Si(OAc)_3$ was found to be highly active in the reaction with 1-hexene. In contrast, $H_2C{=}C(H)Si(OAc)_2Me$ gave only traces of products and $H_2C{=}C(H)Si(OAc)Me_2$ did not show any metathesis activity. In the presence of both of these vinylsilanes the fast decomposition of carbene complex **II** by loss of the carbene moiety was observed.

Cross-metathesis efficiency decreased and small amounts of olefin self-metathesis products **D** were formed when 1-hexene and allyltrimethylsilane were replaced by styrene, allyl ethyl ether, or allyl bromide. When allyl ethyl ether was used as the olefin even the stereoselectivity dropped considerably. Obviously, electron-withdrawing substituents at the olefin used as co-reagent tend to decrease cross-metathesis efficiency.

Unexpectedly, when a large excess of $H_2C{=}C(H)SiCl_2Me$ (15 equivalents) was used, the slow formation of significant amounts of the bis(silyl)ethene $Cl_2MeSi(H)C{=}C(H)SiCl_2Me$ by self-metathesis was observed. Self-metathesis of vinylsilanes in the presence of well-defined carbene complexes has not been observed before. The molar ratio of bis(silyl)ethene to cross-metathesis product **C** in the reaction mixtures was 1/8 for the reaction of $H_2C{=}C(H)SiCl_2Me$ with allyl bromide, 1/4 with allyl ethyl ether, and 1/3 with styrene, as determined by NMR spectroscopy. When the excess of $H_2C{=}C(H)SiCl_2Me$ in the reactions with 1-hexene and allyltrimethylsilane was reduced to 5-fold, the cross-metathesis proceeded highly selectively and only traces of $Cl_2MeSi(H)C{=}C(H)SiCl_2Me$ were detected in the reaction mixture. The formation of the bis(silyl)ethene establishes that a silylcarbene species is formed as an intermediate during the metathesis reaction (for a simplified mechanistic scheme of the catalytic cycles see Scheme 3). The failure to observe the cross-metathesis product in the system containing $H_2C{=}C(H)SiClMe_2$ is very likely due to rapid decomposition of either the silylcarbene intermediate $[Ru]{=}C(H)SiClMe_2$ or the corresponding ruthenacyclobutane. The decomposition presumably follows a mechanism similar to that proposed for the decomposition of **I** in the presence of $H_2C{=}C(H)SiMe_3$ (β-silyl elimination from a ruthenacyclobutane).[13] Despite the detection of a self-metathesis product derived from a silylcarbene intermediate the majority, if not all, of the cross-metathesis products seems to be formed by a catalytic cycle involving $[Ru]{=}CH_2$ and $[Ru]{=}C(R')H$ intermediates (bold cycle in Scheme 3). All attempts to detect a silylcarbene complex have failed so far.

In conclusion, the efficient and highly selective cross-metathesis of chloro- and acetoxy-substituted vinylsilanes with various olefins in the presence of very small loadings of $[Cl_2(PCy_3)(IMesH_2)Ru({=}CHPh)]$ (**II**) offers an attractive route to unsaturated organosilicon compounds. The ability to produce chloro-substituted silyl derivatives makes the method particularly useful for the synthesis of functional (co)monomers for silicone chemistry and of intermediates in organic synthesis.

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   $Cl_3SiCH{=}CHCH_2SiMe_3$: collected fraction: 78–80°C/2 mmHg, $E/Z=25/1$. ^1H NMR (C_6D_6, ppm) δ −0.18 (s, 9H, $SiMe_3$), 1.36 (d, $J=8.2$ Hz, 2H, CH_2), 5.28 (dt, $J=18.0$, 1.2 Hz, 1H, =CHSi), 6.54 (dt, $J=18.0$, 8.2 Hz, 1H, =CH); ^{13}C NMR (C_6D_6, ppm) δ −2.2 ($SiMe_3$), 28.8 (CH_2), 119.3 (=CHSi), 155.8 (=CH).
   $Cl_2MeSiCH{=}CHCH_2SiMe_3$: collected fraction: 79–81°C/2 mmHg, $E/Z=22/1$. ^1H NMR (C_6D_6, ppm) δ −0.12 (s, 9H, $SiMe_3$), 0.53 (s, 3H, SiMe), 1.46 (dd, $J=8.2$ Hz, 1.2, 2H, CH_2); 5.37 (dt, $J=18.2$, 1.2, 1H, =CHSi), 6.41 (dt, $J=18.2$, 8.2 Hz, 1H, =CH). ^{13}C NMR (C_6D_6, ppm) δ −2.1 ($SiMe_3$), 5.4 (SiMe), 28.6 (CH_2), 121.7 (=CHSi), 152.2 (=CH).
   $(AcO)_3SiCH{=}CHC_4H_9$: collected fraction: 93–94°C/4 mmHg, $E/Z=20/1$. ^1H NMR (C_6D_6, ppm) δ 0.50 (s, 3H, SiMe), 0.73–0.80 (m, 3H, CH_3), 1.04–1.17 (m, 4H, CH_2), 1.78–1.88 (m, 2H, CH_2 next to CH=), 5.54 (dt, $J=18.3$ Hz, 1.5, 1H, =CHSi), 6.30 (dt, $J=18.3$, 6.4 Hz, 1H, =CH). ^{13}C NMR (C_6D_6, ppm) δ 13.9 (CH_3), 21.9 (Ac), 22.3 (CH_2), 30.1 (CH_2), 36.4 (CH_2), 116.2 (=CHSi), 158.1 (=CH), 168.9 (Ac).
   $(AcO)_3SiCH{=}CHCH_2SiMe_3$: collected fraction: 119–120°C/3 mmHg, $E/Z=25/1$. ^1H NMR (C_6D_6, ppm) δ −0.05 (s, 9H, $SiMe_3$), 1.56 (dd, $J=8.2$, 1.2 Hz, 2H, CH_2), 1.69 (s, 9H, Ac), 5.67 (dt, $J=18.6$, 1.2 Hz, 1H, =CHSi), 6.90 (dt, $J=18.6$, 8.2, 1H, =CH). ^{13}C NMR (C_6D_6, ppm) δ −2.2 ($SiMe_3$), 21.9 (Ac), 29.4 (CH_2), 113.9 (=CHSi), 156.0 (=CH), 168.9 (Ac).
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