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# Metathesis of silicon-containing olefins

## VI *. Metathesis of vinylphenyl-substituted silanes

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### Abstract

Ruthenium(II) and -(III) complexes have been found to be very efficient catalysts for the metathesis of vinylphenyl-substituted silanes to yield the corresponding $(E)+(Z)$-1,2-bis(silyl)ethenes with a yield above 75%. Rhodium(I) complexes are less effective.

Our study on self-metathesis of vinyltrisubstituted silanes [1,2] and their cross-metathesis with various olefins [2,3] occurring in the presence of ruthenium complexes showed that at least one oxygeneous substituent (alkoxy, siloxy) at silicon was required for the reaction to proceed effectively. The general equations for the two reactions are as follows:

$$(RO)_nMe_{3-n}SiCH{=}CH_2 \xrightarrow[-CH_2{=}CH_2]{} (RO)_nMe_{3-n}SiCH{=}CHSiMe_{3-n}(OR)_n \quad (Z+E) \qquad (1)$$

where $R = CH_3$, $C_2H_5$, $C_3H_7$, iso-$C_3H_7$, $n = 1$–$3$

$$\left.\begin{array}{l} CH_2{=}CH(CH_2)_nR \\ CH_2{=}CHSi(OEt)_3 \end{array}\right] \xrightarrow[-CH_2{=}CH_2]{} (EtO)_3SiCH{=}CH(CH_2)_nR \quad (Z+E) \qquad (2)$$

where $R = CH_3$, $n = 2$–$15$; $R = Ph$, $n = 0$; $R =$ cyclohexyl, $n = 0$;
$R = SiMe_3$, $n = 0$.

No metathetical activity was observed for vinyltrimethylsilane and for vinyl(methyl, chloro)silanes. Furthermore, activation of ruthenium and rhodium catalysts by traces of dioxygen and predominantly by hydride donor cocatalysts as well as the inhibition of the reaction by any solvent were reported [2,3].

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* For Part V see ref. 3.

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Replacement of the vinyl by an allyl substituent decreases markedly the activity of the catalysts, the maximum yield of products after heating under reflux in metathesis being 10–15% [2]. On the other hand, metathesis of allyl(methyl, phenyl)silane was observed to be more effective in the presence of the heterogeneous systems $\mathrm{Re_2O_7/Al_2O_3/SnBu_4}$, giving bis(silyl)butene with a yield of 50–60% [4].

Our previous investigations on vinyl(alkoxy)silanes have been extended to vinyltri(phenyl, methyl)-substituted silanes to determine their metathetical activity in the presence of homogeneous catalysts such as $\mathrm{RuCl_2(PPh_3)_3}$, $\mathrm{Ru(acac)_3}$ and $\mathrm{RhCl(PPh_3)_3}$. The reaction leads to the synthesis of novel bis(silyl)ethenes according to the following equation:

$$2\mathrm{Ph}_n\mathrm{Me}_{3-n}\mathrm{SiCH{=}CH_2} \xrightarrow[-\mathrm{CH_2{=}CH_2}]{} \mathrm{Ph}_n\mathrm{Me}_{3-n}\mathrm{SiCH{=}CHSiMe}_{3-n}\mathrm{Ph}_n \quad (Z+E)$$

$$n = 1\text{–}3 \qquad (3)$$

Preliminary examinations of the above reactions show high yield of metathesis products. Vinylphenyldimethylsilane ($5.5 \times 10^{-2}$ mol) heated at 120 °C for 48 h in the presence of $\mathrm{RuCl_2(PPh_3)_3}$ ($5.5 \times 10^{-4}$ mol) in air afforded a main product which was isolated and identified as 1,2-bis(dimethylphenylsilyl)ethene (mixture of ($E$) and ($Z$) products): yield 80%, m.p. = 28 °C; $^1$H NMR (TMS): $\delta$(SiCH$_3$) 0.34 ppm (s, 12H), $\delta$(=CH) 6.83 ppm (s, 2H), $\delta$(Ph) 7.28–7.53 ppm (m, 10H); $^{13}$C NMR (TMS): $\delta$(SiCH$_3$) $-2.87$ ppm, $\delta$(=CH) 150.78 ppm, $\delta$(Ph) 128.03, 129.17, 134.15 ppm, IR $\nu$(C=C) 1585 cm$^{-1}$ (w); MS $m/e$ 296.4 ($M^+$), 161.2 ($\mathrm{HC{=}^+CHSiPhMe_2}$), 135.1 ($\mathrm{^+SiPhMe_2}$).

Vinylmethyldiphenylsilane ($4.4 \times 10^{-2}$ mol) was heated at 120 °C for 96 h in the presence of $\mathrm{RuCl_2(PPh_3)_3}$ ($4.4 \times 10^{-4}$ mol) to yield 75% of ($Z$) + ($E$) products. The products were isolated and identified as 1,2-bis(methyldiphenylsilyl)ethene; m.p. = 127–128 °C; $^1$H NMR (TMS): $\delta$(SiCH$_3$) 0.65 ppm (s, 6H), $\delta$(=CH) 7.08 ppm (s, 2H), $\delta$(Ph) 7.26–7.58 ppm (m, 20H); $^{13}$C NMR (TMS): $\delta$(SiCH$_3$) $-4.05$ ppm, $\delta$(=CH) 150.98 ppm, $\delta$(Ph) 128.27, 129.70, 135.25 ppm; IR $\nu$(C=C) 1585 (w); MS: $m/e$ 420.4 ($M^+$), 197.1 ($\mathrm{^+SiPh_2Me}$), 223.2 ($\mathrm{HC^+{=}CHSiPh_2Me}$).

The $^1$H NMR (60 Mz) and $^{13}$C NMR spectra were recorded on a Jeol FX 90Q spectrometer equipped with a Texas 980 B computer system. $\mathrm{CD_2Cl_2}$ was used as a solvent. IR spectra were recorded on a Perkin–Elmer 180 spectrophotometer. Mass spectra were measured on a Jeol JMS D-100 mass spectrometer.

Vinyltriphenylsilane also undergoes metathetical conversion to evolve ethylene in 30% yield; the product was isolated and identified as 1,2-bis(triphenyl)silylethene containing substrate impurities.

Metathesis of vinyl(phenyl, methyl)silanes also proceeds in sealed glass ampoules under the increasing pressure caused by ethylene evolving in the ampoule. Under such conditions the corresponding 1,2-bis(silyl)ethenes were also synthesized, although sometimes in lower yield. The results of the preliminary series of vinyltri(phenyl, methyl)silane metathesis experiments are collected in Table 1. Product yields are based on GLC measurements (Chrom 5, 10% SE-30/Chromosorb P).

The results show that the formation of *trans*-1,2-bis(silyl)ethene is favoured in the presence of ruthenium complexes, although when rhodium catalyst is used an ($E$)/($Z$) ratio close to 1 is seen. It seems probable that *cis–trans* isomerization takes place, similarly to the metathesis reaction of vinylalkoxy-substituted silanes [5].

Table 1

Effect of ruthenium and rhodium catalyst on the yield and selectivity of 1,2 bis(silyl)ethenes (150 °C, 24 h, glass ampoules, air, no solvent, $[CH_2{=}CHSiMe_nPh_{3-n}]:[\text{catalyst}] = 100:1$)

$2Me_nPh_{3-n}CH{=}CH_2 \rightarrow Me_nPh_{3-n}SiCH{=}CHSiPh_{3-n}Me_n + CH_2{=}CH_2 \quad (n = 1, 2)$

| Catalyst | Yield (%) | $(E)/(Z)$ |
|---|---|---|
| *$CH_2{=}CHSiMe_2Ph$* | | |
| $RuCl_2(PPh_3)_3$ | 90 | 5/1 |
| $RuCl_3(PPh_3)_3$ | 80 | 5/1 |
| $[RuCl_2(CO)_3]_2$ | 90 | 8/1 |
| $RuH_2(PPh_3)_4$ | 70 | 5/1 |
| $RuHCl(PPh_3)_3$ | 80 | 5/1 |
| $Ru(acac)_3$ | 50 | 5/1 |
| $RhCl(PPh_3)_3$ | 20 | 1/1 |
| *$CH_2{=}CHSiMePh_2$* | | |
| $RuCl_2(PPh_3)_3$ | 70 | 10/1 |
| $Ru(acac)_3$ | 15 | - |
| $RuH_2(PPh_3)_4$ | 60 | 10/1 |
| $[RuCl_2(CO)_3]_2$ | 60 | 10/1 |
| $RhCl(PPh_3)_3$ | 20 | 1/1 |

The main reaction proceeds after an induction period, and the rate of metathesis changes in the following order: $CH_2{=}CHSiPh_3 < CH_2{=}CHSiPh_2Me < CH_2{=}CHSiMe_2Ph < CH_2{=}CHSi(OR)_3$.

In the reaction examined, many solvents were used as for example, alkanes, toluene and hexamethyldisiloxane. All of them inhibit the reaction. The effect is similar to that observed during metathesis of vinylalkoxy-substituted silanes [2,5]. It is noteworthy that an activating role of dioxygen is also observed in the present system; 72 hours heating of a mixture of $CH_2{=}CHSiMe_2Ph$ and $RuCl_2(PPh_3)_3$ at 130 °C in oxygen-free (argon) atmosphere gives no metathesis products.

These preliminary results on the metathesis of phenyl-substituted vinylsilanes suggest the mechanism of catalysis by ruthenium and rhodium complexes to be similar to that responsible for the reaction of vinylsilanes containing oxygenous substituents at silicon. Further synthetic, catalytic and mechanistic study may shed more light on the unusual metathetical conversion of vinylsilanes.

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