

Preliminary communication

METATHESIS OF VINYLTRIALKOXYSILANES

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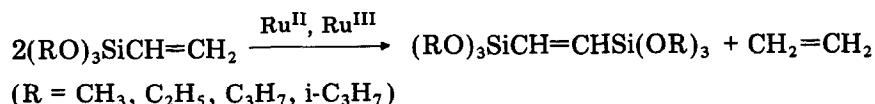
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Summary

Ruthenium(II) and ruthenium(III) complexes have been found to be the first efficient catalysts for the metathesis of organosilicon olefins. *trans*-1,2-Bis(triethoxysilyl)ethene is prepared via metathesis of vinyltriethoxysilane catalyzed by ruthenium complexes with a yield above 80%.

Metathesis of olefins is a well-known disproportionation reaction catalyzed by heterogeneous and homogeneous catalysts. It allows new internal olefins to be synthesized and can be applied to the modification of polymers [1,2]. Alkenylsilanes, like other unsaturated organosilicon compounds, do not easily participate in olefin metathesis. There are only two reports of vinyltrimethylsilanes undergoing metathesis on $\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalytic systems and giving the product $(\text{CH}_3)_3\text{SiCH}=\text{CHSi}(\text{CH}_3)_3$ with a 10–15% yield [3,4]. However, the applications of alkenylsilanes as molecular weight controlling agents in the polymerization of cyclic olefins and in the modification of existing polymers indicate their metathetic activity [5].

Our comprehensive examinations on the hydrosilylation of vinyltrialkoxysilanes by trialkoxysilanes, particularly in the presence of ruthenium complexes, show that besides the β -adduct $(\text{RO})_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{OR})_3$, an unsaturated product, $(\text{RO})_3\text{SiCH}=\text{CHSi}(\text{OR})_3$, is formed [6,7]. The latest product was proposed to be formed via a catalytic cycle including double dehydrogenative hydrosilylation of the vinylsilane [7]. However, the detection of ethylene in the reaction products has revealed that the competitive reaction of disproportionation (metathesis) of vinyltrialkoxysilanes occurs according to the general equation:



Preliminary investigations of the above reactions carried out in the absence of hydrosilanes show high yields of the metathesis product. Vinyltriethoxysilane (5×10^{-2} mol) refluxed for 24 h in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ (5×10^{-5} mol), as well as $\text{RuCl}_3(\text{PPh}_3)_3$, in air afforded the main product (1–2% of a by-product was detected) which was isolated and identified as 1,2-bis(triethoxysilyl)-ethene: yield 82% (for $\text{RuCl}_3(\text{PPh}_3)_3$: 83%), b.p. 122–125°C/4 mmHg, ^1H NMR (TMS): $\delta(\text{CH}_3)$ 1.18 ppm (t, 18H), $\delta(\text{CH}_2\text{O})$ 3.75 ppm (q, 12H), $\delta(\text{CH})$ 6.50 ppm (s, 2H). The ^1H NMR spectra were recorded on a Varian EM 360 (60 MHz) spectrometer.

The above data are consistent with those published previously for the compound isolated from the hydrosilylation product [6]; FT ^{13}C NMR (TMS): $\delta(\text{CH}_3)$ 18.25 ppm, $\delta(\text{CH}_2\text{O})$ 58.60 ppm, $\delta(\text{CH})$ 145.85 ppm. (The spectra were recorded on a Jeol FX 90Q spectrometer equipped with a Texas 980B computer system.)

The absence of the characteristic $\nu(\text{C}=\text{C})$ band in the region close to 1600 cm^{-1} in the IR spectra and the presence of a $\nu(\text{C}=\text{C})$ band at 1565 cm^{-1} in the Raman spectra (Jeol JRS-S1 laser Raman spectrometer) are strong evidence of the *trans*-isomer. The product of vinyltrimethoxysilane metathesis obtained under reflux (48 h) in the presence of $\text{RuCl}_3(\text{PPh}_3)_3$ was also isolated and was identified as 1,2-bis(trimethoxysilyl)ethene (10% of a by-product was detected): yield 57%, b.p. 76–80°C/4 mmHg, ^1H NMR (TMS) $\delta(\text{CH}_3\text{O})$ 3.51 ppm (s, 18H), $\delta(\text{CH})$ 6.50 ppm (s, 2H).

Metathesis of vinyltriethoxysilane also proceeds in sealed glass ampoules under the increasing pressure caused by the ethylene evolved in the closed reaction systems. Under such conditions, 1,2-bis(trialkoxysilyl)ethenes are also formed, though with a lower yield and larger amounts of the above-mentioned by-products. The latter are considered *cis*-isomers based on the IR (Perkin–Elmer 180 spectrophotometer) and ^1H NMR spectral data of the product mixtures, which usually exist in the ratio 5/1. The recorded $\nu(\text{C}=\text{C})$ stretching band (by IR spectroscopy) at 1600 cm^{-1} (w), as well as the appearance of a new signal ($\delta(\text{CH})$ 6.63 ppm) in the ^1H NMR spectrum of the product mixture, seems to be convincing evidence of the existence of the *cis*-isomer in addition to the *trans*-product. The results of the preliminary series of vinyltriethoxysilane metathesis are compiled in Table 1. The product yields are based on GLC measurements (Chrom 4, 10% SE-30/Chromosorb P).

TABLE 1

EFFECT OF THE RUTHENIUM CATALYST ON THE YIELD OF 1,2-BIS(TRIETHOXSILYL)ETHENE (120°C, 24 h, glass ampoules, air, no solvent; $[\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_5)_3]/[\text{catalyst}] = 5 \times 10^2$).

$2(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}=\text{CH}_2 \rightarrow (\text{C}_2\text{H}_5\text{O})_3\text{SiCH}=\text{CHSi}(\text{OC}_2\text{H}_5)_3 + \text{CH}_2=\text{CH}_2$		
Catalyst	Yield (%)	<i>trans/cis</i> product ratio
$\text{RuCl}_2(\text{PPh}_3)_3$	69 (35) ^a	5/1 (5/1) ^a
$\text{RuCl}_3(\text{PPh}_3)_3$	63 (47) ^a	5/1 (1.2/1) ^a
$\text{RuHCl}(\text{PPh}_3)_3$	44	6/1
$\text{RuH}_2(\text{PPh}_3)_4$	42	6/1
$\text{RuCl}_2(\text{CO})_3$	49	6/1
$\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2$	trace	—
$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$	38	5/1
$\text{Ru}(\text{acac})_3$	51	4/1

^a Argon.

Metathesis of vinyltrimethoxysilane furnished, under the same conditions ($\text{RuCl}_2(\text{PPh}_3)_3$), the product in a 58% yield.

Metathesis of vinyltripropoxysilanes leads to the formation of several by-products in addition to the main one. Other vinyl-substituted silanes such as vinyltri-(chloro,alkyl)silanes and vinylalkoxy(alkyl)silanes which underwent the reaction in the presence of ruthenium complexes did not give any metathesis products under the conditions employed.

A further study in the field of metathesis of organosilicon olefins is to be made.

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