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Preliminary communication

METATHESIS OF VINYLTRIALKOXYSILANES

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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 MoO_3/Al_2O_3 and Re_2O_7/Al_2O_3 catalytic systems and giving the product $(CH_3)_3SiCH{=}CHSi(CH_3)_3$ 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 $(RO)_3SiCH_2CH_2Si(OR)_3$, an unsaturated product, $(RO)_3SiCH{=}CHSi(OR)_3$, 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:

$$2(RO)_3SiCH{=}CH_2 \xrightarrow{Ru^{II},\ Ru^{III}} (RO)_3SiCH{=}CHSi(OR)_3 + CH_2{=}CH_2$$

$(R = CH_3,\ C_2H_5,\ C_3H_7,\ i\text{-}C_3H_7)$

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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 $RuCl_2(PPh_3)_3$ (5×10^{-5} mol), as well as $RuCl_3(PPh_3)_3$, 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 $RuCl_3(PPh_3)_3$: 83%), b.p. 122—125°C/4 mmHg, ^{1}H NMR (TMS): $\delta(CH_3)$ 1.18 ppm (t, 18H), $\delta(CH_2O)$ 3.75 ppm (q, 12H), δ(CH) 6.50 ppm (s, 2H). The ^{1}H 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): $\delta(CH_3)$ 18.25 ppm, $\delta(CH_2O)$ 58.60 ppm, δ(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 ν(C=C) band in the region close to 1600 cm^{-1} in the IR spectra and the presence of a ν(C=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 $RuCl_3(PPh_3)_3$ 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, ^{1}H NMR (TMS) $\delta(CH_3O)$ 3.51 ppm (s, 18H), δ(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 ^{1}H NMR spectral data of the product mixtures, which usually exist in the ratio 5/1. The recorded ν(C=C) stretching band (by IR spectroscopy) at 1600 cm^{-1} (w), as well as the appearance of a new signal (δ(CH) 6.63 ppm) in the ^{1}H 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(TRIETHOXYSILYL)ETHENE (120°C, 24 h, glass ampoules, air, no solvent; $[CH_2=CHSi(OC_2H_5)_3]/[\text{catalyst}] = 5 \times 10^2$).

$2(C_2H_5O)_3SiCH=CH_2 \rightarrow (C_2H_5O)_3SiCH=CHSi(OC_2H_5)_3 + CH_2=CH_2$

Catalyst	Yield (%)	*trans*/*cis* product ratio
$RuCl_2(PPh_3)_3$	69 (35)[a]	5/1 (5/1)[a]
$RuCl_3(PPh_3)_3$	63 (47)[a]	5/1 (1.2/1)[a]
$RuHCl(PPh_3)_3$	44	6/1
$RuH_2(PPh_3)_4$	42	6/1
$RuCl_2(CO)_3$	49	6/1
$RuCl_3(NO)(PPh_3)_2$	trace	—
$RuCl_3 \cdot n\ H_2O$	38	5/1
$Ru(acac)_3$	51	4/1

[a] Argon.

Metathesis of vinyltrimethoxysilane furnished, under the same conditions ($RuCl_2(PPh_3)_3$), 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 vinyldialkoxy(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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