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Synthesis of Linear and Cyclic Unsaturated Carbosiloxanes via Catalytic Condensation of Divinyltetramethyldisiloxane

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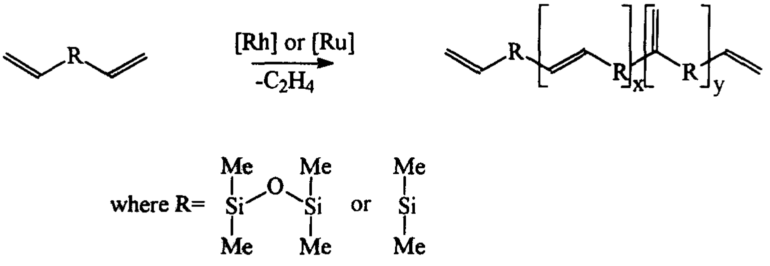
Abstract: Rhodium and ruthenium complex catalyzed condensation of two molecules of divinyltetramethyldisiloxane provides a facile route to cyclic and linear unsaturated carbotetrasiloxanes. © 1997 Elsevier Science Ltd.

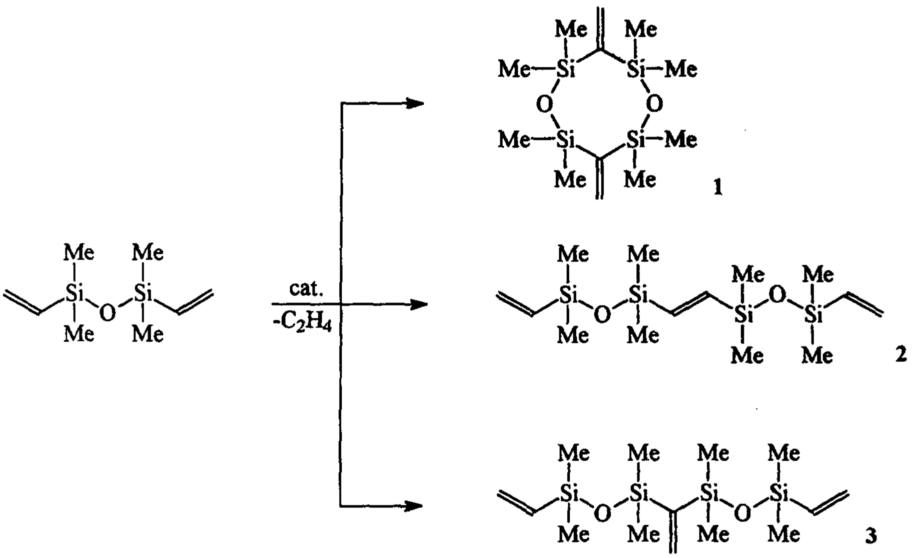
Ruthenium and rhodium complexes appear to be the first effective catalysts for Acyclic Diene Polycondensation (ADPOL) of divinylsubstituted silanes[1] (Mw = 1510, Mw/Mn = 1,19) and siloxanes (Mn=1815, Mw/Mn = 1.16)[2] to give poly(silylene-vinylylene)s and poly(siloxylene-vinylene)s, respectively, according to the following scheme:



The polymers contain chains with trans isomers as well as occasional 1,1-disilyl(disiloxyl)isomers.

Contrary to the Acyclic Diene Metathesis (ADMET) Polymerization developed by Wagener et.al. also for dialkenyl (but except divinyl-) substituted organosilicon compounds[3,4], the reaction occurs via splitting of C_{vinyl}-H bond (non-metathetical conversion) instead of the cleavage of the C=C bond (metathesis). Recent experiments on the insertion of ethylene[5] and vinylsilanes[6] into Ru-Si bond have brought convincing evidence for such a catalytic mechanism.

The ADPOL proceeds via preliminary formation of cyclic and linear oligomers (dienes, trienes, etc.) However, in the beginning of the process, under mild conditions, a catalytic condensation of two molecules of divinyltetramethyldisiloxane (DVTMDS) takes place, giving the following products:



Depending on the catalyst used (Table 1) products I and II can be selectively synthesized with high yields. In the presence of phosphine complexes of ruthenium, product III was isolated from the mixture of products whose distribution can be illustrated by exemplary GLC chromatogram (Fig 1). The structures were determined on the basis of spectroscopic data and GC-MS analysis[7].

Table 1. The Effect of the Catalyst on the Yield and Selectivity of Linear and Cyclic Unsaturated Carbosiloxanes

Catalyst	Monomer conversion	Yield (selectivity of dimers) [%]			
	[%]	1	2	3	oligomers
$[RhCl(cod)]_2$	90	40 (95)	2 (5)	traces	48
$RhH(CO)(PPh_3)_3$	82	7 (15)	25 (48)	19 (37)	31
$RuHCl(CO)(PPh_3)_2$	68	8 (14)	16 (35)	27 (51)	17
$RuCl_2(PPh_3)_3$	65	6 (11)	16 (29)	33 (60)	10
$RuCl_2(CO)_3$	75	traces	49 (96)	2 (4)	24

Synthesis reaction conditions: temperature = 80 °C; reaction time = 48 h; molar ratio monomer/catalyst = 100

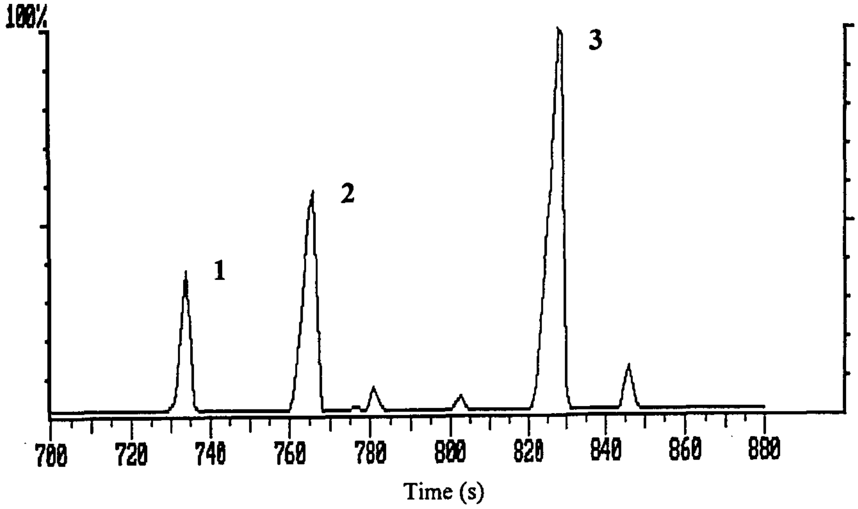


Fig. 1 GC chromatogram of a mixture of (cyclic **1** and linear **2**, **3**) carbosiloxanes obtained in the presence of $RuCl_2(PPh_3)_3$. Reaction conditions: temperature, 80°C; time, 48h; molar ratio (monomer/cat.), 100

It has been recently reported that **II** can be synthesized (in the form of chelate ligand) by co-condensation of nickel vapour onto a liquid nitrogen-cooled matrix of divinyltetramethyldisiloxane to yield (twelve-membered triene)nickel(0) complex[8].

Previous catalytic and mechanistic examinations on the disproportionation (metathesis) of monovinylsubstituted silanes[6,9] allowed utilization of rhodium(I) complexes as well as ruthenium phosphine and non-phosphine complexes as catalysts in this synthesis. Facile removal of the monomer by predistillation and final separation of the higher oligomers from the mixture of dimers by vacuum distillation of the latter makes this method an excellent route for the synthesis of **I** and **II** in the presence of $[RhCl(cod)]_2$ and $RuCl_2(CO)_3$, respectively. Product **III** can be obtained only in the presence of phosphine complexes of ruthenium and it is accompanied by both **I** and **II** compounds. Nevertheless, it can also be easily isolated and characterized.

In conclusion, we describe here a facile synthesis of a new type of linear and cyclic unsaturated carbosiloxanes which can be effectively and commonly used as monomers and particularly as chelate ligands of transition metals **I-III**.

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7. The typical experimental procedure for the synthesis of **I** - **III** is described below:
   5.00 ml (4.07g, 21.8 mmol) of divinyltetramethyldisiloxane and 2.18x10-4 mol of a catalyst were placed in reaction system and heated for 48h at 80 °C. After reaction the soluble part of the catalyst was removed on a SiO_2 column using hexane as mobile phase. The dimers were finally isolated from the mixture of oligomers by vacuum distillation to give 1.61g (40%) of **I** - 2,2,4,4,6,6,8,8-octamethyl-1,5-dimethylene-3,7-dioxa-2,4,6,8-tetrasilacyclooctane (cyclocarbosiloxane) (catalyst $[RhCl(cod)]_2$), bp = 84 °C(1mm Hg), ^1H NMR (300MHz, C_6D_6) δ (ppm): 0.28 (s, $-CH_3$); 6.19 (s, $=CH_2$); ^{13}C NMR (75 MHz, C_6D_6) δ (ppm): 1.16 (CH_3); 139.97 ($=CH_2$ at quaternary carbon atom); 156.61 (quaternary carbon atom) or 1.96g (49%) of **II** - E-1,2 bis-[(vinyltetramethyl)siloxy]ethene (catalyst $RuCl_2(CO)_3$), bp = 88°C(1mm Hg), ^1H NMR (300MHz, C_6D_6) δ (ppm): 0.21 (s, $-CH_3$ at terminal silicon atoms); 0.23 (s $-CH_3$ at internal silicon atoms); 5.85 (dd, $=CH_2$); 6.21 (dd, $=CH$ terminal); 6.86 (s, $=CH$ internal); ^{13}C NMR (75 MHz, C_6D_6) δ (ppm): 1.20 (CH_3 at terminal silicon atoms); 1.35 (CH_3 at internal silicon atoms); 132.40 ($=CH_2$); 140.14 ($=CH$ terminal); 151.27 ($=CH$ internal) or 2.22g (55%) mixture of **I**, **II**, and **III** (catalyst $RuCl_2(PPh_3)_3$), ^1H NMR of **III** - 1,1-bis[(vinyltetramethyl)disiloxy]ethene (300MHz, C_6D_6) δ (ppm): 0.15 (s, $-CH_3$ at terminal silicon atoms); 0.17 (s, $-CH_3$ at internal silicon atoms); 5.78 (dd, $=CH_2$); 6.14 (dd, $=CH$ terminal); 6.41 (s, $=CH_2$ at quaternary carbon atom); ^{13}C NMR of **III** (75 MHz, C_6D_6) δ (ppm): 0.61 (CH_3 at terminal silicon atoms); 1.94 (CH_3 at internal silicon atoms); 131.87 ($=CH_2$); 139.74 ($=CH$ terminal); 141.30 ($=CH_2$ at quaternary carbon atom); 154.95 (quaternary carbon atom).
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