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Dehydrogenative polymerization of disilanes catalysed by titanocene and zirconocene complexes. A novel route to oligo- and poly-silanes

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Abstract

Polymerization of $\text{Me}_3\text{SiSiHMe}_2$, $\text{Me}_2\text{HSiSiHMe}_2$ and $\text{MeH}_2\text{SiSiH}_2\text{Me}$ takes place readily in the presence of Cp_2MR_2 catalyst ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{M} = \text{Ti, Zr}$; $\text{R} = \text{Me, }^n\text{Bu}$) in the absence of a solvent ("polymerization in bulk") to give a mixture containing trisilanes, tetrasilanes, pentasilanes, higher oligosilanes and polysilanes. Depending on the reaction conditions different proportions of linear oligo- and poly-silanes are obtained. $\text{MeH}_2\text{SiSiH}_2\text{Me}$ also yields branched oligo- and poly-silanes. Polymerization of $\text{MeH}_2\text{SiSiH}_2\text{Me}$ "in bulk" in the presence of a catalytic amount of Cp_2MR_2 ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{M} = \text{Ti, Zr}$; $\text{R} = \text{Me, }^n\text{Bu}$) leads to a new type of polysilane polymer, poly(methylsilane), $(\text{MeSiH}_x)_n$, which is thought to be the first organosilicon "living polymer". $\text{MeH}_2\text{SiSiH}_2\text{Me}$ is also polymerized in inert solvents in the presence of Cp_2MR_2 ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{M} = \text{Ti, Zr}$; $\text{R} = \text{Me, }^n\text{Bu, Ph}$) catalysts.

Dehydrogenative polymerization of monosilanes catalysed by metallocene has been described previously [1,2]. Dimethyltitanocene and dimethylzirconocene [2] were the most effective catalysts previously examined.

The reactivity of alkyl- and aryl-silanes depends on the number of hydrogen atoms on silicon. Primary alkyl- and aryl-silanes (RSiH_3) undergo dehydrogenative polymerization at room temperature, whereas secondary alkyl- and aryl-silanes (R_2SiH_2) require vigorous conditions (e.g. reflux temperature). In particular phenylsilane and its derivatives have been thoroughly investigated [2,3,7]. Tertiary alkyl- and aryl-silanes (R_3SiH) do not react at all, and in consequence triethylsilane can be used as an inert solvent for other silanes.

Dehydrogenative polymerization of disilanes has not been previously studied. In the present work it was found to show unexpectedly large differences from that of monosilanes. In contrast to monosilanes, $\text{Me}_2\text{HSiSiHMe}_2$ (tertiary Si–H) readily undergoes polymerization in benzene solution in the presence of a catalytic amount of Cp_2TiMe_2 even at room temperature. Only linear oligosilanes with chain lengths up to 5 Si-atoms were found. At higher temperatures (reflux) the yield of higher oligomers was increased. The interesting feature is that some oligosilanes with an odd-numbered amount of silicon atoms are formed. Evidently the reaction follows a

Table 1

Products from catalysis by Cp_2TiMe_2

Silane	x (RT)	x (MP)	x (130 °C, 2 days)	x (MP)	Polymer
$\text{Me}_3\text{SiSiHMe}_2$	3, 4, 5, 6, 7 ^a	3, 4	3, 4, 5, 6, 7, 8, 9, 10	4, 5, 6	linear, liquid
$\text{Me}_2\text{HSiSiHMe}_2$	3, 4, 5, 6, 7	3, 4	3, 4, 5, 6, 7, 8, 9, 10	3, 4, 5, 6	linear, liquid
$\text{MeH}_2\text{SiSiH}_2\text{Me}$	3, 4, 5, 6, 7, 8 ^b				linear/branched liquid ^b

RT = room temperature; MP = main products; x = number of Si-atoms in each formed polymer; ^a 35 °C; ^b after 2 hours.

pathway involving Si-Si bond cleavage in accord with Tilley's [4-6] suggestion for the dehydrogenative polymerization of silanes.

Other disilanes were found to undergo similar reactions. Polymerization of $\text{MeH}_2\text{SiSiH}_2\text{Me}$ in benzene was carried out at room temperature with Cp_2MR_2 (Cp = C_5H_5 ; M = Ti, Zr; R = Me, ⁿBu, Ph) as catalysts and was found to give linear and branched oligosilanes. At the reflux temperature solid polymers are produced by Zr catalysts (Cp_2ZrMe_2 , $\text{Cp}_2\text{Zr}^i\text{Bu}_2$) and oily liquids by Ti catalysts.

The disilanes $\text{Me}_3\text{SiSiMe}_2\text{H}$ and $\text{Me}_2\text{HSiSiHMe}_2$ were also found to undergo polymerization in inert solvents, and the results were the same as in polymerization without solvent (polymerization "in bulk"). This polymerization "in bulk" starts after an induction period that varies from a few minutes to about two hours, depending on the nature of the disilane and the concentration of the reactants. After the induction period there is a rapid change in colour that marks the beginning of the polymerization. If the reaction mixture is heated immediately after the induction period, larger proportions of higher oligosilanes are formed. Polymerization in the absence of solvent afforded polysilanes with a higher degree of polymerization than did polymerization in solution.

The following order of reactivity was found (with Cp_2MMe_2 (M = Ti, Zr) catalysts): $\text{MeH}_2\text{SiSiH}_2\text{Me} > \text{Me}_2\text{HSiSiHMe}_2 > \text{Me}_3\text{SiSiMe}_2\text{H}$. $\text{Me}_3\text{SiSiMe}_3$ does not react under similar conditions.

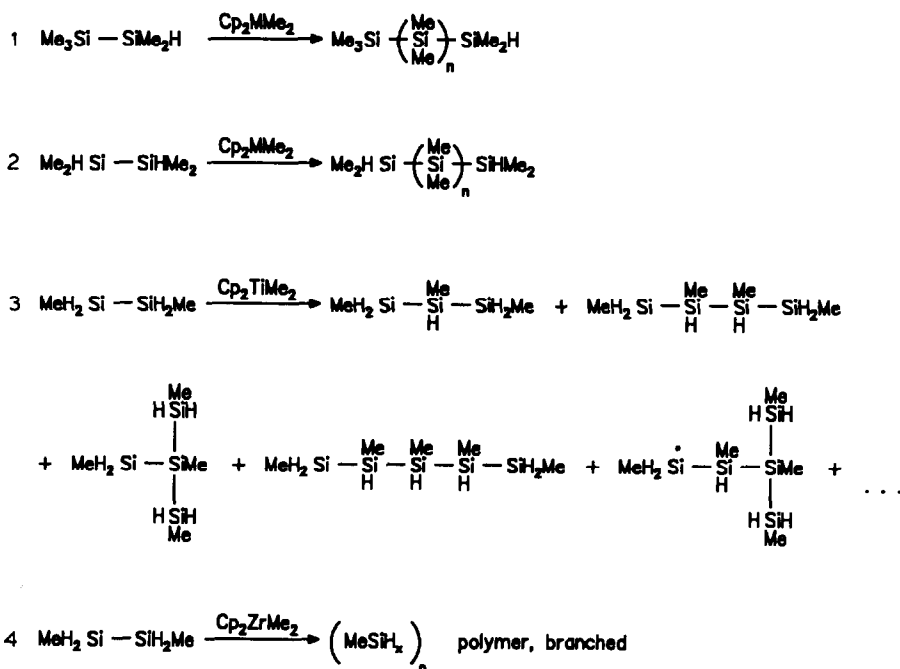
Tables 1 and 2 summarize the results of the polymerization; polysilanes were detected by GLC and GLC-MS, and by ²⁹Si-NMR spectroscopy. There is no reason to doubt that silanes with $x > 10$ were also formed in traces in the polymerization of pentamethyldisilane and 1,1,2,2-tetramethyldisilane, but their detection by GLC is rather difficult.

The tertiary silicon hydrides $\text{Me}_3\text{SiSiHMe}_2$ as well as $\text{Me}_2\text{HSiSiHMe}_2$ (see reactions 1 and 2 in Scheme 1) give linear polysilanes ("in bulk" or with a solvent), whereas $\text{MeH}_2\text{SiSiH}_2\text{Me}$ (reactions 3 and 4) gives linear and branched polysilanes.

Table 2

Products from catalysis by Cp_2ZrMe_2 (abbreviations see Table 1)

Silane	x (RT)	x (130 °C, 1 day)	x (MP)	Polymer
$\text{Me}_3\text{SiSiHMe}_2$	no polymerization	3, 4, 5, 6, 7, 8	2, 3, 4	linear, liquid
$\text{Me}_2\text{HSiSiHMe}_2$	no polymerization	3, 4, 5, 6, 7, 8, 9	4, 5, 6	linear, liquid
$\text{MeH}_2\text{SiSiH}_2\text{Me}$	vigorous reaction, endothermic			branched solid



Scheme 1. Polymerization "in bulk"; M = Ti, Zr.

In the presence of the Zr catalyst, the disilanes $\text{Me}_3\text{SiSiMe}_2\text{H}$ and $\text{Me}_2\text{HSiSiHMe}_2$ undergo no polymerization during several hours' stirring at room temperature, but in both cases a white precipitate separates from the colourless solution; presumably Zr-silyl (previously unknown) compounds are formed. At higher temperatures polymerization occurs.

The course of the polymerization reactions of 1,2-dimethyldisilane in the presence of Cp_2TiR_2 or Cp_2ZrR_2 ($\text{R} = \text{Me}, {}^n\text{Bu}$) is rather unusual. With the Ti catalyst polymerization takes place very slowly, during several weeks. After two hours linear and branched polysilanes up to 8 silicon atoms are detected (eq. 3). After about three weeks a highly viscous, liquid dark green poly(methylsilane) $(\text{MeSiH}_x)_n$ is formed and about two weeks later the polysilane polymer becomes solid. When the solid polysilane is added to pure 1,2-dimethyldisilane further polymerization takes place very slowly, over several weeks, and again a solid poly(methylsilane) is formed. This polymer is stable at room temperature but pyrophoric in air.

The polymerization of 1,2-dimethyldisilane in the presence of the Zr catalyst is unusually vigorous (polymerization is complete within ca. 0.5 h) and slightly endothermic. When the orange solid, highly polymeric poly(methylsilane) $(\text{MeSiH}_x)_n$ is added to pure 1,2-dimethyldisilane, further polymerization takes place vigorously after an induction period of a few minutes and solid orange poly(methylsilane) is again formed. This polymer is also stable at room temperature but pyrophoric in air. These observations lead to the conclusion that this polymer is a "living polymer". Living polymers have been known only in organic chemistry up to now.

Polymerization of other disilanes ($\text{Me}_3\text{SiSiH}_3$, $\text{Me}_3\text{SiSiH}_2\text{Me}$, $\text{Me}_2\text{HSiSiH}_2\text{Me}$, $\text{MeH}_2\text{SiSiH}_3$, $\text{Ph}_3\text{SiSiH}_3$ and $\text{PhH}_2\text{SiSiH}_2\text{Ph}$) with Cp_2MR_2 catalysts ($\text{M} = \text{Ti}, \text{Zr}$;

R = Me, ⁿBu; Cp = C₅H₅ or Cp = Cp* = C₁₀H₁₅) also yield polysilanes. An account of these will be published later.

Preparation of poly(methylsilane) (MeSiH_x)_n

MeH₂SiSiH₂Me (5 ml) is placed in a 25 ml two-necked flask (flushed with argon) fitted with a reflux condenser, and 0.5 mol% Cp₂ZrMe₂ is added. The catalyst quickly dissolves to give a colourless solution. About 15 minutes later the solution becomes slightly yellow and a slight gas evolution begins (CH₄). In the next few seconds the gas evolution accelerates, the colour changes to orange, and gas evolution (H₂) increases to become very violent. A few minutes later the solution becomes more and more viscous until it can no longer be stirred. At this point (gas evolution having meanwhile decreased) the viscous mixture swells like a baking cake. A little time later the "cake" congeals to a glassy, very elastic, orange mass. Further slight gas evolution is observed for a few minutes. After about 30 minutes the (slightly endothermic) reaction is complete. The elasticity of the "cake" decreases, and about two days later the "cake" is hard.

This unusual polymer is stable at room temperature but pyrophoric in the air. The Si : C ratio is 1 : 1 and the Si : H ratio is 1 : 0.58 (MeSiH_{0.58}). The low H : Si ratio indicates cross-linking. The polymer is insoluble in THF, ether, benzene, petroleum ether and acetone. The polymer decomposes at higher temperatures without melting.

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