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A systematic analysis of the structure-reactivity trends for some 'cation-like' early transition metal catalysts for dehydropolymerization of silanes [1,2]

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Abstract

The use of 'cation-like' metallocene combination catalysts $(Cp'_2MCl_2-2BuLi-B(C_6F_5)_3$; $Cp' = \eta^5$-cyclopentadienyl, or substituted η^5-cyclopentadienyl; M = Ti, Zr, Hf, U) for dehydropolymerization of silanes significantly improves the polymer molecular weight. For example, under the same conditions a $Cp(C_5Me_5)ZrCl_2-2BuLi$ catalyst gives $M_n = 1890$, while a $Cp(C_5Me_5)ZrCl_2-2BuLi-B(C_6F_5)_3$ gives $M_n = 7270$. The influence of various factors (steric and electronic effects of the cyclopentadienyl ligands, the nature of the metal, temperature, solvent, concentration and structure of silane) on the build-up of polysilane chains are systematically analyzed.

Keywords: Silicon; Zirconocene; Polysilanes; Cationic; Catalysis; Group 4

1. Introduction

Synthetic routes to polysilanes are of scientific and technological interest as these polymers have a great potential in the field of advanced materials for electronics and integrated optics [2-7]. Wurtz-like coupling of halosilanes with molten alkali metals is currently the most useful industrial method [4-7]. An alternative, less hazardous synthetic strategy is a catalytic dehydropolymerization of silanes discovered by Harrod and coworkers (Eq. (1)) [8]. Transition metal catalysts offer some control over the stereochemistry of the polymeric products and the cyclic/linear chain selectivity [9-12], as well as a greater tolerance towards functional groups, which can be incorporated in the polymer [13-15]. The major drawback of this route is the low molecular weight of polymers [12] which affects mechanical and optical properties. A considerable improvement in polysilane molecular weight has been achieved over the past decade by a combination of an extensive blind screening of various neutral early transition metallocenes [12,16] and studies of the reaction intermediates and mechanisms [8,17-20].

$$PhSiH_3 \xrightarrow{\text{catalyst}} H\left[\begin{array}{c} Ph \\ | \\ Si \\ | \\ H \end{array}\right]_n H + H_2$$

(1)
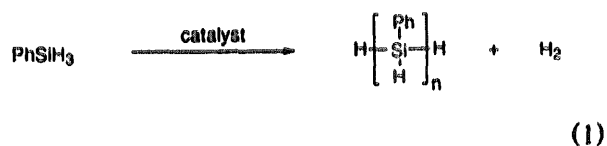
Although the mechanism of the dehydrocoupling reaction is still under discussion, the most widely accepted one is a constant oxidation state σ-bond metathesis [12,19,20] with a transition state similar to that postulated for Ziegler-Natta olefin polymerization. Much of the progress in the field has been based on the results of experimental measurements and theoretical calculations performed for the Ziegler-Natta catalysts.

The highly active olefin polymerization catalysts are believed to be 14-electron cationic Cp_2MR^+ complexes of Group 4 or actinide metals or the neutral $Cp_2M'R$ isoelectronic compounds of Group 3 or lanthanide metals [21,22]. Their activity is attributed to the high degree of electronic and steric unsaturation, which should be an

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[1] Part of this work has appeared as a preliminary communication; see Ref. [1].

[2] Dedicated to Professor Robert Corriu in recognition of his outstanding contributions to organosilicon chemistry and for the inspiration his work has given us.

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important factor for dehydrogenative silane polymerization as well. There are a number of strategies to synthesize cationic Ziegler–Natta catalysts, which can be used in polymerization of silanes. The earlier versions of those catalysts contain a large excess of alkylaluminoxane [22], the presence of which might lead to unwanted side reactions in silane polymerization. Recently developed and well-characterized homogeneous cationic and 'cation-like' Group 4 and actinide metallocene catalysts for olefin polymerization [23,24], which make use of stoichiometric amounts of $B(C_6F_5)_3$ or $[Ph_3C]^+[BR_4]^-$ (where $[BR_4]^-$ is arylborate or carborane) as a cocatalyst, also proved to be active silane dehydrocoupling catalysts [1,25]. Furthermore, the catalysts containing the $[BR(C_6F_5)_3]^-$ anion are often reluctant to form crystals, producing oils instead [26–28]; this is an important property, as the dehydropolymerization reaction proceeds in a low polar and highly viscous medium where solubility could be a limiting factor. Although Imori and Tilley reported no improvements using a $Cp_2'MR_2$–$[NHR_3]^+[BR_4]^-$ system [25], in our experience the $Cp_2'MR_2$–$B(C_6F_5)_3$ catalysts have certain advantages over neutral $Cp_2'MR_2$ catalysts [1]. The above-mentioned considerations prompted us to investigate the factors influencing performance of $Cp_2'MR_2$–

$B(C_6F_5)_3$ and $[Ph_3C]^+[BR_4]^-$ systems towards dehydropolymerization in more detail.

2. Results and discussion

The results of a number of dehydrocoupling reactions are summarized in Tables 1 and 2. A conventional way to evaluate dehydropolymerization catalyst performance is to compare molecular weights of the final products. Molecular weight distributions were estimated by gel permeation chromatography (GPC), calibrated vs. polystyrene standards. At high conversion, the molecular weight of a polysilane sample has a bimodal distribution with the low molecular weight fraction being a mixture of cyclic silanes (approximately 5–8 Si based on the GPC retention time) and a high molecular weight fraction assumed to be linear polymers. In Tables 1 and 2, only the molecular weights of the high molecular weight fractions are reported, since the low molecular weight fraction always has the same weight within the accuracy of the measurements. Furthermore, averaging the weights of the two fractions often masks the actual trends in the linear chain growth and could be misleading, especially when the weights differ by two orders of

Table 1
Some results for the polymerization of phenylsilane in toluene [a]

Entry	Catalyst	Time	Conversion (%)	M_w	M_n	Linear %
1	Cp_2ZrCl_2–2BuLi	0.2 h	95	670	600	n.d.
2		10 d	> 99	2450	2080	55
3	Cp_2ZrCl_2–2BuLi–$B(C_6F_5)_3$	4 d	> 99	3800	2770	85
4		10 d	> 99	4320	3010	85
5	$(MeCp)_2ZrCl_2$–2BuLi	3 d	> 99	2400	1800	60
6	$(MeCp)_2ZrCl_2$–2BuLi–$B(C_6F_5)_3$	4 h	70	1100	810	80
7		3 d	> 99	4650	3180	90
8		10 d	> 99	5150	2840	90
9	$(Me_5C_5)_2ZrCl_2$–2BuLi–$B(C_6F_5)_3$ [b]	0.5 h	10		Dimer	
10		20 h	80		Dimer and trimer	
11		10 d	85		Dimer, trimer and tetramer	
12		10 d + 1 d [c]	> 99		Mostly trimer and tetramer	
13	Cp_2ZrMe_2–$B(C_6F_5)_3$	4 d	< 5	< 500	< 500	n.d.
14	Cp_2ZrMe_2–$B(C_6F_5)_3$	10 d [c]	> 99	2080	1290	65
15	$B(C_6F_5)_3$ [d]	0	n.a.	2450	2080	50
16		8 d	n.a.	2450	2080	50
17	Cp_2TiCl_2–2BuLi–$B(C_6F_5)_3$	1 d	80	780	510	n.d. [e]
18		10 d	95	1050	620	n.d. [e]
19	Cp_2HfCl_2–2BuLi–$B(C_6F_5)_3$	1 d	10	< 500	< 500	n.d.
20		10 d	95	1220	710	60
21	$(Me_5C_5)_2UCl_2$–2BuLi–$B(C_6F_5)_3$ [b]	2 h	20		Mostly dimer	
22		10 d	40	< 500	< 500	n.d.

[a] Reactions at 20°C in a 1:1 monomer–toluene ratio (v/v), and a catalyst concentration of 5 mol%, except where stated otherwise. The molecular weights (Da) are calibrated with respect to polystyrene standards and the values are estimated to be reliable to within ±5%. Where possible the low molecular weight cyclic products were excluded from the calculations of M_w and M_n. MeCp = methylcyclopentadienyl. [b] In this case, product analysis is based on ^1H NMR spectra. [c] The temperature is 60°C. [d] This is a blank reaction in which the substrate was a pre-prepared polyphenylsilane. It establishes that the polymer is inert to the presence of the borane alone. [e] A considerable amount of Ph_2SiH_2 was detected.

magnitude. For cases where the bimodal distribution is not well resolved, there is a certain ambiguity in determining the cut-off point, and thus the calculated molecular weights are somewhat arbitrary. When the molecular weights were too low to show any evidence of the second distribution mode, the entire peak area was used in the calculations and the ratio for the linear vs. cyclic oligomers was not determined. These molecular weights are not strictly comparable with the weights of the linear fractions alone. The apparent weight of the latter is significantly higher, although the actual difference between the samples might be almost negligible. For example, samples with a linear polymer fraction of an $M_w = 900$, $M_n = 700$, or a nonresolved cyclic and linear fraction of $M_w < 500$, $M_n < 500$ give essentially identical chromatograms.

The data in Tables 1 and 2 show that the presence of $B(C_6F_5)_3$ leads to a considerable improvement in the molecular weights and yields of linear polymer produced (entries 1–8 of Table 1; entries 1–3 and 10–14 of Table 2, Figs. 1(a) and 1(b)). Perhaps, the most important feature of this catalytic system is that there is no depolymerization reaction observed. This contrasts with most neutral metallocene catalysts which were reported to depolymerize the long linear chains to produce cyclic compounds [12]. For any polycondensation reaction, high molecular weights can only be achieved at extremely high (higher than 99.9%) conversions, and it is thus mandatory to have the reaction going exclusively in one direction.

$B(C_6F_5)_3$ alone does not react either with monomer or with pre-formed silane polymer (entries 15 and 16 of Table 1) on the time scale of a typical polymerization experiment (less then 24 h for a monomer, 10 days for a polymer), although the broadening of the ^1H NMR resonances indicates some kind of complexation with $RSiH_3$. When the monomer was exposed to $B(C_6F_5)_3$ for 8 days, decomposition into a mixture of unidentified products occurred. However, in most polymerization experiments the monomer was more then 99% consumed within the first 24 h of the reaction, which sets an upper limit on its exposure to $B(C_6F_5)_3$. $[Ph_3C]$-$[B(C_6F_5)_4]$ is more reactive and causes redistribution of silane monomers, vide infra.

2.1. Choice of the central metal

A number of Cp'_2MR_2 metallocenes (Cp'_2 = two substituted cyclopentadienyl ligands or a bridged substituted bis-cyclopentadienyl moiety, M = Ti, Zr, Hf and U) were screened but only zirconocenes and hafnocenes exhibited selectivity for linear high molecular weight products. Uranocene and titanocene have a very low efficiency, both in terms of conversion of the starting monomer and the molecular weight of the final product (entries 17, 18 and 21, 22 of Table 1). The color of the
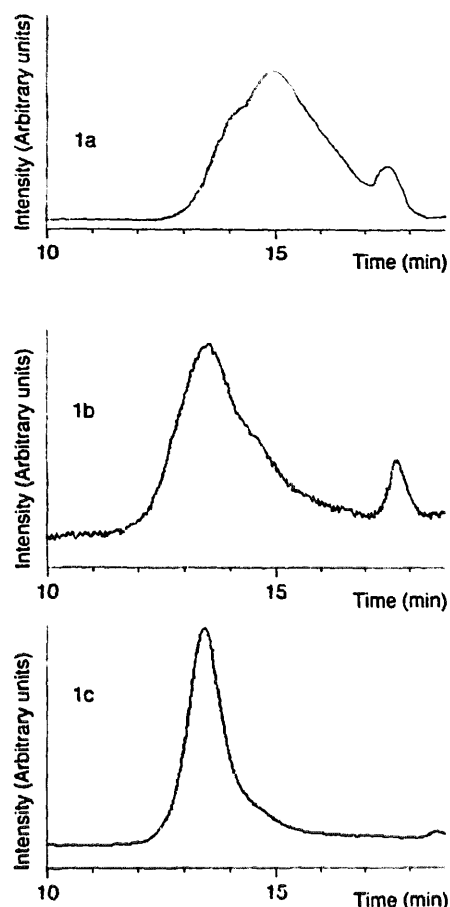

Fig. 1. GPC traces for oligophenylsilane samples. (a) obtained with Cp_2ZrCl_2-$2BuLi$-$B(C_6F_5)_3$ catalyst after 10 days; (b) obtained with $Cp(Me_5C_5)ZrCl_2$-$2BuLi$-$B(C_6F_5)_3$ catalyst after 1 day; (c) improved by fractional precipitation from toluene-petroleum ether.

reaction mixtures indicates reduction of M^{IV} to M^{III}. Zircono- and hafnocene catalytic systems accumulate large amounts of M^{III} only at the late stages, when most of the primary and secondary SiH bonds have been consumed. The reduced forms of uranium and titanium catalysts, however, accumulate in the very early stages of polymerization, which can be attributed to the lower reduction potentials for these metals [29]. There is no final agreement on the mechanism of the dehydrocoupling reaction, but both the constant oxidation state σ-bond metathesis [12] and the one-electron oxidative addition–reductive elimination mechanisms (Figs. 2 and 3 respectively) are consistent with the fact that accumulation of the reduced M^{III} species indicates that the catalytic cycle is not functioning properly. Although there is no a priori reason why M^{III} species could not undergo σ-bond metathesis, there is at the moment no compelling evidence that they do. Further, the olefin polymerization σ-bond metathesis mechanism regards reduction as an abortive side reaction [30,31]. In contrast, in the case of one-electron oxidative addition–reductive elimination mechanisms, formation of M^{III} is an

Table 2

Some results for the polymerization of phenylsilane in neat monomer [a]

Entry	Catalyst	Time	Conversion (%)	M_w	M_n	Linear (%)
1	Cp$_2$ZrCl$_2$–2BuLi	1 d	> 99	3000	1860	75
2		10 d	> 99	2930	1880	75
3	Cp$_2$ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	10 d	> 99	4990	2670	90
4	(MeCp)$_2$ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	10 d	> 99	5640	3020	90
5	(Ind)$_2$ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	12 d	> 99	4840	2730	80
6	(EBI)ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	10 d	> 99	1080	910	n.d.
7	(THI)$_2$ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	12 d	95	< 500	< 500	n.d.
8	[(Me$_3$Si)Cp]$_2$ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	3 h	< 5	< 500	< 500	n.d.
9	[(Me$_3$Si)Cp]$_2$ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	10 d	> 99	10910	4150	95
10	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi	1 d	> 99	3300	1980	80
11	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi	10 d	> 99	3220	1890	80
12	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	0.2 h	90	2570	1560	90
13		3.5 h	95	9640	4800	90
14		1 d	> 99	13790	7270	90
15	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi–2B(C$_6$F$_5$)$_3$	1 d	80	980	700	n.d.
16	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$ [b]	1.5 h	95	5330	3160	95
17		7 d	> 99	10700	5550	95
18	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$ [c]	1 d	95	1600	1140	90
19		17 d	> 99	2710	1640	90
20	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	3 h	95	5640	3330	90
21		3 h + 1 d [d]	> 99	5640	3320	90
22		3 h + 30 d [d]	> 99	3910	2250	90
23	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	3 h	95	6450	3410	90
24		3 h + 1 d [e]	> 99	5090	3320	90
25		3 h + 30 d [e]	> 99	3690	1850	45
26	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	0.5 h + 0.5 h [f]	95	8600	3100	90
27		1 d [f]	> 99	12000	3900	90
28		10 d [f]	> 99	3480	1880	80
29	Cp$_2$ZrMe$_2$–4PhSiH$_3$–B(C$_6$F$_5$)$_3$ [g]	10 d	> 99	2380	1540	80
30	Cp$_2$ZrMe$_2$–4PhSiH$_3$–[Ph$_3$C][B(C$_6$F$_5$)$_4$] [g]	10 d	> 99	870	530	n.d.
31	[(MeCp)$_2$ZrH$_2$]$_2$–B(C$_6$F$_5$)$_3$	7 d	0			
32	[(MeCp)$_2$ZrH$_2$]$_2$–[Ph$_3$C][B(C$_6$F$_5$)$_4$]	7 d	0			
33	Cp$_2$ZrMe$_2$–[Ph$_3$C][B(C$_6$F$_5$)$_4$]	30 d	> 99	680	520	n.d.
34	(MeCp)$_2$ZrCl$_2$–2BuLi–4PhSiH$_3$ –[Ph$_3$C][B(C$_6$F$_5$)$_4$] [g]	30 d	> 99	660	470	n.d.
35	Cp$_2$ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$ [h]	10 d	> 99	< 500	< 500	n.d.
36	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$ [h]	10 d	> 99	> 500	> 500	n.d.
37	Cp(Me$_5$C$_5$)ZrCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$ [i]	5 d	25	< 500	< 500	n.d.
38	Cp$_2$HfCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	10 d [j]	> 99	8030	3780	95
39		1.5 h [k]	> 99	5030	2580	90
40		2 d [k]	> 99	4910	2790	85
41	Cp(Me$_5$C$_5$)HfCl$_2$–2BuLi–B(C$_6$F$_5$)$_3$	1 d [j]	> 99	4510	1840	95
42		10 d [j]	> 99	4530	2600	95
43		1 d [l]	> 99	2630	1510	90
44		10 d [l]	> 99	8670	3050	85

[a] Reactions at 20°C in neat monomer and catalyst concentration of 5 mol%, except where stated otherwise. The molecular weights (Da) are calibrated with respect to polystyrene standards and the values are estimated to be reliable to within ±5%. Where possible the low molecular weight cyclic products were excluded from the calculations of M_w and M_n. MeCp = methylcyclopentadienyl, THI = 4,5,6,7-tetrahydroindenyl, EBI = ethylene-1,2-bis[1-indenyl], Ind = indenyl. [b] 1 mol% catalyst used in this reaction. [c] Only 0.25 mol% catalyst used in this reaction. [d] Small amount of toluene was added; the PhSiH$_3$-toluene ratio is ca. 5:1. [e] Small amount of 1,2-dichloroethane was added; the PhSiH$_3$–C$_2$H$_4$Cl$_2$ ratio is ca. 5:1. [f] PhSiMe$_3$ was used as a solvent (1:1 (v/v) to PhSiH$_3$). [g] The reagents were mixed in the same order as they appear in the table. [h] PhCH$_2$SiH$_3$ was polymerized instead of PhSiH$_3$. [i] (n-C$_6$H$_{11}$)SiH$_3$ was polymerized instead of PhSiH$_3$. [j] Before addition of B(C$_6$F$_5$)$_3$ and PhSiH$_3$, the mixture of Cp$_2$HfCl$_2$ and 2BuLi was stirred for 0.3 h at 80°C. [k] Polymerization was conducted at 80°C. [l] Before addition of B(C$_6$F$_5$)$_3$ and PhSiH$_3$, the mixture of Cp(Me$_5$C$_5$)HfCl$_2$ and 2BuLi was stirred for 1 h at 108°C.
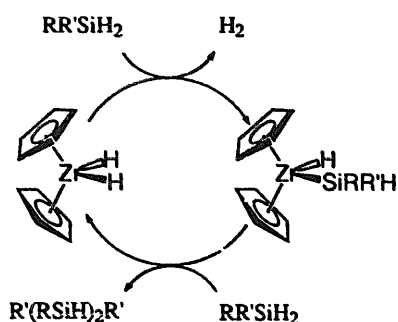
Fig. 2. The Tilley σ-bond metathesis mechanism for silane dehydropolymerization [12] (R = Ar or Alk; R' = H or $(SiHR)_nH$).

important part of the cycle [32,33]. However, in a high performance one-electron oxidative addition–reductive elimination cycle, M^{III} is expected to be a highly reactive intermediate, not a resting state of the system. The vital importance of the catalyst reduction, which favors the latter mechanism vs. σ-bond metathesis, can be illustrated by the behavior of dimethylzirconocene vs. dibutylzirconocene. Dibutylzirconocene is unstable at room temperature and undergoes one-electron reduction spontaneously. We have observed the decomposition of Cp_2ZrBu_2, with a half life of ca. 30 min at room temperature, to a mixture of ca. 50% Zr^{III} and 50% Zr^{IV} products by NMR and EPR spectroscopic analysis [34]. As a result, the catalyst derived from it does not require any thermal activation. In contrast, dimethylzirconocene is a stable compound, and neither the pure complex nor its mixture with borane cocatalyst show any evidence for reduction. A mixture of Cp_2ZrMe_2, $B(C_6F_5)_3$ and $PhSiH_3$ is EPR silent and the performance in dehydropolymerization is extremely poor (entry 13 of Table 1). However, when the sample is heated up to 60°C, the amount of Zr^{III} species increases significantly, and so does the catalytic activity (entry 14 of Table 1). The same trend, although less pronounced, can be observed for hafnocene catalysts. The hafnocene alkyls, in general, are more stable than their zirconocene analogs [35] but undergo similar decomposition and reduction reactions at elevated temperatures. Their dehydrocoupling catalytic activity can be increased by heating the catalyst precursor, dibutylhafnocene, for 30–60 min at 80–110°C (entries 38–44 of Table 2). Dehydropolymerization itself does not need elevated temperatures, but the unreactive precatalysts need thermal activation to either undergo reduction, or to undergo σ-bond metathesis with the silane substrate. Either, or both types of reaction may be a prerequisite to generation of the true catalyst.

From the foregoing, it can be concluded that the relative stability of M^{IV}–M^{III} oxidation states and the energy barrier between them, with regard to the dehydropolymerization reaction, are best balanced for zirconocene. The energy barrier is somewhat unfavorable

for hafnocene-based catalysts, and the higher stability of the M^{III} form decreases the activity of urano- and titanocenes. The critical problem with excessive production of the M^{III} forms may be the tendency of these species to form catalytically sterile dimers.

2.2. Catalyst preparation strategy

A number of catalyst preparation strategies have been tried. Mixtures of Cp'_2ZrMe_2 or $[Cp'_2ZrH(\mu\text{-H})]_2$ with $B(C_6F_5)_3$ (entry 13 of Table 1 and entry 31 of Table 2) proved to be poorer catalytic precursors than the Cp'_2ZrCl_2–2BuLi–$B(C_6F_5)_3$ system. The low activity of these precursors can be attributed to the higher stability of the M^{IV} oxidation state. Indeed, when the metallocene was pre-treated (exposed to elevated temperatures or reacted with $PhSiH_3$) to generate some M^{III} species, before introduction of borane, the performance of the catalyst improved significantly (entry 14 of Table 1 and entry 29 of Table 2).

In general, $[Ph_3C]^+[BR_4]^-$ turned out to be a much poorer cocatalyst than $B(C_6F_5)_3$ (entries 30 and 32–34 of Table 2). One of the obvious drawbacks of $[Ph_3C]^+[BR_4]^-$ is that it reacts with primary aryl silanes, inducing electrophilic redistribution of $RSiH_3$ into SiH_4, R_2SiH_2, R_3SiH and R_4Si. R_2SiH_2 and R_3SiH will either terminate polysilane chain growth, or be unreactive. The SiH_4 acts as a branching agent, causing crosslinking and leading to poorly soluble, intractable products, which are mainly lost during the
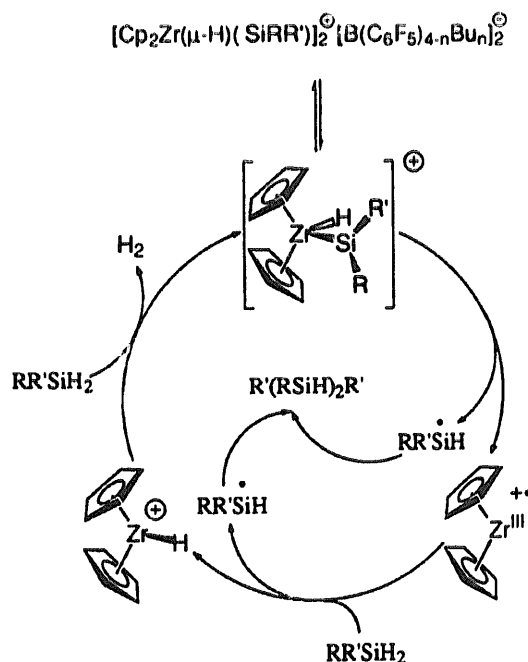
$[Cp_2Zr(\mu\text{-}H)(\,SiRR')]_2^{\oplus}\,[B(C_6F_5)_{4\text{-}n}Bu_n]_2^{\ominus}$

Fig. 3. A tentative one-electron oxidative addition–reductive elimination mechanism for silane dehydropolymerization [32,33] (R = Ar or Alk; R' = H or $(SiHR)_nH$).

workup procedure. If any borate cocatalyst is left unreacted in the system, the above-mentioned problems can interfere and mask the true performance of the catalyst generated in this way. In addition, we have confirmed that trityl cation oxidizes catalytically active Zr^{III} species producing trityl radical, which can be observed by EPR spectroscopy. An analogous redox reaction was recently reported for Ti^{III} [36]. Imori and Tilley recently reported that a very similar $\{Cp_2'ZrMe_2$ or $[Cp_2'ZrH_2]_2\}-[NHR_3]^+[BR_4]^-$ catalytic system produced high molecular weight polymers [25]. It is obvious that the polymers and conditions reported in the present paper for the $Cp_2'ZrX_2-[Ph_3C]^+[BR_4]^-$ combination catalysts are not well optimized, but the above-mentioned arguments discouraged us from concentrating on this system.

In some cases of coordination catalysis, dicationic complexes have certain advantages over monocationic compounds [37,38]. The dehydropolymerization reaction, however, slowed down significantly (only 80% conversion after 1 day) and decreased the product molecular weights by an order of magnitude upon introduction of a second equivalent of borane (entry 15 of Table 2). This suggests that the dication complex is completely inactive towards silane polymerization and the observed reaction is driven by a residual monocationic catalyst. The lack of catalytic activity for the dication is consistent with both the constant oxidation state σ-bond metathesis and the one-electron oxidative addition – reductive elimination mechanisms.

2.3. Solvent, temperature and concentration effects

As previously reported, the highest rates and degrees of polymerization can be achieved in neat monomer [12]. The obvious drawback of the high concentration conditions is that the reaction mixture completely solidifies at high conversions, which puts an end to the polymerization. However, the catalyst performance decreases significantly even when a small amount of solvent (usually toluene) is added. This solvent effect may be due to the ability of aromatic solvents to compete with the SiH groups for the catalyst coordination site. This competition will be particularly important for the more hindered terminal SiH_2 groups, whose reaction is required to produce long chains. Tilley and coworkers earlier suggested a number of compromises to overcome these problems [12]. The most attractive idea is a slow bleeding of monomer into the reaction mixture to keep it at least semiliquid. Unfortunately, the known dehydropolymerization catalysts are significantly more active towards monomer–monomer vs. monomer–chain coupling. The bleeding of the monomer thus results in the build-up of new, short polymer chains instead of propagating the old, long ones. Another approach, a slow introduction of toluene, such that the reaction mixture maintained a slight fluidity, was re

ported to improve the efficiency of neutral zirconocene catalysts [12]. In the case of the cationic $Cp_2'ZrCl_2-BuLi-B(C_6F_5)_3$ combination catalyst, however, neither toluene nor dichloroethane improved the efficiency of the catalyst even if they were added at the point when the mixture appeared to be solid (entries 20–25 of Table 2). Dichloroethane leads to decomposition of the active Zr^{III} catalytic intermediates, judging both from the dramatic color change from brown to yellow and the disappearance of EPR signals. In addition, the behavior of the catalyst changes, in that significant depolymerization can be observed even after 1 day and a large (55%) amount of cyclics is formed after 30 days. The impact of added toluene is much less dramatic; there are no major changes, either in the EPR spectrum or in the color of the sample. The polymerization stops but no depolymerization is observed after 1 day, and very little change occurs even after 30 days. The nature of the solvent influence in this case is obviously different, as the solvent merely blocks coordination sites, vide supra, but does not decompose the catalyst.

An ideal solvent for the dehydropolymerization should be chemically inert and weakly coordinative, yet polar enough to solubilize the catalyst and the polysilane. The latter requirement is not very strict as the catalyst is soluble enough in relatively nonpolar primary silanes and short chain oligosilanes. Tertiary silanes are known to be inert towards dehydropolymerization, presumably because of their steric bulk and inability to coordinate to the metal center [39]. Quaternary silanes should be even more weakly coordinative and inert. However, they do not differ much in terms of polarity from the primary silanes and polysilanes. $PhSiMe_3$ was probed as an inert, sufficiently polar and weakly coordinative solvent candidate (entries 26–28 of Table 2). At the early stages (within the first day) the reaction behaves as predicted; the solvent does not interfere with the built up of the long chains and the amount of cyclics does not increase compared with the neat monomer conditions. The polydispersity index is higher than usual, which indicates that the low molecular weight oligomers are either less efficiently consumed or are gradually formed again in a depolymerization reaction. The latter prevails at longer (10 days) reaction times. It is not clear, though, whether the depolymerization activity is an inherent property of the catalyst and cannot be avoided, or is a result of insufficient stability of the catalyst and a matter of a proper tuning.

A general way to achieve a higher degree of conversion is to raise the temperature. A number of different experiments with temperatures ranging from 20 to 108°C were performed. The samples were either heated for the entire period of the reaction or only at the early or late stages (entries 12 and 14 of Table 1; entries 38–44 of Table 2). Unfortunately, with both Zr and Hf catalysts decomposition occurs faster than the build-up of the

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based catalysts proved to be a good compromise; they are bulky enough to be stable, yet not overcrowded enough to prohibit approach of oligomeric substrates (entries 8, 9 and 12–17 of Table 2) [12]. The constrained geometry catalysts (CGC), which have the two cyclopentadienyls of the sandwich complex connected together by a bridging group, proved to be more reactive towards ethylene polymerization owing to the more accessible metal center [22]. However, neither the neutral [42] nor the cationic-based $(Me_2E(CpCp')M$, where $E = Si$ or C and $M = Ti$, Zr, Hf; $Cp' = Cp$ or C_5Me_5) catalysts reported by the Tilley group [25], showed any advantages in dehydropolymerization. We have studied $(EBI)ZrCl_2$, which has a more flexible two atom bridge, but it exhibited a much poorer activity than the nonbridged $(Ind)_2ZrCl_2$ (entries 5 and 6 of Table 2).

Compared with zirconocene, hafnocene nonbridged catalytic systems are much less sensitive to the steric effects of the cyclopentadienyl ligands due to a larger opening of the metallocene wedge [43]. Thus, the cheap and commercially available Cp_2HfCl_2 has an efficiency as high as $(C_5Me_5)(Cp)HfCl_2$, and is almost approaching $(C_5Me_5)(Cp)ZrCl_2$ (entries 38 and 44 of Table 2).

Electronic effects of substituted cyclopentadienyl ligands are relatively unimportant. Thus, a polyaromatic indenyl has nearly the same performance as cyclopentadienyl and methylcyclopentadienyl-based catalysts (entries 3–5 of Table 2). The slight decrease in activity of the indenyl-based catalyst is probably due to the haptatropic rearrangements, which were reported for the neutral $(Ind)_2TiMe_2$ dehydropolymerization catalyst [44]. Such rearrangements lead to the catalyst dimerization through a bridging polyaromatic ligand, as well as a poorly predictable coordination environment due to the $\eta^5 - \eta^6$ slipping of the indenyl.

3.5. Dehydropolymerization of other monomers

Attempted polymerizations of $PhCH_2SiH_3$ and $(n-C_6H_{13})SiH_3$ lead to low molecular weight products and, in the case of $(n-C_6H_{13})SiH_3$, to low polymerization rates as well (entries 35–37 of Table 2). Similar behavior was reported for dehydropolymerization with neutral metallocene catalysts [11] and can be rationalized by the variable oxidation state model. According to the model (Fig. 3) the building of the silicon chains occurs by one-electron reductive elimination of silyl radicals from the metal center [32], followed by radical coupling to produce Si–Si bonds [45,46]. The yield and stability of silyl radicals decreases in the series $PhSiH_2^-$ $> PhCH_2SiH_2^- > (n-C_6H_{13})SiH_2^-$ [46,47], as does the ability of the silanes to undergo polymerization. To the best of our knowledge, no alternative explanation for the particular activity of $PhSiH_3$ has been offered in terms of the σ-bond metathesis or any other model.

2.6. Fractional precipitation of polysilanes

As can be seen from the molecular weights and the amount of the cyclic compounds (Tables 1 and 2, Fig. 1(b)), even the best catalytic systems furnish a low quality polymer. However, the quality of the raw product can be easily improved by fractional precipitation from toluene–petroleum ether solution (Table 3, Fig. 1(c)). The precipitated polymer was separated from the mother liquor by simple decanting. To illustrate the advantages of this purification technique, a low quality starting polymer ($M_w = 5000$, $M_n = 3000$) was used. No centrifugation or filtering was used to improve the yield. The first, high molecular weight fraction (1:2 toluene–petroleum ether) precipitated rapidly. The lower molecular weight fraction (1:6) was not completely recovered and some of the material was lost, suspended in the mother liquor. Although the fractionation technique was not optimized, the experiment illustrates that dehydropolymerization reactions can furnish high quality linear long chain polysilanes.

3. Conclusions

Careful optimization of the catalyst structure and reaction conditions leads to higher molecular weight polysilanes ($M_w = 13\,800$, $M_n = 7300$) in a dehydropolymerization reaction. Catalyst performance can be rationalized in terms of a one-electron oxidative addition–reductive elimination mechanism. The molecular weight of the polymer can be further improved (e.g. from $M_w = 5000$, $M_n = 2800$ to $M_w = 12\,000$, $M_n = 6600$) by a fractional precipitation technique from a toluene–petroleum ether solution.

4. Experimental details

4.1. General methods

All operations were performed in Schlenk-type glassware on a dual-manifold Schlenk line, equipped with flexible stainless steel tubing, or in an argon-filled M. Braun Labmaster 130 glovebox (less than 0.05 ppm H_2O). Argon was purchased from Matheson (prepurified for the glovebox and UHP for the vacuum line) and was used as-received. Hydrocarbon solvents (protio- and deuterio- benzene and toluene) were dried and stored over Na–K alloy, benzophenone and 18-crown-6 in Teflon-valved bulbs and were vacuum transferred prior to use. Halogenated solvents and silanes (1,2-dichloroethane, $PhSiMe_3$, $PhSiH_3$, (n-C_6H_{13})SiH_3 and $PhCH_2SiH_3$) were degassed and stored over molecular sieves. Cp_2ZrCl_2, Cp_2TiCl_2, Cp_2HfCl_2, Me_5C_5H, $ZrCl_4$, C_6D_6, C_7D_8, 1,2-dichloroethane, C_6F_5Br,

$PhC(O)Ph$, 18-crown-6, BCl_3 (1.0 M in heptane), n-BuLi (2.5 M in hexanes) and CpNa (2.0 M solution in THF) were purchased from Aldrich Chemical Co. and used as-received, unless stated otherwise. $(Me_5C_5)_2$-$ZrCl_2$ and $PhSiMe_3$ were purchased from Strem Chemicals Inc. and United Chemicals respectively.

The compounds Cp_2ZrMe_2 [48], $(MeCp)_2ZrCl_2$ [49], [(MeCp)Zr(μ-H)H]$_2$ [50], $(Me_3SiCp)_2ZrCl_2$ [51], $Cp(Me_5C_5)ZrCl_2$ [52], (Ind)$_2ZrCl_2$ [49], (EBI)$ZrCl_2$ [53], (THI)$_2ZrCl_2$ [49], $Cp(Me_5C_5)HfCl_2$ [54], $(Me_5C_5)_2UCl_2$ [55], $B(C_6F_5)_3$ [56], $[Ph_3C]^+$-$[B(C_6F_5)_4]^-$ [24], and $RSiH_3$ (R = Ph, $PhCH_2$ and n-C_6H_{13}) [57] were prepared according to literature procedures.

NMR spectra were recorded on a Varian Unity 500 (FT, 500 MHz for ^1H), Varian XL-200 or Varian Gemini-200 (FT, 200 MHz for ^1H) spectrometers. Chemical shifts for ^1H and ^{13}C spectra were referenced using internal solvent references and are reported relative to tetramethylsilane. ^{19}F NMR spectra were referenced to external trifluoroacetic acid. EPR spectra were recorded on a Bruker ESP 300E (X-band) spectrometer and were referenced to external DPPH. The molecular weights of the polysilanes were measured with a Varian 5000 liquid chromatograph equipped with a refractive index detector and Waters TSK G2000 HXL and TSK G4000 HXL columns in series. The chromatograph was calibrated with polystyrene standards and THF was used as an eluent.

All air-sensitive NMR samples were prepared in an NMR-tube assembly, consisting of one or more 5 ml round-bottom flasks fitted with a Teflon valve to which an NMR tube has been fused at an angle of 45°. The liquids can be either kept separately in each of the flasks and tubes or can be transferred from one flask of choice to the other by tilting the entire apparatus. A sample and a stirring bar were loaded in the side flask and treated with a small quantity (0.1–0.2 ml) of a deuterated solvent of choice. The solvent was then evaporated and the evaporation–vacuum transfer cycle was repeated to remove any residual nondeuterated solvents. A fresh portion of the same deuterated solvent (0.6–0.7 ml) was then vacuum transferred into the assembly and the solution was carefully decanted into the side NMR-tube. The top part of the tube was washed by touching it with a piece of cotton wool soaked with liquid nitrogen, which caused condensation of the solvent vapors on the inner walls. The sample was then frozen and flame sealed.

4.2. Silane polymerization experiments with $Cp'Cp''$-MCl_2–$2BuLi$–$B(C_6F_5)_3$ (M = Ti, Zr, Hf, U) combination catalyst

The metallocene dichlorides (0.125 mmol) and $(C_6F_5)_3B$ (0.125 mmol, 0.064 g) were loaded in sepa-

rate Schlenk tubes in the glovebox and all further manipulations were performed on a vacuum line. The reaction mixtures were protected from light with aluminum foil. The metallocene dichloride was suspended in 1 ml of toluene at 0°C and a 2.5 M solution of BuLi in hexanes (0.1 ml, 0.25 mmol) was added. The mixture was stirred at room temperature for 30 min (for some hafnocene catalysts 60 to 108°C temperatures were applied for 0.3–1 h). The color gradually changed from light yellow to dark brown. Toluene (5 ml) was added to the $(C_6F_5)_3B$ and the resulting solution was slowly syringed into the butylated metallocene solution. A brown-red oil precipitated (brown-green for $MeCp_2$ $ZrCl_2$–BuLi–$B(C_6F_5)_3$ and $Cp(Me_5C_5)ZrCl_2$–BuLi–$B(C_6F_5)_3$; black for Cp_2TiCl_2–BuLi–$B(C_6F_5)_3$ and $(EBI)_2ZrCl_2$–BuLi–$B(C_6F_5)_3$). After stirring for another 30 min, the solvent was removed in vacuum and the catalyst was spread on the walls of the tube in a thin layer. $RSiH_3$ or $RSiH_3$–toluene mixture $(R = Ph, PhCH_2,$ or $n\text{-}C_6H_{13})$ was added and an immediate vigorous evolution of hydrogen started, accompanied by a color change from brown to light yellow (titano- and uranocene catalysts did not change color upon addition of silane). In the absence of solvent, the mixture solidified within the first 1–10 min and the brown-red color slowly reappeared. In some cases (see Table 2), a specified amount of solvent (toluene, dichloroethane or trimethylphenylsilane) was added within the first 1–3 h after the addition of silane to keep the reaction mixture liquid. The mixture turned light yellow upon addition of dichloroethane.

Polysilane was worked up in air with minimum exposure to light. The sample was dissolved in toluene and passed through a short plug of dry Florisil to remove catalyst. Toluene was removed under vacuum and solutions for GPC analysis were prepared in THF.

4.3. Silane polymerization experiments with Cp'Cp''-ZrCl₂–2BuLi combination catalyst

The title polymerization was carried out according to the procedure above except that $B(C_6F_5)_3$ was not used.

4.4. Silane polymerization experiments with Cp_2ZrR_2–$mB(C_6F_5)_3$ or $Cp'Cp''ZrR_2$–$m[Ph_3C][B(C_6F_5)_4]$ $(R = Me$ or H and $m = 1$ or $2)$ combination catalyst

The appropriate metallocene (0.125 mmol), toluene (2 ml) and $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ (0.125 or 0.250 mmol) were loaded in a Schlenk tube in the glovebox and all further manipulations were performed on a vacuum line. The reaction mixtures were protected from light with aluminum foil. After stirring at room temperature for 4 h, the solvent was removed in vacuum and the catalyst was spread on the walls of the tube in a thin layer. The color of the $Cp'Cp''ZrR_2$–$[Ph_3C]$-$[B(C_6F_5)_4]$ mixture was white and the Cp_2ZrR_2–$B(C_6F_5)_3$ was green or purple. Phenylsilane was added and the mixture was left stirring in the dark for a specified time period. Polysilane was worked up according to the procedure described above.

4.5. Silane polymerization experiments with Cp_2ZrMe_2–$4PhSiH_3$–$B(C_6F_5)_3$ or Cp_2ZrMe_2–$4PhSiH_3$–$[Ph_3C]$-$[B(C_6F_5)_4]$ combination catalyst

In the glovebox, Cp_2ZrMe_2 (0.125 mmol, 0.031 g), toluene (2 ml) and $PhSiH_3$ (0.062 ml, 0.500 mmol) were loaded in a Schlenk tube and the mixture was stirred for 1 h. Then, $(C_6F_5)_3B$ or $[Ph_3C][B(C_6F_5)_4]$ (0.125 mmol) was loaded and all further manipulations were performed on a vacuum line. The solvent was removed in vacuum and the catalyst was spread on the walls of the tube in a thin layer. Phenylsilane was added and the mixture was stirred in the dark for a specified time period (Tables 1 and 2). Polysilane was worked up according to the procedure described above.

4.6. Silane polymerization experiment with $(MeCp)_2$-$ZrCl_2$–$2BuLi$–$4PhSiH_3$–$B(C_6F_5)_3$ combination catalyst

The title polymerization was carried out according to the procedure described above, except that $PhSiH_3$ (0.062 ml, 0.500 mmol) was added to the $(MeCp)_2ZrCl_2$–2BuLi mixture after it was allowed to

Table 3
Some results for the fractional precipitation of polyphenylsilane [a]

Toluene–alkane ratio	Yield (%)	M_w	M_n	Polydispersity index	Linear (%)
1 : 0 (before fractionation)	—	4910	2790	1.77	85
1 : 2	24	11900	6620	1.74	100
1 : 0 (before fractionation)	—	4840	2725	1.78	80
1 : 2	29	8490	4510	1.88	100
1 : 6	12 [b]	4590	3030	1.52	100

[a] The molecular weights (Da) are calibrated with respect to polystyrene standards and the values are estimated to be reliable to within ±5%. The low molecular weight cyclic products were excluded from the calculations of M_w and M_n. [b] This fraction was precipitated from the mother liquor left over after separation of the previous (1 : 2) fraction.

react for 1 h at room temperature. The mixture was stirred for an additional 1 h and $B(C_6F_5)_3$ solution in toluene (5 ml) was introduced by a syringe.

4.7. Fractional separation of polyphenylsilane

A sample of polyphenylsilane (0.300 g) was dissolved in 1.7 ml of dry toluene. Petroleum ether was slowly added from a dropping funnel. Precipitation of the polymer began after approximately 1.5 ml of petroleum ether was added. The white milky suspension was allowed to settle for 0.5 h. The precipitate was separated by decanting the mother liquor and dried in vacuum. The yields and the molecular weights of different fractions are shown in Table 3.

4.8. Reaction of $B(C_6F_5)_3$ with $RSiH_3$ ($R = Ph$, CH_2Ph)

In the glove box, $B(C_6F_5)_3$ (0.10 mmol, 0.051 g), $RSiH_3$ (0.01 mmol) and C_6D_6 (0.5 ml) were loaded in an NMR tube assembly and the sample was prepared as described above. No color change occurred. The spectra were acquired after 1 and 24 h; no changes were observed. Further reaction (8 days) leads to a mixture of at least six compounds (^{19}F NMR), which were not identified.

R = Ph; time, 24 h: NMR (C_6D_6, +25°C) ^1H δ 7.5 (m, Ph), 7.3–7.1 (m, Ph), 4.3 (br s, SiH); ^{19}F δ −131.5 (dt, 21.2, 7.1 Hz, o-C_6F_5), −144.6 (tt, 21.2, 7.1 Hz, p-C_6F_5), −162.8 and −162.9 (tt, m-C_6F_5).

R = CH_2Ph; time, 24 h: NMR (C_6D_6, +25°C) ^1H δ 7.07 (t, Ph), 6.91 (t, Ph), 6.90 (d, Ph), 3.63 (br s, SiH), 1.88 (br s, CH_2); ^{19}F δ = −131.5 (d, 21.2 Hz, o-C_6F_5), = −144.6 (br s, p-C_6F_5), = −162.8 (br s, m-C_6F_5).

4.9. Reaction of $[Ph_3C][B(C_6F_5)_4]$ with $PhSiH_3$

In the glove box, $[Ph_3C][B(C_6F_5)_4]$ (0.08 mmol, 0.075 g) and $PhSiH_3$ (ca 8 mmol, 1 ml) were loaded in a Schlenk tube. The color immediately changed from brown-red to light gray. The mixture was stirred for 16 h, an aliquot was dissolved in C_6D_6 and passed through a short plug of dry Florisil. The components of the mixture were identified by comparison with the ^1H NMR spectra of the authentic tri-, di-, and monophenylsilane; the relative amounts were estimated from the integrals to be 32%, 46% and 22% respectively.

^1H NMR (C_6D_6, +25°C) ^1H δ 7.7–7.5 (m, Ph), 7.2–7.0 (m, Ph), 6.00 (br s, Ph_3SiH), 5.07 (br s, Ph_2SiH_2), 4.22 (br s, $PhSiH_3$).

4.10. Reaction of $B(C_6F_5)_3$ with polyphenylsilane

In the glovebox, $B(C_6F_5)_3$ (0.125 mmol, 0.064 g), polyphenylsilane (2.5 mmol, 0.265 g) and toluene (0.25 ml) were charged in a Schlenk tube. No color change

occurred. The mixture was left stirring for 8 days and was worked up according to the same procedure as used for the metallocene-catalyzed polymerization reactions.

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