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Catalytic Dehydrocoupling of Phenylsilane with "Cation-like" Zirconocene Derivatives: A New Approach to Longer Silicon Chains

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Summary: The use of tris(pentafluorophenyl)borane, $(C_6F_5)_3B$, as a cocatalyst in the dehydrocoupling of phenylsilane, in the presence of zirconocene-derived catalysts, leads to suppression of chain scission reactions and to an increase in polysilane chain length ($M_n > 7000$). An exhaustive multinuclear NMR study of the catalytic species leads to the conclusion that they are zirconocene(IV) hydride bridged dimers, with a "cation-like" silylium ligand on each zirconium: $[Cp_2Zr(SiHPh)(\mu\text{-}H)]_2[Bu_2(C_6F_5)_2B]_2$.

The catalytic dehydrocoupling of silanes provides a clean and simple synthesis for Si-Si bonds.[1] Although early-transition-metal, lanthanide, and actinide organometallic catalysts show high activities for this reaction,[2-8] two major problems remain to be overcome. First, no catalyst has yet been reported which can effectively couple tertiary silanes. Second, catalysts have yet to be found which can give polysilanes of high molecular weight with primary and secondary organosilanes. Fractionation of polymers with M_n values of ca. 1300 yields a higher molecular weight fraction with a number-average molecular weight of ca. 4700.[6] The highest number-average molecular weight reported to date with $PhSiH_3$ is ca. 5300 Da.[1b]

The electronic and photonic properties of polysilicon chains level off at about 40–50 silicon atoms, which corresponds to molecular weights of ca. 3000–4000.[9] On the other hand, it is desirable to have chain lengths an order of magnitude longer than this to provide polymers with good mechanical properties.

Following reports that zirconocene alkyl cations are effective catalysts for the polymerization of olefins,[10] we examined the activity of $[Cp_2ZrMe(THF)][BPh_4]$ as a catalyst for the dehydrocoupling of phenylsilane and found that it did not show significant activity toward catalytic dehydrocoupling. More recently, a slightly different type of "cation-like" catalyst, in which a Lewis acid, $(C_6F_5)_3B$, coordinates to a methide ligand but does not (at least in the solid state) completely remove it from the metal coordination sphere, has been described for olefin polymerization.[11] In this communication we report that $(C_6F_5)_3B$, in combination with zirconocene-based catalysts, results in higher molecular weight poly(phenylsilane) via dehydrocoupling.

The results of a number of screening reactions with some zirconocene-based catalysts are summarized in Table 1. It is clear from these results that the zirconocene catalysts which incorporate $(C_6F_5)_3B$ have properties that are different from those which do not. Although the $(C_6F_5)_3B$ *reduces* the overall *activity* of the catalysts, it also strongly suppresses ring formation, as evidenced by the small size of the typical, near-monodisperse peak at DP ca. 6–8 in the gel permeation chromatograms. The small amounts of cyclics observed in these cases appear to be produced in the course of chain buildup and are not due to depolymerization by chain cleavage, such as is observed with reactions in the absence of $(C_6F_5)_3B$. The suppression of the chain cleavage reaction and subsequent cyclization of short-chain fragments allow the growth of polymer chains to greater lengths. Surprisingly, the dimethylzirconocene/$(C_6F_5)_3B$ catalyst, which Yang et al. found to be quite active for ethylene polymerization,[11] does not exhibit any significant activity for dehydrocoupling at room temperature.

The order of reactivity for the various zirconocenes is the same, both in the presence and absence of $(C_6F_5)_3B$, and follows the sequence previously observed by ourselves and by Tilley and co-workers,[1b] namely $(Me_5C_5)_2Zr \ll Cp_2Zr \approx (MeCp)_2Zr < Cp(Me_5C_5)Zr$.

Attempts to isolate crystals of catalytic intermediates in these reactions have not yet been successful. However, NMR studies reveal the presence of relatively stable and reproducible species in solution and the large number of detectable nuclei permits assignment of the structures of the observed species to be **1a** and **1b**.[12] Through-bond and through-space connectivities were established by a variety of two-dimensional homo- and heteronuclear techniques. Much of the structure is analogous to neutral dimers produced by reaction of silanes with Cp_2ZrMe_2 or $Cp_2ZrCl_2/2BuLi$, and the NMR features for the Cp, Zr–H–Zr, and Si–H groups are very similar.[13] The special features of **1** are the silylium-like ligand (^{29}Si δ 106–108

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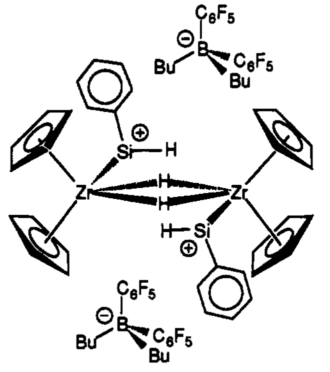
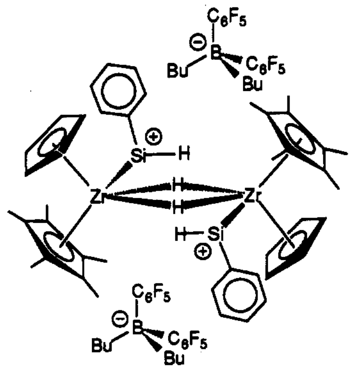
Table 1. Results for the Polymerization of Phenylsilane with Zirconocene-Based Catalysts[a]

catalyst	time, days	% conversn	M_w[b,c]	M_n[b,c]	M_p[d]	linear/ cyclic ratio
		Reactions in 1:1 Monomer/Toluene Mixture (v/v)				
$Cp_2ZrCl_2/2BuLi$	10	>99	2450	2080	1350	55/45
$Cp_2ZrCl_2/2BuLi/(C_6F_5)_3B$	10	>99	4320	3010	3300	85/15
$(MeCp)_2ZrCl_2/2BuLi$	3	>99	2400	1800	2100	60/40
$(MeCp)_2ZrCl_2/2BuLi/(C_6F_5)_3B$	10	>99	5150	2840	4550	90/10
$Cp(Me_5C_5)_2ZrCl_2/2BuLi/(C_6F_5)_3B$	10	>99	5500	3080	4100	95/5
$(Me_5C_5)_2ZrCl_2/2BuLi/(C_6F_5)_3B$[e]	10	85		mixture of dimer, trimer, and tetramer		
$Cp_2ZrMe_2/(C_6F_5)_3B$[e]	4	<5		mixture of low mol wt oligomers		
$(C_6F_5)_3B$[f]	0		2450	2080	1350	50/50
	8		2450	2080	1350	50/50
		Reactions in Neat Monomer				
$Cp_2ZrCl_2/2BuLi$	10	>99	2930	1880	1980	75/25
$Cp_2ZrCl_2/2BuLi/(C_6F_5)_3B$	10	>99	4990	2670	4040	90/10
$(MeCP)_2ZrCl_2/2BuLi/(C_6F_5)_3B$	10	>99	5640	3020	4670	90/10
$[(Me_3Si)Cp]_2ZrCl_2/2BuLi/(C_6F_5)_3B$	10	>99	10910	4150	9960	95/5
$Cp(Me_5C_5)ZrCl_2/2BuLi$	10	>99	3220	1890	2800	80/20
$Cp(Me_5C_5)ZrCl_2/2BuLi/(C_6F_5)_3B$	1	>99	13790	7270	12890	90/10
$Cp(Me_5C_5)ZrCl_2/2BuLi/(C_6F_5)_3B$[g]	7	>99	10700	5550	12240	95/5
$Cp(Me_5C_5)ZrCl_2/2BuLi/(C_6F_5)_3B$[h]	17	>99	2710	1640	2440	90/10
$Cp(Me_5C_5)ZrCl_2/2BuLi/(C_6F_5)_3B$[i]	7	>99	4260	2400	3500	85/15

[a] Reactions at 20 °C and a catalyst concentration of 5 mol %, except where stated otherwise. [b] The molecular weights (in Da) are calibrated with respect to polystyrene standards, and the values are estimated to be reliable to within ±5%. [c] Where possible, the low-molecule-weight cyclic products were excluded from the calculations of M_w, M_n, and M_p. [d] M_p is the molecular weight at the peak maximum. [e] In this case product analysis is based on ^1H NMR spectra. [f] This is a blank reaction in which the substrate was a preprepared polyphenylsilane. It establishes that polymer is inert to the presence of the borane alone. [g] 1 mol % catalyst used in this reaction. [h] Only 0.25 mol % catalyst used in this reaction. [i] A small amount of toluene was added; the $PhSiH_3$/toluene ratio is ca. 5/1.



1a



1b

ppm)[14] and the $[BBu_2(C_6F_5)_2]^-$ anion, whose presence is confirmed by the comparison of its spectrum with that of an independently prepared sample of $[Ph_3C][BBu_2(C_6F_5)_2]$. The presence of diastereotopic hydrides in **1b** strongly suggests that silicon is chiral and is thus nonplanar. This distortion is most likely caused by a tightly coordinated $[BBu_2(C_6F_5)_2]^-$ anion,[15] but attempts to detect such an interaction by variable-temperature ^{19}F NMR have been so far unsuccessful. An important feature of the structure of **1b** is that coordination of the borate anion is determined by the relative orientation of the Cp, Cp*, Si, and Ph groups, which can be changed only by rotation about the Zr–Si bond. If the dissociation–association of the ion pair were fast on the NMR time scale, while rotation

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(12) NMR data for $[Cp_2Zr(\mu\text{-}H)\{(Ph)(H)Si^+\}]_2[B(Bu)_2(C_6F_5)_2]^-{}_2$ (solvent $C_2D_2Cl_4$; all resonances in ppm and *J* values in Hz; spectra acquired at −40 °C) are as follows. C_6F_5: ^{13}C 148.26 (ortho, dm, $^1J_{CF}$ = 236.7), 136.14 (meta, dm, $^1J_{CF}$ = 226.5), 137.10 (para, dm, $^1J_{CF}$ = 244.9), 135.32 (ipso); ^{19}F −136.46 (ortho, d, 4F, J_{FF} = 23.00), −170.14 (meta, t, 4F, J_{FF} = 19.8), −167.55 (para, t, 2F, J_{FF} = 20.50). C_4H_9: ^1H 1.11 (α, br m, 4H), 0.76 (β, br m, 4H), 1.19 (γ, m, 4H), 0.72 (δ, t, 6H, $^2J_{HH}$ = 7.3); ^{13}C 23.18 (α), 30.68 (β), 26.95 (γ), 14.46 (δ). C_5H_5: ^1H 5.71 (s, 5H) 5.79 (s, 5H); ^{13}C 106.43, 106.14. C_6H_5: ^1H 7.6–7.8 (ortho, m, 2H), 7.2–7.6 (m, 3H, meta and para); ^{13}C 135.20, (ortho), 129.14, (meta), 130.89 (para), 135.63 (ipso). Si–H: ^1H 6.17 (br s, $\nu_{1/2}$ = 2.9 Hz, 1H); ^{29}Si 108.04. μ-H: ^1H −2.93 (s, 1H). NMR data for $[CpCp^*Zr(\mu\text{-}H)\{(Ph)(H)Si^+\}]_2[B(Bu)_2(C_6F_5)_2]^-{}_2$ (solvent C_6D_6; spectra acquired at room temperature) are as follows. C_6F_5: ^{19}F −136.44 (ortho, br s, 8F), −167.64 (meta, br s, 8F), −165.34 (para, br s, 4F). C_4H_9: ^1H 1.99 (α, br s, 8H), 1.50 (β, m, 8H), 1.74 (γ, m, 8H), 1.10 (δ, t, 12H, $^2J_{HH}$ = 7.4); ^{13}C 23.7 (α), 31.4 (β), 27.4 (γ), 14.6 (δ). C_5H_5: ^1H 5.16 (s, 5H), 5.10 (s, 5H); ^{13}C: 106.0, 106.9. $C_5(CH_3)_5$: ^1H 1.48 (s, 15H), 1.47 (s, 15H); ^{13}C 11.8, 11.7. C_6H_5: ^1H 7.7–6.8 (m, 10H). Si–H: ^1H 5.53 (br s, 2H, $\nu_{1/2}$ = 4); ^{29}Si 106.0. μ-H: ^1H −1.82 and −2.85 (AB q, 2H, J_{HH} = 1.7 and 15.0). NMR data for $[Ph_3C]^+[B(Bu)_2(C_6F_5)_2]^-{}_2$ (solvent C_6D_6; spectra acquired at room temperature) are as follows. C_4H_9: ^1H 1.89 (α, br m, 4H), 1.45 (β, br m, 4H), 1.70 (γ, m, 4H), 1.07 (δ, t, 6H, $^2J_{HH}$ = 7.25). C_6H_5: ^1H 7.3–6.9 (m, 15H). C_6F_5: ^{19}F −135.65 (ortho, d, 4F, J_{FF} = 21.6), −169.47 (meta, t, 4F, J_{FF} = 21.4), −166.49 (para, t, 2F, J_{FF} = 20.5). ^{13}C and ^{29}Si chemical shifts which are cited to one decimal place were obtained from 2D HMQC and HMBC experiments and are reliable within ±0.2 ppm. Symbols: d = doublet, t = triplet, m = multiplet, br = broad, dm = doublet of multiplets, dd = doublet of doublets. The spectra were recorded on a Varian Unity 500 spectrometer and referenced to the solvent resonances in the case of ^1H and ^{13}C nuclei. External references (CF_3COOH and TMS) were used for observation of ^{19}F and ^{29}Si, respectively. Many of the features of the NMR data reported herein are very similar to those of the related neutral compound $Cp_2Zr(SiH(Me)Ph)(\mu\text{-}H)_2(SiH_2Ph)_2ZrCp$ (solvent C_6D_6). SiH: ^1H 4.87 (m); ^{29}Si 15.81 (dm, J_{HSi} = 168 Hz). SiH_2: ^1H 4.78 (s); ^{29}Si 7.86 (td, J_{HSi} = 147 and 15). μ-H: ^1H −4.96 and −5.09 (AB q, J_{HH} = 11 Hz).[13b]

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about the Zr–Si bond was much slower, there should be no racemization at silicon. Such a dynamic process does not affect the diastereotopic hydrides but renders the coordination unobservable by NMR. The nonplanar geometry of the silylium fragment may shed some light on the surprising stability of 1, which is achieved by a combination of favorable electronic and steric effects provided by zirconium, directly bonded to silicon, and a tightly coordinated borate anion. In view of the highly unusual structure proposed for 1,[14,16] we are pursuing the synthesis of analogs with the $[B(C_6F_5)_4]^-$ counterion, which are more likely to crystallize and furnish X-ray structures. There is precedent for tricoordinate Si ligands coordinated to later transition metals,[17] but these ligands are better formulated as =SiRR′. The $4d^0$ species reported above have insufficient electrons to form a double bond to the silicon.

The chemical reactions which lead to the formation of both the cation and the anion of 1 are complicated and will be reported elsewhere. As with the neutral zirconocene silyl hydride dimers, the true catalyst is more likely to be a monomeric species derived from 1 than 1 itself. There are no grounds to speculate on what special features of the silylium complex lead to suppression of chain cleavage relative to chain growth. It is most likely, however, that there are major mechanistic differences between the neutral and the cationic catalysts.

The present observations confirm that tuning the steric and electronic character of the catalyst site does afford some control over the rates of cyclization and chain scissioning, relative to chain elongation. This is cause for optimism that even higher molecular weights may be achieved by careful design, or lucky accident, using this approach. Since the problem of cyclization is a general one for the synthesis of inorganic polymers, this observation suggests that coordination catalysis may become a useful tool for the selective synthesis of other linear organometallic polymers.

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Supplementary Material Available: Text giving experimental details (1 page). Ordering information is given on any current masthead page.

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(15) Aromatic solvents can also coordinate specifically to the silylium cation (Schleyer, P. v. R.; Buzek, P.; Müller, T.; Apeloig, Y.; Siehl, H.-U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1471), but a sample of **1a** which was recrystallized from benzene and dried (overnight) under high vacuum was found to contain less then 0.5 equiv of solvent per silicone.

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