(Scheme II). Addition of 2,3-dimethylbutadiene to **5** leads to the regeneration of **1** and 1-ethyl-2,3-dimethylbutadiene.

In the presence of excess 2,3-dimethylbutadiene, solutions of **2a,b** will absorb ethylene leading to the formation of 4,5-dimethylhexa-1,4-diene.[15] At 25 °C this reaction is slow, but at 70 °C a mixture of **2a,b** (25 mg; 0.039 mmol) and 2,3-dimethylbutadiene (150 μL; 1.33 mmol) in C_6D_6 (0.7 mL total volume) was found to produce 13.7 equiv of 4,5-dimethylhexa-1,4-diene in 100 min when exposed to 1 atm of ethylene,[16] with greater than 95% of **2a,b** still present in solution.

We believe that both the rearrangement of **2** to **5** and the catalytic cross-coupling of 2,3-dimethylbutadiene and ethylene proceed via the σ-allylic metallacyclic intermediate **2b** (Scheme II). In the absence of 2,3-dimethylbutadiene/C_2H_4, the dimethyltitanacyclohept-3-ene can rearrange via a series of β-hydrogen abstraction/reinsertion steps to generate **5**. However, the initial intermediate alkyl-hydride compound can eliminate 4,5-dimethylhexa-1,4-diene directly in the presence of 2,3-dimethylbutadiene/C_2H_4 to regenerate **2a,b**. The fact that the entire mixture of **2a,b** will cleanly convert to **5** suggests that **2a** and **2b** are in equilibrium with one another. We are currently investigating the scope and stereochemistry of this catalytic cross-coupling reaction.[17]

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Supplementary Material Available: Text describing the data collection, structure solution, and refinement and listings of crystal data, fractional coordinates, anisotropic thermal parameters, and full bond distances and angles for the X-ray diffraction study of 1 (20 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

(15) NMR data for 4,5-dimethylhexa-1,4-diene are as follows. ^{1}H NMR (C_6D_6 30 °C): δ 5.74 (m, =C*H*); δ 5.00 (m, =CH_2); δ 2.72 (broad d, CH_2); δ 1.58 (broad s, Me_2C=C*Me*). ^{13}C NMR (C_6D_6, 30 °C): δ 137.1 (=*C*H); δ 125.9, 125.7 (Me_2*C*=CMe); δ 115.0 (=CH_2); δ 39.4 (CH_2); δ 20.7, 20.3, 18.6 (Me_2C=C*Me*).

(16) The catalytic cross-coupling of ethylene and 2,3-dimethylbutadiene can also be achieved using the titanacyclopentadiene complex [Ar″O)$_2$Ti(C_4Et_4)] as catalyst precursor. This complex has been shown to react with ethylene to produce [Ar″O)$_2$Ti(CH_2)$_4$].[8]

(17) The reaction of 2,3-dimethylbutadiene with propene has been shown to produce exclusively 2,4,5-trimethylhexa-1,4-diene in the presence of 1.

Stereoselectivity in the Catalytic Oligomerization of Phenylsilane

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Summary: A variety of chiral and achiral zirconocene complexes were investigated for the stereoselective dehydrogenative coupling of phenylsilane. Polymerization of $PhSiH_3$ with *rac*-(EBI)$ZrCl_2$/2BuLi or $Cp_2Zr(H)Cl$ yields a stereoregular polymer by ^{29}Si NMR spectroscopy. These results suggest that the stereogenic centers of the growing polymer chain may play a role in the stereochemistry of phenylsilane polymerization. A syndiotactic microstructure for the polyphenylsilanes is tentatively assigned on the basis of comparisons of their ^{29}Si NMR chemical shifts with those of known stereoregular cyclic oligomers.

Polysilanes constitute a novel class of σ-conjugated polymers with unusual electronic properties;[1] these materials absorb strongly in the ultraviolet region, and their electronic properties are sensitive to both the chain length and conformation of the polymer.[2] Because the stereochemistry of macromolecules strongly influences their conformational properties, stereoregular polysilanes should exhibit unique electronic and photochemical properties. Unfortunately, current synthetic methods, such as the Wurtz coupling of dichlorosilanes, show little stereoselectivity.[3]

Harrod's discovery[4] of homogeneously catalyzed silane oligomerization reactions with group 4 metallocenes has stimulated considerable interest in the development of catalytic routes to silicon polymers.[5,6] In view of the remarkable advances in stereospecific olefin polymerization with early-transition-metal metallocenes,[7] we were prompted to investigate the influence of metallocene structure on the stereochemistry of phenylsilane polymerization.

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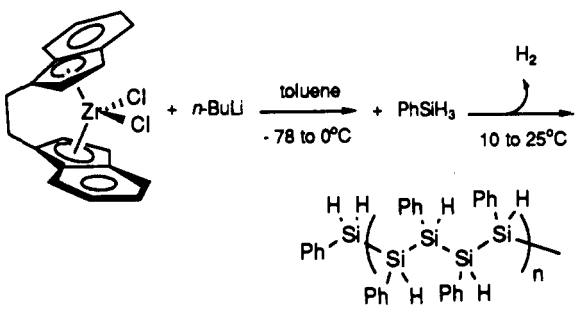
Table I. Phenylsilane Oligomerization

catalyst precursor[a]	[silane], M	temp, °C	time, h	% conversn	raw polymer M_w (M_w/M_n)	raw polymer % cyclics[e]	fractionation polymer M_w (M_w/M_n)
rac-(EBI)$ZrCl_2$/2 *n*-BuLi	1.72	25	28.5	nd[b]	928 (1.95)	49.4 (47.6)	nd
rac-(EBI)$ZrCl_2$/2 *n*-BuLi	5.70	25	7	99	2963 (2.28)	13.8 (19.5)	4902 (1.14)
rac-(EBI)$ZrCl_2$/2 *n*-BuLi	5.64	0	18.5	98	2052 (15.3)	4.8 (4.2)	nd
Cp_2ZrMe_2	1.73	25	63	nd	771 (5.00)	nd	2434 (1.14)
Cp_2ZrMe_2[c]	5.63	25	41	94	2499 (8.46)	nd	5228 (1.12)
Cp_2ZrCl_2/2 *n*-BuLi	5.59	25	7	99	1858 (1.82)	nd	4296 (1.13)
$Cp_2Zr(H)Cl$[d]	5.67	25	66	61	1147 (19.5)	3.5 (nd)	3478 (1.17)

[a] Conditions: [Cat] = 0.014 M, ethylbenzene internal standard. [b] nd = not determined. [c] [Cat] = 0.012 M. [d] [Cat] = 0.018 M. [e] Determined by ^1H NMR (GPC).[17]

Our initial attempts to oligomerize phenylsilane with chiral Brintzinger-type[8] metallocenes such as *rac*-(EBTHI)$ZrMe_2$ and *rac*-(EBI)$ZrMe_2$ (EBTHI = ethylenebis(tetrahydroindenyl), EBI = ethylenebis(indenyl)) were frustrated by variable induction periods,[9] the production of low-molecular-weight oligomers, and significant amounts of cyclic oligomers.[10] In a similar study, Harrod reported that dimethyl derivatives of *ansa*-metallocene complexes yield predominantly cyclic oligomers with some evidence of stereoregularity.[11] We have found that induction periods can be avoided by employing dibutylzirconocene derivatives (generated in situ by treatment of the dichloride with 2 equiv of BuLi[12,13]) as catalyst precursors (eq 1).[14,15] Using this procedure, polymerization of phenylsilane commences at or below room temperature to yield linear oligosilanes, but the molecular weights of the products remained modest (M_w = 1000, vs polystyrene) and approximately 48% of the isolated products were cyclic oligomers (Table I).



(1)

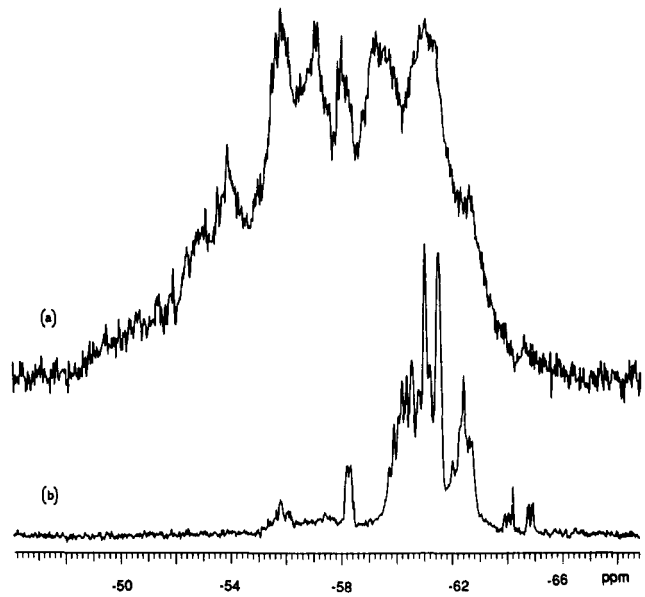


Figure 1. ^{29}Si NMR spectra of oligosilanes in toluene-d_8: (a) synthesized from Cp_2ZrMe_2, [silane] = 1.73 M, M_w = 2434, M_w/M_n = 1.14; (b) synthesized from (EBI)$ZrCl_2$, [silane] = 5.70 M, M_w = 4902, M_w/M_n = 1.14.

The production of cyclic oligomers and the low molecular weights represent two serious shortcomings to transition-metal-mediated syntheses of polysilanes. A key insight into the mechanistic origin of these deficiencies was provided by the Tilley group with the suggestion that the dehydrogenative coupling of silanes proceeds via a step-growth mechanism.[6] On the basis of this suggestion, we investigated the effects of monomer concentration and temperature[16] and found that the selectivity for cyclics decreased with increasing monomer concentration and lower reaction temperatures. Under appropriate conditions, oligophenylsilanes with average molecular weights (M_w vs polystyrene) ranging from 1000 to 3000 can be prepared where the fraction of cyclic oligomers is less than 5% (Table I).[17] Nevertheless, the polydispersity (PDI) of the oligomers produced (M_w/M_n = 1.9–19.5) and the presence of small amounts of cyclic oligomers complicate interpretations of the polymer microstructure. However, by means of preparative gel permeation chromatography we were able to separate higher molecular weight oligomers (M_w = 3400–5000) with narrow polydispersities (M_w/M_n

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(13) Corey has developed a similar procedure and found it to be effective for the oligomerization of secondary silanes.[5b,c]

(14) A control experiment was performed to rule out that BuLi was catalyzing the oligomerization of phenylsilane. BuLi reacts slowly and stoichiometrically with phenylsilane to produce primarily 1-butyl-1,2-diphenyldisilane as well as other butylated silanes. These products were not observed in the oligomerization reactions.

(15) The following procedure is representative. On an inert-atmosphere vacuum line, a 20-mL toluene solution of (EBI)$ZrCl_2$ (0.150 g, 0.36 mmol) was treated with *n*-butyllithium (0.72 mmol) at −78 °C and the mixture warmed to 0 °C to give a dark brown solution. (For experiments with high silane concentration (5.6 M), ethylbenzene was used as a solvent.) After the mixture was stirred for approximately $^1/_2$ h, phenylsilane (5 g, 46 mmol) was added and the solution warmed to room temperature. Polymerization commenced typically at just below room temperature, as evidenced by vigorous bubbling of the solution. Catalyst residues were removed by hot filtration of the reaction solution over a 3 cm × 9 cm column of Florisil. The column was rinsed with hot toluene (3 × 100–150 mL) and the resulting solution evaporated in vacuo to yield an opaque, oily material.

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(17) The fraction of cyclic oligomers were determined both by GPC and by ^1H NMR spectroscopy by comparing the ratio of resonances above 5 ppm to those below 4.8 ppm.

= 1.1-1.2) for spectroscopic investigations (Figure 1).[18]

A variety of catalyst precursors were studied to probe the influence of catalyst structure on the stereochemistry of phenylsilane oligomerization. The microstructure of the fractionated polyphenylsilanes was studied by ^{29}Si NMR spectroscopy (Figure 1). As previously reported,[4] we find that oligomerization of phenylsilane (1.73 M) with Cp_2ZrMe_2 in toluene at room temperature affords oligomers which show a broad series of resonances between -50 and -65 ppm in the ^{29}Si NMR spectrum (Figure 1a).[19] Since the ^{29}Si NMR chemical shift of each stereogenic silicon atom is sensitive to the relative stereochemistry of adjacent silicon atoms, these broad series of resonances are indicative of an atactic microstructure. In contrast, the ^{29}Si NMR spectrum of oligomers obtained from the chiral racemic (ethylenebis(indenyl))zirconocene dibutyl precursors (eq 1) displays a much narrower set of resonances between -60 and -63 ppm, indicative of a stereoregular microstructure (Figure 1b). (DEPT experiments establish that the sharp resonance at -58 ppm is due to SiH_2 end groups.) Remarkably, we find a very similar microstructure when phenylsilane is polymerized at a higher concentration (5.6 M) with achiral catalyst precursors such as Cp_2ZrMe_2 and Cp_2ZrHCl.[20] The effect of concentration on the stereochemistry of phenylsilane polymerization with Cp_2ZrMe_2[21] was unexpected and is not completely understood. Nevertheless, the fact that similar microstructures are obtained in the presence of chiral and achiral metallocenes implies that chiral catalysts, although effective, are not necessary for stereoregulation in the catalytic oligomerization of phenylsilane.

Because there are few stereochemically defined model compounds for spectroscopic comparison, only a tentative assignment of the microstructure is possible. For the atactic material, several broad resonances are discernible in the ^{29}Si NMR spectrum. The narrow set of resonances for the stereoregular oligomers are coincident with the high-field resonance of the atactic material and are centered at δ = -61 ppm. This chemical shift corresponds closely to the ^{29}Si NMR chemical shift (-61.6 ppm) of the known crystalline hexaphenylcyclohexasilane,[22,23] which has been assigned as the trans (or syndiotactic[24]) isomer. On the basis of this, we assign a predominantly syndiotactic microstructure to the linear stereoregular oligosilanes.[25]

In summary, we report the synthesis and characterization of predominantly syndiotactic polyphenylsilane. The stereochemistry of phenylsilane polymerization with chiral and achiral zirconocene derivatives suggests that the stereochemistry of the growing chain end is involved in stereodifferentiation and may be more important than the chirality of the catalyst.

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Supplementary Material Available: Text giving experimental details, a table of experimental data, and ^{29}Si NMR spectra (4 pages). Ordering information is given on any current masthead page.

(18) The absorption properties polysilanes are dependent on molecular weight,[1] and thus for comparisons of samples of different microstructures it is important to have reasonably narrow polydispersities.

(19) A similar microstructure is observed using Cp_2ZrCl_2/*n*-BuLi as a catalyst precursor.

(20) ^{29}Si NMR spectra of oligomers obtained from these precursors are very similar to that shown in Figure 1b (see supplementary material).

(21) There appears to be no concentration dependence on the stereochemistry for polymers produced with (EBI)$ZrCl_2$ or $Cp_2Zr(H)Cl$ catalyst precursors.

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(23) This compound can be isolated from polymerization mixtures obtained with (EBI)$ZrCl_2$ precursors at low phenylsilane concentration. A singlet at -60.2 ppm in the solid-state ^{29}Si NMR spectrum is consistent with the trans isomer.

(24) For assignments of relative stereochemistry for polymers with stereogenic centers at each backbone atom, see: Farina, M. *Top. Stereochem.* **1987**, *17*, 1.

(25) West has used a similar analysis to assign the microstructure of polyphenylmethylsilane.[3]

Reduction of the Heterobimetallic μ-$\eta^1(C)$:$\eta^2(O,O')$-CO_2 Complex $Cp(CO)_2Ru(CO_2)Zr(Cl)Cp_2$ to Its μ-$\eta^1(C)$:$\eta^1(O)$-Formaldehyde Derivative $Cp(CO)_2Ru(CH_2O)Zr(Cl)Cp_2$: Hydride Transfer Occurs at Ligated Carbon Monoxide

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Summary: Treatment of the previously characterized RuZr μ-$\eta^1(C)$:$\eta^2(O,O')$-CO_2 complex $Cp(CO)_2Ru(CO_2)Zr(Cl)Cp_2$ (**5**) with $Cp_2Zr(H)Cl$ (2 equiv) cleanly affords the stable μ-formaldehyde compound $Cp(CO)_2Ru(CH_2O)Zr(Cl)Cp_2$ (**7**), which has been isolated and fully characterized. The ^{13}C-labeled CO_2 complex $Cp(CO)_2Ru(^{13}CO_2)Zr(Cl)Cp_2$ (**5a**) is available from $^{13}CO_2$ (99% labeled); combining **5a** and $Cp_2Zr(H)Cl$ at -78 °C selectively produces $Cp(^{13}CO)(CO)Ru(CH_2O)Zr(Cl)Cp_2$ (**7a**). Complex **5a** transforms to a 1:1.3 mixture of **5a** and its isotopomer $Cp(^{13}CO)(CO)Ru(CO_2)Zr(Cl)Cp_2$ (**5b**) at room temperature (benzene or toluene solutions for 8-12 h). $Cp_2Zr(H)Cl$ then reduces **5a/5b** to a 3:1 mixture of **7a** and its isotopomer $Cp(CO)_2Ru(^{13}CH_2O)Zr(Cl)Cp_2$ (**7b**). IR and NMR (^{1}H, ^{13}C) spectral data are presented for **5/5a/5b** and **7/7a/7b**, and credible mechanistic pathways for ^{13}C-labeled exchange between carboxylate and terminal carbonyl sites for **5a** ⇔ **5b** and for regioselective hydride transfer ($Cp_2Zr(H)Cl$) to a terminal carbonyl (not the carboxylate center) of **5** are discussed.

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