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Ansa-Metallocenes: Catalysts for the Dehydrocoupling of Hydrosilanes

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Abstract: The dehydrocoupling of PhMeSiH₂ to form oligomers and of PhSiH₃ to form polysilanes has been performed with the precatalyst combination of $[Me_2El(C_5H_4)_2MCl_2$ (El = Si, C; M = Ti, Zr, Hf) and nBuLi. The results are compared to those produced from $(\eta^5-C_5H_5)_2MCl_2/nBuLi$.

INTRODUCTION

The σ -conjugation of catenated silicon chains gives rise to conducting, photoconducting and thermochromic behavior, properties that have potential for technological use.¹ A drawback to the applications of polysilanes is the lack of variation of synthetic routes for their production. The general method for the preparation of catenated silicon compounds is a Wurtz-type coupling of a dichlorosilane with an alkali or alkaline earth metal. The vigorous nature of the Wurtz coupling precludes the incorporation of a range of functional groups on the silicon chain and product yields are often low, thus meriting the search for alternative approaches for preparing silicon oligomers and polymers. Recently reported methods that hold some promise include ring-opening polymerization and the anionic polymerization of masked disilenes but both suffer from the requirement that the starting materials for polymerization must first be synthesized from silicon monomers.²

In 1985 Harrod demonstrated that catenated silicon compounds could be formed from hydrosilane monomers by dehydrocoupling in the presence of group IV metallocene compounds.³ Effective catalyst precursors include Cp_2MR_2 ($Cp = \eta^5 - C_5H_5$; M = Ti, Zr; R = Me, Ph) developed by Harrod and coworkers and $CpCp^*M[Si(SiMe_3)_3]R$ ($Cp^* = \eta^5 - C_5Me_5$; M = Zr, Hf; R = H, Cl, Me) developed by Tilley and coworkers.⁴ We have investigated the use of the combined system, $Cp_2MCl_2 + nBuLi$ (M = Ti, Zr, Hf) as precatalysts for the dehydrocoupling of both primary and secondary silanes.^{4,5} This later system utilizes commercially available reagents to generate the catalytic species and eliminates the necessity of first synthesizing and isolating a precursor complex. The H(RSiH)_xH polymers that are formed from the condensation of primary silanes are attractive since the SiH bond represents a useful functional group and conversions occur under mild conditions to Si-O, Si-hal and SiC bonds.⁶ Polymers of the type H(RSiX)_xH (X = H, OR, Cl) are not normally obtained by a Wurtz-type coupling process.⁷

The catalyst precursors that have been the most successful for dehydrocoupling of hydrosilanes are related to the Ziegler-Natta catalysts that have been employed for homogeneous polymerization of olefins. The combination of zirconocene-methylaluminoxane for production of isotactic polypropylene was reported in 1985⁸ and has been under intense investigation since. The Cossee mechanism⁹ is the most widely proposed to account for the polymerization of olefins by heterogeneous Ziegler-Natta systems as well as homogeneous metallocene catalysts and is outlined in the first sequence in Scheme 1. The precursor leading to carbon-carbon bond formation is believed to be a 14-electron, cationic metallocene and recent calculations support a pyramidal geometry for $[Cp'_2ZrMe]^{+.10}$ The olefin forms a π -complex with the metal center followed by a $2\sigma + 2\pi$

cycloaddition to insert the olefin into the Zr-alkyl bond. The mechanism for coupling of hydrosilanes outlined in the second line of Scheme 1 is based on σ -bond metathesis steps as developed by Tilley and coworkers from a study of stoichiometric reactions primarily for the hafnium system.^{3a,e} We have suggested the sequence outlined in Scheme 2 for the formation of the 16-electron complex, Cp₂M(SiRR'H)H which precedes the silicon-silicon bond forming step.¹¹ In the dehydrocoupling sequence, prior coordination of an Si-H σ -bond in H(SiRR')_xH leads to a $2\sigma + 2\sigma$ "cycloaddition" in which a new silicon-silicon bond is formed. Thus, the proposed key step leading to silicon-silicon bond formation and to carbon-carbon bond formation may be viewed as related processes.



Scheme 1. Comparison of Proposed Steps in the Polymerization of Olefins and the Dehydrocoupling of Hydrosilanes Promoted by Metallocene Catalysts.

$$Cp_{2}ZrCl_{2} \xrightarrow{+2 \text{ nBuLi}} Cp_{2}ZrBu_{2} \xrightarrow{-BuH} Cp_{2}Zr \xrightarrow{-BuH} Cp_{2}Zr \xrightarrow{+HSiRR'H} [Cp_{2}Zr] \xrightarrow{HSiRR'H} Cp_{2}Zr \xrightarrow{H} SiRR'H$$

Scheme 2. Proposed route from Cp2ZrCl2 to 16-electron complex Cp2Zr(SiRR'H)H

A major difference between the two processes as outlined in Scheme 1 is direct removal of the silicon product from the metal center after the "cycloadditon" step in dehydrocoupling but retention of the growing polymer chain by the metal center in olefin polymerization. The polymer chain is eventually removed from the metal center either by a β -H or β -Me elimination,^{10,12} with β -Me elimination perhaps thermodynamically favored. Recent calculations have demonstrated that a σ -bond metathesis to give an alkane and a vinylzirconocene may also be a viable chain termination step.¹⁰ If the mechanisms outlined are correct then an additional feature that may influence the two different chemical processes is the presence of two LUMO's on Cp₂MR⁺ and one LUMO on Cp₂M(H)SiRR'H.

First generation catalysts for the formation of polysilanes have produced H(PhSiH)_xH with molecular weights usually in the range of 2000-5000.^{13,4e} It is difficult to compare results from different investigators especially from earlier reports since conditions for the condensation reaction vary. In general, the highest molecular weights are achieved from reactions of neat RSiH₃ (or minimal solvent) at room temperature. Recently, Tilley and Imori have studied the condensation of PhSiH₃ under controlled conditions with a series of zirconocene and hafnocene precursors and report M_w values that vary from about 2000 to 14,000.¹⁴ In most cases studied thus far cyclic polysilanes are also produced in addition to the desired linear materials. The cyclic materials are produced in highest quantities with titanium catalysts and in the smallest percentages with hafnium catalysts.¹⁵ Heating reaction mixtures causes an increase in cyclic products.^{4e} Thus targets for the next generation of catalysts will involve improving the molecular weights of the polymers produced and eliminating cyclic byproducts, a requirement for application purposes.

Ansa-zirconocene catalysts, particularly those with a single silicon atom bridge exhibit a high activity and produce high molecular weight polymers from olefins.¹⁶ The single atom bridge may impose a higher rigidity as

well as provide a favorable electronic influence since silyl-substituents on Cp-rings have been shown to be more electron-donating than carbon-substituents.¹⁷ Similar arguments have been utilized to account for the characteristics of a germanium bridged catalyst system.¹⁸ The possible relationship between olefin polymerization and silane dehydrocoupling as outlined in Scheme 1 suggests that a study of *ansa*-metallocene dichloride catalyst precursors may provide some insight into the factors that influence the condensation of hydrosilanes. We also anticipated that the decrease in Cp(centroid)-M-Cp(centroid) angle that results from a one atom bridge would increase the coordination site somewhat since steric problems in the silicon-silicon bond forming step may be more critical than in a carbon-carbon bond forming step. Recent calculations show that the one atom bridge also increases the electron deficiency of a zirconium center.¹¹ Only scattered examples of *ansa*-metallocenes as silane dehydrocoupling catalysts have been reported. Harrod and Waymouth have briefly investigated LMMe₂ [L = 1,2-bis-(indenyl)ethane and 1,2-bis(tetrahydroindenyl)ethane; M = Ti, Zr^{15,19}] and Tilley has included [Me₂Si(C₅H₄)₂]Zr[Si(SiMe₃)₃]Me and [Me₂Si(C₅H₄)(C₅Me₄)]ZrMeR [R = Me, Si(SiMe₃)₃] in a comparison of catalysts that promote the coupling of PhSiH₃.¹⁴

In this report we compare the results of the condensation of primary and of secondary silanes with the related one atom bridged *ansa*-metallocenes, $Me_2C(C_5H_4)_2MCl_2/nBuLi$ and $Me_2Si(C_5H_4)_2MCl_2/nBuLi$, to those obtained with the parent metallocenes.

RESULTS

Catalyst Synthesis. The ansa-metallocenes with a one atom bridge have been generated by two routes as outlined in Scheme 3. The only derivative that had not been previously reported in the literature was $[Me_2C(C_5H_4)_2]HfCl_2$ which was prepared in the current study by both routes outlined in Scheme 3 although the procedure that utilizes $Me_2C(C_5H_5)_2$ as a starting material provided higher yields of the hafnium complex.



The structures of $[Me_2Si(C_5H_4)_2]MCl_2$ (M = Ti, Zr) have been determined previously^{21b} and the structures of the isomorphous series $[Me_2C(C_5H_4)_2]MCl_2$ (M = Ti, Zr, Hf) were determined for this study.²³ Table 1 summarizes the Cp'-M-Cp' (Cp_{centroid}-M-Cp_{centroid}) angles that have been observed in $[X(C_5H_4)_2]MCl_2$ (and the related $[X(C_5H_4)_2]MMe_2$ when available). When the two Cp rings of Cp₂MCl₂ are "tied" together by a bridging atom or atoms the rings are no longer free to rotate, that is, the structure becomes more rigid. A second effect produced by tying the Cp rings together is that the Cp_{centroid}-M-Cp_{centroid} angle decreases but the decrease is attenuated the greater the number of atoms in the bridge. The most dramatic effect is observed with a single carbon atom bridge which causes a decrease in the Cp'MCp' angle of 10-13°. A two carbon bridge appears to cause a smaller decrease of about 3-5° and the three-atom bridge systems are about the same as the parent metallocenes. The one atom silicon bridge appears to produce about the same type of change as the -(CMe₂)₂- bridge, which is not surprising since the covalent radius of silicon is about 1.5 times that of carbon.³⁶ Although the data are limited it appears that converting the MCl₂ unit in the *ansa*-metallocene to MMe₂ does not significantly change the Cp'MCp' angle and substitution on the Cp-rings also may also produce little change.³⁷

The Cp'-X-Cp'²⁻ unit may be viewed as forming a wedge about the metal center. As the Cp'MCp' angle decreases, the coordination site of the metal opens slightly and the metal protrudes from the wedge created by the Cp ligands. To illustrate this change of position of the metal center a simple parameter was derived which

involves the distance of the metal on a perpendicular to an imaginary line that connects the centers of the two Cp rings. The difference between this distance in the *ansa*-metallocene and the corresponding parent metallocene illustrates the change in this position and is summarized in Table 2. The largest change is observed with the one carbon atom bridge systems for each of the metals.





Bridge Unit X	Metal	Cp'-M-Cp' Angle ^b	Ref. ^c	
none	Ti	131	24	
	Zr	129.5(132.5) 129.1	25(26)	
	Hf	127.1(133.0)	27(26)	
-Me ₂ C-	Ti	121.5(120.9)	23(28)	
2	Zr	116.7(115.9)	23(28)	
	Hf	117.1	23	
-Me ₂ Si-	Ti	128.7	21b	
-	Zr	125.4	21b	
	Hf	126.8	22	
-(CMe2)2-	Ti	128.4	29	
	Zrd	124.8	30	
-(CH2)2-	Ti	128	31	
-(CH ₂)3-	Ti	133	32	
× 205	Zr	129	33	
	Hf	129.5	34	
-(CH2)12-	Zr	133.7	35	

a. Cp'-M-Cp' angle is for Cp_{centroid}-M-Cp_{centroid}

b. Values given are for the chloride derivative; value in parentheses is for the Me analog. c. Reference in parentheses for the Me derivative. d. ^tBu-substituents in 3-position of Cp.

 Table 2. Change in the Metal Position in ansa-Metallocenes Compared to that in the Parent Metallocene.



Metallocene Dichloride	Y (Å)	Δ (Å) ^a	Change
Cp ₂ TiCl ₂	0.853		
Me ₂ Si(C ₅ H ₄) ₂ TiCl ₂	0.898	0.045	5%
$Me_2C(C_5H_4)_2TiCl_2$	1.005	0.152	18%
Cp ₂ ZrCl ₂	0.933		
Me ₂ Si(C ₅ H ₄) ₂ ZrCl ₂	1.008	0.075	8%
$Me_2C(C_5H_4)_2ZrCl_2$	1.152	0.219	23%
Cp ₂ HfCl ₂	0.971		
Me ₂ Si(C ₅ H ₄) ₂ HfCl ₂	1.020	0.049	5%
$Me_2C(C_5H_4)_2HfCl_2$	1.135	0.164	17%

a. Y of the ansa-complex - Y of the parent metallocene dichloride

Condensation of PhMeSiH₂. The silicon oligomers formed in the condensation of PhMeSiH₂ have been previously characterized by GC, GCMS and ¹H, ¹³C and ²⁹Si NMR spectroscopy.^{5a} The reactions of PhMeSiH₂ in the presence of Cp₂MCl₂/nBuLi, $[Me_2C(C_5H_4)_2]MCl_2/nBuLi$ and $[Me_2Si(C_5H_4)_2]MCl_2$ nBuLi were conducted in toluene at 90 °C and run in simultaneous sets for each metal. Aliquots were withdrawn at selected intervals and reaction mixtures quenched in hexane. After removal of the catalyst residues the components in the mixture were determined by gas chromatography. Selected results are given in Table 3.

Consistent with the mechanism outlined in Scheme 1 the first coupling step in the condensation of PhMeSiH₂ results in the formation of disilane through transfer of a silyl unit to a monomeric secondary silane. Chain growth would involve either the reaction of Cp₂M(SiPhMeH)H with HPhMeSiSiMePhH or of Cp₂M(SiPhMeSiPhMeH)H with PhMeSiH₂. According to model studies performed by Tilley^{4a,e} it is likely that the chain growth involves transfer of a single silicon unit to a chain which would favor the first of the two possibilities. Thus, for example, a silyl unit is transferred from the metal to a tertiary silicon center of the disilane. Such a transfer would involve a greater steric requirement.³⁸ Initially the consumption of

Catalyst Precursor	PhMeSiH ₂		Disilane		Trisilane		Tetrasilane	
•	5h	72 h	5h	72h	5h	72h	5h	72h
Cp ₂ TiCl ₂	73	41	21	32	6.1	25	-	2.2
Me ₂ Si(C ₅ H ₄) ₂ TiCl ₂	83	39	17	36	-	23	-	1.8
$Me_2C(C_5H_4)_2TiCl_2$	79	34	21	58	-	7.6	-	-
Cp ₂ ZrCl ₂	68	27	21	15	7.1	34	-	14
Me ₂ Si(C ₅ H ₄) ₂ ZrCl ₂	69	30	26	22	4.4	37	•	5.5
$Me_2C(C_5H_4)_2ZrCl_2$	67	30	28	25	5.7	37	-	4.8
Cp2HfCl2	67	37	30	36	3.6	25	-	1.6
Me ₂ Si(C ₅ H ₄) ₂ HfCl ₂	82	69	19	30	-	1.1	-	-
$Me_2C(C_5H_4)_2HfCl_2$	85	60	15	37	-	3.2	-	-

Table 3. Oligomer Distribution in the Condensation of PhMeSiH₂ as Determined by Gas Chromatography.^a

a. Reactions are run in toluene at 90 °C at a ratio of PhMeSiH₂/Cp₂MCl₂/nBuLi of 22/1/2. Numbers are uncorrected GC percentages.

the starting silane is slower for $Cp'_2MCl_2/nBuLi$ (M = Ti and Hf) systems relative to the parent metallocene but this difference disappears at longer time intervals for Ti but not for Hf. The most direct effect of the *ansa*metallocenes, however, is on the *decrease* in the formation of chains longer than the disilane. This is obvious at the trisilane stage for $Cp'_2HfCl_2/nBuLi$ and $Me_2C(C_5H_4)_2TiCl_2/nBuLi$ but at the tetrasilane stage (Table 3) for $Cp'_2ZrCl_2/nBuLi$.

The disilane and trisilane produced from PhMeSiH₂ were formed as statistical mixtures of diastereomers but this may not be the case for the tetrasilane.^{5a} The trisilane formed with Me₂Si(C₅H₄)₂ZrCl₂ was isolated and characterized and the spectroscopic data are identical to those produced from the parent Cp₂ZrCl₂.

Condensation of PhSiH₃. The condensation of PhSiH₃ with ansa-metallocene dichlorides and the parent metallocene dichloride was studied under various conditions. The polysilane products were characterized by gel permeation chromatography (GPC) to determine the molecular weight and by ¹H NMR spectroscopy to show, qualitatively, the distribution of cyclic and linear materials. Molecular weight data are summarized in Table 4. Overall, the same general trends are observed with the *ansa*-metallocenes as with metallocene derivatives: the molecular weights of the H(PhSiH)_XH produced increase through the sequence Ti < Zr < Hf and are higher for reactions run in the absence of solvents. Under all conditions studied the M_w values of the short polymers produced from the *ansa*-metallocenes are *lower* than those obtained from the parent metallocenes except for [Me₂Si(C₅H₄)₂]HfCl₂/nBuLi in toluene at shorter time periods. There is no distinction in M_w values for H(PhSiH)_xH produced for the three catalyst systems when M = Ti (neat conditions) and M = Zr (in solvent). The M_w values produced from *ansa*-[X(C₅H₄)₂]ZrCl₂ are about 15% lower than those produced from the parent metallocene when reactions are run in the absence of solvent. Only in the case of Hf does there appear to be a difference in the M_w of the polysilanes produced from the two *ansa*-systems.

Fig. 1 provides selected examples of the ¹H NMR spectral data for the polysilanes produced from Hfbased catalysts for the SiH region only. The sharp triplet (centered at 4.49 ppm) that overlaps with the broad SiH massif is due the presence of PhBuSiH₂.³⁹ It is generally believed that the region upfield of 4.8 is due to the SiH resonances in the linear polysilane $H(PhSiH)_XH$ while the region downfield of 4.8 ppm is attributed to SiH resonances in cyclic polysilanes $(PhSiH)_Y^{19c}$ although these regions are by no means well resolved. There are actually two cyclic regions: one centered at ~5.1 ppm and the other at ~5.9 ppm. The region from 4.9-5.3 ppm has been tentatively assigned to a mixture of cyclopentasilane isomers.^{19b} The resonances that appear further downfield result from a mixture of cyclics from cyclohexasilane to cyclononasilane.⁴⁰ We have also demonstrated the presence of a series of cyclics produced in the condensation of BuSiH₃.^{5b} Table 4. Molecular Weights of H(PhSiH)_xH Produced from the Condensation of PhSiH₃ as Determined by Gel Permeation Chromatography.^a

Μ	Conditions sol/°C/hr	Cp2MCl2 ^b wt % ^c M _w		[Me ₂ Si(C ₅ H ₄) ₂]MCl _{2^b} wt % ^c M _W		[Me ₂ C(C ₅ H ₄) ₂]MCl _{2^b} wt % ^c M _W	
Ti	neat/25/24	75	1250	75	10 8 0	75	1060
Zr	neat/25/1	85	2070	85	1680	40	1700
	neat/25/17	85	1600	85	1340	85	1360
	tol/25/17	85	1170	85	1150	85	1170
Hf	neat/25/1	85	3340	85	2080	7	oligomers
	neat/50/13	80	2400	80	2040	73	1490
	tol/50/13	40	oligomers	s 57	1070	22	oligomers
	tol/50/48	75	1520	75	1320	37	1170

a. GPC measurements were conducted with three Waters Styragel columns (100 Å, 500 Å and 10⁴ Å) connected in series. M_w determined relative to polystyrene standards. The values are for the bimodal molecular weight distribution b. Silane/metal complex/nBuLi = 24/1/2. Reactions are run at room temperature. c. (Mass of non-volatile silane residue/mass PhSiH₃) x 100.





The presence of cyclic material is obvious in the condensations carried out in this study with the Ti catalyst series and with the Zr and Hf series when reactions are carried out above room temperature (compare sets of traces for Zr and Hf in Fig. 1). The cyclic region ~5.9 ppm is prominent only in polysilanes produced in toluene solution ($Cp_2HfCl_2/50$ °C).

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DISCUSSION

The most commonly studied primary silane in dehydrocoupling reactions is phenylsilane. The molecular weights of the short polymers that are produced tend to be higher with Zr and Hf catalysts than for Ti and are significantly higher for PhSiH₃ compared to RSiH₃ (R = alkyl > Me). A common problem in almost all cases of dehydrocoupling of primary silanes is the formation of cyclic products.⁴ Cyclics are produced in highest quantities with Ti catalysts and tend to decrease through the sequence Ti>Zr>Hf for catalysts of the same structure. Condensation reactions run above room temperature also increase the percent of cyclics relative to the linear polysilane. The highest molecular weights for the polysilane polymers produced are observed in reactions run in the absence of solvents^{4e,15,41} or in concentrated solutions.^{15,19c} The percentage of cyclic product increases when solvent is present.¹⁵ Although cyclic materials can be removed from the linear fraction by preparative gel permeation chromatography^{19c} this is probably not a practical solution in the long run.

In the evolution of Ziegler-Natta catalysts a major focus has been the design of catalyst structures that prevent regio-errors (for example, 2,1- and 1,3 insertions) and early chain growth termination which leads to lower molecular weight polymer. In the development of the transition metal catalyzed dehydrocoupling reaction the aim of modifications in catalyst structure is to both increase the average molecular weight of the polysilane produced and to decrease or eliminate the relative concentration of cyclic material. The control of stereochemistry in polysilane chemistry has been addressed, but only briefly. Waymouth has shown that stereoregular polysilane polymer was produced with rac-(EBI)ZrCl₂/nBuLi (EBI = ethylene bis(indenyl)) as well as by Cp₂Zr(H)Cl. A syndiotactic microstructure was assigned to H(PhSiH)_xH based on model stereoregular cyclic oligomers.^{19c}

In the current study the effect of tying the two Cp rings of Cp₂MCl₂ with a one atom bridge was examined. With such catalyst systems the dehydrocoupling of PhR'SiH₂ appears to be slower although less obviously so with the one atom silicon bridge. Under conditions that usually promote the formation of higher molecular weight polysilanes from PhSiH₃ the *ansa*-metallocenes, $[Me_2El(C_5H_4)_2]MCl_2$ (El = Si, C), produce lower M_w values compared to the parent metallocene but do provide some evidence for lower cyclic/linear ratios in the case of the one-carbon bridge complexes. Further support for this conclusion was provided with $[Me_2C(C_5H_4)(C_{13}H_8)]ZrCl_2/nBuLi$ ($C_{13}H_8 = \eta^5$ -fluorenyl; $Cp'(cent)M'Cp''(cent) \angle = 118.6^{\circ 42}$). Fig. 2 shows the ¹H NMR spectrum of the SiH region for the polysilane product and illustrates the absence of cyclic material.



Figure 2. ¹H NMR Spectrum of H(PhSiH)_xH Produced from $(\eta^5-C_5H_4CMe_2-\eta^5-C_{13}H_8)ZrCl_2$

In the polymerization of propene "chemical errors" such as 2,1- and 1,3-insertions occur during the polymerization process. These misinsertions occur with frequencies of 1-2% but influence the properties of the polymer that are produced.⁴³ Chemical errors also occur in the condensation of PhSiH₃. The cyclic products may be formed through an "error" in the type of σ -bond metathesis that occurs. A metathesis reaction that involves an internal SiH bond or Si-Si bond of a silicon chain bound to the metal center, would produce cyclic products.^{5b} Both

the parent metallocene and the *ansa*-metallocenes exhibit this type of "error" which can occur with a distressingly high frequency (100% in one case⁴⁰). However, an additional "error" occurs as a result of another type of chemical process although this process can only be detected in the early stages of the condensation reaction. A minor side reaction is phenyl scrambling which results in the formation of -Ph₂Si-units that are incorporated into the growing chain. The *ansa*-metallocenes produce negligible quantities of oligomers that contain Ph₂Si- units compared to the parent metallocene as illustrated by the data in Table 5. The scrambling

may result from a disproportionation of PhSiH₃ to produce Ph_2SiH_2 and SiH_4 . The Ph_2SiH_2 couples with PhSiH₃ to form the "phenyl"-rich short chains listed in Table 5. The other disproportionation product, SiH₄, would be expected to form "phenyl"-poor oligomers but, if formed, the silane must be volatilized from the reaction medium faster than the dehydrocoupling reaction can occur since these "phenyl"-poor oligomers have not been identified in the product mixture.

Condensation reactions promoted by hafnocene complexes are inherently slower than those promoted by zirconium although, in general, hafnocene systems do form high molecular weight polysilanes^{4a,e} and in some cases the M_w values are higher than those produced from the related zirconium and titanium analogs.^{4,15} If the Cp'2HfCl2/nBuLi combination resembles Cp₂ZrCl₂/nBuLi then the sequence shown in Scheme 2 would be expected. The complex Cp₂Hf(isobutylene)PMe₃ has been reported but is generated from a mixed dialkyl precursor, Cp₂Hf(^tBu)R (R = nBu^{44a}, iBu^{44b}) in the presence of PMe₃. The reaction of Cp₂Hf(CH₂=CMe₂)PMe₃ with Ph₃SiH produced Cp₂Hf(SiPh₃)H(PMe₃).⁴⁵ The results from the Me₂C(C₅H₄)₂HfCl₂/nBuLi in the current study could be explained by either incomplete coupling of the dichloride with nBuLi or to the formation of an unusually stable Cp'₂HfBu₂ system.⁴⁶ The reaction of Me₂C(C₅H₄)₂HfCl₂ with 2 eq if nBuLi in toluene cleanly produced Me₂C(C₅H₄)₂HfBu₂ as shown by the ¹H NMR spectrum in Fig. 3. When solutions of Me₂C(C₅H₄)₂HfBu₂ with PhSiH₃ at room temperature does not involve the formation of an olefin complex but that a metathesis reaction with the silane provides Me₂C(C₅H₄)₂Hf(SiPhH₂)Bu which precedes the catalytic cycle.⁴⁷ Subsequent coupling to form chains may be slower.

Table 5. Oligomers Formed from PhSiH₃: Comparison of Results Produced from Cp₂HfCl₂ and Me₂C(C₅H₄)₂HfCl₂.^a

Molecular	Assignment	GC%b		
Ion	-	Cp_2HfCl_2	Cp'2MCl2°	
108	PhSiH ₃	4.1	16	
164	PhBuSiH ₂	2.4	-	
184	Ph ₂ SiH ₂	3.5	2.7	
214	H(PhSiH) ₂ H	38	54	
290	HPh ₂ SiSiPhH ₂	4.4	<0.1	
320	H(PhSiH) ₃ H	21	19	
396	HPh2Si(PhSiH)2Hd	4.5	<0.1	
426	H(PhSiH)4H	14	5.8	
¢	H(PhSiH)5H	3.3 ^f	1.8	





Fig. 3. ¹H NMR Spectrum of Me₂C(C₅H₄)₂HfBu₂: Butyl Region

Conclusion. The condensation of PhSiH₃ and PhMeSiH₂ promoted by ansa-metallocenes of the type $[Me_2El(C_5H_4)_2]MCl_2$ (El = C, Si) in conjunction with nBuLi has been studied for the titanium triad and compared to the parent metallocenes. The major structural change in the ansa-metallocene is a decrease in the Cp'(centroid)-M-Cp(centroid) angle relative to the parent Cp₂MCl₂ and this angle change is greatest for the carbon bridge whereas the silicon bridge produces a change in this parameter similar to that found in an ethanobridge. Description of additional but more complex geometrical features of ansa-metallocenes also have been developed.⁴⁸

The average molecular weight of the oligomers (from PhMeSiH₂) and the polysilanes (from PhSiH₃) that are produced are lower with the [Me₂El(C₅H₄)₂]MCl₂ than with the parent metallocene and this is the case for all three metals of the titanium group. Similar observations have been made by Tilley with [Me₂Si(C₅H₄)₂]Zr-[Si(SiMe₃)₃]Me and [Me₂Si(C₅H₄)(C₅Me₄)]ZrMeR [R = Me, Si(SiMe₃)₃] relative to Cp₂Zr[Si(SiMe₃)₃]Me and CpCp*ZrMeR, respectively.¹⁴ The few results that have been reported with carbon atom bridges are not straight forward but the examples are primarily with Zr-complexes. With *rac*-(EBI)ZrCl₂/nRLi [R = Me, ¹⁹c Bu^{15a}; EBI = ethylenebis-(indenyl)] linear and cyclic polysilanes are produced and the M_w values for the mixture are higher than those produced from Cp₂ZrCl₂/RLi. With *rac*-[EBI]ZrMe₂ and *rac*-[Ind]ZrMe₂ [Ind = bis(indenyl)] only cyclic products are reported.⁴⁰

In no case reported thus far has any *ansa*-metallocene produced polysilane with M_W values as high as those achieved with the non-bridged system CpCp*MXY (X and Y can be H, Hal, alkyl, silyl; M = Zr,^{14,49} Hf¹⁴). The success of this particular combination, Cp and Cp*, most likely results from the stabilization of a mononuclear hydride structure (Schemes 1 and 2). Dimerization generally leads to inactive hydride-bridged species.⁵⁰ The cyclics produced from CpCp*ZrXY are usually around 10%. In the current study only with the *ansa*-metallocene, (η^5 -C₅H₄CMe₂- η^{5-C} Cl₃H₈)ZrCl₂/nBuLi was negligible cyclic formation observed. The only other advantage of the *ansa*-metallocenes catalysts, at least in the hafnium case, is the lack of incorporation of Ph₂Si- units into the growing chain as has been observed with Cp₂HfCl₂/nBuLi.

Although the dehydrocoupling reaction promoted by metallocene based catalysts of Ti, Zr and Hf have been successful in forming polysilanes the molecular weights do not yet compete with those produced from Wurtz-type coupling. This is likely due to factors that include the stepwise nature of the process and that metathesis reactions leading to chain growth compete with reactions that lead to depolymerization and cyclic formation. The structural variations of Cp_2MCl_2 that have been so successful in the improvement of olefin polymerization are not a predictor of success in the dehydrocoupling of hydrosilanes which suggests that the relationship between the two processes as outlined in Scheme 1 is only superficial. It is likely that to overcome these deficiencies in dehydrocoupling catalyst systems with new structures will be required.

EXPERIMENTAL

General. Ether solvents were dried using standard techniques (THF and Et₂O over sodium/benzophenone; hexanes over calcium hydride; CHCl₃ and CH₂Cl₂ over phosphorous pentoxide after prepurification). Glassware was either dried in an oven at 110-120 °C or flame dried prior to use. Transfer of MCl₄, Cp₂ZrCl₂, and [Me₂El(C₅H₄)₂]ZrCl₂ was carried out in a Vacuum Atmospheres HE-43 drybox. All reactions were conducted in an inert atmosphere of nitrogen or argon by standard Schlenk techniques.

Commercial compounds (nBuLi in hexanes, Cp₂MCl₂ and MCl₄) unless otherwise noted, were used as supplied. Literature methods were used to prepare Me₂Si(C₅H₅)₂,⁵¹ Me₂C(C₅H₅)₂,²⁰ Me₂Si(C₅H₄)₂MCl₂ (M = Ti,²¹ Zr,²¹ Hf²²), Me₂C(C₅H₄)₂MCl₂ (M = Ti,²⁰ Zr²⁰) and (η ⁵-C₅H₄CMe₂- η ⁵-C₁₃H₈)ZrCl₂⁴³.

¹H and ¹³C NMR spectra were collected on a Varian XL-300 multinuclear spectrometer. Unless otherwise specified, data were referenced to the residual protons of the solvent. Gas chromatographic separations were performed on a Shimadzu GC-14A gas chromatograph on a J&W Scientific DB-5 capillary column. Mass spectral data were collected on a Hewlett-Packard 5988A GC/MS instrument equipped with an RTE-A data system and molecular weights were determined using three Waters Styragel columns (100 Å, 500 Å and 10⁴ Å) connected in series with chloroform as solvent. The molecular weights were determined relative to polystyrene standards. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, New York.

Preparation of $[Me_2C(C_5H_4)_2]HfCl_2$. nButyllithium (5.00 mL, 2.5 M, 12.5 mmol) was added dropwise to a solution of $Me_2C(C_5H_4)_2$ (1.07 g, 6.24 mmol) in THF/hexanes (75/25 volume ratio; 12.5 mL) at -78 °C. The solution was warmed to room temperature and stirred for 3 h during which time a white precipitate formed. The dilithio salt was added to a dispersion of HfCl₄ (2.00 g, 6.24 mmol) in hexanes (4 mL) at 0 °C. The yellow mixture was warmed to room temperature and stirred for 12 h. The volatiles were removed under reduced pressure and the yellow solid extracted with CHCl₃ (100 mL). Concentration of the CHCl₃ solution yielded $Me_2C(C_5H_4)_2HfCl_2$ as a beige powder (0.97 g, 37%) (decomposes at 200 °C): ¹H NMR (δ ; CDCl₃):

1.80 (s, 6, CMe), 5.68 (t, 4, C₅H₄), 6.56 (t, 4, C₅H₄). ¹³C NMR (δ ; CDCl₃): 124.18, 121.38, 104.52, 37.84, 24.22. Anal. calcd. for C₁₃H₁₄Cl₂Hf: C, 37.21; H, 3.36. Found: C, 36.59; H, 3.52.

 $[Me_2C(C_5H_4)_2]HfCl_2$ was also prepared from $Me_2C(C_5H_4SiMe_3)_2$ and $HfCl_4$ in 29% yield. Condensation of $PhSiH_3$ and $PhMeSiH_2$ in Toluene. In a typical experiment the metallocene dichloride or the ansa-metallocene dichloride (0.37 mmol) was weighed into a Schlenk tube and 2 mL of degassed, dry toluene were added. The slurry was cooled to 0 °C before injection of the nBuLi (0.74 mmol). The mixture was stirred for 10 min or until the dichloride dissolved when PhSiH_3 (1.0 g, 9.2 mmol) was injected into the solution followed by removal of the ice bath. Reactions were run in sets of three (parent metallocene and two ansa-metallocenes) for each of the metals, at 25 °C for Ti and Zr and at 50 °C for Hf. After the appropriate time had elapsed toluene was added and air bubbled through the solution for a few minutes. The resultant slurry was filtered through celite and the volatiles were removed under vacuum. Mass recovery of the oligomers/polymers was usually in the 75-85% range except for Me_2C(C_5H_4)_2HfCl_2 where it was 37%.

The same procedure was followed for the condensation of PhMeSiH₂ except that after the silane was added to the catalyst mixture, the solution was heated at 90 °C. After the reaction period hexanes were added prior to bubbling air through the solution.

Condensation of Neat PhSiH₃. In a typical experiment the metal complex (0.22 mmol) was weighed into a Schlenk tube. Then PhSiH₃ (1.2 g, 11 mmol) was injected at room temperature followed by nBuLi (0.31 mL, 2.5 M, 0.43 mmol). Vigorous bubbling occurred. Reactions were run in sets of three for each of the metals, at 25 °C for Ti, Zr and Hf and also at 50 °C for Hf. After the appropriate time (conditions and times are indicated in Table 4) had elapsed the reaction was quenched by bubbling air through the solution. Toluene was added and the slurry filtered through celite. The volatiles were removed under vacuum and the gummy residue weighed. Mass recovery of the oligomers/polymers was greater than 75% except for Me₂C(C₅H₄)₂ZrCl₂ and Me₂C(C₅H₄)₂HfCl₂ (see Table 4).

Reaction of $Me_2C(C_5H_4)_2HfCl_2$ with 2nBuLi. To a dispersion of $Me_2C(C_5H_4)_2HfCl_2$ (55 mg, 0.13 mmol) in toluene (0.5 mL) was added nBuLi (0.10 mL, 2.5 M, 0.26 mmol) at room temperature. The reaction mixture was stirred for 15 min followed by removal of the volatiles under vacuum (30-60 min). The residue was dissolved in CDCl₃ and the ¹H NMR spectrum immediately recorded. ¹H (δ ; CDCl₃): 0.08 (m, 4, HfCH₂), 0.80 (t, 6, CH₃), 1.09 (sextet, 4, CH₂), 1.37 (m, 4, CH₂), 1.53 (s, 6, CMe), 5.37 (t, 4, C₅H₄), 6.43 (t, 4, C₅H₄).

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