Pergamon

Tetrahedron Vol. 51, No. 15, pp. 4309-4320, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/95 \$9.50+0.00

0040-4020(94)01121-4

Ansa-Metallocenes: Catalysts for the Dehydrocoupling of Hydrosilanes

Raef M. Shaltout and Joyce Y. Corey*

Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO 63121

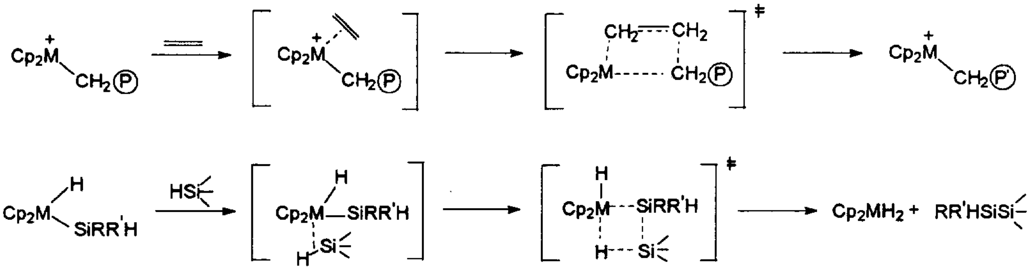
Abstract: The dehydrocoupling of $PhMeSiH_2$ to form oligomers and of $PhSiH_3$ to form polysilanes has been performed with the precatalyst combination of $[Me_2El(C_5H_4)_2MCl_2$ (El = Si, C; M = Ti, Zr, Hf) and nBuLi. The results are compared to those produced from $(\eta^5\text{-}C_5H_5)_2MCl_2$/nBuLi.

INTRODUCTION

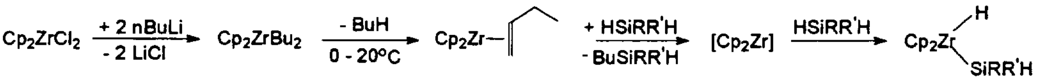
The σ-conjugation of catenated silicon chains gives rise to conducting, photoconducting and thermochromic behavior, properties that have potential for technological use.[1] A drawback to the applications of polysilanes is the lack of variation of synthetic routes for their production. The general method 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 = $\eta^5\text{-}C_5H_5$; M = Ti, Zr; R = Me, Ph) developed by Harrod and coworkers and $CpCp^*M[Si(SiMe_3)_3]R$ ($Cp^* = \eta^5\text{-}C_5Me_5$; 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 1985[8] and has been under intense investigation since. The Cossee mechanism[9] 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 2σ + 2π 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, $Cp_2M(SiRR'H)H$ 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 2σ + 2σ "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.



Scheme 2. Proposed route from Cp_2ZrCl_2 to 16-electron complex $Cp_2Zr(SiRR'H)H$

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 Cp_2MR^+ and one LUMO on $Cp_2M(H)SiRR'H$.

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 $RSiH_3$ (or minimal solvent) at room temperature. Recently, Tilley and Imori have studied the condensation of $PhSiH_3$ 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 $LMMe_2$ [L = 1,2-bis-(indenyl)ethane and 1,2-bis(tetrahydroindenyl)ethane; M = Ti, Zr[15,19]] and Tilley has included $[Me_2Si(C_5H_4)_2]Zr[Si(SiMe_3)_3]Me$ and $[Me_2Si(C_5H_4)(C_5Me_4)]ZrMeR$ [R = Me, $Si(SiMe_3)_3$] in a comparison of catalysts that promote the coupling of $PhSiH_3$.[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.

$$Me_2El(C_5H_5)_2 \xrightarrow[2)\ MCl_4]{1)\ 2\ nBuLi} [Me_2El(C_5H_4)_2]MCl_2 \xleftarrow{MCl_4} Me_2El(C_5H_4SiMe_3)_2$$

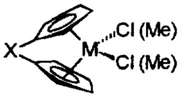
El	M
C	Ti,[20] Zr[20]
Si	Ti,[21] Zr,[21] Hf[22]

Scheme 3: Synthesis of *ansa*-Metallocenes

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 Cp_2MCl_2 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 $-(CMe_2)_2-$ 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 MCl_2 unit in the *ansa*-metallocene to MMe_2 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.

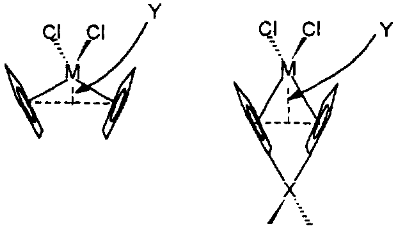
Table 1. Cp'-M-Cp' Angles in $[X(C_5H_4)_2]MCl_2$ and Related $[X(C_5H_4)_2]MMe_2$.[a]



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)
$-Me_2C-$	Ti	121.5(120.9)	23(28)
	Zr	116.7(115.9)	23(28)
	Hf	117.1	23
$-Me_2Si-$	Ti	128.7	21b
	Zr	125.4	21b
	Hf	126.8	22
$-(CMe_2)_2-$	Ti	128.4	29
	Zr[d]	124.8	30
$-(CH_2)_2-$	Ti	128	31
$-(CH_2)_3-$	Ti	133	32
	Zr	129	33
	Hf	129.5	34
$-(CH_2)_{12}-$	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_2TiCl_2	0.853		
$Me_2Si(C_5H_4)_2TiCl_2$	0.898	0.045	5%
$Me_2C(C_5H_4)_2TiCl_2$	1.005	0.152	18%
Cp_2ZrCl_2	0.933		
$Me_2Si(C_5H_4)_2ZrCl_2$	1.008	0.075	8%
$Me_2C(C_5H_4)_2ZrCl_2$	1.152	0.219	23%
Cp_2HfCl_2	0.971		
$Me_2Si(C_5H_4)_2HfCl_2$	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 $PhMeSiH_2$. The silicon oligomers formed in the condensation of $PhMeSiH_2$ have been previously characterized by GC, GCMS and ^1H, ^{13}C and ^{29}Si NMR spectroscopy.[5a] The reactions of $PhMeSiH_2$ in the presence of Cp_2MCl_2/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 $PhMeSiH_2$ 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 $Cp'_2M(SiPhMeH)H$ with HPhMeSiSiMePhH or of $Cp'_2M(SiPhMeSiPhMeH)H$ with $PhMeSiH_2$. 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

Table 3. Oligomer Distribution in the Condensation of $PhMeSiH_2$ as Determined by Gas Chromatography.[a]

Catalyst Precursor	**$PhMeSiH_2$**		**Disilane**		**Trisilane**		**Tetrasilane**	
	5h	**72h**	**5h**	**72h**	**5h**	**72h**	**5h**	**72h**
Cp_2TiCl_2	73	41	21	32	6.1	25	-	2.2
$Me_2Si(C_5H_4)_2TiCl_2$	83	39	17	36	-	23	-	1.8
$Me_2C(C_5H_4)_2TiCl_2$	79	34	21	58	-	7.6	-	-
Cp_2ZrCl_2	68	27	21	15	7.1	34	-	14
$Me_2Si(C_5H_4)_2ZrCl_2$	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
Cp_2HfCl_2	67	37	30	36	3.6	25	-	1.6
$Me_2Si(C_5H_4)_2HfCl_2$	82	69	19	30	-	1.1	-	-
$Me_2C(C_5H_4)_2HfCl_2$	85	60	15	37	-	3.2	-	-

a. Reactions are run in toluene at 90 °C at a ratio of $PhMeSiH_2/Cp_2MCl_2/nBuLi$ 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 $PhMeSiH_2$ were formed as statistical mixtures of diastereomers but this may not be the case for the tetrasilane.[5a] The trisilane formed with $Me_2Si(C_5H_4)_2ZrCl_2$ was isolated and characterized and the spectroscopic data are identical to those produced from the parent Cp_2ZrCl_2.

Condensation of $PhSiH_3$. The condensation of $PhSiH_3$ 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 $[Me_2Si(C_5H_4)_2]HfCl_2/nBuLi$ 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*-$[X(C_5H_4)_2]ZrCl_2$ 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 Hf-based 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 $PhBuSiH_2$.[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 $BuSiH_3$.[5b]

Table 4. Molecular Weights of $H(PhSiH)_xH$ Produced from the Condensation of $PhSiH_3$ as Determined by Gel Permeation Chromatography.[a]

M	**Conditions sol/°C/hr**	**Cp_2MCl_2[b]**		**$[Me_2Si(C_5H_4)_2]MCl_2$[b]**		**$[Me_2C(C_5H_4)_2]MCl_2$[b]**	
		wt %[c]	**M_w**	**wt %[c]**	**M_w**	**wt %[c]**	**M_w**
Ti	neat/25/24	75	1250	75	1080	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	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 10^4 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 $PhSiH_3$) x 100..

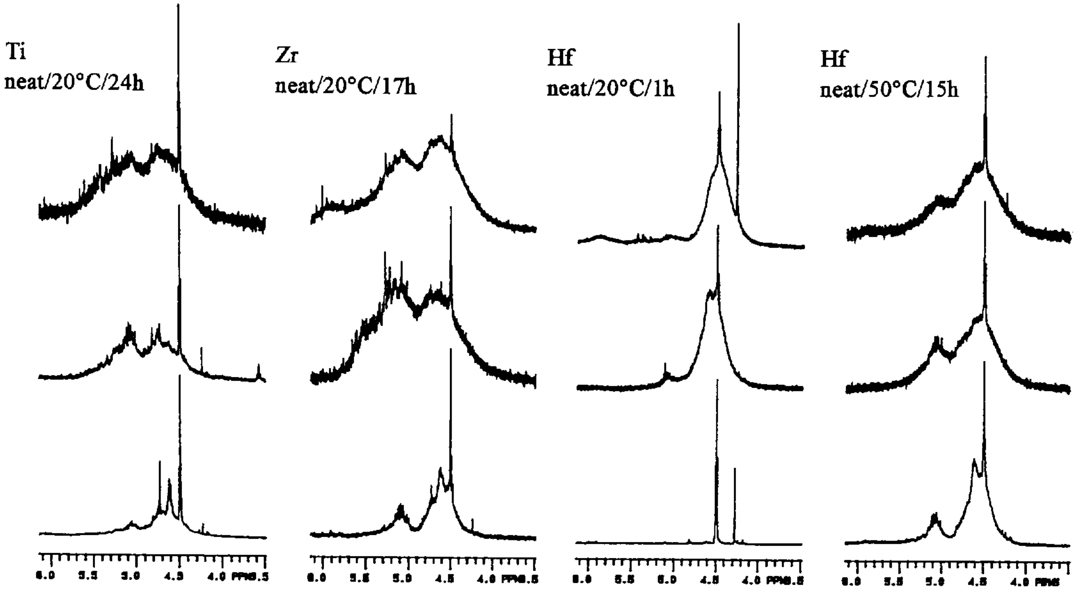


Figure 1. ^{1}NMR Data for SiH region for polysilanes produced from $PhSiH_3$ and metallocene catalysts. Upper trace: Cp_2MCl_2. Middle trace: $Me_2Si(C_5H_4)_2MCl_2$. Lower trace: $Me_2C(C_5H_4)_2MCl_2$.

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).

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 $PhSiH_3$ compared to $RSiH_3$ (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)$ZrCl_2$/nBuLi (EBI = ethylene bis(indenyl)) as well as by $Cp_2Zr(H)Cl$. 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 Cp_2MCl_2 with a one atom bridge was examined. With such catalyst systems the dehydrocoupling of $PhR'SiH_2$ 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 $PhSiH_3$ 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°[42]). Fig. 2 shows the ^1H NMR spectrum of the SiH region for the polysilane product and illustrates the absence of cyclic material.

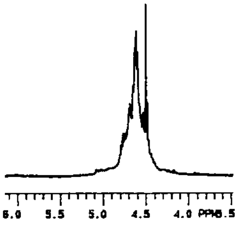


Figure 2. ^1H NMR Spectrum of $H(PhSiH)_xH$ Produced from $(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_{13}H_8)ZrCl_2$

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 $PhSiH_3$. 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 case[40]). 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 $-Ph_2Si$-units that are incorporated into the growing chain. The *ansa*-metallocenes produce negligible quantities of oligomers that contain Ph_2Si- units compared to the parent metallocene as illustrated by the data in Table 5. The scrambling may result from a disproportionation of $PhSiH_3$ to produce Ph_2SiH_2 and SiH_4. The Ph_2SiH_2 couples with $PhSiH_3$ to form the "phenyl"-rich short chains listed in Table 5. The other disproportionation product, SiH_4, 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'_2HfCl_2/nBuLi combination resembles Cp_2ZrCl_2/nBuLi then the sequence shown in Scheme 2 would be expected. The complex Cp_2Hf(isobutylene)PMe_3 has been reported but is generated from a mixed dialkyl precursor, $Cp_2Hf(^tBu)R$ (R = nBu[44a], iBu[44b]) in the presence of PMe_3. The reaction of $Cp_2Hf(CH_2{=}CMe_2)PMe_3$ with Ph_3SiH produced $Cp_2Hf(SiPh_3)H(PMe_3)$.[45] The results from the $Me_2C(C_5H_4)_2HfCl_2$/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'_2HfBu_2 system.[46] The reaction of $Me_2C(C_5H_4)_2HfCl_2$ with 2 eq if nBuLi in toluene cleanly produced $Me_2C(C_5H_4)_2HfBu_2$ as shown by the ^1H NMR spectrum in Fig. 3. When solutions of $Me_2C(C_5H_4)_2HfBu_2$ are heated to 100 °C no obvious decomposition was observed. It is possible that the reaction of $Me_2C(C_5H_4)_2HfBu_2$ with $PhSiH_3$ at room temperature does not involve the formation of an olefin complex but that a metathesis reaction with the silane provides $Me_2C(C_5H_4)_2Hf(SiPhH_2)Bu$ which precedes the catalytic cycle.[47] Subsequent coupling to form chains may be slower.

Table 5. Oligomers Formed from $PhSiH_3$: Comparison of Results Produced from Cp_2HfCl_2 and $Me_2C(C_5H_4)_2HfCl_2$.[a]

Molecular Ion	Assignment	GC%[b]	
		Cp_2HfCl_2	Cp'_2MCl_2[c]
108	$PhSiH_3$	4.1	16
164	$PhBuSiH_2$	2.4	-
184	Ph_2SiH_2	3.5	2.7
214	$H(PhSiH)_2H$	38	54
290	$HPh_2SiSiPhH_2$	4.4	<0.1
320	$H(PhSiH)_3H$	21	19
396	$HPh_2Si(PhSiH)_2H$[d]	4.5	<0.1
426	$H(PhSiH)_4H$	14	5.8
[e]	$H(PhSiH)_5H$	3.3[f]	1.8

a. Reactions conducted in toluene at 50 °C in toluenewith 2 eq of nBuLi. b. Uncorrected GC% values are given. c. Other possible isomer: $(H_2PhSi)_2SiPh_2$. c. $Cp'_2MCl_2 = Me_2C(C_5H_4)_2HfCl_2$.
d. Tentative assignment. Not observed under GCMS conditions
e. Additional components: 6 minor components (4.0% total) and 2 components tentatively assigned to isomers of $Ph_5Si_4H_5$ (3.5%; not observed under GCMS conditions).

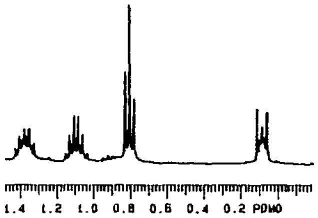


Fig. 3. ^1H NMR Spectrum of $Me_2C(C_5H_4)_2HfBu_2$: Butyl Region

Conclusion. The condensation of $PhSiH_3$ and $PhMeSiH_2$ 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 Cp_2MCl_2 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 ethano-bridge. Description of additional but more complex geometrical features of *ansa*-metallocenes also have been developed.[48]

The average molecular weight of the oligomers (from $PhMeSiH_2$) and the polysilanes (from $PhSiH_3$) that are produced are lower with the $[Me_2El(C_5H_4)_2]MCl_2$ 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 $[Me_2Si(C_5H_4)_2]Zr\text{-}[Si(SiMe_3)_3]Me$ and $[Me_2Si(C_5H_4)(C_5Me_4)]ZrMeR$ [R = Me, $Si(SiMe_3)_3$] relative to $Cp_2Zr[Si(SiMe_3)_3]Me$ 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*-$(EBI)ZrCl_2$/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 Cp_2ZrCl_2/RLi. With *rac*-$[EBI]ZrMe_2$ and *rac*-$[Ind]ZrMe_2$ [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] Hf[14]). 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, $(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_{13}H_8)ZrCl_2$/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 Ph_2Si- units into the growing chain as has been observed with Cp_2HfCl_2/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 Et_2O over sodium/benzophenone; hexanes over calcium hydride; $CHCl_3$ and CH_2Cl_2 over phosphorous pentoxide after prepurification). Glassware was either dried in an oven at 110-120 °C or flame dried prior to use. Transfer of MCl_4, Cp_2ZrCl_2, and $[Me_2El(C_5H_4)_2]ZrCl_2$ 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, Cp_2MCl_2 and MCl_4) unless otherwise noted, were used as supplied. Literature methods were used to prepare $Me_2Si(C_5H_5)_2$,[51] $Me_2C(C_5H_5)_2$,[20] $Me_2Si(C_5H_4)_2MCl_2$ (M = Ti,[21] Zr,[21] Hf[22]), $Me_2C(C_5H_4)_2MCl_2$ (M = Ti,[20] Zr[20]) and $(\eta^5\text{-}C_5H_4CMe_2\text{-}\eta^5\text{-}C_{13}H_8)ZrCl_2$[43].

^1H and ^{13}C 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 10^4 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 $HfCl_4$ (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 $CHCl_3$ (100 mL). Concentration of the $CHCl_3$ solution yielded $Me_2C(C_5H_4)_2HfCl_2$ as a beige powder (0.97 g, 37%) (decomposes at 200 °C): ^1H NMR (δ; $CDCl_3$):

1.80 (s, 6, CMe), 5.68 (t, 4 , C_5H_4), 6.56 (t, 4, C_5H_4). ^{13}C NMR (δ; $CDCl_3$): 124.18, 121.38, 104.52, 37.84, 24.22. Anal. calcd. for $C_{13}H_{14}Cl_2Hf$: 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 $PhMeSiH_2$ 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 $PhSiH_3$. In a typical experiment the metal complex (0.22 mmol) was weighed into a Schlenk tube. Then $PhSiH_3$ (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 $Me_2C(C_5H_4)_2ZrCl_2$ and $Me_2C(C_5H_4)_2HfCl_2$ (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 $CDCl_3$ and the ^1H NMR spectrum immediately recorded. ^1H (δ; $CDCl_3$): 0.08 (m, 4, $HfCH_2$), 0.80 (t, 6, CH_3), 1.09 (sextet, 4, CH_2), 1.37 (m, 4, CH_2), 1.53 (s, 6, CMe), 5.37 (t, 4, C_5H_4), 6.43 (t, 4, C_5H_4).

REFERENCES AND NOTES

1. (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359-1410. (b) West, R. *J. Organomet. Chem.* **1986**, *300*, 327-346.
2. (a) Cypryk, M.; Gupta, Y.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1991**, *113*, 1046-1047. (b) Sakamoto, K.; Ohata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641-7643.
3. Aitken, C.; Harrod, J. F.; Samuel, E. *J. Organomet. Chem.* **1985**, *279*, C11-C13.
4. (a) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37-51. (b) Harrod, J. F.; Mu, Y.; Samuel, E. *Polyhedron* **1991**, *10*, 1239-1245. (c) Corey, J. In *Advances in Silicon Chemistry;* Larson, G., Ed.; JAI Press, Inc.: Greenwich, CT, 1991; Vol. 1, pp. 327-387. (d) Laine, R. M. in *Aspects of Homogeneous Catalysis*, R. Ugo, Ed.; Kluwer Academic Publishers: Amsterdam, 1990, pp. 37-63. (e) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22-29.
5. (a) Corey, J. Y.; Zhu, X.-H.; Bedard, T. C.; Lange, L. D., *Organometallics* **1991**, *10*, 924-930. (b) Zhu, X.-H.; Corey, J.Y. *J. Organomet. Chem.* **1992**, *439*, 1-17.
6. (a) Banovetz, J. P.; Hsiao, Y-L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 2540-2541. (b) Harrod, J. F. *Inorganic and Organometallic Polymers;* Zeldin, M., Wynne, K., Allcock, H. R., Eds.: ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; Chapter 7.
7. A brief report of $H(PhSiH)_xH$ formed from the condensation of $PhHSiCl_2$ is reported in 1a.

8. (a) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507-508. (b) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behn, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1347-1350.

9. (a) Cossee, P. J. *J. Catal.* **1964**, *3*, 80-88. (b) Arlman, E. J.; Cossee, P. J. *J. Catal.* **1964**, *3*, 99-104.

10. (a) Woo, T. K.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 432-433. (b) Woo, T. K.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 2252-2261. Recent calculations for Cp_2TiMe^+ are mixed in support of the Cossee mechanism for titanium.[10c,10d] c. Bierwagen, E. P.; Bercaw, J. E.; Goddard III, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 1481-1489. d. Weiss, H.; Ehrig, M.; Ahlrichs, R. *J. Am. Chem. Soc.* **1994**, *116*, 4919-4928.

11. (a) Negishi and coworkers have provided evidence for the formation of Cp_2ZrBu_2[11b] and $Cp_2Zr(olefin)$[11c] and examples of $Cp_2Zr(olefin)PMe_3$[11d,e], $[Cp_2ZrH(SiRR'H)]_2$[11f] and $Cp_2ZrH(SiRR'H)PMe_3$[11f] have been characterized in the solid state. We have observed the formation of BuSiRR'H in all successful coupling reactions promoted by Cp_2ZrCl_2/nBuLi[5a]. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829-2832. (c) Takahashi, T.; Suzuki, N.; Kageyama, M.; Nitto, Y.; Saburi, M.; Negishi, E. *Chem. Lett.* **1991**, 1579-1582. (d) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761-764. (e) Binger, P.; Müller, P.; Benn, R.; Rufinske, A.; Gabor, B.; Krüger, C.; Blitz, P. *Chem. Ber.* **1989**, *122*, 1035-1042. (f) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negisihi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564-8566

12. Sini, G.; Macgregor, S. A.; Eisenstein, O.; Tueben, *Organometallics* **1994**, *13*, 1049-1051.

13. Corey, J. Y.; Huhmann, J. L.; Shaltout, R. M.; Kraichely, D. M. in *Xth International Symposium on Organosilicon Chemistry;* Marciniec, B., Chojnowski, J. Eds.; Gordon And Breach Publishers, Inc.: Langhorne, PA, in press.

14. Imori, T.; Tilley, T. D. *Polyhedron*, in press.

15. (a) Li, H.; Gauvin, F.; Harrod, J. F. *Organometallics* **1993**, *12*, 575-577. (b) Additional examples appear in Refs. 13 and 14.

16. (a) Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954-963. (b) Stehling, U.; Diebold, J.; Kirsten, R.; Röll, W.; Brintzinger, H-H.; Jüngling, S.; Mülhaupt, R. *Organometallics* **1994**,, *13*, 964-970, and references cited therein.

17. Gassman, P.; Winter, C. H. *Organometallics* **1991**, *10*, 1592-1598.

18. Chen, Y-X.; Rausch, M. D.; Chien, J. C. W. *Organometallics* **1994**, *13*, 748-749.

19. (a) Gauvin, F.; Harrod, J. F. *Polym. Prepr. (Am. Chem. Soc., Div. Poly. Chem.)* **1991**, *32*, 439-440. (b) Gauvin, F.; Harrod, J. F.; Mu, Y. *Polym. Prepr. (Am. Chem. Soc., Div. Poly. Chem.)* **1992**, *33*, 1235-1236. (c) Banovetz, J. P.; Stein, K. M.; Waymouth, R. M. *Organometallics* **1991**, *10*, 3430-3432.

20. Nifant'ev, I. E.; Butakov, K. A.; Aliev, Z. G.; Urazowski, I. F. *Metalloorg. Khim.* **1991**, *4*, 1265-1268.

21. (a) Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1470-1478. (b) Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539-2546.

22. Zhou, X.-Z.; Wang, Y.; Xu, S.-S.; Wang, H.-G.; Yao, X.-K. *Chem. Res. in Chin. Univ.* **1992**, *8*, 239-246.

23. Corey, J. Y.; Shaltout, R. M.; Rath, N. P. Structural details will be published separately.

24. Clearfield, A.; Warner, D.; Saldarriaga-Molina, C.; Ropal, R. *Can. J. Chem.* **1975**, *53*, 1622-1629.

25. Corey, J. Y.; Zhu, X-H.; Brammer, L.; Rath, N. P. *Acta Cryst. C*, in press.

26. Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Pentilla, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750-755.

27. Soloveichik, G. L.; Arkhireeva, T. M.; Bel'skii, V. K.; Bulychev, B. M. *Metalloorg. Khim.* **1988**, *1*, 226-230.

28. Nifant'ev, I. E.; Churakov, A. V.; Urazowski, I. F.; Mhoyan, Sh. G.; Atovmyan, L. O. *J. Organomet. Chem.* **1992**, *435*, 37-42.

29. Urazovskii, I. F.; Nifant'ev, I. E.; Butakov, K. A.; Ponomarev, V. I. *Metalloorg. Khim.* **1991**, *4*, 745-751.

30. Gutmann, S.; Burger, P.; Hund, H-U.; Hofmann, J.; Brintzinger, H. *J. Organomet. Chem.* **1989**, *369*, 343-357.
31. Reid, A. F.; Wailes, P. C. *J. Organomet. Chem.* **1964**, *2*, 329-335.
32. Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422-6433.
33. Petersen, J. L.; Egan, J. W., Jr. *Inorg. Chem.* **1983**, *22*, 3571-3575.
34. Epstein, E. F.; Bernal, I. *Inorg. Chem. Acta* **1973**, *7*, 211-218.
35. Erker, G.; Mollenkopf, C.; Grehl, M.; R. Fröhlich, R.; Krüger, C.; Noe, R.; Riedel, M. *Organometallics* **1994**, *13*, 1950-1955.
36. Corey, J. Y. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley Interscience: New York, 1989; Part 1, Chapter 1.
37. Examples in the *ansa*-titanocenes include *meso*-$(Me)_4C_2(1\text{-}C_5H_3\text{-}3\text{-}SiMe_3)_2TiCl_2$ and *rac*-$(Me)_4C_2(1\text{-}C_5H_3\text{-}3\text{-}SiMe_3)_2TiMe_2$, both of which exhibit a Cp'MCp' angle of 128°.[30]
38. There are no known examples of coupling of two tertiary silanes with an early transition metal catalyst.
39. An authentic sample of $PhBuSiH_2$ was produced from reaction of $PhSiH_3$ with $SnCl_4$ followed by addition of nBuLi.
40. Gauvin, F.; Harrod, J. F. *Can. J. Chem.* **1990**, *68*, 1638-1640.
41. Corey, J. Y.; Joslin, F.; unpublished studies.
42. Razavi, A.; Ferrara, J.; *J. Organomet. Chem.* **1992**, *435*, 299-310.
43. (a) Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 279-280.(b) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 305-310. (c) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzocchi, R. *Macromolecules,* **1988**, *21*, 617-622. (d) Grassi, A.; Amendola, P.; Longo, P.; Albizzati, E.; Resconi, L.; Mazzocchi, R. *Gazz. Chim. Ital.* **1988**, *118*, 539-543.
44. (a) Buchwald, S. L.; Kreutzer, K. A.; Fisher, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4600-4601. (b) Swanson, D. R.; Negishi, *Organometallics* **1991**, *10*, 825-826. (c) A different synthesis was reported for $Cp_2Hf(CH_2{=}CH_2)PMe_3$ from the hafna-cyclopentane derivative: Takashashi, T.; Tamura, M.; Saburi, M.; Uchida, Y.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1989**, 852-853.
45. Kreutzer, K. A.; Fisher, R. A.; Davis, W. M.; Spaltenstein, E.; Buchwald, S. L. *Organometallics* **1991**, *10*, 4031-4035.
46. $Cp^*_2HfBu_2$ has recently been isolated and characterized. Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424-1432.
47. Cp_2HfMe_2 is inactive in promoting dehydrocoupling, although the combination Cp_2HfCl_2/MeLi is an active catalyst.[19c]
48. Burger, P.; Hortmann, K.; Brintzinger, H. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 127-140.
49. Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1994**, *13*, 1548-1550.
50. Dimers have been characterized in the solid state. (a) Mu, Y.; Aitken, C.; Cote, B.; Harrod, J. F. *Can. J. Chem.* **1991**, *69*, 264-276. (b) Ref. 11f
51. Yasuda, H.; Nagasuna, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1470-1478. CpLi was used in place of CpNa. Isolated $Me_2Si(C_5H_4)_2$ was of 93% purity by GC.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the National Science Foundation (CHE-9213688), to the Research Board of the University of Missouri and to a UM-St. Louis Research Award for support of this work.

(*Received* 22 *August* 1994)