

4; fw = 724.39; $D_{\text{calc}} = 1.611$; abs coeff = 38.243; diffractometer, Syntex P2₁; radiation, graphite monochromated Mo K α (0.71073 Å); 2θ range = 3–45°; scan type, θ - 2θ ; scan speed, var. 4–29; standard reflections, 3 standard/100 reflections; reflections collected = 4855; independent reflections = 4684; observed reflections ($F_o > 3\sigma(F_o)$) = 3025; data/parameter = 7.77; final $R(F)$, $R(wF)$ = 6.3%, 7.2%; weighting scheme, $1/w = \sigma^2(I)/4F^2 + 0.000225F^2$; final GOF = 4.408; Δ/σ (mean) = 0.02; highest peak in difference map = 2.18 e/Å³ (all peaks larger than 0.807 e/Å³ were tungsten ghosts).

Synthesis of (CO)₅W(Ph₃P=NNMe₂) (6). To the oil (CO)₅W(THF) (150 mg, 0.42 mmol) was added Ph₃P=NNMe₂ (7) (100 mg, 0.31 mmol) dissolved in 1 mL of CDCl₃. This resulted in the quantitative conversion of 7 to 6. Spectral data for 6 were obtained on this solution. 6: ¹H NMR (CDCl₃) δ 2.53 (s, 6 H), 7.2–7.8 (m, 15 H). ¹³C NMR (CDCl₃) δ 202.06 (CO_{trans}), 199.21 (CO_{cis}), 49.12 (CH₃). ³¹P NMR (CDCl₃) δ 32.69 (s). 7: ¹H NMR (CDCl₃) δ 2.33 (s, 6 H), 7.4–7.7 (m, 15 H). ¹³C NMR δ 51.63 (d, ³J_{P-C} = 10.0 Hz, CH₃). ³¹P NMR (CDCl₃) δ 18.60 (s, broad).

Kinetics of Reaction of 2 with PPh₃ and P(OPh)₃. To three separate NMR tubes containing a 0.5-mL CDCl₃ solution of 2 (0.010 mmol) and cooled to –50 °C were added 1.1 equiv of PPh₃ (3 mg, 0.011 mmol), 3.1

equiv of PPh₃ (8 mg, 0.031 mmol), and 6.0 equiv of PPh₃ (16 mg, 0.060 mmol). The solutions were warmed to –20 °C in the NMR probe, and the disappearance of 2 was monitored every 5 min for 1 h. Similarly, the disappearance of 2 with 1.6 equiv of P(OPh)₃ (5 mg, 0.016 mmol) was monitored. The plot of ln [2] vs time gave a straight line with a slope equal to k_{obs} . Error in k_{obs} was based upon 5% NMR integration error.

Acknowledgment. Funding for this work was provided by the U.S. Army Research Office, the Office of Naval Research, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the NSF-MRL Program through the Center for Materials Research at Stanford University. We thank Professor T. D. P. Stack for helpful discussion regarding the crystallography.

Supplementary Material Available: Tables of bond distances and angles, hydrogen atom coordinates, and thermal parameters (13 pages); table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

A σ -Bond Metathesis Mechanism for Dehydropolymerization of Silanes to Polysilanes by d⁰ Metal Catalysts

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Abstract: A mechanism for the dehydropolymerization of hydrosilanes to polysilanes, as catalyzed by early-transition-metal metallocene derivatives, is proposed. This mechanism is based on two σ -bond metathesis reactions that pass through four-center transition states: (1) the dehydrometalation of silane, H(SiHR)_nH, with a metal hydride to give hydrogen and a silyl derivative, M(SiHR)_nH, and (2) coupling of the metal silyl derivative with more hydrosilane, H(SiHR)_mH, to produce H(SiHR)_n(SiHR)_mH and regenerate the active metal hydride catalyst. This proposal is based on a number of observed, stoichiometric σ -bond metathesis reactions involving zirconocene and hafnocene complexes. These reactions, which involve silicon, hydrogen, and a d⁰ metal center, are rather facile and apparently reflect the tendency of silicon to expand its coordination sphere under these conditions. One reaction of this type is rapid MH/SiH hydrogen exchange, for example between PhSiH₃ and CpCp*MHCl (1, M = Zr, or 2, M = Hf), which is observed via deuterium labeling. Hydrogenolysis of CpCp*M[Si(SiMe₃)₃]Cl (3, M = Zr, and 4, M = Hf) provides a convenient route to the monomeric hydride complexes 1 and 2, respectively. The first step in the proposed polymerization mechanism, which is the reverse of M–Si bond hydrogenolysis, is observed in stoichiometric reactions of 1 or 2 with PhSiH₃ to give hydrogen and the phenylsilyl complexes CpCp*M(SiH₂Ph)Cl (5, M = Zr, and 6, M = Hf). The thermolytic decomposition of 6 to 2 results in Si–Si bond formation, with the production of polysilane oligomers. This second-order reaction exhibits a deuterium isotope effect at 75 °C of 2.9 (2) and activation parameters ($\Delta H^\ddagger = 19.5$ (2) kcal mol^{–1} and $\Delta S^\ddagger = -21$ (6) eu) that suggest a four-center transition state. The second-order reaction of 6 with PhSiH₃ (to give 2 and (SiHPh)_n polysilanes) was also studied kinetically and found to exhibit similar kinetic parameters. This σ -bond metathesis reaction, which corresponds to the second step in the proposed mechanism, is believed to pass through a four-center transition state that results from interaction of the CpCp*(Cl)Hf–SiH₂Ph and H–SiH₂Ph bonds. Evidence for the role of hydride complexes as true catalysts is obtained by comparing gel permeation chromatograms for polysilanes obtained from both 3 and 1 as catalysts. Observed reactions of CpCp*Hf[Si(SiMe₃)₃]Me (7) with PhSiH₃, to give CpCp*Hf(SiH₂Ph)Me (8) and then CpCp*Hf(H)Me (9), model proposed processes for the activation of catalyst precursors. The step-growth character of the reaction is illustrated by the slow dehydrocoupling of PhSiH₃ by Cp*₂HfH₂, which allows observation of early polysilane intermediates (di-, tri-, and tetrasilane). The participation of M(SiHPh)_nH complexes as intermediates in dehydrocoupling was investigated. Partly on the basis of the observed reaction of CpCp*Hf[(SiHPh)₃H]Cl (11) with PhSiH₃ to give 6 and H(SiHPh)₃H, it is concluded that a preferred dehydrocoupling pathway involves monosilyl intermediates, MSiH₂Ph, and chain growth by one monomer unit per catalytic cycle. Implications of the proposed mechanism are discussed.

Current interest in polysilane polymers results from their unusual electronic, optical, and chemical properties and the potential applications derived therefrom.¹ The most convenient route to these polymers, the Wurtz coupling of dichlorosilanes by alkali metals, is severely limited as a general method since it tends to produce only moderate yields and does not tolerate many functional groups.¹ Because substituent effects can significantly in-

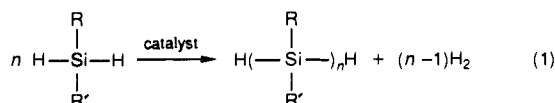
fluence the chemical and physical properties of these polymers,¹ new synthetic routes which allow more control over the polymer structure are desired. Alternative polymerization methods that have been developed include chloride-catalyzed redistribution of methylchlorosilanes,² electrochemical synthesis,³ polymerization

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of masked disilenes,⁴ ring-opening polymerization of strained cyclopolysilanes,⁵ and the dehydropolymerization of silanes with transition-metal catalysts⁶⁻²³ (eq 1).



Because coordination polymerizations offer intriguing possibilities for the controlled synthesis of polymers with tailored properties, attention has been directed toward transition metal-silicon chemistry for the development of new dehydrocoupling catalysts.^{6,7} Recent interest in this approach has been fueled considerably by Harrod's discovery that titanocene and zirconocene complexes are catalysts for the dehydropolymerization of primary

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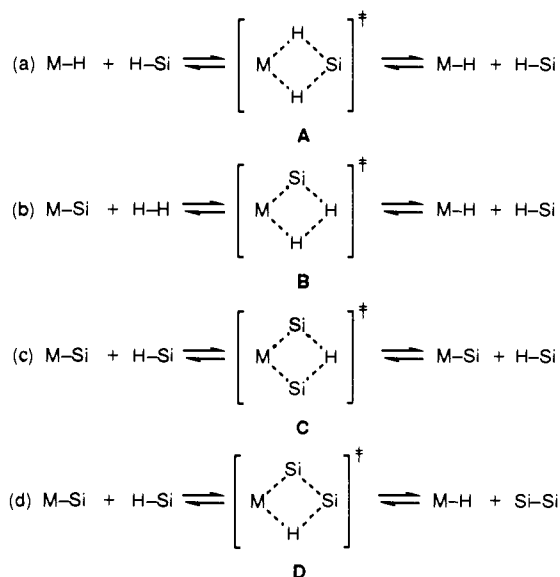
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Scheme I



silanes RSiH_3 to polysilanes of the type $\text{H}(\text{SiHR})_n\text{H}$.^{6a,8} In general this reaction produces linear chains containing ca. 10–30 Si atoms, as well as cyclic species containing ca. 6 Si atoms. Therefore, this method currently appears to be somewhat limited in scope, but applications are beginning to emerge. For example, $\text{H}(\text{SiHMe})_n\text{H}$ polymers obtained in this way have high molecular weights and can be converted in high yields to pure SiC at temperatures below 1000 °C.^{8ij} Further development of this polymerization chemistry relies on a thorough understanding of the polymerization mechanism, which has been a matter of considerable speculation.^{6,7}

Our work in this area stems from an interest in the silicon chemistry of early transition metals and, in particular, the chemistry of d^0 M–Si bonds. We have found that zirconocene and hafnocene silyl complexes are catalyst precursors for silane dehydropolymerization and that polymer molecular weight distributions can vary as a function of reaction conditions and catalyst. In this paper, we describe reactivity patterns for Si–H and d^0 M–Si bonds that suggest a mechanism for the dehydropolymerization of silanes with early-transition-metal catalysts. This “ σ -bond metathesis”²⁴ mechanism (vide infra) represents a new chemical pathway for polymer chain growth and provides a basis for further development of this coordination polymerization method. These mechanistic studies were made possible by the discovery of stable hydrosilyl derivatives such as $\text{Cp}^*\text{Cp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$ (**6**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$),^{15a,25} which undergo stoichiometric transformations that appear to represent fundamental steps in the dehydropolymerization mechanism.

Results

As described below, we have observed a number of σ -bond metathesis reactions involving a d^0 metal center, silicon, and hydrogen. These reactions appear to proceed via concerted, four-center transition states, as do related reactions of d^0 metal complexes with hydrocarbons.^{24,26} The possible four-center

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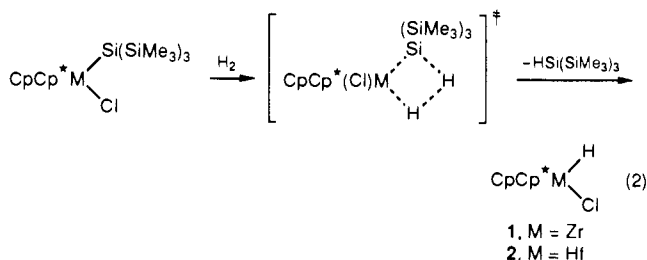
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transition states that involve one d^0 metal center, silicon, and hydrogen are given in Scheme I, together with the reactions that lead to their formation. Examples of all six of the unique processes in Scheme I have been observed for zirconocene and hafnocene derivatives that are catalysts for the dehydrogenative coupling of silanes, which indicates that silicon readily participates in σ -bond metathesis reactions in the presence of d^0 metal centers via expansion of its coordination sphere. The rates of these reactions seem to be governed largely by steric effects (in general, $D > C > B > A$), such that steric crowding in the transition state slows the reaction.

MH/SiH Hydrogen Exchange. Reactions that pass through transition state A (Scheme I) lead to hydrogen exchange between silicon and the transition metal. Hydrogen/deuterium exchange occurs rapidly between PhSiD_3 and CpCp^*MHCl (**1**, $M = \text{Zr}$, or **2**, $M = \text{Hf}$) (by ^1H and ^2H NMR spectroscopy). The exchange reaction involving **2** was complete within ca. 1 h, and there was no detectable deuterium incorporation into the Cp and Cp* ligands after 5 h. Similarly, H/D exchange was observed for reactions of Cp^*HfH_2 with both PhSiD_3 and $\text{PhCH}_2\text{SiD}_3$, without scrambling of deuterium into the Cp* ligand or the methylene group of benzylsilane. Rapid hydrogen scrambling occurs upon interaction of Cp^*HfH_2 with PhSiH_3 , $\text{PhCH}_2\text{SiH}_3$, CySiH_3 , $\text{PhH}_2\text{SiSiH}_2\text{Ph}$, and $\text{PhH}_2\text{Si}(\text{SiHPh})_n\text{SiH}_2\text{Ph}$ ($n = 1, 2$), as indicated by the broadening of ^1H NMR resonances (benzene- d_6 solution) for the MH and SiH_m ($m = 2, 3$) hydrogens at room temperature. The ^1H NMR spectrum of a toluene- d_8 solution of Cp^*HfH_2 and PhSiH_3 contains sharp HfH and SiH resonances at -75°C , which broaden continuously as the sample is heated to 100°C . Such broadening is not observed for mixtures of Cp^*HfH_2 and more sterically hindered silanes such as MesSiH_3 ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$), secondary silanes, and poly(phenylsilylene)s $\text{H}(\text{SiHPh})_n\text{H}$.

Hydrogenolysis of d^0 M-Si Bonds. The forward process of eq b in Scheme I, hydrogenolysis of d^0 M-Si bonds, is rapid compared to the corresponding reactions of d^0 M-C bonds. For example, whereas Cp_2ZrMe_2 reacts slowly with 1 atm of H_2 over days,²⁷ $\text{Cp}_2\text{Zr}(\text{SiMe}_3)\text{Cl}$ and $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{SiMe}_3$ react within a few minutes under comparable conditions.²⁸

Hydrides **1** and **2** are obtained in ca. 80% isolated yield by reaction of the silyl complexes $\text{CpCp}^*\text{M}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (**3**, $M = \text{Zr}$; **4**, $M = \text{Hf}$) with hydrogen (50–100 psi) over 5–10 min (eq 2). These hydride complexes exist as monomers in benzene



solution (isopiestic method) and are pentane-soluble. Spectroscopic data for **1** and **2** are also consistent with a monomeric structure.²⁹ For **1**, the hydride ligand gives rise to a resonance at 6.59 ppm in the ^1H NMR spectrum, and the $\nu(\text{ZrH})$ infrared stretching frequency is 1595 cm^{-1} . The corresponding values for **2** are 12.29 ppm and 1650 cm^{-1} . Compound **1** has previously been prepared by reaction of $\text{CpCp}^*\text{ZrCl}_2$ with 1 equiv of $\text{NaAlH}_2(\text{OCH}_2\text{C}_6\text{H}_4\text{OCH}_3)_2$.³⁰ The above hydrogenolysis reactions presumably

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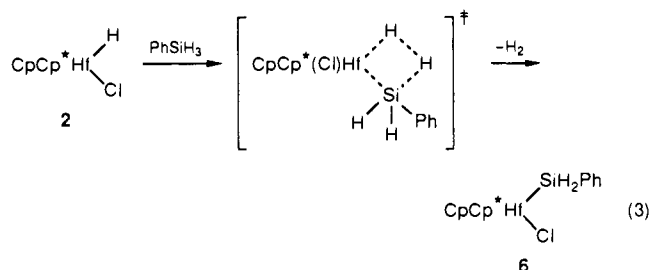
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proceed in a concerted manner via four-center transition states, as has been proposed previously for hydrogenolysis of d^0 M-C bonds.^{29c,31}

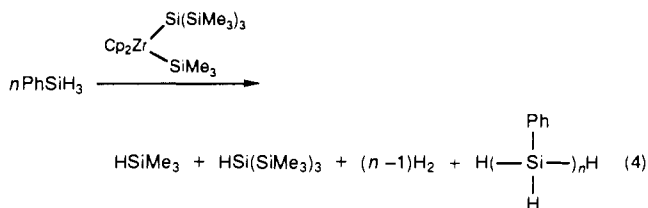
Reactions of d^0 Hydride Complexes with Hydrosilanes. The reverse direction in eq b corresponds to the formation of a silyl complex via the dehydrocoupling of a hydrosilane with a d^0 metal hydride. This process is observed in reactions of hydrides **1** and **2** with PhSiH_3 to produce the phenylsilyl complexes $\text{CpCp}^*\text{M}(\text{SiH}_2\text{Ph})\text{Cl}$ (**5**, $M = \text{Zr}$; **6**, $M = \text{Hf}$)²⁵ and hydrogen. Kinetic data for the reaction of **2** with PhSiH_3 (eq 3) are most consistent with a second-order rate law:

$$\text{rate} = k[\mathbf{2}][\text{PhSiH}_3]$$

Study of the kinetic behavior of this reaction is complicated by competing, further coupling of the silyl product **6** with PhSiH_3 , particularly under conditions of excess silane. Second-order plots of the data based on equivalent initial concentrations of reactants, or with a 2:1 ratio of **2** to PhSiH_3 , are consistent with this rate behavior.



Reactions of d^0 Silyl Complexes with Hydrosilanes. The first reactions of this type to be examined involved zirconocene derivatives that were found to act as efficient dehydropolymerization catalysts for primary silanes. For example, addition of PhSiH_3 to a benzene- d_6 solution of $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{SiMe}_3$ resulted in clean loss of the original silyl ligands, rapid hydrogen evolution, and formation of poly(phenylsilylene) (eq 4). The polymer was identified by comparison of its ^1H NMR spectrum with spectra for authentic samples.



Examination of the catalytic activity of various d^0 silyl complexes established a number of substituent effects for this polymerization reaction. In general, zirconocene derivatives containing a silyl group in combination with another poor π -donor ligand (an alkyl or silyl) are the most active catalysts (as approximated by rates for monomer consumption, measured by ^1H NMR spectroscopy). Thus, $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}^3$ is more active as a dehydropolymerization catalyst than the analogous chloride **3**. Also, as expected, reactions with silanes are significantly slower for the corresponding hafnium derivatives. Therefore, to investigate mechanisms for these reactions we have focused on $\text{CpCp}^*\text{Hf}(\text{Cl})$ derivatives, which often lead to clean, single-step processes and allow for the observation of intermediates. At elevated temperatures ($80\text{--}100^\circ\text{C}$), $\text{CpCp}^*\text{Hf}(\text{SiR}_3)\text{Cl}$ complexes catalyze the dehydropolymerization of primary silanes and are much more effective at producing linear (vs cyclic) polysilanes than zirconocene catalysts.^{15d}

The σ -bond metathesis reactions of $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (**4**) with primary or secondary hydrosilanes have been studied in

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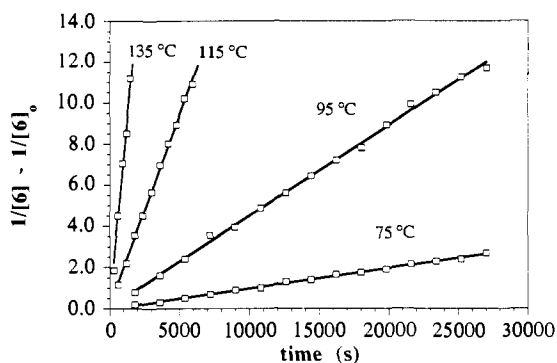
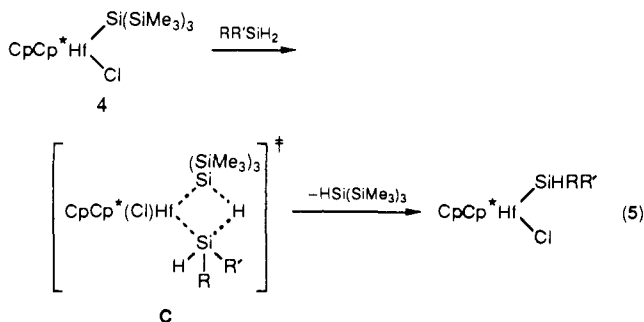


Figure 1. Representative second-order kinetic plots for the thermal decomposition of $\text{CpCp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$ (**6**). Rate constants ($\text{M}^{-1} \text{s}^{-1}$): $k(75^\circ\text{C}) = 1.0(1) \times 10^{-4}$; $k(95^\circ\text{C}) = 4.4(2) \times 10^{-4}$; $k(115^\circ\text{C}) = 2.0(2) \times 10^{-3}$; $k(135^\circ\text{C}) = 7.6(4) \times 10^{-3}$.

detail and are reported elsewhere.²⁵ These reactions produce $\text{HSi}(\text{SiMe}_3)_3$ and new silyl complexes $\text{CpCp}^*\text{Hf}(\text{SiHR}')\text{Cl}$ ($\text{R} = \text{H}$, alkyl, aryl; $\text{R}' = \text{alkyl, aryl}$), apparently via the four-center transition state **C** (eq 5). Such silyl-exchange reactions occur



when the starting metal complex possesses a bulky, easily displaced silyl group. Thus, we have found that $\text{Si}(\text{SiMe}_3)_3$ is a very good leaving group for metathesis reactions of this kind, and **4** serves as a convenient starting material for the synthesis of a wide range of new d^0 hydrosilyl complexes.²⁵

In general, the most encumbered (and highest energy) transition state in Scheme I is the one that leads to Si-Si bond formation or Si-Si bond cleavage (**D**). Therefore, the silyl groups that participate in this coupling reaction must be relatively unhindered. Silicon-silicon bond formation is observed in the thermal decompositions of $\text{CpCp}^*\text{M}(\text{SiH}_2\text{Ph})\text{Cl}$ (**5** and **6**) to $(\text{SiHPh})_n$ oligomers and the corresponding hydrides **1** and **2**. Decomposition of the zirconium derivative **5** occurs within minutes at room temperature,²⁵ but for **6** the reaction requires elevated temperatures. Since MSiH_2Ph derivatives seemed to be likely intermediates in the dehydropolymerization, these reactions which directly produce polysilane were of extreme interest, and mechanistic studies on the thermolysis of **6** were therefore initiated. To test for the possible intermediacy of silylene species (free silylenes or $\text{Hf}=\text{SiHR}$ complexes), the decomposition of **6** was allowed to take place in the presence of hindered hydrosilanes, which are known to be good silylene traps (Et_3SiH , CySiH_3 , Ph_2SiH_2 , and PhMeSiH_2).³³ These traps did not influence the course or rate of decomposition.

The disappearance of **6** follows a second-order rate law (Figure 1):

$$\text{rate} = k[\mathbf{6}]^2$$

By measuring the rate of decomposition of $\text{CpCp}^*\text{Hf}(\text{SiD}_2\text{Ph})\text{Cl}$, a deuterium isotope effect for this reaction at 75°C was determined to be $k_{\text{H}}/k_{\text{D}} = 2.9(2)$. The activation parameters, $\Delta H^\ddagger = 19.5(2) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -21(6) \text{ eu}$, being similar to those for the σ -bond metathesis reaction of **4** with PhSiH_3 ,²⁵ suggest a concerted mechanism for Si-Si bond formation that involves

Scheme II

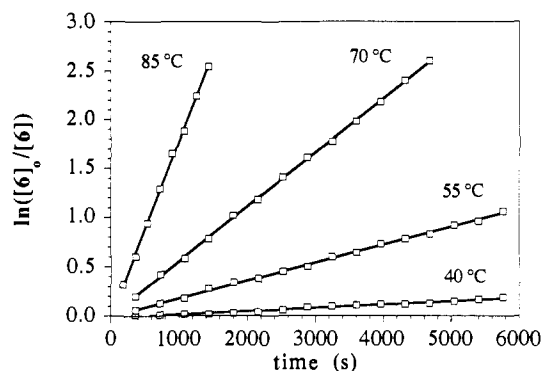
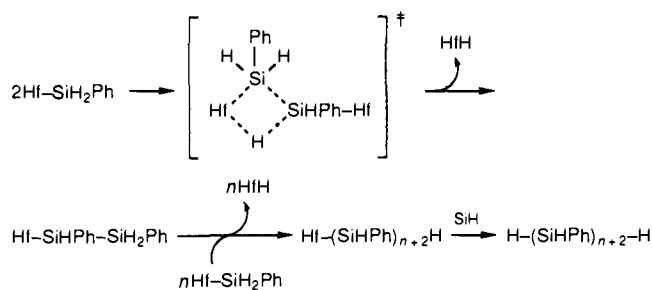
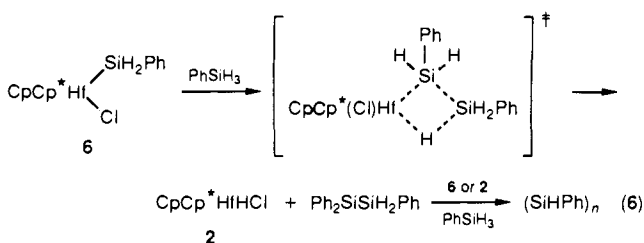


Figure 2. Representative pseudo-first-order kinetic plots for the reaction of $\text{CpCp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$ (**6**) with excess PhSiH_3 (10 equiv). Rate constants ($\text{M}^{-1} \text{s}^{-1}$): $k(40^\circ\text{C}) = 2.4(2) \times 10^{-3}$; $k(55^\circ\text{C}) = 1.2(2) \times 10^{-4}$; $k(70^\circ\text{C}) = 3.7(2) \times 10^{-4}$; $k(85^\circ\text{C}) = 1.2(2) \times 10^{-3}$.

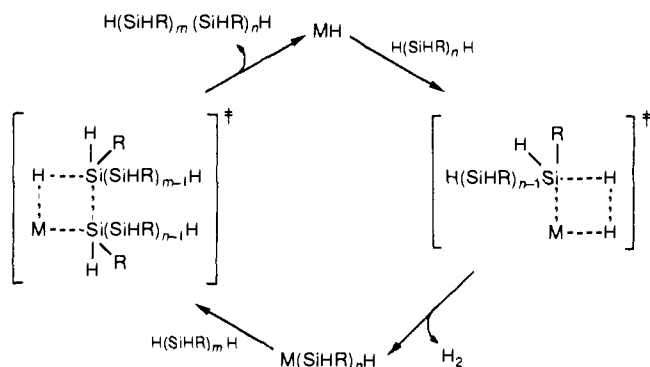
a four-center transition state. Such a mechanism based on bimolecular collisions of **6** is depicted in Scheme II. Formation of free polysilanes could occur by reaction of a $\text{Hf}-(\text{SiHPh})_n\text{H}$ bond with an Si-H bond in the system (e.g., in a cyclization process), but some fraction of the oligomers observed by ^1H NMR spectroscopy is expected to have terminal $-\text{Hf}(\text{Cl})\text{CpCp}^*$ groups.

It then seemed that a mechanism for chain growth could perhaps be based on concerted, σ -bond metathesis steps. Furthermore, the thermolysis of **6** appeared to be related to the metal-catalyzed dehydropolymerization of silanes, since **6** is a catalyst for the slow dehydropolymerization of PhSiH_3 (at room temperature, by ^1H NMR spectroscopy). In both reactions the hydride **2** and $(\text{SiHPh})_n$ polysilanes are produced. Under pseudo-first-order conditions of excess silane, disappearance of **6** is first-order (Figure 2). The reaction is also first-order in silane, as shown by plots of k_{obsd} vs $[\text{PhSiH}_3]$, which intercept the origin. An Eyring plot of the rate data gave the activation parameters $\Delta H^\ddagger = 18.5(5) \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -21(2) \text{ eu}$. The isotope effect, determined at 70°C by comparing the rates of reaction of **6** with PhSiH_3 and PhSiD_3 , is $k_{\text{H}}/k_{\text{D}} = 2.7(2)$. For comparison, note that the kinetic isotope effect for the dehydrocoupling of $\text{PhSiH}_3/\text{PhSiD}_3$ at ambient temperature, under cohydrogenation conditions with cyclohexene and Cp_2TiMe_2 as catalyst, was found to be 3.6.^{3c} On the basis of the above kinetic behavior, we postulate that reaction of **6** with PhSiH_3 occurs initially to give the hydride **2** and 1,2-diphenyldisilane and that the latter two species react further with the excess phenylsilane present to produce the polysilanes that are observed as products (eq 6). The fact that **6** reacts faster with PhSiH_3 than with itself can be explained by a less crowded transition state for the former reaction.



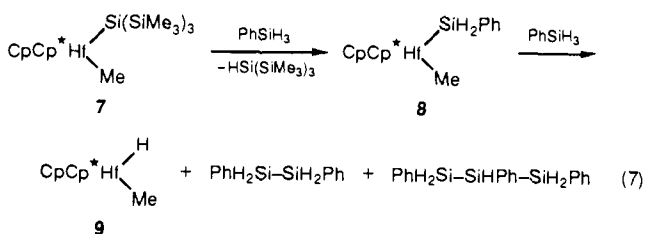
(33) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1981; Vol. 2, p 335 and references therein.

Scheme III



Mechanism for Dehydropolymerization of Silanes by d^0 Catalysts. The σ -bond metathesis chemistry summarized above suggests a mechanism for the dehydrogenative polymerization of hydrosilanes by zirconocene and hafnocene derivatives (Scheme III). The proposed mechanism features a coordinatively unsaturated hydride complex as the active catalyst and is based simply on two σ -bond metathesis reactions: (1) the "dehydrometalation" of a silane with the metal hydride and (2) coupling of the resulting metal silyl complex with a hydrosilane to produce an Si-Si bond, with regeneration of the active hydride. An unusual feature of this coordination-polymerization mechanism is that it is step-growth in nature and describes a transition-metal-catalyzed condensation polymerization. In designing experimental tests for this mechanism, we focused on attempted observation of the predicted intermediates (e.g., the hydride and silyl complexes) and on obtaining supporting evidence for the step-growth character of the polymerization.

If hydride complexes are the real catalysts in dehydropolymerizations, then they must be produced rapidly via reaction of the catalyst precursor with the silane monomer. As described above, such conversions can in fact be quite facile. Sequences of conversions which correspond to "catalyst activation" can be observed with relatively slow catalysts. For example, complex **7** reacts with PhSiH_3 to initially give phenylsilyl **8**, which is then converted by more PhSiH_3 to the hydrido methyl complex **9** and small polysilane oligomers (eq 7). Compounds **8** and **9** were conclusively identified by ^1H NMR spectroscopy, but they could not be isolated in pure form. As expected, addition of PhSiH_3 (0.5 equiv) to **9** regenerates a significant amount of **8**.



Further evidence for the role of hydride complexes as the true catalysts comes from comparing molecular weight distributions (from gel permeation chromatography, GPC) for polysilane samples produced by silyl complexes and their corresponding hydrides under the same conditions. As can be seen by the GPC traces shown in Figure 3, the polysilanes obtained with $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (**3**) and $\text{CpCp}^*\text{ZrHCl}$ (**1**) as catalysts have very similar molecular weight properties. Since these molecular weight distributions tend to be highly sensitive to the nature of the catalyst, we suggest that the same catalyst (probably **1**) is operating in both cases.

The step-growth nature of the dehydrocoupling reaction was suggested earlier by Hilty based on studies of the Cp_2ZrMe_2 -catalyzed dehydropolymerization of $^n\text{BuSiH}_3$, which produced low molecular weight polysilanes during the dehydrocoupling reaction.¹⁴ Under a variety of conditions that result in slow dehydrocoupling, such intermediate oligomers can be observed in re-

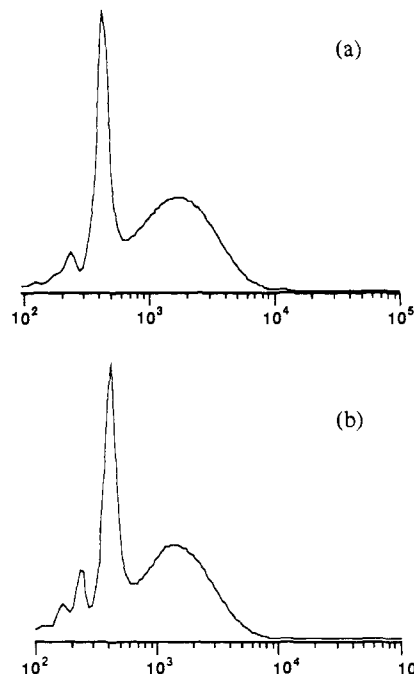


Figure 3. Gel permeation chromatograms of poly(phenylsilylene) samples obtained under analogous conditions with (a) $\text{CpCp}^*\text{ZrHCl}$ (**1**) and (b) $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (**3**) as catalysts. The small, low molecular weight peaks are due to catalyst residue (both traces) and $\text{HSi}(\text{SiMe}_3)_3$ (trace b). The sharp, intense peak is due to the cyclic $(\text{SiHPh})_6$ species, and the higher, broader molecular weight peak corresponds to linear $\text{H}(\text{SiHPh})_n\text{H}$ chains.

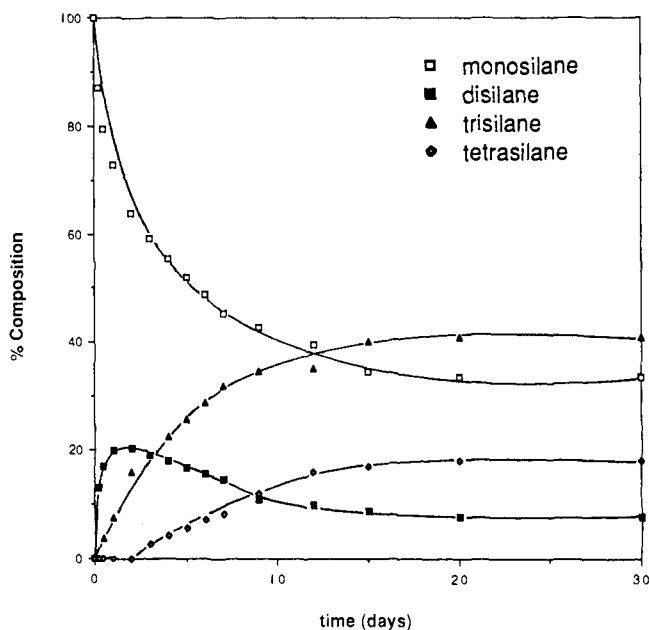


Figure 4. Plots of concentration vs time for the $\text{Cp}^*_2\text{HfH}_2$ -catalyzed dehydrocoupling of PhSiH_3 .

actions catalyzed by silyl complexes (e.g., as in eq 7). Another sluggish dehydrocoupling reaction that allows observation of the first few intermediate polysilanes occurs with $\text{Cp}^*_2\text{HfH}_2$ and excess PhSiH_3 . This reaction is quite slow, probably because of the sterically congested metal center which creates severe crowding in the four-center transition states. Figure 4 compares the disappearance of monomer with the formation of disilane, trisilane, and tetrasilane. It is apparent that dehydrocoupling occurs in a stepwise fashion. Note that this reaction took place in a sealed NMR tube, so that the buildup of hydrogen eventually inhibited dehydrocoupling.

We have also investigated the reaction of $\text{Cp}^*_2\text{HfH}_2$ with excess $\text{Ph}_2\text{SiSiH}_2\text{Ph}$ (Figure 5), which shows that disilane is more

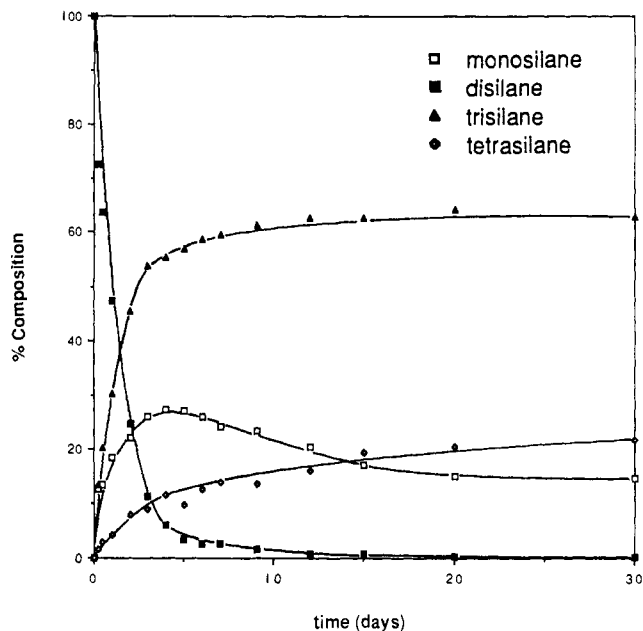
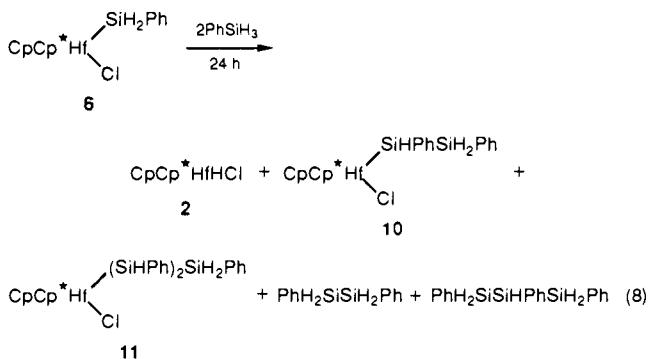


Figure 5. Plots of concentration vs time for the $\text{Cp}^*_2\text{HfH}_2$ -catalyzed dehydrocoupling of $\text{PhH}_2\text{SiSiH}_2\text{Ph}$.

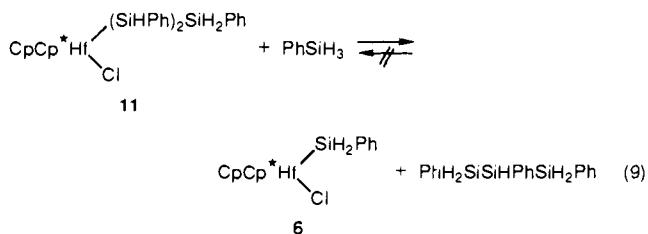
reactive than monosilane. The fairly rapid accumulation of trisilane is interpreted as evidence for facile reversibility of the Si-Si bond-forming process.

Slower, more selective catalysts have also been employed to investigate the importance of $\text{M}(\text{SiHPh})_n\text{H}$ polysilyl intermediates. Two possible intermediates of this type were prepared independently by the σ -bond metathesis reactions of **4** with $\text{PhH}_2\text{SiSiH}_2\text{Ph}$ and $\text{PhH}_2\text{SiSiHPhSiH}_2\text{Ph}$. The resulting complexes, $\text{CpCp}^*\text{Hf}(\text{SiHPhSiH}_2\text{Ph})\text{Cl}$ (**10**)²⁵ and $\text{CpCp}^*\text{Hf}(\text{SiHPhSiHPhSiH}_2\text{Ph})\text{Cl}$ (**11**), have very distinctive ^1H NMR spectra, since they form as statistical mixtures of diastereomers and since their SiH protons appear as multiplets with considerable fine structure. Both **10** and **11** were clearly identified (by ^1H NMR spectroscopy) during the slow oligomerization of PhSiH_3 (2 equiv) by **6** (eq 8). After 24 h (33% conversion of **6**), the four silicon-containing products were present in a ratio of 3:0.1:2:3.



Although the polysilyl hafnium complexes **10** and **11** are observed to form concurrently with small polysilanes, they are not necessarily intermediates in the dehydrocoupling process (as suggested by Scheme III), but are perhaps only side products formed via nonproductive σ -bond metathesis reactions. More insight into preferred dehydrocoupling pathways can be gained by examination of concentration profiles for early polysilane intermediates in the slow polymerization of Figure 4. In this reaction with $\text{Cp}^*_2\text{HfH}_2$ as catalyst, tetrasilane does not appear until after the disilane concentration has reached its maximum. This indicates that, under rather selective conditions, the coupling of polysilane chains is not a major pathway for chain growth. Rather, it seems that the chains tend to grow by one silicon at a time, with tetrasilane being produced by the coupling of monosilyl and trisilyl groups (in Scheme III, n or $m = 1$).

To determine which step in the mechanism of Scheme III might impose the selectivity required for adding one monomer unit per catalytic cycle, reaction of the polysilyl complex **11** with PhSiH_3 was monitored by ^1H NMR spectroscopy (eq 9). This reaction

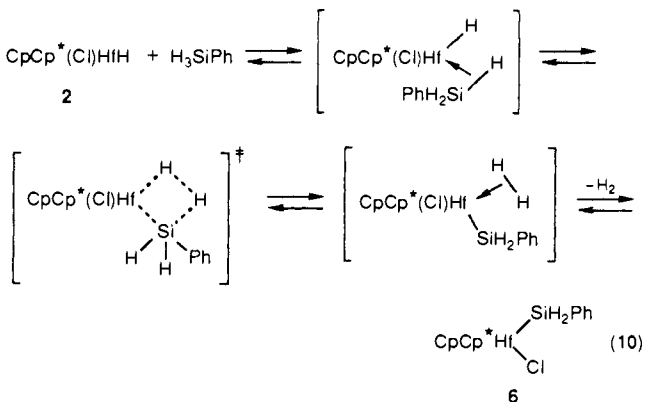


proceeds rapidly via σ -bond metathesis to the trisilane and **6**, which then react slowly to give longer $\text{H}(\text{SiHPh})_n\text{H}$ oligomers and **2**. We interpret these results to mean that the polymerization occurs by predominant dehydrocoupling of the hydride catalyst with monosilane to give an MSiH_2Ph derivative ($n = 1$ in Scheme III). This MSiH_2Ph species then undergoes reaction with a polysilane end group to increment the chain length.

Discussion

It appears that σ -bond metathesis reactions are a characteristic feature of reactants that can form four-center transition states composed of silicon, hydrogen, and a d^0 metal center. Observation of every possible reaction of this type (Scheme I) for zirconocene and hafnocene derivatives indicates that silicon readily takes part in these bond-breaking/bond-making processes via expansion of its coordination number to five. Related σ -bond metathesis reactions are well-known for systems involving carbon, hydrogen, and a d^0 (or f^0) metal center,²⁶ but apparently the corresponding reactions involving silicon are more facile due to the higher susceptibility of silicon toward nucleophilic attack. It is well-known that silicon forms stable compounds with expanded coordination spheres,³⁴ which suggests that hypercoordinate silicon centers may be involved in unstable intermediates along the reaction pathway to or from the four-center transition state. For example, the reaction of a d^0 metal hydride with a hydrosilane may produce (transiently) a complex of the type $\text{L}_n\text{M}(\eta^2\text{-H}_2\text{SiRR}')$, which would be analogous to a $\text{L}_n\text{M}(\eta^2\text{-H}_2\text{BH}_2)$ borohydride complex.

A second type of transient intermediate which may form prior to a four-center transition state is a complex with coordinated Si-H, H-H, or Si-Si σ -bonds. In early studies on hydrogenolysis reactions of zirconocene derivatives, Schwartz proposed such σ -complexes, e.g., $\text{Cp}_2\text{Zr}(\text{R})(\text{H})(\text{H}_2)$, as intermediates.^{29c} Similarly, reaction of **2** with PhSiH_3 may proceed via formation of $\eta^2\text{-HSiH}_2\text{Ph}$ and $\eta^2\text{-H}_2$ complexes (eq 10). Consistent with this,



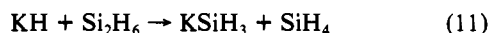
an apparent requirement for the σ -bond metathesis reactions involving silicon is an open coordination site (empty orbital) at the reacting metal center, since the reactions are severely inhibited by the presence of small Lewis donors. Also, σ -bond metathesis

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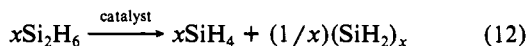
reactions for formally 16-electron ZrCl and HfCl derivatives are significantly slower than reactions for corresponding derivatives that do not have a π -donor ligand (e.g., M-alkyl, MH, or M-silyl derivatives). Presumably this is because π -donation from the chloro ligand to the metal can to some degree compete with coordination of substrate. An analogous effect has been observed for CO insertion reactions of $Cp_2M(alkyl)X$ derivatives.³⁵

The catalytic cycle proposed in Scheme III, composed of two σ -bond metathesis steps, appears to represent a new polymerization mechanism and is unusual as a coordination polymerization in that it involves step growth of polymer rather than chain growth. This explains the relatively low molecular weights that are produced, since extremely high conversion of Si-H to Si-Si bonds would be required for production of high polymer via a step-growth type mechanism.³⁶ Also, conditions which should favor this type of reaction, e.g., high monomer concentrations and high vacuum to remove hydrogen, can be employed to achieve increased molecular weights.³⁷ Therefore dehydropolymerization with early metal catalysts shares many characteristics with another metal-catalyzed condensation, acyclic diene metathesis (ADMET) polymerization, which couples dienes with elimination of a volatile byproduct, ethylene.³⁸ As predicted for a step-growth like mechanism,³⁶ we generally observe polydispersities near 2.0 for the linear $H(SiHPh)_nH$ chains (by GPC).

Related σ -bond metathesis reactions have been observed by Ring and co-workers, in reactions of hydrosilanes with alkali metal salts.³⁹ For example, potassium hydride stoichiometrically cleaves the Si-Si bond of disilane:^{39a,c}



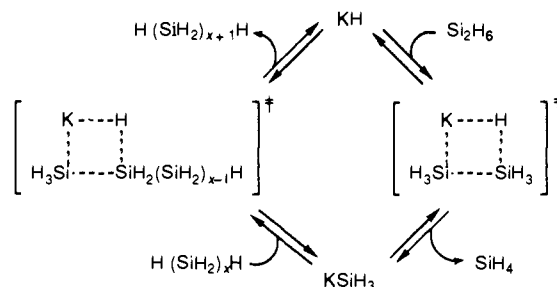
Perhaps more intriguing is the catalytic disproportionation of disilane to SiH_4 and polysilanes, which is catalyzed by KH, LiD, and LiCl (relative rates $KH > LiD > LiCl$):^{39d}



For the latter reaction it was shown that the coupling of free silylenes could not explain the production of polymer, and a concerted, four-center transition state (which did not include the catalyst) was proposed.^{39g} A possible mechanism for the KH-catalyzed polymerization that is similar to that observed above for zirconium and hafnium and is consistent with the observed stoichiometry is shown in Scheme IV. In related work, Corriu and co-workers have reported the redistribution of disilanes $R_2SiSiHMe_2$ ($R = H, Me, Ph$) to oligosilanes (Si_5-Si_7) by KH, and on the basis of trapping studies they propose that the reactions go via elimination of $:SiHR$ silylene species from potassium silyl derivatives.⁴⁰

Most speculation about the mechanism of transition-metal-catalyzed dehydrogenative silane coupling has previously centered on intermediate silylene complexes, $L_nM=SiR_2$.^{6b} In general such mechanisms appear to be viable, but it has yet to be shown that silylene complexes (which are still very rare)⁷ react with silanes via Si-Si bond formation. For the polymerizations discussed here, a metal-silylene-based mechanism seems unlikely, since the reaction of two σ -bonds would be required for formation of a $CpCp^*M=SiHR$ species. Our results are consistent with the

Scheme IV



involvement of only one σ -bond to the metal center, since $CpCp^*M(R)Cl$ ($M = Zr, Hf; R = H, \text{silyl}$) complexes are catalyst precursors for the polymerization of $PhSiH_3$, and in each case the final metal-containing product is the corresponding hydride $CpCp^*MHCl$. If silylene complexes were to form, a likely process for generating them would be α -elimination of RH from a $M-(R)(SiHR'R'')$ complex. An attempt to generate such a complex by thermolysis of $Cp^*_2Zr(Me)SiHMe_2$ gave Me_2SiH_2 (not CH_4) as the elimination product.⁴¹ Finally, added traps (hydrosilanes, alkenes, alkynes, etc.) have failed to intercept a silylene complex during the course of a dehydrocoupling reaction.

The σ -bond metathesis mechanism of Scheme III requires conversion of the catalyst precursor to an active, coordinatively unsaturated hydride complex by reaction with the hydrosilane monomer. Such hydride species are readily formed via σ -bond metathesis reactions (Scheme I), and for silyl complex precursors, the individual steps of this conversion have been observed (e.g., eq 7). The behavior of different catalyst precursors may be explained in terms of the chemistry required to activate them. With Cp_2ZrMe_2 as the catalyst, an induction period is observed, followed by polymerization that is accompanied by formation of the inactive dimer $Cp_2(PhH_2Si)Zr(\mu-H)_2ZrCp_2(SiHMePh)$.^{8d} In contrast, the catalyst precursor $Cp_2Zr[Si(SiMe_3)_3]Me$ gives rapid polymerization of $PhSiH_3$ with no observable induction period. Eventually, this polymerization of $PhSiH_3$ slows as the zirconium species in solution are converted to $Cp_2(PhH_2Si)Zr(\mu-H)_2ZrCp_2(SiHMePh)$. We attribute the higher initial rate of polymerization for $Cp_2Zr[Si(SiMe_3)_3]Me$ to the greater reactivity of Zr-Si bonds relative to Zr-C bonds toward σ -bond metathesis processes that produce active hydride species. This reactivity trend is readily observed, for example, by the fact that $PhSiH_3$ does not react with Cp_2HfMe_2 at 90 °C over 12 h,⁴² but is polymerized at room temperature in the presence of $CpCp^*Hf[Si(SiMe_3)_3]Me$.

A significant consequence of our proposed mechanism is that it provides a basis for the rational design of new catalysts, which are characterized as reactive, coordinatively unsaturated hydride complexes or efficient precursors thereof. Active catalyst precursors are obtained with silyl derivatives such as $CpCp^*Zr[Si(SiMe_3)_3]Me$, which possesses an active Zr-Si bond that is readily converted to a Zr-H bond and a metal center that is sterically crowded enough to inhibit dimerization. This stabilization of monomeric catalysts leads to long-lived activity. Although steric hindrance in bis(pentamethylcyclopentadienyl)zirconium complexes provides very stable monomeric catalysts, crowding in the four-center transition states for σ -bond metathesis appears to severely lower the catalyst's activity. The best dehydropolymerization catalysts for $PhSiH_3$ are currently monomer-stabilized zirconocene hydride derivatives of the type $CpCp^*Zr(H)(R)$ (or direct precursors to these), where R is not a good π -donor ligand ($R = \text{hydride, alkyl, or silyl}$).

More control over molecular weight distributions from the dehydropolymerization of silanes should result from the design of new catalysts. However, there is much yet to be learned about factors that influence σ -bond metathesis reactivity in d^0 metal silyl

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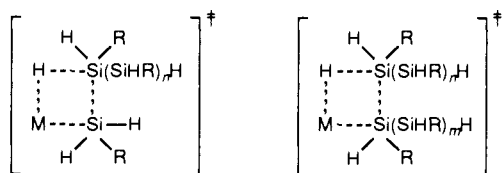
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complexes. Surprisingly, the highly electron-deficient complex $\text{Cp}^*\text{Cl}_2\text{ZrSi}(\text{SiMe}_3)_3$ is unreactive toward PhSiH_3 , even though it is more reactive than $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ toward insertion of ethylene.⁴² Harrod has reported that certain catalysts (e.g., Cp_2V and $\text{Cp}^*_2\text{ThMe}_2$) dehydrocouple silanes to produce disilanes as the principal products.⁴³ Similarly, we have observed that $\text{Cp}_2\text{Ti}(\text{SiMe}_3)\text{Cl}$ and $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$ react with excess PhSiH_3 at room temperature by way of stoichiometric formation of HSiMe_3 and $\text{PhH}_2\text{SiSiH}_2\text{Ph}$.⁴⁴ In the latter case, the tantalum silyl is quantitatively converted to $[\text{Cp}^*\text{Cl}_3\text{TaH}]_n$. We presume that, in these cases, the initially formed MSiH_2Ph derivatives couple with PhSiH_3 to produce disilane and the metal hydride, which is then unreactive toward silane.

The proposed mechanism of Scheme III strongly suggests that active catalysts might be *f* metal hydride derivatives, since scandium group and *f* metal complexes are most closely associated with σ -bond metathesis processes.²⁶ We⁴⁵ and others^{17b,19,20} have therefore investigated Cp^*_2LnR (*R* = alkyl, hydride) complexes as dehydrocoupling catalysts. Generally, relatively slow dehydrocoupling and formation of low molecular weight oligomers are observed. However, the participation of Ln(III) centers in this reaction lends considerable support to the σ -bond metathesis polymerization mechanism, since other mechanisms involving changes in the metal's valency are highly unlikely.

The mechanism of Scheme III can account for many characteristics of the polymerization reaction, including the stringent steric requirements observed for catalysts and silane monomers which result from the inherently crowded four-center transition states. Observed steric constraints on σ -bond metathesis reactions suggest that the catalyst should react predominantly at the polysilane $-\text{SiH}_2\text{R}$ end groups, giving linear chain growth. It also appears that steric factors may heavily influence the types of coupling reactions that can occur, so that chain growth preferentially occurs by one silicon at a time via reaction of a MSiH_2R species with the end group of a polysilane chain. Therefore, as long as monomer is present, the more important polymerization process corresponds to the case where *n* = 1 in Scheme III. This selectivity, which is observed under rather selective conditions (see Figure 4), can be understood in terms of steric hindrance in competing four-center transition states for silyl coupling (monomer-chain vs chain-chain coupling, *n, m* \geq 1):



The least crowded transition state is produced by reaction of a MSiH_2R derivative with the end group of a polysilane chain, since this places the bulky polysilyl group in the β -position relative to the metal center. Of course, this selectivity will be most important early in the polymerization, when the monomer concentration is highest. Later in the reaction, the slower coupling of polysilanes must occur to accomplish an increase in chain lengths.

The mechanistic information provided by the results described above should contribute to the development of transition-metal-catalyzed dehydrocoupling reactions. An encouraging aspect of this mechanistic picture is that, in principle, there are no insurmountable limits to the molecular weights that can be achieved. It is hoped that further investigation will produce a more complete understanding of the factors controlling reactivity and that the proposed mechanism will lead to development of better catalytic systems for controlling stereoregularity^{8h,21} and molecular weights of the polysilanes.

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Experimental Section

All manipulations were performed using rigorously anaerobic and anhydrous conditions. Elemental analyses were performed by Mikroanalytisches Labor Pascher and Schwartzkopf microanalytical laboratories. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were obtained with a GE QE-300 instrument operating at 300 (¹H), 75.5 (¹³C), 59.6 (²⁹Si), and 46.1 MHz (²H). Gel permeation chromatography of polysilanes was carried out on THF solutions, protected from light. A Waters Associates liquid chromatograph comprising Ultrastaygel permeation columns, a 501 HPLC solvent delivery system, an R-400 refractive index detector, and a Model 745 control system was used. All molecular weights are reported versus polystyrene standards. Organosilanes were prepared from the corresponding chlorosilanes (Petrarch) by reduction with LiAlH_4 (deuterated silanes were prepared by reduction with LiAlD_4).⁴⁶ $\text{PhH}_2\text{SiSiH}_2\text{Ph}$ and $\text{PhH}_2\text{SiSiHPhSiH}_2\text{Ph}$ were prepared according to the literature procedure.⁴³ The following compounds were also prepared by literature methods: $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$,³² $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$,²⁵ $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{SiMe}_3$,²⁸ $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$,³² $\text{Cp}^*_2\text{HfH}_2$,⁴⁷ $\text{CpCp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$,²⁵ and $\text{CpCp}^*\text{Hf}(\text{SiHPhSiH}_2\text{Ph})\text{Cl}$.²⁵

CpCp*ZrHCl (1). A pentane (30 mL) solution of $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (0.40 g, 0.70 mmol) in a pressure bottle was charged with 60 psi of hydrogen, resulting in a gradual loss of the solution's color. After 5 min, the H_2 pressure was released, and the solution was filtered, concentrated to 5 mL, and cooled to -40 °C. The white crystals (mp 126 – 128 °C) were isolated in 78% yield (0.18 g) by filtration: molecular weight in benzene, 275 (calcd 328); IR (Nujol, CsI , cm^{-1}) 1595 m (ZrH), 1020 m, 830 m, 810 s, 530 w, 380 m, 340 w; ¹H NMR (benzene-*d*₆, 22 °C, 300 MHz) δ 1.84 (s, 15 H, C₅Me₃), 5.85 (s, 5 H, C₅H₃), 6.59 (s, 1 H, ZrH); ¹³C{¹H} NMR (benzene-*d*₆, 22 °C, 75.5 MHz) δ 12.46 (C₅Me₃), 110.49 (C₅H₃), 120.26 (C₅Me₃). Anal. Calcd for C₁₅H₂₁ClZr: C, 54.9; H, 6.45. Found: C, 54.8; H, 6.60.

CpCp*HfHCl (2). A solution of $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (0.40 g, 0.60 mmol) in pentane (30 mL) was pressurized with H_2 (100 psi), resulting in a gradual color change from yellow to colorless. After 10 min, the H_2 pressure was released, the solution was filtered, and the filtrate was concentrated to 5 mL and cooled to -40 °C. The white crystals (mp 127 – 129 °C) were isolated in 80% yield (0.20 g): molecular weight in benzene, 404 (calcd 415); IR (Nujol, CsI , cm^{-1}) 1650 m (HfH), 1030 m, 830 m, 810 s, 740 m, 560 w, 346 w, 310 w; ¹H NMR (benzene-*d*₆, 22 °C, 300 MHz) δ 1.89 (s, 15 H, C₅Me₃), 5.81 (s, 5 H, C₅H₃), 12.29 (s, 1 H, HfH); ¹³C{¹H} NMR (benzene-*d*₆, 22 °C, 75.5 MHz) δ 12.28 (C₅Me₃), 109.63 (C₅H₃), 118.61 (C₅Me₃). Anal. Calcd for C₁₅H₂₁ClHf: C, 43.4; H, 5.10. Found: C, 43.3; H, 5.19.

CpCp*Hf[Si(SiMe3)3]Me (7). A diethyl ether (30 mL) solution of $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (1.00 g, 1.51 mmol) was cooled to -78 °C. To this stirred solution was added 0.5 mL of 3 M MeMgBr (1.50 mmol) in diethyl ether. The reaction mixture was allowed to slowly warm to room temperature with stirring over 3 h. Volatiles were removed under vacuum, and the product was extracted into pentane (3×20 mL). The combined pentane extracts were concentrated and cooled to -40 °C to afford two crops of yellow crystals (mp 179 – 181 °C) in an overall yield of 81% (0.785 g): IR (Nujol, CsI , cm^{-1}) 1290 w, 1250 m sh, 1238 s, 1140 m, 1070 w, 1028 m, 1015 m, 820 s, 745 m sh, 730 m, 665 s, 620 s, 540 w, 440 w, 330 m; ¹H NMR (benzene-*d*₆, 22 °C, 300 MHz) δ -0.55 (s, 3 H, HfMe), 0.48 (s, 27 H, SiMe₃), 1.82 (s, 15 H, C₅Me₃), 5.88 (s, 5 H, C₅H₃); ¹³C{¹H} NMR (benzene-*d*₆, 22 °C, 75.5 MHz) δ 6.90 (SiMe₃), 13.09 (C₅Me₃), 54.57 (HfMe), 111.15 (C₅H₃), 118.77 (C₅Me₃); ²⁹Si NMR (benzene-*d*₆, 22 °C, 59.6 MHz) δ -83.59 [$\text{Si}(\text{SiMe}_3)_3$], -5.00 [$\text{Si}(\text{SiMe}_3)_3$]. Anal. Calcd for C₂₅H₃₀Si₄Hf: C, 46.8; H, 7.86. Found: C, 46.6; H, 7.79.

CpCp*Hf(SiHPhSiHPhSiH2Ph)Cl (11). To a benzene (20 mL) solution of $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (0.40 g, 0.60 mmol) was added 1,2,3-triphenyltrisilane (0.20 g, 0.62 mmol) (this silane was contaminated with ca. 5% of 1,2,3,4-tetraphenyltetrasilane). Stirring for 3.5 h under ambient fluorescent room lighting resulted in a dark yellow solution. Removal of volatiles, extraction with pentane (30 mL), concentration, and cooling (-40 °C) of the extract resulted in precipitation of a yellow solid that melted at room temperature. This sample of **11**, obtained in about 60% yield, was ca. 90% pure, as judged by ¹H NMR spectroscopy. A mixture of four diastereomers was present in an approximately 1:1:1:1 ratio: IR (Nujol, CsI , cm^{-1}) 2010 s br, 2040 s sh (SiH); ¹H NMR (benzene-*d*₆, 22 °C, 300 MHz) δ 1.70, 1.74, 1.75, 1.77 (s, 15 H, C₅Me₃), 4.6–5.1 (m, 4 H, SiHPhSiHPhSiH₂Ph), 5.72, 5.75, 5.77, 5.78 (s, 5 H, C₅H₃), 7.0–7.9 (m, 15 H, C₆H₅); ¹³C{¹H} NMR (benzene-*d*₆, 22 °C, 75.5

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MHz) δ 12.11, 12.28, 12.33, 12.50 (C_5Me_5), 111.54, 111.76, 111.83, 111.95 (C_5H_5), 119.63, 119.76, 119.88, 119.98 (C_5Me_5), 128.0, 137.0 (m, C_6H_5); ^{29}Si NMR (benzene- d_6 , 22 °C, 59.6 MHz) δ -8.0 (m, α -SiHPh), -50 (m, β -SiHPh), -60 (m, SiH₂Ph).

Polymerization of PhSiH₃ with Cp₂Zr[Si(SiMe₃)₃]SiMe₃. Phenylsilane (1.74 g, 16.0 mmol) was added to a toluene solution (2 mL) of Cp₂Zr[Si(SiMe₃)₃]SiMe₃ (52 mg, 0.10 mmol). The reaction mixture immediately turned dark red-brown with strong gas evolution. The mixture was stirred vigorously under a stream of argon for 48 h and then pumped to dryness under vacuum. The nonvolatile materials were taken up in ca. 10 mL of toluene, the catalyst was allowed to oxidize by exposure to air for a few seconds, and the solution was then passed rapidly through a Florisil column. The effluent was evaporated to dryness, washed with pentane (2 × 10 mL), and dried under vacuum to afford 1.37 g of poly(phenylsilylene); $M_w/M_n = 1900/1100 = 1.7$.

Polymerization of PhSiH₃ with 1 and 3. Phenylsilane (0.61 mL, 4.9 mmol) was added to a rapidly stirred toluene solution (0.30 mL) of **1** (0.080 g, 0.24 mmol) or **3** (0.14 g, 0.24 mmol). The reaction mixture darkened immediately with strong gas evolution. The mixture was stirred for 3 h under a dynamic argon atmosphere. At this point an aliquot was removed, exposed to air to prevent further polymerization, and subjected to GPC analysis. Using **1** as a catalyst, the polymer obtained had the following molecular weight properties: 31% (SiHPh)₆ cyclics; 69% linear polymer with $M_w = 3100$, $M_n = 1700$, $M_w/M_n = 1.8$. Using **3** as a catalyst, the polymer obtained had the following molecular weight properties: 33% (SiHPh)₆ cyclics; 67% linear polymer with $M_w = 2400$, $M_n = 1600$, $M_w/M_n = 1.5$. The cyclic species were independently identified by ^{29}Si NMR experiments.

Reaction of 7 with PhSiH₃. A septum-capped 5-mm NMR tube was charged with CpCp*Hf[Si(SiMe₃)₃]Me (0.02 g, 0.03 mmol), PhSiH₃ (6 mg, 0.06 mmol), and 0.40 mL of benzene- d_6 . After 2 h, the 1H NMR spectrum contained resonances assigned to HSi(SiMe₃)₃ [δ 0.25 (s, 27 H, SiMe₃), 2.53 (s, 1 H, SiH)], CpCp*Hf(SiH₂Ph)Me [δ -0.70 (s, 3 H, HfMe), 1.76 (s, 15 H, C₅Me₅), 4.49 (d, $^2J_{HH} = 2.0$ Hz, 1 H, SiH), 4.82 (d, $^2J_{HH} = 2.0$ Hz, 1 H, SiH), 5.65 (s, 5 H, C₅H₅)], CpCp*Hf(H)Me [δ -0.57 (s, 3 H, HfMe), 1.87 (s, 15 H, C₅Me₅), 5.81 (s, 5 H, C₅H₅), 12.87 (s, 1 H, HfH)], PhH₂SiSiH₂Ph, and PhH₂SiSiHPhSiH₂Ph.

Reactions of PhSiH₃ and PhH₂SiSiH₂Ph with Cp*₂HfH₂. Sealed NMR tubes containing Cp*₂HfH₂ (23 mg, 0.05 mmol), PhSiH₃ (0.32 g, 3.0 mmol) or PhH₂SiSiH₂Ph (0.64 g, 3.0 mmol), and benzene- d_6 (0.4 mL) were allowed to sit at room temperature (21 °C). The reaction was followed by 1H NMR spectroscopy by monitoring the relative ratios of the integrated intensities of the SiH resonances for the silanes PhSiH₃ (δ 4.22), PhH₂SiSiH₂Ph (δ 4.49), PhH₂SiSiHPhSiH₂Ph (δ 4.60), and PhH₂Si(SiHPh)₂SiH₂Ph (δ 4.68). Also, a sealed NMR tube containing

Cp*₂HfH₂ (23 mg, 0.05 mmol), PhH₂SiSiHPhSiH₂Ph (0.96 g, 3.0 mmol), and benzene- d_6 (0.4 mL) was heated to 80 °C for 2 h. The 1H NMR spectrum showed resonances assigned to PhSiH₃ (20%), PhH₂SiSiH₂Ph (22%), PhH₂SiSiHPhSiH₂Ph (46%), and PhH₂Si(SiHPh)₂SiH₂Ph (12%). Upon further heating to 120 °C for 5 h, the 1H NMR spectrum showed resonances assigned to a mixture of higher oligomers at δ 4.1–4.9 (broad unresolved massifs, SiH) and 6.8–7.8 (broad unresolved massifs, C₆H₅).

Reaction of 6 with PhSiH₃. CpCp*Hf(SiH₂Ph)Cl (0.02 g, 0.038 mmol), PhSiH₃ (0.009 mL, 0.08 mmol), and benzene- d_6 (0.4 mL) were loaded into an NMR tube, which was then sealed with a septum cap. After 24 h (33% conversion), the 1H NMR spectrum showed resonances assigned to CpCp*HfHCl, CpCp*Hf(SiHPhSiH₂Ph)Cl, CpCp*Hf(SiHPhSiHPhSiH₂Ph)Cl, PhH₂SiSiH₂Ph, and PhH₂SiSiHPhSiH₂Ph. The latter three silicon-containing products were formed in a ratio of ca. 3:0.1:2:3.

Reaction of 11 with PhSiH₃. Compound **11** (0.02 g, 0.03 mmol), PhSiH₃ (0.004 mL, 0.03 mmol), and benzene- d_6 (0.4 mL) were loaded into an NMR tube, which was then sealed. After 5 h, the 1H NMR spectrum showed quantitative conversion to CpCp*Hf(SiH₂Ph)Cl and PhH₂SiSiHPhSiH₂Ph. At longer times, CpCp*HfHCl and a mixture of (SiHPh)_n oligomers were observed.

Kinetic Studies. The reactions were monitored by 1H NMR spectroscopy. For each kinetic run, a benzene- d_6 solution of the reactants and ferrocene as an internal standard was sealed off under vacuum in a 5-mm NMR tube. The samples were heated in the probe of the NMR spectrometer or in a thermostated oil bath which was kept in the dark. For the reaction of **2** with PhSiH₃, disappearance of the SiH resonance of the silane and the Cp resonance of **2** relative to ferrocene was monitored. For the thermolysis of **6**, disappearance of the Cp* resonance relative to ferrocene was followed, and the reaction was second-order for 3 half-lives over a concentration range of 0.12–0.50 M. For the reaction of **6** with PhSiH₃, pseudo-first-order conditions were established with 10-, 20-, and 30-fold excesses of the silane. Plots of k_{obsd} vs silane concentration were linear and passed through the origin. The disappearance of **6** obeyed first-order kinetics for 3 half-lives.

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