

Enhanced Reactivity of Cationic vs Neutral Hafnocene Complexes in Stoichiometric and Catalytic σ -Bond Metathesis Reactions Involving Si–H and Si–C Bonds

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Summary: A comparison of the cation-like complex $\text{CpCp}^*\text{HfH}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ with the neutral analogue $\text{CpCp}^*\text{HfHCl}$ reveals increased activity toward σ -bond metathesis for the more electrophilic, cationic complex. A catalytic transformation of PhSiH_3 to Ph_2SiH_2 and SiH_4 by $\text{CpCp}^*\text{HfH}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ appears to occur by σ -bond metathesis of the Si–C bond, which occurs concurrently with dehydropolymerization to highly cross-linked polysilanes.

Metal-mediated reactions involving bond cleavage and bond formation via concerted, four-centered transition states (σ -bond metathesis) offer considerable potential for the development of new catalytic conversions. In principle, such processes could be analogous to well-known catalytic cycles based on oxidative addition and reductive elimination but appear to be almost exclusively associated with d^0 transition metal centers. The activation of hydrocarbons by σ -bond metathesis has been well-known for over 20 years,^{1–3} but the development of catalytic reactions involving this chemistry has been hindered by the apparent restriction that carbon cannot adopt the β -position of a four-centered transition state.^{3b} This restriction does not exist for silicon, and therefore, catalytic reactions involving the σ -bond metathesis of Si–H bonds (i.e., dehydropolymerization⁴ and hydrosilylation⁵) have been developed.

Clearly, new metal complexes that are more active in σ -bond metathesis could greatly expand the set of useful catalytic reactions associated with this chemistry. The design of such systems will require a better understanding of the electronic factors that influence

σ -bond metathesis reactivity at d^0 metal centers. Given similarities in the transition states for σ -bond metathesis and the propagation step of alkene polymerization, as catalyzed by metallocene derivatives (both involve four-center, four-electron, electrocyclic transition states), it seemed that cationic complexes⁶ might exhibit enhanced reactivity in σ -bond metathesis. Indeed, a recent theoretical study supports this view,⁷ and whereas $[\text{Cp}^*_2\text{ZrH}][\text{HB}(\text{C}_6\text{F}_5)_3]$ reacts with benzene- d_6 to form $[\text{Cp}^*_2\text{ZrD}][\text{DB}(\text{C}_6\text{F}_5)_3]$,^{6a} $\text{Cp}^*_2\text{ZrH}_2$ is not deuterated by benzene- d_6 .⁸ However, attempts to employ formally 14-electron cationic metallocene catalysts for the dehydropolymerization of silanes have not led to significant increases in polymer chain lengths, and in many cases significant reductions in molecular weight have been observed (implying reduced activity for the cationic catalyst).⁹ Harrod and co-workers have identified a cationic zirconocene system that is active in silane polymerization, and interestingly they suggest that silyl radicals may be involved in the mechanism for polysilane formation.¹⁰ To better understand these reactivity patterns, we have directly compared related cationic and neutral d^0 CpCp^*Hf complexes in simple σ -bond metathesis steps involving Si–H bonds. Here we report evidence that the cationic complexes exhibit remarkably higher reactivities.

The neutral dimethyl complex $\text{CpCp}^*\text{HfMe}_2$ (**1**) does not react with 1 equiv of PhSiH_3 over 1 week in benzene- d_6 (25 °C). In contrast, the cation-like, zwitterionic complex $\text{CpCp}^*\text{HfMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ (**2**) reacts with 1 equiv of PhSiH_3 over 3 h in benzene- d_6 at room temperature to quantitatively form $\text{CpCp}^*\text{HfH}(\mu\text{-H})\text{B}(\text{C}_6\text{F}_5)_3$ (**3**) and PhMe_2SiH (by ^1H NMR spectroscopy; eq 1). During the course of this reaction the intermediate PhMeSiH_2 was observed, and use of 0.5 equiv of PhSiH_3 in the reaction resulted in formation of a 1:1 mixture of

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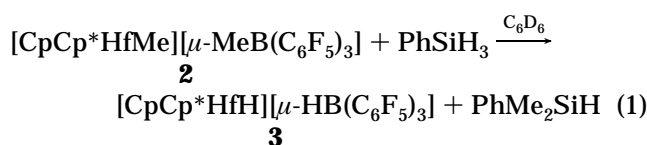
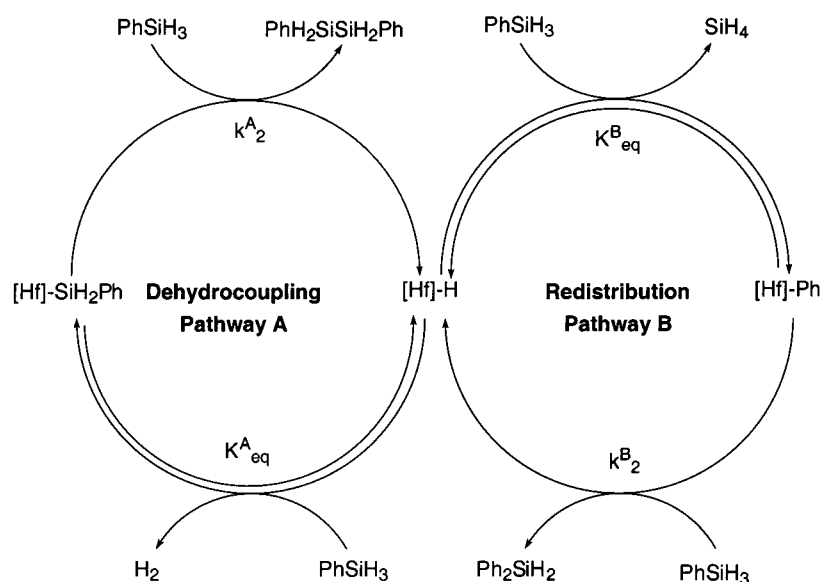
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Scheme 1



2:3, rather than a mixed hafnium hydride/methyl borate complex. While it has been observed that some reactions of early-transition-metal compounds with silanes are accelerated by light,^{3,10,11} this transformation proceeds identically in the presence or absence of ambient light. As might be expected from what is known about steric influences on the rates of σ -bond metathesis reactions,^{4b} bulkier silanes react more slowly with **2** (relative rates: $\text{CySiH}_3 > \text{MesSiH}_3$ ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$), $\text{Ph}_2\text{-SiH}_2 > \text{Mes}_2\text{SiH}_2$). These results suggest that zwitterionic **2** reacts as an associated ion pair with increased electrophilicity due to $\text{CpCp}^*\text{HfMe}^+$ character and is considerably more reactive than neutral **1** toward σ -bond metathesis with Si–H bonds.

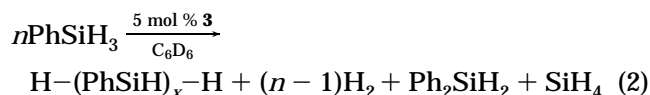
Compound **3** was isolated from the reaction of **2** with 1.5 equiv of PhSiH_3 in pentane, and it may also be prepared by the reaction of **1** with hydrogen (1 atm). Unlike $[\text{Cp}^*_2\text{ZrH}][\text{HB}(\text{C}_6\text{F}_5)_3]$,^{6a} which features a terminal B–H bond and coordination of the anion to Zr via $\text{Zr}\cdots\text{F}\cdots\text{C}$ interactions, **3** appears to possess a Hf–H–B-bonded structure. Thus, no terminal B–H stretch was observed in the infrared spectrum of **3**, but a stretching vibration at 1950 cm^{-1} may be attributed to M–H–B bonding.¹² In addition, the observed $^1J_{\text{BH}}$ coupling constant (50 Hz) reflects the presence of a bridging hydrogen.¹³

In contrast to $[\text{Cp}^*_2\text{ZrH}][\text{HB}(\text{C}_6\text{F}_5)_3]$,^{6a} which reacts with benzene- d_6 via H/D exchange involving the Zr–H and the B–H positions, no deuteration of **3** is observed in benzene- d_6 before thermal decomposition at $100\text{ }^\circ\text{C}$ after 4 days. Though the “cationic” nature of hydride **3**

might be expected to result in higher activity toward the dehydropolymerization of hydrosilanes, relative to similar neutral complexes,⁹ there is little difference in the molecular weight ($M_n \approx 2000$) of polysilane produced by the dehydropolymerization of neat PhSiH_3 with **3** or $\text{CpCp}^*\text{HfHCl}$ (**4**) as the catalyst (2 mol %, 2 days). This result prompted further investigation of the mechanisms of these dehydropolymerizations.

The neutral catalyst **4**, which is known to react with silanes via a four-centered transition state,⁴ reacts with excess PhSiH_3 in benzene- d_6 ($50\text{ }^\circ\text{C}$) to give oligomeric polysilanes and H_2 . The disappearance of PhSiH_3 obeys second-order kinetics (over 3 half-lives), as demonstrated by plots of $1/[\text{PhSiH}_3]$ vs time, and the reaction also displays a first-order dependence on catalyst concentration. This kinetic behavior is consistent with a metal-catalyzed condensation polymerization in which the first step of the catalytic cycle is reversible (Scheme 1, pathway A), and mass balance requires 2 equiv of PhSiH_3 for a single turnover of the cycle. The overall rate law for this mechanism is $\text{rate} = k_{\text{obs}}[\mathbf{4}][\text{PhSiH}_3]^2$, where $k_{\text{obs}} = K^{\text{A}}_{\text{eq}}k^{\text{A}}_2/[\text{H}_2]$ ($k_{\text{obs}} = 3.3 \times 10^{-3}\text{ s}^{-1}\text{ M}^{-2}$ at $51.2\text{ }^\circ\text{C}$), and as expected the reaction rate is inhibited by H_2 . Although this kinetic behavior describes only monomer consumption, we assume that further steps in the polymerization (involving dehydrocoupling of polysilanes) proceed in an analogous fashion.

The cation-like hafnium hydride **3** catalyzes a more complex reaction of PhSiH_3 , in that both dehydrocoupling and redistribution products are observed (eq 2; benzene- d_6 , 5 mol % **3**). Analysis of the reaction products



by NMR spectroscopy revealed that ca. 75% of the starting PhSiH_3 reacted via the redistribution pathway and that SiH_4 is incorporated into the polymer chain, yielding cross-linked oligomers. A $^{29}\text{Si}\{^1\text{H}\}$ DEPT 90° NMR spectrum of the polymer contained resonances for linear poly(phenylsilane) segments,¹⁴ and a group of resonances in the range $\delta -95$ to -120 was ascribed to

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HSi(Si)₃ branching sites. Though the molecular weights of polysilanes produced by the neutral and cationic hydride catalysts are similar, the polysilane backbone structure produced by **3** differs significantly from that derived from **4**, in that cross-linking is not observed with the neutral catalyst (see Supporting Information). Thus, these reaction products reveal an important limitation in the effectiveness of **3** in producing high-molecular-weight polysilanes, in that significant side reactions compete with polymerization.¹⁵ In addition, the observation of Si–C bond cleavage under such mild conditions implicates the presence of highly active catalytic species, since Si–C bonds are generally unreactive in σ -bond metathesis transformations.

During the conversion of eq 2, compound **3** remained unchanged and no identifiable intermediates (e.g., Hf–Ph or Hf–SiH₂Ph species) were observed by ¹H NMR spectroscopy. Despite the complexity of this reaction, its kinetic behavior, in terms of loss of PhSiH₃, is surprisingly well-behaved and analogous to that observed for the dehydrocoupling of PhSiH₃ catalyzed by **4**. Thus, a linear second-order plot of 1/[PhSiH₃] vs time and first-order dependence on catalyst concentration yields a rate law (rate = $K_{\text{obs}}[\mathbf{3}][\text{PhSiH}_3]^2$, $K_{\text{obs}} = 4.5 \times 10^{-2} \text{ s}^{-1} \text{ M}^{-2}$) which suggests operation of only transition-metal-catalyzed coupling reactions. A mechanism that is consistent with the kinetic data, the observed products, and established trends for σ -bond metathesis features two concurrent reaction pathways that employ **3** as a common catalyst (Scheme 1). This mechanism would give rise to second-order dependence on substrate concentration, with a rate law of the form

$$\text{rate} = \left(\frac{K_{\text{eq}}^{\text{A}} k_2^{\text{A}}}{[\text{H}_2]} + \frac{K_{\text{eq}}^{\text{B}} k_2^{\text{B}}}{[\text{SiH}_4]} \right) [\mathbf{3}][\text{PhSiH}_3]^2 \quad (3)$$

From this expression, it can be seen that K_{obs} is a combination of terms corresponding to the two reaction pathways, the first of which results from dehydrocoupling (vide supra). The redistribution pathway is manifested in a second term ($K_{\text{eq}}^{\text{B}} k_2^{\text{B}}/[\text{SiH}_4]$), which arises from an equilibrium involving cleavage of the Si–C bond

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of PhSiH₃ with formation of SiH₄ and a cationic hafnium phenyl complex. Evidence in support of the phenyl-transfer steps in the redistribution cycle was observed in the reaction of CpCp*HfPh(μ -Me)B(C₆F₅)₃ (**5**) with PhSiH₃ (in benzene-*d*₆), to give Ph₂SiH₂. Given the mechanism of Scheme 1, it should be possible to influence the extent of dehydrocoupling vs redistribution by controlling the H₂ and SiH₄ pressures (eq 3). Such an effect was observed in the reaction of **3** with 1 equiv of PhSiH₃ under 1 atm of H₂. As expected, added H₂ inhibits the dehydrocoupling pathway to favor redistribution by a factor of 4:1. In summary, we strongly favor the mechanistic proposal of Scheme 1, and other possibilities (e.g., involving radicals or purely Lewis acidic species) seem less likely.¹⁶ Additional experiments are underway to investigate this issue.

By comparison with well-studied neutral dehydropolymerization catalysts, the results reported here indicate that cationic group 4 metallocenes react with silanes via four-center, four-electron transition states. In addition, the cationic complexes exhibit increased reactivities in σ -bond metathesis. This enhanced activity is seen in increased rates of reaction and in the activation of Si–C bonds, which appear to be generally less reactive than Si–H bonds in σ -bond metathesis.¹⁷ Thus, the design of more reactive catalysts can be based on formation of cationic metal complexes; however, as is often the case, issues of selectivity then come into play.

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Supporting Information Available: Text and figures giving procedures for the synthesis and characterization of **2**, **3**, and **5**, experimental details for the kinetic experiments, kinetics data for the dehydropolymerization reactions, and ²⁹Si NMR spectra for poly(phenylsilanes). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(16) For the reaction mixture involving CpCp*HfH(μ -H)B(C₆F₅)₃ and PhSiH₃, radicals were not observed by EPR spectroscopy, after 1 h and 1 week. To test for the activity of a Lewis acidic catalyst (without a reactive σ -bond) in this system, PhSiH₃ was added to CpCp*Hf(OTf)(μ -Me)B(C₆F₅)₃, generated in solution by addition of B(C₆F₅)₃ to CpCp*Hf(OTf)Me. After 5 days at room temperature, no reaction of the silane had occurred.

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