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σ-Bond Metathesis Reactions for d^0 Metal–Silicon Bonds That Produce Zirconocene and Hafnocene Hydrosilyl Complexes

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Abstract: Reactions of zirconocene and hafnocene silyl derivatives CpCp′M(SiR$_3$)Cl (Cp = η^5-C$_5$H$_5$; Cp′ = Cp or Cp*, Cp* = η^5-C$_5$Me$_5$; M = Zr or Hf; R = Me or SiMe$_3$) with hydrosilanes have been investigated. The observed products depend on the nature of the starting materials, since in some cases the initial σ-bond metathesis products react further via dehydrocoupling processes. For example, Cp$_2$Zr(SiMe$_3$)Cl reacts with PhSiH$_3$ to give the direct products Me$_3$SiH and Cp$_2$Zr(SiH$_2$Ph)Cl, which then combines rapidly with PhSiH$_3$ to produce [Cp$_2$ZrHCl]$_n$, PhH$_2$Si–SiH$_2$Ph, and PhH$_2$Si–SiHPh–SiH$_2$Ph. Thus, hydrosilyl complexes obtained from such reactions can be contaminated by significant quantities of the corresponding hydride. The σ-bond metathesis reactions of CpCp*Hf[Si(SiMe$_3$)$_3$]Cl (**2**) with hydrosilanes RR′SiH$_2$ cleanly give the isolable metal silyl derivatives CpCp*Hf(SiHRR′)Cl (SiHRR′ = SiH$_2$Ph (**8**), SiH$_2$(*p*-Tol) (**9**), SiH$_2$(*p*-MeOC$_6$H$_4$) (**10**), SiH$_2$(*p*-FC$_6$H$_4$) (**11**), SiH$_2$Mes (**12**, Mes = 2,4,6-Me$_3$C$_6$H$_2$), SiH$_2$CH$_2$Ph (**13**), SiH$_2$Cy (**14**), SiHPh$_2$ (**15**), SiHMePh (**16**, as a 7:5 mixture of diastereomers), and SiHPhSiH$_2$Ph (**17**, as a 1:1 mixture of diastereomers)). In general, primary or secondary silanes will undergo such reactions, provided that a less sterically hindered silyl ligand is introduced at hafnium. Tertiary silanes such as Me$_3$SiH and Et$_3$SiH do not react under comparable conditions. Reactions of **2** with bis(silyl) compounds have provided the bimetallic complex 1,4-CpCp*(Cl)HfSiH$_2$C$_6$H$_4$SiH$_2$Hf(Cl)CpCp* (**19**) and the thiophene derivative 2,5-CpCp*(Cl)HfSiH$_2$(C$_4$H$_2$S)SiH$_2$Hf(Cl)CpCp* (**20**). The thermal (dark) reaction of **2** with PhSiH$_3$ obeys a second-order rate law, rate = k[**2**][PhSiH$_3$], with $\Delta H^\ddagger$ = 16.4 (7) kcal mol^{-1}, $\Delta S^\ddagger$ = −27 (2) eu, and k_H/k_D (70 °C) = 2.5 (1). These parameters suggest that the above σ-bond metathesis reactions involve four-center transition states similar to those that have been proposed for "hydrocarbon activation" reactions of d^0 metal complexes. Visible light accelerates the reactions of **2** with hydrosilanes, via excitation of a low-intensity transition at 405 nm (ϵ = 445 dm^3 mol^{-1} cm^{-1}), which appears to have considerable silyl-to-metal charge-transfer character. The quantum yield for the reaction of **2** with 1 or 20 equiv of PhSiH$_3$ is 1.0 ± 0.1. Use of radical traps failed to provide evidence for intermediate radicals in this photochemistry. Possible mechanisms for the observed photochemical conversions are discussed. Reactions of **2** with alkoxyhydrosilanes HSi(OMe)$_2$R′ provide routes to the new complexes CpCp*Hf(SiH$_2$Me)Cl (**23**, R′ = Me) and CpCp*Hf(SiH$_3$)Cl (**24**, R′ = OMe). These reactions appear to proceed via initial, metal-catalyzed redistribution of the alkoxyhydrosilanes (e.g., HSiMe(OMe)$_2$ is redistributed to MeSi(OMe)$_3$ and MeSiH$_3$), followed by trapping of the new hydrosilane by **2**. The Hf–Si distance observed for **2** (2.881 (4) and 2.888 (4) Å for the two independent molecules) is much longer than that observed for **8** (2.729 (3) Å), apparently because of greater ligand–ligand repulsion in **2**.

Many of the recent advances in transition-metal silicon chemistry have resulted from investigations with the early transition metals.[1] These studies have led to discovery of new classes of transition-metal complexes,[2] new methods for the activation of small molecules via migratory insertion into a M–Si bond,[3] new hydrosilation catalysts,[4] and dehydrocoupling reactions for hydrosilanes, which can produce oligomeric or polymeric polysilanes.[5] Historically, the chemistry of d^0 metal–silicon bonds has developed rather slowly compared to that of other types of transition metal–silicon bonds, primarily because of difficulties encountered in the synthesis of d^0 metal silyl complexes. Early-transition-metal silyl complexes have been obtained primarily via reaction of a silyl anion source (such as Al(SiMe$_3$)$_3$·OEt$_2$,[6] (THF)$_3$LiSiPh$_3$,[7] or (THF)$_3$LiSi(SiMe$_3$)$_3$[3c,g,i,8]) with a metal halide complex. This method is therefore severely limited, since relatively few silyl anion reagents are available. For example, hydrosilyl derivatives (with α-hydrogens, L$_n$M–SiHRR′) are not readily accessible via this route. One exception to this generalization is the synthesis of zirconocene derivatives of SiHMes$_2$ (Mes = mesityl), which employs the isolable reagent (THF)$_2$LiSiHMes$_2$.[9] Hydrosilyl complexes of the early transition metals are of interest with respect to their proposed involvement in metal-catalyzed dehydropolymerizations.[5]

Recently, a number of groups have reported routes to early metal silyl complexes based on oxidative addition of an Si–H bond to a low-valent metal complex.[4g,10] In addition, Harrod and

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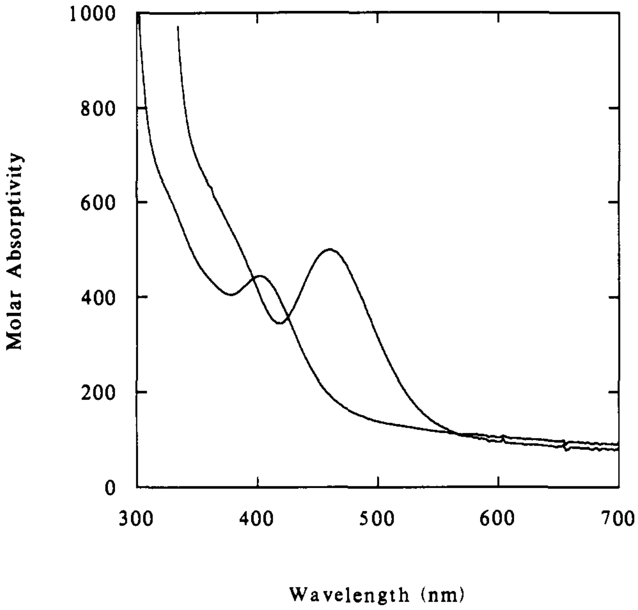


Figure 1. Comparison of the visible electronic spectra for CpCp*Zr-[Si(SiMe$_3$)$_3$]Cl (**1**, λ = 460 nm) and CpCp*Hf[Si(SiMe$_3$)$_3$]Cl (**2**, λ = 405 nm).

co-workers have prepared d^1 titanium(III) silyl complexes of the type Cp$_2$Ti(SiHRR′)(L), via reaction of a silane RR′SiH$_2$ with Cp$_2$TiMe$_2$ in the presence of a donor ligand.[11] Here we report the synthesis and characterization of d^0 hydrosilyl complexes via "σ-bond metathesis"[12] reactions of known silyl complexes with hydrosilanes. In particular, these reactions have been used to obtain a family of stable hafnium hydrosilyl complexes of the type CpCp*Hf(SiHRR′)Cl (Cp* = η^5-C$_5$Me$_5$). We have also observed that alkoxysilanes may serve as reagents for the synthesis of hydrosilyl derivatives via "redistribution chemistry", as in the formation of CpCp*Hf(SiH$_3$)Cl from reaction of CpCp*Hf[Si(SiMe$_3$)$_3$]Cl with excess HSi(OMe)$_3$. Some of this work has been communicated.[13]

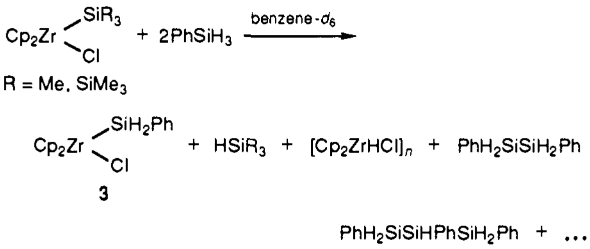
Results

Electronic Properties of Zirconium and Hafnium Silyl Complexes. In general, zirconocene silyl derivatives are orange to dark red in color. The analogous hafnium compounds are yellow. These colors seem to be associated with the silyl ligands since, in general, related alkyl derivatives are colorless. To examine the source of these colors in greater detail, electronic spectra for series of CpCp*M[Si(SiMe$_3$)$_3$]X (M = Zr, Hf) complexes were recorded. In addition to the envelope of UV absorptions usually associated with d^0 metallocene complexes, CpCp*M[Si(SiMe$_3$)$_3$]Cl (**1**, M = Zr,[3g] and **2**, M = Hf) exhibit low-intensity absorptions in pentane at 461 (**1**, ϵ = 500 dm^3 mol^{-1} cm^{-1}) and 405 nm (**2**, ϵ = 445 dm^3 mol^{-1} cm^{-1}) (Figure 1). Upon substitution of the chloro ligands for methyl groups, these transitions shift to higher energy: 435 (ϵ = 250 dm^3 mol^{-1} cm^{-1}) and 398 nm (ϵ = 250 dm^3 mol^{-1} cm^{-1}), respectively, for CpCp*M[Si(SiMe$_3$)$_3$]Me (M = Zr and Hf). Given the observed changes in spectra with variations in the metal and the ligand set and the fact that comparable visible absorptions are not observed in the spectra of related alkyl derivatives (e.g., Cp$_2$ZrMeCl), these transitions may be characterized as silyl ligand-to-metal charge-transfer transitions.

As described previously[3d] and below, these silyl-to-metal charge-transfer transitions appear to be associated with photochemical reactions of the M–Si bonds. Exposure of a toluene-d_8 solution of **1** to direct light from a high-intensity desk lamp results in clean conversion over 2 h to HSi(SiMe$_3$)$_3$ and (η^5:η^5-C$_{10}$H$_8$)[Cp*Zr(μ-Cl)]$_2$ (by ^{1}H NMR spectroscopy).[14] For comparison, the thermolysis of **1** (toluene-d_8, 95 °C, 2 h) produces HSi(SiMe$_3$)$_3$ (quantitatively) and (η^5:η^5-C$_{10}$H$_8$)[Cp*Zr(μ-Cl)]$_2$ in ca. 50% yield, by ^{1}H NMR spectroscopy. Both reactions therefore involve abstraction of a cyclopentadienyl hydrogen atom by the silyl ligand, but further details of the mechanism remain obscure. A concerted process, as has been proposed for Cp$_3$ThR (R = H, ^{i}Pr, ^{n}Bu) compounds,[15] or a radical mechanism can be envisioned. However, a radical mechanism seems less likely given the strong preference for abstraction of hydrogen from a Cp ring over abstraction of hydrogen from the Cp* ligand or the toluene solvent. Toluene solutions of **1** in the dark do not produce an ESR signal. However, irradiation of the sample with light from a high-intensity desk lamp gives rise within minutes to a weak signal at g_{av} = 1.980. After removal of the light source, the signal decays and completely disappears within a few minutes. This signal may be attributed to a Zr(III) species,[16] even though hyperfine splitting by ^{91}Zr (11.3% natural abundance, $I = {}^5/_2$) was not observed, probably because of the low signal-to-noise ratio. Therefore it appears that photochemical Zr–Si bond homolysis may occur to some extent, but given the high sensitivity of the ESR experiment, it is not clear how important this process is.

Preparation of d^0 Hydrosilyl Complexes via σ-Bond Metathesis. The ultimate products that are observed from reaction of zirconocene or hafnocene silyl derivatives with hydrosilanes depend critically on the nature of the reactants, which can allow further reactions of the initial products via dehydrocoupling processes. Also, if the reacting silicon centers are too sterically encumbered, no reaction occurs. Thus in general, zirconocene and hafnocene silyl derivatives do not react with bulky silanes such as Me$_3$SiH, Et$_3$SiH, ^{t}Bu$_2$SiH$_2$, or CyMeSiH$_2$.

In reactions of CpCp′M(SiR$_3$)Cl (Cp′ = Cp or Cp*; M = Zr or Hf; R = Me or SiMe$_3$) derivatives with primary silanes, a commonly observed side product is the corresponding metallocene hydride CpCp′MHCl. For example, Cp$_2$Zr(SiMe$_3$)Cl[6b] and Cp$_2$Zr[Si(SiMe$_3$)$_3$]Cl[3i] react with phenylsilane according to eq 1 to produce the direct metathesis products **3** and HSiR$_3$, along with side products from further silane dehydrocoupling processes ([Cp$_2$ZrHCl]$_n$, PhH$_2$SiSiH$_2$Ph, and PhH$_2$SiSiHPhSiH$_2$Ph). At



$$\mathrm{Cp_2Zr(SiR_3)(Cl)} + 2\mathrm{PhSiH_3} \xrightarrow{\text{benzene-}d_6} \underset{\mathbf{3}}{\mathrm{Cp_2Zr(SiH_2Ph)(Cl)}} + \mathrm{HSiR_3} + [\mathrm{Cp_2ZrHCl}]_n + \mathrm{PhH_2SiSiH_2Ph} + \mathrm{PhH_2SiSiHPhSiH_2Ph} + \ldots \quad (1)$$

R = Me, SiMe$_3$

complete conversion of starting material, these reaction mixtures contain ca. 80% **3** and ca. 10% [Cp$_2$ZrHCl]$_n$ (by NMR spectroscopy, based on the Zr starting material). The primary silyl derivative **3** was identified by comparing its NMR spectrum with spectra for related complexes that were isolated and thoroughly characterized. Reaction of Cp$_2$Hf[Si(SiMe$_3$)$_3$]Cl[3i] with 3 equiv of phenylsilane proceeds similarly, and at 50% conversion (2-h reaction time), resonances assigned to HSi(SiMe$_3$)$_3$, Cp$_2$Hf-(SiH$_2$Ph)Cl (**4**, ca. 5%), [Cp$_2$HfHCl]$_n$ (ca. 10%), PhH$_2$SiSiH$_2$Ph, PhH$_2$SiSiHPhSiH$_2$Ph, and PhH$_2$Si(SiHPh)$_2$SiH$_2$Ph were identified (the latter three silanes were present in a 2:5:1 ratio). If bulkier silanes are used in the reaction with Cp$_2$Hf[Si(SiMe$_3$)$_3$]Cl, higher yields of the silylhafnium compound can be obtained, but the products are still often contaminated by [Cp$_2$HfHCl]$_n$. For

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(14) Identification of (η^5:η^5-C$_{10}$H$_8$)[Cp*Zr(μ-Cl)]$_2$ is based on comparison of its distinctive ^{1}H NMR spectrum [benzene-d_6, δ 1.88 (s, 30 H, Cp*), 4.07 (pseudotriplet, J_{obsd} = 2.7 Hz, 4 H, C$_{10}$H$_8$), 4.79 (pseudotriplet, J_{obsd} = 2.7 Hz, 4 H, C$_{10}$H$_8$)] with the spectrum for (η^5:η^5-C$_{10}$H$_8$)[CpZr(μ-Cl)]$_2$ (Gambarotta, S.; Chiang, M. Y. *Organometallics* **1987**, *6*, 897).

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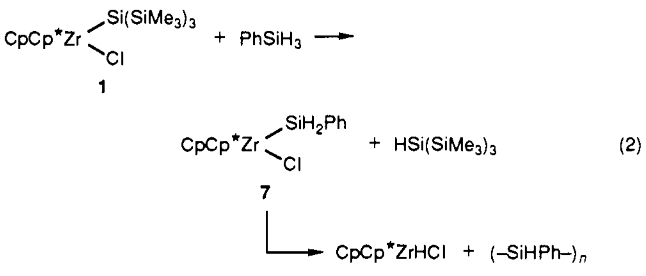
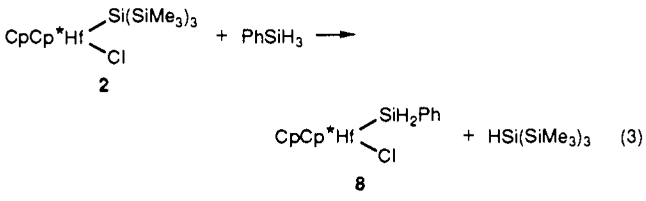
example, the reaction of $Cp_2Hf[Si(SiMe_3)_3]Cl$ with $CySiH_3$ (Cy = cyclohexyl) allowed isolation of a yellow crystalline material that proved to be a 1:1 mixture of $Cp_2Hf(SiH_2Cy)Cl$ (**5**) and $[Cp_2HfHCl]_n$, and similarly $Cp_2Hf(SiHPh_2)Cl$ (**6**) was obtained with ca. 10% of the hydride impurity.

In the dark, benzene-d_6 solutions of **1** react with $PhSiH_3$ over 6 h to give four products identified by ^1H NMR spectroscopy (eq 2). Early in the reaction, the major products are zirconium silyl **7** and $HSi(SiMe_3)_3$. As the reaction proceeds to completion, **7** decomposes to the hydride CpCp*ZrHCl[17] and a mixture of polysilanes. Broad resonances for the polysilanes were assigned on the basis of comparisons to spectra for isolated $(-SiHPh-)_n$ polymer obtained by other methods.[2a,4b,18] In the presence of fluorescent room light, the reaction between **1** and $PhSiH_3$ is complete within 5 min and gives **7** and $HSi(SiMe_3)_3$ cleanly. Compound **7** then slowly decomposes to CpCp*ZrHCl and $(-SiHPh-)_n$.



(2)

Because σ-bond metathesis reactions of $CpCp^*Hf[Si(SiMe_3)_3]Cl$ (**2**) cleanly give more stable metal silyl derivatives, they have been examined in more detail. As expected, the thermal (dark) reaction of **2** with 1 equiv of $PhSiH_3$ is much slower than the corresponding reaction observed for **1** (complete reaction after 1–2 days at room temperature). With illumination by fluorescent room lighting, this reaction is complete within 1 h in pentane or benzene solution, giving quantitative conversion to the σ-bond metathesis products $CpCp^*Hf(SiH_2Ph)Cl$ (**8**) and $HSi(SiMe_3)_3$ (eq 3). The reaction is somewhat slower in diethyl ether or tetrahydrofuran. In contrast to **7**, yellow crystalline **8** is stable indefinitely as a solid at room temperature under an inert atmosphere. The ^1H and ^{29}Si NMR spectra for this compound are shown in Figures 2 and 3, respectively. NMR chemical shifts for the diastereotopic hydrogens on the silicon (δ 4.68, 5.14; $^2J_{HH}$ = 1.2 Hz) and the low $^1J_{SiH}$ coupling constant (155 Hz) are consistent with bonding of the silyl group to a chiral, d^0 metal center.[9]



(3)

Other new hafnium silyl derivatives have been obtained by reaction of **2** with 1 equiv of a primary or secondary silane ($RSiH_3$, R = *p*-Tol, p-$MeOC_6H_4$, p-FC_6H_4, 2,4,6-$Me_3C_6H_2$ (Mes), CH_2Ph, and Cy; Ph_2SiH_2; $PhMeSiH_2$; PhH_2SiSiH_2Ph), under the influence of ambient room light. These reactions are quantitative by ^1H NMR spectroscopy, and isolated yields range from 65 to 75%. For CpCp*Hf(SiHPhMe)Cl (**16**), a 7:5 mixture of diastereomers was observed, while $CpCp^*Hf(SiHPhSiH_2Ph)Cl$ (**17**) was produced as a 1:1 mixture of diastereomers. The rates of these photochemical reactions are quite sensitive to steric effects. Secondary silanes and sterically hindered primary silanes such as $MesSiH_3$ react sluggishly (over 1–2 days for 1:1 reactions) in the presence of room light. Tertiary silanes such as Me_3SiH and Et_3SiH do not react under analogous conditions. In general, we have found that hafnium silyls CpCp*Hf(SiRR′R″)Cl undergo clean σ-bond metathesis reactions with primary or secondary silanes that introduce a smaller silyl ligand. The reaction of **2** with $HSiCl_3$ appears to take a completely different course, quantitatively producing $CpCp^*HfCl_2$ but only a 4% yield of $HSi(SiMe_3)_3$, along with unidentified silicon products.

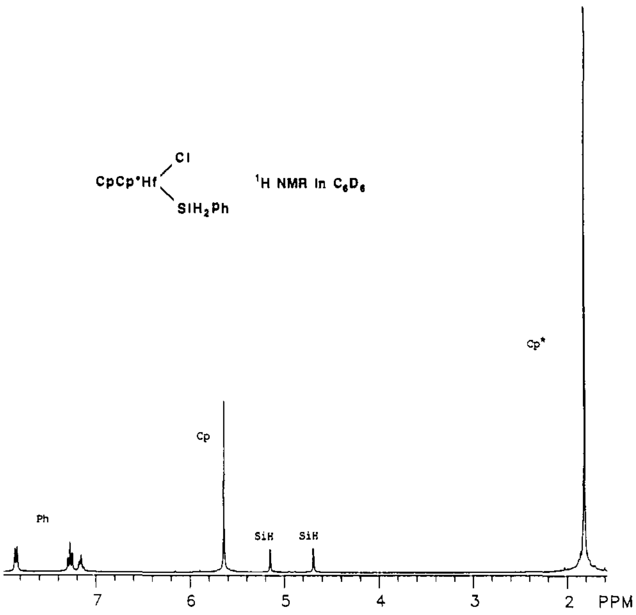


Figure 2. ^1H NMR spectrum for $CpCp^*Hf(SiH_2Ph)Cl$ (**8**). Splitting of the diastereotopic SiH_2 hydrogens into an AB pattern is apparent in high-resolution spectra (J_{HH} = 1.2 Hz).

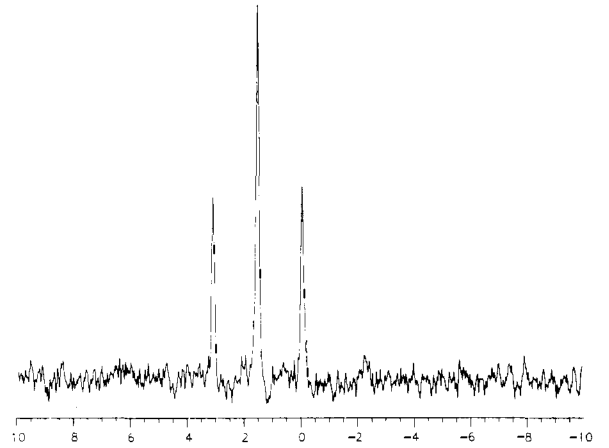


Figure 3. ^{29}Si NMR spectrum for $CpCp^*Hf(SiH_2Ph)Cl$ (**8**) at 99.3 MHz.

Reaction of **2** with bis(silyl) derivatives provides a convenient means for preparing bimetallic silyl complexes. Thus, **2** reacts with 0.5 equiv of p-$H_3SiC_6H_4SiH_3$ to afford the bimetallic complex **19** (eq 4). The 1:1 reaction of these species allowed observation (by NMR spectroscopy) of the intermediate monohafnium complex $CpCp^*Hf(SiH_2C_6H_4SiH_3)Cl$ (**18**). Complexes analogous

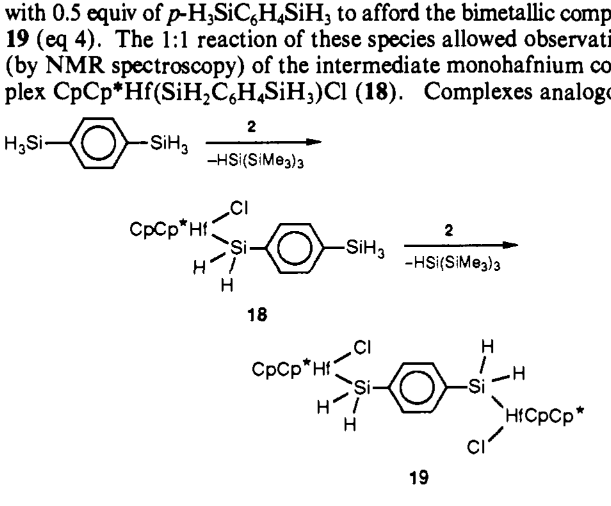


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Table I. ^{29}Si NMR Data for Zirconium and Hafnium Silyl Complexes

compd	^{29}Si NMR, δ^a	$^1J_{\text{SiH}}$, Hz
$\text{CpCp*Zr[Si(SiMe}_3)_3]\text{Cl}^b$ (**1**)		
$\mathit{Si}(\text{SiMe}_3)_3$	−87.30	
$\text{Si}(\mathit{Si}\text{Me}_3)_3$	−6.03	
$\text{CpCp*Hf[Si(SiMe}_3)_3]\text{Cl}$ (**2**)		
$\mathit{Si}(\text{SiMe}_3)_3$	−77.87	
$\text{Si}(\mathit{Si}\text{Me}_3)_3$	−4.85	
$\text{CpCp*Zr(SiH}_2\text{Ph)Cl}$ (**7**)	−14.33 (t)	144
$\text{CpCp*Hf(SiH}_2\text{Ph)Cl}$ (**8**)	1.49 (t)	155
$\text{CpCp*Hf[SiH}_2(p\text{-Tol)]Cl}$ (**9**)	1.46 (t)	157
$\text{CpCp*Hf[SiH}_2(p\text{-Tol)]Br}$ (**21**)	7.74 (t)	153
$\text{CpCp*Hf[SiH}_2(p\text{-MeOC}_6\text{H}_4)]\text{Cl}$ (**10**)	1.56 (t)	159
$\text{CpCp*Hf[SiH}_2(p\text{-FC}_6\text{H}_4)]\text{Cl}$ (**11**)	1.17 (t)	160
$\text{CpCp*Hf(SiH}_2\text{Mes)Cl}$ (**12**)	1.50 (t)	157
$\text{CpCp*Hf(SiH}_2\text{CH}_2\text{Ph)Cl}$ (**13**)	9.69 (t)	153
$\text{CpCp*Hf(SiH}_2\text{Cy)Cl}$ (**14**)	14.83 (t)	145
$\text{Cp}_2\text{Hf(SiH}_2\text{Cy)Cl}$	11.07 (t)	149
$\text{CpCp*Hf(SiHPh}_2\text{)Cl}$ (**15**)	32.25 (d)	158
$\text{Cp}_2\text{Hf(SiHPh}_2\text{)Cl}$	31.88 (d)	148
$\text{CpCp*Zr(SiPh}_3\text{)Cl}^c$	42.42	
$\text{CpCp*Hf(SiPh}_3\text{)Cl}^c$	39.96	
$\text{CpCp*Hf(SiHPhMe)Cl}$ (**16**) (diastereomers)	21.75 (d)	153
	25.10 (d)	153
$\text{CpCp*Hf(SiHPhSiH}_2\text{Ph)Cl}$ (**17**) (diastereomers)		
$\mathit{Si}\text{HPhSiH}_2\text{Ph}$	−9.05 (d)	152
$\mathit{Si}\text{HPhSiH}_2\text{Ph}$	−9.86 (d)	152
$\text{SiHPh}\mathit{Si}\text{H}_2\text{Ph}$	−43.91 (t)	183
$\text{SiHPh}\mathit{Si}\text{H}_2\text{Ph}$	−50.43 (t)	183
$\text{CpCp*Hf(SiH}_2\text{C}_6\text{H}_4\text{SiH}_3\text{)Cl}$ (**18**)		
$\mathit{Si}\text{H}_2\text{C}_6\text{H}_4\text{SiH}_3$	1.16 (t)	162
$\text{SiH}_2\text{C}_6\text{H}_4\mathit{Si}\text{H}_3$	−63.10 (q)	199
$2,5\text{-[CpCp*Hf(Cl)SiH}_2]_2\text{C}_4\text{H}_2\text{S}$ (**20**)	−14.09 (t)	158
$\text{CpCp*Hf(SiH}_2\text{CH}_3\text{)Cl}$ (**23**)	−7.36 (t)	149
$\text{CpCp*Hf(SiH}_3\text{)Cl}$ (**24**)	−46.52 (q)	156

^{a} Benzene-d_6 solvent. ^{b} Reference 3g. ^{c} Reference 7b.

to **18** and **19** are probably intermediates in the $[\text{CpCp*ZrH}_2]_2$-catalyzed dehydropolymerization of p-$\text{H}_3\text{SiC}_6\text{H}_4\text{SiH}_3$.[19] The bimetallic thiophene derivative $2,5\text{-[CpCp*Hf(Cl)SiH}_2]_2\text{C}_4\text{H}_2\text{S}$ (**20**) was obtained similarly. In contrast, a bimetallic complex could not be obtained by reaction of $\text{CpCp*Hf(SiHPhSiH}_2\text{Ph)Cl}$ (**17**) with **2**. The Hf–Cl bonds of **19** and **20** are trans to one another such that the molecules possess a center of symmetry, resulting in only one set of diastereotopic SiH_2 protons, as observed by ^{1}H NMR spectroscopy.

The new hafnium hydrosilyl complexes are yellow in color and possess low-energy electronic absorptions in the range 380–390 nm (ϵ = 750–1000 dm^3 mol^{-1} cm^{-1}). The ^{29}Si NMR chemical shifts for d^0 metal silyl complexes cover a wide range, as seen by the data compiled in Table I. It is readily apparent that substituents bound directly to silicon play the dominant role in defining these ^{29}Si chemical shifts. Note, for example, that replacement of hydrogen atoms with phenyl groups results in pronounced downfield shifts (see entries for **23**, **8**, **15**, and $\text{CpCp*Hf(SiPh}_3\text{)Cl}$ in Table I). Generally, d^0 hydrosilyl complexes are characterized by low $^1J_{\text{SiH}}$ coupling constants (140–160 Hz), which reflect the presence of an electropositive substituent at silicon. The ν(SiH) stretching frequencies for d^0 metal hydrosilyl derivatives are shifted by ca. 100 cm^{-1} to lower energy relative to the corresponding hydrosilanes. For example, **8** exhibits a ν(SiH) stretching frequency of 2050 cm^{-1}, compared to ν(SiH) = 2140 cm^{-1} for PhSiH_3.

The quantitative thermal reaction of eq 3 was subjected to a kinetic study. Reaction rates were monitored by ^{1}H NMR spectroscopy in benzene-d_6 under pseudo-first-order conditions with excess silane. Rates were determined by monitoring the disappearance of **2** and the appearance of $\text{HSi(SiMe}_3)_3$. Under these conditions of excess silane, the only observed hafnium product is CpCp*HfHCl, formed via the dehydrocoupling reaction of **8** with PhSiH_3. The kinetic data (plots of k_{obsd} vs $[\text{PhSiH}_3]$, Figure 4) are consistent with a second order rate law:

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

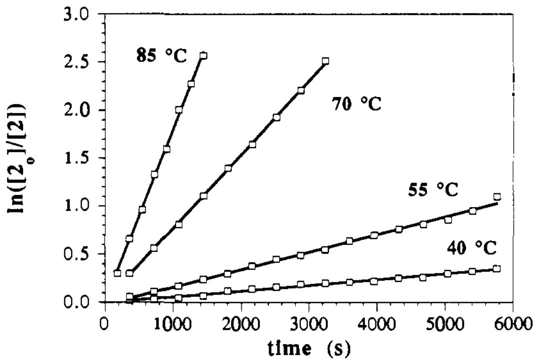

Figure 4. Kinetic plots for the pseudo-first-order reaction of **2** with a 10-fold excess of phenylsilane. Rate constants (M^{-1} s^{-1}): k (40 °C) = 4.3 (3) × 10^{-5}; k (55 °C) = 1.2 (3) × 10^{-4}; k (70 °C) = 5.2 (3) × 10^{-4}; k (85 °C) = 1.2 (3) × 10^{-3}.

An Eyring plot of rate data for the temperature range 40–85 °C provided the activation parameters $\Delta H^\ddagger$ = 16.4 (7) kcal mol^{-1} and $\Delta S^\ddagger$ = −27 (2) eu. Comparison of the reaction rate at 70 °C with that of the reaction of **2** with PhSiD_3 at 70 °C yielded a kinetic deuterium isotope effect of $k_{\text{H}}/k_{\text{D}}$ = 2.5 (1).

As mentioned earlier, fluorescent room light has a dramatic acceleration effect on the reaction of eq 3. Via use of cut-off filters, we have determined that the observed photochemistry results from excitation of the low-intensity transition for **2** at 405 nm. With a 365 (±5) nm band-pass filter, the quantum yield for the reaction of **2** with 1 equiv of PhSiH_3 or 20 equiv of PhSiH_3 in benzene-d_6 is the same, 1.0 ± 0.1.

Currently we have little chemical evidence for photochemically induced homolysis of the metal–silicon bond of **2**. For example, no radical coupling products (e.g., $\text{PhH}_2\text{SiSiH}_2\text{Ph}$ or $\text{PhH}_2\text{SiSi(SiMe}_3)_3$) are observed, and photolysis by visible light does not initiate polymerization of styrene or methyl methacrylate. The reaction is uninhibited in toluene in the presence of added silyl-radical traps such as cyclohexene or 1,4-cyclohexadiene.[20] Also, the photochemical reaction of **2** with ^{t}BuBr, a good silyl radical trapping reagent,[21] is much slower than the corresponding reaction with PhSiH_3. After 24 h (76% conversion), $\text{BrSi(SiMe}_3)_3$ (25%), a mixture of CpCp*HfCl_2, CpCp*HfClBr, and CpCp*HfBr_2 (25%, 1:2:1 ratio), and ^{t}BuH (5%) were observed. (The mixture of hafnocene dihalide species is probably formed by disproportionation of CpCp*HfBrCl.[22]) In the presence of ambient room lighting, the reaction of **2** with PhSiD_3 quantitatively gives $\text{CpCp*Hf(SiD}_2\text{Ph)Cl}$ and $\text{DSi(SiMe}_3)_3$, with no deuterium scrambling (by ^{1}H and ^{2}H NMR). Similarly, the photochemical (room light) reaction of **2** with $\text{PhCH}_2\text{SiD}_3$ in benzene or benzene-d_6 quantitatively gives $\text{CpCp*Hf(SiD}_2\text{CH}_2\text{Ph)Cl}$ and $\text{DSi(SiMe}_3)_3$ (by ^{1}H and ^{2}H NMR), and the same products are produced (at the same rate) in the presence of HSiEt_3.

Reaction times for the photochemical reaction of **2** with silanes are strongly influenced by steric requirements of the incoming silane. Whereas variations in the concentration of small primary silanes do not influence reaction times, for bulkier silanes (e.g., MesSiH_3 and secondary silanes) the reaction rates exhibit a strong concentration dependence. For example, under the same lighting conditions, **2** reacts with 1 equiv of PhSiH_3 and 20 equiv of PhSiH_3 at the same rate (over ca. 1 h), whereas reactions of **2** with 1 equiv of Ph_2SiH_2 and 20 equiv of Ph_2SiH_2 require >48 h and 10 h, respectively. Also, in contrast to the dark reactions of **2** with PhSiH_3 and PhSiD_3, there is no difference in the rates of these reactions when both are exposed to the same lighting conditions. Additionally, small Lewis bases (e.g., pyridine and PMe_2Ph) but

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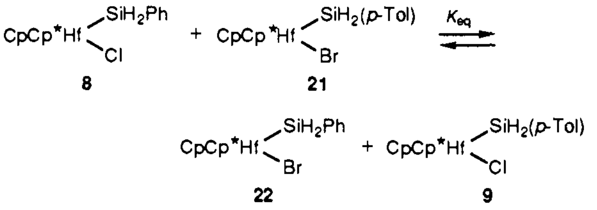
Table II. Equilibrium Constants for Silyl-Group Exchange Reactions

	equilibrium	K_{eq} (25 °C)
1	$CpCp^*(Cl)HfSiH_2Tol$ (**9**) + $PhSiH_3$ ⇌ $CpCp^*(Cl)HfSiH_2Ph$ (**8**) + $TolSiH_3$	1.0 (1)
2	$CpCp^*(Cl)HfSiH_2CH_2Ph$ (**13**) + $PhSiH_3$ ⇌ $CpCp^*(Cl)HfSiH_2Ph$ (**8**) + $PhCH_2SiH_3$	1.3 (1)
3	$CpCp^*(Cl)HfSiH_2Cy$ (**14**) + $MeSiH_3$ ⇌ $CpCp^*(Cl)HfSiH_2Me$ (**23**) + $CySiH_3$	1.8 (1)
4	$CpCp^*(Cl)HfSiH_2Cy$ (**14**) + Ph_2SiH_2 ⇌ $CpCp^*(Cl)HfSiHPh_2$ (**15**) + $CySiH_3$	0.5 (1)
5	$CpCp^*(Cl)HfSiH_2Mes$ (**12**) + Ph_2SiH_2 ⇌ $CpCp^*(Cl)HfSiHPh_2$ (**15**) + $MesSiH_3$	0.6 (1)
6	$CpCp^*(Cl)HfSiHMePh$ (**16**) + Ph_2SiH_2 ⇌ $CpCp^*(Cl)HfSiHPh_2$ (**15**) + $PhMeSiH_2$	1.7 (1)

not large ones (e.g., PCy_3) strongly inhibit the reactions. It therefore appears that these photochemical σ-bond metathesis reactions involve reactive, coordinatively unsaturated intermediates.

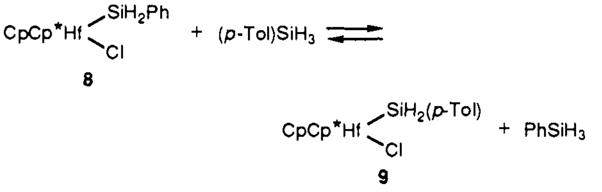
Whereas p-$FC_6H_4SiH_3$ reacts cleanly with **2** under fluorescent room lighting to produce $CpCp^*Hf[SiH_2(p\text{-}FC_6H_4)]Cl$ (**10**) in 1 h, analogous σ-bond metathesis reactions with p-$XC_6H_4SiH_3$ (X = Cl, Br) do not occur at all. Reaction of **2** with the bromide gives a 50% conversion after 24 h to $BrSi(SiMe_3)_3$ (25%), a mixture of $CpCp^*HfCl_2$, $CpCp^*HfClBr$, and $CpCp^*HfBr_2$ (25%, 1:2:1 ratio), and a mixture of $PhSiH_3$ and 4,4′-$(H_3Si)_2C_6H_4C_6H_4$ (50%, 10:3 ratio). The silane $HSi(SiMe_3)_3$ was not observed as a product. Similar product distributions are obtained in the dark, at much slower rates. Analogous results were observed for the reaction of **8** with p-$BrC_6H_4SiH_3$ and for the reaction of **2** with p-$ClC_6H_4SiH_3$. Therefore the aryl halides p-$XC_6H_4SiH_3$ (X = Cl, Br) somehow inhibit the σ-bond metathesis reaction usually observed for **2** and a primary silane and, instead, undergo reactions involving radical intermediates.

Halide Exchange in $CpCp^*Hf(SiH_2Ar)X$ Complexes. To gain further insight into possible reactivity patterns for the new silyl complexes, ligand exchange in the related compounds **8** and $CpCp^*Hf[SiH_2(p\text{-}Tol)]Br$ (**21**) was examined. Compound **21** was obtained via reaction of $CpCp^*Hf[Si(SiMe_3)_3]Br$ with (p-Tol)SiH_3. Within 5 h, an equilibrium is established in benzene-d_6 involving **8**, **21**, **9**, and the new silyl complex **22**, characterized by ^1H NMR spectroscopy (eq 5). An equilibrium constant of 1.0 ± 0.1 was determined for samples either kept in the dark or exposed to normal room lighting. Statistical halide-exchange equilibria were also observed upon reaction of **21** with **2**, **14**, and **15**. These reactions probably occur via halide-bridged intermediates.[22] No products resulting from silyl/halide exchange were observed.



$$\underset{\mathbf{8}}{CpCp^*Hf(SiH_2Ph)(Cl)} + \underset{\mathbf{21}}{CpCp^*Hf(SiH_2(p\text{-}Tol))(Br)} \xrightleftharpoons{K_{eq}} \underset{\mathbf{22}}{CpCp^*Hf(SiH_2Ph)(Br)} + \underset{\mathbf{9}}{CpCp^*Hf(SiH_2(p\text{-}Tol))(Cl)} \quad (5)$$

Silyl-Group Exchange between Hafnium Hydrosilyl Complexes and Hydrosilanes. Hydrosilyl $CpCp^*Hf(SiHRR')Cl$ complexes react intermolecularly with Si–H bonds, to the extent that steric constraints allow. Thus, silyl exchange between the $CpCp^*Hf(Cl)$ group and hydrogen occurs readily, if the smaller silyl group is transferred to hafnium, or if the exchanging silyl groups are of comparable size. In some cases the exchange is balanced such that two silyl complexes exist in equilibrium, as in the reaction shown in eq 6, which has an equilibrium constant of 1.0 ± 0.1 as determined by ^1H NMR spectroscopy. This equilibrium was established after ca. 5 h at room temperature, under ambient laboratory conditions. Other silyl-exchange equilibria are collected in Table II.



$$\underset{\mathbf{8}}{CpCp^*Hf(SiH_2Ph)(Cl)} + (p\text{-}Tol)SiH_3 \rightleftharpoons \underset{\mathbf{9}}{CpCp^*Hf(SiH_2(p\text{-}Tol))(Cl)} + PhSiH_3 \quad (6)$$

Reactions of d^0 M–Si Bonds with Alkoxysilanes. In attempts to introduce alkoxy functional groups at the silicon atom of a d^0 metal silyl complex, σ-bond metathesis reactions with alkoxyhydrosilanes $HSi(OR)_2R'$ were investigated. Harrod and coworkers have reported previously that Cp_2TiMe_2 is an excellent catalyst for the redistribution (disproportionation) of alkoxy- and siloxyhydrosilanes.[23] Thus, $Me_2HSiOSiHMe_2$ can be polymerized to $(\text{–}OSiMe_2\text{–})_n$ species with loss of dimethylsilane. We have found that $[CpCp^*ZrH_2]_2$, a very active catalyst for the dehydrocoupling of hydrosilanes,[19] is quite inferior to Cp_2TiMe_2 as a catalyst for the disproportionation of $HSiMe(OMe)_2$ to $MeSiH_3$ and $MeSi(OMe)_3$ (2500 turnovers/h for Cp_2TiMe_2; 0.4 turnovers/h for $[CpCp^*ZrH_2]_2$). During the latter reaction, the zirconium catalyst is quantitatively converted to $CpCp^*Zr(OMe)_2$, which is also a catalyst for the disproportionation, but only at temperatures ≥80 °C (eq 7). No redistribution of

$$3HSiMe(OMe)_2 \xrightarrow{[CpCp^*ZrH_2]_2 \text{ or } CpCp^*Zr(OMe)_2} MeSiH_3 + 2MeSi(OMe)_3 \quad (7)$$

$Me_2HSiOSiHMe_2$ was observed with $[CpCp^*ZrH_2]_2$ as catalyst. The latter zirconium catalyst is sensitive to the steric properties of the substrate, e.g., $HSiMe(OMe)_2$ is redistributed ca. 3 times faster than is $HSiMe(OEt)_2$. These redistribution reactions are catalyzed by a wide range of Zr and Hf complexes of the types Cp^*MCl_3 and Cp'_2MX_2 (M = Zr, Hf; Cp′ = Cp, Cp*; X = H, alkyl, silyl, alkoxide, halide). The observed influences on catalytic activity are as follows: X = H, alkyl, silyl > halide > alkoxide; M = Zr ≈ Hf. It therefore appears that these complexes act simply as Lewis acid catalysts for the redistribution reactions, in the same way that acidic clays and silica–alumina do.[24]

These redistributions may be combined with the σ-bond metathesis chemistry described above to prepare new d^0 hydrosilyl derivatives of hafnium (eq 8). In these reactions, the metal species apparently acts to redistribute an alkoxyhydrosilane to an alkoxysilane and a hydrosilane, which is then trapped as the metal silyl complex. Alkoxyhydrosilanes may therefore serve as more conveniently handled synthetic equivalents for low-boiling silanes. Due to the volatile nature of the hydrosilanes produced by redistribution, an excess of the starting alkoxysilane is generally employed. The methylsilyl derivative **23** was obtained as a pure, yellow crystalline solid, whereas **24** was contaminated by $CpCp^*Hf(OMe)Cl$ and $CpCp^*HfCl_2$. The $CpCp^*HfCl_2$ is probably produced via reactions with chlorosilanes, which are added to commercial $HSi(OMe)_3$ to inhibit disproportionation.

Descriptions of the Structures of 2 and 8. Given the high reactivity of the mixed-ring, d^0 metal silyl complexes $CpCp^*M[Si(SiMe_3)_3]Cl$ (**1** and **2**)[3d,g,i] and their usefulness as starting materials, it was of interest to determine the molecular structures of these key molecules. The structure of **8** was also of interest, given the role that this and related species appear to play in dehydropolymerization reactions.[5,13b] Initially, we were particularly intrigued by the possibility that the α hydrogens of **8** might be activated toward further reactions by, for example, agostic interactions with the metal center.[25] One structurally charac-

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[23] (a) Xin, S.; Aitken, C.; Harrod, J. F.; Mu, Y.; Samuel, E. *Can. J. Chem.* **1990**, *68*, 471. (b) Laine, R. M.; Rahn, J. A.; Youngdahl, K. A.; Babonneau, F.; Hoppe, M. L.; Zhang, Z.-F.; Harrod, J. F. *Chem. Mater.* **1990**, *2*, 464.

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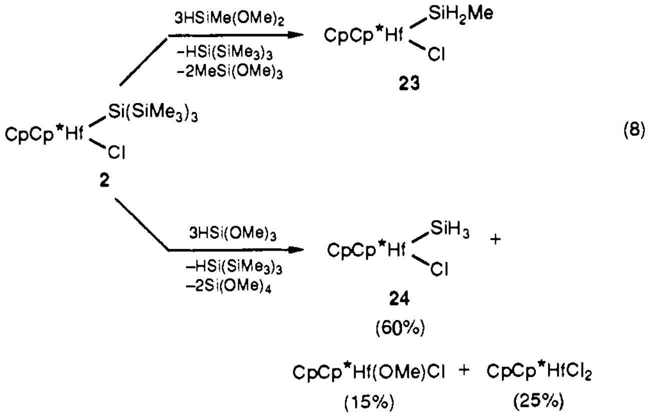

(8)

terized hafnium silyl complex, $Cp^*Cl_3HfSi(SiMe_3)_3$, is available for comparisons.[8a]

An ORTEP view of **2** is given in Figure 5, and relevant geometrical parameters are given in Table III. Two independent molecules/unit cell result in two Hf–Si distances of 2.881 (4) and 2.888 (4) Å. These distances are considerably greater than the one found in $Cp^*Cl_3HfSi(SiMe_3)_3$, 2.748 (4) Å, and exceed d^0 M–Si distances observed for zirconocene derivatives.[1] This probably reflects a high degree of steric crowding in **2**, which is also seen in distortions about the metal-bound silicon atom. The Si–Si–Si bond angles for **2** (average 101°) are compressed relative to those observed for $Cp^*Cl_3HfSi(SiMe_3)_3$ (average 105°). Also, the Hf–Si–Si angles in **2** (106.3 (2), 107.3 (2), 115.3 (2), 115.3 (2), 129.8 (2), and 127.3 (2)°) exhibit wide variations due to intramolecular ligand–ligand repulsions and are greater than those found in $Cp^*Cl_3HfSi(SiMe_3)_3$ (101.1 (2), 114.3 (1), and 124.1 (2)°).

The crystal structure of **8** (Figure 6, Table IV) reveals mononuclear complexes with terminal $Hf–SiH_2Ph$ ligands. The Hf–Si distance in **8**, 2.729 (3) Å, is considerably shorter than the corresponding distance for **2**, presumably because of less steric interaction between the silyl ligand and the bulky Cp* group. The hydrogen atoms bonded to silicon were located by a difference map and were refined. As is evident in Figure 6, these hydrogens adopt roughly normal tetrahedral positions about the silicon atom (∠HSiH = 102 (6)°). The Hf–Si–C angle of 113.5 (2)° is slightly more acute than the analogous angle in $Cp_2Ti(SiH_2Ph)PEt_3$, 114.4 (5)°.[11]

The difference in Hf–Si bond lengths in these two structures (0.16 Å) indicates that d^0 M–Si bond distances (and bond strengths) can be quite sensitive to steric factors. The long M–Si distance in **2** (and presumably also in **1**) is consistent with the observed high reactivity for these silyl complexes.[3d,g,i]

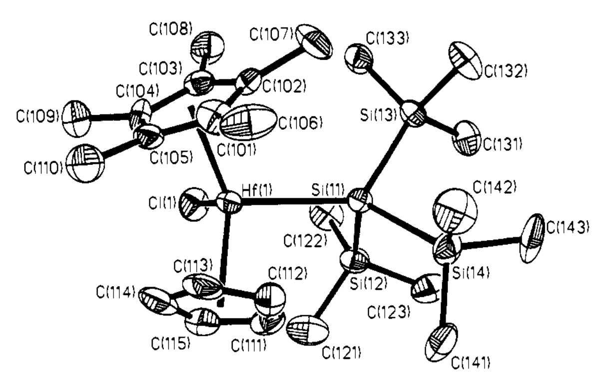

Figure 5. ORTEP view of $CpCp^*Hf[Si(SiMe_3)_3]Cl$ (**2**).

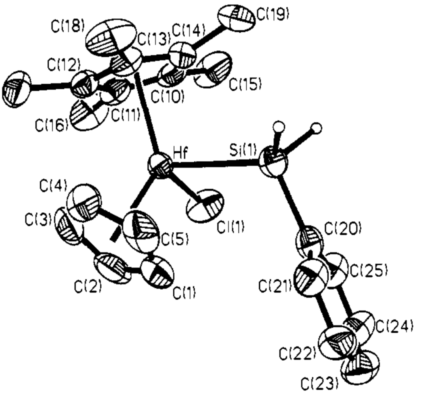

Figure 6. ORTEP view of $CpCp^*Hf(SiH_2Ph)Cl$ (**8**).

Table III. Selected Bond Distances[a] and Angles[b] for **2**

(a) Bond Distances

Hf(1)–Cl(1)	2.395 (3)	Hf(2)–Cl(2)	2.398 (4)
Hf(1)–Si(11)	2.881 (4)	Hf(2)–Si(21)	2.888 (4)
Si(11)–Si(12)	2.394 (5)	Si(21)–Si(22)	2.407 (5)
Si(11)–Si(13)	2.394 (5)	Si(21)–Si(23)	2.385 (5)
Si(11)–Si(14)	2.379 (5)	Si(21)–Si(24)	2.378 (5)

(b) Bond Angles

Cl(1)–Hf(1)–Si(11)	89.4 (1)	Cl(2)–Hf(2)–Si(21)	91.8 (1)
Hf(1)–Si(11)–Si(12)	107.3 (2)	Hf(2)–Si(21)–Si(22)	129.8 (2)
Hf(1)–Si(11)–Si(13)	127.3 (2)	Hf(2)–Si(21)–Si(23)	106.3 (2)
Hf(1)–Si(11)–Si(14)	115.3 (2)	Hf(2)–Si(21)–Si(24)	115.3 (2)
Si(12)–Si(11)–Si(13)	97.8 (2)	Si(22)–Si(21)–Si(23)	99.4 (2)
Si(12)–Si(11)–Si(14)	105.4 (2)	Si(22)–Si(21)–Si(24)	98.2 (2)
Si(13)–Si(11)–Si(14)	100.8 (2)	Si(23)–Si(21)–Si(24)	104.7 (2)

[a] In angstroms. [b] In degrees.

Table IV. Selected Bond Distances[a] and Angles[b] for **8**

(a) Bond Distances

Hf–Cl(1)	2.394 (3)	Si(1)–H(A)	1.43 (11)
Hf–Si(1)	2.729 (3)	Si(1)–H(B)	1.48 (10)
Si(1)–C(20)	1.986 (7)		

(b) Bond Angles

Cl(1)–Hf–Si(1)	89.9 (1)	H(A)–Si(1)–C(20)	107 (4)
Hf–Si(1)–C(20)	113.5 (2)	H(B)–Si(1)–C(20)	105 (4)
Hf–Si(1)–H(A)	115 (4)	H(A)–Si(1)–H(B)	102 (6)
Hf–Si(1)–H(B)	112 (4)		

[a] In angstroms. [b] In degrees.

Discussion

Zirconocene and hafnocene d^0 silyl complexes react with hydrosilanes via silyl-group exchange to give σ-bond metathesis products. Such reactions are generally favorable, but are subject to rather severe steric constraints. Thus, reactions proceed only such that less sterically hindered silyl complexes are formed, and tertiary silanes are generally found to be unreactive. In many cases it is observed that the direct, σ-bond metathesis products are unstable with respect to further reactions to produce hydride complexes and Si–Si bonded species. For reasons that are not entirely clear, the mixed-ring $CpCp^*M(SiR_3)X$ (M = Zr, Hf) complexes participate in cleaner reactions. In particular, the well-behaved CpCp*Hf system has proven most useful in providing numerous examples of stable, d^0 hydrosilyl complexes. Such complexes have been valuable in characterizing the σ-bond metathesis chemistry for d^0 silyl complexes, which has resulted in formulation of a mechanism for the dehydropolymerization of hydrosilanes by early-transition-metal catalysts.[5a,13b,17]

Silyl-exchange reactions can be used to estimate relative Hf–Si bond dissociation energies. Observed silyl-displacement reactions (e.g., the quantitative reactions of complexes **12**, **14**, and **15** with $PhSiH_3$ in benzene-d_6 to produce **8**, along with the corresponding silane) and the equilibrium data compiled in Table III show that steric factors play a large role in determining the relative stabilities of hafnium silyl complexes. In a few cases, electronic effects appear to be more dominant (entries 2 and 6 of Table III). Relevant to these observations, it is known that phenyl substitution at silicon has a slight weakening effect on Si–H bonds.[26] For

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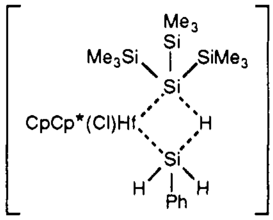
synthetic purposes, complex **2** serves as a good starting material, since $Si(SiMe_3)_3$ acts as a good leaving group in these σ-bond metathesis reactions. Primary and secondary silanes react to give stable, isolable hafnium hydrosilyl complexes, despite the fact that an anomalously weak Si–H bond is formed in the reaction. From published Si–H bond dissociation energies for $H{-}SiH_2Ph$ (88.2 kcal mol^{-1})[26] and $H{-}Si(SiMe_3)_3$ (79.0 kcal mol^{-1}),[27] the Hf–Si bond in **8** appears to be at least 9.2 kcal mol^{-1} stronger than the Hf–Si bond of **2**.

The σ-bond metathesis reactions described above are kinetically well-behaved in the dark. The reaction between **2** and phenylsilane, which was examined in most detail, exhibits a second-order rate law and kinetic behavior that is consistent with other σ-bond metathesis reactions for d^0 metal centers that are thought to proceed via four-center transition states.[12,28] For example, Bercaw and co-workers have determined that the σ-bond metathesis reaction of $(Cp^*\text{-}d_{15})_2ScMe$ with benzene (to give $(Cp^*\text{-}d_{15})_2ScPh$ and methane) is characterized by the activation parameters $\Delta H^{\ddagger} = 18.9$ (2) kcal mol^{-1} and $\Delta S^{\ddagger} = -23$ (2) eu and the isotope effect k_H/k_D (80 °C) = 2.8 (2)[12] (cf. $\Delta H^{\ddagger} = 16.4$ (7) kcal mol^{-1}, $\Delta S^{\ddagger} = -27$ (2) eu, and k_H/k_D (70 °C) = 2.5 (1) for the reaction in eq 3).[28] We therefore propose that the σ-bond metathesis reactions observed for d^0 silyl complexes involve similar four-center transition states. For example, the reaction in eq 3 would involve the transition state:



This transition state is analogous to those previously proposed for σ-bond metathesis reactions involving d^0 M–C and C–H bonds.[12,29] However, it is interesting to note that reactions of the latter type do not readily occur for group 4 bis(cyclopentadienyl) derivatives.[30] A likely explanation for the enhanced behavior of silicon toward this process is that silicon is able to expand its coordination sphere more readily than carbon.[31]

The photochemistry displayed by **1** and **2** in the presence of silanes is remarkable, in that it gives rise to quantitative conversions and high quantum yields. These photochemical reactions apparently result from an electronic LMCT transition (Figure 1) that shifts electron density from the silyl ligand to the metal. This process appears to produce an intermediate (I, eq 9) which exhibits enhanced reactivity toward silanes, especially unhindered silanes.

$$\underset{\mathbf{2}}{CpCp^*Hf[Si(SiMe_3)_3]Cl} \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} I \xrightarrow[-HSi(SiMe_3)_3]{k_2[RR'SiH_2]} CpCp^*Hf(SiHRR')Cl \quad (9)$$

Since **2** is relatively stable to room light (it does decompose in the presence of an intense light source, or after long periods of exposure to normal room lighting), the photochemical formation of I is considered to be reversible. Sterically unhindered hydrosilanes are more efficient traps for the intermediate I than bulky silanes, and the reaction of I with a silane appears to be blocked by donor ligands which can tie up coordination sites.

The photochemistry of related hydrocarbyl group 4 $(\eta^5\text{-}C_5R_5)_2MR'R''$ derivatives has been extensively investigated.[32,33] This chemistry is complex, and mechanisms have proven difficult to probe. However, a number of primary processes have been implicated. Homolysis of a M–C σ-bond produces $(\eta^5\text{-}C_5R_5)_2MR'$ and $^{\bullet}R''$ radical pairs that recombine very rapidly or are trapped by reactive reagents.[32b] Reductive elimination, as in the elimination of biphenyl derivatives from $Cp_2Zr(aryl)_2$ with generation of zirconocene, can also occur.[32c,d] The elimination of the hydrocarbyl group with a hydrogen atom of a cyclopentadienyl ligand has been observed,[32e] as has homolytic rupture of a M–Cp bond.[32f] A recent, thorough study on the photochemistry of $Cp_2Ti(C_6F_5)_2$ is worth noting, given analogies that can be made to the behavior of **2**. Irradiation into the visible absorption band of $Cp_2Ti(C_6F_5)_2$ ($\lambda = 463$ nm) produces a long-lived (~200 μs) transient species with unit efficiency ($\Phi = 0.95 \pm 0.1$). This intermediate quantitatively reverts back to starting material in dry solvents and undergoes reaction with water with a limiting quantum yield of 0.95 ± 0.1. Matrix isolation studies indicate that the transient intermediate is an isomer of $Cp_2Ti(C_6F_5)_2$ with a slipped Cp ring, $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)Ti(C_6F_5)_2$.[33]

On the basis of the information presently available, it is difficult to postulate the identity of intermediate species that may be responsible for the photon-accelerated reactions of **1** and **2**. Solvent-caged radical species such as $CpCp^*MCl$ and $^{\bullet}Si(SiMe_3)_3$ are difficult to exclude, especially since ESR signals are observed upon exposure to room light. Also, compound **1** has previously been observed to undergo a clean photochemical insertion reaction with ethylene, with a quantum yield of 2.5 (λ_{irr} = 380–470 nm), implying a radical-chain mechanism initiated by homolytic cleavage of the Zr–Si bond.[3d] Therefore it seems that light induces M–Si bond rupture in these compounds, but it is difficult to assess the importance of this process in reactions with hydrosilanes. A number of other observations suggest that homolytic cleavage of the M–Si bond cannot explain the σ-bond metathesis reactions. For example, the photochemical reaction of **2** with $PhSiH_3$ is quantitative and does not produce side products from radical-coupling or radical-abstraction processes. The reaction is highly sensitive to the steric properties of the reacting hydrosilane, and in the reaction of **2** with $PhSiD_3$, deuterium is transferred exclusively to the $Si(SiMe_3)_3$ group. Photolysis by room light does not induce polymerization of styrene or methyl methacrylate, and traps that react rapidly with silyl radicals, e.g., 1,4-cyclohexadiene and toluene,[20] do not influence the course of the reaction. Finally ^tBuBr, which is a good silyl-radical trap,[21] reacts much more slowly with **2** under illumination by visible light than does $PhSiH_3$. The absolute rate constant for reaction of $^{\bullet}SiMe_2SiMe_3$ radical with ^tBuBr in isooctane is $2.6 \pm 0.2 \times 10^8$ M^{-1} s^{-1},[34] and in general silyl radicals abstract halogen from carbon much faster than they abstract hydrogen from silicon.[20] In the context of possible silyl-radical reactions, it is also interesting to note that, upon photolysis with visible light, yellow $Hg(SiMe_3)_2$ produces $^{\bullet}SiMe_3$ radicals, which can be trapped by various reagents, including arenes and alkenes.[21,35]

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The photochemical generation of reactive, isomeric species from **1** and **2** appears to be a strong possibility, particularly in light of the studies by Klingert et al. on $Cp_2Ti(C_6F_5)_2$. The observed dependence on size of the reacting silane and the inhibition by phosphines suggest that this intermediate possesses at least one open coordination site. At this time it is difficult to propose a structure for this intermediate, but structures with η^1- or η^3-cyclopentadienyl ligands seem to be good candidates. Other possibilities, such as chlorosilane complexes $CpCp^*M[\leftarrow Cl–Si(SiMe_3)_3]$, also suggest themselves.

The possibility that the observed photochemistry of **1** and **2** is due to a long-lived excited state has been addressed preliminarily by examining fluorescence spectra for **2**. The only emission that was positively identified, at 570 nm, is due to excitation in the 500 ± 60 nm region. Obviously, future investigations should involve more in-depth mechanistic photochemical studies and attempts to observe photogenerated transients.

Experimental Section

All manipulations were performed under an atmosphere of nitrogen or argon using Schlenk techniques and/or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Mikroanalytisches Labor Pascher and Schwartzkopf microanalytical laboratories. Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. Electronic spectra were recorded on an IBM 9420 UV–vis spectrophotometer. Fluorescence spectra were obtained on a SLM-Aminco Model SPF-500C fluorometer with a bandwidth of 5 nm for excitation and emission. NMR spectra were recorded on a GE QE-300 instrument at 300 MHz (^1H), 75.5 MHz (^{13}C), 59.6 MHz (^{29}Si), and 46.1 MHz (^2H). Some ^{29}Si NMR spectra were acquired on a Varian UN-500 instrument at 99.3 MHz. An INEPT sequence was employed to enhance signals in the ^{29}Si NMR spectra.[36] ESR measurements were performed on a Varian E-3 X-band 9.546-GHz spectrometer at room temperature. For quantum-yield measurements, the light intensity entering the photolysis cell through the 365 (±5) nm filters was determined by using the well-known potassium ferrioxalate actinometer.[37] A typical photon flux into the photochemical cell was 1×10^{-7} einstein/min at 365 (±5) nm. A 200-W Hg–Xe short arc lamp (Kratos LH 150) was used. Hydrosilanes were prepared from the corresponding chlorosilanes (Petrarch) by reduction with $LiAlH_4$ (deuterated silanes were prepared by reduction with $LiAlD_4$). PhH_2SiSiH_2Ph was prepared according to the literature procedure,[38] as were p-$H_3SiC_6H_4SiH_3$ and 2,5-$(H_3Si)_2C_4H_2S$,[19] $CpCp^*HfCl_2$,[39] $CpCp^*Zr[Si(SiMe_3)_3]Cl$,[38] and $(THF)_3LiSi(SiMe_3)_3$.[40] Chlorosilanes and alkoxysilanes were used as received. $CpCp^*Hf[Si(SiMe_3)_3]Br$ was prepared by the reaction of $(THF)_3LiSi(SiMe_3)_3$ with $CpCp^*HfBr_2$ (prepared from $CpCp^*HfCl_2$ and BBr_3).

$CpCp^*Hf[Si(SiMe_3)_3]Cl$ (2). A 250-mL round-bottom flask was charged with $CpCp^*HfCl_2$ (4.95 g, 11.0 mmol), $(THF)_3LiSi(SiMe_3)_3$ (5.18 g, 11.0 mmol), and diethyl ether (150 mL) at room temperature. The flask was covered with aluminum foil to protect it from room light, the reaction mixture was stirred for 24 h, and the solvent was then removed by vacuum transfer. The orange residue was extracted with pentane (4 × 50 mL), and the combined extracts were concentrated and cooled (−40 °C) to give orange crystals (mp 175–177 °C) in 67% yield (4.88 g). Anal. Calcd for $C_{24}H_{47}ClSi_4Hf$: C, 43.6; H, 7.16. Found: C, 43.5; H, 7.12. IR (Nujol, CsI, cm^{-1}): 1250 m sh, 1238 m, 1070 vw, 1030 m, 1018 m, 910 vw, 860 m sh, 830 s, 810 s sh, 745 w sh, 670 m, 620 m, 335 w, 312 w. UV–vis (pentane, nm): 226 (6000), 274 (3220), 405 (445). ^1H NMR (benzene-d_6, 22 °C): δ 0.52 (s, 27 H, $SiMe_3$), 1.88 (s, 15 H, C_5Me_5), 5.96 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 6.74 ($SiMe_3$), 13.50 ($C_5\mathit{Me}_5$), 112.48 (C_5H_5), 121.20 (C_5Me_5).

Reaction of $Cp_2Zr[Si(SiMe_3)_3]Cl$ with $PhSiH_3$. An NMR tube was charged with $Cp_2Zr[Si(SiMe_3)_3]Cl$ (0.02 g, 0.04 mmol), $PhSiH_3$ (0.010 mL, 0.08 mmol), and benzene-d_6 (0.4 mL). After 2.5 h (98% conversion, as judged by disappearance of $Cp_2Zr[Si(SiMe_3)_3]Cl$), the ^1H NMR spectrum showed resonances assigned to $Cp_2Zr(SiH_2Ph)Cl$ (**3**, 77%), $[Cp_2ZrHCl]_n$ (9%), PhH_2SiSiH_2Ph (9%), $PhH_2SiSiHPhSiH_2Ph$ (5%), $HSi(SiMe_3)_3$, and as yet unidentified products. ^1H NMR spectrum for **3** (benzene-d_6, 22 °C): δ 4.84 (s, SiH), 5.88 (s, C_5H_5), 7.22 (m, m,p-C_6H_5), 7.80 (d, J = 7.2 Hz, o-C_6H_5).

Reaction of $Cp_2Hf[Si(SiMe_3)_3]Cl$ with $PhSiH_3$. An NMR tube was charged with $Cp_2Hf[Si(SiMe_3)_3]Cl$ (0.02 g, 0.03 mmol), $PhSiH_3$ (0.013 mL, 0.10 mmol), and benzene-d_6 (0.4 mL). After 2 h (ca. 50% conversion, as judged by disappearance of $Cp_2Hf[Si(SiMe_3)_3]Cl$), the ^1H NMR spectrum showed resonances assigned to $Cp_2Hf(SiH_2Ph)Cl$ (**4**, 5%), $[Cp_2HfHCl]_n$ (10%), PhH_2SiSiH_2Ph (23%), $PhH_2SiSiHPhSiH_2Ph$ (52%), $PhH_2Si(SiHPh)_2SiH_2Ph$ (10%), $HSi(SiMe_3)_3$, and as yet unidentified products. ^1H NMR spectrum for **4** (benzene-d_6, 22 °C): δ 4.70 (s, SiH). Other resonances were obscured.

$Cp_2Hf(SiH_2Cy)Cl$ (5). To $Cp_2Hf[Si(SiMe_3)_3]Cl$ (0.50 g, 0.85 mmol) dissolved in benzene (20 mL) was added $CySiH_3$ (0.12 g, 1.0 mmol). Stirring for 16 h under ambient fluorescent room lighting resulted in a yellow solution. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling (−40 °C) of the extract gave yellow crystals (0.25 g). The crystals are a mixture of **5** and $[Cp_2HfHCl]_n$ (1:1 ratio, as judged by ^1H NMR). IR (Nujol, CsI, cm^{-1}): 2030 s (Si–H). ^1H NMR (benzene-d_6, 22 °C): δ 1.16–2.20 (m, 11 H, Cy), 4.43 (d, J_{HH} = 3.3 Hz, 2 H, SiH_2), 5.73 (s, 10 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 27.27, 29.09, 29.32, 33.91 (Cy), 109.75 (C_5H_5).

$Cp_2Hf(SiHPh_2)Cl$ (6). Diphenylsilane (0.19 g, 1.0 mmol), $Cp_2Hf[Si(SiMe_3)_3]Cl$ (0.50 g, 0.85 mmol), and benzene (20 mL) were placed in a Schlenk flask. Stirring for 2.5 days under ambient fluorescent room lighting resulted in a yellow solution. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling (−40 °C) of the extract afforded yellow crystals (0.31 g). The crystals were contaminated with $[Cp_2HfHCl]_n$ (ca. 10%, by ^1H NMR spectroscopy). IR (Nujol, CsI, cm^{-1}): 2030 m (Si–H). ^1H NMR (benzene-d_6, 22 °C): δ 5.63 (s, 10 H, C_5H_5), 5.80 (s, 1 H, SiH), 7.14 (m, 2 H, p-C_6H_5), 7.24 (t, J = 7.2 Hz, 4 H, m-C_6H_5), 7.82 (m, 4 H, o-C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 110.24 (C_5H_5), 127.94, 128.0, 128.13, 136.31 ($SiHPh_2$).

$CpCp^*Zr(SiH_2Ph)Cl$ (7). An NMR tube was charged with **1** (0.06 g, 0.1 mmol), $PhSiH_3$ (0.01 g, 0.1 mmol), and benzene-d_6 (0.5 mL) at room temperature. The NMR tube was left for 10 min under ambient laboratory lighting. By NMR spectroscopy, the reaction was quantitative. ^1H NMR (benzene-d_6, 22 °C): δ 1.73 (s, 15 H, C_5Me_5), 4.27 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, SiH), 4.70 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, SiH), 5.66 (s, 5 H, C_5H_5), 7.15 (t, J = 7.3 Hz, 1 H, p-C_6H_5), 7.26 (t, J = 7.3 Hz, 2 H, m-C_6H_5), 7.85 (d, J = 7.3 Hz, 2 H, o-C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 12.48 ($C_5\mathit{Me}_5$), 110.48 (C_5H_5), 120.24 (C_5Me_5), 127.53, 127.89, 136.07, 136.49 (C_6H_5).

$CpCp^*Hf(SiH_2Ph)Cl$ (8). $PhSiH_3$ (0.082 mL, 0.66 mmol) was added to a benzene (15 mL) solution of **2** (0.40 g, 0.60 mmol). Stirring for 1.5 h under ambient fluorescent room lighting resulted in a yellow solution. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling of the pentane extract gave yellow crystals (mp 123–125 °C) in 70% yield (0.22 g): mol wt in benzene, 561 (calcd 522). Anal. Calcd for $C_{21}H_{27}ClSiHf$: C, 48.4; H, 5.22. Found: C, 48.2; H, 5.38. IR (Nujol, CsI, cm^{-1}): 2050 s (Si–H) [cf. 1475 s for $CpCp^*Hf(SiD_2Ph)Cl$], 1425 m, 1105 w, 1063 w, 1023 m, 1010 m, 915 s, 820 s, 785 s, 724 s, 696 m, 455 w, 395 w, 335 w, 316 w. UV–vis (pentane, nm): 253 (7200), 380 (950). ^1H NMR (benzene-d_6, 22 °C): δ 1.81 (s, 15 H, C_5Me_5) 4.68 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, SiH), 5.14 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, SiH), 5.63 (s, 5 H, C_5H_5), 7.15 (t, J = 7.3 Hz, 1 H, p-C_6H_5), 7.27 (t, J = 7.3 Hz, 2 H, m-C_6H_5), 7.84 (d, J = 7.3 Hz, 2 H, o-C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 11.95 ($C_5\mathit{Me}_5$), 111.54 (C_5H_5), 119.03 (C_5Me_5), 127.51, 127.84, 136.70, 143.17 (C_6H_5). $CpCp^*Hf(SiD_2Ph)Cl$ was prepared by the same procedure by using **2** and $PhSiD_3$.

$CpCp^*Hf[SiH_2(p\text{-}Tol)]Cl$ (9). The method for **8** was employed, using p-$MeC_6H_4SiH_3$ (0.093 mL, 0.66 mmol), benzene (15 mL), and **2** (0.40 g, 0.60 mmol). Yellow crystals (mp 123–125 °C) were obtained in 74% yield (0.24 g). Anal. Calcd for $C_{22}H_{29}ClSiHf$: C, 49.4; H, 5.46. Found: C, 49.3; H, 5.32. IR (Nujol, CsI, cm^{-1}): 2060 s (Si–H), 1596 w, 1308 w, 1255 w, 1185 w, 1090 m, 1014 s, 930 s, 815 s, 752 s, 609 w, 595 w, 478 m, 400 w, 343 m, 315 m. UV–vis (pentane, nm): 226 (6500), 256 (8170), 384 (950). ^1H NMR (benzene-d_6, 22 °C): δ 1.81 (s, 15 H, C_5Me_5), 2.18 (s, 3 H, p-Me), 4.74 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, SiH), 5.22 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, SiH), 5.65 (s, 5 H, C_5H_5), 7.13 (d, J = 7.5 Hz, 2 H, C_6H_4), 7.81 (d, J = 7.5 Hz, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 12.01 ($C_5\mathit{Me}_5$), 21.46 (p-Me), 111.57 (C_5H_5), 119.00 (C_5Me_5), 114.61, 128.78, 136.79, 139.12 (MeC_6H_4).

$CpCp^*Hf[SiH_2(p\text{-}MeOC_6H_4)]Cl$ (10). The method for **8** was employed, using p-$MeOC_6H_4SiH_3$ (0.10 mL, 0.66 mmol), benzene (15 mL), and **2** (0.40 g, 0.60 mmol). Yellow crystals (mp 117–119 °C) were obtained in 71% yield (0.24 g). Anal. Calcd for $C_{22}H_{29}ClOSiHf$: C, 47.9; H, 5.30. Found: C, 47.8; H, 5.30. IR (Nujol, CsI, cm^{-1}): 2035 s (Si–H), 1590 m, 1556 w, 1490 m, 1436 m, 1300 w, 1270 s, 1240 s, 1175 m, 1095 m, 1064 w, 1028 m, 1009 m, 910 s, 820 s, 792 s, 780 s, 745 w sh, 705 w, 510 w, 478 w, 335 m, 310 m. ^1H NMR (benzene-d_6, 22 °C):

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δ 1.81 (s, 15 H, C_5Me_5), 3.33 (s, 3 H, *p*-MeO), 4.78 (d, $^2J_{HH}$ = 1.5 Hz, 1 H, SiH), 5.26 (d, $^2J_{HH}$ = 1.5 Hz, 1 H, SiH), 5.67 (s, 5 H, C_5H_5), 6.92 (d, *J* = 8.7 Hz, 2 H, C_6H_4), 7.80 (d, *J* = 8.7 Hz, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 11.94 ($C_5\mathit{Me}_5$), 54.49 (*p*-Me), 111.58 (C_5H_5), 118.96 (C_5Me_5), 113.88, 132.93, 138.05, 159.93 ($MeO\mathit{C}_6H_4$).

$CpCp^*Hf[SiH_2(p\text{-}FC_6H_4)]Cl$ (11). Using *p*-$FC_6H_4SiH_3$ (0.095 mL, 0.66 mmol), benzene (15 mL), and **2** (0.40 g, 0.60 mmol), the method for compound **8** was followed to obtain yellow crystals (mp 108–110 °C) in 73% yield (0.24 g). Anal. Calcd for $C_{21}H_{26}ClFSiHf$: C, 46.8; H, 4.86; F, 3.52. Found: C, 46.6; H, 4.95; F, 3.31. IR (Nujol, CsI, cm^{-1}): 2040 s (Si–H), 1575 m, 1490 s, 1300 w, 1255 w, 1245 m, 1159 m, 1090 m, 1080 w sh, 1063 w, 1039 m, 1010 m, 915 s, 825 s, 774 s, 695 m, 500 w, 405 w, 335 m, 314 m. ^1H NMR (benzene-d_6, 22 °C): δ 1.79 (s, 15 H, C_5Me_5), 4.63 (d, $^2J_{HH}$ = 1.5 Hz, 1 H, SiH), 5.09 (d, $^2J_{HH}$ = 1.5 Hz, 1 H, SiH), 5.60 (s, 5 H, C_5H_5), 6.93 (dd, *J* = 8.1 Hz, 2 H, C_6H_4), 7.66 (dd, *J* = 8.1 Hz, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 11.88 ($C_5\mathit{Me}_5$), 111.57 (C_5H_5), 119.16 (C_5Me_5), 114.64, 114.90, 138.35, 164.84 ($F\mathit{C}_6H_4$).

$CpCp^*Hf(SiH_2Mes)Cl$ (12). $MesSiH_3$ (0.10 g, 0.66 mmol), **2** (0.40 g, 0.60 mmol), and benzene (15 mL) were placed in a Schlenk flask. Stirring for 2 days under ambient fluorescent room lighting resulted in a yellow solution. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling of the extract gave yellow crystals (mp 144–146 °C) in 71% yield (0.24 g). Anal. Calcd for $C_{24}H_{33}ClSiHf$: C, 51.2; H, 5.90. Found: C, 51.4; H, 5.92. IR (Nujol, CsI, cm^{-1}): 2060 s (Si–H), 1600 w, 1022 m, 1012 m, 954 m, 845 w, 818 s, 783 s, 730 w, 704 m, 600 br, 335 w, 314 m. ^1H NMR (benzene-d_6, 22 °C): δ 1.83 (s, 15 H, C_5Me_5), 2.24 (s, 3 H, *p*-Me), 2.61 (s, 6 H, *o*-Me), 4.61 (d, $^2J_{HH}$ = 2.6 Hz, 1 H, SiH), 4.48 (d, $^2J_{HH}$ = 2.6 Hz, 1 H, SiH), 5.64 (s, 5 H, C_5H_5), 6.93 (s, 2 H, $Me_3C_6\mathit{H}_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 11.86 ($C_5\mathit{Me}_5$), 21.23 (*p*-Me), 24.87 (*o*-Me), 111.52 (C_5H_5), 119.19 (C_5Me_5), 128.60, 136.90, 138.49, 143.82 ($Me_3\mathit{C}_6H_2$).

$CpCp^*Hf(SiH_2CH_2Ph)Cl$ (13). $PhCH_2SiH_3$ (0.093 mL, 0.66 mmol), **2** (0.40 g, 0.60 mmol), and benzene (15 mL) were stirred together in a Schlenk flask for 2 h under ambient laboratory conditions. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling of the extract gave a yellow viscous oil (solid at −40 °C) in 71% yield. Anal. Calcd for $C_{22}H_{29}ClSiHf$: C, 49.4; H, 5.46. Found: C, 49.1; H, 5.43. IR (neat, CsI, cm^{-1}): 3070 m, 3050 m, 3020 m, 2970 m, 2900 s, 2860 m, 2050 s (Si–H), 1600 s, 1490 s, 1200 s, 1150 s, 1060 m, 1020 s, 930 s, 905 m, 815 s, 785 m, 745 s, 726 s, 700 s, 650 m, 610 m, 538 w, 470 m, 400 w, 340 m, 316 s. ^1H NMR (benzene-d_6, 22 °C): δ 1.79 (s, 15 H, C_5Me_5), 2.40 (m, 2 H, $SiC\mathit{H}_2Ph$), 4.27 (m, 1 H, SiH), 4.45 (m, 1 H, SiH), 5.73 (s, 5 H, C_5H_5), 6.98 (t, *J* = 7.8 Hz, 1 H, *p*-C_6H_5), 7.18 (t, *J* = 7.8 Hz, 2 H, *m*-C_6H_5), 7.26 (d, *J* = 7.8 Hz, 2 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 12.01 ($C_5\mathit{Me}_5$), 25.80 ($Si\mathit{C}H_2Ph$), 111.19 (C_5H_5), 119.02 (C_5Me_5), 114.63, 123.95, 128.44, 146.84 (CH_2-C_6H_5).

$CpCp^*Hf(SiH_2Cy)Cl$ (14). To **2** (0.40 g, 0.60 mmol) in benzene (20 mL) was added $CySiH_3$ (0.086 mL, 0.66 mmol) via syringe. Stirring for 2 h under ambient fluorescent room lighting resulted in a yellow solution. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling of the extract gave yellow crystals (mp 103–105 °C) in 76% yield (0.24 g). Anal. Calcd for $C_{21}H_{33}ClSiHf$: C, 47.8; H, 6.31. Found: C, 47.4; H, 6.12. IR (Nujol, CsI, cm^{-1}): 2030 s (Si–H), 1470 w, 1440 m, 1170 w, 1090 w, 1065 w, 1015 m, 991 m, 930 s, 870 m, 860 w, 850 w, 810 s, 790 s, 735 m, 340 m, 315 m. UV–vis (pentane, nm): 223 (4700), 251 (4200), 385 (750). ^1H NMR (benzene-d_6, 22 °C): δ 1.16–2.23 (m, 11 H, Cy), 1.81 (s, 15 H, C_5Me_5), 4.04 (dd, J_{HH} = 1.2, 2.7 Hz, 1 H, SiH), 4.20 (dd, J_{HH} = 1.2, 2.7 Hz, 1 H, SiH), 5.78 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 12.01 ($C_5\mathit{Me}_5$), 27.49, 29.34, 32.92, 35.65 (Cy), 111.03 (C_5H_5), 118.81 (C_5Me_5).

$CpCp^*Hf(SiHPh_2)Cl$ (15). Diphenylsilane (0.12 g, 0.66 mmol), **2** (0.40 g, 0.60 mmol), and benzene (15 mL) were stirred together for 2 days under ambient fluorescent room lighting. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling (−40 °C) of the extract gave yellow crystals (mp 129–131 °C) in 64% yield (0.23 g). Anal. Calcd for $C_{27}H_{31}ClSiHf$: C, 54.3; H, 5.23. Found: C, 54.2; H, 5.45. IR (neat, CsI, cm^{-1}): 2020 m (Si–H), 1425 m, 1100 w, 1065 w, 1021 w, 1010 w, 820 s, 723 s, 700 m, 490 w, 455 w, 400 w, 340 w, 313 w. UV–vis (pentane, nm): 225 (11 165), 263 (9740), 390 (1015). ^1H NMR (benzene-d_6, 22 °C): δ 1.75 (s, 15 H, C_5Me_5), 5.60 (s, 1 H, SiH), 5.70 (s, 5 H, C_5H_5), 7.12 (m, 2 H, *p*-C_6H_5), 7.24 (t, *J* = 6.9 Hz, 4 H, *m*-C_6H_5), 7.73 (d, *J* = 6.9 Hz, 4 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 12.19 ($C_5\mathit{Me}_5$), 111.80 (C_5H_5), 119.58 (C_5Me_5), 127.41, 127.96, 136.85, 145.25 ($SiHPh_2$).

$CpCp^*Hf(SiHPhMe)Cl$ (16). Phenylmethylsilane (0.08 g, 0.66 mmol), **2** (0.40 g, 0.60 mmol), and benzene (15 mL) were stirred together for 1.5 days under ambient fluorescent room lighting. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling (−40 °C) of the extract gave yellow crystals (mp 128–130 °C) in 64% yield (0.21 g). Two diastereomers were formed in a 7:5 ratio. Anal. Calcd for $C_{22}H_{29}ClSiHf$: C, 49.4; H, 5.46. Found: C, 49.1; H, 5.35. IR (Nujol, CsI, cm^{-1}): 2040 s (Si–H, major product), 2000 s (Si–H, minor product), 1480 m, 1425 m, 1258 w, 1238 m, 1100 m, 1062 w, 1020 s, 1010 m, 860 s, 810 s, 728 s, 698 s, 682 w, 655 m, 630 w, 458 w, 390 w, 340 m, 315 m. ^1H NMR (benzene-d_6, 22 °C) for major product: δ 0.58 (d, *J* = 4.5 Hz, 3 H, SiMe), 1.81 (s, 15 H, C_5Me_5), 5.31 (q, *J* = 4.5 Hz, 1 H, SiH), 5.60 (s, 5 H, C_5H_5), 7.17 (m, 1 H, *p*-C_6H_5), 7.31 (m, 2 H, *m*-C_6H_5), 7.78 (d, *J* = 6.6 Hz, 2 H, *o*-C_6H_5). ^1H NMR (benzene-d_6, 22 °C) for minor product: δ 0.81 (d, *J* = 4.5 Hz, 3 H, SiMe), 1.79 (s, 15 H, C_5Me_5), 5.23 (q, *J* = 4.5 Hz, 1 H, SiH), 5.70 (s, 5 H, C_5H_5), 7.17 (m, 1 H, *p*-C_6H_5), 7.31 (m, 2 H, *m*-C_6H_5), 7.72 (d, *J* = 6.6 Hz, 2 H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C) for major product: δ −1.20 (SiMe), 12.13 ($C_5\mathit{Me}_5$), 111.20 (C_5H_5), 118.96 (C_5Me_5), 127.15, 127.58, 135.59, 147.40 ($SiHPh_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C) for minor product: δ 2.75 (SiMe), 12.18 ($C_5\mathit{Me}_5$), 111.69 (C_5H_5), 119.24 (C_5Me_5), 127.35, 127.76, 135.70, 148.27 ($SiHPh_2$). ^{29}Si NMR (benzene-d_6, 22 °C): δ 21.75 (d, J_{SiH} = 153 Hz, major product); 25.10 (d, J_{SiH} = 153 Hz, minor product).

$CpCp^*Hf(SiHPhSiH_2Ph)Cl$ (17). The method for compound **16** was employed using PhH_2SiSiH_2Ph (0.16 mL, 0.66 mmol), benzene (15 mL), and **2** (0.40 g, 0.60 mmol) to obtain a yellow viscous oil (solid at −40 °C) in 65% yield. A mixture of two diastereomers (A and B) were isolated in a 1:1 ratio. The reaction of 2 equiv of **2** with PhH_2SiSiH_2Ph gave the same result; no $[CpCp^*Hf(Cl)SiHPh]_2$ was observed. Anal. Calcd for $C_{27}H_{33}ClSi_2Hf$: C, 51.7; H, 5.30. Found: C, 51.2; H, 5.07. IR (neat, CsI, cm^{-1}): 3060 m, 3040 m, 2980 m sh, 2940 m, 2900 s, 2860 m sh, 2100 s and 2040 s (Si–H, A and B), 1950 w, 1880 w, 1820 w, 1720 vw, 1640 w, 1580 w, 1560 w, 1480 m, 1440 m sh, 1426 s, 1380 s, 1330 w, 1300 w, 1260 w, 1190 w, 1160 w, 1105 m, 1065 m, 1025 m, 1013 m, 1000 w, 920 s, 800 s, 720 s, 625 m, 598 m sh, 485 w, 450 w, 380 m, 315 m. ^1H NMR (benzene-d_6, 22 °C): δ 1.79 (s, 30 H, C_5Me_5, A and B), 4.65–4.92 (m, 6 H, SiH, SiH_2, A and B), 5.73 (s, 5 H, C_5H_5, A), 5.76 (s, 5 H, C_5H_5, B), 7.10 (m, 4 H, *p*-C_6H_5, A and B), 7.19 (m, 8 H, *m*-C_6H_5, A and B), 7.71 (m, 8 H, *o*-C_6H_5, A and B). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 12.26 ($C_5\mathit{Me}_5$, A and B), 111.68, 111.98 (C_5H_5, A and B), 119.78, 119.83 (C_5Me_5, A and B), 127.30, 127.41, 127.68, 127.84, 127.95, 128.14, 128.74, 128.98, 135.66, 136.22, 136.35, 136.50, 137.02, 137.23, 142.89, 143.66 (C_6H_5, A and B). ^{29}Si NMR (benzene-d_6, 22 °C): δ −9.05 and −9.86 (d, J_{SiH} = 152 Hz, $Hf\mathit{Si}HPhSiH_2Ph$, A and B), −43.91 and −50.43 (t, J_{SiH} = 183 Hz, $HfSiHPh\mathit{Si}H_2Ph$, A and B).

$1,4\text{-}[CpCp^*Hf(Cl)SiH_2]_2C_6H_4$ (19). To a benzene (20 mL) solution of **2** (0.40 g, 0.60 mmol) was added *p*-$H_3SiC_6H_4SiH_3$ (0.048 mL, 0.30 mmol). Stirring for 2 h under ambient fluorescent room lighting resulted in a turbid yellow solution and precipitation of a solid. Removal of volatiles, washing with pentane, and drying under reduced pressure afforded a sparingly soluble yellow solid (mp >300 °C) in 39% yield (0.23 g). Anal. Calcd for $C_{36}H_{48}Cl_2Si_2Hf_2$: C, 44.8; H, 5.01. Found: C, 44.9; H, 5.03. IR (Nujol, CsI, cm^{-1}): 2040 s (Si–H), 1115 w, 1060 w, 1028 m, 1010 m, 910 s, 810 s, 755 s, 480 w, 340 w. ^1H NMR (benzene-d_6, 22 °C): δ 1.80 (s, 30 H, C_5Me_5), 4.78 (s, 2 H, SiH), 5.26 (s, 2 H, SiH), 5.66 (s, 10 H, C_5H_5), 7.95 (s, 2 H, C_6H_4), 7.96 (s, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 11.91 ($C_5\mathit{Me}_5$), 111.60 (C_5H_5), 118.87 (C_5Me_5), 128.54, 136.08 (C_6H_4). NMR data for $CpCp^*Hf(SiH_2C_6H_4SiH_3)Cl$ (**18**) were obtained by monitoring the reaction of **2** with 1.5 equiv of *p*-$H_3SiC_6H_4SiH_3$ in benzene-d_6. ^1H NMR (benzene-d_6, 22 °C) for **18**: δ 1.79 (s, 15 H, C_5Me_5), 4.29 (s, 3 H, SiH_3), 4.62 (d, $^2J_{HH}$ = 1.8 Hz, 1 H, SiH), 5.08 (d, $^2J_{HH}$ = 1.8 Hz, 1 H, SiH), 5.59 (s, 5 H, C_5H_5), 7.49 (d, *J* = 7.5 Hz, 2 H, C_6H_4), 7.79 (d, *J* = 7.5 Hz, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C) for **18**: δ 11.94 ($C_5\mathit{Me}_5$), 111.51 (C_5H_5), 119.04 (C_5Me_5), 135.18, 135.60, 136.41, 145.95 (C_6H_4).

$2,5\text{-}[CpCp^*Hf(Cl)SiH_2]_2C_4H_2S$ (20). To a benzene (20 mL) solution of **2** (0.40 g, 0.60 mmol) was added $2,5\text{-}H_3Si(C_4H_2S)SiH_3$ (0.049 mL, 0.30 mmol). Stirring for 3 h under ambient fluorescent room lighting resulted in a yellow solution. Removal of volatiles, washing with pentane, and drying under reduced pressure afforded a yellow solid (mp 185–187 °C dec) in 40% yield (0.23 g). Anal. Calcd for $C_{34}H_{46}Cl_2Si_2SHf_2$: C, 42.06; H, 4.78. Found: C, 42.06; H, 4.89. IR (Nujol, CsI, cm^{-1}): 2040 s (Si–H), 1260 w, 1200 w, 1060 w, 1020 m, 1010 m, 990 m, 952 w, 915 s, 810 s, 776 s, 490 w, 458 m, 400 w, 340 m, 314 m. ^1H NMR (benzene-d_6, 22 °C): δ 1.81 (s, 30 H, C_5Me_5), 5.00 (s, 2 H, SiH), 5.42 (s, 2 H, SiH), 5.75 (s, 10 H, C_5H_5), 7.62 (s, 2 H, C_4H_2S). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 11.96 ($C_5\mathit{Me}_5$), 111.90 (C_5H_5), 119.21 (C_5Me_5), 138.57, 145.21 (C_4H_2S).

Kinetics of the Reaction of 2 with Phenylsilane. Sealed NMR tubes containing **2** (ca. 32 mg, 0.048 mmol), phenylsilane (10, 20, 30, or 40 equiv), ferrocene (7.4 mg, 0.04 mmol), and benzene-d_6 (0.4 mL) were used in the kinetic runs. The reaction was followed by ^1H NMR spectroscopy by monitoring the disappearance of the Cp* resonance of **2** and the appearance of $HSi(SiMe_3)_3$ relative to ferrocene. The kinetics were pseudo-first-order for over 3 half-lives. The linear plots of k_{obsd} vs $[PhSiH_3]$, which intercepted the origin, were used to obtain the second-order rate constants.

Reaction of 2 with ^{t}BuBr. A septum-capped 5-mm NMR tube was charged with **2** (20 mg, 0.030 mmol), ^{t}BuBr (0.007 mL, 0.06 mmol), and benzene-d_6 (0.4 mL). The tube was placed under ambient fluorescent room lighting for 24 h (76% conversion, as judged by the amount of **2** remaining). The ^{1}H NMR spectrum showed resonances assignable to $BrSi(SiMe_3)_3$ (25%), a mixture of $CpCp^*HfCl_2$ [^{1}H NMR δ 1.81 (s, C_5H_5), 5.87 (s, C_5Me_5)], $CpCp^*HfBr_2$ [^{1}H NMR δ 1.84 (s, C_5H_5), 5.89 (s, C_5Me_5)], and $CpCp^*HfBrCl$ [^{1}H NMR δ 1.82 (s, C_5H_5), 5.88 (s, C_5Me_5)] (25%, 1:1:2), and ^{t}BuH (50%) [^{1}H NMR δ 0.85 (d, J = 6.6 Hz, ^{t}*Bu*H), 0.90 (m, ^{t}Bu*H*)]. $HSi(SiMe_3)_3$ was not observed.

Reaction of 8 with p-$BrC_6H_4SiH_3$. A septum-capped 5-mm NMR tube was charged with **8** (20 mg, 0.038 mmol), p-$BrC_6H_4SiH_3$ (0.006 mL, 0.04 mmol), and benzene-d_6 (0.4 mL). The tube was placed under ambient fluorescent room lighting for 24 h (60% conversion, as judged by the amount of **8** remaining). The ^{1}H NMR spectrum showed a mixture of $CpCp^*HfCl_2$, $CpCp^*HfBr_2$, and $CpCp^*HfBrCl$ in a ratio of 1:1:2 (50% total) and a mixture of $PhSiH_3$ and 4,4′-$(H_3Si)_2C_6H_4C_6H_4$ [^{1}H NMR δ 4.29 (s, 6 H, SiH_3), 7.34 (d, J = 8.1 Hz, 4 H, biphenyl), 7.44 (d, J = 8.1 Hz, 4 H, biphenyl)] in a ratio of 10:3 (50% total).

Reaction of 2 with p-$BrC_6H_4SiH_3$ and p-$ClC_6H_4SiH_3$. A septum-capped 5-mm NMR tube was charged with **2** (20 mg, 0.030 mmol), p-$BrC_6H_4SiH_3$ (0.004 mL, 0.03 mmol), and benzene-d_6 (0.4 mL). The tube was placed under ambient fluorescent room lighting for 24 h (50% conversion, as judged by the amount of **2** remaining). The ^{1}H NMR spectrum showed resonances assignable to $BrSi(SiMe_3)_3$ [^{1}H NMR δ 0.023 (s, $SiMe_3$)] (25%), a mixture of $CpCp^*HfCl_2$, $CpCp^*HfBr_2$, and $CpCp^*HfBrCl$ (25%, 1:1:2 ratio), and a mixture of 4,4′-$(H_3Si)_2C_6H_4C_6H_4$ and $PhSiH_3$ in a ratio of 3:10 (50% total). $HSi(SiMe_3)_3$ was not observed in this reaction.

For the reaction with p-$ClC_6H_4SiH_3$, analogous conditions were employed and the tube was placed under ambient fluorescent room lighting for 2 days (100% conversion). The ^{1}H NMR spectrum showed resonances assignable to $ClSi(SiMe_3)_3$ [^{1}H NMR δ 0.22 (s, $SiMe_3$)] (25%), $CpCp^*HfCl_2$ (25%), and a mixture of 4,4′-$(H_3Si)_2C_6H_4C_6H_4$ and $PhSiH_3$ in a ratio of 3:10 (50%). $HSi(SiMe_3)_3$ was not observed.

$CpCp^*Hf[SiH_2(p\text{-}Tol)]Br$ (21). To a benzene (15 mL) solution of $CpCp^*Hf[Si(SiMe_3)_3]Br$ (0.43 g, 0.61 mmol) was added p-$MeC_6H_4SiH_3$ (0.093 mL, 0.66 mmol). Stirring for 1.5 under ambient fluorescent room lighting resulted in a yellow solution. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling of the pentane extract gave yellow crystals (mp 120–122 °C) in 74% yield (0.26 g). Anal. Calcd for $C_{22}H_{29}BrSiHf$: C, 45.6; H, 5.04. Found: C, 44.8; H, 5.42. IR (Nujol, CsI, cm^{-1}): 2035 s (Si–H), 1306 w, 1255 w, 1186 w, 1112 w, 1090 w, 1065 w, 1023 m, 1010 m, 916 s, 820 s, 775 s, 700 m, 625 m, 606 w, 598 w, 480 w, 400 w, 340 m. ^{1}H NMR (benzene-d_6, 22 °C): δ 1.83 (s, 15 H, C_5Me_5), 2.19 (s, 3 H, p-Me), 4.58 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, SiH), 5.13 (d, $^2J_{HH}$ = 1.2 Hz, 1 H, SiH), 5.67 (s, 5 H, C_5H_5), 7.12 (d, J = 7.5 Hz, 2 H, C_6H_4), 7.78 (d, J = 7.5 Hz, 2 H, C_6H_4). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 12.27 ($C_5\mathit{Me}_5$), 21.00 (p-Me), 112.00 (C_5H_5), 119.23 (C_5Me_5), 128.80, 136.81, 137.72, 139.11 ($Me\mathit{C}_6H_4$).

$CpCp^*Hf(SiH_2CH_3)Cl$ (23). To a benzene (20 mL) solution of **2** (0.50 g, 0.76 mmol) was added $HSi(OMe)_2Me$ (0.94 mL, 7.60 mmol). Stirring for 20 h (under a static atmosphere of nitrogen to prevent the loss of gaseous CH_3SiH_3) under ambient fluorescent room lighting resulted in a dark yellow solution. Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling (−40 °C) of the extract afforded yellow crystals (mp 108–110 °C dec) in 65% yield (0.23 g). Anal. Calcd for $C_{16}H_{25}ClSiHf$: C, 41.8; H, 5.49. Found: C, 41.4; H, 5.38. IR (Nujol, CsI, cm^{-1}): 2060 s (Si–H), 2040 s, 1482 m sh, 1260 vw, 1240 m, 1160 w sh, 1140 vw, 1065 w, 1020 s sh, 1010 s, 940 s, 860 s, 825 s, 810 s sh, 695 m, 668 m, 585 vw, 470 vw, 425 w, 405 w, 343 m, 305 m. ^{1}H NMR (benzene-d_6, 22 °C): δ 0.64 (t, $^3J_{HH}$ = 4.8 Hz, 3 H, $SiH_2C\mathit{H}_3$), 1.80 (s, 15 H, C_5Me_5), 4.34 (q, $^3J_{HH}$ = 4.8 Hz, 1 H, SiH), 4.59 (q, $^3J_{HH}$ = 4.8 Hz, 1 H, SiH), 5.74 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ −3.43 (SiH_2CH_3), 11.96 ($C_5\mathit{Me}_5$), 111.20 (C_5H_5), 118.79 (C_5Me_5). The complex **23** slowly decomposed at room temperature in benzene-d_6 solution to give $CpCp^*HfHCl$ and a benzene-insoluble polysilane, presumably $(-SiHMe-)_n$.

$CpCp^*Hf(SiH_3)Cl$ (24). Excess trimethoxysilane (ca. 2 mL) was syringed into a benzene solution of **2** (0.50 g, 0.76 mmol), and the resulting mixture was stirred for 18 h (under a static atmosphere of nitrogen to prevent the loss of gaseous SiH_4). Removal of volatiles, extraction with pentane (30 mL), and concentration and cooling (−40 °C) of the extract gave 0.24 g of a light-yellow solid. As determined by ^{1}NMR spectroscopy, the solid was a mixture of $CpCp^*Hf(SiH_3)Cl$ (60%), $CpCp^*Hf(OMe)Cl$ (15%), and $CpCp^*HfCl_2$ (25%). The $CpCp^*HfCl_2$ probably forms via reactions with chlorosilanes, which are added to commercial $HSi(OMe)_3$ to inhibit disproportionation. IR (Nujol, CsI, cm^{-1}): 2070 (Si–H). ^{1}H NMR (benzene-d_6, 22 °C): δ 1.80 (s, 15 H, C_5Me_5), 3.90 (s, 3 H, SiH_3), 5.73 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (benzene-d_6, 22 °C): δ 11.98 ($C_5\mathit{Me}_5$), 111.53 (C_5H_5), 119.08 (C_5Me_5). The complex **24** slowly decomposed at room temperature in benzene-d_6 solution to give $CpCp^*HfHCl$ and a benzene-insoluble product, presumably $(-SiH_2-)_n$.

X-ray Structure Determinations of 2 and 8. For **2**: A light yellow crystal of approximate dimensions 0.14 × 0.4 × 0.4 mm was mounted under N_2 in a random orientation in a glass capillary and flame-sealed. Centering of 24 randomly selected reflections with $15° \leq 2\theta \leq 30°$ provided unit cell data. The selection of the triclinic cell was confirmed by axial photographs. Data were collected with $\theta/2\theta$ scans ($3° \leq 2\theta \leq 48°$), at a variable scan speed of 3.00–1.95 deg min^{-1}, using Mo Kα radiation (λ = 0.71073 Å), on a Siemens R3m/V automated diffractometer equipped with a highly ordered graphite monochromator. Of the 10841 reflections measured, 8987 were independent (R_{int} = 2.63%), and 5289 were considered observed ($F_o > 6\sigma(F)$). The data were corrected for Lorentz and polarization effects and for a decay in the intensity of three check reflections of approximately 11%. A semiempirical absorption correction based on the Ψ scan method was employed. The minimum and maximum transmission factors for the correction were 0.284 and 0.669, respectively. The structure was solved by direct methods and refined by full-matrix least-squares methods. Refinement of a solution in the space group $P1$ did not provide a chemically reasonable structure. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized, calculated positions (d(C–H) = 0.96 Å), with a fixed thermal parameter approximately equal to 1.2 times the isotropic thermal parameter of the attached carbon atom. R_F = 4.58, R_{wF} = 5.32, GOF = 1.33, data/parameter = 9.8, largest Δ/σ = 0.003, largest difference peak = 1.93 e Å^{-3}, located 1.37 Å from Hf(1).

For **8**: A yellow crystal of approximate dimensions 0.24 × 0.3 × 0.32 mm was mounted under N_2 in a random orientation in a glass capillary and flame-sealed. Centering of 22 randomly selected reflections with $15° \leq 2\theta \leq 30°$ provided unit cell data. The selection of the monoclinic cell was confirmed by axial photographs. Data were collected with ω scans ($3° \leq 2\theta \leq 48°$), at a variable scan speed of 3.00–19.5 deg min^{-1}, using Mo Kα radiation (λ = 0.71073 Å), on a Siemens R3m/V automated diffractometer equipped with a highly ordered graphite monochromator. Of the 3776 reflections measured, 3293 were independent (R_{int} = 1.94%), and 2173 were considered observed ($F_o > 6\sigma(F)$). The data were corrected for Lorentz and polarization effects and for a decay in the intensity of three check reflections of approximately 6%. A semiempirical absorption correction based on the Ψ scan method was employed. The minimum and maximum transmission factors for the correction were 0.585 and 0.963, respectively. Systematic absences uniquely determined the space group $P2_1/c$. The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. The phenyl ring was constrained to be a rigid hexagon (d(C–C) = 1.42 Å). The silicon-bound hydrogen atoms H(A) and H(B) were located by difference Fourier maps and refined. All other hydrogen atoms were placed in idealized, calculated positions (d(C–H) = 0.96 Å), with a fixed thermal parameter approximately equal to 1.2 times the isotropic thermal parameter of the attached carbon atom. R_F = 3.07, R_{wF} = 3.35, GOF = 1.12, data/parameter = 10.2, largest Δ/σ = 0.005, largest difference peak = 0.64 e Å^{-3}, located 1.09 Å from Hf. All calculations were performed with the Siemens SHELXTL PLUS computing package (Siemens Analytical X-ray Instruments, Inc., Madison, WI).

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Supplementary Material Available: Tables of crystal data, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **2** and **8** (22 pages); listings of observed and calculated structure factors for **2** and **8** (45 pages). Ordering information is given on any current masthead page.