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Synthesis and Characterization of Scandium Silyl Complexes of the Type $Cp^*_2ScSiHRR'$. σ-Bond Metathesis Reactions and Catalytic Dehydrogenative Silation of Hydrocarbons

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Abstract: The scandium dihydrosilyl complexes $Cp^*_2ScSiH_2R$ (R = Mes (**4**), Trip (**5**), $SiPh_3$ (**6**), $Si(SiMe_3)_3$ (**7**); Mes = 2,4,6-$Me_3C_6H_2$, Trip = 2,4,6-$^iPr_3C_6H_2$) and $Cp^*_2ScSiH(SiMe_3)_2$ (**8**) were synthesized by addition of the appropriate hydrosilane to Cp^*_2ScMe (**1**). Studies of these complexes in the context of hydrocarbon activation led to discovery of catalytic processes for the dehydrogenative silation of hydrocarbons (including methane, isobutene and cyclopropane) with Ph_2SiH_2 via σ-bond metathesis.

Introduction

The rational design of catalysts for the selective functionalization of hydrocarbons represents an important challenge in chemistry. Efforts directed toward the development of homogeneous catalytic hydrocarbon conversions have identified several mechanisms by which transition metal centers may activate C−H bonds.[1−4] In addition, a few recent examples of homogeneous catalysis involving reactions of alkanes and arenes have been reported, including olefin hydroarylation,[5] hydrocarbon borylation,[6] and alkane dehydrogenation.[7] However, only a few homogeneous catalytic derivatizations of methane (the cheapest and most naturally abundant hydrocarbon) are known.[8−10] Recent advances in the catalytic chemistry of methane have been primarily associated with selective oxidations involving noble metal catalysts in highly acidic media.[9] Although these oxidative processes are promising, they suffer from the limitation that the reaction products are more readily oxidized than methane itself.[8,9] Also, the harsh conditions (highly acidic conditions, >150 °C) for many such reactions make them unattractive for use in routine syntheses.[9] Methane oxidations by metal oxo species in conjunction with an external oxidant (O_2, peroxides) have also been investigated, and this approach appears promising based on the known chemistry of metalloenzymes such as methane monooxygenase.[10] However, synthetic metal oxo catalysts have not yet provided the selectivity and activity that is exhibited by metalloenzymes such as methane monooxygenase and cytochrome P450.[10] Stoichiometric methane activations involving oxidative addition[2] or concerted bond cleavage (e.g., 1,2 addition across a M=N double bond or σ-bond metathesis)[3,4] may provide alternative strategies for catalytic methane conversions. For example, the C−H bond activation of methane (and other light hydrocarbons) by a silica-supported tantalum hydride may involve four-centered transition states.[11]

The development of solution-phase catalytic hydrocarbon functionalizations might be based on C−H bond activation steps via σ-bond metathesis.[3,12−14] In this context, electrophilic

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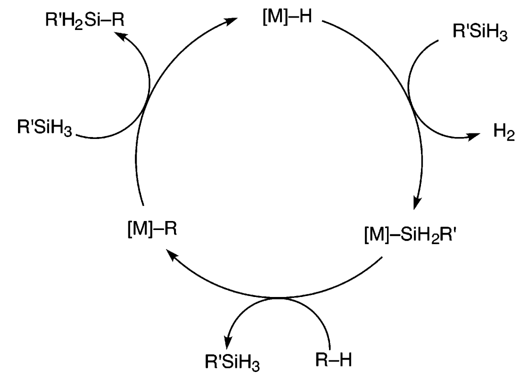
complexes of the type Cp^*_2MR (M = Sc, Lu, Y; R = H, CH_3) are reactive toward unactivated C−H bonds under mild conditions.[12,13] Investigations have shown that these C−H bond activations, including those with methane, proceed through concerted, four-centered, electrocyclic transition states. Although C−H bond activations of this type were reported over 20 years ago,[12] only one example of a productive, selective, catalytic hydrocarbon conversion via C−H σ-bond metathesis has been reported (the alkylation of pyridine derivatives with $[Cp_2ZrH(THF)][BPh_4]$).[15] Activations of methane via well-defined σ-bond metathesis steps have not yet been incorporated into catalytic cycles. On the other hand, several catalytic processes that involve the related activation of Si−H bonds via four-centered transition states have been reported (e.g., hydrosilane dehydropolymerization,[16,17] olefin hydrosilation,[18] organosilane hydrogenolysis[19]).

A strategy for the design of catalysts for hydrocarbon transformations is suggested by the recent observation of arene activation by the electrophilic cationic hafnium hydrosilyl complex $Cp_2Hf(\eta^2\text{-}SiHMes_2)(\mu\text{-}Me)B(C_6F_5)_3$.[20] Based on this reaction and known chemistry for related hafnium alkyl and hydride complexes,[21] a cycle for benzene dehydrosilylation was proposed (Scheme 1). This proposed three-step cycle would involve (1) a C−H bond activation reaction by a metal hydrosilyl complex, (2) the transfer of an organic group from the transition metal center to silicon, and (3) the dehydrocoupling of M−H and Si−H bonds to reform the metal hydrosilyl complex. Precedent for silicon−carbon bond formation (step 2) is provided by stoichiometric reactions of hydrosilanes with hydrocarbyl complexes of d^0 and f^nd^0 metals,[22] and this step

Scheme 1. General Catalytic Cycle for the Dehydrosilation of Hydrocarbons



has been proposed for olefin hydrosilations catalyzed by Group 3 and lanthanide complexes.[18] Dehydrocouplings of M−H (M = Zr, Hf, Y, Sm, Lu) and Si−H bonds to produce metal−silicon bonds (step 3) have also been established.[19,23,24] Unfortunately, $Cp_2Hf(\eta^2\text{-}SiHMes_2)(\mu\text{-}Me)B(C_6F_5)_3$ does not appear to be a suitable catalyst for arene dehydrosilation.[20,26]

A search for more reactive d^0 metal silyl complexes was prompted by the possibility that such complexes might activate C−H bonds and serve as catalysts for hydrocarbon dehydrosilation. In particular, scandium silyl complexes were suggested by the similar covalent radii of hafnium and scandium,[13a] as well as the isoelectronic relationship between complexes of the types Cp_2ScR and Cp_2HfR^+.[27] Additionally, complexes of the type Cp^*_2ScR (R = hydrido, alkyl) have been shown to be highly reactive toward the C−H bonds of hydrocarbons such as methane, benzene, and styrene.[13] A high reactivity for scandium−silicon bonded compounds was also suggested by the weaker nature of M−Si bonds in comparison to M−H and M−C bonded analogues (M = d^0 transition metal or f-element center).[28] Furthermore, M−Si bonds react more rapidly than M−C bonds in σ-bond metathesis reactions with silanes and hydrogen, and metal silyl species have been shown to participate in a number of catalytic cycles (e.g., those involving the dehydropolymerization of silanes).[23]

The few reported compounds containing a scandium−silicon bond are limited to the THF-stabilized complexes $Cp_2Sc(SiR_3)(THF)$ (SiR_3 = $Si(SiMe_3)_3$, Si^tBuPh_2, $SiPh_3$, and $Si(SiMe_3)_2Ph$).[29] Although these complexes are extremely reactive toward polar, unsaturated organic substrates such as CO, xylyl isocyanide, and CO_2, the only σ-bond metathesis process observed for them was in the reaction of $Cp_2Sc[Si(SiMe_3)_3](THF)$ with HC≡CPh to form the dimeric acetylide $[Cp_2ScC{\equiv}CPh]_2$.[29c] Given the rich reactivity associated with 14-electron Cp^*_2Sc-

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derivatives and the expected enhanced reactivity toward σ-bond metathesis for more coordinatively unsaturated complexes,[3] we focused initial efforts on the synthesis of base-free silyl complexes of the type Cp*$_2$ScSiR$_3$. As described herein, complexes of this type may be prepared by reactions of Cp*$_2$ScMe (**1**) with certain hydrosilanes. Related σ-bond metathesis reactions in this system have been investigated, including the more commonly observed alkyl transfer from the metal to silicon, which occurs for many primary and secondary silanes. Finally, σ-bond metathesis reactions of the new scandium hydrosilyl complexes with benzene and methane have been investigated. On the basis of these studies, we have developed a catalytic system for the dehydrosilation of hydrocarbons (eq 1) and describe its application in catalytic methane functionalization.[30]

$$\mathrm{R{-}H + H{-}SiR'_3 \xrightarrow{\text{catalyst}} R{-}SiR'_3 + H{-}H} \qquad (1)$$

Experimental Section

General. All manipulations were performed under an atmosphere of argon using Schlenk techniques and/or a glovebox. Dry, oxygen-free solvents were employed throughout. Removal of thiophenes from benzene and toluene was accomplished by washing each with H_2SO_4 and saturated $NaHCO_3$ followed by drying over $MgSO_4$. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, saturated $NaHCO_3$, and then the drying agent $MgSO_4$. All solvents were distilled from sodium benzophenone ketyl, with the exception of benzene-d_6 and cyclohexane-d_{12}, which were purified by vacuum distillation from Na/K alloy. The compounds Cp*$_2$ScCH$_3$ (**1**), Cp*$_2$ScH (**2**), Cp*$_2$ScPh (**3**) were prepared according to literature procedures.[13b] Silanes were prepared by reduction of the appropriate chlorosilane with $LiAlH_4$ or $LiAlD_4$. Elemental analyses were performed by the microanalytical laboratory at the University of California, Berkeley. Infrared spectra were recorded using a Mattson FTIR spectrometer at a resolution of 4 cm^{-1}. All NMR spectra were recorded at room temperature in benzene-d_6 unless otherwise noted, using a Bruker AMX-300 spectrometer at 300 MHz (^{1}H) or 75.5 MHz (^{13}C) or a Bruker AM-400 spectrometer at 400 MHz (^{1}H) or 377 MHz (^{19}F) and a Bruker DRX-500 at 500 MHz (^{1}H), 125 MHz (^{13}C), or 100 MHz (^{29}Si).

Cp*$_2$ScSiH$_2$Mes (4). Addition of neat MesSiH$_3$ (0.120 g, 0.81 mmol) to solid Cp*$_2$ScMe (0.049 g, 0.147 mmol) resulted in vigorous bubbling. The resulting bright yellow solid was washed with cold pentane (3 × 2 mL) to give 0.030 g of Cp*$_2$ScSiH$_2$Mes (0.065 mmol, 44.1%). The filtrate was cooled to −30 °C to provide **3** as a crystalline solid in 58.8% total yield. ^{1}H NMR (500 MHz): δ 6.99 (s, 2 H, C$_6$*H*$_2$Me$_3$), 4.35 (s, 2 H, SiH), 2.58 (s, 6 H, *o*-C$_6$H$_2$*Me*$_3$), 2.30 (s, 3 H, *p*-C$_6$H$_2$*Me*$_3$), 1.81 (s, 30 H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (125 MHz): δ 160.70 (*C*$_6$H$_2$Me$_3$), 143.98 (*C*$_6$H$_2$Me$_3$), 141.56 (*C*$_6$H$_2$Me$_3$), 135.83 (*C*$_6$H$_2$Me$_3$), 123.00 (*C*$_5$Me$_5$), 26.45 (*o*-C$_6$H$_2$*Me*$_3$), 21.71 (*p*-C$_6$H$_2$*Me*$_3$), 11.86 (C$_5$*Me*$_5$). ^{29}Si{^{1}H} NMR (99 MHz): δ −71.0 ($^1J_{SiH}$ = 135 Hz). IR (KBr, cm^{-1}): 2952 (s), 2908 (s), 2858 (s), 2014 (s), 1601 (w), 1487 (w), 1447 (m), 1378 (m), 1023 (w), 993 (w), 935 (m), 850 (w), 788 (m), 753 (w), 698 (s), 430 (m). Anal. Calcd for C$_{29}$H$_{43}$ScSi: C, 74.96; H, 9.33. Found: C, 74.98; H, 9.31. Mp 175−176 °C.

Cp*$_2$ScSiH$_2$Si(SiMe$_3$)$_3$ (6). Cp*$_2$ScMe (0.275 g, 0.832 mmol) and (Me$_3$Si)$_3$SiSiH$_3$ (0.237 g, 0.851 mmol) were separately dissolved in 15 mL of pentane. The solution of (Me$_3$Si)$_3$SiSiH$_3$ was added to the solution of Cp*$_2$ScMe, producing a bright yellow solution over 20 min. The reaction solution was allowed to stand for 2 h and was then concentrated to 20 mL and cooled to −78 °C. Yellow crystals of Cp*$_2$ScSiH$_2$Si(SiMe$_3$)$_3$ were isolated by filtration (0.341 g, 0.574 mmol, 69%). ^{1}H NMR (500 MHz): δ 2.91 (s, 2 H, Si*H*$_2$Si(SiMe$_3$)$_3$, $^1J_{SiH}$ = 124 Hz), 1.88 (s, 30 H, C$_5$Me$_5$), 0.543 (s, 27 H, SiH$_2$Si(Si*Me*$_3$)$_3$). ^{13}C{^{1}H} NMR: δ 123.56 (*C*$_5$Me$_5$), 12.71 (C$_5$*Me*$_5$), 3.66 [Si(Si*Me*$_3$)$_3$]. ^{29}Si{^{1}H} NMR: δ −8.28 [SiH$_2$Si(*Si*Me$_3$)$_3$], 124.48 [*Si*H$_2$Si(SiMe$_3$)$_3$]. IR (KBr, cm^{-1}): 2949 (s), 2897 (s), 2023 (m), 1439 (w), 1381 (w), 1240 (s), 941 (m), 833 (s), 685 (m), 623 (m), 430 (m). Anal. Calcd for C$_{29}$H$_{59}$ScSi$_5$: C, 58.72; H, 10.03. Found: C, 58.82; H, 10.09. Mp 146.5−149 °C.

Cp*$_2$ScSiH$_2$SiPh$_3$ (7). To a 100-mL Schlenk flask containing Cp*$_2$ScMe (0.240 g, 0.726 mmol) and Ph$_3$SiSiH$_3$ (0.212 g, 0.731 mmol) was added ca. 20 mL of pentane. Toluene (40 mL) was added to the slurry to dissolve all the solids. The resulting yellow solution was filtered, concentrated to 10 mL, and cooled to −30 °C. A yellow microcrystalline solid was isolated, washed with pentane, and dried in vacuo, to yield 0.242 g of **7** (0.401 mmol, 55.2%). ^{1}H NMR (500 MHz): δ 7.94 (d, 6 H, Ph), 7.26 (t, 6 H, Ph), 7.23 (m, 3 H, Ph), 3.47 (s, 2 H, SiH, $^1J_{SiH}$ = 128 Hz), 1.77 (s, 30 H, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (125 MHz): δ 141.33 (C$_6$H$_5$), 137.31 (C$_6$H$_5$), 128.93 (C$_6$H$_5$), 128.67 (C$_6$H$_5$), 123.74 (*C*$_5$Me$_5$), 12.40 (C$_5$*Me*$_5$). ^{29}Si{^{1}H} NMR (99 MHz): δ −3.75 (SiH$_2$*Si*Ph$_3$), −113.83 (*Si*H$_2$SiPh$_3$). IR (KBr, cm^{-1}): 3064 (w), 2960 (w), 2902 (m), 2856 (w), 2031 (m), 2021 (m), 1427 (m), 1261 (w), 1095 (s), 1024 (m) 935 (m), 700 (s), 517 (m). Anal. Calcd for C$_{38}$H$_{47}$ScSi$_2$: C, 75.34; H, 7.83. Found: C, 75.58; H, 7.97. Mp 175−176 °C.

Cp*$_2$ScSiH(SiMe$_3$)$_2$ (8). A pentane solution of (Me$_3$Si)$_2$SiH$_2$ (0.27 g, 1.53 mmol, ca. 10 mL total volume) was added to Cp*$_2$ScMe (0.339 g, 1.02 mmol) dissolved in 20 mL of pentane. The resulting solution turned pale green over 1 h. The solution was concentrated until the green color intensified and was then cooled to −30 °C. An analytically pure solid precipitated from solution, yielding 0.266 g of Cp*$_2$ScSiH(SiMe$_3$)$_2$ (0.543 mmol, 52.2%). ^{1}H NMR (500 MHz): δ 2.53 (s, 1 H, SiH, $^1J_{SiH}$ = 115 Hz), 1.87 (s, 15 H, C$_5$Me$_5$), 1.86 (s, 15 H, C$_5$Me$_5$), 0.54 (s, 18 H, SiMe$_3$). ^{13}C{^{1}H} NMR (100 MHz): δ 123.65 (*C*$_5$Me$_5$), 123.28 (*C*$_5$Me$_5$), 12.75 (C$_5$*Me*$_5$), 12.63 (C$_5$*Me*$_5$), 5.94 (SiMe$_3$). ^{29}Si{^{1}H} NMR (100 MHz): δ −6.41 (SiMe$_3$), −108.23 (SiH). IR (KBr, cm^{-1}): 2941 (s), 2906 (s), 2006 (m), 1439 (w), 1381 (w), 1236 (s), 1024 (w), 829 (s), 754 (w), 679 (m), 615 (m), 426 (m). Anal. Calcd for C$_{26}$H$_{49}$ScSi$_3$: C, 63.62; H, 10.06. Found: C, 63.93; H, 9.95. Mp 163−166 °C.

Methane Dehydrosilation Catalysis. A cyclohexane solution of Cp*$_2$ScMe (**1**) or Cp*$_2$ScH (**2**), Ph$_2$SiH$_2$ (5−20 equiv), and a cyclooctane standard were placed in a glass liner, which was placed in a Parr high-pressure vessel. The Parr vessel was charged with methane (ca. 150 atm) and heated to 80 °C in a constant temperature oil bath for 1−7 days. The reaction mixture was allowed to cool, and the vessel was slowly vented. The cyclohexane solution was quenched with H_2O and filtered through Celite. The amount of Ph$_2$MeSiH formed was determined using a Hewlett-Packard 6890 Series gas chromatograph.

Kinetic Measurements. Reactions were monitored by ^{1}H NMR spectroscopy, with a Bruker DRX500 spectrometer, using 5-mm Wilmad NMR tubes. The samples prepared by dissolution of **1** in toluene-d_8 containing a known concentration of C_8H_{16} standard were cooled to −78 °C followed by addition of the silane via a syringe. The NMR tube was quickly placed in the probe, which was precooled to the required temperature. The probe temperature was calibrated using a neat methanol sample and was monitored with a thermocouple. Single scan spectra were acquired automatically at preset time intervals. The peaks were integrated relative to cyclooctane as an internal standard. Rate constants were obtained by nonweighted linear least-squares fit of the integrated second-order rate law, $\ln\{[\mathrm{Ph_2SiH_2}]_t/[\mathbf{1}]\} = \ln\{[\mathrm{Ph_2SiH_2}]_0/[\mathbf{1}]_0\} + k\Delta_0 t$.

Results and Discussion

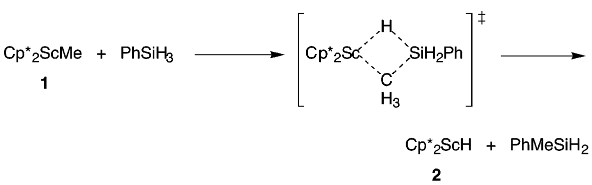
Initial attempts to synthesize compounds of the type Cp*$_2$ScSiR$_3$ involved salt metathesis reactions under conditions analogous to those used for the syntheses of Cp$_2$Sc(SiR$_3$)THF

(30) Sadow, A. D.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 803−805.

complexes.[29] Cp^*_2ScCl was treated with the silyl anion reagents $(THF)_3LiSi(SiMe_3)_3$,[31a] $KSi(SiMe_3)_3$,[31b] $(THF)_3LiSiPh_3$,[31c] $(THF)_3LiSi^tBuPh_2$,[29] or $(THF)_{2.5}LiSiMes_2H$[31d] (Mes = 2,4,6-$Me_3C_6H_2$) in both benzene-d_6 and THF-d_8. However, at room temperature no reactions occurred, and extended reaction times (>1 day) and heating (~80 °C) yielded only $HSiR_3$ and unidentified scandium products. Presumably, unfavorable steric interactions between the Cp* ligands and the bulky tertiary silyl groups prevent the formation of stable compounds.

An alternative approach has precedent in a few reactions of lanthanide alkyl and hydride complexes with hydrosilanes, which produce metal silyl complexes with concurrent elimination of alkane or dihydrogen.[23−25] For example, the reaction of $(Me_3Si)_2SiH_2$ with $Cp^*_2SmCH(SiMe_3)_2$ gives $Cp^*_2SmSiH(SiMe_3)_2$ and $(Me_3Si)_2CH_2$.[24] However, this transformation proceeds via a mechanism involving hydrogenolysis of $Cp^*_2SmCH(SiMe_3)_2$ to Cp^*_2SmH and $(Me_3Si)_2CH_2$ followed by dehydrocoupling of the samarium hydride with $(Me_3Si)_2SiH_2$.[24] More commonly, early metal and lanthanide hydrocarbyl complexes react with silanes via carbon transfer to silicon and formation of Si−C and M−H bonds. For example, the reaction of $CpCp^*HfMe(\mu\text{-}Me)B(C_6F_5)_3$ with $PhSiH_3$ gives $PhMe_2SiH$ and the hafnium hydride $CpCp^*HfH(\mu\text{-}H)B(C_6F_5)_3$.[21]

Reactions of Cp^*_2ScMe (1) with Primary and Secondary Hydrosilanes to Produce Si−C Bonds. Reactions of **1** with unhindered primary silanes ($PhSiH_3$, $C_6H_{11}SiH_3$, *p*-$MeC_6H_4SiH_3$, 3,5-$Me_2C_6H_3SiH_3$, SiH_4, $MeSiH_3$) and small secondary silanes (Ph_2SiH_2, $PhMeSiH_2$, Me_2SiH_2, Et_2SiH_2) yield **2** and the products of Si−C bond formation ($RMeSiH_2$ or R_2MeSiH, respectively). For example, the addition of $PhSiH_3$ (1 equiv, 2 h, room temperature) to a benzene-d_6 solution of **1** produced a yellow solution containing $PhMeSiH_2$ and the scandium hydride **2** (eq 2). A ^1H NMR spectrum of the reaction mixture indicated



(2)

that several minor products also formed, including $Cp^*_2ScPh\text{-}d_5$ (**3**-d_5) and CH_4 (ca. 10% relative to $PhMeSiH_2$). Complex **3**-d_5 presumably forms via the metalation of benzene-d_6 by **2**.[13] Methane may form as a byproduct in the direct reaction of **1** and $PhSiH_3$ to yield the scandium silyl complex $Cp^*_2ScSiH_2Ph$. Additionally, the yellow-colored reaction solution suggests the presence of $Cp^*_2ScSiH_2Ph$, since isolated scandium silyl complexes are similarly colored (vide infra). Unfortunately, the ^1H NMR spectrum is complicated by rapid ScH/SiH exchange that broadens and obscures the SiH resonances of $PhSiH_3$, $PhMeSiH_2$, and the putative $Cp^*_2ScSiH_2Ph$. Although this silyl complex could not be isolated, its formation is suggested by related reactions of **1** with hindered primary silanes which yield isolable scandium silyl complexes (vide infra).

Under pseudo-first-order conditions (5−15 equiv; −81 to −35 °C, in toluene-d_8), the reaction between **1** and Ph_2SiH_2 quantitatively produced **2** and Ph_2MeSiH. Linear plots of $\ln\{[\mathbf{1}]_0/[\mathbf{1}]\}$ vs time indicated that the reaction is first-order in **1**. A plot of k_{obs} vs $[Ph_2SiH_2]$ yielded a straight line that intercepted the *x*-axis at the origin, demonstrating that the reaction is also first-order in Ph_2SiH_2 and that only one pathway is operative. The resulting rate law, rate = $k[\mathbf{1}][Ph_2SiH_2]$, is consistent with a mechanism in which the alkyl group is transferred to silicon in a single, concerted step. The slopes of second-order plots of $\ln\{[Ph_2SiH_2]/[\mathbf{1}]\}$ vs time were used to determine the second-order rate constants (e.g., $k = 6.78(6) \times 10^{-5}$ M^{-1} s^{-1}, −81 °C; $k = 2.24(6) \times 10^{-4}$ M^{-1} s^{-1}, −67 °C; $k = 2.07(6) \times 10^{-3}$ M^{-1} s^{-1}, −36 °C).[32]

For the reaction of **1** with Ph_2SiH_2, a primary kinetic isotope effect of $k_H/k_D = 1.15(5)$ was determined by measuring rates for the reaction with Ph_2SiD_2. This small isotope effect is consistent with an early transition state in which the Si−H(D) bond is not significantly broken. The activation parameters, determined from plots of $\ln(k/T)$ vs $1/T$ over a temperature range of −80 °C to −35 °C, are $\Delta H^\ddagger = 6.66(2)$ kcal/mol and $\Delta S^\ddagger = -42.5(7)$ eu.[32] The low enthalpy of activation indicates that bond cleavage represents a minor component of the reaction barrier, and that loss of translational entropy contributes substantially to the overall activation energy.

The α-agostic SiH interaction in $Cp_2Hf(\eta^2\text{-}SiHMes_2)(\mu\text{-}Me)B(C_6F_5)_3$ appears to activate the Hf−Si bond toward cleavage of the C−H bonds of arenes. In this system, the rates of reaction of benzene with $Cp_2Hf(\eta^2\text{-}SiHMes_2)^+$ and $Cp_2Hf(\eta^2\text{-}SiDMes_2)^+$ are identical [$k_H/k_D = 1.1(1)$],[20] implying that the agostic interaction is maintained throughout the C−H activation process. Compound **1** does not have an α-agostic ground-state structure,[13] but α-agostic assistance in the transition state of its reaction with Ph_2SiH_2 seemed possible. The secondary isotope effect was therefore determined by measuring the rates of reaction for $Cp^*_2ScCD_3$ and $Cp^*_2ScCH_3$. The small value observed ($k_H/k_D = 0.91(5)$ per H) suggests that α-agostic assistance does not play a significant role in this σ-bond metathesis reaction.

The reaction of **1** with Ph_2SiH_2, involving the transfer of a methyl group from scandium to silicon, is relevant to the catalytic dehydrosilation of methane, as discussed below. In addition, the apparent formation of scandium silyl complexes as minor products in reactions of **1** with unhindered primary silanes suggested that via modification of the reaction conditions, it might be possible to produce significant quantities of scandium silyl complexes.

Reactions of Cp^*_2ScMe (1) with Hindered Primary Silanes to Produce Scandium Silyl Complexes. Surprisingly, the reaction of **1** with $MesSiH_3$ (1.2 equiv, cyclohexane-d_{12}, room temperature, 3 h; Mes = 2,4,6-$Me_3C_6H_2$) produced methane and a bright yellow solution of $Cp^*_2ScSiH_2Mes$ (**4**, eq 3).

$$\underset{\mathbf{1}}{Cp^*_2ScCH_3} + MesSiH_3 \xrightarrow{\text{cyclohexane-}d_{12}} \underset{\mathbf{4}}{Cp^*_2ScSiH_2Mes} + CH_4 \quad (3)$$

The ^1H NMR spectrum of **4** contains resonances corresponding to the SiH_2 (s, 3.83 ppm, 2 H), Cp*, and mesityl groups.

(31) (a) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1980**, *225*, 1−3. (b) Kayser, C.; Marschner, C. *Monatsh. Chem.* **1999**, *130*, 203−206. (c) Woo, H.-G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198−2205. (d) Roddick, D. M.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 324−330.

(32) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995; p 155.

Table 1. Spectroscopic Data for **4**, **6**−**8**, and the Respective Silanes

compound	δ (SiH)	$^1J_{SiH}$ (Hz)	^{29}Si{^{1}H} (α–Si) NMR	ν(SiH)
$MesSiH_3$	4.32	198	−77.61	2155
$Cp^*_2ScSiH_2Mes$ (**4**)	4.35	135	−72.00	2014
$(Me_3Si)_3SiSiH_3$	3.52	188	−99.20	2121
$Cp^*_2ScSiH_2Si(SiMe_3)_3$ (**6**)	3.47	128	−124.48	2023
Ph_3SiSiH_3	3.65	191	−99.02	2128
$Cp^*_2ScSiH_2SiPh_3$ (**7**)	2.90	124	−124.48	2031
$(Me_3Si)_2SiH_2$	3.01	166	−104.24	2089
$Cp^*_2ScSiH(SiMe_3)_2$ (**8**)	2.53	115	−108.23	2006

Addition of excess $MesSiH_3$ (2−5 equiv) to a pentane solution of **1**, followed by cooling to −30 °C produced **4** as a yellow powder in 44% yield. A series of dihydrosilylscandium complexes $Cp^*_2ScSiH_2R$ (R = Trip (**5**), $Si(SiMe_3)_3$ (**6**), $SiPh_3$ (**7**); Trip = 2,4,6-$^iPr_3C_6H_2$) were also synthesized via this methane elimination route. When fewer than 1.2 equiv of silane were used, the products were contaminated with small amounts of Cp^*_2ScH and $RMeSiH_2$. Compound **5** could not be isolated free of the excess $TripSiH_3$ starting material, but **4**, **6**, and **7** were purified by crystallization from pentane at −30 °C.

The SiH ^{1}H NMR resonances for the scandium silyl complexes are upfield-shifted vs those for the corresponding free silanes, and this is characteristic for hydrosilyl complexes of electropositive d^0 metals (Table 1).[29d,31d] The $^1J_{SiH}$ values (125−135 Hz) for **4**−**7** are lower than those for the corresponding free silanes (188−200 Hz) and related 16-electron hydrosilyl complexes of zirconium and hafnium (145−155 Hz)[23,31d] but similar to those observed for lanthanide hydrosilyl species.[18,25c] The possibility of an α-agostic SiH is suggested by the detection of a strong interaction of this type in the isoelectronic cationic hafnium complex $Cp_2Hf(\eta^2\text{-}SiHMes_2)(\mu\text{-}Me)B(C_6F_5)_3$ ($^1J_{SiH}$ = 57 Hz; ^{29}Si NMR δ = 158; ν(SiH) = 1414 cm^{-1}).[20] However, the SiH resonance in the ^{1}H NMR spectrum of **7**-d_1 (vide infra) is only slightly upfield-shifted (∼0.05 ppm) relative to the chemical shift for the SiH group in **7**.[13] These data suggest that the scandium silyl complexes **4**−**7** do not contain α-agostic interactions.

The proposed structure of **7** was confirmed by an X-ray crystallographic study (Figure 1; key bond lengths and angles are listed in Table 2, and crystallographic data are listed in Table 3). The Sc−Si1−Si2 (122.43(5)°) and the Sc−Si1−H bond angles (119(1)° and 113(1)°) are inconsistent with an α-agostic

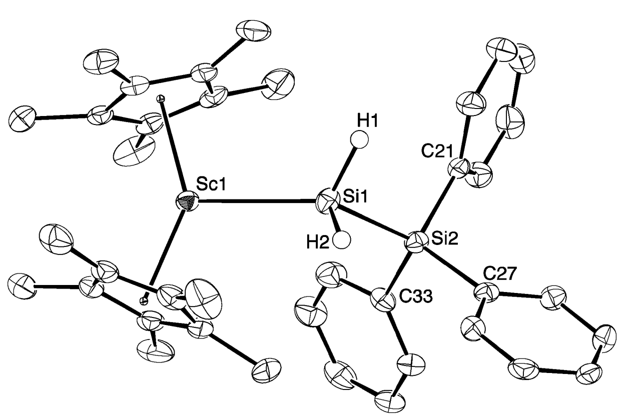


Figure 1. ORTEP diagram of $Cp^*_2ScSiH_2SiPh_3$ (**7**). The hydrogen atoms, with the exception of the two bonded to Si, were removed for clarity. Thermal ellipsoids were drawn to 50% probability.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Cp^*_2ScSiH_2SiPh_3$ (**7**)

Bond Distances			
Sc−Si1	2.797(1)	Si1−Si2	2.364(2)
Si1−H1	1.39(3)	Si1−H2	1.47(3)
Si2−C21	1.896(4)	Si2−C27	1.893(4)
Si2−C33	1.893(4)	Sc−Cp*$_{cent}$	2.1741(6)
Sc−Cp*$_{cent}$	2.1741(7)		
Bond Angles			
Sc−Si1−Si2	122.43(5)	Sc−Si1−H1	119(1)
Sc1−Si1−H2	113(1)	Si2−Si1−H1	98(1)
H1−Si1−H2	96(1)	Si2−Si1−H2	102(1)
Si1−Si2−C21	111.2(1)	Si1−Si2−C27	113.6(1)
Si1−Si2−C33	113.2(1)	Cp*$_{cent}$−Sc−Si1	107.99(3)
Cp*$_{cent}$−Sc−Si1	108.77(3)	Cp*$_{cent}$−Sc−Cp*$_{cent}$	142.96(4)

Table 3. Crystallographic Data for Compounds **7** and **8**

	7	8
empirical formula	$ScSi_2C_{38}H_{37}$	$ScSi_3C_{26}H_{49}$
formula weight	594.84	490.89
crystal color, habit	yellow, blocks	yellow, blocks
crystal size (mm)	0.23 × 0.23 × 0.15	0.30 × 0.21 × 0.16
crystal system	monoclinic	triclinic
space group	$P2_1/n$ (#14)	$P\bar{1}$(#2)
a (Å)	9.9125(8)	9.1426(6)
b (Å)	20.937(2)	10.4602(6)
c (Å)	16.232(1)	17.096(1)
α (deg)	90	94.074(1)
β (deg)	95.289	105.507(1)
γ (deg)	90	103.560(1)
V (Å^3)	3354.3(4)	1515.9(2)
orientation reflections: number, 2θ range (deg)	4204, 3.5−45.0	4330, 3.5−45.0
Z	4	2
D_{calc} (g/cm^3)	1.178	1.075
F_{000}	1256.00	536.00
μ (Mo Kα) (cm^{-1})	3.14	3.71
diffractometer	SMART	SMART
radiation	Mo Kα (λ = 0.710 69 Å) graphite monochromated	Mo Kα (λ = 0.710 69 Å) graphite monochromated
temperature (K)	135	132
scan type	ω (0.3° per frame)	ω (0.3° per frame)
scan rate	10.0 s per frame	10.0 s per frame
data collected, 2θ_{max} (deg)	49.4	49.4
reflections measured	total: 13104 unique: 5548	total: 7647 unique: 4799
R_{int}	0.044	0.036
transmission factors	T_{max} = 0.95 T_{min} = 0.51	T_{max} = 0.94 T_{min} = 0.42
structure solution	direct methods (SIR92)	direct methods (SIR92)
no. of observed data [$I > 3\sigma(I)$]	3349	3756
no. of parameters refined	376	269
reflections/parameter ratio	8.91	13.96
final residuals: R; R_w; R_{all}	0.046; 0.056; 0.081	0.065; 0.090; 0.082
goodness of fit indicator	1.54	2.39
max. shift/error final cycle	0.00	0.00
maximum and minimum peaks, final diff. map (e$^-$/Å^3)	0.36, −0.50	0.68, −0.58

structure (both α-hydrogens were located in the electron density map, and their (x,y,z) coordinates were refined). The Sc−Si1 bond distance (2.797(1) Å) is shorter than the corresponding bond length in the only other crystallographically characterized scandium silyl complex, $Cp_2Sc[Si(SiMe_3)_3](THF)$ (2.863(2) Å).[29c,d] The bond angles around the scandium center in **7** (Cp*$_{cent}$−Sc−Si1 = 107.99(3)°, 108.77(3)°; Cp*$_{cent}$−Sc−Cp*$_{cent}$ = 142.96(4)°) are similar to those reported for the 14-electron

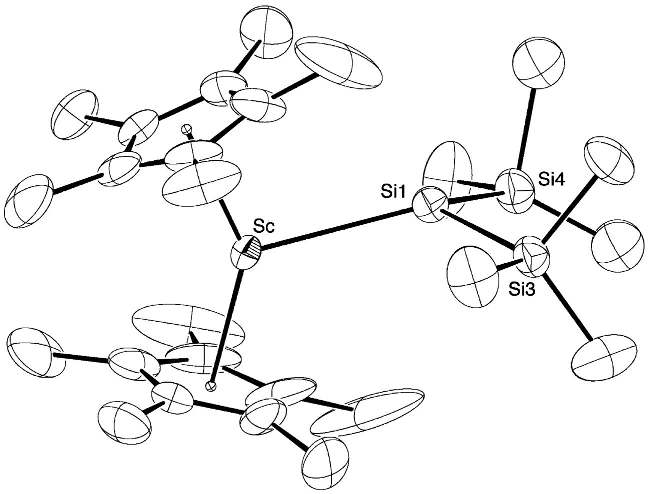


Figure 2. ORTEP diagram of $Cp^*_2ScSiH(SiMe_3)_2$ (**8**) illustrating the molecular connectivity. Hydrogen atoms and the other half of the disordered silyl ligand were omitted for clarity. Thermal ellipsoids are shown at 50% probability.

scandium methyl complex **1** ($Cp^*_{cent}-Sc-C = 108°$, $Cp^*_{cent}-Sc-Cp^*_{cent} = 144°$).[13]

The thermal stability of the silyl complexes follows the trend **4** < **5** ≪ **6** ≈ **7**. Compounds **6** and **7** are stable in the solid state at room temperature for >1 week, whereas **4** decomposed over 12 h. The decompositions are much more rapid for the aryl-substituted complexes (**4** and **5**; $t_{1/2} \approx 24$ h, room temperature). For **6** and **7**, the $t_{1/2}$ values for thermal decomposition are much greater than 1 week.

The reaction of Cp^*_2ScMe (**1**) with 1 equiv of $(Me_3Si)_2SiH_2$ (benzene-d_6, room temperature) yielded a 2:1 mixture of Cp^*_2ScPh-d_5 (**3**-d_5) and $Cp^*_2ScSiH(SiMe_3)_2$ (**8**). However, treatment of **1** with excess $(Me_3Si)_2SiH_2$ (pentane, room temperature) gave the scandium hydrosilyl complex $Cp^*_2ScSiH(SiMe_3)_2$ (**8**, eq 4) in 52% isolated yield.

$$\underset{\mathbf{1}}{Cp^*_2ScMe} + 2(Me_3Si)_2SiH_2 \xrightarrow{\text{pentane}} \underset{\mathbf{8}}{Cp^*_2ScSiH(SiMe_3)_2} + CH_4 + (Me_3Si)_2MeSiH \quad (4)$$

The ^1H NMR spectrum of **8** contains two Cp* resonances (1.87 and 1.85 ppm) and resonances corresponding to the $SiMe_3$ and SiH moieties (0.54 and 2.53 ppm, respectively). This spectrum indicates a structure with C_s symmetry and hindered rotation about the Sc−Si bond. Similar spectroscopic features were observed for the alkyl complexes $Cp^*_2LnCH(SiMe_3)_2$ (Ln = Y, La, Nd, Sm, Lu).[33] Interestingly, the lanthanide silyl complexes $Cp^*_2LnSiH(SiMe_3)_2$ (Ln = Y, Nd, Sm)[22a,24] exhibit equivalent Cp* and $SiMe_3$ groups at room temperature (by ^1H NMR spectroscopy). The structure of **8** was determined by X-ray crystallography (Figure 2). The structure is monomeric, the silicon bonded to scandium is pyramidal, and the two Cp* ligands are inequivalent. Unfortunately, the silicon was disordered over two locations (above and below the plane of the metallocene wedge), precluding meaningful discussion of bond distances and angles. In contrast to **8**, $Cp^*_2SmSiH(SiMe_3)_2$ is dimeric in the solid state.[24]

The more hindered secondary silane Mes_2SiH_2, and the corresponding germane Mes_2GeH_2, did not react with **1** in benzene-d_6 or cyclohexane-d_{12} at room temperature over 1 week. As in the absence of Mes_2SiH_2, heating cyclohexane-d_{12} solutions of Cp^*_2ScMe with Mes_2SiH_2 (80 °C, 2 days) resulted in the formation of $[Cp^*(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)Sc]_2$.

Mechanistic Experiments on the Formation of Scandium Silyl Complexes. Three possible mechanisms for the formation of scandium silyl compounds **4**−**7** are shown in Scheme 2. One pathway involves the direct interaction of **1** with the Si−H bond of a silane to produce a Sc−Si bond and methane. Related second-order processes have been observed for reactions of complexes of the type $Cp^*_2MCH_3$ (M = Sc, Lu, Y) with various hydrocarbons.[12,13] An alternative mechanism is suggested by mechanistic studies on reactions of $Cp^*_2MCH_3$ complexes with methane and benzene, which involve a first-order process in addition to the direct, second-order pathway.[12,13] An analogous pathway for the formation of scandium silyl complexes might involve reaction of the intermediate $[(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)ScCp^*]$ with hydrosilanes. A third possible mechanism involves the reaction of **1** with a catalytic amount of H_2 to form hydride complex **2** and methane. A subsequent dehydrocoupling reaction of the scandium hydride with the silane substrate $RSiH_3$ would then produce $Cp^*_2ScSiH_2R$ and H_2. An analogous chain reaction pathway was reported as the sole mechanism for the reaction of $Cp^*_2SmCH(SiMe_3)_2$ with $(Me_3Si)_2SiH_2$ to form $Cp^*_2SmSiH(SiMe_3)_2$.[24]

The possible role of a pathway involving metalation of a Cp* ligand was addressed with labeling experiments. Treatment of **1** with $MesSiD_3$ quantitatively yielded $Cp^*_2ScSiD_2Mes$ and CH_3D. Since no CH_4 (by ^1H NMR spectroscopy) was detected over the course of the reaction, we conclude that this mechanism is not operative. Unfortunately, deuterium labeling studies cannot distinguish between the direct, single-step reaction and a mechanism involving H_2 catalysis, because identically labeled products would be formed via either pathway (the silane is the source of H_2 in the latter mechanism). Attempts to determine a rate law for the reaction were unsuccessful, as plots of ln{[$MesSiH_3$]/[**1**]} vs time were not linear for three half-lives ($MesSiH_3$ present in >5-fold excess, cyclohexane-d_{12}, −47 °C). Note that the hydrogen-promoted mechanism (Scheme 2) can yield clean pseudo first- and second-order kinetics, as long as the total [metal hydride] + [H_2] concentration does not change over the course of the reaction.[24] Analysis of the ^1H NMR spectra of reactions of **1** with $MesSiH_3$, $TripSiH_3$, or $(Me_3Si)_3SiSiH_3$ revealed that the scandium hydride **2** was present, in each case, in small quantities (∼5%).

A chain reaction involving Cp^*_2ScH/H_2 could be initiated by the expected side reaction of **1** with $RSiH_3$, to form Cp^*_2ScH and $RMeSiH_2$ (vide supra). This H_2-mediated mechanism could occur only if **2** reacts directly with the silanes to form **4**−**7**, as was observed for the reaction of Cp^*_2SmH with $(Me_3Si)_2SiH_2$.[24] In fact, the reactions of **2** with $RSiH_3$ (R = Mes, $Si(SiMe_3)_3$) produced the corresponding scandium silyl complexes in low yield (ca. 10% by ^1H NMR spectroscopy, vida infra). When the reactions of **1** with 1 equiv of $RSiH_3$ (R = Mes, Trip, $(Me_3Si)_3Si$, Ph_3Si) occurred in the presence of a hydride trapping agent (benzene-d_6, which rapidly reacts with **2** to form **3**-d_5 [13]), the amount of the trapped product (**3**-d_5) varied depending on the nature of the silane. Note that complex

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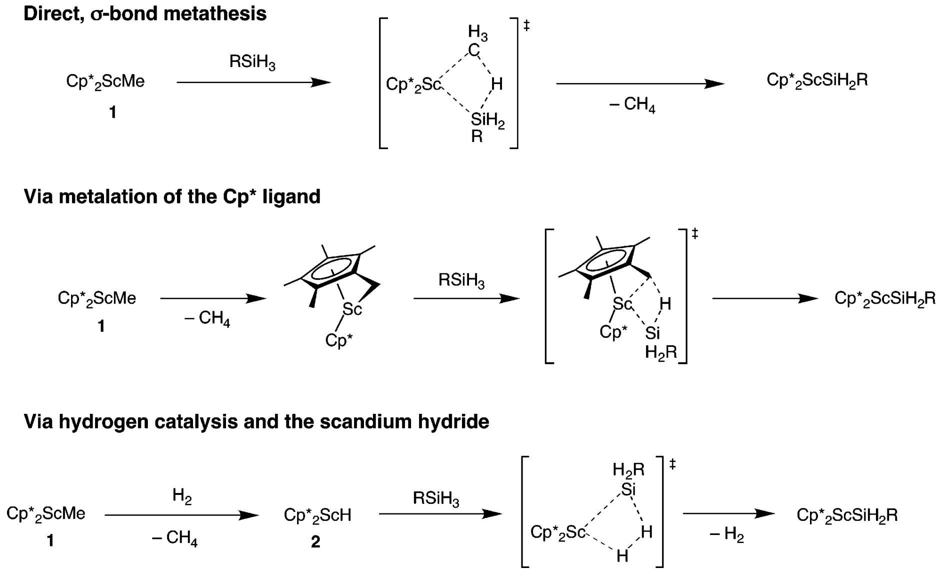
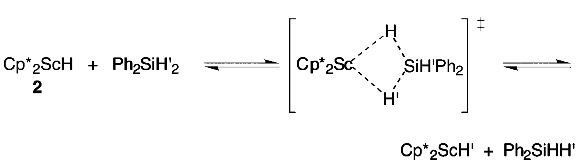
Scheme 2. Possible Mechanisms for Reaction of Cp*$_2$ScMe (**1**) with a Primary Silane



3 reacts much more slowly than **1** with the silanes $MesSiH_3$ and Ph_3SiSiH_3 (vide infra), and at room temperature the reaction between **1** and benzene is slow.[13] The addition of Ph_3SiSiH_3 to **1** (1 equiv, in benzene-d_6) produced **7** in quantitative yield (^{1}H NMR spectroscopy; $Ph_3SiSiMeH_2$, Cp*$_2$ScPh, and Cp*$_2$ScH were not detected). However, treatment of **1** with $(Me_3Si)_2SiH_2$ (in benzene-d_6) led to the formation of a substantial quantity of the scandium phenyl **3**-d_5 (along with $(Me_3Si)_2MeSiH$). The relative amounts of **3** formed in the reaction of **1** with silanes follows the trend: $Ph_3SiSiH_3 < (Me_3Si)_3SiSiH_3 < MesSiH_3 \approx TripSiH_3 < (Me_3Si)_2SiH_2$. Thus, for the secondary silane $(Me_3Si)_2SiH_2$ the pathway involving the scandium hydride intermediate appears to be important for the formation of the silyl complex **8**, whereas the direct interaction of **1** and Ph_3SiSiH_3 via the concerted, single-step reaction mechanism is probably responsible for the formation of **7**. Most likely, the reactions of **1** with $MesSiH_3$, $TripSiH_3$, and $(Me_3Si)_3SiSiH_3$ involve both pathways.

Reactions of Cp*$_2$ScH (2) with Silanes. Given the potential role of hydride **2** in catalytic reactions involving hydrocarbons and silanes, and the possible intermediacy of **2** in the synthesis of scandium silyl complexes, reactions of **2** with hydrosilanes were investigated in detail. Hydrosilanes react rapidly with the scandium hydride **2** via ScH/SiH exchange (eq 5, H′ = H, D).



(5)

This process is rapid for primary and smaller secondary silanes at room temperature, as indicated by the presence of broad SiH resonances in ^{1}H NMR spectra. Within 24 h the SiH resonances disappear, presumably as a result of an H/D exchange process involving benzene-d_6. In the presence of **2**, the SiH resonances of bulky secondary silanes (Mes_2SiH_2 and $^tBu_2SiH_2$) and tertiary silanes ($HSiPh_3$, $HSiEt_3$, $HSiPhMe_2$, $HSiPh_2Me$) are sharp, and $^3J_{HH}$ coupling is observed at room temperature (for $HSiEt_3$, $HSiPhMe_2$, and $HSiPh_2Me$). However, within 4 days at room temperature the SiH resonances disappear, indicating that deuterium exchange occurs at a very slow rate.

Primary silanes containing bulky substituents (e.g., $MesSiH_3$, $(Me_3Si)_3SiSiH_3$, and Ph_3SiSiH_3) were observed to react with Cp*$_2$ScH to form the corresponding scandium silyl only upon removal of H_2 (cyclohexane-d_{12}; one freeze/pump/thaw cycle in a J. Young NMR tube rapidly gave the scandium silyl in ca. 10% yield at room temperature), but Si−Si dehydrocoupling was not observed (by ^{1}H NMR spectroscopy). The hindered secondary silane Mes_2SiH_2 did not react in the presence of **2** (cyclohexane-d_{12}, 1 week).

For less hindered silanes, the scandium hydride **2** slowly catalyzes redistribution via Si−C bond activation.[19,25] For example, over 1 week (80 °C, cyclohexane-d_{12}), the reaction of **2** with $PhSiH_3$ produced Ph_2SiH_2 (ca. 20% yield at 40% conversion of $PhSiH_3$, GC−MS). With $PhMeSiH_2$, the scandium hydride-catalyzed redistribution reactions exhibited an unusual selectivity for Si−CH_3 versus Si−C_6H_5 bond activation. Heating cyclohexane-d_{12} solutions (50 °C, 3 d) of $PhMeSiH_2$ and **2** yielded a mixture of $PhSiH_3$ and $PhMe_2SiH$ (ca. 30% each) in addition to the starting material $PhMeSiH_2$ (ca. 40%, by GC−MS); Ph_2SiH_2 was not observed in the reaction mixture. This selectivity for Si−CH_3 bond activation is likely due to steric factors. The silane Ph_2SiH_2 appears to interact with compound **2** only via the ScH/SiH exchange reaction, since after several days at room temperature $PhSiH_3$, Ph_3SiH, and oligosilanes were not detected by ^{1}H NMR spectroscopy (after H_2O quench) or GC−MS. In comparison to the rapid redistribution reaction of $PhSiH_3$ and Ph_2SiH_2 with early metal and lanthanide hydride catalysts (e.g., Cp*$_2$MH; M = Sm, Lu, Y, and [CpCp*HfH][$B(C_6F_5)_4$]),[19,21,25] the Cp*$_2$ScH-catalyzed redistribution of $PhSiH_3$ is slow.

Reactions of Cp*$_2$ScPh (3) with Hydrosilanes. The reactivity of **3** toward hydrosilanes was of interest for several reasons. First, it was thought that such reactions might provide an alternative route to scandium silyl complexes. Second, the transfer of a phenyl group from scandium to silicon represents a potentially important step in catalytic benzene dehydrosilations. In addition, this type of phenyl transfer would presumably be required for the scandium-catalyzed redistribution of phenylsilanes. Note that redistribution at silicon could compete with a benzene dehydrosilation, if coupled to Si−Ph bond activation by a Sc−H species.[19,21,25] However, the latter process appears to be very slow for Cp^*_2ScH (vide supra).

The scandium phenyl **3** reacted rapidly with excess $PhSiH_3$ (1.5−2 equiv, benzene-d_6, room temperature) to produce a bright yellow solution. The ^1H NMR spectrum of the reaction mixture after 5 min indicated that **3** had been completely consumed and that benzene had quantitatively formed. Interestingly, the major scandium product was Cp^*_2ScH (ca. 60%, eq 6).

$$\underset{\mathbf{3}}{Cp^*_2ScPh} + PhSiH_3 \rightarrow Ph{-}H + \underset{\mathbf{2}}{Cp^*_2ScH} + Ph_2SiH_2 \quad (6)$$

The yellow color of the reaction solution indicated that scandium silyl species were present, since the related scandium silyl complexes **4**−**7** exhibit this color. Indeed, the ^1H NMR spectrum contains a resonance at 4.08 ppm that is tentatively assigned to the SiH_2 group of $Cp^*_2ScSiH_2Ph$. Over 12 h, the SiH resonances of the complex disappeared, apparently as a result of H/D exchange with benzene-d_6. However, prior to complete deuteration, a 1:1:1 triplet corresponding to the SiH resonance of $Cp^*_2ScSiHDPh$ was detected (4.10 ppm). Note that this process was also observed for the related complex **7** (vide supra). After 2 days at room temperature, the reaction mixture contained only a small amount of Ph_2SiH_2 (ca. 5%, by GC−MS after an aqueous quench). Interestingly, PhH_2SiSiH_2Ph and other higher molecular weight dehydrocoupling products were not detected by GC−MS or ^1H NMR spectroscopy.

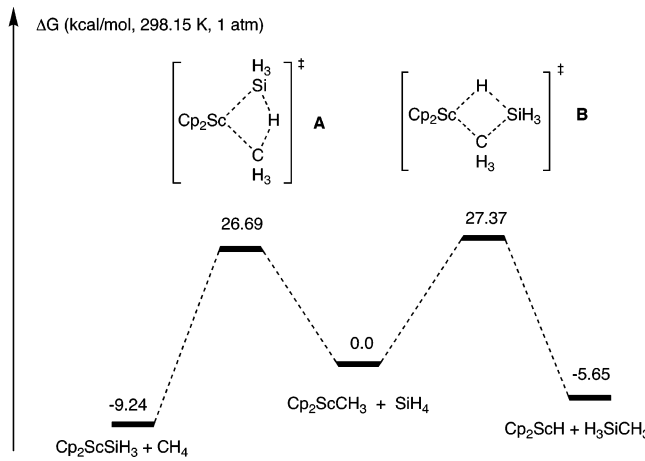
Complex **3** reacted with $MesSiH_3$ (1 equiv, in benzene-d_6, room temperature) to slowly form equivalent amounts of $Cp^*_2ScSiH_2Mes$ (**4**) and benzene ($t_{1/2}$ > 24 h, eq 7).

$$\underset{\mathbf{3}}{Cp^*_2ScPh} + MesSiH_3 \rightarrow \underset{\mathbf{4}}{Cp^*_2ScSiH_2Mes} + C_6H_6 \quad (7)$$

This transformation is reversible in the absence of excess $MesSiH_3$ (i.e., **4** and benzene react to give **3** and $MesSiH_3$, vide infra). Only a trace amount of $MesPhSiH_2$ was observed (<5%), which was identified by comparison of the ^1H NMR spectrum to that of an independently prepared sample (by reaction of $MesSiH_2Cl$ with PhLi). The reaction of **3** with $MesSiH_3$ is significantly slower than the corresponding reaction of **1**. Compound **3** did not react with Ph_2SiH_2 at room temperature over the course of 2 days (benzene-d_6). A ^1H NMR spectrum of a benzene-d_6 solution of **3** and Ph_2SiH_2 heated to 70 °C for several hours contained resonances due to the Cp* group of **3**-d_5 and benzene. Also, the SiH resonance of Ph_2SiH_2 disappeared due to deuterium incorporation from benzene-d_6.

Density Functional Theory (DFT) Calculations on Reactions of Cp_2ScCH_3 with Hydrosilanes. In the reactions of **1** with hydrosilanes, subtle factors appear to control the selectivity for Si−Me (and Sc−H) vs Me−H (and Sc−Si) bond formations. It is of interest to control this reactivity, since it currently offers the only route to 14-electron scandocene silyl complexes. Perhaps more importantly, control over the selectivity for alkyl transfer to silicon could allow the design of catalytic cycles for hydrocarbon dehydrosilations. With these considerations in mind, two primary pathways observed for the reaction of **1** with hydrosilanes (scandium−silicon and silicon−carbon bond formation) were modeled using density functional theory (DFT). Several groups have used computational methods, including extended Hückel MO analysis and DFT studies, to study σ-bond metathesis reactions of dihydrogen, hydrocarbons, and silanes with d^0 transition metal and lanthanide complexes.[34−37] These theoretical investigations implicate concerted transition states involving four-centered ($2\sigma + 2\sigma$) electrocyclic structures[35−37] but have not compared the barriers for the two pathways described above. Given the large number of atoms and variables associated with the Cp* ligand, model scandium species were based on the $(\eta^5\text{-}C_5H_5)_2Sc$ fragment. The geometric structures were minimized at the B3LYP/LACVP**++ level using the Jaguar 4.0 suite,[38−40] and the ground-state structures of Cp_2ScCH_3, Cp_2ScH, Cp_2ScSiH_3, $Cp_2ScSiH_2CH_3$, SiH_4, CH_4, H_2, H_3SiCH_3, and $H_2Si(CH_3)_2$ were verified by frequency calculations as containing exactly zero imaginary normal modes. All transition states contained exactly one imaginary frequency corresponding to a first-order saddle point on the potential energy surface. The electronic energies were adjusted for the zero-point energies (ZPE) and the Gibbs free energy (at 298.15 K) corrections obtained from the normal-mode analyses. The calculated values for entropy and enthalpy obtained from the frequency calculations indicate that entropic factors contribute significantly to the activation barriers.

Scheme 3. Density Functional Theory (DFT) Calculations of the Gas-Phase Gibbs Free Energies of the Two Pathways for the Reaction of Cp_2ScCH_3 with SiH_4[a]



[a] The sum of the energies of the reactants have been arbitrarily set to 0.0 kcal/mol.

The two pathways for the reaction of Cp_2ScCH_3 with SiH_4 are shown in Scheme 3, and the transition states for these pathways are illustrated in Figures 3 and 4. The sum of the energies of Cp_2ScCH_3 and SiH_4 (both electronic and Gibbs free energies) were set at 0.0 kcal/mol; the energies of the transition states and products are reported relative to this arbitrary level. The activation barrier for Sc−Si and Si−C bond formation in

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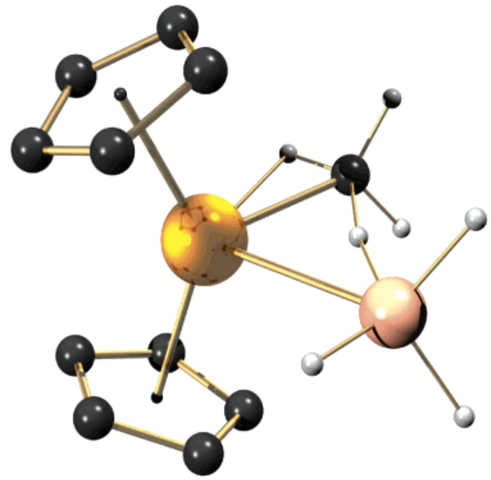


Figure 3. Rendered illustration of the DFT-optimized transition state structure (**A**) for the interaction of Cp_2ScCH_3 with SiH_4 which produces Cp_2ScSiH_3 and CH_4. The hydrogen atoms on the Cp rings were removed for clarity.

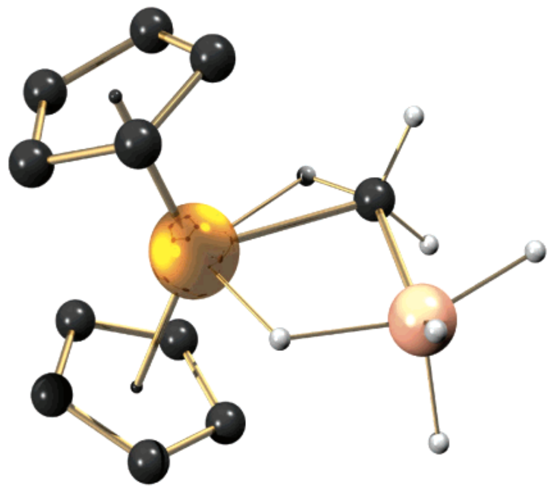


Figure 4. Rendered illustration of the DFT-optimized transition state structure (**B**) for the reaction of Cp_2ScCH_3 with SiH_4 to form Cp_2ScH and H_3CSiH_3. The hydrogen atoms on the Cp rings were removed for clarity.

this simplified system are remarkably similar ($\Delta G^{\ddagger} = 26.7$ and 27.4 kcal/mol, respectively; $\Delta E_{tot}{}^{\ddagger} = 14.0$ and 11.6 kcal/mol, respectively; E_{tot} = electronic energy). This similarity is consistent with the experimental results, which show that both types of reactions occur for **1** with relatively minor variations in the structure of the silane. Note that the experimental value for $\Delta G^{\ddagger}$ for the formation of Ph_2MeSiH from **1** and Ph_2SiH_2 is 19.3 kcal/mol (determined from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ at 298.15 K). The transition states shown in Figures 3 and 4 appear to involve coordination of an α-CH bond to the scandium center in an agostic fashion. However, a three-center two-electron α-agostic interaction should lengthen the coordinated C−H bond distance. Comparisons of the C−H bond lengths calculated for CH_4 (1.09 Å), Cp_2ScCH_3 (1.10 Å), the two nonbridging C−H bonds in transition states **A** and **B** ($[Cp_2ScCH_3{\cdot}SiH_4]^{\ddagger}$, $C-H_{terminal}$, 1.09 and 1.10 Å), and the bridged Sc···H···C structures ($C-H_{bridge}$ for **A** is 1.11 Å, **B** is 1.12 Å) suggest the short Sc···H distances (**A**, 2.41 Å; **B**, 2.15 Å) merely result from the geometric constraints imposed by a rigid, highly ordered transition state. The secondary kinetic isotope effect for the reaction of **1** and Ph_2SiH_2 (eq 2, $k_H/k_D = 0.91(5)$) is also consistent with a transition state that does not require α-agostic assistance.

To assess the potential importance of a chain reaction involving a scandium hydride intermediate, DFT methods were used to model this alternative two-step pathway (i.e., hydrogenolysis of Cp_2ScCH_3 and subsequent dehydrogenative metalation of SiH_4 by Cp_2ScH, eq 8).

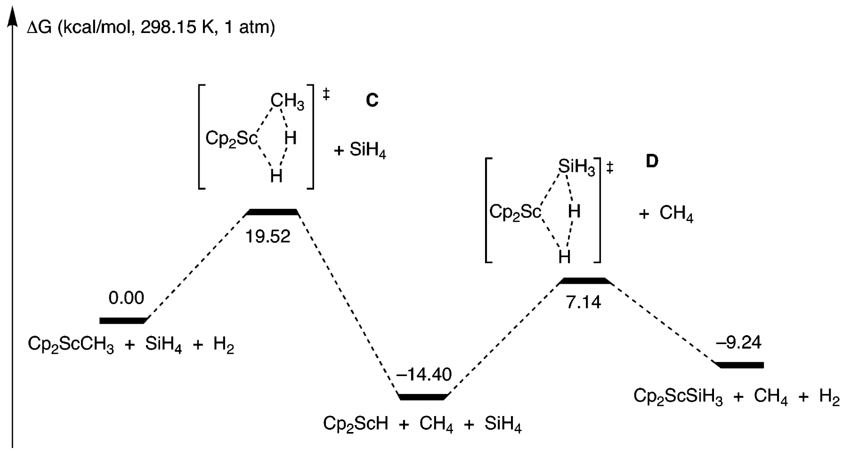
$$\mathrm{Cp2ScCH_3} \xrightarrow[-\mathrm{CH_4}]{\mathrm{H_2}} \mathrm{Cp_2ScH} \xrightarrow[-\mathrm{H_2}]{\mathrm{SiH_4}} \mathrm{Cp_2ScSiH_3} \qquad (8)$$

The sum of the reactant molecules' energies [$Cp_2ScCH_3 + SiH_4 + H_2$] were again set to 0 kcal/mol; all the transition states, intermediates, and product energies are reported relative to this arbitrary value (Scheme 4). As expected, hydrogenolysis of the Sc−C bond of Cp_2ScCH_3 is exothermic by 14.4 kcal/mol, while dehydrocoupling of Cp_2ScH and SiH_4 is endothermic by 5.1 kcal/mol. In contrast, the dehydrocoupling of Cp_2LaH and SiH_4 to Cp_2LaSiH_3 and H_2 was calculated to be exothermic by 4.7 kcal/mol.[37c] The energetic barriers for both steps of the sequence are lower than the barrier for the direct exchange reaction discussed above, indicating that such a pathway is possible for this ligand exchange reaction. The calculated $\Delta G^{\ddagger}$ for the hydrogenolysis of Cp_2ScCH_3 is 19.52 kcal/mol (transition state **C**), and the calculated activation barrier for the metalation of SiH_4 by Cp_2ScH is 21.54 kcal/mol (transition state **D**). Although the calculated activation barrier for this hydrogen-mediated process is lower than the barrier for the direct reaction of Cp_2-$ScCH_3$ with SiH_4, low concentrations of $Cp^*{}_2ScH$ or H_2 in the actual reaction mixture could easily cause the absolute rate of this process to be slower than the one-step pathway.

C−H Bond Activation Reactions of Benzene and Methane with $Cp^*{}_2ScSiH_2R$ Complexes. Given the possibility of productive hydrocarbon activations based on σ-bond metathesis (Scheme 1), we investigated the reactions of benzene and methane with scandium silyl complexes. The silyl complex **4** reacted slowly with benzene (as the solvent) to form the corresponding phenyl complex **3** and $MesSiH_3$ in ∼ 90% yield by ^1H NMR spectroscopy (room temperature, $t_{1/2} \approx 24$ h). Heating benzene-d_6 solutions of **4** at 65 °C produced **3**-d_5 in ca. 70% yield after 60 min (90% conversion by ^1H NMR spectroscopy). This reaction may occur via several mechanisms (Scheme 5) which are analogous to the pathways considered for formation of the scandium silyl compounds (vide supra, Scheme 2). The direct interaction of the scandium−silicon bond with a C−H bond of benzene, via a four-centered transition state, is suggested by an analogous benzene metalation by the isoelectronic hafnium hydrosilyl species, $Cp_2Hf(SiHMes_2)(\mu$-$Me)B(C_6F_5)_3$.[20] Also, **1** is known to react with benzene primarily via an analogous second-order reaction.[13] The second pathway, involving intramolecular Cp* activation and $MesSiH_3$ elimination as the first step, was proposed as a minor pathway for the reaction of benzene with **1**.[13] Finally, the possible participation of the hydride **2** is suggested by its formation in the thermal decomposition of **4** and by its direct reaction with benzene to form **3**.[13] There are several pathways by which **2** may form during the reaction of **4** with benzene, including reactions of **4** with H_2 or $MesSiH_3$, or with a second equivalent of **4**.[23]

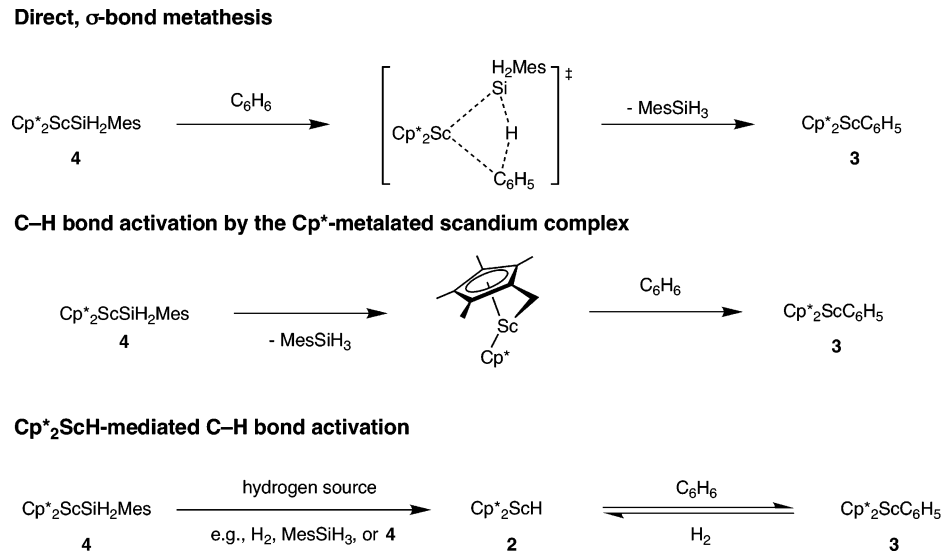
The ^1H NMR spectrum of the reaction mixture of **4** and benzene-d_6 indicated that the conversion of **4** to **3** is quite complicated. After 1 h at 65 °C this mixture contained the

Scheme 4. DFT Calculation of the H_2-Mediated Ligand Exchange Pathway[a]



[a] The sum of the energies of Cp_2ScCH_3, SiH_4, and H_2 has arbitrarily been set to 0.0 kcal/mol, and all of the products' eneriges are reported relative to the initial point. The barrier for the hydrogenolysis of Cp_2ScCH_3 is 19.52 kcal/mol, and the barrier for metalation of SiH_4 by Cp_2ScH is 21.54 kcal/mol.

Scheme 5. Possible Pathways for the Conversion of $Cp^*_2ScSiH_2Mes$ (**4**) to Cp^*_2ScPh (**3**)



starting material **4** (ca. 16% of total scandium present, determined via ^1H NMR spectroscopy by integration of Cp* peaks relative to a cyclooctane standard) and the products $MesSiH_3$-d_1, **3**-d_5 (ca. 70%), and **2**-d_1 (ca. 12%). The presence of the scandium hydride product complicates NMR analysis because the SiH resonances of any primary and unhindered secondary silanes are broadened and shifted by rapid ScH/SiH exchange processes. This exchange reaction, in conjunction with a slower H/D exchange process between benzene-d_6 and the Sc–H of **2**, results in deuteration of the hydrosilanes in the reaction mixture. A ^2H NMR spectrum indicates that $MesD_2SiSiD_2Mes$ (~5%) is a product of this reaction, but there is no evidence for (Cp*-d_x)$Cp^*ScC_6D_5$ in either the ^1H or ^2H NMR spectra. The absence of deuterium in the Cp* ligand rules out a pathway involving activation of a Cp* ligand.

Kinetic studies indicate that the conversion of **4** to **3** in benzene is approximately two times faster than the rate of this conversion in benzene-d_6. However, for the conversion of **4** to **3**, pseudo-first-order plots of $\ln\{[\mathbf{4}]_0/[\mathbf{4}]\}$ vs time are not linear. Plots of [Cp^*_2ScPh] vs time are S-shaped (Figure 5), resulting from an initially slow reaction which then speeds up (probably via catalysis). Although the initial rates for the reactions of benzene with **1** and **4** are similar (as determined from the initial slope of plots of ln[**4**] vs time), the overall reaction time for formation of **3** from the scandium silyl complex is much less than it is for reaction of the methyl complex (**1**) with benzene. Upon addition of small amounts of Ph_2SiH_2 to **4** in benzene-d_6 (~0.1 equiv) to generate trace amounts of **2** and initiate the hydride-mediated pathway, the overall rate of formation of **3** increased. Furthermore, the thermolysis of **4** in cyclohexane-d_{12} at 50 °C yielded Cp^*_2ScH in 95% yield ($t_{1/2} = 8.5$ h). Thus, the metalation of benzene by the scandium hydride intermediate appears to be the primary reaction pathway, although the direct reaction between **4** and benzene may occur during the early stages of the reaction.

Interestingly, $Cp^*_2ScSiH_2SiPh_3$ (**7**) reacted with benzene-d_6 at 65 °C to form $Cp^*_2ScSiHDSiPh_3$ (**7**-d_1) and $Cp^*_2ScSiD_2$-$SiPh_3$ (**7**-d_2) ($t_{1/2} = 24$ h for conversion to **7**-d_2) prior to formation of the scandium phenyl **3**. Only trace amounts of **3**-d_5 (<5%) and the scandium hydride **2** (<5%) were formed at this temperature after 24 h. As in the reaction of **4** with benzene, the rate of conversion of **7** to **7**-d_1 and **7**-d_2 increased as the reaction proceeded. Given the presence of trace amounts of **2**, this H/D exchange could proceed without cleavage of the scandium–silicon bond. Alternatively, the exchange might involve the reaction of benzene-d_6 with **7** to produce Ph_3-

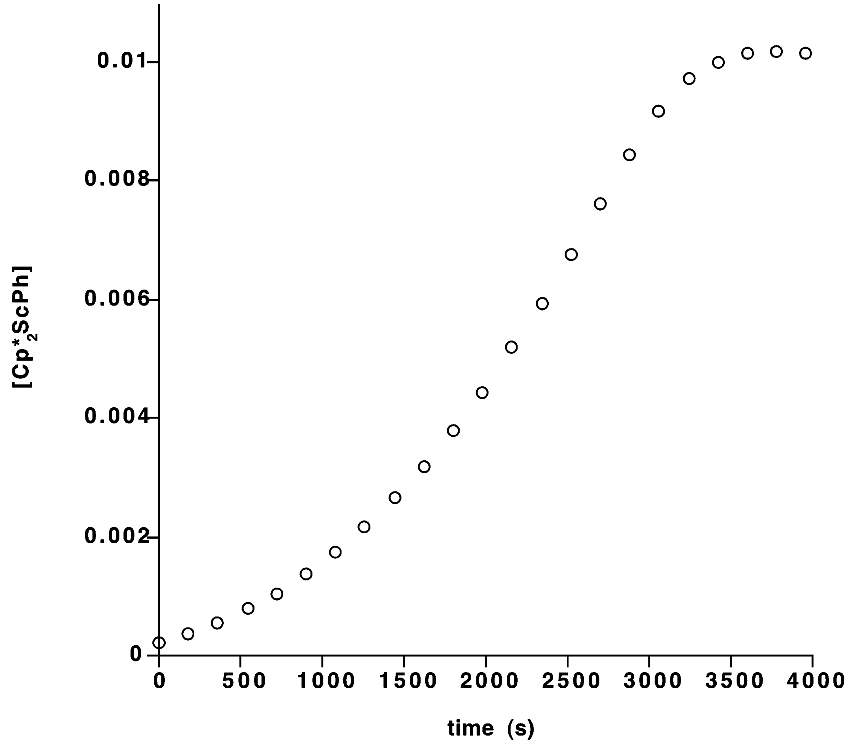


Figure 5. Plot of ln[**7**] vs time for the thermolysis of **3** in benzene-d_6. As the reaction proceeds, the slope of the curve becomes more steep, indicating an autocatalytic rate enhancement.

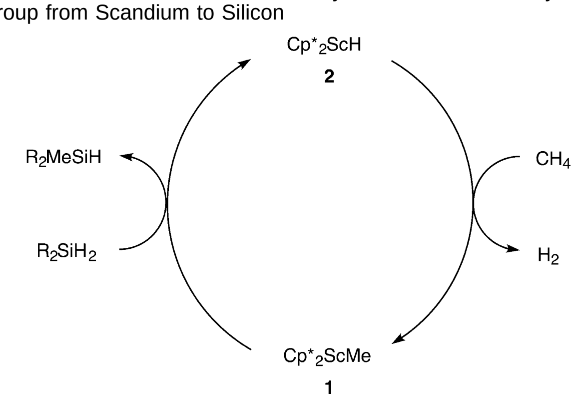
SiSiH$_2$D. Metalation of Ph$_3$SiSiHD−H with concurrent benzene-d_5 elimination would yield **7**-d_1. A third possibility involves scandium−silyl hydrogenolysis to form **2** and Ph$_3$SiSiH$_3$, followed by ScD/SiH exchange and then the dehydrocoupling of Ph$_3$SiSiHD−H with **2**.

The reaction of **4** with methane (ca. 7 atm, 14 equiv in solution) in cyclohexane-d_{12} occurred slowly at room temperature over 4 days to give MesSiH$_3$ and Mes(Me)SiH$_2$ (85% and 15%, respectively, by GC−MS), along with Cp*$_2$ScH (42%) as the major scandium-containing product (eq 9).

$$\underset{\mathbf{4}}{\mathrm{Cp^*_2ScSiH_2Mes}} + \mathrm{CH_4} \rightleftharpoons \underset{\mathbf{1}}{\mathrm{Cp^*_2ScCH_3}} + \mathrm{MesSiH_3} \rightleftharpoons \underset{\mathbf{2}}{\mathrm{Cp^*_2ScH}} + \mathrm{Mes(Me)SiH_2} \quad (9)$$

At intermediate stages of the reaction, the methyl complex **1** was observed in trace quantities. As described above, **1** reacted with MesSiH$_3$ to give **4** and CH$_4$ as the primary kinetic products. Taken together, these results indicate the existence of the coupled equilibria in eq 9, for which the thermodynamic products are Mes(Me)SiH$_2$ and **2**. However, just as in the metalation of benzene discussed above, it is unclear whether the C−H bond of methane is activated by **4** or **2**. It is noteworthy that unlike the reaction of **4** with methane, which produced small but detectable amounts of the scandium methyl complex **1**, the metalation of CH$_4$ by **2** to form **1** could not be directly observed. For example, heating cyclohexane-d_{12} solutions of **2** under 7−150 atm of CH$_4$ to 80 °C for 1−4 days, followed by release of the pressure, did not produce observable quantities of **1** (by ^{1}H NMR spectroscopy). However, a reaction between Cp*$_2$ScD and CH$_4$ is implied by the incorporation of deuterium into methane in the presence of excess D$_2$ or benzene-d_6.[13] Additionally, the mechanism of this exchange likely involves

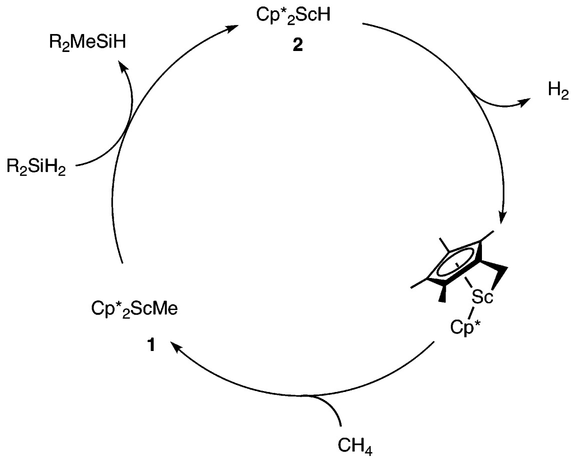
Scheme 6. A Possible Catalytic Cycle for Methane Dehydrosilation via the Metalation of Methane by Cp*$_2$ScH to Form **1** and Eliminate H$_2$, Followed by Transfer of the Methyl Group from Scandium to Silicon



metalation of CH$_4$ by **2** to form **1**. Subsequent reaction of **1** with D$_2$ would then produce CH$_3$D and **2**-d_1.

Catalytic Hydrocarbon Dehydrosilation. Several observations suggested that catalytic methane functionalization via dehydrosilation (eq 1, R = CH$_3$) might be possible with a Cp*$_2$Sc-derived catalyst. For example, the individual steps of the catalytic cycle of Scheme 1 (where R = CH$_3$) have been observed in the stoichiometric reactions of Cp*$_2$ScMe with silanes (Si−CH$_3$ bond formation), the dehydrocoupling of Cp*$_2$ScH with hydrosilanes (Sc−Si bond formation), and the reaction of Cp*$_2$ScSiH$_2$R with hydrocarbons (C−H bond activation). Additionally, C−H bond activations by **2** or (η^1:η^5-C$_5$Me$_4$CH$_2$)ScCp*[13] may participate in a catalytic cycle for hydrocarbon dehydrosilation. A cycle involving methane metalation by **2**, followed by methyl transfer, is shown in Scheme 6.[18e] A third catalytic cycle involves the addition of methane to the Cp*-metalated species (η^1:η^5-C$_5$Me$_4$CH$_2$)ScCp*, which appears to be involved in the activation of ^{13}CH$_4$ by **1** (Scheme 7).[13] The

Scheme 7. A Possible Catalytic Cycle for Methane Dehydrosilation by the Addition of CH_4 Across the Sc−C Bond of the Metalated Complex (η^1:η^5-$C_5Me_4CH_2$)ScCp*, Followed by Transfer of the Methyl Group to Silicon



successful development of catalytic hydrocarbon dehydrosilation via these cycles requires that possible dehydropolymerization and redistribution side reactions of the silanes do not occur. Significantly, the addition of Ph_2SiH_2 or $MesSiH_3$ to cyclohexane-d_{12} solutions of **2** did not lead to formation of dehydropolymerization and redistribution products at room temperature over several days (vide supra).

Cyclohexane-d_{12} solutions of **2** and various silanes (in a J. Young NMR tube) were frozen at −196 °C, and the headspace was evacuated and then replaced with 0.5 atm of CH_4. The solutions were carefully warmed to room temperature, shaken vigorously to dissolve the maximum amount of methane, and then heated to 50−80 °C. A cyclohexane-d_{12} solution of $Cp*_2ScH$ and Ph_2SiH_2 (10 equiv) reacted under ca. 7 atm of CH_4 in a J. Young tube at 80 °C to yield Ph_2MeSiH (by GC−MS and ^1H NMR spectroscopy) in substoichiometric quantities (∼0.4 equiv after 1 week). Although catalytic methane activation was not initially observed, all of the Ph_2MeSiH product was derived from methane. The reaction rate is dependent on methane concentration as demonstrated by the production of 5 equiv of Ph_2MeSiH when a cyclohexane solution of Ph_2SiH_2 and **1** was heated to 80 °C under 150 atm of methane (1 week, 1 equiv from **1**; eq 10).

$$Ph_2SiH_2 + 150\text{ atm } CH_4 \xrightarrow[C_6H_{12},\ 80\ °C,\ 7\text{ days}]{10\%\ Cp*_2ScMe} Ph_2MeSiH \quad (10)$$

Increasing the amount of Ph_2SiH_2 to 20 equiv did not substantially affect the rate of reaction, as the same amount of Ph_2MeSiH product (5 equiv) was observed after 1 week. These observations indicate that the rate-limiting step in the catalytic cycle is C−H bond activation.

Though the methane conversion is slow, the reaction is reasonably selective with 75% of the Ph_2SiH_2 consumed being converted to Ph_2MeSiH. It seems possible that some of the Ph_2SiH_2 was consumed by competitive Si−Ph hydrogenolysis[19,25] and silane dehydrocoupling,[17] but no other products were observed by GC after removal of the catalyst by an aqueous workup. Increasing the temperature to 100 °C decreased the amount of Ph_2MeSiH produced (<1 turnover, by ^1H NMR spectroscopy), apparently as a result of rapid decomposition of the $Cp*_2ScH$ catalyst at this temperature.

Initial mechanistic investigations of the methane dehydrosilation focused on determining the composition of the catalytic reaction mixture. Therefore, the reactions were monitored by ^1H NMR spectroscopy in sealed NMR tubes at low methane pressures (∼7 atm). Unfortunately, identification of the species responsible for C−H bond activation was complicated by the presence of several unidentified scandium species in addition to **2** in the reaction mixture. However, as the concentration of **2** decreased over the course of the reaction due to slow decomposition, the rate of formation of Ph_2MeSiH also decreased (as determined by ^1H NMR spectroscopy through integration relative to a cyclohexane standard). This apparent dependence of rate of product formation on the concentration of **2** suggests that it participates in the catalytic cycle. The pathway for the decomposition of **2** does not involve formation of the insoluble complex [μ-(η^1:η^5-$C_5Me_4CH_2$)ScCp*]$_2$,[13] since the reaction mixtures (cyclohexane-d_{12}, 7 atm of methane, 10 equiv of Ph_2SiH_2) were homogeneous for at least 1 week. Hydride **2** was stable at 80 °C in cyclohexane-d_{12} solution in the presence of 1.2 equiv of Ph_2MeSiH under 150 atm of methane for 4 days.

The mechanism of Si−C bond formation could proceed via a four-centered transition state in which a Sc-Me derivative reacts with Ph_2SiH_2 to yield $Cp*_2ScH$ and Ph_2MeSiH (methyl transfer) or by reaction of a scandium−silyl complex with methane (silyl transfer). The former mechanism is more attractive, since it does not require carbon to occupy the β-position of the four-centered transition state[16b] and since this transformation has been directly observed in the reaction of Ph_2SiH_2 with **1** (vide supra). In addition, the reaction of **4** with a large excess of methane as shown in eq 9 is significantly slower and less efficient than the reaction of **1** with Ph_2SiH_2. These observations lead us to favor methyl transfer from Sc to Si as the Si−C bond-forming step in the catalysis of eq 10. This would indicate that the other product of Si−CH_3 bond formation, $Cp*_2ScH$ (**2**), must be involved in the catalytic cycle.

Study of the methane activation step is complicated by the number of scandium species, including **2**, $Cp*_2ScSiHPh_2$, and (η^1:η^5-$C_5Me_4CH_2$)ScCp*, that might be involved. So far, it has not been possible to directly observe a stoichiometric C−H bond activation that could model this step. For example, attempts to directly observe the metalation of methane by $Cp*_2ScH$ have been unsuccessful, although this metalation is implied by deuteration of CH_4 catalyzed by **2**.[12] Furthermore, studies of the metalation of methane by $Cp*_2ScCH_2CMe_3$ have shown that this reaction is accelerated by the addition of $Cp*_2ScH$ (i.e., a hydride catalyst).[41] This result also implies that **2** reacts directly with CH_4 to form **1** and H_2. However, as suggested by investigations of equilibria between scandium hydride and scandium alkyl species,[42] the metalation of methane by **2** may be an equilibrium process which highly favors the scandium hydride and methane reactants over the products (eq 11). Furthermore, the reaction of $Cp*_2ScMe$ with H_2 is quite fast (the microscopic reverse of methane metalation).[13] In summary, the above observations suggest that the reaction of **2** with CH_4 produces a low equilibrium concentration of **1** (eq 11).

(41) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 7971−7977.
(42) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. *Polyhedron* **1988**, *7*, 1409−1428.

$$\underset{\mathbf{2}}{Cp^*_2ScH} + CH_4 \rightleftharpoons \underset{\mathbf{1}}{Cp^*_2ScMe} + H_2 \quad (11)$$

Methane activation by the Cp*-activated, monomeric species (η^1:η^5-$C_5Me_4CH_2$)ScCp* is suggested by studies of the C−H bond activations of methane and benzene by **1**, which revealed a methane activation process that is zero-order in methane and first-order in scandium.[13] Furthermore, metalation of the Cp* methyl groups is indicated by the rapid incorporation of deuterium into the Cp* methyl groups of **2** and **3** in the presence of benzene-d_6.[13] However, heating cyclohexane-d_{12} suspensions of [μ-(η^1:η^5-$C_5Me_4CH_2$)(η^5-Cp*)Sc]$_2$ with CH_4 (80 °C, 1 week) did not produce detectable quantities of **1** (by ^{1}H NMR spectroscopy), though the insolubility of the dimeric complex may hinder its reactivity.[13] Additionally, the putative species (η^1:η^5-$C_5Me_4CH_2$)ScCp* could not be detected in the catalytic reaction mixture or in reactions of **1** with benzene or methane (by ^{1}H NMR spectroscopy).[13]

A third possibility is that Cp*$_2$ScSiHPh$_2$ mediates the C−H bond activation, as suggested by reactions of isoelectronic Cp$_2$Hf(SiHMes$_2$)(μ-Me)B(C_6F_5)$_3$ with benzene and toluene.[20] In fact, reaction of the scandium silyl **3** with CH_4 produces small quantities of the methyl complex **1** and the methylsilane Mes(Me)SiH$_2$ (vide supra). However, Cp*$_2$ScSiHPh$_2$ could not be observed under the catalytic reaction conditions. All attempts to independently generate and characterize Cp*$_2$ScSiHPh$_2$ failed, including treatment of **3** with excess Ph$_2$SiH$_2$ (2−10 equiv, in benzene-d_6, cyclohexane-d_{12}) at room temperature over 1 week. Addition of neat Ph$_2$SiH$_2$ (10 equiv) to **1**, **2**, and **3**, followed by the addition of cyclohexane-d_{12}, also did not generate Cp*$_2$ScSiHPh$_2$ (by ^{1}H NMR spectroscopy). These reactions produced yellow solutions, but a scandium−silyl complex could not be observed by ^{1}H NMR spectroscopy.

Complex **2** also catalyzes the slow dehydrogenative silylation of other hydrocarbons. For example, the reaction of Ph$_2$SiH$_2$ (8 equiv) with isobutylene (18 equiv) in the presence of **2** produced the vinyl silane Ph$_2$(Me$_2$CCH)SiH (50 °C, ca. 2 turnovers after 20 days in cyclohexane-d_{12}). With PhSiH$_3$ and isobutylene, a mixture of hydrosilation (Me$_2$HCCH$_2$SiH$_2$Ph) and dehydrosilation (Me$_2$CCHSiH$_2$Ph) products were observed (3:2 ratio; cyclohexane-d_{12} solvent), as well as minor amounts of dehydrocoupling products. The scandium hydride complex also catalyzed the very slow dehydrocoupling of cyclopropane and Ph$_2$SiH$_2$ in cyclohexane-d_{12} at 80 °C (2.5 turnovers, 20 days). Hydride **2** reacts directly with cyclopropane and isobutylene to give the scandium complexes Cp*$_2$Sc^{c}Pr and Cp*$_2$ScCHCMe$_2$, respectively. These scandium complexes were also detected (by ^{1}H NMR spectroscopy) in the catalytic reaction mixtures. This observation suggests that the dehydrosilations of cyclopropane and isobutylene proceed via a two step mechanism involving hydrocarbon metalation by **2**, followed by organic group transfer to silicon. Interestingly, benzene is not a suitable substrate for this dehydrosilation process. Though the metalation of benzene by **2** occurs easily, stoichiometric reactions of Cp*$_2$ScPh (**3**) with hydrosilanes demonstrate that transfer of a phenyl group from scandium to silicon is not facile (see above). Thus, in this case, dehydrosilation is inhibited by slow phenyl transfer rather than by the C−H bond activation step.

Concluding Remarks

Reactions of Cp*$_2$ScR (R = hydrido, alkyl) derivatives with silanes proceed via pathways that are well established for early (d^0) transition metal and lanthanide complexes and include rapid MH/SiH exchange and metal-mediated Si−C bond formation (alkyl transfer). However, some aspects to this reactivity are unusual, such as the interaction of methyl complex **1** with certain silanes to produce methane and a Sc−Si bond. Also, it is noteworthy that although Cp*$_2$Sc derivatives are generally quite reactive in σ-bond metathesis processes, the hydride **2** is not an efficient catalyst for the dehydropolymerization or redistribution of silanes. These unusual selectivities appear to allow observation of the first catalytic methane dehydrosilation, which apparently involves only σ-bond metathesis steps. The mechanism of this catalysis appears to be analogous to those previously proposed for d^0 metal-catalyzed dehydropolymerizations of silanes[16b,17e] and stannanes,[43] as well as organosilane redistribution and hydrogenolysis reactions.[19,21,25]

As with several other d^0 transition metal and f-element hydride complexes,[17e,19,23,25] **2** reacts with silanes via relatively rapid ScH/SiH exchange. The rate of this process is very sensitive to steric factors. Thus, for primary and less hindered secondary silanes, the exchange is rapid and results in broad SiH resonances in ^{1}H NMR spectra of the reaction mixtures. Reactions between **2** and more hindered secondary silanes (Mes$_2$SiH$_2$ and ^{t}Bu$_2$SiH$_2$) and tertiary silanes (Et$_3$SiH, Ph$_3$SiH, and Ph$_2$MeSiH) are slow relative to the ^{1}H NMR time scale, as evidenced by sharp SiH resonances which slowly disappear due to deuterium incorporation from benzene-d_6. Similar results have been observed for the Group 4 hydrides CpCp*HfHCl and Cp*$_2$HfH$_2$ and for the lanthanide hydrides (Cp*$_2$LnH)$_2$ (Ln = Lu, Sm, Y).[17e,19,23,25] It was therefore somewhat surprising to observe that **2** exhibits unusually low activities toward the metalation, dehydrocoupling, and redistribution of hydrosilanes. For comparison, the isoelectronic Cp*$_2$LuH reacts rapidly with PhSiH$_3$ at room temperature to yield benzene and short polysilane chains,[19] and the complex Cp*$_2$SmH reacts with PhSiH$_3$ to form mixtures of Ph$_3$SiH, Ph$_2$SiH$_2$, and SiH$_4$.[25c] While these dehydrocoupling and redistribution reactions are catalyzed by **2**, they require forcing conditions (elevated temperatures or active removal of dihydrogen) and only occur with relatively unhindered silanes.

The reactions of Cp*$_2$ScMe (**1**) with RSiH$_3$ (R = Mes, Trip, SiPh$_3$, Si(SiMe$_3$)$_3$) are unusual in that d^0 transition metal and lanthanide alkyl complexes typically react with hydrosilanes to form Si−C bonds and metal hydride complexes. However, the lanthanide complexes Cp*$_2$LnR (Ln = Sm, R = Ph; Ln = Lu, R = Me) react with o-MeOC$_6$H$_4$SiH$_3$ to form the corresponding lanthanide silyl complex,[19,25c] and the reactions of Cp*$_2$LnCH(SiMe$_3$)$_2$ (Ln = Sm, Y, Nd) with (Me$_3$Si)$_2$SiH$_2$ also afford the corresponding lanthanide silyl complexes Cp*$_2$LnSiH(SiMe$_3$)$_2$.[22a] However, note that the latter reaction has been shown to proceed via hydrogenolysis of the Ln−C bond to form Cp*$_2$LnH, which then reacts with the silane (Me$_3$Si)$_2$SiH$_2$.[24]

The reactions of **1** and **2** with silanes and hydrocarbons provide a basis for the development of catalytic dehydrosilations. This reactivity has led to the first dehydrosilation of methane and one of the few examples of catalytic C−H bond activation via σ-bond metathesis.[15,41] Interestingly, although complexes of the type Cp*$_2$MR (M = Sc, Lu, Y; R = H, Me) react with

(43) (a) Imori, T.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1993**, 1607−1609. (b) Imori, T.; Lu, V.; Cai, H.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 9931−9940.

methane under mild conditions,[12,13] the scandium complexes are the least reactive of the series toward stoichiometric methane activation. Thus, more active catalysts might be based on other electrophilic, trivalent transition-metal or lanthanide centers. However, selectivities in the reactions of metal hydride and metal alkyl species with silanes is critical to the catalysis.

As mentioned previously, an important aspect of the chemistry of Cp^*_2ScH (**2**), which allows this complex to function as a catalyst for the dehydrosilation of methane, is its relatively low activity toward the dehydropolymerization and redistribution of silanes. In contrast, the activations of Si−Ph bonds by $(Cp^*_2LuH)_2$ and $(Cp^*_2SmH)_2$ in redistribution and hydrogenolysis processes are rapid.[19,25] Presumably, these trends reflect differences in the steric properties of the Cp^*_2Sc, Cp^*_2Lu, and Cp^*_2Sm fragments, as it is known that σ-bond metathesis reactions are highly sensitive to steric factors. Apparently, steric interactions in the Cp^*_2Sc system are significant enough to impact the selectivities in σ-bond metathesis but not severe enough to prohibit the reactions of interest. Thus **2** reacts with Ph_2SiH_2 via ScH/SiH exchange, and **1** reacts with Ph_2SiH_2 selectively by methyl transfer to silicon.

Although the hydrocarbon conversions reported here are slow and not yet synthetically useful, they suggest a new approach for the development of catalytic processes based on σ-bond metathesis. The search for more efficient processes of this type would be facilitated by a deeper understanding of the factors that influence selectivities. In this regard, the results reported here are promising in that they demonstrate that selectivities in σ-bond metathesis reactions may be readily manipulated via modest changes in the catalyst structure and in the nature of the substrates.

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Supporting Information Available: CIF files for the X-ray structures $Cp^*_2ScSiH_2SiPh_3$ (**6**) and $Cp^*_2ScSiH(SiMe_3)_2$ (**8**). This material is available free of charge via the Internet at http://pubs.acs.org.

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