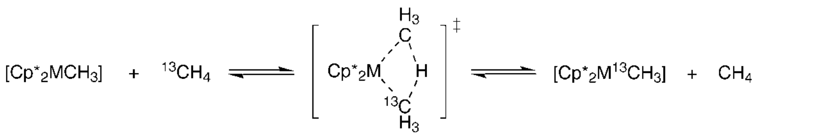
Catalytic Methane Activation

Catalytic Functionalization of Hydrocarbons by σ-Bond-Metathesis Chemistry: Dehydrosilylation of Methane with a Scandium Catalyst**

*Aaron D. Sadow and T. Don Tilley**

The selective, catalytic functionalization of saturated hydrocarbons represents one of the most important challenges in chemical research.[1] While some progress has been made,[2–5] there are very few processes which allow conversion of the cheapest and most abundant hydrocarbon, methane. A few homogeneous catalytic conversions of methane have been developed, but none of these are efficient enough to be employed in routine chemical syntheses. One type of homogeneous catalytic system, originally described by Shilov and co-workers,[1a] features a platinum-group-metal complex as the catalyst and converts methane into simple derivatives of the type MeX (X = Cl, OH, OSO_3H, O_2CCF_3) under acidic conditions.[1,3] Metal oxo complexes, such as $[NBu_4]VO_3$ with pyrazine-2-carboxylic acid and methane monooxygenase, have also been found to catalyze selective oxidations of methane with O_2 and/or peroxides in protic solvents to yield methanol or its derivatives.[4] Although several stoichiometric reactions of transition-metal complexes with methane are known,[1,5] this reactivity has not yet provided useful catalytic processes.

New approaches to the development of catalysts for methane conversion might involve σ-bond metathesis steps. Indeed, the first reports of stoichiometric, homogeneous methane activation, by $[Cp^*_2MMe]$ (M = Sc (**3**), Y, Lu; Cp* = η^5-C_5Me_5) complexes, suggest the reaction proceeds via such transition states [Eq. (1)].[6] Despite this early breakthrough involving the degenerate exchange of methyl groups, productive reactions of methane by σ-bond metathesis have not been reported. A possible limitation to the development of such processes (e.g., carbon–carbon coupling) is the apparent restriction that carbon cannot adopt the position β to the metal center in a four-centered transition state.[7] In contrast, a few catalytic processes involving d^0 (and f^nd^0) metal catalysts and silane substrates have been discovered (e.g., olefin hydrosilation and silane dehydropolymerization).[8,9] Mechanistic investigations indicate that this reactivity is possibly the result of the ability of silicon, unlike carbon, to adopt the β position of a four-centered transition state.[10]



(1)

The recent discovery of arene C–H activation by a cationic, hafnium silyl complex suggests that hydrocarbon conversions might be based on catalysts that possess highly reactive metal–silicon bonds [Eq. (2)].[11] The possibility that scandocene–silicon bonds might be highly reactive in this sense was suggested by the similarity between the electron

$$\text{R-H} + \text{H-SiR}'_3 \xrightarrow{\text{catalyst}} \text{R-SiR}'_3 + \text{H}_2 \qquad (2)$$

count and ionic radius of the metal center in the complexes $[Cp'_2HfSiR_3]^+$ and $[Cp'_2ScSiR_3]$,[12] and by the known ability of $[Cp^*_2Sc]$ derivatives to activate hydrocarbons by σ-bond metathesis.[6b]

Methods for the generation of d^0-metal–silicon bonds have involved σ-bond metathesis reactions of hydrosilanes with hydride or silyl derivatives.[10] However, d^0-metal alkyl derivatives generally react with hydrosilanes by alkyl transfer to silicon and formation of a metal hydride.[8,13] It was surprising, then, to discover that $[Cp^*_2ScMe]$ (**1**) reacted with 1.2 equivalents of $MesSiH_3$ (Mes = 2,4,6-$C_6H_2Me_3$) with elimination of methane to produce a bright-yellow solution of $[Cp^*_2ScSiH_2Mes]$ [**2**; 3 h, room temperature, $[D_{12}]$cyclohexane; Eq. (3)]. The competitive formation of $[Cp^*_2ScH]$ (**3**) and

$$\underset{\mathbf{1}}{[\text{Cp}^*_2\text{ScMe}]} + \text{MesSiH}_3 \xrightarrow{\text{C}_6\text{D}_{12}} \underset{\mathbf{2}}{[\text{Cp}^*_2\text{ScSiH}_2\text{Mes}]} + \text{CH}_4 \qquad (3)$$

$MesMeSiH_2$ (ca. 5 %) was also observed, but addition of a slight excess of $MesSiH_3$ converted the by-product **3** into **2** (an optimized preparation of **2** is given in the Experimental Section).

Complex **2** reacted in $[D_6]$benzene at 65 °C to form the scandium phenyl complex $[Cp^*_2ScC_6D_5]$ ($[D_5]$**4**; ca. 70 % after 60 min at 90 % conversion, by ^{1}H NMR spectroscopy). The primary by-product in this reaction is the hydride $[D_1]$**3** (ca. 12 % after 60 mins at 65 °C), which may form by reaction of a $[Cp^*_2ScR]$ species with hydrogen or $MesSiH_3$, or by the thermal decomposition of **2** ($t_{1/2}$ = 8.5 h at 50 °C in $[D_{12}]$cyclohexane; 95 % yield of **3**). A ^{2}H NMR spectrum of the reaction mixture (in $[D_6]$benzene) indicates that $MesSiD_3$ is the major silane product, but also reveals the presence of a trace amount (< 5 %) of the dehydrocoupling product $MesD_2SiSiD_2Mes$; there is no evidence for the formation of $[([D_n]Cp^*)_2ScC_6D_5]$. The conversion of **2** into the phenyl complex **4** in benzene is approximately two-times faster than it is in $[D_6]$benzene, which indicates that CH bond activation is involved in the rate-determining step. Plots of [**2**] versus time reveal that the reaction rate increases as the thermolysis proceeds, which suggests that a product or intermediate promotes the reaction. A reasonable mechanism

[*] Prof. T. D. Tilley, A. D. Sadow
Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720-1460 (USA)
Fax: (+1) 510-642-8940
E-mail: tilley@cchem.berkeley.edu

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for this reaction, involving hydrogen as a catalyst, is analogous to that proposed for the reaction of $[Cp^*_2SmCH(SiMe_3)_2]$ with $H_2Si(SiMe_3)_2$.[14]

Reaction of **2** with methane (14 equiv) in $[D_{12}]$cyclohexane occurred slowly at room temperature over four days to give $MesSiH_3$ and $MesMeSiH_2$ (85 % and 15 %, respectively, by GC-MS), and **3** (42 %) as the major scandium-containing product [Eq. (4)]. At intermediate stages of the reaction the methyl complex **1** was observed in trace quantities. As

$$\underset{\mathbf{2}}{[Cp^*_2ScSiH_2Mes]} + CH_4 \rightleftharpoons \underset{\mathbf{1}}{[Cp^*_2ScCH_3]} + MesSiH_3 \rightleftharpoons \underset{\mathbf{3}}{[Cp^*_2ScH]} + MesMeSiH_2 \quad (4)$$

described above, **1** reacted with $MesSiH_3$ to give **2** and CH_4 as the primary kinetic products. Taken together, these results indicate the existence of the coupled equilibria of Equation (4), for which the thermodynamic products are $MesMeSiH_2$ and the scandium hydride **3**. However, just as in the metalation of benzene discussed above, it is not clear whether the C–H activation step involves **2** or **3**.

The observed behavior of methane as a methylating reagent suggested that catalytic methane functionalization might be possible with the appropriate organosilane [Eq. (2)], where $RH = CH_4$). A screening of several silanes with the catalyst **3** revealed that Ph_2SiH_2 provided the best results in terms of the minimization of competitive side reactions (e.g., dehydrocoupling and redistribution). A mixture of **3** and 10 equivalents of Ph_2SiH_2 in $[D_{12}]$cyclohexane reacted under approximately 7 atm of CH_4 in a Young's tube at 80 °C to yield Ph_2MeSiH (by GC-MS and NMR spectroscopy) in substoichiometric quantities (ca. 0.4 equiv after 1 week). The reaction rate is dependent on methane concentration; heating a cyclohexane solution of Ph_2SiH_2 and **1** to 80 °C under 150 atm of methane produced five equivalents of Ph_2MeSiH after 1 week, one equivalent of which was derived directly from **1** [Eq. (5)]. Increasing the amount of added Ph_2SiH_2 to

$$Ph_2SiH_2 + 150\text{ atm } CH_4 \xrightarrow[C_6H_{12},\ 80\,°C,\ 7\text{ days}]{10\%\ \mathbf{1}} Ph_2MeSiH + H_2 \quad (5)$$

20 equivalents did not substantially affect the rate of reaction, as approximately five equivalents of Ph_2MeSiH were detected after a week in both cases. Apparently, 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 consumed Ph_2SiH_2 being converted into Ph_2MeSiH. It seems likely that some of the Ph_2SiH_2 reacts by competitive Si–Ph hydrogenolysis and silane dehydropolymerization, but no other products were detected by GC after the catalyst had been removed by an aqueous workup. Increasing the temperature to 100 °C decreased the amount of Ph_2MeSiH produced (< 1 turnover, by NMR spectroscopy), apparently as a result of rapid decomposition of the catalyst **3** at this temperature.

The composition of the catalytic reaction mixture was probed by ^1H NMR spectroscopy at low methane pressures (ca. 8 atm), but attempts to study the mechanism of the catalysis were complicated by the presence of several species in the reaction mixture. The solution remained homogeneous over the course of the reaction and precipitation of insoluble species, such as $[\{(\eta^1{:}\eta^5\text{-}C_5Me_4CH_2)(\eta^5\text{-}Cp^*)Sc\}_2]$,[6b] did not occur. As **3** was depleted over the course of the reaction (because of slow decomposition), the rate of formation of Ph_2MeSiH decreased, which suggests that **3** is involved in the catalytic cycle.

Mechanistic investigations of the catalytic functionalization of methane with Ph_2SiH_2 have thus far focused separately on the Si–C bond formation and C–H activation steps. 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 **3** and Ph_2MeSiH (methyl transfer), or by reaction of a scandium silyl species with methane (silyl transfer). The methylation of Ph_2SiH_2 by **1** to give Ph_2MeSiH and **3** in $[D_6]$benzene or $[D_{12}]$cyclohexane ($t_{1/2} \approx 45$ min at 25 °C) was readily observed; note the sharp contrast between this reaction and that of **1** with $MesSiH_3$, which produced methane and **2** (see above; [Eq. (2)]).[15] In contrast, the reaction of **2** with a large excess of methane was 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 outlined in Equation (5).

Attempts to directly detect the activation of methane by **3** have been unsuccessful. Heating $[D_{12}]$cyclohexane solutions of **3** under 7–150 atm of CH_4 to 80 °C for 4 days, followed by release of the pressure, did not produce observable quantities of **1** (by ^1H NMR spectroscopy). Note, however, that a reaction between $[Cp^*_2ScD]$ ($[D_1]$**3**) and CH_4 is implied by the observed incorporation of deuterium into methane in the presence of excess D_2 or $[D_6]$benzene.[6b] The possible participation of $[Cp^*_2ScSiHPh_2]$ (**5**) in methane activation is suggested by the observed reactions of isoelectronic $[Cp_2Hf(SiHMes_2)]^+$ ($Cp = \eta\text{-}C_5H_5$) with the C–H bonds of both benzene and toluene.[11] However, **5** could not be detected under catalytic conditions, and attempts to isolate it have failed.

The dehydrogenative silylation of other hydrocarbons can also be mediated by $[Cp^*_2Sc]$ derivatives. For example, the vinyl complex $[Cp^*_2ScCHCMe_2]$ slowly catalyzed the coupling of Ph_2SiH_2 (8 equiv) with isobutylene (18 equiv) at 50 °C to produce the vinyl silane $Ph_2(Me_2CCH)SiH$ (ca. 2 turnovers after 20 days in $[D_{12}]$cyclohexane).[6b] With $PhSiH_3$ and isobutylene, a mixture of hydrosilation ($Me_2HCCH_2SiH_2Ph$) and dehydrosilation ($Me_2CCHSiH_2Ph$) products (3:2 ratio; 3 turnovers, 2 days in $[D_{12}]$cyclohexane), as well as minor amounts of dehydrocoupling products, were observed. Compound **3** also catalyzed the dehydrocoupling of cyclopropane and Ph_2SiH_2 in $[D_{12}]$cyclohexane at 80 °C (2.5 turnovers, 20 days). Interestingly, benzene and pentane were not suitable substrates for this dehydrosilation process.

Herein we described a new approach for the selective, catalytic conversion of methane. The catalytic cycles reported (for hydrocarbon dehydrosilations) are believed to involve only σ-bond-metathesis steps. Such mechanisms are therefore quite analogous to those previously proposed for d^0-metal-

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catalyzed dehydropolymerizations of silanes and stannanes.[10,16] Jordan and Taylor have reported the 1,2-addition of a C–H bond of picoline to an olefin (hydroalkylation), which is catalyzed by a cationic d^0 bis(Cp) zirconium complex by a mechanism involving σ-bond metathesis and olefin insertion.[17] Dehydrogenative silation of terminal alkynes has been observed as a competitive process to hydrosilation.[18] Note that the ability of [Cp^*_2ScH] (**3**) to catalyze hydrocarbon dehydrosilation requires that competitive processes, such as silane polymerization and redistribution, are slow relative to C–H bond activation. This characteristic of the scandium system described here is unusual, and further investigations will address mechanistic issues related to this selectivity.

Experimental Section

All manipulations were performed either on a Schlenk line under an Ar atmosphere or in a N_2-filled drybox (M. Braun). All solvents and reagents were purified by standard procedures.

2: Neat $MesSiH_3$ (0.120 g, 0.798 mmol) was added to solid [Cp^*_2ScMe] (**1**; 0.0485 g, 0.1468 mmol). The bright-yellow solid which formed was washed with cold pentane (3 × 2 mL), yielding **2**. The washings were cooled to −30 °C from which additional compound could be isolated: yield 0.030 g, 44 %, m.p. 175 °C, elemental analysis: calcd (%) for $C_{29}H_{43}ScSi$: C 74.96, H 9.33; found: C 74.98, H 9.31; ^1H NMR (500 MHz, [D_6]Benzene, 25 °C, TMS): $\delta = 6.988$ (s, 2H, $C_6H_2Me_3$), 4.345 (s, 2H, SiH), 2.581 (s, 6H, o-$C_6H_2Me_3$), 2.295 (s, 3H, p-$C_6H_2Me_3$), 1.814 ppm (s, 30H, C_5Me_5); $^{13}C\{^1H\}$ NMR (125 MHz): $\delta = 160.70$ ($C_6H_2Me_3$), 143.98 ($C_6H_2Me_3$), 141.56 ($C_6H_2Me_3$), 135.83 ($C_6H_2Me_3$), 123.00 (C_5Me_5), 26.45 (o-$C_6H_2Me_3$), 21.71 (p-$C_6H_2Me_3$), 11.86 ppm (C_5Me_5); $^{29}Si\{^1H\}$ NMR (99 MHz): $\delta = -71.0$ ppm ($^1J_{SiH} =$ 135 Hz); IR (KBr): $\tilde{\nu} = 2014$ cm^{-1} (Si-H).

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[1] a) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507; b) R. H. Crabtree, *J. Chem. Soc. Dalton Trans.* **2001**, 2437; c) A. Sen, *Acc. Chem. Res.* **1998**, *31*, 550; d) S. S. Stahl, J. A. Labinger, J. E. Bercaw, *Angew. Chem.* **1998**, *110*, 2298; *Angew. Chem. Int. Ed.* **1998**, *37*, 2180; e) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879; f) B. A. Arndtsen, R. G. Bergman, T. A. Mobley, T. H. Peterson, *Acc. Chem. Res.* **1995**, *28*, 154.

[2] Some recent representative examples of catalytic hydrocarbon functionalizations: a) H. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, *Science* **2000**, *287*, 1995; b) J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka, M. R. Smith, *Science* **2002**, *295*, 305; c) C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura, Y. Fujiwara, *Science* **2000**, *287*, 1992; d) F. Liu, E. B. Pak, B. Singh, C. M. Jensen, A. S. Goldman, *J. Am. Chem. Soc.* **1999**, *121*, 4086.

[3] R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, *280*, 560.

[4] a) G. V. Nizova, G. Suss-Fink, G. B. Shul'pin, *Chem. Commun.* **1997**, 397; b) M. N. Vargaftik, I. P. Stolarov, I. I. Moiseev, *J. Chem. Soc. Chem. Commun.* **1990**, 1049; c) M. Merkx, D. A. Kopp, M. H. Sazinsky, J. L. Blazyk, J. Müller, S. J. Lippard, *Angew. Chem.* **2001**, *113*, 2860; *Angew. Chem. Int. Ed.* **2001**, *40*, 2782.

[5] R. H. Crabtree, *Chem. Rev.* **1995**, *95*, 987, and references therein.

[6] a) P. L. Watson, G. W. Parshall, *Acc. Chem. Res.* **1985**, *18*, 51; b) M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santarsiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 203; c) C. M. Fendrick, T. J. Marks, *J. Am. Chem. Soc.* **1986**, *108*, 425.

[7] W. E. Piers, P. J. Shapiro, E. E. Bunel, J. E. Bercaw, *Synlett* **1990**, 74.

[8] a) P.-F. Fu, L. Brard, Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1995**, *117*, 7157, and references therein; b) T. I. Gountchev, T. D. Tilley, *Organometallics* **1999**, *18*, 5661; c) G. A. Molander, M. Julius, *J. Am. Chem. Soc.* **1995**, *117*, 4415; d) A. K. Dash, I. Gourevich, J. Q. Wang, J. Wang, M. Kapon, M. S. Eisen, *Organometallics* **2001**, *20*, 5084.

[9] a) C. T. Aitken, J. F. Harrod, E. Samuel, *J. Am. Chem. Soc.* **1986**, *108*, 4059; b) J. Y. Corey, X.-H. Zhu, T. C. Bedard, L. D. Lange, *Organometallics*, **1991**, *10*, 115; c) T. D. Tilley, *Acc. Chem. Res.* **1993**, *26*, 22.

[10] a) H.-G. Woo, J. F. Walzer, T. D. Tilley, *J. Am. Chem. Soc.* **1992**, *114*, 7047; b) G. L. Casty, C. G. Lugmair, N. S. Radu, T. D. Tilley, J. F. Walzer, D. Zargarian, *Organometallics* **1997**, *16*, 8; c) N. S. Radu, T. D. Tilley, *J. Am. Chem. Soc.* **1992**, *114*, 8293.

[11] A. D. Sadow, T. D. Tilley, *J. Am. Chem. Soc.* **2002**, *124*, 6814.

[12] M. E. Thompson, J. E. Bercaw, *Pure Appl. Chem.* **1984**, *56*, 1.

[13] A. Z. Voskoboynikov, I. N. Parshina, A. K. Shestakova, K. P. Butin, I. P. Beletskaya, L. G. Kuz'mina, J. A. K. Howard, *Organometallics* **1997**, *16*, 4041.

[14] N. S. Radu, T. D. Tilley, *J. Am. Chem. Soc.* **1995**, *117*, 5863.

[15] Reactions of **1** with organosilanes are highly sensitive to the nature of substituents at silicon; A. D. Sadow, T. D. Tilley, unpublished results.

[16] T. Imori, V. Lu, H. Cai, T. D. Tilley, *J. Am. Chem. Soc.* **1995**, *117*, 9931.

[17] R. F. Jordan, D. F. Taylor, *J. Am. Chem. Soc.* **1989**, *111*, 778.

[18] A. K. Dash, J. Q. Wang, M. S. Eisen, *Organometallics* **1999**, *18*, 4727.