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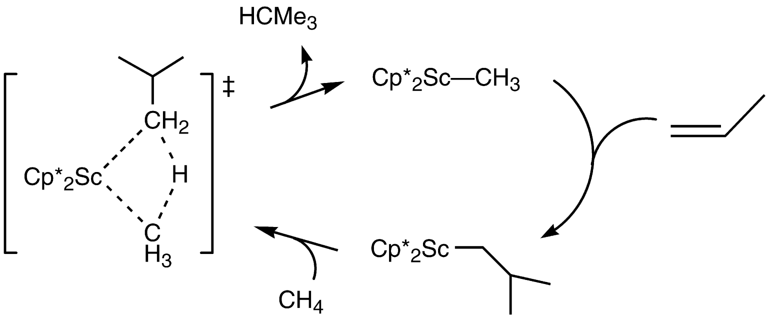
J. Am. Chem. Soc., **2003**, 125 (26), 7971-7977• DOI: 10.1021/ja021341a • Publication Date (Web): 04 June 2003



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Homogeneous Catalysis with Methane. A Strategy for the Hydromethylation of Olefins Based on the Nondegenerate Exchange of Alkyl Groups and σ-Bond Metathesis at Scandium

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Received November 7, 2002

Abstract: The scandium alkyl Cp*$_2$ScCH$_2$CMe$_3$ (**2**) was synthesized by the addition of a pentane solution of LiCH$_2$CMe$_3$ to Cp*$_2$ScCl at low temperature. Compound **2** reacts with the C−H bonds of hydrocarbons including methane, benzene, and cyclopropane to yield the corresponding hydrocarbyl complex and CMe$_4$. Kinetic studies revealed that the metalation of methane proceeds exclusively via a second-order pathway described by the rate law: rate $= k[\mathbf{2}][\mathrm{CH_4}]$ ($k = 4.1(3) \times 10^{-4}$ M^{-1}s^{-1} at 26 °C). The primary inter- and intramolecular kinetic isotope effects ($k_H/k_D = 10.2$ (CH$_4$ vs CD$_4$) and $k_H/k_D = 5.2(1)$ (CH$_2$D$_2$), respectively) are consistent with a linear transfer of hydrogen from methane to the neopentyl ligand in the transition state. Activation parameters indicate that the transformation involves a highly ordered transition state ($\Delta S^\ddagger = -36(1)$ eu) and a modest enthalpic barrier ($\Delta H^\ddagger = 11.4(1)$ kcal/mol). High selectivity toward methane activation suggested the participation of this chemistry in a catalytic hydromethylation, which was observed in the slow, Cp*$_2$ScMe-catalyzed addition of methane across the double bond of propene to form isobutane.

Introduction

The selective conversion of saturated hydrocarbons to functionalized and more valuable products remains an important goal in chemical research.[1−7] Intense interest in this topic has led to many important advances including the discovery of several mechanisms by which transition metal species react with unactivated C−H bonds.[2] Although these studies have revealed a number of interesting stoichiometric transformations, there have been significantly fewer reports describing selective conversions of alkanes via homogeneous catalysis.[3−5] Methane is a particularly attractive substrate for such conversions since it is cheap and readily available, and represents a potentially useful reagent for the incorporation of methyl groups into molecular structures. Research on homogeneous methane conversion has focused on selective oxidations via activations with electrophilic late metal complexes in acidic media, or with reactive metal oxo species.[6−8] Alternative strategies involving non-oxidative mechanisms via electrocyclic transition states (i.e., σ-bond metathesis[9,10] and 1,2-cycloaddition across metal−ligand double bonds[11]) have until recently not been incorporated into catalytic cycles.[12]

Studies on the interactions of silanes with d^0 metal complexes have revealed several pathways for the activation of Si−H and

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Si−C bonds via σ-bond metathesis.[12−15] This rich reaction chemistry suggested that similar activation steps might be used in catalytic hydrocarbon functionalizations, given appropriately active and selective catalysts. We recently reported an initial step in this direction with the description of a catalytic methane dehydrosilylation, which appears to occur via σ-bond metathesis.[12] This discovery prompted further reactivity studies on compounds of the type Cp^*_2ScR[10a] and a search for transformations that might be incorporated into a catalytic cycle.

Useful catalytic processes that might utilize σ-bond metathesis steps involve the formation and cleavage of C−C bonds (e.g., hydrocarbon homologation and hydrocracking, respectively). This possibility has seemed rather remote given some of the apparent limitations associated with such steps. For example, it seems that carbon is disfavored in the β-position of the four-centered transition state for σ-bond metathesis, which should prevent the *direct* formation (and cleavage) of C−C bonds.[16,17] However, a potentially useful product-forming step could involve the nondegenerate exchange of hydrocarbyl groups at the metal center (eq 1)

$$Cp^*_2Sc{-}R + R'{-}H \rightarrow Cp^*_2Sc{-}R' + R{-}H \qquad (1)$$

Very few reactions of this type have been reported, and the majority of these form products that exhibit low reactivities toward further bond activations (e.g., M−Ph, M−C≡R, M−OR, etc).[9,10] Nevertheless, the possibility that highly active metal centers may promote carbon−carbon interactions is suggested by the work of Basset and co-workers on silica-supported catalysts,[18] and by the fact that alkene polymerization occurs by an insertion process that passes through a 4-center transition state with carbon in the β-position.[19] Here, we describe a nondegenerate alkyl exchange reaction involving scandium, and the apparent participation of this reaction type in a catalytic C−C bond formation, the hydromethylation of propene.

Results and Discussion

Synthesis of $Cp^*_2ScCH_2CMe_3$ (2). A search for new catalytic methane activation chemistry began with attempts to observe a nondegenerative alkyl-exchange reaction (eq 1). This reaction seemed likely for the exchange of a sterically hindered alkyl ligand for a methyl group, given the previous observation that Cp^*_2ScMe (**1**) undergoes the thermoneutral exchange of its methyl ligand with methane.[10a] Slow addition of a freshly prepared pentane solution of $LiCH_2CMe_3$ (0.149 M, 1.01 equiv)[20] to a pentane solution of Cp^*_2ScCl at −78 °C in the dark, followed by extraction and repeated fractional crystallization at −78 °C afforded yellow crystals of $Cp^*_2ScCH_2CMe_3$ (**2**) in 50% yield. All manipulations were performed in the dark, because workup under ambient room lighting did not provide **2** and led to formation of deep red solutions and oily decomposition products. The formation of **2** was quantitative in benzene-d_6 but preparative-scale reactions in benzene yielded mixtures contaminated with $Cp^*_2ScC_6H_5$ (**3**)

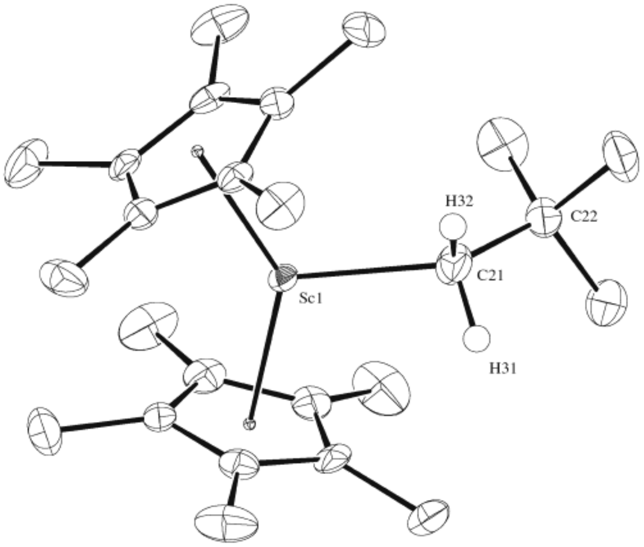

Figure 1. ORTEP diagram of $Cp^*_2ScCH_2CMe_3$ (**1**).

$$Cp^*_2ScCl + LiCH_2CMe_3 \xrightarrow[-78\ °C,\ dark]{pentane} \underset{\mathbf{2}}{Cp^*_2ScCH_2CMe_3} + LiCl \qquad (2)$$

Compound **2** thermally decomposes at room temperature and its solutions are sensitive to ambient light; however, it can be stored in the solid state at −30 °C in the dark for at least three months. The CH coupling constant of the scandium-bound methylene group ($^1J_{CH} = 108$ Hz) and the infrared spectrum (the absence of bands from 1600 to 2700 cm^{-1}) suggest that the neopentyl ligand is not α-agostic. For comparison, spectroscopic data suggest that $Cp^*_2ScCH_3$ ($^1J_{CH} = 111$ Hz) is not α-agostic, whereas $Cp^*_2ScCH_2CH_3$ is β-agostic.[10a] However, the structure of $Cp^*_2Th(CH_2CMe_3)_2$ clearly possesses an α-agostic CH group [$Th{-}C_\alpha{-}C_\beta$ is 158.2(3)°].[10b]

The X-ray crystal structure of **2** was determined (Figure 1) and key crystallographic data are listed in Tables 1 and 2. The Sc1−C21−C22 angle of 128.3(3)° is consistent with a normal σ-bond between scandium and the α-carbon. Furthermore, calculated positions for the α-hydrogens refined to reasonable locations that are beyond bonding distance to the metal. The Sc1−C21 bond distance of 2.286(4) Å is slightly longer than the corresponding distance in the scandium methyl **1** (2.243(11) Å).[10a] The wedge of the bent sandwich is slightly more open in **2** than in **1** due to the steric demand of the larger $-CH_2CMe_3$ ligand. Thus, the $Cp_{cent}{-}Sc{-}Cp_{cent}$ angle in **2** [138.78-

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Table 1. Summary of Crystallographic Data for $Cp^*_2ScCH_2CMe_3$ (2)

formula	$ScC_{25}H_{41}$
MW	386.55
crystal color, habit	yellow, blocks
crystal dimensions	0.30 × 0.25 × 0.24 mm
crystal system	monoclinic
cell determination (2θ range)	2544 (3.5−50.9°)
lattice parameters	$a = 10.4151(6)$ Å $b = 15.7925(8)$ Å $c = 14.2005(7)$ Å $\beta = 95.133(2)°$ $V = 2326.3(2)$ Å^3
space group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.104 g/cm^3
μ(MoKα)	3.21 cm^{-1}
diffractometer	Siemens SMART
radiation	MoKα ($\lambda = 0.71069$ Å)
temperature	−123.0 °C
scan type	ω (0.3° per frame)
no. of reflections measured	total: 8151 unique: 3950 ($R_{int} = 0.054$)
corrections	Lorentz-polarization absorption ($T_{max} = 0.90$, $T_{min} = 0.53$)
structure solution	direct methods (SAPI91)
refinement	full-matrix least-squares
no. observations ($I > 3.00\sigma(I)$)	2297
no. variables	241
R; R_w; R_{all}	0.050; 0.062; 0.090
max peak in final diff. map	0.26 e$^-$/Å^3
min peak in final diff. map	−0.36 e$^-$/Å^3

Table 2. Selected Bond Distances (Å) and Angles (°) for $Cp^*_2ScCH_2CMe_3$

bond distances			
Sc−C21	2.286(4)	C21−C22	1.549(6)
C21−H31	1.07(4)	C21−H32	1.07(4)
Sc−Cp_{cent}	2.2134(7)	Sc−Cp_{cent}	2.2119(7)
bond angles			
Sc−C21−C22	128.3(3)	Sc−C21−H31	105(2)
Sc−C21−H32	104(2)	H31−C21−H32	96(2)
C22−C21−H31	108(2)	C22−C21−H32	108(2)
C21−Sc−Cp_{cent}	112.0(1)	C21−Sc−Cp_{cent}	108.2(1)
Cp_{cent}−Sc−Cp_{cent}	138.78(3)		

(3)°] is smaller by 6.87° than the corresponding angle in $Cp^*_2ScCH_3$. Additionally, the Sc−Cp_{cent} distances [2.2134(7) and 2.2119(7) Å] in **2** are slightly longer than in **1** by (ca. 0.04 Å).

C−H Activation Reactions of $Cp^*_2ScCH_2CMe_3$ (2) with Hydrocarbons. Addition of ca. 0.4 atm of CH_4 to cyclohexane-d_{12} or benzene-d_6 solutions of **2** in an NMR tube with a Teflon-valve at 77 K, followed by warming to room temperature, quantitatively produced the scandium methyl **1** and $C(CH_3)_4$ (eq 3, $t_{1/2} = 45$ min at room temperature in the dark). The conversion of **2** to **1** could proceed either via intramolecular β-methyl elimination or intermolecular C−H bond activation of methane. The quantitative formation of neopentane rather than isobutylene indicates that compound **2** does in fact react with methane. This conclusion was confirmed by second-order kinetics (first order in methane, vide infra) and a labeling study, in which **2** reacted with CD_4 to quantitatively form **1**-d_3. This reaction is similar to the well-known $^{13}CH_4$ exchange mediated by $Cp^*_2MCH_3$ (M = Sc, Lu, Y).[9,10a] Although the latter degenerate reactions are facile, significant reaction rates require slightly elevated temperatures (ca. 70 °C).[9,10a] Thus, **2** is considerably more reactive than **1** toward methane, and this appears to be related to the greater thermodynamic driving force for the reaction of **2** with methane (and Me_4C elimination). Under the conditions employed (with ≥ 5 equiv of CH_4) the elimination of Me_4C is irreversible

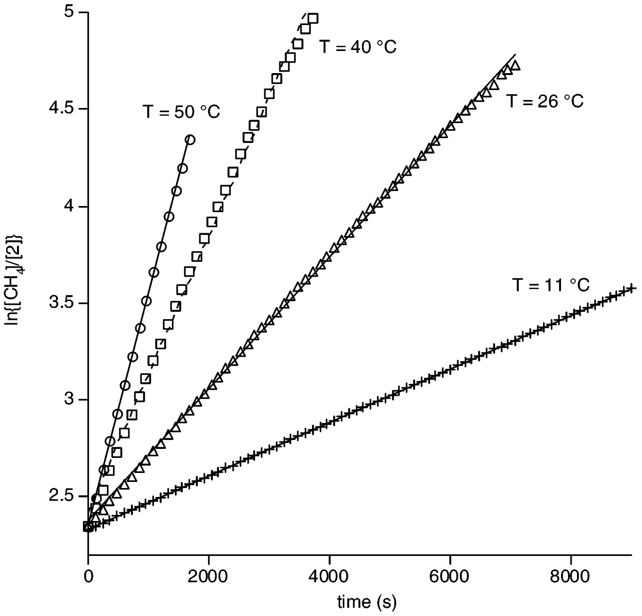

Figure 2. Representative second-order plots of ln{[CH_4]/[$Cp^*_2ScCH_2CMe_3$]} vs time for the reaction of $Cp^*_2ScCH_2CMe_3$ (**2**) with CH_4 in a re-sealable J. Young NMR tube. The second-order rate constants, *k*, were determined by dividing the slope of the linear least squares best fit line by Δ_o ($\Delta_o = [CH_4]_{ini} - [\mathbf{2}]_{ini}$).

$$\underset{\mathbf{2}}{Cp^*_2ScCH_2CMe_3} + CH_4 \xrightarrow{C_8D_{12}\text{ or }C_8D_8} \underset{\mathbf{1}}{Cp^*_2ScCH_3} + Me_4C \qquad (3)$$

Complex **2** is particularly more reactive toward methane (vs other hydrocarbons), such that methane (10 equiv) is selectively activated in benzene-d_6 solvent. This reactivity trend is unusual for C−H activation by transition metal complexes,[1,2,21] and note that the rate of H/D exchange catalyzed by Cp^*_2ScH (**3**) follows the trend H−H ≫ C_6H_6 > CH_4 > cyclooctane.[10a] The complex $[\eta^5\text{-}C_5(CD_3)_5]_2ScCH_2CMe_3$ (**2**-d_{30}) reacted with benzene-d_6 to form $(Cp^*\text{-}d_{15})_2ScC_6D_5$ and CMe_4-d_1, but significant rates required elevated temperatures (70 °C, $t_{1/2} = 305$ min). Proteobenzene reacted more rapidly with **2**-d_{30} ($t_{1/2} = 115$ min; ca. 3 times faster), and these rates are similar to those associated with the reactions of Cp^*_2ScMe with benzene/benzene-d_6.[10a] The reaction of **2** with a large excess of cyclopropane (60 equiv, cyclohexane-d_{12}) proceeded slowly at room temperature with formation of $Cp^*_2Sc^cPr$ and CMe_4 ($t_{1/2} \approx 1$ day). In contrast, Cp^*_2LuMe is reported to react more rapidly with cyclopropane than with methane (by a factor of ca. 4).[9] Compound **2** reacted with ethane (70 equiv, $t_{1/2} \gg 1$ week), but much more slowly than with methane. The latter reaction produced neopentane, but just as in the reaction of $Cp^*_2MCH_3$ (M = Sc, Lu) with ethane,[9,10a] the product of β-H elimination (Cp^*_2ScH) was formed, along with unidentified species (by ^1H NMR spectroscopy).[9,10]

Plots of ln{[CH_4]/[**2**]} vs time (Figure 2) are linear for greater than three half-lives, indicating a second-order rate law, rate =

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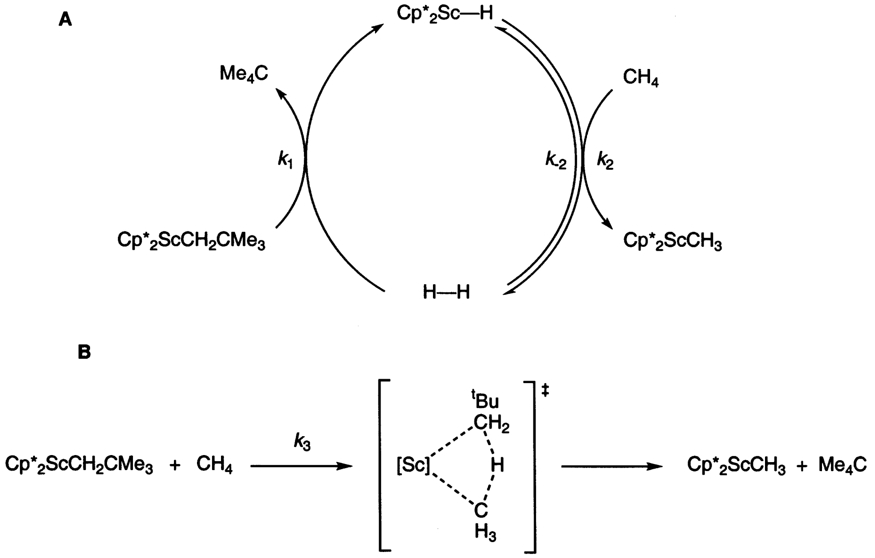
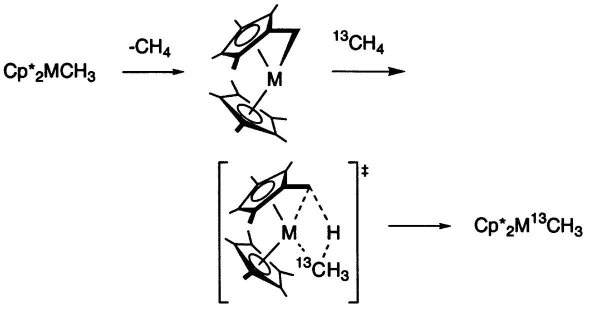
Scheme 1. Two Observed Mechanisms for Methane Activation[a]



[a] Hydrogen catalysis proceeds through the cycle represented by A, whereas the direct reaction proceeds in the absence of added Cp*$_2$ScH (B).

k_3[**2**][CH$_4$] (k_3 = slope/{[CH$_4$]$_{in}$ − [**2**]$_{in}$}; $k_3 = 4.1(3) \times 10^{-4}$ M^{-1}s^{-1}, 26 °C; $k_3 = 2.0 \times 10^{-3}$ M^{-1}s^{-1}, 50 °C). For comparison, the second-order rate constants for methyl exchange in the Cp*$_2$MCH$_3$/CH$_4$ systems are 1×10^{-5} M^{-1}s^{-1} (Sc, 70 °C), 4.6×10^{-4} M^{-1}s^{-1} (Lu, 70 °C) and 2.6×10^{-3} M^{-1}s^{-1} (Y, 70 °C).[9,10a] For the methyl exchange reactions, two competitive processes were proposed: a second-order pathway and a first order, two-step sequence involving a "tuck-in" intermediate species, [η^5-Cp*(η^1:η^5-C$_5$Me$_4$CH$_2$)M] (eq 4; M = Sc, Y, Lu).[9,10a] On the basis of kinetic and isotopic labeling studies, the nondegenerate alkyl exchange of eq 3 does not occur by such a metalation pathway below 50 °C. Thus, with **2**-d_{30} as the reactant, no Me$_4$C-d_1 was observed in the product mixture by ^{1}H NMR spectroscopy. Furthermore, the second-order rate constant for the reaction of **2**-d_{30} with methane was identical to that observed for reaction of the perproteo compound ($k = 4.1(3) \times 10^{-4}$ M^{-1}s^{-1}).



(4)

A third possible mechanism is a chain reaction involving a scandium hydride species, which would metalate CH$_4$ with the elimination of H$_2$. Hydrogen would then react with **2** to produce neopentane and reform the hydride (Scheme 1). This possibility is suggested by the observation that the metalation of benzene by Cp*$_2$LuMe is accelerated by the addition of H$_2$,[9b] and by a study of the reaction of Cp*$_2$SmCH(SiMe$_3$)$_2$ with H$_2$Si(SiMe$_3$)$_2$, which proceeds exclusively via a chain reaction involving Cp*$_2$SmH.[13b] Similarly, trace quantities of Cp*$_2$ScH or H$_2$ could promote the exchange of eq 3. The rate law for a mechanism which proceeds solely through this hydride catalysis would be first order in both [CH$_4$] and [**2**], but would also reflect first-order dependence on [Cp*$_2$ScH]: rate = k[Cp*$_2$ScH][CH$_4$][**2**] {$k = (k_1k_2)/(k_{-2}$[Cp*$_2$ScMe]); k_2 and k_{-2} are rate constants associated with reversible methane metalation by Cp*$_2$ScH and k_1 is the rate constant for hydrogenolysis of **2**}. In fact, the reaction is accelerated by added Cp*$_2$ScH (Figure 3), and this hydride-promoted reaction exhibits first-order dependence on Cp*$_2$ScH. Significantly, the observed rate enhancement is small relative to the rate of reaction in the absence of added Cp*$_2$ScH (e.g., with 0.5 equiv of Cp*$_2$ScH, the observed rate constant increases only 2-fold). Also, the experimentally determined rate constant k_3 (for the direct reaction of **2** with CH$_4$**)** is identical to the value of k_3 obtained by extrapolation to zero [Cp*$_2$ScH] in the plot of Figure 3. This indicates that in the reaction of **2** with methane, the only pathway for alkyl exchange involves direct interaction of the Sc−C bond of **2** with the C−H bond of methane. With added Cp*$_2$ScH, the rate expression becomes rate = k_{obs}[**2**][CH$_4$] where $k_{obs} = k_3 + k$[Cp*$_2$ScH].

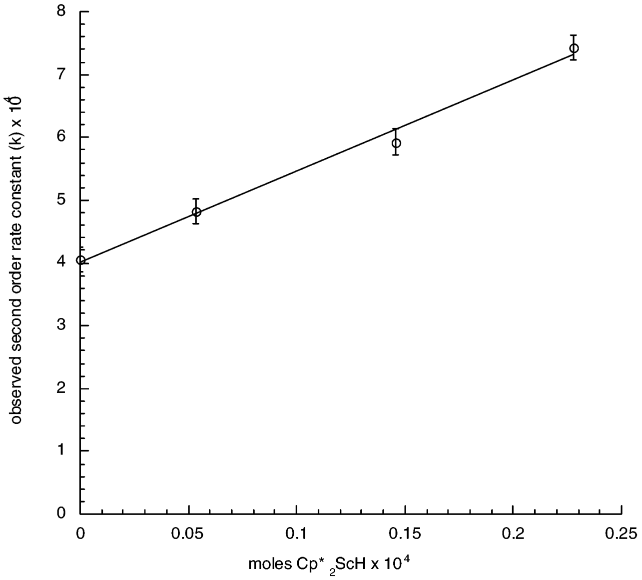


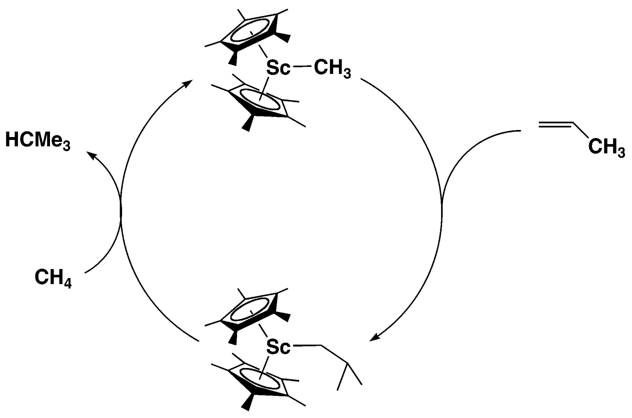
Figure 3. Plot of Cp*$_2$ScH vs the observed second-order rate constant k_{obs}, demonstrating the rate acceleration with added Cp*$_2$ScH.

Interestingly, although methane metalation by Cp^*_2ScH could not be observed directly,[12,22] these kinetic studies of the hydride catalysis indicate that the interaction of Cp^*_2ScH with CH_4 occurs to rapidly produce a low, equilibrium concentration of Cp^*_2ScMe. This direct reaction is also suggested by the Cp^*_2ScH-catalyzed deuteration of methane,[10a] and by the catalytic dehydrosilation of methane by Cp^*_2ScH.[12] Note that the direct metalation of CH_4 by Cp^*_2LuH was also not observed.[23]

As mentioned above, the reaction of **2** with CD_4 yielded the expected products $Cp^*_2ScCD_3$ and Me_4C-d_1 ($k_D = 4.0(1) \times 10^{-5}$ $M^{-1}s^{-1}$). Comparison of second-order rate constants for the activations of CD_4 and CH_4 provided a large intermolecular primary kinetic isotope effect of $k_H/k_D = 10.2$. For comparison, Wolczanski has measured similarly large primary isotope effects ($k_H/k_D = 11.2$) for the metalation of CH_4 vs CD_4 by the transient zirconium imido complex $[(Si^tBu_3)NH]_2Zr{=}N(Si^tBu_3)$.[24] These large isotope effects were attributed to ground state energy differences for proteo vs deutero compounds in highly symmetrical environments. Therefore, the intramolecular kinetic isotope effect was measured by determining the ratio of $Cp^*_2ScCHD_2$ vs $Cp^*_2ScCH_2D$ formed by the reaction of **2** with CH_2D_2. The observed value of 5.2(1) is similar to the intramolecular kinetic isotope effect reported for the metalation of CH_2D_2 by $[(Si^tBu_3)NH]_2Zr{=}N(Si^tBu_3)$ [5.1(6)].[24] These relatively high values indicate that hydrogen is transferred in a linear fashion in the β-position of the transition state. Interestingly, the rate constant for the reaction of CH_2D_2 with **2** ($k = 2.3(1) \times 10^{-4}$ $M^{-1}s^{-1}$) is only 1.78 times slower than the reaction of **2** with CH_4. The activation parameters ($\Delta H^\ddagger = 11.4(1)$ kcal/mol and $\Delta S^\ddagger = -36(1)$ eu, determined for the temperature range of 10−50 °C) for the exchange of eq 3 are consistent with those observed for the $Cp^*_2LuCH_3/CH_4$ system ($\Delta H^\ddagger = 11.6$ kcal/mol; $\Delta S^\ddagger = -38.1$ eu).[9] Although such activation parameters (a high entropy and a modest enthalpy of activation) are frequently attributed to transition states in which bond cleavage is a minor component of the activation barrier, the large, primary isotope effect for the reaction of **2** with methane indicates that the transition state involves significant C−H bond cleavage. This suggests that the relatively small activation enthalpy results from concurrent bond cleavage and bond formation processes.

Small, normal, secondary isotope effects in olefin polymerization reactions have been attributed to α-agostic assistance in the transition state of the insertion step.[25] The similarities between the mechanisms of olefin insertion and σ-bond metathesis (four centered electrocyclic transition states, $2_\sigma + 2_\pi$ vs $2_\sigma + 2_\sigma$) suggest the possibility of an α-agostic participation in C−H bond activation.[26] However, there is not a significant secondary isotope effect associated with the α-hydrogens of **2** [$k_H/k_D = 0.96(5)$], as determined by measurements of the rate constant for the reaction of $Cp^*_2ScCD_2CMe_3$ (**2**-d_2) with CH_4. Thus, this σ-bond metathesis reaction occurs without α-agostic assistance.

Scheme 2. Proposed Catalytic Cycle for Hydromethylation of Propene by Cp^*_2ScMe



Catalytic Hydromethylation of Propene with Cp^*_2ScMe (1). The facile and selective activation of methane by **2** suggested that a related nondegenerate alkyl exchange might be incorporated into a catalytic cycle, if the resulting methyl complex could be readily converted into a higher alkyl derivative (e.g., via alkene insertion). Propene appeared to be a reasonable substrate to test in this regard, since it is known to insert into the Sc−Me bond of **1**.[10a] Note, however, that the insertion product, $Cp^*_2ScCH_2CHMe_2$, is reported to react with a second equivalent of propene via σ-bond metathesis to form isobutane and $Cp^*_2ScCH{=}CHMe$.[10a]

Propene and methane (9 and 10 equiv, respectively) were added to a cyclohexane-d_{12} solution of **1** in a Teflon-sealed NMR tube. Over the course of 3 days at room temperature, $Cp^*_2ScCH_2CHMe_2$, $Cp^*_2ScCH{=}CMe_2$ and isobutane (3 equiv relative to **1**), resulting from the catalytic hydromethylation of propene, were observed in the reaction mixture. After heating a similar mixture to 80 °C overnight, 4 equiv of isobutane formed but the catalyst had completely decomposed to unidentified products (by NMR spectroscopy). Neither Cp^*_2ScH nor propane is observed in the reaction mixture, suggesting that the scandium hydride does not play a role in the observed catalysis. Furthermore, the apparent lack of participation of Cp^*_2ScH in the catalysis suggests that the C−H bond activation step involves the alkyl complex $Cp^*_2ScCH_2CHMe_2$, in a step analogous to the reaction of **2** with methane. Interestingly, β-hydride elimination from the scandium isobutyl complex does not occur, as isobutylene was not observed. The proposed catalytic cycle (Scheme 2) is based on the reactivity of **2** with methane, the known insertion of propylene into **1**, and the observed components in the reaction mixture. The addition of only 4 equiv of propene required 2 weeks to produce 3.5 equiv of isobutane, thus the slow step in the catalytic cycle appears to be olefin insertion into the Sc−Me bond.

Attempts to extend this catalysis to the addition of other hydrocarbons (e.g., arenes and cyclopropane) to propene have been unsuccessful with **1**. For example, propene did not insert into the scandium−carbon bond of $Cp^*_2Sc^cPr$. Both the alkene insertion and C−H bond activation steps appear to be highly sensitive to the nature of the reacting scandium alkyl species.

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The attempted addition of methane to other alkenes or alkynes (*cis*/*trans*-2-butene, 1-hexene, 1-butene, 2-methylpropene, norbornylene, and 2-butyne) did not produce methylated products over several days at room temperature or elevated temperatures (70 °C). Potential difficulties may relate to the fact that internal alkenes, such as *cis*/*trans*-2-butene and norbornylene, do not insert into the scandium−carbon bond of **1**. For example, no reaction was observed between Cp^*_2ScMe and norbornylene (10 equiv, cyclohexane-d_{12}, room temperature, 1 week). Also, larger α-olefins (1-butene, 2-methylpropene, 1-hexene) react with Cp^*_2ScMe via σ-bond metathesis to form the corresponding scandium vinyl complexes.[10a] Although 2-butyne (5 equiv) reacted with Cp^*_2ScMe rapidly via a single insertion (<5 min), the resulting scandium vinyl compound $Cp^*_2ScC(Me){=}CMe_2$ did not react with methane (12 equiv in solution), even upon heating at 70 °C in cyclohexane-d_{12} for 4 days.

Concluding Remarks

The application of σ-bond metathesis chemistry in catalytic hydrocarbon conversions requires metal complexes that are active toward the cleavage of C−H bonds. Such complexes, of the type Cp^*_2MR (M = Sc, Lu, Y; R = H, CH_3), were reported almost twenty years ago.[9,10a] However, productive catalysis also depends critically on the selectivity exhibited by the catalyst toward potential bond activations. For example, the hydromethylation of propene requires that the insertion product ($L_nM{-}CHCHMe_2$) react with methane rather than another equivalent of propene, or the solvent, by σ-bond metathesis. In addition, an intramolecular ligand metalation via C−H activation could lead to inactive or insoluble species.[10a] In this contribution, we have described a highly selective activation of methane by the scandium neopentyl complex **2**, which suggested that a related process might provide the basis for a new type of catalytic methane conversion.

The selective activation of methane by the scandium neopentyl complex **2** is particularly interesting in light of comparisons to related systems. For example, whereas **2** reacts with methane (0.55 M, 10 equiv in solution) in benzene-d_6 to form only Cp^*_2ScMe, the complexes $Cp^*_2MCH_3$ (M = Sc, Lu, Y) react at approximately the same rate with benzene and methane.[9,10a] Unlike the methyl complexes,[9,10a] **2** reacts with methane more rapidly than with cyclopropane. The thoracyclobutane $Cp^*_2Th(\kappa^2\text{-}CH_2CMe_2CH_2)$ exhibits the typical trend in selectivities toward C−H bond activations: cyclopropane > benzene > methane.[10b]

Notably, the enhanced selectivity for methane by $Cp^*_2ScCH_2CMe_3$ is not associated with reduced activity; **2** reacts with methane at a rate that is 2 orders of magnitude faster than that of Cp^*_2ScMe, under similar conditions. The enhanced reactivity of **2** (relative to Cp^*_2ScMe) in the C−H bond activation of methane likely results from a Sc−C bond that is weakened by steric pressure, possibly resulting from the presence of the bulky Cp* and $-CH_2CMe_3$ ligands. Consistent with this, reactions of the scandium neopentyl complex and larger hydrocarbon substrates (e.g., benzene and cyclopropane) are comparatively slow. Thus, it seems that the bulky ligands of **2** create a small, reactive binding site that is selective for methane. Interestingly, compound **2** also exhibits enhanced selectivity for intermolecular vs intramolecular C−H bond activation, as mechanistic investigations reveal that an intramolecular "tuck-in" mechanism does not occur in this system. Apparently, the higher rate for the bimolecular reaction of **2** with methane favors direct C−H activation over a two-step pathway involving a "tuck-in" intermediate, as observed in the reaction of Cp^*_2ScMe with methane.

Another aspect to the selectivity exhibited by **2** in bond activations is seen in its reactivity toward silanes. Although Si−H bonds typically react more rapidly than C−H bonds, when cyclohexane-d_{12} solutions of **2** and Ph_2SiH_2 (0.5 equiv) were exposed to methane (10 equivalents) at room temperature, Ph_2MeSiH (0.5 equiv) and Me_4C (1 equiv) were formed rather than $Ph_2(CH_2CMe_3)SiH$. Note that in contrast to **2**, Cp^*_2ScMe reacts rapidly with Ph_2SiH_2 to form Cp^*_2ScH and Ph_2MeSiH.[12] The enhanced activity and selectivity of **2** in its reaction with methane is unusual, in that complexes (such as Cp^*_2LuMe) that are reactive toward metathesis with C−H bonds are also highly reactive toward Si−H and Si−C bond activations.[14]

On the basis of current mechanistic information, it seems that carbon−carbon coupling reactions are disfavored by purely σ-bond metathesis pathways because such reactions would involve transition states with carbon in the β-position. Experimental and theoretical studies indicate that such transformations are prohibited by high energy transition states, limiting possible strategies for hydrocarbon homologations.[9,10,16,17,26] However, the combination of methane activation and alkene insertion (as in propene hydromethylation) provides an alternative approach for catalytic carbon−carbon bond formations. Although catalytic systems combining C−H bond activation with insertions of unsaturated hydrocarbons have been reported,[4,10c] the scandium system described here represents the only example involving a methane conversion. Future efforts will target modifications of the ancillary ligands and the substrates for the development of new C−H bond activation chemistry.

Experimental Section

General. All manipulations were performed under an atmosphere of argon using Schlenk techniques and/or a M. Braun 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^*_2ScCl, $[\eta^5\text{-}C_5(CD_3)_5]_2ScCl$, $Cp^*_2ScCH_3$ (**1**), Cp^*_2ScH (**2**), Cp^*_2ScPh (**7**),[10a] $LiCH_2CMe_3$ and $LiCD_2CMe_3$[20] were prepared according to literature procedures. Commercial sources were used for CH_4 and propylene (Airgas), CD_4 (Cambridge Isotope Labs), and cyclopropane (Aldrich), and these materials were used as received. 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 AM-400 spectrometer at 400 MHz (^1H) or a Bruker DRX-500 at 500 MHz (^1H) and 125 MHz (^{13}C).

$Cp^*_2ScCH_2CMe_3$ (2). Cp^*_2ScCl (0.529 g, 1.51 mmol) was dissolved in pentane (20 mL) and the resulting solution was cooled to −78 °C. The reaction flask was wrapped in aluminum foil, and a solution of $LiCH_2CMe_3$ in pentane (10.1 mL, 0.149 M) was added slowly with a syringe. The flask was sealed and the solution was stirred at − 78 °C in the dark for 2 h, and then the pentane was removed in vacuo. The resulting solids were warmed to room temperature and extracted with

50 mL of pentane. The resulting solution was concentrated to ca. 30 mL and cooled to −78 °C for 1 day. A white, pyrophoric precipitate was isolated by filtration from the supernatant, which was further concentrated to ca. 5 mL and cooled to −78 °C. Yellow crystals of $Cp^*_2ScCH_2CMe_3$ were isolated by filtration (0.292 g, 0.75 mmol, 49%). ^1H NMR (C_6D_6): δ 1.888 (s, 30 H, $C_5\mathit{Me}_5$), 1.342 (s, 9 H, $CH_2C\mathit{Me}_3$), 0.843 (s, 2 H, $C\mathit{H}_2CMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 121.370 (C_5Me_5), 53.2 ($\mathit{C}H_2CMe_3$), 36.842 ($CH_2C\mathit{Me}_3$), 12.431 ($C_5\mathit{Me}_5$). IR (Nujol, cm^{-1}): 2908 s, 2859 s, 1440 m, 1379 m, 1249 w, 1200, 1087 w, 1022 w, 540 m. Anal. Calcd for $C_{25}H_{41}Sc$: C, 77.68; H, 10.69. Found: C, 77.82; H, 10.77. Mp: 90−92 °C (dec).

[η^5-$C_5(CD_3)_5]_2ScCH_2CMe_3$ (2-d_{30}). The synthesis of **2**-d_{30} was performed in a manner analogous to that of **2**, using [η^5-$C_5(CD_3)_5]_2$-ScCl.

Kinetic Measurements. Reactions were monitored by ^1H NMR spectroscopy, with a Bruker DRX500 spectrometer, using 5 mm Wilmad NMR tubes with a Teflon-valve seal. Samples were prepared by dissolution of **2** in cyclohexane-d_{12} containing a known concentration of C_8H_{16} standard. The samples were cooled to 77 K, the headspace of the NMR tube was evacuated, and CH_4 was admitted. The sample was maintained at 77 K until immediately before being placed in the NMR probe, which was preset to the required temperature. At the appropriate time, the sample was carefully warmed to room temperature and shaken to ensure maximum dissolution of CH_4 into solution. The probe temperature was calibrated using a neat ethylene glycol 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, $\ln\{[CH_4]_t/[\mathbf{2}] = \ln\{[CH_4]_0/[\mathbf{2}]_0\} + k\Delta_0 t$.[27]

Acknowledgment. This work was supported by the National Science Foundation, and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC03-76SF00098. We also thank John Bercaw, Richard Andersen, and Mark Thompson for helpful discussions, and Allen G. Oliver and Fred Hollander for assistance with the X-ray structure determination. CNDOS is supported by Bristol-Myers as a founding member.

Supporting Information Available: Details for the kinetic runs, representative kinetic data (PDF) and X-ray crystallographic data for **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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