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

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Abstract: The scandium alkyl Cp$_2$ScH$_2$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 metatation of methane proceeds exclusively via a second-order pathway described by the rate law: rate = $k[2][\text{CH}_4]$ ($k = 4.1(3) \times 10^{-4} \text{ M}^{-1} \text{s}^{-1}$ at 26 °C). The primary inter- and intramolecular kinetic isotope effects ($k_\text{H}/k_\text{D}$ = 10.2 (CH$_4$ vs CD$_4$) and $k_\text{H}/k_\text{D}$ = 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$^*$ = $-36(1)$ eu) and a modest enthalpic barrier ($\Delta$H$^*$ = 11.4(1) kcal/mol). High selectivity toward methane metathesis 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.8 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 o xo species.6–8 Alternative strategies involving non-oxidative mechanisms via electrolytic transition states (i.e., $\sigma$-bond metathesis9,10 and 1,2-cycloaddition across metal–ligand double bonds11) 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

References:

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 dehydrocyclization, which appears to occur via σ-bond metathesis.12 This discovery prompted further reactivity studies on compounds of the type Cp*2ScR10a 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)

\[
\text{Cp}^\ast_2\text{Sc}^\ast\text{R} + \text{R}^\ast\text{H} \rightleftharpoons \text{Cp}^\ast_2\text{Sc}^\ast\text{R}^\ast + \text{R}^\ast\text{H} \quad (1)
\]

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=CR, 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 the fact that alkene polymerization occurs. 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)

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\]

Results and Discussion

Synthesis of Cp*2ScCH2CM2 (2). A search for new catalytic methane activation chemistry began with attempts to observe a nondegenerate 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.10b Slow addition of a freshly prepared pentane solution of LiCH2CM2 (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*2ScCH2CM2 (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-d8 but preparative-scale reactions in benzene yielded mixtures contaminated with Cp*2ScC2H5 (3)

\[
\text{Cp}^*\text{ScCl} + \text{LiCH}_2\text{CMe}_3 \overset{\text{pentane}}{\longrightarrow} \quad \text{Cp}^*\text{ScCH}_2\text{CMe}_3 + \text{LiCl} \quad (2)
\]

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 (JCM = 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*2ScH (JCM = 111 Hz) is not α-agostic, whereas Cp*2SeC2H5 is β-agostic.10b However, the structure of Cp*2Th(C2H5)2 clearly possesses an α-agostic CH group [Th–C–C β 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 −CH2CM2 ligand. Thus, the Cpent–Sc−Cpent angle in 2 [138.78-
Table 1. Summary of Crystallographic Data for Cp*2ScCH2CMe3 (2)

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Table 2. Selected Bond Distances (Å) and Angles (°) for Cp*2ScCH2CMe3

| bond distances                  | Sc–C21: 2.286(4)       |
|                                 | C21–H31: 1.074(4)       |
|                                 | Sc–Cpcent: 2.2134(7)    |
| bond angles                     | Sc–C21–C22: 128.3(3)    |
|                                 | Sc–C21–H31: 105(2)      |
|                                 | H31–C21–H32: 96(2)      |
|                                 | C22–C21–H31: 108(2)     |
|                                 | C21–Sc–Cpcent: 112.9(1) |
|                                 | Sc–Cpcent–C2: 138.78(3) |

(3°) is smaller by 6.87° than the corresponding angle in Cp2ScCH2. Additionally, the Sc–Cpcent 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*2ScCH2CMe3 (2) with Hydrocarbons. Addition of ca. 0.4 atm of CH4 to cyclohexane-d12 or benzene-d6 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(CH3)4 (eq 3, t1/2 = 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 CD3O to quantitatively form 1-d3. This reaction is similar to the well-known 13CH4 exchange mediated by Cp*2MCH3 (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 MeC elimination). Under the conditions employed (with ≥ 5 equiv of CH4) the elimination of MeC is irreversible.

\[
\text{Cp*}2\text{ScCH2CMe3 + CH}_4 \rightarrow \text{Cp*}2\text{ScCH3} + \text{MeC} \tag{3}
\]

Complex 2 is particularly more reactive toward methane (vs other hydrocarbons), such that methane (10 equiv) is selectively activated in benzene-d6 solvent. This reactivity trend is unusual for C–H activation by transition metal complexesa,1,2,21 and note that the rate of H/D exchange catalyzed by Cp*2ScH (3) follows the trend H–H ≫ C6H6 > CH4 > cyclooctane.10b The complex [η3-C3(CD3)3]2ScCH2CMe3 (2–d30) reacted with benzene-d6 to form (Cp*–d13)2ScC2D6 and CMe4–d1, but significant rates required elevated temperatures (70 °C, t1/2 = 305 min). Protopentane reacted more rapidly with 2–d30 (t1/2 = 115 min; ca. 3 times faster), and these rates are similar to those associated with the reactions of Cp*2ScMe with benzene/benzene-d6.10a The reaction of 2 with a large excess of cyclopropane (60 equiv, cyclohexane-d12) proceeded slowly at room temperature with formation of Cp*2ScPr and CMe4 (t1/2 ≈ 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 ethanol (70 equiv, t1/2 ≈ 1 week), but much more slowly than with methane. The latter reaction produced neopentane, but just as in the reaction of Cp*2MCH3 (M = Sc, Lu) with ethanol,9,10a the product of β-H elimination (Cp*2ScH) was formed, along with unidentified species (by 1H NMR spectroscopy).9,10a

Plots of ln([CH4]/[2]) vs time (Figure 2) are linear for greater than three half-lives, indicating a second-order rate law, rate =

\[
\frac{k}{{}[\text{CH}_4] [\text{Cp*}_2\text{ScCH}_2\text{CMe}_3]} \tag{21}
\]

Scheme 1. Two Observed Mechanisms for Methane Activation

$A$

$B$

$C$

$D$

$E$

$F$

$G$

$H$

$I$

$J$

$K$

$L$

$M$

$N$

$O$

$P$

$Q$

$R$

$S$

$T$

$U$

$V$

$W$

$X$

$Y$

$Z$

$k_3[2][\text{CH}_4]$ (Sadowski $k_3$ = slope/$(2[\text{CH}_4]_0 - 2])$; $k_3 = 4.1(3) \times 10^{-4}$ 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 $1 \times 10^{-5}$ M$^{-1}$s$^{-1}$ (Sc, 70 °C), $4.6 \times 10^{-4}$ M$^{-1}$s$^{-1}$ (Lu, 70 °C) and $2.6 \times 10^{-3}$ M$^{-1}$s$^{-1}$ (Y, 70 °C). 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*($\eta^5$-C$_5$Me$_4$CH$_2$)M] (eq 4; M = Sc, Y, Lu). 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 ($k_3 = 4.1(3) \times 10^{-4}$ M$^{-1}$s$^{-1}$).

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.

A third possible mechanism is a chain reaction involving a scandium hydride species, which would metatate 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 metatation of benzene by Cp*$_2$LuMe is accelerated by the addition of H$_2$ 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. 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

$$\text{rate} = k_{obs}[2][\text{CH}_4]$$

where $k_{obs} = k_3 + k[\text{Cp*$_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 CH₄ 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 dehydroxilatation of methane by Cp*₂ScH.¹² Note that the direct metalation of CH₄ by Cp*₂LuH was also not observed.²³

As mentioned above, the reaction of 2 with Cd₂ yielded the expected products Cp*₂ScCd₁ and Me₂C-d₁ (kd = 4.0(1) × 10⁻⁵ M⁻¹s⁻¹). Comparison of second-order rate constants for the activations of Cd₂ and CH₄ provided a large intermolecular primary kinetic isotope effect of kᵣ/kᵢ = 10.2. For comparison, Wolczanski has measured similarly large primary isotope effects (kᵣ/kᵢ = 11.2) for the metalation of CH₄ vs Cd₂ by the transient zirconium imido complex ([Si(Bu₃)]₂Zr=⁺N(Si(Bu₃))₂.²⁴ These large isotope effects were attributed to ground state energy differences for proto vs deutero compounds in highly symmetrical environments. Therefore, the intramolecular kinetic isotope effect was measured by determining the ratio of Cp*₂ScCd₂ vs Cp*₂ScH₂D formed by the reaction of 2 with CH₄Cd₂. The observed value of 5.2(1) is similar to the intramolecular kinetic isotope effect reported for the metalation of CH₄ by [([Si(Bu₃)]₂Zr=⁺N(Si(Bu₃))₂ [5.16]].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 CH₄Cd₂ with 2 (k = 2.3(1) × 10⁻⁴ M⁻¹s⁻¹) is only 1.78 times slower than the reaction of 2 with CH₄. The activation parameters (ΔH° = 11.4(1) kcal/mol and ΔS° = −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*₂LuCH₃/CH₄ system (ΔH° = 11.6 kcal/mol; ΔS° = −38.1 eu).²⁵ 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 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 α-bond metathesis (four centered electrocyclic transition states, 2α + 2π vs 2α + 2π) 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.

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

[kat/kcb = 0.96(5)], as determined by measurements of the rate constant for the reaction of Cp*₂ScCd₁-CMe₃ (2-d₂) with CH₄. Thus, this α-bond metathesis reaction occurs without α-agostic assistance.

Catalytic Hydromethylation of Propene with Cp*₂ScMe 
(1). The facile and selective activation of methane by 2 suggested that a related nondegenerate allyl 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*₂ScH₂ChMe₂, is reported to react with a second equivalent of propene via α-bond metathesis to form isobutane and Cp*₂ScCH=CHMe.¹⁰a

Propene and methane (9 and 10 equiv, respectively) were added to a cyclohexane-d₂ solution of 1 in a Teflon-sealed NMR tube. Over the course of 3 days at room temperature, Cp*₂ScCH₃ChMe₂, Cp*₂ScCH=CHMe₂ (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*₂ScCH₂ChMe₂, 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 cyclop propane) to propene have been unsuccessful with 1. For example, propene did not insert into the scandium−carbon bond of Cp*₂ScPr. Both the alkene insertion and C−H bond activation steps appear to be highly sensitive to the nature of the reacting scandium alkyl species.
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-d12, room temperature, 1 week). Also, larger α-olefins (1-butene, 2-methylpropene, 1-hexene) react with Cp*2ScMe via α-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)2CM2 did not react with methane (12 equiv in solution), even upon heating at 70 °C in cyclohexane-d12 for 4 days.

Concluding Remarks

The application of α-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, CH3), 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 hydro- methylation of propene requires that the insertion product (L2M(CH2CH2Me2) react with methane rather than another equivalent of propene, or the solvent, by α-bond metathesis. In addition, an intramolecular ligand metalaition 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-d6, to form only Cp*2ScMe, the complexes Cp*2MCH3 (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(κ2-CH2CM2CH2) exhibits the typical trend in selectivities toward C–H bond activations: cyclopropane > benzene > methane.10b

Notably, the enhanced selectivity for methane by Cp*2ScCH2CM3 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 –CH2CM3 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-d12 solutions of 2 and Ph2SiH2 (0.5 equiv) were exposed to methane (10 equivalents) at room temperature, Ph2MeSiH (0.5 equiv) and MeC (1 equiv) were formed rather than Ph2(CH2CM2)SiH. Note that in contrast to 2, Cp*2ScMe reacts rapidly with Ph2SiH3 to form Cp*2ScH and Ph2MeSiH.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 α-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,4,10 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 thiophenones from benzene and toluene was accomplished by washing each with H2SO4 and saturated NaHCO3 followed by drying over MgSO4. Olefin impurities were removed from pentane by treatment with concentrated H2SO4, 0.5 N KMN2O3 in 3 M H2SO4, saturated NaHCO3, and then the drying agent MgSO4. All solvents were distilled from sodium benzenophenone ketyl, with the exception of benzene-d6 and cyclohexane-d12, which were purified by vacuum distillation from Na/K alloy. The compounds Cp*2ScCl, [η5-C5(CD3)5]2ScCl, Cp*2ScCH (1), Cp*2ScH (2), Cp*2ScPh (7),[10a] LiCH2CM3, and LiCD2CM28 were prepared according to literature procedures. Commercial sources were used for CH3 and propylene (Airgas), CD3 (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-d6 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 (13C).

Cp*2ScCH2CM3 (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 LiCH2CM3 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*₂ScCH₂CMe₃ were isolated by filtration (0.292 g, 0.75 mmol, 49%).

1H NMR (C₆D₆): δ 1.888 (s, 30 H, C₅Me₅), 1.342 (s, 9 H, CH₂CMe₃), 0.843 (s, 2 H, CH₂CMe₃). 13C{¹H} NMR (C₆D₆): δ 121.370 (C₅Me₅), 53.2 (CH₂CMe₃), 36.842 (CH₂CMe₃), 12.431 (C₅Me₅). IR (Nujol, cm⁻¹): 2908 s, 2859 s, 1440 m, 1379 m, 1249 w, 1200, 1087 w, 1022 w, 540 m. Anal. Calcd for C₂₅H₄₁Sc: C, 77.68; H, 10.69. Found: C, 77.82; H, 10.77. Mp: 90–92 °C (dec).

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-d₁₂ containing a known concentration of C₈H₁₆ standard. The samples were cooled to 77 K, the headspace of the NMR tube was evacuated, and CH₄ 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 CH₄ 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([CH₄]/[2]) = ln([CH₄]₀/[2]₀) + kΔtd.²⁷

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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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