Control of Selectivity in the Hydromethylation of Olefins via Ligand Modification in Scandocene Catalysts

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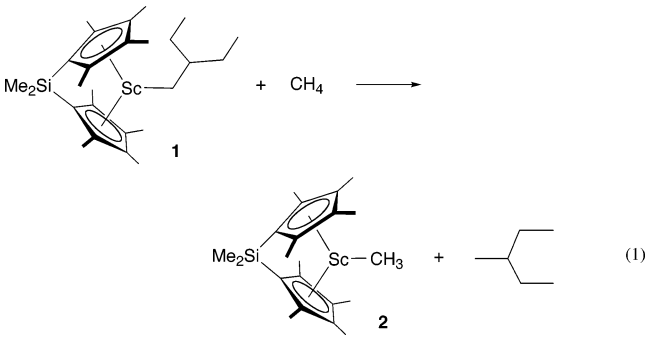
*Summary: The ansa complex $Me_2Si(C_5Me_4)_2ScMe$ (**2**) was isolated in 45% yield from the reaction of $Me_2Si(C_5Me_4)_2ScCH_2CH(CH_2CH_3)_2$ (**1**) with methane. The rate of the C−H bond activation of methane by **2** was found to be 2 orders of magnitude greater than that by Cp^*_2ScMe. Compound **2** is a catalyst for the addition of methane across the double bond of secondary terminal olefins.*

The search for new and effective ways to convert saturated hydrocarbons to more valuable and useful chemicals is a challenge that has led to many significant discoveries in recent years.[1] A particularly attractive substrate is methane, which could serve as an inexpensive and simple reagent for incorporation of a methyl group into molecular structures. In homogeneous catalysis, few transformations that utilize methane are known, and these typically employ electrophilic late metal complexes or oxo species under harsh reaction conditions.[2]

We recently described an alternative strategy for methane functionalization based on a scandium catalyst, Cp^*_2ScMe,[3] and a key methane-activation step that involves nonoxidative σ-bond metathesis under very mild conditions. In this catalysis, methane adds across the double bond of propene to give isobutane as the hydromethylation product. However, the development of such reactions into viable and more general synthetic methods will require the identification of more active and selective catalysts. For Cp^*_2ScMe, hydromethylation is facilitated by the reluctance of this species to act as a catalyst for the potentially competing process of propene polymerization.[4] On the other hand, the slow rate of propene insertion into the Sc−Me bond of Cp^*_2ScMe may limit the efficiency of hydromethylation. Along these lines, it has been shown that *ansa*-cyclopentadienyl ligands may be employed to greatly influence the rates of alkene insertions[5] and σ-bond methathesis.[6] Here we describe initial observations on the influence of an *ansa* ligand on the hydromethylation of olefins, by investigating the reactivity of scandium complexes bearing the ligand $Me_2Si(C_5Me_4)_2^{2-}$.

To our knowledge, the only readily available, base-free scandium alkyl complex bearing the $Me_2Si(C_5Me_4)_2^{2-}$ ligand is $Me_2Si(C_5Me_4)_2ScCH(CH_2CH_3)_2$ (**1**), which was observed to activate a C−H bond of PMe_3.[5a] Complex **1** also activates methane, as shown by exposure of a 0.008 M solution of **1** in cyclohexane-d_{12} to 2 atm of methane. By ^1H NMR spectroscopy, the resulting reaction gives several products, but 3-methylpentane and a new compound that exhibits four resonances between 1.98 and −0.58 ppm in a ratio of 4:4:2:1 were the major species. This information indicates that **1** reacts with methane to form $Me_2Si(C_5Me_4)_2ScCH_3$ (**2**, eq 1).



(1)

The new scandium methyl complex **2** was synthesized on a larger scale by stirring 10 mL of a 0.03 M solution of **1** in pentane under 4 atm of methane. This results in the formation of a yellow suspension, and precipita-

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tion of the product continues over 48 h. The analytically pure, pyrophoric yellow product, isolated in 45% yield by filtration, is slightly soluble in cyclohexane-d_{12} at room temperature, and gentle warming to 60 °C is required for dissolution of significant quantities. The characterization data (^{1}H, ^{13}C NMR, combustion analysis) is consistent with the assigned formula and a highly symmetric structure (a monomer or symmetric dimer). However, some evidence is consistent with fluxional behavior in solution. The broad ^{1}H NMR shift of the Sc-Me resonance is highly dependent on the temperature and the concentration of the solution, and ranges from −0.4 to −0.9 ppm. Moreover, the ^{13}C NMR signal for the methyl group was not detected by various 1D and 2D ^{13}C NMR experiments. A variable-temperature ^{1}H NMR study (in methylcyclohexane-d_{14}) revealed the coalescence of all signals for **2** at 205 K, and at lower temperatures the appearance of two new sets of resonances, including two Sc-Me resonances at −0.85 and −1.16 ppm. From the Holmes−Gutowsky equation, this dynamic process is associated with an energy barrier of 9.5 kcal/mol.[7] This behavior is in accordance with the presence of an unsymmetrical dimer that possesses bridging and terminal methyl groups, as observed for $Cp^*_2M(\mu\text{-Me})M(Me)Cp^*_2$ (M = Y, Lu).[8]

Compound **2** reacted under an atmosphere of $^{13}CH_4$ to give the labeled compound $Me_2Si(C_5Me_4)_2Sc^{13}CH_3$ (**2**-*^{13}C*), as indicated by the presence of ^{13}C satellites for the Sc-Me resonance of the new compound ($^1J_{CH}$ = 110 Hz). A kinetics study of the $^{13}CH_4$ activation by **2** employed pseudo-first-order conditions at 70 °C and revealed first-order behavior for both methane and **2**. The second-order rate constant of the reaction (1.5×10^{-3} M^{-1} s^{-1}) is about 2 orders of magnitude faster than that for Cp^*_2ScMe.[9]

Given the higher rate of **2** (vs Cp^*_2ScMe) for methane activation, this complex was examined as a catalyst for the hydromethylation of propene. The reaction of a 0.01 M solution of **2** with 5 equiv of propene under 4 atm of methane resulted in rapid consumption of the propene and a complex reaction mixture that contained isobutylene, 2-methyl-1-pentene, and isobutane (by various NMR techniques including HMQC, TOCSY). Thus, **2** exhibits far less selectivity for isobutane formation, as compared to the Cp^*_2ScMe catalyst.[3a] A ^{1}H NMR analysis of the nonvolatile components revealed a multitude of peaks attributed to the $Me_2Si(C_5Me_4)_2^{2-}$ ligand and a number of vinylic and allylic proton resonances.[9] Furthermore, under analogous conditions without methane (under nitrogen), the reaction of **2** with 5 equiv of propene gave the same products, in the same ratio. Thus, although it appears that propene insertion occurs to produce an isobutyl complex, catalytic transformation of the methane does not occur. The nature of the competing reactions is suggested by several observations, including those reported for Cp^*_2LuMe.[10] First, activation of the C−H bonds in propene (by, for example, $Me_2Si(C_5Me_4)_2ScMe$) may form stable vinyl or/and allylic complexes that liberate a hydrocarbon such as isobutane. Also, β-H elimination from the isobutyl complex should form isobutylene and a Sc-H species, which may serve as a catalyst for the dimerization of propene to 2-methyl-1-pentene.[11] Under similar conditions, the reaction of **2** with 5 equiv of *cis*-butene under methane gave a very complex mixture of alkanes and olefins, but no 2-methylbutane. Also, **2** reacted with 5 equiv of cyclopentene under methane to produce 1 equiv of 1-methylcyclopentene and cyclopentane. It can be concluded from these results that there are two major differences between **2** and Cp^*_2ScMe. First, olefin insertion is faster with the more "open" ligand system. Also, β-H elimination is much faster for insertion products such as $Me_2Si(C_5Me_4)_2ScCH_2CH(CH_3)_2$, and this seems to be a major limitation for the hydromethylation of α-olefins. These considerations suggested that more sterically hindered olefins with no hydrogen in the β position, such as secondary terminal olefins (e.g., isobutylene), might be adequate substrates for the hydromethylation reaction.

The addition of 5 equiv of isobutylene to a 0.02 M solution of **2** under 4 atm of methane at 25 °C resulted in the formation of 1 equiv of neopentane (1.0 TON by ^{1}H NMR spectroscopy; cyclohexane-d_{12}) as the only organic species after 8 days. The rate of appearance of the alkane was equivalent to the rate of consumption of the alkene, and no other organic side products were observed. During the reaction one other scandium product was observed, which appears to be $Me_2Si(C_5Me_4)_2ScCH{=}C(CH_3)_2$ (**3**), presumably formed by a vinylic C−H bond activation of isobutylene by **2**,[12] based on NMR comparison with the previously characterized complex $Cp^*_2ScCH{=}C(CH_3)_2$.[9] After 2 weeks, **2** and **3** were completely consumed and a very broad ^{1}H NMR resonance between 1.8 and 2.0 ppm, corresponding to a complex mixture of products, was observed. The use of $^{13}CH_4$ in this reaction resulted in incorporation of the labeled methane into 50% of the neopentane, and also into 9% of the methyl groups of the isobutylene that was present, based on integration of the satellites. For this catalytic hydromethylation of isobutylene, concentration effects play a strong role. A higher concentration of isobutylene (10 equiv) or a lower methane pressure (1 atm) decreased the conversion to no more than 0.5 turnover. The optimum temperature was found to be 40 °C, while higher temperatures (55 and 70 °C) gave faster conversion in the first few hours but also led to more rapid decomposition of the catalyst, as shown by the respective TONs of 2.3, 1.5, and 1.2 after 14 days at 4 atm of methane with 5 equiv of isobutylene. Under the best reaction conditions found, 65% conversion of isobutylene to neopentane (3.2 TON) was observed after 25 days.[13]

A proposed catalytic cycle is shown in Scheme 1. The initial insertion step forms an alkyl complex that was not observed, but the incorporation of $^{13}CH_3$ into the

(7) $\Delta G^{\ddagger} = RT_c\{22.96 + \ln(T_c/\Delta\delta)\}$: Abraham, R. J.; Loftus, P. *Proton and Carbon-13 NMR Spectroscopy*; Wiley: New York, 1985; Chapter 7, pp 165−168.

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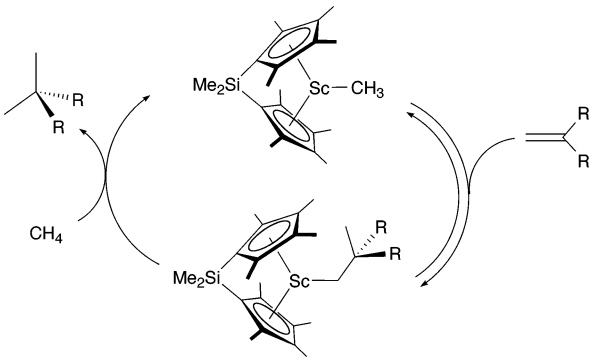
(11) Bercaw demonstrated that $[Me_2Si(C_5Me_4)_2ScH]$ is an efficient catalyst for the dimerization of α-olefins. See ref 5a.

(12) In the absence of methane, this reaction produces **3** and methane (but no neopentane). This implies that $Me_2Si(C_5Me_4)_2ScCH_2C(CH_3)_3$ does not react with isobutylene.

(13) The optimal conditions for hydromethylation of isobutylene and other olefins are 40 °C, 4 atm of CH_4, 0.01 M of **2**, and 0.05 M of the olefin.

Scheme 1



isobutylene indicates that the reverse reaction, β-Me elimination, is relatively rapid. Also consistent with a reversible insertion is a decrease in reactivity at higher temperature, since β-Me elimination should be entropically favored. The second step, which has ample precedent,[3a] is the activation with methane via a concerted metathesis step. It is noteworthy that the formation of neopentane ceases with the complete consumption of **2**, implying the involvement of this species in the catalytic cycle. Also, with **1** as catalyst only 0.5 turnover was observed. Thus, since **1** is known to readily undergo β-H elimination, it appears that the hydride is not an active species.

In summary, the results reported here show that catalyst design principles may be employed to expand the range of olefin substrates that may undergo hydromethylation via a σ-bond metathesis pathway. The more exposed metal center in **2** (vs Cp^*_2ScMe) leads to faster activation of methane and allows for the hydromethylation of 1,1-disubstituted olefins. Preliminary results indicate that a number of such olefins are possible substrates, since 2-ethyl-1-butene, methylenecyclohexane, and methylenecyclopentane are converted in the presence of catalyst **2** under 4 atm of methane to the corresponding, methylated alkane (3,3-dimethylpentane, 1,1-dimethylcyclohexane, and 1,1-dimethylcyclopentane; observed yields were 10 (0.5 TON), 56 (2.8 TON), and 68% (3.4 TON), respectively). Although more selective catalysts are required to make this hydromethylation chemistry synthetically useful, hydromethylation with a d^0 catalyst seems to offer a fundamentally new approach to catalytic carbon−carbon bond formation. The mild conditions associated with this chemistry and the strong influence that catalyst structure appears to have over selectivity are encouraging with respect to the possible development of more efficient catalysts.

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Supporting Information Available: Synthetic procedure and characterization data for **2** and experimental details for kinetic runs. The material is available free of charge via the Internet at http://pubs.acs.org.

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