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# Investigations of the magnitude of steric and $\alpha$ deuterium kinetic isotope effects in a carbon–carbon bond-forming reaction of a permethylscandocene complex *,**

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## Abstract

No measurable isotope effect is observed in the reaction of $(Cp^{\star}\text{-}d_{15})_2Sc\text{-}CH_3$ (**1a**, $Cp^{\star} = \eta^5\text{-}C_5(CH_3)_5$) with $CD_3C{\equiv}CCH_3$ to yield a mixture of $(Cp^{\star}\text{-}d_{15})_2Sc\text{–}C(CD_3)C{=}C(CH_3)_2$ (**2a**) and $(Cp^{\star}\text{-}d_{15})_2Sc\text{–}C(CH_3)C{=}C(CH_3)(CD_3)$ (**2b**) (**2b**:**2a** = 1.01 ± 0.02:1). Thus steric repulsions between the 2-butyne methyl group and the scandium-bound methyl group are not sufficiently severe to give rise to a measurable steric deuterium kinetic isotope effect. Similarly, **1a** reacts with $CH_3C{\equiv}CCH_3$ at approximately the same rate as does $(Cp^{\star}\text{-}d_{15})_2Sc\text{–}CD_3$ (**1b**), producing a mixture of $(Cp^{\star}\text{-}d_{15})_2Sc\text{–}C(CH_3)C{=}C(CH_3)_2$ (**2c**) and $(Cp^{\star}\text{-}d_{15})_2Sc\text{–}C(CH_3)C{=}C(CD_3)(CH_3)$ (**2d**) ($k_{2c}/k_{2d} = 1.02 \pm 0.07$). The implication from the latter finding is that a $[Sc\text{–}(\eta^2\text{-}CH_2\text{–}H)]$ $\alpha$ agostic interaction is likely *not* present in the transition state for 2-butyne insertion into the scandium methyl bond of **1**.

Ziegler–Natta polymerization of olefins has long been among the most industrially important and intellectually stimulating processes promoted by organometallic compounds [1]. The elegant studies by Pino and co-workers of polymer microstructure made a seminal contribution to the evolution of our present understanding of the nature of the active site [2]. Recently several relatively well defined catalyst systems and model compounds have provided an opportunity to investigate the mechanisms of chain propagation and chain transfer. The Cossee–Arlman picture of direct C=C insertion into a M–C bond via a four-center transition state [3] is now widely accepted as the fundamental carbon–carbon bond forming step in polymer growth [4] at least for homogeneous catalysts based on $d^0$ (or $d^0f^n$) metallocenes [5]. Using this transition state geometry as a basis, Pino and co-workers recently have provided a convincing rationale for enantiomorphic site control in propylene polymerizations [6].

Two very recent studies—one from this group of a single-component Ziegler–Natta type system [7], the other by Krauledat and Brintzinger of a zirconocene/

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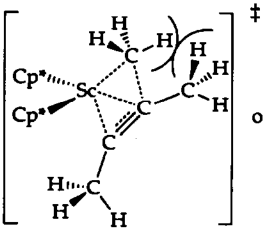
** Dedicated to the memory of Professor Piero Pino.

methylalumoxane system [8]—suggest that the Cossee–Arlman mechanism may not always provide a complete description of olefin insertion. Specifically, it appears that an agostic interaction between the metal center and an $\alpha$ C–H bond in the growing chain, a modification first suggested by Rooney and Green [9], may play an important role in stabilizing the transition state for olefin insertion. This observation has important consequences for understanding tacticity control, as it rigidly defines a particular transition-state geometry for the growing alkyl chain. However, the effect is apparently not general [4,8]. It is therefore important to probe the scope of the effect, and eventually to understand the factors which favor or discourage it.

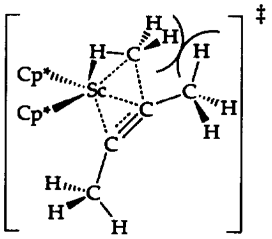
The evidence for (or against) $\alpha$-agostic assistance rests on the observation (or failure to observe) an isotopic perturbation of stereochemistry [4b], measured as an H/D isotope effect in the cyclization or hydrodimerization of singly-$\alpha$-deuterium-labeled substrates. Of course, an observed isotope effect is often open to more than one interpretation. We have considered the possibility that the isotopic perturbation of stereochemistry might have arisen from a steric isotope effect rather than an $\alpha$-agostic interaction. The lower zero-point energy of the C–D bond relative to the C–H bond makes the former a tighter bond and effectively a smaller unit. The steric distinction is only marginal but can lead to observable differences in the rates of reactions which proceed via extremely crowded transition states [10].

To test whether this steric difference could reasonably account for the results attributed to an $\alpha$-agostic effect, we chose a carbon–carbon bond forming reaction at scandium in which steric crowding in the region of the $\alpha$-carbon is maximized: insertion of 2-butyne into the Sc–C bond of $(Cp^\star\text{-}d_{15})_2Sc–CH_3$, **1a**, ($Cp^\star = \eta^5\text{-}C_5(CH_3)_5$) [11]. Since 2-butyne is a linear molecule, the methyl groups on the acetylenic carbons must lie in the same plane as the $Sc–CH_3$ unit in either transition state for insertion, conventional (**A**) or $\alpha$ agostic (**B**).



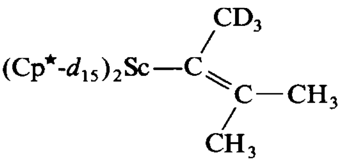
**A**

or



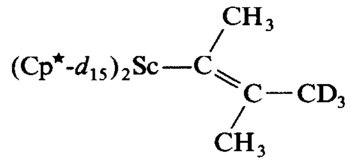
**B**

When 2-butyne-1,1,1-$d_3$, $CD_3C{\equiv}CCH_3$ [12], is allowed to react with **1a**, two regioisomeric products are expected:



$$(Cp^\star\text{-}d_{15})_2Sc-C(CD_3){=}C(CH_3)-CH_3$$

**(2a)**

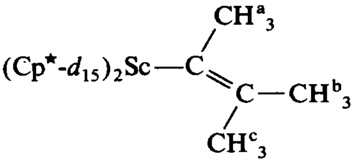


$$(Cp^\star\text{-}d_{15})_2Sc-C(CH_3){=}C(CH_3)-CD_3$$

**(2b)**

If steric interactions between the alkyne methyl groups and the scandium-bound methyl group are sufficiently severe, **2a** and **2b** will be formed in unequal amounts, with **2b** being slightly preferred due to the decreased steric demand of the $CD_3$

group relative to the $CH_3$ group. The relative amounts of **2a** and **2b** in the product mixture can be determined by integrating the $^1$H-NMR resonances of methyl groups ($CH^a_3$, $CH^b_3$, $CH^c_3$) which are cleanly resolved at 400 MHz [13*].

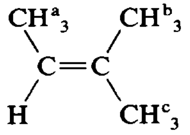


If **2a** and **2b** form in a 1 : 1 ratio, these integrals will appear in the ratio 1.50 : 1.50 : 3.00; deviation from this ratio should be indicative of a steric isotope effect.

**1a** was treated with 2-butyne-1,1,1-$d_3$ in $C_6D_6$ in a sealed NMR tube. The relative integrations of methyl groups a : b : c were 1.50 : 1.48 : 3.00, indicating that no isotopic perturbation of regiochemistry occurs, at least to the limits of NMR detection. Thus, steric repulsions between the 2-butyne methyl group and the scandium-bound methyl group are not sufficiently severe to give rise to a measurable steric deuterium kinetic isotope effect. By extension, we conclude that the kinetic deuterium isotope effects previously attributed to $\alpha$-agostic interactions in olefin insertions [7,8] are unlikely to be due to steric interactions. The transition state for olefin insertion necessarily positions the olefinic substituents out of the equatorial plane of the [$Cp_2M$-R] moiety, away from [M–R] and into the cyclopentadienyl ligands. Hence, steric interactions between the reacting metal alkyl and olefin substituents should be considerably less than those between the metal alkyl and [C–$CH_3$] in 2-butyne insertion.

We next examined this reaction for evidence of $\alpha$-agostic assistance in the transition state, by means of an internal competition experiment between ($Cp^\star$-$d_{15}$)$_2$Sc–$CH_3$ (**1a**) and ($Cp^\star$-$d_{15}$)$_2$Sc–$CD_3$ (**1b**) for unlabeled 2-butyne. If an $\alpha$-agostic interaction plays a significant role in determining the transition state energy, one would expect **1a** to react more quickly than **1b**, given the preference for H to occupy a bridging site [14]. That is, an agostic effect should manifest itself as an isotope effect $k_{CH_3}/k_{CD_3} > 1$. Furthermore, should steric interactions between the scandium methyl group and the pentamethylcyclopentadienyl ligands be severe enough, an inverse isotope effect ($k_{CH_3}/k_{CD_3} < 1$) would be observed.

We chose to monitor this reaction by treating an equimolar mixture of **1a** and **1b** with varying amounts of 2-butyne (0.25, 0.44 and 0.62 equivalents) and subsequently cleaving the [Sc–C($CH^a_3$)C=C($CH^b_3$)($CY^c_3$)] (Y = H, D) groups from scandium *in situ* with water, thereby generating the corresponding 2-methyl-2-butenes, the concentrations of which were measured directly by $^1$H NMR at 500 MHz [15]. The ratio of product olefins may be calculated from the integration of the $CH^c_3$ resonance relative to the sum of the $CH^a_3$ and $CH^b_3$ integrations.



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* Reference number with asterisk indicates a note in the list of references.

Table 1

Normalized methyl integrations for 2-methyl-butenes obtained from hydrolysis of **2c** and **2d**

| Percentage completion | Relative integration of $CH^c_3$ | Total relative integration of $CH^a_3$ and $CH^b_3$ [a] | $\frac{[CH_3(CH_3)C{=}CHCH_3]}{[CH_3(CD_3)C{=}CHCH_3]}$ | $k_{2c}/k_{2d}$ [b] |
|---|---|---|---|---|
| 25 | $1.50 \pm 0.03$ | 6.00 | $0.99 \pm 0.04$ | $1.01 \pm 0.04$ |
| 44 | $1.44 \pm 0.04$ | 6.00 | $0.92 \pm 0.05$ | $1.10 \pm 0.06$ |
| 62 | $1.53 \pm 0.04$ | 6.00 | $1.03 \pm 0.05$ | $0.96 \pm 0.05$ |

[a] Defined as 6.00. [b] Calculated according to the method described by Ingold and Shaw: C.K. Ingold and F.R. Shaw, *J. Chem. Soc.*, (1927) 2918.

The normalized methyl integrations at these three stages are given in Table 1. An isotope effect of essentially unity was observed ($k_{2c}/k_{2d} = 1.02 \pm 0.07$) [16*]. As can be seen, not only does the resonance for $CH^c_3$ integrate to the value of 1.50 expected for no isotope effect, but, importantly, it does not change systematically with percent completion.

The most straightforward conclusion we may draw from the observation that **1a** and **1b** react with 2-butyne with rates that are essentially the same is that the process proceeds by way of the conventional Cossee–Arlman transition state **A**. There is, however, reason to question whether $k_{2c}/k_{2d}$ should differ substantially from 1, even if the $\alpha$ agostic transition state **B** were followed. The earlier experiments designed to probe for $\alpha$ agostic assistance in the hydrocyclization of 1,5-hexadiene and 1,7-heptadiene and hydrodimerization of 1-deutero-1-hexene [17*] differ somewhat from the one used here. Since the $\alpha$ carbon atom was singly labeled with deuterium, those experiments utilized an *internal* H vs D competition, whereas 2-butyne competes *externally* for **1a** or **1b** (i.e. 2-butyne must choose between molecules). Moreover, should transition state **B** operate, **1b** would have two spectator deuteriums in addition to the one involved in the $\alpha$ agostic interaction. Since 2-butyne competes externally for **1a** or **1b**, no isotope effect would be in evidence if the rate determining step is coordination of 2-butyne, rather than C–C bond formation. The very large, negative entropy of activation ($\Delta S^\ddagger = -36(2)$ e.u.) and relatively small enthalpy of activation ($\Delta H^\ddagger = 9.7(3)$ kcal $\cdot$ mol$^{-1}$) associated with this process [5b] does make rate-determining 2-butyne coordination appear plausible. In the experiments utilizing an internal H vs D competition an isotope effect is expected even if olefin coordination also is rate limiting. With regard to the possible effects of the two spectator deuteriums on $k_{2c}/k_{2d}$: to the extent that the $\alpha$ agostic interaction rehybridizes the $\alpha$ carbon atom from $sp^3$ towards $sp^2$, a normal secondary deuterium kinetic isotope effect ($k_H/k_D > 1$) from each is expected [18]. Thus, the isotope effect on the $\alpha$ agostic hydrogen, also expected to be normal, should be reinforced by these secondary effects.

In conclusion, the experimentally determined isotope effect, $k_{2c}/k_{2d} = 1.02 \pm 0.07$, does strongly imply a Cossee–Arlman transition state (**A**) for 2-butyne insertion. As discussed above, only if 2-butyne insertion is rate limiting, could $\alpha$ agostic assistance occur with no observable kinetic deuterium isotope effect. Whereas these experiments have not unambiguously established whether or not $\alpha$ agostic assistance accompanies this process, they have clearly shown that steric effects (both with the 2-butyne methyl group and the $Cp^*$-$d_{15}$ ligands) [19*] are *not* sufficiently severe to give rise to a measurable steric deuterium isotope effect in alkyne insertion, and by extension, in alkene insertion reactions for these scandium alkyls.

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13 $^1$H NMR data ($C_6D_6$). $CH^a_3$: $\delta$ 1.89 (s); $CH^b_3$: $\delta$ 1.12 (q, $^4J$(H–H) $\approx$ 1.5 Hz); $CH^c_3$: $\delta$ 1.52 (m). Fully deuterated Cp$^\star$ rings were used in this experiment because the intense Cp$^\star$ resonance at $\delta$ 1.85 interferes with accurate integration of $CH^a_3$.

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15 $^1$H NMR data ($C_6D_6$): $CH^a_3$: $\delta$ 1.52 (m); $CH^b_3$: $\delta$ 1.51 (m); $CH^c_3$: $\delta$ 1.64 (m).

16 This reaction can also be monitored by integrating the $^1$H NMR resonances due to the methanes produced by hydrolysis of the unreacted Sc–CY$_3$ groups. The ratio of $CH_4$ to $CH_3D$ thus obtained is invariant over all examined levels of conversion, consistent with the absence of a significant isotope effect. However, the observed ratio is not 1 : 1, but rather varies from 1 : 1.2 to 1 : 1.4, depending upon the manner in which the spectra were recorded. We do not understand the source of this apparent systematic error in the integrations of these methanes in solution (spectra were acquired with a relaxation delay of 5–10 $T_1$'s to eliminate saturation effects; integrals were invariant over this range of relaxation delays), although it may be due to the very different peak shapes (singlet vs septet).

17 Preliminary experiments reveal that $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}ScH(PMe_3)$, like the $Cp_2ZrCl_2$/MAO system reported by Krauledat and Brintzinger (ref. 8), catalyzes hydrodimerization of 1-deutero-1-hexene preferentially to *erythro*-5-deuteromethyl-6-deuteroundecane. W.E. Piers and J.E. Bercaw, unpublished results.

18 L. Melander and W.H. Saunders Jr, Reaction Rates of Isotopic Molecules, Wiley, New York, 1980, chap. 6.

19 There is a remote possibility that the steric interactions between [Sc–CY$_3$] (Y = H, D) and $Cp^\star\text{-}d_{15}$ ligands give rise to an inverse $k_{2c}/k_{2d}$ which precisely offsets (or nearly so) the normal $\alpha$ agostic $k_{2c}/k_{2d}$!