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Direct Observation of the Structural Isomerization of a Cationic Group 4 Ziegler−Natta Insertion Product

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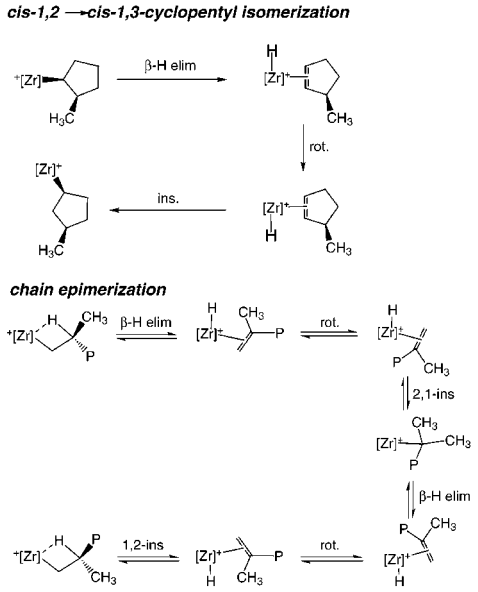
Structural rearrangements within a growing polymer chain that are competitive with propagation are known to strongly influence final polymer microstructure and, hence, the properties of polyolefins prepared through the Ziegler−Natta polymerization of olefins with group 4 metallocene catalysts.[1−3] In particular, epimerization of the chiral center of the last monomer added, prior to chain extension through further insertions, has now been identified as an important source of stereoerrors within predominantly isotactic polypropene prepared with C_2-symmetric *ansa*-bridged zirconocene initiators.[1] Additionally, the Ziegler−Natta polymerization of cyclopentene with this same class of initiator has been shown to exclusively produce isotactic *cis*-poly(1,3-cyclopentene), rather than the expected *cis*-poly(1,2-cyclopentene) material, presumably as a result of rapid isomerization of the initial *cis*-1,2-insertion product to the *cis*-1,3 configuration before complexation and insertion of another cyclopentene unit.[3] Indeed, the apparent ease with which this latter isomerization proceeds has so far been potentially responsible for the inability to observe the initial *cis*-1,2 insertion product in this system, or of that involving the polymerization of cyclopentene with a class of late transition-metal initiators, even at the low temperature of −80 °C.[4] The generally accepted mechanism by which this 1,2 → 1,3 cyclopentyl isomerization proceeds involves a series of single steps comprising β-hydride elimination, rotation of the alkene fragment within the ligand sphere of the resulting metal hydride intermediate, followed by reinsertion according to Scheme 1. For epimerization during propene polymerization, the same elementary steps have also been proposed; however, the total sequence is now considerably longer, and it requires both a 2,1-insertion to produce an intermediate with a tertiary carbon bonded to the metal and a 1,2-insertion, which is the normal mode of propagation, to provide the final epimerized product (see Scheme 1).[1,2,5−7] Unfortunately, although the results of theoretical investigations[2] and of single and double isotopically labeled propene studies[1] appear to support many of the proposed elements of this mechanism, as with 1,2 → 1,3 cyclopentyl isomerization, no experimental model system yet exists for chain epimerization that can be used to provide more definitive verification through direct observation of the isomerization process within a group 4 cationic complex.[8] Herein, we now provide the first experimental model for the 1,2 → 1,3 cyclopentyl isomerization process. Results obtained through structural and kinetic analyses of this system have provided critical clues regarding the factors that appear to drive this process forward.

The cationic monocyclopentadienyl zirconium acetamidinate, $[(\eta^5\text{-}C_5Me_5)ZrMe\{N(Et)C(Me)N(^tBu)\}]^+[B(C_6F_5)_4]^-$ (**1**), has previously been shown to be a highly active initiator for the isospecific living polymerization of α-olefins.[9] Addition of ∼1−2 equiv of cyclopentene to **1** in chlorobenzene-d_5 at either −30° or −10 °C

Scheme 1



resulted in rapid (<1 min) and quantitative formation of a single inserted product that was found to be indefinitely stable in solution at −30 °C as evidenced by NMR spectroscopy.[10] Elucidation of the solution structure of **2** at this temperature was achieved by employing a range of 1- and 2D NMR techniques conducted at high-field strength (500 and 125 MHz for ^{1}H and ^{13}C NMR, respectively), and as Chart 1 shows, this analysis revealed a number of intriguing features. To begin, compound **2** represents the *cis*-1,2 product arising from migratory insertion of the methyl group of **1** into cyclopentene, thus providing the first verification of this previously proposed structural entity. Significantly, a series of 1D NOE ^{1}H NMR spectra conclusively show that the *cis*-2-methyl substituent of the cyclopentyl ring is on the side of, and in close proximity to, the *tert*-butyl group of the acetamidinate ligand. This stereochemical arrangement strongly indicates that cyclopentene must approach, and coordinate to, the less sterically encumbered *N*-ethyl side of the acetamidinate fragment, directing, at the same time, the soon-to-be-inserted methyl group toward the *N*-(*tert*-butyl) group. As shown, **2** also possesses a single strong β-agostic interaction in solution with the hydrogen-labeled, $H_{\beta a}$, that is supported by both a high-field ^{1}H chemical shift (δ −1.43 ppm) and a substantially reduced $^1J(^{13}C-^1H)$ value of 87.7 Hz;[11] the latter being obtained from a 2D *J*-resolved $^{13}C-^1H$ HSQC NMR spectrum. This 2D NMR technique also provided $^1J(^{13}C-^1H)$ values of 146.2 and 141.3 Hz for the geminal hydrogen partner, H_β, and for the hydrogen on the zirconium-bonded carbon atom, H_α, respectively. Both of these values are significantly larger than values observed for typical sp^3-hybridized carbon atoms (e.g., 125−130

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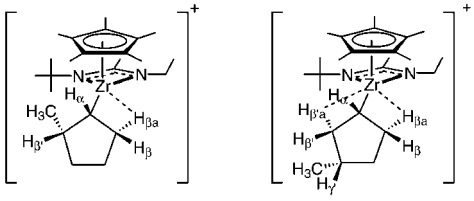
Chart 1



2

$^1J(C_\alpha\text{-}H_\alpha)$ = 141.3 Hz
$^1J(C_\beta\text{-}H_{\beta a})$ = 87.7 Hz
$^1J(C_\beta\text{-}H_\beta)$ = 146.2 Hz
$^1J(C_{\beta'}\text{-}H_{\beta'})$ = 131.6 Hz

3

$^1J(C_\alpha\text{-}H_\alpha)$ = 160.8 Hz
$^1J(C_\beta\text{-}H_{\beta a})$ = 97.5 Hz
$^1J(C_\beta\text{-}H_\beta)$ = 141.3 Hz
$^1J(C_\beta\text{-}H_{\beta' a})$ = 107.2 Hz
$^1J(C_{\beta'}\text{-}H_{\beta'})$ = 126.7 Hz

Hz), and each is the expected result of the strong β-agostic interaction involving $H_{\beta a}$.[12]

The strength of the β-agostic interaction in **2** was further revealed in the nature of the ^{1}H NMR spectra for this compound that appear static, apart from rotation of the η^5-C_5Me_5 group, over the temperature range of −35° to 25 °C as indicated by a narrow line-width, well-defined coupling pattern being observed for $H_{\beta a}$. Despite this static structure, however, upon warming above −30 °C, compound **2** was also observed by ^{1}H NMR to cleanly, and quantitatively, convert to the *cis*-1,3-product **3** through a first-order process. An arsenal of 1- and 2D NMR techniques was again used to confirm the solution structure of this species. To begin, like **2**, the *cis*-3-methyl cyclopentyl substituent is on the same side as the *tert*-butyl group of the acetamidinate fragment as supported by a series of 1D NOE NMR experiments.[10] Compound **3**, however, now sports *two* β-hydrogen agostic interactions rather than the single one of **2**. Interestingly, the chemical shifts and measured $^1J(^{13}C-^1H)$ coupling constants indicate that $H_{\beta a}$ (−1.51 ppm, 97.5 Hz), which is on the more sterically open side of the zirconium center, is engaged in a stronger agostic interaction than $H_{\beta' a}$ (0.6 ppm, 107.2 Hz), whose closest approach to the metal might be hindered by the steric bulk of the *tert*-butyl group (see Chart 1). As a possible result of these dual agostic interactions, the $^1J(^{13}C-^1H)$ coupling constant for H_α has now dramatically increased to 160.8 Hz in **3** relative to the corresponding value of 141.3 Hz in **2**. Here it is important to note that theoretical studies of the proposed chain epimerization mechanism all agree that dual β-agostic interactions help to stabilize the 2,1-insertion product that has a zirconium-bonded tertiary carbon center[2], and Prosenc and Brintzinger[2a] further find that this carbon atom should have hybridization approaching that of a *tert*-butyl cation. Thus, the present structural studies of **2** and **3** appear to support these theories as it is likely that, in addition to steric considerations, formation of the dual β-agostic interactions of **3** also serves to drive the 1,2 → 1,3 cyclopentyl isomerization forward.

To probe the mechanism by which the observed 1,2 → 1,3 cyclopentyl isomerization may be occurring, cyclopentene-1,2-d_2 was prepared and subjected to insertion and isomerization. This study conclusively revealed that $H_{\beta a}$ of **2** becomes $H_{\beta' a}$ of **3**.[10] In other words, an overall stereoselective *syn*-1,2-hydrogen shift has occurred on the same side as that for the migrating zirconium center. This stereochemical course is in agreement with the β-hydride elimination/reinsertion mechanism of Scheme 1. Curiously, however, the results of an Eyring analysis using VT NMR (five data points from −10° to 20 °C), which provided the thermodynamic parameters, $\Delta H^\ddagger = 21.8$ (5) kcal mol^{-1}, $\Delta S^\ddagger = 8.1$ (5) eu, are not in agreement since a negative $\Delta S^\ddagger$ value is normally to be expected if either a β-hydride elimination or a 1,2-insertion step is rate-determining.[13] On first inspection, it is also somewhat surprising that such a large energy barrier exists for a β-hydride elimination process in which the ground-state already possesses a substantial β-agostic interaction with the requisite hydrogen atom. These seeming inconsistencies can be reconciled, however, by considering that the strong β-agostic interaction serves to both stabilize the ground state of **2** and order it in close approximation to the transition state.[13] Thus, under the latter circumstance, the sign for $\Delta S^\ddagger$ might be more strongly influenced by other factors, such as the relative extent of ion-paring in the ground- and transition-state structures. We have also considered that the transition state for rotation of the cycloalkene fragment within the ligand sphere of the first alkene hydride intermediate represents the maximum on the reaction energy profile for the **2** → **3** process. Such a situation would necessitate that a rapid equilibrium exists between **2** and the initial alkene hydride complex, and this cannot be ruled out at the present time. The possibility also exists that 1,2 → 1,3 cyclopentyl isomerization might actually proceed through a concerted pathway where breaking of the $C_\beta-H_{\beta a}$ bond and alkene rotation occur simultaneously within a single transition-state structure.[14] Studies are now in progress that might serve to clarify this isomerization mechanism further.

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Supporting Information Available: Selected 1- and 2D ^{1}H NMR spectra for **2** and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) The mechanisms for both chain epimerization and 1,2 → 1,3 cyclopentyl isomerization are actually more complex than presented as experimental evidence exists to show that the proposed zirconium alkene intermediate can sometimes undergo a switch in which enantiotopic face of the alkene is bound to the metal, even in the presence of excess monomer.[1,3]

(7) Although the alkene hydride complexes of Scheme 1 are drawn as distinct intermediates, it has been recognized that these may actually exist as only transient species due to shallow associated potential energy minima.[1,2]

(8) In contrast, the mechanism for "chain-walking" that occurs during olefin polymerization that is mediated by a class of diimine Ni(II) and Pd(II) catalysts has been well investigated, see: Schultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc*. **2001**, *123*, 11539−11555 and references therein.

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