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Alkene Dissociation from a d^0 Yttrocene−Alkyl−Alkene Complex Generates a Pyramidal Alkyl Yttrium Complex That Inverts Slowly

Charles P. Casey,* Maureen A. Fagan, and Susan L. Hallenbeck

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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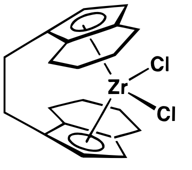
Summary: The d^0 yttrium(III)−alkyl−alkene chelate Cp$_2$Y[η^1:η^2-CH$_2$CH$_2$CH(CH$_3$)CH=CH$_2$] (**5**) was prepared by reaction of 3-methyl-1,4-pentadiene with (Cp*$_2$YH)$_2$. Variable-temperature ^{13}C NMR spectroscopy of **5** showed that the environments of the two diastereotopic Cp* ligands were averaged by a fluxional process which requires both reversible alkene dissociation and inversion at the yttrium center; the energy barrier for alkene dissociation plus yttrium inversion is 9.6 ± 0.3 kcal mol^{-1}.*

Ziegler−Natta polymerization of substituted alkenes catalyzed by group 3 and 4 d^0 metallocenes often produces polymers with high stereospecificity.[1] The key proposed intermediate in the polymerization is a d^0 metal−alkyl−alkene complex that adds a growing polymer chain to the coordinated alkene to produce a pyramidal metal complex with an extended alkyl chain. In Bercaw's model for stereocontrol of propylene polymerization, the geometry of the growing alkyl chain is set by a combination of an α-agostic interaction and steric interaction with the metallocene ligands; the alkene coordinates to minimize the interaction between the growing alkyl chain and the methyl group of propene.[2] For C_2-symmetric metallocene catalysts such as **1**,[3] the formation of highly isotactic polypropylene is not affected by the rate of inversion at the metal center since the same enantioface of propene coordinates selectively to either of the C_2-related sites on the metal.



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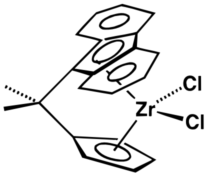

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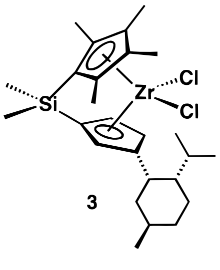

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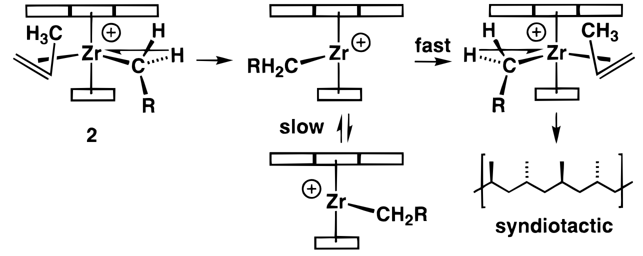
Scheme 1



In other cases, the stereochemistry of the polymer depends on the relative rates of coordination of the next monomer and inversion at the metal center. For example, with Ewen's C_s-symmetric metallocene catalyst **2**,[4] the production of highly syndiotactic polypropylene requires slow inversion at the catalyst's metal center relative to coordination and insertion of the next monomer (Scheme 1). In the case of catalyst **3**,[5] Marks attributed the production of isotactic polypropylene to rapid inversion at the metal center relative to alkene coordination and insertion; chain extension occurs from one sterically favored invertomer. Farina has reported a catalyst for the formation of hemi-isotactic polypropylene that requires slow inversion of a pyramidal metal alkyl intermediate.[6]

Recently we reported the synthesis and spectroscopic characterization of Cp*$_2$YCH$_2$CH$_2$C(CH$_3$)$_2$CH=CH$_2$ (**4**), the first directly observed metal−alkyl−alkene complex.[7] The observation of only a single Cp* resonance for **4** in both ^{1}H and ^{13}C NMR spectra at −100 °C provided evidence for rapid and reversible decomplexation of the alkene. Here we report the related d^0 yttrium(III)−alkyl−alkene chelate Cp*$_2$Y[η^1:η^2-CH$_2$CH$_2$CH(CH$_3$)CH=CH$_2$] (**5**) and ^{13}C NMR spectroscopic evidence for a fluxional process that requires both alkene dissociation and inversion at the yttrium center.

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[4] Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255.

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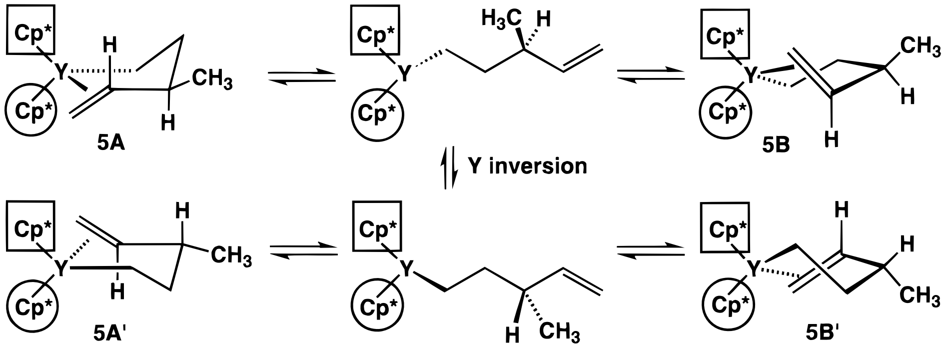
Scheme 2



Reaction of (Cp*$_2$YH)$_2$[8] and 3-methyl-1,4-pentadiene at −78 °C in methylcyclohexane-d_{14} gave the pentenyl chelate **5** in 95% yield (^{1}H NMR integration with CH$_2$(SiMe$_3$)$_2$ internal standard).[9] As in the case of **4**, evidence for alkene coordination was obtained from three lines of evidence: (1) changes in the ^{1}H and ^{13}C NMR chemical shifts of the vinyl hydrogens upon coordination, (2) reversal of these ^{1}H and ^{13}C NMR changes upon displacement of the alkene by THF, and (3) observation of NOE effects between Cp* protons and vinyl hydrogens. In the ^{1}H NMR spectrum of **5** at −50 °C, the vinyl hydrogen resonances are shifted to δ 6.41, 5.26, and 3.81 compared with δ 5.70, 4.95, and 4.90 for 3-methyl-1,4-pentadiene. In the ^{13}C NMR spectrum of **5** at −50 °C, the alkene carbon resonances appear at δ 163.1 and 110.8 compared with δ 142.0 and 113.3 for 3-methyl-1,4-pentadiene. Addition of 1 equiv of THF to **5** led to displacement of the coordinated alkene by THF and formation of Cp*$_2$Y[η^1-CH$_2$CH$_2$CH(CH$_3$)-CH=CH$_2$](THF) (**6**), which has vinyl hydrogen resonances (−50 °C: δ 5.73, 4.82, and 4.76) and alkene carbon resonances (−50 °C: δ 146.7 and 110.4) similar to those of 3-methyl-1,4-pentadiene.[10] At −50 °C, THF exchange with **6** is slow and separate ^{1}H and ^{13}C NMR resonances are seen for the diastereotopic Cp* groups of **6**. In the ^{1}H NOESY spectrum of **5**, evidence for alkene coordination was obtained from the observation of large cross peaks between the Cp* methyl hydrogens and the vinyl hydrogens of the coordinated alkene; cross peaks of the same magnitude are observed between the Cp* methyl groups and the YCH$_2$ group.

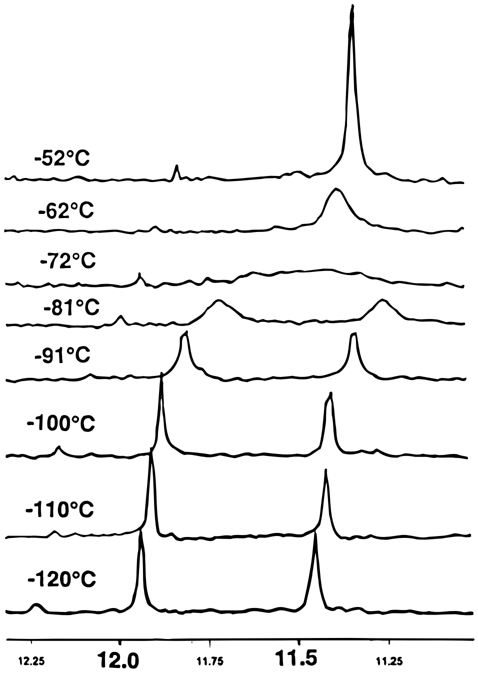


Figure 1. Temperature dependence of ^{13}C NMR Cp* methyl resonances of Cp*$_2$Y[η^1:η^2-CH$_2$CH$_2$CH(CH$_3$)CH=CH$_2$] (**5**) in 1/1 methylcyclohexane-d_{14}/pentane-d_{12}.

The ^{13}C NMR spectrum of **5** at −120 °C in 1/1 methylcyclohexane-d_{14}/pentane-d_{12} showed two inequivalent Cp* resonances at δ 11.9 and 11.5 (Figure 1). Upon warming, the Cp* resonances of **5** broadened, coalesced at −72 °C, and became a sharp singlet ($w_{1/2}$ = 3 Hz) at −52 °C. Spectra between −60 and −90 °C were simulated using the program WinDNMR[11] and gave $\Delta G^\ddagger = 9.6 \pm 0.3$ kcal mol^{-1} at T_c.[12]

The inequivalence of the Cp* resonances of the monomethyl chelate **5** stands in sharp contrast to the equivalence of the Cp* resonances of the dimethyl chelate **4**. For **4**, alkene dissociation and recomplexation to the opposite enantioface without inversion at the yttrium center is sufficient to interchange the environments of the Cp* ligands and is fast at −100 °C. In contrast, for **5**, while rapid alkene dissociation and recoordination to the opposite enantioface changes the environments of the Cp* ligands, it does not interchange their environments (Scheme 2). Without inversion at the yttrium center, this process interconverts two diastereomers: **5A** (tether methyl cis to the secondary

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[8] den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053.

[9] Cp*$_2$Y{η^1:η^2-CH$_2$CH$_2$CH(CH$_3$)CH=CH$_2$] (**5**): ^{1}H NMR (500 MHz, C$_6$D$_{11}$CD$_3$, −50 °C) δ 6.41 (dt, J_{trans} = 17.0 Hz, J_{cis} = J_{CH} = 11.0 Hz, =CH), 5.26 (dd, J_{trans} = 17.0 Hz, J_{gem} = 3.0 Hz, =C*H*H) 3.81 (dd, J_{cis} = 11.0, J_{gem} = 3.0 Hz, =CH*H*) 1.92 (s, C$_5$Me$_5$), 1.46 (m, YCH$_2$C*H$_2$*), 0.91 (d, J = 6.5 Hz, CH$_3$), 0.32 (m, YCH*H*), −1.00 (m, YC*H*H), resonance for C*H*Me is obscured by the C$_5$Me$_5$ resonance; ^{13}C NMR (126 MHz, C$_6$D$_{11}$CD$_3$, −50 °C) δ 163.1 (s, CH=), 116.5 (s, *C$_5$*Me$_5$), 110.8 (s, CH$_2$=), 45.2 (s, *C*HMe), 36.4 (s, YCH$_2$*C*H$_2$), 34.5 (d, J_{YC} = 47.0 Hz, YCH$_2$), 21.1 (s, CH$_3$), 11.6 (s, C$_5$*Me$_5$*).

[10] Cp*$_2$Y[η^1-CH$_2$CH$_2$CH(CH$_3$)CH=CH$_2$](THF) (**6**) was prepared from 0.04 mmol of **5** and 0.04 mmol of THF in 91 ± 5% yield by ^{1}H NMR integration using CH$_2$(SiMe$_3$)$_2$ as an internal standard. ^{1}H NMR (500 MHz, C$_6$D$_{11}$CD$_3$, −50 °C): δ 5.73 (ddd, J = 17.5, 10.0, 7.0 Hz, CH=), 4.82 (dd, J_{trans} = 17.5 Hz, J_{gem} = 2.5 Hz, =CH*H*), 4.76 (dd, J_{cis} = 10.0 Hz, J_{gem} = 2.5 Hz, =C*H*H), 3.68 (m, α-THF), 1.91 (m, β-CH$_2$), 1.89 (s, 15H, C$_5$Me$_5$), 1.88 (s, 15H, C$_5$Me$_5$), 1.32 (m, YCH$_2$C*H$_2$*), 0.96 (d, J = 6.5 Hz, CH$_3$), −0.53 (m, YCH*H*), −0.64 (m, YC*H*H), resonance for YCH$_2$CH$_2$C*H* is obscured by the C$_5$Me$_5$ resonance. ^{13}C NMR (126 MHz, C$_6$D$_{11}$CD$_3$, −50 °C): δ 146.7 (s, CH=), 115.4 (s, *C$_5$*Me$_5$), 110.4 (s, CH$_2$=), 70.8 (s, α-THF), 46.5 (s, *C*HMe), 38.9 (d, J_{YC} = 53.8 Hz, YCH$_2$), 36.4 (s, YCH$_2$*C*H$_2$), 26.0 (s, β-THF), 19.0 (s, CH$_3$), 11.5 (C$_5$Me$_5$).

[11] Reich, H. J. *J. Chem. Educ.* **1995**, *72*, 1086.

[12] A similar barrier is calculated from the coalescence of the ^{1}H NMR (500 MHz, C$_6$D$_{11}$CD$_3$/C$_5$D$_{12}$) resonances of the Cp* methyl hydrogens ($\Delta G^\ddagger = 9.7 \pm 0.3$ kcal mol^{-1}).

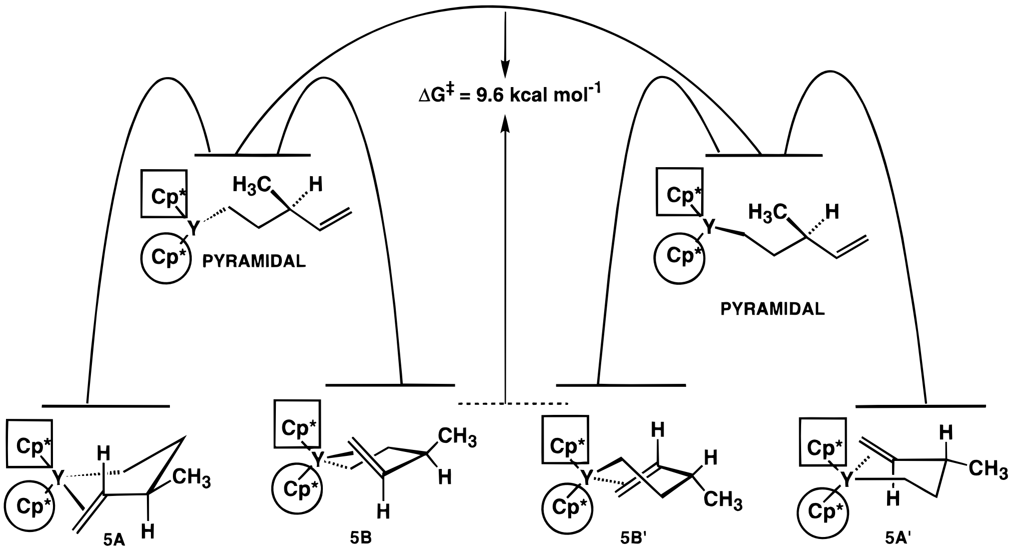

Figure 2. Energy diagram for alkene decomplexation and inversion at Y for **5**.

vinyl hydrogen) and **5B** (tether methyl trans to it). If interconversion of **5A** and **5B** were slow at −120 °C, then two pairs of diastereotopic Cp* resonances would have been seen. Rapid alkene dissociation and recomplexation to the opposite enantioface without inversion at the yttrium center averages one diastereotopic Cp* of **5A** with a Cp* of **5B** and the other diastereotopic Cp* of **5A** with its counterpart on **5B**. As a result, two Cp* resonances are observed at low temperature.

Molecular mechanics calculations (UFF implemented in Cerius^2)[13] suggest that isomer **5A** adopts a chairlike conformation with an equatorial methyl and is 1.5 kcal mol^{-1} more stable than **5B**, which adopts a twist-boat conformation to avoid an axial methyl to Cp* interaction in the chair conformation. The temperature dependence of the chemical shifts of the YCH_2 proton resonances is consistent with a temperature-dependent equilibrium between **5A** and **5B**. The difference between the chemical shifts of the diastereotopic YCH_2 protons of **5** in methylcyclohexane-d_{14} decreased from 1.40 ppm at −100 °C (δ 0.37, −1.03) to 1.15 ppm at 7 °C (δ 0.27, −0.88).

The coalescence of the Cp* resonances of **5** at −72 °C is attributed to alkene dissociation combined with inversion at the yttrium center. This combined process interchanges the environments of the Cp* ligands. When the energy barrier for inversion at yttrium is superimposed on the chelate dissociation energy, the combined process is slow enough to be observed on the NMR time scale (Figure 2).

Why should there be a barrier to inversion at the Y center? Why should a Cp^*_2YR compound not be planar at Y? In the crystal structure of $Cp^*_2YCH(SiMe_3)_2$, there are both α- and γ-agostic interactions that give rise to a nonplanar structure.[14] Perhaps decomplexation of the tethered alkene in **5** produces a Cp^*_2YR complex with an agostic interaction that must be broken to invert the yttrium center. For cationic Zr and Ti metallocene catalysts, ion pairing may help to maintain stereochemistry at the metal center. For example, Marks found that $(1,2\text{-}Me_2C_5H_3)_2ZrCH_3^+CH_3B(C_6F_5)_3^-$ undergoes inversion of stereochemistry at Zr by a process that must involve ion pair dissociation followed by inversion at Zr.[15] The rate of interchange of environments is strongly solvent dependent: barriers of 24 and 12 kcal mol^{-1} were found in toluene and 1,2-dichlorobenzene.

Information concerning the relative rates of inversion at Cp_2MR centers, of alkene coordination to Cp_2MR, and of insertion into Cp_2MR systems will greatly add to our understanding of some of the complex catalytic systems for producing syndiotactic and related polymers. Here we have determined the barrier for alkene decomplexation and inversion at yttrium and shown that recoordination of the alkene to yttrium occurs much more rapidly than inversion at the yttrium center.

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Supporting Information Available: ^{1}H NMR, ^{13}C NMR, ^{1}H NOESY, and ^{1}H−^{13}C HMQC spectra of **5** in methylcyclohexane-d_{14} (4 pages). Ordering information is given on any current masthead page.

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