

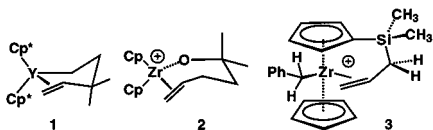
Observation of Zwitterionic d⁰ Zirconium–Alkyl–Alkene Chelates: Models for Intermediates in Metallocene-Catalyzed Alkene Polymerizations

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Metallocene catalysts are becoming increasingly important for the industrial polymerization of alkenes. Group 3 and 4 metallocenes have been used for the stereospecific polymerization of substituted alkenes.¹ Procedures designed to generate group 4 Cp₂MR⁺ species² in the presence of alkenes produce highly active polymerization catalysts. The key proposed intermediate in the polymerization is a d⁰ metal–alkyl–alkene complex, in which the growing polymer chain alkyl group adds to the coordinated alkene to produce a metal complex with an extended polymer chain.^{3,4} These intermediates are transitory in nature, presumably due to weak alkene binding to the d⁰ metal center and rapid alkene insertion, and have never been observed during catalysis. Recently, we reported the first d⁰ metal–alkyl–alkene complexes, a series of neutral d⁰ yttrium–alkyl–alkene chelates such as **1**.⁵ Studies of these complexes indicated that complexation polarizes the alkene π-bond, that alkene decomplexation is exceedingly rapid at low temperature, and that there is a significant barrier to inversion at pyramidal Cp*₂YR centers.



Because of ion-pairing problems, there are additional experimental difficulties in the synthesis of d⁰ Zr–alkyl–alkene cations more closely related to commercial metallocene catalysts. Jordan has synthesized Zr–alkoxy–alkene chelates, including [Cp₂ZrOC(CH₃)₂CH₂CH₂CH=CH₂]⁺[MeB(C₆F₅)₃][−] (**2**);⁶ Royo has prepared the novel Zr–alkyl–alkene complex [(Cp)(η⁵,η²-C₅H₄SiMe₂CH₂-CH=CH₂)Zr(CH₂C₆H₅)⁺[B(C₆F₅)₄][−] (**3**),⁷ in which the alkene is tethered to a Cp ring; Erker has reported Zr–alkyl–alkene complexes with an additional interaction between Zr and a borate carbon;⁸ Bercaw has studied the interconversion of η³- to η¹-

allyl groups in Sc and Y complexes as a model for d⁰ metal–alkene interactions.⁹ Here we report the first example of a stable zwitterionic d⁰ zirconium–alkyl–alkene complex with an all-carbon chelate backbone.

The reaction of Stryker's β-allyl zirconacyclobutane complex Cp*₂Zr[CH₂CH(CH₂CH=CH₂)CH₂] (**4**)¹⁰ with B(C₆F₅)₃¹¹ at −78 °C in CD₂Cl₂ led to the formation of a bright orange solution containing two isomers of Cp*₂Zr⁺[η¹,η²-CH₂CH[CH₂B[−](C₆F₅)₃]CH₂CH=CH₂] (**5a,b**) (Scheme 1).¹² The ¹H and ¹³C NMR spectra at −82 °C showed the presence of a 1.8:1 mixture of two diastereomers of the zwitterionic d⁰ zirconium(IV) chelate complex (**5a,b**).¹³ Evidence for alkene complexation came from perturbation of the vinyl hydrogen chemical shifts compared with those of **4**. The secondary vinyl hydrogen of **5a** appears at δ 7.92, shifted 1.63 ppm to higher frequency than in **4**, and that of **5b** is shifted 1.25 ppm to δ 7.54. Similar shifts of the secondary vinyl hydrogen of d⁰ alkene complexes were seen by us for **1** (1.04 ppm), by Jordan for **2** (1.64 ppm),⁶ and by Royo for **3** (1.58 ppm).⁷ These shifts to higher frequency have been attributed to polarization of the carbon–carbon π-bond that delocalizes positive charge from zirconium onto the secondary vinyl carbon (Scheme 2).^{5b} Perturbations of the terminal vinyl hydrogen resonances also support alkene coordination. There is little difference between these chemical shifts in the uncomplexed alkene of **4** [δ 5.25 (*J*_{trans} = 17.1 Hz), 5.14 (*J*_{cis} = 10.1 Hz), Δδ = 0.09 ppm]. In contrast, there are large chemical shift differences between the terminal vinyl hydrogens in the major chelated complex **5a** [δ 5.85 (*J*_{trans} = 17.1 Hz), 2.44 (*J*_{cis} = 10.1 Hz), Δδ = 3.41 ppm] and the minor isomer **5b** [δ 5.73 (*J*_{trans} = 17.8 Hz), 2.27 (*J*_{cis} = 12.5 Hz), Δδ = 3.46 ppm]. Two Cp* resonances were seen for the major isomer **5a** at δ 1.96 and 1.98 and for **5b** at δ 1.94 and 1.96.

The ¹³C NMR spectrum of **5a,b** also provided evidence of alkene coordination. The internal vinyl carbon resonance of **5a** at δ 163.6 was shifted 22.4 ppm to higher frequency than in **4**, and that of **5b** at δ 166.7 was shifted 25.5 ppm to higher frequency. Similar shifts were seen for yttrium alkene complex **1** and zirconium alkene complexes **2** and **3** and have been attributed to polarization of the alkene π-bond that delocalizes positive charge from zirconium onto the internal vinyl carbon. The chemical shifts of the terminal vinyl carbons of **5a** and **5b** were similar to those of precursor **4**. Resonances at δ 75.7 (**5a**) and 73.2 (**5b**) support the presence of ZrCH₂ groups.

Addition of THF to a CD₂Cl₂ solution of **5a,b** at −78 °C led to the immediate displacement of the coordinated alkene and formation of a bright yellow solution of a single THF adduct, Cp*₂Zr⁺(THF)[CH₂CH(CH₂B[−](C₆F₅)₃)CH₂CH=CH₂] (**6**)¹³ (Scheme 2). The ¹H and ¹³C NMR spectra of the vinyl group of **6** are consistent with a noncoordinated alkene, providing evidence that THF displaces the chelated alkene from the zirconium center.

Further evidence for alkene coordination in **5a** was obtained from 1D NOE difference spectra. The Cp* resonance at δ 1.98 received a 1% NOE enhancement when either the secondary vinyl hydrogen or the terminal vinyl hydrogen cis to it (δ 2.44) was irradiated. The Cp* resonance at δ 1.96 received a 1% NOE enhancement when the other terminal vinyl hydrogen at δ 5.85

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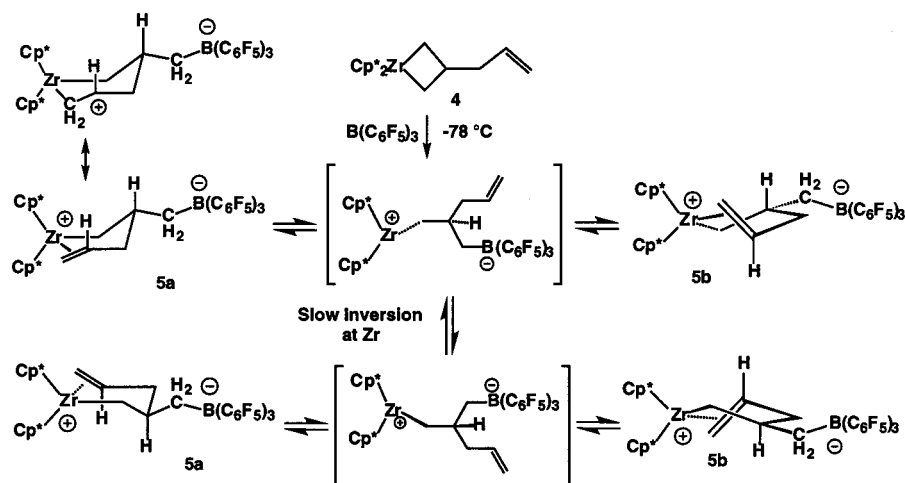
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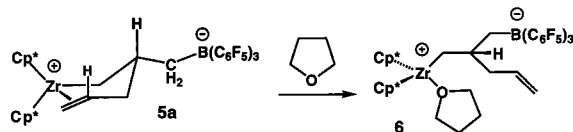
(12) Attempts to generate a zirconium–alkyl–alkene complex by protonation of **4** with a Bronsted acid have been frustrated by the strong interaction of the conjugate base of the protonating agent with the Lewis acidic zirconium center. ¹H NMR data for the reaction of **4** with dimethylanilinium tetrakis(pentafluorophenyl)borate are provided in Supporting Information.

(13) Complete NMR data for **4**, **5a,b**, and **6** are provided as Supporting Information.

Scheme 1



Scheme 2



was irradiated. In contrast, for the nonchelated THF adduct **6**, no enhancements of Cp* peaks were detected when the vinyl hydrogens were irradiated.

At $-32\text{ }^{\circ}\text{C}$, **5a** and **5b** are in rapid equilibrium, and ^1H NMR resonances for the weighted average are observed. Alkene decomplexation and recoordination to the opposite enantioface interconverts **5a** and **5b**. Vinyl hydrogen resonances are seen at δ 7.79, 5.82, and 2.47. Significantly, two Cp* resonances are seen at $-32\text{ }^{\circ}\text{C}$; this requires interchange of a specific Cp* ligand on **5a** with a specific Cp* on **5b**. Alkene decomplexation to give a pyramidal Zr complex that inverts slowly explains this phenomenon.

The rate of interconversion of **5a** and **5b** was measured by dynamic NMR by following the temperature dependence of the resonances for the secondary vinyl hydrogens. Significant broadening of the resonances began at about $-62\text{ }^{\circ}\text{C}$, coalescence occurred at about $-42\text{ }^{\circ}\text{C}$, and the averaged resonance became relatively sharp at $-32\text{ }^{\circ}\text{C}$. Line shape analysis gave $\Delta G^{\ddagger} = 10.5\text{ kcal mol}^{-1}$ for **5a** to **5b** and $\Delta G^{\ddagger} = 10.3\text{ kcal mol}^{-1}$ for **5b** to **5a**. This barrier for alkene dissociation is higher than that for the related neutral yttrium chelate **1** ($\Delta G^{\ddagger} < 8\text{ kcal mol}^{-1}$),¹⁴ presumably due to stronger alkene binding to the cationic zirconium than to the neutral yttrium center. The barrier for **5** is similar to that seen for Jordan's cationic zirconium-alkoxy-

alkene complex **2** ($\Delta G^{\ddagger} = 10.7\text{ kcal mol}^{-1}$).⁶ Royo measured a barrier of $11.7\text{ kcal mol}^{-1}$ for a process that required alkene dissociation and inversion at zirconium for **3**.⁷

In an attempt to observe coalescence of the two Cp* resonances of **5** and obtain a barrier for inversion at zirconium, the NMR spectrum of **5** was observed at higher temperature. All temperature-dependent changes are reversible up to $-35\text{ }^{\circ}\text{C}$, but significant decomposition occurred at higher temperature. Two distinct Cp* resonances are observed up to $-22\text{ }^{\circ}\text{C}$, where decomposition is occurring rapidly. This is consistent with slow inversion at zirconium and places a limit of at least 15 kcal mol^{-1} for the barrier for decomplexation, inversion at Zr, and rotation about Zr-CH₂. Previously, we observed a 9.6 kcal mol^{-1} barrier for alkene dissociation and inversion at yttrium for Cp*₂YCH₂-CH₂CH(CH₃)CH=CH₂;^{5d} Marks found that, for (1,2-Me₂C₂H₃)₂-Zr⁺CH₃ CH₃B(C₆F₅)₃⁻, the barrier for ion pair dissociation and inversion at zirconium was strongly solvent dependent and was 11 kcal mol^{-1} in C₆D₅Cl.¹⁵

Future studies of cationic zirconium-alkyl-alkene complexes generated by this method will lead to better understanding of the role of these key intermediates in metallocene-catalyzed alkene polymerization.

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Supporting Information Available: NMR spectra for **3**, **4**, **5a,b**, **6**, and Cp*₂Zr[N(CH₃)₂C₆H₅]CH₂CH(CH₃)CH₂CH=CH₂ and a figure showing coalescence of secondary vinyl hydrogen resonances of **5** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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