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Models of intermediates in metallocene-catalyzed alkene polymerizations: observation of a d^0 cationic titanium–alkyl-alkene complex and decomposition by β-allyl elimination

Donald W. Carpenetti II *

Department of Chemistry, Trinity University, San Antonio, TX 78212, USA

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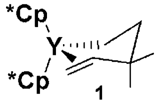
Abstract

Low temperature activation of $Cp^*_2Ti[\eta^1,\eta^1$- $CH_2CH(CH_2CH{=}CH_2)CH_2]$ **(3)** with $[HN(CH_3)(C_6H_5)_2]$ $[B(C_6F_5)_4]$ led to the formation of $Cp^*_2Ti[\eta^1,\eta^2\text{-}CH_2CH(CH_3)CH_2CH{=}CH_2][B(C_6F_5)_4]$ (**6**) as determined by ^1H NMR spectroscopy. $Cp^*_2Ti[\eta^1,\eta^2\text{-}CH_2CH(CH_3)CH_2CH{=}CH_2][B(C_6F_5)_4]$ undergoes rapid quantitative β-allyl elimination at temperatures as low as −140 °C. The resulting cationic titanium allyl complex $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][B(C_6F_5)_4]$ (**4**) exhibits a static structure at low temperatures, but interconversion of η^3–η^1 binding modes can be observed at higher temperatures. Lineshape analysis of this process yielded $\Delta G^\ddagger(-10\ ^\circ C) = 13.7 \pm 0.6$ kcal mol^{-1}, $\Delta H^\ddagger = 9.8 \pm 0.6$ kcal mol^{-1}, and $\Delta S^\ddagger = -15 \pm 3$ eu. The use of neutral borane $B(C_6F_5)_3$ also resulted in β-allyl elimination with the formation of $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][CH_2{=}CHCH_2B(C_6F_5)_3]$ (**8**).

Keywords: Metallocene; Alkyl-alkene Complex; Titanium; β-Allyl elimination

1. Introduction

The commonly accepted mechanism for metallocene-catalyzed alkene polymerization involves a d^0 metal–alkyl-alkene intermediate [1]. The absence of d electrons to stabilize the interaction between the alkene and the metal by d to π^* back-bonding and the high kinetic reactivity of these intermediates are believed to be responsible for these compounds having thus far avoided detection [2,3]. Model systems related to this intermediate that are stabilized by chelation between the alkyl group and the alkene moiety have been studied. Previous work has focused on neutral yttrium and cationic zirconium alkyl-alkene-chelates like **1** and **2** [4–9]. This report details attempts to extend this chemistry to cationic titanium analogues.



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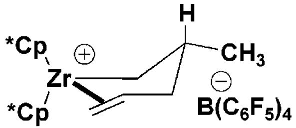

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2. Results and discussion

In order to extend work on zirconium–alkyl-alkene chelates [6,7] to titanium, the analogous β-allyl substituted titanacyclobutane complex, $Cp^*_2Ti[\eta^1,\eta^1\text{-}CH_2CH(CH_2CH{=}CH_2)CH_2]$ (**3**) was prepared. This compound has been prepared by Stryker from Ti(III) precursors [10]. Owing to an abundance of Ti(IV) compounds in inventory the synthesis was attempted in an analogous manner to that published for the zirconium analogue $Cp^*_2Zr[\eta^1,\eta^1\text{-}CH_2CH(CH_2CH{=}CH_2)CH_2]$. [11] Addition of an excess of allylmagnesium chloride to a slurry of $Cp^*_2TiCl_2$ in THF at 0 °C led to the formation of **3** in moderate yields if the reaction temperature was kept at 0 °C for 12 h.

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[*] Corresponding author. Tel.: +1-210-999-7322; fax: +1-210-999-7569.
E-mail address: Donald.Carpenetti@Trinity.edu (D.W. Carpenetti II).

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Protonation of **3** with $[HN(CH_3)(C_6H_5)_2][B(C_6F_5)_4]$ at −78 °C in CD_2Cl_2 led to the formation of $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][B(C_6F_5)_4]$ (**4**) and propene. The η^3-allyl ligand can be clearly identified in ^1H NMR by the triplet of triplets resonance at δ 7.91 ppm and the two doublet resonances at 4.99 ($J = 15.0$ Hz) and 1.57 ppm ($J = 9.7$ Hz) characteristic of a static η^3-allyl structure.

As Bercaw and co-workers [12] have recently observed, the η^3–η^1 transition of an allyl ligand is a special case of alkene dissociation from the metal center and represents the upper limit for the strength of the metal–alkene interaction (Scheme 1). The allyl ligand can be thought of as a three carbon alkyl-alkene chelate. Observation of the temperature dependence of the allyl resonances of **4** revealed that the resonance of the internal hydrogen at δ 7.91 ppm coalesced from a triplet of triplets to a pentet at −20 °C (Fig. 1). The resonances of the *syn* and *anti* hydrogens (δ 1.57 and 4.99 ppm) broadened significantly as the temperature was raised, but due to the extreme separation in frequency coalescence was not observed. Lineshape analysis of the temperature dependent broadening of these resonances yielded rate constants over a 70 °C temperature range. An Eyring plot of the data yielded $\Delta H^{\ddagger} = 9.8 \pm 1.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -15 \pm 4$ eu, corresponding to $\Delta G^{\ddagger}(-20\ °C) = 13.6 \pm 0.6$ kcal mol^{-1}.

The dynamic NMR behavior of $Cp^*_2Sc(\eta^3\text{-}CH_2CHCH_2)$ (**5**), the neutral group III analogue of **4**, was reported by Bercaw and co-workers [12]. Activation parameters for its η^3–η^1 interconversion were found to be $\Delta H^{\ddagger} = 8.0 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14 \pm 4$ eu [$\Delta G^{\ddagger}(-20\ °C) = 11.5$ kcal mol^{-1}] in ether. The free energy barrier for η^3–η^1 interconversion in **4** is 2.1 kcal mol^{-1} higher than the corresponding barrier for neutral scandium. This difference is very similar to those observed between neutral yttrium and cationic zirconium–alkyl-alkene chelates featuring five carbon tethers. Cationic zirconium–alkyl-alkene chelates have an alkene face dissociation barrier ranging from 10 to 11 kcal mol^{-1} [6,7]. The corresponding barrier for neutral yttrium–alkyl-alkene chelates ranges from 7.5 to 8.5 kcal mol^{-1} [4,5].

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Scheme 1.

Although some interesting comparisons can be made by analyzing the rate of η^3–η^1 interconversion for allyl complexes, more information could be gathered by observing the titanium–alkyl-alkene chelate with a five carbon tether. With this goal in mind, **3** was treated with $[HN(CH_3)(C_6H_5)_2]$ $[B(C_6F_5)_4]$ at −140 °C in $CDCl_2F$/$CDClF_2$ [13]. Much lower temperatures were employed in an attempt to observe the titanium–alkyl-alkene complex $Cp^*_2Ti[\eta^1,\eta^2\text{-}CH_2CH(CH_3)CH_2CH{=}CH_2][B(C_6F_5)_4]$ (**6**) before it could β-allyl eliminate (Scheme 2).

Unfortunately, at −140 °C the rate of β-allyl elimination is still fairly rapid ($t_{1/2} < 60$ s) [14]. Complex **6** was partially identified by ^1H NMR at −140 °C. The high frequency shift of the resonance assigned to the secondary vinyl proton of **6** (δ 7.96 ppm) is characteristic of an alkene bound to a d^0 metal center (Fig. 2). **1** and **2** feature similar resonances at δ 6.78 and 7.89 ppm, respectively [4,7]. The difference in chemical shift of the resonances assigned to the two terminal vinyl protons [δ 5.46 and 2.42 ppm, $\Delta\delta({=}CH_2) = 3.04$ ppm] is similar to those observed for related cationic zirconium–alkene chelates [$\Delta\delta({=}CH_2) = 2.99$ ppm for **2**] [7] and more pronounced than those observed for yttrium–alkene chelates [$\Delta\delta({=}CH_2) = 1.38$ ppm for **1**] [4]. Another characteristic of alkyl-alkene chelates is a low frequency shift of one of the diasteriotopic α-methylene protons. In **6**, the broad doublet resonance at δ −0.65 ppm is reminiscent of those observed for more thoroughly

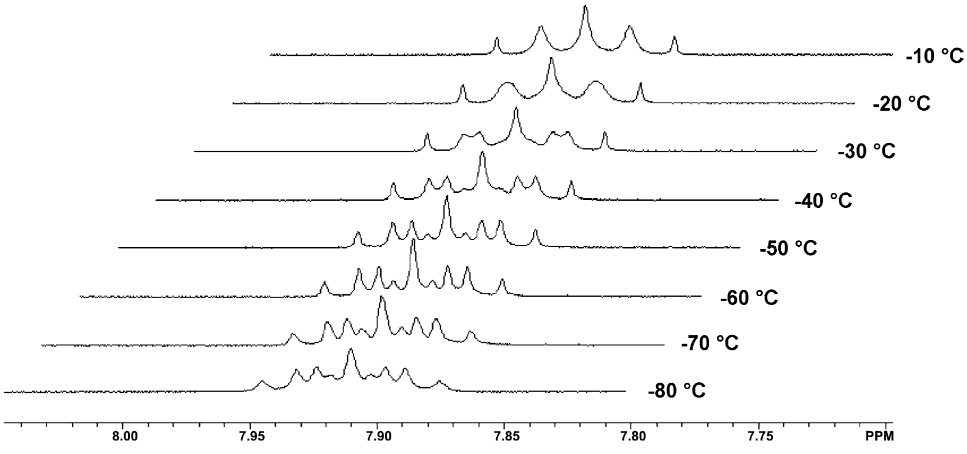
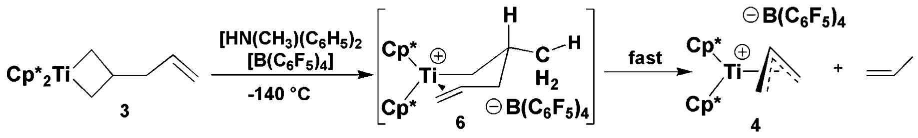


Fig. 1. Interconversion of the internal allyl hydrogen ^1H NMR resonance of **4** from a triplet of triplets to a pentet, a consequence of the *syn* and *anti* hydrogens of the allyl ligand becoming equivalent on the NMR time scale.



Scheme 2.

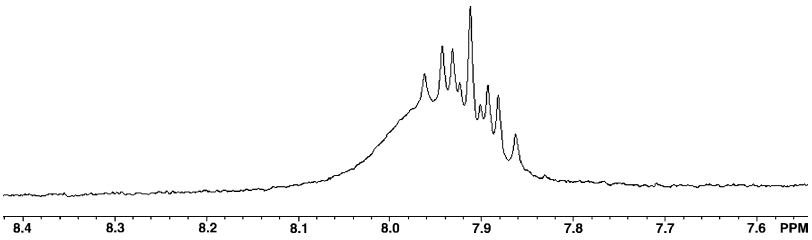


Fig. 2. ^{1}H NMR spectrum of a mixture of $Cp^*_2Ti[\eta^1,\eta^2\text{-}CH_2CH(CH_3)CH_2CH{=}CH_2][B(C_6F_5)_4]$ (**6**) (broad multiplet centered at δ 7.96 ppm) and $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][B(C_6F_5)_4]$ (**4**) (triplet of triplets at δ 7.91 ppm) at −140 °C in $CDCl_2F/CDClF_2$.

characterized complexes **1** (δ −0.44 ppm) and **2** (δ −0.83 ppm). Due to the short lifetime of **6** at −140 °C it could not be fully characterized by NMR, but all evidence from ^{1}H NMR is consistent with the assigned structure.

In contrast to related zirconium–alkyl-alkene chelate **2** [7] where two diastereomers are observed at low temperature, only one diastereomer of **6** is observed. This could be due to a very low barrier for alkene dissociation from the sterically hindered titanium center resulting in an averaging of the resonances of the two diastereomers on the NMR time scale, but is more likely due to a steric interaction between the β-methyl group of the alkyl chain and one of the Cp* ligands which leads to observation of only one orientation which features the methyl group in a pseudo-equatorial position [5].

The reaction of **3** with $B(C_6F_5)_3$ was attempted to see if the zwitterionic titanium–alkyl-alkene complex $Cp^*_2Ti\{\eta^1,\eta^2\text{-}CH_2CH[CH_2B(C_6F_5)_3]CH_2CH{=}CH_2\}$ (**7**) would be more thermally stable. This compound also quickly and quantitatively undergoes β-allyl elimination forming $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][CH_2{=}CHCH_2B(C_6F_5)_3]$ (**8**). Variable temperature NMR analysis of **8** showed that changing the anion from $B(C_6F_5)_4$ to $CH_2{=}CHCH_2B(C_6F_5)_3$ had no effect on the η^3–η^1 interconversion of the allyl ligand.

3. Experimental

3.1. General considerations

All reactions were carried out in an inert atmosphere glovebox or using standard high-vacuum line techniques. All NMR experiments were carried out in 1.9 ml medium-walled resealable NMR tubes that were flamed–dried under vacuum prior to use. NMR spectra were obtained using a Varian Inova 400 spectrometer. Spectrometer temperatures were measured after a 15-min equilibration, using a methanol standard containing 0.03% HCl. CD_2Cl_2 (Cambridge Isotopes) was dried over P_2O_5, then distilled from CaH_2. $CDCl_2F/CDClF_2$ was prepared by a published procedure and stored over CaH_2 [13]. Tetrahydrofuran and pentane were dried over sodium then distilled. Allylmagnesium chloride was obtained from Aldrich as a THF solution and used as received. $[HNCH_3(C_6H_5)_2][B(C_6F_5)_4]$ was prepared by a known procedure [7].

3.2. Preparation of $Cp^*_2Ti[\eta^1,\eta^1\text{-}CH_2CH(CH_2CH{=}CH_2)CH_2]$ (3)

$Cp^*_2TiCl_2$ (1.0 g, 2.57 mmol) was slurried in THF (40 ml). Allylmagnesium chloride (10 ml of a 2.0 M THF solution, 20 mmol) was added by syringe at 0 °C. The reaction was stirred for 12 h at 0 °C and then solvent was removed under reduced pressure. Resulting material was triturated with pentane, chilled to −30 °C and filtered. Removal of solvent from the filtrate yielded **3** as a red powder (0.43 g, 42%). NMR was consistent with literature data [10].

3.3. Reaction of 3 with $[(C_6H_5)_2(CH_3)NH]$ $[B(C_6F_5)_4]$ at −78 °C

CD_2Cl_2 (0.5 ml) was condensed into a resealable NMR tube containing **3** (0.018 g, 0.044 mmol) and $[(C_6H_5)_2(CH_3)NH][B(C_6F_5)_4]$ (0.038 g, 0.044 mmol) at −78 °C. The tube was shaken briefly at −78 °C to give a red solution and was inserted into the precooled probe of the NMR spectrometer. The NMR spectrum shows a mixture of $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][B(C_6F_5)_4]$ **4**, $(C_6H_5)_2(CH_3)N$ and propene, details are given below.

3.3.1. NMR Data for $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][B(C_6F_5)_4]$ (**4**) at −78 °C

^{1}H NMR (400 MHz, CD_2Cl_2, −78 °C) δ 1.54 (d, $J = 9.6$ Hz, CH*H*CHCH*H*), 1.99 (s, C_5Me_5), 5.02 (d, $J = 15$ Hz, C*H*HCHC*H*H), 7.91 (tt, $J = 15$, 9.6 Hz, CHHC*H*CHH). ^{13}C NMR (gated decoupled, 100.5 MHz, CD_2Cl_2, −78 °C) δ 12.8 (s, C_5Me_5), 13.8 (s, C_5Me_5), 91.6, (dd, $J = 156$, 151 Hz, *C*HHCH*C*HH), 124.1 (s, broadened by J_{BC}, *ipso*-C_6F_5), 129.6 (br s, overlapping C_5Me_5), 136.9 (d, $J_{CF} = 245$ Hz, C_6F_5), 139.0 (d, $J_{CF} = 247$ Hz, C_6F_5), 148.3 (d, $J_{CF} = 245$ Hz, C_6F_5), 156.3 (d, $J = 155$ Hz, CHH*C*HCHH).

3.3.2. NMR Data for $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][B(C_6F_5)_4]$ (**4**) at −0 °C

^{1}H NMR (400 MHz, CD_2Cl_2, 0 °C) δ 1.57 (br, CH *H*CHCH*H*), 1.99 (s, C_5Me_5), 4.99 (br, C*H*HCHC*H*H), 7.90 (q, $J = 12$ Hz, CHHC*H*CHH). ^{13}C NMR (gated decoupled, 100.5 MHz, CD_2Cl_2, 0 °C) δ 13.6 (s, C_5Me_5), 91.6, (t, $J = 152$ Hz, *C*HHCH*C*HH), 124.1 (s, broadened by J_{BC}, *ipso*-C_6F_5), 129.6 (br s, overlapping C_5Me_5), 136.9 (d, $J_{CF} = 245$ Hz, C_6F_5), 139.0 (d, $J_{CF} = 247$ Hz, C_6F_5), 148.3 (d, $J_{CF} = 245$ Hz, C_6F_5), 156.0 (d, $J = 155$ Hz, CHH*C*HCHH).

3.3.3. NMR Data for $(C_6H_6)_2NCH_3$

^{1}H NMR (400 MHz, CD_2Cl_2, −78 °C) δ 3.31 (s, NCH_3), 7.03 (m, 4H, Ph), 7.26 (m, 6H, Ph). ^{13}C NMR (gated decoupled, 100.5 MHz, CD_2Cl_2, −78 °C) δ 41.1 (q, $J = 139$ Hz, NCH_3), 121.6 (br, *m*-Ph), 129.9 (br, *p*-Ph), 130.1 (dd, $J = 159$, 7 Hz, *o*-Ph), 149.4 (s, *ipso*-Ph).

3.3.4. NMR data for propene

^{1}H NMR (400 MHz, CD_2Cl_2, −78 °C) δ 1.72 (d, $J = 7$ Hz, CH_3), 4.91 (d, $J = 10$ Hz, CH═CH*H*), 4.94 (d, $J = 15$ Hz, CH═C*H*H), 5.83 (ddq, $J = 15$, 10, 7 Hz).

3.4. Reaction of **3** with $B(C_6F_5)_3$ at −78 °C

CD_2Cl_2 (0.5 ml) was condensed into a resealable NMR tube containing **1** (0.018 g, 0.044 mmol) and $B(C_6F_5)_3$ (0.023 g, 0.044 mmol) at −78 °C. The tube was shaken briefly at −78 °C to give a red solution and was inserted into the precooled probe of the NMR spectrometer. The NMR spectrum shows a mixture of $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][CH_2=CHCH_2B(C_6F_5)_3]$ **8**, and $(C_6H_5)_2(CH_3)N$. The NMR of **8** differs from that of **4** only in the resonances corresponding to the anion, which are given below.

3.4.1. Anion resonances of $[CH_2=CHCH_2B(C_6F_5)_3]$

^{1}H NMR (400 MHz, CD_2Cl_2, −78 °C) δ 0.47 (br d, $J = 7$ Hz, BCH_2), 5.00 (d, $J = 10$ Hz, CH═C*H*H), 5.04 (d, $J = 15$ Hz, CH═CH*H*), 5.52 (ddt, $J = 15$, 10, 7 Hz, C*H*$=CH_2$). ^{13}C NMR (gated decoupled, 100.5 MHz, CD_2Cl_2, −78 °C) Δ 25.2 (br, J_{CH} obscured by J_{BC}, BCH_2), 113.8 (t, $J = 150$ Hz, CH═*C*H_2), 121.1 (br s, *ipso*-BC), 133.4 (d, $J = 154$ Hz, *C*H$=CH_2$) 135.3 (d, $J_{CF} = 238$ Hz, CF), 137.2 (d, $J_{CF} = 245$ Hz, CF), 146.8 (d, $J_{CF} = 240$ Hz, CF).

3.5. Reaction of **3** with $[(C_6H_5)_2(CH_3)NH][B(C_6F_5)_4]$ at −140 °C

$CDCl_2F/CDClF_2$ (0.5 ml) was condensed into a resealable NMR tube containing **3** (0.018 g, 0.044 mmol) and $[(C_6H_5)_2(CH_3)NH]$ $[B(C_6F_5)_4]$ (0.038 g, 0.044 mmol) at −176 °C. The tube was inserted directly into the pre-cooled probe of the NMR spectrometer at −140 °C. The solution was allowed to thaw for 5 min, ejected from the NMR probe, shaken briefly, and reinserted. The initial NMR spectrum shows a mixture of $[Cp^*_2Ti(\eta^3\text{-}CH_2CHCH_2)][B(C_6F_5)_4]$ **4**, $Cp^*_2Ti[\eta^1,\eta^2\text{-}CH_2CH(CH_3)CH_2CH=CH_2][B(C_6F_5)_4]$, **6**, $(C_6H_5)_2(CH_3)N$ and propene, NMR data for **6** is given below.

3.5.1. NMR Data for $Cp^*_2Ti[\eta^1,\eta^2\text{-}CH_2CH(CH_3)CH_2CH=CH_2][B(C_6F_5)_4]$, **6**

^{1}H NMR (400 MHz, $CDCl_2F/CDClF_2$, −140 °C) δ-0.65 (br d, $J = 10$ Hz, TiCH*H*), 1.35 (d, $J = 7$ Hz, $TiCH_2CH(CH_3)$), 1.95 (s, C_5Me_5), 1.97 (s, C_5Me_5), 2.42 (br d, $J = 9$ Hz, CH═C*H* H), 5.46 (br d, $J = 17$ Hz, CH═CH*H*), 7.96 (br m, C*H* $=CH_2$). Resonances were observed at 1.43 ($TiCH_2$C*H*), 1.85 (TiC*H*H), 2.21 and 2.38 ($CH_2CH=CH_2$) ppm, but could only be tentatively assigned.

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