Models for Intermediates in Metallocene-Catalyzed Alkene Polymerization: Alkene Dissociation from $Cp_2Zr[\eta^1,\eta^2\text{-}CH_2Si(CH_3)_2CH_2CH{=}CH_2][B(C_6F_5)_4]$

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The bis(allyldimethylsilylmethyl)bis(cyclopentadienyl)zirconium complex $Cp_2Zr[CH_2Si(CH_3)_2CH_2CH{=}CH_2]_2$ (**5**) reacted rapidly with $[(C_6H_5)_2(CH_3)NH][B(C_6F_5)_4]$ in CD_2Cl_2 at −78 °C to form the cationic zirconium−alkyl−alkene complex $Cp_2Zr[\eta^1,\eta^2\text{-}CH_2Si(CH_3)_2CH_2CH{=}CH_2][B(C_6F_5)_4]$ (**6**). Low-temperature ^1H and ^{13}C NMR spectroscopy established the coordination of the tethered alkene to the d^0 metal center. Line shape analysis of the coalescence of the diastereotopic Cp ligand resonances allowed measurement of the alkene dissociation energy barrier [$\Delta G^{\ddagger}(-28\ ^\circ C) = 12.7 \pm 0.8$ kcal mol^{-1}].

Introduction

The commonly accepted mechanism for metallocene-catalyzed alkene polymerization involves a d^0 metal−alkyl−alkene intermediate.[1,2] However, such alkene complexes have never been observed in catalytic systems, presumably because of their low thermodynamic stability due to weak alkene coordination in the absence of metal d to alkene π^* back-bonding and because of their expected high kinetic reactivity leading to alkyl addition to the coordinated alkene.[3] Our group has studied chelated d^0 metal−alkyl−alkene complexes that are models for this important intermediate in catalysis. We have studied a series of yttrium complexes such as $Cp^*_2Y[\eta^1,\eta^2\text{-}CH_2CH_2C(CH_3)_2CH{=}CH_2]$ (**1**), formed by addition of an yttrium hydride to a diene,[4] and zwitterionic and cationic zirconium complexes $Cp^*_2Zr\{\eta^1,\eta^2\text{-}CH_2CH[CH_2B(C_6F_5)_3]CH_2CH{=}CH_2\}$ (**2**) and $Cp^*_2Zr[\eta^1,\eta^2\text{-}CH_2CH(CH_3)CH_2CH{=}CH_2][B(C_6F_5)_4]$ (**3**), produced by ring-opening reactions of an allyl-substituted zirconacyclobutane complex with Lewis or Bronsted acids.[5] Compounds **2** and **3** suffer from thermal instability, with decomposition starting below −5 °C. Although we have not been able to identify decomposition products unambiguously, evidence from ^1H NMR suggests that free alkenes are formed, possibly by β-hydride, β-methyl, or β-allyl elimination. In an effort to increase the thermal stability of zirconium−alkyl−alkene complexes, we endeavored to produce a complex that did not contain β-hydrogens and that contained a silicon atom β to zirconium in the alkyl chain. This silicon-containing complex should be resistant to β-alkyl elimination which would produce a thermodynamically disfavored carbon−silicon double bond. Here we report the synthesis and characterization of such a zirconium−alkyl−alkene complex.[6−8]

Results and Discussion

Synthesis of $Cp_2Zr[CH_2Si(CH_3)_2CH_2CH{=}CH_2]_2$ (5). The lithium reagent $LiCH_2Si(CH_3)_2CH_2CH{=}CH_2$ (**4**)

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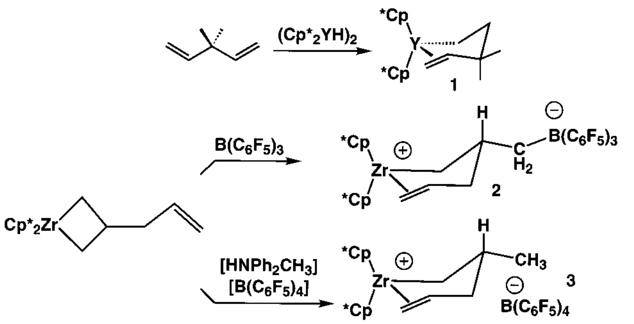
10.1021/om0103658 CCC: \$20.00

Scheme 1



was synthesized by a metal halogen exchange reaction between $ICH_2Si(CH_3)_2CH_2CH{=}CH_2$ and *tert*-butyllithium in diethyl ether at −78 °C. After warming to room temperature, **4** was added to a slurry of Cp_2ZrCl_2 in diethyl ether at −78 °C. Evaporation of solvent gave $Cp_2Zr[CH_2Si(CH_3)_2CH_2CH{=}CH_2]_2$ (**5**) as a viscous yellow oil in 80% yield (Scheme 2). In the ^1H NMR spectrum of **5**, normal chemical shifts were observed for the vinyl hydrogens (δ 4.99, 5.04, 5.95).

Synthesis of $Cp_2Zr[\eta^1,\eta^2\text{-}CH_2Si(CH_3)_2CH_2CH{=}CH_2][B(C_6F_5)_4]$ (6). Protonation of $Cp_2Zr[CH_2Si(CH_3)_2CH_2CH{=}CH_2]_2$ (**5**) with 1 equiv of $[(C_6H_5)_2(CH_3)NH][B(C_6F_5)_4]$ in CD_2Cl_2 at −78 °C led to formation of a yellow-brown solution containing $Cp_2Zr[\eta^1,\eta^2\text{-}CH_2Si(CH_3)_2CH_2CH{=}CH_2][B(C_6F_5)_4]$ (**6**) (Scheme 3). Previously, we had shown that the weak conjugate base, NPh_2Me, does not displace alkenes from Cp^*_2Zr centers;[5b] it is remarkable that NPh_2Me does not complex to the more electron-deficient and less crowded Cp_2Zr center of **6**.

Low-temperature ^1H and ^{13}C NMR spectroscopy established alkene coordination to zirconium in **6**. The strongest evidence for alkene coordination comes from the observation of diastereotopic Cp resonances (δ 6.55 and 6.58), diastereotopic silyl methyl resonances (δ 0.03 and 0.05), and diastereotopic methylene resonances for the $ZrCH_2$ (δ 1.36 and 1.65) and $SiCH_2CH{=}CH_2$ (δ 1.98 and 2.15) groups. Alkene coordination to zirconium in **6** creates a stereocenter at the internal vinyl carbon that renders all these units diastereotopic.

Further support for the coordination of tethered alkene to zirconium in **6** comes from the observation of 3−6% NOE enhancements of the vinyl proton resonances when the Cp resonances of **6** were irradiated.

Alkene coordination also gives rise to dramatic chemical shift changes for the vinyl hydrogens in the ^1H NMR spectrum of **6**. The secondary vinyl hydrogen resonance in **6** is shifted 2.65 ppm to higher frequency (δ 8.60) compared with that of **5** (δ 5.95), which we have found is indicative of alkene coordination to a d^0 metal center.[4,5,7] This shift is significantly greater than those observed for the two diastereomers of zirconium alkene complexes **2** ($\Delta\delta$ 1.63 and 1.25) and **3** ($\Delta\delta$ 1.60 and 1.20).[5] Alkene coordination also results in a marked increase in the chemical shift difference between the two terminal vinyl hydrogen resonances. In the starting compound **4**, this separation is only 0.05 ppm (δ 5.04, 4.99 ppm); but in **6**, the separation increases to 3.58 ppm (δ 2.29, 5.87 ppm). Similar large separations of terminal vinyl hydrogen resonances (3−3.5 ppm) were observed for **2** and **3**.[5] As expected for coordination to a d^0 metal and as observed in **1**, **2**, and **3**, the coupling constants across the C=C bond are basically unchanged upon coordination to Zr in **6**.

^{13}C NMR spectroscopy also provides evidence for alkene coordination in **6**. The internal vinyl carbon is shifted to 175.0 ppm in **6**, 39.8 ppm higher in frequency than the corresponding resonance in **5**. In the ^{13}C NMR spectra of **2** and **3** the observed shifts to higher frequency compared to the starting compounds are 21.8−25.5 ppm. We have attributed these shifts to a contribution from a resonance structure where the positive charge from the metal is delocalized to the internal vinyl carbon. (Scheme 3).[4,5] These much greater chemical shift changes upon alkene coordination in **6** compared with **2** and **3** might be related to a number of factors. The cyclopentadienyl groups of **6** are weaker electron donors than the pentamethylcyclopentadienyl groups of **2** and **3** and are less capable of moderating the high electrophilicity of the cationic zirconium center. Another possible factor is that positive charge at the internal vinyl carbon can be stabilized by interaction with the β-silicon center.[9]

While NPh_2Me does not compete with the tethered alkene for complexation to zirconium, the less crowded base THF displaces the complexed alkene from **6** to form a 1:1 THF adduct. ^1H and ^{13}C NMR chemical shifts of the vinyl resonances of the THF adduct (vinyl hydrogens: δ 5.95, 5.04, and 4.99 ppm; internal vinyl carbon: δ 135.2 ppm) return to values similar to those observed in **5**. No NOE enhancements of the vinyl proton resonances were observed when the Cp resonances of the THF adduct were irradiated, indicating that alkene had been displaced from the metal center.

The use of $B(C_6F_5)_3$ to abstract a methyl group from zirconium often results in the formation of a $Zr{-}CH_3{-}B(C_6F_5)_3$-bridged species, even in the presence of bulky Cp* ligands.[10] Earlier we had found that the $CH_3B(C_6F_5)_3$ anion was not capable of displacing the tethered alkene from zirconium in a salt related to **3**.[5b] To explore whether the smaller steric protection afforded by the Cp ligands of **6** might allow the $CH_3B(C_6F_5)_3$ anion to displace a tethered alkene, we studied protonation of **5** with $[(C_6H_5)_2CH_3NH][CH_3B(C_6F_5)_3]$. We found that $Cp_2Zr[\eta^1,\eta^2\text{-}CH_2Si(CH_3)_2CH_2CH{=}CH_2][CH_3B(C_6F_5)_3]$, **6-$CH_3B(C_6F_5)_3$**, showed no evidence for borate complexation. Its ^1H and ^{13}C NMR spectra were indistinguishable from those of **6** except for the resonances of the anion. Significantly, the ^{13}C NMR chemical shift of the methyl group attached to boron was 10.1 ppm, characteristic of the free anion,[5b,10] with no interaction between the methyl group and zirconium.

Alkene Dissociation Rate from 6. As previously mentioned, the Cp ligands, silyl methyl groups, and methylene units in **6** display diastereotopic resonances in the ^1H NMR spectra at −78 °C. Upon slow warming of a CD_2Cl_2 solution of **6**, a fluxional process was observed that led to the coalesence of pairs of diastereotopic resonances. The coalesence of the Cp resonances of **6** at δ 6.55 and 6.58 occurred at −28 °C. Similarly, the coalescence of the silyl methyl resonances

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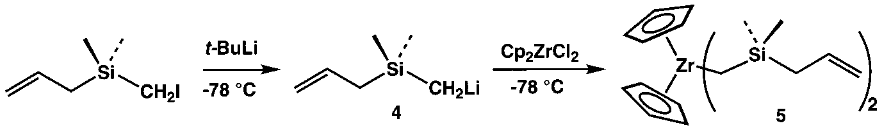
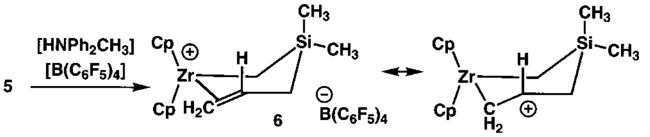
Scheme 2



Scheme 3



at δ 0.03 and 0.05 occurred at −33 °C. All temperature-dependent changes are reversible up to −25 °C, but decomposition begins at −20 °C. Line shape analysis of the coalescence of diasteriotopic Cp resonances using the DNMR program[11] yielded $\Delta G^{\ddagger} = 12.7 \pm 0.8$ kcal mol^{-1} ($\Delta H^{\ddagger} = 16.4 \pm 0.8$ kcal mol^{-1}, $\Delta S^{\ddagger} = 15 \pm 3$ eu). Similarly, line shape analysis of the coalescence of diastereotopic silyl methyl resonances yielded $\Delta G^{\ddagger} = 12.8 \pm 1.2$ kcal mol^{-1} ($\Delta H^{\ddagger} = 16.5 \pm 1.1$ kcal mol^{-1}, $\Delta S^{\ddagger} = 15 \pm 3$ eu).

The fluxional behavior of **6** in C_6D_5Cl was virtually identical to that in CD_2Cl_2.[12] The fluxional behavior of **6-CH$_3$B(C$_6$F$_5$)$_3$** in both C_6D_5Cl and CD_2Cl_2 was also indistinguishable from that of **6**.[12] Similarly, addition of $[C_6H_5N(CH_3)_3][B(C_6F_5)_4]$, $[C_6H_5N(CH_3)_3][CH_3B(C_6F_5)_3]$, or excess $(C_6H_5)_2NCH_3$ had no discernible effect on the fluxional behavior or activation parameters.[12] These results rule out involvement of assistance from solvent, anion, or amine base in the fluxional process.

The fluxional behavior of **6** requires alkene dissociation, rotation within the alkyl chain, and recoordination to the opposite enantioface of the alkene (Scheme 4). Significantly, the resonances for the terminal vinyl protons showed no temperature-dependent broadening. This rules out the possibility of intramolecular insertion, and subsequent ring-opening being responsible for the observed coalescence of diastereotopic resonances.

The higher barrier for alkene dissociation from zirconium in Cp complex **6** compared with Cp* complexes **2** ($\Delta G^{\ddagger} = 10.5$, 10.7 kcal mol^{-1}) and **3** ($\Delta G^{\ddagger} = 10.7$, 11.1 kcal mol^{-1})[5] is consistent with a stronger interaction between the alkene and the metal center, as would be expected for a more electrophilic Cp_2Zr center, but direct comparison is not feasible due to the electronic perturbation of the silicon atom in the alkyl chain of **6** and due to steric differences.

Removal of the possibility of β-hydride and β-alkyl elimination decomposition pathways did not have the desired effect of increasing the stability of the reported zirconium−alkyl−alkene complexes.

Experimental Section

CH$_2$=CHCH$_2$Si[(CH$_3$)$_2$]CH$_2$Li (4). *tert*-Butyllithium (15 mL, 1.7 M in pentane, 25.5 mmol) was added dropwise to a solution of allyl(dimethyl)(iodomethyl)silane[12] (2.63 g, 10.95 mmol) in 25 mL of diethyl ether at −78 °C. The reaction solution was allowed to slowly warm to room temperature (2 h) and was filtered. A small aliquot of **4** was analyzed by NMR, and the remainder of the solution was used directly in the preparation of **5**. ^{1}H NMR (300 MHz, $CDCl_3$): δ −2.24 (br s, SiCH$_2$Li), 0.26 (s, Si(CH$_3$)$_2$), 1.31 (d, $J = 7$ Hz, SiC*H*$_2$CH=CH$_2$), 4.44 (dd, $J = 10$, 5 Hz, CH=C*H*H), 4.54 (dd, $J = 15$, 5 Hz, CH=CH*H*), 5.82 (ddt, $J = 15$, 10, 7 Hz, C*H*=CH$_2$).

(C$_5$H$_5$)$_2$Zr[CH$_2$Si(CH$_3$)$_2$CH$_2$CH=CH$_2$]$_2$ (5). CH$_2$=CHCH$_2$Si[(CH$_3$)$_2$]CH$_2$Li (**4**) (~10.3 mmol) in 25 mL of diethyl ether/pentane was added to a suspension of bis(cyclopentadienyl)zirconium dichloride (1.48 g, 5.06 mmol) in ether at −78 °C. The mixture was stirred at room temperature for 3 h. Solvent was evaporated under reduced pressure, and the residue was extracted with pentane and filtered. Evaporation of solvent gave **5** (1.43 g, 80%) as a viscous yellow oil. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.06 (s, ZrCH$_2$Si), 0.08 (s, Si(CH$_3$)$_2$), 1.57 (d, $J = 7$ Hz, SiC*H*$_2$CH=CH$_2$), 4.99 (dd, $J = 10$, 5 Hz, CH=C*H*H), 5.04 (dd, $J = 15$, 5 Hz, CH=CH*H*), 5.80 (s, Cp), 5.95 (ddt, $J = 15$, 10, 7 Hz, C*H*=CH$_2$). ^{13}C NMR (gated decoupled, 126 MHz, CD_2Cl_2, −78 °C): δ 1.1 (q, $J = 127$ Hz, Si(CH$_3$)$_2$), 28.7 (t, $J = 125$ Hz, *C*H$_2$CH=CH$_2$), 45.3 (t, $J = 108$ Hz, ZrCH$_2$), 110.4 (t, $J = 157$ Hz, CH=*C*H$_2$), 112.2 (d, $J = 150$ Hz, Cp), 135.8 (d, $J = 151$ Hz, CH$_2$*C*H=CH$_2$).

Reaction of (C$_5$H$_5$)$_2$Zr[CH$_2$Si(CH$_3$)$_2$CH$_2$CH=CH$_2$]$_2$ (5) with [(C$_6$H$_5$)$_2$(CH$_3$)NH][B(C$_6$F$_5$)$_4$]. CD_2Cl_2 (0.5 mL) was condensed into a resealable NMR tube containing **5** (0.020 g, 0.049 mmol) and $[(C_6H_5)_2(CH_3)NH][B(C_6F_5)_4]$ (0.039 g, 0.049 mmol) at −78 °C. The tube was shaken briefly at −78 °C to give a bright orange solution and was inserted into the precooled probe of the NMR spectrometer. The NMR spectrum showed a mixture of Cp$_2$Zr[η^1,η^2-CH$_2$Si(CH$_3$)$_2$CH$_2$CH=CH$_2$][B(C$_6$F$_5$)$_4$], **6**, (C$_6$H$_5$)$_2$(CH$_3$)N, and (CH$_3$)$_3$SiCH$_2$CH=CH$_2$; details are given below.

Cp$_2$Zr[η^1,η^2-CH$_2$Si(CH$_3$)$_2$CH$_2$CH=CH$_2$][B(C$_6$F$_5$)$_4$] (6). ^{1}H NMR (500 MHz, CD_2Cl_2, −78 °C): δ 0.03, 0.05 (s, 3H each, Si(CH$_3$)$_2$); 1.36, 1.65 (br s, 1H each, ZrCH$_2$Si); 1.98, 2.15 (br, 1H each, SiC*H*$_2$CH=CH$_2$); 2.29 (d, $J = 10$ Hz, CH=C*H*H); 5.87 (d, $J = 17$ Hz, CH=CH*H*); 6.55, 6.58 (s, 5H each, Cp); 8.60 (m, C*H*=CH$_2$). ^{13}C NMR (gated decoupled, 126 MHz, CD_2Cl_2, −78 °C): δ 1.83, 1.88 (q, $J = 127$ Hz, Si(CH$_3$)$_2$); 32.7 (t, $J = 125$ Hz, *C*H$_2$CH=CH$_2$); 85.9 (t, $J = 108$ Hz, ZrCH$_2$); 99.4 (t, $J = 157$ Hz, CH=*C*H$_2$); 113.0, 115.0 (d, $J = 150$ Hz, Cp); 123.0 (br s, *ipso*-C); 135.9 (d, $J_{CF} = 240$ Hz, C$_6$F$_5$); 137.8 (d, $J_{CF} = 240$ Hz, C$_6$F$_5$); 147.5 (d, $J_{CF} = 240$ Hz, C$_6$F$_5$); 175.0 (d, $J = 151$ Hz, CH$_2$*C*H=CH$_2$). ^{19}F NMR (416.5 MHz, line broadened, CD_2Cl_2, −78 °C): δ −135.9 (br s, 8F), −166.2 (br s, 4F), −170.2 (br s, 8F).

(C$_6$H$_5$)$_2$(CH$_3$)N. ^{1}H NMR (500 MHz, CD_2Cl_2, −78 °C): δ 3.18 (s, NCH$_3$), 7.09 (m, 4H, C$_6$H$_5$), 7.33 (m, 6H, C$_6$H$_5$). ^{13}C NMR (gated decoupled, 126 MHz, CD_2Cl_2, −78 °C): δ 41.5 (q, $J = 139$ Hz, NCH$_3$), 119.4 (br, *m*-C$_6$H$_5$), 123.1 (br, *p*-C$_6$H$_5$), 128.9 (dd, $J = 158$, 7 Hz, *o*-C$_6$H$_5$), 145.3 (s, *ipso*-C).

(CH$_3$)$_3$SiCH$_2$CH=CH$_2$. ^{1}H NMR (500 MHz, CD_2Cl_2, −78 °C): δ 0.02 (s, Si(CH$_3$)$_3$), 1.51 (d, $J = 7$ Hz, SiC*H*$_2$CH=CH$_2$), 4.80 (br d, $J = 10$ Hz, CH=C*H*H), 4.85 (br d, $J = 17$ Hz, CH=CH*H*), 5.78 (m, 1H, C*H*=CH$_2$). ^{13}C NMR (gated decoupled, 126 MHz, CD_2Cl_2, −78 °C): δ −2.1 (q, $J = 125$ Hz, Si(CH$_3$)$_3$), 24.7 (t, $J = 124$ Hz, Si*C*H$_2$CH=CH$_2$), 112.6 (t, $J = 151$ Hz, CH=*C*H$_2$), 135.2 (d, $J = 150$ Hz, *C*H=CH$_2$).

General Procedure for Line Shape Analysis. A CD_2Cl_2 solution of **6** was warmed from −78 to −28 °C. ^{1}H NMR spectra were recorded at five degree intervals following a 20 min equilibration period at each new temperature. Significant broadening of the peaks corresponding to the cyclopentadienyl

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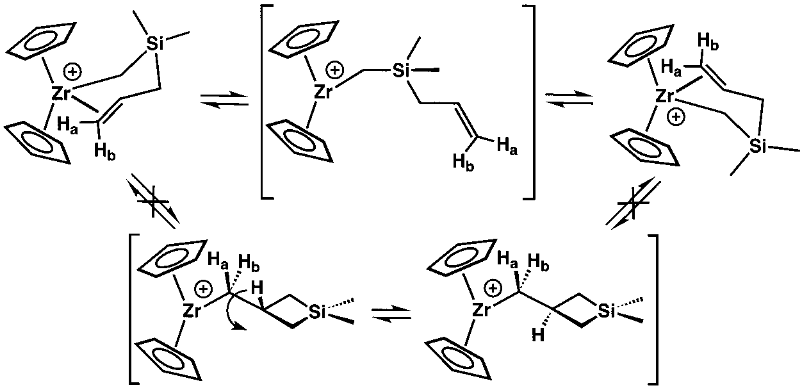
(11) Reich, H. J. *J. Chem. Educ.* **1995**, *72*, 1086.
(12) See Supporting Information.

Scheme 4



resonances was apparent at −48 °C, and these peaks coalesced into one broad peak at −28 °C. Spectra recorded at −23 and −18 °C revealed some sharpening of the Cp resonance, but a nonreversible decomposition was also occurring at these temperatures. This procedure was applied to compounds **6** and **6-$CH_3B(C_6F_5)_3$** in various solvents and with various additives as detailed in Table S-1.[12]

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Supporting Information Available: General experimental preparation of $CH_2{=}CHCH_2Si(CH_3)_3CH_2Cl$ and $CH_2{=}CHCH_2Si(CH_3)_3CH_2I$, the reaction of $(C_5H_5)_2Zr[CH_2Si(CH_3)_2CH_2CH{=}CH_2]_2$ (**5**) with $[(C_6H_5)_2(CH_3)NH][CH_3B(C_6F_5)_3]$, a table of activation parameters, ^1H NMR spectrum of **5**, and a stack plot showing the coalescence of the diastereotopic Cp resonances of **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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