

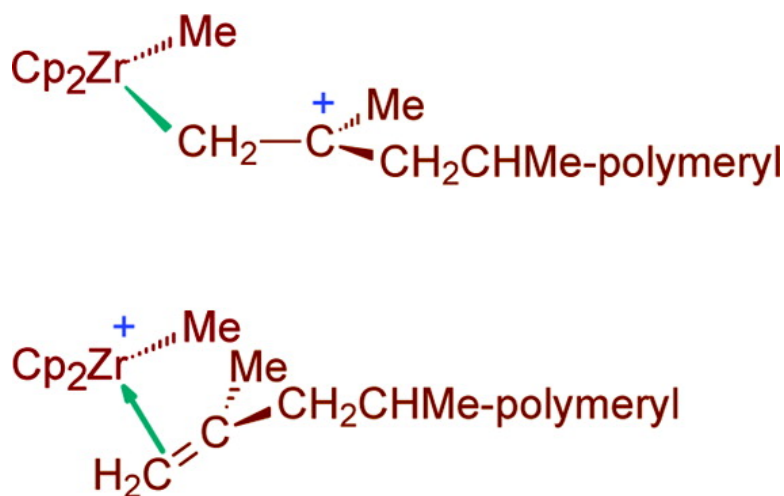
Communication

**Detection of an  $\pi$ -Alkene Intermediate of the Type  $[\text{Cp}_2\text{Zr}(\text{Me})(\pi\text{-alkene})]$ : The Role of Such Species in Metallocene Catalyst Deactivation to Allylic Species**

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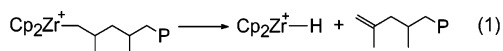
## Detection of an $\eta^1$ -Alkene Intermediate of the Type $[\text{Cp}_2\text{Zr}(\text{Me})(\eta^1\text{-alkene})]^+$ : The Role of Such Species in Metallocene Catalyst Deactivation to Allylic Species

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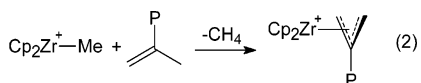
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There has in recent years been considerable research into the use of metallocene catalysts of the type  $[\text{Cp}_2\text{ZrMe}]^+$  for propene polymerization,<sup>1</sup> and it is generally accepted that initiation and propagation involve alkene coordination to the vacant site to give  $[\text{Cp}_2\text{Zr}(\text{Me})(\eta^2\text{-propene})]^+$ . Following a series of 1,2-insertions, chain transfer follows  $\beta$ -hydrogen migration to release a polymer with a terminal vinylidene end group (eq 1).<sup>1</sup>



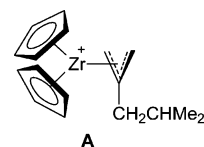
However, attempts are still being made to detect and characterize alkyl alkene intermediates of the type  $[\text{Cp}_2\text{Zr}(\text{Me})(\eta^2\text{-alkene})]^+$ , which are generally quite short-lived because of their pronounced proclivity to undergo insertion and which therefore have never been observed.<sup>2</sup> Indeed, the only  $d^0$  zirconocene-alkene complexes which are known are chelated complexes in which the coordinated alkene is also tethered to the metal via a heteroatom,<sup>2a-d</sup> and the complexes  $[\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)(\text{alkene})]^+$  and  $[\text{Cp}_2\text{Zr}(\text{O}i\text{Bu})(\text{alkene})]^+$  (alkene = 1-alkenes, allyltrimethylsilane, vinylferrocene, *tert*-butyl vinyl ether) in which migratory insertion cannot occur.<sup>2e,f</sup>

There is also considerable interest in related observations that some propene polymerization processes are affected adversely by slow degradation of catalysts to dormant species. It is thought that active catalysts can convert to unreactive allylic species of the type  $[\text{Cp}_2\text{Zr}(\eta^3\text{-allyl})]^+$  via transfer of a methyl hydrogen atom from a coordinated propene to a polymeryl or hydride ligand.<sup>3</sup> Alternatively, compounds of the type  $[\text{Cp}_2\text{ZrMe}]^+$  are found to react slowly with vinylidene compounds  $\text{CH}_2=\text{CMeR}$  to form methane and cationic allylic complexes  $[\text{Cp}_2\text{Zr}(\eta^3\text{-CH}_2\text{C}(\text{R})\text{CH}_2)]^+$ ,<sup>3d,4</sup> and it has been suggested that polypropene-containing vinylidene end groups  $\text{CH}_2=\text{CMe}\sim\text{P}$  (P = polymeryl) (eq 1) may react in the same way (eq 2) rather than just behaving as spectators of the polymerization process.<sup>4c,e</sup>



As part of an ongoing study of the nature of dormant species during alkene polymerization processes,<sup>5</sup> we are investigating reactions of  $[\text{Cp}_2\text{ZrMe}]^+$  with, e.g., 2,4-dimethyl-1-pentene, a model compound for propene macromonomers containing vinylidene end groups. We report here that  $[\text{Cp}_2\text{ZrMe}]^+$  does indeed react with 2,4-dimethyl-1-pentene to form methane and an allyl complex,  $[\text{Cp}_2\text{Zr}(\eta^3\text{-CH}_2\text{C}(\text{CH}_2\text{CHMe}_2)\text{CH}_2)]^+$ , but the reaction involves the unprecedented  $\eta^1$ -vinylidene or near  $\eta^1$ -vinylidene intermediate  $[\text{Cp}_2\text{Zr}(\text{Me})(\eta^1\text{-CH}_2\text{CMeCH}_2\text{CHMe}_2)]^+$ , detected by low-temperature one- and two-dimensional (1D and 2D) <sup>1</sup>H NMR spectroscopy. As an unanticipated corollary, the existence of the  $\eta^1$ -vinylidene complex suggests an alternative and possibly general route to allylic species, one which has not heretofore been considered.

In a typical experiment  $\text{Cp}_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ , generated by reacting  $\text{Cp}_2\text{ZrMe}_2$  with 1.1 equiv of  $\text{B}(\text{C}_6\text{F}_5)_3$ , was reacted with 1.5 equiv of 2,4-dimethyl-1-pentene in  $\text{C}_6\text{D}_5\text{Cl}$  at 21 °C; the reaction was monitored by <sup>1</sup>H NMR spectroscopy over several hours. During the course of the reaction, which was slow, there appeared a singlet at  $\delta$  0.25 (attributable to methane) and a series of exchange-broadened resonances tentatively attributable to the  $[\text{BMe}(\text{C}_6\text{F}_5)_3]^-$  salt of the allylic complex **A**. In order to better identify this product, the sample was cooled to 0 °C where an improved <sup>1</sup>H NMR spectrum facilitated the identification of **A** (see Supporting Information [SI]).



In two complementary but much more rapid NMR experiments  $[\text{Cp}_2\text{Zr}(\text{Me})(\text{C}_6\text{D}_5\text{Cl})][\text{B}(\text{C}_6\text{F}_5)_4]$ , generated in  $\text{C}_6\text{D}_5\text{Cl}$  by reacting  $\text{Cp}_2\text{ZrMe}_2$  with 1.1 equiv of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]^-$ ,<sup>6a</sup> was combined with 1.5 equiv of 2,4-dimethyl-1-pentene at 0 and 21 °C. Both experiments were complete within 10 min, the resonances of the reactants being replaced smoothly by those of methane and the  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  salt of **A**. Similar results were obtained during the course of (much slower) NMR experiments run at  $-40$  °C (see Figure S1 of the SI for a representative spectrum). Interestingly, at the lower temperature a very weak, broad resonance at  $\delta \sim 3.5$  appeared during the first few minutes of the reaction (shown as an inset in Figure S1), but because it was one of several minor, seemingly extraneous resonances which could not readily be assigned, it was ignored until a 2D NOESY spectrum was also run at  $-40$  °C as part of the structural study of the allylic product. In this spectrum (SI, Figure S2), the resonance at  $\delta \sim 3.5$  was observed to exhibit cross-peaks with the two olefinic resonances of unreacted 2,4-dimethyl-1-pentene at  $\delta$  4.82 and 4.75. The phase of these cross-peaks was confirmed in a series of complementary 1D NOESY experiments (Figure S3 shows a representative example) and can *only* be interpreted in terms of exchange between free alkene and the species giving rise to the resonance at  $\delta \sim 3.5$ .<sup>7</sup> Thus, the latter must be attributed to the pair of hydrogens on C(1) of a coordinated 2,4-dimethyl-1-pentene molecule in a zirconium complex of some kind.

Although we cannot as yet identify unambiguously the new alkene complex, several lines of evidence suggest that it is the highly novel species  $[\text{Cp}_2\text{Zr}(\text{Me})(\text{CH}_2=\text{CMeCH}_2\text{CHMe}_2)]^+$  (**B**). For instance, NMR monitoring of the reaction showed that the peak at  $\delta \sim 3.5$  was present from the onset, attaining a maximum, albeit very low, level of intensity (2–5% of that of the total alkene) during the first few minutes of the reaction. However, as the resonances of  $[\text{Cp}_2\text{Zr}(\text{Me})(\text{C}_6\text{D}_5\text{Cl})]^+$  and 2,4-dimethyl-1-pentene were replaced

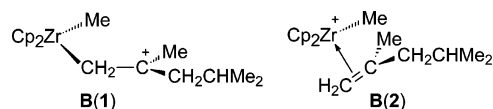
over 2 h by those of **A** and methane, the resonance at  $\delta \sim 3.5$  steadily decreased in intensity until it was barely visible above the baseline. Thus, the species giving rise to the resonance at  $\delta \sim 3.5$  behaves as an intermediate in the formation of **A**, consistent with its identification as **B**. Apparent support for this conclusion comes also from observation in the 2D NOESY spectrum (Figure S4) of a cross-peak between the Zr–Me resonance of  $[\text{Cp}_2\text{Zr}(\text{Me})(\text{C}_6\text{D}_5\text{-Cl})][\text{B}(\text{C}_6\text{F}_5)_4]$  at  $\delta$  0.63 with a very weak resonance at  $\delta \sim 0.25$  which is attributable to the Zr–Me group of  $[\text{B}][\text{B}(\text{C}_6\text{F}_5)_4]$ . As  $[\text{B}][\text{B}(\text{C}_6\text{F}_5)_4]$  was present in very low concentrations, its Cp resonance could not be distinguished among the several very weak singlets present in the region  $\delta$  5.6–6.0 (Figure S1). As a result of the very low intensities of the resonances at  $\delta \sim 3.5$  and  $\sim 0.25$ , it was impossible to relate their integrated intensities as formation of  $[\text{A}][\text{B}(\text{C}_6\text{F}_5)_4]$  proceeded.

To our knowledge, our findings concerning  $[\text{B}][\text{B}(\text{C}_6\text{F}_5)_4]$  provide the first experimental evidence for a  $d^0$  zirconocene alkyl alkene complex, detectable apparently because migratory insertion does not readily occur with vinylidene ligands.<sup>8</sup> Indeed an alternative explanation, that the observed exchange of the  $=\text{CH}_2$  hydrogens of free and coordinated 2,4-dimethyl-1-pentene involves reversible migratory insertion and formation of the alkyl complex  $[\text{Cp}_2\text{Zr}(\text{CH}_2\text{CMe}_2\text{CH}_2\text{CHMe}_2)]^+$ , is ruled out by the lack of a cross-peak between the methyl resonance of  $[\text{Cp}_2\text{ZrMe}]^+$  at  $\delta$  0.63 and the 2-methyl resonance of 2,4-dimethyl-1-pentene at  $\delta$  1.63 in the 2D NOESY spectrum (Figure S5).

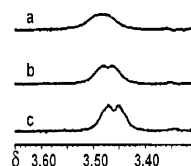
We note tangentially that the 2D NOESY spectrum of Figure S4 also exhibits a cross-peak between the Zr–Me resonance at  $\delta$  0.63 and a very weak resonance at  $\delta$  0.46. The latter is also present in 1D and 2D NOESY spectra of a solution generated as above at  $-40^\circ\text{C}$  in  $\text{C}_6\text{D}_5\text{Cl}$  (but in the absence of alkene<sup>6b</sup>) and is attributed to the  $\text{C}_6\text{D}_5\text{Cl}$ -free ion pair  $[\text{Cp}_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]^{6c}$ .

For most of the above-mentioned cationic complexes,  $[\text{Cp}'_2\text{Zr}(\text{C}_6\text{F}_5)(\text{alkene})]^+$  and  $[\text{Cp}'_2\text{Zr}(\text{OBu}')(\text{alkene})]^{2e,f}$  the resonances of the terminal  $\text{CH}_2$  groups of the alkenes are found to shift downfield on coordination; an exception is the *tert*-butyl vinyl ether complex  $[\text{Cp}'_2\text{Zr}(\text{OBu}')(\text{CH}_2=\text{CHOBu}')]^+$ , for which the  $\text{CH}_2$  resonances shift upfield as is the case with **B**. Vinyl ethers are, of course, of a type of alkene which readily undergoes carbocationic polymerization,<sup>8a</sup> which  $\text{CH}_2=\text{CHOBu}'$  does indeed do in the presence of the  $[\text{Cp}'_2\text{Zr}(\text{C}_6\text{F}_5)]^+$  cation.<sup>2f</sup> Thus, an upfield shift of a  $\text{CH}_2=$  resonance is perhaps to be expected on coordination of an alkene which is readily polymerizable via a carbocationic mechanism, i.e. which can support a significant degree of positive charge on C(2). This would in general be the case with vinylidene compounds such as isobutene and 2,4-dimethyl-1-pentene; thus, the upfield shift from  $\delta$  4.82 and 4.75 of free 2,4-dimethyl-1-pentene to  $\delta \sim 3.5$  for the coordinated olefin of **B** is reasonable.

Of further interest, however, is the fact that the vinylidene hydrogen resonances of **B** are not observed as individual singlets, as is expected and as is the case for the  $\text{CH}_2\text{C}=\text{C}$  resonances of the complexes  $[\text{Cp}'_2\text{Zr}(\text{C}_6\text{F}_5)(\eta^2\text{-alkene})]^+$  and  $[\text{Cp}'_2\text{Zr}(\text{OBu}')(\eta^2\text{-alkene})]^{2e,f}$ . Instead, observation of an apparently exchange-broadened singlet at  $\delta \sim 3.5$  suggests that the vinylidene hydrogens of **B** are undergoing mutual interconversion via rotation about the C(1)–C(2) bond, and this could only be the case if the olefinic bond of the coordinated 2,4-dimethyl-1-pentene had undergone sufficient reduction in  $p_\pi$  overlap on coordination that its bond order had been reduced significantly. A reasonable conclusion is that the coordinated alkene in **B** assumes a near  $\eta^1$  structure close to **B(1)**, in which C(2) is almost carbocationic in nature, rather than the conventional  $\eta^2$  structure.



As a test of this hypothesis, the temperature of the solution was lowered to  $-53^\circ\text{C}$ , at which point the onset of *decoalescence* of the broad singlet was observed. On further lowering of the temperature to  $-60^\circ\text{C}$ , decoalescence resulted in the appearance of two separate resonances (Figure 1) consistent with and unambiguous evidence for the presence of the illustrated  $\eta^1$ -vinylidene complex.



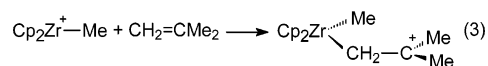
**Figure 1.**  $^1\text{H}$  NMR spectrum of the vinylidene resonance of **B** at (a)  $-50^\circ\text{C}$ , (b)  $-55^\circ\text{C}$ , (c)  $-60^\circ\text{C}$ .

Although the slow exchange limit could not be reached because of freezing of the solution below  $-60^\circ\text{C}$ ,<sup>9</sup>  $\Delta G^\ddagger$  for rotation about the C(1)–C(2) bond was estimated to have an upper limit of  $\sim 47$   $\text{kJ mol}^{-1}$ .<sup>10a</sup>

A consequence of the observed mutual exchange of the vinylidene hydrogens of **B** and exchange between **B** and its precursors,  $[\text{Cp}_2\text{ZrMe}]^+$  and 2,4-dimethyl-1-pentene, is that the vinylidene hydrogens of the free olefin should also be undergoing mutual exchange. That this is in fact so is apparent from the 1D NOESY experiment shown in Figure S3, and thus  $[\text{Cp}_2\text{ZrMe}]^+$  can be said to catalyze the degenerate exchange of the vinylidene hydrogens of 2,4-dimethyl-1-pentene. We are unaware of precedents for this type of behavior.

No evidence for  $[\text{B}][\text{BMe}(\text{C}_6\text{F}_5)_3]$  was observed in low-temperature  $^1\text{H}$  NMR spectra of the reaction of  $\text{Cp}_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  with 2,4-dimethyl-1-pentene. Presumably the fact that the anion  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  is more weakly coordinating than  $[\text{BMe}(\text{C}_6\text{F}_5)_3]^-$  is an important factor,<sup>1f</sup> as the  $[\text{BMe}(\text{C}_6\text{F}_5)_3]^-$  anion is expected to compete more effectively with the alkene for the coordination site. Consistent with this hypothesis and with our suggestion of the intermediacy of **B** in the formation of **A**, a preliminary kinetics study of the reactions of both  $\text{Cp}_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  and  $[\text{Cp}_2\text{ZrMe}][\text{B}(\text{C}_6\text{F}_5)_4]$  with 2,4-dimethyl-1-pentene to form  $[\text{A}][\text{BMe}(\text{C}_6\text{F}_5)_3]$  and  $[\text{A}][\text{B}(\text{C}_6\text{F}_5)_4]$  gives activation energies of 50.9  $\text{kJ mol}^{-1}$  and 46.4  $\text{kJ mol}^{-1}$ , respectively.<sup>11</sup> Thus, the tight ion pair  $\text{Cp}_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  does indeed react more slowly with 2,4-dimethyl-1-pentene.

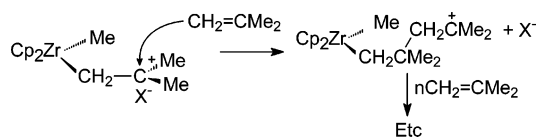
The postulated near  $\eta^1$  interaction involves a mode of bonding for which there are few precedents although the Zr–C(2) bonds of complexes of the types  $[\text{Cp}'_2\text{Zr}(\text{C}_6\text{F}_5)(\eta^2\text{-alkene})]^+$  and  $[\text{Cp}'_2\text{Zr}(\text{OBu}')(\eta^2\text{-alkene})]^{2e,f}$  are believed to be significantly longer than the Zr–C(1) bonds.<sup>2e,f</sup> However, we note that initiation of carbocationic isobutene polymerization by metallocene cations occurs via a process in which the alkene is activated by binding to the Lewis acid as follows (eq 3).<sup>8</sup>



Propagation during isobutene polymerization then involves a sequence of successive nucleophilic attacks by isobutene molecules

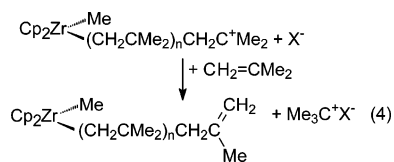
on the carbocationic center, which migrates along the growing polymer chain as in Scheme 1.<sup>8a</sup>

## Scheme 1



Of importance to the thesis being developed here, chain transfer during isobutene polymerization occurs via either methyl end group deprotonation by a molecule of isobutene, to give terminal unsaturation (Scheme 2), or  $\sim\text{CH}_2\text{C}^+\text{Me}_2$  methylene deprotonation to similarly result in internal unsaturation.

## Scheme 2



A structure such as **B(1)** therefore has major implications for the mechanism of formation of allylic complexes. As isobutene is an extremely weak base, it follows that the protons on the three carbon atoms bonded to the carbocationic end group in **B** must be *strongly acidic*. The same would be true for  $\eta^1$ -vinylidene complexes in general, and since Zr-alkyl bonds are sufficiently polarized as  $\text{Zr}^+-\text{R}^-$  that they are readily cleaved by a variety of protic reagents to form alkanes  $\text{RH}$ ,<sup>12</sup> it is expected that formation of species such as **B(1)** would result generally in intramolecular proton transfer to the adjacent methyl group to give methane and an allyl complex, as is observed here with 2,4-dimethyl-1-pentene.

As noted above, chain transfer during propene polymerization results in the formation of vinylidenes  $\text{CH}_2=\text{C}(\text{Me})\text{CH}_2\text{CHMe}\sim\text{P}$  which may well coordinate in a near  $\eta^1$  fashion to cationic  $\text{Cp}_2\text{Zr}-\text{H}$  or  $\text{Cp}_2\text{Zr}$ -polymeryl complexes. It follows that the close proximity of the resulting strongly acidic “allylic” hydrogens to readily protonated hydride (formed as in eq 1) or polymeryl ligands would result in facile proton transfer to the hydride or polymeryl groups to give the corresponding allylic complex and  $\text{H}_2$ <sup>13</sup> or saturated (polymeryl) hydrocarbon, respectively. To our knowledge, this carbocationic mechanism has heretofore not been considered as a rationale for the formation of allylic zirconocene cations  $[\text{Cp}_2\text{Zr}(\eta^3\text{-allyl})]^+$ .

In an effort to synthesize an  $\eta^1$ -vinylidene complex which would be more amenable to study, we reacted 2,4-dimethyl-1-pentene with  $[\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)]^+$ ,<sup>2f</sup> mentioned above as forming relatively stable  $\eta^2$ -alkene complexes; an improved synthetic procedure for the precursor,  $\text{Cp}_2\text{ZrMeC}_6\text{F}_5$ ,<sup>14</sup> is described in the SI. We anticipated that the metal-vinylidene bonding interactions would be stronger than with  $[\text{Cp}_2\text{ZrMe}]^+$  and, hence, that the corresponding  $\eta^1$ -vinylidene complex would be more readily observable. Also, of course, there would be no complications arising from conversion to allylic species. Unfortunately  $[\text{Cp}_2\text{Zr}(\text{C}_6\text{F}_5)]^+$  was found to be an excellent initiator for the carbocationic oligomerization of 2,4-dimethyl-1-pentene. However, research continues with other zirconocene and hafnocene systems as well as with other solvent systems and model vinylidene compounds such as 2,4-dimethyl-1-heptene.

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**Note Added after ASAP Publication.** After this paper was published ASAP October 2, 2007, changes were made at the request of the authors, with the approval of the Editor, in paragraphs 11, 13, 15, 16, 19, and 20, as well as ref 9 and the abstract. The updated version was published December 20, 2007.

**Supporting Information Available:** Synthetic procedures and  $^1\text{H}$  and  $^{13}\text{C}$  NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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