

Observation of non-chelated bis(pentamethylcyclopentadienyl)zirconium-alkyl–alkene complexes is thwarted by competitive arene or amine coordination or by β -hydride elimination

Charles P. Casey *, Donald W. Carpenetti II *

Department of Chemistry, University of Wisconsin—Madison, Madison, WI 53706, USA

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Abstract

The reaction of $\text{Cp}_2^*\text{Zr}(\text{CH}_3)_2$ (**1**) with $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 at -78°C proceeds with the unexpected formation of $[\text{Cp}_2^*\text{Zr}(\text{CH}_3)\eta\text{-C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**). Evidence for the coordination of one of the phenyl rings to zirconium comes from ^1H - and ^{13}C -NMR chemical shifts and from nOe experiments showing spin saturation transfer from the Cp^* methyl protons to the protons of the bound phenyl ring. No chemical exchange between the bound and free phenyl rings is observed up to 0°C , where decomposition to intractable products occurs. Attempts to disfavor coordination of the arene ring by employing a more sterically protective isobutyl substituent in $\text{Cp}_2^*\text{Zr}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2$ (**7**) led to rapid, quantitative β -hydride elimination producing isobutylene and $[\text{Cp}_2^*\text{Zr}(\text{H})\eta\text{-C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**8**) even at temperatures as low as -135°C . Addition of propylene to cold solutions of the trityl-coordinated complexes resulted in very rapid formation of polypropylene. This polymerization resulted in no observable changes in the NMR spectra of the zirconium complexes in solution, implying a very rapid rate of propagation following a much slower first monomer insertion. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Metallocene; Zirconium cation; β -Hydride elimination; Arene complex

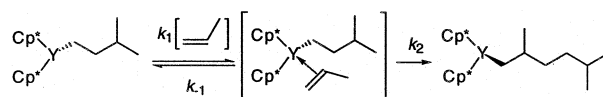
1. Introduction

The ability of trityl cation, $(\text{C}_6\text{H}_5)_3\text{C}^+$, to act as a powerful alkyl-abstracting agent makes it a highly effective co-catalyst for the activation of metallocene and related metal–alkyl complexes. When combined with non-coordinating anions such as $\text{B}(\text{C}_6\text{F}_5)_4^-$ [1] or $\text{Al}(\text{C}_6\text{F}_5)_4^-$ [2], trityl activated metallocenes can be highly efficient alkene polymerization catalysts [3]. Ammonium salts possessing an acidic proton can also be highly effective co-catalysts when used to protonate the Zr–C bond of an appropriate zirconium alkyl complex [4].

Efforts in our group have focused on studying ytrocene polymerization catalysts. At extremely low tem-

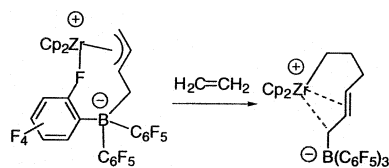
peratures, we have been able to observe propene coordination to an yttrium alkyl complex; this was the first observation of a non-chelated metallocene-alkyl–alkene complex, a key proposed intermediate in metallocene catalyzed alkene polymerization [5,6] (Scheme 1). Also, by taking advantage of increased steric hindrance after one insertion of propene into $\text{Cp}_2^*\text{YCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$, we have been able to arrest the polymerization and observe the product of a single insertion. This has allowed us to measure the kinetic parameters associated with the first monomer addition to a growing polymer chain [5].

Erker's group has also observed the first alkene insertion into a growing polymer chain (Scheme 2). In Erker's system, internal ion-pairing and π -coordination

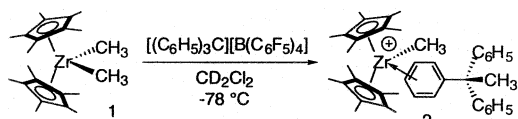


Scheme 1.

* Corresponding authors. Present address: Delphi Automotive Systems, P.O. Box 580970, Tulsa, OK 74158-0970 (D.W. Carpenetti II).
E-mail addresses: casey@chem.wisc.edu (C.P. Casey), donald.w.carpenetti@delphiauto.com (D.W. Carpenetti, II).



Scheme 2.



Scheme 3.

of a C=C to the zirconium center after the first insertion allowed observation of the dormant post-insertion catalyst state [7].

Examples of zirconium–benzyl complexes that insert only one equivalent of an alkene due to stabilization of the mono-insertion product by an interaction between the metal and the phenyl ring have been reported by Pellecchia [8] and Horton [9].

Here we report attempts to extend our studies of non-chelated yttrium–alkyl–alkene complexes to their more catalytically relevant zirconium analogs. We sought a system which would allow observation of a cationic zirconium–propene complex at low temperatures and possibly also allow observation of the first insertion of propene into the growing alkyl chain.

2. Results

2.1. Arene complexation prevents observation of propene complexation

Our first attempt to generate a cationic zirconium complex capable of binding propene involved methyl abstraction from $\text{Cp}_2^*\text{Zr}(\text{CH}_3)_2$ (**1**) with trityl cation. The reaction of **1** with one equivalent of $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 at -78°C led to formation of an orange solution containing $[\text{Cp}_2^*\text{Zr}(\text{CH}_3)\eta\text{-C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**) (Scheme 3). Evaporation of CD_2Cl_2 from a solution of **2** at -78°C gave a viscous oil that resisted all attempts at crystallization. Consequently, **2** was identified as an arene complex by ^1H - and ^{13}C -NMR spectroscopy at -78°C .

The ^1H -NMR of **2** exhibits two sets of resonances in the phenyl region. The 2:1 ratio of the peak intensities indicates that one of the phenyl rings experiences a different chemical environment than its two neighbors (Fig. 1). The hydrogen resonances for the unique phenyl ring at δ 7.67 (*ortho*), 7.87 (*meta*) and 8.25 (*para*) ppm are all shifted to significantly higher frequency. The *para* hydrogen is shifted +1.03 ppm, the *meta* hydrogens +0.60 ppm and the *ortho* hydrogens +0.59 ppm compared to the resonances of the other two phenyl rings. The high frequency shifts of the resonances of the unique phenyl ring are reminiscent of our observations for alkene coordination to a d^0 metal center [10], and are consistent with phenyl coordination to a cationic zirconium(IV) center. This interaction

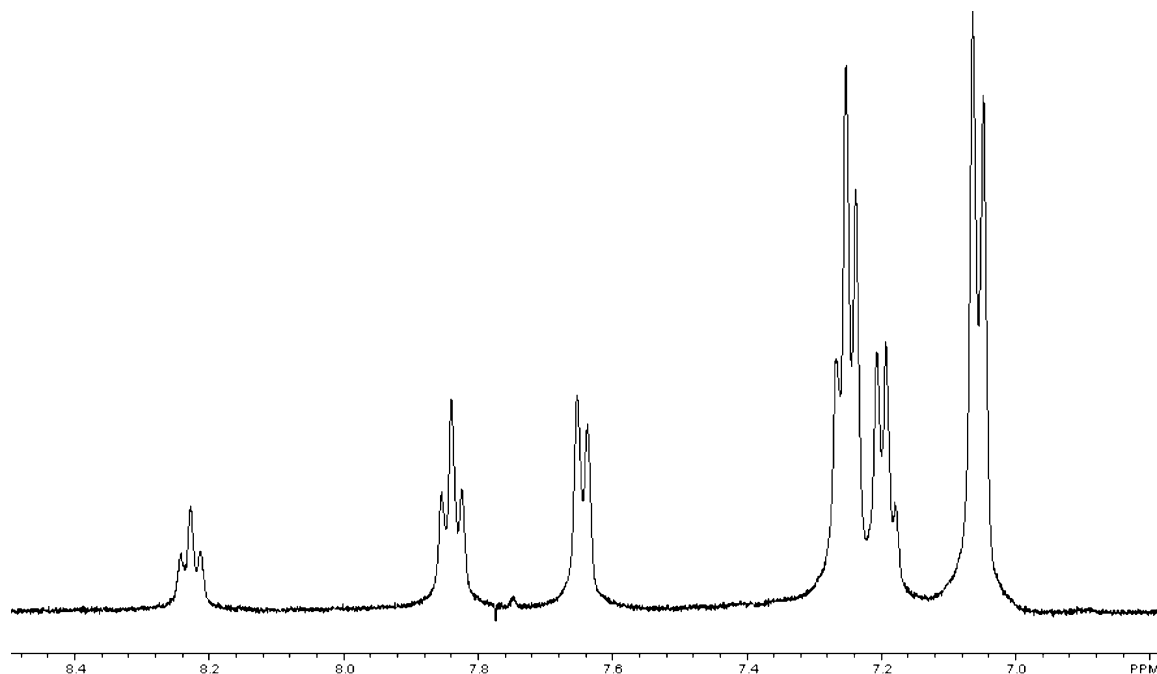
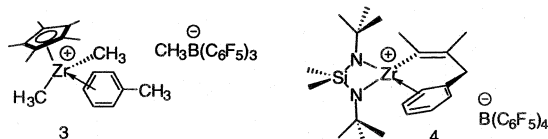


Fig. 1. Phenyl region of ^1H -NMR spectrum of **2** showing 2:1 ratio of resonances corresponding to free and bound phenyl groups.

involves no metal–ligand back-bonding, but significant electron donation from the arene to the metal.

Comparison of the ^1H -NMR chemical shifts of **2** with those of other arenes coordinated to cationic zirconium centers provided further support for coordination of one trityl phenyl ring. Baird reported that the ^1H -NMR resonances of the bound toluene in $[\text{Cp}(\text{CH}_3)_2\text{Zr}(\eta^6\text{-toluene})][\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]$ (**3**) were shifted to higher frequency (δ 7.78, 7.38 and 7.04) compared with uncomplexed toluene (δ 7.09, 7.00 and 6.98) [11]. Horton and de With reported that the ^1H -NMR resonances of the bound phenyl ring of $\{\text{[Si}(\text{CH}_3)_2(t\text{-BuN})_2\text{Zr}[\eta^1, \eta^6\text{-C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5]\}\text{[B}(\text{C}_6\text{F}_5)_4]\}$ (**4**) appeared at higher frequency (δ 8.16, 8.12 and 7.88) than those of the phenyl ring after displacement from zirconium by THF (δ 7.05 and 7.25) [9,12].



The ^{13}C -NMR spectrum of **2** also supports coordination of one of the trityl phenyl rings to zirconium. The *para* carbon of the bound phenyl at δ 143.5 is shifted 16.7 ppm to higher frequency than the *para* carbon of the unbound phenyl. The *meta* carbon of the bound phenyl at δ 142.9 is shifted 13.5 ppm to higher frequency than the *meta* carbon of the free phenyl. Significantly, the more crowded *ortho* carbon is shifted only 1.9 ppm to higher frequency in the coordinated ring. Because three of the phenyl carbons exhibit significant shifts to higher frequency, and two others exhibit minor shifts, we believe that at least three and possibly five of these carbons experience interaction with the cationic zirconium center. This is consistent with either a symmetric structure with η^3 or η^5 binding of the phenyl ring or with rapidly fluxional asymmetric η^2 or η^4 binding.

As observed in related compounds [9,12], addition of THF to a solution of **2** leads to displacement of the bound arene and formation of a 1:1 THF adduct. The ^1H - and ^{13}C -NMR spectra show only one set of arene resonances with shifts corresponding to those observed for an independently synthesized sample of $(\text{C}_6\text{H}_5)_3\text{CCH}_3$. Further support for the coordination of one phenyl group in **2** came from observation of a 2–3% nOe enhancement of the hydrogen resonances assigned to the bound arene from through space saturation transfer from the Cp* methyl groups. No nOe enhancement of arene resonances was observed after addition of THF which displaces the bound arene.

No evidence for dissociation of the bound phenyl group from trityl complex **2** was observed up to its decomposition temperature. The observed resonances for the free and bound phenyl rings remained essen-

tially unchanged up to 0 °C where decomposition to intractable products occurred rapidly. Spin saturation transfer experiments at –20 °C showed no exchange between the free and bound phenyl rings. Also, addition of toluene- d_8 to a solution of **2** resulted in no observable displacement of the bound phenyl ring. Baird made similar observations indicative of tight arene binding in **3** and similar compounds [11].

In light of the steric bulk of the pentamethylcyclopentadienyl ligands, we questioned whether more than two arene carbons could interact with zirconium simultaneously. To distinguish between symmetric structures with η^3 or η^5 binding of the phenyl ring and rapidly fluxional asymmetric η^2 or η^4 structures, we attempted to freeze out fluxional behavior at low temperature. Static η^2 - or η^4 -coordination would result in an asymmetric bound arene with different *ortho* and *meta* hydrogens. The mixture of CDCl_2F and CDClF_2 provides a very low viscosity solvent suitable for use down to –150 °C [13]. The region of the ^1H -NMR spectrum corresponding to the bound phenyl peaks of **2** in CDCl_2F – CDClF_2 at –135 °C is shown in Fig. 2. Although the resolution of the spectrum is much lower than those taken at –78 °C in CD_2Cl_2 , it is apparent that the bound phenyl ring is still symmetric as evidenced by the 1:2:2 ratio of the peak intensities. The *ortho* and *meta* positions on either side of the bound phenyl ring still experience identical magnetic environments on the NMR time scale. This indicates that *if* the high frequency shifts of the five phenyl positions in ^1H - and ^{13}C -NMR are the result of rapid sampling of different η^2 -coordination modes of the bound phenyl ring, then the rate of that interchange is too fast to be frozen out.

In light of the ability of THF to displace the bound phenyl ring from the metal center of **2**, we sought to determine if addition of an alkene monomer such as propene might also displace the bound arene and allow the observation of a zirconium–propene complex. Small amounts of propene (ca. two equivalents) were condensed into NMR tubes containing **2** in CD_2Cl_2 or CDCl_2F – CDClF_2 at –196 °C, the tubes were then placed in the pre-cooled probe of the NMR spectrometer and allowed to thaw at –90 and –135 °C, respectively. The samples were briefly ejected, shaken, and placed back into the cooled spectrometer probe. In both cases, no resonances corresponding to propene were observed; instead, alkyl resonances corresponding to atactic polypropylene (δ 0.9–1.5) were seen. In addition, a small amount of solid (polypropylene?) was observed. The only zirconium species observed was **2**, which showed no change in peak integrations relative to an internal standard. This suggests that the initial propene insertion (initiation) is followed by much faster subsequent insertions (propagation) which consume all of the propene but only a vanishingly small amount of catalyst.

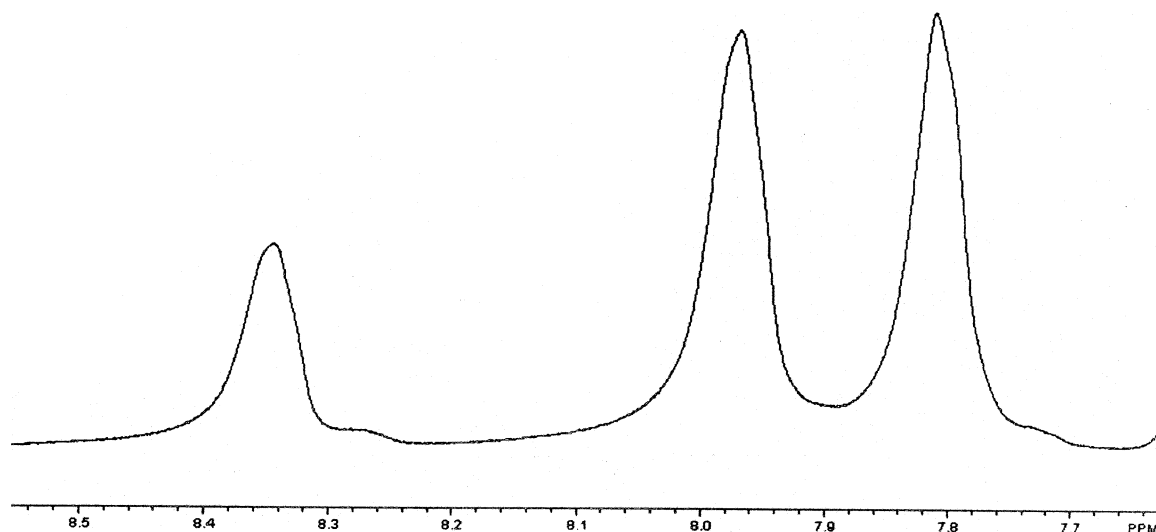
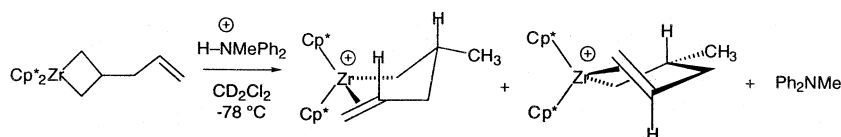


Fig. 2. Bound phenyl region of the ^1H -NMR spectrum of **2** in CDCl_2F – CDClF_2 at $-135\text{ }^\circ\text{C}$.



Scheme 4.

2.2. Amine complexation prevents observation of propene complexation

Our second attempt at generating a cationic zirconium complex capable of binding propene involved protonolysis of **1**. We had previously synthesized cationic zirconium-alkyl-alkene chelates by protonation of 3-allyl-zirconacyclobutanes with $[\text{HNCH}_3(\text{C}_6\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ and found that the conjugate base NMePh_2 did not displace the chelated alkene from zirconium (Scheme 4) [10].

The reaction of **1** with $[\text{HNCH}_3(\text{C}_6\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 at $-78\text{ }^\circ\text{C}$ led to formation of a brown–orange solution containing $[\text{Cp}^*_2\text{Zr}(\text{CH}_3)\text{NCH}_3(\text{C}_6\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**5**) and methane (Scheme 5). The ^1H -NMR chemical shift of the NCH_3 group at δ 4.03 is indicative of coordination to zirconium; the chemical shift of the NCH_3 group of the free amine is δ 3.18 [10].

Complex **5** was also formed in CDCl_2F – CDClF_2 solution. Both the CD_2Cl_2 and the CDCl_2F – CDClF_2 solutions of **5** rapidly polymerized propene at low temperatures. Again, no apparent change in the amount of zirconium complex **5** was observed by ^1H - and ^{13}C -NMR.

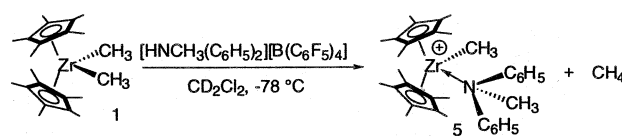
2.3. β -Hydride elimination prevents observation of isobutylzirconium complexes

In a third attempt to generate a cationic zirconium complex capable of binding propene, we sought to

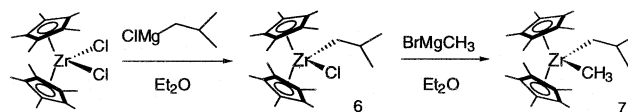
block coordination of arenes and amines by employing a more sterically demanding isobutylzirconium precatalyst.

Addition of excess isobutylmagnesium chloride to $\text{Cp}^*_2\text{ZrCl}_2$ led to the formation of $\text{Cp}^*_2\text{Zr}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$ (**6**) in excellent yield. Apparently, the combined steric bulk of the isobutyl substituent and the Cp^* rings prevents reaction with a second equivalent of isobutylmagnesium chloride. Subsequent addition of methyl magnesium bromide led to formation of $\text{Cp}^*_2\text{Zr}(\text{CH}_3)[\text{CH}_2\text{CH}(\text{CH}_3)_2]$ (**7**) (Scheme 6).

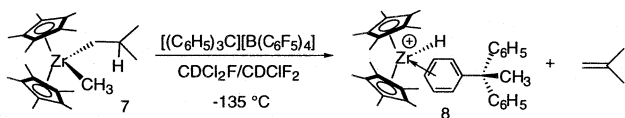
The reaction of **7** with the methide abstracting agent $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 at $-78\text{ }^\circ\text{C}$ was carried out in an attempt to generate the cationic isobutylzirconium complex $\text{Cp}^*_2\text{ZrCH}_2\text{CH}(\text{CH}_3)_2^+$. While methyl abstraction occurred, the desired intermediate apparently



Scheme 5.



Scheme 6.



Scheme 7.

underwent immediate β -hydride elimination and an orange solution containing $[Cp_2^*Zr(H)\eta-C_6H_5C(C_6H_5)_2CH_3][B(C_6F_5)_4]$ (**8**) and isobutylene was formed (Scheme 7) [14]. Similar zirconium alkyls have been shown to undergo facile β -hydride or β -methyl elimination [15,16]. The assignment of the Zr–H resonance of **8** was verified by nOe experiments showing excitation transfer from the Cp^* hydrogens to the one proton singlet at δ 5.57 which is therefore assigned to the hydride. This zirconium hydride chemical shift is similar to those of cationic zirconium hydrides reported by Marks [17]. Experiments attempting to detect nOe between isobutylene and Cp^* ligands were all negative, indicating that isobutylene does not interact with the metal center.

The reaction of **7** with $[(C_6H_5)_3C][B(C_6F_5)_4]$ was attempted in $CDCl_2F-CDClF_2$ at $-135^\circ C$ to determine if the β -hydride elimination could be avoided at lower temperatures. However, even at $-135^\circ C$, rapid formation of **8** and isobutylene occurred. We were therefore unable to determine whether the isobutyl group prevented arene coordination and were unable to study the kinetics of the β -hydride elimination.

In a second attempt to generate the desired cationic isobutylzirconium intermediate $Cp_2^*ZrCH_2CH(CH_3)_2^+$, the reaction of **7** with $[HNCH_3(C_6H_5)_2][B(C_6F_5)_4]$ was investigated. In CD_2Cl_2 at $-78^\circ C$ or in $CDCl_2F-CDClF_2$ at $-135^\circ C$, the reaction proceeded with rapid and quantitative formation of $[Cp_2^*Zr(H)NCH_3(C_6H_5)_2][B(C_6F_5)_4]$ (**9**), isobutylene, and methane (Scheme 8). Apparently protonolysis of the methyl group occurs, but rapid β -hydride elimination and amine coordination ensues. The assignment of the hydride was supported by nOe experiments, in this case from the *N*-methyl group to the resonance at δ 3.28 assigned to the hydride. Once again, experiments attempting to detect nOe between isobutylene and Cp^* ligands were negative, indicating that isobutylene does not interact with the metal center.

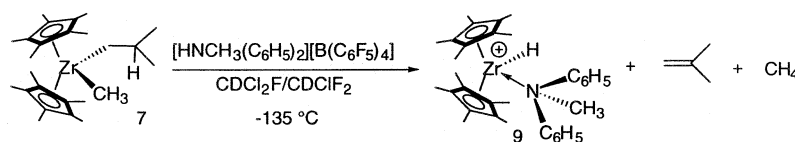
The reactions of solutions of the cationic zirconium hydrides **8** and **9** with propene were monitored at low temperature in an effort to detect formation of a zirco-

nium-alkyl–propene complex. In all cases, propene was completely consumed before the first NMR spectrum could be recorded and only polypropylene and undiminished **8** or **9** were observed. As expected, the isobutylene produced by β -hydride elimination was not incorporated into the polymer. These results suggests that the initial addition of zirconium hydride to propene (initiation) is followed by much faster subsequent insertions of propene (propagation) which consume all of the propene but only a vanishingly small amount of the hydride catalyst.

3. Discussion

For yttrium complexes, we were able to observe d^0 metal-alkyl–alkene complexes for both chelates and non-chelates; but for zirconium, so far, we have been able to observe only chelated d^0 metal-alkyl–alkene complexes. Why is zirconium so different? A major difference is the mode of generating 14-electron zirconium cations capable of coordinating an alkene. Methyl abstraction from **1** with trityl cation generates triphenylethane which complexes strongly with zirconium to give arene complex **2**. Similarly, protonation of **1** with $[HNCH_3(C_6H_5)_2][B(C_6F_5)_4]$ gave the amine complex **5**. While the arene and amine functionalities of $NCH_3(C_6H_5)_2$ do not compete with intramolecular coordination of a chelated alkene to zirconium, they effectively compete with intermolecular coordination of propene. We were able to make cationic zirconium-alkyl–alkene chelates in the presence of $[CH_3B(C_6F_5)_3]$ anion; this anion did not compete with the tethered alkene for coordination to zirconium. Marks has reported that the tight ion pair $[Cp_2^*Zr(CH_3)][CH_3B(C_6F_5)_3]$ was generated from **1** and $B(C_6H_5)_3$ and that this ion pair rapidly polymerizes propene [18]. No evidence for propene complexation was obtained. Either propene does not thermodynamically compete with $[CH_3B(C_6F_5)_3]$ anion for complexation to zirconium or insertion of propene occurs more rapidly than propene substitution for the anion. In the case of yttrium, we were able to generate yttrium alkyls in the absence of arenes, amines, and $[CH_3B(C_6F_5)_3]$ anion; without competition from these complexing agents, propene coordination was observed [5].

Can we imagine an observable $[Cp_2^*Zr(CH_3)-(propene)]^+$ complex with any anion? Not yet! Such a



Scheme 8.

complex will require a much less tightly bound anion than $[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]$; the $\text{B}(\text{C}_6\text{F}_5)_4$ anion is a possibility, but a new way of generating the ion pair will be required. Observation of $[\text{Cp}^*\text{Zr}(\text{CH}_3)(\text{propene})]^+$ will also require that the anion be kinetically displaced by propene at a rate faster than methyl migration to coordinated propene.

In the case of arene complex **2** and amine complex **5**, contact with propene led to polypropylene with no perceptible decrease in the amount of polymerization catalysts **2** or **5**. It is likely that the initial more crowded β -alkyl substituted alkyl zirconium insertion products are more reactive towards propene than the starting methyl zirconium complex. Similar results have been seen by Marks [18] and by Landis [19]. These observations suggest that the more crowded alkyl zirconium complexes might have a more easily displaced anion and might allow observation of a zirconium-alkyl-propene complex.

We attempted to generate the more sterically demanding isobutylzirconium precatalyst. $[\text{Cp}^*\text{ZrCH}_2\text{CH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ either by methyl abstraction from **7** with $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ or by protonation of **7** with $[\text{HNCH}_3(\text{C}_6\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$. In both cases, while the initial cleavage of the methyl zirconium bond was seen, the presumed isobutyl zirconium intermediate apparently underwent immediate β -hydride elimination to give cationic zirconium hydride complexes of the amine or arene.

Can we imagine an observable $[\text{Cp}^*\text{ZrR}(\text{propene})]^+$ complex with any crowded alkyl group? Possibly, but the R group must be resistant to β -hydride elimination. One possibility would be the neopentyl group CH_2CMe_3 , but β -alkyl elimination is likely to be a major problem encountered in related systems [16a,b]. $[\text{Cp}^*\text{Zr}(\text{CH}_2\text{Ph})(\text{propene})]^+$ is a possibility since β -alkyl elimination is impossible, but π -benzyl formation is a serious concern. $[\text{Cp}^*\text{Zr}(\text{CH}_2\text{SiMe}_3)(\text{propene})]^+$ should be resistant to β -alkyl elimination since it would result in an unstable $\text{C}=\text{Si}$ product and offers perhaps the best hope for success.

4. Experimental

4.1. General procedure

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. ^1H -NMR spectra were obtained using a Varian Unity500 spectrometer. ^{13}C - and ^{19}F -NMR spectra were obtained on a Varian Unity500 spectrometer operating at 126 and 416.5 MHz, respectively. ^{19}F spectra were referenced

externally to CFCl_3 . Spectrometer temperatures were measured after a 15 min equilibration, using a methanol standard containing 0.03% HCl [20] or a thermocouple. CD_2Cl_2 (Cambridge Isotopes) was dried over P_2O_5 and then distilled from CaH_2 . Tetrahydrofuran and pentane were dried over sodium and then distilled. Isobutylmagnesium chloride and methylmagnesium bromide were obtained from Aldrich and used as received. Propene was purchased from Aldrich and used as received or dried over Na–K alloy. Cp^*ZrCl_2 was purchased from Strem. $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was supplied by Dow Chemical Company. $[\text{HNCH}_3(\text{C}_6\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ [10,21], $\text{Cp}^*\text{Zr}(\text{CH}_3)_2$ [22], and $\text{CCl}_2\text{FD}-\text{CClF}_2\text{D}$ [13] were prepared by known procedures.

4.2. Preparation of

$[\text{Cp}^*\text{Zr}(\text{CH}_3)\eta\text{-C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**2**)

CD_2Cl_2 (0.5 ml) was condensed into a resealable NMR tube containing $\text{Cp}^*\text{Zr}(\text{CH}_3)_2$ (0.020 g, 3.9×10^{-5} mol) and $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.036 g, 3.9×10^{-5} mol) at -78°C . The tube was shaken briefly at -78°C to give an orange solution of **2**. ^1H -NMR (-78°C , 500 MHz, CD_2Cl_2) δ 0.24 (s, ZrCH_3), 1.98 (s, Cp^*CH_3), 2.14 (s, $(\text{C}_6\text{H}_5)_3\text{CCH}_3$), 7.08 (d, $J = 7$ Hz, 4H, *o*- C_6H_5), 7.22 (t, $J = 7$ Hz, 2H, *p*- C_6H_5), 7.27 (t, $J = 7$ Hz, 4H, *m*- C_6H_5), 7.67 (d, $J = 7$ Hz, 2H, *o*- $\eta\text{-C}_6\text{H}_5$), 7.87 (t, $J = 7$ Hz, 2H, *m*- $\eta\text{-C}_6\text{H}_5$), 8.25 (t, $J = 7$ Hz, 1H, *p*- $\eta\text{-C}_6\text{H}_5$). ^{13}C -NMR (gated decoupled, -78°C , 126 MHz, CD_2Cl_2) δ 11.6 (q, $J = 126$ Hz, Cp^*CH_3), 30.1 (q, $J = 126$ Hz, $(\text{C}_6\text{H}_5)_3\text{CCH}_3$), 52.3 (s, $(\text{C}_6\text{H}_5)_3\text{CCH}_3$), 56.1 (q, $J = 118$ Hz, ZrCH_3), 123.6 (br s, *ipso*-BC), 125.7 (br s, C_5Me_5), 126.0 (dt, $J = 160$, 7 Hz, *p*- C_6H_5), 127.9 (dd, $J = 156$, 7 Hz, *o*- C_6H_5), 128.6 (dt, $J = 156$, 7 Hz, *m*- C_6H_5), 130.5 (dd, $J = 167$, 8 Hz, *o*- $\eta\text{-C}_6\text{H}_5$), 136.1 (d, $J_{\text{CF}} = 242$ Hz, C_6F_5), 138.0 (d, $J_{\text{CF}} = 241$ Hz, C_6F_5), 139.6 (d, $J = 8$ Hz, *ipso*- $\eta\text{-C}_6\text{H}_5$), 142.9 (dt, $J = 165$, 6 Hz, *m*- $\eta\text{-C}_6\text{H}_5$), 143.5 (dt, $J = 164$, 7 Hz, *p*- $\eta\text{-C}_6\text{H}_5$), 147.8 (d, $J_{\text{CF}} = 242$ Hz, C_6F_5), 149.0 (s, *ipso*- C_6H_5). ^{19}F -NMR (416.5 MHz, CD_2Cl_2 , line broadened, -78°C) δ -135.9 (s, 8F, C_6F_5), -166.2 (s, 4F, C_6F_5), -170.2 (s, 8F, C_6F_5).

A 2:1 mixture of CDCl_2F and CDClF_2 (0.5 ml) was condensed into resealable NMR tube containing $\text{Cp}^*\text{Zr}(\text{CH}_3)_2$ (0.020 g, 3.9×10^{-5} mol) and $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.036 g, 3.9×10^{-5} mol) at -196°C . The tube was inserted directly into the NMR probe pre-cooled to -135°C . After allowing the tube to equilibrate at -135°C , it was briefly ejected, shaken, and reinserted into the probe. Upon shaking, the solution immediately took on the orange color of the solute, **2**. ^1H -NMR (-135°C , 500 MHz, $\text{CDCl}_2\text{F}-\text{CDClF}_2$) δ 0.27 (s, ZrCH_3), 1.96 (s, Cp^*CH_3), 2.21 (s, $(\text{C}_6\text{H}_5)_3\text{CCH}_3$), 7.14 (br, 4H, *o*- C_6H_5), 7.25 (br, 2H, *p*- C_6H_5), 7.29 (br, 4H, *m*- C_6H_5), 7.81 (br, 2H,

o- η -C₆H₅), 7.97 (br, 2H, *m*- η -C₆H₅), 8.35 (br, 1H, *p*- η -C₆H₅). ¹³C-NMR (gated decoupled, –135 °C, 126 MHz, CDCl₂F–CDClF₂) δ 11.9 (q, *J* = 126 Hz, Cp*CH₃), 30.9 (q, *J* = 126 Hz, (C₆H₅)₃CCH₃), 50.8 (s, (C₆H₅)₃CCH₃), 57.6 (q, *J* = 118 Hz, ZrCH₃), 123 (br s, *ipso*-BC), 125.7 (br s, C₅Me₅), 126.0 (d, *J* = 160 Hz, *p*-C₆H₅), 127.9 (d, *J* = 156 Hz, *o*-C₆H₅), 128.6 (d, *J* = 156 Hz, *m*-C₆H₅), 130.5 (d, *J* = 167 Hz, *o*- η -C₆H₅), 136.1 (d, *J*_{CF} = 242 Hz, C₆F₅), 138.0 (d, *J*_{CF} = 241 Hz, C₆F₅), 139.6 (s, *ipso*- η -C₆H₅), 142.9 (d, *J* = 165 Hz, *m*- η -C₆H₅), 143.5 (d, *J* = 164 Hz, *p*- η -C₆H₅), 147.8 (d, *J*_{CF} = 242 Hz, C₆F₅), 149.0 (s, *ipso*-C₆H₅). ¹⁹F-NMR (416.5 MHz, CDCl₂F–CDClF₂, line broadened, –135 °C) δ –134.8 (s, 8F, C₆F₅), –167.2 (s, 4F, C₆F₅), –169.1 (s, 8F, C₆F₅).

4.3. Reaction of **2** with THF

A small amount of THF was condensed into a resealable NMR tube containing **2**. Upon shaking at –78 °C, the solution changed from orange to yellow. ¹H-NMR (–78 °C, 500 MHz, CD₂Cl₂) δ 0.27 (s, ZrCH₃), 1.77 (br m, free β -THF), 1.82 (br m, 4H, bound β -THF), 1.89 (s, Cp*CH₃), 2.13 (s, (C₆H₅)₃CCH₃), 3.51 (br m, 2H, bound α -THF), 3.63 (br m, free α -THF), 3.77 (br m, 2H, bound α -THF), 7.04 (d, *J* = 7 Hz, *o*-C₆H₅), 7.17 (t, *J* = 7 Hz, *p*-C₆H₅), 7.23 (t, *J* = 7 Hz, *m*-C₆H₅). ¹³C-NMR (gated decoupled, –78 °C, 126 MHz, CD₂Cl₂) δ 12.1 (q, *J* = 125 Hz, Cp*CH₃), 25.8 (t, *J* = 135 Hz, bound β -THF), 26.4 (t, *J* = 133 Hz, free β -THF), 27.3 (t, *J* = 135 Hz, bound β -THF), 30.8 (q, *J* = 129 Hz, (C₆H₅)₃CCH₃), 50.7 (q, *J* = 118 Hz, ZrCH₃), 53.0 (s, (C₆H₅)₃CCH₃), 68.6 (t, *J* = 155 Hz, free α -THF), 73.2 (t, *J* = 150 Hz, bound α -THF), 77.5 (t, *J* = 155 Hz, bound α -THF), 124.0 (br s, *ipso*-BC), 124.4 (br s, C₅Me₅), 126.8 (dt, *J* = 156, 7 Hz, *p*-C₆H₅), 128.6 (dd, *J* = 156, 7 Hz, *o*-C₆H₅), 129.4 (dt, *J* = 156, 7 Hz, *m*-C₆H₅), 136.9 (d, *J*_{CF} = 242 Hz, C₆F₅), 138.8 (d, *J*_{CF} = 241 Hz, C₆F₅), 148.6 (d, *J*_{CF} = 242 Hz, C₆F₅), 149.7 (s, *ipso*-C₆H₅). ¹⁹F-NMR (416.5 MHz, CD₂Cl₂, line broadened, –78 °C) δ –136.3 (s, 8F, C₆F₅), –167.1 (s, 4F, C₆F₅), –170.5 (s, 8F, C₆F₅).

4.4. Reaction of **2** with propene

Two equivalents of propene were condensed into an NMR tube containing a CD₂Cl₂ solution of **2** at –78 °C. The sample was shaken briefly and inserted directly into the probe of the pre-cooled NMR spectrometer. Resonances corresponding to polypropylene were observed. No resonances for propene were present. Catalyst peaks and their respective integrations versus an internal standard of tetramethylsilane were unchanged within experimental error.

Two equivalents of propene were condensed into an NMR tube containing a CDCl₂F–CDClF₂ solution of

2 at –196 °C. The tube was inserted directly into the NMR probe pre-cooled to –135 °C. After allowing the tube to equilibrate at –135 °C, it was briefly ejected, shaken, and reinserted into the probe. Resonances corresponding to polypropylene were observed. No resonances for propene were present. Catalyst peaks and their respective integrations versus an internal standard of bis(trimethylsilyl)methane were unchanged within experimental error.

4.5. Preparation of

[Cp*₂Zr(CH₃)NCH₃(C₆H₅)₂][B(C₆F₅)₄] (**5**)

CD₂Cl₂ (0.5 ml) was condensed into a resealable NMR tube containing Cp*₂Zr(CH₃)₂ (0.020 g, 3.9 × 10^{–5} mol) and [HNCH₃(C₆H₅)₂][B(C₆F₅)₄] (0.040 g, 4.6 × 10^{–5} mol) at –78 °C. The tube was shaken briefly at –78 °C to give a brown–orange solution of **5** and methane. ¹H-NMR (–78 °C, 500 MHz, CD₂Cl₂) δ –0.38 (s, 4H, CH₄), 0.24 (s, 3H, ZrCH₃), 1.98 (s, 30H, Cp*CH₃), 4.03 (s, 3H, ZrNCH₃), 7.40 (d, *J* = 7 Hz, 4H, *o*-C₆H₅), 7.66 (t, *J* = 7 Hz, 2H, *p*-C₆H₅), 7.67 (t, *J* = 7 Hz, 4H, *m*-C₆H₅). Additional evidence supporting the assignments came from 1D nOe spectroscopy, where through space spin transfer was observed between the *N*-methyl group and the Cp* methyl groups. ¹³C-NMR (gated decoupled, –78 °C, 126 MHz, CD₂Cl₂) δ –3.0 (pentet, *J* = 126 Hz, CH₄), 12.7 (q, *J* = 126 Hz, Cp*CH₃), 41.1 (q, *J* = 127 Hz, NCH₃), 56.1 (q, *J* = 118 Hz, ZrCH₃), 123.6 (br s, *ipso*-BC), 124.5 (br s, C₅Me₅), 130.0 (dd, *J* = 156, 7 Hz, *o*-C₆H₅), 132.0 (dt, *J* = 156, 7 Hz, *m*-C₆H₅), 132.6 (dt, *J* = 160, 7 Hz, *p*-C₆H₅), 136.1 (d, *J*_{CF} = 242 Hz, C₆F₅), 138.0 (d, *J*_{CF} = 241 Hz, C₆F₅), 145.9 (s, *ipso*-C₆H₅), 147.8 (d, *J*_{CF} = 242 Hz, C₆F₅). ¹⁹F-NMR (416.5 MHz, CD₂Cl₂, line broadened, –78 °C) δ –135.9 (s, 8F, C₆F₅), –166.2 (s, 4F, C₆F₅), –170.2 (s, 8F, C₆F₅).

A 2:1 mixture of CDCl₂F and CDClF₂ (0.5 ml) was condensed into resealable NMR tube containing Cp*₂Zr(CH₃)₂ (0.020 g, 3.9 × 10^{–5} mol) and [HNCH₃-(C₆H₅)₂][B(C₆F₅)₄] (0.040 g, 4.6 × 10^{–5} mol) at –196 °C. The tube was inserted directly into the NMR probe pre-cooled to –135 °C. After allowing the tube to equilibrate at –135 °C, it was briefly ejected, shaken, and reinserted into the probe. Upon shaking the solution immediately took on the orange–brown color of the solute **5**. ¹H-NMR (–135 °C, 500 MHz, CDCl₂F–CDClF₂) δ –0.4 (br s, 4H, CH₄), 0.2 (br s, 3H, ZrCH₃), 2.0 (br s, 30H, Cp*CH₃), 4.1 (s, 3H, ZrNCH₃), 7.3 (br, 4H, *o*-C₆H₅), 7.7 (br m, 6H, *p*-C₆H₅ and *m*-C₆H₅). ¹³C-NMR (gated decoupled, –135 °C, 126 MHz, CDCl₂F–CDClF₂) δ –3.2 (pentet, *J* = 123 Hz, CH₄), 13.3 (q, *J* = 125 Hz, Cp*CH₃), 42.7 (q, *J* = 129 Hz, NCH₃), 56.5 (q, *J* = 121 Hz, ZrCH₃), 123.4 (br s, *ipso*-BC), 124.9 (br s, C₅Me₅), 130.7 (d, *J* = 156 Hz, *o*-C₆H₅), 131.9 (d, *J* = 156 Hz, *m*-C₆H₅), 132.6 (d,

$J = 160$ Hz, $p\text{-C}_6\text{H}_5$), 136.4 (d, $J_{\text{CF}} = 242$ Hz, C_6F_5), 138.8 (d, $J_{\text{CF}} = 241$ Hz, C_6F_5), 145.7 (s, *ipso*- C_6H_5), 147.3 (d, $J_{\text{CF}} = 242$ Hz, C_6F_5). ^{19}F -NMR (416.5 MHz, CDCl_2F – CDClF_2 , line broadened, -135 °C) δ -134.9 (s, 8F, C_6F_5), -167.4 (s, 4F, C_6F_5), -169.3 (s, 8F, C_6F_5).

4.6. Reaction of **5** with propene

Two equivalents of propene were condensed into an NMR tube containing a CD_2Cl_2 solution of **5** at -78 °C. The sample was shaken briefly and inserted directly into the probe of the pre-cooled NMR spectrometer. Resonances corresponding to polypropylene were observed. No resonances for propene were present. Catalyst peaks and their respective integrations versus an internal standard of tetramethylsilane were unchanged within experimental error.

Two equivalents of propene were condensed into an NMR tube containing a CDCl_2F – CDClF_2 solution of **5** at -196 °C. The tube was inserted directly into the NMR probe pre-cooled to -135 °C. After allowing the tube to equilibrate at -135 °C it was briefly ejected, shaken, and reinserted into the probe. Resonances corresponding to polypropylene were observed. No resonances for propene were present. Catalyst peaks and their respective integrations versus an internal standard of bis(trimethylsilyl)methane were unchanged within experimental error.

4.7. $\text{Cp}^*_2\text{Zr}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$ (**6**)

$\text{Cp}^*_2\text{ZrCl}_2$ (1.00 g, 2.31 mmol) was slurried in 40 ml of THF in a 100 ml Schlenk flask. The solution was cooled to -78 °C and isobutylmagnesium chloride (3.0 ml of a 2.0 M solution in THF, 6 mmol, 2.6 equivalents) was added via syringe under N_2 flush. The solution was allowed to warm slowly to room temperature (r.t.) and was stirred overnight (ca. 16 h). THF was evaporated under reduced pressure. The resulting solid material was slurried in pentane and filtered to give **6** (0.85 g, 81%) as a light orange powder. ^1H -NMR (24 °C, 500 MHz, CD_2Cl_2) δ 0.26 (d, $J = 5.9$ Hz, ZrCH_2), 0.80 (d, $J = 6.3$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.80 (apparent quintet of triplets; smallest lines of expected septet not resolved; $J = 6.3$, 5.9 Hz, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.94 (s, Cp^*CH_3). ^{13}C -NMR (gated decoupled, 24 °C, 126 MHz, CD_2Cl_2) δ 12.24 (q, $J = 125$ Hz, Cp^*CH_3), 28.7 (q, $J = 123$ Hz, $\text{CH}(\text{CH}_3)_2$), 30.7 (d, $J = 126$ Hz, $\text{CH}(\text{CH}_3)_2$), 65.5 (t, $J = 117$ Hz, ZrCH_2), 121.2 (s, C_5Me_5). MS (MALDI–TOF) Calc. (Found) for $\text{C}_{24}\text{H}_{42}\text{Zr}$ 433.84 (433.9).

4.8. Preparation of $\text{Cp}^*_2\text{Zr}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2$ (**7**)

Compound **6** (1.00 g, 2.20 mmol) was dissolved in

THF (40 ml) in a 100 ml Schlenk flask. CH_3MgBr (1.1 ml of a 3.0 M solution in THF, 3.30 mmol) was added via syringe under N_2 flush at -78 °C. The reaction mixture was warmed slowly to r.t. and stirred overnight. The THF was evaporated under reduced pressure and the resulting material was triturated with pentane and filtered. Evaporation of pentane from the filtrate afforded **7** (0.79 g, 75%). ^1H -NMR (24 °C, 500 MHz, CD_2Cl_2) δ -0.83 (s, 3H, ZrCH_3), -0.33 (d, $J = 6.2$ Hz, ZrCH_2), 0.61 (d, $J = 6.2$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.89 (s, Cp^*CH_3), 3.98 (apparent sextet, $J = 6.2$ Hz, $\text{ZrCH}_2\text{CH}(\text{CH}_3)_2$). ^{13}C -NMR (gated decoupled, 24 °C, 126 MHz, CD_2Cl_2) δ 11.90 (q, $J = 125$ Hz, Cp^*CH_3), 29.0 (q, $J = 127$ Hz, $\text{CH}(\text{CH}_3)_2$), 30.0 (d, $J = 132$ Hz, $\text{CH}(\text{CH}_3)_2$), 41.2 (q, $J = 117$ Hz, ZrCH_3), 64.5 (t, $J = 112$ Hz, ZrCH_2), 118.1 (s, C_5Me_5). MS (MALDI–TOF) Calc. (Found) for $\text{C}_{24}\text{H}_{39}\text{ClZr}$ 454.25 (454.3).

4.9. Reaction of **7** with $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$

CD_2Cl_2 (0.5 ml) was condensed into a resealable NMR tube containing **7** (0.020 g, 4.6×10^{-5} mol) and $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.042 g, 4.6×10^{-5} mol) at -78 °C. The tube was shaken briefly at -78 °C to give a yellow–orange solution of $[\text{Cp}^*_2\text{Zr}(\text{H})\eta\text{-C}_6\text{H}_5\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**8**) and isobutylene. ^1H -NMR (-78 °C, 500 MHz, CD_2Cl_2) δ 1.88 (s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 1.97 (s, Cp^*CH_3), 2.05 (s, $\text{C}_6\text{H}_5\text{CCH}_3$), 4.55 (br s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 5.57 (s, ZrH), 7.08 (d, $J = 7$ Hz, 4H, *o*- C_6H_5), 7.20 (t, $J = 7$ Hz, 2H, *p*- C_6H_5), 7.26 (t, $J = 7$ Hz, 4H, *m*- C_6H_5), 7.65 (d, $J = 7$ Hz, 2H, *o*- $\eta\text{-C}_6\text{H}_5$), 7.85 (t, $J = 7$ Hz, 2H, *m*- $\eta\text{-C}_6\text{H}_5$), 8.24 (t, $J = 7$ Hz, 1H, *p*- $\eta\text{-C}_6\text{H}_5$). Additional evidence supporting the assignment of the zirconium hydride resonance came from 1D nOe spectroscopy, where through space spin transfer was observed between the zirconium hydride and the Cp^* methyl groups and between the zirconium hydride and the protons of the bound phenyl ring. ^{13}C -NMR (gated decoupled, -78 °C, 126 MHz, CD_2Cl_2) δ 12.4 (q, $J = 126$ Hz, Cp^*CH_3), 30.1 (q, $J = 126$ Hz, $(\text{C}_6\text{H}_5)_3\text{CCH}_3$), 30.8 (q, $J = 129$ Hz, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 52.3 (s, $(\text{C}_6\text{H}_5)_3\text{CCH}_3$), 111.1 (t, $J = 155$ Hz, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 123.6 (br s, *ipso*-BC), 126.4 (br s, $\text{Cp}^*\text{-ring C}$), 126.0 (dt, $J = 160$, 7 Hz, *p*- C_6H_5), 127.9 (dd, $J = 156$, 7 Hz, *o*- C_6H_5), 128.6 (dt, $J = 156$, 7 Hz, *m*- C_6H_5), 130.5 (dd, $J = 167$, 8 Hz, *o*-*h*- C_6H_5), 136.1 (d, $J_{\text{CF}} = 242$ Hz, C_6F_5), 138.0 (d, $J_{\text{CF}} = 241$ Hz, C_6F_5), 139.6 (d, $J = 8$ Hz, *ipso*- $\eta\text{-C}_6\text{H}_5$), 142.4 (s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 143.7 (dt, $J = 165$, 6 Hz, *m*- $\eta\text{-C}_6\text{H}_5$), 144.2 (dt, $J = 164$, 7 Hz, *p*- $\eta\text{-C}_6\text{H}_5$), 147.8 (d, $J_{\text{CF}} = 242$ Hz, C_6F_5), 149.0 (s, *ipso*- C_6H_5). ^{19}F -NMR (416.5 MHz, CD_2Cl_2 , line broadened, -78 °C) δ -135.9 (s, 8F, C_6F_5), -166.2 (s, 4F, C_6F_5), -170.2 (s, 8F, C_6F_5).

CDCl_2F – CDClF_2 (0.5 ml) was condensed into a resealable NMR tube containing **7** (0.020 g, 4.6×10^{-5} mol) and $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.042 g, 4.6×10^{-5}

mol) at $-196\text{ }^{\circ}\text{C}$. The tube was inserted directly into the NMR probe pre-cooled to $-135\text{ }^{\circ}\text{C}$. After allowing the tube to equilibrate at $-135\text{ }^{\circ}\text{C}$ it was briefly ejected, shaken, and reinserted into the probe. Upon shaking, the solution immediately took on the yellow–orange color of the solute mixture **8** and isobutylene. ^1H -NMR ($-135\text{ }^{\circ}\text{C}$, 500 MHz, CDCl_2F – CDClF_2) δ 1.87 (s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 1.94 (s, Cp^*CH_3), 2.08 (s, $\text{C}_6\text{H}_5\text{CCH}_3$), 4.5 (br s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 5.6 (s, ZrH), 7.18 (br, 4H, *o*- C_6H_5), 7.29 (br, 2H, *p*- C_6H_5), 7.35 (br, 4H, *m*- C_6H_5), 7.75 (br, 2H, *o*- η - C_6H_5), 7.94 (br, 2H, *m*- η - C_6H_5), 8.31 (br, 1H, *p*- η - C_6H_5). Additional evidence supporting the assignment of the zirconium hydride resonance came from 1D nOe spectroscopy, where through space spin transfer was observed between the zirconium hydride and the Cp^* methyl groups and between the zirconium hydride and the protons of the bound phenyl ring. ^{13}C -NMR (gated decoupled, $-135\text{ }^{\circ}\text{C}$, 126 MHz, CDCl_2F – CDClF_2) δ 12.2 (q, $J=126\text{ Hz}$, Cp^*CH_3), 30.4 (q, $J=126\text{ Hz}$, $(\text{C}_6\text{H}_5)_3\text{CCH}_3$), 31.2 (q, $J=129\text{ Hz}$, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 53.3 (s, $(\text{C}_6\text{H}_5)_3\text{CCH}_3$), 111.1 (t, $J=155\text{ Hz}$, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 123.6 (br s, *ipso*-BC), 126.4 (br s, C_5Me_5), 126.5 (d, $J=160\text{ Hz}$, *p*- C_6H_5), 128.5 (d, $J=156\text{ Hz}$, *o*- C_6H_5), 128.6 (d, $J=156\text{ Hz}$, *m*- C_6H_5), 130.5 (d, $J=167\text{ Hz}$, *o*- η - C_6H_5), 136.1 (d, $J_{\text{CF}}=242\text{ Hz}$, C_6F_5), 138.0 (d, $J_{\text{CF}}=241\text{ Hz}$, C_6F_5), 139.6 (s, *ipso*- η - C_6H_5), 142.4 (s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 144.3 (d, $J=165\text{ Hz}$, *m*- η - C_6H_5), 145.0 (d, $J=164\text{ Hz}$, *p*- η - C_6H_5), 147.8 (d, $J_{\text{CF}}=242\text{ Hz}$, C_6F_5), 149.0 (s, *ipso*- C_6H_5). ^{19}F -NMR (416.5 MHz, CDCl_2F – CDClF_2 , line broadened, $-135\text{ }^{\circ}\text{C}$) δ -136.2 (s, 8F, C_6F_5), -166.8 (s, 4F, C_6F_5), -170.5 (s, 8F, C_6F_5).

4.10. Reaction of **8** with propene

Two equivalents of propene were condensed into an NMR tube containing a CD_2Cl_2 solution of **8** at $-78\text{ }^{\circ}\text{C}$. The sample was shaken briefly and inserted directly into the probe of the pre-cooled NMR spectrometer. Resonances corresponding to polypropylene were observed. No resonances for propene were present. Catalyst peaks and their respective integrations versus an internal standard of tetramethylsilane were unchanged within experimental error.

Two equivalents of propene were condensed into an NMR tube containing a CDCl_2F – CDClF_2 solution of **8** at $-196\text{ }^{\circ}\text{C}$. The tube was inserted directly into the NMR probe pre-cooled to $-135\text{ }^{\circ}\text{C}$. After allowing the tube to equilibrate at $-135\text{ }^{\circ}\text{C}$, it was briefly ejected, shaken, and reinserted into the probe. Resonances corresponding to polypropylene were observed. No resonances for propene were present. Catalyst peaks and their respective integrations versus an internal standard of bis(trimethylsilyl)methane were unchanged within experimental error.

4.11. Reaction of **7** with $[\text{HNCH}_3(\text{C}_6\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$

CD_2Cl_2 (0.5 ml) was condensed into a resealable NMR tube containing **7** (0.020 g, 4.6×10^{-5} mol) and $[\text{HNCH}_3(\text{C}_6\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.040 g, 4.6×10^{-5} mol) at $-78\text{ }^{\circ}\text{C}$. The tube was shaken briefly at $-78\text{ }^{\circ}\text{C}$ to give a brown–orange solution of $[\text{Cp}^*\text{Zr}(\text{H})\text{NCH}_3(\text{C}_6\text{H}_5)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (**9**), isobutylene, and methane. ^1H -NMR ($-78\text{ }^{\circ}\text{C}$, 500 MHz, CD_2Cl_2) δ -0.38 (s, CH_4), 1.90 (s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 1.98 (s, Cp^*CH_3), 3.28 (s, ZrH), 4.03 (s, ZrNCH_3), 4.67 (br s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 7.40 (d, $J=7\text{ Hz}$, *o*- C_6H_5), 7.66 (t, $J=7\text{ Hz}$, *p*- C_6H_5), 7.67 (t, $J=7\text{ Hz}$, *m*- C_6H_5). Additional evidence supporting the assignment of the zirconium hydride resonance came from 1D nOe spectroscopy, where through space spin transfer was observed between the zirconium hydride and the Cp^* methyl groups and between the zirconium hydride and the protons on the methyl group of the bound amine. ^{13}C -NMR (gated decoupled, $-78\text{ }^{\circ}\text{C}$, 126 MHz, CD_2Cl_2) δ -3.0 (pentet, $J=126\text{ Hz}$, CH_4), 12.7 (q, $J=126\text{ Hz}$, Cp^*CH_3), 25.2 (q, $J=130\text{ Hz}$, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 41.1 (q, $J=127\text{ Hz}$, NCH_3), 111.2 (t, $J=155\text{ Hz}$, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 123.6 (br s, *ipso*-BC), 124.5 (br s, C_5Me_5), 130.0 (dd, $J=156, 7\text{ Hz}$, *o*- C_6H_5), 132.0 (dt, $J=156, 7\text{ Hz}$, *m*- C_6H_5), 132.6 (dt, $J=160, 7\text{ Hz}$, *p*- C_6H_5), 136.1 (d, $J_{\text{CF}}=242\text{ Hz}$, C_6F_5), 138.0 (d, $J_{\text{CF}}=241\text{ Hz}$, C_6F_5), 143.9 ($\text{CH}_2=\text{C}(\text{CH}_3)_2$), 145.9 (s, *ipso*- C_6H_5), 147.8 (d, $J_{\text{CF}}=242\text{ Hz}$, C_6F_5). ^{19}F -NMR (416.5 MHz, CD_2Cl_2 , line broadened, $-78\text{ }^{\circ}\text{C}$) δ -135.9 (s, 8F, C_6F_5), -166.2 (s, 4F, C_6F_5), -170.2 (s, 8F, C_6F_5).

CDCl_2F – CDClF_2 (0.5 ml) was condensed into a resealable NMR tube containing **7** (0.020 g, 4.6×10^{-5} mol) and $[(\text{C}_6\text{H}_5)_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (0.042 g, 4.6×10^{-5} mol) at $-196\text{ }^{\circ}\text{C}$. The tube was inserted directly into the NMR probe pre-cooled to $-135\text{ }^{\circ}\text{C}$. After allowing the tube to equilibrate at $-135\text{ }^{\circ}\text{C}$ it was briefly ejected, shaken, and reinserted into the probe. Upon shaking, the solution immediately took on the yellow–orange color of the solute mixture **9**, isobutylene and methane. ^1H -NMR ($-135\text{ }^{\circ}\text{C}$, 500 MHz, CDCl_2F – CDClF_2) δ -0.40 (s, CH_4), 1.92 (s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 1.99 (s, Cp^*CH_3), 3.34 (s, ZrH), 4.11 (s, ZrNCH_3), 4.67 (br s, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 7.40 (br, *o*- C_6H_5), 7.66 (br, *p*- C_6H_5), 7.67 (br, *m*- C_6H_5). Additional evidence supporting the assignment of the zirconium hydride resonance came from 1D nOe spectroscopy, where through space spin transfer was observed between the zirconium hydride and the Cp^* methyl groups and between the zirconium hydride and the protons on the methyl group of the bound amine. ^{13}C -NMR (gated decoupled, $-135\text{ }^{\circ}\text{C}$, 126 MHz, CDCl_2F – CDClF_2) δ -3.2 (pentet, $J=126\text{ Hz}$, CH_4), 12.9 (q, $J=126\text{ Hz}$, Cp^*CH_3), 26.0 (q, $J=130\text{ Hz}$, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 41.1 (q, $J=127\text{ Hz}$, NCH_3), 111.7 (t, $J=155\text{ Hz}$, $\text{CH}_2=\text{C}(\text{CH}_3)_2$), 124 (br s, *ipso*-BC), 124.8 (br s, C_5Me_5), 130.0 (d, $J=156\text{ Hz}$, *o*- C_6H_5), 132.0 (d, $J=156\text{ Hz}$, *m*- C_6H_5), 132.6 (d,

$J = 160$ Hz, p -C₆H₅), 136.1 (d, $J_{\text{CF}} = 242$ Hz, C₆F₅), 138.0 (d, $J_{\text{CF}} = 241$ Hz, C₆F₅), 143.9 (CH₂=C(CH₃)₂), 145.9 (s, *ipso*-C₆H₅), 147.8 (d, $J_{\text{CF}} = 242$ Hz, C₆F₅). ¹⁹F-NMR (416.5 MHz, CD₂Cl₂, line broadened, -78 °C) δ -135.8 (s, 8F, C₆F₅), -166.1 (s, 4F, C₆F₅), -170.1 (s, 8F, C₆F₅).

4.12. Reaction of **9** with propene

Two equivalents of propene were condensed into an NMR tube containing a CD₂Cl₂ solution of mixture **9**, isobutylene, and methane at -78 °C. The sample was shaken briefly and inserted directly into the probe of the pre-cooled NMR spectrometer. Resonances corresponding to polypropylene were observed. No resonances for propene were present. Catalyst peaks and their respective integrations versus an internal standard of tetramethylsilane were unchanged within experimental error.

Two equivalents of propene were condensed into an NMR tube containing a CDCl₂F–CDClF₂ solution of mixture **9**, isobutylene, and methane at -196 °C. The tube was inserted directly into the NMR probe pre-cooled to -135 °C. After allowing the tube to equilibrate at -135 °C, it was briefly ejected, shaken, and reinserted into the probe. Resonances corresponding to polypropylene were observed. No resonances for propene were present. Catalyst peaks and their respective integrations versus an internal standard of bis(trimethylsilyl)methane were unchanged within experimental error.

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