Reactive Intermediates

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Structures and Properties of Nonchelated, d^0 Alkyl Alkene Complexes of the Type [$Cp_2ZrMe(alkene)]^+$: Elusive Intermediates during Ziegler–Natta Polymerizations of Alkenes**

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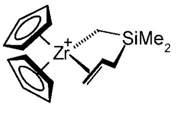
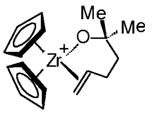
There has for many years been considerable interest in the utilization of metallocenes such as the 14-electron archetype $[Cp_2ZrMe]^+$ as catalysts for polymerization of alkenes $CH_2{=}CHR$ (R = H, alkyl, aryl).[1] It is universally accepted that polymerization involves initial alkene coordination to the vacant site to generate the intermediate $[Cp_2Zr(Me)(\eta^2\text{-}CH_2{=}CHR)]^+$ with a subsequent sequence of migratory insertion/coordination steps, and that polymeryl intermediates $[Cp_2Zr\{(CH_2CHR)_nMe\}(\eta^2\text{-}CH_2{=}CHR)]^+$ are formed and yield polymer by chain transfer.[1] However, in spite of a wealth of available mechanistic information concerning the polymerization process, all attempts to detect and characterize methyl alkene or polymeryl alkene intermediates of the types shown above have failed. Such species exhibit a pronounced proclivity to undergo insertion and are far too short-lived to be detectable,[1] and thus known d^0 alkene zirconocene complexes are typically stabilized by chelation as in **A**[2a,c,d] and/or contain no ligand that can undergo migratory insertion, as in **B** and **C**.[2b,e,f]



A



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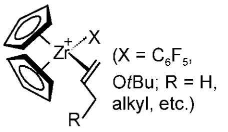
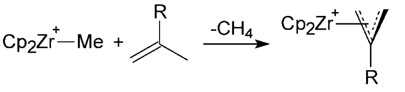


C

An alternative approach to the synthesis of, for example, a cationic methylzirconocene complex containing a coordinated alkene could involve utilization of an alkene that does not readily undergo migratory insertion reactions,[3] and we have recently reported evidence for the existence of complexes of the type $[Cp_2Zr(Me)(CH_2{=}CMeR)]^+$ (R = alkyl) as intermediates during the formation of the allylic complexes $[Cp_2Zr(\eta^3\text{-}CH_2C(R)CH_2]^+$ from 2-methyl-1-alkenes $CH_2{=}CMeR$ [Eq. (1)].[4]



(1)

Thus, while monitoring the course of a reaction of $[Cp_2Zr(Me)(C_6D_5Cl)]^+$ with 2,4-dimethyl-1-pentene (**I**) in C_6D_5Cl at 233 K, a NOESY experiment demonstrated exchange between the resonances of the terminal methylene hydrogen atoms of the free alkene ($\delta = 4.82, 4.75$ ppm) with a very weak resonance at $\delta \approx 3.5$ ppm. The latter was of necessity assigned to the corresponding terminal methylene hydrogen atoms of a zirconium complex containing a coordinated 2,4-dimethyl-1-pentene ligand, apparently the unprecedented complex $[Cp_2Zr(Me)(CH_2{=}CMeCH_2CHMe_2)]^+$ (**II**). Unfortunately, a more definitive study could not be carried out because of exchange phenomena above the freezing point of the solvent (f.p. 228 K), and we initiated an NMR investigation in CD_2Cl_2 (f.p. 176 K) in an attempt to better characterize the putative alkene complex. We report herein the results of a successful study to this end.

Experiments typically involved methide ion abstraction from $[Cp_2ZrMe_2]$ by $[Ph_3C][B(C_6F_5)_4]$ (ca. 1:1 molar ratio) at 293 K to give a mixture of $[Cp_2ZrMe][B(C_6F_5)_4]$ (**III**),[5a,b] the dinuclear complex $[Cp_2ZrMe(\mu\text{-}Me)ZrMeCp_2][B(C_6F_5)_4]$ (**IV**),[5a,b] and a species that we tentatively suggest is $[Cp_2ZrMe(CD_2Cl_2)][B(C_6F_5)_4]$ (**V**).[5c] The sample was rapidly cooled to 176 K and then placed in the probe of a Bruker AV-600 NMR spectrometer at 183 K, where a ^{1}H NMR spectrum was recorded (Figure S1 in the Supporting Information). To replicate the reported formation of the alkene complex,[4a] a ten-fold molar excess of **I** was added slowly (and without shaking in order to minimize polymerization) to a cooled (183 K) solution containing a mixture of **III**, **IV**, and **V** prepared as above. The alkene diffused slowly into the reaction mixture (see Figure S2 in the Supporting Information for a representative ^{1}H NMR spectrum) as NOESY experiments were carried out. We hoped to observe exchange correlations between the terminal methylene hydrogen resonances of free **I** with terminal methylene resonances of coordinated **I** in the region $\delta \approx 3.5$ ppm, and we were immediately successful. In addition to the anticipated NOE

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correlations between the terminal methylene hydrogen singlet resonances of free **I** at $\delta = 4.61$ and 4.55 ppm,[6a] we also observed exchange correlations of these with the high- ($\delta = 3.88$ ppm) and low-field ($\delta = 3.93$ ppm) halves, respectively, of an extremely weak AB quartet (Figure 1) at 193 K and above (see Figure S3a in the Supporting Information for a NOESY spectrum at 193 K).

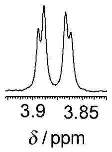
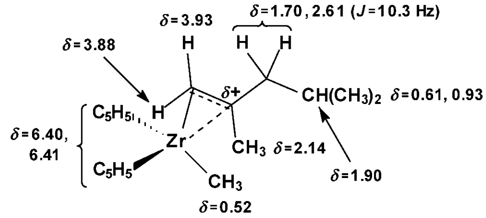


Figure 1. Terminal methylene resonances of coordinated **I** at 193 K.

Thus a zirconocene complex of **I** had formed, albeit at very low concentrations (ca. 1% of the total alkene and zirconium) under the conditions of the experiment. As anticipated, intermolecular exchange with free alkene was facile at 193 K and above, and NMR spectroscopy experiments were carried out from 183 to 238 K. As indicated above, these experiments involved mixtures with constantly varying alkene concentrations and, hence, varying alkene/Zr ratios.

Consistent with the formation of **II**, and aiding in chemical shift assignments, NOESY experiments at 193 K also revealed exchange of the 2-methyl resonance of **I** ($\delta = 1.60$ ppm)[6a] with a resonance at $\delta = 2.14$ ppm, which is therefore assigned to the 2-methyl group of **II** (Figure S4 in the Supporting Information) and of the *gem*-dimethyl resonance of **I** ($\delta = 0.74$ ppm, d)[6a] with a resonance at $\delta = 0.61$ ppm, assigned to one of the *gem*-dimethyl groups of **II** (Figure S5 in the Supporting Information). The resonance at $\delta = 0.61$ ppm is also seen to exchange with a resonance at $\delta = 0.93$ ppm, assigned below on the basis of a COSY experiment to the other *gem*-dimethyl group of **II**. Figure S5 in the Supporting Information also indicates exchange of the methylene resonance of **I** at $\delta = 1.83$ ppm[6a] with a doublet ($J = 10.3$ Hz) at $\delta = 2.61$ ppm, assigned as one of the methylene hydrogen atoms on C(3) of **II**. Aiding determination of the chemical shifts of **II**, NOEs were observed between the 2-methyl resonance of **II** at $\delta = 2.14$ ppm and the above-mentioned terminal methylene resonance at $\delta = 3.88$ ppm, assigned therefore as the hydrogen atom *cis* to the 2-Me group, as well as with a Cp resonance at $\delta = 6.41$ ppm, assigned to **II** (Figure S4 in the Supporting Information; the Cp resonance at $\delta = 6.41$ ppm is decoalesced at 183 K into two closely spaced singlets at $\delta = 6.399$ and 6.402 ppm). Furthermore, the aforementioned Cp resonance at $\delta = 6.41$ ppm exhibited an NOE with the two terminal methylene doublets of **II** at $\delta = 3.88$ and 3.93 ppm, with the doublet at $\delta = 2.61$ ppm, assigned above to one of the methylene hydrogen atoms on C(3) of **II**, and with the ZrMe resonance at $\delta = 0.52$ ppm, (Figures S4–S6 in the Supporting Information).

Assignments were also facilitated by COSY experiments (183 K) in which a cross peak was observed between the doublet at $\delta = 2.61$ ppm ($J = 10.7$ Hz) and a partially obscured doublet at $\delta = 1.70$ ppm (Figure S7 in the Supporting Information) with which it also undergoes exchange (Figure S5 in the Supporting Information); these resonances are attributed to the methylene protons on C(3) of **II**. Moreover, the resonances at $\delta = 0.61$ and 0.93 ppm, attributed above to the two *gem*-dimethyl groups of **II**, exhibited mutual cross peaks in addition to cross peaks with a broad resonance at $\delta = 1.90$ ppm, attributed to the methine proton on C(4) (Figure S8 in the Supporting Information). These results are thus consistent with the coexistence of **I** and a methyl ligand in the zirconocene complex **II**, for which all of the ^{1}H resonances have now been assigned, as summarized in Scheme 1.

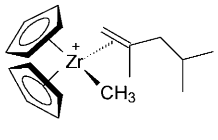


Scheme 1. ^{1}H NMR spectroscopy data for **II** (in ppm).

Note that observations of pairs of resonances for the Cp groups, for the two hydrogen atoms on C(3), and for the two *gem*-dimethyl groups are consistent with these groups constituting diasterotopic pairs as a result of chirality at C(2) of the coordinated alkene. Also of considerable significance is the observation of spin–spin coupling ($^2J = 6.58$ Hz) between the terminal methylene hydrogen atoms of the coordinated alkene. Although lower than the 10–15 Hz normally observed for aliphatic systems, the coupling is considerably greater than the approximately 0 Hz coupling in the free alkene and indicates significant sp^3 character for C(1) of the coordinated alkene.

Furthermore, on the basis of an HMBC experiment at 193 K, the ^{13}C chemical shifts of C(1) and C(2) of the coordinated alkene are $\delta = 99.0$ and 204.6 ppm, respectively, compared with $\delta = 111.3$ and 145.7 ppm for the free alkene. The resonance of C(2) has thus shifted downfield by 58.9 ppm, consistent with C(2) gaining significant carbocationic nature on coordination (as in Scheme 1), although C(2) is not as deshielded as isolated carbocations.[6b]

To complement these experimental findings, we carried out DFT calculations on **II** at the BP86 level of theory[7a] using the ADF program.[7b] We find that the optimized structure of **II** is as depicted in Scheme 2, with the methyl ligand and C(1)–C(2) bond of coordinated **I** both lying essentially in the plane perpendicular to the Cp(centroid)-Zr-Cp(centroid) plane and with the methyl ligand eclipsing C(2). This structure is stabilized relative to free **I** and the contact ion pair **III** by about 19 kcal mol^{-1} in CH_2Cl_2 but only by approximately 2 kcal mol^{-1} relative to the rotational isomer in which the methyl ligand eclipses C(1) of coordinated **I**. Note that this structure places one of the methylene hydrogen atoms on C(3), presumably (on the basis of NOESY experiments) that with chemical shift $\delta = 2.61$ ppm, closer to a Cp ring and its ring current effects than the other, thus offering a



Scheme 2. Structure of **II** as derived from optimization calculations.

rationale for the quite different chemical shifts ($\delta = 1.70$, 2.61 ppm).

The calculated C(1)–C(2) distance is 1.38 Å, slightly elongated from the 1.34 Å calculated for free **I**, but the Zr–C(1) and Zr–C(2) distances are 2.61 and 3.36 Å, respectively. The former is significantly longer than the Zr–Me bonds in [Cp_2ZrMe_2] (2.273(5), 2.280(5) Å)[2g] and [$Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$] (2.251(3) Å),[2h] and indeed it is only slightly shorter than the Zr–C(1) separations in **B** (2.68(2) Å) and other zirconium π complexes of unsaturated ligands.[2b] On the other hand, the Zr–C(2) bond is calculated to be almost 30 % longer than the Zr–C(1) bond, thus suggesting an extremely weak interaction between the metal and C(2).

Complex **II** appears to be very labile. The coalescence of the two closely spaced Cp resonances is mentioned above, and NOESY experiments at 193 K demonstrated exchange correlations between the C(3) methylene resonances at $\delta = 2.61$ and 1.70 ppm as well as between the *gem*-dimethyl resonances at $\delta = 0.61$ and 0.93 ppm. These observations are readily accommodated by intra- or intermolecular interfacial exchange of the coordinated alkene ("alkene flipping")[2f] and, as observed previously for complexes of type **C**,[2f] an intramolecular process seems more likely.[8]

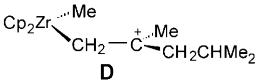
Very similar results were obtained with 2,4-dimethyl-1-heptene, and, since this ligand already contains a chiral center, the resulting alkene complex consisted of unequal amounts of diastereomers.[9] Thus the terminal methylene resonances were observed as two pairs of overlapping AB quartets at $\delta \approx 3.86$ and 3.96 ppm (Figure S9 in the Supporting Information), which coalesced to a single AB quartet at approximately 203 K as a result of interfacial exchange.[8] In an HMBC experiment, the ^{13}C chemical shift of C(2) was found to be $\delta = 204.3$ ppm, comparable with that of **II** and implying a very similar mode of bonding to the zirconium center.

While unsymmetrical bonding of 1-alkenes seems to be the norm for Cp_2Zr^{IV} alkene complexes,[2] the calculated difference between the Zr–C(1) and Zr–C(2) separations of **II** (0.75 Å) is much greater than the differences observed crystallographically for **A** and similar complexes[2a] as well as that determined computationally for the isoelectronic species [$Cp_2Zr(H)(CH_2{=}CMe_2)$]$^+$ (**VI**: Zr–C(1) 2.55 Å, Zr–C(2) 3.01 Å; difference 0.46 Å).[7c] We have replicated the latter result, and we have also found for [$Cp_2Zr(Me)(CH_2{=}CMe_2)$]$^+$ (**VII**) that Zr–C(1) = 2.67 Å and Zr–C(2) = 3.23 Å; difference 0.56 Å. Thus the Zr–C bond lengths *and* the degree of asymmetry increase in the order **VI** < **VII** < **II**, and both structural parameters seem to be strongly affected by steric as well as electronic factors.

Deshielding of the ^{13}C chemical shift of C(2) on coordination of **I** is also significantly greater than that observed for most complexes of types **A**–**C**,[2] consistent with much greater polarization of the more asymmetric C=C bond in **I**.[10] We also note that the large increase in the spin–spin coupling constant of the terminal methylene hydrogen atoms of **I** on coordination stands in stark contrast to alkene complexes of types **A**–**C**, for which little or no change in H–H coupling constants is observed on coordination.[2]

Interestingly, when the sample temperature of the NOESY experiment shown in Figure S3a (in the Supporting Information) was raised from 193 to 213 and then to 223 K, the cross peaks between the terminal methylene resonances of **I** changed sign (Figure S3b,c in the Supporting Information), indicating the onset of intramolecular exchange between the two hydrogen atoms. A ROESY experiment (Figure S10 in the Supporting Information) verified this interesting conclusion, which implies rotation about the C=C bond of **I**. Mechanistically, this process could involve intermolecular exchange, with concomitant magnetization transfer, of **I** with a species containing **I** and in which rotation about the C=C bond is facile. In view of the observed intermolecular exchange of free **I** with **II** but with no other species,[11] we conclude that rotation occurs about the C=C bond of **II**, although an attempt to demonstrate exchange directly failed. The exchange is too slow to be measured at 183 K, where the two resonances are distinct, and the resonances converge (not coalesce; see Figure S12 in the Supporting Information) at higher temperatures, possibly because of rotation of the coordinated alkene to the slightly higher energy conformer in which the methyl ligand eclipses C(1) of coordinated **I** (see above).

In contrast, rotation about the C=C bond does not occur in complexes of type **C**,[2e,f] and it seems that extreme coordination asymmetry and the related polarization of the C=C bond[2e,f,3a] are indicative of increased importance of a near η^1 resonance structure **D**. The latter finds precedent as an intermediate in the carbocationic polymerization of similar alkenes, such as isobutylene,[3a,4a] while near η^1 alkene coordination coupled with facile rotation about the C(1)–C(2) bond has been reported for the cationic complexes [$CpFe(CO)_2(CH_2CHX)$]$^+$, where X is a π-donor substituent (NR_2, OR) that can stabilize a positive charge on C(2).[12]



D

Experimental Section

CD_2Cl_2 was dried over CaH_2 and stored over molecular sieves, **I** and 2,4-dimethyl-heptene (CHEM SAMPCO) were dried over molecular sieves, [Ph_3C][$B(C_6F_5)_4$] (Asahi Glass Co) was used as received, and Cp_2ZrMe_2[13] was prepared as in the literature. All NMR spectroscopy experiments were carried out on a Bruker Avance 600 spectrometer.

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[5] a) M. Bochmann, S. J. Lancaster, *Angew. Chem.* **1994**, *106*, 1715; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1634. b) A representative spectrum is shown in Figure S1 in the Supporting Information. Literature precedents and NOESY experiments resulted in assignments of the resonances of [Cp$_2$ZrMe][B(C$_6$F$_5$)$_4$] (**III**)[5a] at $\delta = 0.65$ (Me) and 6.32 ppm (Cp) and of [Cp$_2$Zr(Me)(μ-Me)Zr(Me)Cp$_2$][B(C$_6$F$_5$)$_4$][5a] (**IV**) at $\delta = 0.195$ (ZrMe), -0.84 (μ-Me), and 6.26 (Cp). c) Also observed here but not in reference [5a] were weak, deshielded resonances at $\delta = 0.83$ (ZrMe) and 6.58 ppm (Cp), which belong (NOE) to the same molecule and are tentatively assigned to [Cp$_2$ZrMe(CD$_2$Cl$_2$)][B(C$_6$F$_5$)$_4$] (**V**).

[6] a) The chemical shifts of **I** are $\delta = 4.61$ (H *cis* to 2-Me), 4.55 (H *trans* to 2-Me), 1.60 (2-Me), 1.81 (CH$_2$), 1.68 (CH), 0.74 ppm (*gem*-dimethyl protons); b) R. N. Young, *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *12*, 261.

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[8] We carried out careful analyses of the relative intensities of the diagonal and cross peaks in the NOESY experiment (193 K) shown in part in Figures S3–S6 (in the Supporting Information), in which intermolecular exchange between free and coordinated **I** occurs simultaneously with intramolecular exchange of the diastereotopic pairs; note that **I** and **II** are present in a molar ratio of approximately 1:2. In general we found that the intensities of the cross peaks for intermolecular exchange were only about 7 % of the intensities of the diagonals, while, for the intramolecular exchanges, the intensities of the cross peaks were about 65 % of the intensities of the diagonals. Thus, qualitatively at least, intramolecular exchange appears to provide the better rationale for the observed interfacial exchange of coordinated **I**. The same conclusion was reached in reference [2f], where a very useful discussion of possible mechanisms can be found.

[9] In addition to the terminal methylene resonances, ^{1}H resonances were observed at $\delta = 6.43$ (Cp), 1.65 and 2.63 (doublets, $J = 10.6$ Hz, H(3)), 1.80 and 2.56 (doublets, $J = 10.4$ Hz, H(3) of the other diastereomer), 1.72 (H(4)), 2.14 (Me on C(2)), 0.58, 0.89 (doublets, Me on C(4)), and 0.51 ppm (ZrMe). Unfortunately, not all resonances of the 2,4-dimethyl-1-heptene complex could be assigned fully because of overlap with resonances of the free alkene.

[10] A referee notes that a complex of type **C** (R = CH$_2$SiMe$_3$) exhibits a $\Delta\delta \approx 50$ ppm for C(2),[2f] implying that the β-Si atom also stabilizes a partial positive charge on C(2).

[11] No exchange cross peaks were observed between the terminal methylene hydrogen atoms of **I** and any species other than **II**. Furthermore, a control experiment (Figure S11 in the Supporting Information) showed that rotation about the C=C bond of **I** is not induced by free trityl ion.

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