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Direct Observation of a Nonchelated Metal−Alkyl−Alkene Complex and Measurement of the Rate of Alkyl Migration to a Coordinated Alkene

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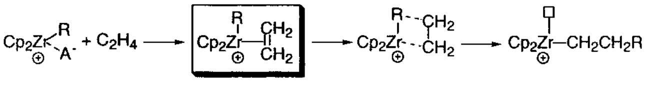
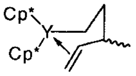
Since the discovery of homogeneous Ziegler−Natta catalysts in 1957,[1] group 3- and 4-based-catalysts have generated a great deal of interest because of their relevance to industrial alkene polymerization.[2] A molecular species featuring complexation of an alkene monomer to a d^0 metal−alkyl complex has been proposed as a key intermediate in metallocene-catalyzed alkene polymerization (Scheme 1).[3] Due to lack of π-back-bonding and rapid insertion of the alkene monomer into the growing polymer chain, the intermediate d^0 metal−alkyl−alkene complexes are highly unstable and have never been observed during catalysis.

Scheme 1

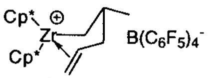


$A^- = B(C_6F_5)_4^-$, $MeB(C_6F_5)_3^-$

Recently, our group and others have reported model compounds related to this proposed intermediate.[4−7] These complexes are stabilized by chelation which has enabled observation and study of d^0 metal−alkyl−alkene complexes. We have reported neutral yttrium−alkyl−alkene complexes such as **1**,[4] and cationic zirconium−alkyl−alkene complexes such as **2**.[5] Similarly, Jordan has reported zirconium−alkoxy−alkene complexes such as **3**[6] and Royo has reported the zirconium−alkyl−alkene complex **4** where the chelating alkene is tethered to a cyclopentadienyl ring.[7]



1



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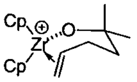

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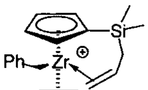

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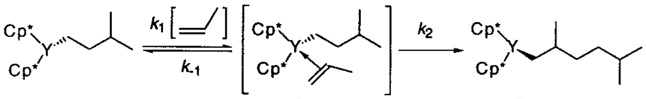
Scheme 2



5 **6** **7**

Our studies of chelated yttrium−alkyl−alkene complexes allowed measurement of $\Delta H° = -4.6$ kcal mol^{-1} for binding of a monosubstituted alkene to yttrium.[4e] This suggested that an yttrium−propene complex might be observable below −130 °C. Here we report the observation of the first nonchelated d^0 metal−alkyl−propene complex and the rate of propene insertion into the metal−alkyl bond.[8]

The reaction of $[Cp^*_2YH]_2$[9] ($Cp^* = C_5(CH_3)_5$) with 3-methyl-1-butene in a 1:1 mixture of methylcyclohexane-d_{14} and pentane-d_{12} produced $Cp^*_2YCH_2CH_2CH(CH_3)_2$ (**5**) in quantitative yield within minutes at −78 °C as determined by ^{1}H NMR spectroscopy using $CH_2(SiMe_3)_2$ as an internal standard. Complex **5** does not insert a second equivalent of 3-methyl-1-butene up to −30 °C at which point decomposition begins.

Propene (0.015 to 0.4 M) was vacuum transferred into the NMR tube containing the solution of **5** (0.025 to 0.04 M) and residual 3-methyl-1-butene (Scheme 2). The solution was shaken at −130 °C and then monitored by ^{1}H NMR spectroscopy between −100 and −150 °C to determine whether propene coordinated to **5**. Upon lowering the temperature from −100 to −150 °C, the resonance of the secondary vinyl hydrogen of propene shifted to higher frequency (from δ 5.72 to 5.96) (Figure 1). The direction of this chemical shift change is the same as that seen for alkene coordination in chelate **1** ($\Delta\delta = +0.68$ ppm). The resonance of the *E*-terminal vinyl hydrogen of propene shifted to lower frequency at lower temperatures (from δ 4.87 to 4.33); a smaller shift to higher frequency is observed in the resonance of the *Z*-terminal vinyl hydrogen (from δ 4.96 to 5.10). Similar shifts have been observed for the *E*- ($\Delta\delta = -0.96$ ppm) and *Z*-protons ($\Delta\delta = +0.44$ ppm) of **1**. These shifts are also consistent with, but smaller than, those observed for cationic zirconium−alkene chelates.[5−7] Excess 3-methyl-1-butene, present from the preparation of **5**, shows only slight shifts/broadening upon cooling, indicating that this more sterically demanding alkene does not complex to **5**. In a control experiment in the absence of yttrium compound **5**, propene showed no temperature dependence of its ^{1}H NMR resonances.[10] We attribute the observed shifts in propene resonances in the presence of **5** to a rapid equilibrium between free and bound propene, such that the proton chemical shifts of propene occur at a population-weighted mean of δ_{free} and δ_{bound}.[11]

1D nOe spectroscopy provides additional evidence for coordination of propene to **5** (Figure 2). In this experiment through-space transfer of excitation is observed from the internal vinyl proton of propene to the methyl protons of the Cp* ligands on yttrium. This result requires that the internal vinyl proton of propene be in close proximity to the Cp* ligands, as expected for an yttrium−propene complex. Due to the relationship between effective correlation time (τ_c) and relaxation processes, rapidly rotating molecules show positive nOes, while slowly tumbling molecules show negative nOes. At −139 °C, free propene shows a positive nOe between its internal vinyl proton and its methyl protons, but in the presence of **5** the nOe is negative, implying

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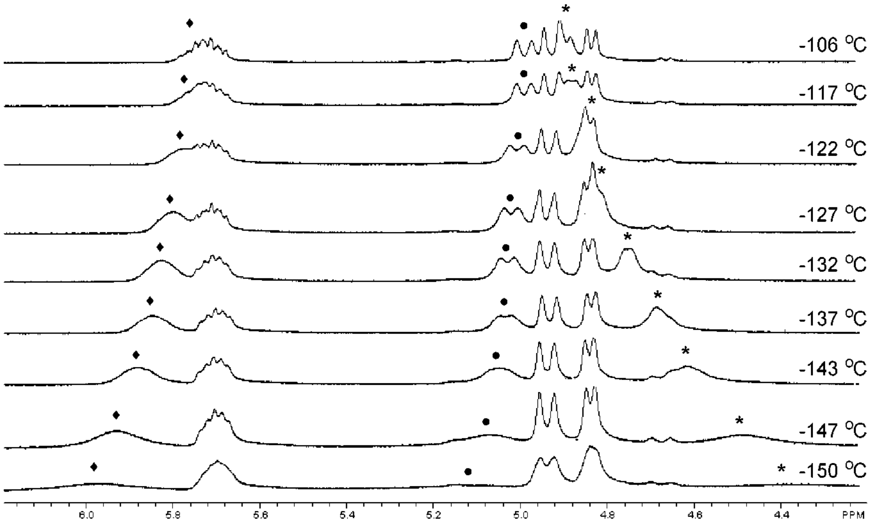

Figure 1. Chemical shifts of 0.020 M propene in the presence of 0.042 M **5**. ◆ = H_{int}, ● = H_Z, * = H_E. Unmarked resonances are due to residual 3-methyl-1-butene.

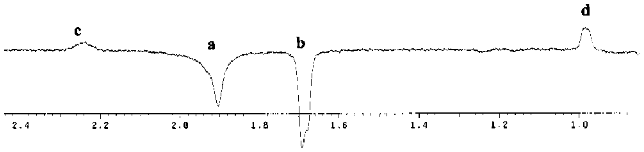

Figure 2. nOe spectrum showing excitation transfer from the secondary vinyl proton of propene to its methyl group (b) and the Cp* of **5** (a). Resonances c and d are a result of excitation transfer from the secondary vinyl proton of 3-methyl-1-butene to its CH (c) and CH_3 (d) groups.

slower tumbling in solution as expected for propene complex **6**. Such behavior is typical of small molecules in rapid equilibrium with a complexed form.[12]

Further evidence for propene coordination comes from ^{13}C NMR spectroscopy.[10] When propene concentrations (<0.02 M) are such that a significant percentage of the propene is coordinated to yttrium, the alkene carbon resonances are severely broadened and could not be located. In contrast, the ^{13}C resonances of free 3-methyl-1-butene remain sharp.

On the basis of model chelates such as **1**, we know that the separation between the *E*- and *Z*-protons ($\Delta\delta = \delta H_Z - \delta H_E$) of alkenes increases from 0.06(2) ppm in the free alkene to 1.46(4) upon alkene binding.[4] Assuming the same 1.40 ppm chemical shift difference for bound versus free propene, the percentage of propene bound was estimated from the observed chemical shifts. Using these percentages, equilibrium constants for propene complexation at various temperatures were determined. A van't Hoff plot yields values of $\Delta H° = -4.6$ kcal mol^{-1} and $\Delta S° = -31$ eu;[10] the average of five experiments at different alkene and yttrium concentrations gives $\Delta H° = -4.5(3)$ kcal mol^{-1} and $\Delta S° = -30(2)$ eu. The value of $\Delta H°$ is very similar to that measured for yttrium–alkene chelates.

The observed broadening of the alkene ^{1}H and ^{13}C resonances occurs because the fast exchange between free and bound propene slows at low temperature. At low temperature, the equilibrium is characterized as near-fast exchange ($k_{\mathrm{exch}} < \pi(\delta\nu)_2$), where line shape is affected by the lifetime of **5** and **6**.[11,12] From analysis of the observed line-broadening of the secondary vinyl proton of propene, we estimate that the rate constant for decomplexation (k_{-1}) is approximately 2.1×10^{-4} s^{-1} at −140 °C ($\Delta G^{\ddagger} = 4.9$ kcal mol^{-1}). Using all line broadening data from −140 to −150 °C gives $\Delta G^{\ddagger} \approx 5.1(2)$ kcal mol^{-1} for decomplexation. Taken together with $\Delta G = -0.5$ kcal mol^{-1} for complexation at −140 °C, this gives $\Delta G^{\ddagger} \approx 4.6(2)$ kcal mol^{-1} for complexation. Unfortunately even at −150 °C, the exchange process is too fast to allow observation of separate resonances for complexed and uncomplexed propene.

Observation of a d^0 metal–alkyl–alkene complex provided the opportunity to monitor propene insertion into a metal–alkyl bond.[13] At −100 °C, **5** reacted with 0.3 M propene over several hours to give mono-insertion product **7**. Reaction of **7** with propene is slowed by the steric influence of the β-methyl substitution on the extended chain. Under pseudo-first-order conditions of excess propene, the rate of propene insertion is first-order in **5** as shown by the linear correlation of ln[**5**] versus time. The linear correlation of k_{obs} versus [propene] shows that the insertion is also first-order in propene (eq 1). The second-order rate constant, *k*, for propene insertion is $1.5(2) \times 10^{-3}$ M^{-1} s^{-1}. Extrapolation gives $K_{\mathrm{eq}} = 0.13(2)$ M^{-1} at −100 °C, so that the rate constant (k_2) for insertion of the yttrium–alkyl into coordinated propene is $1.1(2) \times 10^{-2}$ s^{-1} [$\Delta G^{\ddagger}$ is 11.5(2) kcal mol^{-1}]. Comparison with the estimate for $\Delta G^{\ddagger}$ of propene dissociation (5.1 kcal mol^{-1}) shows that dissociation is much faster than migratory insertion. This establishes that **5** and **6** are in rapid equilibrium prior to insertion.

$$\frac{-\mathrm{d}[\mathbf{5}]}{\mathrm{d}t} = K_{\mathrm{eq}}k_2[\mathbf{5}][\mathrm{C_3H_6}] = k[\mathbf{5}][\mathrm{C_3H_6}] = k_{\mathrm{obs}}[\mathbf{5}] \qquad (1)$$

Although d^0 metal–alkyl–alkene complexes were proposed as polymerization intermediates in the early 1960s, group 3 and 4 d^0 metal–alkene interactions have previously been observed only in systems stabilized by chelation. Observation of a nonchelated yttrium–alkyl–alkene complex has allowed us to measure and compare the rate of propene complexation/decomplexation with the rate of migration of the yttrium–alkyl to coordinated propene; these processes are of great importance to industrial polyolefin manufacture using metallocene catalysts.

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Supporting Information Available: Spectroscopic data, experimental procedures, kinetic and thermodynamic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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