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Synthesis and Spectroscopic Characterization of the d^0 Transition Metal−Alkyl−Alkene Complex $Cp^*_2YCH_2CH_2C(CH_3)_2CH{=}CH_2$

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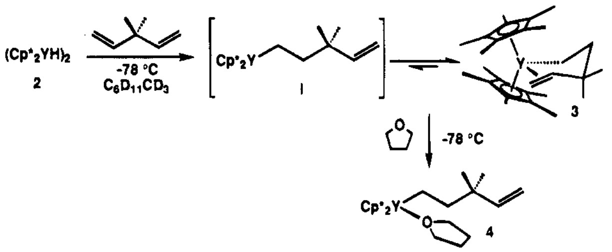
Coordination of an alkene to an electron-deficient metal−alkyl complex has been proposed as a requisite chain propagation step in Ziegler−Natta alkene polymerization.[1,2] Calculations indicate that subsequent alkyl migration to the coordinated alkene via a concerted four-center transition state to generate a growing polymer chain has a very low activation barrier.[3] The d^0 M(alkyl)(alkene) intermediates of group 3, group 4, and lanthanide metals are particularly unstable due to the lack of d−π^* back-bonding to the coordinated alkene.[4] There are only a few examples of d^0 transition metal−alkene complexes, and none possess an additional metal−alkyl bond.[5,6] Jordan recently reported the X-ray crystal structure of the zirconium(IV) pent-4-enyloxo chelate complex $[Cp_2ZrOC(CH_3)_2CH_2CH_2CH{=}CH_2]^+$ $[MeB(C_6F_5)_3]^-$ (**1**), which was designed to model a Cp_2Zr-(alkyl)(alkene)$^+$ intermediate.[6] Here we report the synthesis and spectroscopic characterization of the first d^0 transition metal−alkyl−alkene complex.

We have investigated the reaction of yttrium hydride dimer $(Cp^*_2YH)_2$ (**2**)[7,8] with 3,3-dimethyl-1,4-pentadiene in an effort to generate a stable d^0 transition metal−alkyl−alkene complex. Yttrium was chosen because group 3 metallocene−alkyl−alkene complexes are neutral and because ^{89}Y (100% abundance) is a spin $^1/_2$ nucleus.[9] The 4-pentenyl side chain was chosen to favor alkene complexation by the chelation effect, and the *gem*-dimethyl group was incorporated into the pentenyl backbone to promote ring-forming chelation.[10] Intramolecular alkene insertion is thermodynamically disfavored by the 26 kcal mol^{-1} strain in the resulting methylcyclobutyl complex.

Yttrium hydride **2** reacted rapidly with 3,3-dimethyl-1,4-pentadiene in methylcyclohexane-d_{14} at −78 °C to form a bright yellow solution of the d^0 yttrium(III) 3,3-dimethylpentenyl chelate complex $Cp^*_2YCH_2CH_2C(CH_3)_2CH{=}CH_2$ (**3**) in quantitative yield (^1H NMR spectroscopy, $CH_2(SiMe_3)_2$ internal standard) (Scheme 1). **3** is thermally unstable above −50 ° C and was characterized by ^1H and ^{13}C NMR spectroscopy at −100 °C.[11] In the ^1H NMR spectrum of **3**, methylene resonances at δ −0.44 (YCH_2) and δ 1.84 (YCH_2CH_2) confirm the addition of yttrium hydride to one of the diene double bonds. The substantial differences between the vinyl hydrogen chemical shifts in tethered metal−alkene complex **3** and in the starting diene provide evidence for coordination of the pendant alkene to the d^0 yttrium center. The chemical shift difference ($\Delta\delta$) between the terminal vinyl hydrogens of **3** is 1.38 ppm (δ 3.76 and 5.14) but is only 0.05 ppm (δ 4.87 and 4.92) in the starting diene. The secondary vinyl hydrogen of **3** (δ 6.78) is shifted to substantially higher frequency than in the starting diene (δ 5.74).

Scheme 1



In the ^{13}C NMR spectrum of **3**, a methylene resonance at δ 33.7 (d, J_{YC} = 45.8 Hz, YCH_2) confirms the formation of an alkyl yttrium complex. The 15 ppm shift to higher frequency of the resonance of the internal alkene carbon atom of **3** (δ 161.1, d, J_{CH} = 151 ± 2 Hz) relative to that in 3,3-dimethyl-1,4-pentadiene (δ 146.1, d, J_{CH} = 151 Hz) provides evidence for alkene coordination. The chemical shift of the terminal alkene carbon of **3** (δ 110.5, t, J_{CH} = 154 ± 2 Hz) is similar to that of the starting diene (δ 111.1, J_{CH} = 156 Hz). The similarity of the vinyl J_{CH} coupling constants of **3** and the starting diene is inconsistent with an agostic Y−H−C interaction in **3**.

A static chelate structure for **3** would possess diastereotopic Cp* groups and diastereotopic *gem*-methyl groups. Therefore, the observation of resonances for equivalent Cp* and *gem*-methyl groups in both the ^1H and ^{13}C NMR spectra at −100 °C suggests that a fluxional process interconverts the enantiomers of **3**. Dissociation of the chelated alkene to generate intermediate **I** (Scheme 1) followed by recoordination of the opposite face of the alkene is the minimum process needed to interconvert both the *gem*-methyl groups and the Cp* groups. This rapid fluxional process is consistent with the expected weakness of a d^0 metal−alkene interaction.

Addition of THF to **3** at −78 °C in methylcyclohexane-d_{14} led to immediate displacement of the coordinated alkene and quantitative formation of a colorless solution of the thermally unstable 1:1 yttrium(III) pentenyl THF adduct $Cp^*_2YCH_2CH_2C(CH_3)_2CH{=}CH_2(THF)$ (**4**),[12] which serves as a model for a pentenyl yttrium complex without a coordinated alkene (Scheme 1). The negligible chemical shift difference ($\Delta\delta$) between the terminal vinyl hydrogens of **4** (δ 4.75, br m, $=CH_2$) is very different from that of the complexed alkene of **3** ($\Delta\delta$ = 1.38 ppm) and similar to that observed for the starting diene ($\Delta\delta$ = 0.05 ppm). The ^1H NMR chemical shift of the secondary

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(11) **3:** ^1H NMR (500 MHz, $C_6D_{11}CD_3$, −100 °C) δ −0.44 (br s, YCH_2), 1.03 (br s, CH_3), 1.82 (br s, YCH_2CH_2), 1.93 (br s, C_5Me_5), 3.76 (br d, J_{cis} = 10.7 Hz, $=CHH$), 5.14 (br d, J_{trans} = 17.8 Hz, $=CHH$), 6.78 (br dd, J = 17.8, 10.7 Hz, $CH=$); $^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_{11}CD_3$, −100 °C) δ 11.6 (s, C_5Me_5), 14.6 (s, YCH_2CH_2), 33.7 (d, J_{YC} = 45.8 Hz, YCH_2), 41.2 (s, CMe_2), 43.1 (s, CH_3), 110.5 (s, $=CH_2$), 116.3 (s, C_5Me_5), 161.1 (s, $CH=$).

(12) **4:** ^1H NMR (500 MHz, $C_6D_{11}CD_3$, −100 °C) δ −0.74 (br s, YCH_2), 0.90 (br s, CH_3), 1.35 (br m, β-THF), 1.88 (br s, C_5Me_5), 3.64 (br m, α-THF), 4.75 (br m, $=CH_2$), 5.78 (br dd, J = 17.8, 10.9 Hz, $CH=$), resonance for $YCH_2CH_2CH_2$ obscured by resonance for Cp* ligands; $^{13}C\{^1H\}$ NMR (126 MHz, $C_6D_{11}CD_3$, −100 °C) δ 11.6 (s, C_5Me_5), 14.7 (s, YCH_2CH_2), 25.7 (s, β-THF), 33.7 (d, J_{YC} = 50.3 Hz, YCH_2), 39.6 (s, CMe_2), 43.5 (s, CH_3), 67.7 (s, α-THF), 108.4 (s, $=CH_2$), 115.2 (s, C_5Me_5), 150.7 (s, $CH=$).

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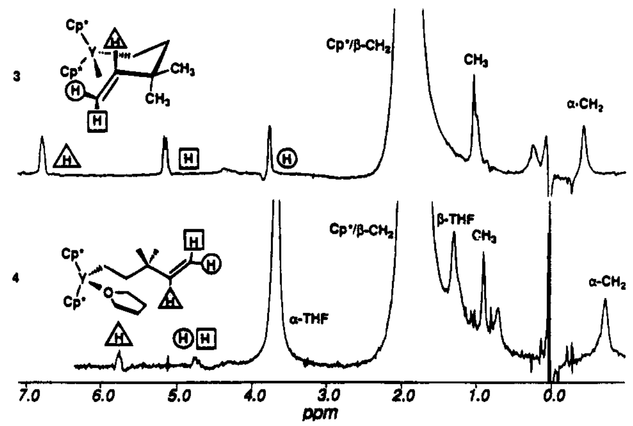
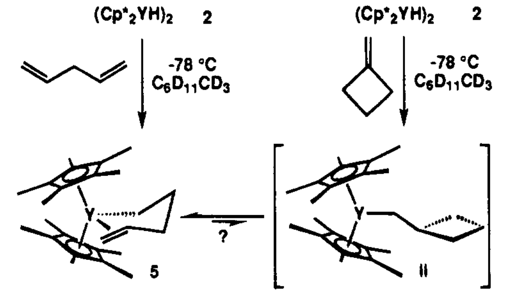


Figure 1. ^{1}H NOESY trace through **3** and **4** in $C_6D_{11}CD_3$ at -100 °C ($\tau_m = 0.050$ s). The spectra are normalized to combined Cp^*/β-CH$_2$ intensities.

vinyl hydrogen of **4** (δ 5.78) and the ^{13}C NMR chemical shifts of the alkene carbons (δ 108.4, =CH$_2$; 150.7, CH=) of **4** are also similar to those of 3,3-dimethyl-1,4-pentadiene and very different from those of **3**.

^{1}H NOESY data support coordination of the alkene to the metal in pentenyl chelate **3**. The chelate ring structure of **3** forces all vinyl hydrogens into the proximity of the methyl groups of the Cp* rings. Hence, we expect NOESY cross peaks between the Cp* resonance and all the vinyl resonances. In contrast, the nonchelate structure of THF adduct **4** should yield weaker Cp* $\leftrightarrow$ vinyl cross peaks, with particularly weak cross peaks to the terminal vinyl hydrogens. Figure 1 presents traces through 2D NOESY spectra at the overlapping Cp^*/β-CH$_2$ resonances in **3** and **4**.[13] The magnitude and the distribution of Cp^*/β-CH$_2$ $\leftrightarrow$ HC=CH$_2$ NOE intensities reveal qualitative information about the structures of **3** and **4**. All of the vinyl hydrogens in **3** show sizable NOEs of nearly equal intensities. The similar intensities imply that all the vinyl hydrogens are roughly equidistant from the Cp^*/β-CH$_2$ protons, as expected for a coordinated alkene. In contrast, the spectrum of THF adduct **4** shows a strong Cp^*/β-CH$_2$ $\leftrightarrow$ α-THF NOE but weak Cp^*/β-CH$_2$ $\leftrightarrow$ HC=CH$_2$ NOEs. As expected, the Cp^*/β-CH$_2$ $\leftrightarrow$ *H*C=CH$_2$ cross peak is larger than the peak to the two terminal vinyl hydrogens. In further support of these interpretations, the spectra of **3** and **4** exhibit similar cross peak intensities correlating the Cp^*/β-CH$_2$ protons to the *gem*-dimethyl and α-CH$_2$ protons.

Scheme 2



Yttrium hydride **2** also reacts with 1,4-pentadiene at -78 °C to form a bright yellow solution of the thermally unstable pentenyl chelate complex $Cp^*_2YCH_2CH_2CH_2CH{=}CH_2$ (**5**), which was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy at -100 °C (Scheme 2).[14] Formation of **5** demonstrates that the *gem*-dimethyl group on the pentenyl backbone is not required to form a stable alkene chelate. Evidence for alkene coordination is seen in the large difference in chemical shift of the =CH$_2$ protons ($\Delta\delta = 1.46$ ppm) and in the shift to higher frequency of the CH= proton (δ 6.58). In the ^{13}C NMR spectrum of **5**, the resonance of the coordinated =CH$_2$ carbon (δ 112.9) shifts 3 ppm to lower frequency than in 1,4-pentadiene and the CH= resonance (δ 158.1) shifts 22 ppm to higher frequency.

Pentenyl chelate **5** also was generated from the reaction of yttrium hydride **2** and methylenecyclobutane, presumably via the methylcyclobutyl intermediate **II** (Scheme 2). Formation of **5** from **2** and methylenecyclobutane demonstrates that ring opening via β-alkyl elimination is facile and that the pentenyl chelate complex is favored over the methylcyclobutyl derivative. The interconversion of methylcyclobutyl and pentenyl ligands has been observed in several similar systems.[15-18]

Nonlocal DFT calculations of $H_2SiCp_2Zr(CH_3)(CH_2{=}CH_2)^+$ indicate that ethylene is strongly polarized and asymmetrically bonded to the d^0 metal center.[3b] Jordan's X-ray structure of zirconium(IV) pentenyloxo complex **1**[6] showed asymmetric bonding of the alkene ligand to Zr with a bond length difference of 0.21 Å (2.68 and 2.89 Å). The similarity of the ^{1}H and ^{13}C NMR chemical shifts of the complexed alkenes of **3** and **5** with those reported by Jordan for **1** suggests that the complexed alkenes of the chelate complexes **3** and **5** also are bound asymmetrically to the d^0 yttrium center and that the internal alkene carbon is positively polarized.

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Supporting Information Available: Experimental procedures for **2**–**5** and ^{1}H NMR and ^{1}H NOESY spectra of **3** and **4** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microflim version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[13] Both **3** and **4** exhibit negative NOEs at 500 MHZ in methylcyclohexane at -100 °C, consistent with slow molecular tumbling. A short mixing time (50 ms) was used to minimize the effects of spin diffusion on the NOESY intensities.

[14] See supporting information for spectral characterization of **5**.

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