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Isolation and Characterization of the Ethylene-Bridged Zirconocene Complex $(Cp_2ZrMe)_2(CH_2CH_2)$

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Summary: An ethylene-bridged zirconocene complex, $(Cp_2ZrMe)_2(CH_2CH_2)$, was prepared by the reaction of Cp_2ZrMe_2 with a zirconocene–ethylene complex, $[Cp_2ZrEt(CH_2{=}CH_2)]MgBr$, and the structure of this complex was determined by a single-crystal X-ray diffraction study. The structure of this complex showed one methyl group on each zirconium and an ethylene ligand simultaneously coordinating to the two zirconocene moieties.

Olefin polymerization reactions by homogeneous Ziegler–Natta catalysts have been studied for over 25 years.[2] Recently, zirconocene complexes have attracted much attention in this area[2] and some intermediate model complexes have been prepared and characterized.[3–10] However, the coordination or interaction of olefins such as ethylene with zirconocene species has remained to be studied.

Recently we have reported the preparation and stoichiometric or catalytic reactions of zirconocene–ethylene complexes.[11] During the course of our study on the reaction of a zirconocene–ethylene complex with Cp_2ZrMe_2, we isolated a novel zirconocene complex having simultaneously both methyl and bridging ethylene ligands. We now report the isolation and characterization of $(Cp_2ZrMe)_2(CH_2CH_2)$.[12]

First we attempted the reaction of ethylene precoordinated to Zr, i.e., $Cp_2Zr(CH_2{=}CH_2)(PMe_3)$,[11a,13] with the cationic complex $[Cp_2ZrMe(THF)][BPh_4]$.[3b] Unfortunately, the desired products were not detected. On the other hand, the reaction of $[Cp_2ZrEt(CH_2{=}CH_2)]MgBr$ (**1**)[11e] with Cp_2ZrMe_2 (**2**) afforded $(Cp_2ZrMe)_2(CH_2CH_2)$ (**3**) in 43% yield. Since the ethylene complex $[Cp_2Zr(CH_2{=}CH_2)]$ can be prepared from **2** and EtMgBr,[11c] the product **3** could be alternatively prepared by the reaction of **2** with about 0.8 equiv of EtMgBr. Golden yellow crystals of **3** were obtained in 37% yield when diethyl ether was slowly added to the reaction mixture.

$$\underset{\mathbf{1}}{[Cp_2ZrEt(CH_2{=}CH_2)]MgBr} + \underset{\mathbf{2}}{Cp_2ZrMe_2} \rightarrow \underset{\mathbf{3}}{(Cp_2ZrMe)_2(CH_2CH_2)} \quad (1)$$

The novel complex **3** has been characterized by NMR and X-ray crystallographic methods. The crystal structure of **3** is shown in Figure 1.[14] It clearly shows a side-on-bridged μ-η^4-ethylene molecule and one methyl group on each zirconium atom. The C–C bond length of the

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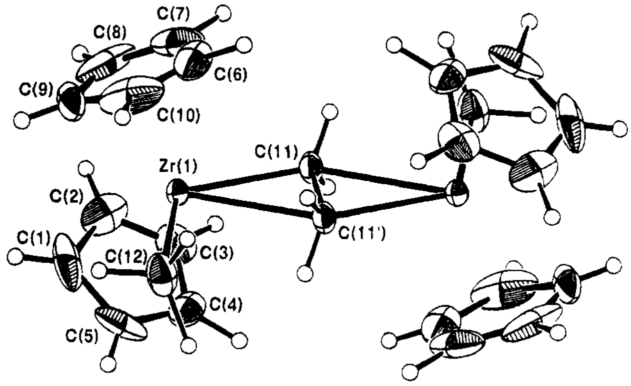


Figure 1. Structure of the complex **3**. Key bond distances (angstroms) and angles (degrees): Zr(1)–C(11), 2.327(6); Zr(1)–C(11′), 2.528(4); Zr(1)–C(12), 2.347(7); C(11)–C(11′), 1.473(7); Zr(1)–C(11)–C(11′), 80.3(3); Zr(1)–C(11′)–C(11), 64.6(3); C(12)–Zr(1)–C(11′), 79.6(2); C(11)–Zr(1)–C(11′), 35.1(2).

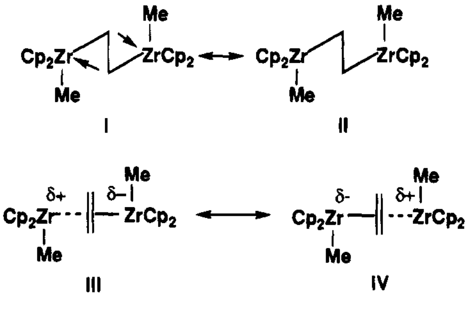
ethylene ligand is 1.473(7) Å. There have been a few examples reported for a side-on-bridged ethylene molecule between two zirconium atoms, i.e., $Zr_2X_6(PEt_3)_4(CH_2CH_2)$ (X = Cl, Br)[17] and $[Cp_2Zr(Et_3AlCl)]_2(CH_2CH_2)$.[16] The C–C bond of ethylene in **3** is shorter than those in $Zr_2X_6(PEt_3)_4(CH_2CH_2)$ (1.69(3) Å, X = Cl; 1.56(3) Å, X = Br)[15] and $[Cp_2Zr(Et_3AlCl)]_2(CH_2CH_2)$ (1.55 Å).[18] It is comparable to the corresponding C–C bond length of a mononuclear ethylene complex, $Cp_2Zr(CH_2CH_2)(PMe_3)$ (1.486(8) Å).[13] The two Zr–ethylene carbon bond distances are different (2.317(6) Å, Zr(1)–C(11); 2.528(4) Å, Zr(1)–C(11′)). The Zr–CH$_3$ bond distance is 2.347(7) Å, which is 0.09 and 0.07 Å longer than the corresponding distances in the cationic complex $[Cp_2ZrMe(THF)][BPh_4]$[3b] and in the neutral complex Cp_2ZrMe_2,[17] respectively.

The reaction of **1** and **2** probably affords **4** as an intermediate, even though **4** could not be detected. Transmetalation of dialkylzirconocene with alkyl Grignard reagents proceeds easily.[11c] Therefore, **4** can be converted into **3** by transmetalation with MeMgBr formed *in situ*. Since **3** is relatively insoluble in the usual organic solvents such as THF and toluene, it precipitated out as yellow crystals from the reaction mixture. An alternative mechanism involving a transmetalation reaction which initially gives $Cp_2ZrMeEt$ and $Cp_2ZrMe(CH_2{=}CH_2)MgBr$ cannot be ruled out. However, the methyl group in $Cp_2ZrMeEt$ easily abstracts a hydrogen from the ethyl group to become a methane molecule. Therefore, this alternative mechanism is unlikely.

$$\underset{\mathbf{4}}{(Cp_2ZrMe)(CH_2CH_2)(EtZrCp_2)} + MeMgBr \rightarrow \underset{\mathbf{3}}{(Cp_2ZrMe)_2(CH_2CH_2)} \quad (2)$$

The ^1H NMR spectrum of **3** in $CDCl_3$ showed the methyl proton signal as a singlet at −0.34 ppm, a broad signal for the two methylenes of the ethylene moiety at −0.49 ppm, and the Cp signal at 5.65 ppm. The ^{13}C NMR spectrum in C_6D_6–THF showed three signals at 13.23, 11.57, and 106.58 ppm assignable to the Me, ethylene, and Cp carbons, respectively. These Me and methylene signals appeared upfield relative to the usual positions for dialkylzirconocenes, e.g. $Cp_2ZrMeEt$, which shows resonances at 44.11 and 30.12 ppm assigned to CH_2–Zr and CH_3–Zr, respectively.[18] The pentacoordinate ethylene carbons[19] of **3** showed a large C–H coupling constant (J_{C-H} = 146 Hz), which indicates that the bridging ethylene carbons have sp^2 character.[20] The reaction of **3** with 4-octyne is similar to that of $Cp_2Zr(CH_2{=}CH_2)$ or $[Cp_2ZrEt(CH_2{=}CH_2)]MgBr$[11e] with 4-octyne. The reaction afforded (*Z*)-4-ethyl-4-octene in 29% yield after hydrolysis along with the formation of the 4-octyne dimer (*E,E*)-5,6-dipropyl-4,6-decadiene in 29% yield. This reaction did not proceed at room temperature or even at 50 °C. At 80 °C after 3 h these coupling products were obtained after hydrolysis.

Four reasonable structures for **3** are I–IV. The data presented herein do not permit us to choose one over the other. A resonance hybrid of these four structures may well be the most reasonable representation of **3**.



Supplementary Material Available: Text describing experimental procedures and tables of crystallographic data, positional and thermal parameters, and selected bond distances and bond angles for **3** (8 pages). Ordering information is given on any current masthead page.

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(14) A prismatic crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm was sealed in the capillary and was used for data collection. Crystallographic data: space group $P2_1/a$, $Z = 2$; $a = 13.040(4)$ Å, $b = 8.105(2)$ Å, $c = 11.300(3)$ Å, $\beta = 115.78(5)°$, $V = 1075.5(5)$ Å^3, $\mu = 9.58$ cm^{-1}. Diffraction data were collected using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å) and $\theta-2\theta$ scan mode (scan range $(1.42 + 0.50 \tan\theta)°$) on a Rigaku AFC-5R diffractometer. Lattice constants were determined from 25 2θ values ($25° < 2\theta < 29°$). Three standard reflections were monitored every 150 reflections and showed no detectable changes during data collection. A total of 3573 independent reflections with $2\theta < 60°$ were collected; 2286 reflections having $|F_o| > 3\sigma(|F_o|)$ were used in the solution and refinement of the structure. The intensities were corrected for Lorentz and polarization effects. The location of zirconium was determined from Patterson functions, and the locations of the remainder of the non-hydrogen atoms were found by the usual Fourier methods. The positions of the methyl and ethylene hydrogen atoms were determined from difference-Fourier maps, and the hydrogen atoms of the cyclopentadienyl rings were calculated or idealized positions. The calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science using the Universal Crystallographic Computation Program System UNICS-III. The final R factor was 0.049 ($R_w = 0.053$).

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