of the alkenyl halides increase in the order I < Br < Cl and the rates of reaction of the haloform are in the sequence I > Br > Cl. Thus, reaction between an aldehyde and chloroform was conducted in THF at 65 °C (runs 4, 8, and 13). When bromoform was employed, a mixture (approximately 1:1) of an alkenyl chloride and the desired bromide was produced (runs 2 and 6). This difficulty was overcome by using a combination of $CrBr_3$ and $LiAlH_4$ (1:0.5 molar ratio) instead of $CrCl_2$ (runs 3, 7, 10, 12, and 15). Although ketones are also converted into the corresponding alkenyl halides, they are less reactive than aldehydes. As shown in Scheme I, selective conversion of an aldehyde into *E*-iodo olefin was performed without affecting the coexisting ketone group.[4]

Because an alkenyl halide adds to an aldehyde with $CrCl_2$ in the presence of a catalytic amount of $NiCl_2$ in DMF,[15] the new method provides a simple route to *E*-allylic alcohols by addition of three components, i.e., two aldehydes and CHI_3 (Scheme II). Iodoform functions as a methine trianion synthon in the reaction sequence.

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(16) Benzaldehyde (0.11 g, 1.0 mmol) was treated at 0 °C with iodoform (0.43 g, 1.1 mmol) and $CrCl_2$ (0.98 g, 8.0 mmol) in THF (15 mL). After the aldehyde was almost consumed (2 h), the THF solvent was replaced by DMF (13 mL). To the mixture was added at 25 °C a solution of nonanal (85 mg, 0.60 mmol) in DMF (2 mL) and then a catalytic amount of $NiCl_2$ (5.2 mg, 0.040 mmol). The resulting dark green mixture was heated at 60 °C for 3 h. The mixture was poured into water and extracted with ether. The combined was poured into water and extracted with ether. The combined extracts were dried (Na_2SO_4) and concentrated. Purification by preparative TLC (hexane–ethyl acetate, 10:1) afforded the desired allylic alcohol **6b** in 62% yield (92 mg, E/Z = >98/<2). The E/Z ratio was determined by NMR.

Ethylene Polymerization by a Cationic Dicyclopentadienylzirconium(IV) Alkyl Complex

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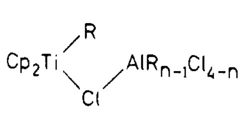
The mechanism of olefin polymerization by soluble Ziegler–Natta catalysts has been the object of continuous study for over 25 years.[1] As early as 1960 Breslow, Long, and Newburg proposed,[2] on the basis of UV–visible spectroscopic and chemical studies, that the active species in Cp_2TiCl_2/AlR_nCl_{3-n} model systems is titanium alkyl complex **1** or a species derived therefrom, possibly cationic complex **2** as recently discussed by Eisch and co-workers.[3] The proposed role of the Al cocatalyst is to alkylate Cp_2TiCl_2 and to activate the resulting Cp_2TiRCl complex by Lewis acid complexation to (as in **1**) or complete removal of (as in **2**) a chloride ligand. Polymerization was proposed to involve coordination of olefin to this activated Ti–R species (presumably with concomitant extrusion of $[AlR_{n-1}Cl_{5-n}]^-$ in the case of **1**) and subsequent insertion into the Ti–R bond (the Cossee–Arlman mechanism[4]). The results of kinetic studies[5] and isotope effect measurements[6] are consistent with this proposed mechanism. Support for the intermediacy of the cationic species **2** or its olefin adduct is provided by (1) the isolation of a cationic complex $Cp_2TiC(SiMe_3){=}C(CH_3)Ph^+$ from the reaction of $(SiMe_3)CCPh$ with $Cp_2TiCl_2/AlMeCl_2$,[3] (2) electrochemical experiments[7] and other observations,[8] (3) the observation that $(C_5Me_5)_2MR$ (M = Lu,[9] Sc[10]) and $[(C_5Me_5)_2MH]_2$ (M = La, Nd, Lu)[11] compounds, which in monomeric form are isoelectronic with **2** (neglecting f electrons), are active ethylene polymerization catalysts, and (4) the direct observation of propylene insertion into the $Lu{-}CH_3$ bond of $(C_5Me_5)_2LuCH_3$.[12] However, cationic Cp_2TiR^+ (R = alkyl) complexes have never been directly observed in Ziegler–Natta model systems nor isolated and characterized. In view of the complexity of these catalytic systems[1] it is important to demonstrate the existence of cationic $Cp_2M(IV)R^+$ complexes and to delineate their chemistry. With these goals in mind we recently reported the synthesis of $Cp_2Zr(R)(L)^+$ (L = labile ligand) complexes.[13] Here we report the X-ray structure of a simple member of this series, $Cp_2Zr(CH_3)(THF)^+$, which polymerizes ethylene in the absence of an Al cocatalyst.



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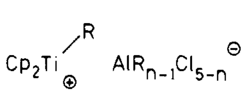

2

$[Cp_2Zr(CH_3)(THF)][BPh_4]$ (**3**) was prepared by reaction of $Cp_2Zr(CH_3)_2$ with 1 equiv of $Ag[BPh_4]$ in CH_3CN followed by recrystallization from THF as previously described.[13] The structure of this compound has been confirmed by X-ray diffraction and is given in Figure 1 along with important molecular parameters.[14] The $Zr{-}CH_3$ and average Zr–Cp distances in **3** are ca. 0.02 and 0.04 Å shorter, respectively, than the corresponding distances in $Cp_2Zr(CH_3)_2$[15] possibly as a result of the greater Lewis acidity of the metal center in the former compound. The THF ligand is oriented nearly perpendicular to the plane defined by the methyl carbon, zirconium, and THF oxygen atoms (dihedral angle C(36)–O–C(39)/(Me–Zr–O = 102.3°). This orientation is more clearly shown in Figure 2. In contrast, in the isoelectronic (neglecting f electrons) lanthanide metal complex,

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(14) Suitable crystals were obtained by slow cooling of a hot THF solution. Crystallographic data: a = 13.707 (12) Å, b = 9.469 (6) Å, c = 24.824 (17) Å, α = 89.97 (5), β = 93.87 (6)°, Γ = 90.00 (6°), v = 3214 (4) Å^3, Z = 4 in space group $P2/c$; R_F = 0.0648, R_{wF} = 0.0646 for 1861 unique reflections ($I \geq 3\sigma(I)$). Disorder of the Cp and THF ligands in two equally populated conformers limited the refinement. The disordered Cp rings were treated as rigid bodies with independent thermal parameters for each C atom and C–H distances fixed at 0.96 Å. The positional and thermal parameters for the two disordered THF molecules were refined independently. No attempt was made to constrain distances and angles (except for H atom positions). It was not possible to refine all thermal parameters anisotropically due to the strong correlation between parameters. In the final refinement the C atoms of the THF molecules except C(36') and C(39') of the conformer not shown were assigned isotropic thermal parameters. Anisotropic thermal parameters were used for all C atoms of the Cp rings except for C(5), C(8), C(9), C(5'), C(9'), and C(10'). Bond distances and bond angles quoted in the text and in Figure 1 are for one of the two conformers; parameters for the other are similar. A low-temperature structure determination of **3** is planned.

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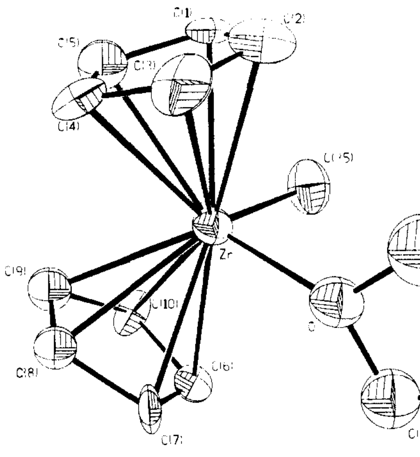

Figure 1. Structure of the Cp$_2$Zr(CH$_3$)(THF)$^+$ cation. The BPh$_4^-$ structure is normal. Important bond lengths (Å) and bond angles (deg) are as follows: Zr–C(35) 2.256 (10); Zr–O 2.122 (14); Zr–Cp(av) 2.487 (41); Zr–CNT(av) 2.174; O–C(36) 1.443 (27); O–C(39) 1.464 (25); CNT–Zr–CNT 129.6; C(35)–Zr–O 97.4 (5); C(39)–O–C(36) 104.5 (16); CNT indicates the centroid of a Cp ring.

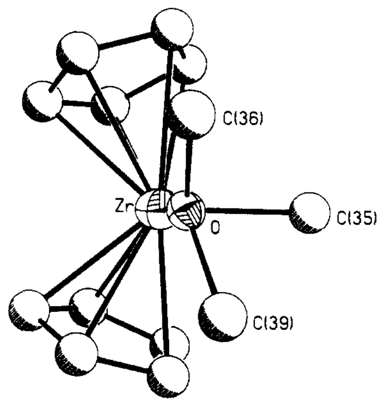

Figure 2. Structure of the Cp$_2$Zr(CH$_3$)(THF)$^+$ cation viewed down the O–Zr bond. The β-carbons of the THF ligand have been removed for clarity.

Cp$_2$Yb(CH$_3$)(THF) (**4**), in which steric effects should dominate directional bonding effects, the THF ligand lies nearly in the Me–Yb–O plane (dihedral angle = 16°).[16] This difference suggests that there is a significant π component in the Zr–O bond of **3**.[17] Consistent with this proposal, after correction for metal size difference,[18] the M–CH$_3$ and average M–Cp distances in **3** are ca. 0.04 Å greater than in **4**, while the M–O distance in **3** in ca. 0.04 Å shorter than in **4**.[19-22]

In CH$_2$Cl$_2$ solvent, cationic complex **3** is an ethylene polymerization catalyst, producing linear polyethylene with a minimum activity of ca. 0.2 g/(mmol of catalyst) min atm at 25 °C and 1–4 atm of ethylene.[23] This activity is relatively low[11] due to the presence of the THF ligand which, though labile, competes with ethylene for the Zr coordination site. Addition of THF or other donor ligands slows the polymerization rate dramatically and in THF or CH$_3$CN solvents no activity is observed.[24]

The observation of ethylene polymerization by **3** supports the original Long–Breslow–Newburg mechanism for olefin polymerization by the soluble Ziegler–Natta systems. It also satisfies a necessary condition of the proposal[3] that cationic complex **2** is the active species; i.e., that Cp$_2$M^{IV}R$^+$ complexes prepared in the absence of Al cocatalysts should polymerize ethylene. Detailed spectroscopic studies of this and related systems are in progress.

Acknowledgment. Support from the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Washington State University Research and Arts Committee is gratefully acknowledged. The X-ray diffraction system was acquired with the aid of NSF grant CHE8408407 and the Boeing Co.

Supplementary Material Available: Summary of X-ray data collection parameters; ORTEP diagram of BPh$_4^-$; stereoview of [Cp$_2$Zr(CH$_3$)(THF)][BPh$_4$]; and tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, H atom coordinates and isotropic thermal parameters (11 pages); tables of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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[19] (a) Other structural comparisons support the proposed Zr–O π-bonding in **3**. The Zr–O bond of **3** is ca. 0.09 Å shorter than the Zr–O bond of Cp$_2$Zr(η^2-CPh$_2$OCH$_3$)Cl[19b] and 0.26 Å shorter (after correction for the difference in O and N radii) than the Zr–N bond of (C$_5$Me$_5$)$_2$Zr(pyridine)(*C,O*-η^2-OCCH$_2$).[19c] (b) Erker, G.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 2251. (c) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068.

[20] The chemical significance of Zr–O π-bonding in **3** is under investigation. For example, it provides an explanation[21] for the observation that **3** undergoes hydrogenolysis slowly (2 days) under conditions (1 atm of H$_2$, room temperature) where the analogous PMe$_3$ complex Cp$_2$Zr(CH$_3$)(PMe$_3$)$^+$ undergoes instantaneous reaction.[22]

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[23] Typical analysis for polymer produced under these conditions: M_w = 18 400; M_z = 33 000; M_w/M_n = 2.58.

[24] The THF-free species Cp$_2$Zr(CH$_3$)$^+$ (**5**) (or its CH$_2$Cl$_2$ solvate) is generated as a transient intermediate in CH$_2$Cl$_2$ solution by reaction of Cp$_2$Zr(CH$_3$)$_2$ with [(C$_5$H$_4$Me)$_2$Fe][BPh$_4$]. In the presence of THF, **5** is trapped as **3**, while in the absence of potential ligands it decomposes principally to Cp$_2$Zr(CH$_3$)Cl. Generation of **5** in the presence of 1 atm of ethylene results in very rapid polymerization. The activity of **5** is considerably greater than that of **3**, confirming the inhibition by THF and indicating that THF is not required for polymerization activity. Activity measurements for **5** and polymer characterization are in progress. Jordan, R. F.; Bajgur, C. S.; Echols, S. F., unpublished results.

The Trimethylphosphine Adduct of the Zirconocene–Benzyne Complex: Synthesis, Reactions, and X-ray Crystal Structure

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Although several η^2-benzyne complexes of transition metals have been reported,[2] there are only two examples of mononuclear benzyne complexes which have been structurally characterized. These are the Cp*TaMe$_2$(benzyne) (Cp* = η^5-C$_5$Me$_5$) complex reported by Schrock[1] and Bennett's 1,2-bis[(dicyclohexylphosphino)ethane]nickel(benzyne) complex.[2] The existence of

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