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Crystal and molecular structure and unusual hydrocarbon solubility properties of $(C_5H_5)_2ZrCl(AlCl_4)$: relevance to Ziegler–Natta polymerization chemistry

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Abstract

$(C_5H_5)_2ZrCl_2$ and $AlCl_3$ react in benzene or toluene to form an adduct that under certain conditions readily dissolves in benzene or toluene to form a binary liquid–liquid phase system ("liquid clathrate"), the denser of which contains the Cp_2Zr moiety and possesses stoichiometry 1/6.3 and 1/5.4 for benzene and toluene, respectively. Cooling of these liquids, or the corresponding dilute hydrocarbon solutions, results in isolation of the 1/1 neutral adduct $(C_5H_5)_2ZrCl(AlCl_4)$ (**4**) which is a model for precursors to cationic Ziegler–Natta polymerization catalysts. **4** crystallizes in the monoclinic space group $C2/c$ with 25.568(9), b 12.710(3), c 9.845(2) Å, β 101.47(2)° and $Z = 8$. An R value of 0.036 was obtained for 1346 observed reflections. The salient feature of the structure is the Zr–Cl–Al bridge. The Zr–Cl bonds are nonequivalent (2.406(3) Å terminal vs. 2.605(2) Å bridging) and the Zr–Cl–Al angle which, at 126.06(7)°, is quite obtuse. The implication of the structure of **4** is therefore that the $AlCl_4^-$ moiety is somewhat loosely held by the Zr atom, thereby facilitating bond rupture to yield cationic Zr^{IV} complexes related to those recently shown to be catalytically active for Ziegler–Natta type polymerizations.

Introduction

Recent interest in homogeneous Ziegler–Natta polymerization chemistry comes from two important developments: (1) an enhancement of the understanding of the mechanism as exemplified by elegant work conducted upon cationic group IV metallocene [1,2] and group VI "half-sandwich" [3] moieties which indicate that

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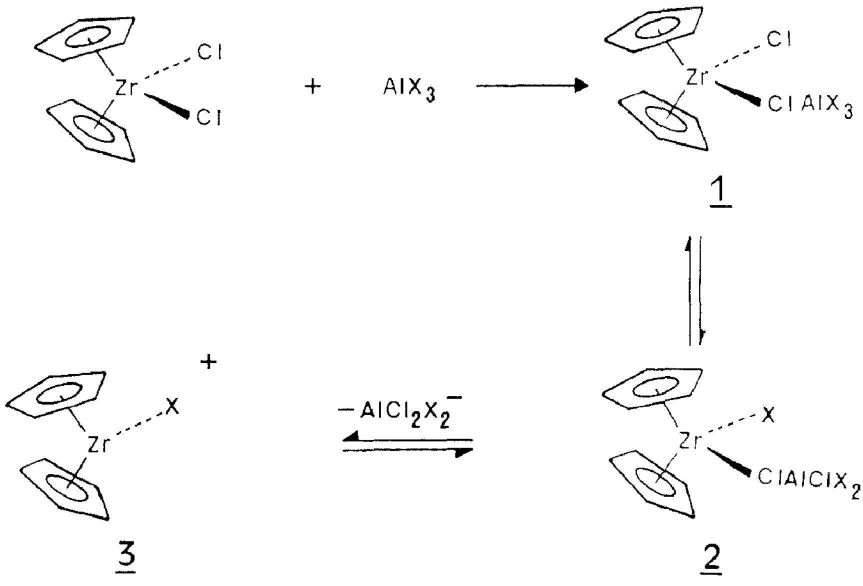

Scheme 1

they are active Lewis acid alkene polymerization catalysts; (2) a realization of the goal of highly stereospecific propylene polymerization via chiral complexes such as Et[Ind]$_2$MCl$_2$ and ethylenebis(4,5,6,7-tetrahydro-1-indenyl)MCl$_2$ (M = Ti [4], Zr [4b,6] or Hf [6]). Scheme 1 is based upon the first of the two developments and upon the well accepted [7] initial step of adduct formation with a Lewis acid cocatalyst (normally AlX$_3$) to give an adduct, **1**. It is clear from this scheme that the nature of intermediates **1** and **2** is crucial to the subsequent formation of the active catalyst, **3**. Unfortunately such adducts, which were originally considered unisolable [8], are still difficult to characterize (see for example the problems encountered with the only other analogue of **1** that has so far been isolated (M = Ti and AlX$_3$ = AlMeCl$_2$ [2,9*])). The situation is further complicated by the unusually high hydrocarbon solubility of many Ziegler–Natta catalysts. In this contribution we report the first structural characterization of a model of a Ziegler–Natta catalyst precursor adduct, $(C_5H_5)_2ZrCl(AlCl_4)$ (**4**) and its intriguing behavior in the presence of benzene and toluene.

Results and discussion

Crystal structure

The structure of **4** was determined by X-ray diffraction and is illustrated in Fig. 1. Final fractional coordinates are given in Table 1 and bond distances and angles are given in Table 2. The most striking feature of **4** is the nonequivalence of the Zr–Cl bonds. The Zr–Cl(bridging) bond length is somewhat long at 2.605(2) Å, although not excessively so [10*], whereas the Zr–Cl(terminal) bond length is only

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* Reference number with asterisk indicates a note in the list of references.

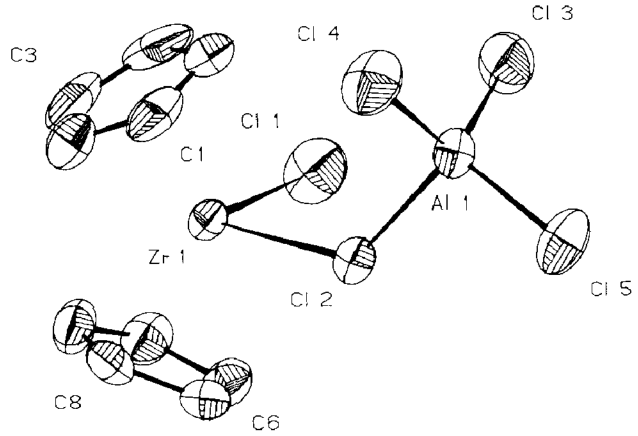

Fig. 1. Perspective view of $(C_5H_5)_2ZrCl(AlCl_4)$.

2.406(3) Å, shorter by ca. 0.04 Å than that typically seen for zirconcene dichlorides [11*]. Another interesting feature of the structure is the Zr–Cl2–Al angle which, at 126.06(7)°, is obtuse compared with the Al–Cl–Al angle observed for $[Al_2Cl_7]^-$ [12] and is probably the result of steric strain. The structure may therefore be regarded as an $AlCl_4^-$ moiety only loosely held by the cationic zirconium moiety **3**, a factor that must to some degree favor rupture of the Zr–Cl(bridge) bond to give the salt $[(C_5H_5)_2ZrCl][AlCl_4]$. The weakness of the Zr–Cl $AlCl_3$ interaction would presumably be even more pronounced in the monomethyl derivative of **4**, $[(C_5H_5)_2Zr(CH_3)(AlCl_4)]$, a direct analogue of Jordan's catalyst.

Table 1

Final fractional coordinates for $(C_5H_5)_2ZrCl(AlCl_4)$

Atom	x/a	y/b	z/c	Equiv. [a] U_{iso}
Al	0.14513(9)	0.3476(2)	0.5081(2)	0.0419
Cl2	0.09066(6)	0.3276(1)	0.3022(2)	0.0441
Cl3	0.1605(1)	0.1964(2)	0.5918(2)	0.0717
Cl4	0.21250(9)	0.4292(2)	0.4733(3)	0.0717
Cl5	0.0994(1)	0.4393(2)	0.6187(2)	0.0694
Zr	0.10613(3)	0.20268(6)	0.10406(6)	0.0349
Cl1	0.0898(1)	0.0472(1)	0.2287(3)	0.0708
C1	0.1930(2)	0.2967(8)	0.1317(9)	0.0601
C2	0.1797(3)	0.2618(8)	−0.0057(9)	0.0654
C3	0.1804(3)	0.1524(9)	−0.0082(10)	0.0693
C4	0.1952(3)	0.1183(8)	0.1286(12)	0.0719
C5	0.2021(2)	0.2060(8)	0.2158(9)	0.0592
C6	0.0072(2)	0.1962(8)	0.0159(8)	0.0550
C7	0.0219(2)	0.3014(8)	0.0085(8)	0.0540
C8	0.0555(3)	0.3069(8)	−0.0893(8)	0.0536
C9	0.0602(3)	0.2061(8)	−0.1405(7)	0.0538
C10	0.0309(3)	0.1381(7)	−0.0750(8)	0.0547

[a] Equiv. $U_{iso} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$.

Table 2

Interatomic distances (Å) and bond angles (°) in $(C_5H_{52}ZrCl(AlCl_4)$

Al–Cl2	2.234(3)	Zr–C8	2.465(8)
Al–Cl3	2.097(4)	Zr–C9	2.460(7)
Al–Cl4	2.097(3)	Zr–C10	2.476(8)
Al–Cl5	2.101(4)	C1–C2	1.400(13)
Zr–Cl1	2.406(3)	Cl–C5	1.411(15)
Zr–Cl2	2.605(2)	C2–C3	1.391(16)
Zr–C1	2.489(8)	C3–C4	1.393(16)
Zr–C2	2.465(10)	C4–C5	1.397(15)
Zr–C3	2.463(10)	C6–C7	1.394(15)
Zr–C4	2.486(9)	C6–C10	1.389(13)
Zr–C5	2.483(7)	C7–C8	1.414(12)
Zr–C6	2.508(7)	C8–C9	1.391(14)
Zr–C7	2.509(8)	C9–C10	1.385(13)
Cl2–Al–Cl3	106.63(9)	C1–C2–C3	109.4(9)
Cl2–Al–Cl4	106.98(9)	C2–C3–C4	107.2(9)
Cl2–Al–Cl5	102.86(9)	C3–C4–C5	108.8(9)
Cl3–Al–Cl4	114.94(10)	Cl–C5–C4	107.8(8)
Cl3–Al–Cl5	112.6(2)	C7–C6–C10	108.6(8)
Cl4–Al–Cl5	111.7(2)	C6–C7–C8	106.9(8)
Zr–Cl2–Al	126.06(7)	C7–C8–C9	108.0(9)
Cl1–Zr–Cl2	92.93(7)	C8–C9–C10	108.1(8)
C2–Cl–C5	106.7(9)	C6–C10–C9	108.3(9)

Other intramolecular bond distances and angles in **4** are within expected ranges. The Zr–C and Zr–(ring plane) distances, average 2.480 and 2.177 Å, respectively, compare with the average distances of 2.494 and 2.195 Å observed for the prototypal compound, $(C_5H_5)_2ZrCl_2$ [13].

*Solubility of **4***

4 is sufficiently soluble in benzene or toluene to obtain NMR spectra but under certain conditions [14*] dramatic increases in solubility of the Cp_2Zr moiety, to the equivalent of 1 g of **4** per 4 g of hydrocarbon solvent, are observed. It is intriguing that under these conditions we observe that two liquid phases are present and that the lower phase contains the Cp_2Zr moiety [15*]. This phenomenon is therefore consistent with a "liquid clathrate" effect which in turn requires the presence of a salt in the lower phase [16*]. Unfortunately, attempts to isolate and determine the exact nature of the species responsible for this behavior, which is presumably a haloaluminate salt of a cationic Zr moiety [17*], have so far proven fruitless as cooling of the apparent "liquid clathrate" phases results in isolation of **4** and complete removal of solvent affords an intractable amorphous solid. We are actively investigating alternate means to isolate the species responsible for this effect.

In conclusion, we have prepared and structurally characterized, for the first time, a model for the initial adducts formed in Ziegler–Natta catalysis. The structure and unusual hydrocarbon solubility of the adduct further support the idea that solvated Zr^{IV} cations are active species in Ziegler–Natta catalysis, even in aromatic hydrocarbon media.

Experimental

General

All manipulations were conducted in an inert atmosphere glove box (Vacuum Atmospheres, Ar atmosphere). Neither **4** nor any of the other compounds subsequently isolated appeared to be oxygen sensitive, although all were hygroscopic. NMR spectra were recorded on Varian EM360 or Nicolet 360NB spectrometers.

Synthesis

4 was prepared via addition of one equivalent of $AlCl_3$ (Johnson–Matthey Aesar, 0.453 g, 3.40 mmol) to 1.00 g (3.42 mmol) of $(C_5H_5)_2ZrCl_2$ (Aldrich) that had been dissolved in 50 ml of freshly distilled dry benzene or toluene. The $AlCl_3$ was observed to dissolve within 5 min at 20 °C and the solution became pale yellow in color. Crystals of **4** were obtained via cooling of the toluene reaction mixture at −15 °C for 3 d. ^1H NMR (60 MHz, benzene-d_6) δ 5.97(s); ^{13}C NMR (91 MHz, benzene) δ 115.97 (d); ^{27}Al NMR (94.07 MHz, benzene) −116.6 (broad singlet).

It must be noted that although **4** was successfully prepared at least ten times we have subsequently discovered that the batch of $AlCl_3$ may considerably affect the outcome of the reaction. In some instances, even with freshly sublimed $AlCl_3$, the reaction does not proceed smoothly and yields only an intractable yellow/orange oily solid.

X-Ray crystallography

A pale yellow air stable crystal of was mounted and sealed in a thin-walled glass capillary and placed on an Enraf–Nonius CAD-4 diffractometer. The unit cell

Table 3

Crystallographic data collection and structure refinement parameters for $(C_5H_5)_2ZrCl(AlCl)_4$ (**4**)

Formula	$C_{10}H_{10}AlCl_5Zr$
Formula wt.	425.7
Radiation	Mo-$K_{\alpha 1}$ (Graphite-monochromated, λ 0.70926 Å)
Crystal system	Monoclinic
Space group	$C2/c$
a	25.568(9) Å
b	12.710(3) Å
c	9.845(2) Å
β	101.47(2)°
V	3135.4 Å^3
Z	8
D_{calc} (g cm^{-3})	1.803
μ (cm^{-1})	15.63
Crystal dimensions (mm)	0.5 × 0.4 × 0.2
Scan type	$\omega-2\theta$
2θ range	4–50
Reflections measured	3,751
Unique reflections	2,752
Reflections observed [a]	1,346
Parameters refined	165
Ratio data/parameter	8.24
R	0.036
R_w	0.036

[a] $I > 2\sigma(I)$.

constants were obtained by least squares analysis of the diffractometer setting angles of 25 well centred reflections with $22° < 2\theta < 28°$. These constants along with other pertinent data collection parameters are shown in Table 3. The intensities were reduced to a standard scale using routine procedures [18]. Corrections for Lorentz and polarization factors were applied but no corrections were made for absorption. Scattering factors for neutral atoms were those recorded in "International Tables for X-ray Crystallography" [19] and were corrected for the real part of the anomalous dispersion effect.

The structure was solved by direct methods (MULTAN-80 [20]) from which all heavy atom positions were obtained. Refinement was carried out using the SHELX-76 [21] system. The structure was refined initially by a full-matrix least squares procedure with independent isotropic temperature factors on the heavy atoms. Some of the hydrogen atom positions could be determined from a difference Fourier synthesis, but all the hydrogen atoms were placed in their geometrically calculated positions with C–H distances of 1.08 Å. The final refinements were with anisotropic temperature factors on the non-hydrogen atoms and individual isotropic temperature factors on the hydrogen atoms. A 2-block matrix least-squares method was employed, minimizing $\Sigma w \Delta F^2$ where $w^{-1} = [\sigma(F)]^2 + 0.01|F_0|^2$. Details of the refinement parameters are given in Table 3. Four reflections were omitted because of suspected extinction. The only significant features in a final difference map were two peaks of approximately 0.8 eÅ^{-3} within 1.0 Å of the zirconium atom.

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15 ^1H NMR spectroscopy showed the presence of 6.3 and 5.4 moles of aromatic hydrocarbon per mole of Cp_2Zr moiety for benzene and toluene, respectively.

16 The existence of a liquid–liquid layering effect when a wide range of trialkylaluminate salts dissolve in benzene or other aromatic hydrocarbon liquids has been well documented and termed the "liquid clathrate" effect. The aromatic contents of the "liquid clathrate" phases are nonstoichiometric and variable but typically lie within the range 5–10 moles of aromatic per mole of salt: J.L. Atwood in J.L. Atwood, J.E.D. Davies and D.D. MacNicol (Eds.), Inclusion Compounds, Vol. 1, Chapter 9, p. 375. Academic Press, New York, 1984.

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