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Synthesis and molecular structure of *meso*-(ethylenebis-(2-(dimethylamino)-1-indenyl))zirconium dichloride

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Abstract

The preparation and molecular structure of *meso*-(ethylenebis(2-(dimethylamino)indenyl))zirconium dichloride (**3**) is reported. Predominant *meso* formation is observed when the ligand dilithium salt is reacted with $ZrCl_4$ in THF. Complex **3** crystallizes in a chiral C_1 symmetric staggered conformation ($\mathrm{Ind}\wedge\mathrm{Ind} = 23.1°$) and reveals shortened hapto–nitrogen bond lengths, 1.456(11) and 1.399(13) Å, indicating extensive orbital overlap between the nitrogen and the hapto carbon atom. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Aminoindenyl; Meso; Metallocene

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1. Introduction

Transition metal based homogeneous polymerization catalysts have gone through a remarkable development in recent years. Especially C_2-symmetric *ansa*-metallocene complexes have been employed in isospecific polymerization of propylene [1] and have been exploited as stereoselective catalysts or reagents for a wide variety of other reactions [2]. Until recently, electronic alteration of group IV metallocene complexes by direct hetero atom substitution on the η^5-rings has remained relatively rare [3–7]. This paper continues our recent studies on hetero atom functionalized bis(indenyl) *ansa*-zirconocenes [3]d[4] and describes the synthesis and molecular structure of *meso*-(ethylenebis(2-(dimethylamino)indenyl))zirconium dichloride.

2. Results and discussion

Double deprotonation of ethylenebis(2-(dimethylamino)indene) (**1**) with two equivalents of *n*-butyllithium and subsequent reaction of the dilithium salt with $ZrCl_4$ in toluene yields *rac*- (**2**) and *meso*- (**3**) (ethylenebis(2-(dimethylamino)indenyl))zirconium dichloride in a 1:1 ratio [3]d. When, however, the same reaction is performed in THF, a *rac*:*meso* ratio of 3:7 is obtained (Scheme 1).

The diastereomers can be separated by fractional crystallization from toluene. Surprisingly an opposite stereochemical outcome has been observed for the dimethylsilylene-bridged analogue, which in toluene yielded *rac*:*meso* = 7:2 and in THF *rac*:*meso* = 1:1 [3]b, c.

In solution **3** gives a highly symmetric ^{1}H-NMR spectrum indicating rapid conformational interconversion. The bridge protons give a characteristic AA'BB' spin pattern [8]. The signal from the H_b-proton of **3** (5.85 ppm) is shielded considerably compared to the corresponding value for *meso*-$Et(Ind)_2ZrCl_2$ (6.70 ppm) [9]a, indicating increased electron density in the C_5 ring.

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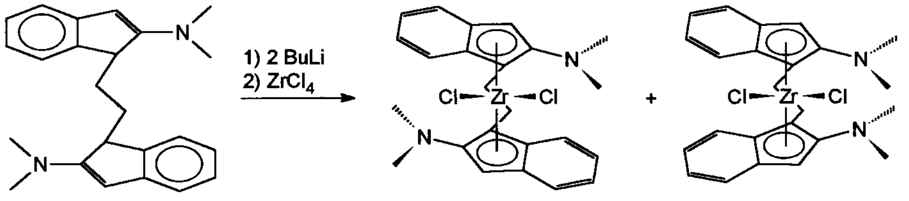

1 **2** **3**

Toluene	1 : 1
THF	3 : 7

Scheme 1.

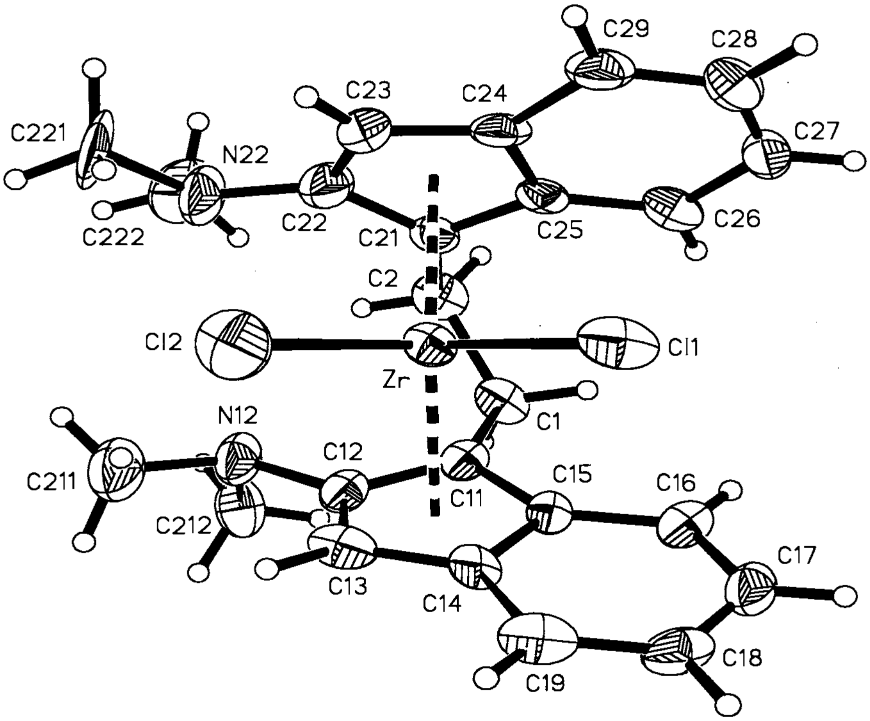

Fig. 1. Molecular structure of **3** (ORTEP view, ellipsoids at 40% probability level).

The molecular structure of **3** (Fig. 1) shows that this complex crystallizes in a chiral C_1 symmetric staggered conformation (Ind ^ Ind = 23.1°) as observed previously for *meso* ethylene-bridged bis(indenyl) [9] and bis(tetrahydroindenyl) [10] zirconium dichlorides. The interatomic distances and angles (Table 1) are unremarkable and well within the range observed for other crystallographically determined molecular structures of *meso* ethylene-bridged bis(indenyl) zirconium dichlorides (Table 2). In fact, the substitutions presented in Table 2 do not alter any of the relevant geometrical parameters.

The R,S *meso* stereoisomer, reported in Fig. 1, has a δ conformation of the Zr–C(11), C(1), C(2), C(21) 'metallacycle'. The hapto-nitrogen bond lengths, C(12)–N(12) = 1.456(11) and C(22)–N(22) = 1.399(13) Å are dissimilar and comparable to those found in the pyrrolidino substituted complex *meso*-$Me_2Si[(2\text{-}C_4H_8N)Ind]_2ZrCl_2$ in which this dissimmilarity has been explained by crystal packing effects [3]b. Steric hindrance forces the dimethylamino substituents out from the η^5-plane [11] which leads to an elongation of the C–N bond lengths compared to the unperturbed non bridged analogue [3]b–d.

Table 1
Selected interatomic distances (Å) and angles (°) for **3**

Zr–Cl(1)	2.418(3)	Zr–Cl(2)	2.462(3)
Zr–C(11)	2.471(8)	Zr–C(21)	2.453(10)
Zr–C(12)	2.548(9)	Zr–C(22)	2.610(11)
Zr–C(13)	2.519(10)	Zr–C(23)	2.560(11)
Zr–C(14)	2.575(10)	Zr–C(24)	2.571(10)
Zr–C(15)	2.552(9)	Zr–C(25)	2.497(9)
Zr–Ce(1)[a]	2.228	Zr–Ce(2)[a]	2.233
Cl(1)–Zr–Cl(2)	96.89(11)	Ce(1)–Zr–Ce(2)[a]	127.5

[a] Ce(1) and Ce(2) denote the centroids of the five-membered portions of the indene rings, with the lowest and highest crystallographic numbering, respectively.

Table 2
Comparison of selected intramolecular distances and angles for *meso ansa*-zirconocenes

meso-Zirconocene	Zr–C(min–max) (Å)	Zr–Cl (Å)[a]	Zr–Cl (Å)	Cl–Zr–Cl (°)	Ce–Zr–Ce (°)[b]	Ref
Et(2–Me_2NInd)$_2ZrCl_2$	2.453–2.610	2.418	2.462	96.89	127.5	This work
Et(1-*t*-BuMe_2SiOInd)$_2ZrCl_2$	2.444–2.661	2.426	2.435	96.19	126.4	4c
Et(4,7-Me_2Ind)$_2ZrCl_2$	2.462–2.602	2.410	2.450	95.91	123.8	9b
Et(Ind)$_2ZrCl_2$	2.470–2.646	2.397	2.455	97.62	126.2	9a
Et(IndH_4)$_2ZrCl_2$	2.436–2.602	2.420	2.457	98.65	125.2	10

[a] Chlorine atom inside the bis-indenyl framework (see Fig. 1).
[b] Centroid–zirconium–centroid angle.

Though similar lithium–nitrogen coordination would be expected for both ethylene- and silylene-bridged ligand salts, opposite *rac*:*meso* ratios of these reactions show, however, that in this case the stereochemical outcome of heteroatom functionalized *ansa*-metallocene formation is unpredictable.

3. Experimental section

Reactions with organometallic compounds were carried out under argon in Schlenk-type glassware. Solvents were dried and distilled under argon prior to use. Ethylenebis(2-(dimethylamino)indene), as a mixture of three double bond isomers, was prepared as described previously [3]d, *n*-butyllithium and zirconium tetrachloride (Aldrich) were used without further purification. NMR spectra were recorded with a JEOL JNM-LA400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) NMR spectrometer. Direct inlet ionization mass spectra (EIMS) were obtained at 70 eV on a Varian VG-7070E mass spectrometer.

*3.1. Synthesis of meso-(ethylenebis(2-(dimethylamino)-indenyl))zirconium dichloride **(3)***

To a solution of ethylenebis(2-*N*,*N*-(dimethylamino)indene) (4.32 g, 12.5 mmol) in THF (40 ml) was added dropwise *n*-butyllithium (10.0 ml of a 2.5 M solution in hexanes, 25.0 mmol) at −40°C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. This solution was added dropwise to a solution of $ZrCl_4$ (2.84 g, 12.2 mmol) in THF (80 ml) at 0°C and the reaction mixture was stirred overnight at room temperature. The orange suspension was evaporated to dryness and extracted with CH_2Cl_2 (100 ml) to remove lithium chloride. Evaporation and crystallization of the residue from toluene (40 ml) at 4°C gave a mixture of **2** and **3** (1.95 g, 3.9 mmol, *rac*:*meso* ~ 2:1). Further crystallization of the mother liquor at −30°C gave pure **3** (2.38 g, 4.7 mmol, 38%) as yellow crystals. Crystals suitable for the X-ray study were obtained by cooling a solution of **3** in CH_2Cl_2-hexane (1:1 v/v) to −30°C. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 7.45 (dd, $^3J = 8.7$ Hz, $^4J = 0.6$ Hz, 2H), 7.16 (dt, $^3J = 8.4$ Hz, $^4J = 1.0$ Hz, 2H), 7.02 (ddd, $^3J = 8.4$, 6.8 Hz, $^4J = 1.0$ Hz, 2H), 6.85 (ddd, $^3J = 8.6$, 6.9 Hz, $^4J = 1.1$ Hz, 2H), 5.85 (d, $^4J = 0.6$ Hz, 2H), 3.98–3.81 (m, AA'BB', 4H), 3.02 (s, 12H). ^{13}C-NMR (400 MHz, CD_2Cl_2): δ 150.16, 127.46, 124.95, 124.56, 123.57, 122.99, 121.72, 104.94, 94.64, 42.84, 28.53. In the mass spectrum of **3**, parent ions of the composition $C_{24}H_{26}N_2ZrCl_2^+$ were obseved in the appropriate isotope ratios at $m/e = 502$–510. The base peak corresponded to $C_{12}H_{12}N^+$, at $m/e = 171$.

3.2. Crystal structure determination

Intensity measurements for X-ray structure analysis were made on a Nicolet R3m diffractometer using M_o–K_α radiation. Three intensity check reflections showed crystal decay of 8% for **3** at the end of data collection, although the crystal was sealed in a glass capillary. The data set was scaled and corrected for Lorentz and polarization factors. The crystal structure was determined by direct methods with SHELX86 [12] and subsequent Fourier synthesis with SHELXL93 [13]. The hydrogens were placed at calculated positions with

Table 3
Crystallographic data for **3**

Empirical formula	$C_{24}H_{26}Cl_2N_2Zr\cdot\frac{1}{4}CH_2Cl_2$
Formula weight	525.85
Crystal system	Tetragonal
Space group	*P*-42_1c No. 114
a (Å)	23.196(3)
b (Å)	23.196(3)
c (Å)	8.570(2)
Z	8
V (Å^3)	4611.1(14)
μ (mm^{-1})	0.781
D_c (Mg m^{-3})	1.515
F (000)	2148
Crystal dimensions (mm)	0.45 × 0.20 × 0.15
2θ limits (°)	2.48–25.00
Scan mode	ω
Reflections collected	4477
Independent reflections	2285 [*R*(int) = 0.0726]
Final *R* indices [$I > 2\sigma(I)$] (%)	$R = 4.59$; $R_w = 7.39$
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$	0.549 ± 0.417

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **3**

Atom	x	y	z	U_{eq}
Zr	4985(1)	2470(1)	2629(1)	33(1)
Cl(1)	4619(1)	2078(1)	5048(3)	51(1)
Cl(2)	5578(1)	3238(1)	3795(4)	71(1)
N(12)	4922(4)	3264(4)	−787(10)	49(3)
N(22)	6129(4)	2561(4)	−63(12)	64(3)
C(1)	4330(4)	2050(4)	−759(10)	39(3)
C(2)	4953(5)	1897(4)	−1087(10)	45(3)
C(11)	4289(4)	2517(5)	449(9)	33(2)
C(12)	4538(4)	3069(5)	449(11)	37(3)
C(13)	4421(5)	3353(5)	1850(12)	44(3)
C(14)	4019(4)	3018(4)	2695(10)	32(3)
C(15)	3926(4)	2503(5)	1826(9)	30(2)
C(16)	3515(4)	2101(4)	2367(11)	38(3)
C(17)	3213(4)	2219(5)	3690(13)	51(3)
C(18)	3298(5)	2744(5)	4508(12)	51(3)
C(19)	3701(5)	3134(5)	4076(12)	52(3)
C(21)	5296(5)	1866(4)	436(12)	36(3)
C(22)	5830(5)	2150(5)	816(14)	51(3)
C(23)	5977(5)	1997(5)	2362(16)	56(4)
C(24)	5611(4)	1560(5)	2864(13)	40(3)
C(25)	5184(4)	1470(4)	1695(11)	34(3)
C(26)	4755(4)	1042(4)	1885(11)	40(3)
C(27)	4778(5)	703(4)	3221(13)	47(3)
C(28)	5201(5)	784(5)	4353(12)	48(3)
C(29)	5613(5)	1192(5)	4193(13)	51(3)
C(211)	5261(5)	3760(5)	−409(14)	71(4)
C(212)	4630(5)	3333(5)	−2299(10)	55(3)
C(221)	6619(5)	2853(6)	651(15)	97(6)
C(222)	6177(5)	2469(6)	−1745(14)	96(5)

$U_{eq} = 1/3\, \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j \times 10^4$.

fixed isotropic thermal parameters (1.2 U_{eq} of the corresponding C atom). The crystallographic data and atomic coordinates for **3** are collected in Tables 3 and 4, respectively.

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[11] (a) Selected torsion angles (°) for **3**: C(211)–N(12)–C(12)–C(13) = 8.3(15), C(212)–N(12)–C(12)–C(11) = 67.3(13), C(221)–N(22)–C(22)–C(23) = −0.3(18), C(222)–N(22)–C(22)–C(21) = −42.5(17).

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