

Bis(2-*N,N'*-methylpiperazinoindenyl)zirconium dichloride. Crystal structure of bis(2-*N,N'*-methylpiperazinoindenyl)ZrCl₂

Markku Hämmäläinen*, Heikki Korpi, Mika Polamo, Markku Leskelä

Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, PO Box 55, FIN-00014 Helsinki, Finland

Received 10 April 2002; accepted 1 July 2002

Abstract

Synthesis of bis(2-*N,N'*-methylpiperazinoindenyl)zirconium dichloride is described. The solid state structure, based on single crystal X-ray diffraction, shows that the compound has a nearly C₂-symmetric conformation. This amino-substituted zirconium metallocene catalyst and methylaluminoxane as a cocatalyst yield polyethylene with narrow molecular weight distribution and very high activity.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Metallocene; Zirconium; Bis(indenyl); Aminoindenyl

1. Introduction

Numerous attempts to improve the activity and the selectivity of metallocene complexes have been reported [1]. Generally, bis(indenyl) compounds are more active than their bis(cyclopentadienyl) analogues. Barsties et al. have reported that 2-dimethylamino substituent increases the electron density noticeably at the Zr center of unbridged (bis)indenyl metallocene [2]. 2-(*N,N'*-Methylpiperazinoindenyl)zirconium dichloride has not been synthesized before even though several other unbridged 2-substituted aminoindenyl zirconium and titanium complexes have been synthesized [3].

Thus, the main focus was to show that the 2-(*N,N'*-methylpiperazinoindenyl)zirconium dichloride is a potential ethylene polymerization catalyst (Fig. 1).

The ligand is prepared by a one-step condensation of 2-indanone [4] and *N*-methylpiperazine. After recrystallization from methanol the ligand was obtained in 29% yield. The ligand was treated with one equivalent of *n*-BuLi and half equivalent of ZrCl₄. After crystallization, yellow bis(2-*N,N'*-methylpiperazinoindenyl)zirconium dichloride was obtained in 27% yield (Scheme 1).

The ¹H-NMR spectrum of the complex shows only six magnetically and chemically different protons indicating time-averaged molecular C₂-symmetry. Comparison between the ligand and the complex ¹H-NMR spectra shows the regions of increased and reduced shielding at the indene part of the molecule. First, the singlet of five-ring methine protons is shifted by about 0.7 ppm to higher shielding relative to the ligand five-ring methine signal. The signals of the aromatic six-ring protons are shifted by about 0.3 ppm to lower shielding. Second, the electron donating effect of the *N*-methylpiperazino substituent can be seen at 4.85 ppm, which is less shielded compared with 2-pyrrolidino substituent (4.42 ppm) but similar to 2-morpholino substituent (4.84 ppm) [5].

The molecule possesses a nearly perfect C₂-symmetry (Fig. 2). Selected bond lengths and angles are given in Table 1. The geometry around zirconium atom can be described as a slightly distorted tetrahedral. Cp(centroid)–Zr–Cp(centroid) angle (132.4°) and Zr–Cp(centroid) bond lengths, 2.217 and 2.215 Å, are typical to unbridged 2-amino substituted indenyl complexes. The bonding of the indenyl five-membered ring to zirconium is unsymmetric, C–Zr distances vary between 2.462(12) and 2.627(10) Å, and, 2.456(11) and 2.630(12) Å, respectively. Also, Cl–Zr–Cl angle, 94.78(13)°, and Zr–Cl distances, 2.444(4) and 2.436(4)

* Corresponding author. Tel.: +358-9-191-50223; fax: +358-9-191-50198

E-mail address: markku.hamalainen@helsinki.fi (M. Hämmäläinen).

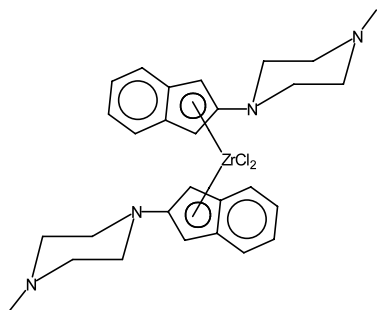
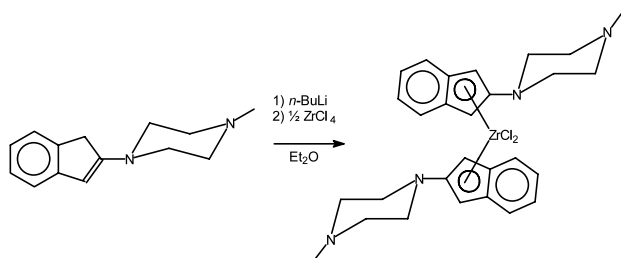


Fig. 1. Bis(2-*N,N'*-methylpiperazinoindenyl)zirconium dichloride.



Scheme 1. Preparation of bis(2-*N,N'*-methylpiperazinoindenyl)zirconium dichloride.

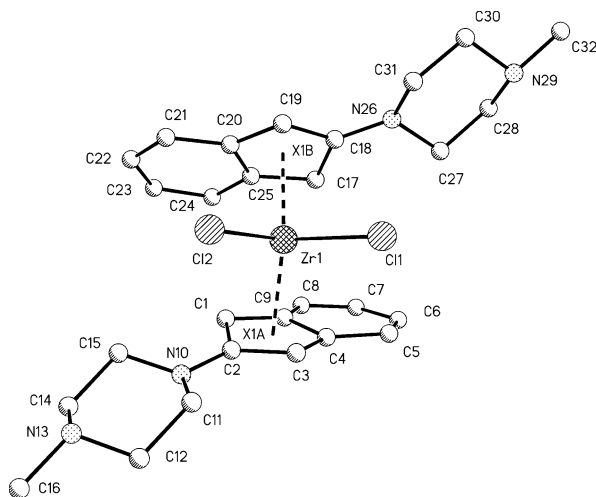


Fig. 2. Crystal structure of complex showing the labelling scheme; displacement ellipsoids are drawn at the 30% probability level; hydrogen atoms and solvent molecule are omitted for clarity.

Å, are common to unbridged 2-aminoindenyl complexes. The single-crystal X-ray structure of the complex reveals that the ligands are disposed in an *anti* conformation. The *N*-methylpiperazino substituents show a chair-like conformation with an almost trigonal-planar nitrogens (sum of angles at N(10) = 355.1°, at N(26) = 352.4°). Bond lengths of C(2)–N(10) = 1.368 Å and C(18)–N(26) = 1.343 Å are similar to Ti(IV) and Zr(IV) bis(aminoindenyl)metallocene complexes. The C(2)–N(10) π -bonding is maximized for a planar structure because the orbitals are better set up for side-on

Table 1
Selected interatomic distances (Å) and angles (°) for the complex

Bond lengths	
C2–N2	1.384(14)
C18–N26	1.343(15)
N10–C11	1.465(15)
N13–C16	1.466(17)
Zr1–X1A	2.217
Zr1–X1B	2.215
Zr1–Cl1	2.444(4)
Zr1–Cl2	2.436(4)
Bond angles	
C11–Zr1–Cl2	94.78(13)
X1A–Zr1–X1B	132.4
X1A–Zr1–Cl1	106.5
X1A–Zr1–Cl2	104.5
X1B–Zr1–Cl1	104.6
X1B–Zr1–Cl2	107.9

interaction. The nitrogen lone pair must be delocalized considerably into the indenyl five-ring and the rotation should be hindered. Nonetheless, planar nitrogen and short C–N bond lengths are disfavored in two known ansa-bridged bis(aminoindenyl) Zr(IV) complexes due to steric hindrance with the ligand bridges [2]. The nitrogen chlorine distances, Cl(1)–N(26) = 3.264(11) Å and Cl(2)–N(10) = 3.262(11) Å, are about the sum of their van der Waals radii (3.30 Å) and there is no significant bonding [3e].

The bis(2-*N,N'*-methylpiperazinoindenyl)zirconium dichloride was examined as an ethylene polymerization catalyst (Table 2) [6a]. The complex proved to be slowly activated by MAO [6b]; it took ca. 15 min at 50 °C before the ethylene consumption started. After the activation period, the ethylene consumption increased slightly towards the end of each polymerization experiment. Preactivation did not have any effect on the activation time. The activity of the complex–MAO system increases with increasing amount of the bis(2-*N,N'*-methylpiperazinoindenyl)zirconium dichloride. The difference in activity obtained in the experiments made at 70 °C cannot be explained by the difference in polymerization time because in none of the polymerizations the catalyst deactivated during the process. The only explanation we have at the moment is the high sensitivity of the system towards catalyst amount.

Various reasons for the very high activity of the compound and narrow molecular distribution of polymers can be proposed. Steric and electronic properties of the complex differ from those of bis(2-*N*-pyrrolidinoindenyl)zirconium dichloride. It is possible that the interactions between MAO and the catalyst differ from bis(2-*N*-pyrrolidinoindenyl)zirconium dichloride because the amino groups can offer suitable binding sites for MAO. The resulting interaction between MAO and the catalyst may cause the long activation period. Evidently, α - or δ -nitrogen to indenyl or the methyl

Table 2

Results of ethylene polymerizations promoted by bis(2-*N,N'*-methylpiperazinoindenyl)zirconium dichloride with MAO^{a,b}

T_p (°C)	Time (s) ^c	n_{cat} (μmol)	Yield (g)	Activity ^d	T_m (°C)	M_w (kg mol ⁻¹)	M_w/M_n
50	4250	1.7	6.56	3270	140	^e	^e
50	4950	2.2	19.8	6550	142	420	1.5
70	3400	0.9	0.9	1060	138	282	2.9
70	1800	1.1	3.8	6910	141	334	1.5

^a Polymerisation conditions: $p_{\text{ethylene}} = 2.6$ bar, [Al]:[M] = 2000:1.^b Bis(2-*N*-pyrrolidinoindenyl)zirconium dichloride ($T_p = 50$ °C; $t_p = 3500$ s; $n_{\text{cat}} = 5.0$ μmol; [Al]:[M] = 2000:1) did not show any activity.^c The times quoted include ca. 15 min activation period.^d Activity of catalyst in kg PE/(mol Zr h).^e Not determined.

group attached to δ -nitrogen must have an effect on the activity of the catalyst.

2. Experimental

All the complexation reactions were done under argon using standard Schlenk techniques. Solvents were dried and distilled before use. NMR spectra were recorded at 200 MHz on a Varian Gemini 200 spectrometer; CDCl₃ as solvent, Me₄Si as internal standard. (a) 2-(*N*-methylpiperazine)indene see [3a]. Yield: 29%, m.p. 155–157 °C, ¹H-NMR (CDCl₃, 25 °C): $\delta = 2.34$ (s, 3H, –CH₃), 2.51 (t, 4H, –CH₂NCH₃), 3.18 (t, 4H, –NCH₂–), 3.39 (s, 2H, IndCH₂–), 5.21 (s, 1H, –CH=C–), 6.85–7.26 (m, 4H, arom.). ¹³C-NMR (CDCl₃, 25 °C): $\delta = 37.2, 46.2, 48.0, 54.5, 100.1, 117.6, 120.8, 122.8, 126.6, 137.1, 145.5, 157.4$. (b) Bis(2-*N,N'*-methylpiperazinoindenyl)zirconium dichloride: to a solution of 2-(*N*-methylpiperazine)indenyl in Et₂O at –78 °C was added drop wise *n*-BuLi, and the reaction mixture was stirred 3 h at room temperature (r.t.). The mixture was cooled to –78 °C, the ZrCl₄ was added and the light yellow suspension was stirred overnight. The solvent was removed in vacuo and the complex crystallized from Et₂O or toluene. Yield 27%. ¹H-NMR (CDCl₃, 25 °C): $\delta = 2.25$ (s, 6H, –NCH₃), 2.34 (t, 8H, –CH₂NCH₃), 3.10 (t, 8H, IndNCH₂–), 4.86 (s, 4H, IndCH–), 7.15 (dd, 4H), 7.62 (dd, 4H). ¹³C-NMR (CDCl₃, 25 °C): $\delta = 45.6, 46.3, 54.5, 84.9, 123.2, 123.6, 125.6, 156.7$. Anal. Calc. for C₃₄H₄₂Cl₂N₄Zr·Et₂O: C, 57.98; H, 6.69; N, 8.45. Found: C, 58.36; H, 6.63; N, 8.93%.

2.1. Crystal data for C₃₄H₄₂Cl₂N₄Zr

Data were collected on a Rigaku AFC-7S diffractometer. The non-hydrogen atoms were refined with full-matrix least-squares on F^2 using SHELXTL 97 program package. Yellow prism 0.25 × 0.25 × 0.20 mm, orthorhombic, space group $P2_12_12_1$, $a = 10.326(2)$, $b = 15.873(3)$, $c = 19.932(4)$ Å, $V = 3267.0(11)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.384$ Mg m⁻³, $T = 193(2)$ K, $\lambda(\text{Mo-K}\alpha) =$

0.71073 Å, $\mu(\text{Mo-K}\alpha) = 0.531$ mm⁻¹, 3321 reflections were collected with $2482 [|F_o| > 2\sigma|F_o|]$, $2.57 < \theta < 25.25^\circ$, number of parameters 174, GOF = 1.209, final R indices [$I > 2\sigma(I)$]: $R = 0.0857$, $wR = 0.1915$. R indices (all data): $R = 0.1223$, $wR = 0.2164$.

3. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 183061. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

References

- [1] H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205.
- [2] E. Barsties, S. Schaible, M.-H. Proscenc, U. Rief, W. Röhl, O. Weyand, B. Dorer, H.-H. Brintzinger, J. Organomet. Chem. 520 (1996) 63.
- [3] (a) H. Plenio, D. Burth, Z. Anorg. Allg. Chem. 622 (1996) 225; (b) H. Plenio, D. Burth, J. Organomet. Chem. 519 (1996) 269; (c) A. Kucht, H. Kucht, W. Song, M.D. Rausch, J.C.W. Chien, Appl. Organomet. Chem. 8 (1994) 437; (d) K.P. Stahl, G. Boche, W. Massa, J. Organomet. Chem. 277 (1984) 113; (e) H.J.G. Luttikhedde, R.P. Leino, C.-E. Wilen, J.H. Näsman, M.J. Ahlgren, T.A. Pakkanen, Organometallics 15 (1996) 3092; (f) H.J.G. Luttikhedde, R.P. Leino, M.J. Ahlgren, T.A. Pakkanen, J.H. Näsman, J. Organomet. Chem. 557 (1998) 227; (g) Y.L. Qian, R.W. Guo, J.L. Huang, K. Jonas, Chin. Chem. Lett. 7 (1996) 1139.
- [4] J.E. Horan, R.W. Schiesster, Org. Synth. 41 (1961) 530.
- [5] S. Knüppel, J.-L. Faure, G. Erker, G. Kehr, M. Nissinen, R. Fröhlich, Organometallics 19 (2000) 1262.
- [6] (a) For ethylene polymerization procedure see T.V. Laine, M. Klinga, A. Maaninen, E. Aitola, M. Leskelä, Acta Chem. Scand. 53 (1999) 968; (b) All of the polymerisations were performed within a week with the same batch of MAO.