

Preliminary communication

Aminozirconocenes: a new class of zirconocenes with a nitrogen atom directly bonded to an η^5 -cyclopentadienyl (indenyl) ligand

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Abstract

The reactions of 2-indanone or 3,4-diphenylcyclopent-2-enone with pyrrolidine and *N,N'*-dimethylethylenediamine respectively lead to the corresponding 2-aminoindenes and 1-amino-3,4-diphenylcyclopentadienes, whose lithium salts can be reacted with $ZrCl_4$ to generate the corresponding moisture-sensitive aminozirconocene dichlorides. The X-ray crystal structure of di-(2-*N*-pyrrolidine- η^5 -indenyl)zirconium dichloride was determined, in which the zirconocene exists exclusively as a racemic-mixture, whereas the meso-rotamer is not present. The (indenyl)carbon–nitrogen bond lengths range from 132.5(7) to 134.9(8) pm, which is indicative of considerable multiple bond character.

Keywords: Zirconocenes; X-ray crystal structure; Aminocyclopentadiene; Zirconium; Cyclopentadienyl

1. Introduction

η^5 -bound metal complexes with aminocyclopentadienes and 2-aminoindenes used to be rare species [1] due to their difficult syntheses [2], but they have recently become readily available [3]. Consequently, a large number of complexes with different metals are now accessible [4]. Cationic zirconocenes are the key component of modern Ziegler–Natta catalysts for the polymerization of ethene and 1-olefins, and are known in large numbers [5] since variations of the metallocene catalysts allow the exertion of a unique degree of microstructural control in the resulting polyolefin [6].

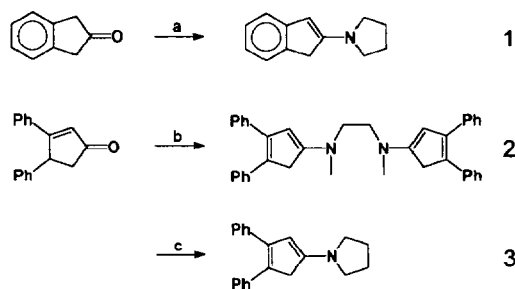
We wish to describe here a new type of substituted zirconocene in which one nitrogen atom is directly bonded to a cyclopentadienyl or indenyl ring, and the X-ray crystal structure of di-(2-*N*-pyrrolidine- η^5 -indenyl)zirconium dichloride. The presence of a nitrogen atom bonded to the aromatic ring may also lead to a new class of Ziegler–Natta catalysts, since it is known that changes in the electron density at the metal center have a pronounced influence on the olefin polymerization behavior [7].

Aminoindene **1** is synthesized from 2-indanone and pyrrolidine in almost quantitative yields, the aminocyclopentadienes **2** and **3** are available from 3,4-diphenylcyclopent-2-enone and pyrrolidine or *N,N'*-dimethylethylenediamine (Scheme 1) using the standard procedure [3]. For the synthesis of the aminozirconocene dichlorides described here, the respective aminoindene **1** or the aminocyclopentadienes **2** and **3** are dissolved in toluene and deprotonated with $nBuLi$. $ZrCl_4$ was added to the Li-salt and the reaction mixture was heated under reflux for 3 days. The aminozirconocene dichlorides **4**, **5** and **6** (Scheme 2) were isolated as yellow to orange-red crystalline, rather moisture-sensitive materials.

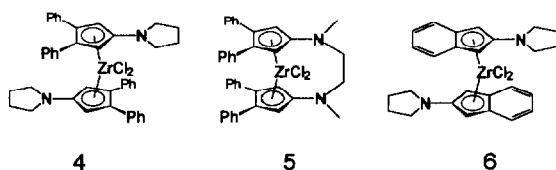
2. X-ray crystal structure [8]

In the crystal the aminozirconocene **6** exists as a mixture of racemic forms, whereas the meso-rotamer is not present (Fig. 1). The indenyl-unit is not planar, and with respect to the reference plane formed by C(1)–C(2)–C(7)–C(8) (or the three sets of stereochemically equivalent carbon atoms) the plane formed by C(3)–C(4)–C(5)–C(6) (or equivalent atoms) is tilted by between 3.6 and 5.3°, whereas the plane formed by C(1)–C(8)–C(9)–N(1) (or equivalent atoms) is tilted by 10.6 to 13.5°. This leads to Zr–C distances ranging from

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Scheme 1. (a) Pyrrolidine, MeOH, 15 min; (b) *N,N'*-dimethylethylenediamine, benzene, 48 h reflux; (c) pyrrolidine, benzene, 48 h reflux.



Scheme 2. Aminozirconocene-dichlorides **4**, **5** and **6** were prepared by reaction of the respective deprotonated aminoindenes (**1**, **2**) and aminocyclopentadienes (**3**) with $ZrCl_4$.

245.9(6) to 264.4(6) pm, with the shorter bonds to atoms like C(1), C(8) (and equivalent atoms) and the longer bonds to indenyl carbons bonded to nitrogen. A large difference in the Zr–C bonds is also typically observed in other bisindenyl–zirconium structures [9], but the almost 20 pm difference between the shortest and the longest Zr–C bond in **6** is unusual and may be due to the bulky pyrrolidin-substituent.

We have noticed previously that indenyl–nitrogen bond lengths in η^5 -bonded aminocyclopentadienes are long in the case of electron-rich organometallic groups (e.g. ferrocenes, ca. 141 pm) and short when electron-deficient organometallic fragments (e.g. $Mn(CO)_3$ in cymantrenes, ca. 136 pm) are bonded to the organic π -ligand. Consequently, for the electron-deficient zirconocene **6** the shortest indenyl–N distances of 132.5(7)–134.9(8) pm are observed. Under these circumstances it is quite likely that cationic zirconocenes will be quite stable since the zirconium(IV)-center should be comparatively electron-rich [10].

Preliminary polymerization data of the zirconocenes in the presence of MAO-cocatalyst indicate that activities for ethylene polymerization are high in the case of the bridged zirconocene **5** but lower for **6** and **4**. Further investigations into the polymerization behavior of aminozirconocenes are underway [11].

3. Experimental

All reactions were performed under dry nitrogen using standard Schlenk techniques. Commercially avail-

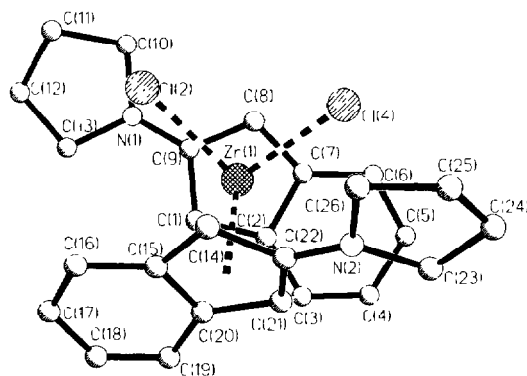


Fig. 1. Crystal structure of **6** (hydrogen atoms omitted) viewed along the vector Zr(1)–Cent(1), which is normal to the best plane of C(1)–C(2)–C(7)–C(8)–C(9). Selected bond lengths (pm) and angles ($^\circ$): Zr(1)–Cl(4) 2.443(2), Zr(1)–Cl(2) 2.449(2), Zr(1)–C(1) 2.459(6), Zr(1)–C(21) 2.484(6), Zr(1)–C(14) 2.504(6), Zr(1)–C(8) 2.519(6), Zr(1)–C(15) 2.529(6), Zr(1)–C(2) 2.537(6), Zr(1)–C(7) 2.549(7), Zr(1)–C(20) 2.549(6), Zr(1)–C(9) 2.631(6), Zr(1)–C(22) 2.644(6), C(9)–N(1) 1.338(9), C(22)–N(2) 1.341(8), C(109)–N(3) 134.8(8), C(122)–N(4) 132.5(7), Zr(1)–Cent 223.2, Zr(1)–Cent 223.4, Cl(4)–Zr(1)–Cl(2) 95.15(7), C(9)–N(1)–C(13) 122.4(6), C(26)–N(2)–C(23) 113.2(6), Cent(1)–Zr(1)–Cent(2) 133.0.

able solvents and reagents were purified according to literature procedures. NMR spectra were recorded at 300 K with a Bruker AC200 F (1H -NMR 200 MHz, ^{13}C -NMR 50 MHz). 1H -NMR data was referenced to residual hydrogen in the deuterated solvents and ^{13}C -NMR data to the signals of $CDCl_3$ (7.26, 77.0 ppm). Elemental analyses were performed at the Mikroanalytisches Laboratorium der Chemischen Laboratorien, Universität Freiburg. Starting materials were commercially available or synthesized according to literature procedures: 3,4-diphenylcyclopentadiene [12], aminocyclopentadienes **2** and **3** [3,4c], 2-(*N*-pyrrolidino)indene [13].

3.1. 1-(*N*-pyrrolidine)-3,4-diphenyl- η^5 -cyclopentadienylzirconium-dichloride (**4**)

A solution of 3,4-diphenyl-1-(*N*-pyrrolidine)-1,3-cyclopentadiene (1.0 g, 4.26 mmol) in toluene (50 ml) was treated with n -BuLi (1.71 ml, 4.26 mmol). After 1 h $ZrCl_4$ (0.49 g, 2.13 mmol) was added and the reaction mixture heated under reflux for 3 days. The hot solution was filtered, the volatiles evaporated and the residue recrystallized from toluene/PE. Yield 0.78 g (50%) orange–red powder. Anal. Found: C, 67.13; H, 5.44; N, 3.65. $C_{42}H_{40}N_2ZrCl_2$ (734.92) Calc.: C, 68.64; H, 5.49; N, 3.81. 1H NMR ($CDCl_3$): δ 1.75 (m, 8H, NCH_2CH_2), 2.96 (m, 8H, NCH_2CH_2), 5.40 (s, 4H, CpH), 7.13–7.25 (m, 20H, ArH). ^{13}C NMR ($CDCl_3$): δ 25.41, 48.81, 97.70, 123.70, 126.84, 127.67, 129.70, 134.96, 146.55.

3.2. [N,N'-dimethyl-N,N'-di(3,4-diphenyl- η^5 -cyclopentadien-1-yl)ethylendiamine]-zirconium-dichloride (5)

A solution of N,N'-dimethyl-N,N'-di-(3,4-diphenyl-cyclopentadien-1-yl)ethylendiamin (1.00 g, 1.91 mmol) in toluene (50 ml) was treated with ⁿBuLi (1.53 ml, 2.5 mol l⁻¹). After 1 h ZrCl₄ (0.44 g, 1.91 mmol) was added and the reaction mixture heated under reflux for 3 days. The hot solution was filtered, the solvent evaporated and the residue recrystallized from CH₂Cl₂/PE. Yield 0.13 g (11%). Anal. Found: C, 68.65; H, 5.62; N, 3.07. C₃₈H₃₄N₂ZrCl₂ · 0.5C₆H₅CH₃ (720.8 g mol⁻¹) Calc.: C, 68.57; H, 5.27; N, 3.85. ¹H NMR (CDCl₃): δ 2.11 (s, 6H, NCH₃), 2.41 (br, 4H, NCH₂), 5.43 (s, 4H, CpH), 6.98–7.20 (m, 20H, ArH). ¹³C NMR (CDCl₃): δ 39.29, 53.20, 125.24, 126.89, 127.62, 128.08, 128.98, 129.44, 134.66.

3.3. Di-(2-N-pyrrolidine- η^5 -indenyl)zirconium-dichloride (6)

2-(N-pyrrolidino)-indene (1.00 g, 5.40 mmol) in toluene (50 ml) was deprotonated with ⁿBuLi (2.16 ml, 5.40 mmol, 2.5 M in n-hexane). After 30 min at room temperature ZrCl₄ (0.63 g, 2.70 mmol) was added and the reaction mixture heated under reflux for 3 days. The hot solution was filtered and reduced in volume. Petrol ether was added to the cold filtrate until the solution became cloudy. The solution was warmed to redissolve the precipitate and slowly cooled to 0°C, resulting in the formation of yellow crystals. Yield 0.87 g (61%). Anal. Found: C, 60.04; H, 5.62; N, 4.70. C₂₆H₂₈N₂ZrCl₂ · 0.25C₆H₅CH₃ (553.6 g mol⁻¹) Calc.: C, 60.20; H, 5.46; N, 5.06. ¹H NMR (CDCl₃): δ 1.80–1.91 (m, 8H, CH₂), 2.97 (t, *J* = 4.8 Hz, 8H, NCH₂), 4.52 (s, 4H, IndH), 7.14–7.18 (AA', 4H, IndH), 7.61–7.66 (BB', 4H, IndH). ¹³C NMR (CDCl₃): δ 25.55, 47.89, 85.17, 122.80, 123.63, 125.85, 154.44.

3.4. X-ray crystal structure

Suitable crystals were grown by slowly cooling a solution of **6** in toluene/PE. The X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer at ambient temperature. Solution and refinement: SHELXS-86 and SHELXL-93 [8]. An empirical absorption correction (psi-scans) was applied. All non-hydrogen atoms in the structures were refined with anisotropic temperature coefficients; hydrogen atoms were placed in calculated positions and refined using isotropic temperature coefficients (riding-model). The unit-cell contains the two enantiomeric forms of the zirconocene together with one molecule of toluene per Zr. Crystal data summary: empirical formula C₃₃H₃₅Cl₂N₂Zr; formula weight 621.75; temperature 293(2) K; wavelength 0.71069 Å; crystal system triclinic; space group *P*1; unit cell di-

mensions *a* = 10.298(2), *b* = 14.957(3), *c* = 19.266(4) Å, α = 85.34(3), β = 85.83(3), γ = 77.57(3); volume 2883.7(10) Å³; *Z* = 4; density (calc.) 1.432 Mg m⁻³; absorption coefficient 0.592 mm⁻¹; *F*(000) 1284; crystal size 0.5 × 0.5 × 0.5 mm³; θ -range for data collection 2.7–23.3°; index ranges 0 ≤ *h* ≤ 11, -16 ≤ *k* ≤ 15, -21 ≤ *l* ≤ 21; reflections (collected/independent) 8667/8156 [*R*(int) = 0.0363]; refinement method full-matrix least-squares on *F*²; data/parameters 6734/659; goodness of fit on *F*² 1.077; final *R*-indices [*I* > 2 σ (*I*)] *R*₁ = 0.0547, *wR*₂ = 0.1312; *R*-indices (all data) *R*₁ = 0.1183, *wR*₂ = 0.1716; largest difference peak and hole +0.68 and -0.42 e Å⁻³. Full details of the X-ray crystal structure determination have been deposited at the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen and are available on quoting the depository number CSD-404405, the names of the authors and the journal citation.

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