

Preliminary communication

Ansa-bis(indenyl) dimethylamido zirconocenes¹

Alexander Vogel, Thomas Priermeier, Wolfgang A. Herrmann^{*}

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching bei München, Germany

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Abstract

Tetrakis(dimethylamido)zirconium (**3**) reacts with dimethylsilylene- and isopropylene-bridged bis(indenyl) ligands **4** and **5** to yield the corresponding *ansa*-bis(dimethylamido)zirconocenes *rac*-**1** and *rac*-**2** containing η^5 -coordinated π -aromatic ligand systems.

Keywords: Zirconium; *ansa*-Metallocene; Metal amide; Bis(indenyl); Crystal structure; Metallocene

1. Introduction

In 1957 Breslow and coworker [1] discovered that bis(cyclopentadienyl)titaniumdichloride in the presence of alkylaluminumchloride can act as a homogeneous catalyst in the Ziegler–Natta polymerization of ethylene. Ever since this discovery, a rapid development in the area of metallocene catalysts has occurred. At present, the catalysts with the best performance in the stereospecific polymerization of α -olefins are rigid, chiral *ansa*-metallocene derivatives of Group 4 metals with methylalumoxane serving as activating agent [2]. These metallocenes are commonly prepared by salt metathesis or amine elimination [3]. The latter method has, in general, higher yields, and in the case of potential *rac*-*meso* isomerism better *rac*-*meso* ratios than the salt metathesis reaction. This amine elimination to synthesize Group 4 metallocenes was first applied by Lapport and coworker [4] in 1968 for the reaction of tetrakis(dimethylamido)zirconium(IV) with excess cyclopentadiene, yielding bis(dimethylamido)bis(cyclopentadienyl)zirconium(IV) and two equivalents of dimethylamine.

It was reported earlier by Jordan and coworkers [5] that the reaction of ethylene-bridged bis(indenyl) with tetrakis(dimethylamido)zirconium gives the corresponding *ansa*-metallocene. The *rac*-dimethylsilylene-bridged bis(indenyl) derivative *rac*-(CH₃)₂Si(C₉H₆)₂Zr-

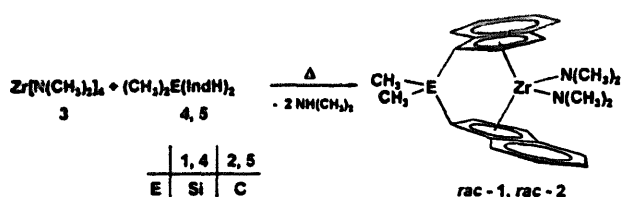
[N(CH₃)₂]₂ (*rac*-**1**) was reported, even though no structural data were given [6]. This prompts us to present our own results, including a crystal structure and NMR data. We also report on the preparation of the isopropylene-bridged bis(indenyl) zirconiumamide *rac*-(CH₃)₂C(C₉H₆)₂Zr[N(CH₃)₂]₂ (*rac*-**2**).

2. Experimental results

It has been shown that the reaction of **4** and tetrakis(dimethylamido)zirconium (**3**) in toluene at 110°C yields a mixture of trisamidozirconium(IV) species which was not further investigated [7]. Upon mixing the two starting solutions of **3** and **4** in mesitylene at –50°C, no reaction was immediately apparent. However, on heating the yellowish reaction mixture up to 165°C under reflux the color of the reaction solution changed to dark red. After 1.5 h the solution was allowed to cool down and the solvent was evaporated to yield a red–brownish oil. The *rac*-*meso* ratio was found to be 9:1 by NMR spectroscopy. The racemic *ansa*-metallocene *rac*-**1** can easily be crystallized from toluene in 51% yield with respect to the starting compounds in the form of red crystals. By means of NMR experiments, every single signal in the ¹H and ¹³C NMR spectra could be assigned to the corresponding atom in the complex. Owing to its C₂ symmetry, the complex gives very simple NMR spectra with only one set of signals for the indenyl substituents, the amido methyl groups, and the methyl groups of the dimethylsilylene bridge.

^{*} Corresponding author.

¹ Dedicated to Professor Rudolf Taube on the occasion of his 65th birthday.



Scheme 1.

The analogous reaction applied to the isopropylene-bridged ligand $(\text{CH}_3)_2\text{C}(\text{C}_9\text{H}_7)_2$ (5) and tetrakis(dimethylamido)zirconium(IV) (3) yields the corresponding racemic *ansa* complex *rac-2* which can be recrystallized from toluene in 53% yield. Similar to the dimethylsilylene-bridged complex, the C_2 symmetry of *rac-2* results in simple NMR spectra.

The reaction of the two amido complexes 1 and 2 with chlorotrimethylsilane at 60°C in C_6D_6 leads to quantitative conversion to the corresponding chloro complexes by NMR spectroscopy (Scheme 1).

3. Molecular and crystal structure

We have carried out a single crystal X-ray structure determination of the complex *rac-1*. Fig. 1 shows its PLATON drawing. According to the spectroscopic results

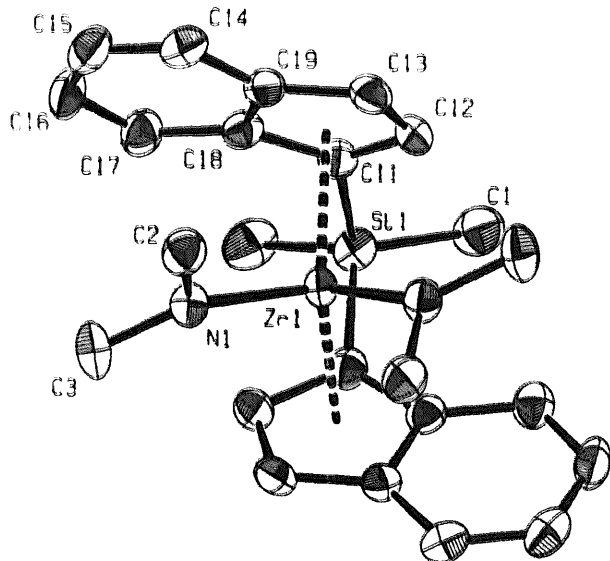


Fig. 1. PLATON representation of *rac-1*. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (pm) and angles (°): Zr(1)–C(11) 256.1(2), Zr(1)–C(12) 253.5(2), Zr(1)–C(13) 261.0(2), Zr(1)–C(18) 264.0(2), Zr(1)–C(19) 270.6(2), Zr(1)–N(1) 207.8(2), Zr(1)–Cg 231.3, Si(1)–C(11) 186.3(2), N(1)–C(2) 146.7(3), N(1)–C(3) 144.3(4), N(1)–Zr(1)–N(1) 96.8(1), C(11)–Si(1)–C(11) 95.6(1), Zr(1)–N(1)–C(2) 118.2(2), Zr(1)–N(1)–C(3) 131.8(2), C(2)–N(1)–C(3) 109.5(2), C_g –Zr(1)– C_g^* 122.9 (C_g defines the centers of gravity of the five-membered rings of the corresponding indenyl systems).

in solution, *rac-1* also exhibits C_2 symmetry in the solid state. The Si and Zr atoms lie on a crystallographically imposed C_2 axis. The coordination geometry around the zirconium and the silicon atom is slightly distorted tetrahedral. Comparison with the analogous *rac*-chloro complexes $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrCl}_2$ [8], $\text{Me}_2\text{Si}(2\text{-Me-Ind})_2\text{ZrCl}_2$ [9], $\text{Me}_2\text{Si}(2\text{-Me-4-Phe-Ind})_2\text{ZrCl}_2$ [10] and $\text{Me}_2\text{Si}(2\text{-Me-[4,5]-Benzo-Ind})_2\text{ZrCl}_2$ [11] shows that variation in steric demand of the π -ligands results only in a minute distortion of the core geometry, that is in the Si–Zr distance and the C_g –Si– C_g^* angles (C_g defines the center of gravity of the five-membered rings of the corresponding indenyl systems).

However, the exchange of chloro ligands by the much bulkier amido ligands leads to significant changes in the geometry of the corresponding complex: the Si–Zr distance amounts to 341 pm, the C_g –Zr– C_g^* angle to 123° (332 pm and 128–129° in the analogous chloro complexes [8–11]). To minimize steric repulsion, each of the two symmetry related amido ligands is oriented such that its virtual C–N–C plane is roughly parallel to the six-membered ring of one of the two indenyl systems. This causes an increased steric interaction between one methyl group and the five-membered ring of the other indenyl substituent. Summarizing these results, by changing the chloro to dimethylamido ligands a shift of the $\text{Zr}(\text{N}(\text{CH}_3)_2)_2$ unit out of the slightly increased 'aperture gap' of the chelating π -ligand sphere is observed.

Atomic coordinates and equivalent isotropic thermal parameters of *rac-1* are given in Table 1. A complete list of bond lengths and angles, and tables of hydrogen atom coordinates and thermal parameters have been deposited at the Fachinformationszentrum Karlsruhe.

Table 1
Atomic coordinates and equivalent isotropic thermal parameters of *rac-1*

Atom	x	y	z	U_{eq} (Å ²)
Zr(1)	0.2500	0.21708(2)	0.0000	0.0249
C(1)	0.280(3)	0.5779(3)	0.0967(2)	0.0458
C(2)	0.1399(2)	0.0100(2)	–0.0902(2)	0.0369
C(3)	0.2363(3)	0.1084(3)	–0.1821(2)	0.0419
C(11)	0.1264(2)	0.3915(2)	0.0003(2)	0.0289
C(12)	0.1164(2)	0.3301(2)	0.0729(2)	0.0305
C(13)	0.0438(2)	0.2376(2)	0.0477(2)	0.0322
C(14)	–0.0802(2)	0.1723(2)	–0.1000(2)	0.0350
C(15)	–0.1055(2)	0.1967(2)	–0.1833(2)	0.0400
C(16)	–0.0514(3)	0.2869(2)	–0.2138(2)	0.0395
C(17)	0.0269(2)	0.3543(2)	–0.1596(2)	0.0353
C(18)	0.0542(2)	0.3336(2)	–0.0713(2)	0.0284
C(19)	0.0014(2)	0.2396(2)	–0.0408(2)	0.0288
Si(1)	0.2500	0.49274(7)	0.0000	0.0310
N(1)	0.2141(2)	0.1055(2)	–0.0984(1)	0.0318

Starred atoms lie on a two-fold axis and have an occupation factor of 0.5.

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4. Experimental section

The metal complexes are air- and moisture-sensitive, thus all reactions and manipulations must be carried out in an atmosphere of pure and dry argon, using either standard high-vacuum techniques and standard Schlenk procedures or a glove-box. Solvents were predried and freshly distilled or vacuum-transferred from Na/K alloy. The ligands and tetrakis(dimethylamido)zirconium were prepared by literature procedures and stored in a glove-box (N_2 atmosphere). NMR spectra were recorded on a Bruker DPX 400 spectrometer.

4.1. *rac*-Bis(dimethylamido)[η^5 : η^5 -bis(1-indenyl)dimethylsilyl]zirconium(IV) (*rac*-1)

A solution of $Zr[N(CH_3)_2]_4$ (3) (300 mg, 1.04 mmol) in 5 ml mesitylene was cooled to $-50^\circ C$ and $(CH_3)_2Si(C_9H_7)_2$ (4) (278 mg, 1.04 mmol) dissolved in 5 ml mesitylene subsequently added. The solution was slowly warmed to room temperature and then refluxed for 1.5 h. A yellow color arose first and then changed to dark orange. The solvent was removed under vacuum and the residue dissolved in pentane. The solution was filtered and after removal of the solvent the product was recrystallized from toluene. Complex *rac*-1 was obtained as red crystals in 51% yield (241 mg, 0.53 mmol).

4.1.1. Spectroscopic data

1H NMR (400 MHz, C_6D_6 , $25^\circ C$): [ppm] 0.81 (s, 6H, $Si(CH_3)_2$), 2.47 (s, 12H, $N(CH_3)_2$), 6.21 (d, 2H, $^3J(H_2, H_3) = 3.12$ Hz, H^2), 6.70 (dd, 2H, $^3J(H^4, H^5) = 8.40$ Hz, $^3J(H^5, H^6) = 6.67$ Hz, H^5), 6.86 (d, 2H, $^3J(H^2, H^3) = 3.12$ Hz, H^3), 6.95 (dd, 2H, $^3J(H^5, H^6) = 6.67$ Hz, $^3J(H^6, H^7) = 8.58$ Hz, H^6), 7.51 (d, 2H, $^3J(H^4, H^5) = 8.40$ Hz, H^4), 7.58 (d, 2H, $^3J(H^6, H^7) = 8.58$ Hz, H^7).

$^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6 , $25^\circ C$): [ppm] -1.2 (s, $Si(CH_3)_2$), 47.8 (s, $N(CH_3)_2$), 97.9 (s, C^1), 110.1 (s, C^3), 116.0 (s, C^2), 123.0 (s, C^7), 124.1 (s, C^5), 124.2 (s, C^6), 125.8 (s, C^4), 128.4 (s, C^9), 131.4 (s, C^8).

4.2. *rac*-Bis(dimethylamido)[η^5 : η^5 -2,2-bis-(1-indenyl)propane]zirconium(IV) (*rac*-2)

Using the same procedure as in the preparation of *rac*-1, $Zr[N(CH_3)_2]_4$ (3) and 332 mg (1.22 mmol) $(CH_3)_2C(C_9H_7)_2$ afforded 291 mg (0.65 mmol, 53%) *rac*-2.

4.2.1. Spectroscopic data

1H NMR (400 MHz, C_6D_6 , $25^\circ C$): [ppm] 2.02 (s, 6H, $C(CH_3)_2$), 2.51 (s, 12H, $N(CH_3)_2$), 6.19 (d, 2H, $^3J(H, H) = 3.13$ Hz, olefinic), 6.49 (d, 2H, $^3J(H, H) = 2.77$ Hz, olefinic), 6.61 (dd, 2H, $^3J(H, H) = 7.38$ Hz, $^3J(H, H) = 7.45$ Hz, aromatic), 6.88 (dd, 2H, $^3J(H, H) = 7.00$ Hz, $^3J(H, H) = 7.99$ Hz, aromatic), 7.38 (d, 2H, $^3J(H, H) = 8.40$ Hz, aromatic), 7.68 (d, 2H, $^3J(H, H) = 8.92$ Hz, aromatic).

$^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6 , $25^\circ C$): [ppm] 28.6 (s, $C(CH_3)_2$), 40.3 (s, $C(CH_3)_2$), 47.5 (s, $N(CH_3)_2$), 102.6, 108.9, 114.6, 118.2, 122.5, 123.1, 123.8, 126.1, 126.5 (aromatic and olefinic C's).

4.3. Crystal structure determination of *rac*-1

X-ray structure of *rac*-1: monoclinic crystal system, space group $I2/a$ (No. 15); $C_{24}H_{30}N_2SiZr$; $a = 1115.3(1)$, $b = 1236.5(1)$, $c = 1627.0(1)$ pm, $\beta = 103.91(1)^\circ$, $Z = 4$, $V = 2178(1) \times 10^6$ pm³, $M = 465.83$, $\rho_{calc} = 1.421$ g cm⁻³, $\mu = 5.7$ cm⁻¹, $F_{000} = 968$; diffractometer type STOE IPDS, graphite monochromated Mo $K\alpha$, measurement at $-80^\circ C$, range of measurement $2.0^\circ < 2\theta < 48.4^\circ$, φ -mode rotation, $\Delta\varphi = 1^\circ$, 12521 measured reflections, 1589 independent reflections with $I > 0$, structure determination with direct methods and subsequent difference Fourier syntheses, 188 least-squares parameters, all hydrogen atoms found and independently refined (isotropic), $R = \sum(|F_o| - |F_c|) / \sum |F_o| = 0.032$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.031$, residual electron density $+0.32$ $\Delta e \text{ \AA}^{-3} / -36 \Delta e \text{ \AA}^{-3}$. All calculations were performed on a DECstation 5000/25 using the programs CRYSTALS [12] and PLATON [13].

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