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(2-(Dimethylamino)indenyl)zirconium Dichlorides

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Summary: Bis(2-(dimethylamino)indenyl)zirconium dichloride and rac-(ethylenebis(2-(dimethylamino)-1-indenyl))zirconium dichloride have been prepared and their molecular structures determined. Both complexes reveal very short η*-nitrogen distances which indicate considerable C−N double-bond character.*

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Introduction

Metallocene complexes in general, and C_2-symmetrical *ansa*-metallocenes in particular, have been employed as catalyst precursors for stereospecific polymerization of α-olefins.[1] Ligand substitution patterns and their influence on the catalyst performance in a series of silicon-bridged bis(indenyl)zirconium dichlorides have been extensively studied by Spaleck *et al.*[2] They showed that the combined influence of a 2-methyl substituent and aromatic substituents on the benzo units drastically improved the catalyst performance. A similar approach was applied to ethylene-bridged bis(indenyl)zirconium dichlorides by Kaminsky *et al.*[3] Coates and Waymouth have reported the preparation of bis(2-phenylindenyl)zirconium dichloride, the first example in which oscillating stereocontrol of the catalyst species gives rise to thermoplastic elastomeric polypropylene.[4] In this note we describe the synthesis and molecular structures of bis(2-(dimethylamino)indenyl)zirconium dichloride and its ethylene-bridged congener, whose accessibility was recently pointed out by Plenio and Burth.[5]

Results and Discussion

2-(Dimethylamino)indene (**1**) was prepared in 90% yield by mixing 2-indanone and dimethylamine in methanol.[6] The conversion of **1** into ethylenebis(2-(dimethylamino)indene) (**2**), which was isolated as a mixture of the expected three double-bond isomers,[7] proceeded in 77% yield via a salt metathesis reaction of Li-**1** with 1,2-dibromoethane. A portion of this material was isomerized for complete characterization. Treatment of $ZrCl_4$ with 2 equiv of Li-**1** in THF yielded, after workup and crystallization, bis(2-(dimethylamino)indenyl)zirconium dichloride (**3**) as a yellow powder in 21% yield. The ^1H and ^{13}C NMR spectra of **3** at room temperature were consistent with molecular C_{2v} symmetry. The dilithium derivative of **2** was treated with $ZrCl_4$ in toluene. After workup and crystallization, *rac*-(ethylenebis(2-(dimethylamino)-1-indenyl))zirconium dichloride (**4**) was obtained as a bright yellow microcrystalline powder in 33% yield. The ^1H and ^{13}C NMR spectra showed only one type of (dimethylamino)indenyl ligand together with a characteristic AA′BB′ pattern for the protons of the ethylene bridge. Both **3** and **4** tended to slowly decompose in solution but were stable in the crystalline state under an inert atmosphere.

The molecular structures of **3** and **4** are shown in Figures 1 and 2, respectively, as elucidated by an X-ray structure determination. The structure of **3** reveals that the 2-(dimethylamino)indenyl ligands are disposed in an *anti* conformation, with bond lengths and angles within the range normally observed for crystallographically determined molecular structures of bis(indenyl) zirconium dichlorides.[9] The η-nitrogen bond lengths, C(12)−N(12) = 1.377(12) Å and C(22)−N(22) = 1.323(12) Å, in which the electron deficiency of zirconium is expressed, are a measure for the $p-\pi$ overlap (*vide infra*) and are, in fact, as short as the C−N double bond in amides. The rotation around the η-nitrogen bond must be hindered because of its considerable double-bond character.[10] Maximum orbital overlap is achieved when the (dimethylamino)indenyl ligand is unperturbed and the deviation from planarity is minimal.[11] These η-nitrogen bond lengths are comparable to those reported for 1,1′-bis(dimethylamino)titanocene dichloride.[12] The nitrogen−chlorine distances Cl(1)−N(22) =

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(1) For a recent review, see: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995,** *34,* 1143.

(2) (a) Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1347. (b) Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994,** *13,* 954.

(3) Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem.* **1995,** *497,* 181.

(4) Coates, G. W.; Waymouth, R. M. *Science* **1995,** *267,* 217.

(5) Plenio, P.; Burth, D. *Angew. Chem., Int. Ed. Engl.* **1995,** *34,* 800.

(6) Edlund, U. *Acta Chem. Scand.* **1973,** *27,* 4027.

(7) Edlund, U. *Chem. Scr.* **1973,** *7,* 85.

(8) 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.

(9) For molecular structures of nonbridged group IV bis(indenyl) complexes, see ref 4 and: (a) O'Hare, D.; Murphy, V. M.; Diamond, G. M.; Arnold, P.; Mountford, P. *Organometallics* **1994,** *13,* 4689. (b) Krüger, C.; Lutz, F.; Nolte, M.; Erker, G.; Aulbach, M. *J. Organomet. Chem.* **1993,** *452,* 79. (c) Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, N.; Werner, S. *J. Am. Chem. Soc.* **1993,** *115,* 4590. (d) Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990,** *9,* 3098. (e) Rausch, M. D.; Moriarty, K. J.; Atwood, J. L.; Hunter, W. E.; Samuel, E. *J. Organomet. Chem.* **1987,** *327,* 39. (f) Atwood, J. L.; Hunter, W. E.; Hrncir, D. C.; Samuel, E.; Alt, H.; Rausch, M. D. *Inorg. Chem.* **1975,** *14,* 1757.

(10) Lide, D. R., Jr. *Tetrahedron* **1962,** 125.

(11) Selected torsion angles (deg) for **3**: C(121)−N(12)−C(12)−C(13) = −2.8(14), C(122)−N(12)−C(12)−C(11) = 7.8(13), C(221)−N(22)−C(22)−C(23) = −0.7(13), C(222)−N(22)−C(22)−C(21) = 9.9(13).

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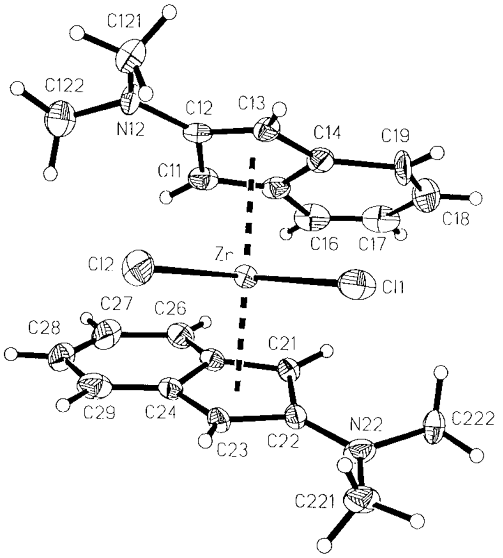

Figure 1. Molecular structure of **3** (ORTEP view, ellipsoids at 50% probability level). Bond lengths (Å): Zr−Cl(1) = 2.446(3), Zr−Cl(2) = 2.465(2), Zr−C(11) = 2.498(9), Zr−C(12) = 2.640(8), Zr−C(13) = 2.519(9), Zr−C(14) = 2.567(8), Zr−C(15) = 2.570(8), C(12)−N(12) = 1.377(12), C(22)−N(22) = 1.323(12). Bond angles (deg): Cl(1)−Zr−Cl(2) = 94.92(3), Ce(1)−Zr−Ce(2) = 132.76(2).[8]

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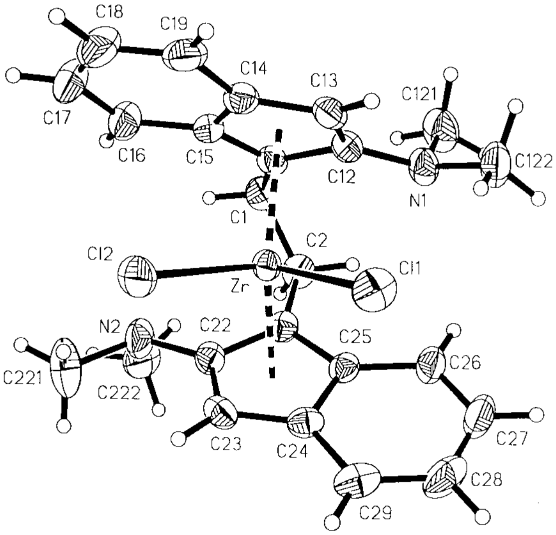

Figure 2. Molecular structure of **4** (ORTEP view, ellipsoids at 40% probability level). Bond lengths (Å): Zr−Cl(1) = 2.4270(14), Zr−Cl(2) = 2.427(2), Zr−C(11) = 2.477(5), Zr−C(12) = 2.543(5), Zr−C(13) = 2.551(5), Zr−C(14) = 2.602(5), Zr−C(15) = 2.552(5), C(12)−N(1) = 1.398(6), C(22)−N(2) = 1.406(6). Bond angles (deg): Cl(1)−Zr−Cl(2) = 94.76(6), Ce(1)−Zr−Ce(2) = 127.21(3).[8]

3.186(9) Å and Cl(2)−N(12) = 3.223(10) Å are shorter than the sum of their relevant van der Waals radii (3.30 Å).

The molecular structure of **4** shows that this complex crystallizes in the indenyl-forward (π) conformation, as is the case for most of the chiral ethylene-bridged bis(indenyl)type metallocenes.[13] The symmetry axis bisecting the Cl−Zr−Cl angles is almost perfectly maintained, although the molecule is not situated on a crystallographic C_2 axis. The coordination sites are framed in an equivalent fashion, in accordance with the requirements for equivalent enantiofacial coordination of prochiral substrates. The *S*,*S* enantiomer, reported in Figure 2, has a δ conformation of the Zr−C(11)−C(1)−C(2),C(21) "metallacycle". Steric hindrance between C(121)H_3 and bridge C(1)H_2 and between C(222)H_3 and bridge C(2)H_2 forces the dimethylamino substituents out from the η^5 plane, which leads to a decrease in p−π overlap and a small but significant increase in the η-nitrogen bond lengths (C(12)−N(1) = 1.398(6) Å and C(22)−N(2) = 1.406(6) Å).[14] The other characteristic bond lengths and angles are comparable to those in analogous (ethylenebis(1-indenyl))zirconium dichlorides.[3,13,15] Preliminary polymerization results show a relatively low ethylene polymerization activity for complex **4** when it is activated with methylaluminoxane (MAO) (A = 500 kg of PE/mol of Zr/h; [Al]:[Zr] = 3000:1; $P(C_2H_4)$ = 1.6 bar; T_p = 80 °C). The melting point and crystallinity of the produced polymer are comparable to those obtained with the Cp_2ZrCl_2/MAO reference system (T_m = 133 °C; crystallinity = 51.3%).

We believe that 2-amino-substituted indenes, also because of the enormous abundance of secondary amines, will open new and exciting possibilities in tuning the electronic as well as the steric environment of the active site in these catalyst precursors. This is currently under investigation.

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. Dimethylamine (Fluka), 2-indanone, *n*-butyllithium, 1,2-dibromoethane, and zirconium tetrachloride (Aldrich) were used without further purification. NMR spectra were recorded with a JEOL GX 400 (^1H, 400 MHz; ^{13}C, 100.6 MHz) NMR spectrometer with Me_4Si as internal standard. Direct inlet ionization mass spectra (EIMS) were obtained at 70 eV with a VG-7070E mass spectrometer. Melting points are uncorrected.

Synthesis of Ethylenebis(2-(dimethylamino)indene) (2). To a solution of 2-(dimethylamino)indene (25.58 g, 160.6 mmol) in THF (200 mL) was added dropwise *n*-butyllithium (65.0 mL of 2.5 M solution in hexanes, 162.5 mmol) at −40 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. To this solution was added dropwise 1,2-dibromoethane (15.03 g, 80.0 mmol) in THF (50 mL) at −78 °C, and the reaction mixture was stirred at room temperature for 12 h. The mixture was poured into water (150 mL) and the organic phase separated and dried over anhydrous Na_2SO_4. The THF was evaporated and the gray residue washed with Et_2O (3 × 50 mL) to afford **2** (21.26 g, 61.71 mmol, 77%) as an off-white powder. A suspension of **2** (3.45 g, 10.00 mmol) was refluxed in triethylamine (80 mL) for 3 h. The mixture was filtered and slowly cooled to 5 °C. This procedure was repeated three times (without further filtration) to yield ethylenebis(2-(dimethylamino)-1-indene) (1.18 g, 3.42 mmol, 34%), which was the major isomer in the original mixture, as slightly pink crystals. ^1H NMR (400 MHz, $CDCl_3$): δ 7.09 (m,

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(12) Stahl, K.-P.; Boche, G.; Massa, W. *J. Organomet. Chem.* **1984,** *227*, 113.

(13) Piemontesi, F.; Camurati, I.; Resconi, L.; Balboni, D.; Sironi, A.; Moret, M.; Ziegler, R.; Piccolrovazzi, N. *Organometallics* **1995,** *14*, 1256 and references therein.

(14) (a) Selected torsion angles (deg) for **4**: C(121)−N(1)−C(12)−C(11) = 57.9(7), C(122)−N(1)−C(12)−C(13) = 8.6(7), C(222)−N(2)−C(22)−C(21) = 60.1(7), C(221)−N(2)−C(22)−C(23) = 8.1(8). (b) In the solid state two interatomic hydrogen distances are shorter than the sum of their relevant van der Waals radii, (see Supporting Information).

(15) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem. Macromol. Symp.* **1991,** *48/49*, 253.

4H), 6.97 (d, $^3J = 7.4$ Hz, 2H), 6.85 (dt, $^3J = 7.3$ Hz, $^4J = 1.2$ Hz, 2H), 5.33 (s, 2H), 3.42 (s(br), 2H), 2.69 (s, 12H), 1.82−1.73 (m, 2H), 1.37−1.28 (m, 2H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.95, 125.53, 125.04, 124.45, 123.54, 123.12, 122.66, 107.64, 98.56, 42.22, 27.13. Mp: 134−135 °C. EIMS (calculated/found): *m*/*e* 344.2252/344.2267. The base peak corresponded to $C_{12}H_{12}N^+$ at *m*/*e* 171.The mass spectrum was identical with that for the original double-bond mixture.

Synthesis of Bis(2-(dimethylamino)indenyl)zirconium Dichloride (3). To a solution of 2-(dimethylamino)indene (6.58 g, 41.35 mmol) in THF (50 mL) was added dropwise *n*-butyllithium (16.6 mL of 2.5 M solution in hexanes, 41.5 mmol) at −40 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. This solution was added dropwise to a suspension of $ZrCl_4$ (4.77 g, 20.47 mmol) in THF (50 mL) at room temperature and stirred overnight. The solvent was evaporated and the residue extracted with CH_2Cl_2 (70 mL) to leave lithium chloride. Diffusion of hexane (30 mL) into this solution at −30 °C yielded **3** (2.08 g, 4.35 mmol, 21%) as a yellow powder. Crystals suitable for the X-ray study were obtained by cooling a solution of **3** in a CH_2Cl_2−hexane (2:1 v/v) mixture to −30 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.66 (dd, $^3J = 6.2$ Hz, $^4J = 3.2$ Hz, 4H), 7.19 (dd, $^3J = 6.2$ Hz, $^4J = 3.2$ Hz, 4H), 4.64 (s, 4H), 2.68 (s,12H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 158.14, 126.14, 124.14, 123.38, 85.12, 39.68. In the mass spectrum of **3**, parent ions of the composition $C_{22}H_{24}N_2ZrCl_2^+$ were observed in the appropriate isotope ratios at *m*/*e* = 476−484. The base peak, however, corresponded to $C_{11}H_{12}NZrCl_2^+$ which gave the correct isotope ratios at *m*/*e* = 318−326.

Synthesis of *rac*-(Ethylenebis(2-(dimethylamino)indenyl))zirconium Dichloride (3). To a suspension of ethylenebis(2-(dimethylamino)indene) (1.26 g, 3.66 mmol) in Et_2O (50 mL) was added dropwise *n*-butyllithium (3.0 mL of 2.5 M solution in hexanes, 7.50 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 12 h. The solvents were evaporated *in vacuo* and the resulting white powder was mixed with $ZrCl_4$ (0.84 g, 3.60 mmol) in toluene (50 mL). The reaction mixture became warm and turned dark red. After 12 h of stirring, the orange suspension was evaporated to dryness and extracted with CH_2Cl_2 (50 mL) to leave lithium chloride. Diffusion of hexane (30 mL) into this solution at −30 °C yielded **4** (0.60 g, 1.19 mmol, 33%) as a yellow powder. Crystals suitable for the X-ray study were obtained by cooling a solution of **4** in a CH_2Cl_2−hexane (2:1 v/v) mixture to −30 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.32 (d, ^3J=8.8 Hz, 2H), 7.21−7.14 (m, 4H), 7.00 (ddd, $^3J = 8.5$, 6.2 Hz, $^4J = 1.3$ Hz, 2H), 5.99 (s, 2H), 4.39−4.28 (m, AA′, 2H), 3.40−3.29 (m, BB′, 2H), 2.82 (s, 12H). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ 147.95, 125.53, 125.04, 124.45, 123.54, 123.12, 122.66, 107.64, 98.56, 42.22, 27.13. In the mass spectrum of **4**, parent ions of the composition $C_{24}H_{26}N_2ZrCl_2^+$ were observed in the appropriate isotope ratios at *m*/*e* = 546−554. The base peak, however, corresponded to $C_{12}H_{12}N^+$, at *m*/*e* = 171.

Crystal Structure Determination. Intensity measurements for X-ray structure analysis were made on a Nicolet R3m diffractometer using Mo Kα radiation. Three intensity check reflections showed crystal decay of about 30% for **3** and 20% for **4** at the end of data collection, although the crystals were sealed in glass capillaries. The data sets were scaled and corrected for Lorentz and polarization factors. The crystal structures were determined by direct methods with SHELX86[16] and subsequent Fourier synthesis with SHELXL93.[17] The hydrogens were placed at calculated positions with fixed isotropic thermal parameters (1.2 times the U_{eq} value for the corresponding C atom).

Crystal data for **3**: $C_{22}H_{24}Cl_2N_2Zr$, $M_r = 478.55$, monoclinic space group *Cc*, $a = 18.461(3)$ Å, $b = 8.2320(10)$ Å, $c = 14.401(2)$ Å, $\beta = 112.580(10)°$, $V = 2020.8(5)$ Å^3, $Z = 4$, $D_c = 1.573$ g cm^{-3}, R (R_w) = 3.2% (7.5%) for 3755 reflections ($I > 2\sigma(I)$). Crystal data for **4**: $C_{24}H_{26}Cl_2N_2Zr$, $M_r = 504.59$, monoclinic space group $P2_1/n$, $a = 11.349(4)$ Å, $b = 16.288(4)$ Å, $c = 12.153(3)$ Å, $\beta = 98.11(2)°$, $V = 2224.0(11)$ Å^3, $Z = 4$, $D_c = 1.507$ g cm^{-3}, R (R_w) = 4.9% (9.6%) for 3950 reflections ($I > 2\sigma(I)$).

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Supporting Information Available: Tables listing positional parameters, thermal parameters, complete bond lengths and angles, and full experimental details for data collection and refinement for **3** and **4**, text giving polymerization details, and ORTEP diagrams of **3** and **4** giving side and top views (21 pages). Ordering information is given on any current masthead page.

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[16] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[17] Sheldrick, G. M. SHELX93: Program for the Refinement of Crystal Structures; University of Göttongen, Göttongen, Germany, 1993.

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