J. Am. Chem. Soc. **1998,** *120,* 9945−9946 9945

A New Class of Chiral Bridged Metallocene: Synthesis, Structure, and Olefin (Co)polymerization Behavior of *rac*- and *meso*-1,2-CH_2CH_2\{4-(7-Me-indenyl)\}$_2$$ZrCl_2$

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Received April 6, 1998

Chiral bridged metallocenes[1] exercise stereocontrol in the polymerization of propylene.[2,3] Extensive investigation of substituent effects has resulted in highly active, highly isospecific homogeneous catalysts.[4] These contain two indenyl groups with a bridge (−CH_2CH_2− or −$SiMe_2$−) linking the 1,1′-positions. We report here a new class of chiral bridged metallocenes which are efficient catalysts, after activation with MAO, for the polymerization of ethylene and propylene, and are very active for their copolymerization. They have an ethylene bridge between the 4,4′-positions, i.e., linking the two phenyl rings,[5] rather than the cyclopentadienyl rings, as is the case with all hitherto known bridged bis(indenyl) ligands.[3]

The synthesis[6] of *rac*- and *meso*-1,2-CH_2CH_2\{4-(7-Me-indenyl)\}$_2$$ZrCl_2$ (**1**) is shown in Figure 1. In contrast to conventional 1,1′-bridged metallocenes, its synthesis requires the stepwise assembly of the cyclopentadienyl ring.

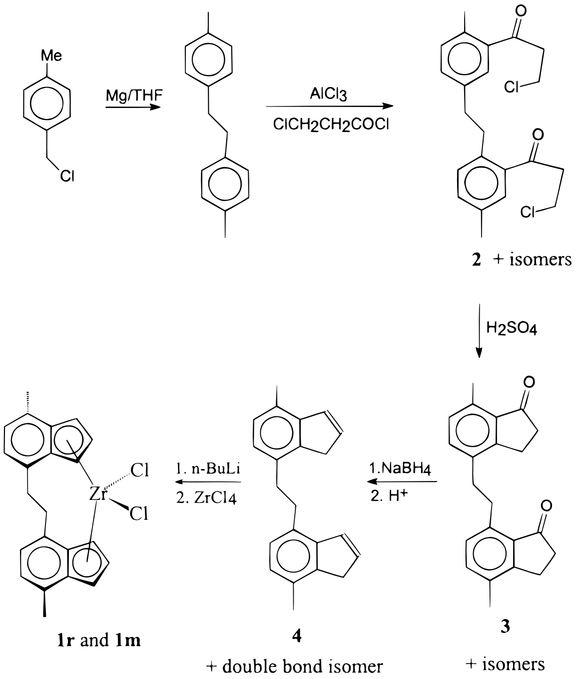

Figure 1. Synthesis of 1,2-CH_2CH_2\{4-(7-Me-indenyl)\}$_2$$ZrCl_2$.

Friedel−Crafts addition of $ClCH_2CH_2COCl$ to para-substituted bis(aryl)ethanes affords the skeleton of the cyclopentadienyl-ring fragment in only one position relative to the ultimate 4,4′-CH_2-CH_2- bridge in the metallocene. Because Friedel−Crafts acylation is not regiospecific, three isomers of **2** are formed.[7] Subsequent ring closure of **2** with concentrated H_2SO_4 afforded three isomers of **3**.[7] Reduction with $NaBH_4$ and dehydration with dilute HCl gave two (double bond) isomers of **4**.[7] Reaction of [**4**]$^{2-}$ with $ZrCl_4$ in ether gave two (diastereo)isomers of **1** in a ca. 4:1 ratio (^{1}H/^{13}C NMR) which could be separated by extraction with toluene.

As well as different 7-Me ^{1}H NMR chemical shifts (δ2.60 ppm for **1r**;[8] δ2.33 ppm for **1m**[9]), the 4,4′-CH_2CH_2 bridge of **1r** gave a deceptively simple aa′bb′ pattern (δ3.04, 3.35 ppm; aa′ = 5.04, ab = a′b′ = −13.1, ab′ = a′b = 4.35, bb′ = 13.97 Hz, simulated), while **1m** gave a more complex pattern (δ3.29, 3.47 ppm; aa′ = 8.85, ab = −14.4, ab′ = 3.77, a′b = 8.51, a′b′ = −14.5, bb′ = 9.26 Hz, simulated).

To confirm that the two isomers were indeed the rac and meso isomers as expected by UFF molecular modeling (vide infra) and to understand the geometric consequences of a 4,4′-bridge, the X-ray crystal structures[7] of both **1r** and **1m** were determined. Their molecular structures are given in Figures 2 and 3.

Molecules of **1m**/**1r** consist of a Zr(IV) center coordinated by two chloride ligands and a bis(indenyl) ligand so as to form the meso(rac) isomer of **1**. The local geometry at zirconium is of

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[1] Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H.-H. *J. Organomet. Chem.* **1982**, *232*, 233. Wild, F. R. W. P.; Wasiuconek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1985**, *288*, 63.

[2] Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.

[3] Horton, A. D. *Trends Polym. Sci.* **1994**, *2*, 158. Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

[4] Ewen, J. A.; Haspeslagh, L.; Elder, M. J.; Atwood, J. L.; Zhang, H.; Cheng, H. N. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, Heidelberg, 1987; p 381. Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. *J. Organomet. Chem.* **1995**, *497*, 181. Spaleck, W.; Küber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954. Diebold, J.; Kirsten, R.; Röll, W.; Brintzinger, H. H.; Jüngling, S.; Mülhaupt, R.; Langhauser, F. *Organometallics* **1994**, *13*, 964.

[5] A bridged metallocene in which the bridge is part of an η-fused bis(tetrahydroindenyl) ligand has been reported. Könemaan, M.; Erker, G.; Fröhlich, R.; Kotila, K. *Organometallics* **1997**, *16*, 2900. Resconi, L.; Nifant'ev, I. E.; Dubitsky, Y. A.; Barbassa, E.; Schaverien, C. J.; Ernst, R. WO 96/38458 to Montell Technology Company. Uchino, H.; Endo, J.; Takahama, T.; Sugano, T.; Katoh, K.; Iwama, N.; Taniyama, E. Eur. Pat. Appl. 693502 to Mitsubishi Chemical Corporation. There was no mention of *rac* and *meso* isomers. Okamoto, T.; Uemura, M.; Watanabe, M.; Ohtani, T. WO 96/04317 (in Japanese) to Idemitsu Kosan.

[6] (i) 100 g (0.71 mol) of *p*-$MeC_6H_4CH_2Cl$ and 0.39 mol of Mg in 650 mL of THF gave 70 g of bis(tolyl)ethane, 93%. (ii) $ClCH_2CH_2COCl$, 1 equiv of $AlCl_3$ in CH_2Cl_2 at 0 °C gave **2** (3 isomers), 86%. (iii) Concentrated H_2SO_4, reflux 4 h, 94%. (iv) $NaBH_4$ added to **3** in THF/MeOH at 0 °C; then dehydration with HCl in ether gave **4**, 46%. (v) 82.5 mL of 1.6 M *n*-BuLi added to 18 g of **4** in ether at −78 °C, warmed to 20 °C; $ZrCl_4$ added at −40 °C and warmed to 20 °C. See the Supporting Information for full details.

[7] See the Supporting Information.

[8] ^{1}H NMR (CD_2Cl_2): δ 7.08−7.21 (dd, J = 6.9 Hz, 4H), 6.72 (t, J = 3.5 Hz, 2H, 5 ring), 6.67 (t, J = 3.5 Hz, 2H, 5 ring), 4.48 (dd, 2H, 5 ring), 3.35 (m, 2H, bridge), 3.04 (m, 2H, bridge), 2.60 (s, 6H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ 19.90 (CH_3), 36.58 (CH_2), 102.18 (CH, 5 ring), 108.48 (CH, 5 ring), 125.13 (CH, 6 ring), 126.48 (C), 126.55 (CH, 6 ring), 126.95 (C), 130.59 (CH), 135.08 (C), 137.08 (C) ppm.

[9] ^{1}H NMR (CD_2Cl_2): δ 7.14 (dd, J = 3.45 Hz, 2H, 5 ring), 6.67 (m, 4H, 6 ring), 6.60 (t, J = 3.45 Hz, 2H, 5 ring), 6.51 (dd, J = 3.45 Hz, 2H, 5 ring), 3.47 (m, 2H, bridge), 3.29 (m, 2H, bridge), 2.33 (s, 6H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ 19.62 (CH_3), 30.83 (CH_2), 99.30 (CH, 5 ring), 106.09 (CH, 5 ring), 121.52 (C), 122.76 (CH, 5 ring), 125.47 (CH, 6 ring), 125.75 (CH, 6 ring), 130.75 (C), 132.96 (C), 134.81 (C) ppm.

S0002-7863(98)01129-9 CCC: $15.00

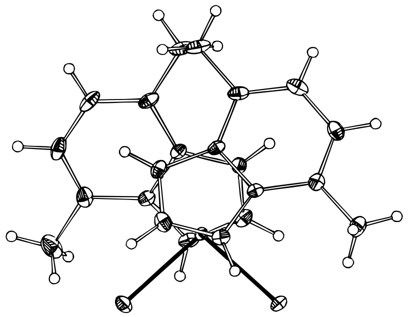

Figure 2. X-ray crystal structure of *rac*-1,2-CH_2CH_2\{4-(7-Me-indenyl)\}$_2$-$ZrCl_2$ (**1r**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are given arbitrary radii.

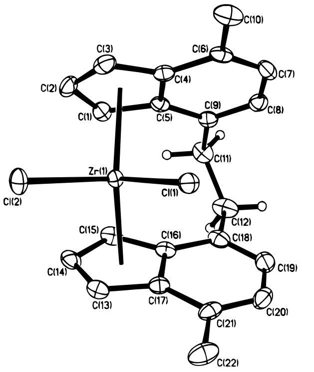

Figure 3. X-ray crystal structure of *meso*-1,2-CH_2CH_2\{4-(7-Me-indenyl)\}$_2$-$ZrCl_2$ (**1m**). Non-hydrogen atoms are represented as ellipsoids enclosing 50% probability density.

the usual distorted pseudo tetrahedral sort typical of group 4 metallocene dichlorides[1] (data for **1m**; **1r** in \{\}) (i.e., bond angles (°) Cl(1)−Zr(1)−Cl(2) 96.38 (3) \{94.50(3)\}, Cl(1)−Zr(1)−cp1 106.1 \{106.12(2)\}, Cl(2)−Zr(1)−cp1 105.1 \{107.64(2)\}, Cl(1)−Zr(1)−cp2 106.9 \{107.09(1)\}, Cl(2)−Zr(1)−cp2 105.7 \{105.43-(2)\}, cp1−Zr(1)−cp2 131.3 \{130.31(1)\}). The zirconium−chloride bond lengths are approximately equal at Zr−Cl(1) = 2.4330(7) Å and Zr−Cl(2) = 2.4464(7) \{2.4358(8), 2.4277(4)\} Å. The Zr−Cp centroid distances are effectively equal at Zr−Cp1 = 2.228 Å and Zr−Cp2 = 2.231 \{2.222, 2.226\} Å. The Zr−Cp bond lengths lie in the range of 2.458−2.634 Å \{2.466−2.586\} (av 2.535 \{2.527\} Å) indicating that the indenyl rings are η^5-coordinated to the zirconium. These parameters are quite normal for zirconium metallocenes.[1]

To gain insight into the geometry and strain energy of the isomers, **1**[10] was modeled using the Universal Force Field.[11,12] Two sets of calculations were performed: with and without Coulombic interactions. In the former case, the atomic charges were calculated using the charge equilibration method.[13] The range of validity of these methods has been previously described.[11−13] The lowest-energy isomer was the rac isomer in a gauche conformation.[7] The structure is in good agreement with that of **1r** as found by X-ray diffraction. The rac-anti bridge conformation was found not to be an equilibrium structure and was found by constraining the dihedral angle $C_{ipso}-CH_2-CH_2C_{ipso}$ to 180°. This led to an unstable rac-anti conformation with a very high strain energy (nonplanar indenyl rings) of 124 kcal mol^{-1}. Upon relaxation of this constraint, a second rac-gauche conformation was found with a strain energy 18 kcal mol^{-1} higher than the first.[7] These two rac-gauche conformations are separated by a transition barrier of 21 kcal mol^{-1} in which the hydrogen atoms in the $-CH_2-CH_2-$ bridge are approximately eclipsed. These UFF results were within 1−2 kcal mol^{-1}, with and without, Coulombic interactions. The strain energy of the meso isomer (also gauche) is 10 kcal mol^{-1} higher in energy than the lowest energy rac-gauche isomer with Coulombic interactions, and 4 kcal mol^{-1} higher without Coulombic interactions.[7] On the basis of these calculations, the isolation of both rac-gauche and *meso* metallocenes was to be expected.

Compound **1r**, after activation with excess MMAO, polymerizes[14,15] ethylene with an activity of 138 kg/g of Zr h to give high molecular weight polyethylene (M_v = 390 000[16]). The complex of **1m**/MMAO is more active (375 kg/g of Zr h) and gives polyethylene with lower molecular weight (M_v = 32 500). The complex of **1r**/MAO, polymerizes[17] propylene with an activity of only 10 kg/g of Zr h. The polymer has M_v = 122 000 and is highly regioregular with 99.7 mol % 1,2- and 0.3 mol % 3,1-insertions. No 2,1-units were observed. The polymer has low isotacticity (mm = 77%; mmmm = 65%). The complex of **1m**/MAO is appreciably more active (204 kg/g of Zr h) and affords atactic-PP (mm = 28%, mr = 49%, rr = 23 mol %) with a molecular weight M_v = 29 000. There were no regioerrors.

These catalysts were significantly more active for the copolymerization[18] of ethylene and propylene; **1r**/MAO afforded a high molecular weight (M_v = 335 000) copolymer with an activity of 230 kg copolymer/g of Zr h. The copolymer contained 60 mol % ethylene and 40 mol % propylene (^{13}C NMR). Under the same conditions, **1m**/MAO was much more active and afforded a high molecular weight (M_v = 224 000) copolymer with very high activity (5350 kg/g of Zr h; = 490 tons copolymer/mol of **1m** h!). ^{13}C NMR analysis indicated 75 mol % ethylene incorporation.

Further research will focus on gaining understanding into the potential of this new class of chiral metallocene and to improve polymer properties.

Acknowledgment. This research was sponsored by Montell Technology Company, Hoofddorp, The Netherlands. We thank Olof Sudmeijer (SRTCA) for running the NMR spectra of the (co)polymers and Tiziano Dall'Occo (Montell, Ferrara) for the ethylene polymerizations.

Note Added in Proof. Similar 4,4′-bridged metallocenes have just been published. Halterman, R. L.; Combs, D.; Khan, M. A. *Organometallics* **1998**, *17*, 3900−3707.

Supporting Information Available: Synthetic methods, polymerization details and results of UFF calculations, as well as tables of data collection parameters, atom coordinates, bond distances and angles for **1m** and **1r** (25 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[10] The 7-Me group was omitted in the UFF calculations. This should have little effect on the strain energy.

[11] Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024. The UFF calculations were performed using the Molecular Classical Mechanics (MCM) software written by Rappé and Skiff.

[12] A pseudoatom was used to attach each cyclopentadienyl ring to the metal center. Castonguay, L. A.; Rappé, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 5832.

[13] Rappé, A. K.; Goddard, W. A., III *J. Phys. Chem.* **1991**, *95*, 3358.

[14] Ethylene polymerizations at 80 °C under 9.6 bar in hexane using "modified" MAO with Al:Zr ratio = 1000.

[15] Under identical conditions, $CH_2CH_2(4,7\text{-dimethylindenyl})_2ZrCl_2/MAO$, as reference compound, gave polyethylene (molecular weight 205 000) with an activity of 420 kg/g of Zr h. See: Resconi, L.; Piemontesi, F.; Camurati, I.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Zeigler, R. *Organometallics* **1996**, *15*, 5046 and references therein.

[16] Polyethylene and atactic and isotactic polypropylene viscosity-averaged molecular weights (M_v) were obtained from the experimentally determined intrinsic viscosities using the correlations reported in the literature. For PE, $[\eta] = (3.8 \times 10^{-4})\ M_v^{0.725}$; for a-PP, $[\eta] = (1.85 \times 10^{-4})\ M_v^{0.74}$; for i-PP, $[\eta] = (1.93 \times 10^{-4})\ M_v^{0.74}$. Moraglio, G.; Gianotti, G.; Bonicello, U. *Eur. Polym. J.* **1973**, *9*, 623. Pearson, D. S.; Fetters, L. J.; Younghouse, L. B.; Mays, J. W. *Macromolecules* **1988**, *21*, 478.

[17] Propylene polymerizations were performed at 50 °C with 4 μmol of metallocene; Al:Zr ratio = 5000 in a 5 L reactor containing 1.6 kg of liquid propylene for 1 h.

[18] Copolymerizations at 50 °C with 0.49 μmol of metallocene, Al:Zr ratio = 40 000, in a 25 L reactor containing 7.5 kg liquid propylene and 6 mol % C_2H_4. The very large Al:Zr ratio is a consequence of the high catalyst activity. From experience, 20 mmol MAO is necessary for efficient and effective scavenging of 7.5 kg of liquid propylene in a 25 L autoclave. The very small amount of metallocene added therefore necessarily implies a very large Al:Zr ratio.