**AnsA-metallocone polymerization catalysts derived from [2 + 2]cycloaddition reactions of bis(1-methylethenyl-cyclopentadienyl)zirconium systems**

Jan Paradies, Gerald Kehr, Roland Fröhlich, and Gerhard Erker†

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, 48149 Münster, Germany

Edited by Tobin J. Marks, Northwestern University, Evanston, IL, and approved June 22, 2006 (received for review April 11, 2006)

Bis(1-methylethenyl-cyclopentadienyl)zirconium dichloride (7a) was prepared by a fulvene route. Photolysis at 0°C with Pyrex-filtered UV light resulted in a rapid and complete intramolecular [2 + 2]cycloaddition reaction to yield the corresponding cyclobutylene-bridged ansa-zirconocene dichloride isomer (8a). This is one of the rare examples of an organic functional group chemistry that leads to carbon-carbon coupling at the framework of an intact sensitive group 4 bent metallocene complex. More sterically hindered open metallocenes that bear bulky isopropyl or tert-butyl substituents at their Cp rings in addition to the active 1-methyl-ethenyl functional group undergo the photochemical ansa-metallocone ring closure reaction equally facile. The metallocene systems used and obtained in this study have served as transition metal components for the generation of active metallocene propene polymerization catalysts.

---

**Metallocene catalysis has become of great significance in olefin polymerization, especially for polyethylene, stereospecific propylene formation, and the production of some copolymers. The ansa-metallocenes of the group 4 metals and related systems play an essential role in this important development (1–3). Various methods have been devised and applied to construct such bent metallocene frameworks that feature a short carbon- or heteroatom-containing bridge between their substituted cyclopentadienyl, indenyl, or fluorenyl ligands. Because of the sensitive character of the organometallic group 4 metal complexes, ligand construction and variation is usually carried out at the free ligand stage before the final transmetallation step to the transition metal in the practical preparative sequences. This is a serious synthetic limitation. It would be highly desirable to have an organic functional group chemistry developed for framework variation at the actual metallocene stage.**

Previously, some addition reactions to metallocene frameworks had been reported, such as catalytic hydrogenation (4), hydrosilylation (5), hydroboration (6–9), or borylation (refs. 10, 11 and references therein, and 12). However, carbon-carbon coupling reactions at the intact group 4 bent metallocene frameworks were close to nonexistent before our work (13–15). Meanwhile, a few leading examples have emerged from the literature, using, e.g., olefin-metathesis (16–19) or even borylation (refs. 10, 11 and references therein, and 12). However, this specific reaction was not synthetically useful for a clean ansa-metallocene catalyst development because of its reversibility under the photochemical conditions to result in a photostationary equilibrium mixture of the open and closed isomers of most investigated examples under practical conditions (23, 24). We later showed that the [2-(1-methylethenyl)indenyl]2ZrCl2 derivative (3) rapidly and completely underwent the intramolecular photolytic [2 + 2]cycloaddition reaction when irradiated with Pyrex-filtered light to yield 4, from which an interesting homogeneous metallocene Ziegler-Natta catalyst system was generated (25–28). This posed the question as to whether the outcome of the intramolecular [2 + 2]photocyclization reaction at the group 4 bent metallocenes might significantly depend on the substituent at the allyl functional group and that the use of, e.g., the 1-methylalkenyl moiety might actually lead to a synthetically favorable situation. We have now prepared a small series of respective (1-methylethenyl-Cp)-derived group 4 metallocenes and found that the systems tested rapidly and completely underwent the intramolecular [2 + 2]cycloaddition to give their cyclobutylene-bridged ansa-zirconocene isomers, which were subsequently used to generate active metallocene Ziegler-Natta catalysts (Scheme 1).

**Results and Discussion**

The alkenyl-functionalized group 4 bent metallocenes (7) were synthesized by fulvene-derived routes (29–31). For the prepara-

Conflict of interest statement: No conflicts declared.

This article is a PNAS direct submission.

Abbreviations: DSC, differential scanning calorimetry; MAO, methylalumoxane.

Data deposition: The crystallographic data have been deposited in the Cambridge Structural Database (CSD), Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (CSD reference nos. 615770–615772).

†To whom correspondence should be addressed. E-mail: erker@uni-muenster.de.

© 2006 by The National Academy of Sciences of the USA
ratiion of the ligands the 6,6-dimethylfulvene derivatives (5) were treated with lithium disopropylamide to give the corresponding alkenyl-Cp lithium reagents (6), which were then reacted with ZrCl4(THF)2 (32) to yield the (1-methylethenyl-Cp)2ZrCl2 complexes (7) (Scheme 2).

Photochemical ansa-Zirconocene Formation. Bis(1-methylethenyl-Cp)ZrCl2 (7a) behaves like a conformationally rapidly equilibrating system of an averaged C2v-symmetry in solution (33) as judged from its NMR spectra. The photolysis of 7a with Pyrex-filtered light in toluene at 0°C led to a practically quantitative formation of the ligands the 6,6-dimethylfulvene derivatives (5) (Scheme 2).

In the crystal, complex meso-7c attains a chiral conformation with both tert-butyl groups pointing to one side but offset by ~1/5 C5 rotation. The C(Me)CH2 functional groups are likewise oriented at the opposite lateral sector of the bent metallocene with the alkenyl planes oriented close to parallel to their adjacent Cp planes [dihedral angles: C7A-C6A-C1A-C2A, 129.8°; C11-Zr-C11*, 96.20(4)°] [bond lengths: C6A-C7A, 1.34(5) Å; C6B-C7B, 1.37(5) Å]. One of the C=C groups (C6B-C7B) points to the front, and the other (C6A-C7A) points to the narrow back side of the bent metallocene wedge. The rac/meso-7b complex mixture (1:1) was photolyzed in toluene solution at room temperature. Within 1 h, a complete conversion to the respective cyclobutylene-bridged ansa-zirconocene isomers (8b) was effected. Principally, a mixture of oriented cis to each other. The bridging C11-C14 bond length inside the four-membered ring is 1.543(4) Å [1.552(4) Å].
three stereoisomers could be formed in this case, namely a rac and two meso (cis-meso and trans-meso) isomers. However, we observed the formation of a 1:1 mixture of rac-8b with only one of the meso isomers. We have tentatively assigned this product the trans-meso-8b structure from ¹H NMR NOE measurements. It features a set of three ¹H NMR C₅H₃ signals of the pair of symmetry-equivalent 1,3-disubstituted Cp ligands [at δ 6.38, 6.00, and 5.56 (each m, each 2H)], two signals of the cyclobutylene—CH₂—CH₂— protons (δ 2.15/1.54), and one set of ¹H NMR signals for the pair of symmetry-equivalent isopropyl substituents [δ 1.28 (d, 6H), 1.11 (d, 6H, CH₃), δ 3.40 (sept, 2H)], as well as a singlet of the pair of CH₃ groups at the cyclobutylene bridge [δ 0.98 (s, 6H)].

The isomer rac-8b features a total of ten C₅H₃R₁R₂ ¹³C NMR signals (δ 146.4, 142.2, 141.3, 139.8, 122.0, 116.5, 109.6, 109.1, 105.4, and 104.9) because of its lower symmetry. Likewise, there are a total of four cyclobutylene ¹³C NMR resonances [δ 49.8/49.5 (quart), δ 30.8/30.3 (CH₂)] and the ¹H NMR signals of a pair of attached methyl substituents [δ 1.01/1.00 (s, 3H each)]. The isopropyl substituents are spectroscopically differentiated because of their different position at the rigid rac-8b metallocene framework [δ (CH): 3.41/3.32 (¹H); 29.1/28.7 (¹³C)], and their attached methyl groups are diastereotopic [¹H NMR, δ 1.35, 1.22, 1.15, and 1.11 (each d, each 3H)].

Photolytic conversion of the 1:1 rac/meso-7c mixture to the ansa-metallocene isomers rac/meso-8c was complete after 1 h in toluene at room temperature. Again, the formation of only one of the two possible meso-8c isomers was observed. Analogous to the isopropyl-substituted system 8b, this isomer was tentatively assigned the trans-meso-8c structure according to its ¹H NMR NOE spectra (see Scheme 4).

From the mixture the meso-8c isomer is easily recognized by NMR because of its C₂-symmetry [three ¹H NMR C₅H₃ signals, δ 6.52 (H-4), 6.10 (H-5), and 5.98 (H-2), each of 2H intensity; five ¹³C NMR C₅H₃ resonances, δ 144.5 (C-3), 139.0 (C-1), 120.2 (C-4), 109.3 (C-2), and 108.5 (C-5)] and distinguished from the
are predominantly responsible for the formation of the rather atactic polymer, whereas the catalyst derived from the markedy higher isotacticity. It remains to be clarified which of the metallocene nucleus (23, 24). The interesting observation that were used as 1:1 meso/MAO mixtures. PDI, polydispersity index.

**Materials and Methods**

**Preparation of the (1-Methylethenyl-Cp)2ZrCl2 Complexes.** For the preparation of the parent compound (7a), 6,6-dimethylfulvene (5a) was treated with lithium disopropylamide to give 6a. The alkyl-lithium reagent (6a, 10.5 g, 94.0 mmol) was reacted with ZrCl4(THF)2 (17.7 g, 47 mmol) in toluene (~78°C to room temperature) to yield 9.45 g (54%) of 7a after recrystallization from dichloromethane. 1H NMR (500 MHz, 298 K, CDCl3): δ 6.51, 6.32 (each m, each 4H, 2-H to 5-H), 5.38/5.14 (4H, 1=CH2), 2.05 (dd, J = 1.5 Hz/0.9 Hz, 6H, CH3); 13C NMR (150.8 MHz, 298 K, CDCl3): δ 137.0 (C6), 131.4 (C1), 115.2/114.7 (C2–5), 113.7 (C7), 21.5 (C8); mp 180°C (decomp 273°C, differential scanning calorimetry (DSC)); anal. calculated for C22H30Cl2Zr (456.6): C 51.60%, H 4.81%; found: C 51.14%, H 4.95%. X-ray crystal structure analysis (single crystals from a concentrated solution in dichloromethane and storage at +4°C): orthorhombic, space group P212121, a = 11.805(1), b = 19.140(1), c = 6.784(1) Å, V = 1913.3(1) Å3, μ = 1.616 g cm–3, μ = 1.051 mm–1, empirical absorption correction (0.710 ≤ T ≤ 0.797), Z = 4, λ = 0.71073 Å, T = 198 K, ω and q scans, 1818 reflections collected (±h, ±k, ±l), |sin(θ)/λ| = 0.66 Å–1, 887 independent reflections (R(int) = 0.032) and 882 observed reflections (I ≥ 2σ(I)), 60 refined parameters, R = 0.020, wR2 = 0.050, =CH2 (CSA) and —CH3 (CSB) group refined independently with occupancy 0.5 for each; hydrogen atoms calculated and refined as riding atoms.

The substituted derivatives were prepared analogously. In theses cases, ~1:1 mixtures of meso/rac-7b and meso/rac-7c were obtained. The reaction of 6b (10.3 g, 66.8 mmol) with ZrCl4(THF)2 (12.6 g, 33.4 mmol) in 150 ml of toluene and recrystallization from dichloromethane gave 11.5 g (76%) of rac-7b (1:1). Anal. calculated for C22H30Cl2Zr (456.6): C 57.87%, H 6.62%; found: C 58.41%, H 6.94%; mp 107°C (decomp 205°C, DSC). 1H NMR (600 MHz, 298 K, d6-benzene): δ 8.37 (m, 2H, H-2), 5.95 (m, 2H, H-5), 5.69 (m, 2H, H-4), 5.17 (br d, J = 2.2 Hz, 2H, H-7), 4.89 (br d, J = 2.2 Hz, 2H, H-7), 3.27 (sept, J = 6.9 Hz, 2H, CHMe2), 1.86 (dd, J = 1.6 Hz/0.8 Hz, 6H, H-8), 1.17 (d, 6H) and 1.09 [d, J = 6.9 Hz, 6H, CH(CH3)2]; 13C NMR (78°C): δ 60.50 (m, 2H, H-2), 5.98 (m, 2H, H-5), 5.57 (m, 2H, H-4), 5.13 (dd, J = 2.2 Hz/1.5 Hz, 2H, H-7), 4.86 (dd, J = 2.2 Hz/0.8 Hz, 2H, H-7), 3.31 (sept, J = 6.9 Hz, 2H, CHMe2), 1.84 (dd, J = 1.5 Hz/0.8 Hz, 6H, H-8), 1.27 (d, J = 6.9 Hz, 6H), and 1.10 [d, 6H, CH(CH3)2]. For additional data, see Supporting Appendix, which is published as supporting information on the PNAS web site.

The 1:1 meso/rac-7c complex mixture was prepared analogously from 500 mg (2.97 mmol) of 6c and 555 mg (1.48 mmol)

### Table 1. Propene polymerization with the metallocene/MAO catalyst systems

<table>
<thead>
<tr>
<th>No.</th>
<th>Catalyst, mg mmol</th>
<th>Polypropylene, g</th>
<th>Activity</th>
<th>% mm/mm</th>
<th>Mw</th>
<th>Mn</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>14 (0.037)</td>
<td>34.3</td>
<td>464</td>
<td>6</td>
<td>1,520</td>
<td>2,690</td>
<td>1.78</td>
</tr>
<tr>
<td>8a</td>
<td>22 (0.059)</td>
<td>36.6</td>
<td>309</td>
<td>2</td>
<td>3,490</td>
<td>7,990</td>
<td>2.29</td>
</tr>
<tr>
<td>7b</td>
<td>20 (0.044)</td>
<td>11.5</td>
<td>131</td>
<td>4</td>
<td>3,830</td>
<td>7,680</td>
<td>2.01</td>
</tr>
<tr>
<td>8b</td>
<td>24 (0.053)</td>
<td>66.8</td>
<td>630</td>
<td>24</td>
<td>1,910</td>
<td>3,580</td>
<td>1.87</td>
</tr>
<tr>
<td>7c</td>
<td>14 (0.028)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8c</td>
<td>14 (0.028)</td>
<td>2.9</td>
<td>52</td>
<td>42</td>
<td>680</td>
<td>1,070</td>
<td>1.58</td>
</tr>
</tbody>
</table>

In toluene solution, MAO activated, 20°C, 2 bar propene, 1-h reaction time. 7b, 8b, 7c, and 8c were employed as 1:1 meso/rac-mixtures. PDI, polydispersity index.

In g polypropylene/mmol [Zr]-h-bar propene.
of ZrCl₄(THF)₂ to yield 539 mg (75%) of product. Anal. calculated for C₂₂H₃₀Cl₂Zr (456.6): C 57.87%, H 6.62%; found: C 56.51%, H 6.77%. Analogously, a 1:1 meso/rac-8c mixture (1.85 g, 82% yield) was isolated from photolysis of 2.00 g (34.13 mmol) of meso/rac-7c (1:1) dissolved in 100 ml of toluene, mp 143°C (decomp 214°C, DSC). Anal. calculated for C₂₄H₃₄Cl₂Zr (482.1): C 59.48%, H 7.07%; found: C 59.40%, H 7.04%. For spectral data, see Supporting Appendix.

Photolysis Reactions. The photolysis of a suspension of 7a (4.25 g, 11.4 mmol) in 30 ml of toluene at 0°C (Philips HPK 125-W, Pyrex filter) was carried out for 2.5 h. Solvent was removed in vacuo, and the product was washed with pentane to yield 4.12 g (97%) of the ansa-metallocene product 8a, mp 207°C (DSC). Anal. calculated for C₂₄H₃₄Cl₂Zr (372.4): C 51.60%, H 4.87%; found: C 51.56%, H 5.00%. X-ray crystal structure analysis (single crystals from a concentrated solution in toluene at room temperature): monoclinic, space group P2₁/n (no. 14), a = 11.746(1), b = 14.878(1), c = 14.452(1), β = 110.35(1), V = 2.368(0.3) Å³, ρcalc = 1.359 g cm⁻³, μ = 6.97 mm⁻¹, empirical absorption correction (0.873 ≤ T ≤ 0.979), Z = 4, λ = 0.7013 Å, T = 198 K, ω and φ scans, 25,904 reflections collected (±h, ±k, ±l), (sinθ/λ) = 0.66 Å⁻¹, 5.624 independent (Rint = 0.068) and 4,464 observed reflections (I ≥ 2σ(I)), 225 refined parameters, R = 0.036, wR² = 0.077. For spectroscopic data, see Supporting Appendix.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.