

The preferred 8-endo mode of cyclization of (alkoxycarbonyl)methyl radicals reflects the conformational bias of these radicals favoring *Z* conformation (*s-trans*) over *E* conformation (*s-cis*) (Scheme III). In line with many theoretical and experimental studies corroborating the relative stability of *Z* ester conformations, the *Z* conformation of the (alkoxycarbonyl)alkyl radicals was also judged to be more stable than the *E* conformation.^{13,14} The selective formation of eight-membered-ring heptanolactones in these cyclization reactions is probably also connected with the finding that the heptanolactone is the smallest lactone for which *Z* conformers are found as low-energy conformers.¹⁵

In conclusion, 8-endo cyclization is the fundamentally preferred mode of reaction for (alkoxycarbonyl)methyl radicals, and eight-membered heptanolactones are obtained in reasonably good yields from bromoacetates. Further mechanistic details and the synthetic utility of these unique reactions will be reported in due course.

Acknowledgment. The authors thank the Organic Chemistry Research Center (KOSEF) and Ukong Corporation for financial support.

(13) (a) Fisher, H.; Wu, L. M. *Helv. Chim. Acta* 1983, 66, 138. (b) Beckwith, A. L. J.; Glover, S. A. *Aust. J. Chem.* 1987, 40, 157.

(14) Atom-transfer cyclization of allyl iodoacetates is much more efficient at 80 °C than at 25 °C. This beneficial effect of temperature arises because at higher temperature there is a relatively larger population of the less stable *E* conformer (which can cyclize in 5-exo mode) of [(allyloxy)carbonyl]methyl radicals than at lower temperature. See: Curran, D. P.; Tamine, J. *J. Org. Chem.* 1991, 56, 2746.

(15) Wiberg, K. B.; Waldron, R. F. *J. Am. Chem. Soc.* 1991, 113, 7697.

Intramolecular [2 + 2] Cycloaddition of Bis(alkenylcyclopentadienyl)zirconium Dihalides: A Novel Way of Synthesizing *ansa*-Metallocene Complexes

Gerhard Erker* and Stephan Wilker

Organisch-Chemisches Institut der
Universität Münster, Corrensstrasse 40
D-4400 Münster, Germany

Carl Krüger and Richard Goddard

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-4330 Mülheim a.d. Ruhr, Germany
Received August 26, 1992

ansa-Metallocene complexes of the group 4 transition metals have played a decisive role for the development of homogeneous Ziegler-type catalysts for stereoselective α -olefin polymerization.¹ Two-carbon containing bridges between the metal bound η^5 -cyclopentadienyl units (or analogues thereof) are usually prepared by means of substitution reactions² or coupling of C_1 -substituted

(1) Ewen, J. A. *J. Am. Chem. Soc.* 1984, 106, 6355. Kaminsky, W.; Kùlper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* 1985, 97, 507. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 507.

(2) Schnutenhaus, H.; Brintzinger, H. H. *Angew. Chem.* 1979, 91, 837. *Angew. Chem., Int. Ed. Engl.* 1979, 18, 777. Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1982, 232, 233. Recent examples: Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* 1988, 7, 1828. Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* 1990, 9, 2695. Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem.* 1990, 102, 339. *Angew. Chem. Int. Ed. Engl.* 1990, 29, 279 and references cited therein. Bandy, J. A.; Green, M. L. H.; Gardiner, I. M.; Prout, K. J. *Chem. Soc., Dalton Trans.* 1991, 2207. Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* 1991, 10, 1501. Lang, H.; Seyferth, D. *Organometallics* 1991, 10, 347. Collins, S.; Gauthier, W. J.; Holden, D. A.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *Organometallics* 1991, 10, 2061. Collins, S.; Hong, Y.; Ramachandran, R.; Taylor, N. J. *Organometallics* 1991, 10, 2349. Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* 1992, 11, 1869.

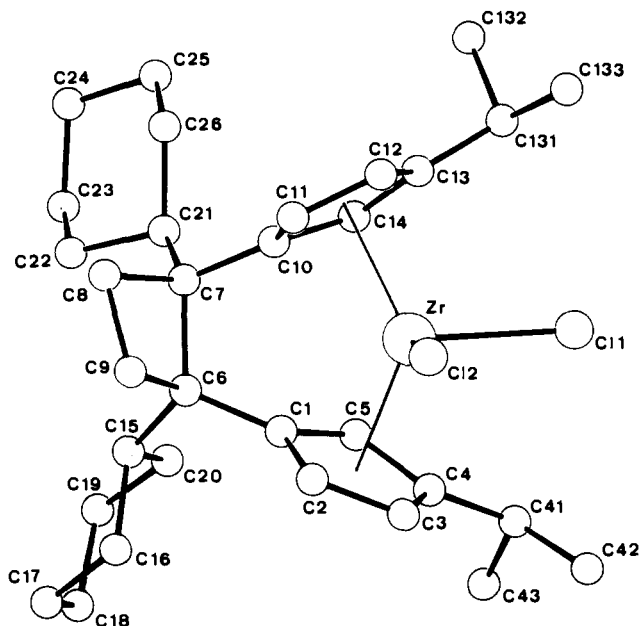


Figure 1. A view of the molecular structure of *meso*-5.

cyclopentadienyls.³ We here describe a novel method of synthesizing C_2 -bridged *ansa*-metallocene complexes by photochemically induced [2 + 2] cycloaddition of bis(alkenyl-Cp)MX₂ complexes.⁴ The two-carbon bridge in these compounds is part of a cyclobutane ring. A representative example is described here.

Bis(1-(cyclohexylethenyl)-3-isopropylcyclopentadienyl)zirconium dichloride (*rac*- and *meso*-4) was prepared by reacting the substituted alkenylcyclopentadienyllithium reagent **2** [generated by treatment of the 3-isopropyl-6-cyclohexylfulvene isomers (**1**) with LDA⁵] with 0.5 M equiv of ZrCl₄(THF)₂ (**3**). The isomers of **4** were separated by fractional crystallization from pentane (the pure diastereomers were isolated in ca. 10% yield each) and then irradiated with UV/vis light.⁶ Irradiation of *meso*-4 with Pyrex-filtered light from a high-pressure mercury lamp (Philips HPK 125, room temperature, 60 min, benzene solution) gave a 90:10

(3) Schwemlein, H.; Brintzinger, H. H. *J. Organomet. Chem.* 1983, 254, 69. Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* 1989, 369, 359. Kawase, T.; Nisato, N.; Oda, M. *J. Chem. Soc., Chem. Commun.* 1989, 1145. Recknagel, A.; Edelmann, F. T. *Angew. Chem.* 1991, 103, 720. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 693. Burger, P.; Brintzinger, H. H. *J. Organomet. Chem.* 1991, 407, 207. Burger, P.; Hortmann, K.; Diebold, J.; Brintzinger, H. H. *J. Organomet. Chem.* 1991, 417, 9. Burger, P.; Diebold, J.; Gutmann, S.; Hund, H.-U.; Brintzinger, H. H. *Organometallics* 1992, 11, 1319. Dorer, B.; Diebold, J.; Weyand, O.; Brintzinger, H. H. *J. Organomet. Chem.* 1992, 427, 245 and references cited therein. For coupling reactions leading to C_1 -bridged *ansa*-metallocene systems, see: Ewen, J. A.; Haspelslagh, L.; Atwood, J. L.; Zhang, H. J. *J. Am. Chem. Soc.* 1987, 109, 6544. Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* 1990, 112, 2030. Llinas, G. H.; Dong, S.-H.; Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Winter, H. H.; Chien, J. C. W. *Macromolecules* 1992, 25, 1242 and literature cited in these references.

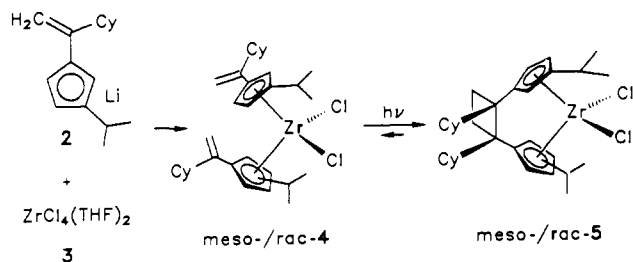
(4) For examples of remotely related organometallic [2 + 2] cycloaddition reactions, see: Nakanishi, K.; Mizuno, K.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* 1990, 3362. Nakadira, Y.; Sakurai, H. *Tetrahedron Lett.* 1971, 1183. Bichler, R. E. J.; Booth, M. R.; Clark, H. C. *Inorg. Nucl. Chem. Lett.* 1967, 3, 71. See, also: Nesmeyanov, A. N.; Sazonova, V. A.; Romanenko, V. I.; Rodionova, N. A.; Zolnikova, G. P. *Dokl. Akad. Nauk. SSSR* 1963, 149, 1354; *Chem. Abstr.* 1963, 59, 3460. Related reviews: Bozak, R. E. *Adv. Photochem.* 1971, 8, 227. Seebach, D. In *Houben-Weyl, Methoden der Organischen Chemie*; Müller, E., Ed.; Thieme: Stuttgart, 1971, Vol. IV/4. Kaupp, G. In *Houben-Weyl, Methoden der Organischen Chemie*; 1975; Vol. IV/5a, pp 278-412.

(5) For leading references concerning the synthetic procedures involved, see: Huang, Q.; Qian, Y. *Synthesis* 1987, 710. Fiaud, J. C.; Malleron, J. L. *Tetrahedron Lett.* 1980, 21, 4437. Stone, K. J.; Little, R. D. *J. Org. Chem.* 1984, 49, 1849. Erker, G.; Aul, R. *Chem. Ber.* 1991, 124, 1301 and references cited therein.

(6) UV/vis absorptions in CH₂Cl₂: *meso*-4, λ_{max} = 242 nm (ϵ = 20 400), 265 (sh, ϵ = 14 600), 340-375 (br, ϵ \approx 3000); *rac*-4, λ_{max} = 239 nm (ϵ = 22 200), 265 (sh, ϵ = 17 200), 340-370 (br, ϵ \approx 4000); *meso*-5, λ_{max} = 240 nm (ϵ = 49 000); *rac*-5, λ_{max} = 234 nm (ϵ = 56 000).

photostationary equilibrium of *meso*-5 and *meso*-4. The [2 + 2] cycloaddition product was crystallized from pentane and analyzed by X-ray diffraction.

The X-ray crystal structure analysis of *meso*-5 revealed that stereoselective head-to-head addition had occurred exclusively at the bent metallocene unit giving only one of two possible *Z*-substituted cyclobutane products, namely the one having the cyclohexyl substituents at the four-membered ring and the isopropyl groups at the Cp rings in a *syn* arrangement. The newly formed cyclobutane moiety is slightly puckered. The carbon-carbon bond between the tetrasubstituted ring carbons C(6)–C(7) is rather long at 1.624 (2) Å; in contrast the C(8)–C(9) distance is as expected for a "normal" C(sp³)–C(sp³) single bond at 1.524 (3) Å.⁷ The Cp(centroid)–Zr–Cp(centroid) angle of the *ansa*-metallocene *meso*-5 is 123.9°. The Cl(1)–Zr–Cl(2) angle is 97.2 (1)°. These values place complex *meso*-5 in a typical range of characteristic structural features of C₂-bridged group 4 *ansa*-metallocenes.⁸



The chiral bis(alkenyl-Cp)metal dihalide complex *rac*-4 produces a slightly different photostationary equilibrium at *rac*-5/*rac*-4 = 75:25⁶ when irradiated under analogous conditions (room temperature, 90 min, toluene solution, Philips HPK-125 lamp, Pyrex-filter). Extraction of the mixture with pentane gave pure *rac*-5 (mp 180–182 °C, 60% isolated). The spectroscopic data again revealed that stereoselective head-to-head [2 + 2] cycloaddition had taken place giving the *Z*-configured cyclobutene-bridged *ansa*-metallocene. Thus, complex *rac*-5 exhibits two sets of cyclopentadienyl NMR resonances (C₁ symmetry), whereas the respective Cp signals of the *meso*-5 isomer (C_s) are symmetry equivalent.⁹

In orientating experiments both 1,2-cyclohexylcyclobutene-bridged *ansa*-metallocenes were used for generating homogeneous propene polymerization catalysts. Activation of *meso*-5 with methylalumoxane in toluene (Al/Zr ratio = 1600) gave a catalyst system which produced atactic polypropylene (–8 °C, activity *a* ≈ 2000 g polymer/g[Zr]·h). The *rac*-5/(MeAlO)_x catalyst (Al/Zr = 400) gave partially isotactic polypropylene at –22 °C

(7) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* 1987, S1.

(8) Smith, J. A.; von Seyler, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1979, 173, 175. Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1985, 288, 63. Wochnner, F.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1985, 288, 69. Schäfer, A.; Karl, E.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1987, 328, 87. Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* 1988, 342, 21. Gutmann, S.; Burger, P.; Hund, H.-U.; Hofmann, J.; Brintzinger, H. H. *J. Organomet. Chem.* 1989, 369, 343. Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem.* 1989, 101, 1536. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1511. Gómez, R.; Cuenca, T.; Royo, P.; Herrmann, W. A.; Herdtweck, E. *J. Organomet. Chem.* 1990, 382, 103. Gómez, R.; Cuenca, T.; Royo, P.; Hovestreydt, E. *Organometallics* 1991, 10, 2516 and references cited therein.

(9) *meso*-5: X-ray crystal structure analysis, space group P2₁/n, *a* = 13.779 (1) Å, *b* = 13.245 (1) Å, *c* = 16.423 (1) Å, β = 95.55 (1)°, 11 101 reflections measured, 7936 observed, V = 2983.4 Å³, d_{calc} = 1.32 g cm⁻³, Z = 4, 500 parameters refined, R = 0.035, R_w = 0.039. Selected ¹H/¹³C NMR data (benzene-d₆) δ 6.12, 6.07, 5.87 (CH, Cp-hydrogens), 3.28 (2 H), 1.18 and 1.08 (6 H each, CH₃, isopropyl)/δ 148.7, 138.4, 115.7, 112.0, 104.9 (Cp carbon atoms), 31.1, 23.4, 22.8 (isopropyl). *rac*-5: Anal. Calcd for C₃₂H₄₆Cl₂Zr: C, 64.83; H, 7.82. Found: C, 64.17; H, 7.97. Selected ¹H/¹³C NMR data (benzene-d₆) δ 6.63, 6.15, 6.01, 5.89 (double intensity), 5.85 (6 H, Cp hydrogens), 3.40, 3.26 (2 H), 1.42, 1.21, 1.18, 1.08 (3 H each, CH₃, isopropyl)/δ 149.0 (double intensity), 141.4, 138.7, 115.0, 112.9, 111.6, 108.7, 106.2, 104.7 (Cp carbon atoms), 33.7, 33.7, 23.6, 22.6, 22.1, 21.4 (isopropyl).

(M_n = 3500, *a* = 126). Stereochemical analysis of this polymer (¹³C NMR methyl pentades with statistical treatment as previously described¹⁰) revealed a typical situation of double stereodifferentiation [formally 60% enantiomeric site control (α = 0.73) and 40% chain end control (σ = 0.81)].^{10,11}

In contrast to the metallocenes of the late transition metals only very few reactions at the Cp rings of the much more sensitive early d- and f-element metallocenes have been found so far. Using photochemical reactions such as the one described here provides attractive alternatives for synthesizing useful metallocene derivatives of these electropositive and very oxophilic elements.

Acknowledgment. Financial support from the Fonds der Chemischen Industrie, the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, and the Alfred Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

Supplementary Material Available: Tables of X-ray crystal structure analysis data for complex *meso*-5 including lists of bond lengths and angles and atomic coordinates (11 pages); listing of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

(10) Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* 1975, 8, 1565. Farina, M. *Top. Stereochem.* 1987, 17, 1. Bovey, F. A.; Tiers, G. V. D. *J. Polym. Sci.* 1960, 44, 173. Sheldon, R. A.; Fueno, T.; Tsuntsuga, T.; Kurukawa, J. *J. Polym. Sci. B* 1965, 3, 23. Inoue, J.; Itabashi, Y.; Chujo, R.; Doi, Y. *Polymer* 1984, 25, 1640. For details concerning the procedures used for the polymer analysis, see: Erker, G.; Nolte, R.; Aul, R.; Wilker, S.; Krüger, C.; Noe, R. *J. Am. Chem. Soc.* 1991, 113, 7594 and references cited therein.

(11) Erker, G.; Nolte, R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* 1989, 101, 642. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 628.

A Double Addition Product of C₆₀: C₆₀[Ir(CO)Cl(PMe₂Ph)₂]₂. Individual Crystallization of Two Conformational Isomers

Alan L. Balch,* Joong W. Lee, Bruce C. Noll, and Marilyn M. Olmstead

Department of Chemistry
University of California, Davis
Davis, California 95616
Received September 8, 1992

Multiple addition reactions, which are frequently reversible, have emerged as a major feature of the chemistry of C₆₀.¹ Often the occurrence of these multiple additions has given rise to mixtures of products that are difficult to separate and fully characterize. The most thoroughly characterized multiple addition products include the brominated derivatives (C₆₀Br₂₄,² C₆₀Br₃₆,³ and C₆₀Br₆₃)³ and organometallic derivatives (C₆₀[Pt(PEt₃)₂]₂,⁴ C₆₀[Pd(PEt₃)₂]₂,⁵

(1) Holloway, J. H.; Hope, E. G.; Taylor, R.; Langley, G. J.; Avent, A. G.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* 1991, 966. Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem.* 1991, 103, 1339. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 1309. Kalsbeck, W. A.; Thorp, H. H. *J. Electroanal. Chem.* 1991, 314, 363. Krusic, P. J.; Wasserman, E.; Keizer, P. N.; Morton, J. R.; Preston, K. F. *Science* 1991, 254, 1183. Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* 1991, 254, 1186. Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* 1991, 113, 9387. Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* 1991, 113, 9385. Tebbe, F. N.; Becker, J. Y.; Chase, D. B.; Firment, L. E.; Holler, E. R.; Malone, B. S.; Krusic, P. J.; Wasserman, E. *J. Am. Chem. Soc.* 1991, 113, 9900. Wudl, F. *Acc. Chem. Res.* 1992, 25, 157. Hawkins, J. M. *Acc. Chem. Res.* 1992, 25, 150.

(2) Tebbe, F. N.; Harlow, R. L.; Chase, D. B.; Thorn, D. L.; Campbell, G. C., Jr.; Calabrese, J. C.; Herron, N.; Young, R. J., Jr.; Wasserman, E. *Science* 1992, 256, 822.

(3) Birkett, P. R.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* 1992, 357, 479.

(4) Fagan, P. J.; Calabrese, J. C.; Malone, B. *J. Am. Chem. Soc.* 1991, 113, 9408.

(5) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* 1992, 25, 134.