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Formation and Structure of a Novel Large-Ring Group 4 *ansa*-Metallocene Complex

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1,12-Dodecanediol was treated with 2 molar equiv of methanesulfonyl chloride and then with indenyllithium to yield 1,12-bis(3-indenyl)dodecane (**4**). Double deprotonation of **4** with *n*-butyllithium gave the corresponding dilithio compound **5**. Its reaction with $ZrCl_4(THF)_2$ in tetrahydrofuran under high dilution conditions gave the large-ring *ansa*-metallocene dihalide complex *rac*-**6** in 15% isolated yield. Under similar conditions the reaction of **5** with $ZrCl_4(THF)_2$ in toluene solvent allowed the isolation of the diastereoisomer *meso*-**6** in 11% yield. The complex *rac*-**6** was hydrogenated to yield the corresponding large-ring *ansa*-bis(tetrahydroindenyl)zirconium dichloride complex *rac*-**8**. Each of the complexes *rac*-**6**, *meso*-**6**, and *rac*-**8** reacted cleanly with methyllithium to yield the corresponding *ansa*-metallocene dimethyl derivatives (*rac*-**7**, *meso*-**7**, *rac*-**9**). The organic compound **4** and the *ansa*-metallocene *rac*-**6** were characterized by X-ray diffraction. In the solid state the metallocene precursor **4** exhibits a $(-CH_2-)_{12}$ chain at its maximal elongation, which separates the indenyl end groups intramolecularly as far as possible. In the large-ring *ansa*-metallocene dichloride complex *rac*-**6** the 1,12-dodecanediyl chain that connects the two η^5-indenyl ligands is oriented in a nearly C_2-symmetric arrangement in the central position in front of the bent-metallocene wedge. In this orientation the mean plane of the $(-CH_2-)_{12}$ loop is arranged orthogonal to the $ZrCl_2$ σ-ligand plane and spatially separates the two segments in front of the bent-metallocene unit where the reactive σ-ligands are located.

ansa-Metallocene complexes of the group 4 transition metals containing small 1,ω-alkanediyl moieties connecting the two Cp or, more importantly, indenyl, tetrahydroindenyl, or fluorenyl ligands and their alkyl-substituted derivatives have been employed in both catalysis and organometallic-mediated organic synthesis.[1,2] Of particular interest are the *ansa*-metallocenes containing methylene, silylene, or ethylene bridges, as they are used for generating extremely active homogeneous Ziegler-type catalysts for the stereoselective polymerization of α-olefins.[3] In addition, a number of special examples have been reported that contain, for example, four-carbon bridges between the η^5-cyclo-C_5 ligand systems.[4] All these complexes have the size of the small alkanediyl moieties in common, allowing only for a few specific conformational arrangements. In these the bridging unit is oriented at the back of the bent-metallocene wedge, i.e. directed away from the σ-ligands at the pseudo-tetrahedrally coordinated group 4 metal center.[5] We thought it would be very interesting to prepare counterparts of the existing *ansa*-metallocenes that contain much longer alkanediyl bridging moieties with the oligomethylene chain oriented in a stable and favored conformational arrangement in front of the bent-metallocene unit.[6] A symmetrical orientation of this $(-CH_2-)_n$ bridging moiety at the open side of the bent-

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[1] Ewen, J. A. *J. Am. Chem. Soc.* **1984,** *106,* 6355. Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* **1985,** *97,* 507; *Angew. Chem., Int. Ed. Engl.* **1985,** *24,* 507. Spaleck, W.; Aulberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem.* **1992,** *104,* 1373; *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1347.

[2] Jordan, R. F.; La Pointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990,** *9,* 1539. Grossman, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991,** *113,* 2321. Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991,** *10,* 1501. Chen, Z.; Halterman, R. L. *J. Am. Chem. Soc.* **1992,** *114,* 2276. Halterman, R. L.; Ramsey, T. M. *Organometallics* **1993,** *12,* 3879 and references cited therein.

[3] Schnutenhaus, H.; Brintzinger, H. H. *Angew. Chem.* **1979,** *91,* 837; *Angew. Chem., Int. Ed. Engl.* **1979,** *18,* 777. Schwemlein, H.; Brintzinger, H. H. *J. Organomet. Chem.* **1983,** *254,* 69. Röll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem.* **1990,** *102,* 339; *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 279. 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. Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987,** *109,* 6544. Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988,** *7,* 1828. Kawase, T.; Nisato, N.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1989,** 1145. Herrmann, W. A.; Rohrmann, J.; Herdtweck, E.; Spaleck, W.; Winter, A. *Angew. Chem.* **1989,** 101, 1536; *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1511. Reddy, K. P.; Petersen, J. L. *Organometallics* **1989,** *8,* 2107. Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990,** *9,* 2695. 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. 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. Bandy, J. A.; Green, M. L. H.; Gardiner, I. M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1991,** 2207. Gomez, R.; Cuenca, T.; Royo, P.; Hovestreydt, E. *Organometallics* **1991,** *10,* 2516. Recknagel, A.; Edelmann, F. T. *Angew. Chem.* **1991,** *103,* 720; *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 693. Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992,** *11,* 1869. Rieger, B. *J. Organomet. Chem.* **1992,** *428,* C33. Nifant'ev, I. E.; Churakov, A. V.; Urazowski, I. F.; Mkoyan, Sh. G.; Atovmyan, L. O. *J. Organomet. Chem.* **1992,** *435,* 37. Erker, G.; Wilker, S.; Krüger, C.; Goddard, R. *J. Am. Chem. Soc.* **1992,** *114,* 10983. Erker, G.; Wilker, S.; Krüger, C.; Nolte, M. *Organometallics* **1993,** *12,* 2140. See also literature cited in these references.

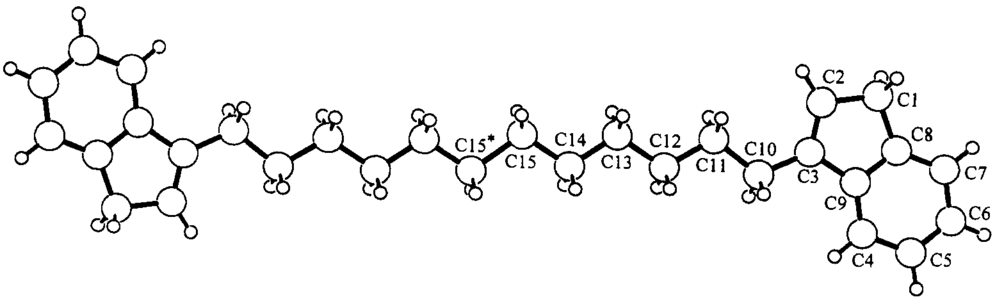


Figure 1. View of the molecular geometry of 1,12-bis(3-indenyl)dodecane (**4**) in the solid state.

metallocene wedge would constitute a separating entity of the segments of space where the σ-ligands and with them the chemically reactive units are located at the (μ-R)Cp_2MX_2 type compounds. Such a physical separation of the active binding sites at the front of the bent-metallocene fragment could eventually have interesting consequences with regard to influencing and controlling reactions at such group 4 metallocene derived reagents and catalysts. We have now developed a route for preparing *ansa*-metallocene complexes with such a characteristic structure. The synthesis and structural characterization of the first typical example are described herein.

Results and Discussion

We have converted 1,12-dodecanediol (**1**) to the bis(methanesulfonate) **2**, which was then treated with 2 molar equiv of indenyllithium in tetrahydrofuran at room temperature. The expected S_N2 substitution product is 1,12-bis(1-indenyl)dodecane (**3**). However, under the applied reaction conditions this is not obtained due to isomerization.[7] 1,12-Bis(3-indenyl)dodecane (**4**) was isolated in 85% yield. This attachment of the substituent at the indene 3-position was evident from the NMR spectra (^{1}H NMR ($CDCl_3$) δ 3.32 (1-H), 6.19 (2-H); ^{13}C NMR ($CDCl_3$) δ 37.7 (C1), 119.0 (C2), 145.7 (C3)). This structural feature was confirmed by an X-ray crystal structure analysis of **4**, showing a center of inversion and the C(2)–C(3) double bond (1.331(2) Å; d[C(1)–C(2)] = 1.494(2) Å) with the substituent attached at carbon atom C(3) ($\angle$C(2)–C(3)–C(10) = 129.4(1)°).

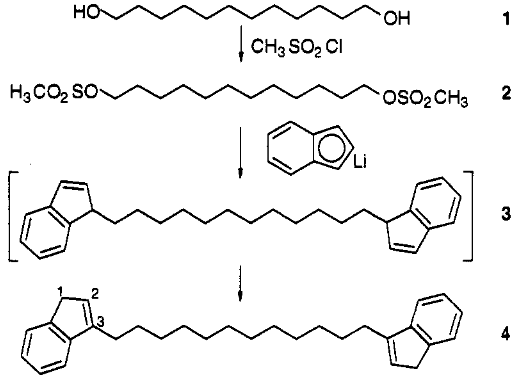
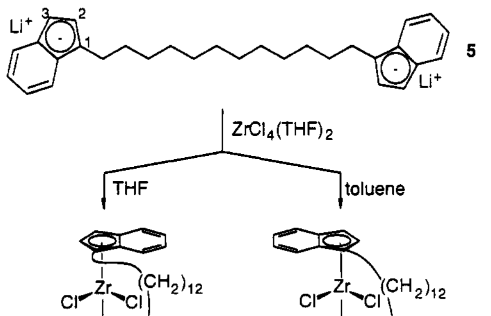


Figure 1 may serve to demonstrate some of the difficulties that arise with the synthesis of an *ansa*-metallocene starting from **4**. The two indenyl moieties in the dodecanediyl-bridged bis(indenyl) ligand system are spatially separated from each other. In the solid state the bis(indenyl)dodecane favors an overall conformational arrangement which takes the two indenyl moieties intramolecularly as far apart from each other as possible.[8] Consequently, this leads to some initial problems in pursuing the planned synthesis.

The dodecamethylene-bridged bis(indenyl) system **4** was treated with 2 molar equiv of n-butyllithium in ether. Double deprotonation gave the corresponding 1,12-bis(lithioindenyl)dodecane system **5** (isolated as a solid in 85% yield; ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8, 8:2) δ 6.58



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(4) Lang, H.; Seyferth, D. *Organometallics* **1991**, *10*, 347. Hollis, T. K.; Rheingold, A. L.; Robinson, N. P.; Whelan, J.; Bosnich, B. *Organometallics* **1992**, *11*, 2812. Huttenloch, M. E.; Diebold, J.; Rief, U.; Brintzinger, H.-H.; Gilbert, A. M.; Katz, T. J. *Organometallics* **1992**, *11*, 3600. Scott, P.; Rief, U.; Diebold, J.; Brintzinger, H. H. *Organometallics* **1993**, *12*, 3094 and references cited therein.

(5) See also: Smith, J. A.; von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175. Röll, W.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1987**, *322*, 65.

(6) For conformational preferences of substituted bent-metallocene complexes see: Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422. Dusausoy, Y.; Protas, J.; Renaut, R.; Gautheron, G.; Tainturier, G. *J. Organomet. Chem.* **1978**, *157*, 167. Broussier, R.; Rold, A. D.; Gautheron, B.; Dromzee, Y.; Jeannin, Y. *Inorg. Chem.* **1990**, *29*, 1817. Howie, R. A.; McQuillan, G. P.; Thompson, D. W. *J. Organomet. Chem.* **1984**, *268*, 149. Howie, R. A.; McQuillan, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213. Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. *Angew. Chem.* **1986**, *98*, 456; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463. Erker, G.; Mühlenbernd, R.; Nolte, R.; Petersen, J. L.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1986**, *314*, C21. Erker, G.; Schlund, R.; Krüger, C. *J. Organomet. Chem.* **1988**, *338*, C4. Erker, G.; Nolte, R.; Tainturier, G.; Rheingold, A. L. *Organometallics* **1989**, *8*, 454. Krüger, C.; Nolte, M.; Erker, G.; Thiele, S. *Z. Naturforsch., B* **1992**, *47B*, 995. Erker, G.; Aulbach, M.; Knickmeier, M.; Wingbermühle, D.; Krüger, C.; Nolte, M.; Werner, S. *J. Am. Chem. Soc.* **1993**, *115*, 4590. Antinolo, A.; Lappert, M. F.; Singh, A.; Winterborn, D. J. W.; Engelhardt, L. M.; Raston, C.; White, A. H.; Carty, A. J.; Taylor, N. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1463. Urazowski, I. F.; Ponomaryov, V. I.; Ellert, O. G.; Nifant'ev, I. E.; Lemenovskii, D. A. *J. Organomet. Chem.* **1988**, *356*, 181. Urazowski, I. F.; Ponomaryev, V. I.; Nifant'ev, I. E.; Lemenovskii, D. A. *J. Organomet. Chem.* **1989**, *368*, 287. Huang, Q.; Qian, Y.; Tang, Y.; Chen, S. *J. Organomet. Chem.* **1988**, *340*, 179. Kapon, M.; Reisner, G. M. *J. Organomet. Chem.* **1989**, *367*, 77. Mallin, D. T.; Rausch, M. D.; Mintz, E. A.; Rheingold, A. L. *J. Organomet. Chem.* **1990**, *381*, 35. Ogasa, M.; Mallin, D. T.; Macomber, D. W.; Rausch, M. D.; Rogers, R. D.; Rollins, A. N. *J. Organomet. Chem.* **1991**, *405*, 41. See also references cited in the articles above.

(7) Dehmlow, E. V.; Bollmann, C. *Tetrahedron Lett.* **1991**, *32*, 5773.

(8) Menger, F. M.; Monnier, C. E. *J. Org. Chem.* **1993**, *58*, 1655.

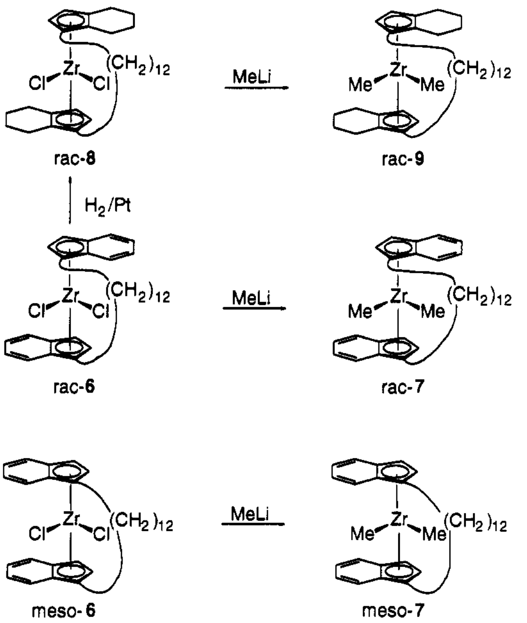
(2-H), 6.04[9] (3H, ^3J(2-H,3-H) = 3.2 Hz, ^5J(3-H,7-H) = 0.7 Hz)[10]). Straightforward treatment of **5** with 0.5 molar equiv of $ZrCl_4(THF)_2$ under the conditions usually applied for metallocene formation (~40 mM concentration of the reagents in THF, addition at −78 °C, warming to 25 °C, followed by workup at ambient temperature) resulted in the formation of a complex mixture of organometallic products whose components could not be separated and completely identified as yet. From a comparison of the ^1H NMR spectra it became evident that the desired *ansa*-metallocenes **6** (vide infra) were among the products formed from zirconium tetrachloride and the 1,12-bis(lithioindenyl)dodecane reagent **5** under these conditions but were obtained admixed with several major unidentified organometallic components. The reaction proceeded much more selectively when it was conducted under special high dilution conditions. Solutions of both reagents were added simultaneously from two separate funnels dropwise to a large volume of refluxing tetrahydrofuran solvent. Under these conditions an instantaneous bimolecular reaction was ensured to take place. Pentane extraction after removal of the THF solvent and crystallization gave a single organometallic product in 15% yield, which was identified as the *rac* diastereomer of the *ansa*-bis(indenyl)zirconium dichloride **6**, containing a 1,12-dodecanediyl moiety connecting the two indenyl ligand systems.

On the NMR time scale complex *rac*-**6** appears to be C_2 symmetric in solution; i.e., it features a pair of symmetry-equivalent η^5-indenyl ligands, substituted at their respective 1-positions and fused by an equally C_2-symmetrical $(-CH_2-)_{12}$ chain. Complex *rac*-**6** thus exhibits a simple set of ^1H NMR signals for the indenyl methine hydrogen atoms 2-H and 3-H at δ 6.26 and 5.30 ($CDCl_3$, ^3J(2-H,3-H) = 3.1 Hz; ^5J(3-H,7-H) = 0.7 Hz; ^{13}C NMR ($CDCl_3$) δ 121.3, 103.9 (C-2, C-3)).

The stereochemical outcome of the reaction between the bis(lithioindenyl) reagent **5** and zirconium tetrachloride is remarkably solvent-dependent.[11] The reaction was carried out under high-dilution conditions similar to those described above but with toluene at reflux temperature as the major solvent medium to which THF solutions of the reagents were simultaneously added. Workup and crystallization gave the *ansa*-metallocene product *meso*-**6** in 11% isolated yield, with a small amount of the more soluble *rac*-**6** diastereomer remaining in the mother liquor. Complex *meso*-**6** exhibits $^1H/^{13}C$ NMR spectra that are markedly different from those for *rac*-**6** (e.g. δ 6.46, 6.43 (3-H,2-H)/δ 113.2, 96.2 (C-2, C-3) in benzene-d_6).

The molecular symmetries of the pair of *rac*-**6** and *meso*-**6** complexes were confirmed by chemical derivatization introducing a symmetry probe. The chiral C_2-symmetric racemate of the *ansa*-metallocene dichloride diastereoisomer *rac*-**6** was treated with 2 molar equiv of methyllithium[12] in ether to yield the corresponding *ansa*-metallocene dimethyl complex *rac*-**7** (65%). The zirconium-bound methyl groups are arranged in the common σ-ligand plane at the bent-metallocene wedge which bisects the Cp–Zr–Cp angle. Therefore, these CH_3 groups are symmetry-equivalent (C_2 operation). Consequently, only a single CH_3 resonance is observed for complex *rac*-**7** in both the ^1H (δ −0.64 in benzene-d_6) and ^{13}C (δ 37.2) NMR spectra.

Scheme 1



The same symmetry effect was observed in the related *ansa*-bis(tetrahydroindenyl)zirconium series. The *ansa*-bis(indenyl)zirconium dichloride *rac*-**6** was hydrogenated (PtO_2, CH_2Cl_2, 60 bar of H_2)[13] to give the *ansa*-bis(tetrahydroindenyl)$ZrCl_2$ complex *rac*-**8** (85% isolated). Subsequent treatment with methyllithium gave the dimethyl *ansa*-metallocene complex *rac*-**9** (oil, 70% yield), which shows a single ^1H NMR methyl resonance at δ −0.20 (in benzene-d_6) and a single $^{13}CH_3$ signal at δ 35.0.

The C_s-symmetric *meso*-**6** diastereoisomer was also converted to the corresponding dimethyl metallocene derivative by treatment with CH_3Li. Due to the position of the zirconium-bonded σ-ligands *in* the molecular mirror plane of the *ansa*-bis(indenyl)$ZrMe_2$ product *meso*-**7**, the methyl groups are not symmetry-equivalent. Therefore, the C_s-symmetric complex *meso*-**7** exhibits a 1:1 pair of CH_3 resonances in both the ^1H (δ −0.58 and −1.02 in benzene-d_6) and ^{13}C (δ 50.8 and 42.2) NMR spectra.

The *ansa*-bis(indenyl)zirconocene dichloride complex *rac*-**6** was characterized by X-ray diffraction. The zirconium center is coordinated to two substituted η^5-indenyl ligands and two chlorides in a pseudotetrahedral environment. In the crystal the complex is close to C_2 symmetric. The Zr–Cl(1)/Cl(2) distances are 2.428(1) and 2.431(1) Å, respectively. The Cl(1)–Zr–Cl(2) angle is 98.4(1)°. These values are in the typical range observed for many zirconocene dichloride complexes. The bonds between zirconium and the indenyl five-membered rings are between 2.442(2) and 2.630(2) Å. The relative orientation of the two five-membered-ring systems is almost staggered (θ = 24.8° (i.e. not too far from the expected value of 36° for this situation)). The annulated six-membered rings are both oriented relatively far toward the narrow back side of the bent-metallocene wedge. This allows the bridging dodecamethylene chain of the large-ring *ansa*-zirconocene complex *rac*-**6** to be oriented in the front of

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(9) See for a comparison: Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776.

(10) Elvidge, J. A.; Foster, R. G. *J. Chem. Soc.* **1963**, 590.

(11) Wiesenfeld, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H.-H. *J. Organomet. Chem.* **1989**, *369*, 359.

(12) Atwood, J. L.; Hunter, W. E.; Hrncir, D. C.; Samuel, E.; Alt, H.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 1757.

(13) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H.-H. *J. Organomet. Chem.* **1982**, *232*, 233. Wild, F. R. W. P.; Wasiucionek, M.; Huttner, G.; Brintzinger, H.-H. *J. Organomet. Chem.* **1985**, *288*, 63.

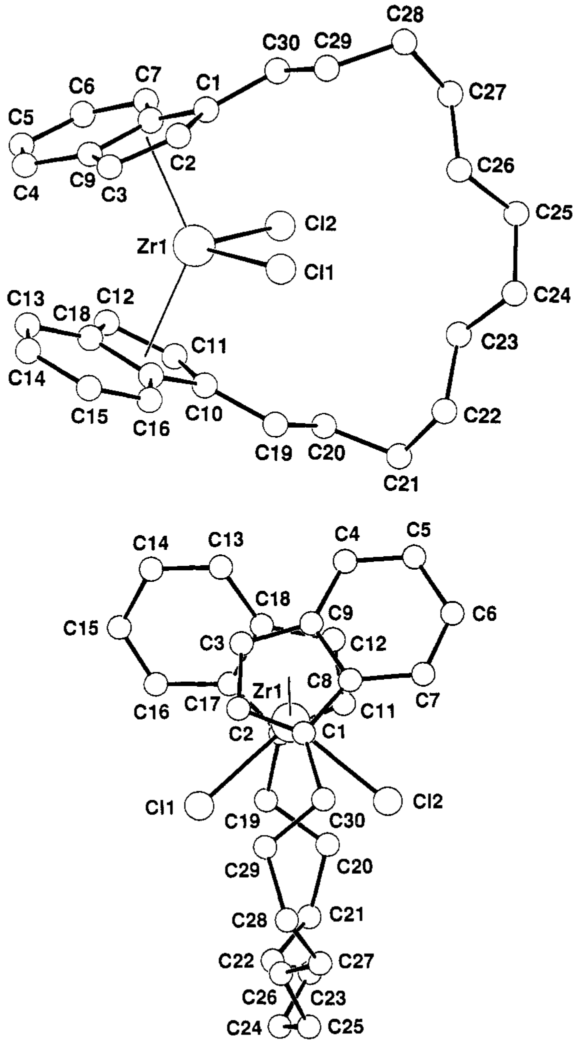

Figure 2. Two projections of the molecular geometry of the large-ring *ansa*-metallocene complex *rac*-6 in the solid state (with unsystematical atom-numbering scheme).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for *rac*-6

Zr(1)–Cl(1)	2.428(1)	Zr(1)–Cl(2)	2.431(1)
Zr(1)–C(1)	2.567(2)	Zr(1)–C(2)	2.524(2)
Zr(1)–C(3)	2.461(2)	Zr(1)–C(8)	2.597(2)
Zr(1)–C(9)	2.574(2)	Zr(1)–C(10)	2.580(2)
Zr(1)–C(11)	2.518(2)	Zr(1)–C(12)	2.442(2)
Zr(1)–C(17)	2.630(2)	Zr(1)–C(18)	2.572(2)
C(1)–C(2)	1.396(3)	C(1)–C(8)	1.429(3)
C(1)–C(30)	1.503(4)	C(2)–C(3)	1.414(3)
C(3)–C(9)	1.432(3)	C(4)–C(5)	1.349(4)
C(4)–C(9)	1.418(3)	C(5)–C(6)	1.400(5)
C(6)–C(7)	1.361(5)	C(7)–C(8)	1.427(3)
C(8)–C(9)	1.426(3)	C(10)–C(11)	1.401(3)
C(10)–C(17)	1.433(3)	C(10)–C(19)	1.498(3)
C(11)–C(12)	1.414(3)	C(12)–C(18)	1.433(3)
C(13)–C(14)	1.349(4)	C(13)–C(18)	1.429(3)
C(14)–C(15)	1.406(4)	C(15)–C(16)	1.351(4)
C(16)–C(17)	1.421(3)	C(17)–C(18)	1.422(3)
C(19)–C(20)	1.513(3)	C(20)–C(21)	1.524(4)
C(21)–C(22)	1.503(5)	C(22)–C(23)	1.502(5)
C(23)–C(24)	1.512(5)	C(24)–C(25)	1.510(6)
C(25)–C(26)	1.500(6)	C(26)–C(27)	1.501(6)
C(27)–C(28)	1.504(6)	C(28)–C(29)	1.534(5)
C(29)–C(30)	1.506(4)		
Cl(2)–Zr(1)–Cl(1)	98.4(1)	C(30)–C(1)–C(8)	125.9(2)
C(30)–C(1)–C(2)	127.5(2)	C(8)–C(1)–C(2)	106.4(2)
C(3)–C(2)–C(1)	110.4(2)	C(9)–C(3)–C(2)	107.0(2)
C(9)–C(4)–C(5)	119.4(2)	C(6)–C(5)–C(4)	120.8(3)
C(7)–C(6)–C(5)	122.5(3)	C(8)–C(7)–C(6)	118.5(3)
C(9)–C(8)–C(7)	118.7(2)	C(9)–C(8)–C(1)	109.0(2)
C(7)–C(8)–C(1)	132.2(2)	C(8)–C(9)–C(4)	120.0(2)
C(8)–C(9)–C(3)	106.8(2)	C(4)–C(9)–C(3)	133.1(2)
C(19)–C(10)–C(17)	124.3(2)	C(19)–C(10)–C(11)	129.0(2)
C(17)–C(10)–C(11)	106.5(2)	C(12)–C(11)–C(10)	110.1(2)
C(18)–C(12)–C(11)	107.1(2)	C(18)–C(13)–C(14)	119.1(2)
C(15)–C(14)–C(13)	121.6(2)	C(16)–C(15)–C(14)	121.7(2)
C(17)–C(16)–C(15)	118.5(2)	C(18)–C(17)–C(16)	120.2(2)
C(18)–C(17)–C(10)	108.8(2)	C(16)–C(17)–C(10)	130.9(2)
C(17)–C(18)–C(13)	118.7(2)	C(17)–C(18)–C(12)	107.2(2)
C(13)–C(18)–C(12)	134.1(2)	C(20)–C(19)–C(10)	115.0(2)
C(21)–C(20)–C(19)	113.0(2)	C(22)–C(21)–C(20)	115.2(3)
C(23)–C(22)–C(21)	114.6(3)	C(24)–C(23)–C(22)	114.9(3)
C(25)–C(24)–C(23)	113.8(3)	C(26)–C(25)–C(24)	115.3(3)
C(27)–C(26)–C(25)	115.5(3)	C(28)–C(27)–C(26)	116.8(4)
C(29)–C(28)–C(27)	116.2(3)	C(30)–C(29)–C(28)	114.4(3)
C(29)–C(30)–C(1)	115.1(2)		

the bent-metallocene moiety (see Figure 2). The (–CH_2–)$_{12}$ unit occupies a narrow band in the center of the open front side of the *ansa*-metallocene molecule. It is also arranged almost in a C_2-symmetric conformation. The mean plane of the *ansa*-fused medium-sized Cp–(CH_2)$_{12}$–Cp ring system bisects the Cl(1)–Zr–Cl(2) angle and thereby separates the segments of space where the chloride ligands Cl(1) and Cl(2) are located, respectively, from one another.

In the structure of complex *rac*-6 the bridging dodecamethylene chain is arranged such that it brings the carbon atoms C(19)–C(21) almost into coplanarity with their attached ring system (C(10)–C(12), C(17), C(18)) (the same is, of course, true for their "near to symmetry counterparts" C(30)–C(28) and the attached C(1)–C(3), C(8), C(9) five-membered ring). The *ansa* bridge thus has achieved its largest possible expansion (normal to the σ-ligand plane) between the methylene ring carbon atoms C(21) and C(28), i.e. at positions three C–C bonds away from the η^5-indenyl ring sections.

This spatial arrangement of the (–CH_2–)$_{12}$ chain causes apparently only minor distortions of the central core of the bent-metallocene framework.[14] In *rac*-6 the separation of the metal center from the centroids of the indenyl five-membered rings is 2.245 Å (Zr–D(1)) and 2.241 Å (Zr–D(2)), which is only slightly larger than found in typical examples of *ansa*-zirconocenes with small ligand-connecting bridges (e.g. Zr–D = 2.214 Å in Brintzinger's [ethylenebis(4,5,6,7-tetrahydroindenyl)]zirconium dichloride **10**).[15]

The D(1)–Zr–D(2) angle in *rac*-6 is 133.7°, whereas in **10** it is 5° smaller (128.8°). It appears that the dodecamethylene unit in *rac*-6 has attained its "natural" position in front of the bent-metallocene wedge, a position where it introduces the least additional strain to the large-ring *ansa*-metallocene complex. It cannot be ruled out that complexes derived from the large-ring *ansa*-metallocene *rac*-6 will adopt other conformations in the course of sterically demanding reactions taking place at the common bent-metallocene binding sites in the σ-ligand plane in front of the bent-metallocene wedge. However, it is conceivable that one may find series of reactions where the orientation found in the crystal structure analysis of *rac*-6 is retained. This would create the interesting situation that the action of reagents or substrates might directly be influenced by the spatial arrangement of the adjacent dodecamethylene unit; it may even be possible

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(14) Cardin, D. J.; Lappert, M. F.; Raston, C. J. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986.

(15) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* 1988, *342*, 21.

Table 2. Atomic Coordinates of *rac*-6

atom	*x*	*y*	*z*
Zr(1)	0.1945(1)	0.3631(1)	–0.2551(1)
Cl(1)	0.2447(1)	0.2232(1)	–0.1399(1)
Cl(2)	–0.0202(1)	0.2189(1)	–0.3549(1)
C(1)	0.3748(3)	0.3105(2)	–0.3786(2)
C(2)	0.4752(2)	0.3607(2)	–0.2974(2)
C(3)	0.4807(3)	0.4820(2)	–0.2814(2)
C(4)	0.3735(3)	0.6238(2)	–0.3909(2)
C(5)	0.2870(3)	0.6257(3)	–0.4734(2)
C(6)	0.2143(4)	0.5196(3)	–0.5290(2)
C(7)	0.2304(3)	0.4111(3)	–0.5047(2)
C(8)	0.3259(2)	0.4060(2)	–0.4197(1)
C(9)	0.3941(2)	0.5133(2)	–0.3614(2)
C(10)	–0.0115(2)	0.3785(2)	–0.1314(1)
C(11)	–0.0527(2)	0.4233(2)	–0.2181(2)
C(12)	0.0761(3)	0.5269(2)	–0.2425(2)
C(13)	0.3412(3)	0.6543(2)	–0.1402(2)
C(14)	0.4224(3)	0.6576(2)	–0.0549(2)
C(15)	0.3682(3)	0.5655(2)	0.0114(2)
C(16)	0.2325(3)	0.4691(2)	–0.0073(2)
C(17)	0.1412(2)	0.4632(2)	–0.0956(1)
C(18)	0.1949(2)	0.5558(2)	–0.1632(2)
C(19)	–0.1086(3)	0.2706(2)	–0.0784(2)
C(20)	–0.2640(3)	0.1920(2)	–0.1314(2)
C(21)	–0.3449(4)	0.0741(3)	–0.0815(2)
C(22)	–0.2483(5)	–0.0130(3)	–0.0779(3)
C(23)	–0.2109(5)	–0.0532(3)	–0.1742(3)
C(24)	–0.1412(5)	–0.1570(3)	–0.1725(3)
C(25)	–0.0710(5)	–0.1779(3)	–0.2656(3)
C(26)	0.0983(5)	–0.0949(3)	–0.2811(3)
C(27)	0.1546(5)	–0.0965(3)	–0.3810(3)
C(28)	0.3333(5)	–0.0329(3)	–0.3949(3)
C(29)	0.4002(4)	0.1004(3)	–0.3613(3)
C(30)	0.3363(3)	0.1845(2)	–0.4205(2)

that the $(-CH_2-)_{12}$ "loop" has to be penetrated or passed through. We are currently searching for examples, if they do exist, where such pathways can be investigated experimentally.

Experimental Section

Reactions with organometallic reagents were carried out under an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. The following instruments were used for physical characterization: Bruker AC 200 P NMR (^1H, 200.1 MHz; ^{13}C, 50.3 MHz) and Bruker ARX 300 NMR (^{13}C: 75.0 MHz) spectrometers; Nicolet 5 DXC FT IR spectrometer; DuPont 910 DSC and Gallenkamp melting point apparatus for melting point; Voss-Heraeus CHNO-Rapid elemental analyzer. $ZrCl_4(THF)_2$ was prepared according to a literature procedure.[16]

1,12-Dodecanediyl Bis(methanesulfonate) (2). 1,12-Dodecanediol (25.0 g, 0.12 mol) was dissolved in 300 mL of freshly distilled pyridine. At 0 °C 56.8 g (38.7 mL, 0.50 mol) of methanesulfonyl chloride was added dropwise over 0.5 h. The mixture was stirred for 3 h at ambient temperature and then poured into ice–water. The precipitate was collected by filtration, washed with water until neutral, and dissolved in methylene chloride, and this solution was washed with dilute H_2SO_4 and then with sodium bicarbonate solution and water. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. The product was crystallized at –30 °C to give 38.6 g (90%) of 2, mp (DSC) 86 °C. Anal. Calcd for $C_{14}H_{30}O_6S_2$ (358.51): C, 46.90; H, 8.43. Found: C, 47.14; H, 8.43. ^1H NMR ($CDCl_3$): δ 4.19 (t, 4H, ^3J = 6.5 Hz, 1-H/12-H), 2.97 (s, 6H, S–Me), 1.80–1.65 (m, 4H, 2-H/11-H), 1.45–1.17 (m, 16H, 3-H-10-H). ^{13}C NMR ($CDCl_3$): $\delta(CH_3)$ 37.2 (2C, S–Me); $\delta(CH_2)$ 70.2, 29.2 (double intensity), 29.0, 28.8, 25.3 (12C, C1–C12).

1,12-Bis(3-indenyl)dodecane (4). Freshly distilled indene (25.5 g, 25.8 mL, 220 mmol) was dissolved in 150 mL of tetrahydrofuran. At 0 °C 125 mL of a 1.6 M *n*-butyllithium solution in hexene (200 mmol) was added dropwise over 30 min. The yellow solution was stirred for 3 h at room temperature and then cooled again to 0 °C. A solution of 20.0 g (56 mmol) of 2 in 100 mL of THF was added dropwise. The mixture was stirred for 2 h at 0 °C and then for 12 h at room temperature. The reaction was brought to completion by refluxing the mixture for 2 h. Ether (50 mL) and water (50 mL) were added. The organic phase was separated and washed with water. The aqueous phase was extracted with ether (3×). The combined organic solutions were dried over magnesium sulfate. Solvent was removed and the remaining solid recrystallized from acetone to give 19.0 g (85%) of 4, mp (DSC) 53 °C. Anal. Calcd for $C_{30}H_{38}$ (398.63): C, 90.39; H, 9.61. Found: C, 90.86; H, 9.75. ^1H NMR ($CDCl_3$): δ 7.48–7.18 (m, 8H, 4-H–7-H), 6.19 (br s, 2H, 2-H), 3.32–3.31 (m, 4H, 1-H), 2.60–2.50 (m, 4H), 1.75–1.60 (m, 4H), 1.60–1.21 (m, 16H, CH_2). ^{13}C NMR ($CDCl_3$): $\delta(CH_2)$ 37.7 (2C, C1), 29.7 (double intensity), 29.6, 28.1, 28.0, 27.9; $\delta(CH)$ 127.6, 126.0, 124.4, 123.7, 119.0; $\delta(C)$ 145.7, 144.8, 144.6. Single crystals of 4 suited for the X-ray crystal structure determination were obtained from CH_2Cl_2 at 0 °C. Compound 4 crystallizes in a monoclinic unit cell (space group $P2_1/n$ (No. 14)) with lattice parameters a = 5.524(1) Å, b = 4.951(1) Å, c = 44.132(4) Å, β = 90.71(1)°, V = 1207(1) Å^3, and Z = 2. The X-ray diffraction data were measured with Mo Kα radiation (λ = 0.710 69 Å) on an automated Enraf-Nonius X-ray diffractometer equipped with a graphite monochromator. A total of 4847 reflections (2188 independent) were measured with ω-scans within a θ range of 1.85–26.96° using variable scan rates of 1.1–5.5°/min. The structure was solved with direct methods, and idealized positions were introduced for the 19 hydrogen atoms as fixed contributions. Full-matrix refinement (based on F^2, SHELXL93) of the positional and anisotropic thermal parameters for the 15 non-hydrogen atoms converged with $R(F_o)$ = 0.041 and GOF = 1.05 for 1441 unique reflections with $I > 2\sigma(I)$.

Deprotonation of 4. Compound 4 (19.0 g, 47.7 mmol) was dissolved in 150 mL of ether. At 0 °C 60.0 mL (96 mmol) of butyllithium (1.6 M hexane solution) was added dropwise over 0.5 h. The mixture was warmed to room temperature and stirred for 12 h. The solution was then concentrated in vacuo to about half its volume, and an equal volume of pentane was added. The resulting precipitate was recovered by filtration, washed with pentane, and dried in vacuo. The dilithio compound 5 (8.3 g, 85%) was only characterized by ^1H NMR spectroscopy at ambient temperature. ^1H NMR (benzene-d_6/THF-d_8): δ 7.60–7.45 (m, 4H, 4-H, 7-H), 6.78–6.65 (m, 4H, 5-H, 6-H), 6.58 (d, 2H, ^3J = 3.2 Hz, 2-H), 6.04 (dd, 2H, ^3J = 3.2 Hz, ^5J = 0.65 Hz, 3-H), 3.00 (t, 4H, ^3J = 7.3 Hz, 1′-H/12′-H), 1.92–1.71 (m, 4H, 2′-H/11′-H), 1.55–1.15 (m, 16H, 3′-H-10′-H).

Preparation of the *ansa*-Metallocene Dichloride *rac*-6. A 500-mL Schlenk flask with reflux condenser and two dropping funnels was charged with 300 mL of tetrahydrofuran. One of the dropping funnels was charged with a solution of 350 mg (1.70 mmol) of the dilithio compound 5 in 20 mL of THF and the other with 324 mg (1.70 mmol) of $ZrCl_4(THF)_2$ dissolved in 20 mL of THF. Both solutions were slowly added simultaneously over 4 h to the refluxing THF solvent. Then the mixture was kept at reflux temperature for another 1 h. Solvent was then removed in vacuo. The residue was dried and extracted with pentane (3 × 50 mL). The combined pentane solutions were concentrated in vacuo to a volume of 15 mL. The resulting precipitate was collected and washed twice with pentane to give 145 mg of *rac*-6 (15%), mp (DSC) 112 °C. IR (KBr): $\tilde{\nu}$ 740, 786, 803, 1024, 1050, 1097, 1262, 2850, 2920, 3160, 3178 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.71–7.52 (m, 2H), 7.43–7.18 (m, 6H, arom), 6.26 (d, 2H, ^3J = 3.1 Hz, 2-H), 5.30 (dd, 2H, ^3J = 3.1 Hz, ^5J = 0.7 Hz, 3-H), 2.92–2.78 (m, 4H, 1′-H/12′-H), 1.75–1.35 (m, 20H, 2′-H-11′-H). ^{13}C NMR ($CDCl_3$): $\delta(CH_2)$ 28.3 (double intensity), 27.5, 27.0 (double intensity), 26.9; $\delta(CH)$ 126.3, 126.0 (double intensity), 123.3, 121.3, 103.9; $\delta(C)$ 127.0, 121.6, one quaternary C not observed. Single crystals of *rac*-6 suited for the X-ray crystal structure analysis were obtained from a saturated pentane solution at –30 °C. The complex *rac*-6 crystallizes in a triclinic unit cell (space group $P\bar{1}$ (No. 2)) with lattice parameters of a = 8.612(1) Å, b = 11.650(1)

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(16) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

Å, $c = 13.982(1)$ Å, $\alpha = 90.77(1)°$, $\beta = 92.68(1)°$, $\gamma = 108.55(1)°$, $V = 1327.9$ Å^3, $Z = 2$. The X-ray diffraction data were measured with Mo Kα radiation ($\lambda = 0.710\,69$ Å) on an automated Enraf-Nonius X-ray diffractometer equipped with a graphite monochromator. A total of 6264 reflections were measured with coupled ω–2θ scans within a θ range of 1.0–27.5° using variable scan rates of 1.0–10.0°/min. The structure was solved with direct methods, and idealized positions were introduced for the 36 hydrogen atoms as fixed contributions. Full-matrix refinement (based on F_o, SHELXL76) of the positional and anisotropic thermal parameters for the 33 non-hydrogen atoms converged with $R(F_o) = 0.030$ and GOF = 1.60 for 5578 unique reflections with $I > 2\sigma(I)$. The SCHAKAL and ORTEP program packages were used for the drawings of the structures of 4 and *rac*-6, respectively (see Figures 1 and 3).

Preparation of the *ansa*-Metallocene Dichloride *meso*-6. Similarly as described above, two separate solutions containing 350 mg (1.70 mmol) of 5 in 20 mL of THF and 324 mg (1.70 mmol) of $ZrCl_4(THF)_2$ in 20 mL of THF, respectively, were simultaneously added dropwise over a period of 4 h to 300 mL of refluxing toluene. The mixture was kept at the reflux temperature for 1 h and then cooled to room temperature. A precipitate was filtered off and the clear filtrate concentrated in vacuo to ca. 25% of its original volume. The product was crystallized at −30 °C, collected by filtration, washed with pentane, and dried. Concentration of the mother liquor and crystallization gave an additional fraction of *meso*-6: combined yield 95 mg (11%); mp (DSC) 165 °C dec. Anal. Calcd for $C_{30}H_{36}Cl_2Zr$ (558.74): C, 64.49; H, 6.49. Found: C, 63.46; H, 6.56. IR (KBr): $\tilde{\nu}$ 428, 451, 473, 485, 500, 508, 524, 748, 808, 1048, 1099, 1340, 1354, 1442, 1456, 2852, 2925 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.55–7.10 (m, 8H, arom), 6.46 (dd, 2H, ^3J = 3.0 Hz, ^5J = 0.7 Hz, 3-H), 6.43 (d, 2H, ^3J = 3.0 Hz, 2-H), 3.0–2.6 (m, 4H, 1′-H/12′-H), 2.4–2.35 (m, 4H, 2′-H/11′-H), 1.65–1.25 (m, 16H, 3′-H–10′-H). ^{13}C NMR ($CDCl_3$): $\delta(CH_2)$ 30.1, 27.9, 27.6, 27.4, 27.3, 27.1; δ(CH) 127.1, 126.0, 125.5, 123.8 (C4–C7), 113.2, 96.2 (C2, C3); δ(C) 139.4, 131.2, one quaternary C not located.

Catalytic Hydrogenation of *rac*-6. Complex *rac*-6 (400 mg, 0.72 mmol) was dissolved in 60 mL of dichloromethane. A small amount (spatula tip) of PtO_2 was added and the mixture stirred for 4 h under 60 bar of hydrogen in an autoclave. The catalyst was then removed by filtration and the solvent removed in vacuo. The residue was extracted with pentane (3 × 20 mL), and the combined pentane extracts were concentrated in vacuo to a volume of 10 mL. The product *rac*-8 was precipitated by cooling to −30 °C to give 325 mg (80%), mp 116 °C. Anal. Calcd for $C_{30}H_{44}Cl_2Zr$ (566.81): C, 63.57; H, 7.82. Found: C, 64.04; H, 8.11. IR (KBr): $\tilde{\nu}$ 804, 819, 1025, 1037, 1042, 1057, 1065, 1095, 1261, 1282, 1333, 1348, 1436, 1447, 1457, 1490, 2855, 2929, 3078 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.13 (d, 2H, ^3J = 3.0 Hz), 5.50 (d, 2H, ^3J = 3.0 H, 2-H, 3-H), 3.00–2.80 (m, 2H), 2.80–2.60 (m, 2H), 2.60–2.40 (m, 4H, tetrahydroindenyl CH_2), 2.40–2.25 (m, 4H), 1.9–1.0 (m, 20H, $(-CH_2-)_{12}$). ^{13}C NMR ($CDCl_3$): $\delta(CH_2)$ 29.6 (double intensity), 28.3, 27.2, 26.9, 26.8, 24.9, 22.7, 22.1 (double intensity); δ(CH) 111.5, 109.2; δ(C) 132.7, 129.8, 126.0.

Generation of the *ansa*-Metallocene Dimethyl Complexes *rac*-7 and *meso*-7. Reaction of *rac*-6 with Methyllithium. The complex *rac*-6 (120 mg, 0.21 mmol) was dissolved in 15 mL of toluene and cooled to −78 °C. Methyllithium (0.50 mmol) in ether (0.33 mL of a 1.6 M solution) was added over 10 min. After 30 min the mixture was warmed to room temperature and then stirred for an additional 3 h. A precipitate was filtered off and washed with toluene. Solvent was removed from the combined toluene/ether solutions in vacuo to give 71 mg of *rac*-7 (65%) as a colorless oil. The product was only characterized by NMR spectroscopy. ^{1}H NMR (benzene-d_6): δ 7.40–6.85 (m, 8H, arom), 5.84 (d, 2H, ^3J = 3.1 Hz, 2-H), 5.27 (dd, 2H, ^3J = 3.1 H, ^5J = 0.7 Hz, 3-H), 2.71–2.40 (m, 4H, 1′-H/12′-H), 1.8–1.1 (m, 20H, 2′-H–11′-H), −0.64 (s, 6H, Zr–CH_3). ^{13}C NMR (benzene-d_6): δ(Zr–CH_3) 37.2; $\delta(CH_2)$ 30.1, 28.8, 28.5, 27.3, 27.2, 27.1; δ(CH) 125.9, 124.0, 123.8, 122.8, 115.9, 100.1; δ(C) 124.7, 115.4, one quaternary C not located.

Reaction of *meso*-6 with Methyllithium. In an NMR experiment 10 mg (0.02 mmol) of *meso*-6 was dissolved in 10 mL of toluene and cooled to −78 °C. A volume of 0.014 mL of a 1.6 M ethereal methyllithium solution (0.022 mmol) was added with stirring. The mixture was warmed to room temperature and then stirred for 3 h. Solvent was removed and the residue extracted with 0.5 mL of benzene-d_6. The product *meso*-7 was not isolated but only characterized by NMR spectroscopy. ^{1}H NMR (benzene-d_6): δ 7.45–6.88 (m, 8H, arom), 5.71 (d, 2H, ^3J = 3.2 Hz, ^5J = 0.7 Hz, 3-H), 5.43 (d, 2H, ^3J = 3.2 H, 2-H), 2.71–2.45 (m, 4H, 1′-H/12′-H), 1.75–1.15 (m, 20H, 2′-H–11′-H), −0.58 (s, 3H, Zr–CH_3), −1.02 (s, 3H, Zr–CH_3). ^{13}C NMR (benzene-d_6): δ(Zr–CH_3) 50.8, 42.2; $\delta(CH_2)$ 30.1, 28.3, 27.8, 27.6, 27.3, 26.8; δ(CH) 126.2, 124.0, 123.8, 123.2, 109.1, 92.7; δ(C) 117.1, two quaternary C not located.

Reaction of *ansa*-Bis(tetrahydroindenyl)zirconium Dichloride Complex *rac*-8 with Methyllithium. The complex *rac*-8 (120 mg, 0.22 mmol) was dissolved in 20 mL of toluene. At −78 °C 0.32 mL of a 1.6 M ethereal methyllithium solution (0.51 mmol) was added dropwise over 10 min with stirring. After 30 min the reaction mixture was warmed to room temperature and then stirred for an additional 3 h. A precipitate was removed by filtration and washed with toluene, and the combined organic solutions were stripped in vacuo to give 81 mg (71%) of *rac*-9 as a colorless oil. Anal. Calcd for $C_{32}H_{50}Zr$ (525.97): C, 73.07; H, 9.58. Found: C, 74.26; H, 9.37. IR (KBr): $\tilde{\nu}$ 453, 470, 794, 946, 1021, 1098, 1261, 1457, 2854, 2927, 3104 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 5.56–5.45 (m, 4H, 2-H/3-H), 2.61–2.04 (m, 12H), 1.75–1.21 (m, 28H), −0.20 (s, 6H, Zr–CH_3). ^{13}C NMR (benzene-d_6): $\delta(ZrCH_3)$ 35.0; $\delta(CH_2)$ 29.2, 28.3, 27.5, 27.2, 26.9, 28.8, 24.9, 23.4, 23.3, 23.1; δ(CH) 107.5, 107.2; δ(C) 125.0, 123.3, 121.6.

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Supplementary Material Available: Details of the crystal structure determinations of 4 and *rac*-6, including listings of crystal data and refinement details, bond lengths and angles, and thermal parameters, and a table of atomic fractional coordinates for 4 (10 pages). Ordering information is given on any current masthead page.

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