Chiral Cyclopentane-1,3-diyl-Bridged *ansa*-Titanocene Dichlorides

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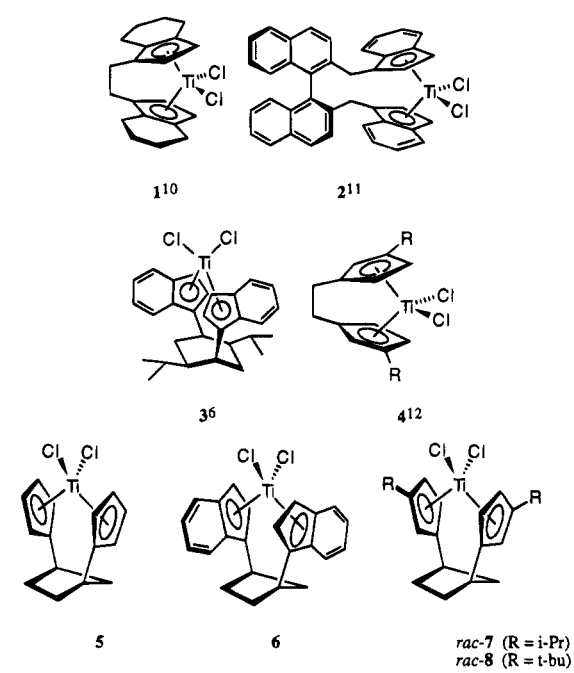
Displacement of cis-1,3-cyclopentanediol bis(tosylate) (**12**) or bis(mesylate) (**11**) with cyclopentadienylmagnesium bromide or indenyllithium afforded cyclopentane-bridged bis(cyclopentadiene) and bis(indene) species **13** and **19**, respectively. Bis(cyclopentadiene) **13** was converted via dimethylpentafulvene **16** to the isopropyl- and *tert*-butyl-substituted bis(cyclopentadienes) **17** and **18**. Each of the ligands **13**, **17**, **18**, and **19** was converted into the corresponding cyclopentane-1,3-diyl-bridged *ansa*-titanocene dichloride complexes **5** (unsubstituted cyclopentadienyl), **7** (3-isopropyl-substituted cyclopentadienyl), **8** (3-*tert*-butyl-substituted cyclopentadienyl), and **6** (indenyl), respectively. Three diastereomers were observed in complexes **7** and **8** in a ratio of *dl*-C_1-symmetrical to C_s-symmetrical (*R* over methano bridge) to C_s-symmetrical (*R* over ethano bridge) of 8:3:1 and 5:5:1, respectively. The major two isomeric components of **7** and **8** were isolated by fractional crystallization. The bis(indenyl) complex **6** was obtained from the initial reaction mixture as a pure C_1-symmetrical diastereomer. Complexes **5** and **6** were characterized by X-ray crystallography. No evidence for hindered interchange between conformations was observed for any of the complexes.

The preparation of new chiral metallocene complexes has proceeded in recent years at a rapid pace, owing to the desire to prepare more selective metallocene catalysts for important stereoselective reactions such as alkene hydrogenations,[2] alkene epoxidations,[3] imine[4] and ketone[5] reductions, alkene isomerizations,[6] and alkene polymerizations.[7] One particularly intense avenue of research has been the prepartion of *ansa*-metallocenes whose chirality is due to a chiral orientation of bridged indenyl or substituted cyclopentadienyl ligands such as complexes **1**–**4** (Chart 1). The majority of published work describing the chemistry of chiral *ansa*-metallocenes has covered simple ethano-bridged complexes with less being known about the effect of changing the nature of the bridging unit.[8] It is known that the simple ethano-bridged *ansa*-metallocenes adopt two conformations in the solid state, but only rapid (on the NMR time scale) conformational mobility has been observed in solution.[9] The interpretation of the reactivity of these complexes depends on a better understanding and controlling of the effects of any conformational

Chart 1



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(1) Experimental portions of this work were carried out at the Department of Chemistry, Boston University.

(2) (a) Cesarotti, E.; Ugo, R.; Kagan, H. B. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 10. (b) Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883. (c) Halterman, R. L.; Vollhardt, K. P. C.; Welker, M. E.; Bläser, D.; Boese, R. *J. Am. Chem. Soc.* **1987**, *109*, 8105. (d) McLaughlin, M. L.; McKinney, J. A.; Paquette, L. A. *Tetrahedron Lett.* **1986**, *27*, 5595. (e) Paquette, L. A.; McKinney, J. A.; McLaughlin, M. L.; Rheingold, A. L. *Tetrahedron Lett.* **1986**, *27*, 5599. (f) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911. (g) Conticello, V. P.; Brard, L.; Giardello, M. A.; Tsuji, Y.; Sabat, M.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 2761.

(3) Colletti, S. L.; Halterman, R. L. *Tetrahedron Lett.* **1992**, *33*, 1005.

(4) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562.

(5) Halterman, R. L.; Ramsey, T. M.; Chen, Z. *J. Org. Chem.* **1994**, *59*, 2642.

(6) Chen, Z.; Halterman, R. L. *J. Am. Chem. Soc.* **1992**, *114*, 2276.

(7) Review: Brintzinger, H. H. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, 1988; p 249. (b) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc* **1987**, *109*, 6544. (c) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (d) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (e) Kaminsky, W.; Kulper, K.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (f) Mallin, D. T.; Rausch, M. D.; Lin, Y. G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030; (g) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (h) 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.

(8) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965–994.

(9) Collins, S.; Hong, Y.; Ramachandran, R.; Taylor, N. J. *Organometallics* **1991**, *10*, 2349.

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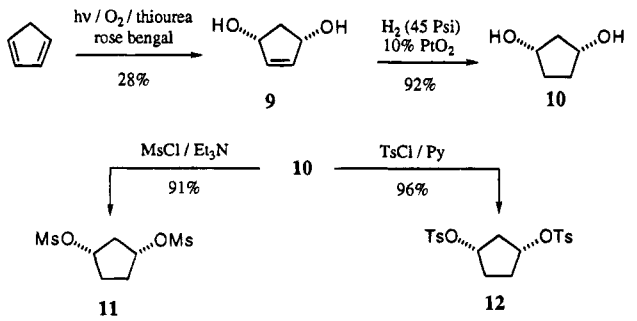
Scheme 1

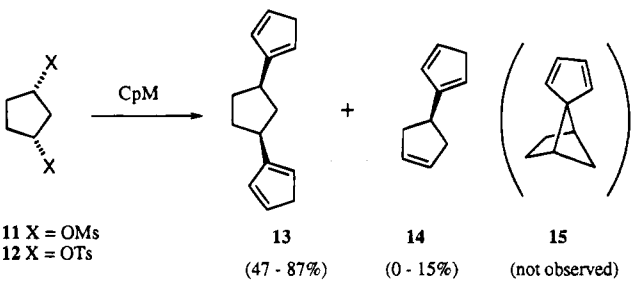


mobility. In an effort to address the role of the bridging units, we prepared and characterized several cyclopentane-1,3-diyl-bridged *ansa*-titanocene dichloride complexes **5**–**8** and report these results herein.

Results and Discussion

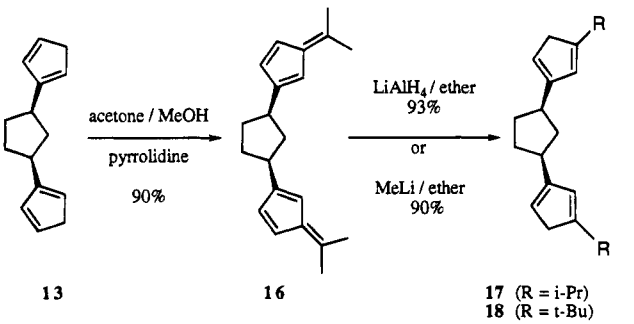
Ligand Synthesis. The key intermediate in the preparation of each of the cyclopentane-1,3-diyl bridged complexes **5**–**8** is the *cis*-1,3-cyclopentanediol bis(methanesulfonate) (**11**). This common intermediate or the related bis(*p*-toluenesulfonate) **12** could be easily prepared in three steps from cyclopentadiene (Scheme 1). The known photooxidation of cyclopentadiene[13] affords *cis*-1,3-dihydroxycyclopent-2-ene (**9**), which can be hydrogenated to *cis*-1,3-cyclopentanediol (**10**).[14] We found that if the crude product after the oxidation was first purified through vacuum distillation and then filtered through a short path of SiO_2, the resulting ene diol **9** could be efficiently hydrogenated with 10% of Adam's catalyst, as compared to the previously reported 50% of the catalyst.[14] Treatment of diol **10** with either methanesulfonyl chloride in the presence of triethylamine or with *p*-toluenesulfonyl chloride in pyridine gave the two bis alkylating reagents **11** and **12.**

Treatment of bis(mesylate) **11** with excess CpLi in THF/HMPA gave the desired bridged bis(cyclopentadiene) **13** in only 47% yield. The reaction of bis(tosylate)



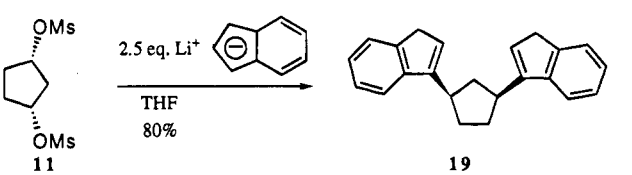
12 with excess CpNa gave 55% of the desired product **13.** These reactions also produced about 15% of the elimination product **14**, which was isolated as what appears to be a Diels–Alder reaction adduct with **13.** The desired product could be readily purified through SiO_2 chromatography. The formation of the elimination product **14** could be completely suppressed by using the less ionic CpMgBr or Cp_2Mg[15] as the cyclopentadienyl alkylating agent. In this manner, ligand **13** was readily prepared as a double bond isomeric mixture in high yields (88% purified yield using CpMgBr and quantitative crude yield using 2 equiv of Cp_2Mg). Spiroannulation products are common when cyclopentadienyllithium is alkylated, but in this case not spiro annulated **15** was observed, presumably due to the large degree of strain in forming this bicyclo[2.1.1]hexane system.

Following established routes in the literature for producing bridged substituted cyclopentadienes, we condensed *cis*-1,3-bis(cyclopentadienyl)cyclopentane (**13**) with acetone in the presence of pyrrolidine,[12,16] to produce bis(fulvene) **16** in 90% yield. Nucleophilic addition of hydride or methyllithium[12] to the latter provided the 3-isopropyl- or 3-*tert*-butyl-substituted bis(cyclopentadienyl) ligand **17** or **18**, respectively. As with



our "parent" bis(cyclopentadiene) ligand **13**, compounds **17** and **18** could be purified through short path SiO_2 chromatography. These bis(cyclopentadienes) were thermally unstable and had to be stored at −25 °C as dilute solutions in petroleum ether or converted to the next step shortly after their formation.

Addition of indenyllithium in THF to bis(mesylate) **11** readily produced an additional bridged ligand, bis(indene) **19**, as a mixture of double bond isomers, with the predominant isomer shown. When HMPA was used as a cosolvent in this reaction, bis(indene) **19** was formed as a single double bond isomer in 80% yield. In contrast to the unstable nature of the bis(cyclopentadienes) **13**, **17**, and **18**, bis(indene) **19** is a stable solid.



Parent Bis(cyclopentadienyl)titanium Dichloride 5. When a standard metalation procedure[9,12] was used, deprotonation of bis(cyclopentadiene) **13** with *n*-BuLi followed by metalation with $TiCl_3$ in dilute THF and oxidation cleanly gave the desired "parent" titanocene dichloride **5.** Inspection of the ^1H NMR spectrum of the crude reaction product indicated very little formation of the oligomeric titanocenes observed in other bis(cyclopentadienyl) metalations. Recrystallization gave *ansa*-titanocene dichloride **5** as a red

(10) 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.

(11) Burk, M.; Colletti, S. L., Halterman, R. L. *Organometallics* **1991**, *10*, 2998.

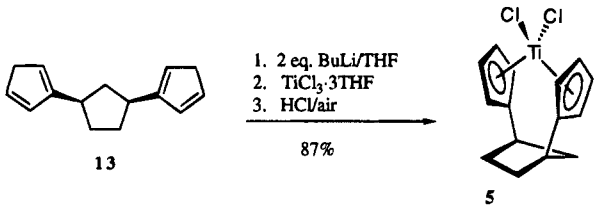
(12) Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* **1990**, *9*, 2695.

(13) Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876.

(14) Sable, H. Z.; Posternak, T. *Helv. Chim. Acta* **1962**, *45*, 370.

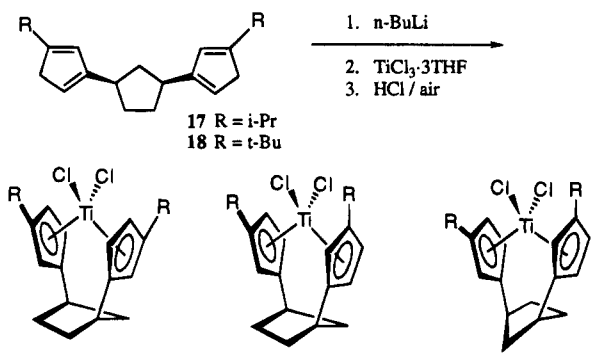
(15) Gutmann, S.; Burger, P.; Prosenc, M-H.; Brintzinger, H. H. *J. Organomet. Chem.* **1990**, *397*, 21.

(16) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849.



crystalline solid in 87% yield. In the ^1H and ^{13}C NMR spectra of **5** only one set of cyclopentadienyl signals was detected, due to the presence of a mirror plane in the molecule. The solid state structure of this product was confirmed by X-ray crystallographic analysis and is discussed below.

Subtituted Bis(cyclopentadienyl)titanium Dichlorides 7 and 8. By the same procedure described for the preparation of metallocene **5**,[9,12] the *n*-BuLi-generated dianion of the isopropyl-substituted ligand **17** was reacted with $TiCl_3$·3THF in a dilute THF solution. The crude products from this reaction, as shown by the ^1H NMR spectrum, contained a mixture of three isomeric titanocenes in a ratio of ca. 8:3:1, in addition to a very small amount of apparantly oligomeric metal complexes. Fortunately, if two recrystallizations from hexane were performed, the major isomer, C_1-symmetrical metallocene **7a**, could be isolated in 16% yield, while the second most abundant isomer, C_s-symmetrical titanocene **7b**, could be separated in 10% yield from the rest of the mixture in the mother liquid after multiple recrystallizations from a *n*-chlorobutane/hexane cosolvent. The total yield of the purified titanocenes was 75%.



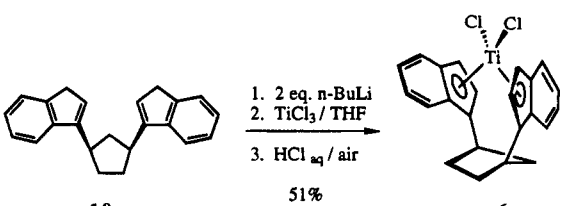
7 R = *i*-Pr	**7a** 8	:	**7b** 3	:	**7c** 1	
(Total Yield, 75%)	(16% istd.)		(10% istd.)			
8 R = *t*-Bu	**8a** 5	:	**8b** 5	:	**8c** 1	
(Total Yield, 34%)	(3% istd.)		(3% istd.)			

In an analogous manner the *tert*-butyl-bearing ligand **18** was subjected to the same metalation procedure to give three *ansa*-titanocenes in a ratio of 5:4:1. The formation of the oligomeric material in this case, however, was much more prevalent. After multiple recrystallizations, the major component, C_1-symmetrical titanocene **8a**, was isolated in only 3% yield while the second most abundant complex, C_s-symmetrical isomer **8b**, was obtained in a similar yield with about 80% isomeric purity. *n*-Chlorobutane was found to be the most appropriate recrystallization solvent to perform the needed purification.

The possible complex products from the metalation of ligand **17** should include one racemic *ansa*-metallocene **7a** and the two *meso* complexes **7b** and **7c**. The same isomeric composition should apply to complex **8**. The major product isomers from both ligands were isolated and both showed six Cp proton resonances in their ^1H NMR spectra. The translation of the demonstrated lack of symmetry in these molecules led to their unambiguous structural assignment as **7a** and **8a**, respectively. Whereas the corresponding spectra of the second most abundant isomer from complexes **7** or **8** showed one triplet at a lower field relative to two closely spaced multiplets in the vinyl proton region, characteristic of their C_s symmetry. The two possible C_s-symmetrical structures differ from each other only in whether the 3-alkyl substituents on the cyclopentadienyl rings are directly above the ethano bridge or directly above the methano bridge. The assignment of the structures of the second most abundant isomers as **7b** and **8b** was made by observing NOE effects (NOESY experiments on the isolated complexes) between the appropriate protons. Ideally, these assignments would be confirmed by comparing the NOE effect data from the remaining isomers, but these complexes **7c** and **8c** were not isolable.

The formation of complexes **7** and **8** represented a 2:1 and 1:1 *rac:meso* selectivity for the metalation of isopropyl-substituted or *tert*-butyl substituted ligand **17** or **18**, respectively. In an analogous metalation study of ethylene bridged 3-alkyl-substituted cyclopentadienyl ligands, Collins[12] found the corresponding *rac:meso* ratio of 1:1.8 or 1:2. They have invoked Brintzinger's interpretation to rationalize the decreased *rac:meso* selectivity as the alkyl group becomes bulkier.[17] In our case, the same trends were observed but the formation of the racemic isomer was not disfavored by the formation of the *meso* ones. The latter result indicates an advantage of using a cyclic bridging unit to prefix the two cyclopentadienyl rings in a direction which favored the formation of the racemic *ansa* complexes. The significantly enhanced formation of a polymeric complex in *tert*-butyl-substituted ligand **18**, however, suggests that the isopropyl substituent on the cyclopentadienyl ring is probably the bulkiest group possible to be comfortably accommodated around the metal center in the *cis*-1,3-cyclopentanediyl bridging system.

Bis(indenyl)titanium Dichloride 6. By a procedure modified from Collins'[18] improved preparative method for the analogous (EBTHI)$TiCl_2$, the bis(indene) ligand **19** was deprotonated with *n*-BuLi. The dianion was then refluxed with $TiCl_3$ in THF at 66 °C to afford, subsequent to the HCl (aqueous)/air workup and purification by a simple recrystallization, a dark green crystalline compound in 51% yield. We note here that the use of the more convenient aqueous HCl rather than gaseous HCl, as used by Collins,[18] worked equally well.



The dark green crystals contained only one isomer, which was also the only product observed by ^1H NMR

(17) Gutmann, S.; Burger, P.; Hund, H.-U.; Hofmann, J.; Brintzinger, H. H. *J. Organomet. Chem.* **1989**, *369*, 343.
(18) Collins, S.; Kuntz, B. A.; Taylor, J. J.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21.

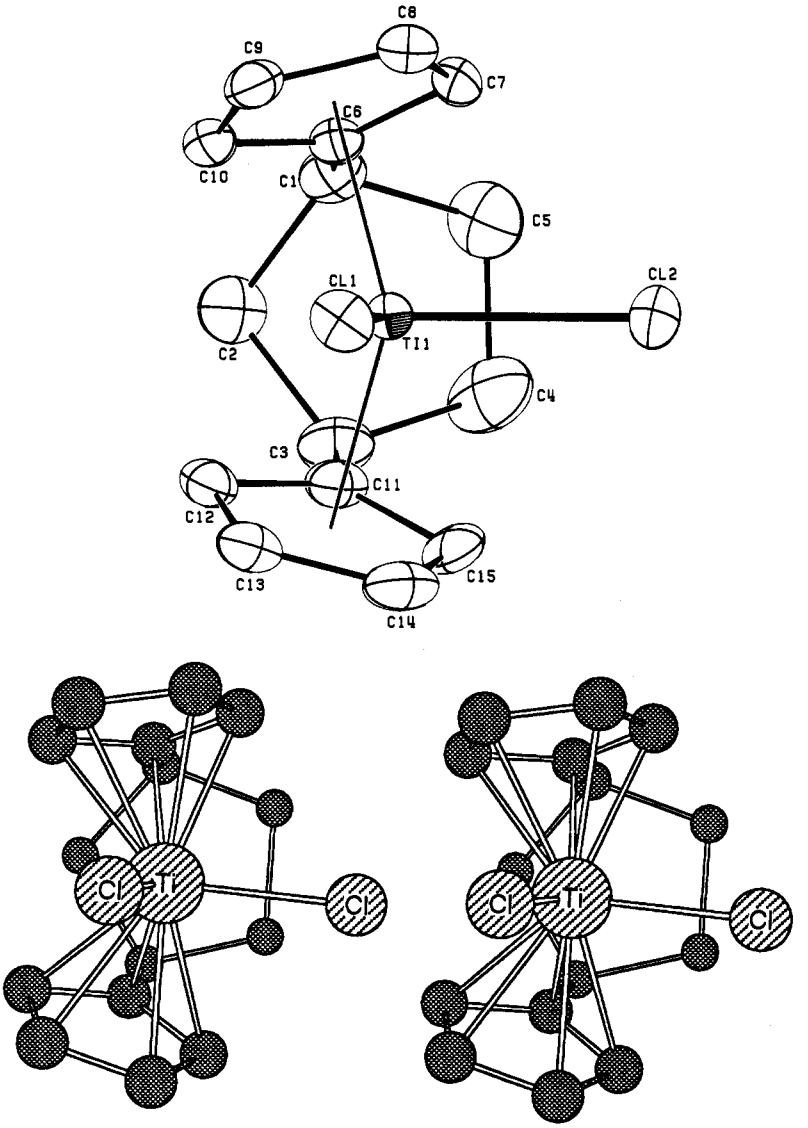


Figure 1. (a, top) ORTEP drawing of **5** drawn at the 50% probability level. (b, bottom) Stereoview of **5**.

spectroscopy in the crude product of the metalation reaction. The ^{1}H NMR spectrum of this isomer showed two pairs of sharp doublets at 6.53 and 6.38 ppm and at 5.71 and 5.64 ppm for the indenyl Cp protons; within each pair each of the doublets were coupled to each other as determined by the COSY experiment. Accordingly, there were 18 aromatic resonances in the ^{13}C NMR spectrum. These spectral characteristics indicated the C_1-symmetrical racemic structure presented in the chiral *ansa* complex **6**, an assignment which was latter confirmed by X-ray crystallography.

The metalation of the *cis*-1,3-cyclopentanediyl bridged bis(indene) ligand **19** led to the formation of only the chiral complex **6** in 51% yield. The appearance of the other two possible *meso* isomers was not observed in the crude product; it may be possible that these isomers were formed but were not stable or isolable under our applied conditions. In the titanocene dichloride formation of the analogous ethylene bridged bis(indene), a 1:2 to 1:10 mixture of *rac* and *meso* isomers were formed in 55% yield, depending on the complex formation conditions.[10a] When the bridging chain was extended to propane, the yield of the metalation step of the relevant bis(indene) ligand was low (the corresponding titanium tetrahydroindenyl complex was formed in 11% yield), although in this case only the racemic isomer was isolated.[19,20] The preexisting closeness of the two indenyl ligands fixed in a rigid cyclopentane framework in bis(indene) ligand **19** appears to contribute to the diastereoselectivity and efficiency observed in the metalation step.

X-ray Analysis of 5. In order to ascertain the conformation of complex **5** in the solid state, an X-ray structure determination was undertaken. The structure of **5** is shown in Figure 1, the crystallographic data are compiled in Table 1, and selected structural data are given in Table 3. Overall, the geometry of the cyclically bridged complex **5** closely resembled that of the unbridged analogue Cp_2TiCl_2[21] and the trimethylene bridged relative $(CH_2)_3(\eta^5\text{-}C_5H_4)TiCl_2$.[22] The Cl—Ti—Cl angle was 94.2° with a normal Ti—Cl bond distance of 2.36 Å (supplementary material and Table 3). In the near-planar cyclopentadienyl ligands (with a <2° deviation) the C—C bond distances narrowly ranged from 1.39

(19) Brintzinger, H. H.; Schnutenhaus, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 777.
(20) Roll, W.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1987**, *322*, 65.
(21) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R. I.; Nernal, I. *Can. J. Chem.* **1975**, *53*, 1622.
(22) Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422.

Table 1. Crystallographic Data for 5

empirical formula	$C_{15}H_{16}TiCl_2$
fw	315.08
cryst color, habit	red plate
cryst dimens	0.25 × 0.2 × 0.05 mm
cryst syst	monoclinic
a	20.89(1) Å
b	11.194(9) Å
c	11.83(14) Å
β	97.93(8)°
V	2742(39) Å^3
space group	*I*2/*a* (No. 15)
Z	8
D_{calcd}	1.5263 g/cm^3
F_{000}	1296
abs coeff	9.889
diffractometer	Nicolet P2$_1$
radiation	Mo Kα (λ = 0.709 260 Å)
temp	20 °C
scan type	$\omega - 2\theta$
scan rate	4−20°/min (in ω)
scan width	(1.42 + 0.30 tan θ)°
$2\theta_{max}$	54°
no. of reflns measd	5879 (total, 3201 unique (R_{int} = 0.061)
cor	Lorentz−polarization
structure soln	direct methods (TEXSAN programs)
refinement	full-matrix least squares
function minimized	$\sigma w(\|F_o\| - \|F_c\|)^2$
least-squares weights	$4F_o^2/s^2(F_o^2)$
p factor	0.03
anomalous dispersion	all non-H atoms
no. of observns ($I > 3.00\sigma(I)$)	1525
no. of variables	163
rfln/param ratio	9.35
residuals: *R*; R_w	0.059, 0.061
goodness-of-fit indicator	2.6
max peak in final diff map	1.2 e/Å^3
min peak in final diff map	−1.3 e/Å^3

Table 2. Positional Parameters and *B*(eq) Values for 5

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ti(1)	0.40521(3)	0.09076(7)	0.16489(6)	2.55(3)
Cl(1)	0.46565(5)	0.2226(1)	0.0647(1)	3.84(5)
Cl(2)	0.36240(5)	−0.0172(1)	0.0000(1)	4.49(6)
C(1)	0.2980(2)	0.0270(5)	0.3618(4)	4.0(2)
C(2)	0.3539(2)	−0.0108(5)	0.4519(4)	4.5(2)
C(3)	0.3873(2)	−0.1073(4)	0.3876(4)	4.4(2)
C(4)	0.3306(3)	−0.1777(5)	0.3241(6)	6.6(3)
C(5)	0.2729(2)	−0.0916(5)	0.3104(5)	5.6(3)
C(6)	0.3180(2)	0.1130(4)	0.2756(3)	3.1(2)
C(7)	0.2921(2)	0.1235(4)	0.1601(4)	3.3(2)
C(8)	0.3182(2)	0.2249(4)	0.1135(4)	3.6(2)
C(9)	0.3596(2)	0.2801(4)	0.2020(4)	3.5(2)
C(10)	0.3607(2)	0.2118(4)	0.3001(3)	3.4(2)
C(11)	0.4315(2)	−0.0553(4)	0.3112(4)	3.5(2)
C(12)	0.4734(2)	0.0444(4)	0.3367(3)	3.5(2)
C(13)	0.5135(2)	0.0540(4)	0.2531(4)	3.9(2)
C(14)	0.4974(2)	−0.0354(5)	0.1737(4)	4.4(2)
C(15)	0.4478(2)	−0.1028(4)	0.2095(4)	4.2(2)

Table 3. Selected Bond Lengths (Å) for 5

Ti(1)−Cl(1)	2.365(9)	Ti(1)−C(15)	2.374(5)
Ti1−Cl(2)	2.360(20)	C(6)−C(7)	1.400(20)
Ti(1)−C(6)	2.400(10)	C(6)−C(10)	1.426(6)
Ti(1)−C(7)	2.385(4)	C(7)−C(8)	1.405(7)
Ti(1)−C(8)	2.371(5)	C(8)−C(9)	1.410(10)
Ti(1)−C(9)	2.389(5)	C(9)−C(10)	1.390(10)
Ti(1)−C(10)	2.380(20)	C(11)−C(12)	1.426(6)
Ti(1)−C(11)	2.390(20)	C(11)−C(15)	1.400(10)
Ti(1)−C(12)	2.370(20)	C(12)−C(13)	1.390(10)
Ti(1)−C(13)	2.394(6)	C(13)−C(14)	1.380(10)
Ti(1)−C(14)	2.379(5)	C(14)−C(15)	1.394(7)

to 1.426 Å, and each of the aromatic carbons was almost evenly bonded to the Ti center (2.37−2.40 Å). The C−C bond distances within the bridging ring were almost uniform (1.52−1.54 Å). As may be seen in Figure 1, both of the bridging bonds C(1)−C(6) and C(3)−C(11)

Table 4. Crystallographic Parameters for 6

empirical formula	$C_{23}H_{22}TiCl_2$
fw	417.23
cryst color, habit	dark red, hexag
cryst dimens	0.25 × 0.25 × 0.11 mm
cryst syst	monoclinic
ω scan peak width at half-height	0.38
a	8.323(2) Å
b	14.449(3) Å
c	15.034(1) Å
β	90.10(1)°
V	1808.0(6)
space group	*P*2$_1$/*n* (No. 14)
Z	4
D_{calcd}	1.533 g/cm^3
F_{000}	864
μ(Cu Kα)	68.37 cm^{-1}
diffractometer	Rigaku AFC5R
radiation	Cu Kα (λ = 1.541 78 Å)
temp	20 °C
takeoff angle	6.0°
detector aperture	6.0 mm horiz, 6.0 mm vert
cryst to detector dist	40 cm
scan type	ω−2θ
scan rate	32.0°/min (in ω; 2 rescans)
scan width	(1.42 + 0.30 tan θ)°
$2\theta_{max}$	120.2
no. of rflns measd	5627 total, 2823 unique (R_{int} = 0.031)
cor	Lorentz−polarization, abs (transmissn factors 0.87−1.25)
structure soln	direct methods
refinement	full-matrix least squares
function minimized	$\sigma w(\|F_o\| - \|F_c\|)^2$
least-squares weights	$4F_o^2/s^2(F_o^2)$
p factor	0.03
anomalous dispersion	all non-H atoms
no. of observns ($I > 3.00\sigma(I)$)	2067
no. of variables	235
rfln/param ratio	8.80
residuals: *R*; R_w	0.032; 0.041
goodness-of-fit indicator	1.53
max shift/error in final cycle	0.00
max peak in final diff map	0.61 e Å^{-3}
min peak in final diff map	−0.25 e Å^{-3}

were out of the mean plane of the Cp rings by a 8−9° angle. Each of these bonds formed angles of about 113° with the adjacent C−C bond on the cyclopentane ring. Similar out-of-plane distortion and positive deviations from a tetrahedral angle had been previously observed in $(CH_2)_3(\eta^5\text{-}C_5H_4)TiCl_2$[22] and other *ansa*-metallocene systems.[23] The conformation of complex **5** has the two cyclopentadienyl rings eclipsed with each other (torsion angles Cl(2)−Ti(1)−C(8)−C(9) = −170.0° vs Cl(2)−Ti(1)−C(14)−C(13) = 170.4°).

X-ray Analysis of 6. The conformation of complex **6** in the solid state was also determined by X-ray crystallography. The experimental data and the selected bond parameters are included in Tables 4−6. Figure 2 shows the structure of the unique molecule found in the unit cell. The geometry around the $TiCl_2$ moiety in **6** was very similar to that of the analogous c-C5CpTiCl$_2$ (**5**). The Cl−Ti bond distances and the Cl−Ti−Cl angle were 2.32 and 2.35 Å and 93.7°, compared to the related parameters of 2.36 Å and 94.2° for **5**. However, a major difference appeared in the η^5-cyclopentadienyl ligand−metal portion. Like other indenyl complexes,[24] complex **6** contains two types of Ti−C

(23) Smith, J. A.; Seyerl, J. V.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175.

(24) (a) Atwood, J. L.; Hunter, W. E.; Hrncir, D. C.; Samuel, E.; Alt, H.; Rausch, M. D. *Inorg. Chem.* **1975**, *14*, 1757. (b) Piccolrovazzi, N.; Pino, P.; Consiglio, G.; Sironi, A.; Moret, M. *Organometallics* **1990**, *9*, 3098.

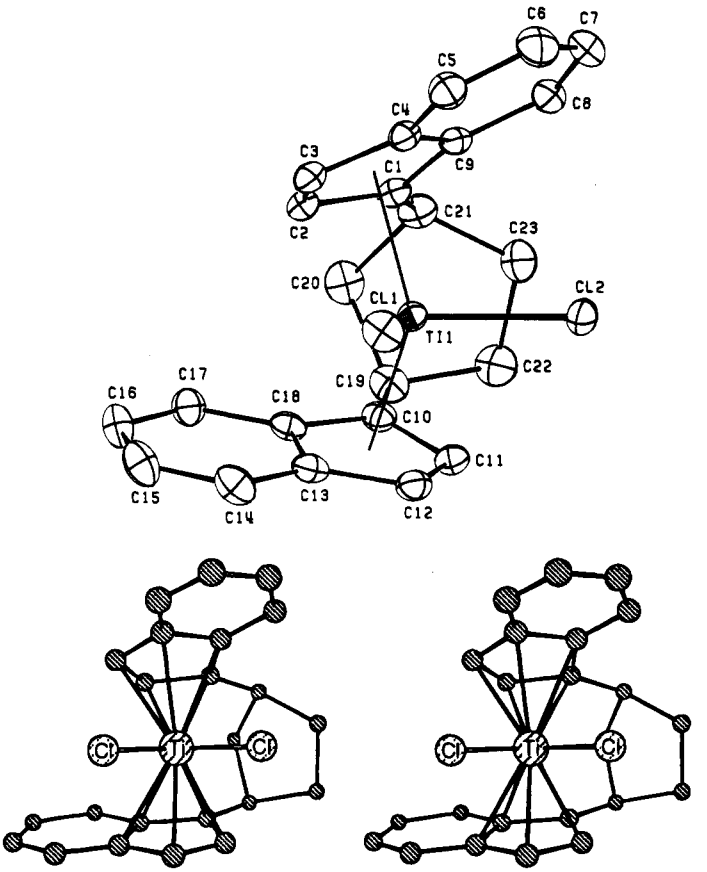


Figure 2. (a, top) ORTEP drawing of **6** drawn at the 50% probability level. (b, bottom) Stereoview of **6**.

Table 5. Positional Parameters and *B*(eq) Values for 6

atom	*x*	*y*	*z*	*B*(eq), Å^2
Ti(1)	0.88869(6)	0.39445(4)	0.79177(4)	2.18(2)
Cl(1)	1.0428(1)	0.37719(6)	0.92200(6)	3.67(4)
Cl(2)	1.10720(9)	0.37268(6)	0.69812(6)	3.25(4)
C(1)	0.7579(4)	0.5170(2)	0.7162(2)	2.6(1)
C(2)	0.7008(4)	0.5145(2)	0.8047(2)	2.7(1)
C(3)	0.8254(4)	0.5361(2)	0.8635(2)	3.0(1)
C(4)	0.9612(4)	0.5626(2)	0.8119(2)	2.7(1)
C(5)	1.1147(4)	0.5953(3)	0.8369(2)	3.7(2)
C(6)	1.2160(4)	0.6243(3)	0.7712(3)	4.2(2)
C(7)	1.1705(4)	0.6202(2)	0.6812(3)	3.9(2)
C(8)	1.0260(4)	0.5850(2)	0.6543(2)	3.2(2)
C(9)	0.9184(4)	0.5552(2)	0.7209(2)	2.7(1)
C(10)	0.6637(4)	0.3124(2)	0.7207(2)	2.7(1)
C(11)	0.8059(4)	0.2603(2)	0.7164(2)	3.0(1)
C(12)	0.8590(4)	0.2373(2)	0.8018(2)	3.0(2)
C(13)	0.7385(4)	0.2667(2)	0.8633(2)	2.9(1)
C(14)	0.7243(4)	0.2576(3)	0.9562(2)	3.7(2)
C(15)	0.5890(4)	0.2902(3)	0.9963(2)	4.2(2)
C(16)	0.4650(4)	0.3324(3)	0.9475(2)	3.8(2)
C(17)	0.4756(4)	0.3439(3)	0.8578(2)	3.2(2)
C(18)	0.6161(3)	0.3125(2)	0.8133(2)	2.7(1)
C(19)	0.5634(4)	0.3458(3)	0.6430(2)	3.3(2)
C(20)	0.5074(4)	0.4461(3)	0.6512(2)	3.5(2)
C(21)	0.6612(4)	0.5015(2)	0.6328(2)	3.1(2)
C(22)	0.6588(4)	0.3505(3)	0.5562(2)	3.9(2)
C(23)	0.7491(4)	0.4427(3)	0.5612(2)	3.5(2)

bonds: longer than normal bonding for the ring fusing carbons (e.g. Ti—C(9) and Ti—C(4) were 2.57 and 2.52 Å) and the usual bonding for the rest of the η^5 moiety (e.g. Ti—C(1), Ti—C(2), and Ti—C(3) were 2.37, 2.34, and 2.37 Å, respectively, compared to the normal Ti—C bonding range of 2.37—2.40 Å in **5**). As may be seen in Figure 2, the geometry adopted by the two indenyl rings was near synclinal, with a deviation of ca. 2° (e.g. torsion angles Cl(1)—Ti(1)—C(3)—C(4) = 91.2° vs Cl(1)—Ti(1)—C(13)—C(12) = 91.2°).

Table 6. Selected Bond Lengths (Å) for 6

Ti(1)—Cl(1)	2.352(1)	C(1)—C(2)	1.415(4)
Ti(1)—Cl(2)	2.323(1)	C(1)—C(9)	1.447(4)
Ti(1)—C(1)	2.368(3)	C(3)—C(4)	1.424(4)
Ti(1)—C(2)	2.344(3)	C(4)—C(9)	1.417(4)
Ti(1)—C(3)	2.373(3)	C(2)—C(3)	1.397(4)
Ti(1)—C(4)	2.522(3)	C(13)—C(18)	1.428(4)
Ti(1)—C(10)	2.459(3)	C(10)—C(11)	1.405(4)
Ti(1)—C(11)	2.348(3)	C(10)—C(18)	1.449(4)
Ti(1)—C(12)	2.289(3)	C(11)—C(12)	1.396(5)
Ti(1)—C(13)	2.476(3)	C(12)—C(13)	1.430(5)

Solution Conformation of 5. Unlike previously prepared C_2-symmetric *ansa*-titanocenes which could interconvert between two identical conformations, our C_s-symmetric complex **5** would interconvert between two diastereomeric conformations and could have a preference for one conformation. In order to address this point, we have compared the NMR spectral data for our complex **5** with several other *ansa*-titanocene complexes. Brintzinger[23] has previously compared the X-ray structures and the NMR data of the methylene-, ethylene- (including tetramethylethylene) and trimethylene-bridged *ansa*-titanocene dichlorides and noted the following: (1) The noncontact Cp—Cp distances at the bridgehead carbons in these complexes were all shorter than the normal van der Waals distance of about 3.30 Å. (2) The resulting extra π-electron density built up at the bridgehead position was shifted to the proximal Cp ring carbons, thus at least partially causing the upfield ^{1}H and ^{13}C NMR chemical shifts on these carbons, relative to the bridgehead carbons, while those on the distal Cp ring carbons fell in between. Other possible factors influencing the relative chemical shifts in the Cp ring include the closeness of a nucleus to the magnetic anisotropic zone imposed by the $TiCl_2$ frag-

Table 7. Comparative Data for Cyclopentadienyl Rings in *ansa*-Titanocene Dichlorides

complex	noncontact bridgehead dist (Å)	δ (ppm, CD_2Cl_2)	
		^{1}H NMR	^{13}C NMR
$[CH_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$[a]	2.30	5.58, 6.95; Δδ = 1.37	145.4, 131.3, 112.8; Δδ = 32.6
$[(CH_2)_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$[a]	2.68	6.09, 6.91; Δδ = 0.82	139.7, 129.4, 114.1; Δδ = 24.5
$[(CH_3)_4C_2(\eta^5\text{-}C_5H_4)_2]TiCl_2$[a,b]		6.21, 6.86; Δδ = 0.65	145.3, 128.0, 112.8; Δδ = 32.5
$[(CH_2)_3(\eta^5\text{-}C_5H_4)_2]TiCl_2$[a]	3.01	6.45, 6.49; Δδ = 0.04	127.6, 122.7, 120.4; Δδ = 7.2
c-C5Cp$_2$TiCl$_2$[b,c]	3.01	6.61, 6.51, 6.39, 6.28; Δδ(max) = 0.33	130.54, 127.25, 125.21, 121.22, 112.47; Δδ(max) = 18.07

[a] Reference 23. [b] Spectra taken in $CDCl_3$. [c] This work.

ment. (3) The extent of the upfield shift decreased as the noncontact distances increased. For example, a Δδ value of 1.37 or 32.6 ppm was found in the ^{1}H NMR or ^{13}C NMR spectrum, respectively, of $CH_2(\eta^5\text{-}C_5H_4)_2TiCl_2$ with a bridgehead carbon distance of 2.30 Å, whereas the corresponding Δδ values and noncontact distance were 0.82 and 24.5 ppm and 2.68 Å for $(CH_2)_2(\eta^5\text{-}C_5H_4)_2TiCl_2$ (see Table 7). (4) Conformational mobility decreased the chemical shift differences. In the case of the rigid methylene-bridged or of the less rigid ethylene-bridged complexes, a large chemical shift difference was observed due to the maintained inequivalence of the proximal and distal carbons of the cyclopentadienyl rings. The larger degree of torsional ring mobility in $(CH_2)_3(\eta^5\text{-}C_5H_4)_2TiCl_2$, however, enabled an interchange of the relatively congested portions of the cyclopentadienyl rings; this averaging of the positions led to a smaller chemical shift difference Δδ of 0.04 or 7.2 ppm in the ^{1}H NMR or ^{13}C NMR spectrum.

In our cyclopentane-bridged complex **5** the bridgehead distance was exactly the same (3.01 Å) as in $(CH_2)_3(\eta^5\text{-}C_5H_4)_2TiCl_2$ but the relevant Δδ values of 0.33 and 18.07 ppm were much larger, resembling more those of the ethylene-bridged analogue. If complex **5** were conformationally mobile between two fairly equivalently occupied conformations, we would expect a much smaller chemical shift difference in accord with the trimethylene-bridged complex. Thus, it is apparent that our complex **5** is behaving either as a conformationally less mobile molecule or as a molecule which has a strong preference for one conformation. A conformational flipping of the $TiCl_2$ fragment in the complex c-C5Cp$_2$TiCl$_2$ would lead to a diastereomeric form which could be less thermodynamically stable due to the steric interactions between the $TiCl_2$ moiety and the centered methano bridge. Even with a small barrier to interconversion, if the compound spent more time in the favored of the two conformations, we could justify the larger observed chemical shift differences due to uneven averaging of the conformational effects.

In order to further study the conformational inversion in the complex c-C$_5$Cp$_2$TiCl$_2$, we carried out a variable temperature ^{1}H NMR experiment of **5** in solution. Throughout the entire attainable NMR solvent temperature range (acetone-d_6, +47 to −85 °C) only one set of constantly sharp signals was observed. Since we did not observe a second set of signals within the detection limit of the ^{1}H NMR method at a temperature as low as −85 °C, the conformational inversion in complex **5** must be either be a low energy process ($\Delta G^{\ddagger}$ < ca. 9 kcal/mol, assuming a nominal ca. 0.5 ppm separation in chemical shifts[25]), or if we assume that coalescence occurs at above −85 °C, the population of the less stable conformation must be beyond the detection limit of the ^{1}H NMR technique. Given our data, however, the most we can say is that it appears that one conformation is significantly favored, but we cannot judge the barrier to interconversion.

A similar set of inconclusive conformational mobility arguments can also be made in the case of **6**. A variable-temperature ^{1}H NMR experiment was performed on **6** and again, as in the case of c-C5Cp$_2$TiCl$_2$ (**5**), only one set of constantly sharp signals was observed throughout the entire attainable NMR solvent temperature range ($CDCl_3$, +27 to −57 °C), indicating again either a low-energy barrier to any conformational changes and/or a preference for one conformation.

Conclusion. We have prepared for the first time *ansa*-bis(cyclopentadienyl)titanium dichloride and *ansa*-bis(indenyl)titanium dichloride complexes bridged by the cis-1,3-cyclopentanediyl group. These complexes were formed in good yield and, in the indenyl case, with complete stereoselectivity, exhibiting selectivity more similar to ethano rather than propano bridges. Two complexes were characterized by X-ray crystallography. The solution conformation of **5** and **6** likely favors one diastereomeric conformation, and no estimate of the barrier to interconversion was obtained.

Experimental Section

General Methods. Unless otherwise noted, all chemicals were obtained from commercial suppliers and used without further purification. Ethereal and aromatic solvents were distilled from sodium benzophenone ketyl under nitrogen or argon. Amine, hydrocarbon, and halogenated solvents were distilled from CaH_2. Pyrrolidine and HMPA were distilled from BaO. All reactions involving air- and moisture-sensitive reagents were carried out under either a nitrogen or an argon atmosphere by utilizing standard Schlenk techniques or a Vacuum Atmospheres drybox (under nitrogen). All glassware was oven-dried prior to use. Routine solvent removal was performed with rotary evaporators using an aspirator and a water bath. Routine vacuum line operations were carried out with a multiple line apparatus (10^{-2} Torr at ambient temperature).

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-400 or JEOL INM GSX-270 instrument. Data are reported as follows: chemical shifts in parts per million (ppm) relative to residual solvent peaks (mutiplicity, coupling constants in hertz (rounded to 0.5 Hz), number of hydrogens, hydrogen numbering in the structure). For ^{1}H NMR spectra, the peaks due to the residual $CHCl_3$, C_6H_6, and acetone are listed at 7.24, 7.15, and 2.04 ppm, respectively, and for ^{13}C NMR spectra, the central peaks of $CDCl_3$, C_6D_6, and acetone-D_6 multiplets are assigned chemical shifts of 77.0, 128.0, and 206.0 ppm, respectively. DEPT and APT ^{13}C NMR spectra were obtained for some compounds. The number of hydrogens on each carbon is indicated as quat (quaternary), CH (methine), CH_2 (methylene), or CH_3 (methyl). Unless otherwise noted, multiplicities

(25) Hirsch, J. *Top. Stereochem.* **1967**, *1*, 199.

and compound ratios are deduced from the electronic integration by the XL-400 or the GSX-270.

Infrared spectra were obtained on a Perkin-Elmer 1800 FT-IR or Perkin-Elmer 1310 infrared spectrometer and were referenced to carbon dioxide or polystyrene, respectively. Only characteristic and/or strong signals are reported. Low-resolution and high resolution mass spectra were measured on a Finnegan MAT-90 mass spectrometer. Low resolution mass spectra are reported as m/z (relative intensity) at 40 or 70 eV. Melting points were determined in open Pyrex capillary tubes with a Thomas-Hoover Unimelt apparatus and are uncorrected. Elemental analyses were conducted by Galbraith Analytical Laboratories (Knoxville, TN), Schwarzkopf Microanalytical Laboratories (Woodside, NY), and Desert Analytics (Tucson, AZ).

Flash chromatography was performed using flash silica gel (E. Merck Reagents silica gel 60, 230–400 mesh ASTM) or neutral alumina (E. Merck Reagents activated alumina F-20, 80–200 mesh) as they were received or deactivated as required. Highly polar crude products were absorbed to the absorbents with the aid of a polar solvent which was removed *in vacuo* before the samples were applied to the column. Preparative thin-layer chromatography was carried out by using 500 μm E. Merck silica gel 60 F-254. Analytical thin-layer chromatography (TLC) was performed on 200 μm thickness E. Merck plastic sheets coated with silica gel 60 F-254.

***cis*-2-Cyclopentene-1,4-diol (9).**[13] To cyclopentadiene (freshly cracked from dicyclopentadiene, 1.62 mL, 24.2 mmol) in methanol (distilled, 450 mL) in a 2 L Hanovia reactor was added thiourea (1.84 g, 16.4 mmol) and rose bengal (50 mg). The mixture was cooled in a 0 °C bath, and oxygen was bubbled through for 5 min, followed by irradiation with a high pressure mercury immersion lamp (Hanovia 679A36) with a Pyrex filter under a current of oxygen for 2.5 h. The irradiation and the oxygen bubbling were stopped, and the reaction mixture was stirred at room temperature for 12 h in the dark. Methanol was removed *via* rotary evaporation to provide a brick red residue. The same reaction was repeated an additional nine times and the combined residue was extracted with THF (4 × 50 mL) until the extract was colorless. THF was distilled off under reduced pressure, and the resulting red oily material (22.88 g) was subjected to vacuum distillation to afford a pink oil fraction (ca. 80–100 °C/10^{-2} Torr, 6.86 g, 28%) as the desired ene diol **9**. Although a clean ^{1}H NMR spectrum, identical with those reported in the literature,[13] could be obtained from this product, its further purification by short path flash chromatography (SiO_2/ethyl acetate and then 50% THF in ethyl acetate) was necessary to ensure a high ratio of substrate to catalyst in the subsequent hydrogenation step. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.98 (s, 2 H), 4.63 (dd, J = 7.0, 3.5 Hz, 2 H), 2.87 (br s, 2 H), 2.68 (ddd, J = 14.5, 7.0, 7.0 Hz, 1 H), 1.55 (ddd, J = 14.5, 3.5, 3.5 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.52, 75.07, 43.79. MS (EI, 70 eV, m/z relative intensity)) 100 (M^+, 1.7%), 83 (M^+ − OH, 100), 82 (M^+ − H_2O, 34), 72 (39), 71 (39), 54 (90).

***cis*-1,3-Cyclopentanediol (10).**[14] The Sable and Posternak procedure[14] used 50% of Adam's catalyst for the hydrogenation. A much lower percentage of the same catalyst is sufficient to calalyze the same reaction, as long as the starting ene diol is purified by chromatography described in the preceding procedure. A new hydrogenation procedure is as follows. Ene diol **9** (3.285 g, 32.9 mmol) in water (60 mL) was hydrogenated in the presence of Adam's catalyst (Strem, 360 mg, 11%) under hydrogen at 50 psi for 93 h. The mixture was filtered through filter paper. Removal of water from the filtrate gave a colorless oil (3.007 g, 92%) as the title compound **10**. IR (thin film): 3350, 2960, 1430, 1350, 1160, 1075, 1000 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73 (br s, 2 H), 2.30 (br s, 2 H), 1.90 (m, 5 H), 1.76 (dt, J = 14.5, 5.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 74.00, 44.13, 33.96. MS (EI, 70 eV; m/z (relative intensity)): 103 (M^+ + 1, 4%), 85 (M^+ − OH, 18), 84 (M^+ − H_2O, 64), 55 (100).

***cis*-1,3-Cyclopentanediol Bis(methanesulfonate) (11).** To diol **10** (4.163 g, 40.8 mmol) in Ch_2Cl_2 (326 mL) was added at 0 °C triethylamine (14.9 mL, 106.08 mmol) and methanesulfonyl chloride (6.93 mL, 87.7 mmol) in CH_2Cl_2 (45 mL) dropwise under nitrogen. The mixture was stirred at 0 °C for 30 min and room temperature for another 30 min and then quenched with a saturated NH_4Cl solution in ice–water (100 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic portion was dried over anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation. Further drying *in vacuo* and recrystallization from methanol (200 mL) afforded pure **11** as a light yellow solid (9.53 g, 91%). Mp: 86–88 °C. IR (KBr) 3018, 2936, 1424, 1360, 1336, 1159, 1068, 980, 930 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.17 (br s, 2 H), 3.02 (s, 6 H), 2.31 (m, 2 H), 2.27 (m, 2 H), 2.07 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.70, 40.30, 38.68, 31.47. MS (CI, isobutane; m/z (relative intensity)): 259 (M^+ + 1, 3%), 258 (M^+, 26), 214 (26), 162 (33), 161 (20), 84 (18), 82 (88), 65 (100), 53 (89).

***cis*-1,3-Cyclopentanediol Bis(tosylate) (12).** Tosyl chloride (98%, 2.563 g, 13.12 mmol) was added to diol **10** (448 mg, 4.39 mmol) in pyridine (10 mL) at −10 °C under nitrogen. The mixture was stirred well for 15 min and stored in a refrigerator (ca. 4 °C) for 18 h. The pink slurry was poured into 30% H_2SO_4 in ice–water and extracted with CH_2Cl_2 (3 × 10 mL). The organic portion was washed with brine (15 mL) and dried with anhydrous Na_2SO_4 to give a pink residue (1.73 g, 96%) upon removal of the solvent. Two recrystallizations from 95% ethanol afforded bis(tosylate) **12** as white crystals (1.07 g, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.0 Hz, 4 H), 7.73 (d, J = 8.0 Hz, 4 H), 4.85 (m, 2 H), 2.43 (s, 6 H), 2.09 (m, 1 H), 1.95 (m, 3 H), 1.79 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.74, 133.93, 129.83, 127.67, 81.03, 39.38, 30.99, 21.62. MS (EI, 70 eV; m/z (relative intensity) 411 (M^+ + 1, 2%), 410 (M^+, 9), 380 (11), 344 (11), 238 (10), 154 (40), 90 (62), 66 (100).

1,3-*cis*-Bis(cyclopentadienyl)cyclopentane (13). Method 1. To a solid mixture of cyclopentadienylmagnesium bromide (ca. 45%, 9.000 g, 14 mmol) and bis(mesylate) **11** (2.064 g, 8 mmol) was added THF (60 mL) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 1 h and then at room temperature for 30 h. The resulting orange slurry was quenched with ice–water (20 mL), diluted with petroleum ether (30 mL), filtered through a SiO_2 pad, and washed with petroleum ether (100 mL). The aqueous portion was washed with petroleum ether (3 × 10 mL). The combined organic portions were washed with brine (30 mL), dried over Na_2SO_4, and concentrated at 20 °C *via* rotary evaporation to afford an orange oil (1.987 g). The crude product was further purified by short path SiO_2 chromatography with petroleum ether as the eluting solvent to give a clear oil (1.400 g, 88%) of the title compound **13** as a mixture of double-bondnd isomers. It was usually stored at −25 °C under nitrogen and converted to the next step within 1 or 2 days. R_f 0.35 (SiO_2/petroleum ether). IR (KBr) 3060, 2949, 2869, 1599, 1522, 1448, 1364, 1345, 948, 890, 810, 676 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (m, 1 H), 6.43 (m, 1.7 H), 6.26 (m, 1.5 H), 6.18 (br s, 1 H), 6.01 (m, 0.8 H), 2.98 (m, 6 H), 2.23 (m, 1 H), 2.01 (m, 2 H), 1.66 (m, 2 H), 1.50 (m, 1 H). MS (EI, 70 eV; m/z (relative intensity)): 199 (M^+ + 1, 12%), 198 (M^+, 74), 156 (19), 131 (51), 117 (14), 91 (100), 79 (33), 65 (22). HRMS (EI, 70 eV): calcd for $C_{15}H_{18}$ 198.1408, found 198.1405.

Method 2. To a solid mixture of lithium cyclopentadienylide (97%, 54 mg, 0.75 mmol) and bis(mesylate) **11** (77.4 mg, 0.3 mmol) was added THF (3 mL) and HMPA (264 μL, 1.5 mmol) at −78 °C under nitrogen. The mixture was slowly warmed to room temperature and stirred for 4 h. The dark brown solution was quenched with ice-water and extracted with petroleum ether (3 × 5 mL) to give a yellow oil upon removal of the solvents. Purification by flash chromatography (SiO_2/petroleum ether) gave first the desired product **13** (28 mg, 47%) and then the Diels–Alder adduct of the elimination

product and the desired product (**13** + **14**; 7 mg, 14%). The isolated desired product **13** showed a different ratio of double-bond isomers compared to that obtained from method 1. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (m, 1.1 H), 6.42 (m, 2 H), 6.25 (m, 0.9 H), 6.17 (br s, 0.9 H), 6.00 (m, 1.1 H), 2.94 (br s, 4 H), 2.90 (br s, 2 H), 2.22 (m, 1 H), 2.01 (m, 2 H), 1.67 (m, 2 H),1.53 (m,1 H). MS (EI, 70 eV; *m*/*z* (relative intensity)): 199 (M^+ + 1, 2%), 198 (M^+, 7), 170 (3), 157 (5), 141 (2), 131 (9), 91 (18), 86 (64), 84 (100). HRMS (EI, 70 eV): calcd for $C_{15}H_{18}$ 198.1408, found 198.1393. Physical properties of the Diels–Alder adduct are as follows. R_f 0.15 (SiO_2/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54 (m, 1 H), 6.44 (br s, 1.4 H), 6.30 (m, 0.8 H), 6.21 (br s, 0.6 H), 6.14 (m, 0.4 H), 6.05 (m, 0.7 H), 5.96 (br s, 0.1 H), 2.97 (m, 6 H), 2.24 (m, 1 H), 2.05 (m, 3.3 H), 1.62 (m, 4 H). MS (EI, 70 eV; *m*/*z* (relative intensity)): 331 (M^+ + 1, 26%), 330 (M^+, 100), 263 (22), 197 (32), 141 (5), 131 (21), 91 (23).

Method 3. By the same procedure as in method 2 sodium cyclopentadienylide (Aldrich, 2.0 M in THF, 1.25 mL, 2.5 mmol) was added to a solution of bis(tosylate) **12** (420 mg, 1 mmol) in THF (12 mL) to afford after purification the desired product **13** (108 mg, 54.5%) and again the Diels–Alder adduct (**13** + **14**; 34 mg, 10%), both of which had ^{1}H NMR spectra identical with those observed in method 2.

Method 4. By the same procedure as in Method 1 bis(cyclopentadienyl)magnesium (46 mg, 0.3 mmol), bis(mesylate) **11** (38.7 mg, 0.15 mmol), HMPA (209 μL, 1.2 mmol), and THF (3 mL) were mixed at −78 °C under nitrogen. The solution was stirred at room temperature for 40 h and worked up as described above to give a pale yellow oil (35 mg, 97%) as the crude product which showed a clean ^{1}H NMR spectrum, identical with that from tetraene **13** in method 2.

[*cis*-1,3-Cyclopentanediylbis(η^5-cyclopentadienyl)]titanium Dichloride (c-C5Cp$_2$TiCl$_2$; 5). To the unsubstituted 1,3-bis(cyclopentadienyl)cyclopentane ligand **13** (148 mg, 0.747 mmol) in THF (37 mL) was added dropwise *n*-butyllithium (1.84 M in hexane, 0.81 mL, 1.50 mmol) at −78 °C under nitrogen. The solution was stirred at 0 °C for 30 min and at room temperature for another 30 min. The resulting light yellow dilithio salt was recooled to −40 °C, and $TiCl_3$·3THF (277 mg, 0.747 mmol) was added in one portion from a side arm. The cold bath was removed, and the slurry was warmed to room temperature and further heated at reflux for 7 h. The dark green solution was recooled to −40 °C, and 6 N HCl (0.5 mL, 3 mmol) was added *via* a syringe over 2 min. The mixture was warmed to room temperature, and then compressed air was bubbled through for 10 min, rendering it a dark red solution. Diethyl ether (10 mL) was added and the mixture was filtered through a short path SiO_2 column and washed with diethyl ether (ca. 50 mL). Removal of the solvent from the dark red solution under reduced pressure afforded **5** as a deep red solid (205 mg, 87%). Analytically pure product can be obtained by recrystallization from CH_2Cl_2/hexane. Mp: 197–197.5 °C (hexane/CH_2Cl_2). IR (KBr) 3100, 2950, 2890, 1490, 1460, 1430, 1330, 1300, 1050, 825 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.61 (m, 2 H), 6.51 (m, 2 H), 6.39 (m, 2 H), 6.28 (m, 2 H), 3.40 (m, 2 H), 2.44 (d, J = 13.0 Hz, 1 H), 2.18 (dt, J = 13.0, 6.0 Hz, 1 H), 1.90 (m, 2 H), 1.77 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.54, 127.25, 125.21, 121.22, 112.47, 38.19, 34.09, 26.69. MS (EI, 70 eV; *m*/*z* (relative intensity)): 318 (M^+ + 4, 8%), 316 (M^++ 2, 39), 314 (M^+, 57), 281 (M^+ + 2 − Cl, 13), 280 (M^+ + 2 − HCl, 16), 279 (M^+ − 2 Cl, 36), 278 (M^+ − 2 Cl − H, 27), 277 (M^+ − 2 HCl, 8), 242 (100), 240 (17). HRMS (EI, 70 eV): calcd for $C_{15}H_{16}TiCl_2$ 314.0109, found 314.0109. Anal. Calcd for $C_{15}H_{16}TiCl_2$: C, 57.16; H, 5.12. Found: C, 57.18; H, 5.10.

X-ray Structure Determinations. A single crystal of **5** was grown from methylene chloride and hexane by slow evaporation. A single crystal of **6** was grown from methylene chloride and hexane by slow evaporation. X-ray intensity data were obtained at 20 °C on a Syntex $P2_1$ four circle autodiffractometer system (for **5**) or a Rigaku automated four circle single crystal diffractometer system (for **6**) using graphite monochromated Mo Kα or Cu radiation, at 20 kV/50 mA or 50 kV/220 mA, respectively. The cell constants and an orientation matrix for data collection were obtained from the setting angles of 15 centered reflections on a Syntex $P2_1$ or from a least-squares refinement by using the setting angles of 25 centered reflections on a Rigaku AFC5R. Scans were made at a maximum speed of 20 or 32°/min in ω (automatically determined in each case) on a Syntex $P2_1$ or a Rigaku AFC5R, respectively. The intensities of 3 standard reflections were measured after every 150 reflections and remained constant throughout the data collection; no decay correction was applied. The crystallogaphic calculations were performed by using the TEXSAN program.[26] The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods. The hydrogen atoms were included in calculated positions for the final full-matrix least-squares refinement cycles but were not refined.

***cis*-1,3-Bis(3-indenyl)cyclopentane (19).** To indene (distilled, 0.446 mL, 3.75 mmol) in THF (7.5 mL) was added at −78 °C *n*-butyllithium (2.25 M in hexane, 1.7 mL, 3.83 mmol) under nitrogen. The yellow brown slurry was stirred at 0 °C for 30 min and at room temperature for 30 min. The brown solution was brought to −78 °C, and bis(mesylate) **11** (387 mg, 1.5 mmol) in THF (7.5 mL) was added *via* a cannula. The cold bath was removed and the mixture was stirred for 4 h, quenched with ice–water (10 mL) and saturated ammonium chloride (10 mL), and diluted with petroleum ether (10 mL). The aqueous portion was extracted with petrolum ether (3 × 10 mL). The combined organic portions were washed with brine (15 mL) and dried with anhydrous Na_2SO_4. Removal of the solvent gave a yellow oily residue which was purified by flash chromatography (SiO_2/0–2% diethyl ether in petroleum ether) to afford **19** as a white powder (356 mg, 80%). Mp: 85–86 °C. R_f 0.50 (SiO_2/3% Et_2O in petroleum ether). IR (KBr) 3072, 3040, 3019, 2954, 2907, 2864, 1603, 1572, 1457, 1397, 1385, 1325, 1016, 966, 916, 761, 726 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (m, 4 H), 7.31 (m, 2 H), 7.20 (t, J = 7.5 Hz, 2 H), 6.25 (d, J = 1.5 Hz, 2 H), 3.33 (s, 4 H), 3.28 (m, 2 H), 2.57 (dt, J = 12.5, 6.5 Hz, 1 H), 2.27 (m, 2 H), 1.90 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.24, 145.39, 144.82, 125.91, 125.69, 124.44, 123.77, 119.64, 38.60, 37.78, 37.58, 30.88. MS (EI, 70 eV; *m*/*z* (relative intensity)): 299 (M^+ + 1, 9%), 298 (M^+, 80), 269 (53), 254 (35), 230 (78), 180 (71), 140 (96), 116 (73), 114 (100). HRMS (EI, 70 eV): calcd for $C_{23}H_{22}$ 298.1721, found 298.1720. Anal. Calcd for $C_{23}H_{22}$: C, 92.56; H, 7.44. Found: C, 91.58; H, 6.94.

In some cases other double bond isomers of compound **19** were observed. The ^{1}H NMR diagnostic signals are as follows: δ 6.82 (m, 1 H), 6.53 (m, 1 H), 6.23 (s, 1 H), 3.49 (m, 1 H), 3.28 (m, 3 H).

***rac*-[1,3-Cyclopentanediylbis(η^5-1-indenyl)]titanium Dichloride (*rac*-c-C5In$_2$TiCl$_2$; 6).** To bis(indene) **13** (168.2 mg, 0.564 mmol) in THF (10 mL) at −78 °C was added *n*-butyllithium (2.0 M, 0.58 mL, 1.16 mmol) under nitrogen. The bath was removed, and the solution was stirred at 0 °C for 30 min and at room temperature for 30 min to give an orange-yellow solution. The dilithio salt was recooled to −78 °C, and $TiCl_3$ (93 mg, 0.59 mmol) was added from a side arm in one portion. The greenish solution was warmed to room temperature and heated at reflux for 14 h and the solvent stripped *in vacuo*. The resulting greenish residue was taken up in $CHCl_3$ (10 mL) and 6 N HCl (10 mL) at −78 °C. While exposed to air, the mixture was vigorously stirred at room temperature for 1 h. The aqueous portion was separated and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic portions were dried over anhydrous $CaCl_2$ and concentrated under reduced pressure to produce a dark greenish residue. Two recrystallizations of the crude product from a CH_2Cl_2/

(26) TEXSAN Structure Analysis Package, Molecular Structure Corp., 1985.

hexane cosolvent provided the title compound **6** as dark green crystals (120.4 mg, 51%). Mp 223–225 °C (hexane/CH_2Cl_2). IR (KBr) 3100, 2950, 2900, 2890, 1610, 1460, 1440, 1315, 1300, 1220, 1060, 845, 800, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, H-12), 7.85 (d, J, 8.5 Hz, H-20), 7.65 (d, J = 8.5 Hz, H-9), 7.43 (m, H-18), 7.27 (m, H-11, 21, 19), 7.15 (m, H-10), 6.53 (d, J = 3.5 Hz, H-7), 6.38 (d, J = 3.5 Hz, H-8), 5.71 (d, J = 4.0 Hz, H-17), 5.64 (d, J = 4.0 Hz, H-16), 4.00 (m, H-1α), 3.85 (m, H-3α), 3.32 (d, J = 12.5 Hz, H-2β), 2.48 (ddd, J = 13.0, 6.5, 5.5 Hz, H-2α), 2.32 (m, H-4α), 2.18 (m, H-5β), 2.03 (m, H-5α, 4β). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.93, 130.47, 130.27, 129.10, 128.41, 127.92, 127.50, 127.03, 126.09, 125.90, 124.80, 122.92, 122.65, 122.52, 122.29, 115.83, 115.47, 111.32, 36.75, 36.38, 32.52, 28.84, 28.03. MS (EI, 70 eV; m/z (relative intensity)): 418 (M^+ + 4, 11%), 417 (M^+ + 3, 14), 416 (M^+ + 2, 46), 415 (M^+ + 1, 24), 414 (M^+, 64), 381 (M^+ + 3 − Cl, 32), 380 (M^+ + 2 − Cl, 57), 379 (M^+ + 1 − HCl, 85), 378 (M^+ − HCl, 100), 342 (M^+ − 2 HCl, 62), 141 (44), 115 (52). HRMS (EI, 70 eV): calcd for $C_{23}H_{20}TiCl_2$ 414.0422, found 414.0425. Anal. Calcd for $C_{23}H_{20}TiCl_2$: C, 66.51; H, 4.86. Found: C, 66.27; H, 4.80.

1,3-*cis*-Bis(6,6-dimethylpentafulven-3-yl)cyclopentane (16). To a suspension of bis(cyclopentadiene) **13** (235 mg, 1.19 mmol) in methanol (5 mL) was added acetone (0.437 mL, 5.95 mmol) and pyrrolidine (0.886 mL, 9.0 mmol). The solution turned yellow and then orange-yellow after being stirred for 12 h. A 10:1 mixture of acetic acid and water was added until pH 4. The mixture was extracted with diethyl ether (3 × 5 mL). The combined organic portions were washed with saturated sodium bicarbonate until the aqueous layer was basic. The yellow organic layer was dried with $MgSO_4$, and the solvent was removed *via* rotary evaporation to give an orange brown oily residue which was further purified by short-path SiO_2 flash chromatography (4% diethyl ether in petroleum ether) to afford **16** as a bright yellow oil (297 mg, 90%). R_f 0.31 (SiO_2/2% Et_2O in petroleum ether). IR (KBr) 3030, 2950, 2867, 1643, 1582, 1496, 1437, 1368, 1265, 1081, 812, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 6.52 (dd, J = 5.50, 2.0 Hz, 2 H), 6.43 (m, 2 H), 6.19 (m, 2 H), 2.98 (m, 2 H), 2.24 (dt, J = 12.0, 7.0 Hz, 1 H), 2.14 (br s, 12 H), 1.98 (m, 2 H), 1.72 (m, 2 H), 1.60 (q, 11.5 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.69, 147.13, 141.94, 131.52, 121.57, 113.61, 40.80, 39.83, 31.72, 22.86, 22.74. MS (EI, 70 eV; m/z (relative intensity)): 279 (M^+ + 1, 21%), 278 (M^+, 100), 263 (72), 235 (20), 207 (12), 133 (10), 132 (11), 131 (16), 91 (13). HRMS (EI, 70 eV) calcd for $C_{21}H_{26}$ 278.2035, found 278.2032.

1,3-*cis*-Bis(3-isopropylcyclopentadienyl)cyclopentane (17). To a vigorously stirred slurry of lithium aluminum hydride (180 mg, 4.50 mmol) in diethyl ether (26 mL) was added bis(pentafulvene) **16** (250 mg, 0.899 mmol) in diethyl ether (1.3 mL) dropwise. The yellow color faded after 4 h. After being stirred for 12 h, the mixture was treated subsequently with ice–water (0.18 mL, 10 mmol), 15% NaOH (0.18 mL), and water (2 mL). The resulting slurry was filtered through a Celite pad and washed well with petroleum ether (10 mL). The aqueous portion was extracted with petroleum ether (2 × 3 mL), and the combined organic portions were dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure at room temperature and purification by short path SiO_2/petroleum ether chromatography afforded **17** as a colorless oil (235 mg, 93%), which was carried to the next step immediately or stored as a dilute solution in petroleum ether at −25 °C. R_f 0.31 (SiO_2/petroleum ether). ^1H NMR (400 MHz, $CDCl_3$) δ 6.12 (br s, 0.6 H), 6.07 (br s, 0.6 H), 6.02 (br s, 0.7 H), 5.99 (br s, 0.7 H), 5.81 (br s, 0.5 H), 5.78 (br s, 0.6 H), 2.88 (m, 6.5 H), 2.68–2.54 (m, 2.3 H), 2.16 (m, 1 H), 1.95 (m, 2 H), 1.64 (m, 2 H), 1.46 (m, 1 H), 1.24–1.00 (m, 12 H). MS (EI, 70 eV; m/z (relative intensity)): 283 (M^+ + 1, 21%), 282 (M^+, 100), 239 (77), 173 (46), 149 (23), 135 (14), 119 (18), 91 (21). HRMS (EI, 70 eV) calcd for $C_{21}H_{30}$ 282.2347, found 282.2340.

1,3-*cis*-Bis(3-*tert*-butylcyclopentadienyl)cyclopentane (18). To bis(pentafulvene) **16** (278 mg, 1 mmol) in diethyl ether (10 mL) was added at 0 °C methyllithium (1.2 M in diethyl ether, 2.08 mL, 2.5 mmol) dropwise. The mixture was stirred vigorously at room temperature for 12 h to give a white slurry. The suspension was quenched with saturated ammonium chloride (0.5 mL) and water (10 mL) and then extracted with petroleum ether (3 × 5 mL). The combined organic portions were dried over anhydrous $MgSO_4$, and the organic solvent was rotary-evaporated at room temperature. The light yellow oily residue (305 mg) was purified by short-path SiO_2/petroleum ether chromatography to afford **18** as a colorless oil (279 mg, 90%), which was carried to the next step immediately or stored as a dilute solution in petroleum ether at −25 °C. R_f 0.28 (SiO_2/petroleum ether). ^1H NMR (400 MHz, $CDCl_3$): δ 6.19 (br s, 0.7 H), 6.07 (br s, 0.6 H), 6.00 (br s, 1 H), 5.82 (br s, 0.6 H), 5.76 (br s, 0.7 H), 2.89 (m, 5.6 H), 2.16 (hep, J = 6.0 Hz, 1 H), 1.97 (m, 2 H), 1.64 (m, 2 H), 1.47 (m, 1 H), 1.30–1.00 (m, 18 H). MS (EI, 70 eV; m/z (relative intensity)): 311 (M^+ + 1, 27%), 310 (M^+, 100), 295 (42), 253 (56), 213 (9), 197 (14), 187 (42), 163 (24), 131 (15), 91 (11), 57 (23). HRMS (EI, 70 eV) calcd for $C_{23}H_{34}$ 310.2661, found 310.2653.

***rac*- and *meso*-[*cis*-1,3-Cyclopentanediylbis(η^5-3-isopropylcyclopentadienyl)]titanium Dichloride (7).** To **16** (179.1 mg, 0.635 mmol) in THF (32 mL) was added dropwise *n*-butyllithium (2.25 M in hexane, 0.565 mL, 1.27 mmol) at 0 °C. The solution was stirred at 0 °C for 10 min and at room temperature for 30 min. The resulting white slurry was recooled to −40 °C, and $TiCl_3$·3THF (235 mg, 0.635 mmol) was added in one portion from a side arm. The cold bath was removed, and the slurry was warmed to room temperature and heated at reflux for 4 h. The dark brown solution was recooled to −40 °C, and 6 N HCl (0.5 mL, 3 mmol) was added *via* a syringe over 2 min. The mixture was warmed to room temperature, and compressed air was bubbled through for 10 min, rendering it an orange-red solution. Diethyl ether (15 mL) was added, and the mixture was filtered through a short-path SiO_2 column and washed with diethyl ether (ca. 50 mL). Removal of the solvent of the dark red solution under reduced pressure afforded a brown-red solid (268 mg) which showed a **7a**:**7b**:**7c** ratio of 65:27:8 by ^1H NMR analysis, in addition to a small amount of oligomeric material. The mixture was washed with hot hexane (ca. 60 mL) and filtered. The filtrate, containing mostly **7a**, was subjected to recrystallization in hexane, while the residue, containing some polymer and most of **7b**, was subjected to recrystallization in a chlorobutane/hexane cosolvent. Several recrystallizations from these two systems efficiently provided pure **7a** as a brown-red solid (38 mg, 16%) and pure **7b** as a dark green solid (24 mg, 10%), along with other crops consisting of three isomers (total 177 mg, 75%). Compound **7a**: mp 161–162.5 °C (hexane); IR (KBr) 3100, 2960, 2930, 2880, 1500, 1460, 1390, 1368, 1315, 1075, 905, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.43 (t, J = 3.0 Hz, 1 H), 6.34 (m, 1 H), 6.23–6.25 (m, 2 H), 6.09 (t, J = 2.5 Hz, 1 H), 6.02 (t, J = 2.5 Hz, 1 H), 3.39 (m, 3 H), 3.19 (hep, J = 7.0 Hz, 1 H), 2.48 (d, J = 13.0 Hz, 1 H), 2.10 (dt, J = 13.0, 6.0 Hz, 1 H), 1.86 (m, 2 H), 1.72 (m, 2 H), 1.29 (d, J = 7.0 Hz, 3 H), 1.25 (d, J = 7.0 Hz, 3 H), 1.15 (d, J = 7.0 Hz, 3 H), 0.89 (d, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.83, 142.55, 128.93, 128.06, 126.91, 125.11, 123.70, 119.28, 111.61, 108.48, 37.31, 34.72, 34.55, 29.93, 28.86, 26.95, 26.32, 24.93, 23.77, 21.99, 20.63; MS (EI, 70 eV; m/z (relative intensity)) 400 (M^+ + 2, 3.4%), 398 (M^+, 4.9), 365 (M^++ 2 − Cl, 22), 364 (M^+ + 2 − HCl, 28), 363 (M^+ − Cl, 62), 362 (M^+ − HCl, 37), 328 (M^+ − 2 Cl, 34), 327 (M^+ − 2 Cl − H, 73), 326 (M^+ − 2 HCl, 100), 321 (13), 307 (6); HRMS (EI, 70 eV) calcd for $C_{21}H_{28}TiCl_2$ 398.1047, found 398.1040. Anal. Calcd for $C_{21}H_{28}TiCl_2$: C, 63.15; H, 7.07. Found: C, 63.24; H, 7.05. Compound **7b**: mp 256–258 °C (hexane/chlorobutane); IR (KBr) 3094, 2962, 1514, 1467, 1380, 1362, 1074, 874, 838 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.24 (t, J = 2.0 Hz, H-7,12), 6.19 (m, H-9,14), 6.16 (m, H-10,15), 3.43 (hep, J = 7.0 Hz, H-16,19), 3.37 (m, H-1α,3α), 2.61 (d, J = 13.0 Hz, H-2β), 2.11 (dt, J = 13.0, 6.0 Hz, H-2α), 1.82 (m, H-4α,5α), 1.65 (d, J = 8.5 Hz,

H-4β,5β), 1.33 (d, J = 7.0 Hz, H-17,19), 1.32 (d, J = 7.0 Hz, H-18,20); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.52, 127.62, 126.77, 125.91, 108.02, 35.94, 34.38, 28.60, 26.71, 23.19, 22.67; MS (EI, 70 eV; m/z (relative intensity)) 400 (M^+ + 2, 5%), 398 (M^+, 7), 365 (M^+ + 2 − Cl, 13), 363 (M^+ − Cl, 36), 362 (M^+ − HCl, 30), 328 (M^+ − 2 Cl, 38), 327 (M^+ − 2 Cl − H, 82), 326 (M^+ − 2 HCl, 100), 325 (46), 324 (49), 323 (11); HRMS (EI, 70 eV) calcd for $C_{21}H_{28}TiCl_2$ 398.1047, found 398.1045. Compound **7c**: ^{1}H NMR (400 MHz, $CDCl_3$) diagnostic signals δ 6.28 (t, J = 3.0 Hz, 1 H), 6.24 (m, 1 H), 6.04 (t, J = 2.0 Hz, 1 H), 1.27 (d, J = 7.5 Hz, 6 H), 1.09 (d, J = 7.0 Hz, 6 H).

***rac*- and *meso*-[*cis*-1,3-Cyclopentanediylbis(η^5-3-*tert*-butylcyclopentadienyl)]titanium Dichloride (8).** To **18** (196 mg, 0.632 mmol) in THF (32 mL) was added dropwise *n*-butyllithium (1.84 M in hexane, 0.68 mL, 1.26 mmol) at 0 °C. The solution was stirred at 0 °C for 10 min and at room temperature for 30 min. The resulting white slurry was recooled to −40 °C, and $TiCl_3$·3THF (234 mg, 0.632 mmol) was added in one portion from a side arm. The cold bath was removed, and the slurry was warmed to room temperature and further heated to reflux for 4 h. The dark purple solution was recooled to −40 °C, and 6 N HCl (0.5 mL, 3 mmol) was added *via* a syringe over 2 min. The mixture was warmed to room temperature, and then compressed air was bubbled for 10 min, rendering it a brown-red solution. Diethyl ether (20 mL) was added, and the mixture was filtered through a short-path SiO_2 column and washed with diethyl ether (ca. 100 mL). Removal of the solvent of the dark red solution under reduced pressure afforded a brown red solid (234 mg) which was further washed with hot hexane (ca. 40 mL) and filtered. The filtrate (155 mg after removal of the solvent) showed a **8a**:**8b**:**8c** ratio of 50:40:10 by ^{1}H NMR analysis, in addition to some polymer. Further multiple recrystallizations from hexane provided pure **8a** as a deep red solid (9 mg, 3%) and a fraction containing 80% **8b** as a dark red solid (11 mg, 3%), along with other crops consisting of three isomers (total 92 mg, 34.1%). Compound **8a**: mp 251−253 °C (hexane); IR (KBr) 3090, 2860, 2820, 1610, 1460, 1260, 1100, 1020, 800 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (t, J = 3.0 Hz, H-15), 6.44 (t, J = 2.5 Hz, H-7), 6.41 (dd, J = 3.5, 2.5 Hz, H-10), 6.39 (t, J = 3.0 Hz, H-14), 6.27 (t, J = 2.5 Hz, H-12), 5.92 (dd, J = 3.5, 2.5 Hz, H-9), 3.35 (m, H-1,3), 2.56 (d, J = 13.0 Hz, H-2β), 2.03 (dt, J = 13.0, 6.0 Hz, H-2α), 1.83−1.73 (m, H-4,5), 1.37 (s, H-21,22,23), 1.18 (s, H-17,18,19); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.19, 147.83, 129.70, 128.72, 128.44, 127.95, 120.10, 117.76, 111.40, 111.20, 36.47, 35.37, 35.26, 34.78, 34.34, 31.28, 30.82, 26.92, 26.15; MS (EI, 70 eV; m/z (relative intensity)) 428 (M^+ + 2, 17%), 427 (M^+ + 1, 9), 426 (M^+, 23), 393 (M^+ + 2 − Cl, 36), 392 (M^+ + 2 − HCl, 44), 391 (M^+ − Cl, 100), 356 (M^+ − 2 Cl, 10), 354 (M^+ − 2 HCl, 67), 340 (41), 335 (14), 270 (16), 169 (28), 69 (16); HRMS (EI, 70 eV) calcd for $C_{23}H_{32}TiCl_2$ 426.1360, found 426.1363. Compound **8b**: IR (KBr) 3094, 2970, 1505, 1410, 1396, 1370, 1265, 1025, 880, 800 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (t, J = 2.5 Hz, H-7,12), 6.15−6.12 (m, H-9,10,14,15), 3.36 (m, H-1α,3α), 2.63 (d, J = 13.0 Hz, H-2β), 2.05 (dt, J = 13.0 Hz, 6.0 Hz, H-2α), 1.82−1.71 (m, H-4,5), 1.40 (s, H-17,18,19,21,22,23); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.27, 129.46, 126.16, 124.11, 106.69, 35.01, 34.86, 34.77, 31.52, 26.60; MS (EI, 70 eV; m/z (relative intensity)) 430 (M^+ + 4, 14%), 429 (M^+ + 3, 22), 428 (M^+ + 2, 59), 427 (M^+ + 1, 37), 426 (M^+, 100), 393 (M^+ + 2 − Cl, 5), 391 (M^+ − Cl, 15), 390 (M^+ − HCl, 30), 354 (M^+ − 2 HCl, 32); HRMS (EI, 70 eV) calcd for $C_{23}H_{32}TiCl_2$ 426.1361, found 426.1376. Compound **8c**: ^{1}H NMR (400 MHz, $CDCl_3$) diagnostic signals δ 6.44 (m, 1 H), 6.21 (m, 1 H), 5.92 (t, J = 3.5 Hz, 1 H), 1.34 (s, 18 H).

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Supplementary Material Available: Complete tables of crystal data, bond lengths and angles, positional parameters, and anisotropic thermal parameters and stereo drawings for **5** and **6** (14 pages). Ordering information is given on any current masthead page.

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