Synthesis, Structure Determination, and Reactivity of C_2-Symmetrical Ethylene-Bridged *ansa*-Bis(DiMeBCOCp)titanium Dichlorides

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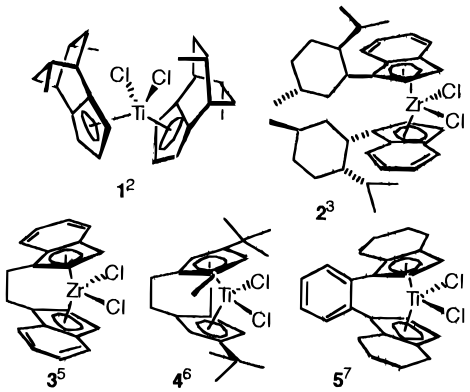
The bridging of C_2-symmetric 8,10-dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadiene (DMeBCOCpH) by silicon, methylene, and ethylene was investigated. The dimethylsilyl-bridged bis(BCOCp) ligand was accessible but could not be converted to its titanium, zirconium, or niobium chloride complexes. 8,10-Dimethyl-4-(1-methylethylidene)tricyclo[5.2.2.0^{2,6}]-2,5-undecadiene (DMeBCOCp-dimethylfulvene) was formed, but did not react with cyclopentadienyl anions. A regioisomeric mixture of 1,2-bis[(*1R,7R,8R,10R*)-8,10-dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadienyl]ethane [en(DMeBCOCpH)] ligands could be formed and metalated to form (+)-[ethylene-1,2-bis[η^5-(*1R,7R,8R,10R*)-8,10-dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadien-4-yl]]titanium dichloride [(+)-β,β-en(DMeBCOCp)$_2$TiCl$_2$, (+)-**11**] along with its α,α- and α,β-bridged regioisomeric titanocene dichlorides. (+)-**11** is unique in that it is a chiral ethylene-bridged *ansa*-metallocene which contains only homotopic cyclopentadienyl faces. (+)-**11** was characterized by X-ray crystallography and was applied as a catalyst for the enantioselective isomerization of alkenes. (+)-**11** was less active and less enantioselective than a known chiral *ansa*-bis(indenyl)titanium catalyst for the enantioselective alkene isomerization.

The use of chiral group 4 metallocene complexes as catalysts for stereoselective reactions has been increasing in the past several years, spawning efforts to develop new chiral metallocene complexes which may prove even more useful.[1] One approach for installing a chiral environment around the metal has been to incorporate unbridged chiral ligands into a metallocene such as in bis(cyclopentadienyl) **1**[2] or bis(indenyl) **2**[3] (Chart 1) in the anticipation that their substituents may create a highly asymmetric conformation around the metal. Although high enantioselectivity has been observed in a few instances in complexes of this type,[4] their conformational mobility makes an efficient transfer of chirality less predictable. A second approach has been to metalate achiral, but bridged, ligands which would then be held in a chiral, helical-type orientation around the metal such as *ansa*-bis(indenyl) **3**[5] or *ansa*-bis(cyclopentadienyl) **4**[6] and **5**.[7] Although metalation of these achiral ligands with their enantiotopic faces may give rise to *meso*- and *dl*-mixtures of metallocenes, the desired *dl*-pair can usually be isolated and resolved.[8] This second type of conformationally constrained complex has been more widely and successfully applied.[9]

Chart 1



1[2] **2**[3] **3**[5] **4**[6] **5**[7]

Through incorporation of a chiral bridge in ansa-metallocenes, the direct formation of a single enantiomer is possible—potentially avoiding the need for separation of stereoisomeric metallocenes. This strat-

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Chart 2

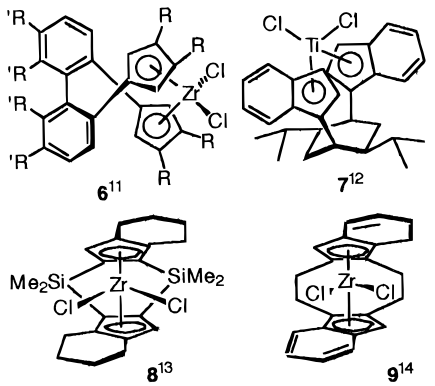
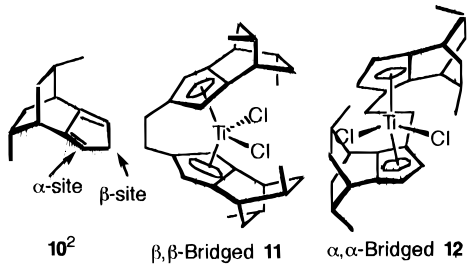


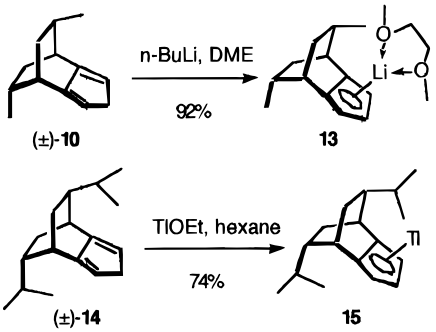
Chart 3



egy for the selective synthesis of essentially helically-chiral metallocenes[10] such as **6**[11] and **7**[12] (Chart 2) has been investigated by several groups. Recently, doubly bridged, achiral ligands have also been used to place substituents in a chiral orientation about the metal as in **8**[13] and **9**.[14]

A third approach to installing chirality around the metal in conformationally constrained metallocenes would be to use an achiral bridge between chiral cyclopentadienyl ligands. Given the good selectivity observed in reactions of unbridged $(BCOCp)_2TiCl_2$ complexes[4a] and the advantages in reducing the number of possible isomers due to its C_2 symmetry, we undertook a study to bridge these accessible cyclopentadienes[2] to see what the effect of constraining the conformational mobility of these complexes would be. Bridging the BCOCp ligand **10**[2] (Chart 3) at the symmetrical β,β-positions would produce ligands with homotopic faces which could form only a single stereoisomeric metallocene complex **11**. The chirality in this molecule is unlike the usual helical chirality such as that found in Brintzinger's complex **3** in that the two bicyclooctane moieties in **11** should be nearly eclipsing, while the methyl substituents aiming toward either side of the metal would provide the asymmetric environment. Bridging the BCOCp ligand **10** at the α,α-positions would produce diastereotopic ligand faces, giving rise to the possibility of diastereotopic metal complexes such as **12** which would possess a combination of helical-type and cylcopentadienyl-based chirality. Herein we report the synthesis, structural characterization, and reactivity of the novel-bridged complexes **11** and **12**.

Scheme 1



Results and Discussion

Whereas the alkylation of indene is electronically favored at the 1-position, we needed to rely on steric and statistical factors to favor either alkylation at the α- or β-positions of **12**. Due to the significance of *ansa*-metallocenes, a variety of methods for introducing one- and two-atom bridges has been developed, and we investigated a number of these methods for bridging two BCOCp ligands.

Lithium and Thallium Complexes of BCOCp. Since several procedures for bridging cyclopentadienes require the use of either lithium or thallium salts of the cyclopentadienyl ligands, we initially prepared and characterized the lithium−DME complex **13** and the thallium complex **15**. The DMeBCOCp·Li complex could be obtained as the DME adduct **13** by the deprotonation[15] of DMeBCOCpH (±)-**12**[2] in dimethoxyethane (DME) (92% yield after hexane recrystallization based on recovered DMeBCOCpH) (Scheme 1). In the ^{1}H NMR spectrum, the three Cp ring protons were seen at 6.15 ppm as a multiplet and the two methyl groups coincided at 0.97 ppm as a broad singlet. The signal broadening and apparent C_2 symmetry observed for lithium complex **13** suggests that the lithium cation was in a rapid exchange between the two homotopic cyclopentadienyl faces. Although complex **13** was sensitive to air and moisture, it provided a convenient way of storing the thermally unstable DMeBCOCpH **10**.

Treatment of the DiPrBCOCpH (±)-**14**[2] with thallium ethoxide[16] produced DiPrBCOCpTl (**15**) as an air-, moisture-, and light-sensitive yellow solid in 74% yield. The mass spectrum of **15** showed the expected molecular ion fragment. As in the case of the◊lithium complex **13**, thallium complex **15** exhibited C_2 symmetry in the NMR spectra, showing only a half set of resonances. In the ^{1}H NMR spectrum the cyclopentadienyl ring protons were located upfield relative to the lithium complex **13**, appearing as broad singlets at 5.87 and 5.49 ppm.

Dimethylsilylene Bridge. We first investigated the use of a one-atom silicon bridge. Such bridges were known to be sensitive to steric effects, forming selectively at the least hindered position of cyclopenta-

(10) The chirality in these complexes is basically helical in the sense that the achiral subsitituents on the cyclopentadienyl ligand are held in a chiral orientation around the metal.

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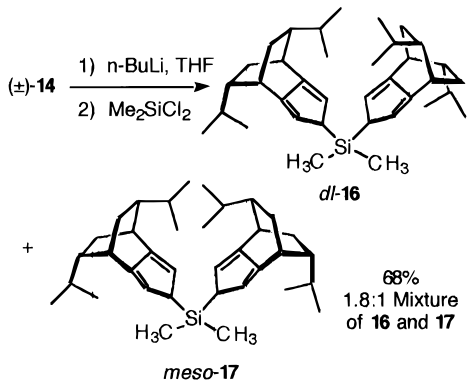
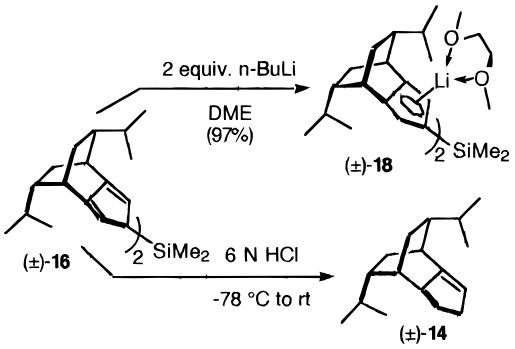
Scheme 2



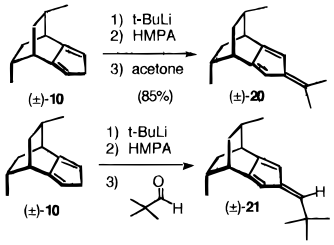
Scheme 3



dienes.[17] Following Brintzinger's bis(alkylation) procedure,[17a] the slow addition of 0.5 equiv of dichlorodimethylsilane to the *n*-BuLi-generated anion of DiPrBCOCpH (±)-**14** produced a 1.8:1 mixture of the desired racemic bis(DiPrBCOCpH)dimethylsilane (±)-**16** and the *meso* isomer **17** in 68% yield, in addition to a 16% recovery (±)-**14** (Scheme 2). As expected, the silyl bridge was found only at the sterically less conjested β-position of the BCOCp units, and due to the homotopic cyclopentadienes only a single diastereomer was possible. The pure C_2-symmetric silane (±)-**16** was separated by recrystallization in hexane and exhibited a singlet for the two homotopic silyl methyl groups at 0.23 ppm in the ^{1}H NMR spectrum. In contrast, in the corresponding spectrum of the C_s-symmetrical isomer **17**, two singlets at −0.23 and 0.27 ppm were observed for the analogous diastereotopic methyl groups.

Attempted metalation of the silyl-bridged ligand (±)-**16** through deprotonation with *n*-BuLi, addition of $TiCl_3$, and oxidation with HCl in chloroform according to established procedures[18] gave no desired titanocene dichloride but rather recovery of the desilyated DiPrBCOCpH (±)-**14**. Several experiments were conducted to determine at which step the breaking of the Si−Cp bond occurred. A mixture of silanes *dl*-**16** and *meso*-**17** was exposed to 2 equiv of *n*-BuLi in DME to give the DME adduct of the dilithium salts *dl*-**18** and *dl*-**19**, whose identities were supported by their ^{1}H NMR spectra (reaction of *dl*-**16** is shown in Scheme 3). The three singlets for the silyl methyl groups (one for the racemic complex and the other two for the *meso* isomer) were observed to shift downfield to 0.80, 0.71, and 0.66 ppm (ratio ca.1:4:1). Exposure of these lithium salts to moist air led to recovery of the intact silyl-bridged ligands. When the same silane mixture was treated with 6 N HCl, only the desilylated DiPrBCOCpH (±)-**14** was isolated. Thus, it is evident that the deprotonation of the silyl-bridged ligand proceeds smoothly, but the metalation and/or workup results in desilylation and recovery of the ligands **16** and **17**. To avoid the acidic workup used in $TiCl_3$ metalations, metalations of the *in situ* generated dianion of **16** or its dilithium salt **18** with $TiCl_4$, $ZrCl_4$, and $NbCl_4(THF)_2$[19] were attempted under various conditions. In each case, only the desilyated DiPrBCOCpH (±)-**14** and a lesser amount of silane (±)-**16** were found in the crude product mixtures. The Si−Cp bond in this hindered ligand was thus too labile in the presence of these metal halides.

Scheme 4



Dimethylmethylene Bridge. Bis(cyclopentadienes) with a dimethylmethylene bridge can be formed through the addition of cyclopentadienyl anions to 6,6-dimethylpentafulvenes.[20] Since the formation of 6,6-dimethylpentafulvenes by the condensation of acetone with substituted cyclopentadienes was known to occur selectively at the least hindered cyclopentadienyl position,[21] this bridging method seemed appropriate to try with the BCOCp ligands.

Initial attempts to prepare the 6,6-dimethylfulvene derivative of (±)-DMeBDCOCp (±)-**10**, via the usually successful secondary amine-induced acetone condensation procedure failed,[21] giving only recovered starting material. By an increase of the reactivity of the hindered cyclopentadiene **10** through *t*-BuLi deprotonation and use of the polar solvent HMPA, addition to excess acetone did lead to formation of the yellow crystalline fulvene (±)-**20** in 85% yield (based on recovered **10**). Only β-site reactivity was observed (Scheme 4). Unfortunately, nucleophilic addition of either the parent cyclopentadienyl anion or an anion of DMeBCOCpH **10** to fulvene (±)-**20** did not occur. A considerable variety of reaction conditions, including the use of different metal salts, different solvents, and co-solvents or reaction in the presence of 12-crown-4 and various reaction temperatures, were examined. In each case, the bridged ligand was not observed and the starting fulvene (±)-**20** was always recovered in high yield. Treatment of fulvene (±)-**20** with *n*-BuLi also gave only recovered fulvene. To test for deprotonation to a vinyl cyclopentadienyl anion, the *n*-BuLi reaction was quenched with D_2O. No deuterium incorporation was

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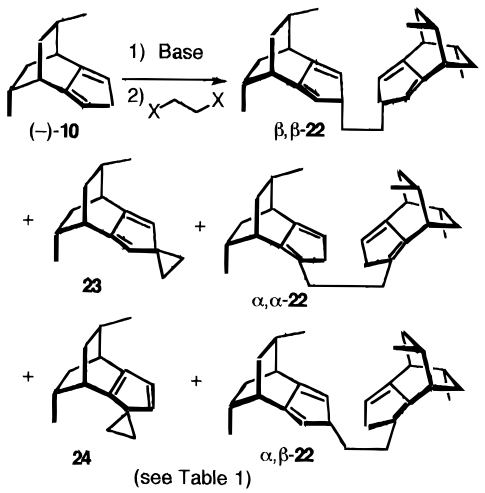
Scheme 5



observed, further supporting the idea that this fulvene is unreactive toward nucleophiles. A second fulvene (±)-**21** was obtained by the condensation of the anion of (±)-**10** with *tert*-butyl carboxaldehyde. Fulvene (±)-**21**, lacking the acidic methyl protons in **20**, also failed to react with cyclopentadienyl anions. Apparently the combination of a sterically hindered and electron-rich fulvene rendered these compounds inert to nucleophilic additions.

Ethylene Bridge. The alkylation of substituted cyclopentadienes with alkyl dihalides or bis(sulfonates) usually affords low regioselectivity and in many cases gives spiro-annulated side products.[1a,22,23] Indeed, the alkylation of (−)-**10** with alkyl dihalides or bis(sulfonates) gave mixtures of α- and *β*-site ethylene-bridged bis(cyclopentadienes) α,α-**22**, *β*,*β*-**22**, and α,*β*-**22** and spiro-annulated products *β*-spiro **23** and α-spiro **24**. Through the variation of the alkylation conditions, we found conditions which favored α- or *β*-site reactivity (see Scheme 5 and Table 1).

Mixing either the DMeBCOCpLi·DME adduct **13** or the *in situ* *n*-BuLi-generated anion of DMeBCOCp (−)-**10** in THF with ethylene glycol bis(methanesulfonate) at −78 °C and subsequent warming to room temperature gave a 1.8:1:2 mixture of the ethylene-bridged bis(cyclopentadienes) **22** (three inseparable isomers), the *β*-spirocyclopropane derivative **23**, and its α-isomer **24**. Carrying out the same reaction in other solvents resulted in little or no improvement in the product distribution. The use of ethylene dibromide at 23 °C gave a 1.3:1:0.7 ratio of bridged **22** to *β*-spiro **23** to α-spiro **24**, while ethylene glycol bis(tosylate) at 23 °C gave much improved selectivity for the bridged product (25:1:7 ratio of **22**:**23**:**24**) (Table 1, entries 1−3). A mixture of the three inseparable bridged products **22** could be isolated from this last reaction by chromatography in 62% yield. The spirocyclopentadienes **23** and **24** could be selectively prepared though the alkylation of the lithium salt of (−)-**10** with ethylene glycol bis(tosylate) at −78 °C in the presence of HMPA (Table 1, entry 4). The ratio of α-site and *β*-site addition corresponds to the statistical ratio of the sites and suggests that steric direction under these conditions is unimportant. The spirocyclopentadienes (−)-**23** and (−)-**24** were characterized as a mixture, and their ^{1}H NMR and ^{13}C NMR spectra showed the characteristic upfield cyclopropane resonances[23] at 1.56−1.38 ppm and 10.89−10.66 ppm, respectively. Their structural assignments were possible through the C_2 symmetry displayed by *β*-spiro **23** in the NMR spectra. The identification of the signals arising from the spiro products **23** and **24** enabled the initial ratio of spiro and bridged products to be estimated from the ^{1}H NMR spectrum of the crude product mixtures. It was apparent from the spectral data that more than one regioisomer of ethylene-bridged bis(cyclopentadienes) **22** was present, but the mixture of regio and double-bond isomers was not separable and was characterized spectroscopically as the mixture. As discussed below, the mixture of **22** was converted to a separable mixture of ansa-titanocene dichlorides which enabled the selectivity in the formation of α,α-**22**, *β*,*β*-**22**, and α,*β*-**22** to be back-estimated.

The softer bacisity or less ionic nature of the cyclopentadienyl moiety in CpMgX has been used to prepare ethylene-bridged bis(cyclopentadienes) with minimal formation of spirocyclopropane side products.[18,24] On the basis of these reports, we replaced the lithium cation with magnesium in the hope of not only solving the spiro-annulation problem but perhaps also altering the regioselectivity in the ethylene bridging of the DMeBCOCp ligand. A magnesium salt of DMeBCOCpH (−)-**10** could could be prepared by refluxing (−)-**10** and EtMgCl in THF for 48 h. Shorter reaction times resulted in incomplete anion formation. The reaction of the unisolated Grignard reagent with 0.25 equiv of 1,2-dibromoethane at an initial temperature of 23 °C and then refluxing at 66 °C gave a mixture of regioisomers of the bridged ligand **22** in 60% yield (based on limiting dibromide reagent). Spirocyclopropanes **23** or **24** were not observed. After some variation of the temperature and time of the alkylation, it was found that lower initial temperatures, followed by heating to reflux provided a higher yield of the desired bridged ligand (75% based on the limiting dibromide reagent) (Table 1, entries 4 and 5). Unlike the lithium salt of (−)-**10** which could cleanly react with 0.5 equiv of ethylene dibromides or bis(sulfonates), when 0.5 equiv of ethylene dibromide was added to the magnesium salt of (−)-**10**, the reaction was not as clean, giving presumably monoalkylated side products. The bridged ligand and the excess BCOCp ligand were readily separated by silica gel chromatography. As above, we were unable to separate the isomers of the bridged ligand and carried the mixture on to the titanocene dichlorides, where we were able to achieve separation and characterization of the isomers.

Metalation of Ethylene-Bridged Bis(DMeBCOCp). The compounds in the mixture of ethylene-bridged bis(cyclopentadienes) **22** prepared according to the conditions in Table 1 were deprotonated by *n*-BuLi in THF and metalated with $TiCl_3$·3thf in dilute THF solutions followed by HCl/$CHCl_3$ workup according to the procedure reported by Collins.[18] The metalation yields, after quick SiO_2 chromatography, were generally high (see Scheme 6 and Table 2). In each case, the product contained three isomers. The distribution of thse

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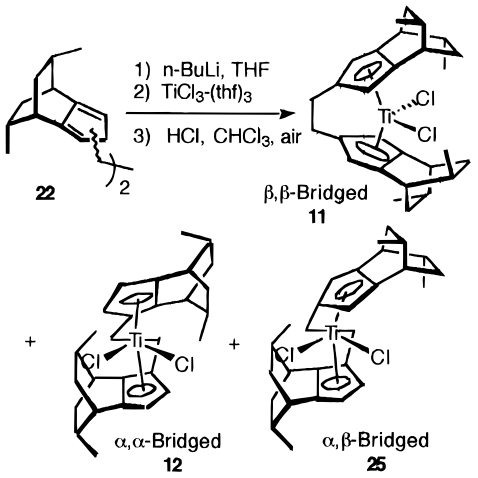
Table 1. Reaction of 10 with XCH_2CH_2X (As in Scheme 5)

entry	base	alkylating agent/conditions	ratio bridged **22**: β-spiro **23**: α-spiro **24**
1	*n*-BuLi	$MsOCH_2CH_2OMs$, THF, −78 to 23 °C	1.8:1:2
2	*n*-BuLi	$BrCH_2CH_2Br$, THF, 23 °C	1.3:1:0.7
3	*n*-BuLi	$TsOCH_2CH_2OTs$, THF, 23 °C	25:1:7
4	*n*-BuLi	$TsOCH_2CH_2OTs$, THF/HMPA, −78 °C	0:1:2
5	EtMgBr	$BrCH_2CH_2Br$, THF, 23− 66 °C	100:0:0
6	EtMgBr	$BrCH_2CH_2Br$, THF, −10 to 66 °C	100:0:0

Scheme 6



isomers should reflect the regioselectivity in the previous bridging reaction. As discussed below, the structures of these isomers were identified, enabling us to estimate the selectivity in the various bridging reactions. The bridging reaction with the Grignard reagent proved to be most selective in providing the β,β-bridged products. The metalation of the bis(cyclopentadiene) **22** formed according to Table 1, entry 6, gave a 73% yield of *ansa*-titanocene dichlorides β,β-**11**, α,α-**12**, and α,β-**25** in a ratio of 71:7:22, from which β,β-**11** could be isolated in 24% yield after two recrystallizations from hexane/*n*-chlorobutane (Table 2, entry 3). The most selective conditions for α-site bridging were with the lithium salt of **10** and ethylene glycol bis(tosylate) (Table 1, entry 3) which gave rise to a 77% yield of *ansa*-titanocene dichlorides β,β-**11**, α,α-**12**, and α,β-**25** in a ratio of 26:35:39, from which α,α-**12** could be isolated in 6% yield (Table 2, entry 1).

Structures of *ansa*-Titanocene Dichlorides. The structures of *ansa*-titanocene dichlorides β,β-**11**, α,α-**12**, and α,β-**25** could be assigned on the basis of their spectral characteristics, in particular their ^{1}H NOESY spectra. The complexes identified as β,β-**11** and α,α-**12** both exhibited C_2 symmetry in their NMR spectra, and the complex identified as α,β-**25** exhibited C_1 symmetry with double the number of signals as seen with the C_2-symmetrical complexes. In the NOESY spectrum of β,β-**11** two pairs of cross peaks, each corresponding to a bridgehead proton interacting with a cyclopentadienyl proton, were exhibited. Only the β,β-bridged complex would be expected to give rise to two such interactions; the α,α-isomer, with only one bridgehead hydrogen neighboring a cyclopentadienyl proton, would be expected to have only one such interaction. An additional NOE interaction was observed between a cyclopentadienyl proton and only one of the protons in the ethylene bridge. As shown in Figure 1, the observed NOE could arise from either the δ- or λ-conformation[25] of β,β-**11** but most likely not both. If both conformations were present on the time scale of the NMR experiment, an interaction between two cyclopentadienyl protons and both unique protons in the bridge would be expected. The presence of only one interaction argues for the presence of a single conformation in solution. As discussed below, the λ-conformation of β,β-**11** was found in its X-ray crystal structure.

With the structure of C_2-symmetrical β,β-**11** established, the structure of α,α-**12**, which also exhibited C_2 symmetry in its NMR spectra, had to be one of the two remaining possible C_2-symmetrical complexes **12** or **26** (Figure 2). Of particular usefulness in the structural assignment of α,α-**12** was the assignment of the methyl groups as being *syn* or *anti* to the metal based on the known *syn*-deshielding and *anti*-shielding effect exerted by the titanium center in related titanocene dichlorides.[2] Thus, in C_2-symmetrical α,α-**12** the two equivalent *syn*-methyl groups were found at 1.08 ppm while the two *anti*-methyl groups were found at 0.38 ppm. In the NOESY spectrum of the α,α-bridged complex **12** the β-cyclopentadienyl vinyl proton (δ 5.85 ppm) was observed to have an NOE with both the *syn*-methyl group (at 1.08 ppm) and one of the interannular bridging ethylene protons. The other possible C_2-symmetric structure, compound **26**, was ruled out since its syn-methyl groups are much further away from the β-cyclopentadienyl protons and is thus unlikely to account for the observed NOE.

The *si*-face selectivity in the metalation of α,α-**22**, leading to the exclusive formation of complex **12**, is presumably of steric origin. With both sterically large groups (the methyl group and the ethylene bridge) on one edge of the cyclopentadienyl ring, a more open region is available for approach of the metal. The diastereotopic faces whose metalation would give α,α-**26** have the large groups flanking both edges of the cyclopentadienyl ring—sterically hindering approach of the metal in its formation.

Complex **25**, which was not isolated in a pure form, must be derived from the unsymmetrically bridged ligand α,β-**22** since the complex exhibited C_1 symmetry in its NMR spectra. In the ^{1}H NMR spectrum of α,β-**25** (characterized as a mixture with **11** and **12**) one vinyl proton showed a higher field resonance relative to the other three vinyl protons (5.62 vs 6.06−6.41 ppm), in the agreement with the presence of one β-proton and three α-protons. On the basis of the assigned *si*-face selectivity for the formation of complex α,α-**12**, the structure of the C_1-symmetrical complex was assigned α,β-**25** as shown in Scheme 6.

X-ray Structure of β,β-11. Crystals of β,β-**11** suitable for X-ray diffraction were obtained by diffusion of hexane into a solution of this *ansa*-titanocene dichloride in 1-chlorobutane. The data were collected and pro-

(25) Corey, E. J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 2620.

Table 2. Preparation of *ansa*-Titanocene Dichlorides from 22 (As in Scheme 6)

			distribn of products (isolated yields)		
entry	source of **22**	tot; tield	β,β-**11**	α,α-**12**	α,β-**25**
1	Table 1, entry 3	77%	26	35 (6%)	39
2	Table 1, entry 5	75%	58	7	35
3	Table 1, entry 6	73%	71 (24%)	7	22

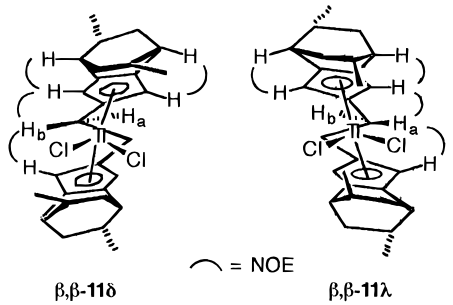


Figure 1. NOE for β,β-bridged **11**.

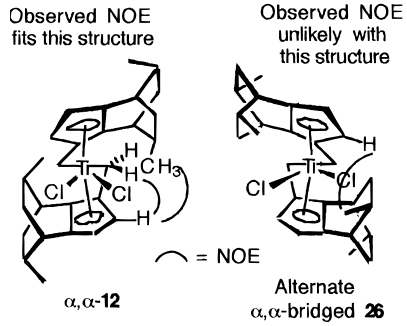


Figure 2. NOE for α,α-bridged **12**.

Table 3. Crystal Data and Structure Refinement for β,β-Bridged (+)-11

empirical formula	$C_{28}H_{36}TiCl_2$
fw	491.37
temp	293(2)
wavelength	0.710 69 Å
cryst system	trigonal
space group	$P3_121$ (No. 152)
unit cell dimens	$a = b = 13.565(6)$ Å, $\alpha = \beta = 90°$, $c = 48.092(10)$, $\gamma = 120°$
v, Z	7664 (5) Å^3, 6
D(calcd)	1.278 g/cm^3
abs coeff	0.56 mm^{-1}
F(000)	3120
cryst size	0.5 × 0.4 × 0.2 mm
θ range for data collcn	1.73−24.94°
limiting indices	$0 \le h \le 13$, $0 \le k \le 13$, $0 \le l \le 56$
reflcns collcd	5078
independ reflcns	5022 ($R_{int} = 0.0904$)
refinement method	full-matrix least-squares on F^2
goodness-of-fit on F^2	1.1
final R indices [$I > 2\sigma(I)$]	$R = 0.0794$ for 3421 reflcns
final R_w	0.0875
largest diff peak and hole	0.689 and −0.647 e Å^{-3}

cessed according to Table 3. Two independent, conformationally similar molecules of β,β-**11** were found in the unit cell. Some important bond lengths and angles for molecule 1 are as follows: Ti−Cp 2.12(2) and 2.11(2) Å, Cp−Ti−Cp 130.9(6)°, Cl−Ti−Cl 108.3(1)°; for molecule 2, Ti−Cp 2.11(2) and 2.14(2) Å, Cp−Ti−−p 129.5(6)°, Cl−Ti−−l 103.0(1)° (complete tables are included as Supporting Information). An ORTEP diagram of β,β-**11** is shown in Figure 3. The Ti−Cp distances and the Cp−Ti−Cp bond angles are in the usual range for Cp_2TiCl_2 structures. The molecules adopt a roughly C_2-symmetrical λ-conformation to place the methyl groups syn to the metal between the chlorine

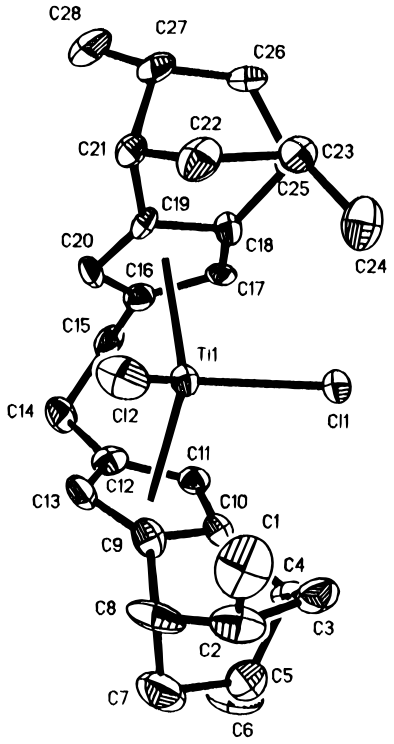


Figure 3. ORTEP of β,β-bridged (+)-**11** with atoms drawn with 50% probability coefficients.

atoms. A model of an alternative δ-conformation indicates a greater steric interaction between these methyl groups and the chlorine atoms.

Reactivity of β,β-11. We have previously published the enantioselective isomerization of an alkene using the chiral bridged bis(indenyl)titanium complex **7**.[12,26] We have now examined this isomerization with unbridged and bridged BCOCp−titanium complexes $(DMeBCOCp)_2TiCl_2$ (**1**), $(DiPrBCOCp)_2TiCl_2$ (**33**),[2] and β,β-**11** and can report a comparison of their reactivity.

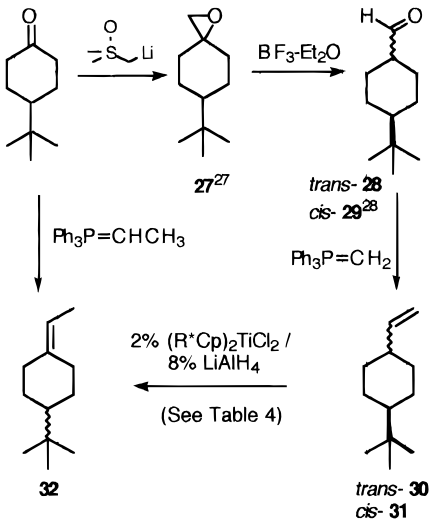
The *meso*-symmetrical substrates *trans*- and *cis*-4-*tert*-butyl-1-vinylcyclohexanes **30** and **31** were prepared according to Scheme 7. Addition of a sulfonium ylide to 4-*tert*-butylcyclohexanone gave a mixture of *cis*- and *trans*-epoxides **27**,[27] which were rearranged in the presence of boron trifluoride to give a mixture of *trans*- and *cis*-4-*tert*-butylcyclohexanecarboxaldehydes **28** and **29** in a ratio of 72:28.[28] The presence of the polar functional group facilitated chromatographic separation of the aldehydes, and each isomer could be obtained in about 98% stereoisomeric purity. The separated aldehydes **28** and **29** were converted via Wittig olefination reactions to the *trans*- and *cis*-4-*tert*-butyl-1-vinylcyclohexanes **30** and **31** without epimerization. Chromato-

(26) (a) Mach, K.; Turecek, F.; Antropiusova, H.; Petrusova, L.; Hanus, V. *Synthesis* **1982**, 53. (b) Lehmkuhl, H.; Qian, Y. *Chem. Ber.* **1983**, *116*, 2437. (c) Akita, M.; Yasuda, H.; Hagasuna, K.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 554.

(27) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

(28) House, H. O.; Lubinkowski, J.; Good, J. J. *J. Org. Chem.* **1975**, *40*, 86.

Scheme 7



graphic separation of these hydrocarbons was not successful. A sample of the racemic 4-*tert*-butyl-1-ethylidenecyclohexane (**32**)[29] was prepared though a Wittig olefination of 4-*tert*-butylcyclohexanone. Conditions for the gas chromatographic separation of the *cis*- and *trans*-4-*tert*-butyl-1-vinylcyclohexanes and the two enantiomers of 4-*tert*-butyl-1-ethylidenecyclohexane were established using a chiral cyclodextrin-based capillary column.

The catalytic isomerization of *cis*- or *trans*-4-*tert*-butyl-1-vinylcyclohexanes (**33** and **30**) to 4-*tert*-butyl-1-(ethylidene)cyclohexane (**32**) using chiral bis(cyclopentadienyl)titanium dichlorides **1**, **33**, and **11** was studied as reported for the bis(indenyl)titanium dichloride **7**. The results are summarized in Table 4. A striking feature of the results is the greatly diminished activity of the bis(cyclopentadienyl) complexes. Whereas the *trans*-substrate **30** was completely converted to product **32** within 2 h at 180 °C using bis(indenyl) **7** (Table 4, entry 1), only 15% or 78% of the product was produced under similar conditions by unbridged $(BCOCp)_2TiCl_2$ complexes **1** and **33**. The bridged complex **11** turned out to be the least active, producing a mere 2% of the product even after a prolonged reaction time (Table 4, entries 3−5). Analogous activity trends were observed in the isomerization of *cis*-alkene **31** (entries 7−11). To what extent the low activity was due to catalyst decomposition or to catalyst unreactivity was not fully determined. The reversible nature of the catalytic reaction makes interpretation of the stereoselectivity difficult, but it is apparent that the bis(cyclopentadienyl)titanium complexes are not only less active but less stereoselective. The bridged complex **11** provides a much inferior enantioselective catalyst for alkene isomerization than the bis(indenyl) complex **7**.

Summary. Two equivalents of the DiMeBCOCp ligand (+)-**10** were bridged at the β-position by ethylene with moderate selectivity. The titanocene dichloride (+)-**11** was formed and characterized crystallographically. The chirality in this complex is not the usual helical type found in previous chiral *ansa*-metallocenes, but (+)-**11** is a much inferior catalyst for enantioselective alkene migrations in comparison to an *ansa*-bis(indenyl)titanium complex.

(29) Hanessian, S.; Delorme, D.; Beaudoin, S.; Leblanc, Y. *J. Am. Chem. Soc.* **1984**, *106*, 5754.

Experimental Section

For general procedures and equipment used see refs 2 and 9b.

DMeBCOCp·Li·DME (13). To a solution of DMeBCOCpH (±)-**10**[2] (0.790 g, 4.54 mmol) in DME (10 mL) at −78 °C was added *n*-BuLi (2.5 M in hexane, 1.9 mL, 4.77 mmol) dropwise over 5 min. The mixture was slowly warmed to −10 °C and stirred for 3 h and then at room temperature overnight. The resulting white slurry was concentrated *in vacuo* to ca. 3 mL, and hexane (5 mL) was added. The mixture was cooled at −78 °C for 1 h and filtered using an insert gas filter tube. The residue was washed with cold hexane (2 × 4 mL) to provide **13** as a moisture- and air-sensitive white powder (0.735 g, 60%, 92% based on starting materials consumed). The filtrate was quenched with ice water (5 mL), extracted with petroleum ether (3 × 5 mL), and concentrated to give recovered DMeBCOCpH **10** as an orange oil (0.28 g, 35%). Compound **13**: ^{1}H NMR (400 MHz, C_6D_6) δ 6.15 (m, 3 H), 2.89 (br s, 2 H), 2.79 (s, 6 H), 2.47 (s, 4 H), 2.60 (m, 3 H), 2.15 (m, 3 H), 0.97 (br s, 6 H).

DiPrBCOCpTl (15). To a solution of DiPrBCOCpH (±)-**14**[2] (0.460 g, 2.0 mmol) in hexane (4 mL) was added at 0 °C thallium ethoxide (Aldrich, 2.0 mmol) [*Caution*: Thallium ethoxide is highly toxic and should be only handled with gloves and appropriate protective clothing!] to provide an instantly yellow cloudy solution. After the solution was stirred at 0 °C for 2 h and at room temperature for 12 h, the solvent was removed *in vacuo* to provide a yellow orange residue. This material was dissolved in diethyl ether (4 mL) and filtered under argon. The filtrate was kept to −25 °C for 2 h. The supernatant was transferred to a second flask under argon *via* cannula. The yellow orange crystals were mixed with cold ether (3 mL) and kept at −25 °C for 2 h. The supernatant was again removed, and the residue was dried *in vacuo* to afford (±)-**15** as air- and moisture-sensitive yellow crystals (0.222 g, 26%) which could be stored at −25 °C in the dark under nitrogen for months without decomposition. The combined supernatant was concentrated *in vacuo* to leave a brown residue (0.422 g, 49%) which was slightly impure **15**. Compound (±)-**15**: IR (Nujol) 3047, 2983, 2981, 1444, 1424, 1383, 1366, 1250, 1153, 1017, 763, 682 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (br s, 2 H), 5.49 (br s, 1 H), 2.93 (br s, 2 H), 1.85 (m, 2 H), 1.23 (m, 2 H), 0.88 (d, J = 6.0 Hz, 6 H), 0.74 (d, J = 5.5 Hz, 6 H), 0.97−0.67 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.19, 101.47, 99.29, 45.14, 40.60, 33.48, 33.09, 21.28, 20.69; MS *m*/*z* (EI, 70 eV, rel intensity) 435 (M^+ + 1, 6%), 434 (M^+, 43), 364 (8), 321 (5), 205 (100), 203 (34), 128 (4), 116 (33); HRMS (EI, 70 eV) calcd for $C_{17}H_{25}$ 434.1701, found 434.1709.

***rac*- and *meso*-Bis(DiPrBCOCpH)dimethylsilane [(±)-16 and *meso*-17].** To a solution of DiPrBCOCpH (±)-**14** (2.07 g, 9.0 mmol) in THF (7.5 mL) and hexane (4.5 mL) was added at −78 °C *n*-BuLi (2.1 M, 4.5 mL, 9.4 mmol). The cold bath was removed, and the mixture was stirred for 45 min during which time the temperature rose to −10 °C. Me_2SiCl_2 (0.55 mL, 4.5 mmol) was added dropwise over 10 min. The mixture was stirred for 4 h and concentrated *in vacuo*. The resulting light yellow oily residue was washed with hexane (70 mL) and filtered. The filtrate was washed with saturated NH_4Cl (20 mL), dried over Na_2SO_4, concentrated to 10 mL, and kept at −25 °C overnight to provide pure (±)-**16** as white crystals (0.530 g). The mother liquid, after being chromatographed on SiO_2/petroleum ether, gave the recovered diisopropyl-BCOCpH **14** (0.338 g, 16%) in the first fraction and a 1.8:1 mixture of (±)-**16** and *meso*-**17** as a yellow oily residue (1.021 g) in the following fraction (total yield 68% based on recovery of **14**). Compound (±)-**16**: Mp 108−110 °C (hexane); R_f 0.50 (SiO_2/petroleum ether); IR (KBr) 3050, 2920, 2860, 1670, 1465, 1450, 1385, 1370, 1250, 1230, 1050, 940, 820, 800, 780 cm^{-1}; ^{1}H NMR

Table 4. Enantioselective Alkene Isomerization of 4-*tert*-Butyl-1-vinylcyclohexane

entry	temp/time (°C/h)	complex[a]	remaining SM: *trans* (%)	remaining SM: *cis* (%)	yield[b] (%)	ee[c] (%)	absolute config[d]
			With *trans*-**30**				
1	180/2	7	0	0	100	44	S
2	180/12	7	0	0	100	14	S
3	180/2.5	33	20	2[e]	78	18	S
4	180/6	1	73	6[e]	15	11	R
5	180/14	11	93	2[e]	4	4	R
6	23/120	7	0	0	100	76	S
			With *cis*-**31**				
7	110/2	7	15	0	84	43	S
8	110/12	7	0	0	100	23	S
9	110/11.5	33	28	21	45	10	S
10	110/24	11	54	11	30	10	R
11	110/24	4	25	60	15	7	S

[a] Complexes: (+)-(DiPrBCOCp)$_2$TiCl$_2$ (**33**), (−)-(DMeBCOCp)$_2$TiCl$_2$ (**1**), (+)-β,β-en(DMeBCOCp)$_2$TiCl$_2$ (**11**), or c-C6(Ind)$_2$TiCl$_2$ (**7**). [b] GC yield based on internal standard. [c] Enantiomeric excess determined by chiral capillary GC. [d] Correlated by the sign of the rotation.[29] [e] Same amount present in the starting mixture (SM).

(400 MHz, $CDCl_3$) δ 5.95 (br s, 2 H), 5.90 (br s, 2 H), 3.11 (br s, 2 H), 2.82 (br s, 4 H), 1.91−1.82 (m, 4 H), 1.31−1.24 (m, 4 H), 1.09−0.80 (m, 8 H), 0.86 (d, J = 8.0 Hz, 6 H), 0.85 (d, J = 6.0 Hz, 6 H), 0.76 (d, J = 6.0 Hz, 6 H), 0.75 (d, J = 6.5 Hz, 6 H), 0.23 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.93, 147.60, 121.27, 120.90, 49.24, 44.93, 44.58, 35.87, 35.82, 33.81, 33.72, 33.68, 33.64, 21.19, 21.16, 20.89, 20.79, −4.14; MS m/z (EI, 70 eV, rel intensity) 517 (M^+ + 1, 6%), 516 (M^+, 13), 288 (24), 287 (100), 231 (3), 146 (4); HRMS (EI, 70 eV) calcd for $C_{36}H_{56}Si$ 516.4151, found 516.4153. Compound *meso*-**17** (in mixture with **16**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (br s, 2 H), 5.92 (br s, 2 H), 3.10 (br s, 2 H), 2.81 (br s, 4 H), 1.86 (m, 4 H), 1.26 (m, 4 H), 1.08−0.70 (m, 8 H), 0.86 (d, J = 5.5 Hz, 6 H), 0.85 (d, J = 5.5 Hz, 6 H), 0.76 (d, J = 6.0 Hz, 6 H), 0.75 (d, J = 6.0 Hz, 6 H), −0.23 (s, 3 H), −0.27 (s, 3 H).

Attempted Metalation of Bis(DiPrBCOCpH)dimethylsilanes (±)-16 and 17. To a suspension of *rac*-silane (±)-**16** (0.487 g, 0.94 mmol) in THF (4 mL) at −78 °C was added *n*-BuLi (2.3 M in hexane, 0.87 mL, 2.00 mmol) dropwise over 5 min. The cold bath was removed, and the mixture was stirred for 1 h to give a brownish orange solution. Into a second flask was placed NaH [washed with petroleum ether (2 × 1 mL), 60% in mineral oil, 12 mg, 0.3 mmol], $TiCl_3$ (98%, 0.154 g, 1.00 mmol), and THF (2 mL) at −10 °C. The dilithio salt, cooled at −10 °C, was cannulated to the second flask, and the mixture was stirred vigorously at room temperature for 3 h before it was concentrated to dryness in vacuo. The resulting dark green residue was then taken up with $CHCl_3$ (20 mL) and concentrated HCl (10 mL) at −78 °C. The cold bath was removed, and the mixture was stirred vigorously for 1.5 h. The aqueous portion was separated and extracted with CH_2Cl_2 (2 × 5 mL). The combined greenish organic portion was dried with $CaCl_2$ and concentrated *via* rotary evaporation to produce a greenish oily residue which contained recovered DiPrBCOCpH (±)-**14**. Under similar conditions in which the reaction mixture was heated to reflux for 6 h before it was worked up with $CHCl_3$−HCl again only DiPrBCOCpH (±)-**14** was found in the resulting green crude product.

Me$_2$Si(diisopropylBCOCp)$_2$·Li·2DME Complexes *dl*-18 and *meso*-19. To a silane mixture [(±)-**16**/*meso*-**17** = 2.1:1, 2.212 g, 4.287 mmol] suspension in DME (18 mL) at −78 °C was added *n*-BuLi (2.0 M in hexane, 4.52 mL, 9.04 mmol) dropwise over 10 min. The mixture was stirred for 30 min to give a clear orange solution which was further stirred at room temperature for an additional 4 h to obtain a brown orange slightly cloudy solution. The solvent was removed *in vacuo* to afford a mixture of **18** and **19** as an air- and moisture-sensitive brownish orange semisolid (2.95 g, 97%): ^{1}H NMR (400 MHz, C_6D_6) δ 6.29 (br s, 4 H), 3.26 (m, 4 H), 2.93 (br s, 12 H), 2.65 (br s, 8 H), 2.08 (m, 4 H), 1.47 (m, 4 H), 1.30−0.81 (m, 52 H), 0.80 (s, 1 H), 0.73 (s, 4 H), 0.66 (s, 1 H). After being exposed to the air at room temperature overnight, the same NMR sample showed a good (>85%) recovery of the starting silane mixture of (±)-**16** and *meso*-**17**.

Treatment of Me$_2$Si(DiPrBCOCpH)$_2$ under Acidic Conditions. To a mixture of silane (±)-**16** and *meso*-**17** (ca. 10 mg) in $CHCl_3$ (3 mL) at −78 °C was added 6 N HCl (1.5 mL). The cold bath was removed, and the mixture was stirred for 2 h. The aqueous portion was separated, and the organic layer was concentrated *in vacuo* to give a yellow oil which contained DiPrBCOCpH (±)-**10** as the major product by ^{1}H NMR analysis.

(1*S,7*S**,8*R**,10*R**)-8,10-Dimethyl-4-(1-methylethylidene)tricyclo[5.2.2.0^{2,6}]-2,5-undecadiene (DMeBCOCp-Dimethylfulvene) ((±)-20).** To DMeBCOCpH (±)-**10** (2.61 g, 15.0 mmol) in THF (30 mL) at −78 °C was added dropwise *t*-BuLi (1.7 M in hexane, 17.6 mL, 30 mmol) to give an orange solution. After being stirred at 0 °C for 1 h, the solution was recooled to −78 °C and HMPA (10.54 mL, 60.0 mmol) was added, followed by acetone (5.5 mL, 75 mmol) in THF (40 mL). The solution was stirred at 0 °C for 2 h. Ice water (15 mL) was added, and the aqueous layer was extracted with petroleum ether (3 × 15 mL). The combined organic portions were washed with aqueous NaCl (15 mL), dried with Na_2SO_4, concentrated, and purified by chromatography (SiO_2, petroleum ether) to give first recovered **10** (1.243 g) and then (±)-**20** as yellow crystals (1.427 g, 44%, 85% based on recovered **10**): R_f 0.58 (SiO_2, petroleum ether); mp 92.5−93.5 °C; IR (KBr) 3080, 2960, 2930, 2860, 1645, 1450, 1370 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (s, 2 H), 2.37 (d, J = 2.5 Hz, 2 H), 2.14 (s, 6 H), 2.03 (ddd, J = 12.5, 10.5, 3.0 Hz, 2 H), 1.76 (m, 2 H), 1.00 (ddd, J = 12.5, 5.0, 2.5 Hz, 2 H), 0.81 (d, J = 7.0 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.54, 142.76, 142.73, 110.33, 37.39, 37.28, 30.68, 22.74, 22.23; MS m/z (EI, 40 eV, rel intensity) 214 (M^+, 100%), 199 (22), 185 (9), 171 (74), 157 (90), 141 (15), 128 (11), 84 (8); HRMS (EI, 40 eV) calcd for $C_{16}H_{22}$ 214.1722, found 214.1725.

(1*S,7*S**,8*R**,10*R**)-8,10-Dimethyl-4-(2,2-dimethyl-1-propylidene)tricyclo[5.2.2.0^{2,6}]-2,5-undecadiene (DMeBCOCp-*tert*-butylpentafulvene) ((±)-21).** The procedure for the preparation of **20** was followed using DMeBCOCpH (±)-**10** (0.348 g, 2.0 mmol) in THF (4 mL), *t*-BuLi (1.7 M in hexane, 2.35 mL, 4.0 mmol), HMPA (1.4 mL, 8.0 mmol), and trimethylacetaldehyde (1.1 mL, 10 mmol) in THF (5 mL) to give after chromatography (SiO_2, petroleum ether) recovered (±)-**10** and then (±)-**21** as a yellow oil (0.20 g, 42%): R_f 0.69 (SiO_2, petroleum ether); IR (thin film) 3060, 2970, 2930, 2880, 1760, 1680, 1660, 1480, 1460, 1375, 1365, 900 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (br s, 1 H), 6.10 (br s, 1 H), 5.61 (br s, 1 H), 2.33 (m, 2 H), 2.03-1.87 (m, 4 H), 1.25 (s, 9 H), 1.03−0.95 (m, 2 H), 0.80 (d, J = 7.0 Hz, 3 H), 0.79 (d, J = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.92, 147.65, 146.10, 143.28, 117.67, 109.85, 37.54, 37.20, 37.10, 36.88, 35.42, 31.34, 30.79, 27.36, 27.30, 22.24; MS m/z (EI, 40 eV, rel intensity) 242 (M^+,

25%), 227 (75), 200 (11), 185 (43), 157 (23), 146 (42), 118 (100), 91 (13), 57 (13); HRMS (EI, 40 eV) calcd for $C_{18}H_{26}$ 242.2035, found 242.2033.

1,2-Bis[(1*R*,7*R*,8*R*,10*R*)-8,10-dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadien-4-yl]ethane (*β*,*β*-22), 1,2-Bis[(1*R*,7*R*,8*R*,-10*R*)-8,10-dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadien-3-yl]ethane (α,α-22), 1-[(1*R*,7*R*,8*R*,10*R*)-8,10-dimethyltricyclo-[5.2.2.0^{2,6}]-2,5-undecadien-4-yl]-2-[(1*R*,7*R*,8*R*,10*R*)-8,10-dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadien-3-yl]ethane (α,*β*-22). Method 1 *via* Lithio Salt (Table 1, Entry 3). To a solution of DMeBCOCpH (−)-**10** (0.696 g, 4.0 mmol) in THF (4 mL) was added at −78 °C *n*-BuLi (2.1 M in hexane, 2.0 mL, 4.2 mmol). The solution was stirred at 0 °C for 30 min and at room temperature for 30 min. To the resulting yellow solution was added at room temperature 1,2-ethanediol bis(4-methylbenzenesulfonate) (0.741 g, 2.0 mmol) from a side arm. A thick white slurry was observed after 5 min. THF (2 mL) was added to loosen the slurry. After the slurry was stirred for 12 h, ice water (15 mL) was added and the mixture was extracted with petroleum ether (3 × 15 mL). The combined organic portions were washed with aqueous NaCl (10 mL) and concentrated at 20 °C to give a pale yellow oil (0.80 g) which showed the following ratio by ^{1}H NMR analysis: DMeBCOCpH (−)-**10**/bridged ligand **22**/*β*-spiro **23**/α-spiro **24** = 26.0:55.6:2.4:16.0. The mixture of these four components was chromatographed (SiO_2, ca. 1 g of sample/700 mL of gel, petroleum ether), to give in order of increasing polarity DMeBCOCpH (−)-**10** (0.10 g, 14%), bridged ligand (+)-**22** as a colorless oil (0.460 g, 62%), and a mixture of α-spiro (−)-**24** and *β*-spiro (−)-**23** in a ratio of 7:1 as a white solid (0.091 g, 11%). Compound (+)-**22** (mixture of isomers): $[\alpha]_D^{23}$ +1.83° (*c* 1.29, hexane); R_f 0.48 (SiO_2/petroleum ether); IR (KBr) 3060, 2950, 2920, 2860, 1445, 1375, 1345, 1170, 1070, 1020, 900, 815, 740 cm^{-1}; ^{1}H NMR (400 MHz, CDCl3) *δ* 6.07−5.78 (m, 2 H), 5.63 (m, 1 H), 3.03 (m, 0.6 H), 2.89−2.81 (m, 2.5 H), 2.53−2.26 (m, 6 H), 1.99−1.07 (m, 10 H), 1.31−1.09 (m, 0.9 H), 0.97−0.57 (m, 9 H), 0.73 (d, *J* = 7.0 Hz, 6 H); MS *m*/*z* (EI, 70 eV, rel intensity) 374 (M$^+$, 6%), 240 (14), 200 (25), 187 (36), 174 (22), 158 (24), 143 (23), 132 (51), 117 (33), 86 (63), 84 (100); HRMS (EI, 70 eV) calcd for $C_{28}H_{38}$ 374.2974, found 374.2973. Due to thermal lability this compound was immediately carried to the next step.

Method 2 *via* Grignard Reagent (Table 1, Entry 6). EtMgBr (3.0 M in Et_2O, 4.0 mL, 12 mmol) was syringed into a 100 mL, three-necked flask equipped with a reflux condenser. The solvent was removed *in vacuo* to provide a white gray residue, to which was added THF (4 mL) and DMeBCOCpH (−)-**10** (1.988 g, 11.43 mmol) in THF (30 mL) *via* cannula. The mixture was heated at reflux for 48 h and then cooled to −10 °C to produce a yellow slurry. 1,2-Dibromoethane (0.245 mL, 2.86 mmol) was added dropwise. The mixture was stirred at −10 °C for 24 h, at room temperature for 8 h, and then at 66 °C for 24 h. Ice water (20 mL) was added to the resulting yellow solution at 0 °C, and the mixture was diluted with petroleum ether (20 mL) and filtered through a SiO_2 pad, which was washed well with petroleum ether (60 mL). The aqueous portion was easily separated and extracted with petroleum ether (3 × 20 mL). The combined organic portions were dried over Na_2SO_4 and concentrated at 20 °C to give a yellow oil (2.1 g) which contained unreacted DMeBCOCpH (−)-**10**, the bridged ligand **22**, and a trace amount of the C_2-symmetric spiro-compound **23** by ^{1}H NMR analysis. Column chromatography on deactivated SiO_2 (pretreated with 6% water 1 night prior to use, ca. 1 g of sample/700 mL of gel) using petroleum ether as an eluent gave first the unreacted DMeBCOCp diene (−)-**10** (0.993 g, 50%; 100% based on limiting dibromide) and then **22** as a colorless oil (0.806 g, 75%). Characterization of mixture of **22**: $[\alpha]_D^{23}$ −0.67° (*c* 1.19, hexane); R_f 0.46; IR (KBr) 3060, 2980, 2930, 2870, 1470, 1380, 1355, 1140, 1080, 1025, 895, 850, 740 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.07 (br s, 0.7 H), 6.05 (br s, 1 H), 5.80 (m, 1.5 H), 5.63 (m, 1 H), 3.05 (m, 0.5 H), 2.94−2.76 (m, 5.3 H), 2.55−2.28 (m, 11.7 H), 2.00−1.62 (m, 15.6 H), 0.98−0.57 (m, 25.4 H); MS *m*/*z* (EI, 70 eV, rel intensity) 374 (M$^+$, 33%), 201 (29), 200 (76), 188 (54), 187 (38), 158 (58), 145 (100), 129 (31), 91 (11); HRMS (EI, 70 eV) calcd for $C_{28}H_{38}$ 374.2974, found 374.2972. Due to thermal lability this compound was immediately carried to the next step.

Method 3 *via* Grignard Reagent (Table 1, Entry 5). Following the procedure described in method 2, DMeBCOCp·MgBr, derived from DMeBCOCpH (−)-**10** (1.591 g, 9.14 mmol) and EtMgBr (3.0 M in Et_2O, 3.2 mL, 9.6 mmol), was mixed with 1,2-dibromoethane (0.196 mL, 2.29 mmol) at room temperature. The mixture was stirred for 8 h, heated to 66 °C for 24 h, and worked up as above to provide a yellow oil (1.65 g) which contained the unreacted DMeBCOCpH (−)-**10** and the bridged ligand **22** by ^{1}H NMR analysis. The crude product was column chromatographed on normal SiO_2 to afford first DMeBCOCpH (−)-**10** (0.497 g, 31%; 63% based on limiting dibromide) and then bridged bis(cyclopentadiene) **22** (0.516 g, 60%). Characterization of the mixture: $[\alpha]_D^{23}$ +1.87° (*c* 1.02, hexane); spectra were similar to those reported above. This mixture was immediately carried to the next step.

(1*S*,7*S*,8*R*,10*R*)-8,10-Dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadiene-4-spirocyclopropane [*β*-spiro-DMBCOCp, 23] and (1*S*,7*S*,8*R*,10*R*)-8,10-Dimethyltricyclo[5.2.2.0^{2,6}]-1-(6),4-undecadiene-3-spirocyclopropane [α-spiro-DMB-COCp, 24] (Table 1, Entry 4). To a solution of DMeBCOCpH (−)-**10** (0.174 g, 1.0 mmol) in Et_2O (3 mL) was added at −78 °C *n*-BuLi (2.2 M in hexane, 0.48 mL, 1.05 mmol). The mixture was stirred at 0 °C for 30 min and at room temperature for an additional 30 min. HMPA (0.37 mL, 2.1 mmol) was added at 0 °C, transforming the original white slurry into a light yellow solution. 1,2-Ethanediol bis(4-methylbenzenesulfonate) (0.185 g, 0.5 mmol) was added at 0 °C from a side arm, and the mixture was stirred at room temperature for 12 h to give a white slurry. Water (3 mL) was added at 0 °C, and the mixture was extracted with petroleum ether (3 × 5 mL). The combined organic portion was washed with saturated aqueous NaCl (5 mL), dried with Na_2SO_4, and then concentrated under reduced pressure to give a yellow oil (0.182 g). The ^{1}H NMR spectrum of this crude product indicated the presence DMeBCOCpH (−)-**10**/*β*-spiro **23**/α-spiro **24** in a ratio of 1:0.3:0.7. A mixture of *β*-spiro **23** and α-spiro **24** was separated from the recovered DMeBCOCpH by column chromatography (SiO_2/petroleum ether) as a light yellow oil. The compounds were characterized as the mixture: $[\alpha]_D^{23}$ −13.0° (*c* 1.72, hexane, 23:24 = 1:7); R_f 0.41 (SiO_2/petroleum ether); IR (KBr) 3070, 3030, 2930, 2900, 2840, 1475, 1440, 1365, 1270, 955 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) for **23** (in mixture with **24**) *δ* 5.50 (s, 2 H), 2.36 (m, 2 H), 2.02−1.75 (m, 4 H), 1.43−1.38 (m, 4 H), 0.97 (ddd, *J* = 12.0, 5.0, 2.5 Hz, 2 H), 0.78 (d, *J* = 7.0 Hz, 6 H); for **24** (in mixture with **23**) *δ* 6.47 (d, *J* = 5.0 Hz, 1 H), 5.90 (d, *J* = 5.0 Hz, 1 H), 2.59 (m, 1 H), 2.14 (m, 1 H), 2.02−1.75 (m, 4 H), 1.56−1.38 (m, 4 H), 0.71 (ddd, *J* = 11.5, 4.0, 3.0 Hz, 1 H), 0.65 (d, *J* = 6.5 Hz, 3 H), 0.59 (d, *J* = 6.5 Hz, 3 H), 0.53 (ddd, *J* = 11.5, 4.0, 3.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) (for **23** and **24**) *δ* 147.23, 145.68, 141.40, 135.87, 129.34, 127.22, 38.32, 37.40, 37.35 (2 C), 37.27, 37.24, 36.73, 35.76, 32.00, 31.83, 30.70, 22.98, 22.80, 22.38, 10.89, 10.83, 10.66; MS *m*/*z* (EI, 20 eV, rel intensity) 201 (M$^+$ + 1, 5.6%), 200 (M$^+$, 37), 143 (100), 129 (10), 128 (9), 104 (4.5); HRMS (EI, 20 eV) calcd for $C_{15}H_{20}$ 200.1565, found 200.1565.

(−)-[Ethylene-1,2-bis[*η*^{5}-(1*R*,7*R*,8*R*,10*R*)-8,10-dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadien-3-yl]]titanium Dichloride [(−)-α,α-en(DMeBCOCp)$_2$TiCl$_2$, (−)-12]. To an isomeric mixture of bridged ligand **22** (0.410 g, 1.10 mmol, prepared according to entry 3 in Table 1) in THF (55 mL) was added at −78 °C MeLi (1.4 M in Et_2O, 1.65 mL, 2.3 mmol). The cold bath was removed, and the mixture was stirred for 1.5 h to give a pink solution, to which was added at −40 °C $TiCl_3$·3THF (0.408 g, 1.10 mmol) from a side arm in one portion. The mixture warmed to room temperature during 30 min and was heated at reflux for 12 h. The resulting dark

green solution was cooled to −40 °C, and 6 N HCl (1.0 mL) was added *via* a syringe over 5 min. The cold bath was removed, and after 30 min air was bubbled through the reaction mixture for 10 min, giving a deep red solution. Et_2O (20 mL) was added, and the mixture was filtered through a short SiO_2 column and washed well with Et_2O (50 mL). The deep red filtrate was concentrated to provide a dark brown residue (0.415 g, 77%) whose ^1H NMR spectrum indicated the presence of *β*,*β*-en(DMeBCOCp)$_2TiCl_2$ ((+)-**11**)/α,α-en(DMeBCOCp)$_2TiCl_2$ ((−)-**12**)/α,*β*-en(DMeBCOCp)$_2TiCl_2$ (**25**) in a ratio of 26:35:39. Pure (−)-**12** was isolated as dark green crystals (26 mg, 6%) after repeated recrystallization from hexane containing a little CH_2Cl_2: Mp 197−199 °C (hexane/CH_2Cl_2); $[\alpha]_D^{23}$ −1.3 × 10^3° (*c* 0.025, CH_2Cl_2); IR (KBr) 3030, 2980, 2970, 2880, 1510, 1380, 1270, 810 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 6.53 (d, *J* = 2.5 Hz, 2 H), 5.85 (d, *J* = 2.5 Hz, 2 H), 3.43−3.05 (m, 4 H), 3.05 (br s, 2 H), 2.86 (m, 2 H), 2.60 (ddd, *J* = 13.0, 6.0, 2.0 Hz, 2 H), 2.03 (ddd, *J* = 12.0, 9.0, 2.0 Hz, 2 H), 1.99−1.89 (m, 4 H), 1.72 (ddd, *J* = 13.0, 10.5, 3.5 Hz, 2 H), 1.08 (d, *J* = 7.5 Hz, 6 H), 0.38 (d, *J* = 6.5 Hz, 6 H), 0.20 (ddd, *J* = 12.0, 5.5, 2.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 153.16, 136.75, 135.71, 122.08, 120.16, 42.33, 40.02, 39.90, 33.34, 32.45, 30.72, 30.28, 21.95, 20.78; MS *m*/*z* (EI, 40 eV, rel intensity) 493 (M^+ + 3, 11%), 492 (M^+ + 2, 33), 491 (M^+ + 1, 19), 490 (M^+, 40), 457 (M^+ − Cl + 2, 27), 455 (M^+ − Cl, 62), 418 (M^+ − 2HCl, 33), 376 (100); HRMS (EI, 40 eV) calcd for $C_{28}H_{36}TiCl_2$ 490.1673, found: 490.1673. Compound α,*β*-en(DMeBCOCp)$_2TiCl_2$ (**25**): ^1H NMR (400 MHz, $CDCl_3$) (in mixture with **11** and **12**) diagnostic signals *δ* 6.41 (d, *J* = 2.5 Hz, 1 H), 6.22 (m, 1 H), 6.06 (m, 1 H), 5.62 (d, *J* = 2.5 Hz, 1 H), 1.17 (d, *J* = 6.5 Hz, 3 H), 0.89 (d, *J* = 7.5 Hz, 3 H), 0.40 (d, *J* = 6.5 Hz, 6 H).

(+)-[Ethylene-1,2-bis[*η*^{5}-(1*R*,7*R*,8*R*,10*R*)-8,10-Dimethyltricyclo[5.2.2.0^{2,6}]-2,5-undecadien-4-yl]]titanium Dichloride [(+)-*β*,*β*-en(DMeBCOCp)$_2TiCl_2$, (+)-11]. To a mixture of bridged ligand **22** (0.680 g, 1.82 mmol, prepared according to Table 1, entry 6) in THF (91 mL) was added at −78 °C MeLi (1.4 M in Et_2O, 2.73 mL, 3.8 mmol). The cold bath was removed, and the mixture was stirred for 1.5 h to give a pink solution, to which was added at −40 °C $TiCl_3$·3THF (0.674 g, 1.82 mmol) from a side arm in one portion. After being stirred at room temperature for 30 min and heated at reflux for 12 h, the resulting dark green solution was cooled to −40 °C and 6 N HCl (1.5 mL) was added *via* a syringe over 5 min. The cold bath was removed, and after 30 min air was bubbled through the reaction mixture for 10 min to produce a deep red solution. Et_2O (50 mL) was added, and the mixture was filtered through a short SiO_2 column, which was washed well with Et_2O (150 mL). The deep red filtrate was concentrated *via* rotary evaporation to provide a brown red residue (0.753 g, 84%) whose ^1H NMR spectrum indicated the presence of (+)-**11**/(−)-**12**/**25** in a ratio of 71:7:22. The crude product was washed with hot hexane (170 mL) and filtered to give after removal of the solvent a brown red solid (0.650 g, 73%). Pure (+)-**11** was isolated as dark green crystals (0.218 g, 24%) after several recrystallizations from hexane/*n*-chlorobutane: Mp 263−264 °C (hexane/*n*-BuCl); $[\alpha]_D^{23}$ +4.7 × 10^3° (*c* 0.030, CH_2Cl_2); IR (KBr) 3100, 3080, 2930, 2870, 1705, 1450, 1375, 1150, 1070, 850 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 5.77 (m, 2 H), 5.68 (m, 2 H), 3.22−2.88 (m, 4 H), 2.91 (br s, 2 H), 2.70 (br s, 2 H), 2.37 (ddd, *J* = 12.0, 7.0, 2.0 Hz, 2 H), 2.02−1.94 (m, 4 H), 1.88−1.81 (m, 2 H), 1.77 (ddd, *J* = 12.0, 10.5, 3.5 Hz, 2 H), 1.06 (d, *J* = 7.0 Hz, 6 H), 0.44 (d, *J* = 6.5 Hz, 6 H), 0.20 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 152.16, 145.27, 139.66, 113.77, 105.32, 42.43, 39.58, 39.50, 33.49, 32.73, 32.04, 30.91, 22.10, 21.46; MS *m*/*z* (EI, 40 eV, rel intensity) 495 (M^+ + 5, 5%), 494 (M^+ + 4, 15), 493 (M^+ + 3, 22), 492 (M^+ + 2, 61), 491 (M^+ + 1, 36), 490 (M^+, 82), 457 (M^+ − Cl + 2, 31), 455 (M^+ − Cl, 74), 420 (M^+ − 2Cl, 16), 376 (100); HRMS (EI, 40 eV) calcd for $C_{28}H_{36}TiCl_2$ 490.1673, found 490.1666. Anal. Calcd for $C_{28}H_{36}TiCl_2$: C, 68.55; H, 7.40. Found: C, 68.45; H, 7.20.

Following the metalation procedure above, a mixture of bridged ligand **22** (0.415 g, 1.11 mmol, prepared according to Table 1, entry 5) in THF (55.5 mL) was deprotonated with MeLi (1.4 M in Et_2O, 1.66 mL, 2.3 mmol), and metalated with $TiCl_3$·3THF (0.411 g, 1.11 mmol) to provide, after workup, a brownish red residue (0.411 g, 75%, (+)-**11**/(−)-**12**/**5** = 58:7:35).

X-ray Crystal Structure of (+)-11. Crystals of (+)-11 suitable for X-ray diffraction were obtained by diffusion of hexane into a solution of this *ansa*-titanocene dichloride in 1-chlorobutane. The data were collected at room temperature on a CAD-4 diffractometer with Mo Kα radiation (*λ* = 0.710 69 Å) and corrected for Lortenz and polarization effects. Absorption correction was not applied because it was judged to be insignificant. The structure was solved and refined using the SHELX 76 program (see Table 3).

4-*tert*-Butyl-1-methylenecyclohexane Epoxide (27).[27] To a 2 L, two-necked flask was placed trimethylsulfonium iodide (79.2 g, 353 mmol), sodium hydride [60% in mineral oil, 15.84 g, 396 mmol, washed with hexane (3 × 30 mL) prior to use], and THF (600 mL). The mixture was heated at reflux for 3.5 h to afford a milky slurry. The solution was cooled to room temperature, and 4-*tert*-butylcyclohexanone (51.0 g, 327 mmol) in THF (120 mL) was added *via* a cannula. The mixture was heated at reflux for 1.2 h followed by removal of most of the THF by rotary evaporation. Water (500 mL) was added, and the mixture was extracted with petroleum ether (400 mL). The aqueous portion was further extracted with petroleum ether (2 × 200 mL). The combined organic portions were washed with saturated aqueous NaCl (200 mL) and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, leading to the desired oxirane **27** as a pale yellow oil (56.95 g, >100%) which contained a 92:8 mixture of the *cis* and *trans* isomers: ^1H NMR (400 MHz, $CDCl_3$) for the major isomer *δ* 2.61 (s, 2 H), 1.88−1.75 (m, 4 H), 1.39−1.29 (m, 4 H) 1.04 (m, 1 H), 0.86 (s, 9 H). The crude product was used in the next step without further purification.

***trans*- and *cis*-4-*tert*-Butylcyclohexanecarboxyladehydes (28 and 29).**[28] In an oven-dried 2 L separatory funnel was placed a solution of oxirane **27** (56.95 g, crude product from previous step) in dry benzene (676 mL), followed by boron trifluoride (20.7 mL, 169 mmol). The solution was swirled, allowed to stand for 1 min, and then washed sequentially with saturated Na_2CO_3 (3 × 20 mL) and saturated aqueous NaCl (150 mL). The organic layer was dried over $MgSO_4$ and concentrated under aspirator pressure (25 °C). The resulting yellow oil (52.5 g) was purified by vacuum distillation (50−55 °C/0.2 Torr) to afford the title compounds **28** and **29** as a clear oil (28.1 g, 51.0%) with a *trans* to *cis* ratio of 72:28. Careful chromatography (SiO_2, petroleum ether) gave the cis-isomer **29** in the first fraction (5.53 g, 10%, *cis*/*trans* = 98.4/1.6), a mixture of both isomers in the second fraction (8.46 g, 15%, *cis*/*trans* = 29.7/70.3), and the *trans* isomer **28** in the third fraction (11.15 g, 20%, *trans*/*cis* = 98.5/1.5). The *cis*/*trans* ratios were determined by capillary GC on a 50 m dimethylsilicon column with the following program: initial 100 °C/15 min, rate 10 °C/1 min, final 170 °C/0.5 min at 15 psi column head pressure. R_f: *cis* =10.84 min, *trans* = 11.10 min. Both isomers were stored in a freezer and converted to the next step within 1−2 days. Decomposition was observed for both isomers at room temperature within 3−4 days. *cis*-Isomer **29**: R_f 0.32 (SiO_2, 3% diethyl ether in petroleum ether); IR (thin film) 2970, 2930, 2700, 1720, 1450, 1390, 1365, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 9.70 (s, 1 H), 2.38 (m, 1 H), 2.27 (br s, *J* = 13.5 Hz, 2 H), 1.66 (br d, *J* = 12.0 Hz, 2 H), 1.50 (m, 3 H), 0.96−0.86 (m, 2 H), 0.78 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 205.91, 47.76, 46.46, 32.45, 27.33, 25.43, 24.05; MS *m*/*z* (EI, 40 eV, rel intensity) 168 (M^+, 4%), 157 (5), 146 (8), 135 (7), 118 (12), 111 (21), 94 (16), 83 (17), 69 (12), 57 (100). *trans*-Isomer **28**: R_f 0.24 (SiO_2, 3% diethyl ether in petroleum ether); IR (thin film) 2980, 2860, 2705, 1720, 1450, 1390, 1370, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 9.59 (d, *J* = 2.0 Hz, 1 H), 2.11 (ttd, *J* = 12.0, 3.5, 2.0 Hz, 1 H), 2.02−1.97 (m, 2 H),

1.92−1.83 (m, 2 H), 1.26−1.16 (m, 2 H), 1.06−0.94 (m, 3 H), 0.83 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.95, 50.51, 47.56, 32.42, 27.45, 26.47, 26.17; MS *m*/*z* (EI, 40 eV, rel intensity) 168 (M^+, 4%), 157 (7), 146 (43), 135 (6), 118 (62), 83 (18), 67 (14), 57 (100).

***trans*-4-*tert*-Butyl-1-vinylcyclohexane (30).** To a slurry of methyltriphenylphosphonium bromide (30.20 g, 82.9 mmol) in THF (414 mL) was added at −78 °C *n*-BuLi (2.5 M in hexane, 31.8 mL, 79.5 mmol) dropwise. The yellow mixture was warmed to room temperature and stirred for 1 h. The solution was cooled to 0 °C, *trans*-aldehyde **28** (11.15 g, 66.28 mmol, containing 1.5% cis isomer **29**) in THF (133 mL) was added *via* cannula, and the cloudy mixture was stirred at room temperature overnight. Water (100 mL) was added, and the aqueous layer was extracted with petroleum ether (3 × 100 mL). The combined organic portions were dried over $MgSO_4$ and concentrated under reduced pressure to give an oily residue. Petroleum ether (ca. 100 mL) was added, and the mixture was vacuum filtered through a SiO_2 pad and washed with petroleum ether. Evaporation of the solvent from the filtrate gave a residue which after a short column (SiO_2, petroleum ether) gave the desired *trans*-alkene **30** as a clear oil (9.59 g, 87%; the *cis*/*trans* ratio remained the same): R_f 0.50 (SiO_2, petroleum ether); IR (thin film) 3080, 2960, 2860, 1640, 1480, 1450, 1390, 1370, 1240, 1000, 920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddd, J = 17.0, 10.5, 6.5 Hz, 1 H), 4.96−4.83 (m, 2 H), 1.85−1.75 (m, 5 H), 1.09-0.91 (m, 5 H), 0.82 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.84, 111.57, 47.76, 41.86, 33.01, 32.42, 27.56, 27.00; MS *m*/*z* (EI, 40 eV, rel intensity) 166 (M^+, 9%), 151 (18), 137 (4), 123 (12), 109 (25), 95 (23), 81 (34), 67 (37), 57 (100); HRMS (EI, 40 eV) calcd for $C_{12}H_{22}$ 166.1722, found 166.1720.

***cis*-4-*tert*-Butyl-1-vinylcyclohexane (31).** Following the procedure used to prepare **30** with methyltriphenylphosphonium bromide (14.3 g, 39.3 mmol), THF (197 mL), *n*-BuLi (2.5 M in hexane, 15.1 mL, 37.8 mmol), and *cis*-aldehyde **29** (5.295 g, 31.47 mmol, containing 1.6% *trans* isomer **28**) in THF (63 mL) gave *cis*-alkene **31** as a clear oil (3.84 g, 73%, the *cis*/*trans* ratio remained the same): R_f 0.50 (SiO_2, petroleum ether); IR (thin film) 3090, 2980, 2860, 1640, 1460, 1450, 1370, 1240, 1000, 915 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (ddd, J = 17.0, 11.0, 6.0 Hz, 1 H), 5.04−4.99 (m, 2 H), 2.38 (br s, 1 H), 1.75 (m, 2 H), 1.55−1.47 (m, 4 H), 1.20−1.09 (m, 2 H), 1.00−0.93 (m, 1 H), 0.81 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.36, 113.56, 48.49, 36.21, 32.57, 31.13, 27.49, 22.24; MS *m*/*z* (EI, 40 eV, rel intensity) 166 (M^+, 5%), 151 (8), 137 (4), 129 (13), 117 (24), 109 (17), 96 (8), 91 (23), 81 (38), 67 (45), 57 (100); HRMS (EI, 40 eV) calcd for $C_{12}H_{22}$ 166.1721, found 166.1711.

(4*R)-(4-*tert*-Butylcyclohexylidene)ethane (32).**[29] To a slurry of ethyltriphenylphosphonium bromide (13.64 g, 36.0 mmol) in THF (180 mL) was added at −78 °C *n*-BuLi (2.6 M in hexane, 15 mL, 39.0 mmol) dropwise. The yellow mixture was stirred for 15 min and warmed to room temperature and stirred for an additional 15 min. The ylide solution was cooled to −30 °C, 4-*tert*-butyl-cyclohexanone (4.67 g, 30.0 mmol) in THF (60 mL) was added *via* cannula, and the cloudy mixture was heated at reflux overnight. The mixture was cooled to room temperature, water (30 mL) was added, and the aqueous layer was extracted with petroleum ether (3 × 30 mL). The combined organic portions were washed with saturated aqueous NaCl (30 mL), dried over $MgSO_4$, and vacuum filtered through a SiO_2 pad with petroleum ether. Evaporation of the solvent from the filtrate gave a residue which after a short column (SiO_2, petroleum ether) gave the desired racemic alkene **32** as a clear oil (3.20 g, 64%): R_f 0.43 (SiO_2, petroleum ether); IR (thin film) 3020, 2950, 2860, 1480, 1450, 1370, 1240, 1020, 920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (q, J = 6.5 Hz, 1 H), 2.65 (dq, J = 13.0, 2.5 Hz, 1 H), 2.19 (dq, J = 13.0, 3.0 Hz, 1 H), 1.96 (m, 1 H), 1.81 (m, 2 H), 1.62 (m, 1 H), 1.55 (d, J = 6.5 Hz, 3 H), 1.13 (tt, J = 12.0, 3.0 Hz, ^{1}H), 0.97 (dtd, J = 20.0 13.0, 4.0 Hz, 2 H), 0.83 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.09, 114.67, 48.52, 36.94, 32.46, 29.17, 28.23, 28.00, 27.63, 12.67; MS *m*/*z* (EI, 40 eV, rel intensity) 166 (M^+, 45%), 157 (89), 151 (13), 142 (21), 129 (19), 110 (49), 109 (43), 95 (30), 81 (61), 67 (49), 57 (100); HRMS (EI, 40 eV) calcd for $C_{12}H_{22}$ 166.1721, found 166.1724.

Procedure for Enantioselective Alkene Migration. A 2 mL round bottom drying ampule was charged with a titanocene dichloride complex (0.01 mmol), $LiAlH_4$ (Fluka, 97%, 1.6 mg, 0.04 mmol), and a spinbar. The tube was capped with a septum and syringe addition adapter and was connected to a Schlenk line through the side tube of the adapter. The flask was evacuated and purged with argon three times. Mesitylene (distilled under Na/benzophenone, 0.3 mL) was added *via* a syringe, and the mixture was heated at 164 °C for 30 min and then cooled to room temperature. To the resulting slurry (the color changed during the heating to give dark greenish, dark blue, dark greenish, or dark purple for (+)-(DiPrBCOCp)$_2$TiCl$_2$ (**33**), (−)-(DMeBCOCp)$_2$TiCl$_2$ (**1**), (+)-β,β-en(DMeBCOCp)$_2$TiCl$_2$ (**11**), or c-C6(Ind)$_2$TiCl$_2$ (**7**), respectively) was introduced *trans*- or *cis*-4-*tert*-butyl-1-vinylcyclohexane (**30** or **31**) (mixed with decane as a GC internal reference, predried with CaH_2, and degassed *via* four freeze−pump−thaw cycles, 0.2 mL, 0.50 mmol). The ampule was cooled and sealed *in vacuo*, and the migration reaction was allowed to proceed at the temperatures listed in Table 4. The product mixture was examined by achiral gas chromatography. The enantiomeric excess of the products was determined on a 50 m chiral GC column (CP-cyclodex β 236) at an isothermal mode (80 °C, 15 psi). R_f: (*R*)-**32** = 77.016, (*S*)-**32** = 77.735 min. The absolute configuration was determined by the sign of the rotation for one sample.[29] Thus, the crude product from entry 6 in Table 4 was first diluted with mesitylene and then purified by filtering through a short path of SiO_2 and washing with petroleum ether: The $[\alpha]_D^{23}$ of this product was dextrotatory, enabling the major isomer to be assigned as (+)-(*S*)-**32**, and enabling the more slowly eluting (major) enantiomer from the chiral GC column to be assigned with the (*S*)-configuration.

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Supporting Information Available: X-ray crystal data for **11**, including tables of data collection parameters, atomic coordinates, anisotropic parameters, bond lengths and angles, and torsion angles (12 pages). Ordering information is given on any current masthead page.

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