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Synthesis of Pure Racemic Isomers of *ansa*-Titanocene Dichlorides: Conformational Preferences Are Determined by Substitution Patterns on the Cyclopentadienyl Rings

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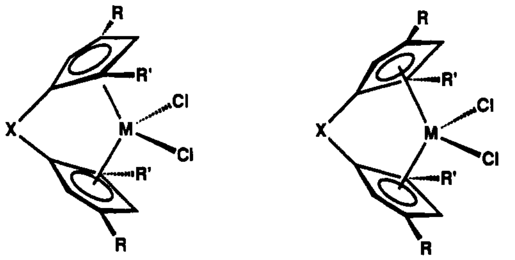
A series of [1,2-ethylene-1,1′-bis(4-alkyl-2-methylcyclopentadienyl)]titanium dichlorides (**3a–c**) have been prepared by a new route wherein the presence of the 2-methyl substituent on the cyclopentadiene rings enables the stereoselective preparation of *racemic* isomers. Racemic ethylene-1,1′-bis(2-methyl-4-*tert*-butylcyclopentadienyl)titanium dichloride (**3c**) was characterized by an X-ray structural determination: triclinic, space group $P\bar{1}$, $a = 9.910$ (1) Å, $b = 14.511$ (1) Å, $c = 15.141$ (2) Å, $\alpha = 83.81$ (1)°, $\beta = 88.62$ (1)°, $\gamma = 81.27$ (1)°, $V = 2139.5$ (4) Å^3, $Z = 4$, final $R = 0.0361$, $R_w = 0.0573$ based on 5944 reflections with $F > 6.0\sigma(F)$. Two independent molecules of compound **3c** are present in the asymmetric unit; the conformations adopted by the ansa ligand in these two molecules are similar, however. The structural features that influence the solid-state conformations of this class of compounds are discussed. Variable-temperature NMR studies reveal that both compound **3c** and its normethyl analogue **3c** (R′ = H) are fluxional at low temperature; the line-broadening behavior is different, however, for the two compounds. The possible origins for these differences are discussed.

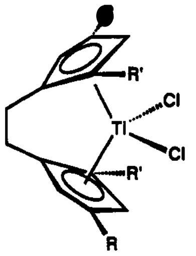
Introduction

Efficient preparative methods for the synthesis of racemic, *ansa*-metallocene compounds of general structure **1** (Chart I) are in great demand; these compounds serve as efficient cataylsts for olefin polymerization[1] and have attracted attention as reagents or catalysts in organic synthesis.[2] In earlier work, we and others have developed synthetic routes to a variety of these compounds,[3] differing mainly in the nature of the bridging group X and, more importantly, synthetic efficiency.[3a] In all cases, however, the concurrent formation of meso stereoisomers **2** in the final step of these routes seriously compromises the overall yields (Chart I). Brintzinger demonstrated that in dimethylsilylene-bridged metallocenes the racemic isomer predominates if the cyclopentadienyl rings bear an additional substituent, R′, at the 2-position (**1**: R = *i*-Pr, *t*-Bu; R′ = Me; X = $SiMe_2$).[3b] We independently observed the same phenomenon in one example of an ethylene-bridged system (**1**: R = *t*-Bu; R′ = *i*-Pr; X = CH_2CH_2).[3a] We report here general and reasonably efficient synthetic routes to compounds **3a–c** (R = Me, *i*-Pr, *t*-Bu, R′ = Me) wherein the presence of the additional methyl substituent leads to stereoselective formation of the racemic isomer. We also report on the conformational properties of these compounds in the solid state and in solution and discuss the possible origins for these preferences particularly with reference to the structures of their normethyl analogues **3** (R′ = H).

Chart I



racemic-1 meso-2
M=Ti, Zr, Hf; X=SiMe₂, CMe₂CMe₂, CH₂CH₂; R=R'=alkyl or H



3a-c: R'=Me; R=Me, *i*-Pr, *t*-Bu

Results and Discussion

We had initially hoped that simple alkylation of ligands **4**[3a] would suffice for the preparation of ligands **5**, required for the synthesis of the target metallocenes. However, even in the most favorable case (compound **4**, R = *t*-Bu), a mixture of compounds was obtained by e.g. direct methylation of the dilithio salt with Me_2SO_4 (eq 1). The

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(1) See inter alia: (a) Ewen, J. A. *J. Am. Chem. Soc.* 1984, *106*, 6355. (b) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. W. R. P. *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 507. (c) Kaminsky, W.; *Angew. Makromol. Chem.* 1986, *145/146*, 149. (d) Ewen, J. A. Ligand Effects on Metallocene Catalyzed Polymerizations. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Elsevier: New York, 1986; p 271. (e) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* 1987, *109*, 6189. (f) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *Ibid.* 1987, *109*, 6544. (g) Soga, K.; Shiono, T.; Takemura, S.; Kaminsky, W. *Makromol. Chem., Rapid Commun.* 1987, *8*, 305. (h) Corradini, P.; Guerra, G.; Vacatello, M.; Villani, V. *Gazz. Chim. Ital.* 1988, *118*, 173. (i) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* 1988, *110*, 6255. (j) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzochi, R. *Macromolecules* 1988, *21*, 617. (k) Kaminsky, W.; Ahlers, A.; Moller-Lindehof, N. *Angew. Chem., Int. Ed. Engl.* 1989, *101*, 1216. (l) Rieger, B.; Chien, J. W. C. *Polym. Bull.* 1989, *21*, 159. (m) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Makromol. Chem.* 1989, *190*, 1177. (n) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. W. C. *J. Am. Chem. Soc.* 1990, *112*, 2030. (o) Roll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* 1990, *29*, 279.

(2) (a) Collins, S.; Kuntz, B. A.; Hong, Y. *J. Org. Chem.* 1988, *54*, 4154. (b) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* 1990, *112*, 4911. (c) Jordan, R. F., personal communication.

(3) (a) Collins, S.; Hong, Y.; Taylor, N. J. *Organometallics* 1990, *9*, 2695. (b) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H. H. *J. Organomet. Chem.* 1989, *369*, 359. (c) Gutmann, S.; Burger, P.; Hund, H.-U.; Hoffmann, J.; Brintzinger, H. H. *Ibid.* 1989, *369*, 343. (d) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* 1989, 1853. (e) HPLC conditions: Waters Radial-Pak-CN normal bonded phase column, 8 mm × 12 cm, with 80:20 hexane–CH_2Cl_2 as eluent at 1.0 mL/min, detection at 540 nm.[3a] (f) From the work reported here and elsewhere,[3a,21] it appears that the racemic isomer is favored in these photoisomerizations because steric repulsion between the two alkyl groups present at the 2-position of the Cp rings (i.e. methyl (this work), isopropyl,[3a] methylene[21]) in the meso compound is absent in the racemic isomer.

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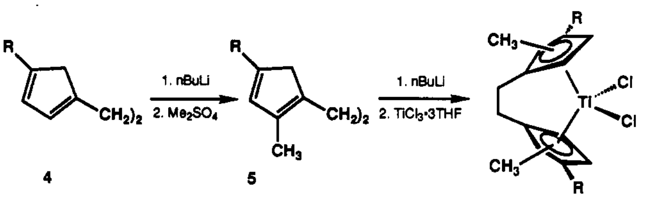
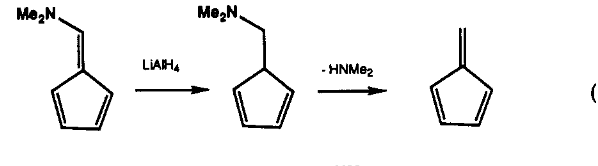
unsuitability of this approach was dramatically revealed when this mixture was used to prepare the corresponding titanocene dichlorides; more than 10 *ansa*-metallocene compounds were generated in this reaction, as revealed by HPLC of the crude reaction mixture![3e]

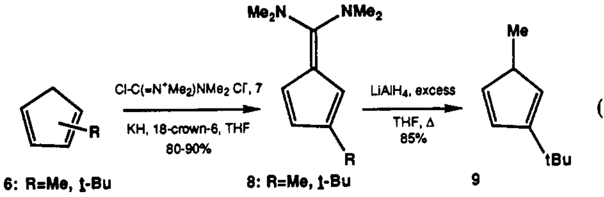


(1)

Other attempts were based on some chemistry developed by Hafner; namely, 6-(dimethylamino)fulvene could serve as surrogates for the parent compound (eq 2a).[4a] On the basis of our earlier work[3a] it seemed probable that, with suitably bulky amine substituents, this approach might be applied to the synthesis of ligand **5**. For example, condensation of cyclopentadiene **6** (R = Me or *t*-Bu) with excess chloroformamidinium salt **7**, excess KH, and catalytic amounts of 18-crown-6 in THF at room temperature provided bis(dimethylamino)fulvenes **8** in high yields (80–90%) with high regioselectivity (1,3:1,2 > 10:1; eq 2b).[4b] Reduction–elimination of compound **8** (R = *t*-Bu) with excess $LiAlH_4$ in refluxing THF provided, in a single operation, 1,3-dialkylcyclopentadiene **9**.[4b] Application of this procedure to the bridged ligand **4** (R = *t*-Bu) was inefficient however; the bis(fulvenes) were formed in maximal yields of 20–30% and the reduction process was complicated by intramolecular condensation reactions.



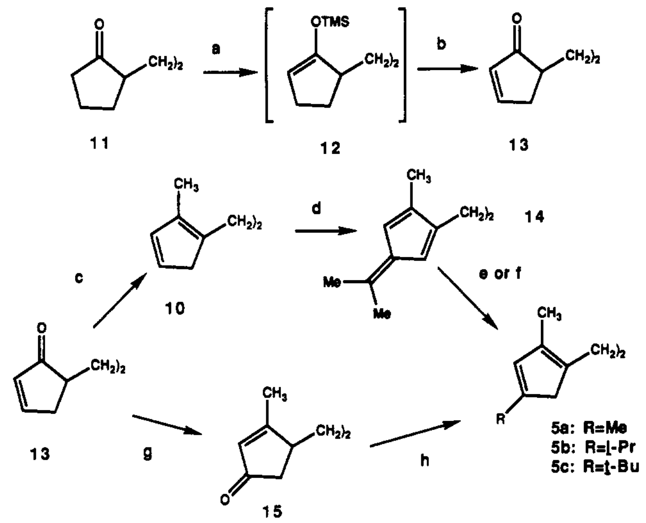
(2a)



(2b)

At this point we recognized that if the bridged ligand **10** could be prepared by some alternate route, it should prove possible to prepare ligands **5** by application of the methods developed earlier for the synthesis of compounds **4**.[3a] In practice, the synthesis of ligands **5** was accomplished as outlined in Scheme I. The starting material, diketone **11**, could be prepared on a large scale from cyclopentanone by using a modification of the literature procedure (see Experimental Section).[5] Kinetic deprotonation of diketone **11** and silylation provided the sensitive bis(enol silane) **12**, which was directly converted to dienone **13** with use of Saegusa's procedure (72%).[6] It should be noted that, in this case, the efficiency of this oxidative desilylation is dramatically improved through the use of ultrasound.[7] Ligand **10** could be prepared by reaction of this dienone with 2 equiv of $MeLa(OTf)_2$,[8] followed by subsequent dehydration of the diol produced (pTSA, C_6H_6), in 75% overall yield.

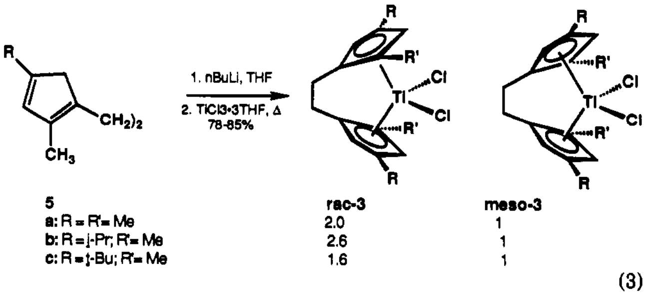
Scheme I[a]



[a] Legend: (a) (1) LDA (2 equiv) and THF/HMPA, (2) TMSCl and NEt_3, ~100%; (b) O_2, $Pd(OAc)_2$ catalyst, $Cu(OAc)_2$ catalyst, CH_3CN, ultrasound, 72%; (c) (1) $MeLa(OTf)_2$ (2 equiv) and THF, (2) pTSA and benzene, ~75%; (d) acetone (excess), pyrrolidine (excess), MeOH, 75%; (e) $LiAlH_4$, THF, ~100%; (f) MeLi, ether, ~100%; (g) (1) MeLa $(OTf)_2$ (2 equiv), and THF, (2) PCC, pyridine, and CH_2Cl_2, 85–90%; (h) (1) $MeLa(OTf)_2$ (2 equiv) and THF, (2) pTSA and THF, 40%.

Condensation of ligand **10** with acetone under the conditions previously developed was somewhat less efficient; a 75% isolated yield of bis(fulvene) **14** was obtained. We attribute this to the decreased acidity of the dialkylated cyclopentadiene **10**. Reduction or methylation of compound **14** proceeded uneventfully to provide ligands **5b** and **5c**, respectively, in essentially quantitative yields. Synthesis of ligand **5a** was also accomplished by starting from dienone **13**. Addition of 2 equiv of $MeLa(OTf)_2$ to dienone **13**, followed by oxidative rearrangement of the derived diol with PCC[9] in the presence of pyridine, afforded dienone **15** in 85–90% yields. Addition of 2 equiv of $MeLa(OTf)_2$, followed by dehydration of the resulting diol (pTSA, THF), provides ligand **5a** in 40% yield from compound **15**.

Preparation of the titanocene dichlorides **3a–c** (R′ = Me) was accomplished in the manner previously reported by reaction of the dianions of compounds **5a–c** with $TiCl_3$·3THF in THF at reflux temperature (78–85% isolated yields).[3a] In each case, small amounts of the corresponding meso isomers were also produced (eq 3). The relative amount of the meso isomer generally increased with increasing steric size of the alkyl substituent at the 4-position. In any event, the amount of racemic isomer present



(3)

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(4) (a) Sturm, E.; Hafner, K. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 749. (b) Collins, S.; Hong, Y. Unpublished results.

(5) Ryu, I.; Ando, M.; Ogawa, A.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 7192.

(6) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.

(7) For the use of ultrasound in improving heterogeneous reactions see: Davidson, R. S. In *Chemistry with Ultrasound*; Mason, T. J., Ed.; Elsevier: New York, 1990; pp 65–113, and references therein.

(8) Collins, S.; Hong, Y.; Hoover, G. J.; Veit, J. R. *J. Org. Chem.* **1990**, *55*, 3566 and references therein.

(9) Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682.

could be increased at the expense of the meso isomer by photoisomerization of the mixture in THF solution.[3a] The position of this "photoequilibrium" increasingly favors the racemic isomer for larger substituents (i.e. 2.5:1 (R = Me), 4:1 (R = *i*-Pr), >15:1 (R = *t*-Bu)).[3f] Chromatography (or even simple solvent extraction in the case of compound **3a**) served to cleanly and efficiently remove the meso contaminants in all cases.

The increasing tendency toward the formation of meso stereoisomers with increasing steric size of the 4-R group when the dianions of compounds **5** are condensed with $TiCl_3$ is consistent with the earlier results obtained in the normethyl series (compounds **3a–c**, R′ = H).[3a] Brintzinger has also observed a similar trend in the formation of tetramethylethylene-bridged analogues and has rationalized this trend on thermodynamic arguments; the meso stereoisomer can readily adopt a conformation wherein simultaneous repulsion between the alkyl groups at the 4-position of the ansa ligand and the equatorial chloride ligands is avoided.[3c] A similar result was also observed during the formation of dimethylsilyl-bridged analogues of compounds **3b** and **3c**.[3b] Although the enhanced formation of racemic isomers in this latter case was rationalized on kinetic grounds,[3b] the fact that the racemic isomer was less predominant in the mixture when a larger substituent was present also argues for an underlying thermodynamic bias toward formation of meso stereoisomers in these systems as well.

The results of the photoisomerization experiments are therefore intriguing; in this case the racemic isomer is increasingly favored with increasing size of the 4-alkyl substituent. The mechanism of these photoisomerizations has not been studied in detail; in unbridged titanocene dichlorides, photodecomposition is observed in halogenated solvents.[10] Products consistent with the formation of metal-centered radicals are obtained (e.g., $CpTiCl_3$ is formed during photolysis of Cp_2TiCl_2 in $CHCl_3$ solution), and the radical itself is stable in non-halogenated solvents.[10] We have also noted that extensive decomposition is observed with these bridged systems if the photoisomerizations are conducted in halogenated solvents, implying that the intermediates involved are also (di)radical in nature. The implication of the photoisomerization experiments then is that radical recombination favors the formation of racemic stereoisomers, increasingly so as the 4-alkyl substituent is made larger. It is difficult to reconcile these results with those seen when compounds **3** are prepared from the dianions of ligands **5** and $TiCl_3$. One might expect that the same thermodynamic (or kinetic) bias should prevail in the photoisomerization experiment if an intermediate diradical in its ground state is involved. Further work is definitely required to clarify thermodynamic and kinetic aspects of the stereochemistry of *ansa*-metallocene formation.[11]

In order to confirm the stereochemistry, an X-ray structure determination was obtained for compound **3c**.

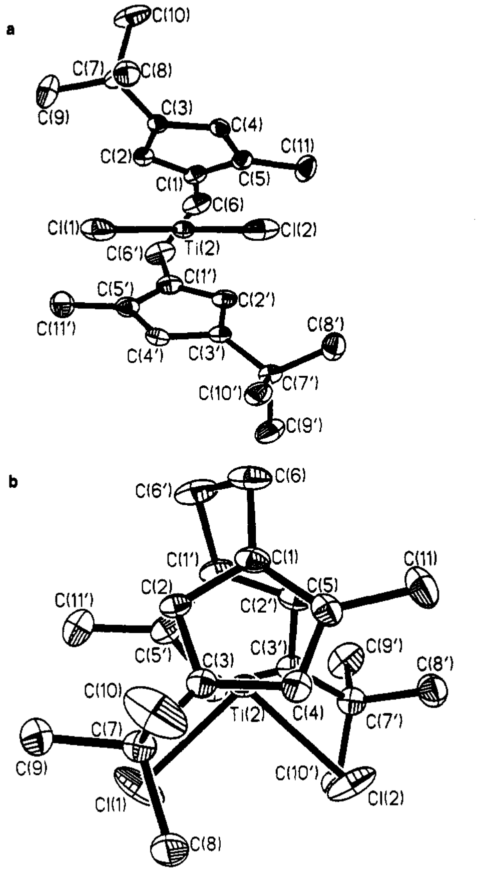

Figure 1. Molecular structure of compound **3c** (molecule 2) with 50% probability thermal ellipsoids depicted and H atoms removed for clarity: (a) projection along the bisector of the Cl(1)–Ti(2)–Cl(2) angle in the $TiCl_2$ plane; (b) projection orthogonal to that depicted in Figure 1a. For selected bond lengths and angles see Table III.

The similarity of the spectral characteristics observed for these series of compounds (see Experimental Section) served to secure the remaining assignments. Single crystals of compound **3c** were grown by slow evaporation of a toluene–isooctane solution. Crystals grown in this manner were triclinic, space group $P\bar{1}$, with $Z = 4$; two independent molecules are present in the asymmetric unit. Since the geometry about the metal and the conformation of the ansa ligand in the two molecules are quite similar, the structure of only one of these (molecule 2; for molecule 1 see the supplementary material) will be discussed in detail; when necessary, the structure of the other molecule will be mentioned, as there are several differences between the two that warrant discussion.

As can be seen from Figure 1a, the conformation adopted by the ansa ligand has approximate C_2 symmetry and the pseudo-C_2 axis is nearly coincident (to within 10°) with the bisector of the Cl(1)–Ti(2)–Cl(2) angle. This is perhaps best appreciated from the projection depicted in Figure 1b. Compound **3c** is the first example of an *ansa*-metallocene dichloride wherein the ansa ligand adopts the λ conformation. This conformation has been observed before, but only in derivatives with bulky ligands in the equatorial positions.[12] In contrast to its normethyl analogue (**3c**; R = *t*-Bu, R′ = H), where, in one modification, the ring carbon–tert-butyl carbon bonds were located within the angle subtended by the Cl–Ti–Cl moiety,[3a] the

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[10] Tsai, Z. T.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1979**, *166*, 199.

[11] It should be pointed out that most of the *ansa*-titanocene preparations, including those reported here, involve the use of $TiCl_3$ rather than $TiCl_4$. Therefore, thermodynamic and kinetic arguments based on the structures and stabilities of the final Ti(IV) metallocene dichlorides (or presumed intermediates that lead to the formation of these compounds) are *not* related to the experimental conditions employed and the intermediates that *are* involved (i.e. Ti(III)) in these reactions. We also note that it is possible to induce isomerization of, e.g., pure meso or racemic titanocene dichloride **3c** (R′ = H) to the equilibrium mixture by treatment with the dianion of the ligand in THF at room temperature or at reflux. It is possible, then, that the racemic:meso ratio observed in these preparations is unrelated to the relative stabilities of the titanocene dichlorides.

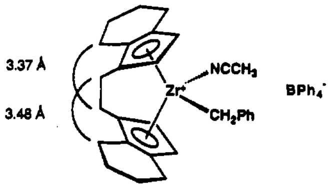
[12] (a) Schafer, A.; Karl, E.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1988**, *328*, 87. (b) Jordan, R. F.; LaPointe, R. E.; Baenziger, N.; Hinch, G. D. *Organometallics* **1990**, *9*, 1539.

corresponding bonds in this structure (C(3)–C(7) and C(3′)–C(7′)) lie outside the corresponding angle (Figure 1b) or in a "lateral" position. This leads to substantial steric repulsion between the *tert*-butyl groups and the equatorial chloride ligands in this structure. This repulsion is evident from a number of structural features. The *tert*-butyl groups lie substantially out of the least-squares planes of the Cp ligands (i.e. the angle of the line defined by C-(3)–C(7) to the Cp(1) plane is 13.6°; the corresponding angle for C(3′)–C(7′) is 14.1°). Also, as can be appreciated from Figure 1a, the Cp ring also tilts so as to further alleviate the interaction of the *tert*-butyl group with its nearest chloride ligand. The angle of the line defined by C(3)–C(4) with respect to the $TiCl_2$ plane is 4.4°, whereas the corresponding angle for C(3′)–C(4′) is 1.6° in the opposite direction—i.e., toward the $TiCl_2$ plane. The degree of tilt away from the $TiCl_2$ plane is determined by how closely the C(3)–C(7) (or C(3′)–C(7′)) bond eclipses the corresponding Ti–Cl bond (Figure 1b). This phenomenon is even more evident in the structure of molecule 1, in which the deviation of the C_2 axis of the ligand from the $TiCl_2$ bisector is more pronounced (~20°) and results in the C(3)–C(7) bond nearly eclipsing the Ti(1)–Cl(1) bond (see the supplementary material). In this case, the out-of-plane bending of the *tert*-butyl groups is 13.8 and 12.4° for C(3)–C(7) and C(3′)–C(7′), respectively, whereas the tilt angles are 7.7 and 6.6° for C(3)–C(4) and C(3′)–C(4′), respectively.

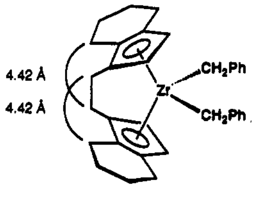
By comparison of the two structures it can be readily concluded that the Cp(1) ligand of molecule 1 is more tilted away from the $TiCl_2$ plane than that of molecule 2 and the *tert*-butyl group (C(3)–C(7)) is more out of plane in the former structure, in agreement with the relative degree of eclipsing of the C(3)–C(7) bond with the Ti–Cl(1) bond. Also, the Cp(1′) ligand is less tilted *toward* the $TiCl_2$ plane in molecule 2 as compared to molecule 1; in the former structure the C(3′)–C(7′) bond more nearly eclipses the Ti–Cl(2) bond than in the latter structure.

Finally, additional evidence for substantial repulsion between the two *tert*-butyl groups and the halide ligands is to be found in a number of nonbonded hydrogen–chlorine contacts, some of which are *well* within the sum of the van der Waals radii (e.g., H(8Y′)–Cl(2) = 2.58 (1) Å and H(8X)–Cl(1) = 2.63 (1) Å!).

Given that the λ conformation obviously introduces substantial steric repulsion between the substituent at the 4-position of the Cp ring and that of the equatorial halogen ligand, why is it that this conformation is adopted in this structure? It is clear that if the δ conformation were adopted, these interactions would be relieved to a certain extent.[3a] However, in doing so, steric repulsion between the methyl groups, C(11) and C(11′), respectively and the methylene groups, C(6′) and C(6), respectively, of the two-carbon bridge would be introduced. Perhaps the best evidence for the existence and presumed importance of this interaction is from two recent structures of [ethylenebis(η^5-tetrahydroindenyl)]zirconium derivatives 16 and 17, accurately determined by Jordan and co-workers.[12b]



16



17

In the structure of the cationic system 16, in which the ansa ligand adopts, in this case, the unfavored λ conformation, the distances between the back methylene groups and the corresponding distal carbon atoms of the ethylene bridge (analogous to the distances C(11)–C(6′) and C-(11′)–C(6) in the present structure) are 3.481 (17) and 3.365 (16) Å, respectively.[13] These distances are well within the sum of the van der Waals radii of two methyl groups (~4.0 Å). In the neutral analogue 17, the favored δ conformation is adopted and the steric interaction between these atoms is relieved; the corresponding distance is 4.416 (7) Å.[13] The latter distance is comparable to those observed in the titanocene structure reported here (C(11)–C(6′) is 4.385 (5) and C(11′)–C(6) is 4.439 (5) Å).

In summary, we believe that it is the interaction of the substituent at the 2-position of the Cp ring with the two-carbon bridge that is critical in determining the solid-state geometry of these metallocene dichlorides. In the case of a 1,2,3-substitution pattern, as is found in the tetrahydroindenyl system, the δ or "forward" conformation will be favored in the absence of bulky equatorial ligands. In the case of a 1,2,4-substitution pattern, as is demonstrated here, the λ or "lateral" conformation will be adopted in the solid state. If no substituent is present at the 2-position, the conformation adopted by the ansa ligand will depend, in part, on the nature of the substituent at the 3-position or on the size of the equatorial ligand or both; a range of conformations is expected and indeed is observed.[3] It is important to note that in the case of silyl-bridged systems only one conformer is possible; interpretation of the stereochemical course of e.g. olefin polymerization is not clouded by the conformational ambiguity seen in the ethylene-bridged systems.

In solution, both compounds **3c** (R′ = Me) and **3c** (R′ = H) exhibit NMR spectral characteristics consistent with the maintenance of 2-fold symmetry at room temperature. We have attempted to obtain information about the conformational dynamics of these systems using low-temperature ^{13}C NMR spectroscopy at high field strengths. Both compound **3c** (R′ = Me) and **3c** (R′ = H) show line-broadening behavior in their ^{13}C NMR spectra at low temperatures. However, even at the lowest temperature studied (−115 °C) and at 125 MHz, decoalescence was not observed and the slow exchange limit was not attained. Interestingly, however, the line-broadening behavior of the two compounds is different. In the spectrum of compound **3c** (R′ = H), signals due to the methyl carbons of the $C(CH_3)_3$ groups, the methylene carbons of the bridge, and three of the Cp carbons (those bearing hydrogen) exhibit similar line-broadening behavior. In contrast, in the spectrum of compound **3c** (R′ = Me), only the methyl groups of the $C(CH_3)_3$ groups exhibit significant line broadening—the other signals are reasonably sharp even at −115 °C in concentrated CD_2Cl_2 solution. We suggest that the natures of the dynamic processes are different in the two cases; in the latter case, hindered *tert*-butyl rotation is probably responsible for the dynamic behavior seen; this seems reasonable in view of the steric repulsion that exists between the *tert*-butyl groups and the halide ligands of compound **3c** (R′ = Me) in the solid state. In the normethyl compound (**3c**, R′ = H), this process may also be occurring, but in addition, conformational exchange processes involving the ligand framework (e.g. interconversion of δ and λ C_2-symmetric conformations or equilibration of two enantiomeric and asymmetric conformers) could also be involved. It is quite clear, however, that these exchange processes have low barriers; caution should be

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(13) We thank Prof. Richard F. Jordan and Prof. Norman Baenziger for providing us with these data.

applied in rationalizing the results of olefin polymerization or other processes as arising from interaction of equatorial ligands with a rigid, C_2-symmetric structure in solution.[14]

Conclusions

Relatively efficient preparative routes to pure, racemic *ansa*-metallocene compounds have been devised. At the same time, the effects of substitution of the Cp rings on the solid-state conformations adopted by the ansa ligand have been delineated; 1,2,3-substitution patterns will favor the δ conformation, whereas 1,2,4-substitution will favor the λ conformation in ethylene-bridged systems. Although it is not yet possible to state whether such considerations are important and apply to the solution chemistry of these systems, in particular the stereoselectivity of asymmetric reactions occurring at the metal center, this is obviously an interesting area for further research.

Experimental Section

All solvents and chemicals were reagent grade and were purified as required. Tetrahydrofuran and diethyl ether were dried by distillation from sodium–benzophenone ketyl. Methylene chloride and acetonitrile were dried by distillation from P_2O_5. Dimethylformamide and HMPA were dried by distillation from CaH_2. All reactions were conducted under an atmosphere of dry argon in dry glassware unless otherwise noted. Alkyllithium reagents were titrated before use. Lanthanum triflate was prepared by the method reported.[15] The compound $TiCl_3{\cdot}3THF$ was prepared by the method of Manzer.[16] ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-250 or AC-200 spectrometer; chemical shifts are referenced with respect to residual undeuterated solvent (δ 7.26 ppm for $CHCl_3$, δ 7.15 for C_6D_5H, and δ 5.32 for $CHDCl_2$). Low-temperature ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-500 spectrometer at McMaster University; temperature calibration was based on the chemical shift separation of a standard methanol sample. IR spectra were obtained with a Perkin-Elmer 983 instrument; spectra were calibrated with poly(styrene) film. Mass spectra were acquired with a KRATOS instrument at the University of Guelph. Elemental analyses were determined by M.H.W. Laboratories of Phoenix, AZ.

Preparation of 1,2-Ethylene-2,2′-bis(cyclopentan-1-one) (11).[5] A solution of cyclopentanone (42.1 g, 0.5 mol), triethylamine (100 g, 1.0 mol), and chlorotrimethylsilane (65.8 g, 0.61 mol) in DMF (200 mL) was heated at reflux for 8 h. The mixture was cooled to ~0 °C and diluted with distilled pentane (500 mL) while the mixture was vigorously stirred. The two-phase mixture was transferred to a 2-L separatory funnel, the lower layer was drawn off, and the pentane layer was set aside. The DMF layer was treated with 200 mL of ice-cold $NaHCO_3$ solution and extracted with 3 × 100 mL of pentane. The combined pentane extracts were rapidly washed with cold aqueous $NaHCO_3$ solution (2 × 150 mL), cold 1.0 N HCl (3 × 100 mL), and cold aqueous $NaHCO_3$ solution (100 mL), the pentane was then dried over $MgSO_4$ and filtered, and the pentane was removed by distillation through a Vigreaux column at atmospheric pressure. The residue was then distilled through a short-path distillation apparatus and the fraction boiling at 125–150 °C collected; this consisted largely (>95% by GC) of the desired enol silane (yield 70.3 g, 90%).[17]

The enol silane (30.0 g, 0.192 mol) was added to an excess of freshly prepared zinc–copper couple (from 0.75 mol of Zn and 0.075 mol of CuCl)[18] in ether (500 mL). Diiodomethane (40.3 g, 0.225 mol) was then added dropwise to the mixture at reflux. The mixture was then heated at reflux for 40 h. The dark mixture was cooled to 0 °C and filtered through Celite, which was washed with ether. The filtrate was washed with saturated NH_4Cl solution (2 × 50 mL), and the aqueous phase was separated and washed with ether (3 × 50 mL). The combined ether extracts were washed with saturated $NaHCO_3$ solution (3 × 50 mL) and brine (2 × 50 mL) and then dried over $MgSO_4$. The mixture was filtered and the ether removed by distillation as described above. The residue was distilled at 8 mmHg and the fraction boiling at 52–58 °C collected. The intermediate siloxycyclopropane[18] was sufficiently pure for the next reaction (yield 32.1 g, 92%).

To a suspension of anhydrous $Cu(BF_4)_2$ (7.12 g, 0.030 mol) in dry ether (15 mL) was added the siloxycyclopropane (2.56 g, 0.015 mol) at 0 °C in one portion. The mixture was immersed in an ultrasonic bath, sonicated at 15 °C for 30 min, and then stirred for another 30 min at this temperature. The mixture was diluted with ether (50 mL) and then quenched by the addition of aqueous NH_4Cl (20 mL). The ether layer was separated and set aside and the aqueous phase washed with ether (3 × 20 mL). The combined ether extracts were washed with aqueous NH_4Cl (2 × 20 mL), and aqueous $NaHCO_3$ (4 × 20 mL), and the ether layer was then dried over $MgSO_4$, filtered, and then concentrated to dryness to provide compound **11** as a low-melting solid (1.195 g, 82% yield). The spectral data indicated that compound **11** was a 2:1 mixture of stereoisomers. ^1H NMR (200 MHz, $CDCl_3$): δ 2.4–1.68 (complex m, 14 H), 1.66–1.08 (complex m, 4 H) ppm. IR ($CHCl_3$): 1745 cm^{-1}. Mass spectrum (EI): m/e 194 (M^+). The yield quoted was reproducible on a scale of up to 50 mmol of siloxycyclopropane, with the ultrasonic bath employed (2-L capacity). Several runs at this scale were conducted to convert all of the siloxycyclopropane to compound **11**.

Preparation of 1,2-Ethylene-5,5′-bis(cyclopent-2-en-1-one) (13). A solution of diisopropylamine (10.12 g, 100 mmol) in THF (200 mL) was treated dropwise with a solution of *n*-butyllithium in hexane (2.44 M, 41.0 mL, 100 mmol) at 0 °C. After 20 min, the solution was cooled to −78 °C and a solution of 1,2-ethylene-2,2′-bis(cyclopentan-1-one) (9.715 g, 50 mmol) in THF (2 × 25 mL) was added dropwise by syringe. After the mixture was stirred for 30 min, 35 mL of dry HMPA was added dropwise by syringe and the solution was stirred for a further 10 min at −78 °C. The solution of the bis(enolate) was treated dropwise with chlorotrimethylsilane (15.0 g, 138 mmol) that had been pretreated with dry triethylamine (10 mL) and then centrifuged to precipitate triethylamine hydrochloride. The solution was then warmed to room temperature over 1.5 h. The mixture was diluted with an equal volume of pentane and the mixture quenched at −20 °C by the addition of cold saturated $NaHCO_3$ (100 mL). The mixture was transferred to a separatory funnel and washed rapidly with saturated $NaHCO_3$ (2 × 50 mL) and then brine (1 × 50 mL). The organic phase was dried over $MgSO_4$ and filtered and the filtrate concentrated in vacuo to provide the crude bis(enol silane) **12** (~100%), which was used without further purification.

Compound **12** (~50 mmol) was dissolved in 50 mL of dry ether under argon. This solution was transferred via cannula to a suspension of $Pd(OAc)_2$ (1.13 g, 5.0 mmol) and $Cu(OAc)_2$ (1.83 g, 10 mmol) in 50 mL of acetonitrile in a flask immersed in a Bransonic ultrasonic bath. The mixture was sonicated at 25 °C while dry oxygen (passage over molecular sieves 4A) was bubbled through the mixture for 14 h. The dark black mixture was diluted with 1:1 ether–ethyl acetate (200 mL) and then filtered through a bed of Celite that was washed with additional ether. The pale yellow filtrate was transferred to a separatory funnel and washed with aqueous NH_4Cl (4.0 M, 3 × 50 mL) and $NaHCO_3$ (2 × 50 mL), and the organic layer was then dried over $MgSO_4$. The mixture was filtered and the filtrate concentrated in vacuo to provide a pale yellow semisolid. The pure dienone **13** could be obtained by crystallization from 5:1 30–60 °C petroleum ether–$CHCl_3$ (6.5 g, 68%). The mother liquor was concentrated in vacuo and the mixture separated by flash chromatography on silica gel eluting with 1:1 to 1:3 hexane–ether as eluent to provide an additional 0.4 g of compound **13** (total 6.9 g, 72%); mp 121–123

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[14] For example, we have found that the enantioselectivities of the additions of the crotyltitanium(III) derivative of compound **3c** (R′ = H) to aldehydes can be partially rationalized by models in which the ansa ligand adopts an asymmetric conformation similar to that observed in one of the two crystalline modifications of compound **3c** (R′ = H):[3a] Collins, S.; Kuntz, B. A., Taylor, N. J., manuscript in preparation.

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°C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 7.65 (m, 2 H), 6.13 (m, 2 H), 2.84 (m, 2 H), 2.37–2.25 (m, 4 H), 1.86–1.38 (m, 4 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ 212.0, 163.6, 133.7, 44.37, 35.32, 28.18 and 211.8, 163.6, 133.7, 44.91, 33.55, 28.95 ppm in a ratio of ~1:2. IR (CHCl$_3$): 3046, 3000, 2926, 2860, 1699, 1588 cm^{-1}. Mass spectrum (EI): *m/e* 190 (M$^+$). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.77; H, 7.42. Found: C, 75.42; H, 7.45.

Preparation of 1,2-Ethylene-1,1-bis(2,6,6-trimethylfulvene) (14). Lanthanum triflate (23.5 g, 40.0 mmol) was suspended in 200 mL of dry THF under argon. A solution of methyllithium in ether (1.4 M, 28.5 mL, 40.0 mmol) was added to this suspension at −78 °C over 15 min and the mixture warmed to 25 °C. The mixture was stirred for 30 min at this temperature and then cooled to −78 °C. A solution of dienone **13** (3.805 g, 20.0 mmol) in THF (2 × 10 mL) was then cannulated into the solution of the methyllanthanum triflate reagent. After 30 min at −78 °C, the solution was quenched by the addition of aqueous NaOH solution (1.0 M, 10 mL). After it was warmed to room temperature, the mixture was transferred to a separatory funnel and diluted with ether (200 mL), and the aqueous layer withdrawn, and the organic phase washed with aqueous NaHCO$_3$ (3 × 40 mL) and brine (4 × 20 mL), dried over K$_2$CO$_3$, filtered, and concentrated in vacuo to provide crude diol (4.4 g, ~100% yield) that was sufficiently pure (^{1}H NMR (250 MHz, CDCl$_3$) δ 5.78 (m, 2 H), 5.67 (m, 2 H), 2.44 (m, 2 H), 2.03 (m, 2 H), 1.30 (br s, 6 H) superimposed on 1.8–1.30 (m, 6 H), 1.1 (br s, 2 H, exchange with D$_2$O)) for further use in the preparation of compound **14**.

The crude diol (4.4 g, 20.0 mmol) was dissolved in 700 mL of benzene under argon. *p*-Toluenesulfonic acid hydrate (2.6 g, 14.0 mmol) was added in one portion to this solution. After 8 min at room temperature, the pale yellow solution was diluted with saturated NaHCO$_3$ solution (80 mL). The aqueous layer was separated, the organic phase washed with NaHCO$_3$ (2 × 80 mL), dried over Na$_2$SO$_4$, and filtered, and the filtrate concentrated in vacuo to provide an oil, which was passed through a short pad of silica gel, with hexane as eluent. The eluate (200 mL) was concentrated in vacuo to provide the crude bis(cyclopentadiene) **10** (2.89 g, ca. 78% from **13**) that was used without further purification in the next step.

The crude bis(cyclopentadiene) was suspended in methanol (50 mL) under argon and treated sequentially with dry acetone (10.0 mL, large excess) and freshly distilled pyrrolidine (20.0 mL, large excess). The mixture turned bright yellow within 10–15 min and became homogeneous. After 16 h at 25 °C, the mixture was filtered to provide 2.50 g of compound **14**. The filtrate was cooled to 0 °C and acetic acid (18.0 mL) added dropwise by syringe. The mixture was washed with 1:1 pentane–ether (5 × 100 mL), and the pentane extracts were combined and washed with aqueous NaHCO$_3$ (2 × 25 mL) and brine (25 mL). The organic phase was separated, dried over Na$_2$SO$_4$, and filtered and the filtrate concentrated in vacuo to provide a brown oil. An additional 0.45 g of compound 14 (total 2.95 g, 56% from dienone **13**) was obtained by recrystallization of this material from methanol–ether; mp 175–177 °C dec. ^{1}H NMR (200 MHz, CDCl$_3$): δ 6.25 (br s, 2 H), 6.23 (dq, *J* = 3.0, 1.5 Hz, 2 H), 2.60 (br s, 4 H), 2.13 (s, 6 H), 2.12 (s, 6 H), 2.04 (d, *J* = 1.5 Hz, 6 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ 147.1, 143.7, 142.3, 140.6, 117.3, 115.7, 27.9, 22.5, 13.9 ppm. IR (CHCl$_3$): 3069, 2997, 2961, 2931, 2922, 285, 1645, 1442, 1370 cm^{-1}. Mass spectrum (EI): *m/e* 266 (M$^+$). High-resolution mass spectrum: calculated for $C_{20}H_{26}$ 266.2034$_5$, found 266.2036$_0$. A satisfactory analysis could not be obtained for this compound, as it decomposes slowly (1–2 days) at room temperature in the solid state.

Preparation of 1,2-Ethylene-4,4′-bis(cyclopent-2-en-1-one) (15). As described above in the preparation of bis(fulvene) **14**, dienone **13** (0.951 g, 5.0 mmol) was treated with MeLa(OSO$_2$CF$_3$)$_2$ (10.0 mmol) in THF to provide the crude diol.

The diol was dissolved in CH$_2$Cl$_2$ (20 mL) and the solution cannulated into a vigorously stirred mixture of pyridinium chlorochromate (3.25 g, 15.0 mmol), pyridine (2.37 g, 30.0 mmol), and Celite (5 g) in CH$_2$Cl$_2$ (200 mL) at room temperature. After 3 h, the dark mixture was diluted with 250 mL of dry ether and filtered through a small pad of Celite that was washed with ethyl acetate (5 × 20 mL). The pale orange filtrate was washed with 2.0 M aqueous acetic acid (20 mL), saturated NH$_4$Cl solution (3 × 20 mL), and brine (3 × 20 mL) and the organic phase then separated and dried over MgSO$_4$. Filtration and concentration of the filtrate in vacuo provided the crude dienone **15** (0.928 g, 85%) as a pale yellow solid, which could be purified by crystallization from ethyl acetate–hexane; mp 121–124 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ 5.92 (br s, 2 H), 2.78 (m, 2 H), 2.56 (dd, *J* = 17.5, 6.5 Hz, 2 H), 2.10 (br s, 6 H), 2.07 (dd, *J* = 17.5, 6.0 Hz, 2 H), 1.78 (m, 2 H), 1.26 (m, 2 H) ppm. ^{13}C NMR (50 MHz, CDCl$_3$): δ 208.0, 180.2, 131.3, 43.9, 41.6, 29.7, 17.4 and 208.0, 180.2, 131.3, 44.2, 41.7, 29.8, 17.4 ppm with separate signals in a ratio of 1:2.5 (mixture of diastereomers). IR (CHCl$_3$): 3066, 2927, 2858, 1683, 1618, 1435 cm^{-1}. Mass spectrum (EI): 218 (M$^+$). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.04; H, 8.31. Found: C, 76.93; H, 8.09.

Preparation of Racemic (and Meso) [1,2-Ethylene-1,1′-bis(2,4-dimethylcyclopentadienyl)]titanium Dichloride (3a). By the procedure outlined above for the preparation of bis(fulvene) 14, a solution of dienone **15** (2.183 g, 10.0 mmol) in THF (10 mL) was added to a solution of MeLa(OSO$_2$CF$_3$)$_2$, prepared from lanthanum triflate (11.75 g, 20.0 mmol) and a solution of methyllithium in ether (1.4 M, 14.3 mL, 20.0 mmol), in THF (100 mL) over a period of 15 min at −78 °C. After it was stirred at this temperature for 1.5 h, the solution was quenched by the addition of 1 M NaOH (20 mL). The mixture was diluted with ether and washed with brine (2 × 10 mL), the organic phase separated, dried over Na$_2$SO$_4$, and filtered, and the filtrate concentrated in vacuo to provide crude diol (2.48 g, 98%) that was directly employed in the next step.

The diol was dissolved in 300 mL of THF and *p*-toluenesulfonic acid hydrate (1.9 g, 10 mmol) added in one portion with stirring at room temperature. After 10 min at this temperature, 100 mL of saturated NaHCO$_3$ was added and the mixture diluted with 300 mL of hexane. The organic phase was washed with saturated NaHCO$_3$ (2 × 80 mL), separated, and then dried over K$_2$CO$_3$. Filtration and concentration of the filtrate in vacuo provided the crude bis(cyclopentadiene) **5a**, which was purified by passage through a short silica gel column, with hexane as eluent (0.858 g, 40% yield from **15**), and used without further purification for the preparation of the title compound.

Compound **5a** (0.858 g, 4.0 mmol) was dissolved in 20 mL of dry THF and cooled to −78 °C. A solution of *n*-butyllithium in hexane (2.45 M, 3.3 mL, 8.1 mmol) was added dropwise by syringe. The solution was warmed to room temperature and stirred at room temperature for 1.0 h. The mixture was then cooled to −40 °C and TiCl$_2$·3THF (1.48 g, 4.0 mmol) added in one portion via a side arm of a solid addition funnel. The dark green mixture was warmed to room temperature and then heated to reflux. After 4 h at reflux, the dark mixture was cooled to −40 °C and 6 M HCl (2.0 mL, 12.0 mmol) added by syringe. The mixture was then warmed to room temperature, while dry air was bubbled through the solution; a deep red solution was obtained. This solution was dried over MgSO$_4$ and then filtered through a short pad of silica gel that was washed with ether. The filtrate was concentrated in vacuo and the residue taken up in 1:1 toluene–CH$_2$Cl$_2$ (100 mL) and filtered through Celite that was washed with CH$_2$Cl$_2$. The filtrate was concentrated in vacuo to provide the crude metallocene, which was freed from polymeric contaminants by passing a toluene solution of this material through a short column of BioBeads SX-1, with toluene as eluent, and collecting the deep red fractions. The eluate was concentrated in vacuo to provide a mixture of the title compound and its meso stereoisomer (0.994 g, 75% yield from ligand **5a**; racemic:meso = 2:1). *rac*-**3a**: ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.33 (d, *J* = 2.3 Hz, 2 H), 5.31 (d, *J* = 2.3 Hz, 2 H), 3.26 (m, 2 H), 2.94 (m, 2 H), 2.28 (s, 6 H), 2.03 (s, 6 H) ppm; ^{13}C NMR (50 MHz, CDCl$_3$) δ 140.1, 135.5, 128.5, 128.3, 110.2, 27.6, 17.1, 15.0 ppm. *meso*-**3a**: ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.10 (d, *J* = 2.3 Hz, 2 H), 5.81 (d, *J* = 2.3 Hz, 2 H), 3.20–2.99 (m, 4 H), 2.22 (s, 6 H), 2.15 (s, 6 H) ppm; ^{13}C NMR (50 MHz, CDCl$_3$) δ 140.6, 134.7, 131.7, 125.8, 112.8, 28.8, 17.2, 15.1 ppm. IR (CHCl$_3$): 3092, 2996, 2959, 2918, 2867, 2810, 1522, 1442 cm^{-1}. Mass spectrum (EI): *m/e* 330 (M$^+$). Anal. Calcd for $C_{16}H_{20}TiCl_2$: C, 58.04; H, 6.09. Found: C, 58.15; H, 6.04. A pure sample of the racemic isomer could be obtained by crystallizing the mixture from 1:1 pentane–ether or by washing the mixture with a small volume of ether (yield of pure *rac*-**3a** (0.453 g). Aditional material could be obtained by photoisomerization.

Photoisomerization of Meso and Racemic Compound 3a. A mixture of the title compounds (0.54 g, racemic:meso = 1:1.6) was dissolved in 50 mL of dry THF in a Schlenk tube under nitrogen. The tube was placed next to a water-cooled glass immersion well, immersed in an aqueous solution of Na_2CrO_7, and fitted with a 450-W Hanovia medium-pressure Hg lamp. The tube was irradiated for 4 h at room temperature with stirring, the progress of the isomerization being monitored by the ^1H NMR spectra of 0.5-mL aliquots that were withdrawn by syringe. The solution and aliquots were then combined, and the solvent was removed in vacuo to provide a mixture of the title compounds (0.54 g, racemic:meso = 2.6:1).

Preparation of Racemic (and Meso) [1,2-Ethylene-1,1′-bis(2-methyl-4-isopropylcyclopentadienyl)]titanium Dichloride (3b). A solution of bis(fulvene) 14 (1.332 g, 5.0 mmol) in THF (10 mL) was added via cannula to a suspension of $LiAlH_4$ (380 mg, 10.0 mmol) in 100 mL of THF at room temperature. The mixture was stirred at room temperature for 20 h and then cooled to 0 °C. Water (0.4 mL), 15% aqueous NaOH (0.4 mL), and water (1.2 mL) were successively added dropwise by syringe with vigorous stirring. The mixture was filtered through Celite that was washed with ether. The filtrate was concentrated in vacuo to provide the crude bis(cyclopentadiene) **5b**, which was used directly in the next step.

A solution of compound **5b** in THF (10 mL) was cooled to −78 °C. A solution of *n*-butyllithium in hexane (2.45 M, 4.5 mL, 11.0 mmol) was added dropwise by syringe over 15 min. The solution was warmed to room temperature and stirred at this temperature for 1.0 h. The mixture was cooled to −40 °C, and $TiCl_3 \cdot 3THF$ (1.853 g, 5.0 mmol) was added in one portion. The mixture was warmed to room temperature and then heated at reflux for 4 h. The reaction mixture was worked up, and the title compounds were isolated and purified as described for the preparation of compound **3a**. Yield: 1.61 g of a mixture of *rac*-**3b** and *meso*-**3b** (racemic:meso = 2.5:1), 83% combined yield from compound 14. *rac*-**3b**: ^1H NMR (200 MHz, $CDCl_3$) δ 6.40 (d, J = 2.4 Hz, 2 H), 5.37 (d, J = 2.4 Hz, 2 H), 3.24 (septet, J = 6.9 Hz, 2 H) superimposed on 3.31–3.18 (m, 2 H), 3.04–2.90 (m, 2 H), 2.06 (s, 6 H), 1.23 (d, J = 6.9 Hz, 6 H), 1.07 (d, J = 6.9 Hz, 6 H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 150.5, 135.3, 128.2, 125.8, 107.9, 29.2, 27.5, 23.3, 21.5, 15.1 ppm. *meso*-**3b**: ^1H NMR (200 MHz, $CDCl_3$) δ 6.14 (d, J = 2.4 Hz, 2 H), 5.98 (d, J = 2.4 Hz, 2 H), 3.20 (septet, J = 6.9 Hz, 2 H) superimposed on 3.17 (m, 4 H), 2.15 (s, 6 H), 1.19 (d, J = 6.9 Hz, 6 H), 0.98 (d, J = 6.9 Hz, 6 H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.3, 134.3, 132.3, 122.6, 110.0, 28.8, 27.5, 23.2, 21.7, 15.4 ppm. IR ($CHCl_3$): 3091, 2997, 2962, 2928, 2868, 1514, 1461, 1450 cm^{-1}. Mass spectrum (EI): *m/e* 386 (M^+). Anal. Calcd for $C_{20}H_{28}TiCl_2$: C, 62.04; H, 7.29. Found: C, 61.95; H, 7.41. A pure sample of the racemic isomer was obtained by photoisomerization of the mixture as described above for compound **3a** (final ratio of *rac*-**3b**:*meso*-**3b** 3.8:1 after 3 h) and flash chromatography[19] of this mixture on 100 g of silica gel with 1:1 petroleum ether–toluene as eluent (yield of pure *rac*-**3b**, 1.25 g). The silica gel column was deactivated by previously flushing with about one column volume of THF (Caledon, H_2O content at least 0.05%) followed by removal of residual THF by elution with the above solvent mixture.

Preparation of Racemic (and Meso) [1,2-Ethylene-1,1′-bis(4-*tert*-butyl-2-methylcyclopentadienyl)]titanium Dichloride (3c). A solution of bis(fulvene) 14 (1.332 g, 5.0 mmol) in 10 mL of THF was cooled to −78 °C. A solution of methyllithium in ether (1.4 M, 7.9 mL, 11 mmol) was added dropwise by syringe. The solution was warmed to room temperature and stirred at this temperature for 16 h. The mixture was cooled to −40 °C, and $TiCl_3 \cdot 3THF$ (1.853 g, 5.0 mmol) was added in one portion. After the mixture was warmed to room temperature, heated to reflux for 4 h, worked up, and purified as described for compound **3a**, a mixture of *rac*- and *meso*-**3c** was obtained (racemic:meso = 1.6:1, 1.77 g, 85% combined yield). *rac*-**3c**: ^1H NMR (200 MHz, $CDCl_3$) δ 6.40 (d, J = 2.4 Hz, 2 H), 5.58 (d, J = 2.4 Hz, 2 H), 3.34–3.12 (m, 2 H), 3.07–2.93 (m, 2 H), 2.12 (s, 6 H), 1.30 (s, 18 H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.8, 135.6, 129.6, 126.7, 106.8, 34.8, 29.9, 27.8, 15.4 ppm. *meso*-**3c**: ^1H NMR (200 MHz, $CDCl_3$) δ 6.38 (d, J = 2.4 Hz, 2 H), 6.22 (d, J = 2.4 Hz, 2 H), 3.11 (m, 4 H), 2.11 (s, 6 H), 1.23 (s, 18 H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ 155.7, 134.7, 134.0, 119.7, 108.9, 30.3, 28.3, 15.8 ppm. IR ($CHCl_3$): 3091, 2994, 2956, 2869, 1510, 1480, 1459 cm^{-1}. Mass spectrum (EI): *m/e* 414 (M^+). Anal. Calcd for $C_{22}H_{32}TiCl_2$: C, 63.63; H, 7.76. Found: C, 63.88; H, 7.55. Photoisomerization of the mixture for 3 h, as described above, provided 1.70 g of almost pure racemic material (racemic:meso = 16:1) from which pure material could be obtained by crystal-

Table I. Crystal, Collection, and Refinement Data for Compound 3c

formula	$C_{22}H_{32}Cl_2Ti$
fw	415.3
color habit	red polyhedron
cryst size, mm	0.42 (100) × 0.52 (010) × 0.48 (011) × 0.40 (110) × 0.42 (012) × 0.30 (01$\bar{2}$)
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.910 (1)
b, Å	14.511 (1)
c, Å	15.141 (2)
α, deg	83.81 (1)
β, deg	88.62 (1)
γ, deg	81.27 (1)
V, Å^3	2139.5 (4)
Z	4
ρ_{calc}, g cm^{-3})	1.289
abs coeff, mm^{-1}	0.650
$F(000)$	880
T, K	200
μ(Mo Kα), cm^{-1}	8.90
scan method	ω
scan speed, deg min^{-1}	2.93–29.3
scan width, deg	1.2
2θ range, deg	4.0–50.0
std rflns	080; 700
std variation, %	2
transmissn factors	0.79–0.84
no. of unique data	7581
no. of obsd data ($I > 6\sigma(I)$)	5944
no. of variables	515
R ($=\sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$)	0.0361
R_w ($=[\sum(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert]^{1/2}$)	0.0573
R (all data)	0.0480
R_w (all data)	0.0642
GOF ($=[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$	1.11
weighting scheme, $w^{-1} = \sigma^2(F) + aF^2$ (a)	0.0020
max residual electron density, e Å^{-3}	0.40

Table II. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10³) for Compound 3c (Molecule 2)

	x	y	z	U(eq)[a]
Ti(2)	7481.4 (4)	2595.3 (3)	6387.6 (3)	28.4 (1)
Cl(1)	9239.9 (8)	3439.3 (6)	6642.9 (8)	72.7 (4)
Cl(2)	7381.4 (9)	1961.5 (6)	7875.5 (4)	63.7 (3)
C(1)	7279 (3)	1674 (2)	5202 (2)	36 (1)
C(2)	8559 (3)	2003 (2)	5111 (2)	31 (1)
C(3)	9422 (2)	1531 (2)	5808 (2)	30 (1)
C(4)	8624 (3)	991 (2)	6359 (2)	33 (1)
C(5)	7299 (3)	1974 (2)	5995 (2)	38 (1)
C(6)	6117 (3)	1973 (2)	4556 (2)	53 (1)
C(7)	10968 (3)	1455 (2)	5848 (2)	35 (1)
C(8)	11480 (3)	1414 (2)	6798 (2)	47 (1)
C(9)	11525 (3)	2229 (3)	5273 (2)	61 (1)
C(10)	11516 (3)	500 (3)	5492 (2)	80 (2)
C(11)	6202 (3)	521 (2)	6366 (2)	59 (1)
C(1′)	5810 (3)	3371 (2)	5356 (2)	42 (1)
C(2′)	5123 (3)	3004 (2)	6113 (2)	39 (1)
C(3′)	5286 (2)	3512 (2)	6839 (2)	33 (1)
C(4′)	6182 (3)	4149 (2)	6534 (2)	37 (1)
C(5′)	6489 (3)	4080 (2)	5620 (2)	41 (1)
C(6′)	5804 (3)	3033 (2)	4446 (2)	56 (1)
C(7′)	4436 (3)	3528 (2)	7687 (2)	39 (1)
C(8′)	3997 (3)	2587 (2)	8008 (2)	57 (1)
C(9′)	3139 (3)	4228 (3)	7458 (2)	66 (1)
C(10′)	5187 (3)	3880 (2)	8443 (2)	49 (1)
C(11′)	7312 (4)	4701 (2)	5043 (2)	59 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Table III. Selected Interatomic Distances and Angles for Compound 3c (Molecule 2)[a]

Bond Lengths (Å)[b]			
Ti(2)–Cl(1)	2.338 (1)	Ti(2)–Cl(2)	2.345 (1)
Ti(2)–C(1)	2.380 (3)	Ti(2)–C(2)	2.365 (2)
Ti(2)–C(3)	2.483 (2)	Ti(2)–C(4)	2.434 (2)
Ti(2)–C(5)	2.381 (3)	Ti(2)–C(1′)	2.373 (3)
Ti(2)–C(2′)	2.358 (3)	Ti(2)–C(3′)	2.493 (2)
Ti(2)–C(4′)	2.450 (2)	Ti(2)–C(5′)	2.415 (3)
Ti(2)–Cen(1)	2.088 (3)	Ti(2)–Cen(1′)	2.098 (3)
Bond Angles (deg)[b]			
Cl(1)–Ti(2)–Cl(2)	93.5 (1)	Cen(1)–Ti(2)–Cen(1′)	128.4 (1)
Cl(1)–Ti(2)–C(1)	128.2 (1)	Cl(1)–Ti(2)–C(2)	93.4 (1)
Cl(1)–Ti(2)–C(3)	81.4 (1)	Cl(1)–Ti(2)–C(4)	104.2 (1)
Cl(1)–Ti(2)–C(5)	136.9 (1)	Cl(1)–Ti(2)–C(1′)	115.2 (1)
Cl(1)–Ti(2)–C(2′)	134.4 (1)	Cl(1)–Ti(2)–C(3′)	108.0 (1)
Cl(1)–Ti(2)–C(4′)	79.1 (1)	Cl(1)–Ti(2)–C(5′)	82.5 (1)
Cl(2)–Ti(2)–C(1)	121.3 (1)	Cl(2)–Ti(2)–C(2)	132.7 (1)
Cl(2)–Ti(2)–C(3)	101.6 (1)	Cl(2)–Ti(2)–C(4)	76.7 (1)
Cl(2)–Ti(2)–C(5)	87.1 (1)	Cl(2)–Ti(2)–C(1′)	133.6 (1)
Cl(2)–Ti(2)–C(2′)	99.1 (1)	Cl(2)–Ti(2)–C(3′)	80.6 (1)
Cl(2)–Ti(2)–C(4′)	98.4 (1)	Cl(2)–Ti(2)–C(5′)	132.3 (1)

[a] A complete list of bond distances and angles for both molecule 1 and molecule 2 is contained in the supplementary material. See Figure 1 for the numbering scheme used. [b] Cen(1) and Cen(1′) are the two centroids of the cyclopentadienyl rings corresponding to the unprimed and primed carbon atoms, respectively.

lization from hexane–toluene solution or flash chromatography on silica gel as described for compound **3b** (yield of *rac*-**3c** 1.55 g). Single crystal of racemic **3c**, suitable for X-ray diffraction studies, were grown by slow evaporation of an isooctane–toluene solution of this compound over several days at room temperature.

X-ray Structure Determination of Compound 3c.[20] Relevant crystal, collection, and refinement data are summarized in Table I.

A crystal of dimensions 0.42 (100) × 0.52 (010) × 0.48 (011) × 0.40 (110) × 0.42 (012) × 0.30 (01$\bar{2}$) mm was mounted on a Nicolet-Siemens R3m/V diffractomer. Intensity data were obtained with use of graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 200) K. Accurate unit cell dimensions were determined with use of 25 general reflections ($21 < 2\theta < 29°$) well distributed in reciprocal space. Background measurements were made at the beginning and end of each scan for a total time equal to half the scan time. Crystal stability was monitored by measuring two standard reflections every 100 measurements. Absorption corrections to the data were made by using a face-indexed numerical method (transmission factors 0.7902–0.8436).

The structure was solved by standard Patterson and Fourier methods with use of Siemens SHELXTL-PLUS software and a DEC Microvax II computer. Anisotropic refinement of all non-hydrogen atoms allowed location of all the hydrogen atoms from a difference map, which were put in at calculated positions (based on the hydrogen most clearly defined on a given carbon atom) and refined with isotropic thermal parameters. The final refinement converged with $R = 0.0361$ and $R_w = 0.0573$.

Selected bond lengths and angles for molecule 2 appear in Table III, and atomic coordinates and isotropic thermal parameters of molecule 2 appear in Table II, while complete lists of atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, H atom coordinates and isotropic thermal parameters, nonbonded intramolecular contacts for both molecules 1 and 2, plots of the structure of molecule 1, and a packing diagram have been deposited as supplementary material along with tables of structure factors.

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Supplementary Material Available: Room-temperature and low-temperature 125-MHz ^{13}C NMR spectra of compounds **3c** (R′ = Me) and **3c** (R′ = H) and tables of crystal and refinement data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, H atom coordinates and isotropic thermal parameters, and nonbonded intramolecular contacts, plots of the structure of compound **3c** (molecule 1), and a packing diagram for compound **3c** (R′ = Me) (22 pages); a table of structure factors for compound **3c** (R′ = Me) (27 pages). Ordering information is given on any current masthead page.

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(20) Compound **3c** also crystallizes from isooctane–benzene solution in a separate form containing benzene in the lattice: monoclinic, space group $C2/c$, $a = 15.484$ (2) Å, $b = 21.667$ (2) Å, $c = 14.832$ (1) Å, $\beta = 102.09$ (1)°, $V = 4865.6$ (8) Å^3, $Z = 8$. Although a satisfactory solution and refinement proved possible ($R = 0.0290$, $R_w = 0.0226$ based on 1472 reflections with $F > 4.0\sigma(F)$), the structure is not included here because of the low data to parameter ratio of 5.1:1. The conformation of the ansa ligand in this structure is very similar to that of molecule 2 presented here: Collins, S.; Ramachandran, R.; Taylor, N. J., unpublished results.

(21) Wild, F. W. R. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* 1982, *232*, 233.