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Isodicyclopentadienes and related molecules

LII *. Comparative analysis of the solid state structural features of bis(η^5-(1*R*,8*R*)- and (η^5-(1*R*,8*R*),η^5-(1*S*,8*S*)-7,7,9,9-tetramethyltricyclo[6.1.1.$0^{2,6}$]deca-3,5-dien-2-yl)-dichlorotitanium

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Abstract

While the major product stemming from the condensation of ((1*R*,8*R*)-7,7,9,9-tetramethyl[6.1.1.$0^{2,6}$]deca-2,5-dienyl)lithium with $TiCl_3 \cdot 3THF$ is the chiral bis(η^5-(1*R*,8*R*)) titanocene dichloride, the optically impure nature of the lithium reagent allows for the isolation of a small amount of the *meso* complex. The latter has been examined by X-ray crystallography and its structural features are compared to those of its chiral counterpart. Although the mutual orientation of the ligands is now synclinal rather than eclipsed, the metal environments in both compounds are closely comparable. The distinctive bond lengths and angles suggest that steric factors having their origin in the CMe_2 fragment play the key role in dictating the molecular dimensions observed.

Introduction

Ligands possessing substantial potential for asymmetric synthesis are produced when a cyclopentadiene ring is laterally fused to an optically active bicyclic ring system. The resultant molecules may, of course, be either C_1- [3–7] or C_2-symmetric [6–10]. The first subset lends itself to face-selective coordination to give diastereomeric transition metal complexes, an area of study that has commanded a

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* For parts LI and L see refs. 1 and 2.
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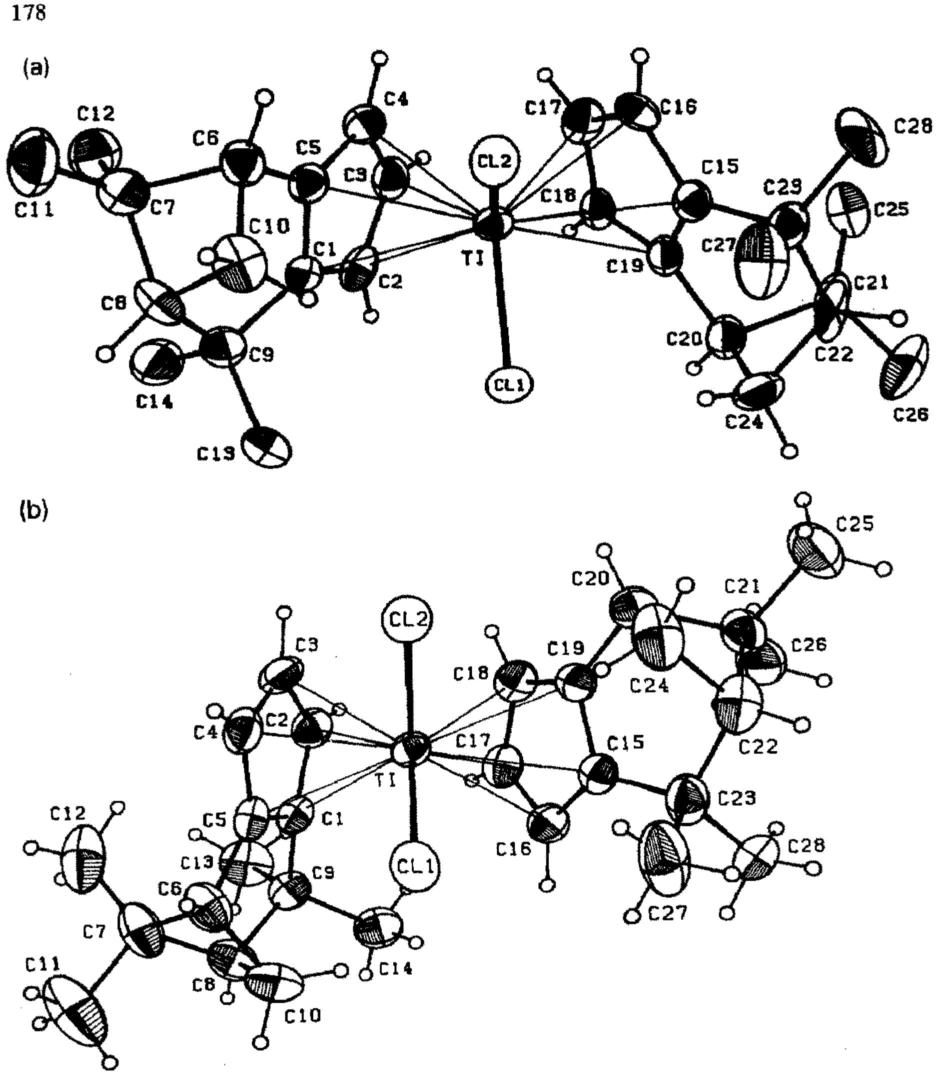

Fig. 1. Edge views of the crystallographically determined molecular structures of 3 (a) and 4 (b) as drawn with 50% probability ellipsoids.

considerable amount of our attention recently [1,5,11–16]. In the course of one of these investigations [14], we had occasion to prepare (1*R*,8*R*)-7,7,9,9-tetramethyltricyclo[6.1.1.0^{2,6}]deca-2,5-diene (**2**) from commercially available * (1*S*,5*S*)-(−)-verbenone (**1**), $[\alpha]_D$ − 140° (*c* 10, C_2H_5OH). Following conversion of **2** to its powdery, white lithium salt, heating with $TiCl_3 \cdot 3THF$ was carried out in dry 1,2-dimethoxyethane for 3 days. An extractive workup gave in 45% yield the titanocene dichloride **3**, the structural assignment to which rests firmly on an X-ray crystallographic analysis (Figs. 1a–3a).

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* Purchased from the Aldrich Chemical Company.

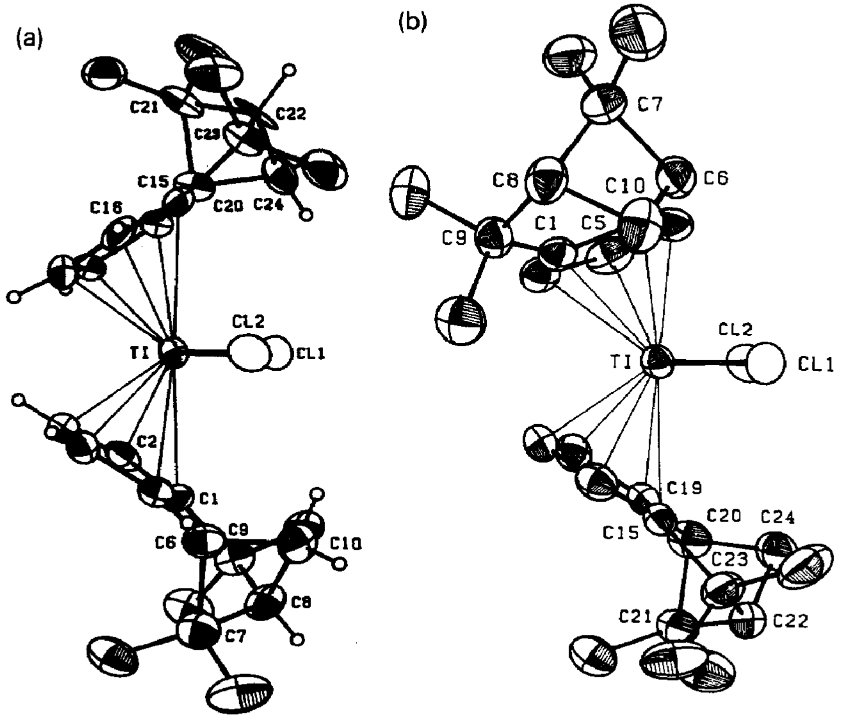
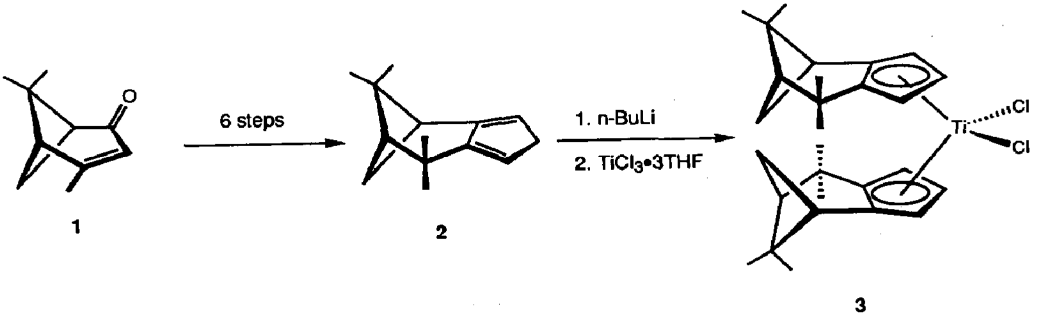
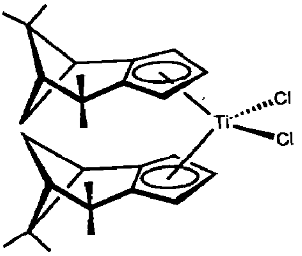


Fig. 2. Side views of the crystallographically determined molecular structures of **3** (a) and **4** (b) as drawn with 50% probability ellipsoids.



Prior to the several recrystallizations needed to obtain **3**, a purple-brown solid exhibiting $[\alpha]_D^{21}$ +491° (*c* 2, toluene), in pure condition, ^{1}H NMR analysis indicated that a minor isomeric complex had been formed concurrently. This substance has now been purified and identified as racemic **4** by X-ray methods. The notably different solid state structural features that distinguish chiral-**3** from *meso*-**4** form the subject matter of this paper.



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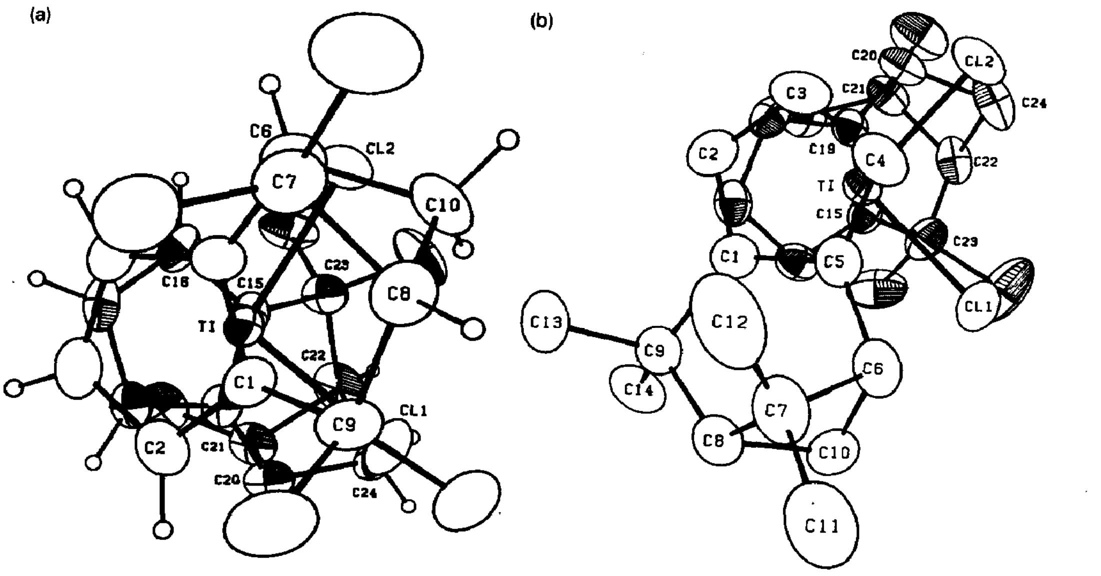

Fig. 3. Projections of **3** (a) and **4** (b) showing the mutual orientation of the tricyclic ligands.

Results and discussion

The isolation of **4** was made possible by the fact that the purchased **1** was not optically pure. The $[\alpha]_D$ of the ketone sample used, when compared to that reported by Blumann and Zeitschel for high quality enantiomer, $[\alpha]_D^{18}$ +229.6° (*c* 9, C_2H_5OH) [17], suggests our material to be only 57% ee *. An independent measure of the optical rotation of **1** by us, $[\alpha]_D^{19}$ −146.5° (*c* 0.97, $CHCl_3$) [19] led to the identical conclusion.

Despite the presence of 21–22% of the (1*R*,5*R*) enantiomer in the sample, the relative quantity of **4** formed during the complexation to titanium was never high. However, insufficient data are presently available to permit the conclusion that a kinetic preference exists for the formation of **3** (and its antipode) via enantiomer recognition. As a consequence of the limited amounts of **4**, suitable crystals of this shiny red-black solid were obtained only after allowing residues from mother liquors to stand in cold (−20 °C) toluene for 2 months.

A crystal structure study of this *meso* complex (Figs. 1b–3b) revealed immediately that the mutual orientation adopted by its tricyclic ligands is significantly different from that seen in **3**. In the chiral complex, the nearly eclipsed arrangement was considered to be perhaps the only one readily attainable by the system on steric grounds. The approximately synclinal geometry of **4** dispels this earlier notion and suggests that other factors may play a more controlling role in deciding the particular solid state conformation.

The 300 MHz ^1H NMR spectrum of **4** (in $CDCl_3$) differs only to a small degree from that of **3** except for the central cyclopentadienide proton in each ligand which finds itself shifted 0.19 ppm to higher field in the *meso* isomer (Table 1). Although

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* Evidently, material of 90% ee was once available from the same vendor [18].

Table 1

Comparative 300 MHz ^{1}H NMR spectral data (δ values, $CDCl_3$ solution) [a]

Protons	3	4
central VCp	6.50 (t, $J = 2.5$ Hz)	6.31 (t, $J = 3.0$ Hz)
peripheral VCp	6.21 (t, $J = 2.5$ hz)	6.22 (t, $J = 2.8$ Hz)
	6.01 (d, $J = 3$ Hz)	5.97 (t, $J = 2.5$ Hz)
bridgehead	2.87 (t, $J = 5.0$ Hz)	2.79 (t, $J = 5.3$ Hz)
	1.66 (m)	1.63 (t, $J = 5.3$ Hz)
anti methano	2.52 (m)	2.54 (m)
syn methano	1.97 (d, $J = 11$ Hz)	2.02 (d, $J = 10.5$ Hz)
apical *syn* methyl	0.44 (s)	0.43 (s)
other methyls	1.40 (s)	1.42 (s)
	1.39 (s)	1.38 (s)
	1.33 (s)	1.32 (s)

[a] VCp = verbenone-derived cyclopentadienyl-fused ligand.

the actual source of this deshielding is unknown, the observed change in local anisotropy is not inconsistent with adoption of different preferred ground state spatial arrangements by **3** and **4** in solution, while making the usual allowance for fluxional behavior.

Despite adoption by **4** of a conformational bias dramatically altered from that present in **3**, the metal environments in these compounds remain entirely comparable, though quite exceptional. Thus, the Ti–C(η^5) separations continue to be subject to rather severe effects as reflected in the sizable variations in the bond lengths from titanium to the individual Cp carbon atoms (Table 2). These actually define a range of 0.31 Å!

The pattern of Ti–C(η^5) distances represents a tilting of the Cp ring with the unsubstituted carbons making the closest approach. Shorter distances are noted for two adjacent unsubstituted carbons on each ring: 2.324(4) and 2.351(4) Å for C(3)–C(4) and 2.313(3) and 2.311(4) Å for C(17)–C(18). Intermediate distances are found for the third unsubstituted carbon in each ring, 2.436(4) Å for C(2) and 2.451(3) Å for C(16). The substituted carbon atoms are farthest from Ti at 2.530(4),

Table 2

Selected bond lengths (in ppm) for **3** and **4**

bond	3	4
Ti–Cl(1)	2.286(3)	2.318(1)
Ti–Cl(2)	2.341(3)	2.380(1)
Ti–C(1)	2.63(1)	2.530(4)
Ti–C(2)	2.48(1)	2.436(4)
Ti–C(3)	2.33(1)	2.324(4)
Ti–C(4)	2.319(9)	2.351(4)
Ti–C(5)	2.502(9)	2.485(4)
Ti–C(15)	2.626(9)	2.624(3)
Ti–C(16)	2.447(8)	2.451(3)
Ti–C(17)	2.31(1)	2.313(3)
Ti–C(18)	2.36(1)	2.311(4)
Ti–C(19)	2.58(1)	2.520(3)

2.485(4), 2.624(3) and 2.520(3) Å for C(1), C(5), C(15), and C(19), respectively. This tilt is greater for the C(15)–C(19) ring which exhibits the longest (C(5)) and shortest (C(18)) Ti–C(η^5) approaches.

Although **3** and **4** are very similar, an interesting structural feature is noted. The range of Ti–C(η^5) separations in **3** (2.63(1)–2.31(1) Å) and the pattern of the distances is nearly identical to those found in **4**. However, both rings in **3** have an almost identical tilt, while this is not the case for **4** as discussed above. The substituted carbon positions making the longest approaches to Ti are 2.63(1) Å (C(1)) and 2.626(9) Å (C(15)) in **3**, while values of 2.530(4) Å (C(1)) and 2.624(3) Å (C(15)) are observed in **4**. Similarly the closest approach of each ring by an unsubstituted carbon are the same in **3** (2.319(9) Å, C(4); 2.31(1) Å, C(17)) while these are different at the 3σ level in **4** (2.324(4) Å, C(3); 2.311(4) Å, C(18)).

The Ti–Cl bonds show an almost identical difference of 0.06 Å in **3** and **4**. An analysis of nonbonded contacts in **4** reveals three Cl(2) · · · C contacts under 3.06 Å and three under 3.40 Å, while Cl(1) has only one contact under 3.06 Å and six under 3.40 Å.

For comparison the ranges of Ti–C(η^5) distances found in CpCp*TiCl$_2$ [20] are 2.344(4)–2.428(3) Å (Cp) and 2.398(3) to 2.440(3) Å (Cp*). Average Ti–Cp distances of 2.366 and 2.44 Å were observed for Cp$_2$TiCl$_2$ [21] and Cp$_2^\star$TiCl$_2$ [22], respectively. The range of Ti–Cl distances in these compounds was observed to be 2.349(4)–2.364(3) Å.

To our knowledge, the availability of **3** and **4** represents the first time that a matching chiral/*meso* pair of titanocene complexes has become available for detailed crystallographic scrutiny (or otherwise). While it is interesting and informative that different conformations are adopted by the ligand pairs in **3** and **4**, the significant conclusion is that their detailed structures are not meaningfully linked to these obvious geometric changes. Rather, the close similarities in bond lengths (Table 2) and bond angles (Table 3) suggest that the severe steric repulsions stemming from the CMe$_2$ fragments C(9) and C(23) likely play the prominent role in dictating molecular dimension. Crystal packing forces probably contribute in a major way to the mutual ligand orientation that is adopted.

Should our conclusions regarding the dominant control elements on structure be accurate, the prediction of trends in structural distortion as the "inner" methyl groups are replaced by substituents having progressively larger steric demands would appear feasible. This we hope to ascertain in the near future. A long-range goal of this effort is to gain insight into the manner in which substantive structural

Table 3

Selected bond angles (°) for **3** and **4**

Angle [a]	**3**	**4**
Cl(1)–Ti–Cl(2)	99.6(1)	95.08(4)
Cent(1)–Ti–Cent(2)	131.0	131.7
Cent(1)–Ti–Cl(1)	105.1	107.0
Cent(2)–Ti–Cl(1)	105.7	106.6
Cent(1)–Ti–Cl(2)	106.6	105.4
Cent(2)–Ti–Cl(2)	104.2	105.1

[a] Cent(1) is the centroid of the C(1)–C(5) ring. Cent(2), C(15)–C(19).

deformation within group 4 metallocenes correlates with chemical reactivity (particularly as reflected in asymmetric synthesis) at the metal center.

Additional structural data for **4** are available on request from the authors.

Experimental

All manipulations were performed under argon, nitrogen, or vacuum by using standard inert-atmosphere techniques. All solvents were predried over molecular sieves and distilled from sodium/benzophenone ketyl.

(η^5-(1R,8R),η^5-(1S,8S)-7,7,9,9-Tetramethyltricyclo[6.1.1.$0^{2,6}$]deca-3,5-dien-2-yl)dichlorotitanium. The mother liquors from three experiments involving the condensation of **2**-Li (1.81 g, 9.30 mmol) with $TiCl_3 \cdot 3THF$ (1.64 g, 4.43 mmol) in the predescribed manner [14], Soxhlet extraction, and crystallization of **3** from toluene and hexane were evaporated to dryness. The resulting residue was redissolved in

Table 4

Experimental crystallographic data for **4**

Formula	$C_{28}H_{38}Cl_2Ti$
Formula wt.	493.40
Space group	$P2_1/c$
Temperature, °C	23
Cell constants [a]	
a, Å	14.236(7)
b, Å	12.610(2)
c, Å	15.431(2)
β, deg	110.57(2)
Cell vol, Å^3	2593.5
Formula units/unit cell	4
D_{calc}, g cm^{-3}	1.26
μ_{calc}, cm^{-1}	5.60
Diffractometer/scan	Enraf-Nonius CAD4/ω–2θ
Radiation, graphite monochromator	Mo-K_α ($\lambda = 0.71073$)
Max crystal dimensions, mm	0.13 × 0.13 × 0.33
Scan width	$0.80 + 0.35 \tan\theta$
Standard reflections	300; 020; 002
Decay of standards	±3%
Reflections measured	4987
2θ range, deg	$2 \leq 2\theta \leq 50$
Range of h, k, l	+16, +15, ±18
Reflections observed [$F_o \geq 5\sigma(F_o)$] [b]	2330
Computer programs [c]	SHELX [23]
Structure solution	SHELXS [25]
No. of parameters varied	304
Weights	$[\sigma(F_o)^2 + 0.00068 F_o^2]^{-1}$
GOF	0.96
$R = \Sigma \| \|F_o\| - \|F_c\| \| / \Sigma \|F_o\|$	0.34
R_w	0.039
Largest feature final diff. map	0.3 e$^-$ Å^{-3}

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 16°$. [b] Corrections: Lorentz-polarization. [c] Neutral scattering factors and anomalous dispersion corrections from ref. 24.

warm toluene and placed in a freezer at −20 °C for 60 d. After this time, filtration gave 6 mg of **4** as a shiny red-black microcrystalline precipitate; ^{1}H NMR (see Table 1).

*X-ray crystallographic analysis of **4**.* A red-black single crystal of **4** was mounted on a pin and transferred to the goniometer. The space group was determined to be the centric $P2_1/c$ from the systematic absences. A summary of data collection parameters is given in Table 4.

Least-squares refinement with isotropic thermal parameters led to $R = 0.092$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, $B = 5.5$ Å^2). Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.034$ and $R_w = 0.039$. The final values of the positional parameters are given in the Supplementary Material (see Results and discussion).

Acknowledgments

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