example, the O(1)—Ni—O(2) angle is greater than 90°, while O(3)—Ni—O(4) is less than 90°. This appears to affect the angles about C(1), C(2) and C(3) in one ring and C(16), C(17) and C(18) in the other. However, the dihedral angles that the phenyl rings make with the corresponding chelate ring are close, with 31·1 and 41·5° observed in the β-ketoenolate containing O(1) and O(2), and 36·6 and 42·2° for the other. Rotations reported for other complexes [32·9 and 44·8° (Hotz *et al.*, 1987); 6·5 and 11° (Shugam, Shkol'nikova & Zelentsov, 1966); 5·5 and 8·5° (Knyazeva, Shugam & Shkol'nikova, (1969) and 25·6 and 15·9° (Cornwell & Harrison, 1979)] are not directly comparable because, in these compounds, the two β-diketones are coordinated in a square-planar configuration about the metal ion. In the present compound, the chelates are forced to be closer by the *cis* coordinated 1,2-ethanediamine, making them sterically more crowded. The relatively large rotations observed by Hotz *et al.* (1987) were attributed to steric interactions with the bulky amines in the axial position. However, the fact that the rotations within a chelate ring are different would indicate that crystal packing is also an important contributor. In the free ligand, twists of 3·8 and 16·9° (Williams, 1966) are observed. This structure has been redetermined by X-rays (Hollander, Templeton & Zalkin, 1973) and by neutrons (Jones, 1976). Repulsion between the enolate ring hydrogens and the phenyl groups, and crystal packing were determined to be the major factors which determine the dihedral angle in this compound.

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The *syn* Tetramethylethano-Bridged 3,3'-Di-*tert*-butyltitanocene Dichloride

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Abstract. [1,1'-(2,3-Dimethyl-2,3-butylidene)-3,3'-di-*tert*-butyl-bis-η^5-cyclopenta-1,3-dienyl]titanium dichloride, [Ti(C$_{24}$H$_{36}$)]Cl$_2$, M_r = 443·4, triclinic, $P\bar{1}$, a = 9·8756 (13), b = 10·2758 (11), c = 13·075 (4) Å, α = 75·60 (2), β = 89·87 (2), γ = 66·10 (1)°, V = 1167·7 (5) Å^3, Z = 2, D_x = 1·261 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 5·99 cm^{-1}, $F(000)$ = 472, T = 296 K, R = 0·040 for 3617 data with $I > 3\sigma(I)$. The two Ti—Cl distances are 2·3276 (6) and 2·3597 (6) Å.

The Cl—Ti—Cl angle is 96·35 (3)°. The *tert*-butyl groups splay out from the Cp planes by 11·0°. The Cp centroid–Ti distances are 2·092 and 2·014 Å. The Cp1 centroid–Ti–Cp2 centroid angle is 128·8°. The cyclopentadienyl-ring carbon atoms attached to the (ansa) tetramethylethano bridge exhibit a torsion angle of 36·0 (3)°.

Introduction. Chiral titanocene dichloride derivatives with twofold molecular symmetry can control the stereochemistry of catalytic reactions at the

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titanium center such as asymmetric hydrogenation (Halterman, Vollhardt, Welker, Bläser & Boese, 1987) and isotactic Ziegler–Natta catalysis (Kaminsky, Kulper, Brintzinger & Wild, 1985). However a 4:1 selectivity for the *syn* tetramethylethano-bridged 3,3'-di-*tert*-butyltitanocene dichloride shown in Fig. 1 was confirmed by the X-ray analysis described below.

Experimental. Treatment of the proton shift isomers of 2,3-bis(cyclopenta-2,4-dienyl)-2,3-dimethylbutane (Schwemlein & Brintzinger, 1983) with excess acetone in methanol and pyrrolidine gave an 82% yield of 2,3-bis[3-(1-methylethylidene)cyclopenta-1,4-dienyl]-2,3-dimethylbutane (Erickson, McLaughlin & Fronczek, 1989). The difulvene reacted with excess methyllithium in ether to give an insoluble gel that was washed three times with ether, dissolved in THF and treated with $TiCl_3.3THF$ at 195 K and refluxed for 18 h. After workup, NMR analysis showed two titanocene isomers in a ratio of 4:1 in a combined 44% yield (Erickson, Fronczek & McLaughlin, 1990; Guttmann, Burger, Hund, Hofmann & Brintzinger, 1989). A similar isomer ratio was found when $TiCl_4$ was used. Crystallization of the isomer mixture from toluene at room temperature gave orange rectangular plates suitable for X-ray structure determination.

Intensity data were obtained from an irregular fragment of dimensions $0.10 \times 0.23 \times 0.45$ mm mounted in a random orientation on an Enraf–Nonius CAD-4 diffractometer. Cell dimensions were determined at 296 K by a least-squares fit to setting angles of 25 reflections having $24 > 2\theta > 20°$. The theta values were derived from measurements at $\pm 2\theta$. One hemisphere of data having $2 < 2\theta < 55°$, $0 \le h \le 12$, $-13 \le k \le 13$, $-17 \le l \le 17$ was measured using graphite-monochromated Mo $K\alpha$ radiation. The ω–2θ scans were made at speeds ranging from 1.0 to $4.0°$ min^{-1}. Three standard reflections (100, 020, 002) measured every 10000 s of exposure time, decreased in intensity by 9.1% during data collection, and a linear correction was applied. Data reduction also included corrections for background, Lorentz, polarization and absorption. Absorption corrections were based on ψ scans, with minimum relative transmission 0.945, maximum 0.998. Of 5352
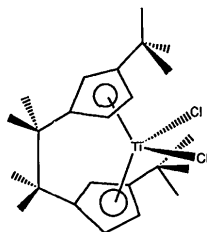
Fig. 1. [1,1'-(2,3-Dimethyl-2,3-butylidene)-3,3'-di-*tert*-butyl-bis-η^5-cyclopenta-1,3-dienyl]titanium dichloride.

Table 1. *Coordinates and equivalent isotropic thermal parameters*

	x	y	z	$B_{eq}(Å^2)$*
Ti	0.04562 (4)	0.94370 (4)	0.78451 (3)	2.238 (8)
Cl1	−0.05387 (8)	0.91136 (7)	0.63643 (5)	3.93 (2)
Cl2	−0.15571 (7)	0.95740 (7)	0.88544 (6)	3.97 (2)
C1	0.3072 (3)	0.8049 (2)	0.8259 (2)	2.84 (6)
C2	0.2601 (3)	0.7271 (2)	0.7695 (2)	2.76 (5)
C3	0.1700 (2)	0.6669 (2)	0.8297 (2)	2.59 (5)
C4	0.1558 (3)	0.7133 (3)	0.9224 (2)	3.12 (6)
C5	0.2382 (3)	0.7975 (3)	0.9210 (2)	3.25 (6)
C6	0.4152 (3)	0.8752 (3)	0.7928 (2)	3.51 (6)
C7	0.3320 (3)	1.0214 (3)	0.7008 (2)	3.12 (6)
C8	0.1703 (2)	1.0941 (2)	0.7227 (2)	2.64 (5)
C9	0.0415 (3)	1.1556 (2)	0.6490 (2)	2.69 (5)
C10	−0.0873 (2)	1.2184 (2)	0.6985 (2)	2.72 (5)
C11	−0.0372 (3)	1.1928 (2)	0.8052 (2)	2.85 (5)
C12	0.1170 (3)	1.1183 (3)	0.8208 (2)	2.73 (5)
C13	0.5515 (3)	0.7628 (3)	0.7575 (3)	5.29 (9)
C14	0.4750 (3)	0.9029 (3)	0.8904 (3)	5.05 (8)
C15	0.3334 (3)	0.9922 (3)	0.5913 (2)	4.13 (7)
C16	0.4022 (3)	1.1327 (3)	0.6940 (3)	4.50 (7)
C17	0.1230 (3)	0.5499 (2)	0.8107 (2)	3.16 (6)
C18	−0.0375 (3)	0.5832 (3)	0.8326 (3)	4.24 (7)
C19	0.1444 (3)	0.5304 (3)	0.6988 (2)	4.00 (7)
C20	0.2285 (3)	0.4048 (3)	0.8904 (3)	4.52 (8)
C21	−0.2432 (3)	1.3227 (3)	0.6433 (2)	3.62 (7)
C22	−0.2368 (3)	1.4722 (3)	0.5918 (3)	4.92 (9)
C23	−0.3594 (3)	1.3458 (4)	0.7215 (3)	5.6 (1)
C24	−0.2902 (3)	1.2719 (3)	0.5556 (3)	5.18 (9)

* The equivalent isotropic thermal parameter, for atoms refined anisotropically, is defined by the equation: $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_i.a_j$.
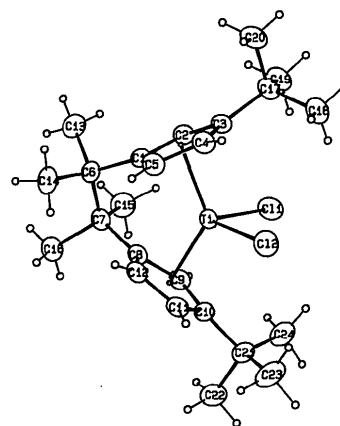
Fig. 2. *ORTEP* drawing (Johnson, 1965) of the molecule. Heavy atoms are represented by 40% probability ellipsoids and hydrogen atoms by circles of arbitrary radius.

independent data, 3617 had $I > 3\sigma(I)$, and were used in the refinement.

The space group was determined by successful refinement of a centrosymmetric model. The structure was solved by heavy-atom methods and refined by full-matrix least squares based upon F, with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ using the *Enraf–Nonius Structure Determination Package* (Frenz, 1985), scattering factors of Cromer & Waber (1974), and anomalous coefficients of Cromer (1974). Non-hydrogen atomic coordinates were refined with

$[Ti(C_{24}H_{36})]Cl_2$

Table 2. *Bond distances (Å) and selected angles (°)*

Ti—Cl1	2·3276 (6)	Ti—Cl2	2·322 (2)
C2—C3	1·413 (3)	C8—C12	1·426 (3)
Ti—C2	2·424 (2)	C10—C11	1·406 (3)
C4—C5	1·405 (3)	C21—C22	1·543 (4)
Ti—C5	2·329 (2)	C17—C18	1·522 (3)
C6—C14	1·543 (4)	C17—C19	1·528 (3)
Ti—C10	2·526 (2)	Ti—Cl2	2·3597 (6)
C7—C16	1·544 (3)	C3—C4	1·396 (3)
C1—C2	1·412 (3)	Ti—C3	2·507 (2)
C9—C10	1·411 (3)	C6—C7	1·576 (3)
C10—C21	1·524 (3)	Ti—C8	2·339 (2)
C21—C23	1·521 (4)	C7—C8	1·526 (3)
C1—C6	1·521 (3)	Ti—C11	2·437 (2)
Ti—C1	2·374 (2)	C8—C9	1·413 (3)
C3—C17	1·525 (3)	C1—C5	1·417 (3)
Ti—C4	2·416 (2)	C17—C20	1·539 (3)
C6—C13	1·536 (3)	C11—C12	1·388 (3)
Ti—C9	2·427 (2)	C21—C24	1·517 (4)
C7—C15	1·533 (3)		

Cl1—Ti—Cl2	96·35 (3)	C2—C1—C6	126·6 (2)
C5—C1—C6	127·7 (2)	C1—C2—C3	110·2 (2)
C2—C3—C4	106·3 (2)	C2—C3—C17	127·6 (2)
C4—C3—C17	125·1 (2)	C2—C1—C5	105·6 (2)
C3—C4—C5	109·2 (2)	C15—C7—C16	106·9 (2)
C1—C5—C4	108·6 (2)	C1—C6—C7	108·5 (2)
C1—C6—C13	108·4 (2)	C7—C8—C9	127·2 (2)
C1—C6—C14	109·4 (2)	C7—C8—C12	127·5 (2)
C7—C6—C13	112·1 (2)	C9—C8—C12	105·3 (2)
C7—C6—C14	112·7 (2)	C13—C6—C14	105·7 (2)
C6—C7—C8	108·3 (2)	C8—C9—C10	110·3 (2)
C6—C7—C15	112·5 (2)	C6—C7—C16	112·2 (2)
C8—C7—C15	108·4 (2)	C8—C7—C16	108·4 (2)
C9—C10—C11	105·9 (2)	C9—C10—C21	126·7 (2)
C3—C17—C20	104·9 (2)	C11—C10—C21	126·0 (2)
C18—C17—C19	110·1 (2)	C18—C17—C20	109·5 (2)
C19—C17—C20	108·1 (2)	C10—C11—C12	109·5 (2)
C10—C21—C22	106·1 (2)	C10—C21—C23	111·9 (2)
C10—C21—C24	112·9 (2)	C8—C12—C11	108·9 (2)
C22—C21—C23	108·7 (2)	C3—C17—C18	111·6 (2)
C22—C21—C24	107·7 (2)	C3—C17—C19	112·5 (2)
C23—C21—C24	109·4 (2)		

anisotropic thermal parameters; the hydrogen atomic coordinates were located in a ΔF map and were refined with isotropic thermal parameters. Final $R = 0·040$ ($R = 0·075$ for all 5352 data), $wR = 0·045$, $S = 1·727$ for 389 variables. The largest shift was $0·02\sigma$ in the final cycle, maximum residual density 0·34, minimum $-0·30$ e $Å^{-3}$.

Discussion. The fractional coordinates of the title compound are given in Table 1. Fig. 2 is a perspective drawing showing the atom numbering. Distances, angles that do not invole Ti—C bonding and selected torsion angles are presented in Table 2.*

The X-ray structure verified the *syn* stereochemistry of the *tert*-butyl groups and revealed how effectively the bulky 3,3' substituents shield the titanium from approach by external nucleophiles.

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* Lists of H-atom parameters, structure factors, torsion angles, least-squares-planes data and cyclopentadienyl-centroid calculations, and fuller lists of distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52979 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The title molecule is unusually stable in that it can be purified by silica-gel column chromatography without losses from hydrolysis or irreversible binding. The chlorines are in different environments; Ti—Cl1 and Ti—Cl2 distances are 2·3276 (6) and 2·3597 (6) Å, respectively. The Cl1—Ti—Cl2 angle, 96·35 (3)°, is 1–2° wider than the analogous angles in titanocene dichloride (Clearfield, Warner, Saldarriaga-Molina, Ropal & Bernal, 1975) and the ethano-bridged titanocene dichloride derivative (Smith, Seyerl, Huttner & Brintzinger, 1979). This appears to accommodate better the crowded Cl1 in the groove of the *tert*-butyl groups. The *tert*-butyl groups splay out from the Cp1 and Cp2 plane by 11·0° and the cyclopentadienyl-ring carbons attached to the tetramethylethano bridge exhibit a torsion angle, C1—C6—C7—C8, of 36·0 (3)°. Similar structures have been reported for closely related metal-locenes (Erickson, Fronczek & McLaughlin, 1990; Guttmann *et al.*, 1989). The Cp1 centroid–Ti and Cp2 centroid–Ti distances are 2·092 and 2·014 Å, respectively, and the Cp1 centroid–Ti–Cp2 centroid angle is 128·8°; these are normal values.

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