

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: JZ1000). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 1063–1064

syn-[2,2-Bis(3-isopropyl- η^5 -cyclopentadienyl)propane]dichlorotitanium

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(Received 11 July 1994; accepted 2 December 1994)

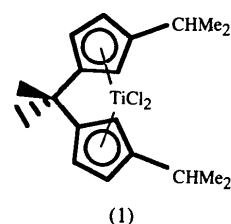
Abstract

The title complex, $[\text{TiCl}_2(\text{C}_{19}\text{H}_{26})]$, belongs to the short-bridged *ansa*-metallocene family, members of which are useful in polymerization processes. It was obtained in a three-step reaction sequence from 2,2-bis(cyclopentadienyl)propane in moderate overall yield. The most important structural feature is the distortion in

the angles caused by the short bridge; the two isopropyl groups do not contribute significantly to the intramolecular tension in the molecule.

Comment

The *ansa*-metallocene complexes of Group IV transition metals are of interest because of their activity in terminal olefin polymerization processes. Most of the literature in this area, including reports of structure determinations, concerns *ansa*-metallocene molecules with C_2 symmetry (*anti* isomers) which are isolated as racemic mixtures, and which are useful in isospecific polymerization processes (Halterman, 1992). In contrast, there are few reports of the structures of the corresponding molecules with C_s symmetry (*meso* or *syn* isomers) (Erikson, Fronczek & McLaughlin, 1990; Erker, Wilker, Krüger & Goddard, 1992), such as the title complex, (1).



The crystal structure of (1) shows important distortion caused by the short C(CH₃)₂ bridge. The ring C—C bond distances are in the range 1.397 (9)–1.412 (7) Å, which is, however, typical for titanium-dicyclopentadienyl complexes (Tkachev & Atovmyan, 1972). The ring angles lie in the range 105.5 (4)–110.9 (5)°, with the smallest angles, 105.5 (4) and 105.9 (5)°, at the ring atoms C(4) and C(6), which are bonded to the bridging group and to the isopropyl substituent, respectively. The mean Ti—C(ring) distance of 2.379 Å is practically the same as in 1,1'-(2,2-propylidene)dicyclopentadienyldimethyltitanium (2.378 Å; Nifant'ev, Churakov, Urazowski,

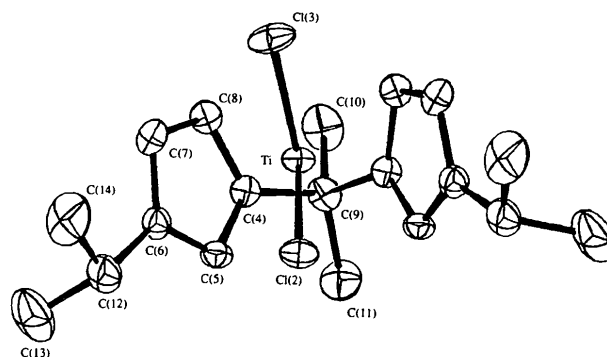


Fig. 1. Molecular structure of the title complex with the atomic labelling scheme. Displacement ellipsoids are shown at 50% probability.

Mkoyan & Atovmyan, 1992). The angle between the least-squares planes through the cyclopentadienyl rings C(4)–C(8) and C(4ⁱ)–C(8ⁱ) in each molecule is 67.8°, and the angle Cp–Ti–Cp', where Cp is the centroid of the cyclopentadienyl ring C(4)–C(8) and Cp' is the centroid of the ring C(4ⁱ)–C(8ⁱ), is 120.9° [symmetry code: (i) $\frac{1}{2} - x, y, z$]. The angle between Cp–Ti and the normal to the least-squares plane through the ring C(4)–C(8) is 4.7°. The results of the X-ray analysis suggest that the two isopropyl groups do not contribute significantly to molecular tension in the molecule.

Experimental

The bis(cyclopentadienyl) ligand used for preparing the title *syn* stereoisomer (1) was obtained in a three-step reaction: (i) synthesis of fulvene (Erickson, McLaughlin & Fronczek, 1989) from 2,2-bis(cyclopentadienyl)propane (mixture of isomers) (Kronig, Slongo & Neuenschwander, 1982) and propane; (ii) reduction (LiAlH₄) of the fulvene; (iii) action of ⁿBuLi. The complexation was finally achieved by reaction of the adduct TiCl₃·3thf with the lithium salt and oxidation with HCl. Brown crystals of the title compound, m.p. 473 K, were recrystallized from hexane in an overall yield of 30%.

Crystal data

[TiCl₂(C₁₉H₂₆)]

M_r = 373.3

Orthorhombic

Pmn

a = 16.881 (9) Å

b = 12.659 (9) Å

c = 9.201 (6) Å

V = 1966.5 Å³

Z = 4

D_x = 1.260 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 10–25°

μ = 0.70 mm⁻¹

T = 298 K

Irregular

0.5 × 0.05 × 0.02 mm

Brown

Data collection

KM-4 diffractometer

ω/2θ scans

Absorption correction: none

1475 measured reflections

1461 independent reflections

865 observed reflections

[*I* > 3σ(*I*)]

R_{int} = 0.026

θ_{max} = 25°

h = 0 → 17

k = 0 → 13

l = 0 → 9

1 standard reflection

monitored every 865

reflections

intensity decay: 5.2%

Refinement

Refinement on *F*²

R = 0.049

wR = 0.055

S = 1.4

865 reflections

175 parameters

H-atom parameters not refined

w = 1/[σ²(*F*) + 0.005707*F*²]

(Δ/σ)_{max} = 0.26

Δρ_{max} = 0.35 e Å⁻³

Δρ_{min} = -0.28 e Å⁻³

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1992, Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ti	1/4	0.2286 (1)	0.2396 (1)	0.039 (1)
Cl(2)	1/4	0.0896 (1)	0.4061 (2)	0.054 (1)
Cl(3)	1/4	0.3650 (2)	0.4121 (2)	0.071 (1)
C(4)	0.1830 (3)	0.2244 (4)	0.0182 (5)	0.044 (1)
C(5)	0.1538 (3)	0.1396 (4)	0.0994 (5)	0.046 (1)
C(6)	0.1086 (3)	0.1758 (5)	0.2184 (6)	0.051 (1)
C(7)	0.1144 (4)	0.2859 (5)	0.2161 (6)	0.060 (2)
C(8)	0.1598 (3)	0.3161 (4)	0.0945 (5)	0.051 (1)
C(9)	1/4	0.2202 (6)	-0.0907 (8)	0.052 (2)
C(10)	1/4	0.3164 (8)	-0.1923 (9)	0.082 (2)
C(11)	1/4	0.1195 (8)	-0.1795 (9)	0.079 (2)
C(12)	0.0597 (4)	0.1096 (5)	0.3208 (7)	0.074 (2)
C(13)	-0.0171 (5)	0.0801 (7)	0.2442 (9)	0.122 (2)
C(14)	0.0412 (5)	0.1673 (7)	0.4624 (8)	0.120 (2)

Table 2. Selected geometric parameters (Å, °)

Ti–Cl(2)	2.333 (2)	Ti–Cl(3)	2.345 (3)
Ti–C(4)	2.331 (5)	Ti–C(5)	2.360 (5)
Ti–C(6)	2.486 (5)	Ti–C(7)	2.411 (7)
Ti–C(8)	2.308 (5)	C(4)–C(5)	1.398 (7)
C(4)–C(8)	1.412 (7)	C(4)–C(9)	1.512 (7)
C(5)–C(6)	1.411 (7)	C(6)–C(7)	1.397 (9)
C(6)–C(12)	1.507 (9)	C(7)–C(8)	1.409 (8)
C(9)–C(10)	1.54 (1)	C(9)–C(11)	1.51 (1)
C(12)–C(13)	1.52 (1)	C(12)–C(14)	1.53 (1)
Cl(2)–Ti–Cl(3)	96.37 (6)	C(5)–C(4)–C(8)	105.5 (4)
C(4)–C(5)–C(6)	110.9 (5)	C(5)–C(6)–C(7)	105.9 (5)
C(6)–C(7)–C(8)	108.7 (5)	C(4)–C(8)–C(7)	108.8 (5)
C(4)–C(9)–C(10)	112.1 (5)	C(4)–C(9)–C(11)	112.8 (5)
C(10)–C(9)–C(11)	109.8 (6)	C(6)–C(12)–C(13)	108.3 (6)
C(6)–C(12)–C(14)	112.3 (6)	C(13)–C(12)–C(14)	109.8 (6)

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