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Acta Cryst. (1996). C**52**, 2402–2404

Chlorobis(η^5-methylcyclopentadienyl)(2,3,4,5,6-pentafluorophenyl)titanium(IV)

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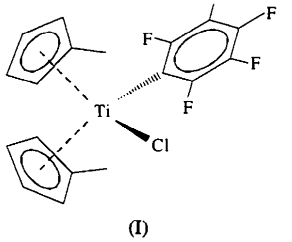
(*Received 23 April 1996; accepted 28 May 1996*)

Abstract

The title compound, [$TiCl(C_6F_5)(C_6H_7)_2$], displays distorted tetrahedral geometry at the Ti atom, as is also observed in other bis(cyclopentadienyl) complexes of titanium(IV). The Cl and the Ti atoms lie in the pentafluorophenyl plane, which bisects the interplanar angle between the methylcyclopentadienyl rings.

Comment

The title compound, (I), displays distorted tetrahedral geometry at the metal centre, which is typical for bis(cyclopentadienyl) complexes of titanium(IV) (if the cyclopentadienyl ligands are regarded as being attached through their ring centres *X*1*A* and *X*1*B*).



(I)

The *X*1*A*—Ti1—*X*1*B* angle of 133.5° lies in the usual range. The value of 100.41 (7)° for the Cl1—Ti1—C31 angle is much greater than the corresponding angles of *ca* 94° found in dihalogeno complexes (Clearfield, Warner, Saldarriaga-Molina, Ropal & Bernal, 1975; Petersen & Dahl, 1975; Klouras, Nastopoulos, Demakopoulos & Leban, 1993; Jones, Kienitz & Thöne, 1994). This may be due to a repulsive interaction between the F1 and Cl1 atoms, because the Ti and Cl atoms lie in the plane of the pentafluorophenyl ring [with respective deviations of 0.016 and 0.004 (2) Å, and a mean deviation of the 11 ring atoms from the ring plane of 0.007 Å], which almost ideally bisects the interplanar angle between the methylcyclopentadienyl rings [51.08 (11)°; the interplanar angle between cyclopentadienyl (Cp) ring 1 and C_6F_5 is 25.86 (13)°, and that between Cp ring 2 and C_6F_5 is 25.23 (14)°].

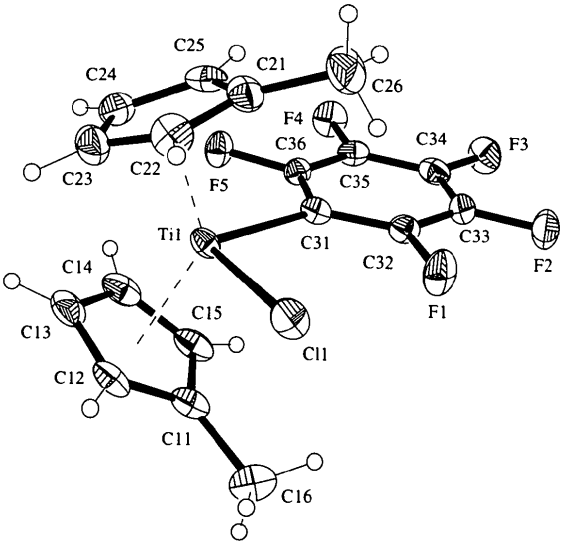


Fig. 1. The molecule of the title compound in the crystal. Ellipsoids correspond to 50% probability levels and H-atom radii are arbitrary.

The pentafluorophenyl ring shows a narrowing of the C32—C31—C36 angle to 112.3 (2)°, a well known phenomenon associated with this ligand (Jones, 1988).

The methyl groups of the Cp rings are oriented towards the space between the chlorine and pentafluorophenyl groups. The relative conformation of the methylcyclopentadienyl rings is between eclipsed and staggered (although they are not parallel), as can be seen from the C16—C11···C21—C26 torsion angle of 21.9 (3)° (ideal values: 0° for eclipsed and 36° for staggered).

The Ti—Cl bond is slightly shorter than in the dichloro complexes with cyclopentadienyl and methylcyclopentadienyl ligands [2.3340 (8) *versus* 2.359 (2)–2.367 (2), average 2.362 Å] (Clearfield *et al.*, 1975; Petersen & Dahl, 1975). Similarly, for the Ti—C31 bond, the value of 2.259 (2) Å is somewhat smaller than the Ti—C_{Ph} distance in [Cp_2TiPh_2] of 2.272 (14) Å (Kocman, Rucklidge, O'Brien & Santo, 1971), although the C_6H_5 and C_6F_5 ligands may not be directly comparable.

The Ti—C_{Cp} bond lengths lie in the range 2.343 (3) to 2.443 (3) Å. The perpendicular distances from the Ti atom to the rings are 2.070 (1) for Cp ring 1 and 2.062 (1) Å for Cp ring 2.

Short intramolecular H···F contacts are observed; H14···F5 of 2.40 Å and H25···F5 of 2.51 Å.

Experimental

The title compound was prepared in 51% yield using a modified version of the procedure of Chaudari, Treichel & Stone (1964) by addition of a cold (195 K) solution of pentafluorophenyllithium in diethyl ether to a cooled (273 K) solution of dichlorobis(methylcyclopentadienyl)titanium in tetrahydrofuran. The pure product was obtained by chromatography on a silica column using toluene as eluent and recrystallization from toluene/*n*-heptane at 243 K.

Crystal data

$[TiCl(C_6F_5)(C_6H_7)_2]$
$M_r = 408.64$
Monoclinic
$P2_1/c$
$a = 7.3431\ (9)$ Å
$b = 15.305\ (2)$ Å
$c = 14.475\ (3)$ Å
$\beta = 97.25\ (2)°$
$V = 1613.8\ (4)$ Å^3
$Z = 4$
$D_x = 1.682$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 54 reflections
$\theta = 10–11.5°$
$\mu = 0.746$ mm^{-1}
$T = 143\ (2)$ K
Plate
0.90 × 0.70 × 0.08 mm
Orange

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1990)
$T_{min} = 0.337$, $T_{max} = 0.989$
3413 measured reflections
2841 independent reflections

2516 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0488$
$\theta_{max} = 25.03°$
$h = -8 \rightarrow 8$
$k = -18 \rightarrow 2$
$l = -17 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F) = 0.0401$
$wR(F^2) = 0.1236$
$S = 1.068$
2827 reflections
228 parameters
Methyl H atoms refined as rigid groups, others refined as riding

$w = 1/[\sigma^2(F_o^2) + (0.0674P)^2 + 1.08P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.006$
$\Delta\rho_{max} = 0.323$ e Å^{-3}
$\Delta\rho_{min} = -0.595$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ti1	0.13947 (6)	0.66064 (3)	0.21791 (3)	0.0188 (2)
Cl1	0.41497 (9)	0.70398 (4)	0.16714 (5)	0.0296 (2)
F1	0.5568 (2)	0.55924 (11)	0.29503 (12)	0.0349 (4)
F2	0.6516 (2)	0.42806 (11)	0.40979 (12)	0.0337 (4)
F3	0.3978 (2)	0.34347 (10)	0.49795 (11)	0.0334 (4)
F4	0.0402 (2)	0.39276 (10)	0.46522 (11)	0.0303 (4)
F5	−0.0624 (2)	0.52238 (10)	0.34905 (10)	0.0261 (4)
C11	0.2290 (4)	0.7788 (2)	0.3278 (2)	0.0266 (6)
C12	0.1075 (4)	0.8116 (2)	0.2523 (2)	0.0288 (6)
C13	−0.0648 (4)	0.7722 (2)	0.2536 (2)	0.0321 (7)
C14	−0.0482 (4)	0.7116 (2)	0.3276 (2)	0.0305 (6)
C15	0.1328 (4)	0.7161 (2)	0.3726 (2)	0.0288 (6)
C16	0.4204 (4)	0.8101 (2)	0.3570 (2)	0.0421 (8)
C21	0.1263 (4)	0.5525 (2)	0.0943 (2)	0.0286 (6)
C22	0.0825 (4)	0.6343 (2)	0.0535 (2)	0.0310 (6)
C23	−0.0776 (4)	0.6649 (2)	0.0847 (2)	0.0325 (7)
C24	−0.1372 (4)	0.6020 (2)	0.1449 (2)	0.0288 (6)
C25	−0.0124 (4)	0.5329 (2)	0.1499 (2)	0.0277 (6)
C26	0.2870 (5)	0.4963 (3)	0.0817 (2)	0.0505 (9)
C31	0.2395 (3)	0.5499 (2)	0.3143 (2)	0.0198 (5)
C32	0.4190 (3)	0.5207 (2)	0.3342 (2)	0.0221 (5)
C33	0.4745 (3)	0.4523 (2)	0.3938 (2)	0.0234 (6)
C34	0.3475 (4)	0.4091 (2)	0.4387 (2)	0.0236 (6)
C35	0.1672 (3)	0.4350 (2)	0.4225 (2)	0.0207 (5)
C36	0.1194 (3)	0.5031 (2)	0.3619 (2)	0.0191 (5)

Table 2. *Selected geometric parameters (Å, °)*

Ti1—Cl1	2.3340 (8)	Ti1—*X*1*A**	2.071
Ti1—C31	2.259 (2)	Ti1—*X*1*B**	2.064
C31—Ti1—Cl1	100.41 (7)	*X*1*A*—Ti1—*X*1*B*	133.5
C31—Ti1—*X*1*A*	104.0	C36—C31—C32	112.3 (2)
C31—Ti1—*X*1*B*	103.2	C36—C31—Ti1	121.1 (2)
Cl1—Ti1—*X*1*A*	106.1	C32—C31—Ti1	126.6 (2)
Cl1—Ti1—*X*1*B*	105.1		
Cl1—Ti1—C31—C36	179.9 (2)	Ti1—C31—C32—F1	0.4 (3)
Cl1—Ti1—C31—C32	0.4 (2)	Ti1—C31—C36—F5	1.6 (3)

* *X*1*A* and *X*1*B* are the centroids of the C11–C15 and C21–C25 rings, respectively.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

The authors thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1195). 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. (1996). C**52**, 2404–2406

1,5-Diferrocenylnaphthalene

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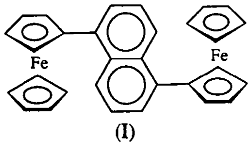
(*Received 10 May 1996; accepted 4 June 1996*)

Abstract

The title compound, [$Fe_2(C_5H_5)_2(C_{20}H_{14})$], was prepared by a palladium-catalyzed coupling reaction. The molecule lies about an inversion centre with the two ferrocenyl moieties bound to the 1 and 5 positions of the naphthalene unit and inclined at an angle of 47.0 (2)° with respect to the naphthalene mean plane.

Comment

As part of our continuing investigations on the formation of compounds in which redox centres are linked by conductive bridges (Elder, Robinson & Simpson, 1990; Robinson, Simpson & Worth, 1992; Duffy, McAdam, Robinson & Simpson, 1996), we have prepared 1,5-diferrocenylnaphthalene, (I), in yields of 10–20% by the palladium-catalyzed coupling of ferrocenyl zinc chloride with 1,5-diiodonaphthalene. The structure of the resulting product is the subject of this report.



(I)

The structure of (I) consists of well separated molecules lying about inversion centres with all intermolecular contacts < 3.5 Å involving H atoms (Nardelli, 1983). The naphthalene-bound cyclopentadiene rings of the ferrocenyl groups are inclined at angles of 47.0 (2)° with respect to the naphthalene mean plane. In contrast, the outer naphthyl substituents in 2′,6′-diethyl-1,1′:5′,1″-trinaphthyl are inclined at angles of 98° with respect to the central naphthalene unit in the centrosymmetric *meso* form and at angles of 106 and 93° in the DL-isomer (Anton, Adam, Wagner, Qi-Lin & Müllen, 1993). The twisting of the ferrocene moieties found in the title compound is similar to that observed for the more sterically crowded 1,8-diferrocenylnaphthalene (Lee, Foxman & Rosenblum, 1985) and its ruthenium analogue (Arnold, Foxman, Rosenblum & Euler, 1988), but the severe distortions of the naphthalene moiety observed in these compounds are not displayed here. Furthermore, the displacement of the C6 atom, which links the cyclopentadiene ring to the naphthalene, from the naphthalene ring plane is only 0.021 (9) Å compared with values in excess of 0.07 Å in the 1,8-substituted complex. Despite these observations, the C6—C12 bond length of 1.495 (5) Å compares well with the values obtained for the 1,8-ferrocene and ruthenocene analogues. Bond lengths and angles within the naphthalene and ferrocenyl moieties are unremarkable, as is the angle of 1.0 (2)° between the cyclopentadienyl ring planes. The cyclopentadiene rings are approximately eclipsed with a mean *Cn*—*Cg*1—*Cg*2—*Cm* torsion angle of −6.3 (2)° (*Cg*1 and *Cg*2 are the centroids of the cyclopentadienyl rings, n = 1–5 when m = 7–10, 6).

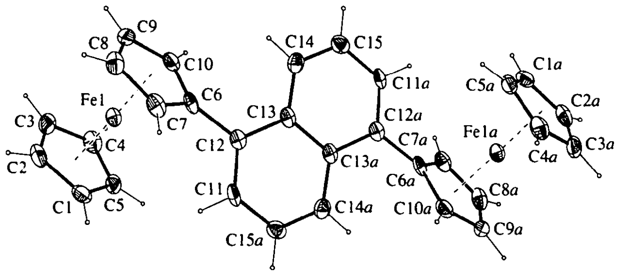


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title molecule showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

Experimental

The title compound was obtained by the Pd(dppf)Cl_2-catalyzed coupling of 1,5-diiodonaphthalene and ferrocenyl zinc chloride (Lee, Foxman & Rosenblum, 1985). Following separation by column chromatography (SiO_2/hexane), the product was crystallized from CH_2Cl_2 layered with hexane. Analysis calculated for $C_{30}H_{24}Fe_2$: C 72.62, H 4.88%; found C 72.32, H 4.65%. ^{1}H NMR ($CDCl_3$): δ 4.21 (*s*, 10H, C_5H_5), 4.40 (*t*, $^3J_{HH}$ = 1.8 Hz, 4H, C_5H_4), 4.64 (*t*, $^3J_{HH}$ = 1.8 Hz, 4H, C_5H_4),