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Dichlorobis(η^5-1,2,4-trimethylcyclopentadienyl)-titanium(IV)

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Key indicators

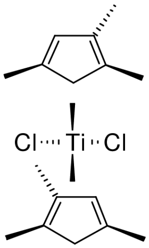
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.100
Data-to-parameter ratio = 24.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, [$TiCl_2(C_{16}H_{22})$], (I), is isomorphous with the corresponding and previously described Zr compound [(II); Kimura *et al.* (1998), *Chem. Lett.* pp. 571–572] and, apart from the difference in space group used in the structure refinements [*C*2/*c* for (I) and *Cc* for (II)], the compounds are isostructural.

Comment

The molecules of the title compound, (I), are subject to the operation of a twofold crystallographic axis passing through Ti and the midpoint of the Cl—Cl^{i} vector [symmetry operation: (i) $-x, y, -z + \frac{1}{2}$]. Therefore, the asymmetric unit consists of Ti, one Cl and one complete cylopentadienyl (hereafter Cp) ligand. The Cp ring C atoms are labelled in a manner compatible with the 1,2,4 distribution of the methyl substituents (C6, C7 and C8 respectively; see Fig. 1).



(I)

The Cp ring is itself essentially planar but the methyl substituents are displaced from the ring plane in a direction away from Ti (and the other Cp ligand) by distances of 0.174 (3), 0.123 (3) and 0.157 (3) Å for C6, C7 and C8, respectively. There is significant variation in the Ti—C distances, *viz*. 2.484 (3) (C1), 2.425 (2) and 2.421 (3) (C5 and C2), and 2.391 (2) and 2.381 (2) Å (C4 and C3). Small variations are also observed in the distances and angles within the Cp ring itself. Of the C—C distances which range from 1.402 (3) to 1.418 (3) Å, it is notable that whereas the longest is C1—C2, between adjacent methyl subsituted C atoms, the remaining short and intermediate C—C bonds alternate round the ring. The ring angles all differ somewhat from the ideal value of 108° and while those at C3 and C5 are greater than the ideal, those at C1, C2 and C4 are less. This variation in the angular values, although small and in which C3 and C5 are forced slightly in toward the ring centroid, is consistent with an extended scissor or lazy-tong-like effect provoked by increasing the separation of the methyl groups C6 and C7, so reducing the interaction between them.

In simple terms, Ti is in a tetrahedral environment coordinated to two Cl and to two Cp (Table 1). The Cp ligands and

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their methyl substituents are primarily related to one another by the operation of the crystallographic twofold axis alluded to above. The C atoms of the cyclopentadienyl rings are almost eclipsed but with a small rotation (approximately 11°) relative to one another. The distribution of the methyl substituents is more complex. Thus, while C7 of one ring almost eclipses C8 of the other, C6 of both rings tends to eclipse one or other of the Cl. This situation is much more complicated than that described by Howie *et al.* (1985), and references therein, for other analogous compounds.

The Cambridge Structural Database (Allen & Kennard, 1993), accessed by means of the Chemical Database Service of the EPSRC at Daresbury (Fletcher *et al.*, 1996), includes an entry with reference code HOBYAY describing the structure of the corresponding Zr compound, (II), as determined in the space group *Cc* by Kimura *et al.* (1998). Despite the difference in space group, the structures of (I) and (II) are virtually identical (see, for example, Table 1). Thus, the compounds can reasonably be regarded as isostructural although the situation with regard to the crystallographic nature of the twofold axial molecular symmetry remains in doubt.

Experimental

The title compound was prepared using the method of Sullivan & Little (1967) and recrystallized from dichloromethane.

Crystal data

$[TiCl_2(C_{16}H_{22})]$
$M_r = 333.14$
Monoclinic, $C2/c$
$a = 16.788\ (13)$ Å
$b = 6.791\ (7)$ Å
$c = 15.814\ (13)$ Å
$\beta = 119.89\ (6)°$
$V = 1563\ (2)$ Å^3
$Z = 4$

$D_x = 1.416$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
$\theta = 17–26°$
$\mu = 0.87$ mm^{-1}
$T = 298\ (2)$ K
Rhomb, dark red
0.88 × 0.30 × 0.24 mm

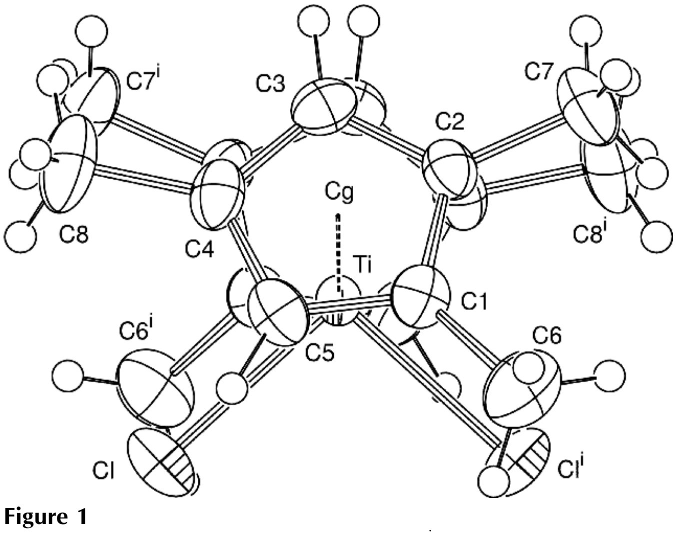

Figure 1
The title molecule projected on to the Ti/Cl/Cl^i plane [symmetry code: (i) $-x, y, -z + \frac{1}{2}$], *i.e.* viewed along the vector joining the centroids (*Cg*) of the Cp rings. Non-H atoms are shown as 50% ellipsoids and H atoms as spheres of arbitrary radii. All non-H atoms of the asymmetric unit, *i.e.* Ti, Cl and C of the uppermost ligand are labelled along with selected symmetry-related atoms.

Data collection

Nicolet *P*3 diffractometer
$\theta–2\theta$ scans
2207 measured reflections
2207 independent reflections
2147 reflections with $I > 2\sigma(I)$
$\theta_{max} = 30.1°$

$h = 0 \rightarrow 23$
$k = 0 \rightarrow 9$
$l = -22 \rightarrow 18$
2 standard reflections every 50 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.100$
$S = 1.17$
2207 reflections
90 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 2.0290P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Comparative table of bond distances and angles (Å, °) in the coordination of M in (I) and (II).

	(I) (M = Ti)	(II) (M = Zr)	
$M—Cg$	2.102 (2)	2.201 (8)	2.247 (8)
M—Cl	2.3605 (18)	2.439 (6)	2.455 (7)
$Cg—M—Cg^i$	133.51 (9)	132.6 (3)	
Cl—M—Cl^i	95.41 (9)	97.7 (2)	
$Cg—M$—Cl	104.59 (9)	104.2 (3)	104.8 (3)
$Cg—M$—Cl^i	106.22 (9)	105.8 (3)	106.5 (3)

Note: the geometric parameters are determined in terms of the centroids (*Cg*) of the cyclopentadienyl (Cp) rings. They are expressed in conformity with the axial molecular symmetry of (I) and hence the occurrence of entries in pairs for (II) [symmetry code: (i) $-x, y, \frac{1}{2} - z$].

H atoms were placed in calculated positions and refined as riding.

Data collection and cell refinement: *Nicolet P*3 *Software* (Nicolet, 1980); data reduction: *RDNIC* (Howie, 1980); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
Howie, R. A. (1980). *RDNIC*. University of Aberdeen, Scotland.
Howie, R. A., McQuillan, G. P. & Thompson, D. W. (1985). *Acta Cryst.* C**41**, 1045–1047.
Kimura, K., Takaishi, K., Matsukawa, T., Yoshimura, T. & Yamazaki, H. (1998). *Chem. Lett.* pp. 571–572.
Nicolet. (1980). *Nicolet P*3/*R*3 *Software*. Nicolet XRD Corporation, 10061 Bubb Road, Cupertino, CA 95014, USA.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Sullivan, M. F. & Little, W. F. (1967). *J. Organomet. Chem.* **8**, 277–285.