

## CRYSTAL AND MOLECULAR STRUCTURE OF DICHLOROBIS( $\eta^5$ -t-BUTYLCYCLOPENTADIENYL)TITANIUM(IV)

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### Summary

Dichlorobis( $\eta^5$ -t-butylcyclopentadienyl)titanium(IV),  $(t\text{-BuCp})_2\text{TiCl}_2$ , crystallises in space group  $P2_12_12$  (orthorhombic) with  $a$  12.862(14),  $b$  10.709(9),  $c$  6.602(9) Å,  $Z = 2$ . The two t-butyl groups are directed away from each other on opposite sides of the molecule; the overall molecular symmetry is  $C_2$ . The individual titanium-ring carbon atom distances are not all equal, but vary from 2.330(5) to 2.475(4) Å, the distortion from an exactly symmetric conformation being in a direction which increases the separation between the titanium atom and the carbon atom carrying the t-butyl substituent group.

### Introduction

Compounds containing a bis( $\eta^5$ -cyclopentadienyl)titanium group continue to be widely used and studied [1]. Titanocene dichloride and its ring-substituted analogues are commonly used as precursors in the synthesis of other bis( $\eta^5$ -cyclopentadienyl) compounds, including, for example,  $(\eta^5\text{-Cp})_2\text{Ti}(\text{CO})_2$  [2],  $(\eta^5\text{-Cp})_2\text{Ti-}\mu\text{-CH}_2\text{-}\mu\text{-ClAlMe}_2$  [3], decamethyltitanocene [4] and  $(\eta^5\text{-Cp})\text{TiCH}_2\text{CH}(\text{i-Pr})\text{CH}_2$  [5]. Titanocene dichloride has been studied extensively as a catalyst/promoter component in olefin polymerisation [6], in the hydrometallation of alkenes [7], and in the carbometallation of alkene and alkyne functionalities [8–11]. Overall, much less attention has been given to the effect of ring-substituents on the chemistry of bis( $\eta^5$ -cyclopentadienyl)titanium systems even though methyl and pentamethylcyclopentadienyl compounds do show significant modifications of chemical behaviour relative to their unsubstituted analogues [4,12,13].

Recently [8,14], we have been investigating the influence of ring-substitution on the carbometallation of unsaturated alcohols using  $(\eta^5\text{-Cp})_2\text{TiCl}_2/\text{AlR}_x\text{Cl}_{3-x}$  reagents (R = Me or Et; Cp = substituted or unsubstituted cyclopentadienyl ligand). In this work little variation in the regioselectivity of the carbotitanation reaction was observed for the series  $(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{TiCl}_2$ , R = H, Me, t-Bu. This prompted us to determine the crystal and molecular structure of the t-butyl compound  $(\text{t-BuCp})_2\text{TiCl}_2$  in order to compare it with the known structures of  $\text{Cp}_2\text{TiCl}_2$  [15] and  $(\text{MeCp})_2\text{TiCl}_2$  [16] and to provide a basis for the interpretation of reactivity patterns.

## Experimental

Dichlorobis( $\eta^5$ -t-butylcyclopentadienyl)titanium(IV) was prepared using a method devised by Lock [17], following the general syntheses reported by Sullivan and Little [18]. The compound was obtained as long deep-red needles by slow recrystallisation from dichloromethane solution.

### Structure determination

*Crystal data.*  $\text{C}_{18}\text{H}_{26}\text{Cl}_2\text{Ti}$ , *MW* 361.2; orthorhombic, space group  $P2_12_12$  (No. 18); *a* 12.862(14), *b* 10.709(9), *c* 6.602(9) Å; *V* 909.5 Å<sup>3</sup>, *d*<sub>calc</sub> 1.32 g cm<sup>-3</sup>, *Z* = 2;  $\mu$  7.53 cm<sup>-1</sup>,  $\lambda$  0.71069 Å (Mo- $K_\alpha$ ).

Intensity data were collected at room temperature for a wedge-shaped crystal fragment approximately 1.00 mm long and 0.14 mm square in section at the midpoint, using a Nicolet P3 automatic four circle X-ray diffractometer with Mo- $K_\alpha$  radiation ( $\lambda$  0.71069 Å). The unit-cell data listed above were obtained by least-squares refinement of the accurately-determined setting angles of twelve strong high-angle reflections, and the space group ( $P2_12_12$ ) was identified from the systematic absences ( $h00$ ,  $h \neq 2n$ ;  $0k0$ ,  $k \neq 2n$ ) in the complete data set.

Intensities were measured over a half-cell in reciprocal space, using the  $\theta$ - $2\theta$  scan technique ( $0^\circ < 2\theta < 40^\circ$ ) with variable scan speed. Two strong reference reflections monitored at intervals during the data collection process showed no detectable variation in intensity as a function of time. After application of Lorentz and polarisation corrections, a total of 1682 individually measured intensities was averaged over equivalent indices to yield 524 independent observed reflections [ $I > 3\sigma(I)$ ] for use in the structure determination. No correction was made for absorption.

The structure was solved by conventional heavy-atom techniques [19,20]. In space group  $P2_12_12$  with two molecules in the unit cell the titanium atoms must occupy special positions on the twofold *c*-axes; the molecules have  $C_2$  symmetry with the titanium, one chlorine, nine carbon and thirteen hydrogen atoms in the asymmetric unit. The titanium and chlorine atoms were located from an initial Patterson synthesis and a subsequent Fourier synthesis provided approximate coordinates for the nine carbon atoms. Block-diagonal least-squares refinement with all atoms anisotropic converged at  $R = 5.29\%$ . Two successive difference maps calculated at this point showed significant areas of electron-density in appropriate positions for the thirteen hydrogen atoms. Continued refinement with the hydrogen atom coordinates included as fixed contributions, with  $B_{\text{iso}}$  6.0 Å<sup>3</sup>, reduced  $R$  to 2.98% with all parameter shifts  $< 0.15$  e.s.d. A final series of least-squares cycles, with the hydrogen

TABLE 1  
ATOMIC COORDINATES (e.s.d.'s in last significant figure)

Atom	$x/a$	$y/b$	$z/c$	$B_{\text{iso}}(\text{eq}) (\text{\AA}^2)^b$
Ti	0.5000	0.5000	0.8433(2)	3.46(6)
Cl	0.4030(1)	0.6095(1)	1.0915(2)	5.59(11)
C(1)	0.3576(4)	0.3508(4)	0.8706(8)	4.4(4)
C(2)	0.4465(4)	0.2892(4)	0.7937(9)	5.1(5)
C(3)	0.4728(3)	0.3403(4)	0.6096(8)	4.1(4)
C(4)	0.3973(3)	0.4323(4)	0.5637(7)	3.4(3)
C(5)	0.3255(3)	0.4373(4)	0.7226(7)	3.8(3)
C(6)	0.2215(3)	0.5069(5)	0.7136(7)	4.7(4)
C(7)	0.2379(4)	0.6443(4)	0.6510(10)	5.9(5)
C(8)	0.1645(4)	0.5013(6)	0.9171(10)	7.6(7)
C(9)	0.1578(4)	0.4412(6)	0.5502(13)	8.2(7)
H(1)	0.333(4)	0.341(4)	1.002(8)	6 (1)
H(2)	0.486(4)	0.225(4)	0.877(7)	4 (1)
H(3)	0.526(3)	0.323(4)	0.521(7)	3 (1)
H(4)	0.389(3)	0.481(4)	0.444(6)	3 (1)

<sup>a</sup> Coordinates for methyl hydrogens, determined from difference map, are available from the authors.

<sup>b</sup>  $B_{\text{iso}}(\text{eq}) = 4/3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2)$ . Data for H atoms are those obtained directly from final cycles of least-squares refinement.

atoms refining isotropically, produced a further reduction in  $R$  to 2.48% with a significant improvement in the definition of the ring hydrogen positions, but not in those of the methyl hydrogens. A concluding difference map revealed no detectable areas of residual electron density.

The weighting scheme used throughout was of the form  $w = \{1 + |F_o| - 12)/20\}^2\}^{-1}$ . No reflections were rejected in the course of the refinement. The calculated atomic coordinates and equivalent isotropic temperature factors are listed in Table 1. Details of the observed and calculated structure factors and of the anisotropic thermal vibrational parameters are available from the authors.

## Discussion

The molecular structure of  $(t\text{-BuCp})_2\text{TiCl}_2$  is illustrated in Fig. 1, and bond length and angle data are listed in Table 2. The atomic numbering system is indicated in the Figure.

The coordination of the titanium atom is similar to that in other bis( $\eta^5$ -cyclopentadienyl)titanium dihalides, with the chlorine atoms and the centroids of the cyclopentadienyl rings occupying pseudotetrahedral sites around the metal atom. The  $\text{ClTiCl}$  ( $92.5^\circ$ ) and  $\text{Cp}(c)\text{TiCp}(c)$  ( $131.5^\circ$ ) angles are within the observed ranges for similar structures. The non-bonded contacts  $\text{C}(4)\text{--}\text{C}(4)'$ , 3.014(6) Å and  $\text{C}(4)\text{--}\text{C}(3)'$ , 2.969(6) Å, between the approaching ring edges effectively prevent any further tilting towards a more nearly tetrahedral  $\text{Cp}(c)\text{TiCp}(c)$  angle. The rings are partially staggered, with a relative displacement of about  $20^\circ$ , compared with  $36^\circ$  required for a 'perfect' staggered conformation. Variations in the precise angle of stagger in other bis( $\eta^5$ -cyclopentadienyl) compounds have been attributed to local crystal-packing requirements [21].

The *t*-butyl groups are located at opposite sides of the molecule, directed away

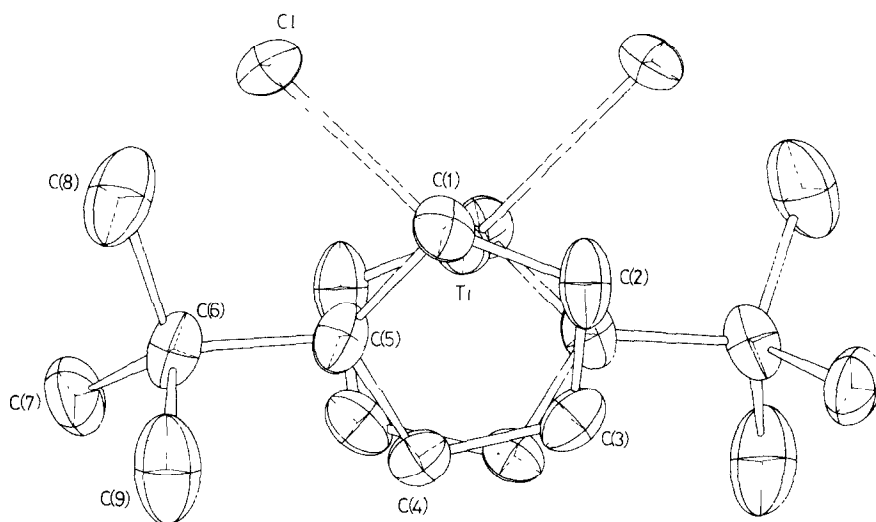


Fig. 1. ORTEP representation of  $(\eta^5\text{-t-BuCp})_2\text{TiCl}_2$  (hydrogen atoms omitted). Thermal ellipsoids are drawn at 30% probability limit.

from each other and from the chlorine atoms. The only molecular symmetry element is a  $C_2$  axis bisecting the  $\text{TiCl}_2$  angle. The structure contrasts markedly with those of the methyl-substituted compounds  $(\text{MeCp})_2\text{TiCl}_2$  and  $(\text{MeCp})_2\text{VCl}_2$  [16], in which

TABLE 2\*

BOND LENGTHS AND ANGLES<sup>a</sup> (e.s.d.'s in last significant figure)

Bond lengths (Å)		Bond angles (°)	
Ti-Cl	2.370(2)	Cl-Ti-Cl	92.5(5)
Ti-C(1)	2.437(5)	C(1)C(2)C(3)	109.3(4)
Ti-C(2)	2.383(4)	C(2)C(1)C(5)	107.2(4)
Ti-C(3)	2.330(5)	C(2)C(3)C(4)	107.3(4)
Ti-C(4)	2.383(5)	C(3)C(4)C(5)	108.6(4)
Ti-C(5)	2.475(4)	C(4)C(5)C(1)	107.5(4)
C(1)-C(2)	1.413(7)	C(4)C(5)C(6)	124.5(4)
C(1)-C(5)	1.408(7)	C(1)C(5)C(6)	127.1(4)
C(2)-C(3)	1.375(8)	C(5)C(6)C(7)	110.7(4)
C(3)-C(4)	1.416(6)	C(5)C(6)C(8)	111.4(4)
C(4)-C(5)	1.399(6)	C(5)C(6)C(9)	105.8(4)
C(5)-C(6)	1.533(6)	C(7)C(6)C(8)	109.8(4)
C(6)-C(7)	1.543(7)	C(7)C(6)C(9)	108.9(4)
C(6)-C(8)	1.531(8)	C(8)C(6)C(9)	110.2(4)
C(6)-C(9)	1.526(9)	C(2)C(1)H(1)	124(3)
C(1)-H(1)	0.93(5)	C(5)C(1)H(1)	128(3)
C(2)-H(2)	1.02(5)	C(1)C(2)H(2)	122(3)
C(3)-H(3)	0.92(4)	C(3)C(2)H(2)	128(3)
C(4)-H(4)	0.95(4)	C(2)C(3)H(3)	132(3)
Ti-Cp(c) <sup>b</sup>	2.093	C(4)C(3)H(3)	121(3)
		C(3)C(4)H(4)	129(3)
		C(5)C(4)H(4)	122(3)

\* A diagram of the molecule with the hydrogen atoms included is available from the authors. Angle subtended at Ti by ring centroids is 131.5°; angle between perpendiculars to planes of rings is 126.0°.

the methyl groups are situated above and below the  $\text{MCl}_2$  'wedge'. It would not be possible to incorporate the sterically more demanding *t*-butyl groups in a similar structure without intolerably crowding the inward-directed methyl groups and the chlorine atoms: the less compact structure adopted by  $(t\text{-BuCp})_2\text{TiCl}_2$  is the only feasible conformation in which a highly branched substituent group can be accommodated. The removal of the *t*-butyl groups to positions well away from the titanium atom means that despite their bulk these groups can have little effect on reagents approaching the titanium centre along the direction defined by the  $C_2$  axis. Thus, if we assume that the conformation in the crystal, or something close to it, is preserved in solution, we can account for the general similarity in reactivity between  $(t\text{-BuCp})_2\text{TiCl}_2$  and unsubstituted  $\text{Cp}_2\text{TiCl}_2$ .

The C–C distances around the cyclopentadienyl ring cover a narrow range between 1.375(8) and 1.416(6) Å; the differences between them are within the conventional uncertainty limits of  $3 \times \text{e.s.d}$  and hence are not significant. The Ti–C distances, in contrast, vary by 0.145 Å from 2.330(5) for Ti–C(3) to 2.475(4) Å for Ti–C(5). The average C–C bond length of 1.40 Å is close to the ideal value of 1.41 Å suggested by Prout et al. [21] for a 'good' structure unaffected by disorder or excessive thermal vibration, and the narrow spread of the measured C–C distances is further evidence that the carbon atom positions are accurately determined. Accordingly, we conclude that the asymmetry in the titanium-ring interaction is real and is not simply an artefact of the structure analysis. The displacement of the rings relative to the titanium atom is in a direction which increases the separation between the titanium atom and the carbon atom C(5) carrying the *t*-butyl group. The closest intra-molecular non-bonded distances between atoms of the *t*-butyl groups in one ring and C or H atoms in the other ring are C(7)–C(3)', 3.73 Å, and C(7)–H(3)', 3.18 Å. Taking the Van der Waals radii of carbon, hydrogen and the methyl group as 1.70, 1.20 and 2.00 Å, respectively, these are normal non-bonded contacts with no undue crowding, and suggest that the asymmetry in the titanium-ring interaction must be electronic rather than steric in origin.

The ring carbon atoms all lie within 0.015 Å of the calculated C(1–5) mean plane, with the *t*-butyl group (i.e. the C(5)–C(6) bond) displaced outwards by  $10.5^\circ$  from the plane of the ring. This displacement of the substituent group is closely comparable with those ( $\sim 8^\circ$ ) observed for the most nearly equivalent methyl groups in  $(\eta^5\text{-Me}_3\text{Cp})_2\text{TiCl}_2$  [22]. Because of the slight asymmetry in the position of the titanium atom relative to the cyclopentadienyl rings, the angle between the perpendiculars from the titanium atom to the rings ( $126.1^\circ$ ) is slightly less than the  $\text{Cp}(c)\text{TiCp}(c)$  angle ( $131.5^\circ$ ).

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### References

- 1 M. Battrill, P.D. Gavens, J.W. Kelland and J. McMeeking, Anionic  $\pi$ -Bonded Derivatives of Titanium(IV), in Vol. 3 of *Comprehensive Organometallic Chemistry*, Pergamon Press, 1982.

- 2 J.L. Atwood, K.E. Stone, H.G. Alt, D.C. Hrcir and M.D. Rausch, *J. Organomet. Chem.*, 132 (1977) 367.
- 3 F.N. Tebbe, G.W. Parshall and G.S. Reddy, *J. Am. Chem. Soc.*, 100 (1978) 3611.
- 4 J.E. Bercaw, *J. Am. Chem. Soc.*, 96 (1974) 5087.
- 5 D.A. Strauss and R.H. Grubbs, *Organometallics*, 1 (1983) 1658.
- 6 H. Sinn and W. Kaminsky, *Adv. Organometal. Chem.*, 18 (1980) 99.
- 7 E.C. Ashby and S.A. Noding, *J. Org. Chem.*, 44 (1979) 4364.
- 8 M.D. Schiavelli, J.J. Plunkett and D.W. Thompson, *J. Org. Chem.*, 46 (1981) 807.
- 9 E. Negishi, *Pure Appl. Chem.*, 53 (1981) 2333.
- 10 J.J. Eisch, R.J. Manfre and D.A. Komar, *J. Organomet. Chem.*, 159 (1978) C13.
- 11 B.B. Snider and M. Karras, *J. Organomet. Chem.*, 179 (1979) C37.
- 12 E. Samuel, *J. Organomet. Chem.*, 19 (1969) 87.
- 13 R. Jungst, D. Sekutowski, J. Davis, M. Luly and G. Stucky, *Inorg. Chem.*, 16 (1977) 1645
- 14 D.W. Thompson, unpublished observations.
- 15 A. Clearfield, D.K. Warner, C.H. Saldarriaga-Molina, R. Ropal and I. Bernal, *Can. J. Chem.*, 53 (1975) 1622.
- 16 J.L. Petersen and L.F. Dahl, *J. Am. Chem. Soc.*, 97 (1975) 6422
- 17 G.A. Lock, Hercules Inc., private communication.
- 18 M.E. Sullivan and W.F. Little, *J. Organomet. Chem.*, 8 (1967) 277.
- 19 Neutral-atom scattering factors taken from International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.
- 20 F.R. Ahmed, S.R. Hall, M.E. Pippy and C.P. Huber, NRC Crystallographic Programs, Ottawa, 1966, Variously modified by R.A. Howie, J.S. Knowles and H.F.W. Taylor (Univer. Aberdeen).
- 21 K. Prout, T.S. Cameron, R.A. Forder, S.R. Critchley, B. Denton and G.V. Rees, *Acta Cryst.*, B30 (1974) 2290.
- 22 T.C. McKenzie, R.D. Sanner and J.E. Bercaw, *J. Organomet. Chem.*, 102 (1975) 457.