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THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(PENTAMETHYLCYCLOPENTADIENYL)DICHLOROTITANIUM(IV)

THOMAS C. McKENZIE*, ROBERT D. SANNER and JOHN E. BERCAW*

*A.A. Noyes Laboratory of Chemical Physics, California Institute of Technology**, Pasadena, California 91125 (U.S.A.)*

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Summary

The structure of bis(pentamethylcyclopentadienyl)dichlorotitanium(IV) has been investigated by single-crystal X-ray diffraction techniques. $[\eta\text{-}C_5(CH_3)_5]_2TiCl_2$ crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions $a = 10.816(1)$, $b = 8.132(1)$, $c = 22.259(1)$ Å; $Z = 4$. Full matrix, least-squares refinement converged to a final R index of 0.032 based on 1429 reflections. The configuration about the titanium atom is a distorted tetrahedron comprised of the two chlorine atoms and the centroids of the two η-cyclopentadienyl rings. Several ring methyl groups are bent considerably out of the cyclopentadienyl plane and away from the titanium atom. These out-of-plane deviations are attributable to chlorine—methyl crowding and methyl—methyl contacts between the two rings.

Introduction

Reaction systems derived from the electron-deficient sandwich compound dicyclopentadienyltitanium(II), $(\eta\text{-}C_5H_5)_2Ti$ are of current interest, especially in connection with the fixation and reduction of dinitrogen [1-3]. Efforts toward the isolation and characterization of low-valent titanocene derivatives from these systems are often thwarted, however, owing to side reactions involving rearrangement to titanium hydride species via a ring-to-titanium α-hydrogen shift [1,4-6]. In view of these complicating features inherent in $(\eta\text{-}C_5H_5)_2Ti$ based systems, we have more recently investigated the closely related bis(cyclopentadienyl)titanium(II) derivative, $[\eta\text{-}C_5(CH_3)_5]_2Ti$, and its behavior toward N_2 [7,8].

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While the chemistry of $[\eta\text{-}C_5(CH_3)_5]_2Ti$ and $(\eta\text{-}C_5H_5)_2Ti$ derivatives are in many respects quite similar, we have noted a definite preference for monomeric $[\eta\text{-}C_5(CH_3)_5]_2$ Ti derivatives [1,8], apparently as a result of steric crowding of bulky $[\eta\text{-}C_5(CH_3)_5]$ rings in dimeric or polymeric species. Furthermore, a recent structure determination of $[\eta\text{-}C_5(CH_3)_5](\eta\text{-}C_5H_5)TiCl_2$ shows ring methyl groups to be pushed out of the plane of the ring carbons, apparently as a result of intramolecular $(\eta\text{-}C_5H_5)[\eta\text{-}C_5(CH_3)_5]$ crowding [9]. In order to establish the extent of such crowding in a complex containing two $[\eta\text{-}C_5(CH_3)_5]$ rings and to provide a basis for interpreting the structures of $[\{\eta\text{-}C_5(CH_3)_5\}_2M]_2\text{-}(N_2)_n$ (M = Ti, $n = 1$; M = Zr, $n = 3$) presently under investigation, we have undertaken an X-ray structure determination of $[\eta\text{-}C_5(CH_3)_5]_2TiCl_2$.

Experimental

$[\eta\text{-}C_5(CH_3)_5]_2TiCl_2$ was prepared as described previously [8] and obtained as dark purple-brown needles from chloroform. A series of Weissenberg and precession photographs (taken with Cu-K_α and Mo-K_α radiation) indicated an orthorhombic unit cell of space group $P2_12_12_1$ (systematic absences: $h00$, h odd; $0k0$, k odd; $00l$, l odd). Unit cell dimensions were obtained by a least-squares fit to the observed $\sin^2\theta/\lambda^2$ values for 29 reflections measured on a diffractometer. The density was measured by flotation in aqueous zinc chloride/HCl solution. Crystal data are given in Table 1.

A crystal (elongated along its b axis) was mounted with its b axis slightly skew to the ϕ axis of a G.E. XRD-5 quarter-circle diffractometer automated by Datex. Using Mo-K_α radiation monochromated with a graphite crystal, one octant of intensity data was measured between 4° and 45° in 2θ (corresponding to a spacing of 0.93 Å) employing the $\theta - 2\theta$ step scan technique. A scan rate of 1°/min and scan width of 1.75° were selected, and 30-sec background counts were taken before and after each scan. Intensities of three check reflections measured every 45 reflections showed no crystal decomposition during the data collection. A variance $\sigma^2(I)$ was calculated for each reflection based on counting statistics and a term in $(0.02\ S)^2$, where S is the scan count. Intensities and their variances were corrected for Lorentz and polarization effects but not for absorption ($\mu = 7.2\ \text{cm}^{-1}$). The data were then placed on an absolute scale by means of a Wilson plot [10]. Scattering factors for all atoms were calculated by the method of Cromer and Mann [11]. The intensities of 1516 reflections were collected; 20 were deleted as systematic absences, 66 were given zero weight

TABLE 1

CRYSTAL DATA

$C_{20}H_{30}TiCl_2$	Orthorhombic space group $P2_12_12_1$
$a = 10.816(1)$ Å	$FW = 389.2$
$b = 8.132(1)$ Å	$\rho_{obs} = 1.31(1)\ \text{g cm}^{-3}$
$c = 22.259(1)$ Å	$\rho_{calc} = 1.32\ \text{g cm}^{-3}$
$V = 1958$ Å^3	$Z = 4$
$\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å	$\mu = 7.2\ \text{cm}^{-1}$

TABLE 2

FINAL NONHYDROGEN ATOM PARAMETERS (Coordinates × 10^5, U_{ij} × 10^4, Esd's in parentheses)[a,b]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	27847(7)	97604(8)	12722(3)	327(4)	209(4)	315(4)	3(3)	18(4)	−16(3)
Cl(1)	38795(11)	115982(14)	18910(5)	582(8)	513(8)	567(8)	−210(6)	98(7)	−246(6)
Cl(2)	17039(11)	118844(13)	7894(6)	591(8)	427(7)	659(9)	204(6)	179(7)	220(6)
C(1)	6407(37)	91848(49)	15393(20)	318(26)	411(28)	484(29)	−33(21)	60(23)	50(23)
C(2)	11770(37)	100147(52)	20322(17)	418(26)	419(26)	383(26)	−13(26)	147(23)	−50(23)
C(3)	20899(40)	89708(47)	22820(17)	463(29)	397(25)	319(25)	−115(25)	−10(23)	66(19)
C(4)	21373(40)	75299(44)	19371(18)	404(25)	314(24)	432(26)	12(22)	72(26)	104(20)
C(5)	12283(39)	76567(48)	14788(18)	392(26)	357(25)	422(28)	−123(22)	83(24)	−44(20)
C(11)	38843(38)	100928(49)	3001(17)	448(26)	398(26)	354(24)	78(25)	113(23)	−7(22)
C(12)	32617(39)	85531(50)	3087(18)	407(27)	490(30)	371(27)	3(23)	48(23)	−190(22)
C(13)	38417(42)	75591(46)	7441(19)	455(28)	251(23)	520(30)	53(22)	170(27)	−25(20)
C(14)	47483(38)	85331(49)	10383(17)	374(27)	415(26)	375(27)	139(22)	70(22)	29(21)
C(15)	47817(35)	100565(48)	7413(17)	343(24)	390(27)	342(25)	−13(22)	63(21)	−59(21)
C(6)	−5077(42)	97186(64)	12122(26)	414(32)	761(42)	1047(51)	−46(31)	−135(36)	104(42)
C(7)	8042(48)	116551(59)	22906(23)	824(50)	461(33)	783(43)	−21(33)	451(41)	−132(30)
C(8)	27324(56)	92363(64)	28660(21)	948(50)	845(46)	451(33)	−295(40)	−148(35)	74(30)
C(9)	27568(51)	59885(55)	21519(22)	729(38)	531(34)	720(40)	164(34)	203(38)	288(28)
C(10)	7343(47)	62762(60)	11093(24)	682(43)	582(40)	869(49)	−292(33)	139(38)	−248(34)
C(16)	37198(53)	114085(60)	−1647(22)	915(48)	646(39)	552(39)	300(39)	263(37)	235(29)
C(17)	23197(52)	80654(73)	−1408(23)	607(41)	1166(53)	616(39)	−88(43)	76(36)	−360(40)
C(18)	37840(62)	57107(56)	7570(29)	1164(65)	346(33)	1183(66)	11(37)	677(59)	−81(34)
C(19)	56214(49)	80095(72)	15140(24)	691(41)	975(50)	650(43)	363(43)	−6(39)	120(38)
C(20)	57432(48)	113663(62)	8246(25)	690(44)	659(39)	823(44)	−232(34)	255(37)	−208(37)

[a] The final value of the scale factor is 0.9329(19). [b] The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2klb^*c^*U_{23})]$.

TABLE 3

FINAL HYDROGEN ATOM PARAMETERS (coordinates × 10^4)[a]

	x	y	z	B
H(6A)	−680(48)	10809(61)	1282(25)	6.50
H(6B)	−1265(49)	9132(60)	1413(23)	6.50
H(6C)	−602(48)	8906(63)	896(24)	6.50
H(7A)	1511(47)	12095(64)	2245(22)	6.00
H(7B)	120(52)	11598(60)	2611(23)	6.00
H(7C)	554(46)	12058(66)	1933(23)	6.00
H(8A)	3015(47)	10439(61)	2940(22)	6.50
H(8B)	3563(47)	8736(69)	2855(23)	6.50
H(8C)	2245(47)	8623(61)	3162(22)	6.50
H(9A)	3613(46)	6139(63)	2191(22)	6.00
H(9B)	2770(47)	5280(63)	1850(22)	6.00
H(9C)	2447(47)	5944(57)	2567(22)	6.00
H(10A)	464(50)	6612(68)	792(24)	6.25
H(10B)	−69(50)	6009(59)	1236(24)	6.25
H(10C)	1337(48)	5457(65)	1076(22)	6.25
H(16A)	3595(51)	12317(65)	54(25)	6.25
H(16B)	2843(49)	11249(59)	−353(22)	6.25
H(16C)	4374(46)	11444(61)	−481(22)	6.25
H(17A)	1517(50)	8444(68)	−45(24)	7.00
H(17B)	2074(50)	6909(65)	−89(23)	7.00
H(17C)	2698(53)	8254(66)	−519(22)	7.00
H(18A)	4002(52)	5373(70)	1125(23)	7.00
H(18B)	3018(47)	5441(69)	650(25)	7.00
H(18C)	4406(50)	5682(68)	508(25)	7.00
H(19A)	5504(55)	8490(73)	1807(26)	7.00
H(19B)	6382(50)	7814(67)	1420(26)	7.00
H(19C)	5478(53)	6921(68)	1528(25)	7.00
H(20A)	5534(48)	12402(61)	894(23)	6.50
H(20B)	6471(50)	11214(61)	538(23)	6.50
H(20C)	6150(52)	11303(66)	1182(24)	6.50

[a] Thermal parameters were not refined and are of the form $\exp[-B(\sin^2\theta/\lambda^2)]$.

and zero structure factor since for these $F < \sigma(F)$, and one reflection (102) exceeded the counter capacity and was accordingly given a structure factor and weight of zero.

Solution and refinement

The remaining 1429 reflections were used to generate a three-dimensional sharpened Patterson map from which the titanium and two chlorine atoms were located. Structure factors calculated using these positions yielded an R index $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0.39. Two successive structure factor calculations interspersed with Fourier syntheses revealed the locations of all remaining nonhydrogen atoms. Refinement was by least-squares minimization of the quantity $\Sigma w|F_o^2 - s^2F_c^2|^2$, where $1/s$ is the scale factor for F_o and $w = 1/\sigma^2(F_o)^2$. In the initial least-squares cycles, positions of all nonhydrogen atoms, isotropic temperature factors for the carbon atoms, and anisotropic temperature factors for titanium and chlorine atoms were refined to an R index of 0.074. At this point a difference Fourier was generated from which all 30 hydrogen atoms were located. The titanium and chlorine atoms were then treated as anomalous scatterers using values from the "International Tables" [12], and final full matrix least-squares refinement was performed using two matrices*, one containing hydrogen coordinates, the scale factor, and anisotropic temperature factors for all nonhydrogen atoms, the other containing nonhydrogen positional parameters. Isotropic thermal parameters for the hydrogen atoms were set approximately 1 Å^2 larger than those for their respective carbon atoms, but these hydrogen thermal parameters were not refined.

The final R index was 0.032 and the goodness of fit, $[\Sigma w(F_o^2 - s^2F_c^2)/(N-P)]^{1/2}$ was 1.53 for $N = 1429$ reflections and $P = 298$ parameters**. All crystallographic computations were performed under the CRYM system [13] with an IBM 370/155 computer***. Final parameters are shown in Tables 2 and 3.

Results and discussion

The molecular configuration of $[C_5(CH_3)_5]_2TiCl_2$ is given in Fig. 1, a stereoscopic view in Fig. 2, and the packing of molecules in the unit cell is shown in Fig. 3. The geometry about the titanium atom may be viewed as a distorted tetrahedral configuration with centroid—Ti—centroid and Cl—Ti—Cl angles of 137.4(1)° and 92.94(4)°, respectively. The two π-bonded rings are staggered with centroid—Ti distances of 2.13 Å and an average Ti—C distance of 2.44 Å (Table 4), values comparable to those found for derivatives of the type $(\eta\text{-}C_5H_5)_2TiX_2$ (X = Cl, Ph, S, η^1-C_5H_5) [14-18]. Both rings are very nearly planar (maximum out-of-plane deviations < 0.03 Å) (Table 6), and the $(C\text{—}C\text{—}C)_{ring}$ bond angles range from 107.0(3)° to 109.6(3)° (Table 5) with an average angle of 108° as expected for a planar pentagon. The Ti—Cl distances of 2.352(1) and 2.346(1) Å are not unlike those reported for $[(CH_2)_3(C_5H_4)_2]TiCl_2$, 2.368(4) Å [15]; $(C_5H_5)[C_5(CH_3)_5]TiCl_2$, 2.329(8) Å [9]; and $(C_5H_5)_2TiCl_2$, 2.36 Å [14].

An interesting feature of this structure is the fact that several of the methyl groups are bent considerably out of the cyclopentadienyl plane and away from the titanium atom (Table 6) by an amount which ranges from only 2° for C(19) to as much as 19° for C(18). The trend for these out-of-plane deviations indicates that this strain results from chlorine—methyl crowding and methyl—methyl contacts between the two rings‡. Thus the 0.49 Å out-of-plane deviation for C(18) arises from crowding of its hydrogen atoms with those of C(9) and C(10) (Table 7). Smaller out-of-plane deviations of ring methyl groups (0.025-0.191 Å) have been reported for $[\eta\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CH(C_6H_5)$

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* Space limitations in the least-squares program prohibited refinement of all parameters in a single matrix.

** Structure factors calculated using the atomic coordinates and thermal parameters of the other enantiomer resulted in an increase of the R index to 0.035 and the goodness to fit to 1.73, thus indicating the original enantiomer was in fact the correct choice.

*** The table of structure factors has been deposited as NAPS Document No. 0000 (00 pages). Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting $000 for photocopies or $000 for microfiche. Advance payment is required. Make check payable to Microfiche Publications.

‡ The out of plane deviations of the methyl groups could be argued to arise through intrinsic electronic factors rather than by crowding; however, we see no compelling reason to suspect that the Ti-ring bonding is exceptional for $(C_5(CH_3)_5)_2TiCl_2$.

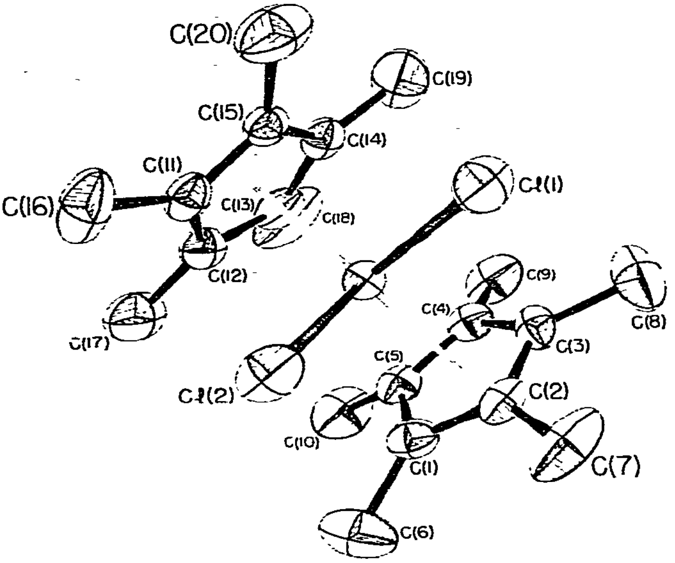

Fig. 1. The molecular configuration of $[C_5(CH_3)_5]_2TiCl_2$. In this and subsequent figures, the thermal ellipsoids are drawn at the 50% probability level [22].

[19,20]. The two shortest H—H nonbonded distances for this interaction average 2.07(7) Å, significantly less than twice the Van der Waals contact radius of a hydrogen atom (ca. 2.4 Å). C(9) and C(10) appear to distribute the strain associated with this contact and thus exhibit similar and somewhat smaller out-of-plane deviations of 0.345 and 0.332 Å, respectively. Similarly, several hydrogen—chlorine and carbon—chlorine distances smaller than Van der Waals contacts of ca. 3.0 and 3.4 Å, respectively, reflect the steric crowding and accompanying deviations from planarity exhibited by C(6), C(8), C(16), and C(20). C(7) is pushed only slightly out of the ring plane despite the fact that two of its hydrogen atoms are pointed toward the two chlorine atoms with H—Cl(1) and H—Cl(2) contacts of only 2.71(5) and 2.84(5) Å, respectively. The relatively long C(7)—Cl

(continued on p. 465)

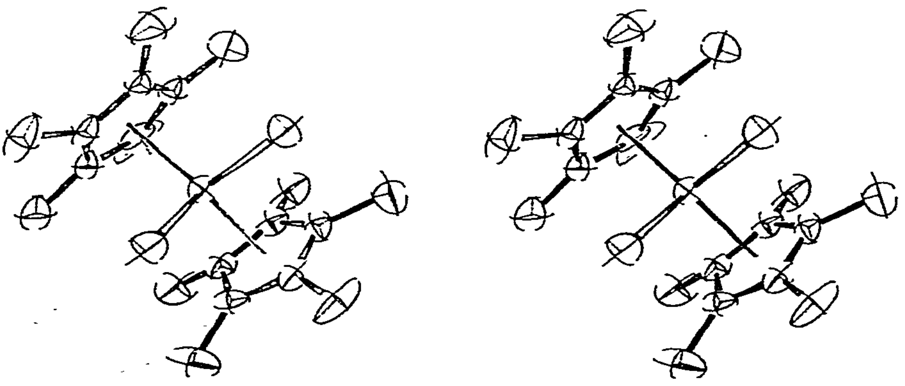

Fig. 2. Stereoscopic view of $[C_5(CH_3)_5]_2TiCl_2$. The figure is oriented to match the labeled Fig. 1.

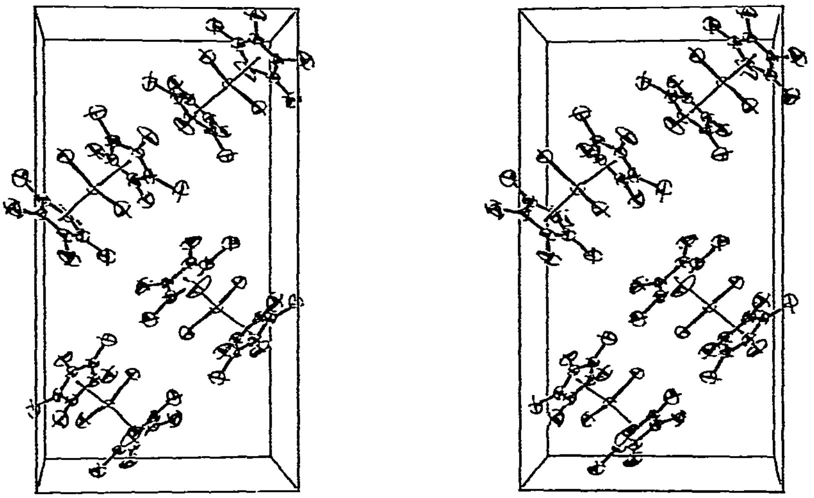

Fig. 3. Stereoscopic view of the packing of the molecules in the unit cell. Positive x runs from left to right; positive y runs from front to back; positive z runs from bottom to top.

TABLE 4

BOND DISTANCES (Å)

Ti—Cl(1)	2.352(1)	C(1)—C(2)	1.413(5)
Ti—Cl(2)	2.346(1)	C(2)—C(3)	1.416(5)
Ti—R(1)[a]	2.127(4)	C(3)—C(4)	1.402(5)
Ti—R(2)[a]	2.128(4)	C(4)—C(5)	1.420(5)
		C(1)—C(5)	1.402(5)
Ti—C(1)	2.439(4)	C(11)—C(12)	1.422(5)
Ti—C(2)	2.435(4)	C(12)—C(13)	1.409(5)
Ti—C(3)	2.455(4)	C(13)—C(14)	1.421(5)
Ti—C(4)	2.444(4)	C(14)—C(15)	1.405(5)
Ti—C(5)	2.444(4)	C(11)—C(15)	1.381(5)
Ti—C(11)	2.484(4)		
Ti—C(12)	2.415(4)		
Ti—C(13)	2.428(4)		
Ti—C(14)	2.404(4)		
Ti—C(15)	2.474(3)		
C(1)—C(6)	1.504(6)		
C(2)—C(7)	1.508(6)		
C(3)—C(8)	1.490(6)		
C(4)—C(9)	1.500(6)		
C(5)—C(10)	1.491(6)		
C(11)—C(16)	1.499(6)		
C(12)—C(17)	1.482(6)		
C(13)—C(18)	1.505(7)		
C(14)—C(19)	1.481(6)		
C(15)—C(20)	1.500(6)		

[a] R(1) = C(1)—C(5) ring centroid, R(2) = C(11)—C(15) ring centroid.

TABLE 5

BOND ANGLES (deg)

Cl(1)—Ti—Cl(2)	92.94(4)	C(12)—C(11)—C(16)	125.6(4)
R(1)—Ti—R(2)	137.4(1)	C(15)—C(11)—C(16)	126.1(4)
R(1)—Ti—Cl(1)	104.6(1)	C(11)—C(12)—C(17)	123.5(4)
R(1)—Ti—Cl(2)	104.5(1)	C(13)—C(12)—C(17)	128.0(4)
R(2)—Ti—Cl(1)	104.4(1)	C(12)—C(13)—C(18)	124.6(4)
R(2)—Ti—Cl(2)	104.4(1)	C(14)—C(13)—C(18)	125.2(4)
		C(13)—C(14)—C(19)	127.5(4)
C(1)—C(2)—C(3)	107.8(3)	C(15)—C(14)—C(19)	125.0(4)
C(2)—C(3)—C(4)	108.2(3)	C(14)—C(15)—C(20)	125.9(4)
C(3)—C(4)—C(5)	108.0(3)	C(11)—C(15)—C(20)	124.0(4)
C(4)—C(5)—C(1)	107.9(3)		
C(5)—C(1)—C(2)	108.2(3)		
C(11)—C(12)—C(13)	107.7(3)		
C(12)—C(13)—C(14)	107.7(3)		
C(13)—C(14)—C(15)	107.0(3)		
C(14)—C(15)—C(11)	109.6(3)		
C(15)—C(11)—C(12)	107.7(3)		
C(2)—C(1)—C(6)	125.3(4)		
C(5)—C(1)—C(6)	125.7(4)		
C(1)—C(2)—C(7)	127.5(4)		
C(3)—C(2)—C(7)	124.6(4)		
C(2)—C(3)—C(8)	125.5(4)		
C(4)—C(3)—C(8)	125.6(4)		
C(3)—C(4)—C(9)	122.7(4)		
C(5)—C(4)—C(9)	126.8(4)		
C(4)—C(5)—C(10)	126.1(4)		
C(1)—C(5)—C(10)	123.9(4)		

TABLE 6

LEAST-SQUARES PLANES OF CYCLOPENTADIENYL RINGS[a]

Ring I			Ring II		
Atom	Deviation (Å)	Angle (deg)[b]	Atom	Deviation (Å)	Angle (deg)[b]
C(1)	−0.003		C(11)	−0.007	
C(2)	0.007		C(12)	0.023	
C(3)	−0.008		C(13)	−0.030	
C(4)	0.007		C(14)	0.025	
C(5)	−0.022		C(15)	−0.011	
C(6)	−0.228	8.7	C(16)	−0.207	7.9
C(7)	−0.064	2.4	C(17)	−0.100	3.9
C(8)	−0.233	9.0	C(18)	−0.490	19.0
C(9)	−0.345	13.3	C(19)	−0.047	1.8
C(10)	−0.332	12.9	C(20)	−0.214	8.2

[a] A positive deviation is a deviation toward the titanium atom. [b] The angle (away from Ti) from the cyclopentadienyl ring plane.

TABLE 7

INTRAMOLECULAR NON-BONDED DISTANCES (Å) LESS THAN OR APPROXIMATING VAN DER WAALS CONTACTS[a]

C(4)—C(13)	3.233(3)	Cl(1)—C(8)	3.153(5)
C(5)—C(13)	3.267(5)	Cl(1)—C(7)	3.444(5)
C(9)—C(18)	3.305(7)	Cl(1)—C(20)	3.120(5)
C(10)—C(18)	3.422(7)	Cl(2)—C(7)	3.486(5)
		Cl(2)—C(16)	3.068(5)
H(9A)—H(18A)	2.49(7)	Cl(2)—C(6)	3.116(5)
H(9B)—H(18A)	2.10(7)		
H(10C)—H(18B)	2.05(7)	Cl(1)—Cl(2)	3.407(1)
Cl(1)—C(3)	3.012(4)	Cl(1)—H(7A)	2.71(5)
Cl(1)—C(2)	3.210(4)	Cl(1)—H(8A)	2.69(5)
Cl(1)—C(15)	3.012(3)	Cl(1)—H(20A)	2.92(5)
Cl(2)—C(1)	2.988(4)	Cl(1)—H(20C)	2.93(5)
Cl(2)—C(2)	3.208(4)	Cl(2)—H(6A)	2.94(5)
Cl(2)—C(11)	2.978(4)	Cl(2)—H(7C)	2.84(5)
		Cl(2)—H(16A)	2.64(5)
		Cl(2)—H(16B)	2.88(5)

[a] Listed are all intramolecular nonbonding distances less than 3.50 Å for C—C, 3.50 Å for Cl—C, 3.00 Å for Cl—H, 2.50 Å for H—H.

distances of 3.44(4) and 3.49(4) Å appear to indicate a reduction in crowding here, however.

Previous structure determinations for (η-C_5H_5)$_2$TiX_2 (X = Cl, Ph, S, η^1-C_5H_5) and (C_5H_5)[$C_5(CH_3)_5$]TiCl_2 have shown the cyclopentadienyl rings to be tilted at a Cp—Ti—Cp angle of 130 to 136° [9,15-18]. For [$C_5(CH_3)_5$]$_2$-TiCl_2, this angle is somewhat expanded (137.4°), apparently as a result of methyl—methyl contacts between the two rings. Further expansion is probably opposed largely by increased methyl—chlorine crowding, since the strength of the titanium—ring bonding should depend only slightly on the angle of tilt over this small range [21]. The final ring positions are thus viewed as that balance which minimizes chlorine—methyl and methyl—methyl nonbonding interactions in the molecule.

In view of the extent of intramolecular crowding, it is indeed remarkable to note that the ^{1}H NMR spectrum of [η-$C_5(CH_3)_5$]$_2$TiCl_2 remains a sharp singlet at −50°C, thus indicating that "free" rotation of rings and ring methyl groups is maintained even at this temperature [1]. This process must therefore resemble a set of rapidly turning, closely meshed gears.

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