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THE CRYSTAL AND MOLECULAR STRUCTURE OF (1,1'-TRIMETHYLENEDICYCLOPENTADIENYL)TITANIUM DICHLORIDE[*,**]

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SUMMARY

The crystal and molecular structure of (1,1'-trimethylenedicyclopentadienyl)-titanium dichloride, $[(CH_2)_3(C_5H_4)_2]TiCl_2$, has been determined from three-dimensional X-ray data collected by counter techniques. The coordination about the titanium atom is a distorted tetrahedron comprised of the two chlorine atoms and the centroids of the π-cyclopentadienyl rings of the 1,1'-trimethylenedicyclopentadienyl group. The Cl–Ti–Cl bond angle is 93.69(5)° and the (centroid)–Ti–(centroid) angle is 132.64°. The Ti–Cl bond distances are 2.372(1) and 2.364(3) Å. The titanium–(ring centroid) distances are 2.061 and 2.060 Å and the range of the Ti–C distances associated with the π-cyclopentadienyl rings, 2.407(3) to 2.360(4) Å, establishes the pentahapto coordination mode of these groups. Crystal data: $a = 8.490(2)$, $b = 14.209(4)$, $c = 10.185(2)$ Å, $\beta = 90.43(2)°$, space group $P2_1/n$, $Z = 4$, $D_o = 1.57(1)$ and $D_c = 1.57$ g·cm^{-3}. The structure was refined by least-squares techniques, using 1668 independent reflections for which $F_o^2 > 3\sigma(F_o^2)$, and the refinement converged to a conventional R factor (on F) of 2.9%.

INTRODUCTION

In a recent structural study[1] of Cp_2TiS_5[***] it was found that the two cyclopentadienyl rings exhibit different degrees of librational freedom. Concomitantly, there was an *apparent* difference in the length of the C–C bonds of the two rings such that the one with the larger torsional motion (about 12°) had a smaller C–C length (1.32 Å *vs.* 1.38 Å) than the one with the smaller (about 7°) librational motion. In order to demonstrate that this effect is an artifact of the torsional motion and in order to obtain proper values of the C–C distance for Cp compounds of the type Cp_2MX_2 (with M = a metal such as Ti, Mo, W, etc... and X a monodentate ligand) we sought a system in which torsional motional effects were minimized without having to resort to low temperature techniques. $[(CH_2)_3(C_5H_4)_2]TiCl_2$ was chosen because

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[*] Work performed under the auspices of the U.S. Atomic Energy Commission.

[**] After this manuscript was completed a short note appeared (see ref. 24), which describes the results of an electron diffraction study of Cp_2ZrCl_2. These results, where relevant, agree with ours.

[***] Cp = cyclopentadienyl

in this substance the two Cp rings are connected by a chain whose length is just about that necessary to span across two cyclopentadienyl rings canted approximately 130° to one another[1]. Therefore, the thermal motion should be intramolecularly restricted and no cooling should be necessary to reduce the librational freedom associated with the apparently low values of the C–C distances.

It is of more than passing interest that the structure of the parent compound, Cp_2TiCl_2, has not yet been studied in the crystalline state. This apparent omission may very well be connected with the fact that the crystals obtained from most solvents are twinned. Therefore, our study should provide some insight into the structural details of the parent compound, whose importance as a catalyst in the polymerization of α-olefins is well known (see, for instance, ref. 21 and references therein).

EXPERIMENTAL

The compound, $[(CH_2)_3(C_5H_4)_2]TiCl_2$, was prepared by M. Hillman and A Weiss who kindly provided samples. The crystal selected for the X-ray study was a dark red-brown parallelepiped whose dimensions were 0.58 x 0.38 x 0.33 mm along the $(\bar{1}01)$, (101), and (010) directions, respectively. A series of Weissenberg and precession photographs taken with Cu $K_{\bar{\alpha}}$ and Mo $K_{\bar{\alpha}}$ radiation showed the crystal to be monoclinic with $2/m$ Laue symmetry. The systematic extinctions were: $(h0l)$ for $h+l$ odd and $(0k0)$ for k odd. These absences are consistent with the space group $P2_1/n$, whose fourfold set of general positions is $\pm(x, y, z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$. The observed density is 1.57(1) while the calculated density is 1.57 $g \cdot cm^{-3}$ for a formula weight of 289.05 g/mol and four molecules in a unit cell of volume 1228.6 $Å^3$. The unit cell parameters of $a=8.490(2)$, $b=14.209(4)$, $c=10.185(2)$ Å, $\beta=90.43(2)°$ were obtained from a least-squares refinement of twenty sets of setting angles for reflections which were centered, at 22°, on a Picker Automated diffractometer equipped with a graphite monochromator and using Mo $K_{\bar{\alpha}}$ radiation ($\lambda=0.71069$ Å).

Data were collected with a Picker diffractometer controlled by the Brookhaven Multiple Spectrometer Control System. The scintillation counter system included a pulse height analyzer and pulse shape discriminator and was set to accept approximately 90% of the diffracted intensity. The b^* axis of the crystal coincided with the φ axis of the instrument and the data were collected using a θ–2θ step scan technique. A reflection was scanned in steps of $\Delta(2\theta)=0.02°$, with a counting time of two seconds for each step. The total scan range of $1.2(1.0+1.0 \tan\theta)$ was centered about the Bragg angle which corresponds to the unweighted average wavelength of 0.7104 Å for Mo K_{α_1} and Mo K_{α_2} radiation. The background was taken to be the total count for the five points at each end of the scan and no attempt was made to fit the data points to a polynomial. The intensities of 2754 reflections, of which 2264 were unique, were measured for $2\theta \leqslant 50.4°$. Two standard reflections were measured every 30 reflections as a check on electronic and crystal stability. Individual measurements were within 3% of the average values of these standard reflections indicating no crystal decomposition.

The data were corrected for Lorentz-polarization effects and absorption. The absorption coefficient, μ, for Mo $K_{\bar{\alpha}}$ radiation is estimated to be 11.26 cm^{-1} from the atomic absorption coefficients[2]. The absorption correction[3] was made based on the equations of the crystal faces of the form (101) and (010) and the transmission factors ranged from 0.58 to 0.70. Reflections for which equivalent forms were collected were averaged and this gave 1668 reflections for which $F_o^2 \geqslant 3\sigma(F_o^2)$ with $\sigma(F_o^2) = 1/Lp[(I+B)^2 + (0.05\ I)^2]^{\frac{1}{2}}$, where Lp is the Lorentz-polarization factor, I is the total integrated peak, and B is the time scaled background[4].

SOLUTION AND REFINEMENT

The 1668 reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used to solve and refine the structure. All least-squares refinements were carried out on F, the function minimized being $\Sigma\omega(|F_o|-|F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and $\omega = 4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factors for the titanium, chlorine, carbon, and hydrogen atoms were taken from the tabulation by Cromer[5]. The effects of anomalous dispersion ($\Delta f'$, $\Delta f''$)[6] of the titanium and chlorine atoms were included in the calculation of F_c.

A Patterson function yielded approximate coordinates for the titanium atom and the two chlorine atoms. This was followed by an observed Fourier synthesis based on F^2 which gave approximate coordinates for the thirteen carbon atoms. Two cycles of full-matrix, isotropic, least-squares refinement of the positions of the titanium atom, the two chlorine atoms, the three methylene carbon atoms, and the group parameters of the C_5H_4 rings were carried out. For the planar rigid groups, the values of the C–C and C–H bond lengths were taken as 1.419 Å and 0.98 Å, respectively. After one cycle of refinement where the titanium and two chlorine atoms were refined with anisotropic thermal parameters, the positions of the methylene hydrogen atoms were calculated assuming tetrahedral geometry about the methylene carbon atoms and a C–H distance of 0.98 Å. The methylene carbon atoms were then allowed to refine with anisotropic thermal parameters and the positions of the methylene hydrogen atoms were recalculated. Three cycles of refinement in which the sixteen non-hydrogen atoms were refined with anisotropic thermal parameters, the hydrogen atoms were not refined and assigned a thermal parameter of 6.0 Å^2, and the isotropic extinction coefficient was refined gave discrepancy factors $R_1 = 0.032$ and $R_2 = 0.045$ where $R_1 = \Sigma|(|F_o|-|F_c|)|/\Sigma|F_o|$ and $R_2 = \{\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega F_o^2\}^{\frac{1}{2}}$. In the final two cycles of refinement the titanium, two chlorine, and the thirteen carbon atoms were refined with anisotropic thermal parameters, the positional and isotropic thermal parameters of the fourteen hydrogen atoms were refined, and an isotropic extinction coefficient was refined. The refinement converged to give final values of $R_1 = 0.029$ and $R_2 = 0.040$. For the 202 variables and 1668 observations, the error in an observation of unit weight was 1.20 electrons.

The refined isotropic extinction parameter[7] corresponds to a mosaic spread parameter of 114 sec or a domain size of 3.6×10^{-6} cm depending upon whether a Zachariasen[7] type I or type II description is chosen. The calculated structure amplitudes were multiplied by the extinction correction

$$E = \left[1 + \frac{2\bar{T}\cdot F_c^2\cdot g\cdot \lambda^3(1+\cos^4 2\theta)}{12.593\ V^2\cdot 10^{-4}\cdot(\sin 2\theta)\cdot(1+\cos^2 2\theta)}\right]$$

where F_c^2 is on an absolute scale, λ is in Å, the cell volume, V, is in Å^3, $\bar{T}$ is average path length in the crystal for each reflection appropriately modified for absorption, and g (the refined extinction parameter) has the value of 510(20) e^{-2}.

TABLE 1

POSITIONAL AND THERMAL PARAMETERS

A. Fractional coordinates

Atom	x	y	z
Ti	−0.23670(5)	0.07583(3)	0.21761(4)
Cl1	−0.29165(10)	−0.05870(5)	0.08718(7)
Cl2	0.01133(9)	0.01830(6)	0.28978(8)
C1	−0.6149(4)	0.1725(2)	0.2682(4)
C2	−0.5711(4)	0.2653(2)	0.2072(3)
C3	−0.4822(4)	0.2535(2)	0.0803(3)
C1-1	−0.4811(3)	0.1151(2)	0.3216(2)
C1-2	−0.4696(4)	0.0168(2)	0.3185(3)
C1-3	−0.3403(4)	−0.0114(2)	0.3954(3)
C1-4	−0.2713(4)	0.0691(2)	0.4496(3)
C1-5	−0.3557(3)	0.1471(2)	0.4035(2)
C2-1	−0.3218(3)	0.2101(2)	0.0915(3)
C2-2	−0.2607(5)	0.1439(2)	0.0037(3)
C2-3	−0.1017(5)	0.1306(3)	0.0309(4)
C2-4	−0.0609(4)	0.1904(3)	0.1343(5)
C2-5	−0.1966(4)	0.2377(2)	0.1746(3)
H11	−0.683(5)	0.184(3)	0.349(5)
H12	−0.676(5)	0.134(3)	0.201(4)
H21	−0.505(3)	0.303(2)	0.275(3)
H22	−0.667(5)	0.305(3)	0.194(4)
H31	−0.467(4)	0.316(3)	0.039(3)
H32	−0.550(4)	0.214(3)	0.011(4)
H1-2	−0.546(3)	−0.022(2)	0.264(2)
H1-3	−0.289(4)	−0.069(2)	0.408(3)
H1-4	−0.181(4)	0.071(2)	0.504(3)
H1-5	−0.329(3)	0.214(2)	0.428(3)
H2-2	−0.315(3)	0.112(2)	−0.060(3)
H2-3	−0.041(4)	0.087(2)	−0.010(3)
H2-4	0.027(5)	0.194(3)	0.177(4)
H2-5	−0.206(4)	0.281(2)	0.242(3)

B. Thermal parameters

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti[a]	934(8)	272(2)	606(5)	10(3)	109(4)	17(2)
Cl1[a]	1848(14)	404(4)	878(8)	−44(6)	199(8)	−172(4)
Cl2[a]	1141(12)	626(5)	1200(9)	185(6)	−43(8)	216(5)
C1[b]	100(4)	65(2)	117(4)	14(3)	15(4)	−1(2)
C2[b]	136(5)	56(2)	122(4)	33(3)	10(4)	4(2)
C3[b]	149(5)	51(2)	106(4)	15(3)	−8(4)	10(2)
C1-1[b]	106(4)	46(2)	69(3)	0(2)	23(3)	−5(2)
C1-2[b]	132(5)	44(2)	89(3)	−24(2)	42(3)	−11(2)
C1-3[b]	177(6)	40(2)	78(3)	2(3)	41(3)	11(2)
C1-4[b]	158(6)	56(2)	55(3)	7(3)	8(3)	2(2)
C1-5[b]	133(5)	41(2)	64(3)	1(2)	15(3)	−10(2)
C2-1[b]	118(4)	32(2)	84(3)	3(2)	12(3)	10(2)
C2-2[b]	234(7)	44(2)	65(3)	17(3)	22(4)	13(2)
C2-3[b]	211(7)	54(2)	138(5)	36(3)	104(5)	40(3)
C2-4[b]	104(6)	58(2)	217(7)	−11(3)	11(5)	65(3)
C2-5[b]	169(6)	29(1)	114(4)	−10(2)	−2(4)	13(2)

(*Table continued*)

TABLE 1 (*continued*)

Atom	β_{11}
H11[c]	4.4(1.1)
H12[c]	2.5(1.1)
H21[c]	1.9(5)
H22[c]	4.5(9)
H31[c]	3.2(7)
H32[c]	4.1(8)
H1-2[c]	1.4(4)
H1-3[c]	2.6(6)
H1-4[c]	2.7(6)
H1-5[c]	3.0(6)
H2-2[c]	2.4(6)
H2-3[c]	2.9(6)
H2-4[c]	3.3(9)
H2-5[c]	3.7(8)

C. RMS amplitudes of vibration along the three principal axes of the thermal ellipsoid (*Å*)

Atom	Axis 1	Axis 2	Axis 3
Ti	0.165	0.169	0.194
Cl1	0.175	0.229	0.267
Cl2	0.184	0.233	0.284
C1	0.181	0.250	0.263
C2	0.181	0.250	0.275
C3	0.200	0.243	0.251
C1-1	0.163	0.212	0.223
C1-2	0.166	0.195	0.272
C1-3	0.167	0.209	0.273
C1-4	0.169	0.231	0.249
C1-5	0.166	0.213	0.226
C2-1	0.169	0.199	0.226
C2-2	0.168	0.214	0.300
C2-3	0.163	0.204	0.367
C2-4	0.161	0.208	0.376
C2-5	0.161	0.244	0.256

[a,b] Multiplied by 10^5 and 10^4, respectively. The form of the thermal ellipsoid is $\exp-[\beta_{11}\cdot h^2+\beta_{22}\cdot k^2+\beta_{33}\cdot l^2+2\beta_{12}\cdot h\cdot k+2\beta_{13}\cdot h\cdot l+2\beta_{23}\cdot k\cdot l]$. [c] Isotropic temperature factor in Å^2.

The positional and thermal parameters derived from the last cycle of refinement are presented in Table 1, along with the associated standard deviations in these parameters as estimated from the inverse of the normal equations matrix. The final value of 10 $|F_o|$ and 10 $|F_c|$ (in electrons) are given in Table 2 for the 1668 reflections which were used in the refinement.

The following programs were used: PROCH (initial processing of data); DATAPH (Lorentz-polarization and absorption corrections); ECSORTH (sorting and averaging of data); JIMDAP (local version of the Zalkin Fourier summation program); LINUS (modification of the Busing, Martin, and Levy ORFLS least-squares program)[8]; ORFFE (function and error)[9]; RBANG (rigid group parameter)[10]; PLANET (least squares planes)[11]; ORTEP (molecular plotting)[12].

TABLE 2

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

K	L	FO	SIG	FC	K	L	FO	SIG	FC	K	L	FO	SIG	FC	K	L	FO	SIG	FC	K	L	FO	SIG	FC	K	L	FO	SIG	FC	K	L	FO	SIG	FC	K	L	FO	SIG	FC	K	L	FO	SIG	FC	K	L	FO	SIG	FC
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

In the preparation of this list, the observed structure amplitude, its estimated standard deviation and the calculated structure amplitude were multiplied by 10.

DISCUSSION

The molecular configuration of $[(CH_2)_3(C_5H_4)_2]TiCl_2$ is given in Fig. 1. A stereoscopic view of the molecule is given in Fig. 2 and the packing of the molecules in the unit cell is shown in Fig. 3. A selection of bond distances and bond angles,

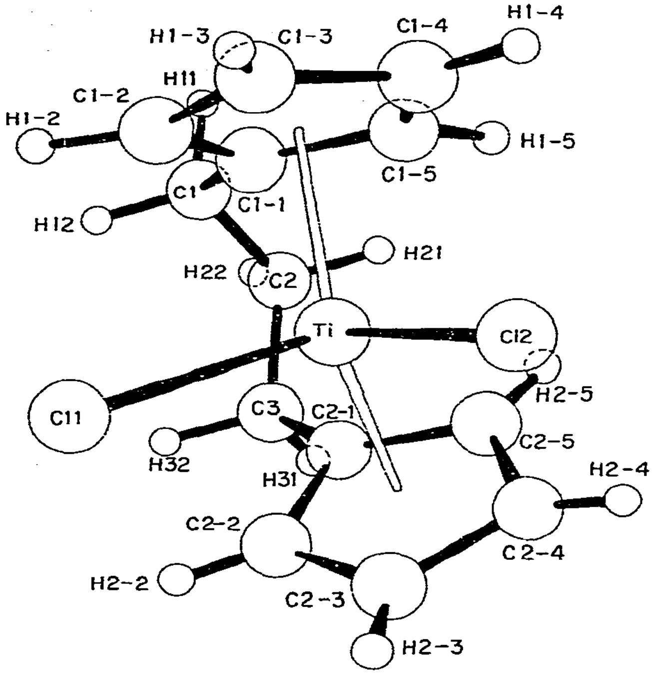

Fig. 1. The molecular configuration of $[(CH_2)_3(C_5H_4)_2]TiCl_2$. All atoms are isotropic and of arbitrary magnitude.

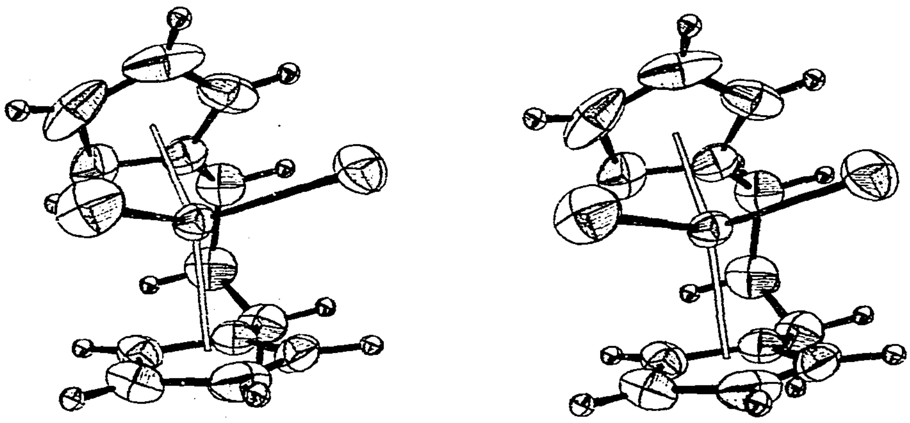

Fig. 2. Stereoscopic view of the $[(CH_2)_3(C_5H_4)_2]TiCl_2$ molecule. The Fig. is oriented to match the labelled Fig. 1, thus there is a one-to-one correspondence between Figs. 1 and 2.

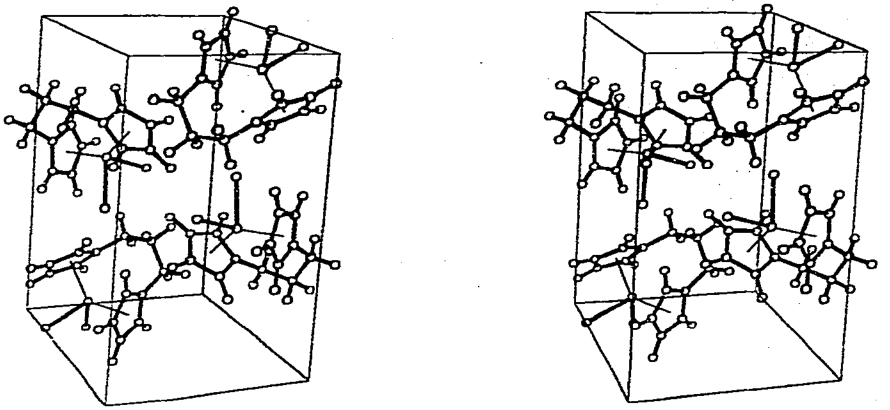

Fig. 3. The packing of the molecules in a monoclinic unit cell. The axes of the right-handed cell are as follows: positive x runs from left to right; positive y runs from the bottom to the top of the Fig.

together with estimated standard deviations which include correlation effects, is given in Table 3. Least-squares planes through selected atoms and deviations of atoms from these planes are given in Table 4. The geometry about the titanium atom may be viewed as a distorted tetrahedron with centroid–Ti–centroid and Cl–Ti–Cl angles of 132.64° and 93.69(5)°, respectively.

The Ti–Cl distances in this structure are 2.372(1) and 2.364(3) Å. In complexes for which there are no π-cyclopentadienyl groups coordinated to the titanium atom, a regular increase has been observed in Ti–Cl bond distances as the coordination number increases[13]. In tetrahedral $TiCl_4$[14], the Ti–Cl distance is 2.185 Å and in the distorted trigonal bipyramidal complex, $TiCl_2(OC_6H_5)_2$ dimer[15], they are 2.209(6) and 2.219(6) Å. In the octahedral complex $TiCl_2(C_9H_6NO)_2$[13], the Ti–Cl bond distance is 2.283(16) Å and in another octahedral complex, $[TiCl(C_5H_7O_2)_2]O\cdot CHCl_3$[16], the distances are 2.32(2) and 2.30(1) Å. When there is one π-cyclopentadienyl ring coordinated to the titanium atom, the Ti–Cl bond distances are longer than those observed in complexes which have the same geometry but contain no π-cyclopentadienyl groups. In the tetrahedral complex $[(C_5H_5)TiClO]_4$[17], the Ti–Cl bond distances are 2.263(4), 2.270(4), and 2.264(4) Å and in the octahedral complex $TiCl(C_5H_5)(C_9H_6NO)_2$[18] the distance is 2.37 Å. In $[(CH_2)_3(C_5H_4)_2]TiCl_2$ the coordination about the titanium atom is a distorted tetrahedron with two π-cyclopentadienyl groups coordinated to the titanium atom and two long Ti–Cl bonds having a mean length of 2.368 (esd 0.004) Å.

An interesting feature of this structure is the fact that the π-cyclopentadienyl rings are identical and symmetrically displaced with respect to the titanium atom. The Ti–(ring centroid) distances are both 2.06 Å and are typical of the distances found in other π-cyclopentadienyltitanium complexes[19]. The ten Ti–C distances associated with the π-cyclopentadienyl rings range from 2.360(4) to 2.407(3) Å with a mean value of 2.381 (esd 0.005) Å. This is essentially equal to the value of 2.374(5) Å found in $(C_5H_5)_2TiS_5$[1], 2.38 Å found in $(C_5H_5)_2Ti(SC_6H_5)_2$[20], and 2.38 Å found in $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$[21]. The chlorine–metal–chlorine plane in $[(CH_2)_3(C_5H_4)_2]TiCl_2$ is the approximate bisector of the centroid–metal–centroid angle of 132.6°, just as the sulfur–metal–sulfur plane is the approximate bisector in $(C_5H_5)_2Ti(SC_6H_5)_2$[20] and in $(C_5H_5)_2Mo$(3,4-toluenedithiol)[22]. The normal to the chlorine–titanium–chlorine

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (°)

A. Bond distances

Ti-Cl1	2.372(1)		
Ti-Cl2	2.364(3)		
Ti-(ring 1 centroid)	2.061(–)		
Ti-(ring 2 centroid)	2.060(–)		
Ti-C1-1	2.400(4)	C1-1-C1-2	1.401(4)
Ti-C1-2	2.384(4)	C1-2-C1-3	1.398(5)
Ti-C1-3	2.369(4)	C1-3-C1-4	1.396(4)
Ti-C1-4	2.385(4)	C1-4-C1-5	1.397(4)
Ti-C1-5	2.379(3)	C1-5-C1-1	1.419(4)
Ti-C2-1	2.407(3)	C2-1-C2-2	1.401(4)
Ti-C2-2	2.390(4)	C2-2-C2-3	1.385(6)
Ti-C2-3	2.360(4)	C2-3-C2-4	1.395(6)
Ti-C2-4	2.369(3)	C2-4-C2-5	1.396(5)
Ti-C2-5	2.367(3)	C2-5-C2-1	1.406(4)
C1-C1-1	1.494(4)	C1-H11	1.02(5)
C1-C2	1.505(5)	C1-H12	1.02(5)
C2-C3	1.511(5)	C2-H21	1.04(3)
C3-C2-1	1.495(5)	C2-H22	1.00(4)
		C3-H31	0.99(4)
		C3-H32	1.06(4)
C1-2-H1-2	1.01(3)	C2-2-H2-2	0.91(3)
C1-3-H1-3	0.94(3)	C2-3-H2-3	0.91(3)
C1-4-H1-4	0.94(3)	C2-4-H2-4	0.86(4)
C1-5-H1-5	1.01(3)	C2-5-H2-5	0.92(4)

B. Bond angles

Cl1–Ti–Cl2	93.69(5)	R1–Ti–Cl2	105.93
R1[a]–Ti–R2	132.64	R2–Ti–Cl1	105.80
R1–Ti–Cl1	106.20	R2–Ti–Cl2	105.87

[a] R_i=centroid of ring *i*

C1–C1-1–C1-2	126.1(3)	H1-2–C1-2–C1-1	121(1)
C1–C1-1–C1-5	126.8(3)	H1-2–C1-2–C1-3	130(1)
C1-2–C1-1–C1-5	106.3(3)	H1-3–C1-3–C1-2	133(2)
C1-1–C1-2–C1-3	109.1(3)	H1-3–C1-3–C1-4	119(2)
C1-2–C1-3–C1-4	108.0(3)	H1-4–C1-4–C1-3	126(2)
C1-3–C1-4–C1-5	107.8(3)	H1-4–C1-4–C1-5	126(2)
C1-4–C1-5–C1-1	108.7(3)	H1-5–C1-5–C1-4	123(2)
C3–C2-1–C2-2	124.7(3)	H1-5–C1-5–C1-1	128(2)
C3–C2-1–C2-5	127.6(3)	H2-2–C2-2–C2-1	127(2)
C2-2–C2-1–C2-5	106.9(3)	H2-2–C2-2–C2-3	124(2)
C2-1–C2-2–C2-3	109.1(3)	H2-3–C2-3–C2-2	124(2)
C2-2–C2-3–C2-4	107.6(3)	H2-3–C2-3–C2-4	129(2)
C2-3–C2-4–C2-5	108.4(4)	H2-4–C2-4–C2-3	129(3)
C2-4–C2-5–C2-1	107.8(3)	H2-4–C2-4–C2-5	122(3)
		H2-5–C2-5–C2-4	128(2)
C1-1–C1–C2	116.1(3)	H2-5–C2-5–C2-1	124(2)
C1–C2–C3	112.5(3)		
C2–C3–C2-1	116.1(3)		

(Table continued)

TABLE 3 (*continued*)

H11–C1–C1-1	103(3)	H21–C2–C1	108(2)	H31–C3–C2-1	106(2)
H11–C1–C2	110(3)	H21–C2–C3	111(2)	H31–C3–C2	110(2)
H11–C1–H12	110(4)	H21–C2–H22	103(3)	H31–C3–H32	105(3)
H12–C1–C2	109(2)	H22–C2–C1	111(2)	H32–C3–C2	111(2)
H12–C1–C1-1	109(3)	H22–C2–C3	111(2)	H32–C3–C2-1	109(2)

C. Non-bonded intramolecular contacts less than 3.5 *Å about the Ti, Cl1, and Cl2 atoms*

Ti–H1-2	3.00	Cl1–H1-2	2.87
Ti–H1-3	2.87	Cl1–H1-3	3.27
Ti–H1-4	2.95	Cl1–H2-2	2.86
Ti–H1-5	3.02	Cl1–H2-3	3.14
Ti–H2-2	2.95		
Ti–H2-3	2.87	Cl2–C1-3	3.20
Ti–H2-4	2.83	Cl2–C1-4	3.00
Ti–H2-5	2.94	Cl2–C2-3	3.22
		Cl2–C2-4	2.97
Cl1–Cl2	3.45	Cl2–H1-3	3.09
Cl1–C1-2	3.01	Cl2–H1-4	2.84
Cl1–C1-3	3.24	Cl2–H2-3	3.23
Cl1–C2-2	3.01	Cl2–H2-4	2.75
Cl1–C2-3	3.18		

D. Intermolecular contacts less than 3.50 *Å about the Cl1 and Cl2 atoms*

Cl1–H2-3	2.96	000	2[a]
Cl1–H12	3.13	$\bar{1}00$	2
Cl1–H32	2.77	$\bar{1}00$	2
Cl1–H2-2	3.43	$\bar{1}00$	2
Cl1–H21	3.47	$\bar{1}\bar{1}0$	3
Cl1–H1-5	3.39	$\bar{1}\bar{1}0$	3
Cl1–H2-5	2.87	$\bar{1}\bar{1}0$	3
Cl2–H2-3	3.23	000	2
Cl2–H31	3.47	000	4
Cl2–H21	3.13	$\bar{1}\bar{1}0$	3
Cl2–H22	3.30	$\bar{1}\bar{1}0$	3
Cl2–H31	3.39	$\bar{1}\bar{1}0$	3
H12–Cl2	3.25	$\bar{1}00$	1

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[a] The notation 000 2 indicates the second atom is in the symmetry position 2 with no cell translations. The symmetry positions 1, 2, 3, and 4 are: x, y, z; $\bar{x}, \bar{y}, \bar{z}$, $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

plane makes an angle of 24° with both Ti–centroid vectors. In $(C_5H_5)_2TiS_5$[1], where the rings were asymmetrically disposed with respect to the TiS_5 fragment, these angles were 17° and 32°.

The identical nature of the two π-cyclopentadienyl rings is further demonstrated by the RMS amplitudes of vibration for motion along the three principal axes of the thermal ellipsoid given in Table 1 and by the C–C distances associated with the rings. These distances range from 1.419(5) Å to 1.385(5) Å to give an average value of 1.399 (esd 0.003) Å. The C–C–C bond angles range from 106.3(3)° to 109.1(3)° and have an average value of 108°, as expected for a planar pentagon. The average C–C bond distance is similar to that of 1.381 Å found in $(C_5H_5)_2TiS_5$[1] for the π-cyclopentadienyl ring in which variation of the carbon–carbon bond lengths was not observed. It is

TABLE 4

PLANES[a]

A. Equations of planes and distances (Å) from these planes

a. Plane containing Ti, Cl1, and Cl2.

$0.4451\,x+0.4373\,y-0.7814\,z=-2.1613$

Ring 1 centroid	−1.88
Ring 2 centroid	1.89

b. Plane containing C1-1, C1-2, C1-3, C1-4, and C1-5.

$0.6052\,x+0.0627\,y-0.7936\,z=-4.9790$

C1-1	−0.001	H1-2	0.010
C1-2	−0.004	H1-3	0.117
C1-3	0.008	H1-4	0.010
C1-4	−0.008	H1-5	0.002
C1-5	0.004		
Ti	2.063		
C1	−0.200		

c. Plane containing C2-1, C2-2, C2-3, C2-4, and C2-5.

$0.2258\,x+0.7360\,y-0.6382=0.9815$

C2-1	0.005	H2-2	−0.014
C2-2	0.000	H2-3	−0.081
C2-3	−0.011	H2-4	−0.056
C2-4	0.018	H2-5	−0.013
C2-5	−0.010		
Ti	−2.060		
C3	0.225		

d. Plane containing Ti and the centroids of the two rings.

$-0.7405\,x-0.3142\,y-0.5941\,z=-0.1563$

Cl1	1.725
Cl2	−1.729

B. Angles (°) between the normals to planes

a–b	23.5	b–c	46.4
a–c	22.9	b–d	89.8
a–d	90.2	c–d	91.1

C. Angles (°) between interatomic vectors and the normals to planes

Vector	Plane	Angle
Ti–ring 1 centroid	a	23.9
Ti–ring 1 centroid	b	0.4
Ti–ring 2 centroid	a	23.5
Ti–ring 2 centroid	c	1.3
Cl1–Cl2	d	0.3

[a] The equations of the planes and distances and angles were obtained with the Smith plane program. Weights used in the calculation equalled $1/(EX\cdot EY\cdot EZ\cdot A\cdot B\cdot C)^{\frac{1}{3}}$ where EX, EY, and EZ equal the errors in the fractional coordinates of the atom which are listed in Table 1 and A, B, and C are the cell constants. The equation of the plane is expressed in orthogonal coordinates which are related to the fractional coordinates x, y, z by the transformation: $x=a\cdot x+c\cdot z\cdot\cos\beta$; $y=b\cdot y$; $o=c\cdot z\cdot\sin\beta$.

equal to that of 1.399 Å found in $(C_5H_5)CuP(C_6H_5)_3$[23]. This symmetrical nature of the rings is most probably due to the fact that there are no unusually close intra- or intermolecular chlorine–hydrogen contacts in this structure, (see Table 3).

In the $[(CH_2)_3(C_5H_4)_2]$ group, the average value of the methylene carbon to ring carbon bond distances is 1.495(5) Å and the methylene carbon–methylene carbon average bond distance is 1.508(5) Å. The methylene carbon atoms attached to the π-cyclopentadienyl rings are 0.2 Å out of the planes of the rings, away from the metal atom. The trimethylene bridge is apparently rather rigid and in maintaining approximate tetrahedral geometry about the methylene carbon atoms the two π-cyclopentadienyl groups are found eclipsed, rather than staggered, as may be seen by examining Figs. 1 and 2. All three carbons atoms of the exocyclic chain are to one side of the plane defined by the titanium atom and the two ring centroids, the distances being 1.67, 1.32 and 1.55 Å, respectively, for C1, C2 and C3.

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REFERENCES

1 E. F. Epstein, I. Bernal and H. Köpf, *J. Organometal. Chem.*, 26 (1971) 229.
2 *International Tables for X-Ray Crystallography*, Vol. 3, Kynoch, Birmingham, England, 1967, p. 162.
3 P. Coppens, L. Leiserowitz and D. Rabinowitz, *Acta Crystallogr.*, 18 (1965) 1035.
4 P. W. R. Corfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6 (1967) 197.
5 D. T. Cromer, to be published in the new edition of the *International Tables for X-Ray Crystallography*.
6 *International Tables for X-Ray Crystallography*, Vol. 3, Kynoch, Birmingham, England, 1967, p. 215.
7 W. H. Zachariasen, *Acta Crystallogr.*, 23 (1967) 558.
8 W. R. Busing, K. O. Martin and H. Levy, *ORFLS, A Fortran Crystallographic Least Squares Program*, ORNL-TM-305, Oak Ridge National Laboratory, 1962.
9 W. R. Busing, K. O. Martin and H. Levy, *ORFFE, A Fortran Crystallographic Function and Error Program*, ORNL-TM-306, Oak Ridge National Laboratory, 1962.
10 S. F. Watkins, Ph.D. Thesis, University of Wisconsin, 1967.
11 D. L. Smith, Ph.D. Thesis, University of Wisconsin, 1962.
12 C. K. Johnson, *ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL-3794-Revised, Oak Ridge National Laboratory, 1965.
13 B. J. Studd and A. G. Swallow, *J. Chem. Soc.*, (1968) 1961.
14 *Tables of Interatomic Distance and Configuration in Molecules and Ions*, Supplement Special Publication No. 18, Chem. Soc., London, 1965, p. M205.
15 K. Watenpaugh and C. W. Caughlan, *Inorg. Chem.*, 5 (1966) 1782.
16 K. Watenpaugh and C. W. Caughlan, *Inorg. Chem.*, 6 (1967) 963.
17 A. C. Skapski and P. G. H. Troughton, *Acta Crystallogr.*, Sect. B26 (1970) 716.
18 J. D. Matthews, *Chem. Commun.*, (1969) 883.
19 P. J. Wheatley, in J. D. Dunitz and J. A. Ibers (Eds.), *Perspectives in Structural Chemistry*, Vol. 1, Wiley and Sons, New York, N.Y., 1967, p. 1.
20 S. F. Watkins and L. F. Dahl, to be published.
21 G. Natta, P. Corradini and I. W. Bassi, *J. Amer. Chem. Soc.*, 80 (1958) 755.
22 J. R. Knox and C. K. Prout, *Acta Crystallogr.*, Sect. B25 (1969) 2013.
23 F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, 92 (1970) 2353.
24 I. A. Ronova, N. V. Alekseev, N. I. Gapotchenko and Yu. T. Struchkov, *J. Organometal. Chem.*, 25 (1970) 149.