paring the present structure with that of $Cu(PPQ)Cl_2$ it can be seen that the organic ligand maintains its geometry even if there is a substantial change in the environment of the metal, *i.e.* five-coordinate Cu(II). The dimeric character of the Co(II) complex is obviously due to the SCN groups which show a tendency to act as bridges. These groups show small distortions from linearity, as is usually observed. Their structural behaviour is particularly interesting as they are not all in the same situation: two of them act as bridges and two are terminal. This fact influences the infrared spectrum in which the bands of the two types of SCN are found: two strong ν(C–N) bands at 2085 (bridging) and 2070 cm^{-1} (terminal), two weak ν(C–S) bands at 790 (bridging) and 845 cm^{-1} (terminal) and a medium δ(NCS) at 479 cm^{-1} (terminal). These assignments are made on the basis of the observation that the C–N stretching frequency in a bridging thiocyanate group is higher than in a terminal one, while the reverse is observed for the C–S stretching (Nardelli, Gasparri, Musatti & Manfredotti, 1966).

Packing is determined by normal van der Waals contacts, the most significant of which are quoted in Table 4. The absence of hydrogen bonds can be related with the value of ν(N–H) which is higher (3260 cm^{-1}) than that observed in the Cu(II) complex (3160 cm^{-1}) where two rather strong N–H···Cl hydrogen bonds occurred.

Table 4. *Most significant van der Waals interactions* (Å)

Standard deviations are in the range 0·007–0·013 Å.

S(1)·····N(9)	3·348	C(20)···C(41)	3·299
S(1)·····N(12)	3·302	O(1)····C(30^{i})	3·330
S(3)·····N(2)	3·170	N(11)···S(2^{i})	3·354
S(3)·····N(5)	3·338	C(4)····O(2^{i})	3·191
N(6)····N(13)	3·359	N(2)····N(11^{ii})	3·377
N(6)····C(41)	3·143	N(4)····C(42^{ii})	3·179
N(13)···C(20)	3·111	O(1)····C(9^{iii})	3·253

Code for symmetry-related atoms:

Superscript	Atom at
none	$x, \quad y, \quad z$
i	$1-x, \quad \frac{1}{2}+y, \quad \frac{1}{2}-z$
ii	$x-1, \quad \frac{1}{2}-y, \quad z-\frac{1}{2}$
iii	$1-x, \quad 1-y, \quad \bar{z}$

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The Crystal and Molecular Structure of Tris(cyclopentadienyl)titanium

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Tris(cyclopentadienyl)titanium crystallizes in space group *Pbca* with $a = 13{\cdot}468$, $b = 10{\cdot}229$, $c = 17{\cdot}180$ Å and $Z = 8$. The structure has been determined from four-circle diffractometer data and refined by least-squares calculations to $R = 0{\cdot}052$ for 1461 reflexions. It consists of isolated $(C_5H_5)_3Ti$ molecules containing two normal $5e$-π-cyclopentadienyl groups with a third cyclopentadienyl ring which is bonded to the metal by two carbon atoms only. It is suggested that this group is acting as a 3-electron ligand

It is a feature of many organotitanium(III) compounds (Coutts & Wailes, 1970) that the metal atom increases its coordination number by chelation, as in $(C_5H_5)_2$–$Ti(O_2CR)$, by dimerization, as in $[(C_5H_5)_2TiCl]_2$, or by solvation. However, the physical properties of tris(cyclopentadienyl)titanium, first described by Fischer & Lochner (1960), suggest that it is monomeric. The structures of a number of other compounds containing more than two cyclopentadienyl rings around one metal atom, such as $(C_5H_5)_4Ti$ (Calderon, Cotton, DeBoer & Takats, 1971), $(C_5H_5)_3MoNO$ (Calderon, Cotton & Legzdins, 1969), and $(C_5H_5)_3In$ (Einstein, Gilbert & Tuck, 1972), have proved valuable in exploring the nature of the C_5H_5 ligand. The structure of tris(cyclopentadienyl)titanium has therefore been determined by single-crystal X-ray diffraction. A preliminary account of this work has appeared (Lucas, Green, Forder & Prout, 1973).

Experimental

$(C_5H_5)_3Ti$, prepared as dark green-black crystals by the reaction of $[(C_5H_5)_2TiCl]_2$ and NaC_5H_5 in tetrahydrofuran and purified by vacuum sublimation, was kindly supplied by Dr C. R. Lucas and Dr M. L. H. Green. Crystals suitable for X-ray work were difficult to obtain, but eventually an irregular fragment in the form of a thin, dished plate about 0·3 mm in diameter was used. The compound is very sensitive to air and moisture and was mounted under dry nitrogen in a glass capillary. It was not possible to measure its density.

Preliminary oscillation and Weissenberg photographs showed the material to be orthorhombic, mounted about [10$\bar{1}$]. The crystal was then set up on a Hilger and Watts PDP8-controlled four-circle diffractometer and accurate cell dimensions and orientation matrix obtained by a least-squares fit to the accurately determined setting angles of 20 reflexions.

Crystal data

$C_{15}H_{15}Ti$, $M=243\cdot2$.
Orthorhombic, $a=13\cdot468$ (6), $b=10\cdot229$ (5), $c=17\cdot180$ (7) Å, $U=2366\cdot8$ Å^3, space group $Pbca$ (D_{2h}^{15}, No. 61), $d_{calc}=1\cdot37$ g cm^{-3} for $Z=8$.
$F(000)=1016$. Cu $K\alpha$, $\lambda=1\cdot5418$ Å, $\mu=60$ cm^{-1}.

The intensities of at least two equivalents of each independent reflexion with $\theta\le 70°$ were measured with an $\omega/2\theta$ scan and the ordinate analysis method (Watson, Shotton, Cox & Muirhead, 1970) with 60 steps of 0·02°. The 30 consecutive steps giving the highest total count were treated as peak and the remaining 30 as background. Counting times at each step ranged from 1 to 4 s depending on the Bragg angle. Cu $K\alpha$ radiation was used with a nickel β-filter, except for data with $\theta<10°$ where balanced filters (nickel and cobalt) were used. Reflexions with intensity less than 3σ, where σ is the standard deviation based on simple counting statistics, or whose apparent centre was more than 0·2° from the predicted position were not included in subsequent calculations, which were based on the remaining 1461 independent reflexions. An empirical absorption correction was applied by the method of North, Phillips & Mathews (1968).

Structure solution and refinement

A Patterson synthesis showed that the y coordinate of the titanium atom was close to 0·25, which leads to the metal atom array halving the cell in the z direction. A Fourier synthesis phased on the metal atoms was therefore difficult to interpret on account of pseudosymmetry. A solution by weighted, multi-solution tangent refinement with the program *XTAN* (Sheldrick, 1972) was therefore attempted, with three origin-determining (722, 2,11,1, 3,10,1) and three multisolution phases (3,10,7, 1,11,1, 512). An E map (333 reflexions) calculated from the phase set with the best figure of merit after ten cycles showed the titanium and seven of the 15 carbon atoms; the remaining carbon atoms were found from a difference synthesis. This model was refined by full-matrix least-squares calculations to $R=0\cdot098$ with isotropic temperature factors, and then to $R=0\cdot063$ when anisotropic variation was permitted. A further difference synthesis placed the hydrogen atoms which were introduced into the refinement with individual isotropic temperature factors; two further cycles reduced R to its final value of 0·052. In the last stages of refinement, each reflexion was assigned a weight according to $w=(50-|F_o|+0\cdot04F_o^2)^{-1}$, which was chosen to minimize the variation of mean $w(|F_o|-|F_c|)^2$ with F_o. The final weighted R index was 0·055.

Results

The final atomic parameters are given in Table 1.* Projections of the crystal and molecular structures are shown in Figs. 1 and 2. Bonded distances and interbond angles, with estimated standard deviations calculated from the full variance–covariance matrix, and the equations of important molecular planes are given in Tables 2 and 3.

* A copy of the observed structure amplitudes and structure factors calculated from the final atomic parameters has been deposited at the British Library Lending Division, as Supplementary Publication No. 30244 (12 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates and temperature factors*

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0·3986 (1)	0·2364 (1)	0·3793 (1)	0·043 (1)	0·037 (1)	0·037 (1)	−0·003 (1)	−0·001 (1)	−0·001 (1)
C(11)	0·5465 (4)	0·3634 (6)	0·3726 (3)	0·056 (3)	0·072 (3)	0·060 (3)	−0·005 (3)	0·006 (3)	−0·020 (3)
C(12)	0·4713 (4)	0·4436 (5)	0·3464 (3)	0·075 (4)	0·040 (3)	0·077 (4)	−0·005 (3)	0·021 (3)	−0·013 (3)
C(13)	0·4322 (4)	0·3898 (5)	0·2788 (3)	0·069 (3)	0·062 (3)	0·060 (3)	0·027 (3)	0·006 (3)	−0·015 (3)
C(14)	0·4849 (5)	0·2782 (6)	0·2624 (3)	0·085 (4)	0·073 (4)	0·044 (3)	−0·004 (3)	0·017 (3)	−0·022 (3)
C(15)	0·5540 (4)	0·2603 (6)	0·3200 (4)	0·051 (3)	0·060 (3)	0·096 (5)	0·007 (3)	0·029 (3)	0·009 (3)
C(21)	0·3143 (5)	0·0384 (6)	0·4002 (4)	0·080 (4)	0·071 (4)	0·070 (4)	0·023 (3)	−0·015 (4)	−0·034 (3)
C(22)	0·3493 (4)	0·0352 (5)	0·3267 (4)	0·059 (3)	0·044 (3)	0·110 (5)	−0·029 (3)	0·017 (3)	−0·010 (3)
C(23)	0·3012 (6)	0·1313 (7)	0·2851 (4)	0·119 (6)	0·085 (5)	0·043 (3)	0·000 (3)	−0·023 (4)	−0·061 (5)
C(24)	0·2376 (5)	0·1937 (6)	0·3366 (6)	0·061 (4)	0·049 (3)	0·158 (8)	−0·023 (4)	−0·061 (5)	0·009 (3)
C(25)	0·2473 (5)	0·1335 (8)	0·4063 (4)	0·054 (4)	0·109 (6)	0·079 (4)	−0·041 (4)	0·020 (4)	−0·038 (4)
C(31)	0·3955 (5)	0·3254 (6)	0·5116 (3)	0·085 (4)	0·063 (3)	0·042 (3)	−0·015 (2)	−0·002 (3)	−0·004 (3)
C(32)	0·4606 (4)	0·2153 (6)	0·5147 (3)	0·053 (3)	0·092 (4)	0·045 (3)	−0·003 (3)	−0·011 (2)	0·000 (3)
C(33)	0·4138 (5)	0·1222 (7)	0·5615 (3)	0·076 (4)	0·091 (5)	0·048 (3)	0·011 (3)	−0·006 (3)	0·016 (4)
C(34)	0·3239 (4)	0·1706 (6)	0·5875 (3)	0·071 (4)	0·098 (4)	0·038 (3)	0·007 (3)	0·001 (3)	0·003 (3)
C(35)	0·3114 (4)	0·2943 (6)	0·5559 (3)	0·074 (3)	0·083 (4)	0·046 (3)	−0·016 (3)	0·001 (3)	0·012 (3)

Table 1 (*cont.*)

	x/a	y/b	z/c	U
H(11)	0·576 (6)	0·377 (8)	0·416 (5)	0·09 (3)
H(12)	0·455 (4)	0·507 (6)	0·369 (3)	0·04 (2)
H(13)	0·373 (4)	0·424 (5)	0·250 (3)	0·04 (1)
H(14)	0·473 (4)	0·225 (5)	0·218 (3)	0·03 (1)
H(15)	0·592 (3)	0·208 (5)	0·323 (3)	0·01 (1)
H(21)	0·334 (4)	−0·020 (5)	0·445 (3)	0·04 (1)
H(22)	0·399 (4)	−0·016 (5)	0·310 (3)	0·04 (2)
H(23)	0·310 (6)	0·143 (7)	0·244 (5)	0·08 (3)
H(24)	0·204 (5)	0·256 (7)	0·325 (4)	0·07 (2)
H(25)	0·220 (6)	0·148 (8)	0·446 (5)	0·10 (3)
H(31)	0·412 (4)	0·408 (6)	0·496 (3)	0·03 (1)
H(32)	0·528 (4)	0·214 (5)	0·499 (3)	0·03 (1)
H(33)	0·433 (4)	0·045 (6)	0·571 (3)	0·05 (2)
H(34)	0·278 (4)	0·120 (5)	0·618 (3)	0·03 (1)
H(35)	0·246 (4)	0·349 (5)	0·560 (3)	0·04 (1)

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Ti–C(11)	2·380 (5)	Ti–C(21)	2·350 (5)
Ti–C(12)	2·402 (5)	Ti–C(22)	2·344 (5)
Ti–C(13)	2·377 (5)	Ti–C(23)	2·345 (5)
Ti–C(14)	2·360 (5)	Ti–C(24)	2·331 (6)
Ti–C(15)	2·340 (5)	Ti–C(25)	2·340 (6)
Ti–C(31)	2·448 (5)	Ti···C(33)	3·346 (6)
Ti–C(32)	2·481 (5)	Ti···C(34)	3·775 (6)
		Ti···C(35)	3·307 (6)

C(11)–C(12)	1·380 (8)	C(15)–C(11)–C(12)	107·0 (6)
C(12)–C(13)	1·389 (8)	C(11)–C(12)–C(13)	108·4 (5)
C(13)–C(14)	1·373 (8)	C(12)–C(13)–C(14)	107·8 (5)
C(14)–C(15)	1·371 (9)	C(13)–C(14)–C(15)	108·2 (5)
C(15)–C(11)	1·392 (8)	C(14)–C(15)–C(11)	108·6 (6)
C(21)–C(22)	1·348 (9)	C(25)–C(21)–C(22)	109·2 (6)
C(22)–C(23)	1·378 (9)	C(21)–C(22)–C(23)	107·7 (6)
C(23)–C(24)	1·387 (10)	C(22)–C(23)–C(24)	106·7 (6)
C(24)–C(25)	1·353 (10)	C(23)–C(24)–C(25)	107·2 (6)
C(25)–C(21)	1·331 (10)	C(24)–C(25)–C(21)	109·1 (6)
C(31)–C(32)	1·428 (8)	C(35)–C(31)–C(32)	107·3 (5)
C(32)–C(33)	1·397 (8)	C(31)–C(32)–C(33)	106·4 (5)
C(33)–C(34)	1·382 (8)	C(32)–C(33)–C(34)	109·7 (6)
C(34)–C(35)	1·387 (8)	C(33)–C(34)–C(35)	107·9 (6)
C(35)–C(31)	1·402 (8)	C(34)–C(35)–C(31)	108·7 (5)

Table 3. *Mean planes through cyclopentadienyl groups*

The planes have been calculated from carbon atom positions only. In the equations, x, y and z represent fractional coordinates with respect to the crystallographic axes. The tables give the displacement (Å) of the specified atom from the plane.

Ring C(11) to C(15)

Equation of plane: $8{\cdot}882x+5{\cdot}392y-9{\cdot}207z=3{\cdot}383$

Constituent atoms		Other atoms	
C(11)	0·000	H(11)	−0·061
C(12)	0·005	H(12)	−0·011
C(13)	−0·009	H(13)	−0·085
C(14)	0·009	H(14)	0·021
C(15)	−0·005	H(15)	0·016
		Ti	−2·060

Ring C(21) to C(25)

Equation of plane: $9{\cdot}742x+6{\cdot}594y+4{\cdot}251z=5{\cdot}019$

Constituent atoms		Other atoms	
C(21)	−0·002	H(21)	−0·002
C(22)	0·005	H(22)	0·082
C(23)	−0·006	H(23)	−0·017
C(24)	0·005	H(24)	0·040
C(25)	−0·002	H(25)	−0·010
		Ti	2·037

Ring C(31) to C(35)

Equation of plane: $5{\cdot}996x+3{\cdot}990y+13{\cdot}847z=10{\cdot}749$

Constituent atoms		Other atoms	
C(31)	0·006	H(31)	0·217
C(32)	0·000	H(32)	0·176
C(33)	−0·006	H(33)	−0·064
C(34)	0·009	H(34)	−0·055
C(35)	−0·009	H(35)	−0·124
		Ti	−2·164

Discussion

The structure consists of an array of $(C_5H_5)_3Ti$ molecules with no intermolecular contacts less than 2·6 Å (no C···C contacts less than 3·6 Å). Two of the cyclopentadienyl rings are the familiar $5e$-π-systems, each making five equivalent metal–carbon contacts to the

Table 2 (*cont.*)

C(11)–H(11)	0·86 (8)	C(21)–H(21)	1·02 (6)	C(31)–H(31)	0·91 (5)
C(12)–H(12)	0·79 (6)	C(22)–H(22)	0·90 (6)	C(32)–H(32)	0·95 (5)
C(13)–H(13)	1·01 (5)	C(23)–H(23)	0·73 (8)	C(33)–H(33)	0·85 (6)
C(14)–H(14)	0·96 (6)	C(24)–H(24)	0·81 (7)	C(34)–H(34)	0·96 (5)
C(15)–H(15)	0·74 (5)	C(25)–H(25)	0·79 (9)	C(35)–H(35)	1·04 (6)

H(11)–C(11)–C(12)	122 (6)	H(11)–C(11)–C(15)	131 (6)
H(12)–C(12)–C(13)	129 (4)	H(12)–C(12)–C(11)	122 (4)
H(13)–C(13)–C(14)	127 (3)	H(13)–C(13)–C(12)	125 (3)
H(14)–C(14)–C(15)	128 (3)	H(14)–C(14)–C(13)	124 (3)
H(15)–C(15)–C(11)	124 (4)	H(15)–C(15)–C(14)	128 (4)
H(21)–C(21)–C(22)	127 (3)	H(21)–C(21)–C(25)	124 (3)
H(22)–C(22)–C(23)	127 (4)	H(22)–C(22)–C(21)	125 (4)
H(23)–C(23)–C(24)	130 (6)	H(23)–C(23)–C(22)	123 (6)
H(24)–C(24)–C(25)	130 (5)	H(24)–C(24)–C(23)	123 (5)
H(25)–C(25)–C(21)	122 (7)	H(25)–C(25)–C(24)	129 (7)
H(31)–C(31)–C(32)	126 (3)	H(31)–C(31)–C(35)	125 (3)
H(32)–C(32)–C(33)	126 (3)	H(32)–C(32)–C(31)	126 (3)
H(33)–C(33)–C(34)	123 (4)	H(33)–C(33)–C(32)	128 (4)
H(34)–C(34)–C(35)	129 (3)	H(34)–C(34)–C(33)	123 (4)
H(35)–C(35)–C(31)	127 (3)	H(35)–C(35)–C(34)	124 (3)

titanium, whilst the third is bonded to the metal by only two carbon atoms, the first observation of a cyclopentadienyl ligand in this configuration. The mean planes of the rings are perpendicular (±1·5°) to the plane containing their centroids, which also passes within 0·02 Å of the titanium.

The two $5e$-π-C_5H_5 groups, including the hydrogen atoms, are planar within experimental error (Table 3). The C–C distances range from 1·331 to 1·392 Å (individual e.s.d.'s 0·008–0·010); such a variation has often been observed and has been attributed to librational motion of the rings (Calderon, Cotton, DeBoer & Takats, 1971). This is consistent with the observation that ring C(11) to C(15) (mean C–C bond length 1·381 Å) has a smaller average temperature factor than C(21) to C(25) (mean C–C 1·359 Å), probably as a consequence of the unfavourable contacts between H(11) and H(31) and H(32) which would result from any large oscillation of ring 1.

The geometry of the $(5e$-π-$C_5H_5)_2Ti$ grouping is similar to that observed in other compounds, such as $(C_5H_5)_4Ti$ (Calderon, Cotton, DeBoer & Takats, 1971), $(C_5H_5)_2TiS_5$ (Epstein, Bernal & Kopf, 1971), and $(C_5H_5)_2Ti(C_3H_3Me_2)$ (Helmholdt, Jellinek, Martin & Vos, 1967). The titanium–carbon distances vary between 2·331 and 2·402 Å, whilst the normals from the metal to the mean ring planes are 2·060 and 2·037 Å in length and meet the rings 0·05 and 0·03 Å from their centroids; the angle between them is 133·2°. A projection of the molecule on to the plane which bisects this angle shows that the two rings adopt a staggered conformation.

The carbon atom skeleton of the odd C_5H_5 group is planar within experimental error, but H(31), H(32) and H(35) lie somewhat out of plane (Table 3, Fig. 2), though not to such an extent as to require the abandonment of the π-delocalized model for the bonding in the ring. The scatter of C–C bond lengths about their mean of 1·399 Å is on the verge of significance, but since it is no larger than that observed in the $5e$-π-systems it would be unwise to base any conclusions of a chemical nature upon it. The ring is bonded to the titanium *via* C(31) (2·45 Å) and C(32) (2·48 Å); the other Ti–C distances are greater than 3·3 Å. The two bonding distances are thus longer than those to the $5e$-π-rings and also those to the allyl carbons in bis-(π-cyclopentadienyl)-(1,2-dimethylallyl)titanium (III) (Helmholdt, Jellinek, Martin & Vos, 1967) (2·34, 2·43, 2·35 Å). Nonbonded contacts between the rings presumably make a closer approach impossible. The best plane of ring C(31) to C(35) makes an angle of 109·8° with the Ti–C(31)–C(32) plane.

It seems likely that this cyclopentadienyl group is acting as a 3-electron ligand, resulting in a 17-electron configuration for the titanium. On this basis, the bonding may be simply described in terms of the model recently proposed for bent bis-(π-cyclopentadienyl) compounds by Green, Green & Prout (1972). Nonzero overlap is permitted between ψ_0 and ψ_{-1} on the ring and ψ_B on the metal (σ-symmetry), and between ψ_{+1} on the ring and ψ_C on the metal (π-symmetry) [Fig. 3(*a*) and (*b*)]. The suggestion is therefore that one

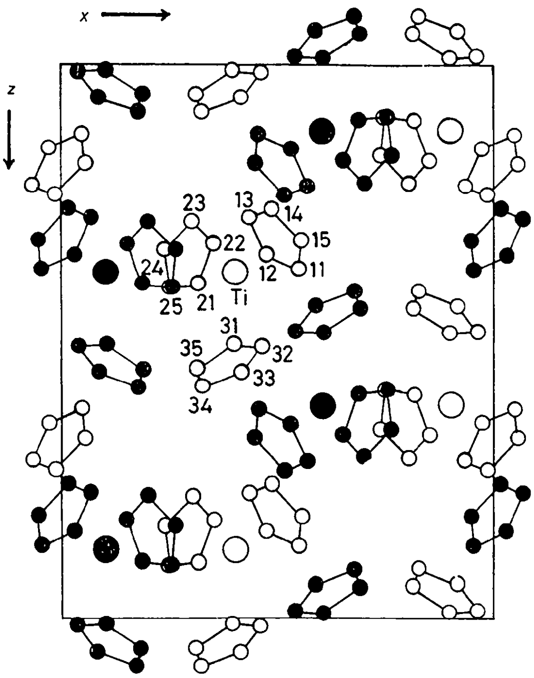

Fig. 1. The structure in projection down the y axis. The labelled atoms are those whose coordinates are given in Table 1; for clarity, hydrogen atoms have been omitted and carbon atoms referred to by their numbers only. Shaded titanium atoms are at $y/b=0·764$ and 0·736, others at $y/b=0·236$ and 0·264.

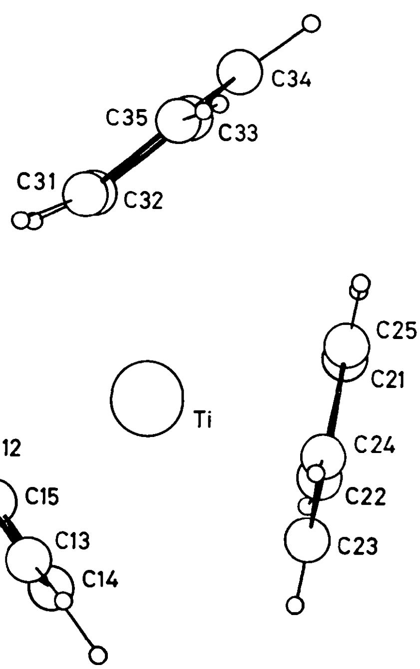

Fig. 2. The molecule projected on to the plane of the ring centroids.

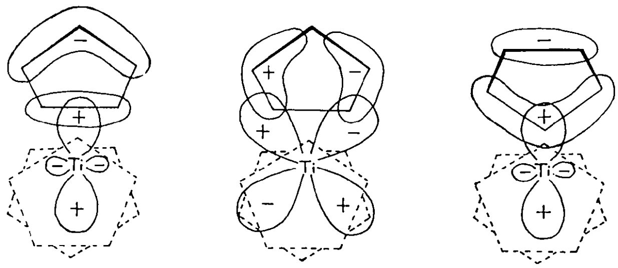

Fig. 3. (*a*) The σ-symmetry interaction between ψ_B and ψ_{-1}. (*b*) The π-symmetry interaction between $\psi_C(d_{xy})$ and ψ_{+1}. (*c*) The $\psi_B-\psi_{-1}$ interaction for the inverted configuration. ψ_B and ψ_C are the titanium orbitals and ψ_{+1} and ψ_{-1} are those of the cyclopentadienyl group. For these latter, only the part on the same side of the ligand as the titanium atom is shown.

of the molecular orbitals arising from the former interaction is localized mainly on the ligand. This might be quite similar to ψ_0, in which case little variation of C–C bond lengths around the ring would be expected, and the interaction could be simply regarded as one between ψ_{-1} and ψ_B. The resulting bonding molecular orbital, together with that from ψ_{+1} and ψ_C, then permits the formation of the postulated 3-centre, 4-electron bond.

This description of the bonding could apply equally to a hypothetical compound where the odd cyclopentadienyl group was inverted [Fig. 3(*c*)] and the bonding would mainly involve three carbon atoms in an allylic type system. However, if, as would be expected, the three carbons were essentially equidistant from the metal, it follows (Cotton, 1969) that all five metal–carbon distances would, in fact, be the same. Such a model, with three pseudo-equivalent π-cyclopentadienyl groups, would be grossly overcrowded and much less favourable than the observed configuration. Exactly comparable overcrowding would be observed in the genuine allyl complex bis-(π-cyclopentadienyl)-(1,2-dimethylallyl)titanium(III) (Helmholdt, Jellinek, Martin & Vos, 1967) if the 1-methyl group occupied the *anti*-position, and this molecule therefore adopts the *syn*-conformation.

The configuration adopted by the $3e$-π-cyclopentadienyl group in this molecule may serve as a model for the intermediate in the 1,2-shift mechanism in fluxional π-cyclopentadienyl metal systems (Bennett, Cotton, Davison, Faller, Lippard & Morehouse, 1966).

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