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STRUCTURAL STUDIES OF (π-C_5H_5)$_2$$MX_2$ COMPLEXES AND THEIR DERIVATIVES

THE STRUCTURE OF 1,1'-TRIMETHYLENEDICYCLOPENTADIENYLDICHLOROZIRCONIUM*

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Summary

1,1'-Trimethylene-π-dicyclopentadienedichlorozirconium, $(CH_2)_3(C_5H_4)_2$-$ZrCl_2$, is orthorhombic, space group *Pbca*. The unit cell dimensions found were $a = 8.277(2)$, $b = 13.922(4)$, $c = 22.568(5)$, $Z = 8$. The structure was determined from three-dimensional X-ray data (1049 independent reflections) refined to an R factor of 2.64%. The coordination about the zirconium atom is that of a distorted tetrahedron comprised of the chlorine atoms and the centroids of the π-cyclopentadienyl rings. The Cl—Zr—Cl bond angle is 96.92(7)° and the centroid —Zr—centroid angle 129.5°. The Zr—Cl bond distances found are 2.451(2) and 2.431(2) Å which are very close to the sum of the Pauling radii. Zirconium—ring centroid distances are 2.192 and 2.193 Å and the range of Zr—C distances is 2.477—2.516 Å. The carbon—carbon distances within the π-cyclopentadiene rings average 1.395(10) Å and range from 1.363(9) to 1.413(9) Å. These values establish the *pentahapto* nature of the metal—ring bonding.

Introduction

Recently, the crystal and molecular structure of $(CH_2)_3(\pi\text{-}C_5H_4)_2TiCl_2$ was studied by X-ray [1] and neutron [2] diffraction methods. In this compound the *pentahapto*-cyclopentadienyl rings are severely limited in their librational motion by the bridging methylene chain. It was found that the carbon—carbon bond distances in the rings are fairly uniform in length. In a related compound,

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(π-C_5H_5)$_2$$TiS_5$, the librational motion of the rings is rather large and so is the spread of C—C bond lengths (1.31—1.41 Å) [3]. Therefore, it was suggested [1] that thermal motion was the origin of the variations in the C—C bond distances. In order to explore this suggestion experimentally, we have initiated a study of the crystal and molecular structures of the compounds (π-C_5H_5)$_2$$MCl_2$ and $(CH_2)_3$(π-C_5H_4)$_2$$MCl_2$ (M = Ti, Zr and Hf). This report is a description of our study of the $(CH_2)_3$(π-C_5H_4)$_2$$ZrCl_2$ derivative. The structure of the unbridged, parent compound will be described in a subsequent paper. An electron diffraction study of that molecule is available [4] which is discussed in the text along with the structure of related compounds (vide infra).

Experimental

Crystals of 1,1′-trimethylenedicyclopentadienyldichlorozirconium were kindly provided by Dr. M. Hillman (Brookhaven National Laboratory). The crystals, had the shape of square antiprisms with two opposite corners cut, roughly half-way from the crystal centers. Since they were too large to use without a severe absorption problem, they were ground into spheres [5].

The crystal data are summarized in Table 1.

Results and discussion

X-ray data

The space group (Table 1) was determined from precession and Weissenberg photographs. It was found necessary to seal the spherically shaped specimen of the subject compound in a low-absorbing glass capillary tube, since it had been noticed during the preliminary film work that the crystal decomposed under the influence of X-rays in the open air. The data set was collected on a CAD-4 computer controlled four-circle diffractometer (Enraf-Nonius) using Mo-K_α radiation (λ = 0.71070 Å, graphite monochromator) at a take-off angle of 4.0°.

Previous to the gathering of intensity data an accurate set of cell parameters and a refined orientation matrix were obtained by means of the subroutines Search, Index and Detcell [6].

The unit cell dimensions given in Table 1 were refined by least-squares method [7] from a set of Bragg (θ) angles of 18 reflections accurately centered at room

TABLE 1

CRYSTAL DATA

Chemical formula	$(CH_2)_3(C_5H_4)_2ZrCl_2$
Molecular weight	332.4 g mole^{-1}
Crystal system	Orthorhombic
Cell dimensions	a = 8.277 (2), b = 13.922 (4), c = 22.568 (5) Å
Cell volume	2601 Å^3
Systematic absences	$0kl$ for $k \neq 2n$, $h0l$ for $l \neq 2n$, $hk0$ for $h \neq 2n$
Space group	*Pbca*
λ (Mo-K_{α_1})	0.71070 Å
D_c	1.714 g cm^{-3}
Z	8
μ (Mo-K_α)	12.24 cm^{-1}
$F(000)$	1328 $\bar{e}$

temperature on the diffractometer. The set of cell parameters was then used to calculate the density, $D_c = 1.714$ g cm^{-3}, and with the density the linear absorption coefficient [8], $\mu = 12.24$ cm^{-1}, was obtained.

Since the crystal system was orthorhombic, data were collected only in the *hkl* octant out to a maximum θ angle of 45°. The intensities of several equivalent reflections were determined in all octants and found to agree within about 5%. Crystal-to-counter and crystal-to-aperture distances of 208 and 173 mm, respectively, were used. Intensity data were collected by the θ—2θ scan technique using a variable 2θ scan rate ranging from a minimum of about 0.53° per minute for weak reflections to a maximum of 5.3° per minute for the strong ones. The variable angular scan width used, $0.8 + 0.4 \tan\theta$ degrees, was selected after a search for high and low angle reflections revealed that all of them had peak widths at half-height in the range of about 0.25 to 0.35°. In this way it was ensured that the whole peak and part of its background were scanned. The left and right background counts were obtained simultaneously with the peak scan being counted as the initial and final 25% of the scan. During the data collection three standard reflections of high, medium and low intensities were recorded every time a set of 32 reflections were on a common scale. The change in the intensities of the standards was small and random (maximum fluctuation about 3.4%). Of the 7857 independent reciprocal lattice points examined 1049 had intensities greater than or equal to 3σ where $\sigma = (\text{total counts} + \text{background counts})^{1/2}$ and were considered to be observed.

The data were corrected for the Lorentz and polarization effects but not extinction or absorption ($\mu R = 0.122$). The data reduction procedure was carried out with the "Data Reduction and Tape Generation" program of Ahmed and Saunderson [9].

Solution and refinement of the structure

A Patterson function was computed which gave a simple, straightforward, solution for the position of the Zr atom. Refinement of the scale factor and of the positional parameters of the heavy atom gave an R_F index of 0.39, where $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. From successive Fourier syntheses, the coordinates of the chlorine and carbon atoms were readily determined. Including the coordinates of all non-hydrogen atoms in the structure and assuming isotropic temperature factors for all of them, convergence was obtained to an R_F index of 6.13%. Anisotropic refinement, however, lowered this residual index to 3.64%.

Most of the hydrogen atoms were found on an electron-density difference synthesis map made at this point on which they appeared with peak heights having minimum and maximum values of about 0.47 and 0.62 e Å^{-3}, respectively. However, the hydrogen atom positions were idealized at distances of 0.95 Å from the carbon atoms and making the proper angles (109.5° in the case of tetrahedral carbons, etc.) with them. The hydrogens were included in subsequent structure factor calculations with their coordinates fixed and isotropic thermal parameters one unit greater than for the corresponding carbons to which they are bonded. In this way the following final set of agreement parameters were obtained. R_F 2.64% and Rw_F 2.58% where $Rw_F = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$. The goodness of fit, $[\Sigma w(\Delta|F|)^2/(m-n)]^{1/2}$, was 1.495; m is the number of observed reflections and n the number of variables refined.

The shifts applied to the parameters from cycle to cycle were damped by a factor of 0.5 to speed-up convergence [10]. In the last cycle they were on the average less than one-tenth of the corresponding standard deviation. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights given for every reflection by $w = 1/\{1 + [(|F_o| - 105.0)/40.0]^2\}$.

A final difference Fourier map was featureless with maxima and minima ranging from 0.27 to −0.35 e Å^{-3}, respectively. The atomic scattering factors for the non-hydrogen atoms used in the present structure refinement were those of Hanson, Herman, Lea and Skillman [11], and inclusion was made of the real term of an anomalous dispersion correction factor for zirconium and chlorine [12]. The hydrogen atom scattering factors used were those reported by Stewart, Davidson and Simpson [13].

The final set of coordinates and isotropic temperature parameters determined for the zirconium and all chlorine and carbon atoms is given in Table 2. Table 3 lists the anisotropic thermal parameters. The hydrogen atom coordinates together with the temperature factors assumed are presented in Table 4. Final observed and calculated structure factors are available*.

Description of the structure

The molecular configuration of $(CH_2)_3(C_5H_4)_2ZrCl_2$ appears in Fig. 1, where the numbering scheme used in the solution and refinement of its structure is also given. A stereoscopic view of the molecule is shown in Fig. 2. As suggested by the figures, the coordination of the zirconium atom is that of a distorted

TABLE 2

FINAL POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	B_{iso}
Zr	0.12043 (7)	0.15699 (4)	0.11265 (2)	2.09
Cl(1)	0.2928 (2)	0.0544 (1)	0.0503 (1)	3.75
Cl(2)	0.0001 (3)	0.0285 (1)	0.1714 (1)	4.51
C(1)	0 0551 (9)	0 3599 (5)	0 2097 (3)	4 30
C(2)	−0.0577 (9)	0.4069 (5)	0.1659 (4)	4.66
C(3)	−0.1780 (8)	0.3439 (6)	0.1355 (3)	4.84
C(4)	0.0029 (10)	0.2837 (4)	0.0478 (3)	4.42
C(5)	0.0129 (11)	0.2003 (6)	0.0134 (3)	5.14
C(6)	−0.0932 (10)	0.1341 (5)	0.0357 (3)	4.94
C(7)	−0.1711 (7)	0.1761 (5)	0.0837 (3)	4.69
C(8)	−0.1130 (9)	0.2701 (4)	0.0933 (3)	3.79
C(9)	0.1771 (7)	0.2882 (4)	0.1862 (3)	2.33
C(10)	0.2876 (8)	0.3011 (4)	0.1388 (3)	3.11
C(11)	0.3923 (8)	0.2231 (4)	0.1384 (3)	3.25
C(12)	0.3522 (8)	0.1609 (5)	0.1836 (3)	3.38
C(13)	0.2187 (9)	0.2016 (5)	0.2141 (3)	3.51

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[*] The table of structure factors has been deposited as NAPS Document No. 02440, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 3

ANISOTROPIC THERMAL PARAMETERS FOR $(CH_2)_3(C_5H_4)_2ZrCl_2$ [a]

Atom	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Zr	0.00812 (6)	0.00242 (2)	0.00113 (1)	−0.00037 (14)	−0.00042 (8)	−0.00024 (5)
Cl(1)	0.0158 (3)	0.0049 (1)	0.0020 (0)	0.0032 (3)	0.0013 (2)	−0.0017 (1)
Cl(2)	0.0218 (4)	0.0047 (1)	0.0025 (1)	−0.0085 (4)	0.0018 (2)	0.0013 (1)
C(1)	0.0190 (14)	0.0046 (5)	0.0025 (2)	0.0038 (13)	−0.0002 (8)	−0.0028 (5)
C(2)	0.0158 (14)	0.0051 (5)	0.0041 (3)	0.0045 (13)	0.0007 (10)	−0.0029 (6)
C(3)	0.0152 (12)	0.0059 (4)	0.0038 (2)	0.0080 (16)	−0.0010 (8)	−0.0027 (6)
C(4)	0.0193 (15)	0.0048 (4)	0.0021 (2)	0.0059 (14)	−0.0043 (9)	0.0004 (5)
C(5)	0.0257 (19)	0.0090 (6)	0.0015 (2)	0.0150 (18)	−0.0047 (10)	−0.0004 (5)
C(6)	0.0209 (17)	0.0062 (5)	0.0033 (2)	0.0081 (15)	−0.0103 (10)	−0.0047 (5)
C(7)	0.0094 (11)	0.0054 (5)	0.0034 (2)	−0.0004 (12)	−0.0046 (8)	0.0001 (5)
C(8)	0.0107 (10)	0.0016 (4)	0.0023 (2)	0.0033 (14)	−0.0028 (9)	−0.0003 (4)
C(9)	0.0107 (11)	0.0034 (3)	0.0015 (1)	-0.0006 (10)	−0.0020 (6)	−0.0017 (4)
C(10)	0.0122 (12)	0.0036 (3)	0.0019 (2)	−0.0028 (11)	−0.0005 (8)	−0.0009 (4)
C(11)	0.0091 (9)	0.0054 (4)	0.0021 (1)	−0.0016 (13)	−0.0010 (9)	−0.0016 (4)
C(12)	0.0138 (12)	0.0013 (3)	0.0019 (1)	0.0034 (15)	−0.0045 (7)	−0.0009 (5)
C(13)	0.0170 (14)	0.0051 (4)	0.0011 (1)	−0.0059 (13)	−0.0017 (8)	−0.0004 (14)

[a] The form of the anisotropic thermal parameters is exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE 4

HYDROGEN ATOM POSITIONAL PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS

Atom	x	y	z	B_{iso}
H(1)	−0.0127	0.3270	0.2389	5.30
H(2)	0.1131	0.4095	0.2312	5.30
H(3)	0.0092	0.4356	0.1352	5.66
H(4)	−0.1152	0.4590	0.1850	5.66
H(5)	−0.2526	0.3865	0.1140	5.84
H(6)	−0.2400	0.3134	0.1659	5.84
H(7)	0.0680	9.3434	0.0420	5.42
H(8)	0.0828	0.1880	−0.0206	6.14
H(9)	−0.1110	0.0701	0.0201	5.94
H(10)	−0.2552	0.1430	0.1086	5.69
H(11)	0.2894	0.3557	0.1108	4.11
H(12)	0.4812	0.2118	0.1104	4.25
H(13)	0.4060	0.1004	0.1931	4.38
H(14)	0.1665	0.1735	0.2486	4.51

tetrahedron comprised of bonds to two chlorine atoms and to the centroids of the π-cyclopentadienyl rings of the 1,1′-trimethylenedicyclopentadienyl group.

The distances from the heavy atom to the centroids of the cyclopentadienyl rings of 2.192 and 2.193 Å (Table 5) and the Zr—C distances associated with the five-membered rings, which are all in the narrow range of from 2.477(7) to 2.516(7) Å, establish the *pentahapto* coordination mode of these groups [14]. These zirconium to carbon distances are comparable to those reported by Bush and Sim [15] who found a mean Zr—C length of 2.50(1) Å in bis-(π-dicyclopentadienyl)difluorozirconium(IV) [$(C_5H_5)_2ZrF_2$] from X-ray diffraction studies. These

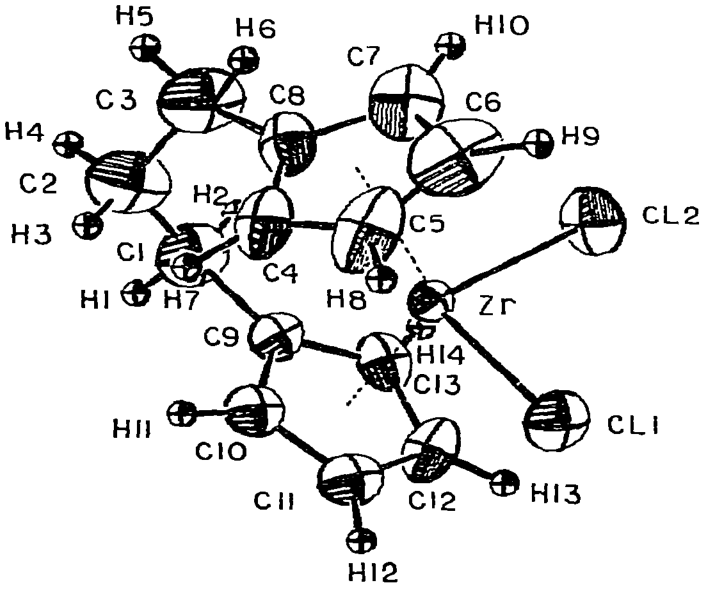

Fig. 1. Configuration of the 1,1′-trimethylenedicyclopentadienyldichlorozirconium molecule showing the numbering scheme used in the Tables.

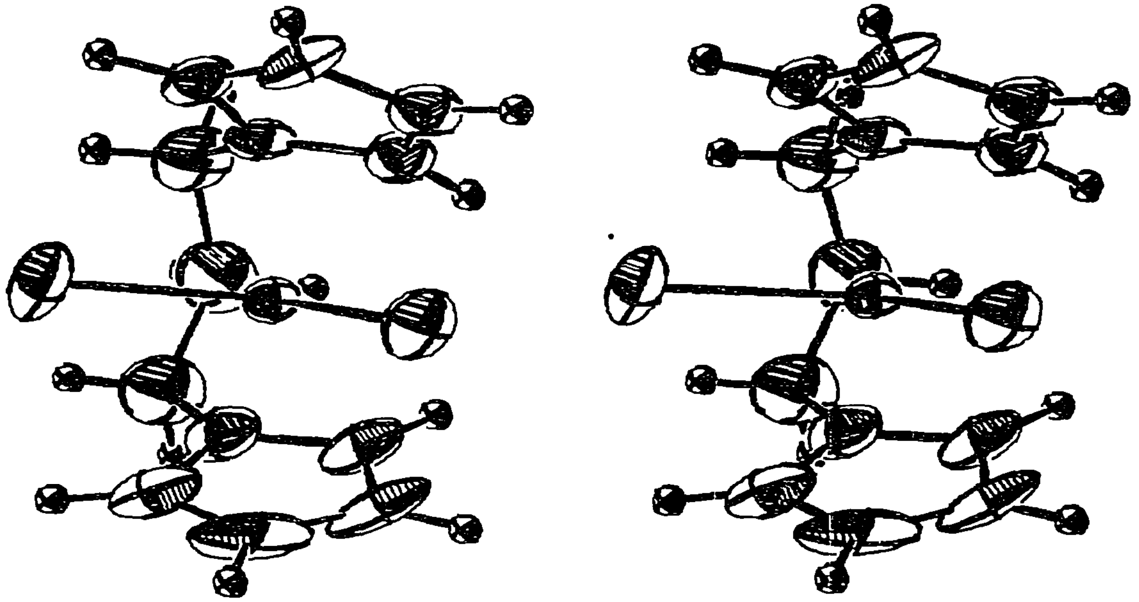

Fig. 2. Stereoscopic view of $(CH_2)_3(C_5H_4)_2ZrCl_2$

workers also obtained a mean Zr—C distance of 2.48(2) Å in the corresponding diiodo compound $(C_5H_5)_2ZrI_2$. A vapor-phase electron-diffraction study [4] of the $(C_5H_5)_2ZrCl_2$ molecule, however, gave a mean Zr—C separation of 2.522(5) Å which is slightly larger but still in substantial agreement with the values listed in Table 5. Table 6 provides further comparisons of intramolecular parameters in $(CH_2)_3(C_5H_4)_2ZrCl_2$ and several other related molecules [16, 17].

The Zr—Cl bond lengths of 2.451(2) and 2.431(2) Å, with an average of 2.441(10) Å, calculated for the title molecule are significantly longer than those reported by Ronova et al. [4], from a vapor-phase electron-diffraction study,

TABLE 5

INTERATOMIC DISTANCES (Å) AND ANGLES (°) ABOUT THE ZIRCONIUM ATOM

Bond distances			
Zr—Cl(1)	2.451 (2)	Zr—Cl(2)	2.431 (2)
av. Zr—Cl dist	2.441 (10)		
Zr—R(1) [a]	2.192	Zr—R(2) [a]	2.193
Zr—C(4)	2.482 (7)	Zr—C(9)	2.506 (6)
Zr—C(5)	2.477 (7)	Zr—C(10)	2.496 (6)
Zr—C(6)	2.487 (8)	Zr—C(11)	2.483 (7)
Zr—C(7)	2.496 (6)	Zr—C(12)	2.487 (6)
Zr—C(8)	2.516 (7)	Zr—C(13)	2.502 (6)
av. Zr—C dist. ring 1	2.492 (7)		
av. Zr—C dist. ring 2	2.495 (4)		
av. Zr—C dist. both rings	2.494 (4)		
Bond angles			
Cl(1)—Zr—Cl(2)	96.92 (7)	Cl(2)—Zr—R(1)	106.8
Cl(1)—Zr—R(1)	106.4	Cl(2)—Zr—R(2)	106.3
Cl(1)—Zr—R(2)	106.2	R(1)—Zr—R(2)	129.5

[a] R(1) and R(2) are the two rings centroids.

TABLE 6

BOND DISTANCES (Å) AND ANGLES (°) OF THE $[(CH_2)_3(C_5H_4)_2]$ GROUP

Bond distances in trimethylene group			
C(1)—C(2)			1.503 (11)
C(1)—C(9)			1.509 (9)
C(2)—C(3)			1.485 (11)
C(3)—C(8)			1.497 (10)
av. C—C dist.	1.499 (5)		
Bond distances in rings			
C(4)—C(5)	1.396 (10)	C(9)—C(10)	1.413 (9)
C(5)—C(6)	1.363 (11)	C(10)—C(11)	1.383 (9)
C(6)—C(7)	1.385 (10)	C(11)—C(12)	1.377 (9)
C(7)—C(8)	1.406 (9)	C(12)—C(13)	1.412 (9)
C(4)—C(8)	1.412 (10)	C(9)—C(13)	1.398 (9)
av. C—C dist. ring 1	1.392 (9)		
av. C—C dist. ring 2	1.397 (7)		
av. C—C dist. both rings	1.395 (5)		
Interatomic angles in trimethylene group			
C(9)—C(1)—C(2)			117.8 (6)
C(1)—C(2)—C(3)			117.2 (6)
C(2)—C(3)—C(8)			117.2 (6)
av. C—C—C angle about trimethylene carbons			117.4 (6)
C(1)—C(9)—C(10)	127.5 (5)	C(3)—C(8)—C(4)	127.6 (6)
C(1)—C(9)—C(13)	124.9 (6)	C(3)—C(8)—C(7)	127.8 (6)
av. C—C—C angle between trimethylene and ring carbons			127.0 (6)
Interatomic angles in cyclopentadienyl rings			
C(4)—C(5)—C(6)	108.5 (7)	C(9)—C(10)—C(11)	107.8 (5)
C(5)—C(6)—C(7)	107.5 (7)	C(10)—C(11)—C(12)	109.7 (6)
C(6)—C(7)—C(8)	110.7 (6)	C(11)—C(12)—C(13)	107.1 (6)
C(4)—C(8)—C(7)	104.0 (6)	C(9)—C(13)—C(12)	108.4 (6)
C(5)—C(4)—C(8)	109.3 (6)	C(10)—C(9)—C(13)	107.0 (5)
av. C—C—C angle, ring 1	108.0 (11)		
av. C—C—C angle, ring 2	108.0 (6)		
av. C—C—C angle, both rings	108.0 (6)		

but are typical of values found in other complexes in which the zirconium atom is bound to π-cyclopentadienyl groups (Table 7). Stezowski and Eick [17], for example, report a Zr—Cl distance of 2.50 Å in π-cyclopentadienylbis(acetylacetonato)chlorozirconium(IV), while Bush and Sim [15] cite a distance of 2.430(3) Å in $(C_5H_5)_2ZrCl(SiPh_3)$ obtained by Muir. As expected, the mean Zr—Cl bond length in $(CH_2)_3(C_5H_4)_2ZrCl_2$ is intermediate between the values of 1.975(5) and 2.832(2) Å obtained for the Zr—F and Zr—I distances, respectively, in $(C_5H_5)_2ZrF_2$ and $(C_5H_5)_2ZrI_2$ [15].

The Cl—Zr—Cl angle of 96.92(7)°, agrees closely with F—Zr—F and I—Zr—I angles of 96.2(3) and 96.2(1)°, respectively, reported for the difluorozirconocene and diiodozirconocene molecules [15], but not with the approximate value of 104(2)° obtained for $(C_5H_5)_2ZrCl_2$ from electron-diffraction studies [4]. Similarly, the centroid—Zr—centroid angle is smaller than the corresponding angle found for $(C_5H_5)_2ZrCl_2$ in the vapor phase, but again agrees well with those found in $(C_5H_5)ZrF_2$ and $(C_5H_5)ZrI_2$ (Table 7).

TABLE 7

INTRAMOLECULAR PARAMETERS IN SOME $(CP')_mZrXY$ COMPLEXES

Complex	Zr—X dist. (Å)	Zr—C dist. (Å)	C—C (ring) dist. (Å)	Cp—Zr—Cp angle (°)	X—Zr—X angle (°)	Ref.
$(CH_2)_3(C_5H_4)_2ZrCl_2$	2.441 (10)	2.494 (4)	1.39 (1)	129.46	96.92 (7)	This work
$(C_5H_5)_2ZrCl_2$ [a]	2.309 (5)	2.522 (5)	1.42 (1)	134 (5)	104 (2)	4
$(C_5H_5)_2ZrF_2$	1.975 (5)	2.50 (1)	1.36 (2)	127.8 (7)	96.2 (3)	15
$(C_5H_5)_2ZrI_2$	2.832 (2)	2.48 (2)	1.35 (4)	126.3 (7)	96.2 (1)	15
$(C_5H_5)_2ZrCl(SiPh_3)$	2.430	2.49 (1)				15
$(C_5H_5)(CF_3COCH_2COCF_3)_3Zr$		2.527 (6)	1.40 (2)			16
$(C_5H_5)(MeCOCH_2COMe)_2ZrCl$	2.50 (1)	2.55 (5)	1.43 (5)			17

[a] Vapour phase electron-diffraction study.

From the equation of the plane calculated through the zirconium and the two chlorine atoms: $-0.7422x - 0.081y - 0.6651z + 2.6005 = 0$, and through the zirconium and the two rings centroids: $+0.6601x + 0.0959y - 0.7451z + 1.0285 = 0$, it can be shown that the second plane is the approximate bisector of the Cl—Zr—Cl angle. Using the "Mean Plane" program of Pippy and Ahmed [18] distances out of the centroid—metal—centroid plane of 1.845 and 1.809 Å are calculated for C(11) and C(12), respectively. In the same way, the chlorine—metal—chlorine plane bisects the centroid—metal—centroid angle of 129.46°, with the ring centroids being separated by distances of 1.978 Å for the centroid of ring 1 and of 1.988 Å for that of ring 2.

Table 6 gives a list of calculated bond lengths and angles in the 1,1′-trimethylenedicyclopentadienyl group. The C—C distances range from 1.363(11) to 1.412(10) Å [average 1.392(9) Å] in ring 1 and from 1.377(9) to 1.413(9) Å [average 1.397(7) Å] in ring 2. The mean carbon—carbon bond length of 1.395 (5) Å for all ten aromatic bonds is essentially equal to the value of 1.399(5) Å found in $(CH_2)_3(C_5H_4)_2TiCl_2$ [1, 2]. This compares to the C—C distances of 1.36(2) and 1.35(4) Å obtained for $(C_5H_5)_2ZrF_2$ and $(C_5H_5)_2ZrI_2$, respectively, where there is no exocyclic carbon chain connecting the rings. It may also be compared to the average C—C distance of 1.40(2) Å in $(C_5H_5)(CF_3COCH_2COCF_3)_3$-Zr [16] and of 1.43(5) Å in $(C_5H_5)(CH_3COCH_2COCH_3)_2ZrCl$ [17]. The bond angles at the carbon atoms in both rings average 108°, the ideal value for a regular pentagon. The mean methylene-carbon to ring-carbon bond distance is 1.503(6) Å and the average methylene-carbon—methylene-carbon distance is 1.494(9) Å. These distances between sp^2 and sp^3, and between sp^3 and sp^3 types of carbon atoms are comparable to those found between similar types of atoms [1.495(5) and 1.508(5) Å, respectively] in $(CH_2)_3(C_5H_4)_2TiCl_2$ [1, 2]. Bonding angles at the *exocyclic* carbons, on the other hand, deviate considerably [average 117.4(2)°] from the expected tetrahedral value of 109.5°, indicating a fair amount of strain in the trimethylene moiety. It is apparent that those angles have to deform more in $(CH_2)_3(C_5H_4)_2ZrCl_2$, where there is a bigger atom sandwiched between the cyclopentadienyl rings than in $(CH_2)_3(C_5H_4)_2TiCl_2$. In the latter molecule, the angles about the trimethylene carbons average 114.9(3)°. All three carbon atoms of the exocyclic chain are to one side of the plane defined by the zirconium atom and the two ring centroids, the distances being 1.713(2), 1.526(8) and 1.753(8) Å respectively, for C(1), C(2) and C(3).

Cyclopentadienyl ring 1 is strictly planar and may be represented by the equation: $-0.7139x + 0.3538y - 0.6043z - 0.7233 = 0$, with a χ^2-value of 1.313 [19]. The largest displacement of a carbon atom from the mean plane is 0.005(7) Å (Fig. 3a), while the largest displacement of the idealized hydrogen ator is 0.005 Å. C(3) of the trimethylene chain, however, deviates from the plane by 0.166(7) Å which, again, indicates some degree of strain in the $[(CH_2)_3(C_5H_4)_2]$ group caused by the accomodation of the larger metal atom between the two aromatic rings.

Ring 2 is also perfectly planar, the largest deviation of any ring carbon atom from the mean plane being 0.005(7) Å (Fig. 3b). The hydrogen atoms deviate fron the plane by distances no less than 0.001 and no greater than 0.018 Å but of course were originally placed in ideal positions relative to the ring. As was found in ring 1, the exocyclic atom C(1) is out of the mean plane of the carbon atoms by 0.180(7) Å in the direction of the zirconium atom. The best-fit, mean plane, of ring 2 is represented by the equation: $-0.6247x - 0.4894y - 0.6088z - 5.4125 = 0$, with an index of planarity, χ^2, of 1.723. Rings 1 and 2 make a dihedra angle of 50.2° in this structure as compared to an angle of 46.4° in $(CH_2)_3$-$(C_5H_4)_2TiCl_2$ [1, 2] where the two aromatic rings are closer to each other.

The molecular structure of $(CH_2)_3(C_5H_4)_2ZrCl_2$ has the interesting feature that the two cyclopentadienyl rings are almost identical and symmetrically displaced with respect to the metal atom, as shown before by the equal Zr—ring centroid distances and the narrow range of Zr—C distances. This is further illustrated by the fact that the angles between the chlorine—metal—chlorine mean plane and the planes of rings 1 and 2 are 25.5 and 24.7°, respectively. That is, the Cl—Zr—Cl plane not only bisects the centroid—metal—centroid angle but also the dihedral angle between the rings. This symmetrical disposition of the two cyclopentadienyl moieties about the heavy atom is attributed to the fact that there are no unusually short intra- or inter-molecular contacts in the structure (Table 8). It should also be mentioned that the two rings are eclipsed in the molecule as may be seen by examining Figs. 1 and 2, and by the fact that

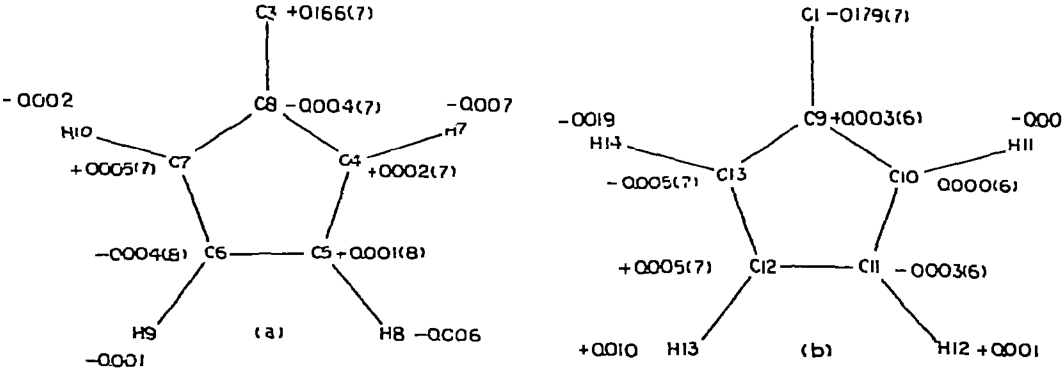

Fig. 3 Displacements in Ångstroms of atoms from the best-fit mean plane through the cyclopentadiene rings. Ring 1, (a). Ring 2, (b). The e.s.d.'s are given in parentheses.

TABLE 8

NONBONDED INTRA- AND INTER-MOLECULAR CONTACTS OF LESS THAN 3.60 Å ABOUT THE ZIRCONIUM AND CHLORINE ATOMS

Intramolecular distances (Å)

Zr—H(7)	3.07	Zr—H(11)	3.09
Zr—H(8)	3.05	Zr—H(12)	3.06
Zr—H(9)	3 07	Zr—H(13)	3.07
Zr—H(10)	3.09	Zr—H(14)	3.09
Cl(1)—C(12)	3.65	Cl(2)—C(6)	3.48
Cl(1)—C(5)	3 17	Cl(2)—C(7)	3.17
Cl(1)—C(6)	3 38	Cl(2)—C(12)	3.44
Cl(1)—C(11)	3.18	Cl(2)—C(13)	3.15
Cl(1)—C(2)	3.38	Cl(2)—H(9)	3.58
Cl(1)—H(8)	2.99	Cl(2)—H(10)	2.99
Cl(1)—H(9)	3.39	Cl(2)—H(13)	3.51
Cl(1)—H(12)	3 00	Cl(2)—H(14)	2.99
Cl(1)—H(13)	3.41		

Intermolecular contacts about Cl(1) and Cl(2)

Cl(1)—H(9)	2.78	100 1 [a]
Cl(1)—H(7)	3.38	100 5
Cl(1)—H(3)	3.00	000 3
Cl(1)—H(7)	3.15	000 3
Cl(1)—H(11)	3.25	000 3
Cl(2)—H(4)	3.32	000 3
Cl(2)—H(5)	3.11	000 3
Cl(2)—H(11)	3.26	000 3
Cl(2)—H(1)	3.45	100 2
Cl(2)—H(4)	3 50	100 2
Cl(2)—H(2)	2.90	000 2
Cl(2)—H(13)	3.30	000 4

[a] The notation 100 1 indicates that the first atom is in symmetry position 1 translated one unit cell along the x direction. The symmetry positions 1, 2, 3, 4 and 5 are, respectively, x, y, z; $x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}-x, \frac{1}{2}+y, z$; $\frac{1}{2}+x, y, \frac{1}{2}-z$; $\frac{1}{2}+x, \frac{1}{2}+y, z$

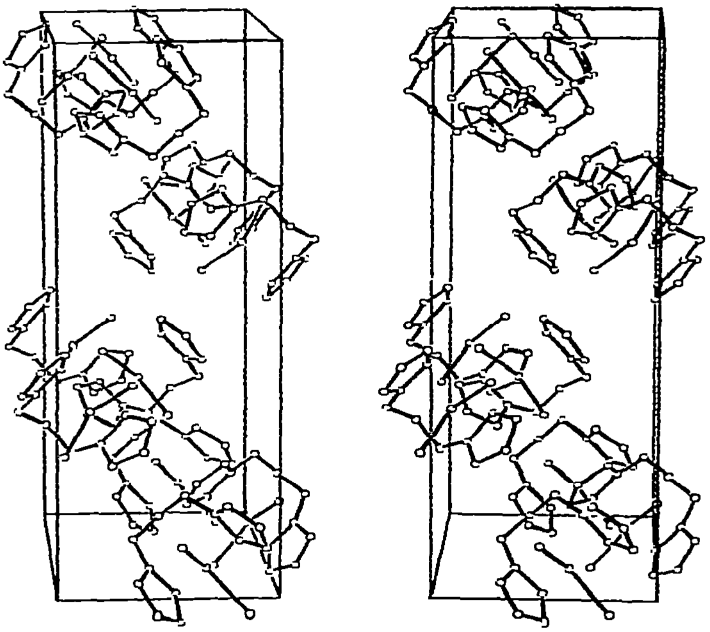

Fig. 4. Stereoscopic view of packing in the $(CH_2)_3(C_5H_4)_2ZrCl_2$ unit cell.

the distances of atoms C(4) through C(13) from the centroid—metal—centroid plane are correspondingly equal in the two rings. A packing diagram of the molecules in the unit cell of $(CH_2)_3(C_5H_4)_2ZrCl_2$ is shown in Fig. 4.

A full discussion of the effect of thermal motion on the magnitude of the ring carbon—carbon distances will be deferred until the projected study of the remaining cyclopentadiene compounds is completed. However, it is of interest to note that the spread in the C—C bond lengths for $(C_5H_5)_2ZrF_2$ and $(C_5H_5)_2$-ZrI_2 is about twice that observed for the subject compound. This is in substantial agreement with results quoted in the introduction for analogous titanium compounds.

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