Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE STRUCTURE OF BIS(CYCLOOCTATETRAENE)(TETRAHYDROFURAN)ZIRCONIUM

DAVID J. BRAUER and CARL KRÜGER
Max-Planck-Institut für Kohlenforschung 433 Mülheim/Ruhr, Lembkestrasse 5 (Germany)

(Received March 13th, 1972)

SUMMARY

The structure of bis(cyclooctatetraene)(tetrahydrofuran)zirconium, $(C_8H_8)_2$-$Zr(C_4H_8O)$, has been determined from 1600 non-zero, single crystal X-ray data collected at room temperature by counter methods. The molecule crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell of dimensions:

$$a = 18.0655(4), \quad b = 10.6894(4), \quad c = 8.6810(5)\ \text{Å}$$

The calculated density is 1.472 g/cm^3. Using anisotropic thermal parameters the structure was refined by least-squares techniques to a conventional discrepancy index of 0.048. In the crystal the molecule exists as discrete units with an h^8-C_8H_8 ring, an h^4-C_8H_8 ring and a C_4H_8O group bonded to the zirconium atom. The h^8-C_8H_8 ligand is planar, and the C–C and Zr–C bond lengths do not deviate significantly from their average values of 1.374(15) and 2.461(7) Å, respectively. The Zr–C bond lengths of 2.849(14), 2.399(18), 2.315(17), and 2.584(12) Å indicate a distorted "butadiene" bonding mode for the h^4-C_8H_8 ring. The Zr–O distance of 2.447(4) Å is very long.

INTRODUCTION

Cyclooctatetraene (COT) is known to show a variety of different bonding modes to transition metals. A review on this subject has been published[1]. Recently a number of bis(COT)metal complexes have been prepared, and some of their structures have been established by X-ray and IR techniques. The compounds of the lathanides and actinides [K(COT)$_2$Ln[2]; (COT)$_2$U[3]] apparently possess sandwich structures. The structures of (COT)$_2$Ti[4] and (COT)$_2$Fe[5] have been reported. Neither structure is of good quality, either because of high thermal motion or because of disorder of the COT groups, but the latter reveals an h^6-COT and an h^4-COT simultaneously bonded to the iron atom. The structure of (COT)$_3$Ti$_2$ is known as well[6]; here two different types of COT bonding were also found. Each titanium atom is symmetrically coordinated to a planar COT ligand; the third COT ligand acts as a bridging group between the two metal atoms.

A number of COT complexes of zirconium have been prepared in this laboratory in order to compare their chemistry to the corresponding titanium[7,8] compounds.

We have undertaken a crystallographic investigation of some of these, and we wish to report the results of the first of these studies, *viz.* the crystal structure of $(COT)_2Zr \cdot THF$ (THF = tetrahydrofuran).

EXPERIMENTAL

A deep red crystal, kindly supplied by Dr. J. Kablitz of our institute, of the extremely oxygen- and moisture-sensitive compound $(COT)_2Zr \cdot THF$ was mounted in a glass capillary under dry, THF-saturated argon. The space group and initial cell data were determined from precession and Weissenberg photographs. The crystal was transferred to an automated diffractometer (PDP-8 + Siemens-Hoppe) and mounted with c^* coincident to the φ axis. The lattice constants, which appear with other crystal data in Table 1, were refined by a least-squares treatment using the 2θ maxima of 42 reflections as a basis.

TABLE 1

CRYSTAL DATA

Formula $C_{20}H_{24}OZr$
Molecular weight 371.64
Color red
Habit rectangular block
Crystal size 0.26 × 0.26 × 0.75 mm
Crystal system orthorhombic
Wavelength (Mo–$K\alpha$) 0.71069 Å

Temp. 22°
Unit cell: $a = 18.0655(4)$ Å
$b = 10.6894(4)$ Å
$c = 8.6810(5)$ Å
$V = 1676.4$ Å^3
$Z = 4$

d (calcd.) 1.472 g/cm^3
$\mu = 6.461$ cm^{-1}
Systematic absences $h00$, $h = 2n+1$
$0k0$, $k = 2n+1$
$00l$, $l = 2n+1$
Space group D_2^4 $P2_12_12_1$

One octant of intensity data ($2\theta \leqslant 50°$) was collected and reduced to F's as described previously[9]. The fluctuations of the monitor reflection, which was measured after each batch of twenty reflections, were small and random. Of the 1716 reflections measured, 7 exceeded the linearity of our counter and 10 were shown to suffer from counter errors, severe missetting, or white streak distortions; therefore, these 17 reflections were excluded from the data set. Of the remaining 1699 data, 1600 had intensities greater than $2\sigma(I)$, and only these were used in the subsequent analysis. These observed reflections were assigned weights based solely on Poisson statistics.

The structure was solved by the heavy-atom method. The position of the zirconium atom was derived from a sharpened Patterson map. An electron density synthesis clearly revealed the positions of the heavy atoms of the THF group; however, those of the COT rings were more difficult to locate.

The structure was refined by full-matrix least-squares techniques. The function minimized was $w \cdot (|F_o| - s \cdot |F_c|)^2$ where $w = 1/\sigma^2(|F_o|)$. The scattering factors for Zr^0, O, and C were those of Cromer[10], and anomalous scattering factors of Zr[11] were applied to the calculated structure factors. Isotropic refinement reduced the discrepancy indices $R_1 = \Sigma(|F_o| - s \cdot |F_c|)/\Sigma|F_o|$ and $R_2 = [\Sigma w \cdot (|F_o| - s|F_c|)^2/\Sigma w \cdot |F_o|^2]^{0.5}$ to 0.107 and 0.129 respectively. A difference Fourier map showed peaks as large as 1.0 e/Å^3 between each COT ring atom and the need for anisotropic temperature factors for the remaining atoms. Further cycles of least-squares refinement with all atoms given anisotropic temperature factors reduced R_1 and R_2 to 0.0479 and

0.0450, respectively. The final value for the error of fit was 4.32 which implies that the weights chosen for the reflections were too small. The absolute configuration of the molecule was established as that indicated by the positional parameters since an analogous refinement with the opposite value of $\Delta f''$ for zirconium yields a final R_2 of 0.0521[12]. A final difference Fourier calculation gave no consistent evidence for hydrogen atom positions and contained densities ranging from -0.61 e/Å^3 to 0.36 e/Å^3. On earlier electron density maps, peak maxima of the COT carbon atoms ranged between 3 and 6 e/Å^3. The final positional and thermal parameters are listed in Table 2, bonded and nonbonded distances are given in Table 3, and bond angles are shown in Table 4. The numbering system is defined by Fig. 1. The results of best weighted least-squares plane calculations are given in Table 5.

The stereoscopic drawing (Fig. 2) illustrates the relatively high thermal displacements for the COT and THF atoms. The average value for the maximum root-mean-square displacements of these atoms is 0.45 Å, the individual values ranging from 0.27 to 0.58 Å. While our neglect of an absorption correction ($\mu = 6.161$ cm^{-1}) should bias our derived thermal parameters to some extent, similar compounds also show large thermal motion. This feature has been ascribed to either disorder or reorientation of the ligand as well as ring torsions. Since ring torsions can be interpreted as rigid body motions. we analyzed the thermal parameters of the individual ligands with the rigid body motion treatment of Shomaker and Trueblood[13]. Physically reasonable results were obtained only for the Zr, C(11)–C(18) system. The average of the C–C bond length correction was 0.043 Å.. Considering the relatively low precision of our carbon thermal parameters, we must treat the rigid body assumption and the derived bond length corrections with caution. All bond lengths in Table 3 are therefore not corrected for rigid body librations.

RESULTS AND DISCUSSION

The structure of the molecule (COT)$_2$Zr·THF is shown in Figs. 1 and 2. The disposition of ligands about the zirconium atom may be described approximately

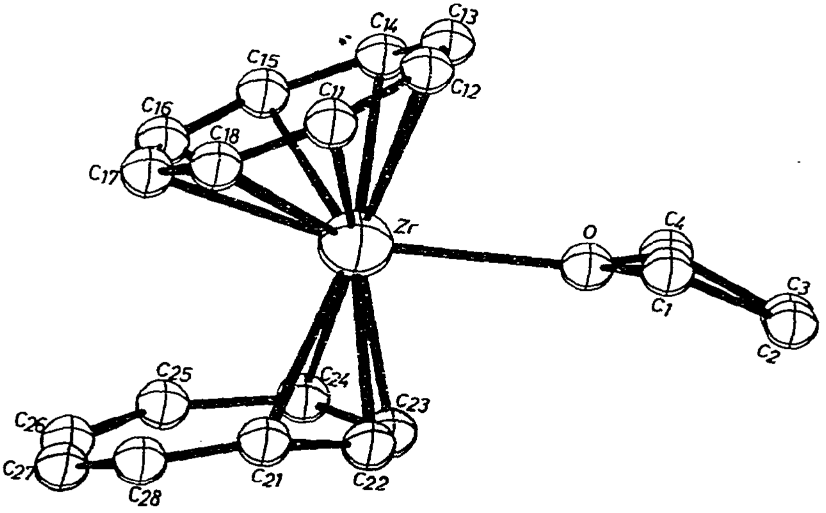


Fig. 1. A drawing of the $(C_8H_8)_2Zr \cdot THF$ molecule with arbitrary spheres.

TABLE 2

POSITIONAL AND THERMAL PARAMETERS FOR $(C_8H_8)_2Zr\cdot THF$

Atom	x	y	z	U_{11}^a	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	0.38195(4)	0.13207(7)	0.45758(9)	0.0382(4)	0.0349(4)	0.0366(4)	−0.0005(5)	0.0092(5)	0.0028(5)
C(11)	0.5128(9)	0.194(3)	0.474(2)	0.07(1)	0.17(2)	0.08(1)	−0.05(1)	−0.02(1)	0.05(1)
C(12)	0.5129(9)	0.099(2)	0.374(3)	0.06(1)	0.12(2)	0.17(2)	0.03(9)	0.06(1)	0.06(1)
C(13)	0.467(2)	0.064(1)	0.250(3)	0.14(2)	0.09(1)	0.12(2)	−0.02(1)	0.09(1)	−0.01(1)
C(14)	0.403(2)	0.110(3)	0.179(2)	0.16(2)	0.18(2)	0.034(7)	−0.09(2)	0.02(1)	−0.01(1)
C(15)	0.365(1)	0.217(3)	0.197(3)	0.07(1)	0.25(3)	0.11(2)	−0.03(2)	0.00(1)	0.12(2)
C(16)	0.368(1)	0.318(3)	0.293(4)	0.13(2)	0.12(2)	0.19(3)	0.05(2)	0.10(2)	0.12(2)
C(17)	0.415(2)	0.351(1)	0.423(3)	0.19(2)	0.032(7)	0.17(2)	−0.01(1)	0.15(2)	−0.01(1)
C(18)	0.473(1)	0.299(2)	0.495(2)	0.13(2)	0.11(2)	0.15(2)	−0.07(1)	0.05(2)	0.01(2)
C(21)	0.3662(9)	0.213(2)	0.768(2)	0.09(1)	0.16(1)	0.060(9)	0.00(1)	0.006(8)	0.05(1)
C(22)	0.338(1)	0.103(2)	0.716(2)	0.13(1)	0.10(1)	0.10(1)	0.05(1)	0.09(1)	0.07(1)
C(23)	0.2818(9)	0.071(1)	0.606(2)	0.08(1)	0.064(8)	0.15(2)	−0.033(8)	0.09(1)	−0.04(1)
C(24)	0.2406(7)	0.149(2)	0.498(2)	0.044(7)	0.19(2)	0.10(1)	−0.07(1)	0.033(7)	−0.09(1)
C(25)	0.2226(6)	0.283(2)	0.499(1)	0.068(8)	0.15(1)	0.06(1)	−0.036(9)	0.018(6)	−0.012(9)
C(26)	0.2388(6)	0.378(1)	0.596(2)	0.058(7)	0.10(1)	0.10(1)	0.14(8)	0.030(7)	0.030(9)
C(27)	0.2884(8)	0.395(1)	0.719(2)	0.10(1)	0.064(9)	0.08(1)	−0.015(7)	0.037(8)	−0.003(7)
C(28)	0.3426(9)	0.330(2)	0.781(2)	0.11(1)	0.14(2)	0.08(1)	−0.01(1)	0.021(9)	0.01(1)
C(1)	0.4494(6)	−0.1623(9)	0.561(1)	0.090(7)	0.064(7)	0.15(1)	0.016(6)	−0.063(8)	0.026(8)
C(2)	0.4180(6)	−0.2929(9)	0.582(1)	0.117(9)	0.054(6)	0.09(1)	−0.011(6)	−0.050(7)	−0.001(6)
C(3)	0.3543(6)	−0.3038(8)	0.472(2)	0.103(8)	0.047(6)	0.15(1)	0.001(5)	−0.048(9)	0.034(8)
C(4)	0.3501(6)	−0.1840(8)	0.377(1)	0.098(8)	0.044(5)	0.084(7)	−0.003(5)	−0.047(6)	−0.013(5)
O	0.3931(3)	−0.0954(4)	0.4774(7)	0.055(3)	0.041(3)	0.070(4)	0.003(3)	−0.006(4)	−0.005(3)

[a] The form of the anisotropic thermal ellipsoid is: $\exp[-2\pi^2\cdot(U_{11}\cdot h^2\cdot a^{*2}+U_{22}\cdot k^2\cdot b^{*2}+U_{33}\cdot l^2\cdot c^{*2}+2U_{12}\cdot h\cdot k\cdot a^*\cdot b^*+2U_{13}\cdot h\cdot l\cdot a^*\cdot c^*+2U_{23}\cdot k\cdot l\cdot b^*\cdot c^*)]$.

TABLE 3

INTERATOMIC DISTANCES (Å) IN $(C_8H_8)_2ZrTHF$

Bonded distances					
Zr–C(11)	2.46(2)	C(11)–C(12)	1.34(3)	C(25)–C(26)	1.36(2)
Zr–C(12)	2.50(2)	C(11)–C(18)	1.34(3)	C(26)–C(27)	1.41(2)
Zr–C(13)	2.48(2)	C(12)–C(13)	1.42(3)	C(27)–C(28)	1.32(2)
Zr–C(14)	2.46(1)	C(13)–C(14)	1.39(3)	O–C(1)	1.44(1)
Zr–C(15)	2.46(2)	C(14)–C(15)	1.35(4)	O–C(4)	1.50(1)
Zr–C(16)	2.46(3)	C(15)–C(16)	1.36(4)	C(1)–C(2)	1.52(1)
Zr–C(17)	2.43(1)	C(16)–C(17)	1.45(4)	C(2)–C(3)	1.49(2)
Zr–C(18)	2.45(3)	C(17)–C(18)	1.35(3)	C(3)–C(4)	1.53(1)
Zr–C(21)	2.85(1)	C(21)–C(22)	1.36(3)		
Zr–C(22)	2.40(2)	C(21)–C(28)	1.33(3)		
Zr–C(23)	2.32(2)	C(22)–C(23)	1.44(3)		
Zr–C(24)	2.58(1)	C(23)–C(24)	1.45(2)		
Zr–O	2.447(4)	C(24)–C(25)	1.47(3)		
Selected[a] nonbonded distances					
C(12)–C(1)	3.43(2)	C(17)–C(28)	3.38(3)	C(24)–C(4′)	3.69(2)
C(13)–O	2.93(2)	C(18)–C(21)	3.20(3)	C(25)–C(4′)	3.69(2)
C(13)–C(1)	3.64(2)	C(23)–O	2.90(2)	C(26)–C(4′)	3.58(2)
C(13)–C(4)	3.56(2)	C(23)–C(4)	3.59(2)	C(27)–C(3′)	3.53(2)
C(14)–C(4)	3.71(2)	C(23)–C(4′)[b]	3.56(2)	C(27)–C(4′)	3.64(2)
C(16)–C(25)	3.20(3)				

[a] Only those contacts less than the following Van der Waals radii are included: CH (1.70 Å), CH_2 (2.00 Å), O (1.40 Å). [b] The positions of the primed atoms are related to those in the asymmetric unit as follows: $x', y', z' = \frac{1}{2}-x, -y, \frac{1}{2}+z$.

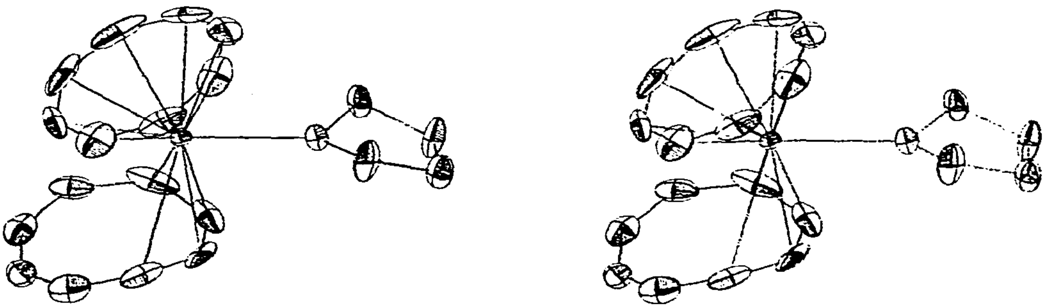


Fig. 2. A stereodrawing of $(C_8H_8)_2Zr \cdot THF$ with 20% probability thermal ellipsoids.

as octahedral with a planar COT ring, four carbon atoms of the second COT ring, and the THF oxygen atom occupying a face, a corner, and an edge of the octahedron, respectively. The COT ligands are essentially eclipsed, and the dihedral angle between their two coordination planes is 146.2°. The molecule possesses approximate $C_s(m)$ symmetry, the mirror plane passing through the Zr and O atoms and the midpoints of the bonds C(12)–C(13), C (16)–C(17), C(22)–C(23), C(26)–C(27), C(2)–C(3).

The variation of C–C bond lengths, the deviations from planarity, and the spread of Zr–C distances are not significant for the h^8-COT ligand. The weighted

TABLE 4

BOND ANGLES (°) FOR $(C_8H_8)_2Zr \cdot THF$

C(12)–C(11)–C(18)	136(2)	C(24)–C(25)–C(26)	134(1)
C(11)–C(12)–C(13)	134(2)	C(25)–C(26)–C(27)	135(1)
C(12)–C(13)–C(14)	137(2)	C(26)–C(27)–C(28)	136(1)
C(13)–C(14)–C(15)	132(2)	C(27)–C(28)–C(21)	135(2)
C(14)–C(15)–C(16)	136(2)	Zr–O–C(1)	125.9(5)
C(15)–C(16)–C(17)	133(2)	Zr–O–C(4)	122.9(5)
C(16)–C(17)–C(18)	136(2)	C(1)–O–C(4)	110.2(6)
C(17)–C(18)–C(11)	134(2)	O–C(1)–C(2)	104.5(8)
C(22)–C(21)–C(18)	136(2)	O–C(4)–C(3)	100.9(7)
C(21)–C(22)–C(23)	134(2)	C(1)–C(2)–C(3)	106.6(8)
C(22)–C(23)–C(24)	131(1)	C(2)–C(3)–C(4)	108.4(8)
C(23)–C(24)–C(25)	132(1)		

TABLE 5

BEST WEIGHTED[a] LEAST-SQUARES PLANES FOR $(C_8H_8)_2Zr \cdot THF$

Plane	*Equation of plane*[b]	x^2
1	$-0.60476x-0.48870y+0.62884z-4.04713=0$	9.5
2	$-0.72494x+0.07778y+0.68440z-0.06127=0$	5.0
3	$-0.67701x-0.27732y+0.68173z-0.52111=0$	129.0
4	$0.67072x+0.02276y-0.74136z+1.71510=0$	152.7

Plane	*Deviation* ($\AA \times 10^2$) *of the included atoms from the plane*
1	C(11), 2(2); C(12), −3(2); C(13), −2(2); C(14), 5(2); C(15), 0(3); C(16), −4(3); C(17), 0(3); C(18), 2(2); Zr[c], 168.2(1)
2	C(21), 1(1); C(22), −3(2); C(23), 3(2); C(24), −1(1); Zr[c], −211.3(1)
3	C(21), −4(2); C(24), 9(1); C(25), −9(1); C(26), 1(1); C(27), 8(1); C(28), −3(2)
4	Zr, 0.0(1); O, −4.8(6); C(1), 8(1); C(4), 6(1)

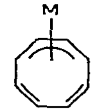
[a] The weight of each atom was the reciprocal of the variance of the atom in the direction of the normal to the plane. [b] The Cartesian unit cell vectors x,y,z are those of the orthorhombic crystal. [c] This atom was not included in the best plane calculation.

average C–C bond length is 1.374(15) Å* with librational corrections increasing this value to 1.417 Å. The uncorrected distances found in other compounds are comparable: $(COT)_2U$[3], 1.395(15) Å, $[(CH_3)_4C_8H_4]_2U$[14], 1.41(3) Å; $(COT)_3Ti_2$[6], 1.399(12) Å; $(COT)(C_5H_5)Ti$[15], 1.395 Å. The weighted average Zr–C bond length is 2.461(7) Å, 2.506 Å corrected for libration. For related h^5-C_5H_5 complexes, average Zr–C distances of 2.48(11) to 2.55 Å have been reported[16]. As expected, the average Zr–C (h^8-COT) distance lies between the average bond lengths of the titanium compounds[6,15], 2.34 Å, and the uranium compounds[3,14], 2.66 Å; moreover, the entire trend is consistent with that of the atomic radii of these atoms: Ti (1.40 Å), Zr (1.55 Å), U (1.75 Å)[17].

---

* When possible, standard deviations have been calculated from population distributions as described in ref. 26.

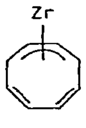
The structural features of the second COT ligand are rather unusual. The distributions of C–C bond lengths are not consistent with those found in (COT)Fe$(CO)_3$[18] and (COT)Ru$(CO)_3$[19], for which the following bonding scheme is appropriate;



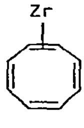
indeed, we have been unable to formulate any other simple bonding scheme. At least in part, disorder, reorientation, and/or torsional motion of these atoms (effects not properly accounted for in our least-squares model) must be responsible for this. Therefore we will limit our discussion to the gross features of Zr–C bonding and ring conformation.

Distances between 2.315(17) and 2.849(14) Å are found for the four shortest metal–ring contacts and are indicative of varying degrees of π-bonding. The longer bonds are formed by C(21) and C(24), the shorter by C(22) and C(23). Similar butadiene-like bonding trends are shown in $(COT)_2Fe$[5], (COT)Fe$(CO)_3$[18], and (COT)Ru$(CO)_3$[19], but the metal–carbon bond lengths do not show similar wide variations. The dihedral angle between the two quasi-planar segments C(21), C(22), C(23), C(24) and C(21), C(24), C(25), C(26), C(27), C(28) is 159.4°. This angle is larger than those found respectively in the above compounds: 147.0(5)°, 137.5(5)° (ref. 18), 136.3(3)° (ref. 19).

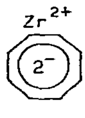
The observed differences in metal–COT bonding modes are probably due to the character of the other ligand about the metal atoms, the ability of iron and ruthenium atoms to engage in back-bonding to the butadiene moiety, and the pronounced tendency of iron and ruthenium atoms to form closed shell compounds. Back-donation is less important in zirconium chemistry, and this metal rarely forms compounds with more than 16 electrons, π-C_5H_5Zr(HFAC)*[20] and perhaps $(C_5H_5)_4$Zr[21,22] being the only exceptions known to us. In addition, Fe–C and Ru–C bonds are expected to be more covalent than Zr–C bonds. Thus we believe that the bonding of the second COT ligand to the zirconium atom may be represented by the following resonance forms:



(I)



(II)



(III)

The first two forms are covalent in character and allot 18 electrons [form (I)] and 16 electrons [form(II)] to the metal; (III) is mainly ionic. Only (I) is important in the above iron and ruthenium compounds, but combinations of (I), (II), and (III) would be necessary to explain the variation of Zr–C bond lengths and the larger dihedral angle in the COT ligand. Finally, (III) is supported by the insolubility of the complex in nonpolar solvents[7].

The IR spectrum of $(COT)_2Zr \cdot THF$ shows an absorption at 1509 cm^{-1} which has been assigned to stretching frequencies of the uncoordinated double bonds in the

---

* HFAC = hexafluoroacetylacetonato.

nonplanar COT ligand. This value is lower than that found in $(COT)_2Fe^5$, 1527 cm^{-1}, or $(COT)Fe(CO)_3$, 1562 cm^{-1}, which in turn are lower than those found in the free ligand. For $(COT)Fe(CO)_3$, it has been proposed that the lowering is due to both increased conjugation in the uncoordinated butadiene fragment due to its planarity and further conjugation throughout the COT ligand because of the overlap between the uncoordinated and coordinated butadiene fragments[23]. The second argument is apparently supported by the correlation of the decrease in the stretching frequency with the increase in the dihedral angle.

The Zr–O bond length [2.447(4) Å] is very long in comparison to the distances (2.07–2.26 Å) reported even in crowded inorganic zirconium complexes[20,24]. This observed bond length implies that the THF group is coordinated weakly, a fact consistent with the loss of THF by crystals of the compound under a flow of dry argon at room temperature. An examination of the intramolecular nonbonded contacts of the THF group (Table 3) indicates that they are not unusually short with respect to the intermolecular contacts; however, a 0.2 Å shortening of the Zr–O distances would change this situation considerably. The increased nonbonded repulsions would probably force the second COT group further from the metal atom, thus making it, at best, a two-electron donor. Therefore we interpret the long Zr–O bond as demonstrating the interplay of nonbonded repulsions and the desire of the zirconium atom to obtain an 18 electron configuration.

The major features of the coordination of the THF group can be seen in Fig. 1. The envelope conformation of the ligand is emphasized by the dihedral angle of 149.0° between the planes through O, C(1), C(4) and C(1), C(2), C(3), C(4); furthermore, the bent donor is incorporated into the complex so as to diminish the overall molecular asphericity. The weighted average C–C bond length and the average C–O bond length are 1.513(10) and 1.472(43) Å, respectively. Presently, we can offer no explanation for the large apparent difference in the two C–O bond lengths. The above values may be compared with those reported for the envelope conformation of free THF in the gas phase: 1.538(2) (C–C) and 1.430(2) Å (C–O)[25]. The atoms Zr, O, C(1), C(4) deviate significantly from planarity with the Zr–O bond forming a 9.0° angle with the O, C(1), C(4) plane. A qualitative examination of the intra- and intermolecular nonbonded distances did not support a steric explanation for the nonplanarity of these four atoms.

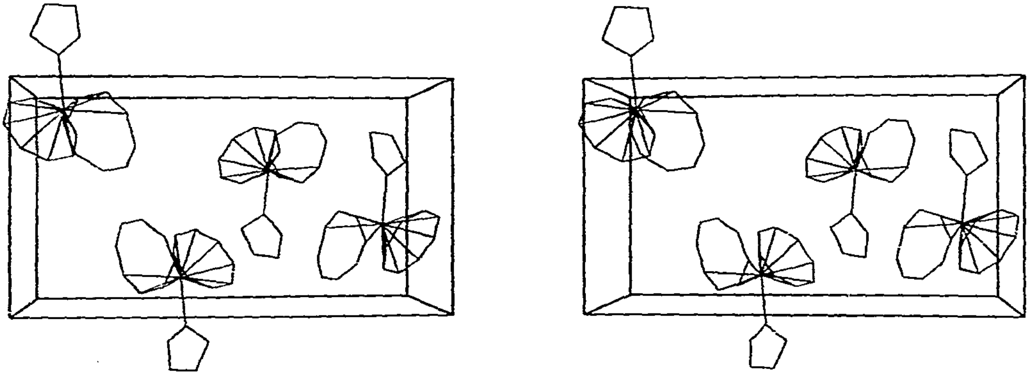


Fig. 3. A stereodrawing of the unit cell packing in $(C_8H_8)_2Zr\cdot THF$. The *a* axis is horizontal and the *b* axis is vertical.

A unit cell packing diagram is shown in Fig. 3. The only intermolecular non-bonded contacts less than Van der Waals' radii are between several THF carbon atoms and carbon atoms of the second COT ligand; even those contacts are not unusually short.

REFERENCES

1 M. A. Bennett, *Advan. Organometal. Chem.*, 4 (1966) 375.
2 F. Mares, K. Hodgson and A. Streitwieser Jr., *J. Organometal. Chem.*, 24 (1970) C68.
3 A. Zalkin and K. N. Raymond, *J. Amer. Chem., Soc.*, 91 (1969) 5667.
4 H. Dietrich and M. Soltwisch, *Angew. Chem.*, 81 (1969) 785; C. Krüger, unpublished results.
5 G. Allegra, A. Colombo and A. Immirzi, *J. Amer. Chem. Soc.*, 90 (1968) 4455; A. Carbonaro, A. L. Segre, A. Greco, C. Tosi and G. Dall'Asta, *J. Amer. Chem. Soc.*, 90 (1968) 4453.
6 H. Dierks and H. Dietrich, *Acta Crystallogr., Sect., B*, 24 (1968) 58.
7 J. Kablitz, Dissertation, Univ. Bochum (1971); J. Kablitz and G. Wilke, to be published.
8 H. Breil and G. Wilke, *Angew. Chem.*, 78 (1966) 942.
9 C. Krueger, *J. Organometal. Chem.*, 22 (1970) 697.
10 D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18 (1965) 104.
11 D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.
12 W. C. Hamilton, *Acta Crystallogr.*, 18 (1965) 502.
13 V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 24 (1968) 63.
14 K. O. Hodgson, D. Dempf and K. N. Raymond, *J. Chem. Soc. D*, (1971) 1592.
15 P. A. Kroon and R. B. Helmholdt, *J. Organometal. Chem.*, 25 (1970) 451.
16 K. W. Muir, *J. Chem. Soc. A*, (1971) 2663, and references cited therein.
17 J. C. Slater, *J. Chem. Phys.*, 41 (1964) 3199.
18 B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, 37 (1962) 2084.
19 F. A. Cotton and R. Eiss, *J. Amer. Chem. Soc.*, 91 (1969) 6593.
20 M. Elder, *Inorg. Chem.*, 8 (1969) 2103.
21 V. J. Kulishov, E. M. Brainina, N. G. Bokiy and Yu. T. Struchkov, *J. Chem. Soc. D*, (1970) 475.
22 J. L. Calderon, F. A. Cotton, B. G. DeBoer and J. Takats, *J. Amer. Chem. Soc.*, 93 (1971) 3592.
23 R. T. Bailey, E. R. Lippincott and D. Steele, *J. Amer. Chem. Soc.*, 87 (1965) 5346.
24 R. B. VonDreele, J. J. Stezowski and R. C. Fay, *J. Amer. Chem. Soc.*, 93 (1971) 2887.
25 H. J. Geise, W. J. Adams and L. S. Bartell, *Tetrahedron*, 25 (1969) 3045.
26 Stout and Jensen, *X-Ray Structural Determination*, Macmillian, Toronto, 1968, pp. 421–425.