Contribution from the Max-Planck-Institut für Kohlenforschung,
433 Mülheim a. d. Ruhr, West Germany

Stereochemistry of Transition Metal–Cyclooctatetraenyl Complexes. Molecular Structure of η-Cyclooctatetraenyl(tetrahydrofuran)dichlorozirconium

D. J. BRAUER and C. KRÜGER*

Received June 24, 1975

AIC50444Y

The structure of η-cyclooctatetraenyl(tetrahydrofuran)dichlorozirconium, η-$C_8H_8(C_4H_8O)Cl_2Zr$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the orthorhombic system with unit cell dimensions $a = 12.328$ (2), $b = 11.973$ (2), and $c = 17.581$ (3) Å, and it has a calculated density of 1.732 g/cm^3 based on $Z = 8$. The space group is *Cmca*. Least-squares refinement yielded a conventional R value of 0.025 for 1364 observed reflections. The molecules possess crystallographic m (C_s) symmetry, the mirror plane passing through two carbon atoms of the cyclooctatetraenyl (COT) ring, the zirconium atom, and the oxygen atom. Therefore the COT C–C bond lengths cannot alternate, and their average value is 1.398 (7) Å. The Zr–C bond distances to the η-COT ring show small (±0.02 Å) but significant deviations from their average value, 2.461 Å. Longer distances are found approximately trans to the Cl atoms. The COT carbon atoms deviate (±0.03 Å) significantly from planarity. The COT hydrogen atoms are located on the Zr atom side of the best plane through COT carbon atoms. The average angle formed by this plane and the C–H bonds is 6.8°. The Zr–Cl bond length is 2.496 (1) Å, and the Zr–O bond distance is 2.274 (2) Å. The Cl–Zr–Cl' angle is 87.2 (1)°. The tetrahydrofuran moiety is in the envelope conformation. The C–O bond lengths are significantly longer than in the free tetrahydrofuran molecule, 1.452 (3) vs. 1.430 Å.

Introduction

Recently the synthesis of a number of new 1,3,5,7-cyclooctatetraene (COT) complexes of zirconium has been reported.[1] In many of these compounds, the presence of planar η-COT ligands has been proposed. In our investigation of one of these complexes, $(COT)_2Zr \cdot THF$ (I) (THF = tetrahydrofuran), both 1–4-η-COT and η-COT ligands were found.[2]

$(COT)ZrCl_2 \cdot THF$ (II) may be prepared by protolysis of $(COT)_2Zr$ with HCl[1] or by electrolytic techniques.[3] In order to gain further knowledge of the COT–Zr interaction, we have examined the structure of II by single-crystal X-ray diffraction techniques.

A peculiarity of I is the unusually long Zr–O bond length, 2.447 (4) Å. When I and II are heated under vacuum, I is reported to lose its THF near 50°C while this process starts at 70°C for II.[1] Whether or not this difference in thermal stabilities would be reflected by different Zr–O bond lengths was also of interest.

Experimental Section

Orange crystals of II were kindly supplied by Dr. Lehmkuhl of this institute. It was possible to cut a small, octagonal plate from a piece of the supplied material. This crystal was then sealed in a glass capillary under argon.

Space group information was obtained from precession and Weissenberg photographs. The systematic absences were consistent with either the centric space group *Cmca* or the acentric space group *C2cb*, a nonstandard setting of *Aba*2. The centric space group was indicated by the refinement.

After transferring the crystal to an automated diffractometer (Siemens + PDP-8/s), it was aligned with b^* parallel to the ϕ axis. Forty values of θ (Mo Kα_1, Mo Kα_2) for a number of high-order reflections were determined by step scanning the peaks with a thin slit collimator inserted in front of the detector window. Accurate lattice cell constants were then obtained by a least-squares procedure on these θ values, taking the Kα_1–Kα_2 doublets into account. Cell constants and other crystal data are included in Table I.

ω scans of three large, low-angle reflections indicated that the crystalline quality was satisfactory. The centering of several diffracted beams in the counter window was checked photographically.

Intensity data were measured by the θ–2θ scan technique using zirconium-filtered Mo Kα radiation. Symmetrical 2θ scans varied as a function of 2θ from 1.08 to 1.60°. For each reflection, two scans of the peak were made, and the left and right backgrounds were measured by the stationary-crystal, stationary-counter technique. To minimize counter losses and to keep the total number of counts approximately constant for all reflections, automatic selection of one of three scanning speeds (20, 10, and 5°/min) and of one of six Zr attenuators was made on the basis of a prior sampling of the peak intensity. In order to check the alignment of the crystal and the stability of the diffractometer system, one reflection (0,0,14) was periodically measured with and without a half-slit occulator placed before the counter window. The intensity of this reflection showed only random fluctuations during data collection. One octant ($\theta \leq 28°$) of data was measured. Thereafter, the crystal faces were measured and indexed.

Table I. Crystal Data

Formula: $C_{12}H_{16}Cl_2OZr$
Mol wt 338.39
Crystal system: orthorhombic
Crystal size: 0.05 × 0.078 × 0.011 mm
$a = 12.328$ (2) Å
$b = 11.973$ (2) Å
$c = 17.581$ (3) Å
$T = 20°C$
$V = 2595$ Å^3
$Z = 8$
$d_{calcd} = 1.732$ g/cm^3
$\mu = 12.09$ cm^{-1}
λ(Mo Kα) 0.71069 Å
Space group: *Cmca*,[a] *C2cb*
Absences: hkl, $h + k = 2n + 1$; $hk0$, $h = 2n + 1$, $k = 2n + 1$; $h0l$, $l = 2n + 1$, $k = 2n + 1$

[a] This space group was indicated by the refinement.

The intensity data were converted to structure factor amplitudes by corrections for Lorentz, polarization, and absorption effects.[23] The calculated transmission factors ranged from 0.563 to 0.875. Of the 1645 reflections measured, 1364 reflections had net intensities I greater than $3\sigma(I)$ and were considered to be "observed". For observed reflections, F was derived[4] from $\sigma(I)$ where $\sigma^2(I) = [\sigma^2(I)_{counting} + 0.0009I^2]$; weights w were set equal to $1/\sigma^2(F)$. "Unobserved" reflections were given zero weights.

Solution and Refinement of the Crystal Structure

If $Z = 8$, no symmetry is imposed on the molecules by space group *Aba*2; however, space group *Cmca* requires the molecules to possess either m (C_s), 2 (C_2), or $\bar{1}$ (C_i) symmetry. Since the structure of II might reasonably be expected to possess m symmetry, space group *Cmca* was initially assumed. This choice was justified by the distribution of Zr–Zr, Cl–Cl, and Zr–Cl vectors in a sharpened Patterson map, the Zr atom located on the mirror plane. A Fourier map was calculated using the phases determined by the Zr and Cl atoms ($R = 0.26$). This map revealed the positions of all carbon and oxygen atoms; three of them (C(1), C(5), O) were found on the mirror plane.

The structure was refined by full-matrix least-squares methods. The function minimized was $\sum w\Delta^2$, where $\Delta = \|F_o| - |F_c\|$. Isolated neutral atom scattering factors[5a] were used for all atoms except H.[5b] The real and imaginary parts of the anomalous scattering factors of Zr and Cl[6] were applied to F. The discrepancy indices R and R_w are defined as $\sum\Delta/\sum|F_o|$ and $[\sum w\Delta^2/\sum w|F_o|^2]^{1/2}$, respectively.

Isotropic refinement yielded $R = 0.072$ and $R_w = 0.087$. An-

Table II. Positional and Thermal Parameters for $(C_8H_8)ZrCl_2\cdot C_4H_8O$

	x	y	z	U_{11}[a] or U_{iso}[b]	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Zr	0.0	0.11876 (3)	0.14745 (2)	0.0291 (2)	0.0232 (2)	0.0279 (2)	0.0	0.0014 (1)	0.0
Cl	0.13956 (5)	−0.03169 (5)	0.15577 (4)	0.0358 (3)	0.0346 (3)	0.0451 (4)	0.0085 (2)	0.0028 (3)	0.0013 (3)
C(1)	0.0	0.1579 (3)	0.0109 (2)	0.0797 (30)	0.0298 (18)	0.0314 (20)	0.0	0.0042 (16)	0.0
C(2)	0.1048 (3)	0.1810 (2)	0.0370 (2)	0.0580 (17)	0.0434 (16)	0.0481 (17)	0.0088 (13)	0.0165 (13)	0.0215 (15)
C(3)	0.1483 (2)	0.2398 (2)	0.0992 (2)	0.0377 (14)	0.0450 (16)	0.0641 (20)	−0.0056 (13)	0.0200 (15)	0.0035 (14)
C(4)	0.1046 (3)	0.2927 (2)	0.1626 (2)	0.0550 (17)	0.0347 (14)	0.0549 (18)	−0.0172 (13)	0.0083 (12)	−0.0135 (15)
C(5)	0.0	0.3140 (3)	0.1892 (3)	0.0725 (29)	0.0228 (17)	0.0454 (23)	0.0	0.0000 (16)	0.0
C(6)	0.0948 (3)	0.1152 (3)	0.3240 (2)	0.0530 (19)	0.0797 (25)	0.0397 (15)	−0.0124 (18)	0.0014 (16)	−0.0135 (14)
C(7)	0.0609 (3)	0.0790 (3)	0.4024 (2)	0.0938 (26)	0.0691 (22)	0.0353 (16)	0.0148 (21)	−0.0098 (16)	−0.0091 (16)
O	0.0	0.0994 (2)	0.2761 (1)	0.0374 (12)	0.0429 (14)	0.0312 (12)	0.0	−0.0020 (11)	0.0
H(1)	0.0	0.111 (4)	−0.028 (3)	0.050 (13)					
H(2)	0.158 (2)	0.137 (2)	0.009 (2)	0.045 (8)					
H(3)	0.224 (2)	0.232 (2)	0.101 (2)	0.046 (8)					
H(4)	0.155 (3)	0.321 (2)	0.198 (2)	0.051 (9)					
H(5)	0.0	0.349 (3)	0.241 (2)	0.035 (10)					
H(6B)	0.155 (4)	0.100 (3)	0.293 (2)	0.080 (13)					
H(6A)	0.105 (3)	0.211 (3)	0.335 (2)	0.076 (12)					
H(7B)	0.092 (3)	−0.000 (4)	0.396 (2)	0.086 (12)					
H(7A)	0.091 (3)	0.128 (3)	0.449 (2)	0.070 (10)					

[a] The form of the anisotropic thermal ellipsoids is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] The form of the isotropic temperature factor is $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

Table III. Bond Distances (Å) in $(C_8H_8)ZrCl_2\cdot C_4H_8O$[a]

Zr–Cl	2.496 (1)	C(6)–C(7)	1.505 (5)
Zr–C(1)	2.446 (4)	C(7)–C(7)′[b]	1.502 (6)
Zr–C(2)	2.449 (3)	C(1)–H(1)	0.89 (5)
Zr–C(3)	2.482 (3)	C(2)–H(2)	0.97 (3)
Zr–C(4)	2.464 (3)	C(3)–H(3)	0.94 (3)
Zr–C(5)	2.450 (5)	C(4)–H(4)	0.94 (3)
Zr–O	2.274 (2)	C(5)–H(5)	1.00 (4)
C(1)–C(2)	1.398 (3)	C(6)–H(6A)	1.17 (4)
C(2)–C(3)	1.408 (4)	C(6)–H(6B)	0.94 (4)
C(3)–C(4)	1.391 (4)	C(7)–H(7A)	1.08 (4)
C(4)–C(5)	1.395 (3)	C(7)–H(7B)	1.03 (4)
O–C(6)	1.452 (3)		

[a] These bond distances have not been corrected for thermal libration. [b] Primed atoms are related to those in the asymmetric unit as follows: $-x, y, z = x, y, z$.

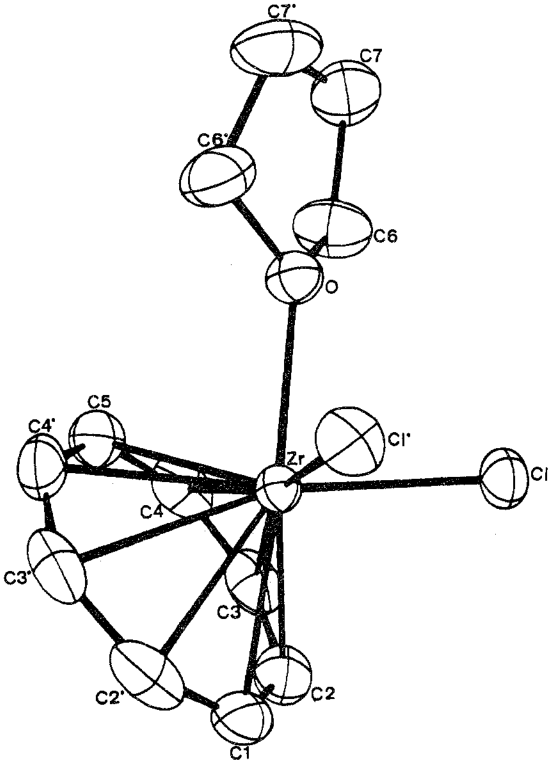

Figure 1. A perspective drawing of η-$C_8H_8ZrCl_2\cdot$THF with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Table IV. Selected Bond Angles[a] (deg) in $(C_8H_8)ZrCl_2\cdot C_4H_8O$

Cl–Zr–Cl′	87.2 (1)	C(4)–C(5)–C(4)′	135.2 (4)
Cl–Zr–O	82.4 (1)	Zr–O–C(6)	124.3 (1)
C(2)–C(1)–C(2)′	135.0 (4)	C(6)–O–C(6)′	107.1 (2)
C(1)–C(2)–C(3)	134.9 (3)	O–C(6)–C(7)	105.7 (3)
C(2)–C(3)–C(4)	134.7 (3)	C(6)–C(7)–C(7)′	106.1 (3)
C(3)–C(4)–C(5)	135.2 (3)		

[a] See footnotes in Table III.

isotropic refinement lowered these values to 0.036 and 0.051, respectively. A difference Fourier map was calculated, and it contained peaks of height 0.28–0.60 e/Å^3 near the expected H atom positions. These peaks were the most prominent electron density features on this map, and they may be compared with the peak heights (4.0–6.4 e/Å^3) for the carbon atoms in this structure. Refinement was continued with the positional and isotropic thermal parameters of the H atoms also being varied. It converged with $R = 0.030$ and $R_w = 0.035$. Examination of a $|F_o| - |F_c|$ list indicated that $|F_c|$ was larger than $|F_o|$ for a few reflections with large $|F_o|$. Therefore, the structure was further refined with an extinction parameter,[7] the path lengths of the beam in the crystal arbitrarily set at 1 cm. The final values of R are 0.025 (without "unobserved" reflections) and 0.029 (all reflections); R_w is 0.034. On the final cycle the largest ratio of shift to error was 0.2. The value of the extinction parameter settled at 151 (52). A plot of $\langle w\Delta^2\rangle$ against $|F_o|$ showed no unusual trends. The final value for the error of fit is 1.58. A list of positional and thermal parameters is given in Table II, errors being calculated from the least-squares matrix. The numbering scheme is shown in Figure 1, the hydrogen atoms being numbered after the carbon atoms to which they are attached. Bond distances and bond angles are given in Tables III and IV, respectively. No attempt to refine the structure in the acentric space group was made because the derived structural parameters are chemically reasonable.

Results and Discussion

Crystals of II have been found to contain monomeric molecules of (COT)$ZrCl_2$·THF. No unusually short intermolecular contacts exist, the shortest being H(3)–H(6B) $(0.5 - x, y, 0.5 - z)$, 2.40 (5) Å.

The zirconium atom bonds to each carbon atom of the COT ligand, to two chlorine atoms, and to the oxygen atom of the THF ring. The spatial distribution of ligands about the zirconium atom may be described as octahedral with the COT moiety occupying a face and the remaining three ligands occupying corners of the octahedron. The zirconium atom has a 16-electron configuration.

The Zr–O bond length is 2.274 (2) Å. This distance is 0.173 (5) Å shorter than the Zr–O bond length in I, 2.447 (4) Å.

Table V. Interligand Intramolecular Contacts (Å)[a]

Cl–C(2)	3.322 (3)	Cl–C(6)	3.485 (4)
Cl–C(3)	3.402 (3)	C(5)–O	2.990 (5)
Cl–O	3.147 (1)	Cl–Cl′[b]	3.441 (1)
Cl–H(6B)	2.88 (4)		

[a] Only distances less than the van der Waals radii sums[13] are tabulated. [b] See footnote *b* of Table III.

This observation is consistent with the greater thermal stability of the Zr–THF attachment in II mentioned above. As we have previously noted, shorter Zr–O bond lengths (2.07–2.26 Å) have been observed even in some crowded zirconium compounds.[2] It seems reasonable that the two Cl atoms of II can remove more electron density from the (η-COT)Zr system than the 1–4-η-COT moiety of I can; thus the Zr atom of II should be a better Lewis acid than the Zr atom of I. Besides this electronic factor, steric factors may also be important. The angles formed by the Zr–O vector with the normal to the η-COT ring are 53.0° in II and 61.3° in I. If the aforementioned ideal octahedral distribution of ligands about the Zr atoms in these compounds was realized, these angles would be 54.8°. The larger angle in I is consistent with the greater steric requirement of 1–4-η-COT as compared to that of two chlorine atoms. The THF ligand possesses rigorous m (C_s) symmetry. The dihedral angle of 149.8° between the planes O–C(6)–C(6)′ and C(6)–C(7)–C(6)′–C(7)′ compares well with the 149.0° angle reported in I. The oxygen atom is pyramidally bonded as shown by the 18.6° angle formed by the Zr–O vector with the O–C(6)–C(6)′ plane.

Due to high thermal motion and(or) disorder of the C and O atoms, accurate structural parameters for coordinated THF are not available.[8] Since we have been able to locate the H atoms of the THF ligand, we feel that the THF structural parameters of this investigation are the most accurate reported to date. The C–O distance, 1.452 (3) Å, is significantly longer than the 1.430-Å distance reported in the envelope conformation of THF in the gas phase.[9] In other systems, observations have been reported of similar changes in ligand bond lengths upon coordination.[10] A second-order hybridization effect may be proposed in our case. By donation of a pair of electrons to the Zr atom, the O atom receives a formal positive charge. As a result the O atom of the complex should have a greater effective electronegativity than the O atom of the free ligand. Supposedly the carbon atom C(6) increases the 2p character of its hybrid orbital used in bonding to the oxygen atom; therefore, the corresponding bond would be expected to be longer than in the free ligand.[11] The average C–C distance, 1.504 (6) Å, appears to be shorter than that, 1.538 Å, in the gas phase. While this is the expected trend, we think that some of the difference, 0.01–0.02 Å, is likely to be due to librational shortening.[12] Unfortunately attempts to fit the anisotropic thermal motion tensors of Zr, O, C(6), C(6)′, C(7), and C(7)′ to a rigid-body model did not yield physically reasonable results; therefore, reliable estimates of the librational shortening of these bonds are not available.

The angle formed by the normals of the Zr–Cl–Cl′ and COT planes is 63.6°. This angle is larger than that expected for an octahedral arrangement of ligands about the Zr atom, 54.8°. This distortion is reflected in the O–Zr–Cl angle, 82.4 (1)°, which is significantly smaller than 90°. The Cl–Zr–Cl′ angle, 87.2 (1)°, is also less than 90°. While the interligand, intramolecular contacts are not unusually short, a few are less than the van der Waals radii sums;[13] these contacts are listed in Table V. The Zr–Cl bond length is 2.496 (1) Å. The difference between the Zr–Cl and Zr–O bond lengths of 0.222 (3) Å is significantly less than the difference between the tetrahedral covalent radii of Cl and O atoms, 0.33 Å.[13] Apparently the Zr–Cl interaction is stronger than the Zr–O interaction. This observation is not surprising since the oxygen atom is trivalent. Thus the distortions mentioned above are toward seven-coordination for the Zr atom as derived from the trigonal prism, the COT ring and the Cl atoms occupying a rectangular face and corners of an edge, respectively, and the O atom centered above one of the remaining rectangular faces.

The Zr–Cl bond length is somewhat longer than reported in $(\eta\text{-C}_5\text{H}_5)_2[(\text{C}_6\text{H}_5)_3\text{Si}]\text{ZrCl}$ (2.430 (3) Å),[14] $[(\text{CH}_2)_3(\eta\text{-C}_5\text{H}_4)_2]\text{ZrCl}_2$ (2.431 (2) and 2.451 (2) Å),[15] and $(\eta\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ (2.441 (5) Å).[16] A Zr–Cl bond length of comparable length (2.50 Å) to that in II was reported in $(\eta\text{-C}_5\text{H}_5)(\text{acac})_2\text{ZrCl}$, (acac = acetylacetonate).[17] In each of these structures the Zr atom has a 16-electron configuration.

We have analyzed the thermal motion of the Zr atom and COT carbon atoms in terms of a rigid-body motion model.[12] The rms difference of the observed and calculated temperature factors (U) is 0.0015 Å, which compares well with the standard deviations of the U's of the carbon atoms. While the translational tensor is approximately isotropic, the librational tensor is anisotropic. The rms amplitude of libration about the principal axis of greatest libration forms an angle of 8.2° with the normal to the best plane of the COT ring. A similar observation was noted for I.[2] When the Zr–C and C–C bond lengths were corrected for librational shortening,[12] these distances increased on the average by 0.011 (2) and 0.010 (1) Å, respectively.

The average Zr–C bond length is 2.461 (15) Å (corrected 2.472 (16) Å). These values compare well with those of I, 2.461 (17) Å (corrected 2.506 (17) Å). In II the Zr–C bond lengths range from 2.446 (4) to 2.482 (3) Å. The longer Zr–C bonds involve C(3) (2.482 (3) Å, corrected 2.494 Å) and C(4) (2.464 (3) Å, corrected 2.477 Å). Since the Cl′–Zr–C angles are largest for these two C atoms, 161.7 (1) and 164.7 (1)°, respectively, the slight variation in Zr–C bond lengths might be interpreted as resulting from the trans influence of the Cl atoms. On the other hand, the variation is small; therefore intermolecular forces cannot be excluded. The shortest intermolecular contact between hydrogen atoms involves H(3) and H(6B) ($0.5 - x, y, 0.5 - z$). The repulsion between these atoms is such as to force H(3), and presumably also C(3), away from the Zr atom. Intramolecular Cl–C repulsions do not seem to be causing the distortion since Zr–C(2) is shorter than Zr–C(3) while Cl–C(2) is shorter than Cl–C(3) (Table V).

The COT ring possess approximate C_{8v} symmetry. The C–C bond lengths do not vary significantly from their average value (1.398 (7) Å, corrected 1.408 Å). The scatter of these distances about their mean is approximately twice as great as would be expected considering the standard deviations calculated from least squares. The average values compare well with those found in I (1.374 (15) Å, corrected 1.417 Å).[2] The average C–C–C bond angle is 135.0 (2)°. The Zr atom lies −1.6506 (3) Å from the best weighted least-squares plane through the eight COT C atoms.

The deviation of the carbon atoms from this plane—C(1), −0.011 (4) Å; C(2), −0.011 (3) Å; C(3), 0.029 (3) Å; C(4), −0.005 (3) Å; C(5), −0.027 (4) Å—reflect the slight asymmetry of the COT–Zr attachment. The average angle formed by CH bonds with the plane of the COT ring is 6.7°, the bonds being inclined toward the Zr atom. If we assume the true C–H distance to be 1.09 Å, each H atom would be located, on the average, 0.13 Å further away from the best plane than the carbon atom to which it is attached. Noteworthy here is the lack of any evidence indicating deviations from D_{8h} symmetry for the "free" COT dianion.[18] Packing forces, intramolecular nonbonded repulsions, and electronic effects could conceivably lead to deviations of H atoms from the COT best plane. An examination of intramolecular and intermolecular H(COT)–H, H(COT)–C, and H(COT)–Cl contacts did not indicate that these interactions are responsible for the observed deformation. Thus we are led to the conclusion that the distortion of the COT ligand results from the electronic nature of the COT–metal interaction.

Similar conclusions were also reached by Hodgson and Raymond in their analysis of $[C_8H_4(CH_3)_4]_2U$[19] and by Rees and Coppens in their study of $C_6H_6Cr(CO)_3$.[20] In these two compounds the substituents were also located on the metal side of the ring planes. Average substituent angles of 4.1° for the methyl groups[19] and 1.7° for the hydrogen atoms[20] were reported for the former and latter complexes, respectively.

Hodgson and Raymond offered two possible explanations for their observations. The first invoked a rehybridization of the ring carbon atoms from trigonal to slightly pyramidal. The ring carbon π orbitals would then be inclined toward the metal atom; thus better ring–metal overlap would be possible. The second requires a volume contraction and an inward polarization of the π density on the metal side of the ring relative to that on the other side, the electron density in the bonds to the ring substituents being forced away from the noncontracted π-electron density.[19] Rees and Coppens' argument retains the trigonal character of the ring carbon atom hybridization; however, they postulated a tilting of these hybrid orbitals so that the carbon π orbitals are directed more along the metal–carbon vector. This rationalization is quite similar to the first given by Hodgson and Raymond.[20] We might add that the third argument bears some similarity to the explanation of the deformation experienced by π-allyl[21] and butadiene[22] moieties π bonded to transition metals. It should be noted that the above arguments consider only the interaction between the metal atom and the π orbitals of the carbocyclic ring. In some cases interactions between the metal atom and the ring σ system may also be important. A differentiation between these two possibilities cannot be derived from substituent angles alone.

Registry No. II, 50648-05-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50444Y-12-75.

References and Notes

(1) H.-J. Kablitz and G. Wilke, *J. Organomet. Chem.*, **51**, 241 (1973).

(2) D. J. Brauer and C. Krüger, *J. Organomet. Chem.*, **42**, 129 (1972).

(3) H. Lehmkuhl, S. Kintopf, and K. Mehler, *J. Organomet. Chem.*, **46**, C1 (1972).

(4) D. J. Brauer and C. Krüger, *Acta Crystallogr., Sect. B*, **29**, 1684 (1973).

(5) (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(6) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(7) A. Larson in "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, pp 291–294.

(8) D. J. Brauer and G. D. Stucky, *J. Organomet. Chem.*, **37**, 217 (1972).

(9) H. J. Geise, W. J. Adams, and L. S. Bartell, *Tetrahedron*, **25**, 3045 (1969).

(10) G. A. Anderson, F. R. Forgaard, and A. Haaland, *Acta Chem. Scand.*, **26**, 1947 (1972).

(11) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 60 (1947); H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(12) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 63 (1968).

(13) L. Pauling, "The Nature of Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(14) K. W. Muir, *J. Chem. Soc. A*, 2663 (1971).

(15) C. H. Saldarriaga-Molina, A. Clearfield, and I. Bernal, *J. Organomet. Chem.*, **80**, 79 (1974).

(16) K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B*, **30**, 2290 (1974).

(17) J. J. Stezowski and H. A. Eick, *J. Am. Chem. Soc.*, **91**, 2890 (1969).

(18) H. P. Fritz and H. Keller, *Z. Naturforsch., B*, **16**, 231 (1961).

(19) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **12**, 458 (1973).

(20) B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, **29**, 2516 (1973); *J. Organomet. Chem.*, **42**, C102 (1972).

(21) B. L. Barnett and C. Krüger, *J. Organomet. Chem.*, **77**, 407 (1974).

(22) R. Eiss, *Inorg. Chem.*, **9**, 1651 (1970).

(23) Aside from various local programs for the PDP 10, other computer programs used in this investigation include modified versions of Coppens, Leiserowitz, and Rabinovich's DATAP absorption program, Ahmed's FOSUM Fourier program, Weizmann Institute's BDLS least-squares program, Davis' DAESD distance and angle program, Roberts' XANADU molecular geometry program, and Johnson's ORTEP thermal ellipsoid plotting program.

Contribution from the Department of Chemistry,
University of Canterbury, Christchurch, New Zealand

Crystal and Molecular Structure of 2-Methyl-1,7-bis(η^5-cyclopentadienyl)-1,7,2,4-dicobaltadicarbaheptaborane(7), a Triple-Decked Sandwich Compound

WARD T. ROBINSON and RUSSELL N. GRIMES*[1]

Received July 28, 1975 AIC50546O

A single-crystal X-ray diffraction investigation of the dicobalt metallocarborane 2-CH_3-1,7,2,4-(η-C_5H_5)$_2$$Co_2C_2B_3H_4$ has established the structure as that of a triple-decked sandwich containing a central planar ring formally designated in the parent molecule as $C_2B_3H_5^{4-}$, isoelectronic with $C_5H_5^-$. The compound crystallizes in the orthorhombic space group *Pnam* with $a = 13.596$ (6), $b = 9.968$ (3), and $c = 10.008$ (4) Å and a calculated density of 1.58 g cm^{-3} for $Z = 4$. The structure was refined by full-matrix least-squares procedures to a final R value of 0.046. The 1,7,2,3- and 1,7,2,4-(η-C_5H_5)$_2$$Co_2C_2B_3H_5$ systems are the only known electrically neutral triple-decked sandwich species, the sole "pure metallocene" member of this class being the (η-C_5H_5)$_3$$Ni_2^+$ ion.

Introduction

The metallocarboranes 1,7,2,3- and 1,7,2,4-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$ occupy a key position in both metallocene and metallocarborane chemistry and can realistically be viewed as members of both classes. Inasmuch as the only known and characterized triple-decked sandwich metallocene is the (η^5-C_5H_5)$_3$$Ni_2^+$ cation prepared by Werner and Salzer,[2-4] the (η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$ species[5-8] are the first electrically neutral examples of true triple-decked complexes containing three planar aromatic rings; in addition, these compounds, in association with the closely related $C_2B_3H_7^{2-}$ complexes,[6,8-10] represent the first metallocarboranes which are direct steric analogs of known metallocenes.[11]

Four isomers of (η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$ have been isolated and characterized[5-8] and together with the related species (CO)$_6$$Fe_2C_2B_3H_5$[7] these are the smallest known metallo-