sistance of W. Gray and L. Jones are gratefully acknowledged.

Registry No. 1, 79568-54-0; **2**, 79568-55-1; **3**, 79645-21-9; **4**, 79645-22-0; **5**, 79645-23-1; **6**, 79568-57-3; **7a**, 79645-25-3; **7b**, 79645-26-4; $[Ir(P(CH_3)_3)_4][PF_6]$, 75593-00-9; $Ir(CH_3)(P(CH_3)_3)_4$, 75613-61-5; $[Ir(CO)(P(CH_3)_3)_4][Cl]$, 67215-74-1; $IrCl(P(CH_3)_3)_3(C_8H_{14})$, 59390-28-2; $[IrCl(C_8H_{14})_2]_2$, 12246-51-4; $[IrHCl(CO)(P(CH_3)_3)_3][BF_4]$, 79568-59-5; $IrH(CO)(P(CH_3)_3)_3$, 79568-60-8; $[IrH_2(CO)(P(CH_3)_3)_3][BF_4]$, 79568-62-0.

Stereochemistry of Transition Metal Cyclooctatetraenyl Complexes. Molecular Structure of (η-Cyclooctatetraenyl)(η-allyl)-*tert*-butoxyzirconium

D. J. Brauer and Carl Krüger*

Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim-Ruhr, West Germany

Received July 14, 1981

Crystals of (η-cyclooctatetraenyl)(η-allyl)-*tert*-butoxyzirconium belong to the monoclinic space group $P2_1/n$ with $a = 15.696$ (6) Å, $b = 16.117$ (3) Å, $c = 12.531$ (6) Å, $\beta = 111.05$ (1)°, $Z = 8$, and $d_{calcd} = 1.39$ g/cm^3. The structure was derived from 4418 counter-measured X-ray data and refined to a conventional R value of 0.039. Two crystallographically independent molecules were found, the second molecule displaying two distinct conformations of the *tert*-butoxy groups. Strong Zr–O bonding is indicated by the short Zr–O bond lengths, average 1.91 (1) Å, and the large Zr–O–C bond angles, average 169 (1)°. The Zr–allyl linkages are slightly asymmetric with a mean Zr–C(allyl) separation of 2.481 Å. The metal atoms are bonded to the COT ligands in an η^8 fashion, although highly significant deviations are found in the Zr–C(COT) bond lengths. These deviations are related to the patterns of nonplanarity revealed for the COT carbon atoms. In the first molecule the ring assumes a shallow tub confirmation while that of the second is slightly folded along a diagonal. The departures from C_{8v} symmetry in the Zr–COT bonding apparently relate to the orientation of the COT moiety with respect to the allyl and *tert*-butoxy groups, the longest Zr–C bond lengths being approximately trans to those ligands. The C–H bonds show an average tilt of 9.2 (9)° out of the COT carbon atom planes toward the metal atoms.

Introduction

Structural investigations of $(COT)_2Zr \cdot THF$[1] (COT = 1,3,5,7-cyclooctatetraene and THF = tetrahydrofuran) and $(COT)ZrCl_2 \cdot THF$[2] showed that both compounds contained a nearly planar COT ligand bonded η^8 to the Zr atoms. In addition, the study of the dichloride revealed that the four Zr–C bonds approximately trans to the Zr–Cl linkages were elongated compared to the other four even though the Zr–Cl interactions appeared not to be particularly strong.[2] This evidence hints at a degree of compliance in the Zr–C(COT) bonds. To gain more information on this phenomenon, we have examined the structure of $(COT)(C_3H_5)(t\text{-}C_4H_9O)Zr$ (I)[3] and now wish to report the results.

Experimental Section

For the X-ray study, crystals of I, which were kindly supplied by Dr. R. Kallweit of this institute, were mounted in glass capillaries under argon. The space group was determined from Weissenberg photographs. Lattice constants were determined by a least-squares procedure from Bragg angles measured with a PDP-8/s automated Siemens diffractometer employing Zr-filtered Mo Kα radiation (λ(Mo K$\bar{\alpha}$) = 0.71069 Å) and are given in the summary. Intensity data (hkl, $\bar{h}kl$, $2 \leq \theta \leq 25°$) were measured and reduced as described previously.[2] No absorption correction was applied because of the irregular crystal shape; however, corrections would have been small ($\mu = 7.2$ cm^{-1}). Of the 5158 data collected, 4418 were unique and had $I \geq 2\sigma(I)$. Only the corresponding $|F_o|$'s were assigned nonzero weights (w) and were used in subsequent calculations.

The structure was solved by the heavy-atom method and refined by least-squares techniques. Computing details have been cited previously.[2] After anisotropic refinement, a difference Fourier calculation indicated the presence of a second orientation (occupancy 0.7) of the *tert*-butoxy group in molecule 2 which was related to the first by a rotation of ~60° about the O–C(12) bond. The additional three carbon atoms were included isotropically in the refinement along with a constrained occupancy factor. Positional parameters for the hydrogen atoms of the COT and allyl ligands in both molecules as well as those of the *tert*-butoxy group of molecule 1 were obtained from a subsequent difference density map, and these atoms were refined isotropically. Methyl hydrogen atoms were not located for molecule 2. After several additional large-block least-squares cycles, convergence was reached with $R = \sum\Delta/\sum|F_o| = 0.039$, $\Delta = ||F_o| - |F_c||$, and $R_w = [\sum w\Delta^2/\sum w|F_o|^2]^{1/2} = 0.048$. Positional parameters are given in Table I, the numbering scheme for both molecules being indicated in Figure 1. The mean C–H distance is 0.97 (11) Å.

Thermal ellipsoids of each Zr–C(1)–C(8) fragment are well fit by a TLS rigid-body-motion model.[4] On the average, librational corrections increase the C–C and Zr–C bond lengths by 0.018 and 0.025 Å, respectively. Unless specified to the contrary, uncorrected values are given in the text.

Description of the Crystal Structure

Crystals of I are composed of discrete molecules, two of which make up the asymmetric unit. Both independent

---

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

(2) D. J. Brauer and C. Krüger, *Inorg. Chem.*, **14**, 3053 (1975).

(3) R. Kallweit, Dissertation, Universität Bochum, 1974.

(4) V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **B24**, 63 (1968).

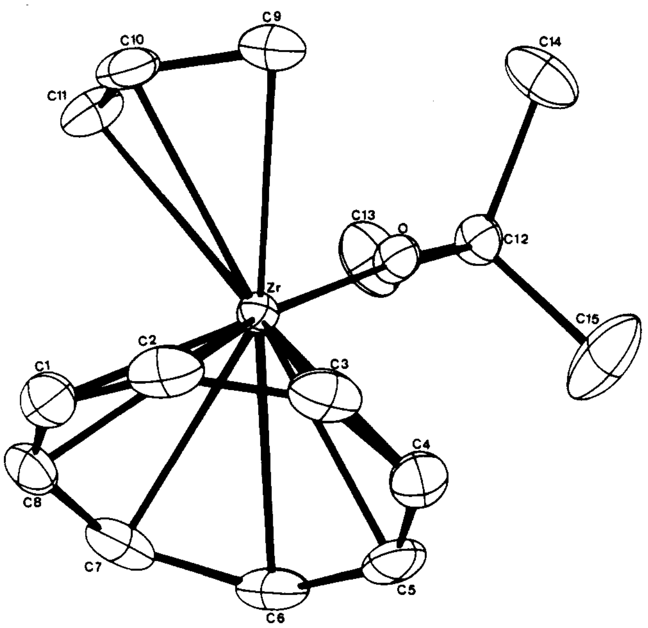


Figure 1. A perspective drawing of I with hydrogen atoms omitted.

molecules contain an octahapto COT ligand, a π-allyl group, and a *tert*-butoxy moiety which are coordinated to the zirconium atoms.

Comparison of structural parameters in these two molecules might reveal which, if any, are compliant toward packing forces. The angles formed by the vectors Zr→O and Zr→G, where G is the center of mass of the allyl carbon atoms, and the COT carbon atom plane normal to it are compared in Figure 2a. Good agreement is found for these gross structural features. The relative rotation of the COT ligand with respect to the allyl and *tert*-butoxy species, which is defined as the angle formed by the projection of the vector C(10)→O on the COT plane with C(1)→C(5), is shown in Figure 2b. Perhaps packing forces have caused the deviations of these values from 22.5°, the angle which would minimize intramolecular steric interactions. Since the observed rotamers are neither staggered nor eclipsed, the molecular symmetry in the solid state, C_1, is lower than the highest conceivable symmetry, C_s.

Librationally corrected C–C(η-COT) bond lengths in I, (COT)ZrCl$_2$·THF, and (COT)$_2$Zr·THF compare well—1.401 (5), 1.408 (4),[2] and 1.417 (15) Å,[1] respectively. The COT carbon atoms in each molecule are significantly nonplanar (Figure 3). This nonplanarity may be described as a shallow tub conformation in molecule 1 while the COT ligand in molecule 2 is folded away from the zirconium atom along the C(3)–C(7) line. The patterns in nonplanarity and differences in Zr–C bond lengths are correlated, which indicates the η^8 nature of the COT–Zr interaction. Those carbon atoms furthest from the metal atom are those trans to and closest to the allyl and *tert*-butoxy

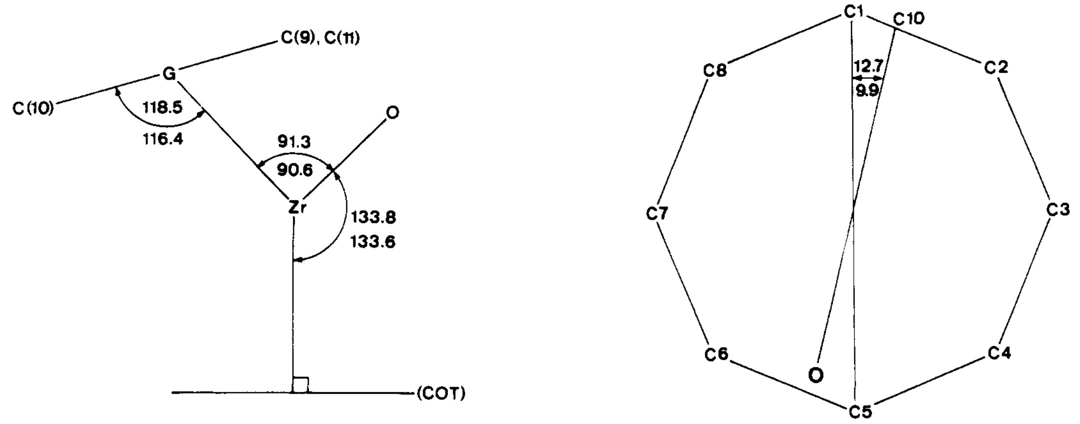


Figure 2. Conformational details of the zirconium coordination with angles in degrees, upper and lower values being for molecule 1 and molecule 2, respectively.

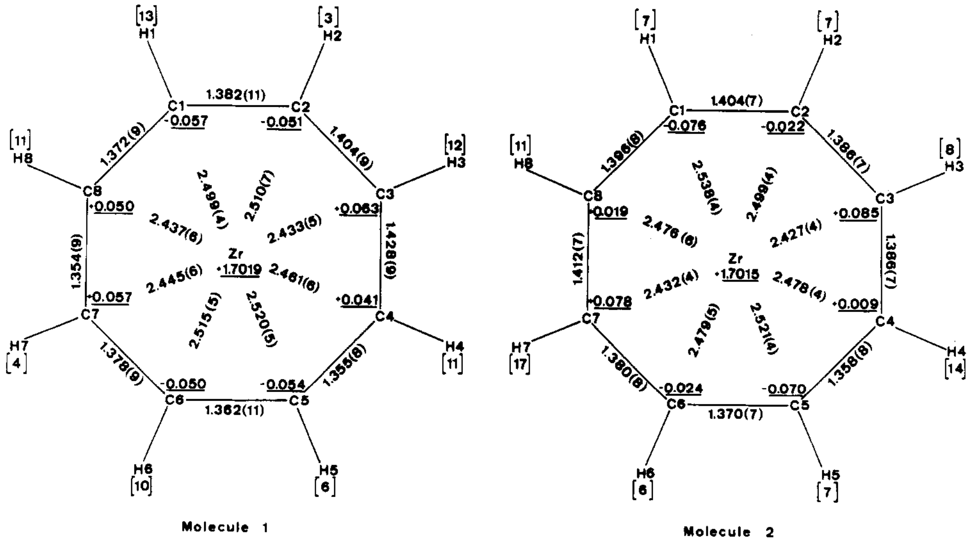


Figure 3. Selected details of the (η-COT)Zr interactions including bond distances (Å), deviations (Å) of carbon and zirconium atoms from the COT planes being underscored, and inclinations (deg) of the C–H vectors out of the COT planes toward the zirconium atoms in brackets.

Table I. Final Atomic Coordinates and Their Standard Deviations ($\times 10^5$)

atom	x	y	z
	Molecule 1		
Zr	3761.4 (2)	1463.8 (2)	1847.7 (3)
C(1)	4202 (3)	−34 (3)	2010 (7)
C(2)	4329 (3)	221 (4)	3110 (6)
C(3)	4684 (4)	945 (4)	3732 (4)
C(4)	5158 (3)	1651 (4)	3540 (5)
C(5)	5414 (3)	1894 (3)	2664 (6)
C(6)	5267 (3)	1622 (4)	1583 (6)
C(7)	4789 (4)	980 (5)	905 (5)
C(8)	4354 (4)	299 (4)	1087 (5)
C(9)	2389 (3)	1346 (3)	2334 (5)
C(10)	2213 (3)	863 (3)	1393 (6)
C(11)	2226 (3)	1119 (3)	372 (5)
C(12)	3262 (3)	3390 (2)	945 (3)
C(13)	3032 (4)	3302 (4)	−322 (5)
C(14)	2432 (4)	3747 (3)	1156 (5)
C(15)	4085 (4)	3926 (3)	1535 (6)
O	3440 (2)	2603 (1)	1454 (2)
H(1)	3871 (30)	−360 (30)	1733 (39)
H(2)	4065 (41)	−108 (35)	3552 (48)
H(3)	4578 (34)	994 (34)	4252 (43)
H(4)	5297 (28)	2111 (24)	4074 (35)
H(5)	5676 (34)	2434 (32)	2870 (43)
H(6)	5407 (33)	2019 (28)	1231 (42)
H(7)	4756 (30)	980 (30)	79 (38)
H(8)	4097 (30)	61 (26)	518 (37)
H(9A)	2523 (32)	1154 (31)	3001 (39)
H(9B)	2304 (30)	1948 (27)	2246 (37)
H(10)	2249 (36)	184 (34)	1347 (45)
H(11A)	2179 (32)	647 (30)	−212 (41)
H(11B)	2030 (28)	1714 (27)	150 (35)
H(13A)	2276 (49)	2895 (42)	−758 (60)
H(13B)	3479 (36)	2974 (30)	−481 (44)
H(13C)	2864 (28)	3967 (30)	−636 (37)
H(14A)	2335 (39)	4267 (38)	784 (51)
H(14B)	2809 (49)	3930 (49)	1932 (64)
H(14C)	2006 (45)	3253 (46)	887 (57)
H(15A)	4421 (36)	3634 (33)	942 (47)
H(15B)	4645 (50)	3832 (48)	2231 (64)
H(15C)	3916 (28)	4503 (29)	1308 (35)
	Molecule 2		
Zr	8861.9 (2)	2022.0 (2)	1383.5 (3)
C(1)	9617 (3)	705 (3)	1052 (5)
C(2)	9217 (3)	527 (2)	1864 (4)
C(3)	8395 (3)	721 (2)	1981 (4)
C(4)	7588 (3)	1078 (2)	1273 (5)
C(5)	7307 (2)	1453 (2)	234 (4)
C(6)	7701 (3)	1688 (3)	−532 (4)
C(7)	8560 (4)	1615 (3)	−587 (4)
C(8)	9362 (3)	1184 (3)	60 (5)
C(9)	9904 (3)	2321 (3)	3386 (4)
C(10)	10424 (2)	2321 (3)	2710 (4)
C(11)	10292 (3)	2812 (3)	1787 (4)
C(12)	7810 (3)	3754 (2)	1606 (3)
C(13)[a]	7405 (10)	3529 (6)	2485 (13)
C(14)[a]	6997 (6)	3888 (6)	494 (8)
C(15)[a]	8412 (5)	4497 (4)	1923 (11)
C(13*)[b]	8345 (12)	4056 (12)	2902 (15)
C(14*)[b]	8044 (18)	4371 (17)	856 (23)
C(15*)[b]	6859 (21)	3545 (19)	1399 (32)
H(1)	10261 (33)	595 (30)	1257 (43)
H(2)	9632(24)	287 (22)	2547 (29)
H(3)	8465 (30)	540 (28)	2720 (39)
H(4)	7204 (25)	1184 (23)	1588 (32)
H(5)	6717 (33)	1715 (32)	74 (40)
H(6)	7334 (29)	2020 (24)	−1072 (36)
H(7)	8623 (35)	1951 (32)	−1064 (47)
H(8)	9817 (35)	1343 (30)	−255 (44)
H(9A)	10042 (30)	1815 (30)	3891 (37)
H(9B)	9591 (30)	2825 (25)	3442 (38)
H(10)	10741 (28)	1879 (26)	2753 (36)
H(11A)	9999 (25)	3346 (24)	1772 (32)
H(11B)	10657 (27)	2671 (25)	1406 (34)

[a] Occupancy 0.80 (1). [b] Occupancy 0.20 (1).

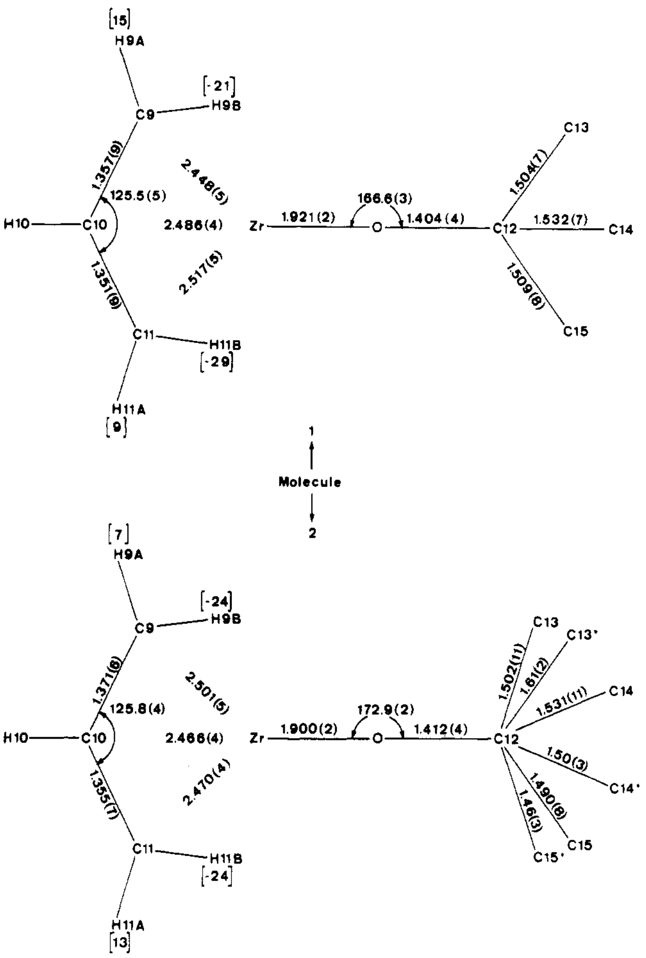


Figure 4. Selected distances (Å) and angles (deg) in the (η-C_3H_5)$ZrOC_4H_9$ fragments with inclinations (deg in brackets) of the C–H bonds out of the allyl carbon atom planes toward the zirconium atoms having a positive sign.

groups. As in (COT)$ZrCl_2$·THF,[2] the C–H bonds of the COT rings are inclined toward the zirconium atom, the average angle between the C–H vectors and the COT planes being 9.2 (9)° in this case.

While the allylic C–C distances do not deviate significantly from their mean value of 1.358 (4) Å, the Zr–C(allyl) distances vary significantly about their mean of 2.481 Å (Figure 4). Thus the C_3H_5–Zr interactions in I are slightly asymmetric in the solid state. Lack of coplanarity of allyl substituents with the C_3 fragments has been found in other π-allyl complexes,[5] but the clear detection of such distortions in this case in which all substituents are hydrogen atoms is noteworthy. The syn and meso hydrogen atoms are on the zirconium side of the plane while the anti hydrogen atoms are on the other side (Figure 4).

The Zr–O bonds (Figure 4), mean 1.91 (1) Å, are short compared to the sum of the covalent radii, 2.11 Å,[6] and thus are indicative of a strong bonding. Since the Zr–O–C angles, which are apparently not uneffected by packing forces, are very large, sp hybridization for the oxygen atom may be invoked. This would be stabilized by O(2pπ)→Zr(dπ) bonding which would impart partial triple-bond character to this linkage. Interestingly, the conformation of the $ZrOC(CH_3)_3$ fragment in molecule 1 approximately corresponds to that of only 20% occupancy in molecule 2.

---

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

[6] L. Pauling, "The Chemical Bond", Cornell University Press, Ithaca, NY, 1967, pp 148–150.

Discussion

The conformation of the COT carbon atoms could be related to the rotamer angle which was defined previously. Thus tub and folded ring stereochemistries are expected for rotamer angles of 22.5 and 0°, respectively. Despite the fact that the rotamer (12.7°) found in molecule 1 is more like the former while that (9.9°) of molecule 2 most closely resembles the latter, it is not understandable why a small change in conformation angle (3°) leads to such a large difference in ring stereochemistry.

Asymmetric π bonding of other carbocyclic ligands to metal atoms has been detected previously,[7] but the interesting feature of the (COT)Zr systems is the larger degree of flexibility in this linkage. While the effects of steric repulsions on the Zr–C(COT) bond distances are difficult to dismiss, we feel that the following electronic factors merit attention. Consider a coordinate system on the Zr atom with z along the COT plane normal, y along the normal to the C(10)–Zr–O plane, and x chosen to complete a right-handed framework. The interaction of the allyl fragment and alkoxy group with the Zr atom will lift the degeneracy of the $4d_{xz}$ and $4d_{yz}$ orbitals, forcing the former to higher energy. Now an important part of the COT–Zr bonding will be the interaction of the ring e_1 orbitals with the higher lying $4d_{xz}$ and $4d_{yz}$ functions of the metal atom.[8] Since the energy difference between the ring orbital and $4d_{xz}$ will be greater than that involving $4d_{yz}$, the latter interaction will be stronger. In other words, the shorter Zr–C(COT) bonds should be those most nearly perpendicular to the C(10)$\rightarrow$O vector. This is observed.

Registry No. I, 79703-91-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

---

[7] L. R. Byers and L. F. Dahl, *Inorg. Chem.*, 19, 277 (1980).

[8] S. Evans, J. C. Green, S. E. Jackson, and B. Higginson, *J. Chem. Soc., Dalton Trans.*, 304 (1974).

Stereochemistry of Transition Metal Cyclooctatetraenyl Complexes. Molecular Structure of (η-Cyclooctatetraenyl)(η^3,$\eta^{3'}$-deca-2,7-diene-4,9-diyl)zirconium

David J. Brauer and Carl Krüger*

Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim-Ruhr, West Germany

Received July 14, 1981

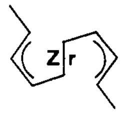
(η-Cyclooctatetraenyl)(η^3,$\eta^{3'}$-deca-2,7-diene-4,9-diyl)zirconium crystallizes in the space group $P2_1/n$ with a = 12.646 (4) Å, b = 14.185 (4) Å, c = 8.373 (2) Å, β = 95.89 (2)°, d_{calcd} = 1.474 g/cm^3, and Z = 4. Least-squares refinement of the structure converged with a conventional R value of 0.020 for 3506 counter-measured X-ray data with $I > 2\sigma(I)$. The monomeric molecules have approximate C_2 symmetry. Highly asymmetric Zr–allyl bonding is found. The Zr–C(allyl) distances average 2.385 (6), 2.532 (3), and 2.824 (2) Å, the longest and shortest distances being associated with methyl- and methylene-substituted carbon atoms, respectively. While the former pair displays trigonal hydridization, the stereochemistry of the latter pair is more nearly tetrahedral. The reason for the asymmetrical bonding is traced to the relief of nonbonded repulsion between the zirconium and methylene carbon atoms. The Zr–C(COT) bond distances display significant variations which cannot be traced to a trans effect induced by the asymmetrical Zr–allyl bonding but rather to steric repulsion between the two hydrocarbyl ligands. On the average, the C–H vectors of the COT ligand are tilted 6.1 (9)° out of the COT carbon atom plane toward the metal atom.

Introduction

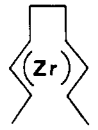
While $Zr(C_3H_5)_4$ catalytically converts butadiene into low molecular weight polybutadienes,[1] the catalytic oligomerization of butadiene by (η-COT)$Zr(C_3H_5)_2$ (I), COT = 1,3,5,7-cyclooctatetraene, yields mainly the dimer octa-1,3,6-triene and only traces of higher polymers.[2] This contrast in product distributions suggests that the (COT)Zr fragment remains intact during the latter reaction. Indeed, the isolation of an intermediate (II) was reported which contained a butadiene dimer attached via two allyl fragments to a (η-COT)Zr moiety.[2] IR and NMR investigations of II suggested an asymmetric π-allyl-bonding mode with terminal C atoms being further from the Zr atom than those C atoms adjacent to the C–C bond joining the two butadiene species.[2]

The catalytic polymerization of *cis*-piperylene by I is more complex. In addition to lesser amounts of higher oligomerics, mixtures of 4-nonatrienes and decatrienes were obtained. Intermediates were also detected by NMR in this case, the one containing a C_{10} chain (III) being isolated. According to the NMR results, III would correspond to a 1,8-dimethyl derivative of II,[3] that is, (η-COT)(η^3-$CH_3CHCHCHCH_2)_2Zr$.

An X-ray structural study on III appeared desirable. First, establishment of the C_{10} chain symmetry, both C_s (A) and C_2 (B) geometries being compatible with the



A



B

spectroscopic data, might help clarify the mechanism of hydrogen transfer occurring during displacement of the

---

[1] E. Steinrücke, Dissertation, Technische Hochschule Aachen (1966).

[2] H. J. Kablitz and G. Wilke, *J. Organomet. Chem.*, 51, 241 (1973).

[3] H. J. Kablitz, unpublished results.

0276-7333/82/2301-0207$01.25/0