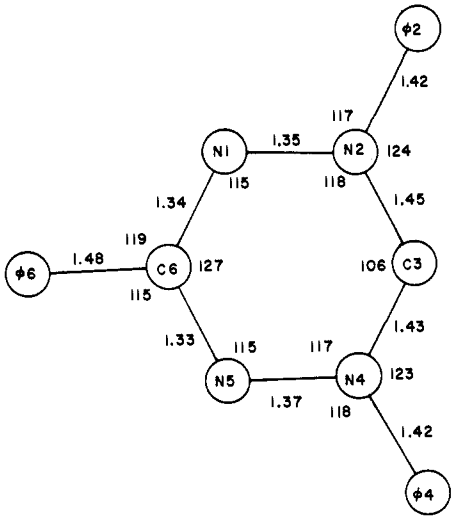

Figure 1. Bond distances (Å) and angles (deg) in and around the verdazyl ring. The estimated standard deviations are 0.01 Å and 1 deg, respectively.

in the ring bond angles from regular trigonal geometry at N_1, N_5, and C_6 are also observed in *s*-tetrazine itself, where the N–C–N angle is 125° and C–N–N angle is 118°.[4] The C(6)–N(1) and C(6)–N(5) bond lengths are also very similar to the C–N bond length of 1.34 Å in *s*-tetrazine.

The nonplanarity of C(3) is apparently the indirect result of intramolecular strain between ϕ_2 and ϕ_4. The repulsions due to the *ortho* hydrogens on these groups are partly relieved by rotating the rings and warping them upwards. The methylene group is then forced downward in order to preserve approximate planarity around N(2) and N(4). The *ortho* hydrogens remain staggered between the two hydrogens of the methylene group.

Acknowledgment. We thank Dr. F. A. Neugebauer for supplying crystals of this compound.

(4) A. J. Merer and K. K. Innes, *Proc. Roy. Soc.* (London), **A302**, 271 (1968).

Donald E. Williams
Chemistry Department, University of Louisville
Louisville, Kentucky 40208
Received December 13, 1968

Tris(hexafluoroacetylacetonato)-π-cyclopentadienylzirconium. Structure and Stereochemical Nonrigidity

Sir:

We have been engaged in nmr studies of π-cyclopentadienyl derivatives of titanium, zirconium, and hafnium involving fluorinated β-diketones as ligands; examples are $(\pi\text{-}C_5H_5)Ti(hfac)_2Cl$, $(\pi\text{-}C_5H_5)Zr(tfac)_3$, and $(\pi\text{-}C_5H_5)Zr(hfac)_3$.[1,2] A very recent communication by Pinnavaia, Howe, and Butler[3] reports closely related though complementary work, and prompts us to submit this preliminary account of our own investigation.

Nmr studies on $(\pi\text{-}C_5H_5)Zr(hfac)_3$ led us to assume a pentagonal-bipyramidal geometry for the molecule. In view of the rarity of this form of heptacoordination[4] among organometallic compounds, an X-ray single-crystal structural determination was undertaken. Crystal data are $a = 13.42 \pm 0.02$, $b = 22.94 \pm 0.02$, $c = 8.90 \pm 0.02$ Å; $\beta = 95.0 \pm 0.2°$ for space group $P2_1/n$ with four molecules per unit cell. A total of 2009 unique reflections above background were collected on a fully automated PAILRED diffractometer using crystal-monochromatized Mo Kα radiation. The data came from the nine levels, *hk*0–*hk*8, perpendicular to *c*. A correction for decomposition in the X-ray beam was applied, based upon the measurement of a set of standard reflections after each layer was collected. Patterson and Fourier methods established the positions of all nonhydrogen atoms. During refinement, some difficulty was experienced with the fluorine atoms, which had relatively high isotropic temperature parameters.

At the present stage of refinement, the conventional residual is 9.2%, with the zirconium and fluorine atoms allowed to vibrate anisotropically. We propose to continue refinement after the possibility of partial or complete disorder in the fluorine atom positions has been investigated.

The molecular structure is shown in Figure 1, from which trifluoromethyl groups have been omitted for

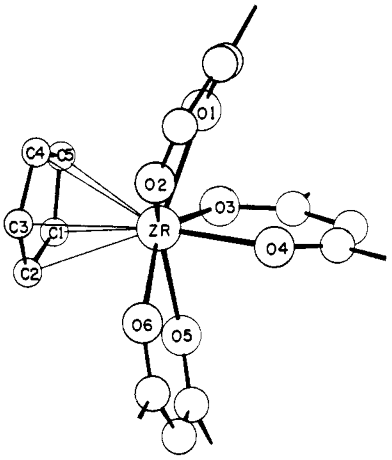

Figure 1. A view of the π-$C_5H_5Zr(hfac)_3$ molecule with trifluoromethyl groups omitted for clarity. Oxygen atoms labeled 1, 3, 5, 6, and 2 are in equatorial positions of the pentagonal-bipyramidal structure.

---

(1) The new compounds have been characterized by microanalysis and mass spectra. A full account of their preparation and properties will be submitted later.

(2) Abbreviations: acac = $CH_3COCHCOCH_3$; tfac = $CF_3COCHCOCH_3$; hfac = $CF_3COCHCOCF_3$.

(3) T. J. Pinnavaia, J. J. Howe, and E. D. Butler, *J. Am. Chem. Soc.*, **90**, 5288 (1968).

(4) We take the view that the π-cyclopentadienyl group is most conveniently regarded in this case as occupying a single coordination position. An easily visualized description of the over-all geometry is then possible. The π-cyclopentadienyl group occupies a larger share of the coordination sphere than typical ligands, as implied by the displacement of equatorial ligands in Figure 1.

The π-cyclopentadienyl ring is often regarded as tridentate, which would here imply nonacoordinate zirconium. The actual arrangement of ligands resembles neither of the regular polyhedra for nine coordination (E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967)), so that the molecular geometry is not aptly described in these terms. A referee has pointed out that zirconium is in fact undecacoordinate (*i.e.*, five carbons and six oxygens), and that the idealized geometry of the complex could be derived from an eicosahedron by suppressing one vertex. We do not consider that such a description is advantageous, however, since it is less familiar and less easily visualized, and deviations from eicosahedral geometry are appreciable.

Table I. Selected Bond Lengths and Angles in π-$C_5H_5Zr(hfac)_3$

Bond	Length, Å	Angle	Deg
$Zr-C_1$	2.51	O_1-Zr-O_2	73.5
$Zr-C_2$	2.55	O_1-Zr-O_3	68.2
$Zr-C_3$	2.53	O_3-Zr-O_5	68.1
$Zr-C_4$	2.51	O_5-Zr-O_6	74.5
$Zr-C_5$	2.54	O_6-Zr-O_2	69.7
$Zr-O_1$	2.22		
$Zr-O_2$	2.23	O_4-Zr-O_1	80.9
$Zr-O_3$	2.28	O_4-Zr-O_2	80.2
$Zr-O_4$	2.16	O_4-Zr-O_3	79.6
$Zr-O_5$	2.20	O_4-Zr-O_5	80.6
$Zr-O_6$	2.24	O_4-Zr-O_6	79.6
	Mean Values (Å)		
O-C	1.27	$C-CF_3$	1.49
C-C	1.38	C-F	1.32

clarity. Pertinent bond lengths and angles are listed in Table I; the accuracy of these figures may be judged from the estimated standard deviations in atomic positions obtained from the inverse matrix: Zr = 0.002, F = 0.015, C = 0.021, O = 0.011 Å. The structure is most conveniently described as a pentagonal bipyramid.[4] Two of the bidentate ligands (designated 1, 2 and 5, 6 with reference to the oxygen atoms as labeled in Figure 1) lie in the equatorial plane, while the third ligand (3, 4) occupies one of the axial positions and the remaining equatorial one. The other axial position is occupied by the cyclopentadienyl group,[4] which is symmetrically placed, within error, on the axis of the bipyramid. Presumably as a consequence of the greater steric effect of the cyclopentadienyl group, the five equatorial Zr-O bonds are tilted away by a surprisingly regular 10°.

The temperature variation of the ^{19}F nmr spectrum of π-$C_5H_5Zr(hfac)_3$ is shown in Figure 2. The pentagonal-bipyramidal model predicts four bands of intensity ratio 2:2:1:1, and this is observed at −30°. As the temperature is raised, the more intense pair (due to the equatorial ligands) coalesces, becoming fully averaged near 50°. The less intense pair (due to the 3, 4 ligand) becomes involved in a general exchange process only at higher temperatures. The barrier to exchange of CF_3 groups on the more rigid 3, 4 ligand may be related to the $Zr-O_4$ bond length, which is 0.07 Å shorter than the average of the other five Zr-O bonds.[5]

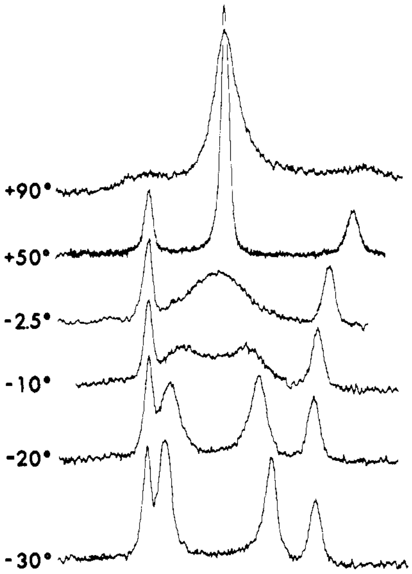

Figure 2. Temperature variation of the ^{19}F nmr spectrum of π-$C_5H_5Zr(hfac)_3$ in methylcyclohexane at 50 and 90° and acetone at lower temperatures. Chemical shifts differ appreciably in the two solvents and the spectra shown have been aligned vertically for illustrative purposes. Spectra were recorded at 56.4 MHz, and a 44-cps segment is shown.

Both proton and ^{19}F spectra of the unsymmetrical chelate π-$C_5H_5Zr(tfac)_3$ can be similarly interpreted. The room-temperature spectra show that two isomers are present in a molar ratio of *ca.* 3:2; the isomers differ in the orientation of the 3, 4 ligand (*i.e.*, CF_3 equatorial or CF_3 axial). Exchange of CH_3 and CF_3 on the equatorial ligands is rapid at room temperature, so that each isomer is characterized in the CH_3 or CF_3 region by two peaks in 1:2 intensity ratio.

Finally, we have observed in the ^{19}F spectrum of π-$C_5H_5Ti(hfac)_2Cl$ two sets of four equal-intensity bands, with one set relatively weak and due to an isomer. The existence of more than one isomer having all CF_3 groups nonequivalent rules out an octahedral coordination for this molecule in solution. We can confirm, however, the observation[3] that only one isomer of the related molecule π-$C_5H_5Zr(acac)_2Cl$ is observable in its proton nmr spectra.

Acknowledgment. We thank the National Research Council of Canada for financial support.

---

(5) The statistical significance of the differing Zr–O distances will be finally assessed when the structure is fully refined. It is also worth noting that the two bonds to the unique (3, 4) ligand are 0.06 Å longer and 0.06 Å shorter than the mean of the four Zr–O bonds in the two similar ligands (2.22 Å).

M. Elder, J. G. Evans, W. A. G. Graham
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

Received November 12, 1968

The Structure of Poly-2′-O-methyladenylic Acid at Acidic and Neutral pH

Sir:

The presence of minor components is a highly characteristic feature of the primary structure of RNA, in particular of transfer RNA. Many subtle variations in the three-dimensional structure of RNA may become possible by changing number, distribution, and kind of the minor components in a given sequence of major nucleotides. Such a "fine structure" may be needed for the full biological activity of RNA. As part of our efforts to understand the effects of specific minor nucleotides on RNA conformation[1,2] we have studied the structure of poly-2′-O-methyladenylic acid[3,4] in weakly acidic and neutral solutions. The presence of 2′-O-methylribonucleotides has been detected in transfer,[5] ribosomal,[6] and

---

(1) P. A. Cerutti, H. T. Miles, and J. Frazier, *Biochem. Biophys. Res. Commun.*, **22**, 466 (1966).

(2) P. A. Cerutti and N. Miller, *J. Mol. Biol.*, **26**, 55 (1967).

(3) F. Rottman and K. Heinlein, *Biochemistry*, **7**, 2634 (1968).

(4) Abbreviations: poly-2′-O-methyladenylic acid, poly 2′-O-mA; polyadenylic acid, poly A.

(5) R. H. Hall, *Biochemistry*, **3**, 876, (1964).

(6) E. K. Wagner, S. Penman, and V. M. Ingram, *J. Mol. Biol.*, **29**, 371 (1967).