bonds from Na to oxygens in adjacent CO_3 groups. The motions of the CO_3 atoms are fairly complex. They may be described as being approximately symmetrical about the O(1)–C–Ca–C′–O(1′) line, which is a pseudosymmetry element of the triplet.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

The Crystal Structure of Tris(hexafluoroacetylacetonato)-π-cyclopentadienylzirconium

BY M. ELDER

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The structure of tris(hexafluoroacetylacetonato)-π-cyclopentadienylzirconium, (π-C_5H_5)Zr($CF_3COCHCOCF_3$)$_3$, has been elucidated by single-crystal X-ray techniques and refined to a conventional residual of 6.1%. A total of 2009 observations above background, collected by counter methods, was used in the determination. The space group is monoclinic, $P2_1/n$, with $a = 13.48$ (2) Å, $b = 23.03$ (2) Å, $c = 8.95$ (1) Å, and $\beta = 94°\ 52\ (8')$. The calculated density is 1.86 g cm^{-3} for four molecules per unit cell. The molecular complex exhibits pentagonal-bipyramidyl geometry. Five of the six coordinated oxygen atoms lie in an equatorial plane about the zirconium while the sixth oxygen and the π-cyclopentadienyl group occupy the two axial positions. The zirconium atom is displaced 0.39 Å from the equatorial plane toward the latter group. Two of the chelate rings exhibit folding of 4.5 and 8.4°, respectively, about the O···O line while the third ring, occupying axial and equatorial oxygen atom coordination positions, is planar. The two Zr–O distances in this ring differ by 0.10 Å.

Introduction

Nuclear magnetic resonance studies of high coordination number metal β-diketonates[1] have indicated that these complexes exhibit a considerable degree of lability in solution.[2-4] Even at low temperatures single-resonance lines in complexes such as Zr(acac)$_4$, Zr(acac)$_3$Cl,[5] Y(tfac)$_4^-$, and Y(hfac)$_4^-$[4] indicate that a rapid intramolecular rearrangement averages the expected nonequivalent $-CH_3$ and $-CF_3$ environments. However, the presence of a π-cyclopentadienyl group in such complexes as (π-C_5H_5)Zr(acac)$_2$Cl[6] and (π-C_5H_5)Zr(hfac)$_3$[7] influences the stereochemical nonrigidity of the β-diketone groups sufficiently to allow the observation of nonequivalent methyl proton and fluorine environments. The crystal structure determination of (π-C_5H_5)Zr(hfac)$_3$ was undertaken in order to provide some structural information toward the interpretation of this effect and to confirm the structural prediction based upon the nmr study.

Experimental Section

Crystals of (π-C_5H_5)Zr($CF_3COCHCOCF_3$)$_3$ grown from acetone solution were kindly supplied by Mr. J. G. Evans. They were large, yellow parallelpipeds, many of which showed evidence of occluded solvent and air cavities under microscopic examination. Small, apparently flawless crystals were chosen for photographic purposes. Examination of Cu Kα radiation Weissenberg photographs of levels ($hk0$)–($hk2$) and Mo Kα radiation precession photographs of levels ($h0l$) and ($0kl$) showed 2/m Laue symmetry. The systematic absences ($0k0$) absent, k odd, and ($h0l$) absent, $h + l$ odd, indicated the monoclinic space group $P2_1/n$. This unconventional setting of space group C_{2h}^5-$P2_1/c$ was used throughout because of the near orthogonality of its axes. The general positions are: $\pm(x, y, z)$, $\pm(^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$. Cell dimensions were determined from the precession photographs of the levels $0kl$ and $h0l$ taken with Mo Kα radiation (λ 0.71069 Å) at 26°. They were $a = 13.48 \pm 0.02$ Å, $b = 23.02 \pm 0.02$ Å, $c = 8.95 \pm 0.01$ Å, and $\beta = 94°\ 52' \pm 8'$. The calculated density is 1.86 g cm^{-3} assuming four molecules per unit cell. An experimental density of 1.71 g cm^{-3} was determined using a pycnometer with water as the displacing liquid. The discrepancy between the two figures is not regarded as serious owing to the air cavities in the crystals which would be expected to cause a low experimental density for a bulk sample.

Intensity data were collected on a PAILRED fully automated diffractometer using a small single crystal mounted in a thin

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(1) Abbreviations: acac, $CH_3COCHCOCH_3$; tfac, $CF_3COCHCOCH_3$; hfac, $CF_3COCHCOCF_3$.

(2) A. C. Adams and E. M. Larsen, *Inorg. Chem.*, **5**, 228 (1966).

(3) T. J. Pinnavaia and R. C. Fay, *ibid.*, **5**, 233 (1966).

(4) F. A. Cotton, P. Legzdins, and S. J. Lippard, *J. Chem. Phys.*, **45**, 3461 (1966).

(5) T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **7**, 502 (1968).

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

(7) M. Elder, J. G. Evans, and W. A. G. Graham, *ibid.*, **91**, 1245 (1969).

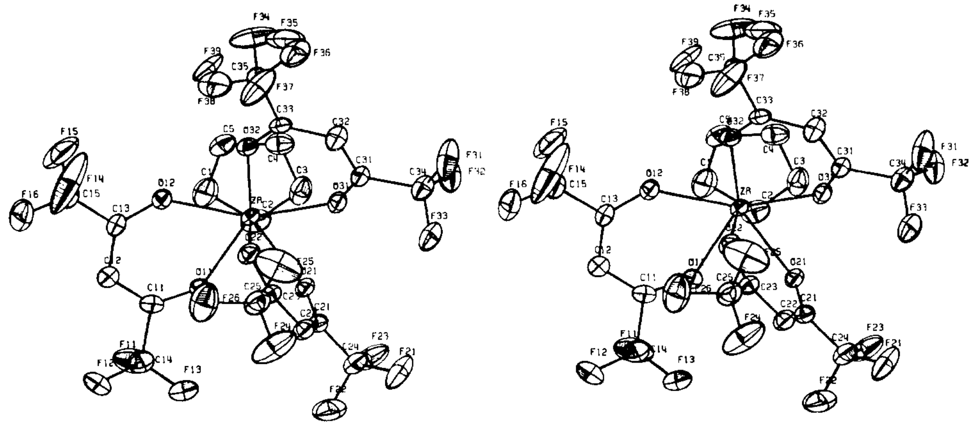

Figure 1.—Stereogram showing a molecule of tris(hexafluoroacetylacetonato)-π-cyclopentadienylzirconium. The positions of three of the disordered fluorine atoms are indicated in outline and the bonds to these atoms are not shown. Ellipsoids are scaled to enclose 20% probability.

glass capillary. The crystal was a needle of nearly square cross section, length 0.9 mm, and mean radius 0.21 mm. It was so mounted since the first crystals used, exposed to the atmosphere, showed considerable surface decomposition in the X-ray beam. A total of 2009 unique observations above background were collected from nine reciprocal lattice levels perpendicular to *c*. Reflections within $\sin\theta \leq 0.37$ (Mo Kα) were scanned but there is some asymmetry in the data since $\sin\theta_{\max} = 0.32$ in the *c* direction. Scanning procedure, determination of the significance of an observation, and other details pertinent to data collection have been discussed in a previous paper:[8] relevant differences in procedure are noted here. Crystal-monochromatized Mo Kα radiation was used, with a counter aperture of 2.5°. The scanning speed was 1°/min with the scan range varying from 1.4° for *hk*0 to 2.5° for *hk*8. Background was counted for 0.4 min with the crystal stationary at either end of the scan range. A correction for decomposition was applied to the data of each layer. Twelve standard reflections from different regions of the *hk*0 layer were scanned after each layer had been collected and a decomposition curve calculated from a plot of the average values against time. The correction factor for each layer was found by interpolation of this curve at a time corresponding to the midpoint of the layer. This relatively crude method was used since the rate of decomposition was not great, amounting to no more than 16% of the starting intensity by the end of the *hk*8 layer.

Data were corrected for Lorentz and polarization effects, but no absorption correction was applied. The linear absorption coefficient for Mo Kα radiation is 6.2 cm^{-1}. The value of μR_{mean} for the crystal used was 0.13 and the neglect of absorption corrections is estimated to cause a maximum error in intensity of 5% in a few extreme cases.

The unsharpened Patterson map was used to place the zirconium atom and remaining atoms were located by three successive difference Fourier maps. Refinement was carried out with a full-matrix least-squares program,[9] with minimization of the function $\Sigma w[|F_o| - |F_c|]^2$ using the 2009 unique reflections. The weighting scheme used was of the form $w = a^2/[a^2 + (F_o - b)^2]$ where $a = 16.7$ and $b = 16.7$ on the absolute scale were chosen to minimize the variation of the mean value of $\Sigma w|F_o - F_c|^2$ for groups of reflections computed for increasing $|F_o|$. Atomic scattering factors for neutral zirconium, fluorine, oxygen, and carbon were taken from the compilations of Ibers[10a] with the zirconium curve corrected for the real part of the anomalous dispersion effect.[10b]

Some difficulties were experienced with the fluorine atom locations owing to the predictably large amplitude of oscillation of the $-CF_3$ groups about the $C-CF_3$ bonds. Finally a difference map based upon the refined positions of the nonfluorine atoms ($R = 28\%$) was prepared. The degree of resolution of the fluorine atoms in the resulting map varied considerably. For five of the $-CF_3$ groups it was possible to locate the three fluorine atoms as resolved peaks with the regions between peaks at least as low as half the height of the peaks. For the sixth group, six nearly equal, evenly spaced, and fairly well-resolved peaks required that six half-weight fluorine atoms be used in the model. All atoms were then refined to $R_1 = 0.149$ and $R_2 = 0.210$[11] with individual isotropic temperature factors. The zirconium atom and all of the fluorine atoms were then allowed to refine anisotropically. A significant improvement in structure factor agreement dropped R_1 and R_2 to 0.107 and 0.150, respectively. Finally the remaining atoms were refined with anisotropic temperature factors. Refinement terminated after six cycles, refining about 240 parameters at a time, with $R_1 = 0.061$ and $R_2 = 0.088$, indicating a significant improvement in the model, judged by Hamilton's criteria.[12] In the final cycle, in which all positional parameters were refined, there was no parameter shift greater than 10% of the corresponding standard error. The positional and thermal parameters, together with their standard errors derived from the inverse matrix, are listed in Tables I and II. The shape and orientation of the thermal ellipsoids can be seen in the stereopair of Figure 1. The fluorine atom ellipsoids show their greatest elongation in the directions that would be expected for $-CF_3$ groups oscillating about the $C-CF_3$ bonds. The inadequacy of the standard anisotropic model in handling an oscillation of this type is admitted; its use, on the basis of computing expediency, is justified by the relative unimportance of the $-CF_3$ positions to the structure and the assumption that the method of handling them will have little effect upon the important region of the structure around the zirconium atom position. The final difference Fourier map is indeed clean in this region, residual electron density ranging from 0.6 to -0.4 e$^-$/Å^2; the largest positive peak is about one-sixth the height of the smallest carbon atom peak in an observed Fourier map on the same scale. Residual electron density near the fluorine atoms varies considerably with the amplitudes of thermal motion of these atoms. For the least well-defined $-CF_3$ group the fluorine atom peaks on the final observed Fourier map range from 3.3 to 2.9 e$^-$/Å^2 on the absolute scale: the residual electron density is in the

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(8) M. Elder and D. Hall, *Inorg. Chem.*, **8**, 1268 (1969).

(9) Programs for the IBM 360/67 computer used in this work were of local origin, together with Busing and Levy's least-squares program ORFLS, Johnson's plotter program ORTEP, and the system of crystallographic programs from F. R. Ahmed of the National Research Council, Ottawa, Canada.

(10) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962: (a) p 202–211; (b) p 216.

(11) The agreement ratios are defined by $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$ and $R_2 = [\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2]^{1/2}$.

(12) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1962, p 160.

TABLE I

ATOMIC POSITIONAL PARAMETERS[a]

Atom	x/a	y/b	z/c
Zr	0.21999 (6)	0.14355 (4)	0.23148 (9)
C_1	0.0406 (9)	0.1155 (7)	0.1607 (17)
C_2	0.0828 (9)	0.1315 (6)	0.0214 (14)
C_3	0.1036 (9)	0.1908 (6)	0.0303 (15)
C_4	0.0732 (9)	0.2121 (5)	0.1671 (14)
C_5	0.0365 (8)	0.1668 (6)	0.2460 (14)
O_{11}	0.2336 (5)	0.0503 (3)	0.1679 (7)
O_{12}	0.1807 (5)	0.0920 (3)	0.4314 (7)
C_{11}	0.2319 (7)	0.0033 (4)	0.2331 (11)
C_{12}	0.2099 (9)	−0.0068 (5)	0.3790 (13)
C_{13}	0.1842 (7)	0.0392 (4)	0.4681 (10)
C_{14}	0.2549 (9)	−0.0494 (5)	0.1280 (13)
C_{15}	0.1516 (8)	0.0263 (5)	0.6149 (11)
F_{11}	0.1758 (8)	−0.0613 (4)	0.0433 (12)
F_{12}	0.2839 (6)	−0.0961 (3)	0.2087 (10)
F_{13}	0.3237 (7)	−0.0369 (3)	0.0434 (10)
F_{14}	0.2037 (13)	0.0414 (10)	0.7211 (12)
F_{15}	0.0699 (10)	0.0495 (7)	0.6433 (14)
F_{16}	0.1270 (12)	−0.0253 (5)	0.6395 (13)
O_{21}	0.3057 (5)	0.1318 (3)	0.0251 (7)
O_{22}	0.3690 (5)	0.1254 (3)	0.3345 (7)
C_{21}	0.3960 (7)	0.1197 (4)	0.0160 (10)
C_{22}	0.4702 (8)	0.1110 (4)	0.1322 (11)
C_{23}	0.4519 (6)	0.1148 (4)	0.2819 (10)
C_{24}	0.4258 (8)	0.1168 (5)	−0.1402 (12)
C_{25}	0.5338 (9)	0.1055 (6)	0.4014 (15)
F_{21}	0.5053 (7)	0.1475 (4)	−0.1588 (11)
F_{22}	0.4524 (9)	0.0612 (4)	−0.1731 (10)
F_{23}	0.3600 (6)	0.1274 (4)	−0.2490 (8)
F_{24}	0.6181 (6)	0.0885 (6)	0.3525 (10)
F_{25}	0.5533 (9)	0.1530 (5)	0.4814 (14)
F_{26}	0.5148 (7)	0.0667 (5)	0.4998 (11)
O_{31}	0.2963 (5)	0.2245 (3)	0.1726 (7)
O_{32}	0.2219 (5)	0.1999 (3)	0.4363 (7)
C_{31}	0.3371 (7)	0.2662 (4)	0.2468 (11)
C_{32}	0.3292 (8)	0.2801 (5)	0.3959 (12)
C_{33}	0.2660 (6)	0.2450 (4)	0.4771 (10)
C_{34}	0.3968 (8)	0.3064 (5)	0.1514 (13)
C_{35}	0.2437 (9)	0.2661 (5)	0.6320 (13)
F_{31}	0.4356 (8)	0.3514 (4)	0.2248 (9)
F_{32}	0.3372 (6)	0.3305 (3)	0.0422 (8)
F_{33}	0.4627 (8)	0.2777 (4)	0.0876 (14)
F_{34}[b]	0.1477 (12)	0.2882 (13)	0.6258 (27)
F_{35}	0.2028 (24)	0.3145 (10)	0.6210 (26)
F_{36}	0.2851 (16)	0.3175 (8)	0.6695 (19)
F_{37}	0.3285 (12)	0.2663 (12)	0.7199 (16)
F_{38}	0.2517 (30)	0.2309 (12)	0.7247 (25)
F_{39}	0.1894 (12)	0.2344 (9)	0.7036 (18)

[a] Numbers in parentheses are the standard errors in the last significant figures, obtained from the inverse least-squares matrix. [b] Half-weight fluorine atoms are F_{34} through F_{39}.

TABLE II

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zr	61.0 (7)	19.4 (2)	111 (2)	−0.9 (3)	31.1 (7)	2.0 (4)
C_1	78 (10)	48 (5)	282 (32)	−15 (6)	18 (14)	12 (10)
C_2	91 (10)	47 (5)	189 (24)	10 (5)	0 (12)	−9 (8)
C_3	75 (9)	47 (5)	261 (30)	7 (5)	17 (13)	52 (9)
C_4	90 (10)	39 (4)	213 (25)	16 (5)	−3 (12)	−9 (8)
C_5	65 (8)	45 (4)	200 (22)	8 (5)	29 (11)	1 (9)
O_{11}	98 (6)	19 (2)	151 (11)	−2 (2)	33 (6)	−3 (3)
O_{12}	94 (6)	22 (2)	140 (11)	−5 (2)	39 (6)	−2 (3)
C_{11}	61 (7)	23 (2)	171 (19)	4 (3)	5 (9)	−13 (6)
C_{12}	97 (9)	27 (3)	193 (23)	3 (4)	44 (11)	5 (6)
C_{13}	61 (7)	26 (3)	131 (17)	−7 (3)	18 (8)	6 (5)
C_{14}	105 (10)	33 (3)	169 (20)	1 (4)	22 (11)	−10 (6)
C_{15}	93 (9)	29 (3)	135 (17)	−13 (4)	15 (9)	3 (5)
F_{11}	167 (9)	45 (2)	392 (21)	8 (4)	−21 (10)	72 (6)
F_{12}	160 (8)	23 (1)	355 (18)	16 (3)	48 (9)	0 (4)
F_{13}	179 (9)	38 (2)	327 (18)	13 (3)	133 (10)	−14 (4)
F_{14}	330 (22)	216 (13)	172 (19)	−190 (14)	46 (14)	−1 (11)
F_{15}	240 (14)	111 (6)	337 (25)	63 (8)	201 (16)	82 (9)
F_{16}	442 (24)	45 (3)	391 (27)	−5 (6)	281 (22)	28 (7)
O_{21}	69 (5)	24 (2)	115 (9)	4 (2)	26 (5)	9 (3)
O_{22}	76 (6)	29 (2)	122 (11)	3 (2)	23 (6)	5 (3)
C_{21}	69 (8)	20 (2)	126 (16)	−2 (3)	22 (9)	−6 (4)
C_{22}	77 (8)	29 (3)	133 (18)	3 (4)	27 (9)	3 (5)
C_{23}	53 (7)	23 (2)	142 (18)	1 (3)	24 (9)	2 (5)
C_{24}	67 (8)	40 (3)	163 (20)	6 (4)	31 (9)	8 (6)
C_{25}	81 (9)	40 (4)	226 (25)	11 (5)	37 (12)	18 (7)
F_{21}	153 (8)	75 (4)	258 (16)	−35 (4)	108 (9)	4 (5)
F_{22}	221 (11)	54 (3)	261 (17)	30 (4)	98 (10)	−20 (5)
F_{23}	122 (6)	83 (3)	129 (11)	28 (4)	33 (6)	4 (4)
F_{24}	95 (6)	132 (6)	220 (16)	42 (5)	11 (7)	18 (7)
F_{25}	196 (11)	63 (3)	444 (27)	19 (5)	−154 (14)	−62 (7)
F_{26}	152 (8)	73 (3)	278 (17)	−5 (4)	−12 (9)	66 (6)
O_{31}	97 (6)	23 (2)	133 (11)	−10 (3)	43 (6)	−3 (4)
O_{32}	77 (5)	21 (2)	141 (11)	−4 (2)	35 (6)	−13 (3)
C_{31}	68 (8)	24 (3)	140 (18)	−1 (4)	29 (9)	8 (5)
C_{32}	86 (9)	34 (3)	161 (21)	−9 (4)	24 (10)	6 (6)
C_{33}	59 (7)	23 (2)	108 (15)	11 (3)	14 (8)	−5 (5)
C_{34}	80 (9)	36 (3)	174 (20)	−15 (4)	27 (10)	0 (6)
C_{35}	97 (9)	22 (2)	197 (21)	−2 (4)	35 (11)	4 (5)
F_{31}	191 (9)	63 (3)	213 (14)	−70 (4)	5 (9)	23 (5)
F_{32}	169 (8)	40 (2)	211 (13)	−20 (3)	−3 (7)	31 (4)
F_{33}	174 (9)	51 (3)	551 (31)	4 (4)	222 (15)	51 (7)
F_{34}	84 (16)	94 (17)	372 (65)	42 (13)	12 (27)	−78 (28)
F_{35}	244 (42)	58 (13)	311 (62)	71 (24)	93 (65)	−7 (23)
F_{36}	159 (23)	49 (6)	195 (40)	−29 (12)	55 (25)	−44 (13)
F_{37}	112 (16)	103 (16)	107 (27)	−44 (15)	11 (14)	−25 (15)
F_{38}	457 (69)	63 (13)	227 (42)	94 (29)	214 (53)	73 (18)
F_{39}	113 (16)	63 (10)	209 (32)	−48 (12)	110 (19)	−63 (16)

[a] The anisotropic ellipsoid is given by: $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

range 0.7 to $-0.2\ e^-/\text{Å}^2$ near these atoms with the highest positive regions lying between pairs of atoms. For the $-CF_3$ groups with the best degree of resolution corresponding figures are 7.0 to 5.6 $e^-/\text{Å}^2$ for the fluorine atoms peaks and 0.4 to $-0.2\ e^-/\text{Å}^2$ for the range of residual electron density; for the half-weight fluorine atoms, 4.4 to 2.5 and 0.3 to $-0.2\ e^-/\text{Å}^2$, respectively.

The agreement between observed and calculated structure factors, listed on a scale 10 times absolute in Table III, showed no evidence of the need for a secondary extinction correction.

Discussion

Intramolecular bond lengths and angles are tabulated in Tables IV and V, respectively. The cyclopentadienyl group is symmetrically placed with respect to the zirconium atom; the perpendicular distance from the zirconium atom to the ring is 2.23 (1) Å, and the five Zr–C distances agree within error, mean value 2.527 (6) Å. There are no significant differences between the carbon–carbon distances in the cyclopentadienyl ring, and the mean value, 1.40 (1) Å, compares well with other reported values.[13]

The zirconium atom is formally eleven-coordinate and its stereochemistry is based upon that of an icosahedron with one vertex suppressed. The major distortion is caused by the compact cyclopentadienyl group and the unoccupied vertex is above the pentagonal face defined by this group. The distortions, however, are such as to maintain approximate C_{5v} symmetry (considering the coordinated atoms alone) as may be seen in Figure 2. An alternative and possibly more descriptive designation is in terms of a pentagonal bipyramid. This description is preferred since it involves little distortion; it is not intended to imply that the zirconium atom is seven-coordinate or that there is necessarily one bond to the $\pi\text{-}C_5H_5$ group. Five oxygen atoms form the equa-

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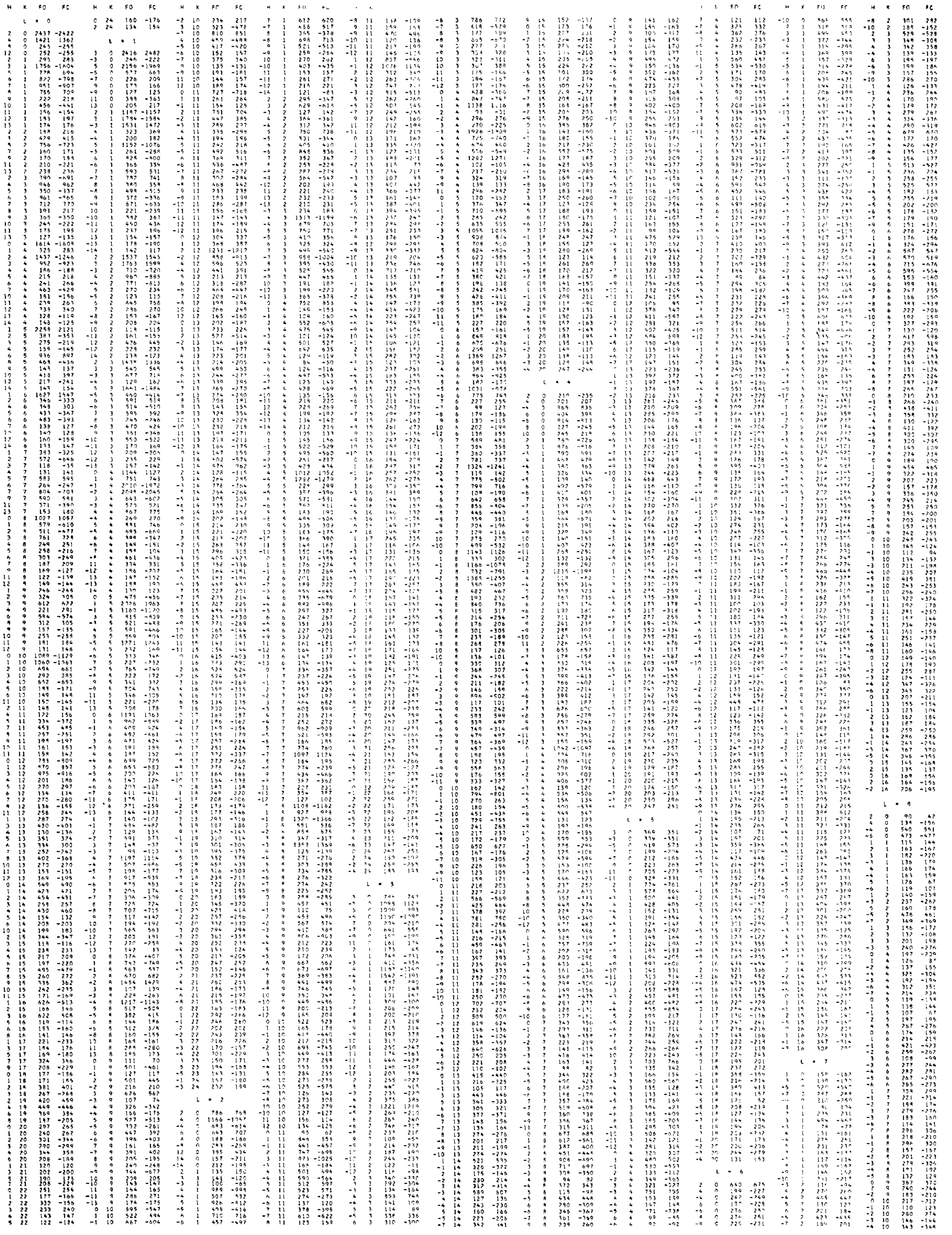
(13) P. J. Wheatley in "Perspectives in Structural Chemistry," Vol. 1, John Wiley & Sons, Inc., New York, N. Y., 1967, p 9.

Table III

Observed and Calculated Structure Factors (×10)



torial plane of the bipyramid with the unique oxygen, O_{22}, occupying one axial position and the cyclopentadienyl group the other. Thus two of the diketonate ligands lie in the equatorial plane while the third bridges equatorial and axial positions. For the purposes of the argument the cyclopentadienyl group is regarded as occupying one coordination position. Hereafter, "equatorial" and "axial" will be used in this context to describe the oxygen atom positions.

The zirconium atom is displaced 0.39 Å toward the cyclopentadienyl group from the plane of the equatorial oxygen atoms, which distortion can be attributed to the greater size of the cyclopentadienyl group compared with the axial oxygen atom. Table VI lists relevant least-squares planes calculated with program NRC-22.[9] The cyclopentadienyl group is planar within error limits, and while this is not true of the equatorial oxygen atoms, the deviations of the atoms from the least-

TABLE IV

INTRAMOLECULAR BOND LENGTHS (Å)

$Zr-C_1$	2.52 (1)	$O_{22}-C_{23}$	1.27 (1)	$C_{15}-F_{15}$	1.26 (2)
$Zr-C_2$	2.52 (1)	$O_{31}-C_{31}$	1.26 (1)	$C_{15}-F_{16}$	1.25 (2)
$Zr-C_3$	2.52 (1)	$O_{32}-C_{33}$	1.23 (1)	$C_{24}-F_{21}$	1.30 (2)
$Zr-C_4$	2.55 (1)	$C_{11}-C_{12}$	1.38 (2)	$C_{24}-F_{22}$	1.36 (2)
$Zr-C_5$	2.53 (1)	$C_{12}-C_{13}$	1.38 (2)	$C_{24}-F_{23}$	1.28 (2)
$Zr-O_{11}$	2.225 (6)	$C_{21}-C_{22}$	1.39 (2)	$C_{25}-F_{24}$	1.31 (2)
$Zr-O_{12}$	2.236 (6)	$C_{22}-C_{23}$	1.38 (2)	$C_{25}-F_{25}$	1.32 (2)
$Zr-O_{21}$	2.266 (6)	$C_{31}-C_{32}$	1.38 (2)	$C_{25}-F_{26}$	1.29 (2)
$Zr-O_{22}$	2.166 (6)	$C_{32}-C_{33}$	1.41 (2)	$C_{34}-F_{31}$	1.31 (2)
$Zr-O_{31}$	2.206 (6)	$C_{11}-C_{14}$	1.58 (2)	$C_{34}-F_{32}$	1.33 (2)
$Zr-O_{32}$	2.231 (6)	$C_{13}-C_{15}$	1.44 (2)	$C_{34}-F_{33}$	1.28 (2)
C_1-C_2	1.45 (2)	$C_{21}-C_{24}$	1.48 (2)	$C_{35}-F_{34}$	1.38 (3)
C_2-C_3	1.39 (2)	$C_{23}-C_{25}$	1.48 (2)	$C_{35}-F_{35}$	1.24 (3)
C_3-C_4	1.41 (2)	$C_{31}-C_{34}$	1.53 (2)	$C_{35}-F_{36}$	1.33 (3)
C_4-C_5	1.37 (2)	$C_{33}-C_{35}$	1.52 (2)	$C_{35}-F_{37}$	1.32 (3)
C_5-C_1	1.40 (2)	$C_{14}-F_{11}$	1.28 (2)	$C_{35}-F_{38}$	1.15 (3)
$O_{11}-C_{11}$	1.23 (1)	$C_{14}-F_{12}$	1.32 (2)	$C_{35}-F_{39}$	1.24 (3)
$O_{12}-C_{13}$	1.26 (1)	$C_{14}-F_{13}$	1.27 (2)		
$O_{21}-C_{21}$	1.25 (1)	$C_{15}-F_{14}$	1.18 (2)		

TABLE V

BOND ANGLES (DEGREES)

$C_1-C_2-C_3$	108 (1)	C_5-Zr-O_{12}	76.9 (3)	$C_{22}-C_{23}-C_{25}$	120.2 (9)
$C_2-C_3-C_4$	109 (1)	$Zr-O_{11}-C_{11}$	136.1 (6)	$C_{32}-C_{31}-C_{34}$	118.9 (9)
$C_3-C_4-C_5$	109 (1)	$Zr-O_{12}-C_{13}$	135.3 (6)	$C_{32}-C_{33}-C_{35}$	117.2 (8)
$C_4-C_5-C_1$	109 (1)	$Zr-O_{21}-C_{21}$	129.9 (6)	$F_{11}-C_{14}-F_{12}$	109.6 (10)
$C_5-C_1-C_2$	107 (1)	$Zr-O_{22}-C_{23}$	133.5 (6)	$F_{12}-C_{14}-F_{13}$	108.0 (10)
$O_{11}-Zr-O_{12}$	74.0 (2)	$Zr-O_{31}-C_{31}$	134.7 (6)	$F_{13}-C_{14}-F_{11}$	107.9 (10)
$O_{21}-Zr-O_{22}$	78.8 (2)	$Zr-O_{32}-C_{33}$	134.2 (6)	$F_{14}-C_{15}-F_{15}$	100.4 (13)
$O_{31}-Zr-O_{33}$	74.6 (2)	$O_{11}-C_{11}-C_{12}$	127.5 (9)	$F_{15}-C_{15}-F_{16}$	96.8 (11)
$O_{11}-Zr-O_{21}$	67.7 (3)	$O_{12}-C_{13}-C_{12}$	126.4 (9)	$F_{16}-C_{15}-F_{14}$	106.5 (13)
$O_{21}-Zr-O_{31}$	68.2 (3)	$O_{21}-C_{21}-C_{22}$	128.3 (9)	$F_{24}-C_{25}-F_{25}$	104.3 (10)
$O_{12}-Zr-O_{32}$	69.0 (2)	$O_{22}-C_{23}-C_{22}$	127.3 (9)	$F_{25}-C_{25}-F_{26}$	101.1 (9)
$O_{22}-Zr-O_{11}$	80.2 (2)	$O_{31}-C_{31}-C_{32}$	127.9 (9)	$F_{26}-C_{25}-F_{24}$	108.7 (10)
$O_{22}-Zr-O_{12}$	80.5 (2)	$O_{32}-C_{33}-C_{32}$	128.6 (9)	$F_{21}-C_{24}-F_{22}$	106.9 (11)
$O_{22}-Zr-O_{31}$	80.4 (2)	$C_{11}-C_{12}-C_{13}$	119.9 (10)	$F_{22}-C_{24}-F_{23}$	104.2 (11)
$O_{22}-Zr-O_{32}$	79.7 (2)	$C_{21}-C_{22}-C_{23}$	122.3 (9)	$F_{23}-C_{24}-F_{21}$	104.1 (11)
C_1-Zr-O_{11}	77.8 (4)	$C_{31}-C_{32}-C_{33}$	117.4 (9)	$F_{31}-C_{34}-F_{32}$	103.0 (9)
C_1-Zr-O_{12}	77.2 (4)	$O_{11}-C_{11}-C_{14}$	112.4 (8)	$F_{32}-C_{34}-F_{33}$	106.7 (10)
C_2-Zr-O_{11}	77.1 (3)	$O_{12}-C_{13}-C_{15}$	115.2 (8)	$F_{33}-C_{34}-F_{31}$	111.7 (11)
C_2-Zr-O_{21}	77.0 (3)	$O_{21}-C_{21}-C_{24}$	114.4 (8)	$F_{34}-C_{35}-F_{35}$	42.4 (16)
C_3-Zr-O_{21}	78.6 (3)	$O_{22}-C_{23}-C_{25}$	112.6 (8)	$F_{35}-C_{35}-F_{36}$	53.1 (15)
C_3-Zr-O_{31}	75.0 (4)	$O_{31}-C_{31}-C_{34}$	113.1 (8)	$F_{36}-C_{35}-F_{37}$	62.0 (13)
C_4-Zr-O_{31}	78.0 (3)	$O_{32}-C_{33}-C_{35}$	114.1 (8)	$F_{37}-C_{35}-F_{38}$	63.8 (19)
C_4-Zr-O_{32}	77.3 (3)	$C_{12}-C_{11}-C_{14}$	120.0 (9)	$F_{38}-C_{35}-F_{39}$	41.1 (18)
C_5-Zr-O_{32}	77.2 (3)	$C_{12}-C_{13}-C_{15}$	118.3 (9)	$F_{39}-C_{35}-F_{34}$	69.4 (14)
		$C_{22}-C_{21}-C_{24}$	117.2 (9)		

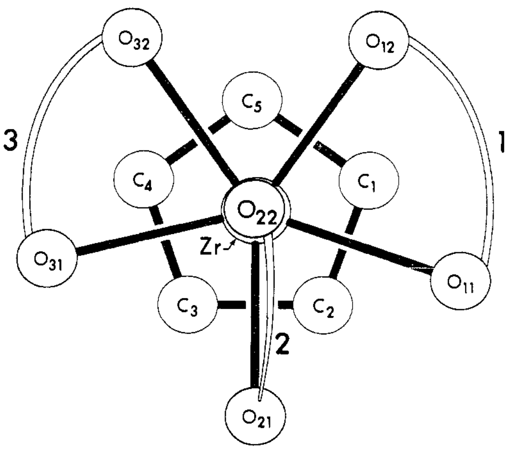


Figure 2.—The zirconium atom coordination polyhedron projected onto the plane of the π-cyclopentadienyl group.

squares plane are small. The angle between these two planes is less than 0.5°. The two diketone groups that provide four of the equatorial oxygen atoms (groups 1 and 3 in Figure 2) show some deviations from planarity. However, the greatest deviations from the least-squares planes are shown by the carbon atoms of the $-CF_3$ groups and these would be expected to be poorly positioned owing to the inadequacy of the fluorine atom treatment. The deviations are not attributed to distortive intramolecular forces but rather to deficiencies in the calculated model and possibly to residual errors in the data. The zirconium atom is displaced 0.14 and 0.26 Å, respectively, from the two planes implying bending of 4.5 and 8.4°, respectively, about the line joining the ligand oxygen atoms. In both cases the direction of bending is such as to move the uncoordinated parts of the two diketonate groups away from the side of the molecule occupied by the cyclopentadienyl group and closer to the axial oxygen atom. Since the carbon atoms of the cyclopentadienyl group have their closest nonbonded contacts with the oxygen atoms of the two equatorial diketonate groups and not with the uncoordinated atoms of these groups, it seems unlikely that the bending is an intramolecular effect. More probably, the distortion enables better molecular packing through minimization of intermolecular forces. Similar bending has been commonly observed by previous workers.[14,15] The unique diketonate group, bridging axial and equatorial positions, is planar within error limits and the zirconium atom lies on the least-squares plane. There is no bending about the O···O line, reinforcing the observation of Cotton and Wood[16] that such bending, though common, is not essential.

Table VII lists mean values for chemically equivalent bond distances and angles. The standard deviation of a number of such values provides a check of the accuracy of the error estimates for the values concerned. These error estimates were calculated from the inverse full-matrix parameter esd's but do not include an allowance for the correlation between the parameters. Program NRC-12[9] was used. The agreement between the standard deviations and the mean errors is good, except where the $-CF_3$ groups are involved. This seems to confirm the assumption that the approximation of the $-CF_3$ motion by anisotropic thermal parameters would have little effect upon the more important parameters. The mean values agree well with values averaged over a series of acetylacetonato complexes[17] and with previously observed values for similar fluorine-substituted ligands.[14,18]

There are some small, just significant differences between the modes of coordination of the three hexafluoroacetylacetonate groups. In addition to the absence of bending about the O···O line in the unique group, the two Zr–O distances for the group differ significantly by 0.10 Å or 16 times the standard deviation of one of them. The four Zr–O distances for the equatorial groups agree closely, with mean value 2.225 (11) Å, which is close to the average of the other two differing figures, 2.216 Å. The unique group subtends a greater angle at the zirconium atom and has a greater O···O

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TABLE VI

WEIGHTED LEAST-SQUARES PLANES

$LX + MY + NZ = D^a$

Atoms	L	M	N	D	χ^2	χ^{2b} $n-3$ 0.05	Dev[c]	
			Plane through Cyclopentadienyl Group					
C_1–C_2–C_3–C_4–C_5	0.8810	−0.1881	0.4341	0.4870	1.6	6.0		
			Plane through Equatorial Atoms of the Bipyramid					
O_{11}–O_{12}–O_{21}–O_{31}–O_{32}	0.8819	−0.1933	0.4300	3.0844	62.0	6.0	O(21)	−0.027 (6)
							O(31)	0.034 (7)
							O(32)	−0.020 (6)
			Planes through Chelate Rings					
O_{11}–O_{12}–C_{11}–C_{12}–C_{13}–C_{14}–C_{15}	0.9364	0.0845	0.3406	3.4336	93.1	9.5	C(12)	−0.059 (12)
							C(13)	−0.031 (9)
							C(15)	0.068 (11)
O_{21}–O_{22}–C_{21}–C_{22}–C_{23}–C_{24}–C_{25}–Zr	0.2099	0.9777	0.0057	3.8135	8.9	11.1		
O_{31}–O_{32}–C_{31}–C_{32}–C_{33}–C_{34}–C_{35}	0.7892	−0.5322	0.3066	0.8027	314.9	9.5	O(31)	0.043 (7)
							O(32)	−0.026 (6)
							C(31)	−0.097 (11)
							C(32)	−0.037 (9)
							C(35)	0.139 (11)

[a] The equation is in ångström units with atomic coordinates expressed in the orthogonal Cartesian system: $X \equiv a$, $Y \equiv b$, $Z \equiv c^*$. The weights were calculated according to $w = 1/\sigma^2 = 3/[\sigma^2(x) + \sigma^2(y) + \sigma^2(z)]$. [b] The tabulated value of χ^2 at significance level $\alpha = 0.05$ and for $n - 3$ degrees of freedom where n is the number of atoms in the particular plane. [c] Deviations from the plane greater than 3 esd's are listed. The parenthetical values are the relevant esd's for the atoms concerned calculated from the σ^2 defined in *a*.

TABLE VII

MEAN VALUES OF CHEMICALLY EQUIVALENT BOND LENGTHS AND ANGLES

Atoms	Mean value[a]	Rms dev[b]	Av error
	Bond, Å		
Zr–O	2.222[c]		
Zr–C	2.527 (6)	0.013	0.013
C–C	1.404 (14)	0.028	0.020
O–C	1.248 (7)	0.015	0.011
C–CH	1.386 (6)	0.013	0.014
C–CF_3	1.50 (2)	0.04	0.02
C–F	1.28 (1)	0.05	0.02
	Angle, deg		
O–Zr–O	75.7[c]		
Zr–O–C	133.9[c]		
O–C–CH	127.7 (3)	0.7	0.9
C–CH–C	119.9 (14)	2.0	1.0
O–C–CF_3	113.6 (5)	1.0	0.8
CH–C–CF_3	118.6 (5)	1.2	0.9

[a] The error in the mean is given by $[\Sigma_i(x_i - \bar{x})^2/n(n-1)]^{1/2}$. [b] The rms deviation, $[\Sigma_i(x_i - \bar{x})^2/n]^{1/2}$, is compared with average value of the errors derived from the least-squares matrix for the group of distances or angles involved. [c] Involves averaging over groups where apparent nonequivalence is reinforced by a physical explanation.

TABLE VIII

NONBONDED DISTANCES (Å)

Intramolecular		Intermolecular	
$O_{11}\cdots O_{12}$	2.69 (1)	$C_2\cdots F_{31}$	3.18 (2)[a]
$O_{21}\cdots O_{22}$	2.81 (1)	$C_3\cdots F_{39}$	3.37 (2)[b]
$O_{31}\cdots O_{32}$	2.69 (1)	$C_4\cdots F_{37}$	3.29 (2)[c]
$O_{22}\cdots O_{11}$	2.83 (1)	$C_5\cdots F_{37}$	3.18 (2)[c]
$O_{22}\cdots O_{12}$	2.84 (1)	$C_5\cdots F_{36}$	3.40 (2)[c]
$O_{22}\cdots O_{31}$	2.82 (1)	$F_{11}\cdots F_{31}$	3.32 (1)[d]
$O_{22}\cdots O_{32}$	2.82 (1)	$F_{12}\cdots F_{21}$	3.13 (1)[e]
$O_{11}\cdots O_{21}$	2.50 (1)	$F_{12}\cdots F_{32}$	3.32 (1)[d]
$O_{21}\cdots O_{31}$	2.51 (1)	$F_{13}\cdots F_{22}$	3.17 (1)[e]
$O_{32}\cdots O_{12}$	2.53 (1)	$F_{15}\cdots F_{31}$	3.03 (2)[c]
$C_1\cdots O_{11}$	2.99 (2)	$F_{21}\cdots F_{25}$	3.32 (2)[b]
$C_1\cdots O_{12}$	2.97 (2)	$F_{22}\cdots F_{26}$	3.10 (1)[b]
$C_2\cdots O_{11}$	2.97 (2)	$F_{23}\cdots F_{14}$	2.88 (2)[b]
$C_2\cdots O_{21}$	2.99 (2)	$F_{23}\cdots F_{37}$	3.22 (3)[b]
$C_3\cdots O_{21}$	3.03 (2)	$F_{23}\cdots F_{39}$	3.36 (2)[b]
$C_3\cdots O_{31}$	2.88 (2)	$F_{24}\cdots F_{35}$	3.30 (3)[f]
$C_4\cdots O_{31}$	3.00 (2)	$F_{26}\cdots F_{26}$	3.09 (2)[g]
$C_4\cdots O_{32}$	2.99 (2)	$F_{32}\cdots F_{36}$	3.34 (2)[b]
$C_5\cdots O_{32}$	2.98 (2)	$F_{32}\cdots F_{37}$	3.22 (2)[b]
$C_5\cdots O_{12}$	2.98 (2)	$F_{33}\cdots F_{34}$	2.90 (2)[f]
		$F_{33}\cdots F_{39}$	3.14 (2)[f]
		$F_{38}\cdots F_{23}$	2.78 (3)[h]

[a–h] The symmetry operation relating the molecule containing the first atom to that containing the second is indicated by the following codes: (*a*) $x - 1/2, 1/2 - y, z - 1/2$; (*b*) $x, y, z - 1$; (*c*) $x - 1/2, 1/2 - y, z + 1/2$; (*d*) $1/2 - x, y - 1/2, 1/2 - z$; (*e*) $1 - x, -y, -z$; (*f*) $x + 1/2, 1/2 - y, z + 1/2$; (*g*) $1 - z, -y, 1 - z$; (*h*) $x, y, z + 1$.

distance than the other two groups. Finally, the Zr–O–C angle involving O_{21}, the equatorial oxygen atom of the unique group, is 5° less than the mean of the other five (closely agreeing) Zr–O–C angles. Evidently the (Zr–O) axial bond is strengthened at the expense of the other Zr–O bond of the same ligand, causing some distortion of the angle the ligand subtends. One hesitates to invoke intermolecular forces to explain such an effect and yet there seems to be no explanation in terms of intramolecular repulsive forces. Possibly the explanation lies in the orientation of the bonding zirconium orbitals and the positional requirements imposed upon the ligand atoms. If these differences in the solid-state structure persist in solution, they could well provide an explanation of the different time-averaging rates observed for the diketonate groups in the fluorine nmr spectra.[7] Evidence from this source indicates that the unique group is less labile than the other two.

The shortest nonbonded contacts are listed in Table VIII. The cyclopentadienyl group has a staggered conformation with respect to the five equatorial oxygen atoms and the carbon–oxygen contacts that result are extremely regular. There is a similar regularity in the five O_{axial}–$O_{equatorial}$ distances which reinforces the observation that regularity in the coordination polyhedron has been achieved at the expense of slight distortions in the coordination of individual chelate rings. Intermolecular contacts all involve fluorine–fluorine or fluorine to cyclopentadienyl carbon contacts. None is abnormally short in view of the fluorine van der Waals radius of 1.35 Å.[19] It is not evident from these contacts why one $-CF_3$ group should show greater disordering than the others. The number of short F···F contacts per $-CF_3$ group varies from 2 to 8, however, which would account for the considerable variation in the amplitudes of thermal motion of the various groups.

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CONTRIBUTION FROM ISTITUTO DI CHIMICA GENERALE ED INORGANICA,
UNIVERSITÀ DEGLI STUDI, MILAN 20133, ITALY

A Tetrahedral Platinum(0) Carbonyl. The Crystal and Molecular Structure of Tris(triphenylphosphine)carbonylplatinum[1]

BY V. G. ALBANO, G. M. BASSO RICCI, AND P. L. BELLON[2]

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The crystal and molecular structure of tris(triphenylphosphine)carbonylplatinum, $Pt(P(C_6H_5)_3)_3CO$, was determined from three-dimensional X-ray data measured by counter methods. The structure was refined by full-matrix least squares using 1408 reflections, to an R factor of 0.051. The complex crystallizes in the monoclinic space group $P2_1/n$ (C_{2h}^5) with the cell parameters: $a = 11.275\ (5)$ Å, $b = 30.904\ (8)$ Å, $c = 13.298\ (5)$ Å, $\beta = 91.6\ (1)°$. There are four monomeric molecules per cell; the coordination around the metal atom is approximately tetrahedral. The three metal–phosphorus bond lengths are 2.333 (8), 2.335 (6), and 2.352 (8) Å, and the metal–carbon distance is 1.86 (3) Å. On the basis of these and other results for noncarbonylated and carbonylated phosphine–platinum complexes, it is suggested that d_π–d_π interactions play an important role in metal–phosphorus bonds whenever no π acceptors competing with phosphorus are present.

It is known that compounds of zerovalent platinum such as $Pt(P(C_6H_5)_3)_3$ and $Pt(P(C_6H_5)_3)_4$ react in solution with carbon monoxide to give variously carbonylated products.[3–5] Booth, *et al.*,[6] have characterized, among the number of mono- and polynuclear platinum carbonyls, the complex $Pt(P(C_6H_5)_3)_3CO$, an orange-yellow monoclinic solid decomposing at 95°. The metal–carbon interaction deduced from the CO stretching band (at 1908 cm^{-1}) is not as weak as should be expected in view of the very high ionization potential, 8.2 eV,[7] of the spin-paired d^{10} state of Pt(0). This value suggests that metal-to-carbon back-donation would take place with difficulty.

An explanation of the stability of compounds such as $Pt(PR_3)_3CO$ and $Pt(PR_3)_2(CO)_2$ has been proposed by Nyholm:[8] the availability of d_π electrons on Pt is increased by the presence of donor bonds from PR_3 ligands which create an excess of negative charge on the metal.

At the beginning of the present investigation no structural reports of any kind on platinum(0) carbonyls had yet appeared. However, two papers dealing with structures and properties of platinum(II) carbonyls were available. In $PtCl(P(C_2H_5)_3)_2CO^+$ [9] and in $PtCl_2(ONC_2H_4OCH_3)CO$,[10] a pyridine N-oxide complex, distances of 1.78 and 1.74 Å and CO stretching frequencies of about 2100 cm^{-1} have been reported. These metal–carbon distances are the shortest interactions reported for a group VIII metal carbonyl of the second and third transition series.[11] On the basis of the lower stretching frequency, one should expect a more pronounced, d_π–π^* interaction in $Pt(P(C_6H_5)_3)_3CO$; therefore, the existence of a metal–carbonyl interaction significantly shorter than the above ones would be expected.

Recently Chini has obtained, by carbonylation of $Pt(P(C_6H_5)_3)_3$ in presence of an excess of triphenylphosphine, a pale yellow polymorph of $Pt(P(C_6H_5)_3)_3CO$

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(2) Author to whom inquiries should be addressed.

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