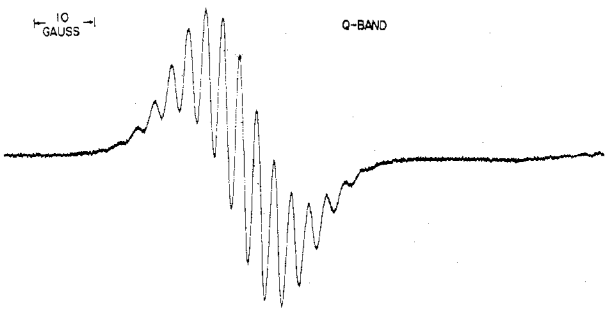

Figure 5. Q-Band EPR spectrum of a ^{63}Cu-doped single crystal of Ni(TTP)(BF$_4$)$_2$ for one of the ^{63}Cu hyperfine lines at the parallel orientation showing superhyperfine structure. Magnetic field increases from left to right.

inequivalencies among the hydrogens. Superhyperfine structure can be seen at other orientations, but it is less well resolved. The effect may indicate greater magnetic inequivalencies among the hydrogens at these orientations. Although the general magnitude of the superhyperfine coupling is not surprising, the near equivalence of all the γ hydrogens is noteworthy. Evidently, in the Cu(TTP)$^{2+}$ complex the spin density is spread out onto the carbon skeleton in an especially uniform way.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Professors E. Kent Barefield and Iain C. Paul for valuable contributions and discussions.

Registry No. Ni(TTP)(BF$_4$)$_2$, 25460-51-9; ^{63}Cu, 14191-84-5.

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 mmm 24× reduction, negatives) containing all of the supplementary material for papers in this issue may be obtained from the Journals Department, 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 AIC40765U.

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Contribution from the Department of Chemistry, University of Alabama, University, Alabama 35486,
from the Laboratoire de chimie de coordination, Paris 5°, France, and from the
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

Molecular Structures of the Bis(η^5-indenyl)dimethyl Derivatives of Titanium, Zirconium, and Hafnium

JERRY L. ATWOOD,*[1a] WILLIAM E. HUNTER,[1a] DUANE C. HRNCIR,[1a] EDMOND SAMUEL,[1b]
HELMUT ALT,[1c] and MARVIN D. RAUSCH*[1c]

Received November 19, 1974

AIC40796P

The crystal structures of the series (η^5-C$_9$H$_7$)$_2$M(CH$_3$)$_2$, where M = Ti, Zr, and Hf, have been determined from three-dimensional X-ray data measured by counter methods. The compounds are isostructural and crystallize in the orthorhombic space group $P2_12_12$ [D_2^3; No. 18]. For bis(η^5-indenyl)dimethyltitanium(IV) the unit cell dimensions are a = 14.124 (7) Å, b = 8.073 (5) Å, c = 6.844 (5) Å, and Z = 2. Full-matrix least-squares refinement has led to a final R value of 0.070 based on 280 independent observed reflections. For bis(η^5-indenyl)dimethylzirconium(IV) the cell dimensions are a = 14.248 (4), b = 8.244 (3), and c = 6.929 (3) Å. The refinement led to a final R value of 0.025 based on 904 reflections. For bis(η^5-indenyl)dimethylhafnium(IV) the cell dimensions are a = 14.243 (6), b = 8.215 (4), and c = 6.918 (4) Å. The refinement led to a final R value of 0.031 based on 965 reflections. The effect of the lanthanide contraction is evident even with the cell parameters: that of hafnium has a volume of 5 Å^3 less than that of zirconium. The molecules have crystallographically imposed twofold symmetry. In each case the metal–carbon σ-bond length is 0.2–0.3 Å shorter than the metal–carbon distances for the η^5 ligands. Although the Hf–C(η^5) approach (2.53 Å average) is closer than with the Zr analog (2.55 Å average), the Hf–C(σ) length (2.332 (12) Å) is significantly longer than the Zr–C(σ) distance (2.251 (6) Å). The values for the titanium complex are Ti–C(η^5) = 2.44 Å (average) and Ti–C(σ) = 2.21 (2) Å.

Introduction

The organometallic chemistry of titanium has been rather extensively developed over the past two decades, while that of zirconium and hafnium is only now beginning to emerge. Structural studies have done much to elucidate the nature of the titanium–carbon bond in compounds which contain ligands coordinated in a polyhapto fashion.[2-10] Likewise, the geometry of several cyclopentadienylzirconium compounds has been established: (η^5-C$_5$H$_5$)$_2$ZrF$_2$,[11] (η^5-C$_5$H$_5$)$_2$ZrCl$_2$,[12] (CH$_2$)$_3$(η^5-C$_5$H$_4$)$_2$ZrCl$_2$,[13] (η^5-C$_5$H$_5$)$_2$ZrI$_2$,[11] (η^5-C$_5$H$_5$)-

Table I. Crystal Data

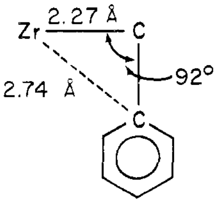
Compd	$(C_9H_7)_2Ti(CH_3)_2$	$(C_9H_7)_2Zr(CH_3)_2$	$(C_9H_7)_2Hf(CH_3)_2$
Mol wt	308.2	351.6	438.8
Linear abs coeff	5.4	6.3	65.5
Obsd density, g cm^{-3}	1.24 (4)	1.37 (2)	1.72 (3)
Calcd density, g cm^{-3}	1.27	1.38	1.74
Max crystal dimensions, mm	0.80 × 0.12 × 0.08	0.60 × 0.25 × 0.20	0.45 × 0.45 × 0.45
Space group	$P2_12_12$	$P2_12_12$	$P2_12_12$
Molecules/unit cell	2	2	2
Cell constants,[a] Å			
a	14.124 (7)	14.248 (4)	14.243 (6)
b	8.073 (5)	8.244 (3)	8.215 (4)
c	6.844 (5)	6.929 (3)	6.918 (4)
Cell vol, Å^3	780.4	814.9	809.6

[a] Mo Kα radiation, λ 0.71069 Å. Ambient temperature of 23°.

$(C_5H_7O_2)_2ZrCl$,[14] $(\eta^5\text{-}C_5H_5)Zr(CF_3COCHCOCF_3)_3$,[15] and $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$.[16] However, for hafnium only $(CH_2)_3(\eta^5\text{-}C_5H_4)_2HfCl_2$[17] and $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$[18] are known.

It is of interest to note that in one of the two complete series to be characterized, $(C_5H_5)_4M$, two rings are η^5 and two are η^1 for M = Ti,[6] three are η^5 and one is η^1 for Zr,[16] and two are η^5 and two are η^1 for Hf.[18] The difference between the zirconium and hafnium analogs is especially surprising in view of the extreme similarity of the chemistry of the two elements (the radii of the Zr^{4+} and Hf^{4+} ions are 0.74 and 0.75 Å, respectively).[19]

The only structural study of a σ-bonded organometallic complex to be reported (other than the $\eta^1\text{-}C_5H_5$ derivatives) is that of tetrabenzylzirconium.[20] The average zirconium–carbon σ-bond distance, 2.27 Å, is much shorter than the $\eta^5\text{-}C_5H_5$ lengths, 2.53 Å, or the $\eta^1\text{-}C_5H_5$ length, 2.47 Å. However, the extent to which the Zr–C linkage in tetrabenzylzirconium may be regarded as "σ" in character is open to question. The average angle at the methylene carbon atom is small (92°), and the carbon atom of the aromatic ring bonded to the methylene carbon atom is quite close to the zirconium atom (2.74 Å), i.e.



In order to draw meaningful structural comparisons among the group 4B organometallic compounds, and to characterize accurately the metal–carbon σ bond in alkyl derivatives, we report here the crystal structures of $(\eta^5\text{-}C_9H_7)_2M(CH_3)_2$, where M = Ti, Zr, and Hf.[21]

Experimental Section

X-Ray Data Collection and Structure Determination for $(\eta^5\text{-}C_9H_7)_2Zr(CH_3)_2$. Single crystals of the air-sensitive substance were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 14 reflections ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. The space group was uniquely determined to be $P2_12_12$ [$D_2{}^3$; No. 18] from the systematic absences in $h00$ for $h = 2n + 1$ and in $0k0$ for $k = 2n + 1$. The density was measured by flotation methods, and it indicated that there are two formula units per unit cell.

Data were taken on an Enraf-Nonius CAD-4 diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω–2θ scan technique with a takeoff angle of 3.0°. The scan rate was variable and was determined by a fast (20° min^{-1}) prescan. Calculated speeds based on the net intensity gathered in the prescan ranged from 7 to 0.3 min^{-1}. Moving-crystal, moving-counter backgrounds were collected for 25% of the total scan width at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan\theta$$

where $A = 0.70°$ and $B = 0.35°$. Aperture settings were determined in a like manner with $A = 4$ mm and $B = 4$ mm. Other diffractometer parameters have been described previously.[22] As a check on the stability of the instrument and the crystal, three reflections, (221), (101), and ($\bar{2}$21), were measured after every 25 reflections; in no case was a variation of greater than ±5% noted.

The integrated intensity of a reflection, I, and its estimated standard deviation, $\sigma(I)$, were calculated with the equations

$$I = [C - 2(B_1 + B_2)]/S$$

$$\sigma(I) = [C + B_1 + B_2 + 0.03^2(C + B_1 + B_2)^2]^{1/2}$$

where C is the counts collected during the scan and B_1 and B_2 are the background counts. S is an integer which is proportional to the total scan time.

One independent octant of data was measured out to $2\theta = 54°$; a slow scan was performed on a total of 904 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations[22] were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 30 was obtained in the prescan. Based on these considerations, the data set of 904 reflections (used in the subsequent structure determination and refinement) was considered observed and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz, polarization, and absorption effects[23] (the transmission factors varied from 0.75 to 0.86).

Fourier calculations were made with the ALFF[24] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[25] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral atom scattering factors for Zr and C were taken from Cromer and Waber,[26] and the scattering for zirconium was corrected for the real and imaginary components of anomalous dispersion using Cromer's table.[27] Scattering factors for hydrogen were from ref 28. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE program.[29] Crystal structure illustrations were obtained with the program ORTEP.[30]

The existence of two molecules per unit cell constrained the molecule to lie on a crystallographic twofold axis in the space group $P2_12_12$. The position of the zirconium atom along the axis was revealed by inspection of a Patterson map. A difference Fourier map phased on the zirconium atom readily revealed the positions of the remaining nonhydrogen atoms. Isotropic least-squares refinement led to a discrepancy factor of $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.080$. The hydrogen atoms of the indenyl ring were then placed at calculated positions of 0.98 Å from the bonded carbon atoms, and the methyl hydrogen atoms were located on a three-dimensional difference Fourier map (at values of ~0.6 e/Å^3). Subsequent anisotropic refinement of all nonhydrogen atoms led to final values of $R_1 = 0.025$ and $R_2 = \{\sum(|F_o| - |F_c|)^2/\sum(F_o)^2\}^{1/2} = 0.030$. (For the inverse absolute configuration the values were $R_1 = 0.027$ and $R_2 = 0.032$.) The largest parameter shifts in the final cycle of refinement were less than 0.02 of their estimated standard deviations. A final difference Fourier map showed no feature greater than 0.2 e/Å^3. The standard deviation of an observation of unit weight was 0.92. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of

Table II. Final Fractional Coordinates and Thermal Parameters[a]

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
a. Bis(indenyl)dimethyltitanium(IV)									
Ti	0.0000	0.0000	0.0749 (8)	0.0052 (3)	0.0156 (12)	0.0097 (12)	0.0000	0.0000	0.0000
C1	0.1114 (24)	0.0889 (35)	−0.1596 (42)	0.0075 (22)	0.0297 (82)	0.0199 (84)	−0.0085 (34)	0.0039 (36)	0.0066 (60)
C2	0.0280 (19)	0.1884 (32)	−0.1800 (41)	0.0058 (25)	0.0118 (60)	0.0292 (82)	−0.0055 (28)	−0.0048 (39)	0.0052 (55)
C3	0.0158 (29)	0.2910 (30)	−0.0170 (40)	0.0088 (27)	0.0133 (51)	0.0218 (69)	−0.0012 (37)	−0.0046 (49)	0.0062 (46)
C4	0.0966 (21)	0.2578 (29)	0.1114 (45)	0.0071 (18)	0.0100 (51)	0.0266 (88)	−0.0031 (34)	0.0076 (40)	−0.0017 (60)
C5	0.1210 (20)	0.3337 (35)	0.2884 (45)	0.0052 (19)	0.0268 (72)	0.0256 (90)	−0.0061 (32)	−0.0026 (36)	−0.0019 (69)
C6	0.2079 (24)	0.2874 (36)	0.3737 (38)	0.0103 (24)	0.0218 (71)	0.0183 (79)	−0.0064 (34)	0.0020 (43)	−0.0070 (67)
C7	0.2724 (23)	0.1665 (42)	0.2913 (50)	0.0106 (27)	0.0254 (86)	0.0283 (99)	−0.0055 (39)	−0.0022 (48)	0.0024 (74)
C8	0.2511 (17)	0.0940 (34)	0.1038 (47)	0.0031 (15)	0.0277 (65)	0.0333 (92)	−0.0029 (25)	0.0041 (38)	0.0113 (76)
C9	0.1587 (18)	0.1384 (31)	0.0193 (35)	0.0057 (19)	0.0106 (51)	0.0137 (73)	−0.0050 (29)	0.0051 (33)	−0.0013 (44)
C10	0.0894 (16)	−0.1213 (27)	0.2971 (35)	0.0046 (14)	0.0136 (56)	0.0176 (60)	0.0030 (24)	−0.0002 (30)	0.0064 (51)
b. Bis(indenyl)dimethylzirconium(IV)									
Zr	0.00000	0.00000	−0.07562 (7)	0.00312 (2)	0.00869 (5)	0.01047 (8)	0.00000	0.00000	0.00000
C1	−0.1162 (5)	−0.1036 (8)	0.1661 (8)	0.0073 (4)	0.0173 (10)	0.0178 (12)	−0.0041 (5)	0.0041 (6)	−0.0009 (10)
C2	−0.0362 (5)	−0.1974 (8)	0.1884 (9)	0.0078 (4)	0.0167 (10)	0.0210 (14)	−0.0035 (5)	−0.0025 (6)	0.0086 (10)
C3	−0.0222 (4)	−0.2903 (6)	0.0248 (9)	0.0060 (4)	0.0105 (6)	0.0283 (15)	−0.0005 (4)	−0.0009 (5)	0.0059 (8)
C4	−0.0989 (4)	−0.2643 (6)	−0.0995 (8)	0.0046 (2)	0.0110 (7)	0.0203 (12)	−0.0024 (4)	0.0010 (5)	−0.0001 (8)
C5	−0.1227 (4)	−0.3300 (7)	−0.2827 (10)	0.0062 (4)	0.0152 (9)	0.0266 (16)	−0.0039 (5)	0.0005 (6)	−0.0036 (11)
C6	−0.2054 (4)	−0.2822 (9)	−0.3633 (10)	0.0066 (4)	0.0258 (13)	0.0268 (18)	−0.0073 (6)	−0.0009 (7)	−0.0024 (12)
C7	−0.2664 (4)	−0.1723 (9)	−0.2755 (11)	0.0046 (4)	0.0255 (13)	0.0371 (21)	−0.0045 (6)	−0.0040 (7)	0.0057 (14)
C8	−0.2450 (4)	−0.1043 (8)	−0.1023 (12)	0.0036 (2)	0.0203 (11)	0.0423 (22)	−0.0019 (5)	0.0035 (7)	−0.0008 (15)
C9	−0.1593 (4)	−0.1493 (7)	−0.0100 (8)	0.0042 (2)	0.0124 (8)	0.0224 (11)	−0.0020 (5)	0.0028 (6)	0.0017 (10)
C10	−0.0925 (4)	0.1272 (8)	−0.2912 (10)	0.0052 (3)	0.0160 (10)	0.0224 (14)	−0.0013 (5)	−0.0034 (6)	0.0063 (10)
H1(C1)	−0.152 (5)	−0.039 (8)	0.256 (9)	*b*					
H2(C2)	0.003 (7)	−0.218 (8)	0.306 (9)						
H3(C3)	0.033 (4)	−0.379 (7)	−0.028 (11)						
H4(C5)	−0.075 (5)	−0.427 (8)	−0.346 (10)						
H5(C6)	−0.214 (4)	−0.332 (8)	−0.511 (11)						
H6(C7)	−0.328 (5)	−0.117 (8)	−0.335 (11)						
H7(C8)	−0.286 (4)	−0.024 (9)	−0.026 (9)						
H8(C10)	−0.122 (5)	0.067 (8)	−0.363 (10)						
H9(C10)	−0.059 (5)	0.216 (9)	−0.387 (10)						
H10(C10)	−0.138 (5)	0.214 (9)	−0.275 (13)						
c. Bis(indenyl)dimethylhafnium(IV)									
Hf	0.00000	0.00000	0.07598 (8)	0.00335 (2)	0.00981 (7)	0.01061 (9)	0.00000	0.00000	0.00000
C1	0.1163 (13)	0.1007 (21)	−0.1628 (21)	0.0087 (11)	0.0199 (27)	0.0168 (29)	−0.0056 (16)	0.0038 (16)	−0.0028 (26)
C2	0.0356 (11)	0.1966 (22)	−0.1856 (20)	0.0072 (10)	0.0200 (28)	0.0168 (29)	−0.0021 (14)	−0.0030 (13)	0.0067 (25)
C3	0.0213 (11)	0.2886 (17)	−0.0236 (22)	0.0058 (13)	0.0128 (19)	0.0249 (33)	−0.0005 (11)	−0.0007 (13)	0.0047 (21)
C4	0.0978 (9)	0.2637 (14)	0.0988 (21)	0.0045 (7)	0.0095 (17)	0.0244 (32)	−0.0019 (9)	0.0010 (12)	−0.0020 (20)
C5	0.1206 (11)	0.3316 (18)	0.2854 (24)	0.0051 (8)	0.0160 (23)	0.0247 (36)	−0.0026 (12)	−0.0013 (14)	−0.0018 (25)
C6	0.2055 (12)	0.2858 (21)	0.3630 (24)	0.0075 (10)	0.0241 (33)	0.0255 (37)	−0.0074 (16)	−0.0014 (17)	−0.0007 (32)
C7	0.2669 (10)	0.1732 (24)	0.2778 (31)	0.0041 (8)	0.0252 (37)	0.0393 (56)	−0.0031 (15)	−0.0033 (18)	0.0052 (43)
C8	0.2456 (11)	0.1026 (22)	0.1057 (30)	0.0041 (8)	0.0181 (29)	0.0402 (55)	−0.0010 (13)	0.0030 (18)	0.0007 (35)
C9	0.1592 (9)	0.1476 (17)	0.0145 (20)	0.0042 (7)	0.0139 (21)	0.0205 (29)	−0.0024 (10)	0.0031 (12)	−0.0013 (21)
C10	0.0928 (8)	−0.1367 (15)	0.3015 (18)	0.0022 (5)	0.0143 (20)	0.0158 (25)	−0.0017 (8)	−0.0014 (9)	0.0006 (18)
H1(C1)	0.153 (10)	−0.026 (24)	−0.265 (23)	*b*					
H2(C2)	0.005 (20)	0.197 (19)	−0.320 (21)						
H3(C3)	−0.014 (17)	0.383 (18)	0.006 (23)						
H4(C5)	0.090 (11)	0.422 (19)	0.337 (25)						
H5(C6)	0.225 (11)	0.359 (16)	0.484 (29)						
H6(C7)	0.335 (11)	0.117 (20)	0.342 (27)						
H7(C8)	0.290 (10)	0.041 (20)	0.046 (22)						
H8(C10)	0.126	−0.034	0.356						
H9(C10)	0.052	−0.199	0.366						
H10(C10)	0.132	−0.172	0.190						

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic thermal parameters of 5.0 Å^2 were assumed for all hydrogen atoms.

the positional and thermal parameters are given in Table IIb.[31]

Data and Structure Refinement for (η^5-C_9H_7)$_2$Hf(CH_3)$_2$. Following the data collection procedures given above, 965 unique observed reflections in the range $2\theta < 55°$ were obtained and subsequently corrected for absorption effects[23] (the transmission factors varied from 0.56 to 0.83).

After two cycles of anisotropic refinement ($R_1 = 0.069$) starting with the atomic parameters of the zirconium analog, a difference map afforded the location of the methyl hydrogen atoms. Least-squares refinement and corrections for anomalous scattering by hafnium[26,27] gave $R_1 = 0.035$ and $R_2 = 0.045$. At this point the inverse absolute configuration was found to yield $R_1 = 0.030$ and $R_2 = 0.039$, and all subsequent parameters refer to this configuration. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. A final difference Fourier map showed no feature greater than 0.9 e/Å^3 (which was near the Hf atom). The standard deviation of an observation of unit weight was 1.63. The final values of the positional and thermal parameters are given in Table IIc.[31]

Data and Structure Refinement for (η^5-C_9H_7)$_2$Ti(CH_3)$_2$. Difficulty in obtaining good crystals of the titanium analog ultimately limited the observed data set to 280 reflections in the range $2\theta < 40°$. No absorption correction was made.

Five cycles of anisotropic refinement, starting with the atomic parameters of the hafnium analog, led to final values of $R_1 = 0.070$ and $R_2 = 0.078$. (For the inverse absolute configuration the values were $R_1 = 0.074$ and $R_2 = 0.082$.) Hydrogen atoms were not located. The largest parameter shifts in the final cycle of refinement were less than 0.10 of their estimated standard deviations. The final values of the positional and thermal parameters are given in Table IIa.[31]

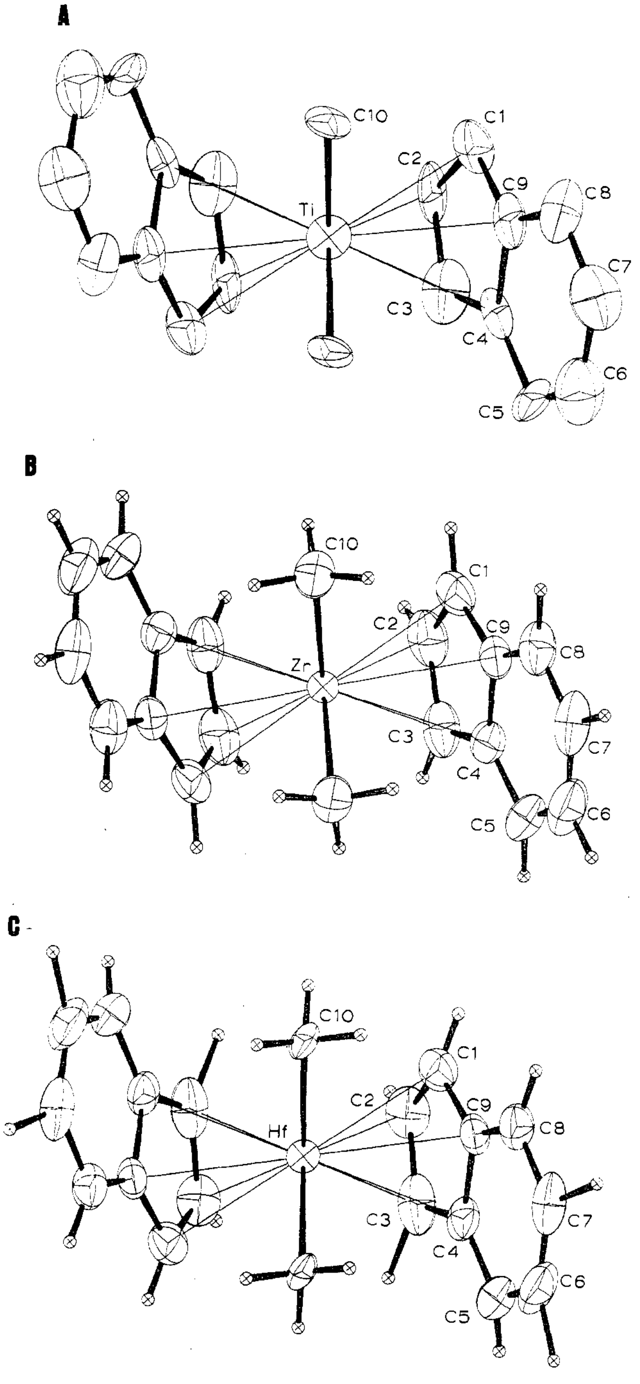


Figure 1. Molecular structures of $(C_9H_7)_2M(CH_3)_2$, where M = Ti (A), Zr (B), and Hf (C), with the atoms represented by their 40% probability ellipsoids for thermal motion.

Sample Preparations. The compounds were prepared by the literature method[21] and sublimed at 120°. The sublimate was dissolved in pentane at room temperature and the resulting solution was filtered. X-Ray diffraction quality crystals of the air-sensitive bis(indenyl)dimethylmetal derivatives were then grown at 0°. $(\eta^5\text{-}C_9H_7)_2Ti(CH_3)_2$ crystals grew as fragile, orange-yellow needles. $(\eta^5\text{-}C_9H_7)_2Zr(CH_3)_2$ crystals were obtained as straw-colored, elongated plates, and those of $(\eta^5\text{-}C_9H_7)_2Hf(CH_3)_2$ were straw-colored polyhedra.

Table III. Comparison of Structural Parameters for $(C_9H_7)_2M(CH_3)_2$

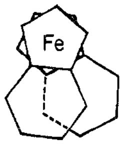
	Titanium	Zirconium	Hafnium
	Bond Lengths, Å		
M-C1	2.36 (3)	2.505 (5)	2.482 (14)
M-C2	2.35 (2)	2.502 (6)	2.477 (14)
M-C3	2.44 (2)	2.513 (5)	2.488 (13)
M-C4	2.50 (2)	2.600 (5)	2.580 (11)
M-C9	2.53 (2)	2.622 (5)	2.609 (12)
M-C10(σ)	2.21 (2)	2.251 (6)	2.332 (12)
C10-H8	*a*	0.82 (7)	1.04
C10-H9		1.10 (7)	0.89
C10-H10		0.96 (8)	1.00
	Bond Angles, Deg		
Cent.-M-Cent.'[b]	119.8 (14)	120.8 (5)	121.0 (9)
C10(σ)-M-C10(σ)'	92.8 (12)	96.9 (3)	96.0 (6)
C10(σ)-M-Cent.	111.0 (13)	110.4 (5)	111.7 (8)
C10(σ)-M-Cent.'	109.5 (13)	107.9 (5)	106.8 (8)

[a] Hydrogen atoms were not located. [b] Cent. indicates the centroid of the five-membered portion of the indenyl group; Cent.' is related to Cent. by $(-x, -y, z)$.

Discussion

The crystal data given in Table I clearly demonstrate that the bis(indenyl)dimethyl derivatives of titanium, zirconium, and hafnium are all isostructural. It is interesting to note the effect of the lanthanide contraction on the unit cell parameters: that of hafnium has a volume 5 Å^3 *less* than that of zirconium. The molecules themselves have crystallographically imposed twofold symmetry (Figure 1).

If one omits the methyl groups in Figures 1 and 2, it is possible to see a striking resemblance between the structures of the $(C_9H_7)_2M-$ fragment and that of diindenyliron[32]



Just as the indenyl groups exhibit a gauche configuration in $(C_9H_7)_2Fe$, so also do they in $(C_9H_7)_2M(CH_3)_2$. In reality, of course, the ring systems are forced apart by the methyl groups.

The metal–carbon bond distances (Table III) afford two worthwhile comparisons. The first involves the σ-bond lengths, while the second concerns group trends.

In every case the M–C σ-bond length is 0.2–0.3 Å shorter than the M–C distances for the polyhapto ligands. This appears as a rather general effect which has recently been observed for organometallic compounds of the main group

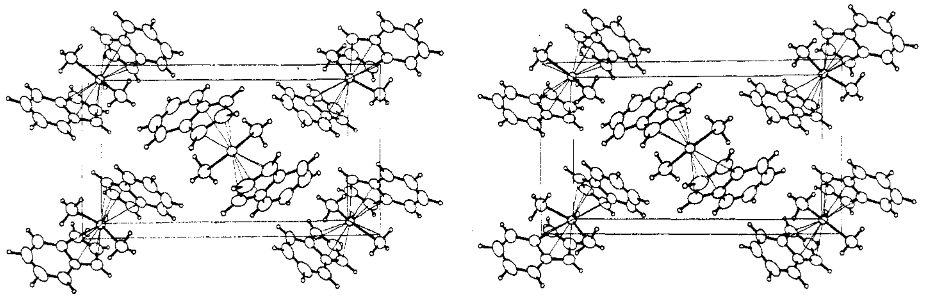


Figure 2. Stereoscopic drawing showing the packing of $(C_9H_7)_2Hf(CH_3)_2$ in the unit cell.

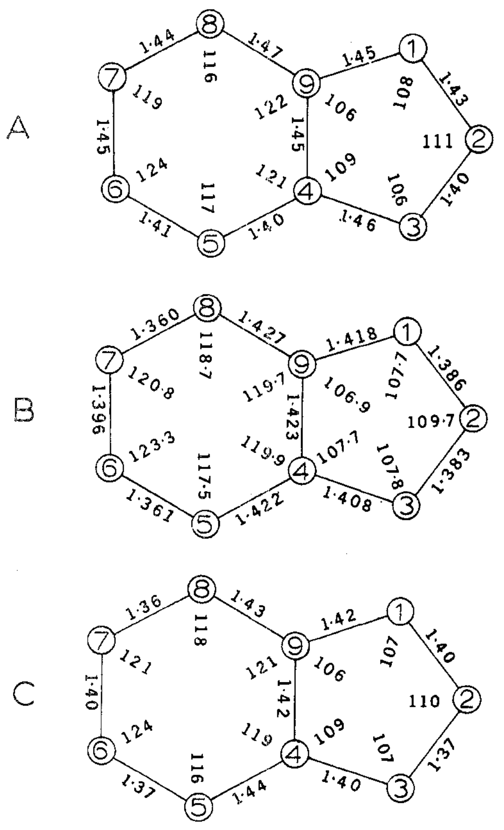


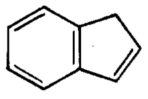
Figure 3. Bond distances and angles in the indenyl rings of $(C_9H_7)_2M(CH_3)_2$, where M = Ti (A), Zr (B), and Hf (C). For A, the standard deviations in bond lengths are less than 0.03 Å, and those in bond angles, 2°; for B, they are 0.008 Å and 0.3°; for C, they are 0.015 Å and 0.9°.

$(Mg(C_9H_7)_2$[33]) and inner transition ($(C_5H_5)_3UC{\equiv}CC_6H_5$,[34] $[Li(C_4H_8O)_4][(CH_3)_2C_6H_4]_4Lu$[35]) elements as well. The 2.21 (2) Å value for the Ti–C bond is in reasonable agreement with those determined recently for $(C_5H_5)_2TiC_4(C_6H_4)_4$,[36] 2.141 (5) and 2.172 (5) Å, but is significantly shorter than the σ-bond lengths reported for $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$,[4] 2.272 (14) Å, and for $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$,[6] 2.32 (2) Å. The only available check on the Zr–C bond length, 2.251 (6) Å, is that quoted for tetrabenzylzirconium, 2.27 Å.[20]

Within the group there is an interesting fluctuation in the metal–carbon σ-bond lengths; although the unit cell of the hafnium compound is smaller than that of the zirconium analog and although the hafnium–carbon polyhapto approach is closer than with the zirconium case, the Hf–C(σ) length is significantly longer, 2.332 (12) Å, than the Zr–C(σ) distance, 2.251 (6) Å.

The bonds between the indenyl ligands and the metal atoms show obvious distortions which may well be due to steric interactions between the nonbonded portions of the indenyl systems and the methyl groups (Figure 1). The range of M–C distances is therefore greater for Ti ($\Delta = (M\text{–}C_{max}) - (M\text{–}C_{min}) = 0.19$ Å) than for Zr ($\Delta = 0.12$ Å) or Hf ($\Delta = 0.13$ Å). The average for the Zr–C1, –C2, and –C3 lengths, 2.48 Å, compares favorably with the average for cyclopentadienylzirconium compounds: 2.48 Å for $(C_5H_5)_2ZrI_2$;[11] 2.50 Å for $(C_5H_5)_2ZrF_2$;[11] 2.53 Å for $(C_5H_5)(CF_3COCH_2COCF_3)_3Zr$.[15]

Even though the metal–carbon (indenyl) distances do not necessarily show any tendency for the indenyl group to behave as an η^1 or η^3 ligand, the rings do exhibit an interesting picture within themselves. In the case of the accurately determined hafnium and very accurately determined zirconium structures, the bond lengths within the rings (Figure 3) show a pattern of alternation consistent with the dominance of resonance structure **1**, which promotes enhanced electron density at the



1

C1 position. This does not appear, because of either limitations in structural accuracy (i.e., $(C_9H_7)_2Ti(CH_3)_2$) or electronic effects, in other recently reported indenyl structures: $Sm(C_9H_7)_3$,[38] $(C_9H_7)_3UCl$,[39] $Mg(C_9H_7)_2$.[33]

The indenyl groups stray significantly from planarity;[31] the maximum deviation for any atom from the least-squares plane is 0.11 Å for the titanium complex, 0.06 Å for zirconium, and 0.07 Å for hafnium. Most of the variance is associated with the C1, C2, and C3 atoms, as the zirconium complex illustrates. The six-membered ring is planar to within 0.01 Å, but the five-membered portion is only planar to 0.03 Å.

The metal atoms reside 2.05 Å (Ti), 2.23 Å (Zr), and 2.22 Å (Hf) out of the plane of the five-membered ring fragments. The value for titanium is near those reported for $(C_5H_5)_2TiCl_2$,[8] 2.059 Å, and $(CH_2)_3(C_5H_4)_2TiCl_2$,[7] 2.061 Å, but those for zirconium and hafnium are appreciably longer than the ones given for $(C_5H_5)_2ZrCl_2$,[12] 2.20 Å, for $(CH_2)_3(C_5H_4)_2ZrCl_2$,[13] 2.193 Å, and for $(CH_2)_3(C_5H_4)_2HfCl_2$,[17] 2.176 Å.

The centroid–metal–centroid angles in the $(CH_2)_3(C_5H_4)_2MCl_2$ series are 129.5° for Hf,[17] 129.5° for Zr,[13] and 132.6° for Ti,[8] while for the nonbridged $(C_5H_5)_2MCl_2$ species they are 126.7° for Zr[12] and 131.0° for Ti.[7] The explanation for the larger values with the bridged compounds is found in the configuration of the cyclopentadienyl groups: eclipsed for $(CH_2)_3(C_5H_4)_2MCl_2$ but staggered for $(C_5H_5)_2MCl_2$. For the $(C_9H_7)_2M(CH_3)_2$ series, the gauche configuration might be expected to produce centroid–metal–centroid angles intermediate between those for $(CH_2)_3(C_5H_4)_2MCl_2$ and $(C_5H_5)_2MCl_2$. The fact that the angles are significantly smaller for $(C_9H_7)_2M(CH_3)_2$, 121.0° for Hf, 120.8° for Zr, and 119.8° for Ti, is probably attributable to the nonbonded indenyl–methyl contacts (Figure 1).

The unit cell packing, shown in Figure 2, is typical of a molecular compound of this type. The only nonbonded intermolecular approaches less than 4.0 Å in $(C_9H_7)_2Zr(CH_3)_2$ are between ring-carbon and methyl-carbon atoms (3.82, 3.97 Å).

Acknowledgment. The authors are grateful to the National Science Foundation for a grant to M.D.R. in support of this research program and to the Deutsche Akademischer Austausdienst, Bonn/Bad Godesberg, Germany, for a fellowship for H.A. We also wish to thank Dr. W. J. Cook for aid in obtaining the crystal structure illustrations.

Registry No. $(\eta^5\text{-}C_9H_7)_2Ti(CH_3)_2$, 49596-02-3; $(\eta^5\text{-}C_9H_7)_2Zr(CH_3)_2$, 49596-04-5; $(\eta^5\text{-}C_9H_7)_2Hf(CH_3)_2$, 49596-06-7.

Supplementary Material Available. Listings of structure factor amplitudes and Table IV giving complete least-squares plane results for all three structures 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 Journals Department, 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 AIC40796P.

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Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163

Crystal and Molecular Structure of ΔΔΔΛ-*cis,trans*(*N–O*)-*uns-cis*-Ethylenediamine-*N,N'*-diacetato((*R*)-1,2-diaminopropane)cobalt(III) Chloride Monohydrate. Effect of Denticity on Chelate Ring Strain

LEON J. HALLORAN, RUTH E. CAPUTO, ROGER D. WILLETT,* and J. IVAN LEGG*

Received December 9, 1974 AIC40821R

The crystal and molecular structure of ΔΔΔΛ-*cis,trans*(*N–O*)-*uns-cis*-ethylenediamine-*N,N'*-diacetato((*R*)-1,2-diaminopropane)cobalt(III) chloride monohydrate (ΔΔΔΛ-*cis,trans*(*N–O*)-*uns-cis*-[Co(EDDA)(*R*-pn)]Cl·H_2O) has been determined from three-dimensional X-ray counter data. The complex crystallizes in the monoclinic system, space group $P2_1$ with a = 9.260 (8) Å, b = 7.255 (9) Å, c = 12.253 (13) Å, and β = 111.05 (6)°. With Z = 2, the observed and calculated densities are 1.56 and 1.559 g cm^{-3}, respectively. The structure was refined by full-matrix least-squares methods to a final value of R_1 = 0.055 for 1305 independent reflections with $F_o > 3\sigma(F_o)$. The geometry about the cobalt atom is distorted octahedral with the tetradentate EDDA assuming the unsymmetrical-cis configuration in which the secondary nitrogen configurations are found to be *R,S* rather than the *S,S* configurations originally predicted. The *R*-pn ring conformation is λ with the methyl group in the stable equatorial position. The optically active carbon of *R*-pn is adjacent to the nitrogen trans to the nonplanar acetate oxygen (O_R) of EDDA. This isomer is similar to chelated EDTA, possessing an in-plane girdling glycinate ring (G ring), the backbone ethylenediamine ring (E ring), and an out-of-plane glycinate ring (R ring). A structural study of [Co(EDTA)]$^-$ has shown that the G rings are quite strained compared to the E and R rings,[1] but for tetradentate uns-cis coordinated EDDA, the ring strain is found to be partially averaged over all three rings with the G ring exhibiting the most distortion. ΔΔΔΛ-*cis,trans*(*N–O*)-*uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ is one of the four possible isomers of this compound which have been isolated and whose absolute configurations have been tentatively assigned by spectroscopic means. The crystal and molecular structure determination confirms these assignments and this structure serves as a reference by which the absolute configuration of other uns-cis EDDA complexes can be assigned by correlation of circular dichroism spectra.

Introduction

X-Ray crystal structure investigations of transition metal–amino acid chelates have played an important role in elucidating the relationship between structure and observed properties of these compounds. Of these studies, the crystal and molecular structure of ammonium ethylenediaminetetraacetatocobaltate(III), NH_4[Co(EDTA)], determined by Weakliem and Hoard[1] and a later study of the closely related compound potassium trimethylenediaminetetraacetatocobaltate(III), K[Co(TRDTA)], by Saito and coworkers,[2] have served as an important source of structural information in studies involving polyaminepolycarboxylic acid chelates. Comparisons between [Co(EDTA)]$^-$ and cobalt(III) complexes of the linear tetradentate ethylenediamine-*N,N'*-diacetate (EDDA)[3–5] have proved to be of particular interest because of the structural similarity between the chelate systems, Figure 1.

For complexes of the type [Co(EDDA)(L)]^n where L represents a bidentate ligand, two geometric isomers are possible, Figure 1, symmetrical-cis (s-cis) and