Journal of Organometallic Chemistry, 354 (1988) 169–176
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The crystal and molecular structures of (η^5-pentamethylcyclopentadienyl)(η^7-cycloheptatrienyl)-zirconium and -hafnium

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(Received April 19th, 1988)

Abstract

The crystal structures of (η^5-C_5Me_5)(η^7-C_7H_7)M (M = Zr, Hf) were determined utilizing single crystal X-ray diffraction data. The two compounds are isostructural with the previously determined Ti analog [1], crystallizing in the orthorhombic space group *Pnma*. Cell data at −140 °C are: M = Zr, *a* 10.464(4), *b* 12.318(5), *c* 11.277(3) Å and D_{calc} 1.45 g cm^{-3} for $Z = 4$; M = Hf, *a* 10.442(2), *b* 12.354(4), *c* 11.246(2) Å, and D_{calc} 1.85 g cm^{-3} for $Z = 4$. The metal atom and one carbon of each aromatic ring reside on a crystallographic mirror plane. The M–C(η^5) and M–C(η^7) separations average 2.485(2) and 2.332(3) Å, respectively for M = Zr and 2.455(3) and 2.296(6) Å for M = Hf. The centroid(η^5)–M–centroid(η^7) angles deviate significantly from linearity, 170.3° for M = Zr and 172.2° for M = Hf.

Introduction

Sandwich complexes of titanium, which contain effectively planar organic rings including, (η^5-C_5H_5)(η^8-C_8H_8)Ti [2,3] and (η^5-C_5H_5)(η^7-C_7H_7)Ti [4–6], have been known and structurally characterized for several years. More recently the pentamethylcyclopentadienyl analogs of these compounds were prepared and structurally characterized [1]. In contrast, little is known regarding the structures of similar sandwich complexes of Zr and Hf, and no structures containing η^7-cycloheptatrienyl ligands with these metals have been reported. In order to more fully characterize this class of compounds for the heavier group 14 congeners and in order to further study the M–(η^7-C_7H_7) interaction, the title compounds were synthesized and spectroscopically characterized [7]. This paper reports the detailed single crystal X-ray diffraction studies of these compounds.

0022-328X/88/$03.50

Results and discussion

The molecular structure and atom labelling scheme for $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)Zr$ are given in Fig. 1. Bond distances and angles for both the Zr and Hf (side-view Fig. 2) are given in Tab. 1. Both compounds are isostructural with the previously determined Ti analog [1]. In each, the metal atom, one carbon atom in each aromatic ring, and one methyl group reside on a crystallographic mirror plane. The ring atom in the η^5-ligand on the mirror (C(5)) is effectively *trans* to the ring atom

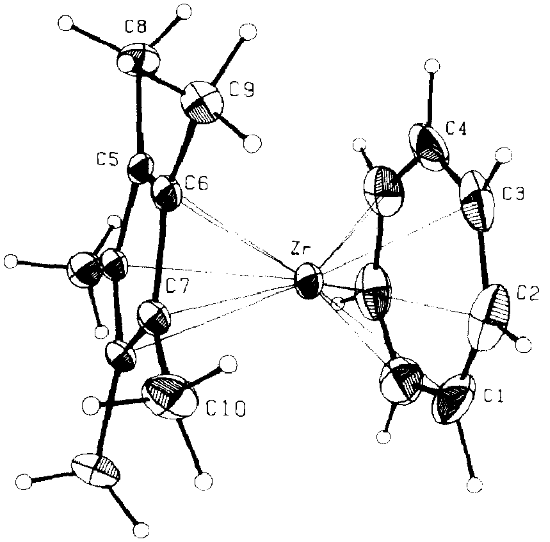

Fig. 1. Molecular structure and atom labelling scheme for $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)M$, M = Zr (shown) and Hf; 50% probability thermal ellipsoids; hydrogen atoms arbitrarily reduced.

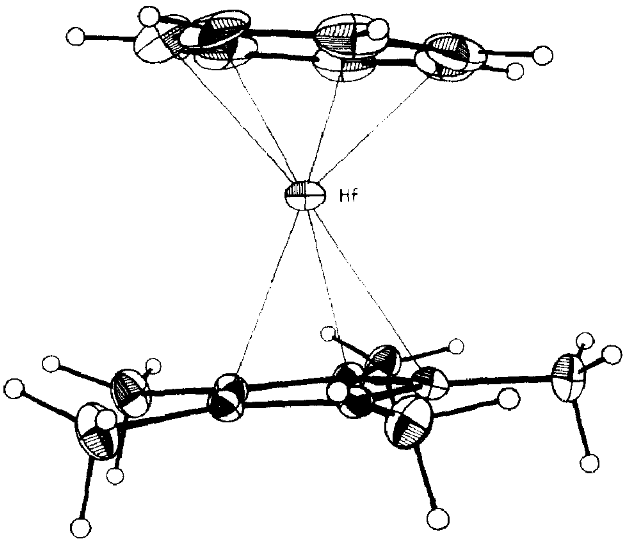

Fig. 2. Side view of M = Hf.

Table 1

Bond distances (Å) and angles (deg) for $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)M$ (M = Zr, Hf)

Atoms	Distance (M = Zr)	Distance (M = Hf)
M–C(1)	2.337(6)	2.290(8)
M–C(2)	2.330(4)	2.306(5)
M–C(3)	2.328(3)	2.293(5)
M–C(4)	2.334(3)	2.295(5)
M–C(5)	2.484(4)	2.455(6)
M–C(6)	2.488(3)	2.451(4)
M–C(7)	2.483(3)	2.458(4)
C(1)–C(2)	1.429(5)	1.433(7)
C(2)–C(3)	1.406(6)	1.408(8)
C(3)–C(4)	1.419(5)	1.415(7)
C(4)–C(4)′ [a]	1.421(8)	1.41(1)
C(5)–C(6)	1.420(4)	1.427(6)
C(5)–C(8)	1.502(6)	1.508(9)
C(6)–C(7)	1.424(4)	1.413(6)
C(6)–C(9)	1.495(5)	1.499(6)
C(7)–C(10)	1.498(4)	1.502(6)
C(7)–C(7)′	1.413(6)	1.445(8)
Cent1 [b]–M	1.66	1.62
Cent2–M	2.17	2.13
Atoms	**Angle**	**Angle**
C(2)–C(1)–C(2)′	128.1(7)	128(1)
C(1)–C(2)–C(3)	128.5(4)	127.8(6)
C(2)–C(3)–C(4)	129.2(4)	129.3(5)
C(3)–C(4)–C(4)′	128.3(2)	128.6(3)
C(6)–C(5)–C(6)′	108.3(4)	107.4(5)
C(6)–C(5)–C(8)	125.8(2)	126.3(3)
C(5)–C(6)–C(7)	107.7(3)	108.6(4)
C(5)–C(6)–C(9)	126.1(3)	126.0(4)
C(7)–C(6)–C(9)	126.2(3)	125.3(4)
C(6)–C(7)–C(10)	126.0(3)	127.2(4)
C(6)–C(7)–C(7)′	108.2(2)	107.6(2)
C(7)′–C(7)–C(10)	125.7(2)	125.1(2)
Cent1–M–Cent2	170.3	172.2

[a] Primed atoms are related to those in Tables 4 and 5 by the crystallographic mirror plane. [b] Cent1 refers to the centroid of the C_7 ring; Cent2 to the C_5 ring.

in the η^7-ligand on the mirror (C(1)), a situation opposite to the eclipsed conformation found in $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)M$ (M = Ti [6], V [8]).

Short Ti–C(η^7) separations in cycloheptatrienyl compounds have previously been observed, and when compared to results found for similar V and Cr compounds, agree with theoretical calculations that indicate the M-C_7H_7 bond strength decreases in the order Ti, V, Cr [9]. Although not as many compounds are available for comparison, review of the data for $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)Ti$, $(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)M$ (M = Ti [1], Zr [10]) and the title compounds reveals the strong nature of the M–C_7H_7 interaction for Zr and Hf. A comparison of the bonding parameters for these compounds is presented in Tab. 2.

The results in Tab. 2 suggest the major differences in the isostructural sandwich complexes of group 14 can be related directly to changes in metal radius. Thus, the

Table 2

Comparison of the bonding parameters in the series $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)M$ (M = Ti, Zr, Hf) and related data

Compound	M–C(η^5) av. (Å)	Range (Å)	M–Cent(η^5) (Å)	M–C(η^n) (Å), n = 7, 8	Range (Å)	M–Cent(η^n) (Å), n = 7, 8	Cent–M–Cent (°)	Ref.
$(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)M$								
M = Ti [a]	2.32(1)	2.315(4)–2.335(2)	1.98	2.21(1)	2.195(5)–2.218(3)	1.49	176.2	1
M = Zr [b]	2.485(2)	2.483(3)–2.488(3)	2.17	2.332(3)	2.328(3)–2.337(6)	1.66	170.3	This study
M = Hf [b]	2.455(3)	2.451(4)–2.458(4)	2.13	2.296(6)	2.290(8)–2.306(5)	1.62	172.2	This study
$(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)M$								
M = Ti	2.32			2.19				6
M = V	2.23			2.25				8
M = Cr	2.18			2.16				9
$(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_8)Ti$								
	2.353		2.03	2.323				3
$(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_8)M$ [c]								
M = Ti	2.338(5)		2.01	2.34(2)		1.43, 1.46	179.1, 179.0	1
M = Zr [b]	2.478(6)		2.17	2.45(3)		1.59, 1.67	173.9, 173.6	10

[a] Structure determined at −90 °C. [b] Structure determined at −140 °C. [c] Disordered structures, cyclooctatetraene ligands have two orientations related to the crystallographic mirror plane.

nature of the M–C_7H_7 interaction itself does not change among the group 14 congeners. The average M–C(η^7) separation is shorter than the average M–C(η^5) distance in all three compounds: by 0.11 Å for M = Ti, 0.15 Å for M = Zr, and 0.16 Å for M = Hf.

It is possible that small steric influences are also present. In the Ti analog and in (η^5-C_5Me_5)(η^8-C_8H_8)Ti the centroid–Ti–centroid angles (176.2 and 179.0° average, respectively) are closer to linearity than observed in the title compounds (170.3°, Zr and 172.2°, Hf) or in (η^5-C_5Me_5)(η^8-C_8H_8)Zr (173.8° average). On the other hand, the methyl groups in the MC_7 complexes bend away from the metal and out of the C_5 plane an average of only 0.032 Å for the M = Ti compound with 0.047 Å for M = Zr and 0.048 Å for M = Hf observed. If these values are considered statistically significant, they imply an electronic origin-optimization of the overlap

Table 3

Crystal data and summary of intensity data collection and structure refinement

	Compound (η^5-C_5Me_5)(η^7-C_7H_7)M	
	M = Zr	M = Hf
Color/Shape	dark red/parallelepiped	translucent orange/parallelepiped
Formula weight	317.6	404.9
Space group	Pnma	Pnma
Temperature (°C)	−140	−140
Cell constants [a]		
a, Å	10.464(4)	10.442(2)
b, Å	12.318(5)	12.354(4)
c, Å	11.277(4)	11.246(2)
Cell volume (Å^3)	1453.6	1450.7
Formula units/unit cell	4	4
D_{calc} (g cm^{-3})	1.45	1.85
μ_{calc} (cm^{-1})	7.24	75.4
Diffractometer/Scan	Enraf–Nonius CAD-4/θ–2θ	Enraf–Nonius CAD-4/θ–2θ
Range of transmission factors	0.90/0.94	0.22/0.32
Radiation, graphite monochromator	Mo-K_α (λ 0.71073)	Mo-K_α (λ 0.71073)
Maximum crystal dimensions, mm	0.08 × 0.15 × 0.40	0.15 × 0.20 × 0.30
Scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
Standard reflections	600; 080; 0, 0, 10	800; 0, 12, 0; 0, 0, 10
Decay of standards	±2%	±2%
Reflections measured	1540	1536
2θ range, deg	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$
Range of h, k, l	+12, +14, +13	+12, +14, +13
Reflections observed ($F_o \geqslant 5\sigma(F_o)$) [b]	1052	1185
Computer programs [c]	SHELX [12]	SHELX [12]
Structure solution	Coordinates from M = Ti [1]	Coordinates from M = Zr
Number of parameters varied	134	88
Weights	$[\sigma(F_o)^2 + 0.004F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00004F_0^2]^{-1}$
GOF	0.66	0.98
$R = \Sigma \| \|F_o\| - \|F_c\| \| / \Sigma \|F_o\|$	0.036	0.024
R_w	0.049	0.026
Largest feature final difference map	0.3e Å^{-3}	0.5e Å^{-3}

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] Corrections: Lorentz-polarization and absorption (empirical, psi scan, M = Hf). [c] Neutral scattering factors and anomalous dispersion corrections from ref. 13.

of the η^5-C_5Me_5 π-orbitals and the more diffuse $4d$ or $5d$ orbitals on the metal.

The average M–C(η^5) distances in the TiC_7 and ZrC_7 compounds are identical at 3σ to the corresponding averages in (η^5-C_5Me_5)(η^8-C_8H_8)M (M = Ti, Zr). In each case the M–C_8 separations are longer than the M–C_7 distances and by the same amount for M = Ti (0.13 Å) and M = Zr (0.12 Å).

The internal bonding parameters of the aromatic rings appear normal. The average values for the C_5Me_5 ring for M = Zr are C–C 1.419(5) Å, C–Me 1.498(3) Å, C–C–C 108.1(3)°, and C–C–Me 126.0(1)° (M = Hf: 1.43(1) Å, 1.503(4) Å, 107.9(5)°, and 126.0(8)°, respectively). Corresponding averages for the C_7H_7 moiety are for M = Zr C–C = 1.419(8) Å and C–C–C 128.5(4)° (M = Hf: 1.42(1) Å and 128.4(6)°, respectively). Although the hydrogen atoms of the cycloheptatrienyl ligand for M = Zr were fully refined, no consistent trend in the bending of the hydrogen atoms out of the C_7 plane was observed. In (η^5-C_5Me_5)(η^7-C_7H_7)Ti the average bending of the C_7 hydrogen atoms of 10° toward the Ti atom was taken as evidence of reorientation of the ring for better metal overlap as discussed in ref. 11. It appears that the larger Zr will fit better than Ti and no inward bending and consequent rehybridization is necessary.

Experimental

X-ray data collection, structure determination, and refinement for (η^5-C_5Me_5)(η^7-C_7H_7)M (M = Zr, Hf). Single crystals of the title compounds were mounted on

Table 4

Final fractional coordinates for (η^5-C_5Me_5)(η^7-C_7H_7)Zr

Atom	x/a	y/b	z/c	U_{eqv} ^{a}
Zr	0.36059(4)	0.7500	0.50685(3)	0.019
C(1)	0.5816(5)	0.7500	0.5370(6)	0.047
C(2)	0.5335(4)	0.6457(4)	0.5699(4)	0.045
C(3)	0.4291(4)	0.6209(3)	0.6436(3)	0.039
C(4)	0.3445(4)	0.6923(3)	0.7035(3)	0.036
C(5)	0.1304(4)	0.7500	0.4532(4)	0.018
C(6)	0.1846(3)	0.6565(2)	0.3992(2)	0.018
C(7)	0.2733(3)	0.6926(2)	0.3119(2)	0.018
C(8)	0.0286(5)	0.7500	0.5471(4)	0.025
C(9)	0.1522(3)	0.5412(3)	0.4273(3)	0.024
C(10)	0.3486(4)	0.6216(3)	0.2298(3)	0.029
H(1)[C(1)]	0.67(1)	0.750	0.480(8)	(iso)
H(2)[C(2)]	0.574(4)	0.587(4)	0.535(4)	(iso)
H(3)[C(3)]	0.409(3)	0.543(3)	0.646(3)	(iso)
H(4)[C(4)]	0.276(4)	0.654(4)	0.754(5)	(iso)
H(5)[C(8)]	−0.060(6)	0.750	0.512(4)	(iso)
H(6)[C(8)]	0.031(4)	0.688(3)	0.591(4)	(iso)
H(7)[C(9)]	0.078(4)	0.514(3)	0.379(4)	(iso)
H(8)[C(9)]	0.127(3)	0.525(4)	0.510(3)	(iso)
H(9)[C(9)]	0.222(4)	0.499(4)	0.407(4)	(iso)
H(10)[C(10)]	0.365(3)	0.548(3)	0.258(4)	(iso)
H(11)[C(10)]	0.435(4)	0.651(3)	0.208(3)	(iso)
H(12)[C(10)]	0.301(5)	0.617(3)	0.165(5)	(iso)

[a] U_{eqv} is equal to $(U_{11}+U_{22}+U_{33})/3$.

Table 5

Final fractional coordinates for $(\eta^5\text{-}C_5Me_5)(\eta^7\text{-}C_7H_7)Hf$

Atom	x/a	y/b	z/c	U_{eqv}
Hf	0.35830(3)	0.7500	0.51127(3)	0.016
C(1)	0.5761(8)	0.7500	0.5349(8)	0.042
C(2)	0.5300(5)	0.6455(5)	0.5700(5)	0.039
C(3)	0.4255(5)	0.6216(4)	0.6447(5)	0.033
C(4)	0.3417(5)	0.6931(4)	0.7049(5)	0.033
C(5)	0.1310(6)	0.7500	0.4553(6)	0.016
C(6)	0.1878(4)	0.6569(4)	0.4018(4)	0.013
C(7)	0.2778(4)	0.6915(3)	0.3162(4)	0.015
C(8)	0.0278(6)	0.7500	0.5491(6)	0.023
C(9)	0.1545(4)	0.5413(4)	0.4281(5)	0.022
C(10)	0.3554(5)	0.6216(4)	0.2340(5)	0.026
H(1)[C(1)]	0.645	0.750	0.480	(iso)
H(2)[C(2)]	0.575	0.585	0.539	(iso)
H(3)[C(3)]	0.409	0.547	0.656	(iso)
H(4)[C(4)]	0.276	0.660	0.751	(iso)
H(5)[C(8)]	−0.049	0.750	0.500	(iso)
H(6)[C(8)]	0.026	0.683	0.590	(iso)
H(7)[C(9)]	0.083	0.516	0.386	(iso)
H(8)[C(9)]	0.104	0.534	0.497	(iso)
H(9)[C(9)]	0.225	0.498	0.412	(iso)
H(10)[C(10)]	0.357	0.554	0.261	(iso)
H(11)[C(10)]	0.443	0.650	0.207	(iso)
H(12)[C(10)]	0.306	0.626	0.159	(iso)

pins and transferred to the goniometer. The crystals were cooled to −140 °C during data collection using a stream of cold nitrogen gas. The space groups were determined to be either the centric *Pnma* or acentric $Pn2_1a$ from the systematic absences. The isostructural titanium analog was satisfactorily refined in the centric space group *Pnma*. The subsequent successful refinements of the title structures in this space group confirmed this choice. A summary of data collection parameters is given in Tab. 3.

The methyl hydrogen atoms were located from difference Fourier maps and refined for $M = Zr$, but included with fixed contributions (B 5.5 Å^2) for $M = Hf$. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to the final values of R and R_w given in Tab. 3. The final values of the positional parameters are given in Tables 4 and 5.

Acknowledgements

We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (RDR), for support of this work. The U.S. National Science Foundation's Chemical Instrumentation Program provided funds used to purchase the diffractometer (NIU).

Supplementary material

Tables of thermal parameters, least-squares planes results, and calculated and observed structure factors for both compounds are available. See NAPS document

No. 04625 for 9 pages of supplementary material which may be ordered from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only, $7.75 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada, add postage of $4.50 for the first 20 pages and $1.00 for each 10 pages of material thereafter. $1.50 for microfiche postage.

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