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THE CRYSTAL STRUCTURE OF 1,1-BIS(η^5-CYCLOPENTADIENYL)-2,3,4,5-TETRAPHENYLZIRCONOLE

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Summary

The crystal and molecular structure of $(\eta^5\text{-}C_5H_5)_2Zr[C_4(C_6H_5)_4]$ has been determined by single crystal X-ray diffraction methods. The compound is isostructural with its titanium and hafnium analogues, and crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 13.790(5)$, $b = 11.136(5)$, $c = 18.692(7)$ Å, $\beta = 92.82(4)°$, and $\rho_{calc} = 1.34$ g cm^{-3} for $Z = 4$. Full-matrix least-squares refinement converged with a conventional R value of 0.049 for 2986 observed reflections. The metallocyclic ring is planar to within 0.05 Å, and the π-electron density is largely localized. The two independent Zr—C(σ) bond lengths are 2.250(5) and 2.265(6) Å. The Zr—C(η^5) distances range from 2.482(6) to 2.546(7) Å, and average 2.521(20) Å. A comparison of zirconium— and hafnium—carbon bonds based on the data available shows that for M = Hf the M—C bonds are shorter for all cases: C(sp), C(sp^2), C(sp^3), C(η^5).

Introduction

The inorganic chemistry of zirconium and hafnium is quite similar due in large measure to the atomic (1.45 vs. 1.44 Å) and 4+ ionic radii (0.74 vs. 0.75 Å) [1]. However, substantial but unexpected differences in metal—carbon(σ) bond lengths have been reported. In $(\eta^5\text{-}C_9H_7)_2M(CH_3)_2$ (M = Zr, Hf) [2] the Zr—C(σ) bond length, 2.251(6) Å, is significantly shorter than the Hf—C(σ) length, 2.332(12) Å *. Similar Zr—C(σ) bond distances have been found in

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* The X-ray crystal structures of $(\eta^5\text{-}C_5H_5)_2M[CH(C_6H_5)_2]_2$ (M = Zr, Hf) have been reported [3], but electronic effects involving the M—C(σ) bond appear to be overridden by the steric requirements of the diphenylmethyl ligand.

$(\eta^5\text{-}C_5H_5)_2Zr[CH_2Si(CH_3)_3]_2$, [4], 2.278(4) Å, and in $(\eta^5\text{-}C_5H_5)_2Zr[CH_2C(CH_3)_3]_2$ [4], 2.289(11) Å, while the Hf—C(σ) length has seemingly been substantiated in the structures of $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$ [5], 2.35(3) Å, and of $[(\eta^5\text{-}C_5H_5)_2Hf(CH_3)]_2O$ [5], 2.295(14) Å.

In view of the above mentioned studies it was surprising to find the Hf—C(σ) distance given as 2.20(3) Å in $(\eta^5\text{-}C_5H_5)_2Hf[C_4(C_6H_5)_4]$ [6]. Clearly the large discrepancy between Hf—C(sp^3) and Hf—C(sp^2) lengths could not be attributed simply to the change in carbon atom hybridization. To add to this body of conflicting data, the previous report of the structure of $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$ is now thought to be in fact that of $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)Cl$ with crystallographic disorder of the sigma-bonded ligands [7].

Our interest in $(\eta^5\text{-}C_5H_5)_2Zr[C_4(C_6H_5)_4]$ was thus two-fold. Firstly, the structure of the title compound was needed for comparison with those of the titanium and hafnium analogues in order to further clarify the M—C(σ) situation. Secondly, the reaction of $(\eta^5\text{-}C_5H_5)_2Zr[C_4(C_6H_5)_4]$ and $(\eta^5\text{-}C_5H_5)_2Ti[C_4(C_6H_5)_4]$ shows significant differences. Attempts to isolate $(\eta^5\text{-}C_5H_5)_2Zr(CO)[C_2(C_6H_5)_2]$ have been unsuccessful [8,9], and the catalytic properties of hydrocarbon solutions containing $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$ and $C_2(C_6H_5)_2$ with respect to hydrogenation are very low compared with those of solutions of $(\eta^5\text{-}C_5H_5)_2Ti(CO)[C_2(C_6H_5)_2]$ [8,10].

Experimental

A. Reaction between $(\eta^5\text{-}C_5H_5)Zr(CO)_2$ and $(C_6H_5)_2C_2$

$(\eta^5\text{-}C_5H_5)Zr(CO)_2$ (0.728 g, 2.63 mmol) was dissolved in heptane (50 ml) to which diphenylacetylene (1.90 g, 10.7 mmol) was added. The solution was kept in vacuo for several hours, then heated at 80°C for 4 h. The color of the solution became red-brown and the IR spectrum showed the absence of $(\eta^5\text{-}C_5H_5)_2Zr(CO)_2$. The solution on cooling gave orange crystals of $(\eta^5\text{-}C_5H_5)_2Zr[C_4(C_6H_5)_4]$ (ca. 51%), which were filtered and dried in vacuo. Analytical and spectroscopic data agreed with those reported in the literature [9,11].

TABLE 1

CRYSTAL DATA FOR $(\eta^5\text{-}C_5H_5)_2M[C_4(C_6H_5)_4]$ (M = Ti [a], Zr, Hf [a])

	Ti	Zr	Hf
Mol. wt.	534.6	577.9	665.2
Linear abs. coeff., μ(cm^{-1})	3.47	4.04	38.55
Calcd. density (g cm^{-3})	1.26	1.34	1.54
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Molecules/unit cell	4	4	4
Cell constants [b],			
a(Å)	13.758(5)	13.790(5)	13.822(8)
b(Å)	11.059(5)	11.136(5)	11.149(8)
c(Å)	18.492(6)	18.692(7)	18.694(9)
β(deg)	93.76(3)	92.82(4)	93.18(5)
Cell vol. (Å^3)	2807.4	2867.0	2876.4

[a] From ref. 6. [b] Mo-K_α radiation, λ 0.71069 Å. Ambient temperature of 22°C.

B. X-ray data collection, solution and refinement of the structure

Crystals suitable for the X-ray study were grown by slow cooling of a toluene solution, and sealed in thin-walled glass capillaries. The final lattice parameters, determined from a least-squares refinement of the angular settings of 15 accurately centered reflections, are given in Table 1. The diffracted intensities were collected on an Enraf-Nonius CAD-4 diffractometer in the usual manner [12].

One independent quadrant of data was measured out to $2\theta = 50°$. A total of 2986 observed reflections $[I \geqslant 3\sigma(I)]$ were obtained. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The full-matrix least-squares refinement was carried out using the Busing and Levy program ORFLS *. The function $w(|F_0| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral atom scattering factors were taken from the compilations of Cromer and Waber [13] for Zr and C. The scattering for zirconium was corrected for the real and imaginary components of anomalous dispersion with the table of Cromer and Liberman [14]. The hydrogen atom scattering factors were from ref. 15.

Since $(\eta^5\text{-}C_5H_5)_2Zr[C_4(C_6H_5)_4]$ is isostructural with its titanium and hafnium analogues, the coordinates for the titanium compound were used for the refinement. Two cycles with isotropic thermal parameters followed by two with anisotropic ones gave

$$R_1 = [\Sigma(|F_0| - |F_c|)/\Sigma|F_0|] = 0.062$$

$$R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w(F_0)^2]^{1/2} = 0.065\ .$$

Placement of the hydrogen atoms in calculated positions followed by further refinement of the nonhydrogen parameters led to final values of $R_1 = 0.049$ and $R_2 = 0.053$. Unit weights were used at all stages and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.02 of their estimated standard deviations. The final value of the e.s.d. of an observation of unit weight was 2.07. The final values of the positional and thermal parameters are given in Table 2 **.

Discussion

The range of Zr—C(sp^3) bond lengths extends from 2.251(6) Å in $(\eta^5\text{-}C_9H_7)_2\text{-}Zr(CH_3)_2$ [2] to 2.447(6) Å in $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$ [17]. The "normal" value may be taken as the 2.283(3) Å found for $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ [7]. Several determinations have been carried out on organohafnium compounds, but the most reliable Hf—C(sp^3) distance is the 2.236(5) Å in $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$ [7].

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* Other crystallographic programs used on a UNIVAC 1110 include ORFFE (distance and angles with e.s.d.'s, by W.R. Busing, K.O. Martin and H.A. Levy), FOURIER (Fourier synthesis, D.J. Hodgson's version of Dellaca and Robinson's program), ORABS (absorption correction, by D.J. Wehe, W.R. Busing and H.A. Levy), ORTEP (thermal ellipsoid drawings, by C.K. Johnson), and BPL (least-squares planes, by W.E. Hunter).

** See NAPS Document No. 03722 for 23 pages of supplementary material. Order from NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only. $ 5.75 for photocopies or $ 3.00 for microfiche. Outside the U.S. and Canada add postage of $ 3 for photocopy and $ 1 for microfiche.

TABLE 2

ATOMIC POSITIONS IN FRACTIONAL COORDINATES AND THERMAL PARAMETERS FOR $(C_5H_5)_2Zr[C_4(C_6H_5)_4]$ [a]

Atom	*x/a*	*y/b*	*z/c*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zr	0.53773(4)	0.22545(5)	0.27320(3)	0.00377(3)	0.00584(5)	0.00259(2)	−0.00003(4)	−0.00036(2)	−0.00001(3)
C(1)	0.5502(4)	0.2189(5)	0.1529(3)	0.0037(3)	0.0053(5)	0.0028(2)	0.0006(4)	0.0002(2)	−0.0003(3)
C(2)	0.4615(4)	0.2227(5)	0.1174(3)	0.0038(3)	0.0044(4)	0.0024(2)	0.0003(3)	−0.0000(2)	−0.0003(3)
C(3)	0.3726(4)	0.2146(5)	0.1602(3)	0.0030(3)	0.0045(5)	0.0030(2)	0.0001(3)	0.0002(2)	0.0001(3)
C(4)	0.3814(4)	0.2243(5)	0.2327(3)	0.0042(3)	0.0039(4)	0.0026(2)	−0.0001(4)	0.0003(2)	−0.0000(3)
C(5)	0.5751(6)	0.4415(6)	0.2429(4)	0.0070(5)	0.0051(6)	0.0039(3)	−0.0022(4)	0.0001(3)	−0.0002(3)
C(6)	0.5069(5)	0.4462(6)	0.2977(4)	0.0051(4)	0.0060(6)	0.0035(3)	0.0001(4)	−0.0005(3)	−0.0012(3)
C(7)	0.5516(5)	0.3950(6)	0.3596(4)	0.0071(5)	0.0076(7)	0.0033(3)	−0.0010(5)	−0.0001(3)	−0.0007(3)
C(8)	0.6477(6)	0.3657(7)	0.3444(5)	0.0058(5)	0.0094(8)	0.0049(3)	−0.0001(5)	−0.0024(3)	−0.0019(4)
C(9)	0.6608(5)	0.3935(7)	0.2733(5)	0.0044(4)	0.0076(7)	0.0061(4)	−0.0022(4)	0.0006(3)	−0.0020(4)
C(10)	0.6446(5)	0.0600(7)	0.3186(4)	0.0057(5)	0.0089(7)	0.0039(3)	0.0016(5)	−0.0014(3)	0.0006(4)
C(11)	0.5871(7)	0.0893(7)	0.3755(4)	0.0100(7)	0.0097(8)	0.0031(3)	0.0022(6)	−0.0008(4)	0.0008(4)
C(12)	0.4915(6)	0.0583(7)	0.3566(5)	0.0089(6)	0.0088(8)	0.0044(3)	0.0023(6)	0.0023(4)	0.0030(4)
C(13)	0.4887(6)	0.0070(6)	0.2890(5)	0.0065(5)	0.0057(6)	0.0049(3)	−0.0003(4)	0.0002(3)	0.0019(4)
C(14)	0.5842(6)	0.0063(6)	0.2644(4)	0.0070(3)	0.0057(6)	0.0035(3)	0.0012(4)	−0.0002(3)	0.0005(3)
C(15)	0.6427(4)	0.2410(5)	0.1186(3)	0.0037(3)	0.0055(5)	0.0027(2)	0.0001(3)	0.0000(2)	−0.0004(3)
C(16)	0.7235(5)	0.1678(6)	0.1351(4)	0.0042(4)	0.0091(7)	0.0044(3)	0.0010(4)	0.0003(3)	0.0011(4)
C(17)	0.8136(5)	0.1947(7)	0.1096(5)	0.0037(4)	0.0119(9)	0.0055(3)	0.0022(5)	0.0003(3)	0.0007(4)
C(18)	0.8263(5)	0.2920(7)	0.0668(4)	0.0041(4)	0.0117(9)	0.0047(3)	−0.0003(5)	0.0011(3)	−0.0002(4)
C(19)	0.7484(5)	0.3650(6)	0.0494(4)	0.0049(6)	0.0083(7)	0.0036(3)	−0.0010(4)	0.0004(3)	0.0000(3)
C(20)	0.6580(4)	0.3392(6)	0.0746(3)	0.0037(3)	0.0070(6)	0.0033(2)	−0.0002(4)	−0.0001(2)	0.0000(3)
C(21)	0.4481(4)	0.2354(5)	0.0378(3)	0.0033(3)	0.0054(5)	0.0025(2)	−0.0004(3)	0.0001(2)	−0.0003(3)
C(22)	0.3880(4)	0.3222(5)	0.0057(4)	0.0043(3)	0.0062(5)	0.0032(2)	0.0006(4)	−0.0002(2)	−0.0002(3)
C(23)	0.3727(5)	0.3290(6)	−0.0674(4)	0.0054(4)	0.0090(7)	0.0032(3)	−0.0004(5)	−0.0009(3)	0.0011(3)
C(24)	0.4149(5)	0.2461(7)	−0.1111(3)	0.0073(5)	0.0098(8)	0.0024(2)	−0.0014(5)	−0.0005(3)	0.0001(3)
C(25)	0.4749(5)	0.1590(7)	−0.0805(4)	0.0065(5)	0.0089(7)	0.0031(3)	−0.0008(5)	0.0004(3)	−0.0014(3)
C(26)	0.4919(4)	0.1544(5)	−0.0073(3)	0.0040(3)	0.0065(5)	0.0028(2)	0.0000(4)	0.0001(2)	−0.0002(3)
C(27)	0.2769(4)	0.1900(5)	0.1211(3)	0.0037(3)	0.0063(6)	0.0022(2)	−0.0002(3)	−0.0000(2)	0.0000(2)
C(28)	0.1968(4)	0.2612(6)	0.1325(3)	0.0039(3)	0.0084(7)	0.0033(2)	0.0006(4)	−0.0003(2)	−0.0004(3)
C(29)	0.1070(4)	0.2354(7)	0.1011(4)	0.0043(4)	0.0100(7)	0.0041(3)	0.0006(4)	−0.0005(2)	−0.0001(4)
C(30)	0.0955(5)	0.1373(7)	0.0575(4)	0.0044(4)	0.0129(9)	0.0033(3)	−0.0020(5)	−0.0005(3)	0.0004(4)
C(31)	0.1730(5)	0.0651(6)	0.0444(4)	0.0063(5)	0.0086(7)	0.0030(2)	−0.0024(5)	0.0001(3)	−0.0007(3)
C(32)	0.2640(4)	0.0914(5)	0.0759(3)	0.0050(4)	0.0063(6)	0.0025(6)	−0.0008(4)	0.0002(2)	−0.0003(3)

C(33)	0.3004(4)	0.2001(5)	0.2790(3)	0.0036(3)	0.0069(6)	0.0026(2)	0.0003(3)	−0.0002(2)	−0.0005(3)
C(34)	0.2787(4)	0.2778(6)	0.3345(3)	0.0049(4)	0.0064(5)	0.0032(2)	−0.0006(4)	0.0006(2)	−0.0006(3)
C(35)	0.2087(5)	0.2513(6)	0.3820(4)	0.0075(5)	0.0069(7)	0.0032(2)	0.0004(4)	0.0016(3)	−0.0004(3)
C(36)	0.1582(5)	0.1436(7)	0.3766(4)	0.0052(4)	0.0095(7)	0.0037(3)	−0.0002(4)	−0.0014(3)	0.0005(4)
C(37)	0.1794(4)	0.0634(6)	0.3240(4)	0.0041(4)	0.0080(6)	0.0034(2)	−0.0014(4)	0.0000(2)	0.0006(3)
C(38)	0.2486(4)	0.0902(6)	0.2757(4)	0.0042(4)	0.0073(6)	0.0035(3)	−0.0009(4)	0.0001(2)	−0.0000(3)
H(1)	0.5632	0.4693	0.1906	5.5000					
H(2)	0.4371	0.4788	0.2933	5.5000					
H(3)	0.5203	0.3821	0.4086	5.5000					
H(4)	0.6976	0.3297	0.3802	5.5000					
H(5)	0.7238	0.3627	0.2473	5.5000					
H(6)	0.7181	0.0737	0.3179	5.5000					
H(7)	0.6110	0.1281	0.4239	5.5000					
H(8)	0.4333	0.0710	0.3894	5.5000					
H(9)	0.4276	−0.0231	0.2612	5.5000					
H(10)	0.6053	−0.0262	0.2151	5.5000					
H(11)	0.7158	0.0962	0.1682	5.5000					
H(12)	0.8711	0.1612	0.1232	5.5000					
H(13)	0.8933	0.3093	0.0474	5.5000					
H(14)	0.7569	0.4383	0.0175	5.5000					
H(15)	0.6008	0.3943	0.0608	5.5000					
H(16)	0.3546	0.3828	0.0377	5.5000					
H(17)	0.3307	0.3968	−0.0895	5.5000					
H(18)	0.4021	0.2500	−0.1658	5.5000					
H(19)	0.5067	0.0978	−0.1121	5.5000					
H(20)	0.5372	0.0898	0.0147	5.5000					
H(21)	0.2044	0.3310	0.1672	5.5000					
H(22)	0.0487	0.2905	0.1107	5.5000					
H(23)	0.0291	0.1184	0.0341	5.5000					
H(24)	0.1639	−0.0082	0.0117	5.5000					
H(25)	0.3226	0.0392	0.0653	5.5000					
H(26)	0.3165	0.3554	0.3399	5.5000					
H(27)	0.1939	0.3093	0.4218	5.5000					
H(28)	0.1063	0.1251	0.4125	5.5000					
H(29)	0.1440	−0.0174	0.3215	5.5000					
H(30)	0.2622	0.0288	0.2360	5.5000					

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[a] Anisotropic thermal parameters defined by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

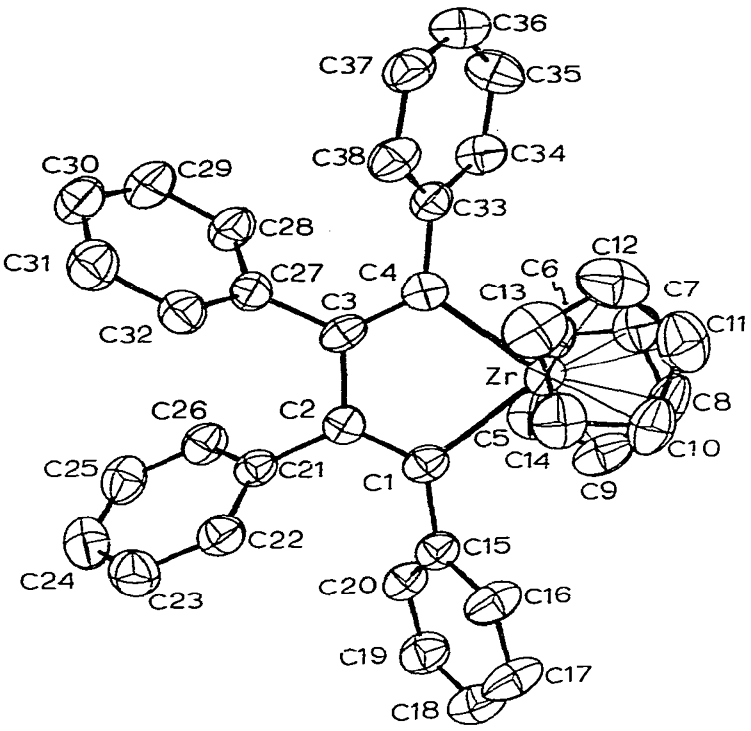

Fig. 1. Molecular structure of 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconole.

In the only previous structural report on a compound containing a Zr—C(sp^2) bond, $(\eta^5\text{-}C_5H_5)_2Zr(C_6H_5)[CH\{Si(CH_3)_3\}_2]$ [17] the length is 2.324(7) Å. This, however, is elongated due to steric problems. In $(\eta^5\text{-}C_5H_5)_2Zr[C_4(C_6H_5)_4]$ (Figure 1, Table 3), the two independent sigma bond lengths are 2.250(5) and 2.265(6) Å. These are near the expected value based on the Zr—C(sp^3) distance and the change in carbon atom hybridization.

If one neglects the reports on the hafnium-containing compounds given in references 2 and 5 the metal—carbon lengths fall into a reasonable pattern (Table 4) *. The sigma bond lengths follow closely the trend expected from a consideration of carbon atom hybridization. For M = Hf, the M—C bonds are shorter than for M = Zr in all cases: C(sp), C(sp^2), C(sp^3), C(η^5-).

It is difficult to compare the title compound to its hafnium analogue because of the relative inaccuracy of the structure of the latter. Similarities with $(\eta^5\text{-}C_5H_5)_2Ti[C_4(C_6H_5)_4]$, especially with respect to the five-membered heterocyclic ring, bear mentioning. The two Zr—C(σ) lengths are different, but not significantly: $\Delta = 0.015$ Å $= 1.9\sigma$. For the titanium analogue the sigma distances exhibited $\Delta = 4.4\sigma$. Even though discrepancies such as these have been

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* Reference 7 gives the details of the structures of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$, $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$, $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)Cl$, and $[(\eta^5\text{-}C_5H_5)_2Zr(CH_3)]_2O$. Therein an analysis of the crystallographic disorder in $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)Cl$ affords the strong indication that the previously reported structure of $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$ is actually that of $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)Cl$. There is also a possibility that the same problem pertains to the study of $(\eta^5\text{-}C_9H_7)_2Hf(CH_3)_2$ given in reference 2.

TABLE 3

COMPARISON OF BOND LENGTHS AND ANGLES FOR 1,1-BIS(η^5-CYCLOPENTADIENYL)-2,3,4,5-TETRAPHENYLZIRCONOLE AND ITS TITANIUM AND HAFNIUM ANALOGUES [a]

Bond	Bond length (Å)		
	Titanium	Zirconium	Hafnium
M—C(1)	2.172(5)	2.265(6)	2.22(2)
M—C(4)	2.141(5)	2.250(5)	2.18(2)
M—C(5)	2.404(6)	2.531(6)	2.52(3)
M—C(6)	2.380(6)	2.540(6)	2.48(2)
M—C(7)	2.364(6)	2.486(7)	2.44(2)
M—C(8)	2.384(5)	2.512(7)	2.49(3)
M—C(9)	2.408(6)	2.527(6)	2.51(2)
M—C(10)	2.338(6)	2.482(6)	2.45(3)
M—C(11)	2.389(6)	2.508(7)	2.49(3)
M—C(12)	2.413(6)	2.529(7)	2.51(2)
M—C(13)	2.402(6)	2.546(7)	2.54(3)
M—C(14)	2.374(6)	2.531(7)	2.50(2)
M—C(η^5)AV	2.386(22)	2.521(20)	2.49(3)
C(1)—C(2)	1.369(6)	1.363(7)	1.39(3)
C(2)—C(3)	1.495(6)	1.500(7)	1.51(3)
C(3)—C(4)	1.370(6)	1.358(8)	1.36(2)
	Bond angle (deg)		
	Titanium	Zirconium	Hafnium
C(1)—M—C(4)	80.3(2)	77.5(2)	78.7(8)
M—C(1)—C(2)	111.0(3)	111.8(4)	114.1(8)
M—C(4)—C(3)	112.5(3)	112.0(4)	113.1(8)
C(1)—C(2)—C(3)	118.5(4)	118.5(5)	114(2)
C(2)—C(3)—C(4)	117.4(4)	119.4(5)	120(2)
Cent1—M—Cent2	134.8(3)	134.3	134(1)
Cent1—M—C(1)	104.1(3)	104.2	103(1)
Cent1—M—C(4)	111.0(3)	112.1	113(1)
Cent2—M—C(1)	109.6(3)	110.7	111(1)
Cent2—M—C(4)	103.7(3)	103.7	103(1)

[a] Data for titanium and hafnium are taken from ref. 6.

TABLE 4

VARIATION OF BOND LENGTHS WITH CARBON ATOM HYBRIDIZATION

Length	Compound	M		Ref.	
		Zr	Hf	Zr	Hf
M—C(sp)	$(\eta^5\text{-}C_5H_5)_2M(CO)_2$	2.187(4)	2.171(9)	20	21
M—C(sp^2)	$(\eta^5\text{-}C_5H_5)_2M[C_4(C_6H_5)_4]$	2.258(11)	2.20(3)	this study	6
M—C(sp^3)	$(\eta^5\text{-}C_9H_7)_2M(CH_3)_2$	2.251(6)	2.332(12)	2	2
	$(\eta^5\text{-}C_5H_5)_2M(CH_3)_2$	2.283(6)	2.236(5)	7	7
	$[(\eta^5\text{-}C_5H_5)_2M(CH_3)]_2O$	2.266(7)	2.295(14)	7	5
M—C(η^5)	$\{(\eta^5\text{-}C_5H_4)_2(CH_2)_3\}MCl_2$	2.494(4)	2.482(4)	22	23
	$(\eta^5\text{-}C_5H_5)_2M[CH(C_6H_5)_2]_2$	2.513(15)	2.46(5)	3	3
	$(\eta^5\text{-}C_5H_5)_2M(CH_3)_2$	2.52(1)	2.50(2)	7	7
	$(\eta^5\text{-}C_5H_5)_2M[C_4(C_6H_5)_4]$	2.52(2)	2.49(3)	this study	6
	$[(\eta^5\text{-}C_5H_5)_2M(CH_3)]_2O$	2.53(2)	2.51(1)	7	5

discussed in some detail [6,18], it is likely that they are only crystallographic artifacts. Other parameters of the metallocyclic ring are comparable to the titanium case. One finds the presence of isolated double bonds with C(1)—C(2), 1.363(7) Å, and C(3)—C(4), 1.358(8) Å. The C=C standard is 1.334 Å [19]. The C(2)—C(3) single bond distance, 1.500(7) Å, is as expected for two sp^2 hybridized carbon atoms. The ring defined by Zr, C(1), C(2), C(3), and C(4) is planar to within 0.05 Å *. The only apparent major difference is the 3° contraction of the C(1)—Zr—C(4) angle compared to the titanium analogue, but this is attributed to the difference in M—C(σ) bond lengths.

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* For best plane results see supplementary data.